

**Global Atmosphere Watch
World Calibration Centre for Surface Ozone
and Carbon Monoxide**



**Swiss Federal Laboratories for Materials Testing
and Research (EMPA)**

REPORT

**Submitted to the
World Meteorological Organization**

**SYSTEM AND PERFORMANCE AUDIT
FOR SURFACE OZONE
GLOBAL GAW STATION ZEPPELIN MOUNTAIN
AT NY-ÅLESUND, SVALBARD, SEPTEMBER 1997**

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1. Abstract

A system and performance audit was conducted by the World Calibration Centre for Surface Ozone, at the global GAW station Zeppelin Mountain at Ny-Ålesund, Svalbard. Below, the findings, comments and recommendations are summarised:

Air Inlet System:

The teflon tube and the rain protection of the inlet were clean and free of dust. The inlet system, concerning construction materials as well as residence time, is adequate for gas analysis. No loss of ozone could be detected.

Although no loss of ozone could be detected still it is regarded as necessary to move the analyser closer to the manifold and use the former shorter line as soon as possible. This since the shorter the line the lower the loss of ozone will be over the time, i.e. particle deposition.

Instrumentation:

The measurement technique used is the UV-method which is the preferred method in the GAW programme.

The non-linearity of the Monitor Labs analyser (see 4.2.) has serious effects on data of the very low concentration range. Depending on how the instrument had been calibrated (see 4.4.), these values are either over or underestimated. For global GAW sites outside the polar regions ozone values below 5 ppb do not occur. But at Zeppelin Mountain this non-linearity causes a problem when investigating episodes of very low ozone concentrations (0 and 5 ppb) which are an observed feature during several days in spring. Therefore a special correction function for very low ozone value has to be developed or the instrument has to be exchanged by a ozone analyser being linear at low concentrations as well.

For a proper quality assurance it is seen as essential that additionally to the ozone standard in the calibration laboratory at NILU another so-called transfer standard is available for multipoint calibrations on site (see also Operation and Maintenance).

Data Handling:

The procedure of data treatment is clearly arranged and transparent which increases the re-liability of the data. Though, it is considered as important that criterias for calculating a valid mean value should be worked out and integrated in the processor programme. Further is noted that with the described data treatment procedure only serious instrument malfunctions can be seen.

Concerning the zero point correction a data treatment that deviates from the actual practice is strongly recommended. For further details see Appendix I.

Operation and Maintenance:

The appearance of the station is clean and functional.

To achieve the GAW objectives and with regard to the quality assurance guidelines for surface ozone, in the WMO-GAW Report No. 97, it is required to perform multipoint calibrations twice a year on site. As a consequence, an ozone transfer standard has to be purchased.

Although access to the site is costly it is necessary to follow NILU's ozone SOP more strictly in terms of regular preventive maintenance to improve the operation of the ozone analyser. During such a station visit the operator is advised to follow a maintenance schedule. It should at least incorporate a leak test, exchange of the inlet filter and checking of the pressure transducer every three month, cleaning of the instruments glass cells and testing the scrubber performance (and exchanging if necessary) once a year.

A good co-operation with the Norwegian Polar Research Institute is seen as fundamental for a further successful operation of the Zeppelin Mountain station. However, concerning maintenance works on the ozone analyser by the NP staff, it was noted that some tasks were not carried out. Questionnaire forms to be filled in by the operators during the maintenance, containing the tasks and the intervals, could help improving the reliability.

Documentation:

The documentation of the ozone measurement meets the requirements of the GAW guidelines. It consists of logbooks as well as graphical plots of the data. However, a detailed questionnaire-like single sheet which is filled in during maintenance, for the purpose of traceability, is suggested.

Competence:

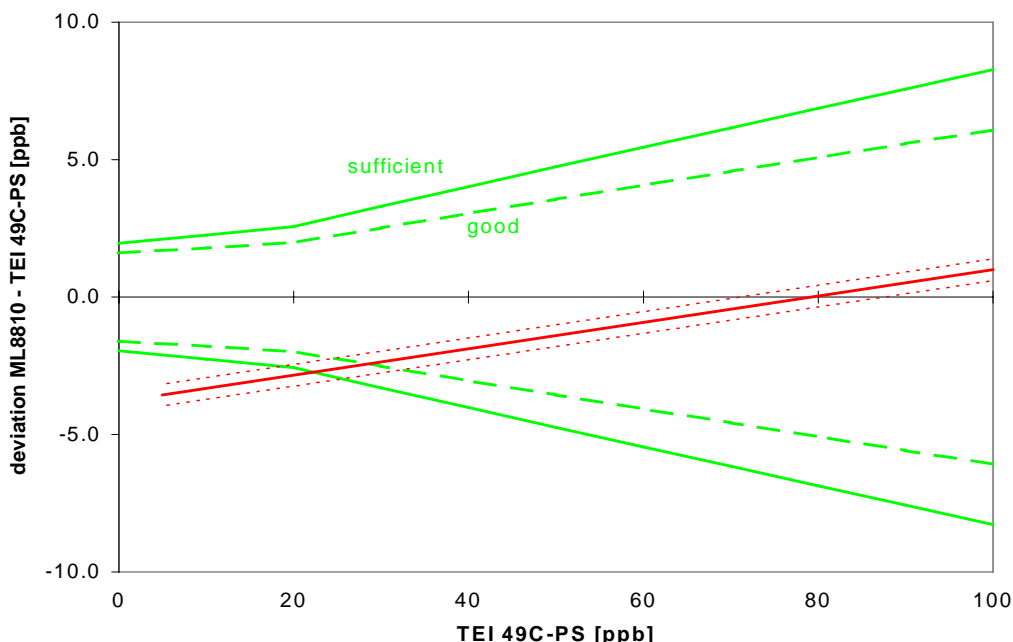
All persons at NILU associated directly or indirectly with the operation of the station are highly motivated and experts in their fields. Obviously, due to long-standing experience and adequate education, the operators were very familiar with the techniques and problems connected with ozone measurements. With the high fluctuation rate of the staff working for NP in Ny-Ålesund NILU responsables should prove the potential of an intensive maintenance training and make sure that such know-how is then handed over to new co-workers.

Instrument Intercomparisons:

The ozone concentrations observed at Ny-Ålesund (1996) usually ranged between 23 and 45 ppb (5- and 95-percentile of hourly mean values). But episodes of very low ozone concentrations (0 and 5 ppb) are a common feature in spring which are atmospheric chemically interesting events. Therefore, by assessing the results it has to be distinguished between the usual and the very low concentrations. For the usual concentrations, higher 23 ppb, the resulting mean linear regression of the field instrument lies partly in the "sufficient" and "good" range and fulfils the assessment criterias (figure 1). However, for the lower values (< 20 ppb) the instrument is assessed outside tolerance. Since the deviations are mainly according the non-adequate calibration procedure (which should consider the analyser's non-linearity), the problem can be easily solved by applying the adequate correction function (see Appendix I).

Fairly small deviation among the three intercomparisons is the reason for a narrow prediction interval for the analyser which implies that the instrument is in reasonable condition.

Figure 1: Intercomparison of instrument ML 8810



Dübendorf, 14. October 1997

EMPA Dübendorf, WCC-O₃

Project engineer

Project manager

A. Herzog

Dr. B. Buchmann

Technical assistant: M. Hill

2. Introduction

In establishing a co-ordinated quality assurance programme for the WMO Global Atmosphere Watch programme, the air pollution and environmental technology section of the Swiss Federal Laboratories for Materials Testing and Research (EMPA) was assigned by the WMO to operate the WMO-GAW World Calibration Centre for Surface Ozone for Europe and Africa (WCC-O₃). At the beginning of 1996 our work started within the GAW programme. The detailed goals and tasks of the WCC-O₃ are described in WMO-GAW Report No. 104.

