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Laboratory Air Pollution / Environmental Technology

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IV TROPOSPHERIC OZONE ANALYZER
INTERCOMPARISON
SERVICIO METEOROLÓGICO NACIONAL
OBSERVATORIO CENTRAL DE BUENOS AIRES
BUENOS AIRES, ARGENTINA.

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EXECUTIVE SUMMARY AND RECOMMENDATIONS

The IV tropospheric ozone analyzer inter-comparison was co-organized by the Regional Calibration Centre for Surface Ozone in Buenos Aires (RCC-BsAs) run by the National Weather Service (Servicio Meteorológico Nacional - SMN) and the World Calibration Centre for Surface Ozone (WCC-Empa). Eight GAW stations from five South American countries participated in the workshop. The aim of the comparison exercise was to ensure traceability of ozone measurements carried out within the WMO-GAW region III against the WMO ozone standard maintained by the Central Calibration Laboratory (CCL) for Surface Ozone at the National Institute for Standard (NIST). It focused on the following topics:

- Assessment of surface ozone analyzers operated at global and regional stations of the WMO-GAW region III through comparisons against NIST traceable ozone standards from RCC-BsAs and WCC-Empa.
- Diagnostics and repair of instruments.
- Review and validation of existing surface ozone data series from the WMO-GAW region III, with the aim to submit these data to the World Data Centre for Greenhouse Gases (WDCGG).
- Operator training in surface ozone chemistry, measurement techniques, instrument maintenance and data handling.

The following people contributed to the workshop:

| | |
|--------------------------------|---------------------------------------|
| Dr. Monica Marino | SMN Headquarters, Buenos Aires |
| MSc. Gerardo Carbajal Beneítez | SMN Central Observatory, Buenos Aires |
| Mr. Ricardo Sánchez | SMN Central Observatory, Buenos Aires |
| Ing. María Elena Barlasina | SMN Central Observatory, Buenos Aires |
| Dr. Christoph Zellweger | Empa Dübendorf, WCC-Empa |

A list of all participants is given in Appendix I.

This report summarizes the assessment of the Regional Calibration Centre for Surface Ozone in Buenos Aires (RCC-BsAs) in general, as well as the surface ozone comparisons performed during the workshop. The assessment criteria for ozone comparisons were developed by WCC-Empa and QA/SAC Switzerland [Hofer et al., 2000; J. Klausen et al., 2003].

The report is distributed to the National Weather Service SMN, to all participants of the comparison workshop, and the World Meteorological Organization in Geneva. The report will be posted on the internet.

The recommendations found in this report are complemented with a priority (*** indicating highest priority) and a suggested completion date.

Facilities at RCC-BsAs, SMN – Villa Ortuzar

The Regional Calibration Centre for Surface Ozone in Buenos Aires (RCC-BsAs) is located at the Central Observatory of Buenos Aires. The location as well as the infrastructure at the site serves well for the operation of the calibration centre. RCC-BsAs is equipped with one ozone calibrator (TEI 49C-PS) and a small stock of spare parts mainly for TEI 49 ozone analyzers. This equipment is suitable; however, an additional ozone reference as well as larger stock of spare parts would be beneficial for the operation of the RCC-BsAs.

Recommendation 1 (*, 2011-13)

The purchase of an additional ozone reference instrument, preferably a NIST standard reference photometer, should be considered.

Recommendation 2 (, 2011-13)**

The RCC-BsAs should have a budget for spare parts; the most important parts should be available in stock at the RCC.

Review of available ozone time series of WMO/GAW region III

Comparison activities such as the current workshop organized by RCC-BsAs are only useful if the ambient ozone data will be made available. Until today, only very few data has been submitted to the World Data Centre for Greenhouse Gases (WDCGG). The following stations have been doing surface ozone measurements within WMO/GAW region III (Table 1):

Table 1. Surface ozone measurement sites within WMO/GAW region III

| Station | GAW ID | Participation in current workshop | Station registered in GAWSIS | O ₃ series registered in GAWSIS | Data submitted to WDCGG |
|-------------|--------|-----------------------------------|------------------------------|--|-------------------------|
| Arembepe | ABP | N | Y | Y | N |
| El Tololo | -* | Y | Y | N | N |
| La Quiaca | -* | Y | Y | N | N |
| Natal | NAT | Y | Y | N | N |
| Paramaribo | PMO | N | Y | Y | N |
| Pilar | -* | Y | Y | N | N |
| Salto | SAG | Y | Y | N | N |
| San Julián | -* | Y | Y | N | N |
| San Lorenzo | -* | Y | Y | N | N |
| Ushuaia | USH | Y | Y | Y | 1994-11-25 - 2008-11-26 |

* No GAW ID has been assigned yet.

With the exception of USH, no ozone data has been submitted to WDCGG. Since data submission is one of the obligations of stations participating in GAW, this fact is clearly not acceptable and will jeopardize future support of the South American surface ozone program if data availability does not improve. The following recommendations are made:

Recommendation 3 (***, 2011)

Data submission to the WDCs is an obligation of stations participating in GAW. Existing surface ozone data of the from WMO/GAW region III must be reviewed and submitted to WDCGG (responsibility: individual GAW stations with support from RCC-BsAs).

Recommendation 4 (***, starting now)

Most surface ozone instruments were in good working condition after the current workshop. Future data acquired with these instruments must be submitted to WDCGG with a maximum delay of one year (responsibility: individual GAW stations).

Recommendation 5 (***, 2011, afterwards ongoing)

Most stations are insufficiently registered in GAWSIS. Station IDs need to be assigned, the site description, measurement programme and contact information must be updated (responsibility: individual GAW stations).

Recommendation 6 (**, 2012)

Biannual calibration workshops at RCC-BsAs are an ongoing task of the GAW strategic plan [WMO, 2007]; these calibrations make only sense if data are submitted. Future workshops should only be organized if at least 50% of the stations submit data (RCC-BsAs is requested to supervise data submission and actively interact with the stations).

Recommendation 7 (***, before next comparison workshop)

All stations doing surface ozone measurements within WMO/GAW region III should be contacted before the comparison exercise. During the current workshop, most stations participated; however, not all potential candidates have been contacted (e.g. PMO).

Allocation of three refurbished ozone analyzers

WCC-Empa was able to provide three refurbished TEI 49C surface ozone analyzers to the GAW stations La Quiaca, Salto and El Tololo. The donation of the instruments by the Swiss Federal Office for the Environment (FOEN) as well as support from WMO is acknowledged. The instruments were handed over to the new owners during the workshop, and the operators were trained in using the new equipment. The instruments were refurbished and calibrated at the WCC-Empa laboratories. The calibration results are shown in Appendix II

Comparison activities during the workshop

An overview of the participating stations and the corresponding ozone instruments is given in Table 2.

Table 2. Participating stations / ozone instruments.

| Station | Instrument | Contact Person |
|-------------|--|--|
| RCC-BsAs | TEI 49C-PS #56084-306 | Ricardo Sánchez |
| Ushuaia | TEI 49C #56546-318 TEI 49 #4703-278 | Manuel Ángel Cupeiro, Sergio Lupo |
| San Julián | TEI 49 #49983-285 | Gabriel Gustavo Arenas |
| Pilar | TEI 49 #49981-285 | José Luis Arce |
| La Quiaca | TEI 49 #54577-300 | Gimena Silvia Mariscal, Luciano Javier Bras |
| San Lorenzo | TEI 49 #54501-300 | Víctor Ariel Ayala Rojas |
| El Tololo | TEI 49 #49978-285 | Gilberto Segundo Lara Azocar |
| Natal | TEI 49C #62170-334 | Francisco Raimundo da Silva |
| Salto | TEI 49 #54947-302 | Sergio Francisco Arizcorreta Medina |

In a first step, all instruments were tested for general operation. In many cases the instruments were in such condition that a following meaningful comparison was not possible. In those cases, the instrument was first repaired and compared afterwards. All instruments were compared against the ozone travelling standard (TS) TEI 49i-PS from WCC-Empa, which was calibrated against the WCC-Empa ozone reference (standard reference photometer SRP#15) before and after the comparison workshop (see Appendix IV). The results of the comparisons are summarized in Table 3.

With the exception of the San Julian instrument, no calibration factors were changed during the comparison exercise (see Appendix III, Table 8). For this particular instrument, a change was necessary because the whole optical bench had to be replaced.

The unbiased ozone mole fraction can be described as follows:

$$\text{Unbiased O}_3 \text{ mixing ratio (ppb}^1\text{:} \quad X_{O_3} \text{ (ppb)} = ([\text{Analyzer reading}] - A) / B \quad (1a)$$

$$\text{Remaining combined standard uncertainty:} \quad u_{O_3} \text{ (ppb)} = \sqrt{C^2 + D * X_{O_3}^2} \quad (1b)$$

The parameters (A-D) obtained during the comparisons are summarized in Table 3.

¹ We use ppb, or parts per billion, as a shorthand for nmol mol⁻¹.

Table 3. Results of the instrument comparisons.

| <i>Station</i> | <i>Instrument</i> | <i>A</i> | <i>sdA</i> | <i>B</i> | <i>sdB</i> | <i>C</i> | <i>D</i> |
|----------------|-----------------------|----------|------------|----------|------------|----------|----------|
| RCC-BsAs | TEI 49C-PS #56084-306 | 0.38 | 0.06 | 0.986 | 0.001 | 0.32 | 2.77e-5 |
| Ushuaia | TEI 49C #56546-318# | -0.10 | 0.05 | 0.944 | 0.001 | 0.41 | 3.01e-5 |
| Ushuaia | TEI 49C #56546-318## | -0.52 | 0.08 | 0.979 | 0.001 | 0.38 | 2.80e-5 |
| Ushuaia | TEI 49 #47306-278 | -0.25 | 0.12 | 0.995 | 0.001 | 0.31 | 2.73e-5 |
| San Julián | TEI 49 #49983-285 | -0.98 | 0.10 | 0.986 | 0.002 | 0.64 | 2.92e-5 |
| Pilar | TEI 49 #49981-285 | -0.87 | 0.10 | 1.032 | 0.001 | 3.23 | 2.50e-5 |
| La Quiaca | TEI 49 #54577-300 | -0.49 | 0.11 | 1.019 | 0.001 | 0.31 | 2.61e-5 |
| San Lorenzo | TEI 49 #54501-300 | 0.19 | 0.08 | 1.046 | 0.001 | 0.30 | 2.49e-5 |
| El Tololo | TEI 49 #49978-285 | 0.48 | 0.05 | 0.993 | 0.001 | 0.33 | 2.74e-5 |
| Natal* | TEI 49C #62170-334 | 0.20 | 0.07 | 0.759 | 0.001 | 13.6 | 4.64e-5 |
| Natal** | TEI 49C #62170-334 | 0.08 | 0.11 | 1.002 | 0.000 | 0.39 | 2.59e-5 |
| Salto | TEI 49 #54947-302 | 0.12 | 0.08 | 1.039 | 0.001 | 0.31 | 2.51e-5 |

#before cleaning ##after cleaning *before repair **after repair at Empa

In the following, the major results of each analyzer and corresponding recommendations are presented. More details including the individual measurement data are given in Appendix III.

RCC-BsAs – TEI 49C-PS #56084-306

Instrument condition prior to comparison:

Besides the following minor issues the instrument was in a good condition:

- Deviation of pressure sensor exceeded normal values (23 mmHg) and was adjusted to ambient pressure. It was further noticed that the pressure reading was not stable over time; replacement of the pressure sensor did not solve the problem.
- Leak check reached only a pressure of 280 mmHg after 20 s (should be <250 mmHg), probably due to a weak pump. Replacement of the pump diaphragm is recommended.
- The instrument was assessed during the WCC-Empa audit in 2008 [Zellweger *et al.*, 2008]; since then, the instrument readings became slightly lower compared to the WCC-Empa TS. The span factor of the calibrator is already relatively high (1.035); if further degradation is observed, a full instrument service is needed.

The results of the comparison are shown in Figure 1.

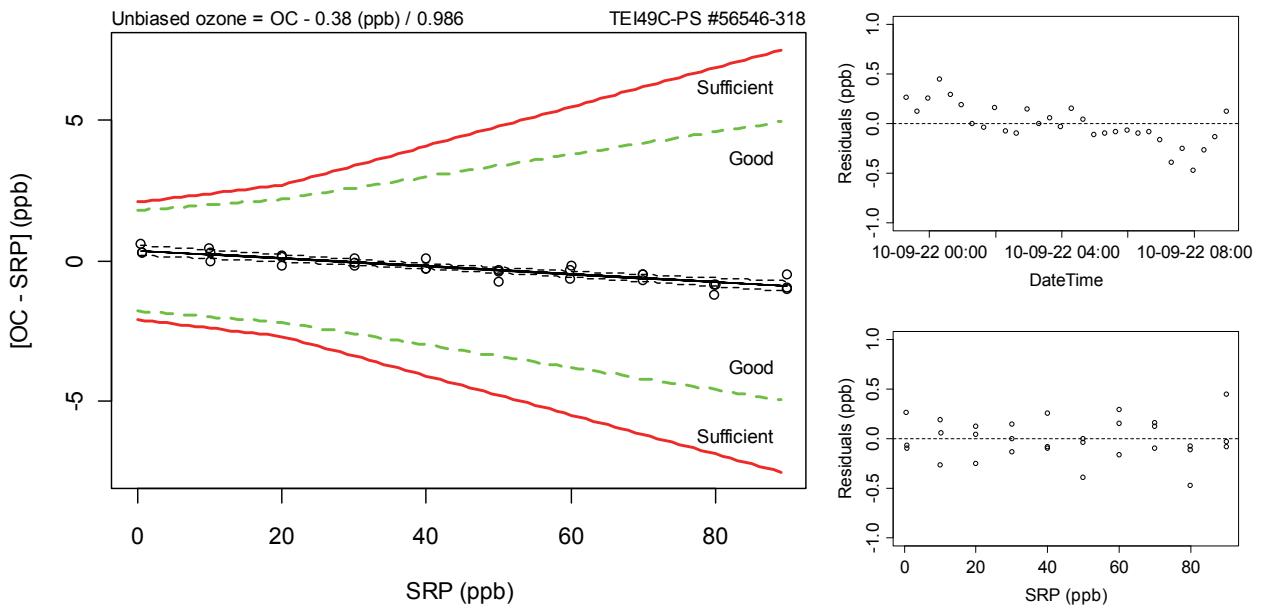


Figure 1. Left: Bias of the RCC-BsAs ozone calibrator (TEI 49C-PS) with respect to the SRP as a function of mole fraction. Each point represents the average of the last 10 one-minute values at a given level. Areas defining ‘good’ and ‘sufficient’ agreement according to GAW assessment criteria [J. Klausen et al., 2003] are delimited by green and red lines. The dashed lines about the regression lines are the Working-Hotelling 95% confidence bands. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).

