

**EMEP Co-operative Programme for Monitoring and Evaluation of the Long-  
Range Transmission of Air Pollutants  
in Europe**

**DRAFT for discussion at the TFMM4;**

**PART A; The EMEP monitoring  
strategy 2004-2009**

**PART B; Justification and  
specification of the EMEP monitoring  
programme, 2004-2009**



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## **How to read/use this draft (this page will not appear in the final document)**

This draft has been prepared the EMEP-CCC in consultation with the EMEP bureau, MSC-W and MSC-E. In addition helpful contributions have been received from experts outside EMEP (Spranger and Erisman).

The objective of this draft is to present the need for observations in order to meet the objectives of EMEP. The draft specifically addresses;

- the need for a revised monitoring activity by reviewing its strengths, weaknesses, opportunities and threats in relation to its objectives (chapters 1-4)
- to present the importance of EMEP data for national as well as other regional or global initiatives in order to improve the harmonisation and use of resources (chapter 5)
- the need to establish more binding monitoring requirements for the participants applying a level approach (chapter 6)
- to define the activities needed for the individual topics (Chapter 7)
- It is proposed to present the monitoring requirements on a component basis (Chapter 8)
- The monitoring requirements for the individual EMEP parties will be presented in Chapter 9.

Chapters 8 and 9 are to be completed in consultation with the TFMM and only a first outline is given here.

Part A will form the EMEP strategy for adoption by the Executive body. It can be maximum 10 pages and the deadline is by June. Part A will be a summary of Part B. The current version of part A should only be considered as a preliminary draft, and the focus of the discussions should thus be on part B.

Part B is to be considered by the TFMM4 meeting in Valencia 9-11 April. Later a revised version will be prepared.



## Preface

The long-term data series of air and precipitation chemistry observation now available for EMEP was generally established through the OECD-project LRTAP in the early 1970ies. Ever since has the monitoring data formed one of the basic legs on which EMEP rests, providing high quality data on the state of the environment, for model validation and national air quality assessments, national involvement and for independent validation of abatement measures. Key elements in the monitoring strategy of EMEP have always been to assure that measurements are made using comparable and reliable methodologies and being operational across Europe. The latter has also been the reason for employing fairly simple, robust and cost efficient methods. In addition these have the advantage of being fairly easy to assess in terms of precision and reproducibility. Even globally, the EMEP dataset is unique in these respects.

During the evolution of the programme new topics and priorities in air pollution policies have entered the arena, but have generally not been associated with additional funding. This has resulted in large variations between different regions of Europe on the ability to implement the full or even parts of the programme or to provide data of adequate quality. A shortcoming of the EMEP protocol is that it does not set specific requirements on the number of sites or parameters to be monitored. One the major objectives of the new strategy is to identify more clearly the monitoring requirements needed to underpin work within, but also outside of the Convention to improve air quality in Europe by defining countries minimum monitoring requirements and also to more directly describe how the monitoring efforts funded in support of EMEP must be complemented by monitoring efforts undertaken by other Conventions (e.g. HELCOM, OSPARCOM, MEDPOL and AMAP), the European Community Air Quality Directives and the Research Community at large.

The European Monitoring and Evaluation Programme (EMEP) is currently facing new challenges with respect to its monitoring and modelling activities. New priorities have set new requirements to the monitoring programme with respect to parameters being monitored and to the density of sites. These challenges can briefly be summarized to be improved spatial resolution, i.e. the influence of regional input to suburban and urban areas, site-specific exposure estimates to ecosystems or even modelling of stomatal uptake of ozone in vegetation, the importance of hemispheric scale transport and understanding the complex behaviour of particulate matter. At the same time new technologies and tools are becoming available that can significantly improve our basis for making sound air pollution abatement (e.g. earth observation systems and data assimilation).

This report outlines the monitoring strategy and the detailed monitoring requirements of EMEP for the period 2004-2009 (the exact formulation here will be improved after the TFMM4).

As a long-term perspective and conservatism is essential for any monitoring activity where tracking the changes over time is a major objective, it aims at ensuring the continuation of the existing data series. At the same time new priorities for policy making are evident (e.g. health issues becoming of relatively

larger political concern). The new technologies and techniques becoming available have a large potential for improving our ability to evaluate the sources, chemical conversion in the atmosphere and the depositions of transboundary air pollution. This calls for the strategy to revisit and evaluate which adjustments to the programme that may be required. Also the financial situation may require elements of the strategy to need more frequent adjustments through the Task Force on Measurements and Modelling as required. The monitoring strategy will be closely linked to the EMEP manual for Sampling and Chemical analysis.



## **PART A: THE EMEP MONITORING STRATEGY 2004-2009**

*This part will be extended to a maximum of 10 pages and will be the strategy the SB and EB will consider and hopefully adopt. It will contain both strategic views on the importance of EMEP measurements as well as specify the monitoring requirements. The detailed justifications will be presented in part B It is likely that Part A and Part B will form two separate documents in the end. Part B is to be considered as a background document for the further discussions while part A will be finalised after the TFMM discussions and in cooperation with the UNECE secretariat.*

### The need for a new strategy:

The EMEP observation network is essential to provide boundary conditions

- for health assessments of in particular PM, O<sub>3</sub> and NO<sub>2</sub>;
- for determining the temporal and spatial variability in the radiative forcing from regional PM (probably a large number; as much as -10 or -20 W/m<sup>2</sup>; may already give rise to the observed shifts in regional precipitation and storm patterns of significant direct impact on societies)
- for eutrophication (NO<sub>x</sub>, NH<sub>3</sub>)
- for determining the contribution of atmospheric deposition of S, N, cations, HM, POPs on changes in biodiversity;
- for determining the role of atmospheric deposition of S, N, cations, HM and POPs on changes in water quality, of importance in the implementation of the EU water framework directive

The monitoring of atmospheric air pollutants in rural and background areas is the responsibility of EMEP. There is currently an emphasis on the "close to citizen"-monitoring in the EU countries as well as in the accession countries as a response to the implementation of the daughter directives of the Framework Directive for Air Quality Management. The EMEP network as such needs to be revised and strengthened in order to serve the needs of CLRTAP as well as of the daughter directives related to air pollutants in the EU and to other international conventions like the UN Framework Convention on Climate Change (UNFCCC) and the biodiversity convention.

This report describes the monitoring requirements for meeting the EMEP objectives of providing data of high and known quality required to assess temporal and spatial trends in atmospheric chemistry and deposition amounts including the validation and further development of chemical transport models in Europe.

### External pressures on the EMEP network

The EMEP monitoring network is under pressure because the sanctions for non-compliance with monitoring requirements are stronger in the EU daughter directives than under the CLRTAP. Even though there already is a substantially larger number of urban/roadside sites compared to rural sites, the number of sites "close to citizens" is expanding on the cost of the rural sites. This shift in balance more and more in disfavour of rural EMEP sites is most unfortunate because it causes larger and larger uncertainties to propagate into the evaluations of the effect of emission reduction measures. The EMEP system has a coherent history

of QA and QC and has traditionally a strong bottom up and top down approach to monitoring at the same time; so that there is a good link between national data producers and the central core of EMEP. This is much less so in many of the data in support of the air quality directives collected by a multitude of players (central, regional or local authorities; sector authorities) where the link from the top layer to the individual data providers is much weaker and where the QA-QC rests in the hands of national systems.

#### Internal pressures on the EMEP monitoring system

The EMEP monitoring network is not seen in the comprehensive role that is now required in order to solve the interrelated policy issues discussed above. It is a challenge for the countries to review their national activities so that all air pollution related monitoring is considered together to ensure that the demands imposed by current and future legislation both related to EU, CLRTAP and other international bodies is served in a cost-effective way. If the revision of national monitoring networks is dealt with in such a comprehensive way, modifications and even cost reductions may be identified without compromising the value and strength of the information that is derived from the monitoring network and which is essential for the technical underpinning of how the implementation of current air pollution legislation works, and for the work to revise and improve current policy. The EMEP observations are essential to establish a reliable picture of the air pollution situation in Europe; even in urban areas.

#### Mission of the EMEP monitoring

1. Assess regional concentrations and deposition of pollutants;
2. Improve the understanding of atmospheric chemical and physical processes and use that for CTM validation and model development;
3. Assess the success of international abatement strategies for atmospheric pollutants;
4. Provide information on the state of the environment to allow comparisons with effects thresholds indicating environmental sustainability (Critical Loads/Levels);
5. Provide input data required to assess the effects of atmospheric pollution on ecosystems, crops, materials and health.

#### Monitoring strategy

The monitoring strategy introduces the term “EMEP Core sites” representing the minimum monitoring requirements (the mandatory programme). Measurements at EMEP core sites are distinguished between so called level 1 sites comprising a relatively large number of sites (>125) with a complete programme covering major inorganic compounds in air and precipitation, ozone and particulate matter mass, and level 2 sites which comprise more technically or economically demanding measurements which can not be implemented at all EMEP sites. The required minimum number of Level 1 and level 2 sites is defined for individual countries (level 1) and for regions (level 2). Level 2 sites are also different between the various topics EMEP considers (Acidification and Eutrophication, Photochemical oxidants, Heavy Metals, Persistent Organic Pollutants and particulate matter. There is a need for regional cooperation in providing sufficient number of core sites level 2 in order to minimise costs and a cost sharing option is proposed. Monitoring performed in support of the marine conventions

(HELCOM, OSPARCOM and AMAP) will contribute significantly to level 2 sites for heavy metals and for POPs.

EMEP also needs highly specialised and demanding measurement generally only available from state of the art monitoring sites either continuously operated or data from research experiments. Such sites are nominated as EMEP level 3 sites or EMEP supersites. These sites will partly be joint sites with the WMO-Global Atmosphere Watch programme.

Finally, EMEP will make use of relevant data from other networks either from the CLRTAP itself (Working Group of Effects) and from the monitoring activities performed under the Air Quality Directives of the European Union.

Criteria for various site levels;

Core sites level 1; A minimum site density of 1 site per 50.000 km<sup>2</sup>, higher resolution if complex terrain, all countries with a geographical area exceeding xxx km<sup>2</sup> are required to operate at least one level 1 site.

Core sites level 2; A minimum site density of 1 site per 100.000 km<sup>2</sup>, density will vary between topics depending on region (photooxidants and particles should have a higher site density in the South and Central parts, while acidification and POPs should have a higher density towards North and East. Regional cooperation towards cost sharing is encouraged.

Table **“level table”** summarises the monitoring requirements for the individual levels of sites (see excel file “strategitabell.xls).

Table **“sites per country”** presents the minimum monitoring obligations for the individual countries at the different levels.

Table **“sites per region”** presents the minimum monitoring obligations for the individual regions at the different levels.

More to come.....

Activities in 2004-2009

to be specified



## **PART B: JUSTIFICATION AND SPECIFICATION OF THE EMEP MONITORING PROGRAMME 2004-2009**

### **1. Introduction**

The “Cooperative programme for monitoring and evaluation of long-range transmission of air pollutants in Europe” (EMEP) was launched in 1977 as a response to the growing concern over the effects on the environment caused by acid deposition. EMEP was organized under the auspices of the United Nations Economic Commission for Europe (ECE). Today EMEP is an integral component of the activities under the Convention on Long-range Transboundary Air Pollution.

International air pollution agreements depend on scientific credibility. CLRTAP, FCCC and other conventions have formed their own ways of achieving this. Within the CLRTAP, a system has evolved over the two decades since the original signing of the Convention in 1979. It consists today of a complex system of working groups, task forces and centres through which the scientific credibility and technical underpinning is formed. Within the system scientific evaluations, assessments and workshops have been important ingredients in the consensus forming process.

One of the main objectives of EMEP is to provide governments with information on deposition and concentration of air pollutants, as well as on the quantity and significance of long-range transmission of pollutants and transboundary fluxes. The programme includes four main elements: emission data, measurements of air and precipitation quality, atmospheric chemistry transport modelling and integrated assessment modelling.

The vision of EMEP is to be the main science-based and policy-driven instrument for international cooperation in atmospheric monitoring and modelling, emission inventories and projections, and integrated assessment to help solve transboundary air pollution problems in Europe. To achieve this EMEP seeks to develop: SCIENCE - EMEP establishes sound scientific evidence and provides guidance to underpin, develop and evaluate environmental policies; PARTNERSHIP - EMEP fosters international partnership to find solutions to environmental problems OPENNESS - EMEP encourages the open use of intellectual resources and products; SHARING - EMEP is transparent and shares information and expertise with research programmes, expert institutions, national and international organizations, and environmental agreements; ORGANIZATION - EMEP is organized to integrate information on emissions, environmental quality, effects and abatement options, and to provide the basis for solutions. The EMEP strategy can be found at <http://www.unece.org/env/emep/> while the complete programme is described at <http://www.emep.int/>.

Most countries in Europe have implemented monitoring programmes for air and precipitation chemistry and it is in the national interests to make sure that the data quality is as good as possible and comparable with similar observations over a larger geographical area. These measurements are in part just registrations of

ambient air quality, while others have more permanent objectives like understanding the causes of changes in the atmospheric composition including the effect of legislation and abatement measures. Due to the fact that air pollutants are advected across national boundaries EMEP has played the central role for international cooperation in this field in Europe the last 25 years. Priority has been put on meeting the national interest through bottom up structures and to increase the understanding and awareness on the national level and providing information being transparent and of high quality.

The EMEP monitoring data forms one of the basic legs on which EMEP rests, providing high quality data on the state of the environment, for model validation and national air quality assessments, national involvement and for independent validation of abatement measures. The data are essential for the technical underpinning of how the implementation of current air pollution legislation works, and for the work to revise and improve current policy. The EMEP observations are essential to establish a reliable picture of the air pollution situation in Europe; even in urban areas.

EMEP has in the past had substantial success in linking East and West together, now an important challenge for EMEP is to extend its activity eastwards into the new states of the former USSR so as to ensure a monitoring system that can help quantifying the fate of European pollution moving eastwards while new emissions are being added. Here EMEP has a particularly important role going beyond the political boundaries of the EU.

Following the adoption of the 1998 Protocols on Heavy Metals and Persistent Organic Pollutants and the 1999 Gothenburg Protocol to Abate Acidification, Eutrophication and Ground-level Ozone, the main priorities for the Convention are now a) the review and extension of existing protocols and b) the implementation of, and compliance with, existing agreements.

The EMEP data are used by a range of conventions and organisations and which include The Convention on Long-range Transboundary Air Pollution, especially through the Working Group on Effects and its International Cooperative Programmes (in particular the ICPs on Forests, Integrated Monitoring, Vegetation, Waters, Materials and Mapping); The World Meteorological Organization (WMO); The World Health Organization (WHO); The Arctic Monitoring and Assessment Programme (AMAP); The European Environment Agency (EEA); The Marine conventions (HELCOM, OSPARCOM, MEDPOL/Barcelona Convention); Intergovernmental Panel on Climate Change (IPCC) as well as Non-governmental organizations and National governments.

EMEP data are also widely used by the individual citizens and the atmospheric research community. While no exact overview can be provided it is assumed that EMEP data have been used in several thousands of papers and scientific reports and thus been fundamental for improved scientific understanding, policy formulation and public awareness in relation to transboundary air pollution issues.

The EMEP observing and modelling system serves the national interests of the member countries by allowing them to assess the regional component of their air

quality problems, and hence to arrive at cost-effective air pollution abatement strategies.

The EMEP data are also being increasingly more used by new groups of scientist like e.g. the Earth Observation Community and the Climate modelling community as there is a strong requirement for high quality observational data on atmospheric composition also for assessment of global change effects on, e.g., climate, chemical weather forecasting, air quality, and terrestrial and aquatic ecosystem. In this way, EMEP data can significantly support regulations and directives for sustainability of our environment in the widest sense. For instance, the effects of green house gases and aerosols on climate are similar in magnitude but of different sign, with the effect of aerosols one of the largest uncertainties (IPCC). It is thus obvious that the compounds regulated by the EMEP protocols also contribute to other air pollution issues ranging from urban air quality to climate change and associated effects (biodiversity etc.). Aerosols and tropospheric ozone are examples of parameters now being recognised as important for other issues than the original. Further, the EMEP region constitutes an important part of the global atmospheric environment and should contribute to relevant global monitoring activities (reference to be made to WMO-GAW and to GMES).

The new monitoring strategy considers the current strengths, weaknesses, opportunities and threats of the programme, including the level of reporting by Parties, new requirements from the users of data and recent technical developments. Special areas for discussion include the linking of scales (hemispheric-regional-local), improvements in the ability to estimate site-specific deposition and exposure are requested in order to assess the negative effects to ecosystems and human health; improvements in the cooperation within CLRTAP, i.e. between EMEP and WGE & their programmes, the availability of new techniques, such as data assimilation, the use of remote sensing techniques and flux monitoring which have the potential to significantly improve our capabilities.

## 2. Objectives of the monitoring programme

Observations are fundamental to the progress of our understanding of atmospheric chemistry, in the estimation of regional emissions of pollutants, in the follow-up of emission reduction policies and in the assessment of regional concentrations and deposition of pollutants. Observations are fundamental to the progress of our understanding of atmospheric chemistry.

Monitoring may be defined as measuring any parameter reflecting the air quality over an extended period for the purpose of public warning or tracking the temporal changes. Monitoring at several sites is also essential for describing spatial trends and understanding the climatology of the parameter. Of particular importance is the monitoring in relation to health and air quality standards, and the use of monitoring data to verify that emission reductions and other control measures have given the expected results. The latter purpose of monitoring is related to the establishment of a proper cause-effect relationship between emissions and the observed air quality through numerical models.

The purpose of the EMEP measurement programme is to provide necessary air concentration and deposition data for the model development and improvement of the understanding of large-scale atmospheric dispersion and deposition processes. While no strict priority between the various objectives has been given the monitoring serves to meet at least the following 4 (or 5, see comment below) objectives; as it allows to:

1. Assess regional concentrations and deposition of pollutants;
2. Providing the observational data for the validation of the EMEP models and improvement of the understanding of atmospheric chemical and physical processes for further development of model parameterisations.
3. Assess the success of international abatement strategies for atmospheric pollutants;
4. Provide information on the state of the environment to allow comparisons with effects thresholds indicating environmental sustainability (Critical Loads/Levels);
5. Provide input data required to assess the effects of atmospheric pollution on ecosystems, crops, materials and health.

The monitoring activities also serve to raise awareness in the participating countries and to provide relevant information to the public as well as to the atmospheric research community.

The main objective (Article 2) of the Gothenburg Protocol is to control and reduce emission of sulphur, nitrogen oxides, ammonia and volatile organic compounds that are caused by anthropogenic activities and are likely to cause adverse effects on human health, natural ecosystems, materials and crops, due to acidification, eutrophication or ground-level ozone as a result of long-range transboundary atmospheric transport, and to ensure, as far as possible, that in the long term and in a stepwise approach, taking into account advances in scientific knowledge, atmospheric depositions or concentrations do not exceed: critical loads of acidity, critical loads of nutrient nitrogen and critical levels of ozone.



In the future using monitoring data for estimating emissions might be one of the important elements for evaluating compliance with protocols and an important use for the data.

