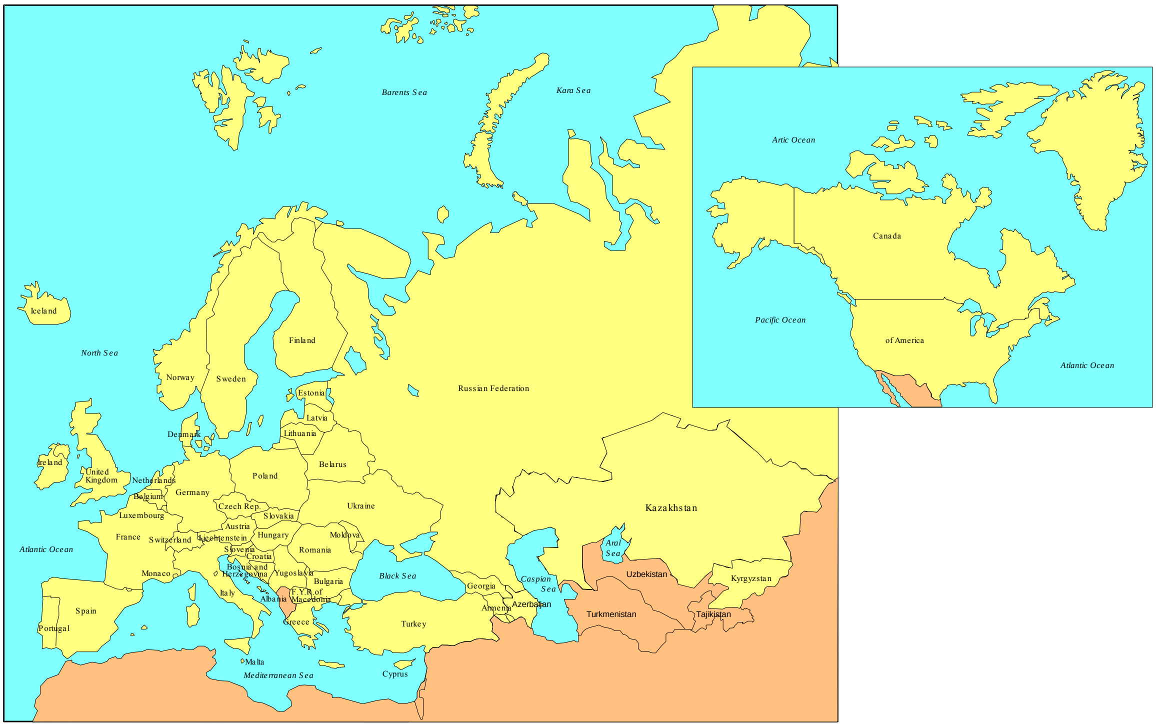
EMEP/CCC-Report 2/2005

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

Workshop on the implementation of the EMEP monitoring strategy

Oslo, 22-24 November 2004



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1. Introduction

Norwegian Institute for Air Research (NILU) arranged an EMEP Task Force on Measurements and Modelling (TFMM) workshop on the implementation of the EMEP monitoring strategy (EB.AIR/GE.1/2004/5) in Oslo 22-24 November 2004.

The workshop was held at the Norwegian Pollution Control Agency's premises. The objective of the workshop was to discuss methodologies and technical requirements needed to implement the level 2 and level 3 activities defined by the EMEP monitoring strategy. Experts from 22 countries attended together with representatives from MSC-W and CCC (see participant list in appendix A). Presentations were given by experts on four focused topics, followed by presentations from the CCC on their experiences (see appendix C). The emphasis was on the four topics; size resolved aerosol chemistry (A), gas/particle distribution of semi-volatile nitrogen species (B), EC and OC determination (C) and methodologies for VOC determination (D).

The workshop mainly addressed the needs in relation to supersite activities being initiated nationally. International experts in the various fields were invited for main presentations

The expected output from the workshop was to come up with advice to Parties on methodologies and proposal for methodologies and SOPs to be included in the EMEP manual.

The workshop was held in parallel with the 9th EIONET Workshop on Air Quality Management and Assessment. A half-day common session was devoted to air quality monitoring strategies in Europe to highlight the main requirements in the AQ monitoring efforts in Europe.

The rapporteurs (Urs Baltensberger, Mark Sutton, Rainer Steinberger and Jean Phillippe Putaud) are greatly acknowledged. Cinzia Perrino has also contributed with valuable information after the workshop was held.

2. Group A. Gas/Particle distribution

2.1 Clarification of sampling in the different levels

***Level 1 sites*:**

EMEP Filter Pack (FP), daily

- Total inorganic nitrate (TIN), Total inorganic ammonium (TIA)
- Separate gas + aerosol (with quality flag)

Low cost denuder (monthly)

- Separate gas and aerosol (monthly) for independent QA/QC of FP
- May be used at additional national sites to improve site density

Level 2 sites:

- Annular denuder + Filterpack system as the best daily reference, or
- Honeycombe denuder + Filterpack system, or
- Continuous denuder + steam jet aerosol collector systems

Level 3 sites:

- Different continuous methods applied in intensive campaign mode
- Inclusion of research campaigns with multiple groups at key sites
- Intensive comparison of different sampling methods

Interchange between Levels and Implementation Plan

- A flexible interchange between Level 2 and Level 3. It is not realistic for daily/hourly Level 2 methods to be performed 365 days a year in Level 2, noting that the Level 1 methods provide the long-term daily record.

