

Deliverable D3.8: Report on Procedure for QC of reactive gases

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1. Procedure for QC of Volatile Organic Compounds

1.1. Production of the VOC dataset

In ACTRIS-2 concentrations of atmospheric VOC species are analysed by gas chromatography with subsequent detection by flame ionization or mass spectrometry. From chromatograms concentrations of VOC species are calculated in a semi-automated way, where the automatic peak integration and comparison of the calculated area against a certified standard of similar concentration is followed by a visual inspection. In addition to the air measurements regular zero air and target gas measurements have to be performed, according to the ACTRIS-VOC measurement guideline.

1.2. Regular quality checks

Furthermore, it is mandatory that data providers check the consistency of the data on a regular basis against historic data from their own site or against historic data from a reference site. The suggested time frame for these checks is on a monthly basis. These consistency checks are available at <ftp://ftp.empa.ch/pub/empa/outgoing/Abt503/rei/ACTRIS-2> and they also build the backbone of the quality assurance before final, annual submission of the data (see section 3).

At the FTP site an individual folder for each ACTRIS site is available, which contains an xls file with the historic data from the individual site and the historic data from the Hohenpeissenberg station (which acts as a reference).

1.3. Annual quality checks and submission of data to EBAS

Before final submission of the data on 30 June the dataset of the previous year undergoes a thorough check which is graphically described in Figure 1. A lot emphasize is laid on the interaction between the data provider and DWD/Empa/NILU who are responsible for the end-of-the year data check.

The first step is performed by Empa, who opens a new thread on the so-called “issue tracker” (available at <http://ebas-feedback.nilu.no/>), which informs the data provider that data, which has already been checked using the tool described in section 2, has to be submitted via the EBAS submission tool, located at <http://ebas-submit.nilu.no/> by 31 March. This submission tool has been newly devised in 2016 in ACTRIS-2 (deliverable 3.6) to facilitate the data submission and accelerate the publication of the final data set under EBAS.

Data is then automatically transferred to the ftp server for incoming data <ftp://ebas-submissions.nilu.no/incoming> from where it is retrieved for an extended quality check described in Annex 1. After the check feedback is provided to the data submitter until 30 April via the issue tracker, pointing to inconsistencies against the historical data from both the site itself and the reference site. Furthermore, other issues such as wrongly assigned or missing flags are addressed.

The data provider can then address these issues and potentially resolve them until mid May. In mid May the annual data quality workshop takes place. The attendance at this workshop is mandatory for the data provider under the ACTRIS label. Here more severe issues are discussed, which cannot be resolved by the data providers on their own or which have implications on the whole network (e.g. inconsistencies of standards, shifting blank values for certain methods). Furthermore, the method of the data quality checks is discussed and further developed. The remaining issues have to be resolved by the data providers in discussion with EMAP/DWD/NILU before final submission to EBAS on 30 June.