Instrument condition after comparison: unchanged.

Recommendation 8 (, 2011-13)**

The TEI 49C-PS of the RCC-BsAs is still in good working condition; however, some degrading has been observed since the last comparison by WCC-Empa in 2008. An instrument service is recommended.

Ushuaia (USH) – TEI 49C #56546-318

Instrument condition prior to comparison:

This instrument is the main analyzer of the USH station since its installation by WCC-Empa in 2008 [Zellweger et al., 2008]. In 2008, the instrument was in good calibration. Several instrument checks were made with the analyzer prior to the first comparison. The instrument passed all checks (A/B ozone at 500 ppb, leak check, visual inspection of cells). Nevertheless, a significant bias was found during the comparison with only sufficient agreement according to the GAW DQOs [J. Klausen et al., 2003] for elevated ozone mixing ratios. The results of the first comparison are shown in Figure 2.

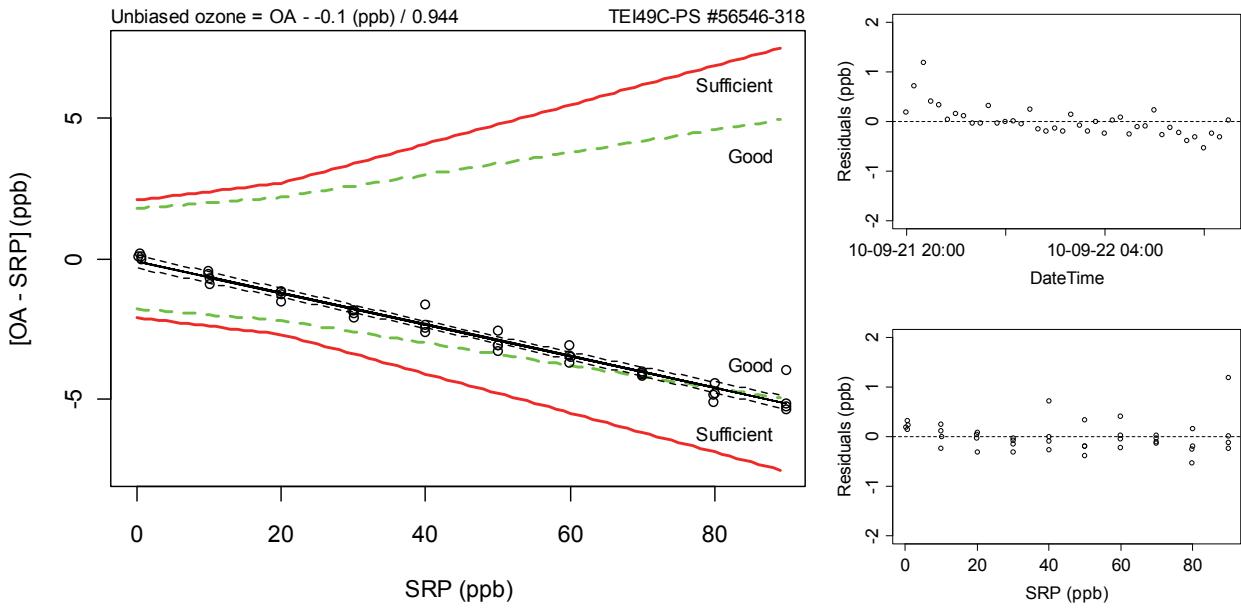


Figure 2. Left: Bias of the USH ozone analyzer (TEI 49C, first comparison) with respect to the SRP as a function of mole fraction. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).

As a consequence of the comparison result, the instrument was cleaned (cells) despite no visible dirt could be seen. Again, the leak check and the A/B ozone test were within the acceptable limits. After this, a second comparison was made; the results which slightly improved are presented in Figure 3.

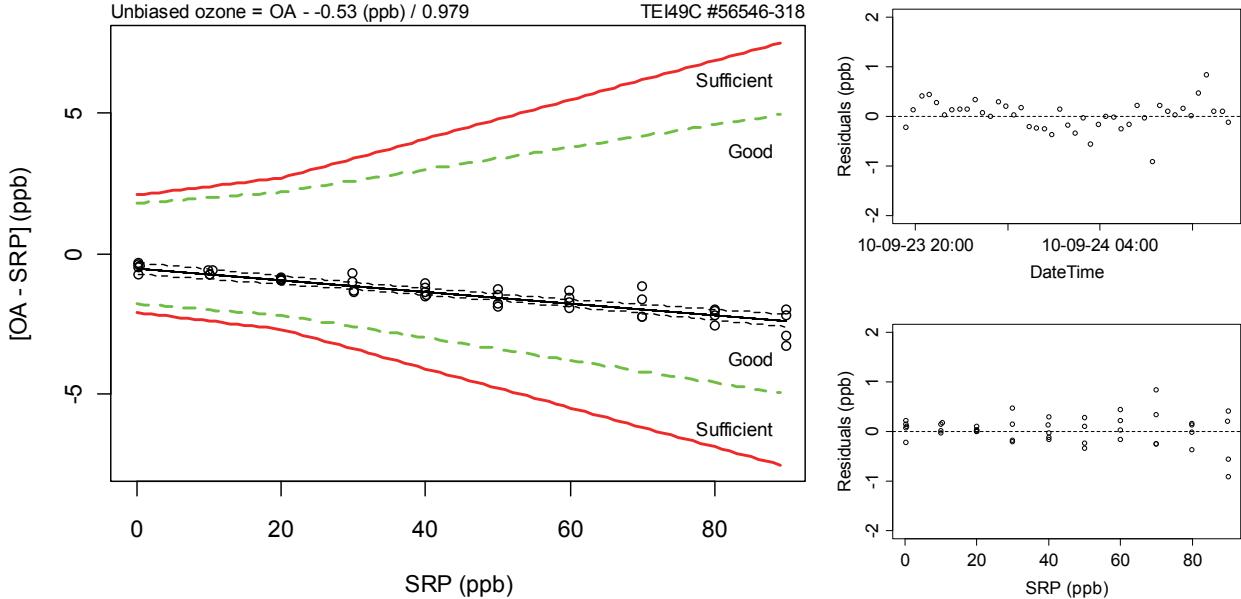


Figure 3. Same as Figure 2, second comparison after cleaning.

Instrument condition after comparison: cleaned, otherwise unchanged.

Recommendation 9 – USH TEI 49C (*, 2011)**

The deviation of the USH TEI 49C was larger than expected from previous comparisons. The TEI 49C USH data should be compared with the TEI 49 instrument, which was found to be in good calibration (see below).

Recommendation 10 – USH TEI 49C (*, 2011)**

In addition to the relatively large deviation the instrument noise was also found to be high compared to a typical instrument of this type; therefore, an instrument service is indicated.

USH – TEI 49 #47306-278

Instrument condition prior to comparison:

The instrument has been used as a back-up analyzer at the USH station since 2008. In 2008, the instrument was in good calibration [Zellweger et al., 2008]. Several instrument checks were made with the analyzer prior to the first comparison. The instrument passed all checks (A/B ozone at 500 ppb, leak check, visual inspection of cells). The results of the comparison confirmed the findings of the audit in 2008 and are presented in Figure 4.

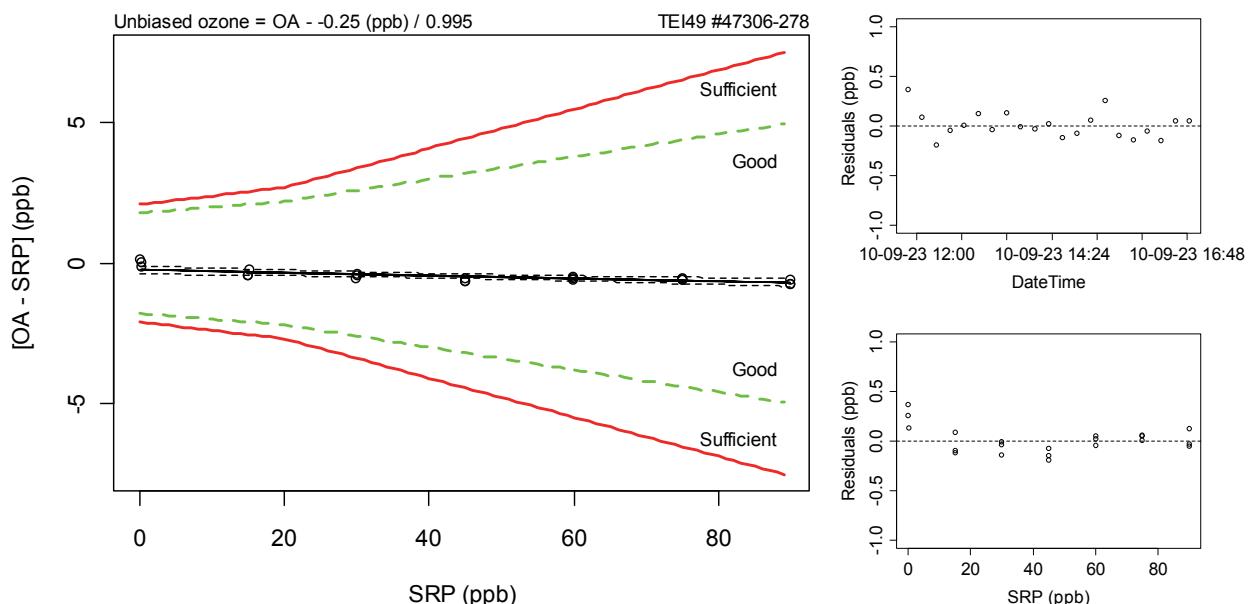


Figure 4. Left: Bias of the USH ozone analyzer (TEI 49) with respect to the SRP as a function of mole fraction. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).

Instrument condition after comparison: unchanged.

Recommendation 11 – USH TEI 49 (*, 2011)

If the findings of the comparison will be confirmed by the ambient USH ozone data, the data of the TEI 49 instrument should be considered for data submission.

Figure 5 shows ambient surface ozone data measured with the TEI 49 and the TEI 49C analyzer at USH, and the difference between the two instruments is presented in Figure 6.

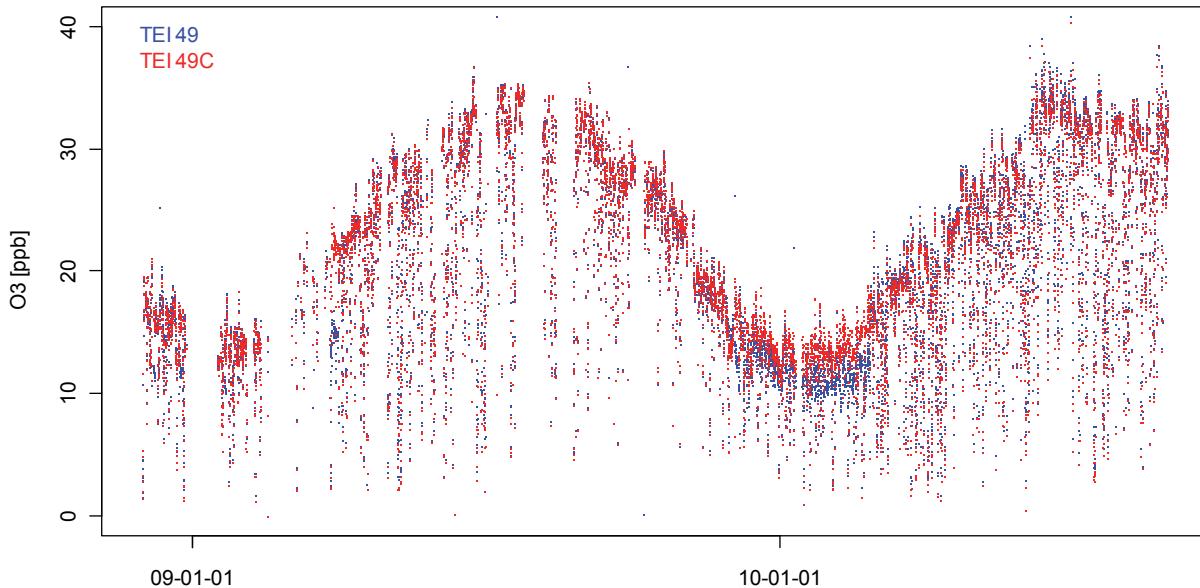


Figure 5. Time series of the two different USH ozone analyzers from December 2008 to August 2010 (1-hourly data corrected according to WCC-Empa audit in 2008).