- Sites may be Level 1, but take on board selected Level 2 activities with eventual aim of eventually being Level 2 compliant – need to agree “critical threshold” of when Level 2 status achieved.

- Need for an implementation plan of the strategy (additional to the strategy and the EMEP sampling manual). This is necessary as a basis to clarify stages of ambition and help facilitate national underpinning funding.

2.2 Sampling frequency at Level 2 and Level 3

Diurnal sampling

- The importance of quantifying the diurnal variations was recognized.

- One proposal to address this was to sample 12-hour day/night separately under Level 2. This proposal was rejected,

- It was agreed that a better solution is to sample full diurnal variation properly (e.g. hourly) on a campaign/intensive period basis in Level 2.

- Given the range of techniques available, it is agreed to be fundamental that a flexible approach is necessary, and parties may choose between providing campaigns/intensive periods of hourly measurements or longer-term 24-hour records using manual daily denuder/filter pack systems as valid contributions to both Level 2 and Level 3.

2.3 Campaigns and Intensive Periods

It is strongly recommended that campaign and research studies (Level 3) at EMEP sites are better coordinated. ACCENT could be a means of facilitating this.

A distinction is needed to clarify the definition of different types of campaigns:

- ***Research campaigns:*** Multiple groups, chemical components and comparison of methods, mainly relevant for Level 3 sites.
- ***Intensive periods:*** Sampling at Level 2 sites during key periods of a year on a repeated long-term basis during which high cost/high frequency methods are deployed.

Intensive periods and hourly/daily denuder measurements

- Recognizing that it is not realistic to require Level 2 sites to conduct daily annular denuder/FP or SJAC measurements 365 days a year,
- Accepting that there is a need to focus attention on the use of the these Level 2 measurements in modelling,
- It is recommended to define specific intensive periods of the year when the daily/hourly denuder and SJAC measurements should be made.
- It is agreed to that the timing of such intensive periods should be coordinated between Level 2 sites. Agreement is needed on the timing strategy and the level of ambition. The conclusions should be incorporated in the Implementation Plan.
- It is recognized that the timing of the intensive periods depends on the methods to be deployed, e.g. for manual denuders, the first week of each month might be preferred; for continuous denuder/SJAC systems, two specified months per year would be preferred. However the periods may differ between components. E.g. the NH_3 emission in the spring is very short and if one week a month is chosen, these periods may be missed. Modellers need on the other hand longer periods so they can look at the transport pattern.
- The coordination of Level 2 intensive periods is recommended to be a joint task for experimentalists and modellers within the TFMM.

Funding of intensive periods and campaign measurements

- It is essential that Parties recognize the funding requirements for intensive periods as an integral part of the long term EMEP monitoring effort at the Super Sites.
- The funding basis for research campaigns at Level 3 sites should be considered by parties, but is also expected to be supplemented by specific national and European research projects.

2.4 Coating material for denuders and filters

- Acid coatings of denuders are used to capture ammonia, while basic coatings used to capture acid gases.
- Similar acid/basic impregnations may be used for post denuder filters

Denuder coating for gaseous ammonia (denuder coating)

- Oxalic acid: too volatile and is not recommend
- Citric acid: develops nice crystals on the denuder surface, making it good for visual QC in preparing denuders. In warm climate it is observed a migration of citric acid to the second denuder and NH_4 may migrate together with this.
- Phosphorous acid is more stable in warmer climate. Experience is documented in the temperature range between -5 and +40 degrees. No experience at lower temperatures.
- Some groups suggest that the denuders should be soaked in NaOH and then rinsed thoroughly in deionized water prior to acid coating to rinse the glass surface to ensure an effective coating. However, one should be careful storing uncoated and coated denuders since ammonia is easily absorbed also on uncoated denuders. In Italy they never store uncoated denuders, but clean them in a dilute HNO_3-solution before rinsing thoroughly in deionized water.
- It is important to ensure complete coating of the denuder, which can be checked visually, and to avoid contamination.

Denuder coating for gaseous nitric acid (+HCl, SO_2 etc)

- KOH with glycerine is recommended, with the KOH converting to K_2CO_3.
- Another option is to use a NaCl-coated denuder for the sampling of nitric acid and Na_2CO_3 + glycerol coating for the sampling of SO_2.
- Glass denuders should be soaked in acid and rinsed thoroughly with deionized water prior to KOH coating to activate glass surface and ensure effective coating.