In agreement with the responsible persons at the Norwegian Institute for Air Research (NILU) who are in charge of the tropospheric ozone measurements a system and performance audit at the global GAW station Ny-Ålesund was conducted. The station on Zeppelin Mountain is an established site for long-term measurements of several chemical compounds and physical and meteorological parameters. It is located on the north western coast of Spitsbergen (Svalbard), in the Arctic. The site offers excellent exposure to polluted air that is transported into the Arctic, in particular during late winter and early spring, when the transport from polluted areas is at its maximum.

The scope of the audit, which took place from September 17 to 22 in 1997, was confined to the tropospheric ozone measurements. The entire process, beginning with the inlet system and continuing up to the data processing, and also the supporting measures of quality assurance, were inspected during the audit. The audit at Zeppelin Mountain was performed according to the "Standard Operating Procedure (SOP) for performance auditing ozone analysers at global and regional WMO-GAW sites", WMO-GAW Report No. 97. The assessment criteria for the intercomparison have been developed by EMPA and are based on WMO-GAW Report No. 97 ("Traceability, Uncertainty and Assessment Criteria of ground based Ozone Measurements" by P. Hofer, B. Buchmann and A. Herzog, 1996, available on request from the authors at: EMPA, 134, Ueberlandstr. 129, CH-8600 Dübendorf).

The present audit report is submitted to the station manager from the Norwegian Polar Research Institute, the responsible persons at NILU, the World Meteorological Organization in Geneva and the Quality Assurance and Scientific Activity Centre (QA / SAC) for Europe and Africa.

System and performance audits at global GAW stations will be regularly conducted on mutual arrangement every 12 to 18 month.

3. Global GAW Site Zeppelin Mountain, Ny-Ålesund

3.1. Site Characteristics

Ny-Ålesund in the European Arctic is one of the world's northernmost human settlements. It is situated on Kongsfjorden - the King's fjord - on north-western Spitsbergen, which is the largest of the Svalbard islands. The town lies surrounded by mountains and glaciers, which at several places stretch well out into the sea. Large areas of Svalbard (about 60 %) are covered with glaciers. Svalbard with an area of 62'049 km² is very sparsely populated. The about 3'200 inhabitants are living in one of the five small settlements on Spitsbergen. The Norwegian town Ny-Ålesund is permanently maintained by about 30 people and additional approx. 150 scientists during summer peak season.

The global GAW station Zeppelin Mountain (coordinates: 78°54'29" N, 11°52'53" E) near Ny-Ålesund lies south of the town. The monitoring station was built in 1988 / 89 on a small plateau 473 m.a.s.l, easterly of the near top of the Zeppelin Mountain (station encircled on the picture below). The station is easy accessed by cable car and consists of a one story building with a 6.6.m x 6 m measuring room and a separated pump room. Several equal air inlets and some meteorological equipment are mounted on the top of the flat roof.

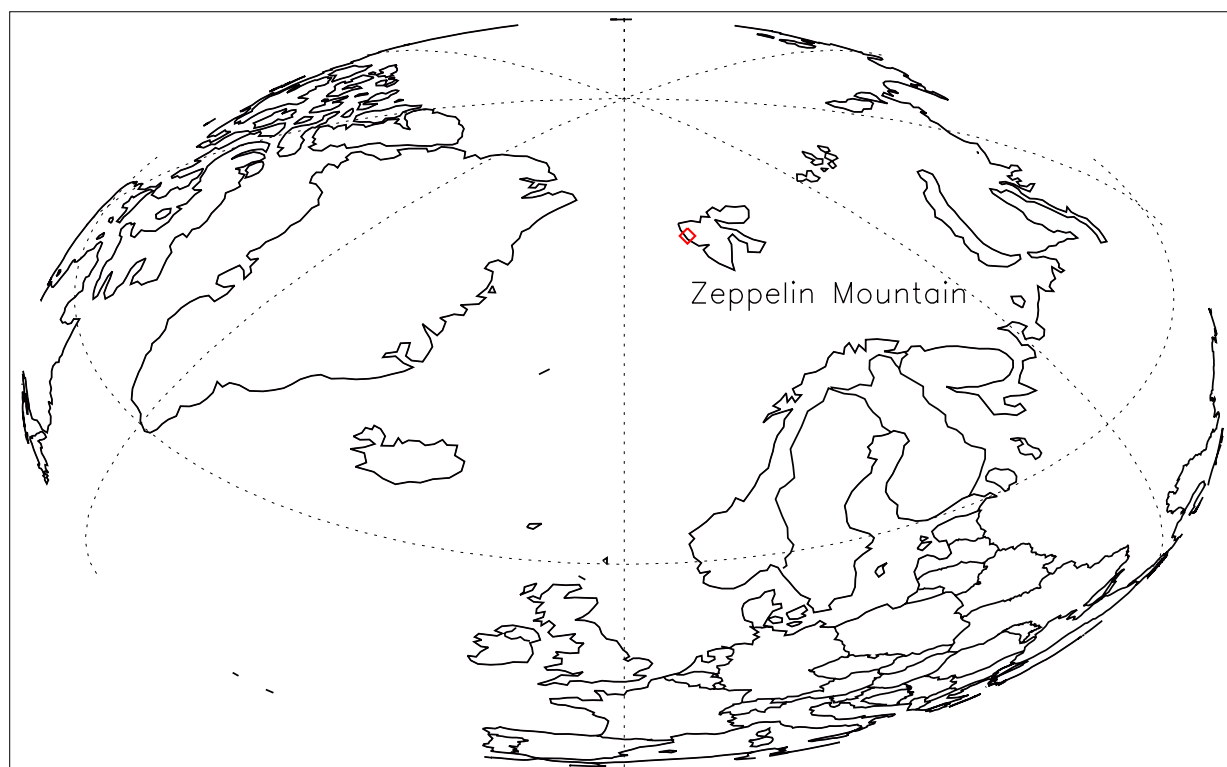
Before the new station at Zeppelin Mountain was built NILU had operated a measuring site for many years in Ny-Ålesund close to the community in the so-called "Gruvebadet" (Minor's Bath). But the measuring site on the valley floor, at the foot of the Zeppelin Mountain, was particular during low wind and inversion conditions influenced by local pollution of Ny-Ålesund. To establish a clean air site it had been decided to build a station on the Zeppelin Mountain.

Figure 2: Picture of Ny-Ålesund and Zeppelin Mountain in the background (station encircled):



Svalbard has a milder climate than might be expected in an area so far north. This is because a branch of the North Atlantic Current flows north along the west coast of Spitsbergen. The average temperature for Ny-Ålesund in February, which is the coldest month, is about -15°C . In July, which commonly is the warmest month, the average temperature is about $+5^{\circ}\text{C}$. Strong winds are common during the winter months, while fog is a typical summer phenomenon. Svalbard is often described as an 'Arctic desert' because of its low precipitation. Average precipitation in Ny-Ålesund is about 370 mm / year (measurements from 1975 to 1989).

Figure 3: Map from satellite view



3.2. Operators

Ny-Ålesund is an old mining settlement where mining activity was closed in 1962. All facilities are owned and run by the old coal company: Kings Bay Kull Company (KBKC). In 1968 the Norwegian government decided to have the Norwegian Polar Research Institute (NP) establish a research station in Ny-Ålesund. Today Ny-Ålesund is an international centre for arctic research where several projects are run in co-operation with national and international research institutions. Among other things NP is therefore also responsible for running the atmospheric chemistry station Zeppelin Mountain. The actual station is owned by NP and is in operation since October 1989. The Norwegian Institute for Air Research (NILU) has the scientific responsibility over the conducted measurements and runs its year-round air sampling programmes, including measurements of several trace compounds of the air including tropospheric ozone. The site was recently adopted as part of the GAW programme as a GAW global station.