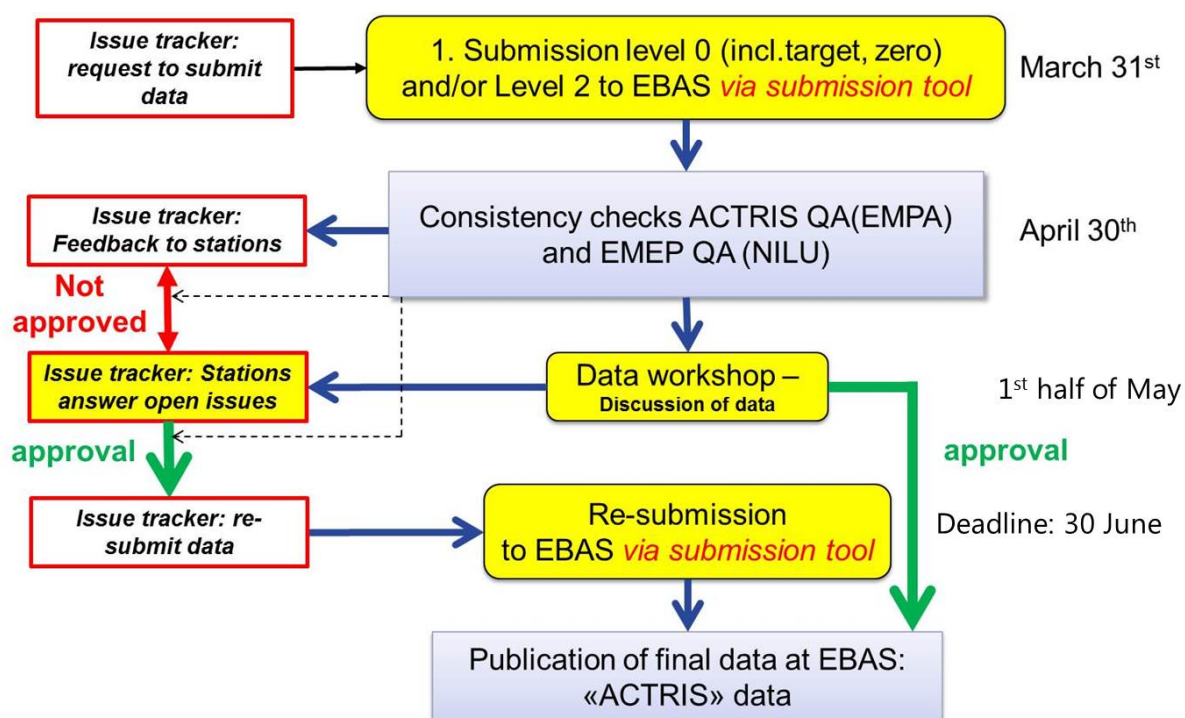


Figure 1 Flow scheme agreed within ACTRIS-2 for the quality assurance of VOC measurements to be submitted as ACTRIS data under EBAS.

2. Procedure for QC of NO_x

2.1. Production of the NO_x dataset

Concentrations of atmospheric NO_x are analysed by instruments using chemiluminescence detection (CLD) for NO coupled with blue-light converter (BLC) for NO₂, or molybdenum converter for NO₂+. Additionally, for NO₂ instruments are available using optical techniques with iterative cavity DOAS (ICAD) and cavity attenuated phase shift (CAPS). The time resolution of these measurements differs between 1s to 1min. Due to artefacts in the NO_x determination by ambient air O₃ (titration of NO with ambient O₃ in the inlet line) and H₂O vapour (quenching of the chemiluminescence) levels, corrections need to be applied. The correction procedures are available at the World Calibration Centre for NO_x (WCC-NO_x, FZ Juelich), which monitors and accompanies the quality assurance process.

The NO_x data are available in three different data levels:

- 0) NO_x mixing ratio in the original time resolution as produced by the instrument
- 1) Corrected NO_x mixing ratio in the original time resolution as produced by the instrument
- 2) Corrected NO_x mixing ratio 1h averages

2.2. Regular quality checks

To achieve the required quality to perform ambient air measurements at background conditions the following requirements/checks/setups are essential at an ACTRIS site:

- ➔ Inlet and other line materials: PFA ('dark'), short residence time of few secs.
- ➔ Gas phase titration unit with O₂ and zero air supply
- ➔ Zero air generator and / or zero air supply
- ➔ Laboratory standard (certified), working standard, and regular measurements of those gases
- ➔ A (automated) plumbing system
- ➔ Data acquisition system
- ➔ Skilled personnel
- ➔ Parallel Ozone measurements
- ➔ Parallel Water vapour measurements

Regular measurements of zero air are needed to monitor the instrumental offsets of the CLDs. Further, parallel O₃ and H₂O vapour measurements enable the correction for artefacts.

The data will be corrected by the WCC-NO_x in the submission process (see below). In future years, this expertise should be available at the individual measurement sites. At this point in the project, each site is encouraged to perform the required corrections for O₃, H₂O and offset individually. Only if a site is not capable to perform this correction, the WCC-NO_x steps in.

2.3. Annual quality checks and submission of data to EBAS

The annual data submission process is graphically described in Figure 2 is led by the WCC-NO_x. Each station is required to send at least level "0" data via the EBAS submission tool (<http://ebas-submit-tool.nilu.no>) by March 31st. From there the data is transferred to the WCC-NO_x, where level 0 data are processed and the O₃/H₂O-correction procedures are applied. Level 1 and level 2 data produced by the WCC-NO_x are then compared with the submitted Level 1 and 2 data and consistency checks (offset assessment etc.) are performed.