Post denuder filters

- The same coating solutions may be used as impregnation solutions for filters
- Current practice suggests that pre-cleaning filters does not improve the results and is not recommended.
- For daily denuders, practice has been to use a post filterpack system. One common option is to use a standard three-pack system with a Teflon filter followed by a KOH filter followed by a citric acid coated filter. Aerosol base cations and sulphate are collected on the Teflon filter with part of the ammonium nitrate and ammonium chloride. Volatilized nitrate and chloride are captured on the KOH filter; volatilized ammonium is captured on the citric acid coated filter.
- Another option is to use a post-denuder filter-pack comprised of one Teflon filter, one Nylon filter and one H_3PO_3 impregnated paper filter. Aerosol base cations and sulphate are collected on the Teflon filter together with a fraction of the ammonium nitrate and ammonium chloride. Volatilized nitrate and chloride are captured on the Nylon filter; while volatilized ammonium is captured on the phosphorous acid coated filter. In order to simplify the procedure on can eliminate the Teflon filter and used a filter pack comprised of one Nylon filter and one phosphorous acid impregnated filter only. Sulphate and base cations as well as nitrate and chloride are collected on the Nylon filter, which retains also nitric acid volatilised from ammonium salts, while volatilised ammonia is collected on the phosphorous acid coated filter. This allows us to give an accurate value for

ammonium salts even if the distribution between volatilised and non-volatilised nitrate is unknown.

- For low-cost denuders, practice has avoided use of the Teflon filter and used the KOH filter to capture nitrate, sulphate, chloride and base cations and the citric acid filter to capture ammonium (which is fully volatilized from the KOH filter). This method reduces cost, but excludes determination of aerosol potassium and maybe sodium because of contamination of Na in KOH. If ion chromatography is used, the K-peak covers the Ca- and Mg-peaks.

2.5 Methodological artefacts

- It is well established that there are significant artefacts associated with filter pack sampling of NH_3/NH_4^+ and HNO_3/NO_3^-, as well as of HCl/Cl. In warm conditions NH_4NO_3 and NH_4Cl aerosol may volatilize from prefilters (and be recorded as the gases). In moist conditions gases may collect on prefilters.

- While these artefacts are a known problem with the EMEP daily filterpack, it is nevertheless recommended to report each of the gas and aerosol components separately, which should then be flagged appropriately as an FP estimate.

- The use of denuder/filter pack combination provides an approach to minimize the artefacts. Even these methods, however, may still associated with some smaller artefacts.

- HNO_3 and HCl losses in inlet lines are significant. Therefore a minimum inlet line should be used, as required to develop laminar flow (e.g. 2-10 cm, according to the system). Long inlet lines (e.g. >0.2 m must be avoided). Short polyethylene (not Teflon!) inlet is the best solution.

- Potential losses of volatile aerosol inside the annular denuders are negligible.

- By contrast, for NH_3, an inlet line (polyethylene or PFA) of >1 m can be used without significant differences.

- The high surface affinity of HNO_3 and HCl has the consequence that size selection inlets (cyclones or impactors) may cause artefacts if used upstream of collection of these gases. This problem cannot be avoided where size selection inlets are used for filterpacks. With denuder sampling, the particle size selection device should be located after the denuder and before the post-denuder filter pack used to collect aerosols. Also because of desorption of ammonia from coarse particles cyclones have to be located after the denuder and before the post-denuder filter pack used to collect aerosols.

- Potential losses of volatile aerosol can occur inside or following denuders. This is because the gas-aerosol equilibrium is disturbed following depletion of the gases, making the aerosol liable to volatilize. It is generally assumed that this effect is small, due to the small residence time in denuders, but the effect may increase volatilization from a post denuder cyclone/impactor or the Teflon filter of the filterpack.

- Given these interactions it is recommended that EMEP filterpacks are continued without the use of a size segregating inlet (i.e. continue the current well established method).

2.6 Corrections for imperfect or incomplete sampling

Imperfections in denuder coating vs. particle deposition

- In annular denuders, where two denuders are used in series, practice has often assumed that the denuders are 100% efficient, so that material collected in the second denuder represents aerosol deposition. In this case the amount in the second denuder is subtracted from the first.

- In the low-cost denuders, two denuders are always used in series, but here the purpose is to check on the denuder capture efficiency. Experience here suggests that occasional failure is due to imperfectly coated denuders (or migration of ammonium citrate in warm conditions). In this case material collected in the second denuder is added to the first, together with a small correction for uncollected gas. The correction is subtracted from the aerosol.

- These two approaches in principle will result in different calculation of air concentrations between gas and aerosol.

- Where the systems operate well (i.e. only a small amount is captured in the second denuder), these differences make little effect on the calculations. However, further consideration of this issue is needed be made to ensure comparability of approaches.

Estimation of ammonium correction from nitrate

- In some implementations of post denuder filter system (see above) a filter pack following denuders to remove acid gases and ammonia need only consist of a Teflon filter followed by a nylon filter.

- In this method the nitrate is estimated by the sum of nitrates collected on the Teflon and nylon filters. For ammonium, it is assumed that the same amount of ammonium volatilizes from the Teflon filter as for nitrate. As the volatilized ammonium is not measured, this assumption is used as a means to correct for the volatilization of ammonium from the Teflon filter.

- This method has been motivated by difficulties to obtain sufficiently low blanks for ammonium, but introduces the uncertainty that the amount of ammonium volatilized from the Teflon filter is generally larger than amount of nitrate volatilized. This is probably due to desorption of the gaseous ammonia adsorbed on both coarse and fine particles

- Given these uncertainties, where possible it is recommended to measure each component directly.