The group of Dr K. Tørseth, manager of the Norwegian ozone network, is in charge of the operation of the tropospheric ozone measurements at Zeppelin Mountain. For measurements that are carried out in collaboration between NP and NILU the tasks and duties are divided up. This since NILU has no permanent staff at Ny-Ålesund. A co-worker of NP visits the station daily for basic maintenance and routine works and observation. General maintenance of the instruments

and data review is conducted by NILU. The structure of the station management at Ny-Ålesund (concerning tropospheric ozone) is shown in Table 1.

During the entire audit procedure Rolf Dreiem, station operator of NILU was present for question and answer on site.

Table 1: Operators

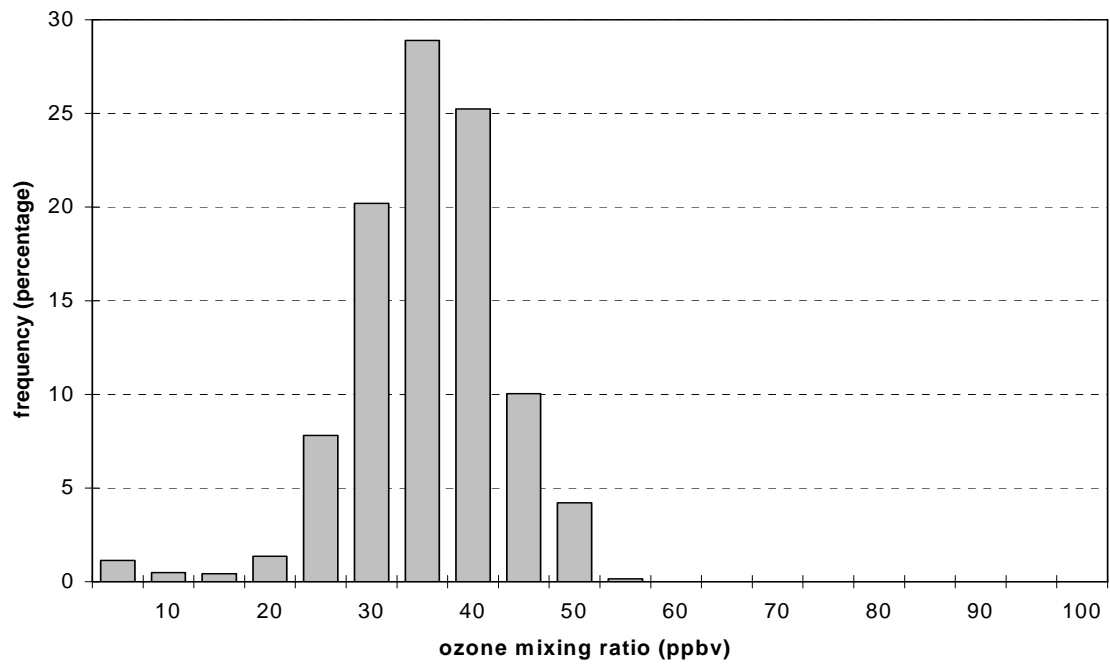
| |
|---|
| Mr Ånung Grimnes, station manager Zeppelin Mountain (NP) |
| Mr Frode Stordal, Co-ordinator of GAW activities at Zeppelin (NILU) |
| Mr Kjetil Tørseth, Norwegian ozone network responsible (NILU) |
| Operator (NILU) Mr Rolf Dreiem, (Chemical engineer), air measurement specialist, data reviewer Ms Jane Østnes Hansen, data correction |
| Observers / Operators at Ny-Ålesund (NP) Mr Einar D. Kaarbø, operation engineer Mr Lars E. Svaasand, operation engineer |

3.3. Ozone Level

The site characteristics and the relevant ozone concentration range can be well defined by the frequency distribution. In figure 4 the frequency distribution of the hourly mean values from the year 1996 is shown. The relevant ozone concentrations were calculated, ranging between 23 and 45 ppb according to the 5 and 95 percentile values. However, episodes of very low ozone concentrations (0 and 5 ppb) are a common feature in spring and are referred to as the boundary-layer ozone depletion in the arctic.

Source of data: received from NILU, September 1997

Figure 4: Frequency distribution of the hourly mean values of the ozone mixing ratio (ppb) at Ny-Ålesund of the year 1996. Data capture nearly 100 per cent.



4. Measurement Technique

4.1. Air Inlet System

The air inlet system for the ozone measurements is mounted on the flat roof of the station. The inlet part of the system is 4.5 m above the flat roof and about 7 m above the ground and consists of an inverse eloxated aluminium bucket, stacked on a eloxated aluminium tube (90 mm i.d.), shielding the system from rain and snow. The sampling line is a 5.5 m long eloxated aluminium tube (4.5 m outside, 1 m indoors) leading directly through a hole in the ceiling into the measuring cabin. The tube is continuously flushed with ambient air at a flow rate of 3 m/s. For the ozone measurements, a PFA teflon tube (4 mm i.d., actually 6 m long) branches off from the manifold leading to the ozone analyser. Two weeks before the audit took place the manifold that is been used for gas analysis was shifted by about 3 m to the middle of the room. Because the ordered instrument rack had not been delivered the ozone analyser was still on the former bench and made therefore the long temporary teflon tube installation necessary. An external pump of the analyser is being used to draw 0.5 l / minute ambient air through this teflon tube, according to the instrument's specified internal flow. The analyser is further protected from dust and particles with a teflon inlet filter at the analyser inlet. The total residence time of the ambient air, through the inlet line to the instrument, lies around 11 seconds but will be reduced to 5 seconds when the former short teflon line (1.5 to 2 m) will be used.

The 6 m long inlet line (although it will be only temporarily used) was checked with regard to loss of ozone in an additional run of the intercomparison. For this experiment the short connection tube (less than 0.9 m) between the ozone producing transfer standard and the analyser was replaced by the actually used 6 m inlet line. No relevant difference between measurements with the dust-free short tube and the relatively long inlet line was found.

Comment

The teflon tube and the rain protection of the inlet were clean and free of dust. The inlet system, concerning construction materials as well as residence time, is adequate for gas analysis. No loss of ozone could be detected.

Although no loss of ozone could be detected still it is regarded as necessary to move the analyser closer to the manifold and use the former shorter line as soon as possible. This since the shorter the line the lower the loss of ozone will be over the time, i.e. particle deposition.

4.2. Instrumentation

The instrument is installed on a bench in a temperature controlled room (air-condition) where the daily variations are rather small and within ± 1 °C. As well the seasonal indoor temperature variations are moderate.

Specifically elderly Monitor Labs instruments of the type 8810 show a non linearity in the very low ppb range (0-5 ppb) which leads to an instrument dependent offset of about 2 to up to 4 ppb. This observation is based on experience from laboratory and field tests conducted by EMPA.

The instrumentation used for measuring ozone at Zeppelin Mountain during the audit is shown in table 2 below.

Table 2: Field instrument

| | |
|--------------------------|---|
| type | ML 8810 #1150 |
| method | UV absorption |
| usage | basic instrument |
| at Ny-Ålesund | since 18. May 1997 |
| range | 0-500 ppb |
| analog output | 0-1 V (not used) |
| electronic offset | 0 (units) |
| electronic coeff. | 282 (absorption coeff.) |
| last calibration by NILU | 7. May '97, at NILU |
| instruments specials | <ul style="list-style-type: none"> • internal zero air unit and ozone generator for automatic zero and span checks • data output directly from the digital signal of the analyser display |

At the moment no multipoint calibrations of the analyser on site are carried out since a so-called transfer standard is not available within the Norwegian ozone network.

Comment

The measurement technique used is the UV-method which is the preferred method in the GAW programme.