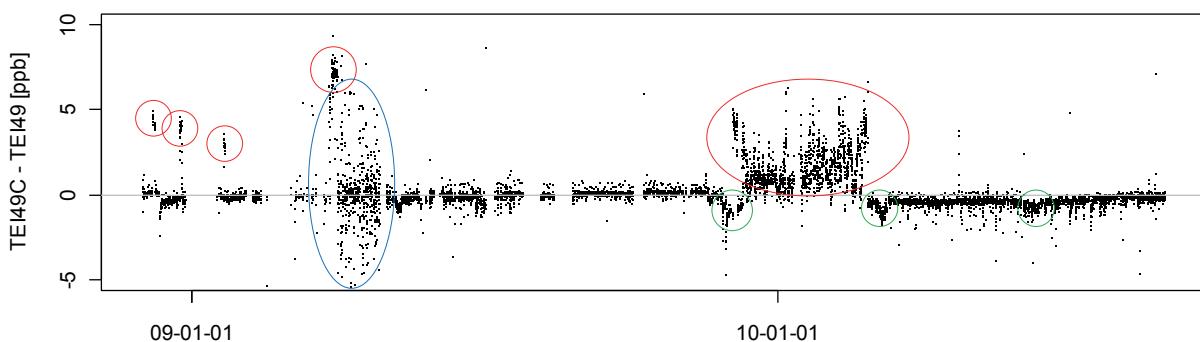


Figure 6. Difference between TEI 49C and TEI 49 measured at USH for 1-hourly averages. Only differences ranging from -5 to +10 ppb are shown.

It can be seen from Figures 5 and 6 that the overall agreement between the two instruments was good for most periods; however, there are a few exceptions. A possible reason for the deviations in the periods when the readings of the TEI 49C were higher compared to the TEI 49 (red circles in Figure 6) could be a leak in the filter holder of the TEI 49 instrument. The type of filter holder that is used with the TEI 49 instrument (Galtek PFA filter holder) is known to be very delicate concerning tightening. Alternatively, it can also be a problem of the TEI 49 instrument, because similar behaviour was already observed in other instruments [Jörg Klausen *et al.*, 2006]. There was also one period where the scatter of the deviation was larger than usual (blue oval). During this period, one or both instruments were not working properly; however, it is difficult to identify which instrument caused the deviation, because the time series of both instruments look reasonable during this period. And finally, there are a few occasions when the TEI 49C readings were significantly lower compared to the TEI 49 instruments (green circles, although this feature can be seen in most of the 2010 data). The deviations during this period were in the same order of magnitude (a few tenths up to 2 ppb) as observed during the current comparison.

San Julian – TEI 49 #49983-285

Instrument condition prior to comparison:

Initial instrument checks revealed several problems, and a comparison in current state of the analyzer was not possible. The following problems were identified:

- Issue: The instrument did not power up. Solution: Replacement of the power supply board.
- Issue: The ozone lamp did not light up: Solution: Ozone lamp was replaced.
- Issue: The cells were completely corroded due to water inside the analyzer. Cleaning was not possible. Solution: The whole optical bench was replaced.
- Issue: Flow B was low. Solution: Capillary B was cleaned.

The initial calibration settings (Zero 51, Span 623) were no longer valid after the above maintenance. The factors were changed to 50 (Zero) and 531 (Span) during instrument conditioning. The initial span settings using a value of 623 were made to compensate for an instrument bias due to the condition of the instrument. Such a high span value is far outside the expected range of meaningful settings. Therefore, data acquired with this instrument need to be carefully re-analyzed considering the instrument log books. Data acquired with high span settings need to be flagged as invalid.

The results of the comparison after repair are shown in Figure 7.

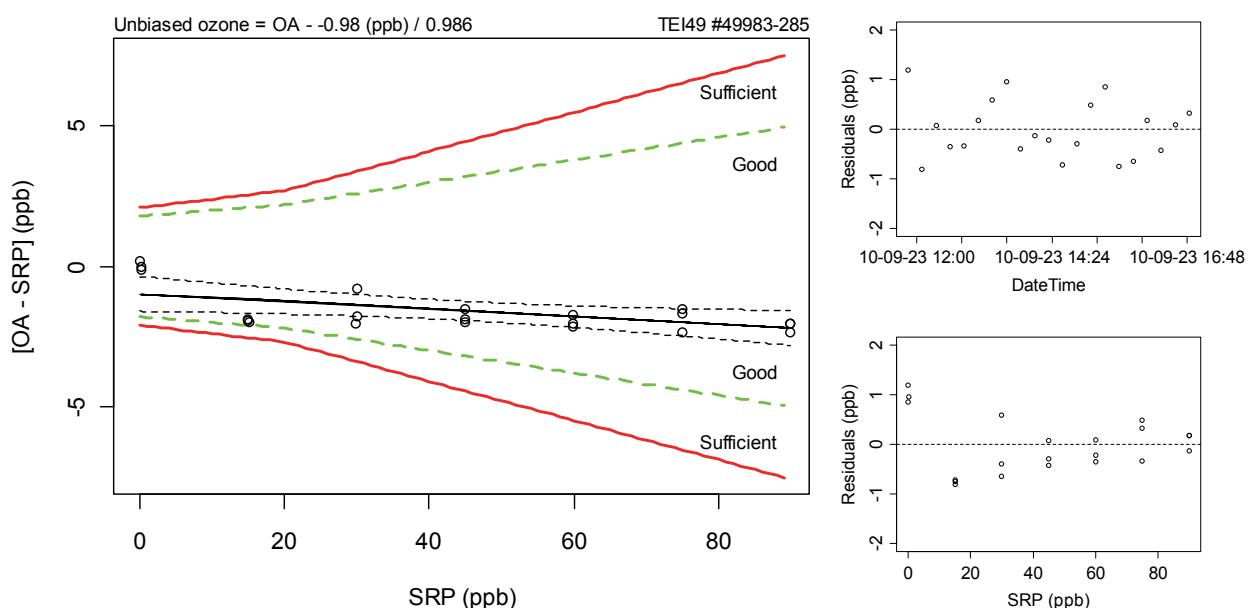


Figure 7. Left: Bias of the San Julian ozone analyzer (TEI 49, after repair) with respect to the SRP as a function of mole fraction. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).

Recommendation 12 – San Julian TEI 49 (***, 2011)

Existing data need to be reviewed. Data acquired using high span factors (>550) need to be flagged as invalid.

Recommendation 13 – San Julian TEI 49 (***, 2011)

The instrument was repaired during the comparison workshop; however, the analyzer remains in a poor working condition. Replacement by a new instrument is of utmost importance.

Instrument condition after comparison: The instrument was repaired and in working condition. The comparison showed some non-linearity at low mixing ratios, but the overall agreement was good according to the GAW DQOs. However, WCC-Empa recommends replacement of the instrument due to fact that extended repair was needed and due to the age of the analyzer.

Pilar – TEI 49 #49981-285

Instrument condition prior to comparison:

Initial instrument checks revealed several problems, and a comparison in current state of the analyzer was not possible. The following issues were identified:

- Issue: The ozone lamp did not light up: Solution: Lamp power supply was replaced.
- Issue: Insufficient flow. Solution: Pump replacement.

Additionally, the shutter of the cell B was almost completely closed, and it was re-adjusted after replacement of the lamp power supply board. The final cell frequency readings were 111 KHz (A) and 90 kHz (B). This instrument had also very high calibration settings (Zero 52, Span 571). No changes of the settings were made for the comparison; the results after repair are shown in Figure 8.

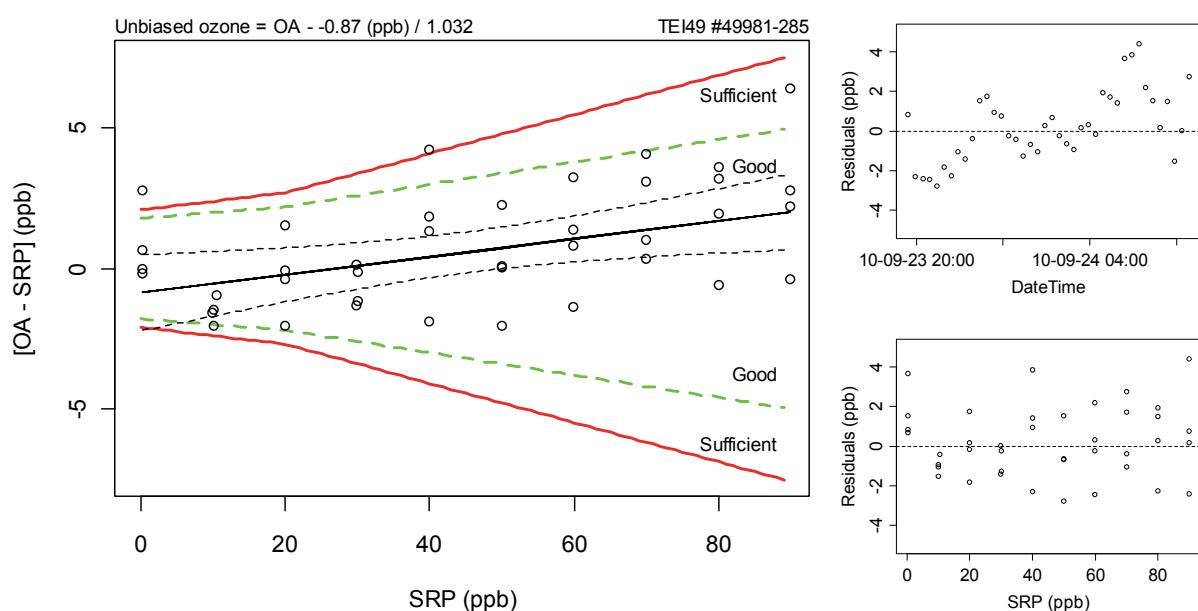


Figure 8. Left: Bias of the Pilar ozone analyzer (TEI 49, after repair) with respect to the SRP as a function of mole fraction. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).

The results show that the instrument was drifting during the comparison, and the noise of the analyzer exceeded acceptable values. Data must be evaluated with care, and will be associated with a high uncertainty.

Recommendation 14 – Pilar TEI 49 (***, 2011)

The instrument was repaired during the comparison workshop; however, the analyzer remains in a poor working condition. Replacement by a new instrument is of utmost importance; WCC-Empa recommends the use of the La Quiaca analyzer as a temporary solution.

Instrument condition after comparison: The instrument was repaired and in working condition. The comparison showed drift over time and poor reproducibility, but the average agreement was good according to the GAW DQOs. However, a few individual 10-min averages showed either only sufficient or insufficient agreement due to the large instrument noise. WCC-Empa recommends replacement of the instrument due to these facts and the age of the analyzer.

La Quiaca – TEI 49 #54577-300

Instrument condition prior to comparison:

Several instrument checks were made with the analyzer prior to the first comparison. The instrument passed the leak and A/B ozone check at 500 ppb; however, the cells were slightly dirty and have been cleaned before the comparison. The results of the comparison are shown in Figure 9.

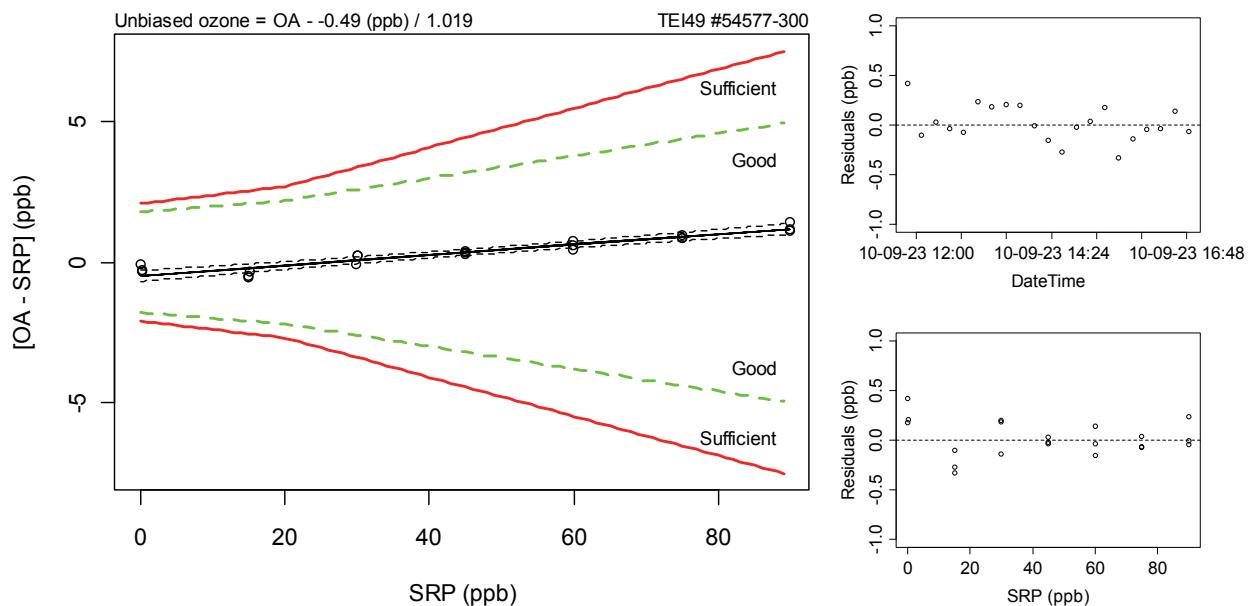


Figure 9. Left: Bias of the La Quiaca ozone analyzer (TEI 49) with respect to the SRP as a function of mole fraction. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).