Estimation of aerosol nitrate and ammonium by difference between methods

- Another method proposed to obtain the correct partitioning between aerosol and gas for nitrogen species is to combine filter pack sampling of TIN, TIA with daily denuder sampling. In this possible approach, the aerosol would be calculated as:

$$\text{Aerosol } NO_3^- = \text{TINfilterpack} - HNO_3\text{denuder}$$
$$\text{Aerosol } NH_4^+ = \text{TIAfilterpack} - NH_3\text{denuder}$$

- This approach has been motivated by the concern that there might be losses of aerosol in denuder systems that do not reach the post denuder filter packs (e.g. in denuders, or inlet lines).

- Groups with experience of using denuders suggest that (with the possible exception of large particles) the internal deposition of particles appears to be trivial. Therefore the disbenefit of additional uncertainty due to calculations by difference would outweigh the potential advantage. The approach is therefore not in general recommended.

- By contrast, it is recommended that this approach would be useful as a basis for further tests of internal losses for large particles (Level 3 activity).

- This point may not be an issue for open-face filterpacks and low-cost denuders, since these do not efficiently sample large particle sizes.

2.7 QA/QC

It was agreed that sound quality assurance and quality control is vital for measurements of the gas/particle components. Each method used needs to incorporate both sound QA and QC approaches.

Daily filterpacks and daily annular denuders
The QA and QC approaches are already described in the EMEP sampling manual.

Low cost denuders
Standard good laboratory and field practice form the basis of the QA approaches, including a design with short 2 cm "end tubes" onto which closure caps are placed (avoiding site operator contact with the open ends of the denuders for analysis).

- For QC two main elements are used:
  - ✓ Two denuders in series are used for every sample (to calculate denuder sampling efficiency, in relation to the quality of denuder coating).
  - ✓ A minimum sample flow rate is applied, to highlight problems of pump failure or system leaks.
  - ✓ Based on discussion in the group it is recommended that parallel sampling with the low cost denuders is recommended to demonstrate robust results. In particular groups applying the approach for the first time are recommended to run 2-3 systems in parallel for at least 1 year.

- A manual for the DELTA low cost denuder method is available and will be made available for parties applying the approach, and it will be included in the EMEP Manual as well. A training and evaluation workshop in this method will be held in July 2005.

Passive sampling

- Passive sampling methods are not currently available for HNO_3, or aerosol NH_4^+ or NO_3^-. However, methods for passive sampling of NH_3 are widely established.

- Passive sampling of ammonia can provide a valuable technique for assessing local spatial variability as well as the representativity of EMEP sites.

- While passive sampling of ammonia has been shown by some groups to work well, it can also fail spectacularly, usually with overestimation of ammonia concentrations.

- Methods tend to fail when they are applied at levels lower than the suitable detection limit of the approach and when poor attention is made to treatment of blanks and pre-post-sample storage.

- Artefacts can be minimized by using high sensitivity passive samplers (e.g. IVL Ferm sampler, CEH Alpha sampler), by careful handling in the field (gloves) and by protection of samplers before and after exposure.

- A common artefact is occasional contamination of a sampler. To deal with this, it recommended as essential that all passive sampling utilize replicate sampling (e.g. at least triplicate samplers used for every sample period). Where the coefficient of variation is larger than an acceptable threshold (e.g. 25%) then samplers fail the quality control standard. Glass body samplers should be avoided since ammonia adsorbs on glass surfaces and can be released later on

- Given the range of different methods in use, it is not reasonable to impose a standard method. By contrast, if a method is to be used in the EMEP program, the method should be demonstrated as equivalent (or calibrated) to a denuder reference method.

- The demonstration of equivalence should include permanent parallel sampling of passive and denuder methods at common sites across the full range of encountered air concentrations. This is necessary, as performance needs to be demonstrated across relevant concentration ranges and to deal with the known changes in sampler performance associated with changes of the chemical analyst.

Calibration methods for continuous sampling techniques

- It is recognized that calibration of the continuous sampling methods is critical for their operation in the EMEP network. This issue applies both for gas sampling, e.g. AMANDA and AMOR denuders, mini-WEDD systems and steam jet aerosol collection systems.

- These systems are generally calibrated by measuring mass airflow and by conducting calibration against aqueous standards in the field. It is recognized that regular calibration is essential as performance of these systems can vary substantially over days and weeks.

- It is noted that in the new GRAEGOR/SJAC systems that a standard calibration including bromide is used for all samples as an additional quality check.

- It is also recommended that these systems are checked against permeation sources, where available (e.g. for SO_2).

3. Group B. EC/OC

3.1 Prefiring of quartz fibre filters

Pre-firing should be avoided if possible, as it activates the filters. Providing quartz fibre filters from the "right" manufacturer could be a good start. Based on experiences from JRC (ISPRA) the OC level of filters from Schleicher and Schuell provide low levels (0.4 µg C cm^{-2}) (0.3 µg C m^{-3} using a flowrate of 20 lpm) even when not prefired. Alternative ways to prepare quartz fibre filters were discussed, but this needs to be tested.