In addition to the scientific objectives mentioned, the national monitoring within EMEP is also instrumental in building up national competence in atmospheric chemistry and in understanding the environmental impact of atmospheric pollution. The active involvement by national experts has been essential for the success of EMEP and is expected to be so also in the future.

### 3. Requirements for meeting the objectives

In order to address the objectives specified above some general requirements to the monitoring activities are obvious. These are in a general form presented in this chapter, while specific requirements for individual topics can be found in chapter 7.

#### 3.1 Data quality

In order to meet the EMEP objectives, the monitoring methods must satisfy certain criteria. It is essential that the measurements reflect the air quality in a representative and that methods applied are consistent and reasonably free of artefacts. Long-term monitoring, in particular, requires that measurement series can be continued consistently for many years.

The purpose of the monitoring must be reflected in the measurement method. One purpose, that of warning the public, or assuring that the air quality is acceptable in relation to recommended air quality criteria, requires that concentrations at or above the level of the air quality limit is measured reproducibly and with an acceptable accuracy. This is the aim of most currently available commercial instrumentation as well as providing on-line access to data. If however the purpose is long-term monitoring for detection of trends, mean concentrations will carry more weight. These concentrations are generally much lower than the air quality limit values, but it is still important that they are measured correctly. In order to indicate trends over several (5-10) years, precision of individual measurements should be within  $\pm 10\%$ , and any systematic change over time should be less than the expected trend (1%/a). This could be hard to achieve with automatic monitors requiring periodic calibration. An example here is the experience from ozone monitoring in Europe. Only few sites have provided data of a satisfactory quality in order to assess the trends, and in particular missing information about calibrations and changes of instruments have the major problem. This is one example of the stricter requirements to EMEP data compared to networks mainly aiming at assessing exceedance to air quality guidelines, where such shifts obviously are less critical. The situation is better for chemical or gravimetric methods, but procedures and details needs to be rigorously followed and documented.

For assessing long-term trends, quality assurance, high precision and consistency of data are of the utmost importance. Measurement sites should not be subject to changes in surroundings, or to changes in instrumentation, unless the impact of changes is carefully evaluated and documented. Similarly, any changes in sampling and analysis procedures should be documented and evaluated, and sampling period and data completeness should meet the existing data quality objectives.

Experience has shown that measurements should be standardized as much as possible to obtain data that are comparable and of sufficient quality. In addition, quality assurance has to be carried out on both the national level and by the CCC to ensure satisfactory data quality. This applies to individual samples and to long-term aggregated values, such as seasonal or yearly mean values including trends.

It is particularly important to avoid systematic errors and undefined changes in the data quality over time, which may cause problems in trend analyses.

For the majority of the methods, the necessary quality assurance is facilitated by a combination of simple and robust sampling techniques with well-described sampling equipment, and use of synthetic control samples for the chemical analyses.

*What have we learnt about data quality from the assessment?*

### **3.2 Site criteria and representativity**

*(items 3.2 and 3.3 could be combined, as some of the problems are almost identical and the provided information partly redundant.)*

The representativity of a site is a highly relevant question for a measurement network such as EMEP. This can only be determined in relation to the purpose of the measurements. For EMEP the site must be positioned in such a way that the air quality and the precipitation is representative of a larger region. In order for the site to be representative, influences and contamination from local sources must be avoided. Obviously monitoring data from regions more directly affected by local emission sources may provide essential information in order to evaluate their relative contribution. It is not recommended that the existing EMEP sites are relocated to measure in such regions however, this is one way monitoring being performed in support of the EC Air Quality Directives may directly support EMEP. For parameters being subject to local emission sources at rural sites (like ammonia) monitoring should be complemented with a programme making it possible to assess their relative importance.

*The representativity/range of measurements of compounds x, y, z is something like X, Y, Z km (in Central/peripheral Europe) (state x, y, z, ..., X, Y, Z, ...)*

### **3.3 Spatial resolution**

To map concentrations and exposure on a European level, data are required at a resolution matching the spatial variability of the pollutant concerned and reflecting the resolution of the models being applied. With respect to slowly forming aerosol species, with low spatial variability, the current EMEP network density is sufficient in large parts of Europe, but insufficient in eastern and Mediterranean parts of the Continent. For more spatially variable species, there is a need for denser monitoring as well as integration of data from different programmes (e.g. for wet deposition and ozone measurements). For some substances, the variability is expected to be much larger than can be resolved by integrating even all available measurements, and the studies need to be supported by assessment of local scale variability, e.g. by passive samplers. Dry deposition monitoring is more demanding but should be made at a few sites only primarily to develop and test the inferential models. *(It is probably better to devote a separate chapter to dry deposition requirements, e.g. 3.3.2.)*

The (spatial) correlation between measured concentrations of air pollutants in Europe is highly anisotropic, and depends on the position and strength of emission

sources, wind directions, topography and the chemical and physical properties of the various pollutants. An earlier evaluation by the EMEP Bureau recommended a distance between the sites of 150–200 km in central parts of Europe, and about 300 km in areas which are mainly influenced by emissions more than 500 km away. Spatial covariance analyses of annual average concentration values give rather variable ranges of covariance from one year to another, but the range is usually 300–600 km (this text is old and should be adjusted to fit with the recommendations given in chapter 6). Recently, EMEP has changed its special resolution for CTM modelling from a grid size of 150x150 km<sup>2</sup> to 50x50 km<sup>2</sup>.

Networks for trend evaluation need to cover in a representative way the climatic zones across the domain. In order to understand the temporal evolution (trends) there is also a particular need for high quality measurements at sites with little influence from local or even regional emission sources.

### ***3.3.1 For improving air quality abatement in populated areas***

*The objective is here to stress the importance of having good boundary conditions when assessing local air quality. It is mentioned that CAFE uses EMEP models, which need validation using EMEP observations.*

#### **City Delta**

As a contribution to the modelling activities in the CAFE programme, an open model inter-comparison exercise is launched by the JRC-IES in collaboration with EMEP, IIASA and EUROTRAC to explore the changes in urban air quality predicted by different atmospheric chemistry-transport (CTM) dispersion models in response to changes in urban emissions. The range of response resulting from this model inter-comparison will be used in the cost-effectiveness analysis of CAFE with the aim to balance Europe-wide emission controls against local measures. The model inter-comparison focuses on ambient levels of particulate matter and ozone in urban areas. It addresses health-relevant matrices of exposure (e.g., long-term concentrations) to fine and coarse particles and ozone. It will enhance the co-operation between European modelling capabilities at urban and regional level and propose a common understanding of the benefits and limitations of regional emission control against local measures. The measurements of the EMEP network are essential for the validation of the calculation of the regional component of the urban air pollution problem.

### ***3.3.2 Ecosystem deposition or exposure***

Deposition of air pollutants is an important loss process for pollutants from the atmosphere and can cause severe damage to ecosystems. In order to develop effective emission reduction options and in order to monitor the progress in terms of reduced deposition levels a combination of modelling and measurement activities has been developed. In this procedure the measurements serve as independent checks on the modelled concentration and deposition fields. Wet deposition can be routinely monitored and provide spatial aggregated fluxes, this is not the case for dry deposition of gasses and particulate matter which is much more difficult to measure and impossible to provide area specific fluxes. The approach for deposition of sulphur, nitrogen ozone and base cations should

therefore based on a combination of detailed monitoring at some (super) sites providing process information, cheap methods applied in regions and models. Requirements for these sites are different for air quality sites with respect to measurement accuracy. Accuracy should be very high to measure the vertical concentration differences resulting in dry deposition estimates.

Already in 1997, the EMEP/WMO workshop on Monitoring Strategies (1997) (see [www.nilu.no/projects/ccc/aspenes98/](http://www.nilu.no/projects/ccc/aspenes98/)) produced a large number of conclusions and recommendations of relevance to this strategy as a whole. With respect to spatial resolution and representativity of measurements, there were many conclusions and recommendations reinforcing and adding to the recommendations listed in the previous paragraph: Effects-related monitoring is needed to define exposure-effect relationships at experimental sites, to provide high-resolution regional maps of exposure, and to help validate atmospheric transport models. The spatial coverage of sites has to be improved, especially in S and E Europe. POPs are inadequately measured. Base cation concentration measurements in air are needed. EMEP should aim to estimate dry deposition at a large number of sites by using inferential modelling and at a small number of sites by continuous measurements. The latter should be used primarily to develop and test inferential models. Techniques need to be developed to monitor cloud concentrations and deposition in order to estimate exposure to them. Monitoring at experimental sites is performed at an international level by ICPs, as well as by national effects assessment projects. These data, mostly relying on throughfall measurements in forests, should be used by EMEP, considering their lack of representativity (see Ch.5.1). Passive samplers should be applied to support high resolution models and measurement networks for substances with a high spatial variability. Concentration measurements and high resolution inferential modelling should be combined. Sub-grid evaluations are of importance in all regions including those where CL are exceeded. This is because of the scale dependence of critical load exceedances, Future changes in critical load exceedances and because they are necessary for dynamic modelling, independent from whether critical loads are presently exceeded.

### ***3.3.3 Intercontinental transport***

Intercontinental transport of pollutants and emissions from marine and atmospheric sources outside Europe influence the air pollution climate and thus also abatement policies within Europe. The importance of this transport varies between the different compounds due to differences in their atmospheric residence times. The background concentrations of ozone and particulate matter are of particular importance, since they may severely influence the control needs and strategies. Even the background deposition of sulphur and nitrogen is large enough to influence the control needs for the achievement of environmental objectives in Europe (critical loads). Background concentrations of ozone, particles as well as of sulphur and nitrogen compounds are also of importance for global policies on climate change.

In order to properly address the issue of intercontinental transport the measurement programme need further developments. This includes establishing

stations in areas not yet sufficiently covered. In particular it would be important to establish new sites in the far east of the EMEP region (Khazakstan etc.).

A modern network of for monitoring should integrate “multi purpose” networks ranging from urban (surface) to rural (transboundary surface (low local influence) and further with ITCT-type sites (surface, low local/regional influence) and global sites. Further new techniques like remote sensing from satellites and necessary calibration and validation data (surface and vertical profiles) should be utilised. Only by doing this can new challenges like “global change” where – the earth system and its biogeochemical cycles (fluxes, air-water-soil) be fully addressed.

For compounds with significant influence from intercontinental scale transport, improved understanding of the vertical gradients, as well as the free troposphere concentrations would be very valuable. We know that significant parts of the transport may occur above the PBL, particularly for cross-Atlantic transport from the US but also within the continent. One could therefore argue that some of the EMEP sites should also be running regular vertical ozone soundings or aircraft measurement programmes. Ozone soundings networks are presently in operation under other initiatives and data could be made available for EMEP use. While these data are of high relevance it remains an important question whether EMEP should in its monitoring strategy initiate such measurements as part of its own programme or make use of data being collected in other frameworks. This should in case be defined as a super site activity (as described elsewhere) and could be considered at a selection of sites at the western border of the European continent (like e.g. Mace Head) and perhaps also in central Europe.

The intercontinental transport issue can be addressed through the upgrading of the EMEP network to integrate and enhance the regional and global observational capacities in Europe of atmospheric trace constituents. These capacities include earth observation from satellites, remote sensing from the ground, in-situ measurements from sondes and aircraft including routine observations from commercial airliners, surface measurements including mountain peak and remote region sites. A collaborative structure needs to be reinforced to ensure that the information value is extracted from the observational capacity. Through such a collaborative structure also the choice of instrumentation and quality control and data assimilation schemes can be addressed. Protection of data owners' intellectual property rights is another issue that such a collaborative structure needs to handle.

### **3.4 Need for complementary data**

EMEP depends on the integration of observation data with the chemistry transport modelling and which allows for linking emissions with deposition fluxes or exposure levels. If the atmospheric physical and chemical processes and their reaction rates are sufficiently well known the models can be used for assign the benefit of introducing various abatement measures. This requires however that the interdependence of the various species atmospheric processes is known and can be properly numerically formulated. The validation of models thus requires the full spectrum of involved compounds both in air and precipitation to be measured. To illustrate this it is obvious that PM10 concentrations alone can't be modelled but needs to be estimated by considering the emissions of the various gaseous precursors, particles emitted from primary sources, their atmospheric

intermediates and finally their removal mechanisms. This calls for the measurement of the full spectre of compounds including all major inorganic compounds in gaseous as well as particulate form, their physical characterisation and precipitation chemistry routinely measured at a relatively large number of sites. Realising what is practicable an assembly of parameters is thus proposed to be mandatory at EMEP Core sites Level 1 and Core sites level 2 sites (is defined in Chapter 6).

### 3.5 Dry deposition

For pollutants that exchange rapidly with the ground surface, e.g. ozone, there are large vertical concentration gradients above the surface and being important since the exposure is considered in relation to air concentrations. Gradients are also significant for  $\text{HNO}_3$ ,  $\text{SO}_2$  and  $\text{NH}_3$ . The sampling height needs to be known when measurements are used for inferential modelling, i.e. calculating fluxes using deposition velocities or other resistance analogies. In the case of  $\text{NH}_3$ , the problem is particularly tricky since both upward and downward vertical gradients are possible. To limit the occurrence of upward  $\text{NH}_3$  gradients (related to emissions), monitoring should take place over grass without fertilisers or grazing. For slowly exchanging species, such as aerosol, this issue is not so important

Dry deposition is a major contributor to the impact of deposited sulphur and nitrogen species, as well as base cations. In large areas of Europe dry deposition is larger than wet deposition, but there is very rarely any validation of the calculated inputs. This is normally done either by atmospheric transport models directly, or using inferential modelling. Very few sites in Europe now continuously measure dry deposition allowing a full assessment of the model approaches, and further effort needs to be made in this area. EMEP should aim to estimate dry deposition at a limited number of sites by using flux based monitoring for comparison with inferential approaches.

The use of integrated assessment models are until now based on the assumption that there is a linear relationship between emission reductions and its impact. There are however many observations indicating that there are large deviations from this assumption, in particular for sulphur. Some of the processes which are responsible for these non-linearities are understood, although the scale of the effects and their consequence for policy development have not been evaluated over Europe. The known effects include important feedbacks between ambient concentrations of  $\text{SO}_2$  and  $\text{NH}_3$  on the dry deposition rates of both gases. For reduced nitrogen, important feedbacks occur at a very local scale, in which the large ambient  $\text{NH}_3$  concentrations suppress the local deposition rate. These effects, which are not detectable at the regional scale and are largely missing from the source–receptor modelling, studies introduce considerable uncertainty in the assessment of impacts of the deposited nitrogen. These effects lead to regional variability in the dry deposition rate, which has not been included in the current generation of source receptor models for Europe. Until recently, dry deposition monitoring methods have been expensive and only available from a limited number of research sites. The EUROTRAC2 – BIATEX2 community have however developed methodologies proven to be applicable also for long term monitoring at a low cost, provided the sites fulfil specific site criteria.

O<sub>3</sub> concentrations at canopy level are needed for AOT40. In the future policy might adopt the flux-based approach. In that case fluxes need to be measured in order to determine the stomatal uptake. The requirements are: measure fluxes of S, N and O<sub>3</sub> at a selected number of sites in different environmental pollution climates.

### 3.6 Supersites

*Why do we need supersites; high quality, high time resolution, large number of parameters allowing for interpreting mechanisms and the study of processes, model development, costly or difficult measurements,*

As described above a detailed description of atmospheric physical and chemical processes are required in order to evaluate and further develop atmospheric models linking emissions with deposition rates or exposure levels. Measurements allowing for describing the atmospheric mechanisms in detail are of special interest for this purpose, but it is obvious that such measurements cannot be established at a large number of sites due to financial or other practical reasons.

There is a need for more advanced measurements which in general are available only from research groups, and which seek to integrate state of the art measurements. This includes also the use of new techniques and platforms like flux based monitoring, remote sensing and earth observations. In order to meet these requirements a number of so-called supersites are to be established. Supersites could also include data from short-term research campaigns.

The supersites needs to fill several criteria, including meeting the Data Quality Objectives for all parameters measured and would include measurements being difficult to perform or being expensive. For some parameters even discontinuous data from individual measurement campaigns would be useful for process studies.

EMEP supersites will be nominated according to topics and would not necessarily need to cover all topics. It is advised that countries cooperate for cost sharing purposes. A number of so called "Large scale facilities" already exists and the further development of these into covering the wide range of EMEP relevant but highly advanced parameters is encouraged. A close cooperation with GAW on this issue is essential. (*PM supersites and GAW cooperation (CREATE).*)

Sites that are capable of representing regional or global concentrations should also be encouraged to develop supersite status; High quality EMEP stations should be encouraged to acquire supersite status by implementing extended measurement programmes or highly specialised programmes for a particular pollutant, documenting high quality and well trained technical staff, offering high quality calibrated data. Supersites will include unique locations being well representative of large regional areas or even global scale.

### 3.7 Accompanying meteorological data

As mentioned above, EMEP monitoring sites should be representative of a larger region and negligibly affected by local conditions. In practice, however, any location will to a certain extent be influenced of its local environment. A suite of



accompanying meteorological measurements at the EMEP sites could be useful for evaluating the local influence of the station. Such data could help reveal both any local emissions and the importance of local scale meteorology.

To evaluate the influence of local emissions, at least wind speed and direction would be needed. These data would also be relevant for studies of local meteorology. In addition, the thermal stability measured by the vertical temperature gradient (e.g. by the temperature difference at 2 m and 10 m) would be valuable for judging the mixing processes near the ground. Probably many of the present EMEP sites experience frequent situations when a shallow boundary layer is "decoupled" from the troposphere above, particularly during night-time inversions. During these periods, the stations are actually not regionally representative. Furthermore, such situations complicate the comparisons with regional scale models significantly, as the models have problems resolving these small-scale inversions.

In addition, local meteorological data could be used for direct evaluation of the other compounds observed at the site in various ways. Temperature and humidity can be used to estimate the stability of semi-volatile components as sNO<sub>3</sub>, sNH<sub>4</sub>, POP etc. Furthermore, knowledge of local wind speed and humidity is important for calculation of surface dry deposition and resuspension of dust and in other aspects.

*More text is being prepared describing other reasons for having met. observations.*

## **4. Strengths, weaknesses and opportunities of the EMEP measurement programme**

*This chapter summarizes the status of the EMEP measurement programme in relation to its objectives, and explains the need to improve the measurements and the network to meet the above-defined objectives. It is based on the information available at CCC, from the comparison of models with observations, interlaboratory test and field intercomparison activities and from information provided by the countries or as seen from their reported data.*

### **4.1 Current status and shortcomings**

The EMEP project organization is intended and set up to detect trends in pollutant concentrations and deposition. A network of sites is in operation, instrument requirements are specified and quality assurance and quality control systems are in place, but still need to be improved in most countries. It is essential that all Parties to the Convention comply with the current requirements of the measurement programme and their future revisions, including instrumentation and quality assurance and quality control systems. Today, the network does not function well, in particular in eastern and southern Europe.

Sulphur, nitrogen, ozone and VOCs are well characterised through observations in some parts of Europe. There is still a lack of observations however, and in particular in eastern and southern Europe.

Long time series of measurements in Europe are available for specific chemical constituents of aerosol, viz. for sulphate and to some extent for nitrate and some other species. The sulphate series go back to 1972, and although the equipment and the data quality have improved over the years, some of the data series are fully consistent over this long time period. Much less information is available for nitrate and ammonium, and these data are much more susceptible to sampling artifacts.