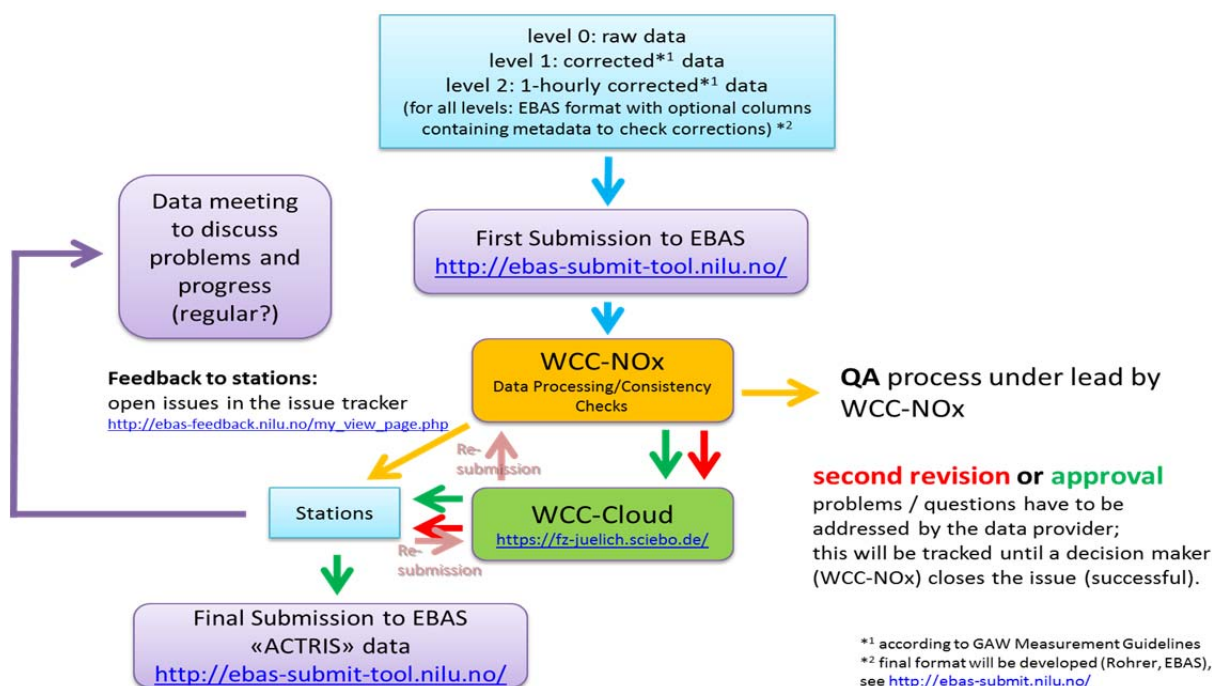


Figure 2 Flow scheme agreed within ACTRIS-2 for the quality assurance of NO_x measurements to be submitted as ACTRIS data under EBAS.

The processed data are subsequently transferred to the WCC-cloud, where the ACTRIS sites can access their data. Problems and open issues are discussed bi-lateral between the WCC-NO_x and each site. This process will be monitored in future submission cycles by an issue tracker (see 1.3.) similar to the VOC data flow.

The data provider can then address these issues and potentially resolve them until mid-May. In mid-May the annual data quality workshop takes place. The attendance at this workshop is mandatory for the data provider under the ACTRIS label. Here more severe issues are discussed, which cannot be resolved by the data providers on their own or which have implications on the whole network (e.g. inconsistencies of standards, shifting blank values for certain methods). Furthermore, the method of the data quality checks is discussed and further developed. The remaining issues have to be resolved by the data providers in discussion with WCC-NO_x before final submission to EBAS on 30 June.

ANNEX1

The consistency of the newly produced dataset with the historic data from the station itself and from comparable stations in Europe is the most important tool to check the quality of the data. For detection of potentially erroneous measurements in ACTRIS the following two methods are used. Currently these checks are still done manually but in the further course of ACTRIS-2 these checks will be automated and managed in conjunction with EBAS.