The non-linearity of the Monitor Labs analyser (see 4.2.) has serious effects on data of the very low concentration range. Depending on how the instrument had been calibrated (see 4.4.), these values are either over or underestimated. For global GAW sites outside the polar regions ozone values below 5 ppb do not occur. But at Zeppelin Mountain this non-linearity causes a problem when investigating episodes of very low ozone concentrations (0 and 5 ppb) which are an observed feature during several days in spring. Therefore a special correction function for very low ozone value has to be developed or the instrument has to be exchanged by a ozone analyser being linear at low concentrations as well.

For a proper quality assurance it is seen as essential that additionally to the ozone standard in the calibration laboratory at NILU another so-called transfer standard is available for multipoint calibrations on site (see also 4.4. Operation and Maintenance).

4.3. Data Handling

A NILU constructed data logger is installed at the site next to the ozone analyser. It consists of several processor boards and a modem card to transfer the data (hourly means only) daily, via telephone connection, to NILU. The processor board of the ozone analyser is equipped with 1 MB RAM to store the 1- 5- and 60-minute means temporary. No conditions of a minimal percentage of

valid 1-minute data are defined on the processor programme under which a 5- or 60-minute mean is becoming accepted. That means that in extreme even a single 1-minute mean could represent an hour mean value, although this is thought as rather unlikely to be common. Data during a zero and span controlling procedure are automatically excluded from the 5- and 60-minute mean calculation.

Data processing is prepared at NILU and consists in a first phase of a brief, weekly raw data review in graphical form (plots). This is to detect irregularities early and minimise loss of data. In a second, monthly stage a closer look at the data is taken. Since, as mentioned, zero and span values are already excluded so finally only data that seems implausible and unreasonable, due to the operator's experience, needs to be marked as invalid data. A copy of the raw data in ppb units is then converted in $\mu\text{g}/\text{m}^3$ unit, by applying the factor $\times 2$, and becoming the final data set. However, the raw data set is archived as well. Further the data are quality controlled by the responsible scientist before placed in the NILU database. During the entire process no additional function is applied to the data.

Comment

The procedure of data treatment is clearly arranged and transparent which increases the re-liability of the data. Though, it is considered as important that criterias for calculating a valid mean value should be worked out and integrated in the processor programme. Further is noted that with the described data treatment procedure only serious instrument malfunctions can be seen.

Concerning the zero point correction a data treatment that deviates from the actual practice is strongly recommended. For further details see Appendix I.

4.4. Operation and Maintenance

As mentioned in chapter "3.2. Operators" the Zeppelin Mountain station is maintained in co-operation with the Norwegian Polar Research Institute (NP) that is situated in Ny-Ålesund. The tasks and duties by NP concerning the ozone measurements consist of a daily visit of the station for basic maintenance includes checking of the operation of the analyser and, if unsure or on suspicion of malfunction, reporting to NILU. Further, has the teflon inlet filter to be exchanged every three month and documented in a list. The lamp voltage needs to be controlled and adjusted if it is below 1.2 Volt. All additional maintenance of the instrument which requires experienced staff is performed by people of NILU. Considering the remote location of Ny-Ålesund and the distance to the NILU in Kjeller (near Oslo) they usually visit the station only about once a year for maintenance reason of the ozone analyser (this in deviation to the ozone SOP by NILU where it is marked that it should be conducted on a three monthly interval). However, extensive instrument maintenance like cleaning glass cells or multipoint calibration is only carried out at NILU either when the instrument had broken down or after about 18 month (or longer). The instrument is then exchanged with a fresh-serviced and calibrated analyser. As a weekly routine, for the purpose of remote control from NILU, a zero, span and general check is triggered and automatically performed.

The ozone standard of the calibration laboratory at NILU, the ML 9811 #459, is calibrated with the NIST Standard Reference Photometer #11 of the Stockholm University every 18 month.

Comment

The appearance of the station is clean and functional.

To achieve the GAW objectives and with regard to the quality assurance guidelines for surface ozone, in the WMO-GAW Report No. 97, it is required to perform multipoint calibrations twice a year on site. As a consequence, an ozone transfer standard has to be purchased.

Although access to the site is costly it is necessary to follow NILU's ozone SOP more strictly in terms of regular preventive maintenance to improve the operation of the ozone analyser. During such a station visit the operator is advised to follow a maintenance schedule. It should at least incorporate a leak test, exchange of the inlet filter and checking of the pressure transducer every three month, cleaning of the instruments glass cells and testing the scrubber performance (and exchanging if necessary) once a year.

A good co-operation with the Norwegian Polar Research Institute is seen as fundamental for a further successful operation of the Zeppelin Mountain station. However, concerning maintenance works on the ozone analyser by the NP staff, it was noted that some tasks were not carried out. Questionnaire forms to be filled in by the operators during the maintenance, containing the tasks and the intervals, could help improving the reliability.

4.5. Documentation

Within the GAW guidelines for documentation, the transparency of and the access to the station documents are required. During the audit the documentation was reviewed for availability and usefulness. Because the instrument calibration, data review and most of the maintenance is performed at NILU the available documents are located there. An exception is a copy of a calendar which is used as maintenance logbook on site. The ozone logbook of the Zeppelin Mountain consists of weekly printouts of the automatic instrument check (general check, span, zero) and contained also the necessary information about maintenance, changes, events and special investigations listed chronologically in a file. Further documents are an SOP for the ozone measurements, a file with all weekly graph plots (ppb / time), a detailed calibration logbook for each instrument and the monthly data plots.

Comment

The documentation of the ozone measurement meets the requirements of the GAW guidelines. It consists of logbooks as well as graphical plots of the data. However, a detailed questionnaire-like single sheet which is filled in during maintenance, for the purpose of traceability, is suggested.

4.6. Competence

All persons at NILU associated directly or indirectly with the operation of the station are highly motivated and experts in their fields. Obviously, due to long-standing experience and adequate education, the operators were very familiar with the techniques and problems connected with ozone measurements. With the high fluctuation rate of the staff working for NP in Ny-Ålesund NILU responsables should prove the potential of an intensive maintenance training and make sure that such know-how is then handed over to new co-workers.

5. Intercomparison of Ozone Instruments

5.1. Experimental Procedure

At the site, the transfer standard (detailed description see Appendix I) was hooked up to power for warming up over night in deviation to the GAW report No. 97 which recommends only one hour of warm-up time. In the morning, before the intercomparison runs were started the transfer standard, the PFA tubing connections to the instrument and the instrument itself were conditioned with about 200 ppb ozone for 20 min. Between 18. and 22. September, three comparison runs between the field instrument and the EMPA transfer standard were performed. In the meantime the inlet system and the instrument maintenance were inspected and discussed. Table 3 shows the experimental details and figure 5 the experimental set up of the audit. In general, no modifications of the ozone analyser which could influence the measurements were made for the intercomparisons.

The EMPA acquisition system, which was used for the audit, consists of a 16 channel ADC circuit board and a PC with the corresponding software. Hooked up to the analog output of the field instrument and of the transfer standard the data was collected by the data acquisition system of EMPA. The analog output of the field instrument is not used as data output in routine. Instead, NILU modified the analyser that way that a digital data signal is taken directly from the analyser display and is transferred to the NILU data logger (no D/A conversion). Therefore, prior starting the intercomparison, it was checked that the readings of the analyser display agreed with the reading on the EMPA acquisition system. The EMPA transfer standard was tested accordingly. For data interpretation the EMPA data is used. Finally, the observed results were discussed at NILU in an informal review with the following persons:

- Mr. Frode Stordal, Co-ordinator of GAW activities at Zeppelin (NILU)
- Mr. Jan E. Hanssen, Head of Quality Control Department (NILU)
- Mr. Rolf Dreiem, Operator, air measurement specialist and data reviewer (NILU)
- Mr. Matthias Hill, GAW Calibration Centre (EMPA)
- Mr. Alex Herzog, GAW Calibration Centre (EMPA)

The audit procedure included a direct intercomparison of the TEI 49C-PS transfer standard with the Standard Reference Photometer SRP#15 (NIST UV photometer) before and after the audit in the calibration laboratory at EMPA. The results are shown in the Appendix IV.