Some EMEP observations are of sufficient quality to derive trends in particular for sulphur and to some extent also for nitrogen compounds and ozone, but not really for VOCs since the time series for VOCs are short and the spatial coverage is still poor.

The performance of the laboratories is documented in the annual interlaboratory exercises. In general there has been a significant improvement in laboratory performance during the last years and at present, the performances are generally good for sulphate and nitrate in precipitation and for nitrogen dioxide in air. Some laboratories experience problems with the determination of ammonium and calcium. This may be due to contamination problems. The concentration levels for calcium in the test samples are low relative to the concentrations at EMEP sites in these countries. The determination of pH is also less accurate than for the other components, and the criteria for acceptable results may have to be relaxed somewhat for this component. However, laboratories are also reminded that pH measurements may need particular attention, checking the performance of electrodes with appropriate test solutions at regular intervals. The performance is strongly related to available equipment and resources.

Even if the laboratory performance is satisfactory, results at many EMEP sites are poor because inadequate sampling methods are used. The number of days with concentration values below the respective detection limits is given in the annexes to the annual EMEP data reports (e.g. EMEP/CCC Report 6/2002). However, these detection limits are generally lower than the typical deviation experienced in the interlaboratory tests. Therefore, it is likely that some of the reported air concentration data may not be satisfactory, even if the laboratory performance is acceptable.

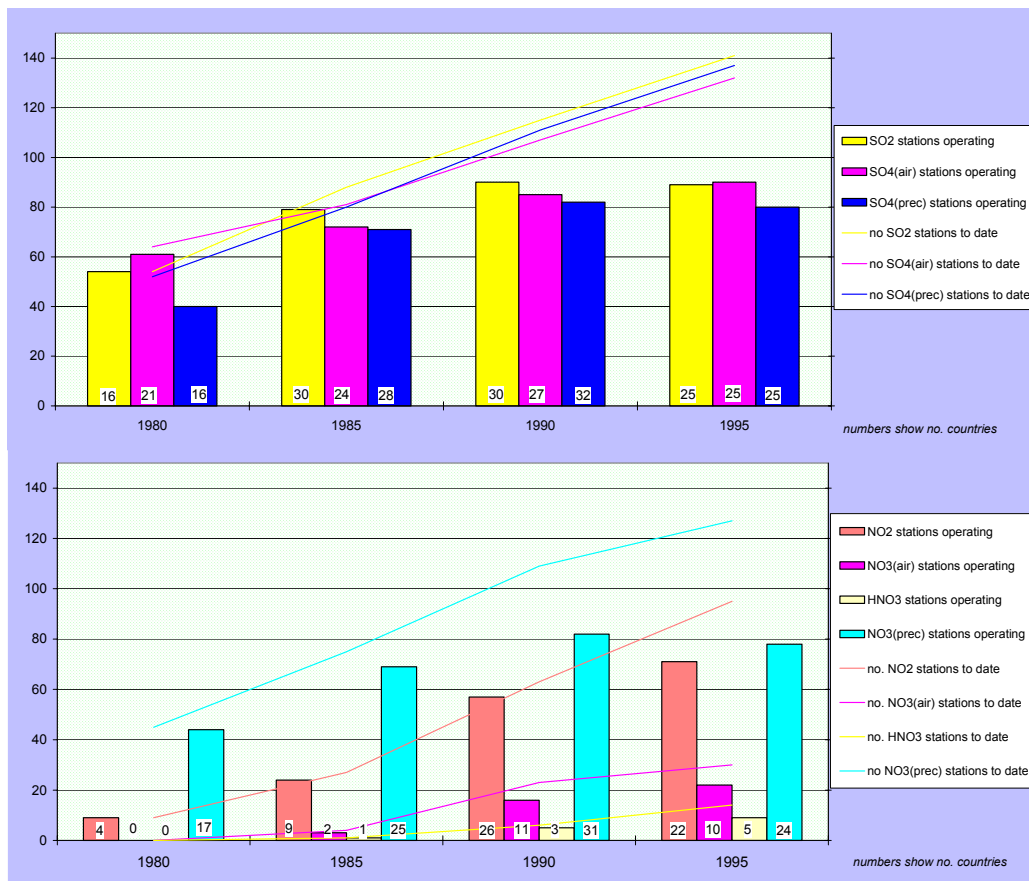
The laboratories in North Western- and Central Europe serving the sites in this area are also generally well equipped and perform satisfactorily in the laboratory intercomparisons. Many of these sites also have excellent long-term records, which are particularly valuable in trend analyses. France, Spain and Portugal apply methods for determining sulphur dioxide and nitrogen dioxide (mainly wet absorption solutions) that are not sensitive enough for the low concentrations usually experienced at the EMEP sites. In Spain and Portugal, measurements often deviate widely from model results. The ambient concentrations in these countries are to a large extent caused by indigenous emissions, and the concentration and deposition fields are not well described by the current EMEP models. This is due partly to the climatic conditions, and also to the high proportion of the emissions from large point sources.

The Balkan-peninsula has been subject to much turmoil and unstable political and economical conditions during the past ten years. Laboratories Croatia and Yugoslavia, as well as the former Yugoslavian Republic of Macedonia, have all struggled to maintain their network of measurement sites, but lack resources and equipment. Bulgaria has not been able to establish EMEP sites, and Romania has not been able to achieve satisfactory laboratory performance and has not reported data for recent years. All these countries have the necessary infrastructure to operate a network through their national hydrometeorological services, however. The same has to some extent been the case also for the three Baltic countries. However there have been great improvements and better conditions in the recent years.

Italy has failed to establish a proper national network of rural background stations for the EMEP programme. The two sites currently in operation are run by a research organization and the European Union's Joint Research Centre in Ispra. Both sites are located near these two research centres, and are not satisfying the siting criteria of rural background sites. Greece has established one EMEP site, but the laboratory performance has never been satisfactory. Turkey operates one EMEP site, with a good performance record, and is establishing two more sites: one closer to the Mediterranean Sea and one in the northeast. A new site has been established in Cyprus, and Malta has shown interest in joining the network. In Russia, Belarus, and the Ukraine the measurement networks are suffering because of the general deterioration in public services. It is also difficult to arrange the transport of samples from the sampling sites to the laboratory, which is well equipped with ion chromatographs. Consequently, there is only one monitoring site over the vast areas between the Baltic countries and the Urals.

The situation in the Balkans and in the Baltic countries calls for a general transfer of technology, including both equipment and training of personnel. Relatively modest investments are needed, but it is important that the national governments welcome such efforts, and that the facilities will also be used to serve national interests in addition to the countries' EMEP involvement. The strategy towards improving the situation in the Russian Federation, Belarus, and Ukraine is much less obvious. First priority should be given to the establishment of 3-5 additional properly located sampling sites, and to the operation of these sites, with proper transport of samples and materials. Then the central laboratory or laboratories must be given the necessary resources for the chemical analyses and for quality assurance. Technical cooperation between the three countries should be encouraged.

For the remaining countries, priority should be given to maintaining and documenting the quality of the existing time series. In some cases, improvements in sampling methods and chemical analyses may still be necessary. Nitrate and nitric acid, and ammonia and ammonium in ambient air should be measured in all the participating countries, in order to provide a satisfactory data basis for the evaluation of model performance for these components.



*We need text also for the other topics (Ox/VOC, HM, POPs, PM here)*

## 4.2 Methods and new developments

*The intention here is to review if we still are recommending proper methods, and further to identify new methods being available (flux monitoring, remote sensing/earth observations etc.).*

### 4.2.1 Traditional methods

At the time EMEP was established, the monitoring procedures developed during the OECD-project were prolonged. The OECD-project however did mainly focus on examining the atmospheric dynamics and focussed on interpreting episodes in a more physical sense. Only barely was the issue of maintaining long-term time series for decades addressed. While precipitation samples and sulphate in aerosols is fairly straight forward, the introduction of impregnated filters was a major invention. Most countries did however not change their methods until about 1988, resulting in very few consistent data series for SO<sub>2</sub> going further back in time (the Norwegian data goes back to 1978?).

The EMEP monitoring has always been based on employing fairly simple, robust and cost efficient methods. In an international programme where concentration and deposition level are compared across national boundaries and with many parties involved it is essential that the methods employed can be properly evaluated in terms of quality.

Below a brief evaluation of the appropriateness of the various candidate methods for air chemistry monitoring at Core sites level 1. Precipitation chemistry is not further discussed as the applied method can still be considered as appropriate for the purpose.

#### 4.2.1.1 Manual methods

- Filter pack samples have traditionally been the reference method for sampling inorganic major compounds in both gaseous form and in particles. Its advantages include being suitable for simultaneously sample both gases and particles (and which then are directly comparable), it can be combined with size segregated sampling of PM, in combination with advanced analytical instrumentation it is very reliable even at very low concentration levels and with short time resolution (daily). The performance can also easily be documented by intercomparisons (field or laboratory). The method is easy to employ, requires little training for field operators and typically not handling of the filter materials in field. The method is also relative cheap as a number of compounds can be determined at once. While the method is subject to artefacts in the separation of semi-volatile species (like HNO<sub>3</sub>/NO<sub>3</sub>, NH<sub>3</sub>/NH<sub>4</sub>), it can be combined with denuders to deliver artefact free results. Experience has however shown that in temperate regions, the gas to particle ratio as seen on impregnated filters do not deviate significantly from as determined with artefact free methods. The filter pack method is subject to some manual labour in preparation and chemical analysis and it also requires a pump and air volume recording.

- Passive samplers have a growing interest over the last years. While resembling many of the advantages of the filter-pack, this method is particularly interesting as it does not require electricity, pump or recording of air volume and can easily be employed in large numbers. It thus provides a relatively cheap alternative for gaseous compounds. Detection limits are however significantly higher and thus it requires a longer sampling time compared to the filter-pack method (typically weekly or bi-weekly). A number of samplers also do not follow the theoretical geometry and thus requires empirical scaling. Some of the methods are not freely available. Countries have experienced mixed success with passive samplers, and quality control issues are critical.

#### 4.2.1.2 *Monitors*

- The use of continuous recording monitors has had a rapid growth in the air quality networks. Their major advantages include high time resolution (~0.5h or less, typically 1 hour), rapid data acquisition and presentation and that also some quality control can be performed “on-line”. Monitors are thus particularly suited for critical limit exceedance assessment and the short time resolution may be useful in process studies or to detect temporary influence by local emission sources. Monitors neither require a chemical laboratory. Monitors do however generally give high detection limits, though “trace level monitors” are available. A monitor generally also gives information for one component only and only for gases. They are more difficult to intercompare and quality control for external bodies. It is also our experience that monitors tend to be overvalued by inexperienced users and that maintenance often is insufficient. This also may lead to costs being underestimated if operations are performed with required attention and maintenance. Monitors are also more unreliable at low concentration levels and that makes trend assessments over long time-spans more difficult compared with manual methods. Also monitors requires housing, electrical power, etc.
- Spectroscopic methods (DOAS) have also had a growing interest over the last years. Their advantages comprise some of those of the monitors given above, and in addition this method integrates over a long path and thus is less influenced by individual sources and features. DOAS instruments are also capable of determining several gaseous components at once. DOAS instruments are however subject to significant uncertainties which make them less attractive for application in EMEP. First of all they are difficult to calibrate and also the possible interference by other factors may be difficult to assess in most commercial systems available. DOAS instruments are also more difficult to intercompare with other measurements due to the different “siting criteria”. Experience has also shown that many commercial systems often provide low data capture and in some cases it is sold as a black box with poor possibility to assess quality.

As can be seen from the above, only the filter-pack method facilitates the simultaneous determination of all parameters requested at the core sites in EMEP (i.e. SO<sub>2</sub>, SO<sub>4</sub>, NH<sub>3</sub>/NH<sub>4</sub>, HNO/NO<sub>3</sub>, Na, Mg, Ca, K). Still, passive samplers (or other low cost methods) have a great potential for improving some aspects of

relevance for EMEP. These include site representativeness studies, studies in source areas, assessment of gas/particle distribution in combination with the filter pack method,. There are also recommendations from the ammonia WG (Sutton) which can be found in chapter 7. More.....?

#### **4.2.2 New methods**

##### **4.2.2.1 Flux based monitoring**

- Low cost methods for dry deposition monitoring have become available (COTAG). Specific site criteria required. Still an expert system?
- EMEP should perhaps recruit new sites satisfying the site requirements and having experienced staff (e.g. the Life sites (Erisman et al)). In addition some existing EMEP sites fulfilling the siting criteria and which have the required capabilities should be encouraged to establish flux measurements using the COTAG method.

##### **4.2.2.2 Earth observation**

- Here we could introduce earth observation systems and their current capabilities, their potential and their limitations. Further we should argue how important ground truth data are for calibration and validation. Data assimilation could also be discussed here.
- Application of new technologies like earth observation systems provides a two-way synergy as the new techniques can significantly improve our understanding and at the same time ground observations are essential for calibration and validation of remote sensing data. EMEP should make use of satellite and other remote sensing observations as well as surface based measurements in the future and contribute to the European part of “Global Monitoring for Environment and Security”, Integrated Global Observing Strategy (IGOS) or similar activities being established. Space-borne sensors have the ability to add information on key parameters with wide spatial coverage. While each of the individual observing systems delivers only incomplete and insufficient information, the combination of ground-based and space-borne observations will improve the retrieval of chemical composition at the regional scale. Satellite observations further connects the various network stations and provide the information on spatial variability for network data interpretation. Auxiliary data as provided by the networks and models increase the value of the retrieved parameters substantially, and continuous ground-truth efforts will allow to assess the quality of the satellite data products (CEOS, 2002). The retrieval of coherent aerosol products at the regional scale combining observations from multiple satellite and ground-based measurements is an important goal prior to a good understanding of processes.

### **4.3 Integration of observations and model calculations**

Here we could review the way we compare model estimates with observations and the associated limitations. Then we could argue that this may significantly improve our abilities if measurements are more directly linked to the modelling

activity. Finally we should outline the requirements (site density, parameters, time resolution, data availability).

Improve the integration of observations with modelling activities (application of data-assimilation technologies (incl. increased computational power)).

Modelling and data assimilation: Three-dimensional chemical transport models (CTMs) are an indispensable tool for comprehensive exploitation of information on atmospheric composition and state contained in the data of station networks (GAW, EMEP, EARLINET) and satellites. Using existing and new methods of four-dimensional chemical data assimilation improved evaluations can be made of observations and analysis of atmospheric composition and its changes over Europe. This includes the assessment of all relevant processes, i.e. anthropogenic and natural emissions, transport, chemical and physical transformation, cloud activity, and deposition.

More text required....



## 5. Cooperation with other programmes in Europe

*This chapter aims at presenting how EMEP seeks integrate its activity with monitoring being performed under other programmes and to stress the importance of EMEP monitoring. It is also important to open for the use of data from sites not officially appointed as EMEP sites in the technical work provided it fills the defined criteria.*

EMEP should strengthen the observational basis through intense interaction with other air quality networks in Europe. These networks include national networks and those of the Global Atmospheric Watch (GAW), AMAP, the Convention for the Protection of the Marine Environment of North-East Atlantic (OSPARCOM), the Convention on the Protection of the Marine Environment of the Baltic Sea Area (HELCOM), the International Cooperative Programmes (ICPs) and others. Such interaction should include data exchange, training procedures and quality assurance/quality control activities.

National authorities should be challenged so that all monitoring is considered together to ensure that the demands imposed by EU, CLRTAP and other international bodies are served in a cost-effective way. If the revision of national monitoring networks is dealt with in such a comprehensive way, modifications and even cost reductions may be identified without compromising the value and strength of the information.

### 5.1 The CLRTAP – Working group on Effects and its International Cooperative Programmes (ICPs)

The 1997 EMEP/WMO Workshop at Aspenäs (cited in Ch. 3.3.2) recommended that "... EMEP should strengthen the observational basis by taking advantage of other air quality networks in Europe, e.g. (...) International Co-operative Programmes (ICPs)". There cooperation between the various effect programmes and EMEP is close and as far as possible trying to make use of common methodologies, site sharing etc. A number of EMEP sites thus directly supports the effect work and vice-versa. The use of ICP observation data by EMEP can still be improved.

- The ICP-Forest's Level II programme comprises bulk/wet deposition measurements and throughfall/stemflow measurements with canopy budget modelling at several hundred sites. In addition, inferential models have been applied by the Forest intensive Monitoring Coordinating Institute (FIMCI) at many sites (see <http://www.icp-forests.org/Programme.htm#FIMCI>).
- Within ICP-Vegetation's monitoring programme heavy metals bulk/wet deposition rates and ozone concentrations are measured (see <http://icpvegetation.ceh.ac.uk/>).
- ICP-Integrated Monitoring performs bulk deposition and throughfall measurements at all of its sites; canopy budget models or inferential models are not regularly applied (see <http://www.unece.org/env/wge/im.htm>).

- ICP Modelling and Mapping (<http://www.icpmapping.org/>) does not have a formally installed deposition network. However, national measurement and modelling networks are applied by National Focal Centres, especially for the mapping of base cation deposition rates needed for critical loads assessment, and for mapping critical loads exceedances at a national scale.

## 5.2 HELCOM

The Helsinki Commission, or HELCOM, works to protect the marine environment of the Baltic Sea from all sources of pollution through intergovernmental co-operation between Denmark, Estonia, the European Community, Finland, Germany, Latvia, Lithuania, Poland, Russia and Sweden. HELCOM is the governing body of the "Convention on the Protection of the Marine Environment of the Baltic Sea Area" - more usually known as the Helsinki Convention. The present contracting parties to HELCOM are Denmark, Estonia, European Community, Finland, Germany, Latvia, Lithuania, Poland, Russia and Sweden.

Atmospheric emissions and atmospheric deposition into the sea are mainly monitored under HELCOM's Pollution Load Compilation Programmes (PLC-Air). A close relationship between EMEP and HELCOM has been established which includes use of the EMEP infrastructure for monitoring data reporting as well as numerical CTM (also emissions?). All data (?) reported in support of HELCOM are thus available also for EMEP use.

Measurements of nitrogen compounds in air are available from about 16 sites, heavy metals is measured at 11 sites, while lindane is measured at three sites. All HELCOM sites are fully integrated with the EMEP network and provides a very good example on how national interest could be met through coordination of measurement activities.

Does HELCOM also have voluntary parameters like specified for CAMP below?  
Does HELCOM have a similar siting criteria as CAMP described below?

## 5.3 OSPARCOM

The Convention for the Protection of the Marine Environment of the North-East Atlantic ("OSPAR Convention") was opened for signature at the Ministerial Meeting of the Oslo and Paris Commissions in Paris on 22 September 1992. The Convention has been signed and ratified by all of the Contracting Parties to the Oslo or Paris Conventions (Belgium, Denmark, the Commission of the European Communities, Finland, France, Germany, Iceland, Ireland, the Netherlands, Norway, Portugal, Spain, Sweden and the United Kingdom of Great Britain and Northern Ireland) and by Luxembourg and Switzerland.