It can be seen from the results that the instrument was in good condition and calibration; the station will be equipped with a refurbished TEI 49C analyzer, and WCC-Empa therefore suggest that this instrument should replace the Pilar analyzer, which needs to be decommissioned.

Recommendation 15 – La Quiaca TEI 49 (***, 2011)

Due to the addition of a TEI 49C at the La Quiaca station, the TEI 49 instrument should be transferred to the Pilar station.

Instrument condition after comparison: unchanged.

San Lorenzo – TEI 49 #54501-300

Instrument condition prior to comparison:

Several instrument checks were made with the analyzer prior to the first comparison. The instrument passed all checks (A/B ozone at 500 ppb, leak check, visual inspection of cells). No changes of the settings were made for the comparison; the results are shown in Figure 10.

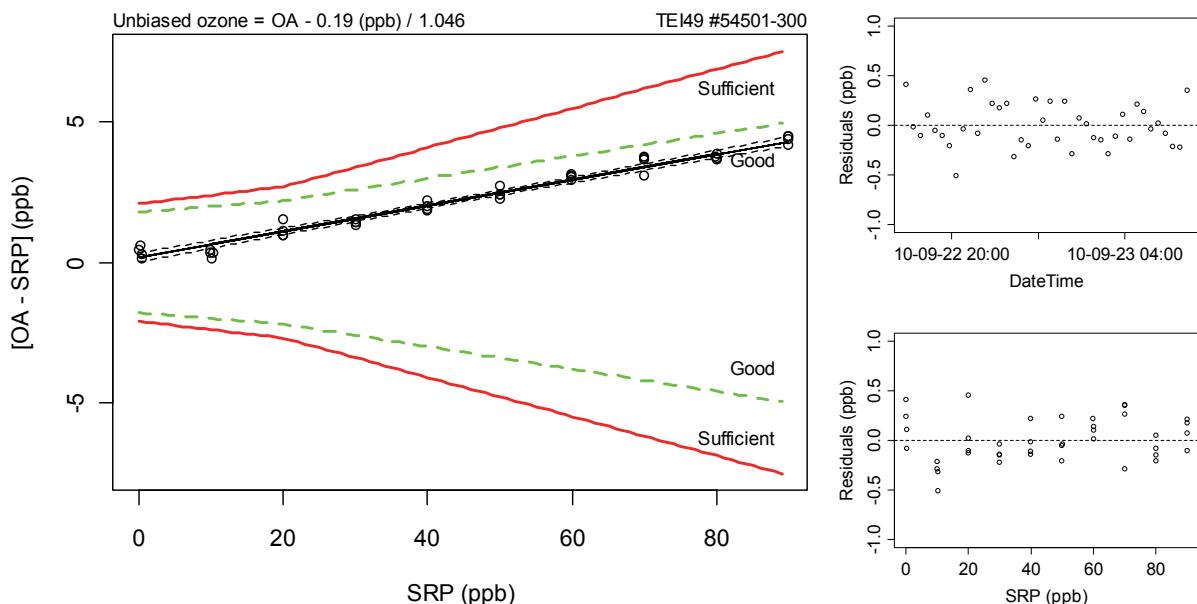


Figure 10. Left: Bias of the San Lorenzo ozone analyzer (TEI 49) with respect to the SRP as a function of mole fraction. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).

The results show that the instrument was functioning well but the readings were relatively high compared to the WCC-Empa reference instrument. This is expected due to the high settings of the span factor (529); to obtain better agreement, the span value needs to be changed to 506. It is recommended that the data acquired with the current span settings are corrected using equation 1a.

Recommendation 16 – San Lorenzo TEI 49 (**, 2011)

The instrument was found to be in good working condition but data acquired with the current calibration setting should be corrected. Furthermore, it is recommended to change the span factor from 529 to 506 to compensate the bias. With the new settings, no further corrections are necessary.

Recommendation 17 (***, immediately)

Despite the good working condition of the instrument, measurements at the San Lorenzo station have been discontinued because no data acquisition system is available at the site. It is necessary to immediately install a data acquisition system (or data logger) and continue with measurements.

Instrument condition after comparison: unchanged.

El Tololo – TEI 49 #49978-285

Instrument condition prior to comparison:

Initial instrument checks revealed several problems, and a comparison in current state of the analyzer was not possible. The following issues were identified:

- Ozone lamp did not light up: Solution: Ozone lamp and lamp power supply were replaced.
- Insufficient flow. Solution: Pump replacement.

Afterwards, the instrument passed all checks (A/B ozone at 500 ppb, leak check, visual inspection of cells). No changes of the settings were made for the comparison; the results are shown in Figure 11.

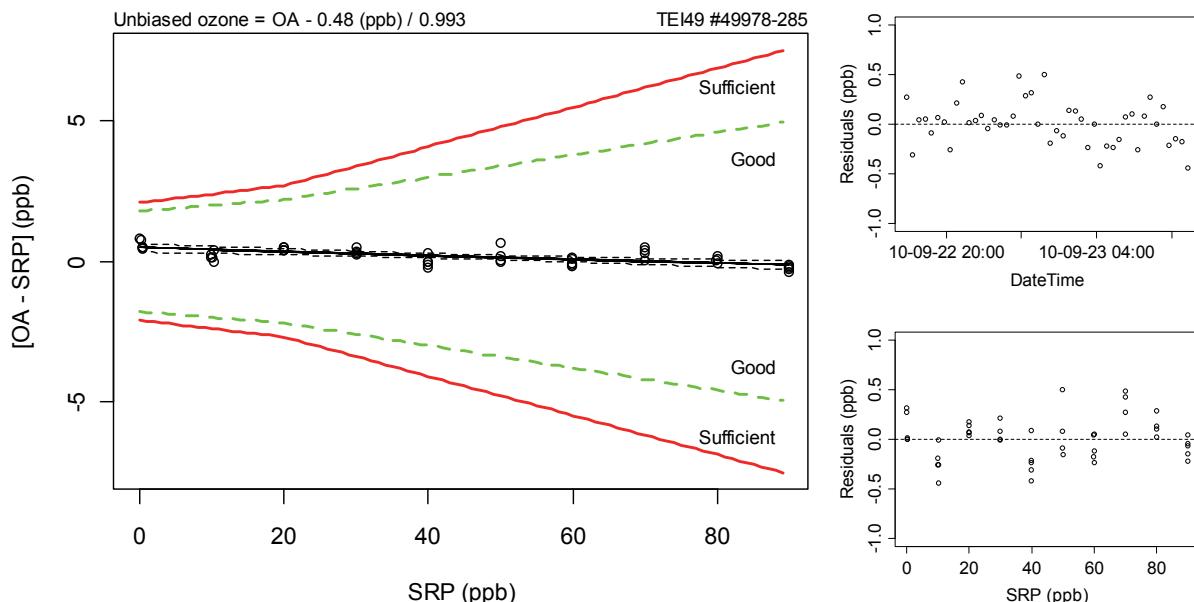


Figure 11. Left: Bias of the El Tololo ozone analyzer (TEI 49) with respect to the SRP as a function of mole fraction. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).

The results show that the instrument was functioning well after repair, and also the calibration of the instrument was still valid. Therefore, no further action is required for this instrument. It should be considered to use this analyzer at another site (e.g. San Julian) due to the fact that a replacement TEI 49C was provided to the El Tololo station.

Recommendation 18 – El Tololo TEI 49 (*, 2011)

Due to instrument replacement at the El Tololo site, use of the current TEI 49 analyzer at another station is recommended.

Instrument condition after comparison: Pump, ozone lamp and lamp power supply replaced, otherwise unchanged. The maintenance is expected to have no influence on the instrument calibration.

Natal – TEI 49C #62170-334

Instrument condition prior to comparison:

The instrument did not pass the A/B ozone check; the readings were unstable, and cell A ozone was reading approximately 30% lower than cell B ozone (acceptable limit: 3%). Several new solenoid valves which were individually leak checked have been tried, but without success. As a consequence, the following parts were exchanged, and ozone conditioning (A/B ozone check) was repeated:

- Scrubber.
- All electronic boards.
- Capillaries.
- Flow sensors.
- Optical bench including lamp and detectors.
- Power supply and lamp power supply.

Despite the fact that almost every part of the analyzer was exchanged, the instrument remained very unstable. Consequently, a comparison in the current state was made. The results are shown in Figure 12.

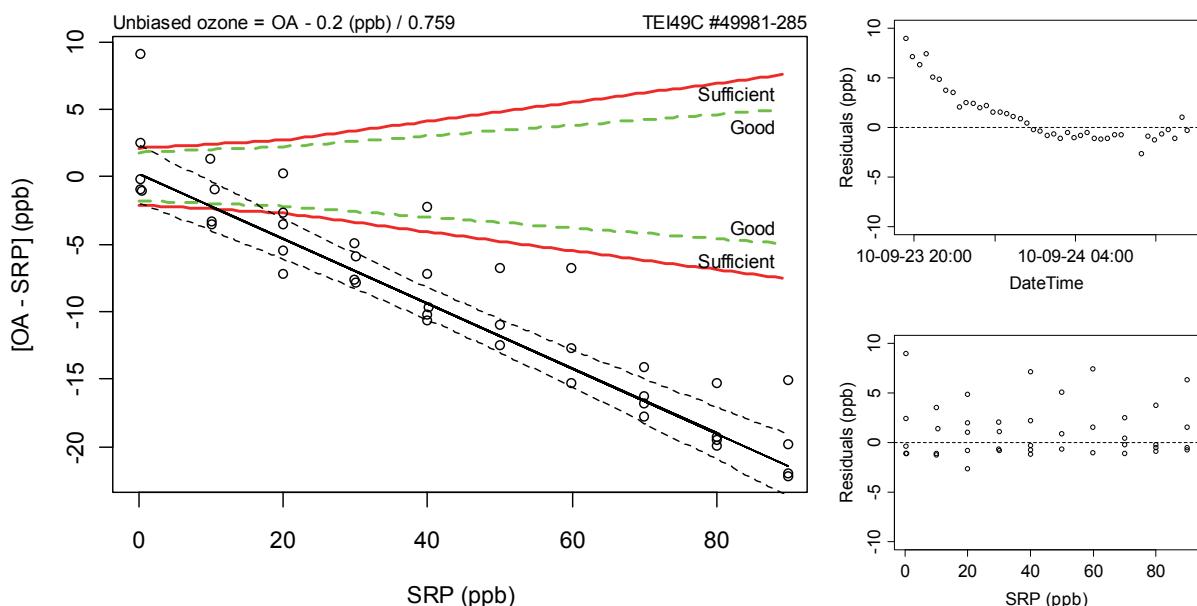


Figure 12. Left: Bias of the Brazilian ozone analyzer (TEI 49C, planned to be placed at Natal) with respect to the SRP as a function of mole fraction. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).

The raw data of the comparison is shown in Figure 13. The red and blue lines are the ozone readings of the reference and Natal ozone instruments, and the circles are the last 10-min averages after stabilization time that were used for the assessment. It can be seen that the instrument was drifting over time and the analyzer was reading significantly lower compared to the reference instrument, despite a span setting of 1.135. Furthermore, the analyzer was sometimes very unstable during the comparison (green circles in Figure 13). The instrument was clearly not in working condition, although the reason could not be identified during the comparison exercise.

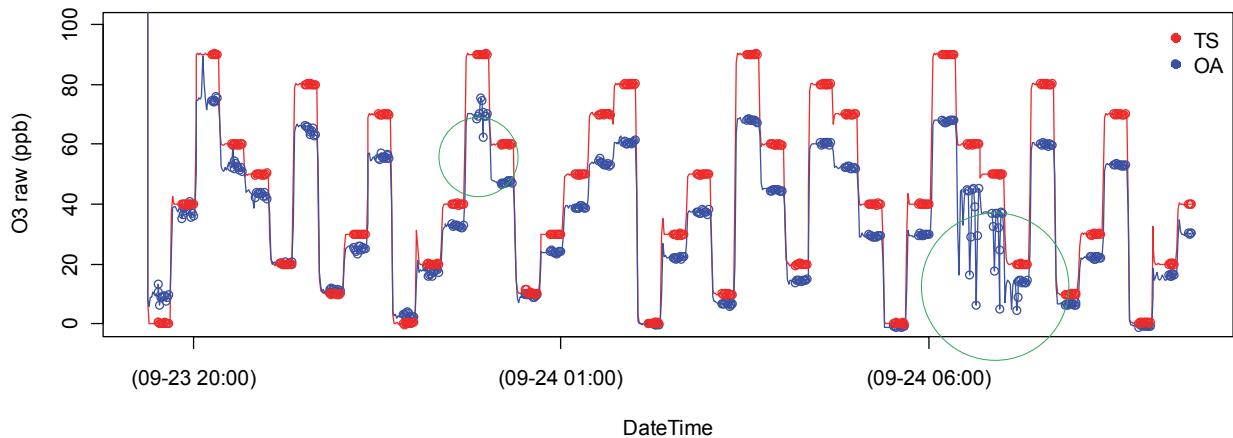


Figure 13. Raw data of the comparison; red and blue lines are raw ozone readings of the reference (TS) and Natal ozone instruments (OA); circles are the 1-min averages after stabilisation time.

It was agreed that the instrument will be shipped to WCC-Empa for further diagnostics and test, which was done in April 2011. Initial instrument checks at Empa showed that the instrument was still not working, and the following repair was made at Empa:

- Battery replaced.
- Flow sensor of cell A replaced.
- IC U4 on power supply board replaced.

