Conclusions and recommendations from the technical workshop on data quality and data reporting to EBAS

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At NILU, Kjeller, Norway
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Background

The workshop was covering two connected topics related to data submission to EBAS, one with hands on technical training in creating NASA Ames files for data submission, the other on the assessment of quality of some specific EMEP data and how to best document this information. The topics was discussed in parallel sessions.

The data reporting session included procedures for data and meta data reporting to EBAS and was thus relevant for EMEP, GAW (WDCA WDCRG), ACTRIS, HELCOM, OSPARCOM and AMAP site operators.

The data quality session focused on various topics, which have either had little attention the last years in EMEP (Inorganic ions, heavy metals and POPs) and components for which there has been large changes in assessment of quality and metadata information, i.e. ozone and EC/OC. The current understanding of the quality of these measurements and recommendations for improvements was discussed. Further, new metadata information on measurement methodology and quality assurance in the current templates was discussed. Recommendation from each sessions are summarized below. Agenda, participant list and presentations are found at: http://www.nilu.no/projects/ccc/tfmm/kjeller_2016/index.html

Formatting data for submission to EBAS

In the hands on training, participants formatted their own data and used the newly developed tool (http://ebas-submit-tool.nilu.no) for checking and correct for mistakes. Two general comments were that too frequent changes and updates in data format is very challenging for the data submitters, and information on where and how to use the different metadata can be improved.

More specifically on recommendations and follow up items:

- ***Python IO module,***
    - generating nasa ames files with python module - have one example for each template
    - Add the EBAS I/O module as a open source project on GitHub
    - Build UI on top of EBAS I/O- Enabling file generation through a user interface
- **ebas-submit-tool**

    - Fix EBAS submit tool documentation - specify UTF-8 error- bug fix and troubleshooting of encoding
    - Help section for converting excel to NASA AMES format. Tools and suggested workflow
- **QA-measures**
    - QA measures (bias and variability) for SMPS and DMPS should be given for concentration only, not for size bins.
        - Explanation should be added this specific template
- ***Template pages:***
    - Launch new template pages
    - Remove specific list of instrument type, manufacturer and model combination- instead link to instrument types, and then a commonly used list of all instrument, models and manufacturers
    - Secure static links to documents at NILU for SOP docs etc.

Inorganic compounds

- ***Status of the program –compliance with monitoring strategy***
  A majority of the sites measure in accordance to the reference methods and with daily sampling frequency. However, there is a worry that more sites change sampling frequency for the precipitation measurements from daily to weekly and even biweekly, and that Parties change their long-term filterpack measurements to the requirements as describes in the EU Air Quality Directive with chemical speciation in $PM_{2.5}$.

  Very few sites measure precipitation amount with a rain gauge in parallel. It is recommended that more sites start measuring and reporting these measurements.

  There are continuous methods like ToF- and Q-ACSM and MARGA, which are being used at some sites and these can be very useful supplement to the EMEP program and some (like MARGA) may replace filterpack measurements if it gives comparable results for assessing trends in space and time and has sufficient data coverage.

- ***Status of the data quality***
  Trends in performance in lab intercomparison show that the bias in lab performance has decreases substantially since 1977. However, the major improvements was the first ten years. After that it is not any significant improvements. For most ions and sites the bias is less than 5%; below 10% for Cl and Ca.

- ***Revision of the data quality objectives (DQO)***
  The current DQO in EMEP was defined in 1995, and these do not necessarily reflect the present need for accuracy to detect spatial and temporal variations. The labs capabilities have also improved over the years, with stricter accreditation regimes

etc. The group agreed that there is a need to revise the EMEP DQO and it was decided that EMEP should adopt the DQO as defined by the WMO/GAW TAD (total atmospheric deposition) programme.

- ***Defining the QA measure items***
  CCC suggested to use a statistical approach which was developed in 2003 (EMEP/CCC-Report 6/2003) to calculate relative standard deviation (RSD) and relative bias (RB) from the annual laboratory intercomparison, which should be used as input to QA variability and bias respectively.

  The calculations will be done by CCC, and the results can be downloaded from: http://www.nilu.no/projects/ccc/intercomparison/. Data submitters should download these data to be included together with in the annual reporting.