OSPARCOM Comprehensive Atmospheric Monitoring Programme (CAMP) lists mandatory and voluntary components to be observed at background stations not more than 10km from the coastline. These are:

	Manadatory	Voluntary
<b>Precipitation</b>	As, Cd, Cr, Cu, Pb, Hg, Ni, Zn, $\gamma$ -HCH, NH <sub>4</sub> , NO <sub>3</sub>	PCB 28,52,101,118,138,153,180 Phenanthrene, anthracene, flouranthene, pyrene, benzo(a)anthracene, chrysene, benzo(a)pyrene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene
<b>Airborne</b>	NO <sub>2</sub> , HNO <sub>3</sub> , NH <sub>3</sub> , NH <sub>4</sub> , NO <sub>3</sub>	As, Cd, Cr, Cu, Pb, Hg, Ni, Zn, $\gamma$ -HCH, PCB 28,52,101,118,138,153,180, Phenanthrene, anthracene, flouranthene, pyrene, benzo(a)anthracene, chrysene, benzo(a)pyrene, benzo(ghi)perylene, indeno(1,2,3-cd)pyrene, NO

In 1999, twenty-one stations reported data, most of these report heavy metals in precipitation while a number of these also report nitrogen concentrations in precipitation.  $\gamma$ -HCH was only reported from three stations. There is a large overlap with EMEP sites. CAMP currently do not have a policy to put all data freely accessible on the internet, but the data from sites reported also for EMEP will be available. NILU act as the data consultant for storing the CAMP data, but has no responsibilities for quality assurance activities like in EMEP. All data flow is according to EMEP infrastructure (file formats etc) however.

#### 5.4 MEDPOL

*This description of the status of the MEDPOL activities may need updating.*

National Coordinators for MEDPOL (Programme for the Assessment and Control of Pollution in the Mediterranean Region, Phase III) are appointed and met in 2001. The programme deals mainly with measurements of various pollutants in marine biota and sediments, in effluents and direct discharges to the sea as well as eutrophication parameters (N and P components) in sea water. There are also some activities to measure trace metals (as well as N and P) in precipitation and in air (on filters of high volume samplers) to assess the atmospheric input of these pollutants into the Mediterranean Sea. Some reports seems to be available. At the present time there are several MED POL monitoring stations in Slovenia, Croatia, Turkey, Israel, Italy and France. A number of these stations also serve as EMEP stations.

In a MEDPOL publication which was being prepared in 2001 the following measurement results seems to have been presented:

- Turkey,
  - south of the Mediterranean coast, concentrations of Al, Na, Ca, Fe, Mn, Pb, Zn and Cd in air (high volume sampling) for the period August 1991 □ December 1992 and January 1996, December 1998.
  - Turkey, south of the Mediterranean coast, Central Turkey (EMEP station) and the Black Sea coast; concentrations of Na, Ca, K, Mg,

Al, Pb, Cu, Cd, Ni, V, Cr, Fe, Zn, SO<sub>4</sub>, NO<sub>3</sub>, Cl, NH<sub>4</sub> and pH in precipitation (wet only) for 1992, 1998.

- France, Corsica, bulk concentrations of Al, Fe, Pb, Zn, and Cd for March 1995, March 1997 and May 1999-November 2000.
- Israel, 3 stations; concentrations of TSP, Pb, Cd, Cu, Zn, Cr, Mn, Fe, Al, Ca and Na in air (high volume sampling) for October 1994 to December 1997 and concentrations of PO<sub>4</sub>, NO<sub>3</sub>, NO<sub>2</sub>, NH<sub>4</sub>, Cl, SO<sub>4</sub>, Ca, Na and pH in precipitation for 1992/1995, March 1998.
- Croatia, several stations (EMEP stations), bulk (sometimes wet only) concentrations of HCO<sub>3</sub>, Cl, NH<sub>4</sub>, SO<sub>4</sub>, NO<sub>3</sub>, Na, K, Ca, Mg and pH for 1981-1995.

Most of these countries participate in EMEP. Unfortunately no raw data from most of these stations have ever been reported to the MEDPOL office in Athens, Greece or to WMO. Formats for data submission have however been discussed but no information about the outcome of this is available.

## 5.5 AMAP

AMAP's current objective is "providing reliable and sufficient information on the status of, and threats to, the Arctic environment, and providing scientific advice on actions to be taken in order to support Arctic governments in their efforts to take remedial and preventive actions relating to contaminants".

The monitoring work within AMAP is based, as far as possible, on existing national and international monitoring and research programs, aiming to harmonize these to the extent possible. Each country defines its own National Implementation Plan (NIP) to meet the AMAP monitoring objectives. Monitoring projects are carried out within each of the participating countries and across borders under bilateral and multilateral cooperations. Efforts continue to be made to harmonize existing and new programs with respect to methodologies and quality assurance.

AMAP's assessments are based to a large extent on information and results from recent (largely unpublished) monitoring and research work. Data from such activities are compiled together with routine monitoring data within AMAP Thematic Data Centres (TDCs). Data are made available from the TDCs to scientists engaged in AMAP assessments under strict conditions that protect the rights of data originators. These conditions are described in AMAP's data policy documentation. Consideration of quality assurance issues is an integral component of the AMAP monitoring and assessment process.

AMAP Thematic Data Centres have been established to meet the following objectives:

- to provide access to data from recent monitoring and research activities conducted as part of the AMAP NIPs;

- to provide a means to ensure that data are treated in a consistent manner, undergo uniform statistical analysis, etc., including application of objective quality assurance procedures;
- to begin the process of establishing a long-term archive of Arctic-relevant monitoring data, for use in future assessments of, e.g. temporal trends, etc.; and
- to meet the terms of reference of the Ministerial declarations, charging AMAP with establishing databases of sources, types, and levels of radionuclide contamination of the atmospheric, aquatic and terrestrial environments of the Arctic and northern areas.

The TDC for atmospheric contaminants is operated by the Norwegian Institute for Air Research (NILU) and employs EMEP infrastructure and formats for its data flow.

All European data reported to AMAP is fully integrated with the EMEP network (?)

## **5.6 Monitoring in support of the EC Air Quality Framework Directive**

*EU regulatory monitoring mainly considers if air quality standards are exceeded, for public warning etc. It is based on monitoring in regions where people live. Monitoring is also required in rural areas and it would be an advantage if this was closely integrated with the EMEP work nationally. Data quality is an important issue here as the methodologies applied are less suited for meeting the EMEP objectives (e.g. precision and comparability at low concentration level (described elsewhere)).*

### **The European Community - Air Quality Framework Directive**

The EC aim has been to develop an overall strategy through the setting of long-term air quality objectives. A series of Directives has been introduced to control levels of certain pollutants and to monitor their concentrations in the air. In 1996, the Environment Council adopted Framework Directive 96/62/EC on ambient air quality assessment and management. This Directive covers the revision of previously existing legislation and the introduction of new air quality standards for previously unregulated air pollutants, setting the timetable for the development of daughter directives on a range of pollutants. The list of atmospheric pollutants to be considered includes sulphur dioxide, nitrogen dioxide, particulate matter, lead and ozone – pollutants governed by already existing ambient air quality objectives- and benzene, carbon monoxide, poly-aromatic hydrocarbons, cadmium, arsenic, nickel and mercury.

A Community-wide procedure for the exchange of information and data on ambient air quality in the European Community is established by the Council Decision 97/101/EC. The decision introduces a reciprocal exchange of information and data relating to the networks and stations set up in the Member States to measure air pollution and the air quality measurements taken by those stations. The information exchange relates to the pollutants listed in Annex I of Directive 96/62/EC

The Framework Directive was followed by daughter directives, which will set the numerical limit values, or in the case of ozone, target values for each of the identified pollutants. Besides setting air quality limit and alert thresholds, the objectives of the daughter directives are to harmonize monitoring strategies, measuring methods, calibration and quality assessment methods to arrive at comparable measurements throughout the EU and to provide for good public information.

The Framework Directive, as well as its Daughter Directives, requires the assessment of the ambient air quality existing in Member States on the basis of common methods and criteria

EU has established a Community-wide procedure for the exchange of information and data on ambient air quality in the European Union by the Council Decision 97/101/EC of 27 January 1997 as amended by Commission Decision 2001/752/EC. It applies to:

- detailed information on networks and stations describing the air pollution monitoring networks and stations operating in the Member States,
- measurements of air quality obtained from stations: the exchange covers data calculated from measurements of air pollution by stations in the Member States.

### **Clean Air for Europe**

*We also need a description of the Clean Air for Europe (CAFE) and the relationship between EMEP and the AQSG and TAG.*

*Strong and effective links with the CLRTAP is seen as crucial in order to add real value to policy-making, to avoid duplication of effort, to exploit synergies for resource efficiency purposes, but also to maintain the credibility of the EC as a Party of the Convention.*

*A Technical analysis group has been set up to help ensure the technical analysis work is well coordinated between CAFE and CLRTAP. The Executive Body of the CLRTAP participates in the TAG and a co-ordination group between the two programmes has been established.*

### **EEA (maybe combined with CAFE and EU-AQFD-sub chapter above)**

EIONET is a collaborative network of the European Environment Agency and its Member Countries, connecting National Focal Points in the EU and accession countries, European Topic Centres, National Reference Centres, and Main Component Elements. These organisations jointly provide the information that is used for making decisions for improving the state of environment in Europe and making EU policies more effective.

AirBase is the air quality information system of the EEA. It contains a database carrying information submitted by participating countries from across Europe. This information comprises of air quality data for a selection of stations and a number of components, and meta information on air quality monitoring networks

and stations. The current database contains information which was transmitted by EIONET partner states in the framework of 'Exchange of Information' (EoI) Decisions, or as part of EuroAirnet. The AirBase information system is developed and maintained by the European Topic Centre on Air Quality on behalf of the European Environment Agency.

Monitoring requirements as specified by the EC directives;

These are the monitoring obligations in the European directive 1999/30/CE (SO<sub>x</sub>, NO<sub>x</sub>, Pm<sub>10</sub>, Pb)

winter mean or annual mean of SO<sub>x</sub> concentration > 12 µg/m<sup>3</sup> : 1 station for 20 000 km<sup>2</sup>

winter mean or annual mean of SO<sub>x</sub> concentration > 8 µg but < 12 µg/m<sup>3</sup> : 1 station for 40 000 km<sup>2</sup>

annual mean of NO<sub>x</sub> concentration > 24 µg/m<sup>3</sup> : 1 station for 20 000 km<sup>2</sup>

annual mean of NO<sub>x</sub> concentration > 19,5 µg but < 24 µg/m<sup>3</sup> : 1 station for 40 000 km<sup>2</sup>

These are the monitoring obligations in the European directive 2002/3/CE (O<sub>3</sub>) says :

on average 1 station for 50 000 km<sup>2</sup> in the country but 1 station for 25 000 km<sup>2</sup> if the topography is complex.

It can drop to 1 station for 100 000 km<sup>2</sup> if 8h daily mean < 120 µg/m<sup>3</sup> and AOT40 < 6 000 µg.h/m<sup>3</sup>.

At least 50% of stations monitoring O<sub>3</sub>, should too monitor NO<sub>x</sub>.

One station have to monitor O<sub>3</sub> precursors (VOC)

## **5.7 World Meteorological Organisation – Global Atmosphere Watch (GAW)**

The purpose and long term objective of the GAW is to provide data and other information on the atmospheric chemical composition and related physical characteristics of the background atmosphere from all parts of the globe required to improve the understanding of the behaviour of the atmosphere and its interactions with the oceans and the biosphere, and to enable predictions of the future states of the Earth system. The objectives of GAW are thus in part identical with those of EMEP. Also with respect to parameters being monitored a there is a great overlap with those being monitored in EMEP. Further, many of the sites are associated with both networks.

GAW aims to be organized to the extent feasible, in cooperation with other international programmes. A close cooperation has been established between the EMEP and GAW both on an administrative level as well as on a technical level. EMEP makes use of the recommendations given by the GAW Scientific advisory Groups (and also has a representative in the SAG on Precipitation Chemistry.), and the technical manuals are identical or compatible between the programmes. Also with respect to Quality Assurance activities cooperation is in place. The EMEP Task Force on Measurements and Modelling (TFMM) is co-chaired by the WMO Atmospheric Research and Environment Programme (AREP) Environment Division secretariat. The development of the EMEP monitoring strategy for particulate matter also was based on the joint EMEP-GAW workshop in Interlaken 1999 and later discussions at the TFMM.

Still efforts could be made on facilitating a further harmonisation between the two networks. In particular in relation to selection of joint supersites there is a good potential for serving the needs of both networks. Regional sites operated in support of GAW should be encouraged to also report their data to EMEP. Duplication of efforts between EMEP and GAW should however be avoided, and in particular in relation to data submission and storage.

There are nine major types of measurement parameters in the GAW programme, of these 5 are also covered in the EMEP programme, namely Ozone, Precipitation chemistry, chemical and physical properties of aerosols (including optical depth), Reactive gases (SO<sub>2</sub>, NO<sub>x</sub> and VOC), POPs and Heavy metals (greenhouse gases, solar radiation and Radionuclides are not part of the EMEP programme. Both programmes recommend meteorological parameters to be monitored (none has so far not requested met. data to be submitted to the database).

### **5.8 National and EU funded research projects**

EU-DG Research (FP4 and FP5) funded research as well as EUROTRAC and EUROTRAC2 has been essential for establishing the current scientific understanding of atmospheric processes. These range from controlled laboratory experiments to large-scale measurement campaigns. Without these developments the technical capabilities of EMEP would be significantly less developed. It is therefore essential for EMEP that also future research activities are made which can support the requirements. EMEP should thus continue to exploit the scientific results from national and international research projects. In particular short-term campaigns comprising advanced and comprehensive measurement programmes are important.



## 6. Definition of the level system and classification of sites

*This chapter aims at presenting the level system in the new strategy and points to how we by harmonising monitoring efforts can secure sufficient data for EMEP.*

The new monitoring strategy will be based on a "level" approach where sites undertake monitoring at different ambition levels with respect to site densities and number of parameters being monitored. This approach will facilitate the use of other relevant sources of information as presented in chapter 5.

The revised EMEP monitoring strategy thus aims at assuring adequate data provision by combining resources from four major sources. These are

- a) official (national) budgets in support of EMEP,
- b) data collected by other bodies of the CLRTAP or other Conventions (WGE, HELCOM, OSPARCOM, AMAP...) available for mutual use,
- c) data available from national monitoring activities in support of the EC-Air Quality Directives, and
- d) the scientific community including national and international research and monitoring programmes (WMO-GAW, DG-RESEARCH ++).

The monitoring strategy introduces the term "**EMEP Core sites**" representing the minimum monitoring requirements (the mandatory programme). Measurements at EMEP core sites are distinguished between so called level 1 sites comprising a relatively large number of sites (>125) with a complete programme covering major inorganic compounds in air and precipitation, ozone and particulate matter mass, and level 2 sites which comprise more technically or economically demanding measurements which can not be implemented at all EMEP sites.

The required minimum number of Level 1 and level 2 sites is defined for individual countries (level 1) and for regions (level 2). Level 2 sites are also different between the various topics EMEP considers (Acidification and Eutrophication, Photochemical oxidants, Heavy Metals, Persistent Organic Pollutants and particulate matter). There is a need for regional cooperation in providing sufficient number of core sites level 2 in order to minimise costs and a cost sharing option is proposed. Monitoring performed in support of the marine conventions (HELCOM, OSPARCOM and AMAP) will contribute significantly to level 2 sites for heavy metals and for POPs.

EMEP also needs highly specialised and demanding measurement generally only available from state of the art monitoring sites either continuously operated or data from research experiments (refer to Chapter 3.7).

Finally, EMEP will make use of relevant data from other networks either from the CLRTAP itself (Working Group of Effects) and from the monitoring activities performed under the Air Quality Directives of the European Union.

The following Criteria for the various site levels have been defined;

**Core sites level 1;** A minimum site density of 1 site per 50.000 km<sup>2</sup>, higher resolution if complex terrain, all countries with a geographical area exceeding xxx km<sup>2</sup> are required to operate at least one level 1 site. Level 1 would be mandatory for all Parties. This should ensure participation of a large number of sites with a main objective to provide spatial and temporal trends and will require continuous sampling.

The objective of the EMEP Core sites is to support the evaluation of trends and validation of models. These objectives puts requirements the network like good geographical coverage as well as long-term operation. In addition the Core sites involve all EMEP parties and ensure that there is a permanent and operational activity that links all EMEP countries and the Centres together. The monitoring thus serves as one of the most important ways countries can actively take part in the EMEP work, as well as serving national interest and needs in particular.

**Core sites level 2;** A minimum site density of 1 site per 100.000 km<sup>2</sup>, density will vary between topics depending on region (photooxidants and particles should have a higher site density in the South, while Acidification and POPs should have a higher density towards North and East). Regional cooperation towards cost sharing is encouraged. Level 2 would cover advanced measurements at selected sites, which would be more expensive or technically demanding. The data should be more process oriented and will also provide basis for the analysis of spatial and temporal trends.

Core sites level 2 serves the same objectives as level 1 sites, but have a monitoring programme being more advanced than what is realistic to expect at all level 1 sites.

**Level 3 sites;** would relate to research data aiming at process studies or very demanding methodologies, including data from sources external to EMEP (ref. chapter 3.6).

Level 2 and level 3 sites will be nominated as "EMEP supersites", as this would be an important motivation factor and provides appropriate recognition to the data providers. Supersites could be topic specific and would not need to cover all substances. The geographic distribution of level 2 and 3 sites should provide a good regional coverage. Super sites should be encouraged to support both EMEP as well as GAW.

See the separate excel file for tables;

Table "**level table**" summerises the monitoring requirements for the individual levels of sites.

Table "**sites per country**" presents the minimum monitoring obligations for the individual countries at the different levels

Table "**sites per region**" presents the minimum monitoring obligations for the individual countries at the different levels

There is no rigorous verification of the national implementation of the monitoring requirements as embedded in the CLRTAP and in the ensuing, and history shows that the rather informal implementation of national monitoring within EMEP has left data coverage and data comparability at a level which is less than satisfactory in many places even after more than 20 years of operation. The new monitoring strategy will point out in a rigorous manner that the national commitment as a party to CLRTAP to carry out national monitoring in line with the minimum requirements described here, must be honoured.

The activity defined for EMEP core sites reflects the minimum requirements for monitoring to be performed in order to underpin the traditional objectives of EMEP. It should further be stressed that new priorities like improved spatial resolution and site specific deposition, linking of scales (local vs. regional vs. global scale), flux based monitoring, model improvement etc, cannot be supported by the core sites alone.

EMEP has in the past and will also in the future build on data available from other bodies of the Convention, and from other national and international legislation. In most countries these resources are well coordinated nationally. Most measurement sites operated through HELCOM, OSPARCOM and AMAP are excellent examples of this, and they share the same organizational set-up with respect to technical solutions. These are thus candidates to serve as joint Core sites Level 2 for e.g. POPs and HM. (UNEP could be an important partner for joint funding of POP monitoring activities in the future)

EMEP will further complement its monitoring requirements by using data available from the national monitoring performed in support of European Community Air Quality Directives which can improve the data coverage significantly for a few compounds. It should be noted that the networks operated under the air quality directives of the European Union have their main focus on populated areas to provide ambient concentrations for comparison with limit and target values for the protection of human health. However, there are also limit and target values for the protection of ecosystems and vegetation ( $\text{NO}_x$ ;  $\text{SO}_2$ ;  $\text{O}_3$ ), which require measurements and assessment on a regional scale. Further harmonisation of the rural sites between EMEP and the sites operated under the air quality directives is important, and these data can support improvements of the spatial resolution and the linking of scales. The quality control and quality assurance of monitoring under the EU air quality directives is, however, an issue here.