The instrument was extensively tested afterwards, and the calibration settings were changed to BKG 0.0 (initial +1.5) and SPAN 1.005 (initial 1.135). The results after repair of a comparison against SRP15 are shown in Figure 14.

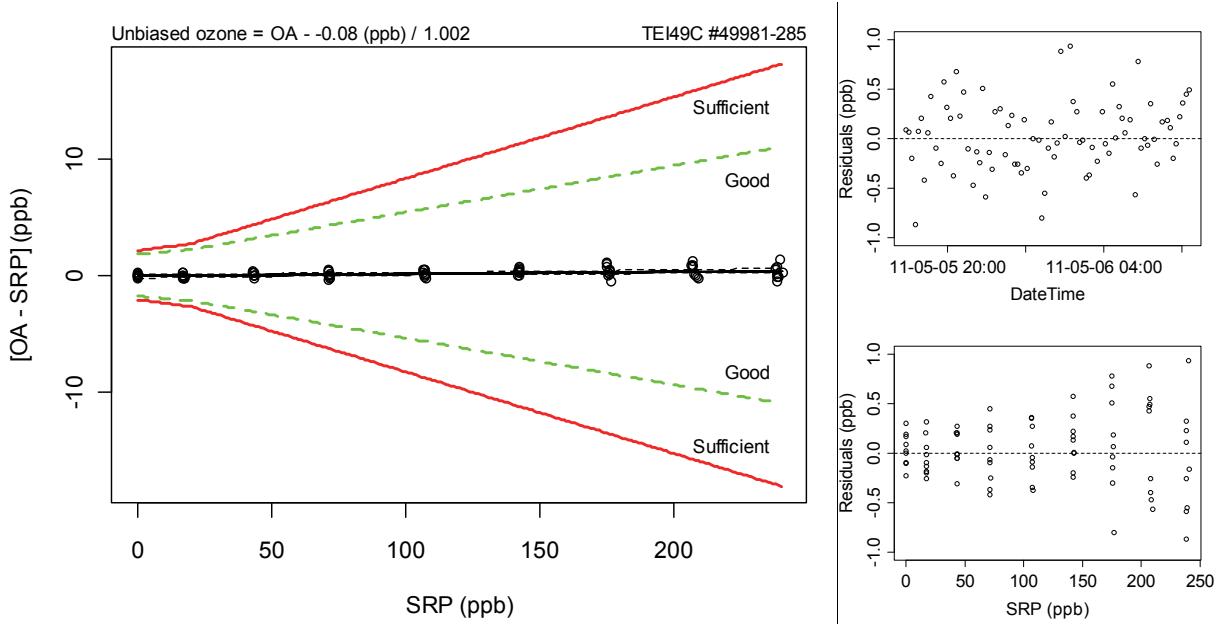


Figure 14. Left: Bias of the Brazilian ozone analyzer (TEI 49C, after repair at Empa) with respect to the SRP as a function of mole fraction. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).

Salto – TEI 49 #54947-302

Instrument condition prior to comparison:

The ozone lamp did not light up and was replaced. Afterwards, the instrument passed all checks (A/B ozone at 500 ppb, leak check, visual inspection of cells). No changes of the settings were made for the comparison; the results of the comparison are shown in Figure 15.

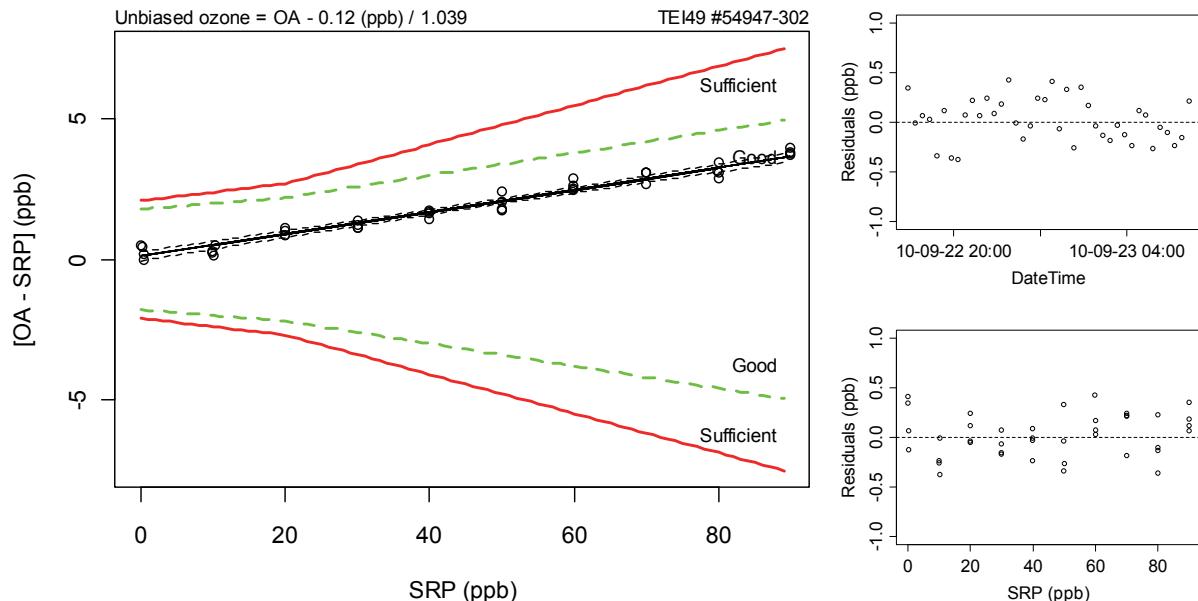


Figure 15. Left: Bias of the Salto ozone analyzer (TEI 49) with respect to the SRP as a function of mole fraction. Right: Regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).

The results show that the instrument was functioning well after lamp replacement. However, the readings were relatively high compared to the WCC-Empa reference instrument. This is expected due to the high settings of the span factor (524); to obtain good agreement, the span value needs to be changed to 504. It is recommended that the data acquired with the current span settings are corrected using equation 1a.

Recommendation 20 – Salto TEI 49 (**, 2011)

The instrument was found to be in good working condition but data acquired with the current calibration setting should be corrected. Furthermore, it is recommended to change the span factor from 524 to 504 to compensate the bias. With the new settings, no further corrections are necessary.

Recommendation 21 (*, 2011)

Due to instrument replacement at the Salto GAW station, use of the current TEI 49 analyzer at another station is recommended.

Instrument condition after comparison: Ozone lamp replaced, otherwise unchanged.

Conclusions

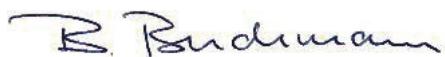
The IV tropospheric ozone analyzer inter-comparison organized by the Regional Calibration Centre for Surface Ozone in Buenos Aires (RCC-BsAs) re-initiated ozone measurements at many sites in South America. Most of the analyzers could be repaired and calibrated, and three additional newer surface ozone instruments were provided to the La Quiaca, Salto and El Tololo GAW stations. Nevertheless, the current instrumentation at most sites should be renewed.

The situation concerning data availability and submission to WDCGG remains unsatisfactory. It is absolutely necessary that progress will be made in this respect in the very near future to maintain visibility of the South American GAW activities and to ensure support by external partners.

Dübendorf, October 2011



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APPENDIX I – NEW OZONE INSTRUMENTATS FOR LA QUIACA, EL TOLOLO AND SALTO

Instruments that have been used in the Swiss National Air Pollution Monitoring Network were provided to the GAW stations La Quiaca, Salto and El Tololo. The instruments were equipped with new pumps and have been carefully serviced at the Empa calibration laboratories. Before shipment to RCC-BsAs, the instruments were directly calibrated using the WCC-Empa Standard Reference Photometer SRP#15. The calibration factors of the instruments were set for minimal bias compared to the reference, and the following relationships between the SRP and the refurbished instruments were found:

GAW Station La Quiaca: TEI 49C #61161-330 (SPAN 1.013, BKG 0.1)

$$\text{Reference value (SRP#15)} = (0.9980 \times \text{TEI 49C } \#61161-330 + 0.16) \text{ ppb} \quad (2a)$$

GAW Station El Tololo: TEI 49C #72417-371 (SPAN 1.010, BKG -0.9)

$$\text{Reference value (SRP#15)} = (0.9988 \times \text{TEI 49C } \#72417-371 + 0.16) \text{ ppb} \quad (2b)$$

GAW Station Salto: TEI 49C #72419-371 (SPAN 1.009, BKG 0.0)

$$\text{Reference value (SRP#15)} = (0.9993 \times \text{TEI 49C } \#72419-371 - 0.03) \text{ ppb} \quad (2c)$$

Figure 16 shows the calibration results including an estimate of the expanded standard uncertainties, which also accounts for the uncertainty of the absorption cross section [Viallon et al., 2006]. The individual measurement data are listed in Tables 4 to 6.

It can be seen from the comparisons that the deviations between the instruments and the WCC-Empa ozone reference is not significant in the range from 0 – 250 ppb ozone. Therefore, data of these instruments can directly be used, but it is recommended to verify the current calibration settings by comparison with an ozone standard in at least yearly intervals (preferably every 3 months).

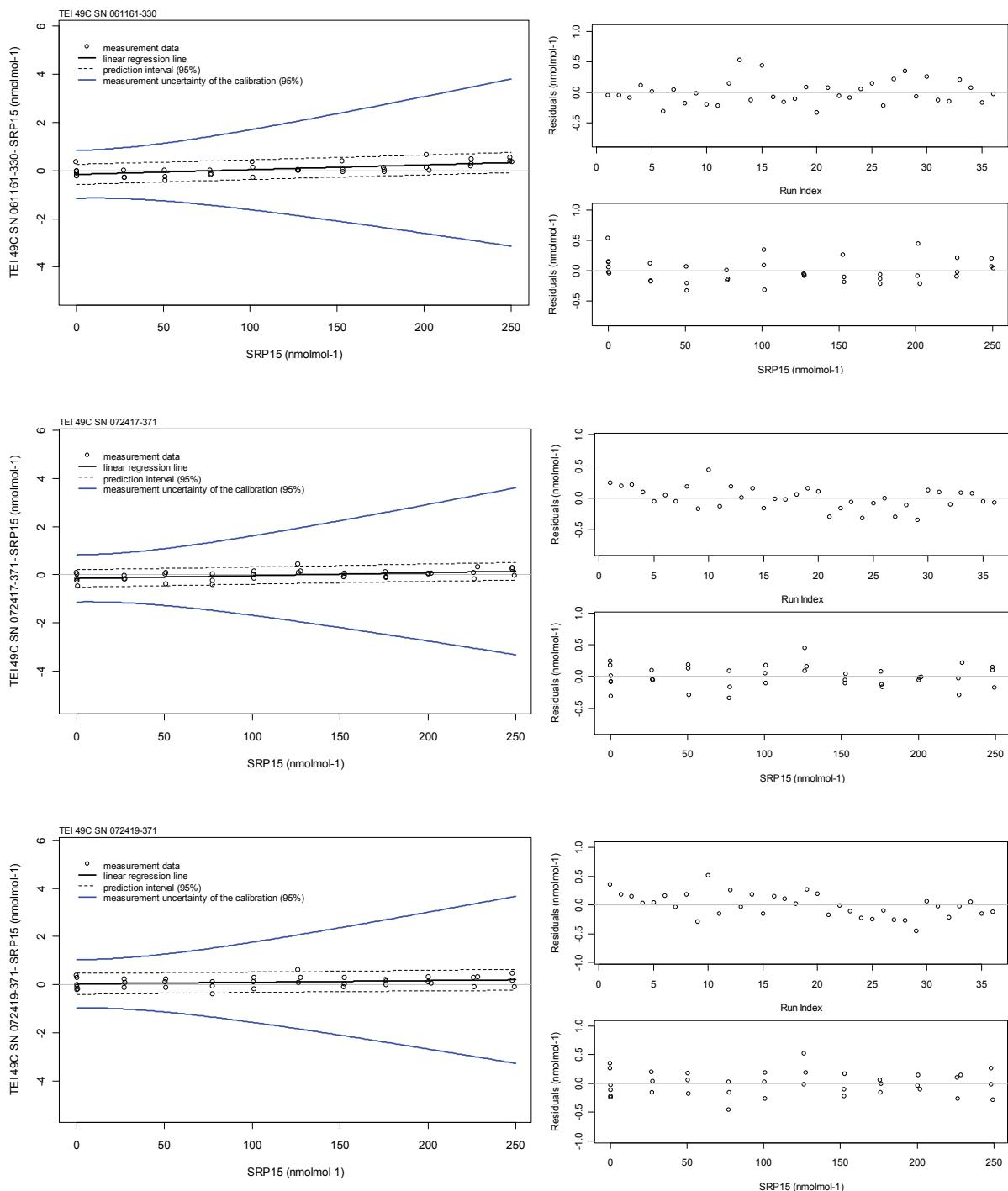


Figure 16. Left panel: Bias of the refurbished ozone analyzers (TEI 49C, top: La Quiaca, middle: El Tololo, bottom: Salto) with respect to the SRP as a function of mole fraction. Right panel: Corresponding regression residuals of the ozone comparisons as a function of time (top) and mole fraction (bottom).