Prefired filters could be an alternative as an adsorbent in the combination denuder-quartz fibre filter-sorbent, addressed later.

3.2 Mass and the carbonaceous content from the same filters?

Mass concentration and the carbonaceous content should preferably not be obtained from the same filters. The common approach applied, dealing with EC and OC measurements of aerosols, is separate measurements of this.

3.3 Filter face velocity

An increase in filter face velocity will be important in order to reduce the positive artefacts of OC. However, since an increased filter face velocity potentially will promote negative artefacts, it is difficult to come up with a solution concerning this question. We need to know whether the positive or negative artefact is the most important to address. At this stage it is not possible to reach a conclusion on this topic until we know whether correction for artefacts shall be applied or not.

3.4 Instrumentation in laboratory

It can be large differences between the instruments available. I.e. the difference between Sunset and DRI (Desert Research Institute) is a factor 2 when it comes to EC. Between Sunset and the others it could be a factor 10. The same instrument should be applied for all filter samples devoted for EC/OC analysis within EMEP. Sunset is more common than DRI in Europe and should be looked at as reference instrument; other instruments need to be checked against this. Laboratory intercomparisons are necessary.

As long as the temperature programme provides BC as BC and OC as OC (std.), a given temperature programme should not be rejected. The results also depend on the monitoring system for charring – transmission or reflectance. The comparison between the different sites will benefit on such an approach.

Using one centralized laboratory for analysis of all samples was discussed. But this is a question of manpower and finances. But Parties interested in doing EC/OC measurements without the necessary laboratory facilities can of course order the analysis of the samples from an established laboratory.

The correction of charring in the stationary EGA-instruments is not optimal either, but it is the best that we've got. The soot produced during analysis is most likely not of the same quality as the soot present in ambient aerosols. However, some correction, all though not 100% correct, is better than none.

3.5 TC and Aethalometer, an alternative approach

The aethalometer has a high time resolution and can be used for monitoring total carbon. Based on this monitoring, interesting events can be identified and filter samples can be picked out for EGA-analysis. By this approach filter sampling needs to be performed according to the protocol even though only a fraction of the filters will be of interest for further analysis.

Hans Christen Hansson suggested that measurements of BC by aethalometers can be used as a supplement to EGA-measurements of EC (refractory carbon). Good agreements between the two approaches are reported from campaigns in Sweden.

Different aethalometer calibration slopes are seen for air masses dominated by different sources; different slopes for wood burning and for long range transport.

3.6 Water soluble organic carbon

WSOC is important as a proxi for SOC. It is easy to obtain and gives extra information. Levoglucosan is an example of a useful tracer species. It is recommended to measure WSOC as a level 3 activity in EMEP.

3.7 Sampling method/design

Quartz behind Teflon (QBT):
As the negative artefact is not addressed we could provide a lower estimate of OC by using this approach.

Poor knowledge concerning use in background areas.

The teflon filters could be used for chemical analysis or mass concentration. However, artefacts will be encountered for some of the chemical species.

Sampling requires 2 samplers and 3 filters, which costs a lot more than using just a single quartz fibre filter.

0.7 µg C cm^{-2} were found on the backup filters at ISPRA. Does this indicate that 0.4 µg C cm^{-2} as a field blank level still is too much?

Denuder-quartz-fibre filter-sorbent:
The combination of a denuder-quartz fibre filter and an active sorbent is perhaps a better alternative than QBT. However, the approach is expensive, and the active sorbent requires another temperature programme to estimate the negative artefact, than the particulate OC level.

Carbon impregnated filters can introduce problems concerning blank levels and dynamic blank levels

Contemporary conclusion:
It is difficult to come up with a final conclusion. A campaign is needed in order to evaluate the usefulness of these approaches in rural background areas.

When denuded filters are corrected for negative artefacts and not-denuded filters are corrected for positive artefacts the levels of particulate OC are comparable.

3.8 Sampling time

It is important that we address these problems, as it will affect the mass. Less than 12 hour is necessary to avoid gas/particle problems, but this will give less particles in the air passing through, which will strip the particles trapped on the filter. In addition it is recommended to have particulate mass measurements of the same time intervals.

4. Group C. Size segregated aerosol chemistry

4.1 Which PM sizes to priorities

It was recommend to measure two size fraction, either PM_{10} and $PM_{2.5}$ or PM_{10} and PM_1, the latter is more attractive from a modelling point of view, in addition it is in line with the GAW recommendation. However, $PM_{2.5}$ is important for the EU directives and here there are standard methods. But PM_1 measurements are very much welcomed in the EMEP network even though no standard reference method is available yet.

4.2 Denuder

Independent of the filter, it is recommended that a denuder should be put in front of the intake. However, one need to take care of which denuder type chosen e.g. depending on the chemical analysis that will be done. E.g. organic coating not possible if EC/OC measurements shall be performed.

However, there are some general concerns about the denuders which not are commercially available. So the implementation at the EMEP sites is difficult, and at this stage this can only be a suggested method and not required.