- ***Flagging of data below detection limits and quantification limit***
  It was a general confusion of how to use the flags related to detection limits, which currently are defined as:
  - ✓ *781 V Value below detection limit, data element contains detection limit*
  - ✓ *780 V Value below detection or quantification limit, data element contains estimated or measured value*

  In general laboratory practice, the detection limit is defined as 3 x standard deviation of lab blanks, while quantification limit is 10 times the standard deviation. It was therefore decided to clearly distinguish between these two terms and redefine 780 to:
  - *780 V Value below quantification limit, data element contains measured value*

  One should notice that 781 should be used when it is not possible to measure anything, and when used in aggregation half the value is being used in the calculations. Before changing the content of the flag, we must be sure that this does not hamper the historical use of the flag. CCC will make an evaluation of the historical use of 780 to see if the suggested changes will influence the status of these data.

  Use of flag 147 is an alternative to 780. Flag 147 has a better definition for typical measurements by monitors:
  - *147 V Below theoretical detection limit or formal Q/A limit, but a value has been measured and reported and is considered valid*

  After the workshop CCC has looked into the possibility to change the wording of flag 780, and it is not recommended since it can change the meaning of historical data. So it has been decided to keep the flag as they are for now, and if necessary new

flags may be created for purpose of clearer identify data under quantification limit, but not under detection limit.

- ***Measurement uncertainty***
  It is possible and a wish, to include a metadata item describing the measurement uncertainty for most components being reported to EBAS. However, it is necessary to define how these calculations should be done so they are comparable. There are many contribution factors to the uncertainty and how to quantify these can vary between methods. One may use GUM method as described in the "Guide to the Expression of Uncertainty in Measurement" (JCGM 100:2008), but the most challenging thing is to describe all possible contributions. One useful tool to visualize how different sources contribute to the overall measurement uncertainty is Ishikawa diagram also known as a 'fishbone'. Most of the accredited labs do have procedures where they need to report upon their measurement uncertainty, but there is not a harmonized procedure for doing this. It was therefore decided that EMEP/CCC ask the EMEP laboratories to report on how they calculate their measurements uncertainty and the results from this survey will be presented at the TFMM meeting and possibly then decide a common approach on how to report this.

- ***Common problems and challenges***
  There was an open discussion on various challenges the representatives' experience. I.e. in Norway, they have had for several years had much problems with contamination of NH_4NO_3 with Zeflour filters from Pall. Pall has stopped producing these filters and Norway have started using Millipore filters. Other labs has similar experience.

  It was a clear wish for more frequent discussions of this type to share experiences on small and larger problems and question people have in the laboratory and in the field. It was discussed the possibility for more dedicated workshops on data quality and maybe generating a facebook group where it is possible to discuss common problems.

Ozone and NOx

- ***New measurement guidelines and SOP***
  In WMO/GAW, new measurement guidelines for tropospheric ozone (WMO/GAW report No209) has been developed, and it was agreed that EMEP will adopt and harmonize with these. Also for NOx, there is a new guideline being developed by WMO/GAW and ACTRIS, and this will soon be published and it is recommended that this will be endorsed by the EMEP programme.

- ***New reference method for NO_2 and NOx***

In EMEP, the reference method for NO_2 is the manual method with impregnated glass sinters, and many Parties have used this for several years. However, there is an increased use of monitors, though the majority of these are chemiluminisence with molybdenum converters, which is not selective for NOx. In the later years new type of NOx monitors with selective detection of NOx has been developed, i.e. chemiluminisence with photolytic converters or cavity ring down spectroscopy method. It was agreed that these selective monitors should be the new reference methods in EMEP, though it is still ok to use the manual method.

- **New reporting guidelines for units**
  Ozone should from now on be reported in mixing ratio given as [nmol/mol] and not as $\mu g/m^3$ as previously done. Mixing ratio is measured by the instrument, and it is therefore recommended to report this to avoid possible errors in conversion between mixing ratio and mass unit. Secondly, with the transfer of ozone data from WDCGG to WDCRG at NILU there is a need for harmonisation. It is still allowed, though not recommended, to report the data in ug/m^3, provided that the data reporter include information on how the conversion have been done. In practice, this should be done by stating a standard temperature and pressure, which the conversion factor refers to. A temperature of 293.15 K and pressure of 1013.25 hPa corresponds to a factor of 2.00, which should normally be used. Export from EBAS will be given in both ug/m^3 and nmol/mol if the conversion factor is known. EMEP/CCC will not change historical data in the database, but Parties are may resubmit full time series for their ozone measurements in mixing ratio, including extended metadata information.

  For NO_2 there are two units in use. For manual method it is necessary to report ugN/m^3, but it is recommended to report monitor data in mixing ratio and CCC will convert between units during import as well as export in a unified way.