Table 4. Comparison data of TEI 49C #61161-330 (La Quiaca).

| Run # | SRP#15 (ppb) | sdSRP#15 (ppb) | TEI49C (ppb) | sdTEI49C (ppb) | TEI49C-SRP (ppb) | TEI49C-SRP (%) |
|-------|--------------|----------------|--------------|----------------|------------------|----------------|
| 1 | 0.17 | 0.55 | -0.03 | 0.14 | -0.20 | NA |
| 2 | 127.23 | 0.32 | 127.27 | 0.12 | 0.04 | 0.03 |
| 3 | 201.29 | 0.49 | 201.44 | 0.17 | 0.15 | 0.08 |
| 4 | 26.97 | 0.50 | 26.99 | 0.13 | 0.02 | 0.06 |
| 5 | 76.90 | 0.36 | 76.91 | 0.08 | 0.01 | 0.01 |
| 6 | 101.36 | 0.67 | 101.09 | 0.13 | -0.27 | -0.27 |
| 7 | 250.39 | 0.23 | 250.77 | 0.19 | 0.38 | 0.15 |
| 8 | 153.23 | 0.21 | 153.19 | 0.25 | -0.04 | -0.02 |
| 9 | 227.18 | 0.24 | 227.46 | 0.21 | 0.28 | 0.12 |
| 10 | 51.02 | 0.39 | 50.76 | 0.12 | -0.26 | -0.50 |
| 11 | 176.99 | 0.30 | 176.97 | 0.19 | -0.02 | -0.01 |
| 12 | -0.11 | 0.44 | -0.12 | 0.10 | -0.01 | NA |
| 13 | -0.49 | 0.63 | -0.10 | 0.14 | 0.38 | NA |
| 14 | 77.57 | 0.23 | 77.43 | 0.08 | -0.14 | -0.17 |
| 15 | 201.43 | 0.59 | 202.12 | 0.42 | 0.69 | 0.34 |
| 16 | 127.54 | 0.45 | 127.55 | 0.13 | 0.02 | 0.01 |
| 17 | 27.47 | 0.78 | 27.21 | 0.16 | -0.26 | -0.95 |
| 18 | 153.34 | 0.31 | 153.39 | 0.24 | 0.04 | 0.03 |
| 19 | 101.24 | 0.26 | 101.38 | 0.11 | 0.13 | 0.13 |
| 20 | 51.11 | 0.48 | 50.72 | 0.09 | -0.38 | -0.75 |
| 21 | 249.53 | 0.41 | 249.94 | 0.12 | 0.41 | 0.16 |
| 22 | 176.75 | 0.29 | 176.89 | 0.12 | 0.13 | 0.08 |
| 23 | 226.55 | 0.24 | 226.75 | 0.14 | 0.20 | 0.09 |
| 24 | -0.05 | 0.24 | -0.15 | 0.14 | -0.10 | NA |
| 25 | -0.06 | 0.29 | -0.07 | 0.11 | -0.01 | NA |
| 26 | 202.90 | 0.25 | 202.93 | 0.11 | 0.03 | 0.01 |
| 27 | 227.10 | 0.41 | 227.61 | 0.18 | 0.51 | 0.22 |
| 28 | 101.04 | 0.20 | 101.43 | 0.10 | 0.39 | 0.39 |
| 29 | 127.43 | 0.33 | 127.46 | 0.10 | 0.03 | 0.02 |
| 30 | 152.73 | 0.41 | 153.14 | 0.14 | 0.41 | 0.27 |
| 31 | 176.87 | 0.14 | 176.93 | 0.07 | 0.06 | 0.04 |
| 32 | 77.12 | 0.29 | 76.96 | 0.14 | -0.15 | -0.20 |
| 33 | 249.38 | 0.37 | 249.92 | 0.15 | 0.54 | 0.22 |
| 34 | 50.58 | 0.43 | 50.59 | 0.12 | 0.02 | 0.03 |
| 35 | 27.46 | 0.31 | 27.19 | 0.14 | -0.27 | -0.99 |
| 36 | -0.07 | 0.40 | -0.25 | 0.07 | -0.18 | NA |

Table 5. Comparison data of TEI 49C #72417-371 (El Tololo).

| Run # | SRP#15 (ppb) | sdSRP#15 (ppb) | TEI49C (ppb) | sdTEI49C (ppb) | TEI49C-SRP (ppb) | TEI49C-SRP (%) |
|-------|--------------|----------------|--------------|----------------|------------------|----------------|
| 1 | -0.21 | 0.29 | -0.12 | 0.15 | 0.09 | NA |
| 2 | 50.65 | 0.50 | 50.75 | 0.11 | 0.10 | 0.20 |
| 3 | 228.33 | 0.31 | 228.67 | 0.20 | 0.34 | 0.15 |
| 4 | 76.98 | 0.40 | 77.01 | 0.08 | 0.04 | 0.05 |
| 5 | 27.37 | 0.51 | 27.20 | 0.13 | -0.17 | -0.63 |
| 6 | 152.49 | 0.42 | 152.56 | 0.24 | 0.08 | 0.05 |
| 7 | 200.00 | 0.37 | 200.04 | 0.09 | 0.04 | 0.02 |
| 8 | 100.83 | 0.24 | 100.98 | 0.09 | 0.15 | 0.15 |
| 9 | 249.03 | 0.54 | 249.01 | 0.13 | -0.02 | -0.01 |
| 10 | 126.00 | 0.26 | 126.45 | 0.09 | 0.45 | 0.36 |
| 11 | 176.06 | 0.46 | 176.00 | 0.06 | -0.07 | -0.04 |
| 12 | -0.07 | 0.40 | -0.04 | 0.07 | 0.03 | NA |
| 13 | 0.05 | 0.32 | -0.09 | 0.08 | -0.14 | NA |
| 14 | 127.45 | 0.35 | 127.61 | 0.11 | 0.16 | 0.13 |
| 15 | 77.25 | 0.27 | 77.04 | 0.07 | -0.22 | -0.28 |
| 16 | 200.33 | 0.33 | 200.40 | 0.15 | 0.08 | 0.04 |
| 17 | 225.85 | 0.36 | 225.95 | 0.07 | 0.10 | 0.04 |
| 18 | 100.47 | 0.31 | 100.49 | 0.09 | 0.02 | 0.02 |
| 19 | 248.15 | 0.45 | 248.45 | 0.21 | 0.30 | 0.12 |
| 20 | 26.87 | 0.35 | 26.85 | 0.19 | -0.02 | -0.05 |
| 21 | 50.83 | 0.50 | 50.45 | 0.06 | -0.38 | -0.75 |
| 22 | 176.19 | 0.40 | 176.09 | 0.12 | -0.10 | -0.06 |
| 23 | 152.26 | 0.45 | 152.23 | 0.07 | -0.03 | -0.02 |
| 24 | 0.26 | 0.60 | -0.20 | 0.07 | -0.46 | NA |
| 25 | 0.16 | 0.31 | -0.07 | 0.09 | -0.23 | NA |
| 26 | 201.80 | 0.42 | 201.89 | 0.14 | 0.09 | 0.04 |
| 27 | 226.23 | 0.50 | 226.06 | 0.11 | -0.17 | -0.08 |
| 28 | 100.82 | 0.31 | 100.68 | 0.11 | -0.14 | -0.14 |
| 29 | 76.99 | 0.60 | 76.59 | 0.08 | -0.40 | -0.52 |
| 30 | 50.35 | 0.30 | 50.38 | 0.09 | 0.04 | 0.07 |
| 31 | 248.12 | 0.45 | 248.36 | 0.13 | 0.24 | 0.10 |
| 32 | 152.07 | 0.39 | 152.00 | 0.20 | -0.07 | -0.05 |
| 33 | 126.01 | 0.35 | 126.09 | 0.07 | 0.09 | 0.07 |
| 34 | 175.58 | 0.22 | 175.71 | 0.10 | 0.14 | 0.08 |
| 35 | 27.12 | 0.58 | 26.95 | 0.08 | -0.17 | -0.61 |
| 36 | 0.03 | 0.52 | -0.20 | 0.06 | -0.23 | NA |

Table 6. Comparison data of TEI 49C #72419-371 (Salto).

| Run # | SRP#15 (ppb) | sdSRP#15 (ppb) | TEI49C (ppb) | sdTEI49C (ppb) | TEI49C-SRP (ppb) | TEI49C-SRP (%) |
|-------|--------------|----------------|--------------|----------------|------------------|----------------|
| 1 | -0.21 | 0.29 | 0.17 | 0.06 | 0.38 | NA |
| 2 | 50.65 | 0.50 | 50.89 | 0.12 | 0.24 | 0.48 |
| 3 | 228.33 | 0.31 | 228.66 | 0.20 | 0.33 | 0.15 |
| 4 | 76.98 | 0.40 | 77.09 | 0.08 | 0.11 | 0.14 |
| 5 | 27.37 | 0.51 | 27.47 | 0.06 | 0.09 | 0.34 |
| 6 | 152.49 | 0.42 | 152.79 | 0.12 | 0.30 | 0.20 |
| 7 | 200.00 | 0.37 | 200.13 | 0.10 | 0.13 | 0.06 |
| 8 | 100.83 | 0.24 | 101.12 | 0.08 | 0.29 | 0.28 |
| 9 | 249.03 | 0.54 | 248.94 | 0.14 | -0.09 | -0.04 |
| 10 | 126.00 | 0.26 | 126.63 | 0.10 | 0.63 | 0.50 |
| 11 | 176.06 | 0.46 | 176.06 | 0.14 | 0.00 | 0.00 |
| 12 | -0.07 | 0.40 | 0.22 | 0.07 | 0.29 | NA |
| 13 | 0.05 | 0.32 | 0.05 | 0.18 | 0.00 | 3.70 |
| 14 | 127.45 | 0.35 | 127.75 | 0.12 | 0.30 | 0.24 |
| 15 | 77.25 | 0.27 | 77.18 | 0.14 | -0.07 | -0.09 |
| 16 | 200.33 | 0.33 | 200.64 | 0.09 | 0.32 | 0.16 |
| 17 | 225.85 | 0.36 | 226.14 | 0.08 | 0.29 | 0.13 |
| 18 | 100.47 | 0.31 | 100.59 | 0.08 | 0.12 | 0.12 |
| 19 | 248.15 | 0.45 | 248.61 | 0.27 | 0.46 | 0.19 |
| 20 | 26.87 | 0.35 | 27.11 | 0.09 | 0.25 | 0.92 |
| 21 | 50.83 | 0.50 | 50.72 | 0.06 | -0.11 | -0.22 |
| 22 | 176.19 | 0.40 | 176.33 | 0.19 | 0.14 | 0.08 |
| 23 | 152.26 | 0.45 | 152.29 | 0.17 | 0.03 | 0.02 |
| 24 | 0.26 | 0.60 | 0.07 | 0.07 | -0.19 | NA |
| 25 | 0.16 | 0.31 | -0.05 | 0.12 | -0.21 | NA |
| 26 | 201.80 | 0.42 | 201.87 | 0.25 | 0.07 | 0.03 |
| 27 | 226.23 | 0.50 | 226.15 | 0.20 | -0.08 | -0.03 |
| 28 | 100.82 | 0.31 | 100.65 | 0.10 | -0.17 | -0.17 |
| 29 | 76.99 | 0.60 | 76.61 | 0.10 | -0.37 | -0.48 |
| 30 | 50.35 | 0.30 | 50.47 | 0.05 | 0.13 | 0.25 |
| 31 | 248.12 | 0.45 | 248.29 | 0.05 | 0.18 | 0.07 |
| 32 | 152.07 | 0.39 | 151.98 | 0.11 | -0.09 | -0.06 |
| 33 | 126.01 | 0.35 | 126.10 | 0.16 | 0.10 | 0.08 |
| 34 | 175.58 | 0.22 | 175.78 | 0.14 | 0.21 | 0.12 |
| 35 | 27.12 | 0.58 | 27.01 | 0.06 | -0.10 | -0.38 |
| 36 | 0.03 | 0.52 | -0.05 | 0.16 | -0.08 | NA |

APPENDIX II – COMPARISON DATA

All comparisons were done according to Standard Operating Procedures [WMO, in preparation] at the laboratory of RCC-BsAs and included comparisons of the traveling standard with the Standard Reference Photometer at Empa before and after the comparison workshop at RCC-BsAs. The ozone laboratory was not air conditioned but it is expected that this has no significant influence on the comparison results.

All comparisons were conducted according to the Standard Operating Procedure [WMO, in preparation]. The set-up is summarized in Table 7.

Table 7. Experimental details of the ozone comparison.

| | | |
|--------------------------------|--|---|
| Transfer standard (TS) | Model, S/N | TEI 49i-PS #0810-153 (WCC-Empa) |
| | Settings | BKG = 0.0; COEFF = 1.009 |
| Ozone source | Internal generator of TS | |
| Zero air supply | Custom built, consisting of: silica gel - inlet filter 5 µm - metal bellow pump - Purafil (potassium permanganate) - activated charcoal - outlet filter 5 µm (WCC-Empa) | |
| Connection between instruments | Maximum 1.5 meter of 1/4" PFA tubing between TS manifold and OA | |
| Data acquisition | TS / TEI 49C | 1- min aggregates from digital output (custom designed LabView program of WCC-Empa) |
| | TEI 49 | 1-min averages acquired with a Hunter&Caprez A/D data acquisition system |
| Levels (ppb) | 0, 10, 20, 30, 40, 50, 60, 70, 80, 90 (OA) | |
| Duration per level (min) | 15 | |
| Sequence of levels | Repeated runs of randomized fixed sequence | |

The instrument calibration settings as well as pressure sensor readings before the comparison are shown in Table 8.