4.3 Filter type

- Quartz (20 lpm) may be used for inorganics as well as for OC. Quartz filters are fragile and many (except S&S) not suited for mass; for heavy metals, impurity of quartz may be a problem.
- Whatman may shrink when prefired, so care should be taken when using this filterers when prefiring is necessary.
- Teflon may be the better option for sites without OC. Teflon because of lower blank (possibly to be specified as well).
- Other membrane filters, e.g. with mixed cellulose esters, may be used.
- Cellulose filters may be acceptable as well, provided that blanks are (made) acceptable and proper denuder combinations are used. A problem can be uptake of HNO_3.
- Nucleopore filters may be used as well if done in a research project if accompanied by appropriate QC; but one needs backup filter for ammonium nitrate.

4.4 Mass closure

Mass closures is important for QA, source apportionment and are therefore recommended

Major concerns:

- Conversion factor for OC to OM.
- Missing compounds, water.
- Non-identical sampling between mass and chemistry.

- Dust. Si only measured with PIXE and XRF. However, XRF may suffer from absorption problems. Si may also be determined from the Al/Si ratio or from Mn/Si. For mass closure these elements are usually calculated as oxides. A centralized laboratory with e.g. synchrotron measurements may be an option.

4.5 Mass and chemical speciation separated?

Ideally, mass and chemistry should not be measured on the same filter because of problems with evaporation as well as contamination. If done on the same, evidence should be given that artifacts are negligible. Critical components are ammonium nitrate and OC.

It is not recommended to use filterpack in combination with a PM_{10}/$PM_{2.5}$ intake because of loss of HNO_3 (and potential other problems).

4.6 Continuous PM_{10} monitors

In general EMEP wants to use reference methods. Monitors can be accepted in EMEP if proven to be equivalent, so a documentation of equivalence is necessary. There are concerns about the quality of the monitors, and especially the jungle of correction factors that are used. The equivalent tests are often done at higher concentrations and may not be representative for the low concentration at EMEP sites. On the other hand, PM_{10} mass is not of critical importance for EMEP and less quality data may be acceptable if flagged properly. The optical measurements using e.g. GRIM are useful method for studying the size distribution. However, mass concentrations from these are doubtful and it is important that the correction factors used are transparent and not totally hidden in the reported values. EMEP sites are good platforms to document the quality of monitors since many measurements are going on to do QA/QC.

5. Group D. VOC

5.1 VOC species to be considered

The presently measured VOC species within EMEP are based on the capabilities of the GC-FID (for light hydrocarbons) and HPLC (for carbonyls). This, however, excludes a range of potentially important components. A revision and extension of the species to measure could for example be based on the VOC speciated emissions provided by UK's National Atmospheric Emissions Inventory (NAEI) as reported by Dore et al. (2004). Table 5.1, adopted from Dore et al. (2004), shows the photochemical ozone creation potential (POCP) for the top 50 VOCs (with respect to POCP) for the UK. The POCP identifies, on a relative basis, the ozone creation potential for each NMVOC compound through modelling studies. The creation potentials are then normalised by defining ethene as a creation potential of 1. Many of the components in Table 5.1 are not measured by the present EMEP VOC program due to limitations by the methods presently used, as e.g. alcohols, chlorinated compounds and long-chained alkanes. An extension to include these compounds in the monitoring program will require additional sampling devices as e.g. adsorption tubes.

5.2 Interpretation and use of monitoring data

- Trend analysis
    - Analysis of the long-term trends in selected species (emission tracers) can be used for compliance studies.
- Validation of compound specific emission inventories by EMEP modelling
    - By including speciated VOC emission profiles, the EMEP model could be used to model individual components and thereby check the model's VOC emission split. Furthermore, comparisons between modelled and observed individual components could be carried out.
- Tracer analysis and compound ratios for characterising air masses
    - (benzene, formaldehyde, isoprene, α-pinene, acetonitril…) could be used to identifying emission source types. Compound ratios could be used to characterize the air masses (toluene/benzene, n-/iso-butane, n-/iso-pentane, ethene/propene)
- halocarbon ratios (TCE/PCE) could be used as a possible parameter to estimate OH radical mixing ratios

5.3 Methodologies for sampling and chemical analyses

An extension of the compound list to be analysed requires different analytical methods. There is no standard procedure for C_7 to C_{13} VOC defined yet. But, up-coming activities within ACCENT and GAW will contribute to evaluate methods. Sampling methods are based on specific enrichment techniques, cartridges and adsorbents, at least 3 different ones. Artefact formation has to be carefully assessed, e.g. need of oxidant scrubbers e.g. DNPH method for oxidant scrubbers for carbonyls and reactive hydrocarbons.

5.4 QA/QC activities

- EMEP should use Audit questionnaire from WMO-GAW
- Joint GAW/EMEP courses are recommended
- Use DQO (data quality objectives) and metadata form from GAW

Table 5.1: POCP Weighted NMVOC emissions (adopted from UK's NAEI emissions reported by Dore et al., 2004).