1) Check for absolute concentration errors

The rationale for this test is, that changes in VOC sources which influence the concentrations at a certain site do normally not change abruptly but rather continuously and over a long time horizon (e.g. by tightening emission values from catalytic converter systems or from industrial emissions). The check of the absolute concentrations has to be performed by comparison of the new dataset with the historic dataset from the same site and with the historic dataset of Hohenpeissenberg (Figure A1). Rapid changes especially at the beginning of the year are the most obvious potential mistakes. However, also abnormal high or low concentrations have to be checked, which could be due to mistakes in the chromatography.

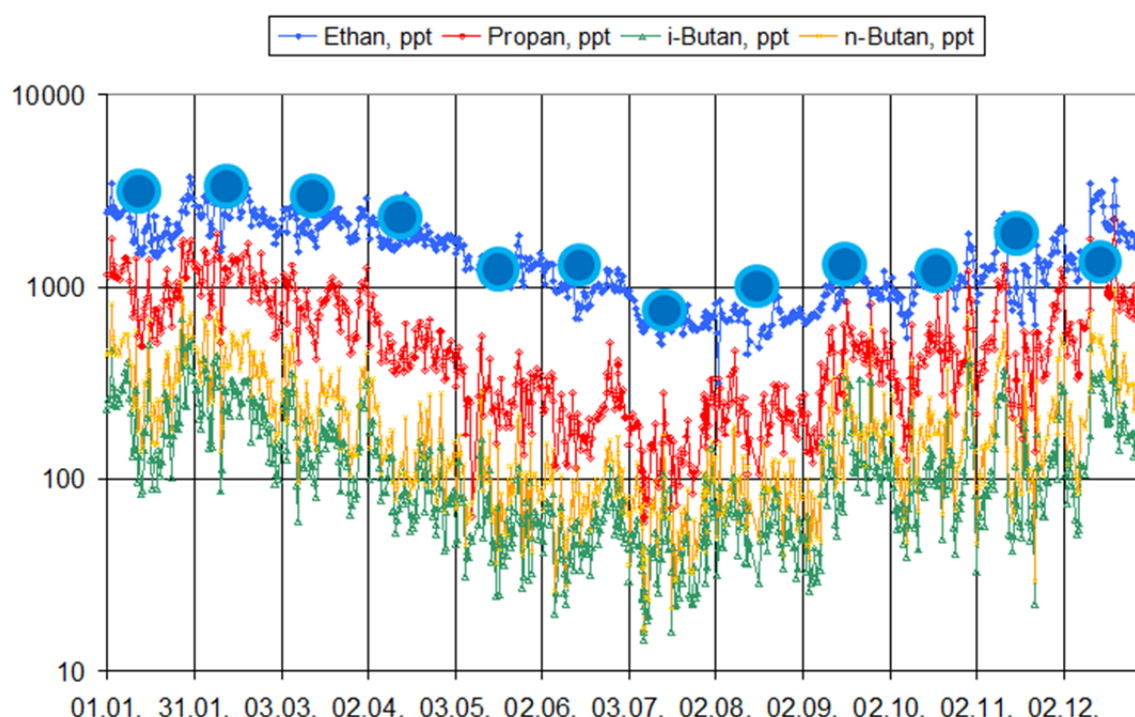


Figure A1: Check of the measured ethane concentrations from the current year against concentrations from the former year (shown as monthly averages).

2) Check for relative concentration errors

The rationale for this test is, that the ratios between VOC species at a certain site in Europe are comparable. This is due to the fact that European sites detect similar sources (e.g. traffic, use of solvents, biofuel emissions). These sources have very stable ratios of specific VOCs, which as for absolute values above, only underlie very slow changes. Therefore, ratios of similar VOC species (e.g. alkane 1 against alkane 2) provide extremely good checks for mistakes. Data points which clearly lie out of the normal cloud of data in a xy-plot have a high probability of being incorrect. They are only taken as approved data points after a thorough check of conditions (e.g. special meteorological conditions, unusual sources). Figure A2 shows an example for benzene vs. ethyne. These two VOC species are emitted predominantly by the exhaust of cars. Red data points below of the normal data cloud were flagged because after the

restart of the system. Red data points above the normal cloud were also flagged because of a local contamination event in August.