Table 8. Instrument calibration settings and pressure sensor readings.

| Station | Instrument | Calibration settings | | Deviation of pressure sensor (%) |
|-------------------------|-----------------------|----------------------|------|----------------------------------|
| | | SPAN | BKG | |
| RCC-BsAs | TEI 49C-PS #56084-306 | 1.035 | -0.5 | 2.3 (-0.1)* |
| Ushuaia | TEI 49C #56546-318 | 1.012 | 0.0 | -0.2 |
| Ushuaia | TEI 49 #4703-278 | 510 | 50 | -0.1 |
| San Julián [#] | TEI 49 #49983-285 | 531 | 50 | -0.1 |
| Pilar | TEI 49 #49981-285 | 571 | 52 | 0.7 |
| La Quiaca | TEI 49 #54577-300 | 523 | 50 | 0.4 |
| San Lorenzo | TEI 49 #54501-300 | 529 | 50 | 0.1 |
| El Tololo | TEI 49 #49978-285 | 503 | 50 | 0.6 |
| Natal | TEI 49C #62170-334 | 1.135 | 1.4 | -0.2 |
| Natal [#] | TEI 49C #62170-334 | 1.005 | 0.0 | -0.2 |
| Salto | TEI 49 #54947-302 | 524 | 50 | 0.5 |

*Pressure sensor was adjusted. [#]Settings after instrument repair.

Results of the individual comparisons

The following tables show the results of the individual comparisons carried out during the workshop. During these comparisons, each ozone level was applied for at least 15 minutes, and the last 10 one-minute averages were aggregated. These aggregates were used in the assessment of the comparison as described elsewhere [J. Klausen et al., 2003]. The results are shown in the following Tables, whereas Figures as well as the calculated bias for individual instruments are presented in the Executive Summary. All results refer to the calibration factors as given in Table 8. The readings of the transfer standard (TS) were compensated for bias with respect to the Standard Reference Photometer (SRP) prior to the evaluation of the ozone analyzer (OA) values.

Table 9. Results of the RCC-BsAs ozone calibrator (OC) TEI 49C-PS #56546-318 compared to the WCC-Empa transfer standard (TS).

| Date Time | Run # | Level (ppb) | TS (ppb) | OC (ppb) | sd TS (ppb) | sd OC (ppb) | OC-TS (ppb) | OC-TS (%) |
|------------------|-------|-------------|----------|----------|-------------|-------------|-------------|-----------|
| 2010-09-21 23:17 | 1 | 0 | 0.48 | 1.09 | 0.12 | 0.02 | 0.61 | NA |
| 2010-09-21 23:37 | 1 | 20 | 19.96 | 20.14 | 0.16 | 0.05 | 0.18 | 0.90 |
| 2010-09-21 23:57 | 1 | 40 | 39.98 | 39.99 | 0.14 | 0.08 | 0.01 | 0.00 |
| 2010-09-22 00:17 | 1 | 90 | 90.00 | 89.44 | 0.09 | 0.09 | -0.56 | -0.60 |
| 2010-09-22 00:37 | 1 | 60 | 60.04 | 59.79 | 0.05 | 0.05 | -0.25 | -0.40 |
| 2010-09-22 00:57 | 1 | 10 | 9.96 | 10.36 | 0.15 | 0.05 | 0.40 | 4.00 |
| 2010-09-22 01:17 | 1 | 30 | 30.01 | 29.91 | 0.14 | 0.05 | -0.10 | -0.30 |
| 2010-09-22 01:37 | 1 | 50 | 50.01 | 49.58 | 0.06 | 0.05 | -0.43 | -0.90 |
| 2010-09-22 01:57 | 1 | 70 | 69.94 | 69.40 | 0.11 | 0.10 | -0.54 | -0.80 |
| 2010-09-22 02:17 | 1 | 80 | 80.01 | 79.08 | 0.08 | 0.06 | -0.93 | -1.20 |
| 2010-09-22 02:37 | 2 | 0 | 0.67 | 0.93 | 0.20 | 0.03 | 0.26 | NA |
| 2010-09-22 02:57 | 2 | 30 | 29.99 | 30.04 | 0.10 | 0.09 | 0.05 | 0.20 |
| 2010-09-22 03:17 | 2 | 50 | 50.03 | 49.63 | 0.08 | 0.06 | -0.40 | -0.80 |
| 2010-09-22 03:37 | 2 | 10 | 10.19 | 10.46 | 0.27 | 0.08 | 0.27 | 2.60 |
| 2010-09-22 03:57 | 2 | 90 | 89.98 | 88.94 | 0.06 | 0.06 | -1.04 | -1.20 |
| 2010-09-22 04:17 | 2 | 60 | 60.01 | 59.61 | 0.12 | 0.07 | -0.40 | -0.70 |
| 2010-09-22 04:37 | 2 | 20 | 20.04 | 20.14 | 0.12 | 0.04 | 0.10 | 0.50 |
| 2010-09-22 04:57 | 2 | 80 | 79.99 | 79.02 | 0.08 | 0.06 | -0.97 | -1.20 |
| 2010-09-22 05:17 | 2 | 70 | 69.99 | 69.19 | 0.09 | 0.08 | -0.80 | -1.10 |
| 2010-09-22 05:37 | 2 | 40 | 40.00 | 39.66 | 0.13 | 0.07 | -0.34 | -0.80 |
| 2010-09-22 05:57 | 3 | 0 | 0.73 | 1.01 | 0.15 | 0.04 | 0.28 | NA |
| 2010-09-22 06:17 | 3 | 40 | 40.02 | 39.68 | 0.07 | 0.04 | -0.34 | -0.80 |
| 2010-09-22 06:37 | 3 | 90 | 90.02 | 88.92 | 0.12 | 0.06 | -1.10 | -1.20 |
| 2010-09-22 06:57 | 3 | 60 | 59.99 | 59.27 | 0.09 | 0.06 | -0.72 | -1.20 |
| 2010-09-22 07:17 | 3 | 50 | 50.00 | 49.21 | 0.10 | 0.08 | -0.79 | -1.60 |
| 2010-09-22 07:37 | 3 | 20 | 20.01 | 19.82 | 0.11 | 0.04 | -0.19 | -0.90 |
| 2010-09-22 07:57 | 3 | 80 | 79.99 | 78.66 | 0.11 | 0.07 | -1.33 | -1.70 |
| 2010-09-22 08:17 | 3 | 10 | 10.02 | 9.96 | 0.15 | 0.04 | -0.06 | -0.60 |
| 2010-09-22 08:37 | 3 | 30 | 30.03 | 29.80 | 0.13 | 0.09 | -0.23 | -0.80 |
| 2010-09-22 08:57 | 3 | 70 | 69.99 | 69.42 | 0.07 | 0.07 | -0.57 | -0.80 |

Table 10. Results of the Ushuaia ozone analyzer (OA) TEI 49C #56546-318 (before cleaning) compared to the WCC-Empa transfer standard (TS).

| Date/Time | Run # | Level (ppb) | TS (ppb) | OA (ppb) | sdTS (ppb) | sdOA (ppb) | OA-TS (ppb) | OA-TS (%) |
|------------------|-------|-------------|----------|----------|------------|------------|-------------|-----------|
| 2010-09-21 19:57 | 1 | 0 | 0.14 | 0.22 | 0.21 | 0.03 | 0.08 | NA |
| 2010-09-21 20:17 | 1 | 40 | 40.01 | 38.34 | 0.09 | 0.05 | -1.67 | -4.20 |
| 2010-09-21 20:39 | 1 | 90 | 90.02 | 85.95 | 0.03 | 0.09 | -4.07 | -4.50 |
| 2010-09-21 20:57 | 1 | 60 | 60.02 | 56.88 | 0.09 | 0.07 | -3.14 | -5.20 |
| 2010-09-21 21:17 | 1 | 50 | 49.95 | 47.33 | 0.08 | 0.07 | -2.62 | -5.20 |
| 2010-09-21 21:37 | 1 | 20 | 19.96 | 18.75 | 0.23 | 0.11 | -1.21 | -6.10 |
| 2010-09-21 21:57 | 1 | 80 | 80.03 | 75.50 | 0.07 | 0.06 | -4.53 | -5.70 |
| 2010-09-21 22:17 | 1 | 10 | 9.96 | 9.38 | 0.23 | 0.06 | -0.58 | -5.80 |
| 2010-09-21 22:37 | 1 | 30 | 29.98 | 28.12 | 0.14 | 0.11 | -1.86 | -6.20 |
| 2010-09-21 22:57 | 1 | 70 | 69.99 | 65.85 | 0.08 | 0.09 | -4.14 | -5.90 |
| 2010-09-21 23:17 | 2 | 0 | 0.48 | 0.65 | 0.12 | 0.06 | 0.17 | NA |
| 2010-09-21 23:37 | 2 | 20 | 19.96 | 18.67 | 0.16 | 0.05 | -1.29 | -6.50 |
| 2010-09-21 23:57 | 2 | 40 | 39.98 | 37.58 | 0.14 | 0.09 | -2.40 | -6.00 |
| 2010-09-22 00:17 | 2 | 90 | 90.00 | 84.76 | 0.09 | 0.12 | -5.24 | -5.80 |
| 2010-09-22 00:37 | 2 | 60 | 60.04 | 56.45 | 0.05 | 0.05 | -3.59 | -6.00 |
| 2010-09-22 00:57 | 2 | 10 | 9.96 | 9.52 | 0.15 | 0.05 | -0.44 | -4.40 |
| 2010-09-22 01:17 | 2 | 30 | 30.01 | 28.04 | 0.14 | 0.06 | -1.97 | -6.60 |
| 2010-09-22 01:37 | 2 | 50 | 50.01 | 46.84 | 0.06 | 0.06 | -3.17 | -6.30 |
| 2010-09-22 01:57 | 2 | 70 | 69.94 | 65.71 | 0.11 | 0.06 | -4.23 | -6.00 |
| 2010-09-22 02:17 | 2 | 80 | 80.01 | 75.14 | 0.08 | 0.05 | -4.87 | -6.10 |
| 2010-09-22 02:37 | 3 | 0 | 0.67 | 0.66 | 0.20 | 0.05 | -0.01 | NA |
| 2010-09-22 02:57 | 3 | 30 | 29.99 | 28.08 | 0.10 | 0.06 | -1.91 | -6.40 |
| 2010-09-22 03:17 | 3 | 50 | 50.03 | 46.86 | 0.08 | 0.05 | -3.17 | -6.30 |
| 2010-09-22 03:37 | 3 | 10 | 10.19 | 9.49 | 0.27 | 0.08 | -0.70 | -6.90 |
| 2010-09-22 03:57 | 3 | 90 | 89.98 | 84.49 | 0.06 | 0.05 | -5.49 | -6.10 |
| 2010-09-22 04:17 | 3 | 60 | 60.01 | 56.51 | 0.12 | 0.10 | -3.50 | -5.80 |
| 2010-09-22 04:37 | 3 | 20 | 20.04 | 18.86 | 0.12 | 0.07 | -1.18 | -5.90 |
| 2010-09-22 04:57 | 3 | 80 | 79.99 | 75.05 | 0.08 | 0.07 | -4.94 | -6.20 |
| 2010-09-22 05:17 | 3 | 70 | 69.99 | 65.78 | 0.09 | 0.08 | -4.21 | -6.00 |
| 2010-09-22 05:37 | 3 | 40 | 40.00 | 37.50 | 0.13 | 0.08 | -2.50 | -6.20 |
| 2010-09-22 05:57 | 4 | 0 | 0.73 | 0.81 | 0.15 | 0.05 | 0.08 | NA |
| 2010-09-22 06:17 | 4 | 40 | 40.02 | 37.36 | 0.07 | 0.07 | -2.66 | -6.60 |
| 2010-09-22 06:37 | 4 | 90 | 90.02 | 84.64 | 0.12 | 0.10 | -5.38 | -6.00 |
| 2010-09-22 06:57 | 4 | 60 | 59.99 | 56.23 | 0.09 | 0.05 | -3.76 | -6.30 |
| 2010-09-22 07:17 | 4 | 50 | 50.00 | 46.66 | 0.10 | 0.08 | -3.34 | -6.70 |
| 2010-09-22 07:37 | 4 | 20 | 20.01 | 18.45 | 0.11 | 0.06 | -1.56 | -7.80 |
| 2010-09-22 07:57 | 4 | 80 | 79.99 | 74.78 | 0.11 | 0.08 | -5.21 | -6.50 |
| 2010-09-22 08:17 | 4 | 10 | 10.02 | 9.09 | 0.15 | 0.06 | -0.93 | -9.30 |
| 2010-09-22 08:37 | 4 | 30 | 30.03 | 27.89 | 0.13 | 0.08 | -2.14 | -7.10 |
| 2010-09-22 08:57 | 4 | 70 | 69.99 | 65.92 | 0.07 | 0.06 | -4.07 | -5.80 |

Table 11. Results of the Ushuaia ozone analyzer (OA) TEI 49C #56546-318 (after cleaning) compared to the WCC-Empa transfer standard (TS).