	POCP	code	Stationary Combustion	Production Processes	Extraction and Distrib_ Fossil Fuels	Solvent Use	Road Transport	Other Transport	Waste Treatment	TOTAL (Mass Emission)	TOTAL (POCP Weighted)	TOTAL (POCP Weighted %)
butane	35.2	a	4.37	4.52	70.21	19.61	13.30	0.47	0.02	112	40	7.2%
ethanol	39.9	a	1.39	53.56		40.27			0.27	95	38	6.9%
ethylene	100.0	a	3.29	5.65	0.03		14.22	3.55	1.07	28	28	5.0%
toluene	63.7	a	2.03	4.06	0.24	11.44	16.95	3.10	0.16	38	24	4.4%
m-xylene	110.8	a	0.75	2.14	0.09	10.90	5.04	0.70	0.07	20	22	3.9%
propylene	112.3	a	1.65	6.01	0.02	0.00	6.80	1.37	0.06	16	18	3.2%
pentane	39.5	a	2.66	2.00	28.93	0.41	8.64	0.29	0.02	43	17	3.1%
hexane	48.2	a	0.51	4.39	14.93	2.32	7.92	0.20	0.10	30	15	2.7%
1,2,4-trimethylbenzene	127.8	a	0.00	0.52	0.01	5.44	4.69	0.51		11	14	2.6%
2-methylbutane	40.5	a	3.48	1.08	11.11	0.04	17.74	0.77	0.01	34	14	2.5%
formaldehyde	51.9	a	9.05	0.38	0.21	0.03	6.26	1.50	3.40	21	11	2.0%
o-xylene	105.3	a	0.25	0.75	0.04	2.74	5.05	0.80	0.04	10	10	1.8%
heptane	49.4	a	0.77	0.30	15.07	1.26	1.61	0.09		19	9	1.7%
propane	17.6	a	3.22	2.26	36.90	3.81	1.18	0.38	5.11	53	9	1.7%
ethylbenzene	73.0	a	0.24	1.75	0.03	4.17	4.93	0.77	0.12	12	9	1.6%
p-xylene	101.0	a	0.19	0.92	0.02	2.92	3.90	0.54	0.06	9	9	1.6%
ethane	12.3	a	5.84	1.46	49.57	0.00	3.15	0.57	5.44	66	8	1.5%
octane	45.3	a	0.06	0.18	13.27	1.10	0.77	0.09		15	7	1.3%
2-methylpropane	30.7	a	1.01	0.24	13.24	0.89	5.96	0.22	0.01	22	7	1.2%
trichloroethene	32.5	a		0.87		18.97			0.06	20	6	1.2%
1,3,5-trimethylbenzene	138.1	a	0.00	0.19		1.82	1.85	0.24		4	6	1.0%
2-butene	113.9	a	0.60	0.14	0.81		2.67	0.21	0.02	4	5	0.9%
2-methylpropene	62.7	a	0.15	0.68	0.26		5.23	1.03	0.00	7	5	0.8%
2-butanone	37.3	a		0.68		11.38	0.24	0.02	0.01	12	5	0.8%
1,2,3-trimethylbenzene	126.7	a	0.00	0.18		1.84	1.07	0.15		3	4	0.7%
methanol	14.0	a		2.01	0.00	26.09			0.07	28	4	0.7%
2-pentene	111.9	a	0.34	0.01	1.41		1.57	0.04	0.00	3	4	0.7%
decane	38.4	a	0.03	0.84	0.03	7.38	0.92	0.47		10	4	0.7%
1,3-butadiene	85.1	a	0.00	0.29	0.01		2.74	0.61	0.01	4	3	0.6%
butyl acetate	26.9	a		0.19		11.19			0.02	11	3	0.6%
1-butanol	62.0	a		0.23		4.58			0.01	5	3	0.5%
methylethylbenzene	94.1	c		0.23		2.91				3	3	0.5%
benzene	21.8	a	3.88	1.41	0.84	0.00	5.06	1.44	0.89	14	3	0.5%
4-methyl-2-pentanone	49.0	a		0.65		5.07				6	3	0.5%
acetaldehyde	64.1	a	0.00	0.75			2.86	0.67		4	3	0.5%
ethyldimethylbenzene	132.0	c		0.11		1.98				2	3	0.5%
1-butene	107.9	a	0.34	0.62	0.23	0.00	1.21	0.12	0.01	3	3	0.5%
naphthalene	97.7	b	0.48	0.02		1.43		0.01		2	2	0.3%
nonane	41.4	a	0.05	0.52	0.08	4.44	0.21	0.11		5	2	0.4%
2-butoxyethanol	48.3	a		0.10		4.48				5	2	0.4%
dipentene	74.5	b		0.01		2.84				3	2	0.4%
1-propanol	56.1	a		0.06		3.29			0.04	3	2	0.3%
acetone	9.4	a	0.19	1.93		17.04	0.81	0.08	0.00	20	2	0.3%
2-methylpentane	42.0	a	0.03	0.99	2.17	1.09		0.01	0.05	4	2	0.3%
2-propanol	18.8	a	0.01	0.73		8.92			0.02	10	2	0.3%
ethyl acetate	20.9	a		1.31		6.98			0.02	8	2	0.3%
undecane	38.4	a	0.00	0.44		3.85		0.19		4	2	0.3%
1-pentene	97.7	a	0.14	0.06	0.29		0.93	0.04	0.00	1	1	0.3%
3-methylpentane	47.9	a	0.02	0.67	1.21	0.86			0.03	3	1	0.2%
1,2,3,5-tetramethylbenzene	136.0	b		0.06		0.84				1	1	0.2%
Total Top 50 (POCP)			**47**	**109**	**261**	**257**	**155**	**21**	**17**	**868**	**399**	**72.3%**
unspeciated	51.3	c	1.86	32.11	1.20	7.06	1.22	0.36	0.01	44	22	4.1%
other grouped species			0.72	23.31	9.51	6.69	34.54	32.53	1.13	108	68	12.3%
other VOC			1.50	29.87	1.80	106.06	19.80	4.44	1.78	165	62	11.3%
Total VOC			**51**	**194**	**274**	**376**	**211**	**59**	**20**	**1186**	**552**	**100%**