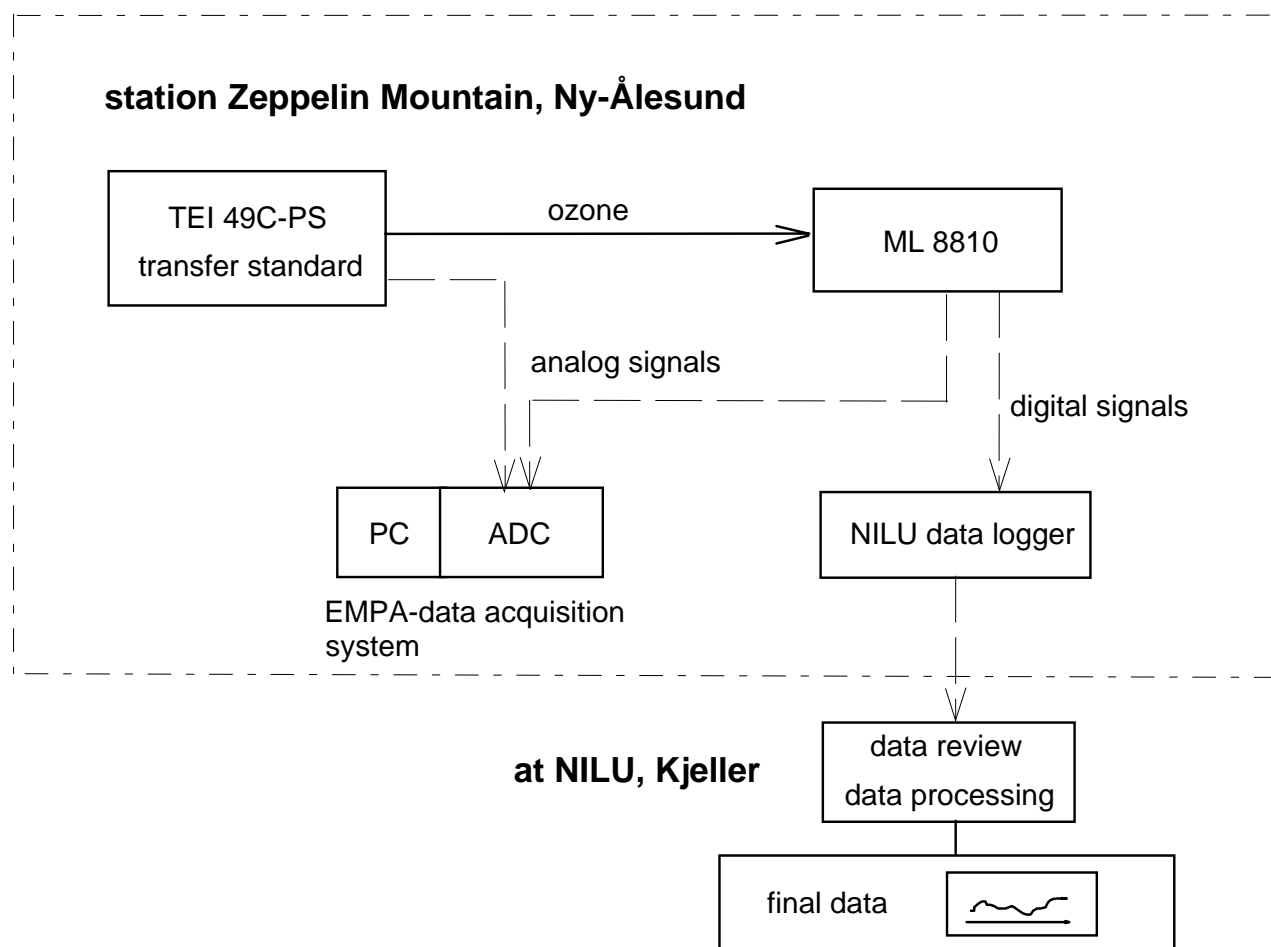
Table 3: Experimental details

| | |
|-------------------------------|---|
| audit-team, EMPA | M. Hill, A. Herzog |
| reference: | EMPA: TEI 49C-PS #54509-300 transfer standard |
| field instrument: | ML 8810 #1150, |
| ozone source: | EMPA: TEI 49C-PS, internal generator |
| zero air supply: | EMPA: silica gel - inlet filter 5 µm - metal bellow pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 µm |
| data acquisition systems: | EMPA: 16 channel ADC circuit board, software |
| pressure transducers reading: | * reference: 946 hPa ML 8810: 945 hPa TEI 49C-PS: 946 (adjusted before audit) |

| | |
|---------------------------------------|--|
| concentration range | 0 - 100 ppb |
| number of concentrations: | 5 + zero air at start and end |
| approx. concentration levels: | 10 / 25 / 40 / 55 / 70 ppb |
| sequence of concentration: | random |
| averaging interval per concentration: | 10 minutes |
| number of runs: | 1 x September 18, 1997 1 x September 19, 1997 1 x September 22, 1997 |
| connection between instruments: | 0.9 meter of 1/4" PFA tubing |

* pressure transducer reference: DVR-1 (EMPA), agreed with the pressure reading of the Synoptic Station (NP) down at Ny-Ålesund.

Figure 5: Experimental set up



5.2. Results

The results comprise three runs of the intercomparisons between the field instrument ML 8810 and the transfer standard TEI 49C-PS, carried out between September 18 and 22 , 1997.

In the following tables the resulting mean values of each ozone concentration and the standard deviations (s_d) of 20 x 30-second-means are presented. For each mean value the differences between the tested instrument and the transfer standard are calculated in ppb and in %.

Furthermore, the diagrams show the results of the linear regression analysis of the field instrument compared to the EMPA transfer standard. The results of the three runs are then summarised to the mean regression equation and presented with the assessment criteria for GAW field instruments (Figure 8).

The data used for the evaluation were recorded by the EMPA data acquisition system.

In table 4 to 6 the acquired data is listed.

Table 4: 1. Intercomparison, ML 8810 field instrument

| No. | reference TEI 49C-PS | | ML 8810 #1150 | | | |
|-----|----------------------|----------------|---------------|----------------|--------------------------|-------|
| | conc. | S _d | conc. | S _d | deviation from reference | |
| | ppb | ppb | ppb | ppb | ppb | % |
| 1 | 0.1 | 0.11 | 0.0 | 0.01 | -0.1 | |
| 2 | 24.9 | 0.12 | 22.2 | 0.55 | -2.7 | -11.0 |
| 3 | 70.0 | 0.12 | 69.2 | 0.58 | -0.8 | -1.1 |
| 4 | 40.0 | 0.12 | 37.8 | 0.73 | -2.2 | -5.4 |
| 5 | 55.1 | 0.14 | 54.1 | 0.61 | -1.0 | -1.8 |
| 6 | 10.1 | 0.18 | 7.0 | 0.53 | -3.1 | -30.6 |
| 7 | -0.2 | 0.06 | 0.0 | 0.00 | 0.2 | |

Table 5: 2. Intercomparison, ML 8810 field instrument

| No. | reference TEI 49C-PS | | ML 8810 #1150 | | | |
|-----|----------------------|----------------|---------------|----------------|--------------------------|-------|
| | conc. | S _d | conc. | S _d | deviation from reference | |
| | ppb | ppb | ppb | ppb | ppb | % |
| 1 | 0.2 | 0.16 | -0.1 | 0.31 | -0.3 | |
| 2 | 39.9 | 0.16 | 37.4 | 0.54 | -2.5 | -6.2 |
| 3 | 10.0 | 0.13 | 6.6 | 0.57 | -3.4 | -33.9 |
| 4 | 24.9 | 0.11 | 22.0 | 0.47 | -2.9 | -11.5 |
| 5 | 69.9 | 0.16 | 69.5 | 0.57 | -0.4 | -0.6 |
| 6 | 54.9 | 0.13 | 54.1 | 0.96 | -0.9 | -1.6 |
| 7 | -0.1 | 0.12 | 0.0 | 0.01 | 0.1 | |