The EMEP Core sites Level 1 and 2 should provide the necessary data also for the monitoring requirements within the EC on regional scale for CTM support (i.e. chemical composition and deposition fluxes).

### *Need for campaigns*

EMEP has arranged a number of campaigns in order to provide data being to expensive or demanding to have as part of the continuous programme. Examples here are the “Pilot measurements of nitrogen containing species in air” in 1993-1994, “the OC/OC-campaign” during 2002-2003, others....

Such campaigns provide useful insight and information and should be considered also in the future as a necessary complement to the continuous sampling.

## 7. Specific requirements for individual topics

*The ambition here is to outline monitoring requirements for individual topics in a relatively detailed sense (but not parameters in detail). This means that this is the place where we would indicate the parameters, the required site densities and argue for the required super site activities.*

### 7.1 Acidification and Eutrophication

#### 7.1.1 Introduction;

Acidification results from long-term deposition of sulphur and nitrogen species in ecosystems. Deposition of base cations adds buffering capacity to the soils. During the recent years it has been realised that sea salt episodes play a very important role in surface water acidification through the “sea-salt effect”. Eutrophication result from the increased deposition of nutrients (nitrogen compounds, phosphorous and base cations. Ammonia and nitrogen oxides are key components in the air pollution strategies and their role for acidification and eutrophication needs thorough evaluation. Fossil fuel combustion, mineral fertilizers and livestock manures all provide major sources of fixed reactive nitrogen (N). This leads to a cascade of effects as the N is transported and transformed through the environment. Excess nitrogen deposition also may increase the nitrate concentrations in surface water, thus also directly contributing to acidification. Dealing with the whole N cycle is clearly a major challenge. The aspects of acidification and Eutrophication are closely linked in terms of atmospheric chemistry and deposition as well as effects in the ecosystems. The same holds true when it comes to developing abatement policies. These are currently widely separated, with for example, the EU Nitrates Directive dealing with eutrophication of ground and fresh waters from agriculture, the UNECE Convention on Long-Range Transboundary Air Pollution (CLRTAP) and the EU National Emissions Ceilings (NEC) Directive dealing with regional air pollution (acidification, eutrophication and photochemical oxidants), and the Framework Convention on Climate Change (FCCC) dealing with emissions of nitrous oxide as a greenhouse gas.

Measuring and assessing the long-term deposition of atmospheric sulphur and nitrogen (oxidized and reduced) compounds and of base cations and sea-salt compounds are the most important issues for acidification and eutrophication.

#### 7.1.2 Current situation and further needs

number of sites, areas with few sites, missing parameters (N-compounds, base cations, lack of flux data, non.linearities.....

Precipitation sampling and analysis is still important as it serves as the main removal mechanism over large regions and which can be determined with high reliability. Samples should be taken daily at all sites which improves the data quality as well as make it possible to asses the associated air mass trajectories.

Sulphur, nitrogen, base cations and sea-salts in air needs to be monitored with the same time resolution as precipitation. Daily air samples are required with a similar

site density in order to assess the relation between emission changes and the observed trends by allowing for linking the observation with air mass origin.

Daily air concentration measurements combined with precipitation chemistry measurements allows for studies of scavenging efficiencies, as well as an improved basis for interpreting the concentrations of ions in precipitation (detect contamination).

To quantify deposition, wet deposition and air concentrations need to be monitored with a site density of one site per 50 000 km<sup>2</sup>, but with higher density in regions with complex terrain or large gradients.

Monitoring of compounds related to acidification and eutrophication for assessments of trends and of effects on ecosystems and materials can be based on weekly samples, data from WGE should also be used but quality assurance is required between different monitoring programmes to integrate data sets;

Gaseous and particulate nitrogen species need to be measured separately at more sites to assess the transport distance of nitrogen species. The gaseous and particulate fractions of NH<sub>3</sub>/NH<sub>4</sub> and HNO<sub>3</sub>/NO<sub>3</sub> should be reported separately from sites employing the reference method (realizing that the gas/particle distribution is subject to artefact). This should be combined with low cost methods for the gaseous fraction with a monthly time resolution. At Core sites level 2 the gas particle distribution should be measured using denuder/filter pack methods. Measurements of NH<sub>3</sub> and HNO<sub>3</sub> concentrations on an hourly basis should be initiated at a limited number of level 3 sites.

There is a need for a limited number of sites also monitoring dry deposition fluxes of sulphur and nitrogen species. These will assist in assessing non-linear effects in deposition fluxes compared to changes in ambient concentrations. COTAG method .....

Low cost methods for NH<sub>3</sub> (Suttons method) and the use of passive samplers should be employed in regions with significant local emission rates (Northern France, The Netherlands, UK, Ireland, Denmark ...). Such networks may need a significantly higher site density compared with level 1 or level 2 sites and could be considered as a level 3 activity.

## **7.2 Photochemical oxidants**

### **7.2.1 Introduction**

Ozone and other photochemical oxidants have negative effects on health, vegetation and materials, are formed from NO<sub>x</sub> and VOC and produced in photochemical reactions. more text....?

The monitoring of ozone and VOC in EMEP is founded on several specific objectives and is limited by a number of restrictions (economical, practical, historical etc.) and at the same time has to meet specified quality standards. Thus, the design of the monitoring network should be a best possible compromise taken all constraints into consideration.

The models are now in a testing and exploratory phase. To assess model reliability in VOC-NO<sub>x</sub> emission change scenarios, one must know that the chemical processes and the model are described correctly regardless of VOC and NO<sub>x</sub> levels. This requires process-oriented measurements (NO, NO<sub>x</sub>, etc.) and EUROTRAC and EU/DG XII projects are important sources of such information.

Process studies is an important way of evaluating model performance. This requires monitoring of other constituents, as e.g. RO<sub>2</sub>, H<sub>2</sub>O<sub>2</sub>, PAN etc than required for effect assessment, and is a reason for establishing super sites. Dynamic process studies require monitoring also of the vertical distribution of ozone, e.g. by vertical soundings.

## **7.2.2 Ozone (and other oxidants)**

### **7.2.2.1 Current situation and further needs – ozone**

The ozone monitoring was established in 1985 in the fourth phase of EMEP but due to financial reasons a systematic collection and checking of ozone data did not start until 1987. The main objectives are

- Establishing the current ambient concentrations
- Compliance monitoring (“Do the emission control programme lead to a reduction of atmospheric concentrations?”)
- Support to the transboundary oxidant modelling (prognostic and diagnostic)

Ozone measurements also have the crucial aim of quantifying regional scale exposure to harmful levels. Other oxidants are also important but more difficult to measure (PAN, RO<sub>2</sub>, ROOH, OH, etc.). (*move to Ch. 8?*)

Improved effect estimates requires direct ozone flux measurements and parameters that can be used for flux modelling. Improved cooperation with other bodies monitoring ozone is furthermore needed to extend the regional coverage.

For ozone there are tough requirements in terms of instrument precision and quality control. A selection of sites should be designated to detect measurable changes in ozone concentrations.

The ozone measurement network presently consisting of about 100 stations is insufficient in several areas of the continent, but at the same time there are totally about thousand sites in operation in Europe. Improved cooperation and exchange with other bodies and programmes are needed.

There is a need for both surface sites and free troposphere measurements, as well as urban and rural sites for trends. The number of sites should be increased especially south of the Alps. Vertical ozone soundings could be an extension at selected sites.

The Level-II (ozone flux) approach (measured and modelled) should perhaps be mentioned here?

### **7.2.3 Volatile organic Compounds**

#### **7.2.3.1 Current situation and further needs – VOCs**

The EMEP VOC monitoring programme was initiated at the EMEP Workshop on Measurements of Hydrocarbons/VOC in Lindau, 1989 (EMEP, 1990). A three-fold objective of the measurement programme was defined at the workshop:

- Establishing the current ambient concentrations
- Compliance monitoring (“Do the emission control programme lead to a reduction of atmospheric concentrations?”)
- Support to the transboundary oxidant modelling (prognostic and diagnostic)

Still the goals set in the original Lindau workshop (see above) are more or less valid. The first aim of establishing the ambient concentration levels is partly solved, as we have several years of regular monitoring data available. The spatial cover is, however, still unsatisfactory, and parts of Europe still lacks any VOC monitoring data. The importance of VOCs in air chemistry and the requirement of the Protocol to reduce their emissions by 30% in five years necessitates measurements of VOCs.

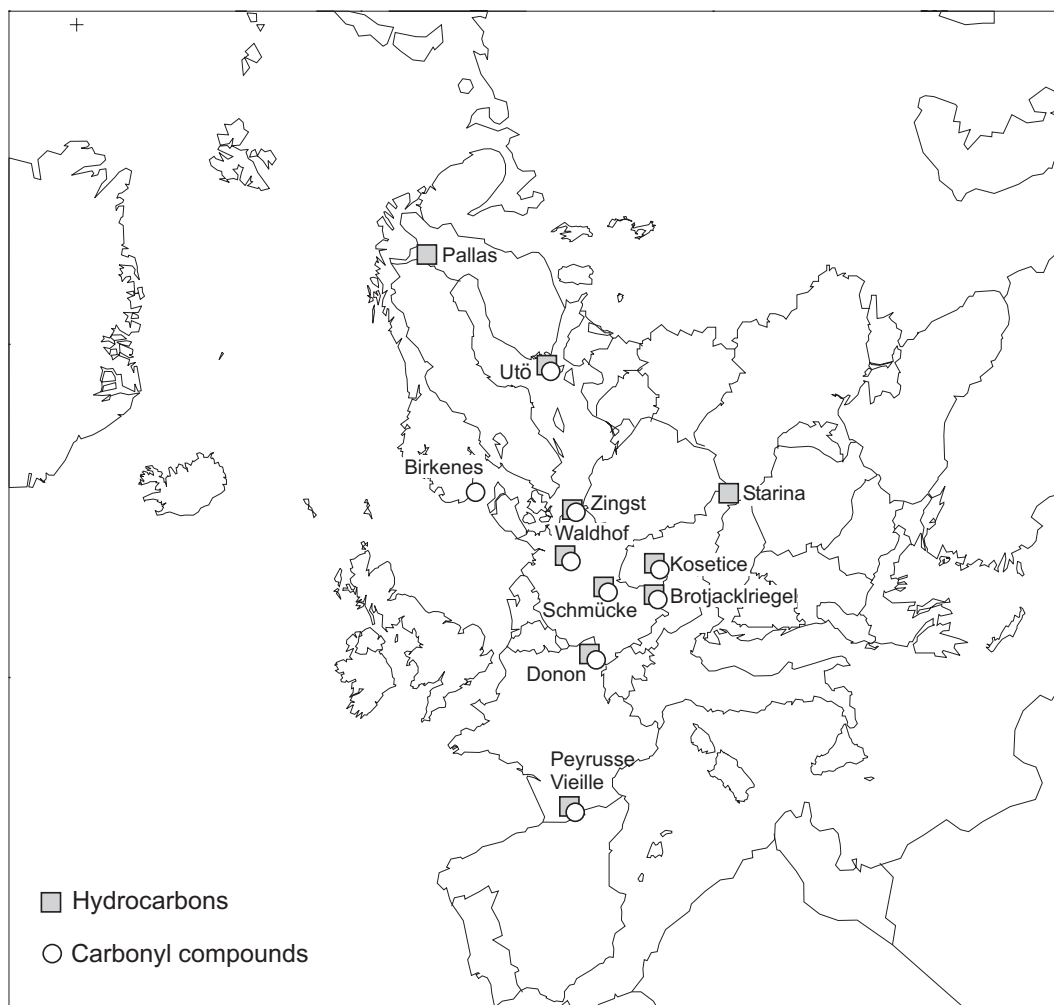
Furthermore, the VOC monitoring programme has to face a number of limitations of different kinds. The programme has to be economically and practically feasible. Thus, manual grab samples have been recommended instead of e.g. expensive monitors, and daily sampling has not been possible. Additionally, the VOC monitoring to some extent is still not routine work, but also includes a method development part, at least for the carbonyl analysis.

For emission inventories, there is a need to know both natural and man-made emissions of VOC. Emission inventory VOC speciation can be assessed by using ambient concentration measurements of individual hydrocarbons, and comparing them with EMEP model type calculations using state-of-the-art chemistry of all the most important VOC species in the inventory. In this way, one may discover disagreement between measurements and model calculations.

#### **7.2.3.2 Distribution of VOC monitoring sites**

A revision of the monitoring programme is needed to be able to adapt the strategy according to the experience gained through the years with monitoring. At the same time it is equally important to partly keep a continuation of previous practices in order not to lose the long-term trends, i.e. a complete shift of stations and monitoring procedures is not recommended. The question to answer is how to modify the present monitoring strategy in order to respond to the main aims in the best way, keeping the previous monitoring history in mind.





*Figure 1: Monitoring sites for VOC in 2000.*

The stations included in the last EMEP VOC report (data for 2000) is shown in Figure 1. In addition VOC was monitored by a GC-MS at Tänikon in Switzerland. It should be noted that several of the given sites have been in operation for a short time only. VOC measurements started in 2000 at Zingst and Brotjacklriegel and in 1999 at Peyrusse Vieille and Schmücke. Furthermore, there have been numerous technical problems with the hydrocarbon sampling at Starina. Thus, only a very few sites have long-term reliable VOC measurements, and it's thus important to continue the VOC activity at these sites. These include Birkenes (1987), Waldhof (1992) and Košetice (1992) with the starting year for VOC monitoring given in brackets. The stations with shorter monitoring history Pallas, Utö and Donon have, however, all shown very valuable results, and the monitoring activity has lead to a substantial build-up of competence which is also important to keep. In Switzerland VOC measurements are carried out by a continuous GC-MC monitor which is recently moved to the more rural EMEP site Rigi. These data will clearly be of very high value for EMEP. The Starina station has, as mentioned, suffered technical problems during certain periods, however, the location of site at the outflow eastern part of Europe makes it also a very important part of the network. Increased support and cooperation with CCC would be a solution when needed.

The map in Figure 1 also indicates obvious holes in the small VOC network. A site at the inflow coast of Europe, preferably in UK/Ireland would be highly valuable. Unfortunately the VOC monitoring at Mace Head which was in operation in the mid 1990-ies was stopped some years ago. However, recently, VOC monitoring has been started up again, using a continuous GC-MS monitor. Furthermore, VOC sites at rural areas in south Europe (Spain, Italy, Greece, Balkan) are highly needed, not only to assess geographical variations in the general concentration levels, but also in the VOC *speciation*, i.e. the mix of individual species, as this is likely to differ from North Europe due to higher influence of biogenic emissions (terpenes, isoprene). Thus, a total number of approx. 15 sites would seem sufficient for a minimum VOC network. This is also in line with the original recommendations from the Lindau workshop (EMEP, 1989). We note, however, that the "representativity range" is likely to be smaller in South Europe due to faster photochemistry and stronger biogenic emissions, thus requiring a denser network in that area.

Lastly, it should be stressed that the exchange of information, measurement data etc between EMEP and other programmes (national, EU, etc) should be improved.

The VOC monitoring today consists of measurements of light hydrocarbons by 10-20 min grab samples in canisters and measurements of carbonyls by 8 h sampling in DNPH tubes. Presently, these measurements are carried out on the same days, normally twice a week through the year. Although there are sound reasons for this practice, it is also a question if this should be changed. One general experience is that the carbonyl data have shown best suited for model evaluation purposes, whereas the data on light hydrocarbons have shown better suited for trend studies (compliance monitoring). Another experience is that the sampling frequency of two samples pr week, particularly combined with the short sampling time of the light hydrocarbons, has limited the application potential of the VOC data significantly particularly for trend studies. The present sampling rate for the hydrocarbon canisters combined with the large scatter in these data (which may be partly caused by the short sampling time) makes any evaluation of long-term trends and compliance to the protocols, statistically uncertain and difficult to carry out in a reasonable way.

One possible solution to this is to sample the hydrocarbons only during winter but at a higher rate, and also with a longer sampling time if technically possible. During winter the compounds are little influenced by photochemical degradation, thus more indicative of the emissions (and – of course – the meteorology). A denser sampling rate and longer sampling time would reduce the uncertainty when calculating monthly and seasonal means and strengthen the confidence in trend studies. Furthermore, methods to increase the sampling time should be evaluated. Today fairly simple automatic equipment which collects a canister sample during several hours, filling the bottle only partly each time is commercially available and is not technically demanding. This could be used to e.g. make a "quasi 8-h average" sample, filling the canister by a fixed fraction every hour through a 8-h period. This would not be a true 8-h sampling as the filling time every hour would still be of the order of 10 min, but it would mix the fractional samples equally from the whole period. This procedure, combined with a dense sampling rate through the week (e.g. daily samples or somewhat less) could be a way to increase

the value of these data considerably. Lack of hydrocarbon data from the summer season would still be a loss though, and questions regarding seasonal variations in the emissions (e.g. evaporative fuel emissions) would be more difficult to answer. Furthermore, the concentration level of biogenic compounds (isoprene) could not be studied by this approach.

In line with this, carbonyls could be measured only during the summer season, also at an increased sampling rate, as these compounds are more valuable as indicators of the photochemical oxidation processes and has mostly been used for model evaluation purposes (for the chemistry). The 8-h sampling time of the carbonyls seems to be well suited and the spread in these data are much lower than for the hydrocarbons.

For example five months sampling of hydrocarbons (November-March) and carbonyls (April-August) could be a minimum requirement. With a sampling rate of 5 samples pr week (Monday-Friday) the total number of samples would be approximately the same as today. Sampling every day during these periods would of course be even better, but could be practically difficult due to the requirement of manual sampling.

In addition, it has been discussed to have regular campaigns of parallel measurements every year with all EMEP VOC laboratories included as part of the QA work and to ensure that different laboratories carry out the sampling and analyses in an acceptable and comparable way. Typically campaign periods of 1-2 weeks would be sufficient

#### **7.2.3.3 VOC speciation**

At the Lindau workshop in 1989, a list of required and desirable VOC components for reporting was defined and is given below (). All the required components are actually reported today (with the exception of trimethylbenzenes), and the desirable compounds are partly reported.

Based on the many years with parallel sampling as well as with method validation studies in the laboratory and the precision of each individual compounds, the VOC speciation list should be revised and agreed upon among the laboratories that have participated in the VOC monitoring. Additionally, the fact that a significant fraction of the VOC emission are solvents should also set constraints on the speciation so that these compounds are also measured.