5.5 References

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Appendix B

Agenda

Monday 22 November

08:30 - 09:00	Registration	
09:00 - 09:20	Welcome and practical information	
09:20 - 09:50	Introduction to EMEP monitoring strategy and expected outcome of the workshop	Kjetil Tørseth
09:50 - 10:20	Modellers needs	Dave Simpson
10:20 - 10:40	Low-cost methods for gas/particle distribution of nitrogen species	Mark Sutton
10:40 - 11:00	*Break*	
11:00 - 11:20	Continuous denuder/steam-jet methods	Eiko Nemitz
11:20 - 11:40	Sampling and chemistry of size segregated aerosols	Urs Baltensperger
11:40 - 12:00	Experience from EMEP aerosol and gas measurements	Wenche Aas
12:30	*Lunch*	
14:00 -14:30	Sampling and analysis of EC/OC	Jean-Philippe Putaud
14:30 - 15:00	Experience from the EMEP EC/OC campaign	Karl Espen Yttri
15:00 - 15:30	*Break*	
1530 - 16:00	VOC measurements in the GAW network: State-of-the-art and perspectives	Rainer Steinbrecher
16:00 - 16:30	Experience from EMEP VOC measurements	Sverre Solberg
16:45	*The bus leaves for NILU*	
17:30 – 19:00	*Excursion to NILU's laboratories*	
19:30	*Dinner (in Lillestrøm)*	

Tuesday 23 November

09:00 - 09:30	Introduction to working groups and expected outcome
09:30 – 12:30	Working groups to be held 2 and 2 in parallel:

09:30 – 11:00	**A**	Gas/Particle distribution	**B**	EC/OC
11:00 – 12:30	**C**	Size segregated aerosol chemistry	**D**	VOC

12:30 – 14:00	*Lunch*

14:00 – 17:00 Common session with EIONET

Air Quality monitoring strategies in Europe

Welcome, scope and goal of the common session

The scope of the session is to discuss improvements in the AQ monitoring efforts in Europe, to highlight the main requirements and the development of a strategy, which will support a harmonisation of objectives of all main activities.

Some expected inputs:

EMEP monitoring strategy	*EMEP*
Analysis of air quality monitoring networks in relation to protecting human health, indication of deficiency in European monitoring networks with respect to AQ Directives requirements etc.	*ETC-ACC*
Use of PM Airbase data for Health Impact Assessment – practical experiences of the APHEIS project	*WHO* *H.-Guido Mücke*

National contributions on how countries are planning to (re)-structure their monitoring systems in the light of the objectives from EMEP and requirements in the Framework and related Directives are welcomed.

Wednesday 24 November

09:00 - 10:00 Final discussions in the working groups
(**A** and **C** together; **B** and **D** together)

10:00 - 11:00 Presentations by the working groups in plenum (two topics)

11:00 - 11:20 Break

11:20 - 12:30 Presentations by the working groups in plenum (two topics)

12:30 - 13:30 Lunch

13:30 - 14:30 Writing up conclusions by the working group leaders -
advice to EMEP/CCC for extending the EMEP manual.

Appendix C

Presentations

Presentations

available at http://www.nilu.no/projects/ccc/tfmm/index.html

Introduction to the monitoring strategy and expected outcome of the workshop	Kjetil Tørseth	ppt, 3.2MB
Modellers needs	David Simpson	pdf, 2.7MB
Low-cost methods for gas/particle distribution of nitrogen species	Mark Sutton	ppt, 8.5MB
(Semi-) Continuous Measurement Techniques for Reactive Aerosol Components and Gases	Eiko Nemitz	ppt, 1.8MB
Sampling and chemistry of size segregated aerosols	Urs Baltensperger	pdf, 1.1MB
EMEP's experience Measurements of gas/particles with focus on nitrogen compounds	Wenche Aas	ppt, 4MB
Sampling and Analysing Organic and Black or Elemental Carbon	Jean-Philippe Putaud	ppt, 18MB
Experience from the EMEP EC/OC campaign	Karl Espen Yttri	ppt, 0.3MB
VOC measurements in the GAW network: State-of-the-art and perspectives	Rainer Steinbrecher	ppt, 1.8MB
Experience from EMEP VOC measurements	Sverre Solberg	ppt, 0.5MB
Implementation of the EMEP new monitoring strategy in France	Nathalie Poisson	ppt, 1.4MB