Table 6: 3. Intercomparison, ML 8810 field instrument

| No. | reference TEI 49C-PS | | ML 8810 #1150 | | | |
|-----|----------------------|----------------|---------------|----------------|--------------------------|-------|
| | conc. | S _d | conc. | S _d | deviation from reference | |
| | ppb | ppb | ppb | ppb | ppb | % |
| 1 | 0.2 | 0.19 | 0.0 | 0.23 | -0.2 | |
| 2 | 54.8 | 0.15 | 53.8 | 0.14 | -0.9 | -1.7 |
| 3 | 24.7 | 0.11 | 22.7 | 0.77 | -2.0 | -8.1 |
| 4 | 69.8 | 0.18 | 69.2 | 0.63 | -0.6 | -0.8 |
| 5 | 9.9 | 0.11 | 6.2 | 0.75 | -3.7 | -37.2 |
| 6 | 39.8 | 0.16 | 38.4 | 0.86 | -1.4 | -3.5 |
| 7 | -0.1 | 0.12 | -0.1 | 0.45 | 0.0 | |

Figure 6: Individual linear regressions of intercomparisons 1 to 3, ML 8810

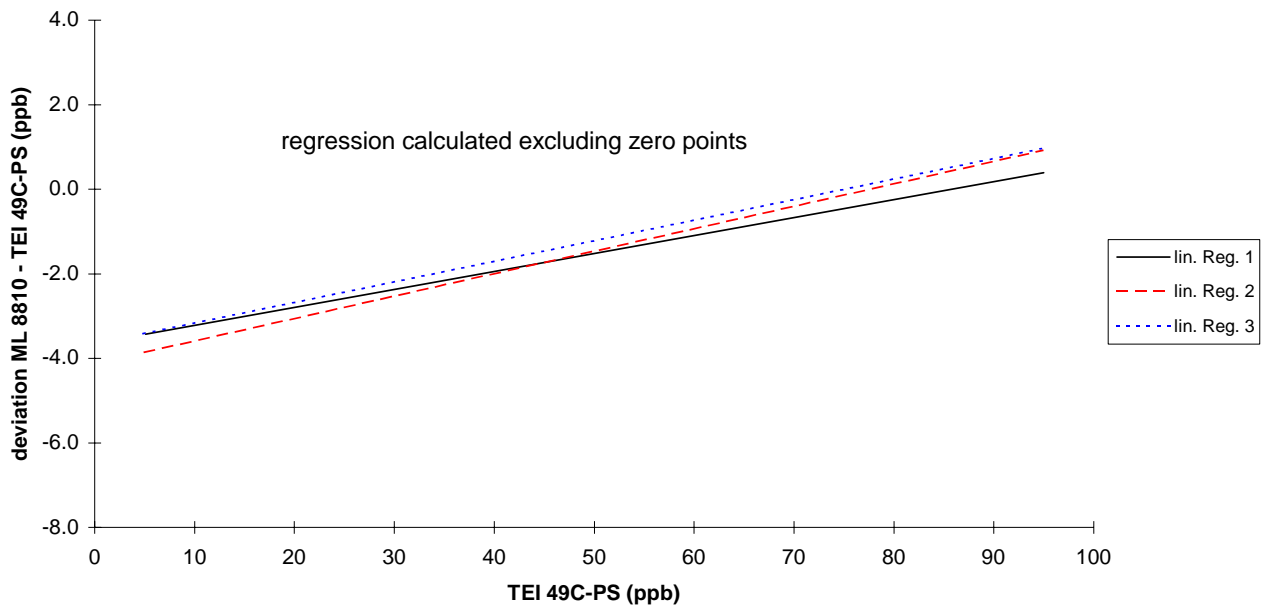
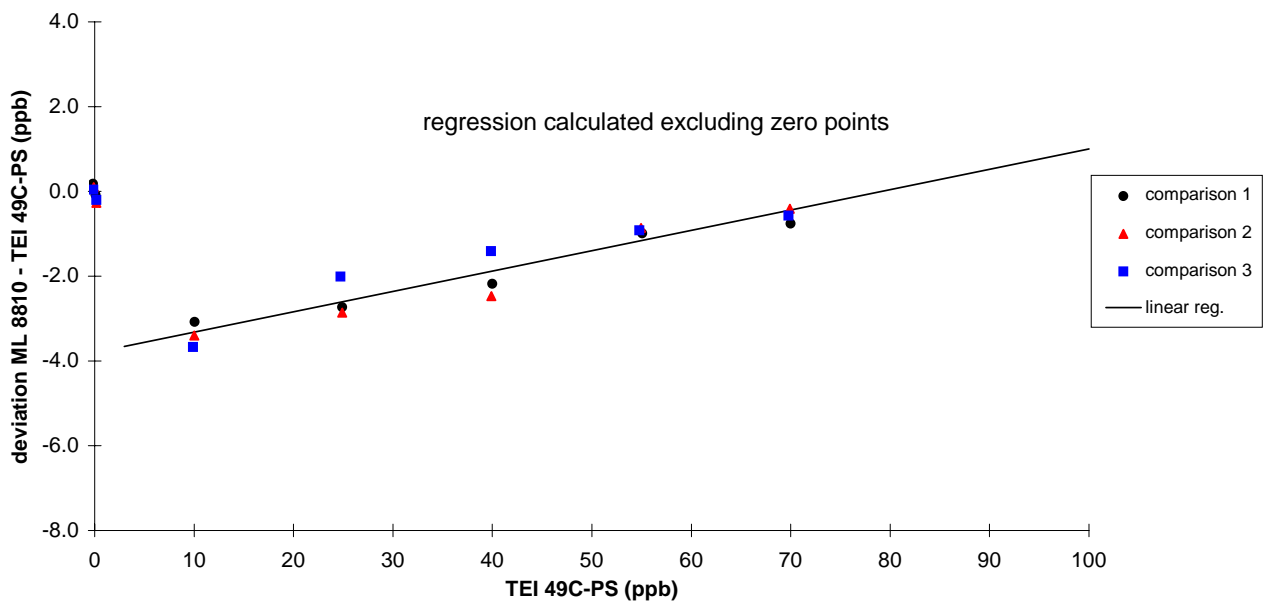


Figure 7: Mean linear regression of intercomparisons 1 to 3, ML 8810



From the intercomparison of the ML 8810 #1150 with the TEI 49C-PS transfer standard from EMPA the resulting linear regression (for the range of 0-100 ppb ozone) is:

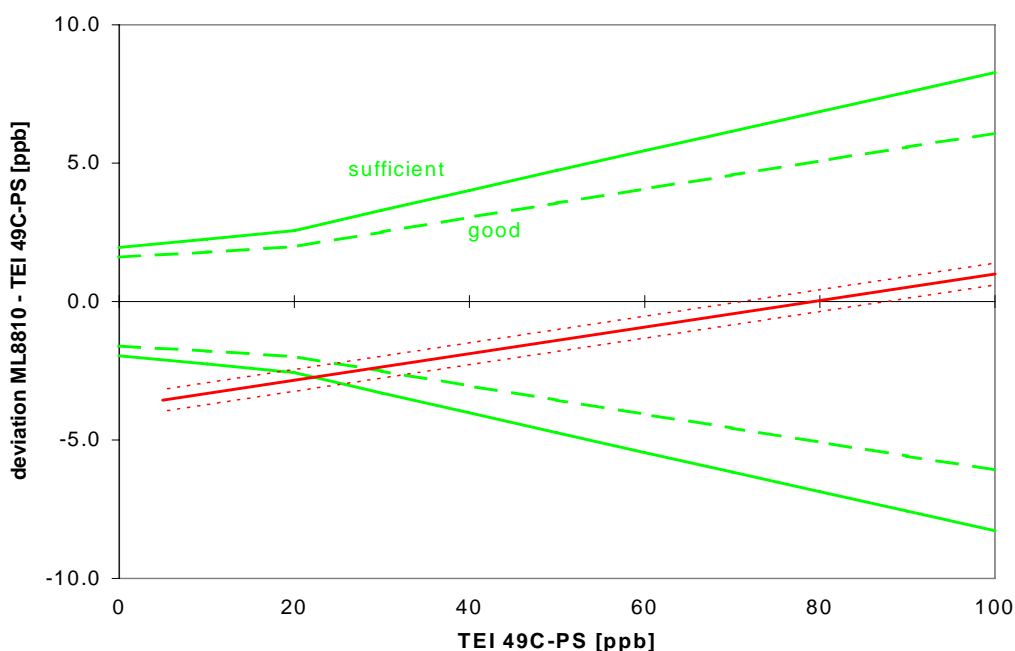
$$\text{ML 8810} = 1.048 \times \text{TEI 49C-PS} - 3.8 \text{ ppb}$$

ML 8810 = O₃ mixing ratio in ppb, determined for ML 8810 #1150

TEI 49C-PS = O₃ mixing ratio in ppb, related to TEI 49C-PS #54509-300

| | |
|--------------------------------------|---|
| Standard deviation of: - slope s_m | 0.0043 (f = 3) <small>f=degree of freedom</small> |
| - offset S_b in ppb | 0.19 (f = 3) |
| - residuals in ppb | 1.26 (f = 13) |

Figure 8: Intercomparison of instrument ML 8810



Comment

In figure 6 of the linear regressions no trend could be observed over the period of five days when the intercomparisons took place.

The ozone concentrations observed at Ny-Ålesund (1996) usually ranged between 23 and 45 ppb (5- and 95-percentile of hourly mean values). But episodes of very low ozone concentrations (0 and 5 ppb) are a common feature in spring which are atmospheric chemically interesting events.

Therefore, by assessing the results it has to be distinguished between the usual and the very low concentrations. For the usual concentrations, higher 23 ppb, the resulting mean linear regression of the field instrument lies partly in the "sufficient" and "good" range and fulfils the assessment criterias (figure 8). However, for the lower values (< 20 ppb) the instrument is assessed outside tolerance. Since the deviations are mainly due to the analyser's non-linearity that has been not considered, the problem can be easy solved by applying the adequate correction function (see Appendix I).

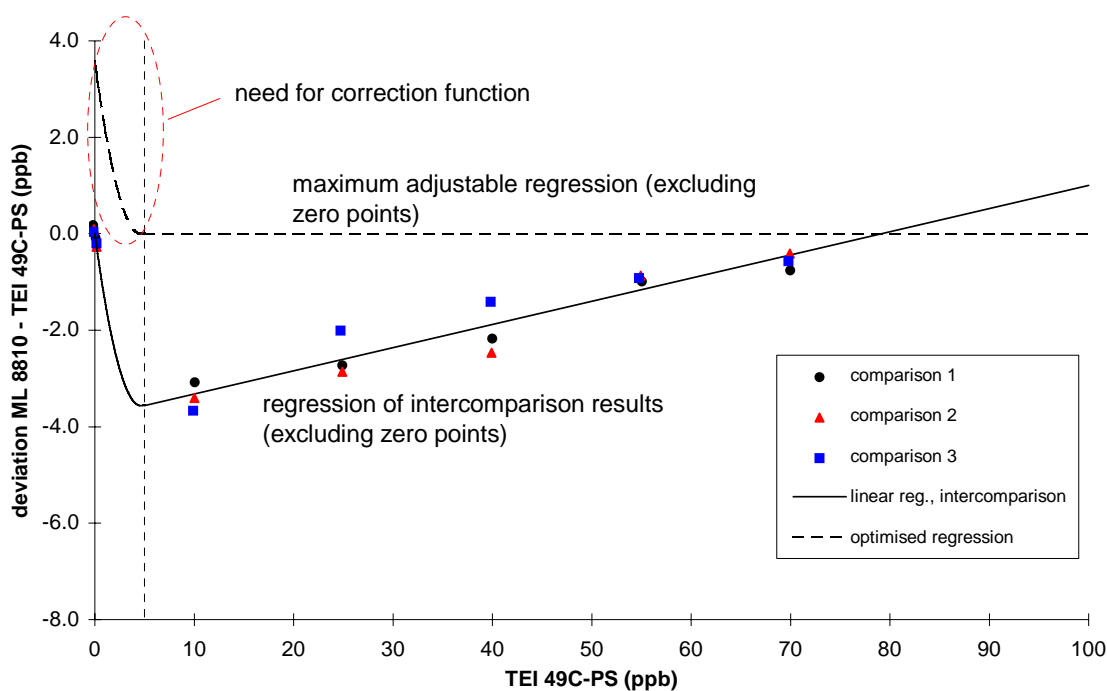
Fairly small deviation among the three intercomparisons is the reason for a narrow prediction interval for the analyser which implies that the instrument is in reasonable condition.

Appendix

I Consideration of Non-Linearity of the Ozone Analyser ML 8810

In chapter 4.4. it is mentioned that elderly Monitor Labs instruments of the type 8810 show a non linearity in the very low ppb range (0-5 ppb) which leads to an instrument dependent offset of about 2 to up to 4 ppb. The consequence in practice for the ML 8810 #1150 of NILU is that the calibration procedure and the data reprocessing has to be changed. Concerning calibration it is important that the zero points are not taken into account when calculating the regression. But even if the analyser would be adjusted to the transfer standard to have virtually no deviation the very low ppb range will still require special data treatment (see figure 9). It is recommended, since the exact function is not known, to apply a linear function for correcting ozone concentrations lower 5 ppb.

Figure 9: Non-linearity of instrument ML 8810 #1150



II Recommendation Concerning Calibration Procedure at NILU

Concerning the data quality objectives for ozone within the GAW programme, the requirements for operators of global stations are relatively high. Beside numerous tasks a carefully performed calibration procedure helps in meeting the aims of quality. In the following several points are noted that are recommended to be changed in the actual calibration procedure at NILU .

Table 7: Recommended calibration procedure

| ACTUAL | RECOMMENDED |
|---|--|
| <ul style="list-style-type: none"> • One multipoint calibration run • Including zero point readings for calculating the regression of the multipoint calibration • A more or less subjective reading of a one minute mean value is taken as representative value (stability is seen on a screen). • The results for each ozone level are reviewed (no regression is calculated) and, if considered as necessary, adjustment of the instrument settings is made accordingly. • The instrument settings (before and after calibration) are not marked. | <ul style="list-style-type: none"> • Three multipoint calibration runs • Considering the non-linearity of the instrument (see Appendix I). Therefore, excluding the zero point readings for calculating the regression of the multipoint calibration is necessary. • The output resolution of the actual analyser is 1 ppb and the instrument is switching between ± 1 ppb. Thus, an averaging of the 1 minute means to a 10 minute mean value results in a more accurate calibration curve. • To put the adjustment procedure on a more certain basis the regression must be calculated prior any change on the offset or absorption coefficient settings. • Mark the instrument settings (before and after calibration) on the calibration sheet in a table. |