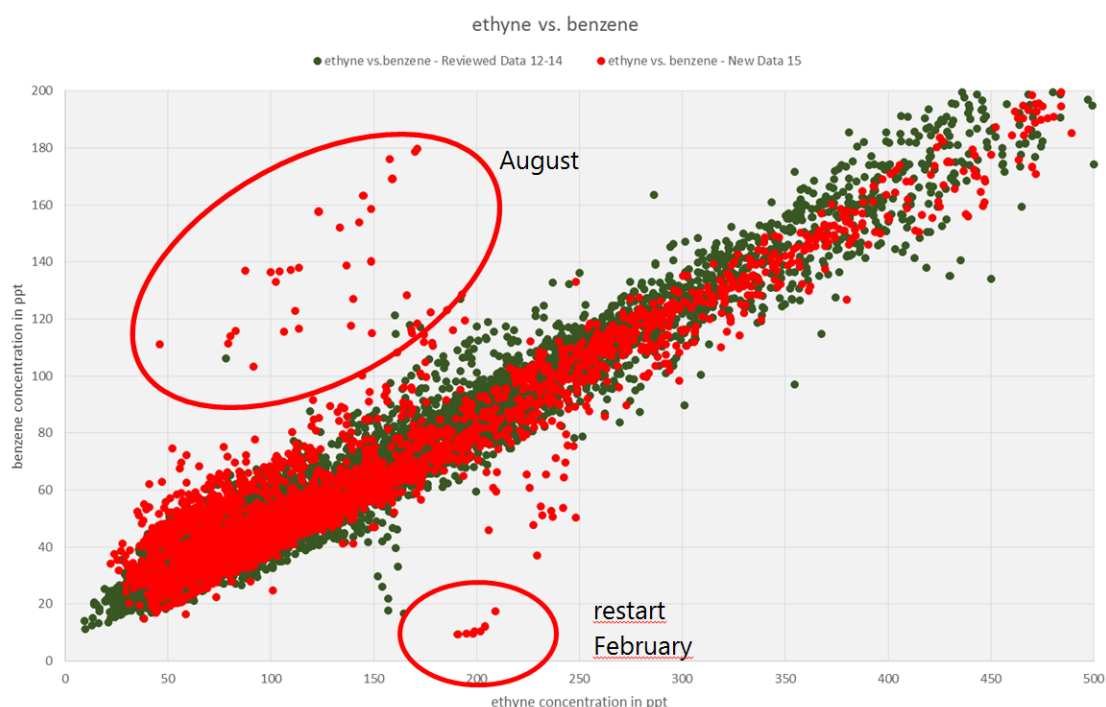


Figure A2. Example for the use of xy-plots for checking the consistency of submitted data. Red data points show measurements from 2015; green data points show measurements from the same site during 2012-14. Outliers in February could be identified as issues during the restart of the instrument. Outliers in August were identified as caused by local contamination.

In Table A1 the ratios used in ACTRIS-2 for quality checks are shown together with their slope and the y-axis value. These values together with the respective confidence intervals will be the basis for a test method to automatically check VOC data: new data can be compared to the climatology of slopes; in case a significant deviation is observed, the data are marked (e.g. by a flag) and this information is returned to the data provider. Such a procedure is currently tested and will be implemented within ACTRIS-2. However, before implementation further statistical analysis of all ACTRIS sites is required to yield robust measures covering all regions and station characteristics.

Table 1: xy-plots used as proxies in ACTRIS-2 for detection of incorrect concentrations of VOC species, related to the data of Rigi (Switzerland). Indicated are the slope (y/z , e.g. propane vs. ethane = 0.517) and the y-intercept in [ppt].

x-axis	y-axis	slope	y-axis intercept [ppt]
ethane	propane	0.517	- 267
ethane	n-butane	0.180	- 82
ethene	propene	0.105	+ 14
ethene	ethine	0.587	+ 75
ethine	benzene	0.356	- 3
propane	n-butane	0.377	- 5
methylpropane	n-butane	1.652	+ 14
methylpropane	2-methylbutane	0.958	+ 46
n-butane	n-pentane	0.525	+ 2
2-methylbutane	n-pentane	0.835	- 21
benzene	toluene	0.682	+ 44
benzene	1,3-butadiene	0.045	+ 4
ethylbenzene	m/p-xylene	2.518	- 4
toluene	m/p-xylene	0.328	- 1
m/p-xylene	o-xylene	0.386	+ 0