### 7.2.3.4 Recommendations

Table 1: List of volatile organic compounds that are “required” or “desirable” to measure within the EMEP programme as defined at the EMEP Workshop in Lindau, 1989 (EMEP, 1990).

	required	desirable
<b>Alkanes</b>	ethane	hexane
	propane	branched hexanes
	i-butane	heptane
	n-butane	branched heptanes
	i-pentane	octane
	n-pentane	
<b>Alkenes</b>	ethene	butenes
	propene	pentenes
	isoprene	
<b>Alkynes</b>	acetylene	
<b>Aromatics</b>	benzene	styrene
	toluene	propylbenzenes
	o-xylene	ethyltoluenes
	m,p-xylene	
	ethylbenzene	
	trimethylbenzenes	
<b>Aldehydes</b>	formaldehyde	propionaldehyde
	acetaldehyde	
<b>Ketones</b>	acetone	methylethylketone
		methylvinylketone

1) A rural VOC monitoring network requires at least of the order of 10-15 sites throughout Europe to give a representative view of the rural concentration level. Presently there are particularly a need for VOC data from UK/Ireland and from south Europe (Spain, Italy, Greece, Balkan)

2) Experience indicate that light hydrocarbons are best suited for compliance monitoring purposes whereas carbonyls are better suited for model validation. Thus hydrocarbon measurements could be carried out at with a dense sampling rate in winter only. Equipment to increase the hydrocarbon sampling to a quasi 8-h sampling should be studied and used if feasible. Carbonyl sampling could be done at a dense sampling rate in the summer season only.

3) An assessment of the carbonyl analyses is needed, particularly for the higher carbonyls. This should be based on general method development work (using LC-MS) and on the previous experience with parallel sampling in EMEP.

4) A list of species to report to CCC in the future should be agreed upon, based on the original recommendations and on the experience with the VOC monitoring and the precision and reliability for the individual compounds. The list should if possible be supplied with an uncertainty estimate for each single compound.

Remarks by Jurgen:

1. Dick Derwent raised the point of solvent use, one of the major sources according to emission inventories. Typically, these (relatively long chained) VOCs are not captured by current measurements.
2. How to proceed? This chapter contains some suggestions, but it clearly needs some additional thinking and discussions. You could e.g. consider to establish a small task group (CCC with a few other experts) to come up with a more concrete proposal.

Comment: That could be a good idea.

## 7.3 Heavy metals

### 7.3.1 Introduction

From 1999, heavy metals have been part of the EMEP program. The recommendations and main conclusions from the EMEP and WMO-GAW workshops in Durham, Beekbergen, Moscow and Aspenäs, and at the two first meetings in the task force of measurements and modelling (TFMM) are still valid. Heavy metals of the first priority are mercury, cadmium and lead; of the second priority copper, zinc, arsenic, chromium, and nickel.

### 7.3.2 Current situation and further needs

In 2000 the measurement network of heavy metals is seen in Figure 2. There are 59 heavy metal sites in Europe connected to either of the EMEP, CAMP or HELCOM monitoring programs. 20 of these measure both heavy metals in air and precipitation. For mercury the site density is much smaller, 15 sites in Europe measure at least one form of mercury.

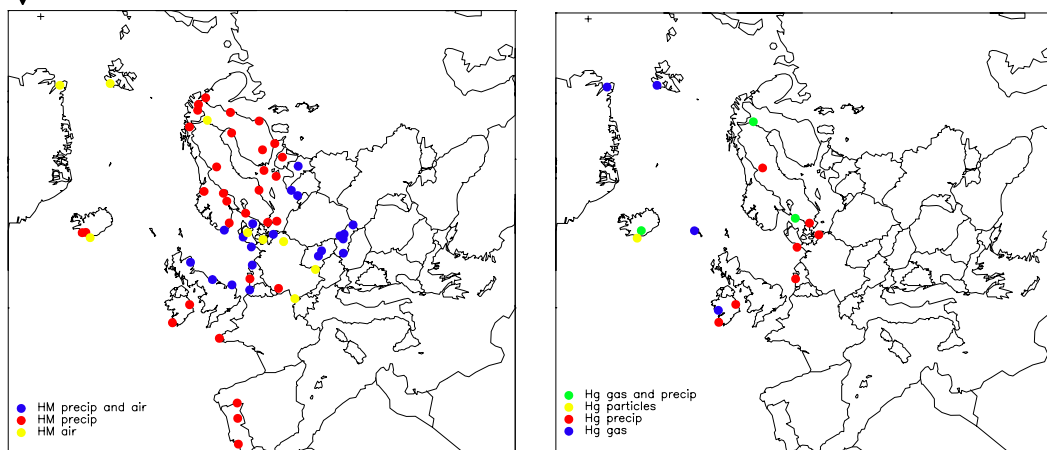




Figure 2: Measurements of heavy metals in air and precipitation at EMEP, CAMP and/or HELCOM sites in 2000.

The spatial distribution of the heavy metal sites is not satisfactory, the sites are mainly distributed in north of Europe. The modellers need a better site coverage to be able to compare the measurements with modelling results.

It is important to have information of HM in air and precipitation at the same time to improve model parameterization of HM scavenging with precipitation. It is believed that 20 stations with a full programme covering both air- and precipitation chemistry would be enough to provide modelling deposition fields within Factor-2 uncertainty over the whole domain. In addition more sites with wet deposition measurements are needed for model validation and for more accurate deposition estimates. There should be a uniform coverage of the domain meaning that the minimum number of sites for HMs to be used for model evaluation should be located in the following regions: Northern Scandinavia, Southern Scandinavia, Western Russia/Belarus, Southern Finland/Baltic States, Baltic States/Poland, Central Europe/Czech-Rep./Slovakia/Hungary, Balkans, Ireland/United Kingdom, Iberian peninsula, Southern France/Italy, Germany/Netherlands.

 Furthermore, there should be additional information from “background” areas on the borders of the domain (including those over ocean areas). Recently obtained experience has showed that in unpolluted areas (for example, Northern Scandinavia) external sources of HMs can provide significant contribution to pollution levels. For the domain as a whole, external sources can contribute as much as internal anthropogenic sources in Europe. E.g. the region of South-Eastern Asia is going through a period of booming industrialization. Already now the region gives the highest contribution to worldwide mercury emission. So, to improve reliability of modelling results on global scale it is important to get monitoring information from the whole region. In this respect it might be an idea to expand the EMEP database to also cover the Northern hemisphere. This should be further discussed also in cooperation with UNEP. Today the information on HM concentrations in the atmosphere and in the other geospheres is very uncoordinated. Creation of a unified database could give an opportunity to assess pollution levels and their trends more completely and easily.

The arctic is a region of special interest and additional stations are needed. It is especially important for mercury, which can be accumulated in vulnerable Arctic ecosystems. Three forms of mercury should be measured. Until now only TGM is measured on routine base. However, it is widely recognized now that M and TPM contribute a lot into pollution levels of industrialized areas.

In addition to the measurements in air and precipitation, there should be a closer cooperation to programs monitoring HM concentrations in different environmental compartments (sea water, soils and so on). Development of multi-compartment models for mercury requires knowledge of mercury contents in different media: fresh water, seawater, bottom sediments, and soils.

Further steps need to be done to evaluate the overall data quality of the heavy metal measurements. Until now analytical methods are being checked in the annual laboratory comparisons. Uncertainties contributed by sampling, shipping, sample processing should also be assessed.

## 7.4 Persistent Organic Pollutants

### 7.4.1 Introduction

Persistent organic pollutants (POPs) are organic compounds of anthropogenic origin, which resist photolytic, biological or chemical degradation, leading to bioaccumulation in the food chain. They can be transported over long distances in the atmosphere resulting in widespread distribution across the earth, including regions where they have never been used. Due to their toxic characteristics they can pose a threat to humans and the environment, and therefore, in recent years the international community has called for urgent global actions to identify their possible risk to human health and the environment and to reduce and eliminate the release of POPs.

### 7.4.2 Current situation and further needs

POP sampling sites in Europe are few and mostly found around the North and Baltic Seas, in the Arctic and in northern Finland, Figure 3.

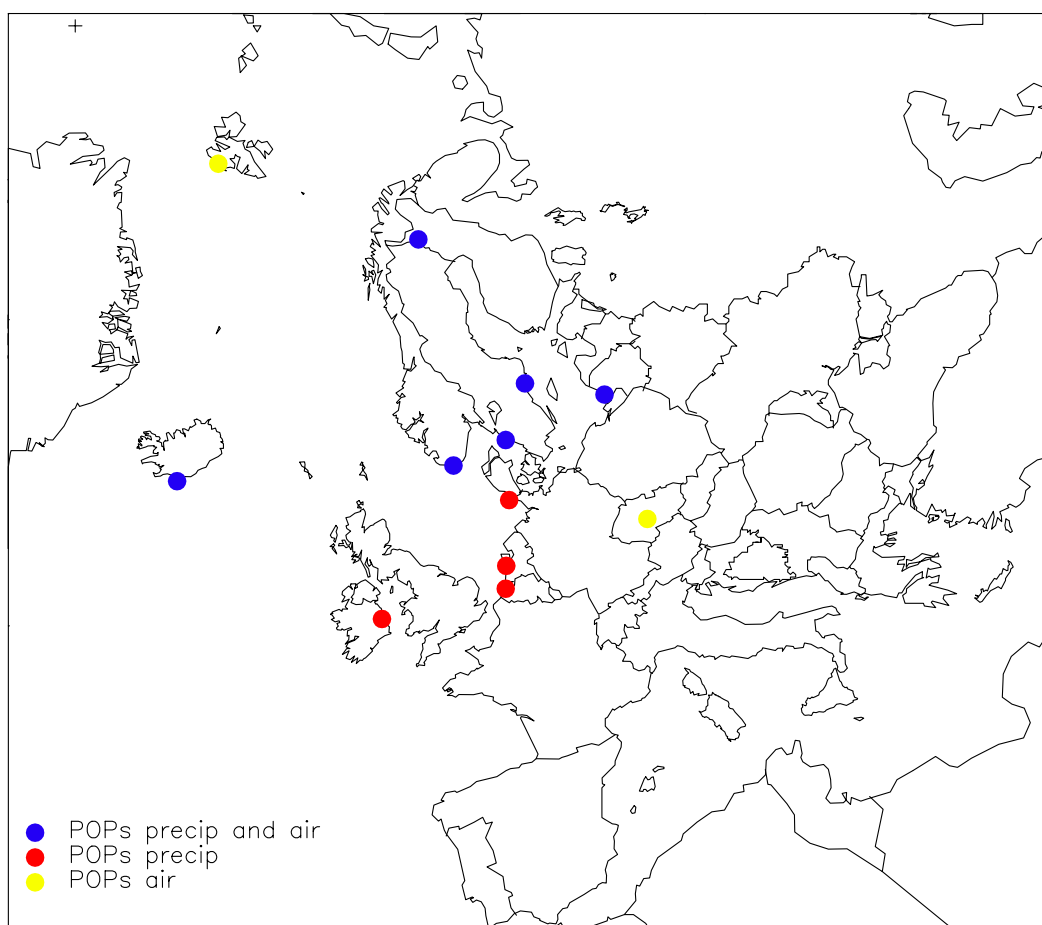


Figure 3: Measurements of POPs in air and precipitation at EMEP, CAMP and/or HELCOM sites in 2000.

To increase the number of sites measuring POPs, a central laboratory may be financed through the EMEP system to carry out all the chemical analyses in the first phase to ensure appropriate procedures and quality as the national

laboratories acquire sufficient skills to continue on their own. In a first step it is recommended that PAHs, PCBs, HCB, chlordane, lindane,  $\alpha$ -HCH and DDT/DDE should be monitored. These compounds may all be determined in one series of chemical operations.

The aims of monitoring POPs as formulated in the various international conventions (CLRTAP, HELCOM, OSPAR, AMAP and UNEP) have much in common. In particular, the following tasks are to be accomplished in the framework of monitoring activities:

- Revealing pathways of POP transport from sources to remote regions;
- Evaluation of level and spatial distribution of POP contamination in various environmental compartments;
- Establishing long-term trends of POP environmental contamination;
- Evaluation of POP long-range transport and source-receptor relationships;
- Evaluation of adverse effects of POP contamination on human health and the environment;
- Evaluation of media response to different emission scenarios;
- Evaluation of new substances to be included into international agreements.

For obtaining more full set of information on POP environmental contamination a complex measurement/modelling approach to monitoring is used under EMEP.

The requirements to measurement data from the viewpoint of modelling are formulated below on the basis of discussions at numerous international conferences and Workshops. In particular these requirements were clearly summarized in conclusions and recommendations of the Geneva Workshop on modelling of atmospheric transport and deposition of persistent organic pollutants and heavy metals held in Geneva, Switzerland in November 1999.

1. Data of POP measurements from different parts of the globe (or at least of the Northern Hemisphere) are very important for global/hemispheric modelling of POP transport and accumulation in the environment.

The importance of measuring POP concentrations in the environment at the hemispheric scale is conditioned by high ability of some POPs to long-range transport all over the globe. Therefore for such POPs modelling is to be performed by hemispheric models. To validate these models it is necessary to have measurements in different regions of the Northern Hemisphere. Particular attention is to be paid to such regions as the Arctic and South-Eastern Asia. Measurements of POP concentrations in various environmental compartments in the Arctic are of special interest for evaluation of the impact of POP contamination to the vulnerable Arctic ecosystems. Asian regions give great contribution to the overall POP emissions, and POP measurements in these regions will rise reliability of modelling results on global scale.

2. It is important to have measurements in environmental compartments other than atmosphere (soil, seawater, vegetation). Possibly, measurements in



environmental media other than air and precipitation may be included into the measurement program in the future.

The necessity of measuring POP concentrations in different environmental compartments is conditioned by the fact that these substances accumulated in these compartments during long time periods can be re-emitted into the atmosphere and undergo further atmospheric transport (grasshopper effect). Thus POP transport modelling is to be performed by multicompartment models. To validate such models it is necessary to have measurements in additional environmental compartments as soil, seawater and vegetation.

Apart from model validation purposes, pollution levels in soil, seawater and vegetation are important since these levels determine accumulation of POPs along food chains and, as a consequence, are considered as essential input information for exposure and risk assessment studies.

As mentioned above, the exchange processes play an important role in long-range transport of some POPs. To refine model descriptions of exchange processes and to validate the performance of corresponding model blocks, simultaneous measurements in pairs of media (atmosphere/soil, atmosphere/seawater, atmosphere/vegetation) are needed. Simultaneous measurements of concentrations in the atmosphere and precipitation are important for correct model description of wet scavenging process. Possibly, such measurements can be performed at superstations.


3. Measurements of atmospheric concentrations are to be done separately for particulate and gaseous phases of a pollutant.

The transport potential of persistent organic pollutants in particulate and gaseous phases are quite different, due to differences in processes that contributes to their dispersion and fate in the environment. For instance, particulate phase POPs (e.g. more chlorinated PCBs) are more easily scavenged from the atmosphere via dry and wet deposition processes. For some of the more volatile POPs (e.g. HCHs) gaseous exchange processes between atmosphere and underlying surface are of particular importance. Therefore, discrimination between these two phases is an important parameter in the description of long-range transport, accumulation and fate of POPs in the environment.

4. Congener-specific measurements are important for complex chemical mixtures such as PCBs, PCDD/Fs, PAHs, etc. because of the substantial variation in physical-chemical properties, which affect their long-range transport potential. In addition, environmental lifetimes and toxicity are usually highly variable within groups of chemical mixtures. For example, among the 210 possible PCDD/F congeners, only 17 possess significant toxic properties, according to NATO toxicity equivalent system. Further, toxicity equivalents of different congeners are different. Besides, in the course of their transport, complex chemical mixtures can change their congener composition (fractionation). To assess the overall toxicity of complex chemical mixtures and to evaluate source-receptor relationships of such pollutants in the environment, it is therefore necessary to monitor the congener composition and its variability in space and time.

5. Weekly measurements throughout the year are desirable for model validation and formulation.

As it was mentioned in Conclusions of the Geneva Workshop, weekly sampling is considered to be sufficient for EMEP objectives. The information on emissions is usually reported on the level of annual totals. Besides in some cases the information on seasonal variations (on the level of monthly data) is available. As a consequence, the results of long-range transport models are considered reliable on the level of annual/monthly averages. To obtain similar averages from measurement data weekly measurements seem to be the best compromise between modellers' demands and feasibility.

6. As it is stated in the document, additional sites covering Eastern and Southern Europe are strongly desirable to improve the spatial coverage for POP model validation purposes. 

The necessity of measurements in different regions of Europe is conditioned by behavioural peculiarities of POPs in the environment within different climatic zones. For most other pollutants, concentrations tend to decrease from source areas, due to dispersion, degradation and dilution. However, for some POPs, concentrations may be surprisingly high, due to effects such as prolonged persistence in cold climates and cold condensation. Because of the strong impact of temperature on environmental phase partitioning and environmental lifetimes, it is therefore a need to extend the spatial coverage of POP monitoring to better facilitate model validation.

## 7.5 Particulate matter

### 7.5.1 Introduction

Particulate matter may cause a variety of negative effects on our environment including impacts on human health, reduced visibility, new cloud formation and cloud properties, it contributes to the deposition of chemical compounds to ecosystems, it affects the radiative properties of the atmosphere and also contributes to soiling of materials (xxxx)

The EMEP/CCC-Report 8/99; Long-range transport of aerosol particles, A literature review. Summarises the key information available on the physical and chemical characteristics of PM, their monitoring, sampling and analysis methodology, their emissions and sources and their concentrations over Europe. In addition the Report provides background information on exposure aspects and related health effects. The report also provides a summary on the effect of particulate matter on visibility, climate effects, material damage and acidification/eutrophication.

It is apparent that particulate matter is not a single pollutant and its mass includes a mixture of many pollutants in a complex multiphase system. Long-range transboundary transport is responsible for a significant fraction of the particulate pollution in European cities as well as in rural areas (EMEP-WMO, 1999) and particulate matter is also subject of intercontinental transport. Long-range transport of aerosol particles (PM) was specifically added to the EMEP work programme in 1998. Recently, aerosol concentrations in several European cities

have been found to contain a significant long-range transported component. If aerosols are shown to be not only a local but also a transboundary problem, the monitoring and assessment will realistically fall under EMEP. The same will hold for visibility, if it is regarded as an environmental degradation problem. Part of the aerosol mass will be sulphur and nitrogen compounds, which are already part of EMEP, but some will also be elemental carbon and other combustion products.

The establishment of an adequate monitoring programme is a crucial step in the development of abatement strategies for particulate matter. After the inclusion of particulate matter in the work plan of EMEP, a monitoring strategy has been developed in close cooperation with the scientific community and national experts through the Task Force on Measurements and Modelling.

### ***7.5.2 Current situation and further needs***

A number of countries have initiated measurements during 2001 and 2002. Measurements of parameters other than PM mass are still sparse and countries are strongly encouraged to expand their activities to meet the requirements. The EMEP monitoring programme thus still provides insufficient data for model validation. This is particularly the case for information on the chemical composition of the aerosol. Although secondary inorganic aerosol components such as nitrate and ammonium have been part of the programme for many years, only few countries report data obtained from measurements that allow for the separation of gas and aerosol phase for these compounds. Apart from their essential role in developing an improved description with respect to acidification and eutrophication, these compounds are also needed for the ongoing development of PM modelling. The initial testing of a particle dynamic module in the EMEP Unified model also highlights the need for accurate descriptions of size dependent dry and wet removal processes.