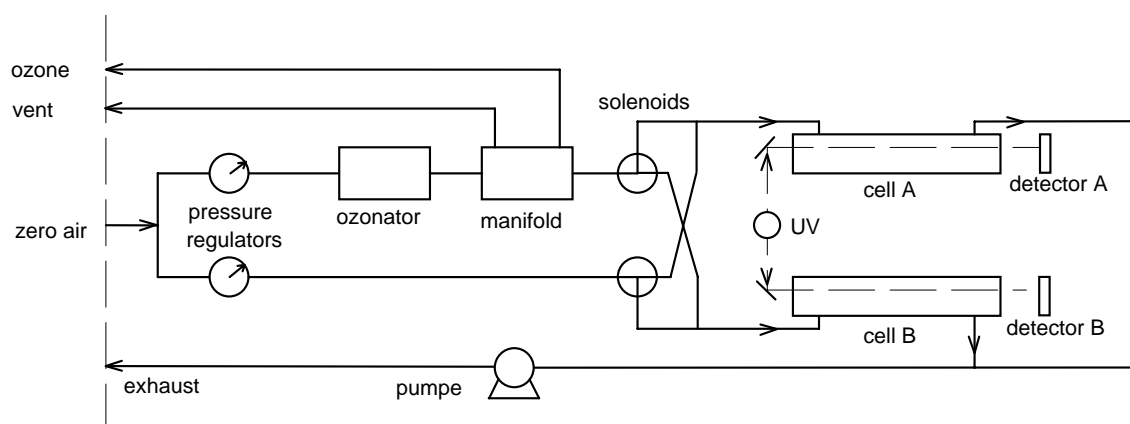
III EMPA Transfer Standard TEI 49C-PS

The Model 49C-PS is based on the principle that ozone molecules absorb UV light at a wavelength of 254 nm. The degree to which the UV light is absorbed is directly related to the concentration as described by the Lambert-Beer Law.

Zero air is supplied to the Model 49C-PS through the zero air bulkhead and is split into two gas streams, as shown in figure 10. One gas stream flows through a pressure regulator to the reference solenoid valve to become the reference gas. The second zero air stream flows through a pressure regulator, ozonator, manifold and the sample solenoid valve to become the sample gas. Ozone from the manifold is delivered to the ozone bulkhead. The solenoid valves alternate the reference and sample gas streams between cells A and B every 10 seconds. When cell A contains reference gas, cell B contains sample gas and vice versa.

The UV light intensities of each cell are measured by detectors A and B. When the solenoid valves switch the reference and sample gas streams to opposite cells, the light intensities are ignored for several seconds to allow the cells to be flushed. The Model 49C-PS calculates the ozone concentration for each cell and outputs the average concentration.

Figure 10: Flow schematic of TEI 49C-PS



IV Stability of the Transfer Standard TEI 49C-PS

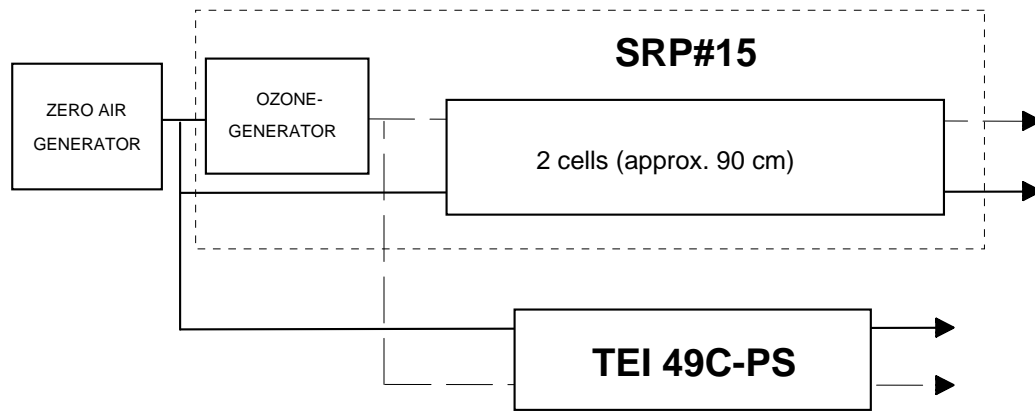
To exclude errors which might occur through transportation of the transfer standard, the TEI 49C-PS #54509-300 has to be compared with the SRP#15 before and after the field audit.

The procedure and the instruments set up of this intercomparison in the calibration laboratory at EMPA are summarised in Table 8 and Figure 11.

Table 8: Intercomparison procedure SRP - TEI 49C-PS

| | |
|---------------------------------------|--|
| pressure transducer: | zero and span check (calibrated barometer) at start and end of procedure |
| concentration range: | 0 - 200 ppb |
| number of concentrations: | 5 + zero air at start and end |
| approx. concentration levels: | 30 / 60 / 90 / 125 / 185 ppb |
| sequence of concentration: | random |
| averaging interval per concentration: | 5 minutes |
| number of runs: | 4 before and 3 after audit |
| zero air supply: | Pressurised air - zero air generator (CO catalyst, Purafil, charcoal) |
| ozone generator: | SRP's internal generator |
| data acquisition system: | SRP's ADC and acquisition |

Figure 11: Instruments set up SRP - TEI 49C-PS



The stability of the transfer standard is thoroughly examined with respect to the uncertainties of the different components (systematic error and precision). For the GAW transfer standard of the WCC-O₃ (TEI 49C-PS) the assessment criteria, taking into account the uncertainty of the SRP, are defined to ###(1 ppb + 0.7%).

Figures 12 and 13 show the resulting linear regression and the corresponding 95% precision interval for the comparisons of TEI 49C-PS vs. SRP#15. Clearly, the results show that the EMPA transfer standard fulfilled the recommended criterias for the period of the audit, including transportation.

Figure 12: Comparison transfer standard - SRP, before audit

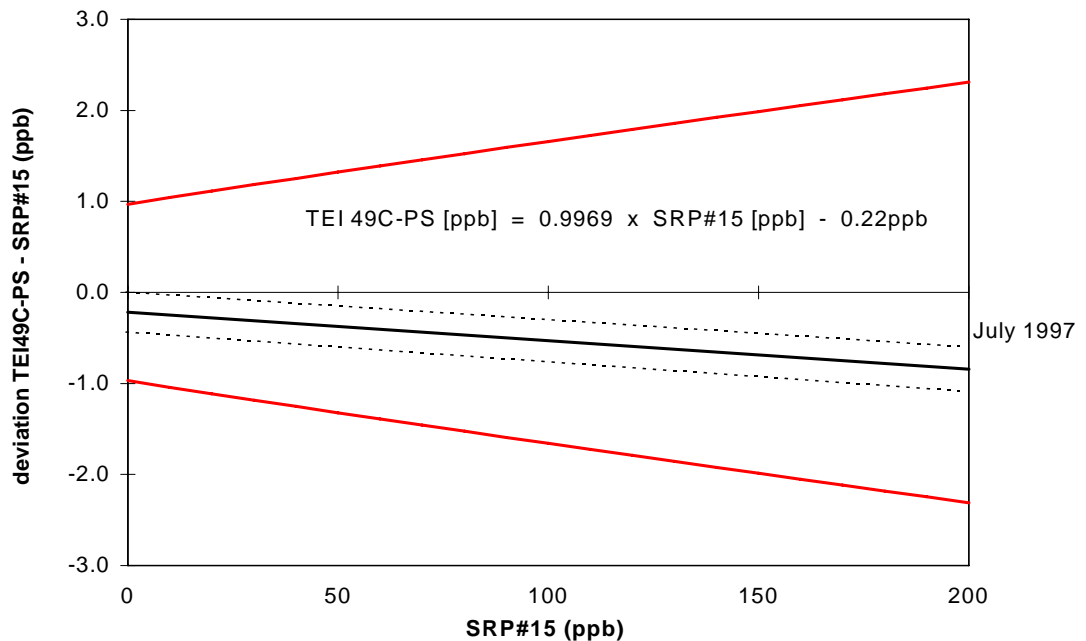


Figure 13: Comparison transfer standard - SRP, after audit