- ***Improved and new metadata items***
  To distinguish between selective and nonselective chemiluminisence monitors, two different instrument_names have been defined: chemiluminescence_molybdenum and chemiluminescence_photolytic. Using the instrument type ‘chemiluminescence’ is not allowed.

  There has been defined some new metadata points to better include detailed information of measurement procedures and maintenance, which is important to evaluate the quality of the data. I.e. for ozone in the “Maintenance description" element include information on filter test, leak tests, ozone scrubber test.

- ***Flagging when low data capture***
  In the new guidelines for ozone the data captures should be higher than 66%. Now the flags include data completeness less than 90%, 75% and 50%. It was therefore decided to add another flag to be in line with the guidelines, i.e:

389 Invalid Data completeness less than 66%
388 Valid Data completeness less than 66%

- ***Ozone absorption cross section***
  In all ozone monitors, the conversion from instrument signal to ozone mixing ratio relies on an assumed value for the ozone absorption cross section. This value has been unchanged for decades, but some recent publications have suggested a slight adjustment of this value. If this value is changed it is critical to report that in the ozone metadata and there is a special metadata element for doing so in the template.

- ***QA measure***
  For ozone there are two QA measures, either calibration and audit by the World calibration Centre (WCC EMPA), and/or calibrations performed using a laboratory standard traceable to a national standard. The QA bias should be calculated from the slope from the calibration curve. CCC will write a procedure how this should be done and include this in the guidelines for reporting

OC/EC

- ***Improved template for reporting***
  CCC emphasized that it is important that those submitting OC/EC data needs to use the updated format, which includes important information for evaluating the comparability and quality of the data, i.e. information on artefact correction or not, filter face velocity, detection limit. For calculating the measurements uncertainty there is an excel template developed by JRC, which should be used (http://ebas-submit.nilu.no/Submit-Data/Regular-Annual-Data-Reporting/EC-OC).

- ***Accounting for carbonate (CO_3^{2-})***
  Carbonate may vary from negligible (e.g. Scandinavia) to noticeable (e.g. the Mediterranean) causing potential overestimation of OC and EC. The Parties are encourage to make studies to evaluate whether carbonate may be of importance or not. Currently, there is no recommendation in the EMEP manual on how to account for carbonate but methods that can be applied are either acidification or Thermal-Oxidative pretreatment.

- ***Calibration of temperature in TOA instrument***
  CCC emphasized the importance of temperature calibration of the thermal-optical instruments. Studies have showed that there can be large differences between the observed temperature and the protocol defined temperature if calibration has not been done, and this could have a noticeable impact on the OC/EC split.

EUSAAR-2 will be adopted in the new CEN standard, and temperature calibration is part of the standard operating procedure.

- ***QA measure***
  The results from the laboratory intercomparison, which is conducted under the EU-funded project ACTRIS-2 in co-operation with EMEP, should be used as QA measure. The QA bias and the QA variability will be calculated centrally and these results will be posted on the EMEP CCC web. The data submitters should use these results in their annual reporting.

Heavy metals

- ***Laboratory intercomparison and QA measure***
  The laboratory intercomparison has two low and two high concentration samples. However the high concentrations are not realistic levels in the network anymore, and it was decided that this intercomparison should change to be similar as for the inorganics with four samples with similar concentration range and with a level representative for most sites. This will also make it possible to use the same statistical approach as for the inorganics to calculate QA bias and QA variability. One should use the results from this laboratory intercomparison also for measurements in aerosols.

- ***Common problems***
  It was discussed how the different labs use the results from field blanks. France correct data while others don't. The number and frequency of field blanks also vary. It is important that if field blanks are used to correct data that this is indicated with the data reporting. It was also expressed wished to have more discussion on this item to share experience and to potentially harmonize how to use field blanks in the network.

Mercury

- ***Component name***
  In EBAS the component names used for different forms of mercury is somewhat a mess, and there has not yet been developed a new template for this compound. It is a strong need to clean up and harmonize the reporting of mercury.

  It was suggested to simplify and decrease the reporting to three compounds:

  - ✓ **Mercury.** This will include both elemental_gaseous_mercury, (or gaseous elemental mercury (GEM)) and total_gaseous_mercury (TGM). To difference between TGM and GEM it is necessary to indicate this by using the metadata actively, i.e. whether soda lime absorbent has been used or not. Particulate_mercury should also be called mercury only, since by using the matrix aerosol, pm10 or pm25, it is implicit that it is particulate form.