For other parameters even less data are available. In particular for carbonaceous species information on the ambient concentration and chemical composition is generally lacking. Thus a comprehensive campaign aiming at determining concentrations of elemental and organic carbon concentrations at a number of sites across Europe has thus recently been initiated. Detailed information about this campaign can be found in EMEP CCC-Report 4/2002. The experiences from the EC/OC campaign will give guidance on the further development of the monitoring strategy for these compounds.

More specifically, in relation to aerosol particles, the task is to provide data for both individual chemical components and for the contribution of sources and source areas to the total particulate mass. Providing a detailed chemical mass balance is not simple, sampling and analysing the individual components should be consistent with the determination of the total mass. The problems related to volatility and of water content, are both of concern in this connection. Data on aerosol mass alone is thus by far not sufficient to improve the understanding of particulate matter behaviour in the atmosphere and the associated emission rates and exposure levels.

Text about the advantages of  $PM_{10}$  vs.  $PM_{2.5}$ .  $PM_{10}$  likely to be less effected by local re-suspension and also separating the bi-modal distribution typically seen in rural aerosol.

Further, the model validation requires sufficient measurement data both in terms of site density, data quality and chemical/physical parameters determined.

A comprehensive description of the atmospheric particles also requires the evaluation of particle number, surface and volume distributions in addition to their mass and their chemical composition. Size distribution measurements combined with chemical speciation are also necessary for identifying also the sources of atmospheric particulate matter.

*More about the need for size/number distribution here?*

Scientific developments by within the Eurotrac2 AEROSOL programme have provided useful input during the formulation of the monitoring strategy for particulate matter. The strategy includes monitoring at regional representative rural sites by standard methodologies but also have the ambition to utilize research data available at fewer sites or during shorter campaigns. The strategy aims to improve the chemical mass closure i.e. full characterisation of inorganic compounds, EC/OC determination at selected sites, improved OC characterization, chemical speciation as function of size as well as physical characterisation (number size distribution and surface area distribution).

## 8. Monitoring requirements for individual parameters

*We frequently experience that people are not really able to identify why the various components are included to the EMEP programme. I thus think it would be useful to prepare a general overview of the various species role in atmospheric chemistry and also their potential effect. Obviously this is a challenging task but I think this will prove useful, not at least to convince funding agencies about the importance of monitoring parameters which may seem unimportant from a deposition or exposure perspective. It will also help showing the multiple effects a parameter can have on various topics (as also highlighted earlier).*

*My idea was to on one argue for all good reasons monitoring each compound, what is the proposed site density and required sampling frequency We drop mentioning reference methods, DQO, etc. and just refer to the EMEP manual ....*

### 8.1 Major ions in precipitation

Wet deposition represents the major deposition flux in large areas of Europe and it can fairly reliable be quantified (as compared to dry deposition). Still there are large local variations in precipitation amount which current models are not able to resolve. Representative regional sites may thus be combined with observations from more dense meteorological network to provide wet deposition estimates for critical load exceedance calculations (references to be added)

Precipitation chemistry data are valuable because of their low cost and their reproducibility. It is also recognised important that precipitation data integrate vertically, so that the spatial representativeness of precipitation chemistry measurements is usually suited for determining air quality, in particular for highly reactive species. This is not the case for ammonium in precipitation, which may be seriously influenced by local ammonia concentrations.

Precipitation scavenging is the most important sink for fine particulate matter, which gives additional reasons for monitoring precipitation chemistry.

Table to be prepared showing; appropriate time resolution; a) daily at a minimum site density of 1 site per 50.000 km<sup>2</sup>, and b) should be supplemented with weekly samples for additional sites in regions requiring higher site density (with complex topography etc.).

#### Monitoring programme

Core sites level 1

Core sites level 2

Level 3 sites

----text from EMEP manual chapter 3.1.3---

In order for the measurements to be useful for validation of models of long-range transport and deposition of air pollutants the site for precipitation collection should be chosen, and the collection of rain and snow for analyses should be made in such a way that the concentrations are representative of rainfall composition over a larger area. For this purpose, the following requirements have been worked out:

1. The annual precipitation amount at the site, as measured by an ordinary meteorological precipitation gauge, should not differ markedly from the precipitation amounts at adjacent sites in the national precipitation network, and the daily precipitation amounts should also be correlated with those from the adjacent sites.
2. The location of the sampler should conform to WMO site requirements for precipitation gauges (WMO, 1971). There should be no obstacles, such as trees, above 30° from the rim of the precipitation collector, and buildings, hedges, or topographical features which may give rise to updraughts or downdraughts should be avoided. Consideration of the prevailing wind directions during precipitation events is recommended in connection with locating the sampler.
3. Of particular concern is the sedimentation of soil dust particles from the immediate surroundings. Gravel roads, farmyards, and tilled agricultural fields in the near surroundings within a distance of 100 m to 1 km should be avoided. Other potential local contamination sources include local residential heating with wood, peat or coal. Potassium is an indicator of such contamination. Local high ammonia concentrations from farming activities should also be avoided.

Supply of electricity is necessary for the operation of wet-only precipitation samplers. For the operation of the sampling site a small room is needed to store samples, equipment, and documents. This must be equipped with a refrigerator for the storage of collected precipitation samples.

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## 8.2 SO<sub>2</sub>

To document emission changes and to improve CTM, Important for the formation of particulate matter etc.. Not so much for evaluating exceedance of air quality guidelines.

Low levels-> filterpack monitoring

Short time resolution monitors allows for inverse modelling...

### Monitoring programme

Core sites level 1

Core sites level 2

Level 3 sites

## 8.3 SO<sub>4</sub>

The reduction in atmospheric sulphur has been one of the successes of EMEP. It is important to continue and maintain enough stations to determine trends and to confirm that emission abatement strategies are being carried out.

Most important compound to PM mass at the regional scale and also in urban scales contributes xxxx?!

Climate impacts, direct and indirect

Visibility...

### **Monitoring programme**

Core sites level 1

Core sites level 2

Level 3 sites

### **8.4 Reduced Nitrogen (NH<sub>3</sub>, NH<sub>4</sub>, sNH<sub>4</sub>)**

The current nitrogen sampling in EMEP is for total NH<sub>x</sub> or NO<sub>3</sub> combining aerosol and gas phases. Since the atmospheric behaviour of these components, including their removal rates, and consequently the ecosystem impact are very different, is considered important to separate these phases during sampling.

Need to include the recommendations from Sutton here. The expert panel on Ammonia will meet early.

To validate models, ammonia concentration data which have good spatial coverage and reasonable time resolution are needed. Because of the very different dry deposition velocities, it is very important to know the fractions of reduced nitrogen which are in the gaseous and in the particulate phase.

### **Monitoring programme**

Core sites level 1

Core sites level 2

Level 3 sites

### **Proposal by the Ammonia expert group;**

Key conclusions from Aspenäs and Bern are listed in the Bern report (Menzi and Achermann, 2001), and can be summarized as:

- Less effort needs to be put on *daily* monitoring of NH<sub>x</sub> concentrations and wet deposition. The main purpose of daily measurements is to relate to back trajectories and for real time comparison with models. This detailed analysis is not generally done, but would be feasible for only selected sites.
- Few sites speciate between gaseous NH<sub>3</sub> and aerosol NH<sub>4</sub><sup>+</sup>. This is a key limitation to data interpretation and to comparison with models, since spatial and temporal patterns of these two components are very different.
- Detailed temporal measurements (e.g. hourly) and dry deposition monitoring is possible at a very limited number of “super sites”.
- Further measurements are required in source areas to assess compliance of abatement policies, but need to account for local variability in NH<sub>3</sub> concentrations.
- Filter-pack sampling is not adequate for long term (e.g. weekly or monthly sampling) for which denuder sampling (for NH<sub>3</sub> + NH<sub>4</sub><sup>+</sup>) or calibrated passive sampling (for NH<sub>3</sub> only) is necessary.

3. Following these and other points, a large number of recommendations were made at the Bern Meeting (see page 31, Section 6.2 of the Bern Report). A key question, however, is why the recommendations regarding  $\text{NH}_x$  from Aspenäs Herrgaard were largely not adopted. In the absence of a clear answer, it appears that a revised monitoring strategy for  $\text{NH}_x$  (linked to that for acidifying components) needs to be made.

#### ***8.4.1.1 Difficulties in implementing the recommendations***

4. Part of the answer to the lack of implementation of may concern the resources required to implement existing classical methodologies. Given the limitations of filter pack sampling, daily denuder measurements with a post denuder filter have been recommended (EMEP/CCC Report 1/95). This approach however, is extremely time-consuming and expensive, especially when combined with parallel analysis for acidic species. The annular denuders and post-denuder filter-packs are fragile and need careful transport to sites, while time consuming preparation and extraction procedures combined with daily sampling give a huge workload. Given the costs and difficulties, it is clear that this approach can only be afforded at a very few sites in the EMEP network.

#### ***8.4.1.2 Distinct objectives and tasks in monitoring $\text{NH}_x$***

5. Given that widespread daily sampling of  $\text{NH}_3$  and  $\text{NH}_4^+$  is not economically feasible, it is important to investigate more cost effective monitoring solutions. This needs to focus clearly on the purposes for which the concentration monitoring is made. These purposes include:

- To assess long-term trends, to consider the relationship with anticipated increases or decreases in emissions between years, and understand the differences between years.
- To provide validation data for models, both in terms of long-term trends and short-term fluctuations related to different air masses
- To investigate interactions with detailed processes, such as differences between daytime and night-time conditions and the response to environmental conditions, such as temperature
- To assess spatial patterns directly, by making measurements at many sites, including providing a contrast between areas dominated by different source types.

6. The above needs imply two major tasks for monitoring  $\text{NH}_x$  concentrations:

- **Task 1:** Detailed time-resolved measurements separating  $\text{NH}_3$  and  $\text{NH}_4^+$ , with measurements at an hourly to daily frequency, implemented at a few sites across Europe
- **Task 2:** Low-frequency sampling separating  $\text{NH}_3$  and  $\text{NH}_4^+$ , with measurements at a weekly to monthly frequency, implemented at many sites across Europe.

The first approach would include the current daily denuder sampling, but could also cover the application of intensive continuous monitoring of  $\text{NH}_3$  and  $\text{NH}_4^+$  (e.g. using AMANDA and SJAC combinations, as developed by ECN, The Netherlands). In order for the second approach to be successful, there is a need for reliable, low-cost methods to be implemented.



7. Given the architecture of the classical annular denuder, this is not well suited to long-term (low frequency) monitoring, because high sampling rates lead to denuder saturation. Similarly, the equipment is expensive and fragile. By contrast, it is possible to design a denuder system that is tuned to low frequency sampling and low cost.

**A low-cost denuder for long-term, regional monitoring of ammonia.**

8. An inexpensive denuder system has been developed by CEH Edinburgh specifically to meet the need for low frequency sampling. The system, referred to as the DENuder for Long-Term Ammonia (DELTA), samples at a slower flow rate than classical denuders. By doing so, much shorter and more robust denuder tubes can be used, while denuder saturation becomes less of an issue. By using two 10 cm citric-acid-coated glass denuders in series, capture efficiency can be established for every sample, providing an important element for quality control of the collected data. A subsequent acidified filter is used to collect aerosol  $\text{NH}_4^+$ . The method is described by Sutton et al. (2001) and has been implemented in the UK at over 50 sites.

9. The DELTA denuder has been shown to operate reliably against continuous  $\text{NH}_3$  sampling, and can be implemented with basic equipment at low cost. The UK network (which also includes passive sampling in selected source regions) samples with a monthly frequency, and is operated with one full-time staff equivalent. The method is estimated to be *two orders of magnitude* cheaper per site (both staff-time and hardware) than daily denuder measurements.

10. A variant on the DELTA method has also been developed by CEH to sample for nitric acid, hydrochloric acid, and aerosol anions. In this approach, two additional 14 cm denuders coated with potassium carbonate precede the ammonia denuders. This has been implemented at 12 of the UK  $\text{NH}_3/\text{NH}_4^+$  sampling sites and also operates on monthly basis.

**Suggested strategy for monitoring  $\text{NH}_x$  within EMEP.**

12. Given the positive experience in the UK, it is suggested that the DELTA method would provide the necessary complement to EMEP sampling for  $\text{NH}_x$ . Noting the low cost of the approach compared with daily measurements, it could easily be implemented at many (or all) EMEP acidifying pollutant monitoring stations.

13. A basic monitoring strategy for  $\text{NH}_x$  could match to the three levels of monitoring envisaged in the EMEP PM10 monitoring strategy.

**Level 1:** Speciated  $\text{NH}_3$  and  $\text{NH}_4^+$  sampling at a monthly level (DELTA). Daily  $\text{NH}_x$  sampling using filter-packs (continue existing measurements, where resources permit, supposing that there is a call for this).

**Level 2:** Daily  $\text{NH}_3$  and  $\text{NH}_4^+$  sampling (classical annular denuders – at a few (5-10) sites across Europe).

**Level 3:** Hourly  $\text{NH}_3$  and  $\text{NH}_4^+$  sampling on a campaign basis or continuously at 1-4 sites across Europe (e.g. AMANDA and SJAC continuous analyzers).

14. The need for long-term trends in  $\text{NH}_3$  and  $\text{NH}_4^+$  would be met at a low cost using the DELTA approach, while the Level 2 and Level 3 approaches would provide detailed data linking to short term meteorological changes.

15. It should be noted that certain passive samplers may be useful as a complement to active sampling methods in EMEP. Such methods should only be implemented where their accuracy is continuously monitored alongside an active reference. Given this, and the fact that passive samplers do not require electricity, they may be used to investigate local variability and establish site representativity in relation to each of the three sampling Levels listed above.

16. Finally, it should be noted that urgent action is required in implementing speciated  $\text{NH}_x$  monitoring in Europe to assess long-term trends over the period of the Gothenburg Protocol. The Ammonia Expert Group set a target of 8 years monitoring by 2010, which implies that changes need to be made by 2002.

#### 8.4.1.3 References

Menzi H. and Achermann B. (2001) *UNECE Ammonia Expert Group (Berne 18-20 Sept 2000) Proceedings* (Eds.) Swiss Agency for Environment, Forest and Landscape (SAEFL), Bern.

Schaug J. and Uhse K. (1997) EMEP/WMO Workshop on strategies for monitoring of regional air pollution in relation to the need within EMEP, GAW and other international bodies. [Aspenaas Herrgaard, Sweden 2-4 June 1997] EMEP/CCC Report 10/97. NILU, Kjeller, Norway.

Sutton M.A., Tang Y.S., Miners B. and Fowler D. (2001) A new diffusion denuder system for long-term, regional monitoring of atmospheric ammonia and ammonium. *Water Air & Soil Pol.* (in press).

Comment to the proposal of Sutton et al by Kjetil; I think the proposal you currently find in the Excel tables are better (they are still quite similar). The main difference is that I think we should strongly argue that we need the filterpacks also in the future, we do indeed use air mass origin analysis (ref. Assessment report), we need the complete inorganics also for other purposes as well (e.g.  $\text{SO}_2$ ,  $\text{SO}_4$ , base cations, particles) (and when using the reference method these come “for free”). We have already said that we prefer the gas and particulate fraction be reported separately and I have in the proposal suggested that the filterpacks should be combined with long-term data for the gaseous fraction either from passive samplers or Suttons Delta method. The proposal of having denuder measurements at a limited number of level 2 sites is similar for both proposals. This would improve our understanding of gas/particle distribution significantly without changing the general approach. For regions with high emission rates more dense networks should be implemented, but this needs to be a level 3 activity as I see it. Mark; it is also an issue that some degree of conservatism is considered very important, and I think the long term data series from filter-pack measurements needs to be continued at core sites level 1.

### **8.5 Oxidised Nitrogen (NO, NO<sub>2</sub>, HNO<sub>2</sub>, HNO<sub>3</sub>, NO<sub>3</sub> (others?))**

See above

Because of the relatively short lifetime of the highly reactive nitrogen compounds, measuring these species is particularly challenging. This is particularly the case for gaseous nitric acid, which is even more rapidly dry-deposited than ammonia. Ammonium nitrate, on the other hand, has the form of sub-micron particles and is deposited more slowly.

The probably best-known and also most important example of a semi-volatile component is ammonium nitrate. The problem with quantifying its concentration is the shift in the balance between gas and aerosol-bound material during collection, resulting in (sometimes complete) evaporation of the sampled ammonium nitrate.

#### **Monitoring programme**

Core sites level 1

Core sites level 2

Level 3 sites

### **8.6 Other inorganic major ions (Base cations, sea salts and mineral dust)**

In many areas, atmospheric deposition of anthropogenic base cations is comparable to the release from weathering of soil minerals. The base cation deposition is therefore important in determining the exceedance of critical loads.

Base cations, sea salts and mineral dust contribute to aerosol mass and is important for chemical mass closure.

Sea salt concentrations (Na, Mg (Cl)) allows for estimating the fraction of aerosol SO<sub>4</sub>, Ca and K originating from sea spray.

There is a lack of measurements of aerosol concentrations of base cations, which are currently derived solely from calculations based on wet deposition, which is highly uncertain.

#### **Monitoring programme**

Core sites level 1

Core sites level 2

Level 3 sites

### **8.7 Photochemical oxidants and precursors (O<sub>3</sub>, other oxidants, VOC)**

A recent survey of the applied QA procedures for ozone monitoring showed that there are still significant gaps compared with the recommendations in the Manual. Long-term trend evaluations of ozone set particularly strong requirements on the precision of ozone monitoring, and stringer focus on the QA requirements is thus needed. Furthermore, flux monitoring at super sites etc. ..

## **Monitoring programme**

Core sites level 1

Core sites level 2

Level 3 sites

### **8.8 Monitoring of VOC**

For emission inventories, there is a need to know both natural and man-made emissions of VOC.

Emission inventory VOC speciation can be assessed by using ambient concentration measurements of individual hydrocarbons, and comparing them with EMEP model type calculations using state-of-the-art chemistry of all the most important VOC species in the inventory. In this way, one may discover disagreement between measurements and model calculations.

Only a very few sites have long-term reliable VOC measurements, and it's thus important to continue the VOC activity at these sites.

The map in Figure 1 also indicates obvious holes in the small VOC network. A site at the inflow coast of Europe, preferably in UK/Ireland would be highly valuable. Unfortunately the VOC monitoring at Mace Head which was in operation in the mid 1990-ies was stopped some years ago. However, recently, VOC monitoring has been started up again, using a continuous GC-MS monitor. Furthermore, VOC sites at rural areas in south Europe (Spain, Italy, Greece, Balkan) are highly needed, not only to assess geographical variations in the general concentration levels, but also in the VOC *speciation*, i.e. the mix of individual species, as this is likely to differ from North Europe due to higher influence of biogenic emissions (terpenes, isoprene). Thus, a total number of approx. 15 sites would seem sufficient for a minimum VOC network. This is also in line with the original recommendations from the Lindau workshop (EMEP, 1989). We note, however, that the "representativity range" is likely to be smaller in South Europe due to faster photochemistry and stronger biogenic emissions, thus requiring a denser network in that area.

#### **8.8.1 Sampling rates and seasonal coverage**

The VOC monitoring today consists of measurements of light hydrocarbons by 10-20 min grab samples in canisters and measurements of carbonyls by 8 h sampling in DNPH tubes. Presently, these measurements are carried out on the same days, normally twice a week through the year. Although there are sound reasons for this practice, it is also a question if this should be changed. One general experience is that the carbonyl data have shown best suited for model evaluation purposes, whereas the data on light hydrocarbons have shown better suited for trend studies (compliance monitoring). Another experience is that the sampling frequency of two samples pr week, particularly combined with the short sampling time of the light hydrocarbons, has limited the application potential of the VOC data significantly particularly for trend studies. The present sampling rate for the hydrocarbon canisters combined with the large scatter in these data (which may be partly caused by the short sampling time) makes any evaluation of

long-term trends and compliance to the protocols, statistically uncertain and difficult to carry out in a reasonable way.

One possible solution to this is to sample the hydrocarbons only during winter but at a higher rate, and also with a longer sampling time if technically possible. During winter the compounds are little influenced by photochemical degradation, thus more indicative of the emissions (and – of course – the meteorology). A denser sampling rate and longer sampling time would reduce the uncertainty when calculating monthly and seasonal means and strengthen the confidence in trend studies. Furthermore, methods to increase the sampling time should be evaluated. Today fairly simple automatic equipment which collects a canister sample during several hours, filling the bottle only partly each time is commercially available and is not technically demanding. This could be used to e.g. make a "quasi 8-h average" sample, filling the canister by a fixed fraction every hour through an 8-h period. This would not be a true 8-h sampling as the filling time every hour would still be of the order of 10 min, but it would mix the fractional samples equally from the whole period. This procedure, combined with a dense sampling rate through the week (e.g. daily samples or somewhat less) could be a way to increase the value of these data considerably. Lack of hydrocarbon data from the summer season would still be a loss though, and questions regarding seasonal variations in the emissions (e.g. evaporative fuel emissions) would be more difficult to answer. Furthermore, the concentration level of biogenic compounds (isoprene) could not be studied by this approach.

In line with this, carbonyls could be measured only during the summer season, also at an increased sampling rate, as these compounds are more valuable as indicators of the photochemical oxidation processes and has mostly been used for model evaluation purposes (for the chemistry). The 8-h sampling time of the carbonyls seems to be well suited and the spread in these data are much lower than for the hydrocarbons.

For example five months sampling of hydrocarbons (November-March) and carbonyls (April-August) could be a minimum requirement. With a sampling rate of 5 samples pr week (Monday-Friday) the total number of samples would be approximately the same as today. Sampling every day during these periods would of course be even better, but could be practically difficult due to the requirement of manual sampling.

In addition, it has been discussed to have regular campaigns of parallel measurements every year with all EMEP VOC laboratories included as part of the QA work and to ensure that different laboratories carry out the sampling and analyses in an acceptable and comparable way. Typically campaign periods of 1-2 weeks would be sufficient

### **8.8.2 VOC speciation**

At the Lindau workshop in 1989, a list of required and desirable VOC components for reporting was defined. All the required components are actually reported today (with the exception of trimethylbenzenes), and the desirable compounds are partly reported. The VOC reporting varies, however, between the

laboratories. Some report the required components and some report a wide range of compounds extending far beyond also the original list of desirable compounds.

Thus, the VOC compounds to report should be revised and settled and adopted by all participating laboratories. This would also set the focus on the QA work and validation of some of the higher-order compounds, where the documentation and precision is less known. Based on the many years with parallel sampling as well as with method validation studies in the laboratory, a common list of species to report should then be agreed upon, also to ease to data base handling of the VOC species.

Remarks by Jurgen:

3. Dick Derwent raised the point of solvent use, one of the major sources according to emission inventories. Typically, these (relatively long chained) VOCs are not captured by current measurements.
4. How to proceed? This chapter contains some suggestions, but it clearly needs some additional thinking and discussions. You could e.g. consider to establish a small task group (CCC with a few other experts) to come up with a more concrete proposal.

Comment: That could be a good idea.

Ozone is an essential trace gas to monitor due to its adverse effects on vegetation and on human health. The standard equipment for ozone monitoring is by commercial available UV-monitors.

Monitoring of VOC are also needed, mainly by two reasons: Firstly, regular measurements or monitoring of VOC are the only way to evaluate the compliance with the VOC abatement protocols. Some countries have national monitoring programmes for VOC, but only a few. Regional VOC monitoring at a sufficient number of sites throughout Europe is thus required. Secondly, VOC monitoring data has proven particularly valuable for validation of the numerical models. Thus, a good agreement with the model calculations for VOC makes out part of the quality assurance of the model predictions.

Ozone plays a central role in physical, chemical and radiative processes in the troposphere. Our knowledge of trends is still incomplete on the regional as well as the global scale, and high precision measurements are fundamental.

Hemispheric issue and linking of scales important

Vertical distribution, linking boundary layer with the free troposphere (stratosphere).

DELETE?

what about ozone and its importance for atmospheric oxidation ?

Ozone and climate....?

Refer to flux based approach again here?

## **Monitoring programme**

Core sites level 1

Core sites level 2

Level 3 sites

### **8.9 Heavy metals (Pd, Cd, Hg) (others)**

On a global scale and even more so within Europe, anthropogenic releases of the priority metals considerably outweigh natural emissions. These metals are all toxic to humans/biota. Metal and metalloid compounds can be incorporated to biota in the ecosystems, either directly via deposition, or indirectly via uptake from soil. Effects caused by the exposure of organisms to heavy metal deposition may be related either to current deposition rates or to accumulated amounts in the ecosystems. The knowledge of possible effects of some of the HMs like arsenic, cadmium and nickel, on ecosystems is still rather limited. The HM species occurring in ambient air, but also their physico-chemical properties have not been properly characterized so far by measurements. Consequently, the assessment of effects is impaired by considerable uncertainties, and more information on speciation is needed.

Lead:

Lead is enriched in the fine particle mode about 2  $\mu\text{m}$ , and can penetrate deeply into the respiratory system. Lead deposited from the atmosphere can enter ecosystems/food chains. Lead additives in petrol is still the main anthropogenic source.

Cadmium:

Cadmium is enriched in the fine particle mode about or below 1  $\mu\text{m}$  and, consequently, can penetrate deeply into the respiratory system and have long residence times in the atmosphere. Cadmium is carcinogens and act as systemic pollutants and as their transfer into the food chain is of particular relevance. Non-ferrous metal industry is the main source.

Mercury:

Unlike the other priority metals, mercury is in the atmosphere mainly found in its elemental form, which is relatively un-reactive. However, close to anthropogenic sources the main species can be so-called reactive gaseous mercury and/or particulate mercury which are much more reactive and have a considerably higher deposition rate than elemental mercury to sources. These species may also be found in the Arctic during special occasions. Methyl mercury is bio-accumulative. Anthropogenic sources are combustion of fossil fuels.

As to elemental mercury, some processes in the atmosphere can be very quick (for example, Arctic depletion). So temporal resolution should be corresponding to rate of such processes. Modern TGM analyzers can provide such a possibility.

Arsenic:

Arsenic is enriched in the fine particle mode about or below 1  $\mu\text{m}$  and, consequently, can penetrate deeply into the respiratory system and have long residence times in the atmosphere. Methylation of inorganic arsenic is known to occur in water and soil and minor amounts of methylated species might be present

in air as well. Arsenics transfer into the food chain is of particular relevance. Arsenic are carcinogens. Anthropogenic sources are non-ferrous-industry and partly combustion of fossil fuels.

Nickel:

In contrast to arsenic, lead and cadmium, up to 30% of the total nickel compounds may be found up to 30% in the coarse mode. Several nickel compounds are classified as human carcinogens in the EU system. Anthropogenic sources are combustion of fossil fuels.

### **Core sites level 1**

A minimum activity comprising the measurement of heavy metals in precipitation is required at a relatively large number of sites. Current number of sites is in the order of 80?, but some regions obviously having poor site densities. The recommendation is thus to sample Pb, Cd, As, Ni, Cr? at an intermediate number of sites compared to Core sites level 1 and Core sites level 2. It may not be feasible to monitor Hg at the same number of sites....

From modelling viewpoint, sampling should be as often as possible. However, it totally unrealistic from monitoring viewpoint – any short period cannot provide collection of materials needed for analyses.

Weekly sampling can provide reliable bases for model verification on annual base. Weekly bulk sampling with at least two samplers is thus recommended and the chemical analysis should at least be performed on a monthly basis. **Number of sites → less than all level 1 sites, but more than Level 2 sites, current number is around 80 .... and may be considered as being close to maximum realistic?**

### **Core Sites level 2**

To improve model parameterization of HM scavenging with precipitation it is important to have information at the same time for air and precipitation. At least weekly sampling of heavy metals in air is recommended.

**For mercury, monthly bulk sampling is recommended for precipitation. For air sampling, gold traps are recommended for TGM and the 24-hour sampling time should not be exceeded for manual sampling.** Automatic TGM monitors can also be used.

Simultaneous measurements of HMs both in precipitation and air should be performed at Core sites level 2. To improve model parameterization of HM scavenging with precipitation it is important to have information at the same time for air and precipitation.

### **Level 3 sites**

At level 3 sites, measurement campaigns should be carried out to meet the requirements for improving the understanding of mechanisms in order to support further model development. These measurements could e.g. include high time resolution measurements of special compounds, defined fraction of compounds and measurements which still not are at a level necessary for monitoring (e.g. reactive gaseous mercury, chromium species). As to elemental mercury, some



processes in the atmosphere can be very quick (for example, Arctic depletion). So temporal resolution should be corresponding to rate of such processes. Modern TGM analyzers can provide such a possibility.

### 8.10 Persistent Organic Pollutants

also here initiate with why do we measure the individual compounds ...  
Later define the requirements...

Refer to WHO/ECEH - UNECE Task Force on Health Aspects of Long Range Transboundary Air Pollution Health Risks Of Persistent Organic Pollutants From Long-Range Transboundary Air Pollution (contains a detailed description for individual compounds)

In a first step five POP sampling sites would be sufficient. Due to the importance of the air/water exchange, these first sites should preferably be located near the coast or at lakesides. The preferred locations are: Scandinavia/Baltic States, North Europe Atlantic region, Continental Europe including (or in addition) Russia/Belarus, Mediterranean region, South Europe Atlantic region.

80. Measurements of POPs in the start-up phase should be restricted to high volume sampling of air, making use of a filter/polyurethane foam (PUF) as sampling medium. Deposition measurements should be included in the second step. The sampling period and frequency for air samples in the start-up phase should be one 24 (48)-hour sample every week. Possibilities for longer sampling periods should be seen in connection with the compounds chosen for the initial step.

Five sampling sites may be sufficient in a first step, preferably close to lakes/the sea in Scandinavia/Baltic States, North Europe Atlantic region, Continental Europe, Mediterranean region and in the South Europe Atlantic region. In the start-up phase high volume sampling may be performed on polyurethane foam (PUF) as sampling medium, later deposition measurements should be included. One 24- (48-) hour sample should be taken per week. A central laboratory should be financed through the EMEP system to carry out all the chemical analyses in the first phase to ensure appropriate procedures and quality as the national laboratories acquire sufficient skills to continue on their own;

One 24- (48-) hour sample should be taken per week

This is from an earlier proposal. What about Lista and Zeppelin ? other sites from CAMP or HELCOM?

For POPs, the EMEP measurement programme will include five sampling sites:

- A: Scandinavia/Baltic,
- B: Northern Atlantic region,
- C: Continental Europe,
- D: Mediterranean region,
- E: South Atlantic region.

For POPs, the EMEP measurement programme will include PAH, PCB, HCB, chlordanes, lindane,  $\alpha$ -HCH, DDT/DDE. POPs in precipitation will be collected on weekly basis. It is still finally not decided if wet-only or bulk samplers will be used. Weekly air samples (particle and vapour-phase combined) will be used.

	Progress	POP Prec.	POP Air.	Area
SE2: Rörvik	Yes	x	x	A
DE2: Waldhof	?			C
IS91:	?	x	x	A
CZ3: Košetice	Yes		x	F

### 8.11 Particulate matter

From S&I;

The multiphase system of aerosols and clouds is an extremely challenging one to sample properly. In contrast to gases (which are essentially scalar quantities), aerosols and clouds are matrix quantities in the sense that it requires a number of different measurements to quantify their thermodynamic state. Aerosol particles and cloud elements vary in size from a few nanometers for particles just produced from the gas phase, to millimeter sizes for raindrops. The chemical composition of the aerosol varies as a function of size, as does the state of mixing of the particles (the degree to which the particles are *internally* or *externally* mixed). The physical properties of particles and cloud elements vary widely as a function of size and composition, making it necessary to use a large number of different sampling and analysis techniques to characterize aerosols and clouds. All of these properties vary with the relative humidity of the air.

The chemical composition and physical properties of aerosols contain information about the particles' sources. These properties also determine the aerosols' interaction with the human respiratory system, but also the transport, transformation, and deposition of particles. Aerosols can be classified according to their origin as either primary or secondary, or as natural or anthropogenic. Secondary aerosols originate from homogeneous or heterogeneous chemical reactions of precursors or by photochemical mechanisms (Pandis et al., 1991). Typical precursor gases are sulphur dioxide, nitrogen oxides, ammonia, and volatile organic compounds (VOC). The precursors can be of natural or anthropogenic origin, where the latter are usually predominant in Europe. The precursor gases can form particles either by homogeneous nucleation, by condensation onto existing particles, or by chemical and photochemical reactions. Primary natural aerosols originate from sea spray (salt aerosols) (Savoie and Prospero, 1982), soil resuspension by wind (Nicholson, 1988) (e.g. Saharan dust (Rahn et al., 1979)), or volcano emissions (Hauet et al., 1977). The most important anthropogenic sources of aerosols or precursor gases of secondary particles are road transport, combustion sources, fossil fuel power plants, and agriculture.

The mass measurement part is based on standard EN 12341 of the European Committee for Standardization (CEN) (CEN, 1998) and recommends employing the gravimetric method, which has proven to be the most accurate method. Gravimetric methods also have the advantage of allowing chemical analysis of the collected PM<sub>10</sub> sample after weighing. The application of the methods and quality

assurance procedures recommended by the manual is important in order to harmonise the ongoing PM<sub>10</sub> measurements (EMEP, 2001; Lazaridis et al., 2002) throughout the EMEP network.

From S&I:

Technology for sampling and determining some of the pertinent properties of aerosols and clouds is in a mature state. For instance, the approaches for measuring aerosol number concentration, or the mass concentration of sulphate in submicrometer particles is well developed and reliable.

From S&I:

Collection of aerosols on a suitable filter and weighing is reasonably straightforward, provided that a suitable size-discriminating air inlet is being used. The construction of the air inlet is not critical for the >10 micron size range. With respect to a lower size cut-off, it has been discussed whether this should be 2.5 or 1. Problems are generally related to the volatility problem. As much as 30% of the sample weight may be ammonium nitrate in some areas (the Netherlands), and many chemical compounds in the organic fraction have appreciable vapour pressures at ambient temperatures. We still need to know how these constituents behave in the "conditioning" process.

An alternative to weighing is quantification by chemical methods. Actually, long measurement series of measurements in Europe are available for specific chemical constituents of aerosol, e.g., for sulphate and to some extent for nitrate and some other species. The sulphate series go back to 1972, and although the equipment and the data quality have improved over the years, some of the data series are fully consistent over this long time period. Much less information is available for nitrate, and these data are much more susceptible to sampling artifacts. Inorganic elemental analysis using several methods has also been performed, with a very high quality both with respect to sampling and chemical analysis, allowing quantification of the inorganic mineral mass, as well as the sea-salt contribution. If the organic and the elementary carbon fractions could be quantified by chemical analysis in the same way, simple weighing of the filters (or mass quantification by other means) could be replaced by chemical analyses, giving more specific as well as more precise information. However, as discussed above, these sampling and analysis techniques are still under development. Ideally, aerosol measurements should also be size-specified. However, cascade impactors require relatively long sampling periods and are expensive to run over extended periods.

Artefacts in OC sampling; from S&I;

From evaporative losses during the collection of organic carbon it was deduced that a substantial fraction of this material is semi-volatile. However, since the molecular composition of the organics cannot yet be determined, it is not known which organic species have this semi-volatile character. This in turn makes focused investigations and resolution of the sampling artefacts impossible. A complication is that, at the same time that evaporation of semi-volatiles occurs, gaseous material adsorbs to the collection substrates. Notorious in this respect are the quartz and especially the glass-fibre filters that are prescribed as the filter material in the EU guidelines for sampling of PM<sub>10</sub> and PM<sub>2.5</sub>. This leads to potentially large overestimates of the actual concentrations of these parameters. A

way to overcome this positive interference is the removal of the adsorptive gaseous organics with so-called gas denuders. However, the proper adsorptive material has not yet been found. To assess the evaporative losses, filter packs, consisting of a series of filters, are being used. Such approaches would seem to be simple, but are very costly and prone to contamination by all the necessary handling. To prevent this handling and for short-term measurements a commercial carbon-monitor (ACPM) is in principle available, and it has been tested in a field intercomparison campaign.

### **Monitoring programme for particulate matter;**

#### **Core site level 1;**

- PM<sub>10</sub> mass

- Daily measurements of inorganic compounds by filter pack

SO<sub>4</sub>, NH<sub>4</sub>, NO<sub>3</sub>, Na, Mg, Ca, K (Cl) (NH<sub>4</sub> and NO<sub>3</sub> to be estimated using values from filter packs (gas and particle fractions should be reported separately) and values for the gaseous fraction measured by low cost methods on a bi-weekly or monthly basis (cfr. "acidification and eutrophication chapter)

Time resolution; daily

#### **Core sites level 2;**

In addition to level 1 parameters also include

PM<sub>2,5</sub> or PM<sub>1</sub> mass, (daily)

Speciation of inorganics by size using impactors (weekly or longer)

Mineral dust (weekly or longer)

Elemental Carbon (weekly or longer)

Organic Carbon (weekly or longer)

Gas/particle distribution for NH<sub>3</sub>/NH<sub>4</sub> and HNO<sub>3</sub>/NO<sub>3</sub> with denuder-filterpack method (see also level 2 sites for acidification and eutrophication)

#### **Level 3 sites;**

Size/number distribution (hourly, size bins to be determined in cooperation with GAW)

Light scattering (hourly)

OC-speciation (grab samples or weekly samples)? experience from EC/OC campaign will give advise

BC

#### **Candidate level2/level3 sites for PM;**

Birkenes (NO), Zeppelin (NO), Pallas (Fi), Virolahti (Fi), Hyetäle (FI), Mace Head (IE), Aspveten (SE), Jungfraujoch (CH), Hohen Peissenberg (DE), Ispra (IT/JRC), Mt Cimone/Bologna? (IT), Inzana (ES), Ilmitz (AT), Kollumerwaard (NL), Braganza (PT), Waldhof (DE), Finokalia (GR), K-Puzta (HU), Košetice (CZ), Gent(BE), =20. other candidates??

Need also one in the Balkan area, one in Turkie, one in Spain, One in UK, one in Poland/Slovakia (Stara Lesna?), to in Russia, One in the Baltics, and one in the far east. =8 -> total 28).

## **9. National monitoring obligations for monitoring at the various levels**

*Here I suggest to present something similar like the excel table showing the number of sites required after having agreed upon minimum site densities for the individual compounds and levels. This should be prepared in cooperation with the countries....*