- ✓ **Gaseous oxidized mercury (GOM).** This is the same as reactive_mercury and reactive_gaseous_mercury (RGM). GOM is preferred since it is a better description of what it is and the fact that GOM is now being more used as the reference name in other networks like in US.
- ✓ **Methyl mercury.** It includes both gaseous_methyl_mercury and methyl_mercury (air and precipitation)

- ***Define a template for reporting of mercury***
  There is a need to come up with a template for mercury including more stringent possibilities for reporting as well as open up for more information of quality, methods, include more information on how instrument is treated and calibration. CCC will make a suggestion and circulate this with the data reporters of mercury and other experts to get necessary input on which metadata is necessary to include and how.

- **Reference methods and standard operating procedures**
  The monitor measurements are presently not defined in the Manual. CCC will contact experts in the EMEP and AMAP networks and others for suggestion on how to proceed. The EU project GMOS has developed an SOP, which may be possible to implement.

- **Data quality**
  There are measurements in EMEP, which obviously struggle with low detection limits or inconsequent data. There is a need to focus more on data quality on mercury measurements. It was suggested that it is time to initiate another field intercomparison on mercury.

POPs

- ***Define a template***
  Also for POPs a template is missing. CCC will make a suggestion and circulate this with the data reporters of POPs and other experts to get necessary input on which metadata is necessary to include and how. Two important metadata points where discussed and approved at the meeting:

  Medium:
  This is the place to indicate what type of filter and/or other adsorbents used for collecting the air samples. For POPs this is usually either a filter or a filter/PUF/XAD combination. The different combination used needs to be predefined, and when submitting data only these defined options can be used. Currently the labs have indicated the following use:

  Quartz
  Quartz+PUF
  Quartz+PUF+PUF

Quartz+PUF+XAD+PUF

Glass fiber
Glass fiber+PUF
Glass fiber+PUF+PUF
Glass fiber+PUF+ XAD+PUF

Teflon
Teflon+PUF
Teflon+PUF+PUF
Teflon+PUF+XAD+PUF

If other options are used, this should be informed to the EBAS data base group, i.e. send an email to ebas@ebas.no

Sample preparation:
Under this item, it is possible to indicate how the sample has been prepared after being received in the lab. It is been identified four important steps and various combination of how these are performed needs to be reported.

The steps that should be addressed:
extraction+solvent+internal std+clean

The different combination used will be predefined, and when submitting data only these defined options can be used. Currently the labs have indicated following use:

Soxhlet+Dichloromethane+13C+Silica
Soxhlet+Dichloromethane+No+Silica
Soxhlet+Dichloromethane+13C+Silica/acid
Soxhlet+Dichloromethane+No+Silica/acid
Soxhlet+Di-ethyl ether/Hexane+13C+Silica
Soxhlet+Di-ethyl ether/Hexane+No+Silica/acid
Soxhlet+Hexane+13C+Silica
Soxhlet+Hexane+No+Silica

Ultrasonication+ Di-ethyl ether/Hexane+13C+Silica
Ultrasonication+ Di-ethyl ether/Hexane+No+Silica

microwave+ Di-ethyl ether/Hexane+No+Silica

If other options are used, this should be informed to the EBAS data base group, i.e. send an email to ebas@ebas.no

- ***QA measure***
  There are not laboratory intercomparison of POPs on an annual interval in EMEP, but there has been are a few ones which are relevant. I.e. in 2010, it was one in cooperation

with AMAP and the northern contaminate programme (NCP) in Canada. NCP has annual lab intercomparison, and there are also others which several labs participate in. These are not necessarily focused on air measurements, but is relevant for assessing the performance of the laboratory. The results from these laboratory intercomparison are difficult to use to assess QA accuracy and QA bias, and it will be also too complicated to do these for all species. However, it is relevant to know whether the lab take part in international or national intercomparison and it is therefore recommended that one report upon this, i.e:

QA1 measure ID:	AMAP/EMEP/NCP _2010
QA1 measure description:	AMAP/EMEP/NCP inter-laboratory study for POP analysis 2010
QA1 document name:	EMEP/CCC-Report 7/2011
QA1 document URL:	http://www.nilu.no/projects/ccc/reports/cccr7-2011.pdf

It was discussed whether it is due time to initiate another intercomparison in EMEP, maybe this could be also looking at methodological differences which may cause problems with breakthrough etc.