| Date/Time | Run # | Level (ppb) | TS (ppb) | OA (ppb) | sdTS (ppb) | sdOA (ppb) | OA-TS (ppb) | OA-TS (%) |
|------------------|-------|-------------|----------|----------|------------|------------|-------------|-----------|
| 2010-09-23 19:35 | 1 | 0 | 0.29 | -0.48 | 0.16 | 0.08 | -0.77 | NA |
| 2010-09-23 19:55 | 1 | 40 | 39.98 | 38.70 | 0.14 | 0.10 | -1.28 | -3.20 |
| 2010-09-23 20:17 | 1 | 90 | 90.00 | 87.92 | 0.12 | 0.08 | -2.08 | -2.30 |
| 2010-09-23 20:35 | 1 | 60 | 60.01 | 58.60 | 0.15 | 0.06 | -1.41 | -2.30 |
| 2010-09-23 20:55 | 1 | 50 | 50.01 | 48.67 | 0.18 | 0.08 | -1.34 | -2.70 |
| 2010-09-23 21:15 | 1 | 20 | 19.99 | 19.05 | 0.26 | 0.08 | -0.94 | -4.70 |
| 2010-09-23 21:35 | 1 | 80 | 79.99 | 77.85 | 0.11 | 0.08 | -2.14 | -2.70 |
| 2010-09-23 21:55 | 1 | 10 | 10.01 | 9.39 | 0.25 | 0.05 | -0.62 | -6.20 |
| 2010-09-23 22:15 | 1 | 30 | 29.98 | 28.94 | 0.12 | 0.09 | -1.04 | -3.50 |
| 2010-09-23 22:35 | 1 | 70 | 70.01 | 68.29 | 0.09 | 0.08 | -1.72 | -2.50 |
| 2010-09-23 22:55 | 2 | 0 | 0.33 | -0.14 | 0.18 | 0.05 | -0.47 | NA |
| 2010-09-23 23:15 | 2 | 20 | 20.03 | 19.05 | 0.16 | 0.10 | -0.98 | -4.90 |
| 2010-09-23 23:35 | 2 | 40 | 40.03 | 38.91 | 0.18 | 0.08 | -1.12 | -2.80 |
| 2010-09-23 23:55 | 2 | 90 | 89.97 | 87.68 | 0.12 | 0.09 | -2.29 | -2.50 |
| 2010-09-24 00:15 | 2 | 60 | 60.01 | 58.20 | 0.12 | 0.06 | -1.81 | -3.00 |
| 2010-09-24 00:35 | 2 | 10 | 10.52 | 9.92 | 0.57 | 0.12 | -0.60 | -5.70 |
| 2010-09-24 00:55 | 2 | 30 | 30.02 | 28.62 | 0.09 | 0.06 | -1.40 | -4.70 |
| 2010-09-24 01:15 | 2 | 50 | 49.97 | 48.10 | 0.10 | 0.07 | -1.87 | -3.70 |
| 2010-09-24 01:35 | 2 | 70 | 70.02 | 67.70 | 0.07 | 0.06 | -2.32 | -3.30 |
| 2010-09-24 01:55 | 2 | 80 | 80.00 | 77.35 | 0.12 | 0.09 | -2.65 | -3.30 |
| 2010-09-24 02:15 | 3 | 0 | 0.32 | -0.08 | 0.21 | 0.04 | -0.40 | NA |
| 2010-09-24 02:35 | 3 | 30 | 30.00 | 28.63 | 0.19 | 0.04 | -1.37 | -4.60 |
| 2010-09-24 02:55 | 3 | 50 | 49.96 | 47.99 | 0.10 | 0.06 | -1.97 | -3.90 |
| 2010-09-24 03:15 | 3 | 10 | 10.03 | 9.24 | 0.14 | 0.05 | -0.79 | -7.90 |
| 2010-09-24 03:35 | 3 | 90 | 90.03 | 86.98 | 0.08 | 0.11 | -3.05 | -3.40 |
| 2010-09-24 03:55 | 3 | 60 | 59.97 | 57.96 | 0.15 | 0.08 | -2.01 | -3.40 |
| 2010-09-24 04:15 | 3 | 20 | 19.96 | 18.98 | 0.19 | 0.08 | -0.98 | -4.90 |
| 2010-09-24 04:35 | 3 | 80 | 80.01 | 77.73 | 0.17 | 0.10 | -2.28 | -2.80 |
| 2010-09-24 04:55 | 3 | 70 | 70.03 | 67.71 | 0.16 | 0.10 | -2.32 | -3.30 |
| 2010-09-24 05:15 | 3 | 40 | 40.03 | 38.46 | 0.18 | 0.12 | -1.57 | -3.90 |
| 2010-09-24 05:35 | 4 | 0 | 0.24 | -0.09 | 0.20 | 0.04 | -0.33 | NA |
| 2010-09-24 05:55 | 4 | 40 | 40.02 | 38.59 | 0.14 | 0.08 | -1.43 | -3.60 |
| 2010-09-24 06:15 | 4 | 90 | 89.99 | 86.58 | 0.13 | 0.70 | -3.41 | -3.80 |
| 2010-09-24 06:35 | 4 | 60 | 60.01 | 58.38 | 0.14 | 0.12 | -1.63 | -2.70 |
| 2010-09-24 06:55 | 4 | 50 | 50.00 | 48.48 | 0.11 | 0.10 | -1.52 | -3.00 |
| 2010-09-24 07:15 | 4 | 20 | 19.98 | 19.04 | 0.10 | 0.09 | -0.94 | -4.70 |
| 2010-09-24 07:35 | 4 | 80 | 80.02 | 77.91 | 0.15 | 0.05 | -2.11 | -2.60 |
| 2010-09-24 07:55 | 4 | 10 | 10.07 | 9.32 | 0.19 | 0.10 | -0.75 | -7.40 |
| 2010-09-24 08:15 | 4 | 30 | 29.95 | 29.22 | 0.17 | 0.09 | -0.73 | -2.40 |
| 2010-09-24 08:35 | 4 | 70 | 70.02 | 68.80 | 0.13 | 0.10 | -1.22 | -1.70 |

Table 12. Results of the Ushuaia ozone analyzer (OA) TEI 49 #4703-278 compared to the WCC-Empa transfer standard (TS).

| DateTime | Run # | Level (ppb) | TS (ppb) | OA (ppb) | sdTS (ppb) | sdOA (ppb) | OA-TS (ppb) | OA-TS (%) |
|------------------|-------|-------------|----------|----------|------------|------------|-------------|-----------|
| 2010-09-23 11:50 | 1 | 0 | -0.01 | 0.10 | 0.32 | 0.03 | 0.11 | -NA |
| 2010-09-23 12:05 | 1 | 15 | 15.14 | 14.88 | 0.52 | 0.15 | -0.26 | -1.70 |
| 2010-09-23 12:20 | 1 | 45 | 44.99 | 44.28 | 0.17 | 0.09 | -0.71 | -1.60 |
| 2010-09-23 12:35 | 1 | 60 | 60.01 | 59.35 | 0.12 | 0.08 | -0.66 | -1.10 |
| 2010-09-23 12:50 | 1 | 75 | 75.02 | 74.31 | 0.08 | 0.03 | -0.71 | -0.90 |
| 2010-09-23 13:05 | 1 | 90 | 90.01 | 89.34 | 0.15 | 0.07 | -0.67 | -0.70 |
| 2010-09-23 13:20 | 1 | 30 | 30.00 | 29.53 | 0.08 | 0.11 | -0.47 | -1.60 |
| 2010-09-23 13:35 | 2 | 0 | 0.25 | 0.12 | 0.26 | 0.04 | -0.13 | NA |
| 2010-09-23 13:50 | 2 | 30 | 29.98 | 29.54 | 0.28 | 0.11 | -0.44 | -1.50 |
| 2010-09-23 14:05 | 2 | 90 | 89.99 | 89.17 | 0.13 | 0.05 | -0.82 | -0.90 |
| 2010-09-23 14:20 | 2 | 60 | 59.99 | 59.40 | 0.15 | 0.08 | -0.59 | -1.00 |
| 2010-09-23 14:35 | 2 | 15 | 15.02 | 14.55 | 0.15 | 0.07 | -0.47 | -3.10 |
| 2010-09-23 14:50 | 2 | 45 | 45.02 | 44.41 | 0.13 | 0.11 | -0.61 | -1.40 |
| 2010-09-23 15:05 | 2 | 75 | 75.02 | 74.37 | 0.07 | 0.05 | -0.65 | -0.90 |
| 2010-09-23 15:20 | 3 | 0 | 0.15 | 0.15 | 0.16 | 0.03 | 0.00 | NA |
| 2010-09-23 15:35 | 3 | 15 | 15.02 | 14.58 | 0.15 | 0.05 | -0.44 | -2.90 |
| 2010-09-23 15:50 | 3 | 30 | 29.97 | 29.39 | 0.15 | 0.09 | -0.58 | -1.90 |
| 2010-09-23 16:05 | 3 | 90 | 90.03 | 89.18 | 0.13 | 0.10 | -0.85 | -0.90 |
| 2010-09-23 16:20 | 3 | 45 | 45.02 | 44.34 | 0.18 | 0.05 | -0.68 | -1.50 |
| 2010-09-23 16:35 | 3 | 60 | 60.02 | 59.45 | 0.12 | 0.11 | -0.57 | -0.90 |
| 2010-09-23 16:50 | 3 | 75 | 75.01 | 74.35 | 0.11 | 0.09 | -0.66 | -0.90 |

Table 13. Results of the San Julian ozone analyzer (OA) TEI 49 #49983-285 (after repair) compared to the WCC-Empa transfer standard (TS).

| Date/Time | Run # | Level (ppb) | TS (ppb) | OA (ppb) | sdTS (ppb) | sdOA (ppb) | OA-TS (ppb) | OA-TS (%) |
|------------------|-------|-------------|----------|----------|------------|------------|-------------|-----------|
| 2010-09-23 11:50 | 1 | 0 | -0.01 | 0.19 | 0.32 | 0.05 | 0.20 | -NA |
| 2010-09-23 12:05 | 1 | 15 | 15.14 | 13.11 | 0.52 | 0.18 | -2.03 | -13.40 |
| 2010-09-23 12:20 | 1 | 45 | 44.99 | 43.41 | 0.17 | 0.44 | -1.58 | -3.50 |
| 2010-09-23 12:35 | 1 | 60 | 60.01 | 57.78 | 0.12 | 0.49 | -2.23 | -3.70 |
| 2010-09-23 12:50 | 1 | 75 | 75.02 | 72.58 | 0.08 | 0.28 | -2.44 | -3.30 |
| 2010-09-23 13:05 | 1 | 90 | 90.01 | 87.88 | 0.15 | 0.28 | -2.13 | -2.40 |
| 2010-09-23 13:20 | 1 | 30 | 30.00 | 29.16 | 0.08 | 0.38 | -0.84 | -2.80 |
| 2010-09-23 13:35 | 2 | 0 | 0.25 | 0.21 | 0.26 | 0.08 | -0.04 | -NA |
| 2010-09-23 13:50 | 2 | 30 | 29.98 | 28.15 | 0.28 | 0.12 | -1.83 | -6.10 |
| 2010-09-23 14:05 | 2 | 90 | 89.99 | 87.55 | 0.13 | 0.19 | -2.44 | -2.70 |
| 2010-09-23 14:20 | 2 | 60 | 59.99 | 57.90 | 0.15 | 0.11 | -2.09 | -3.50 |
| 2010-09-23 14:35 | 2 | 15 | 15.02 | 13.09 | 0.15 | 0.11 | -1.93 | -12.80 |
| 2010-09-23 14:50 | 2 | 45 | 45.02 | 43.07 | 0.13 | 0.12 | -1.95 | -4.30 |
| 2010-09-23 15:05 | 2 | 75 | 75.02 | 73.41 | 0.07 | 0.15 | -1.61 | -2.10 |
| 2010-09-23 15:20 | 3 | 0 | 0.15 | 0.01 | 0.16 | 0.01 | -0.14 | NA |
| 2010-09-23 15:35 | 3 | 15 | 15.02 | 13.06 | 0.15 | 0.07 | -1.96 | -13.00 |
| 2010-09-23 15:50 | 3 | 30 | 29.97 | 27.89 | 0.15 | 0.13 | -2.08 | -6.90 |
| 2010-09-23 16:05 | 3 | 90 | 90.03 | 87.90 | 0.13 | 0.25 | -2.13 | -2.40 |
| 2010-09-23 16:20 | 3 | 45 | 45.02 | 42.95 | 0.18 | 0.18 | -2.07 | -4.60 |
| 2010-09-23 16:35 | 3 | 60 | 60.02 | 58.23 | 0.12 | 0.13 | -1.79 | -3.00 |
| 2010-09-23 16:50 | 3 | 75 | 75.01 | 73.25 | 0.11 | 0.09 | -1.76 | -2.30 |

Table 14. Results of the Pilar ozone analyzer (OA) TEI 49 #49981-285 compared to the WCC-Empa transfer standard (TS).

| Date/Time | Run # | Level (ppb) | TS (ppb) | OA (ppb) | sdTS (ppb) | sdOA (ppb) | OA-TS (ppb) | OA-TS (%) |
|------------------|-------|-------------|----------|----------|------------|------------|-------------|-----------|
| 2010-09-23 19:35 | 1 | 0 | 0.29 | 0.25 | 0.16 | 0.07 | -0.04 | NA |
| 2010-09-23 19:55 | 1 | 40 | 39.98 | 38.05 | 0.14 | 0.13 | -1.93 | -4.80 |
| 2010-09-23 20:17 | 1 | 90 | 90.00 | 89.50 | 0.12 | 0.07 | -0.50 | -0.60 |
| 2010-09-23 20:35 | 1 | 60 | 60.01 | 58.55 | 0.15 | 0.13 | -1.46 | -2.40 |
| 2010-09-23 20:55 | 1 | 50 | 50.01 | 47.91 | 0.18 | 0.15 | -2.10 | -4.20 |
| 2010-09-23 21:15 | 1 | 20 | 19.99 | 17.90 | 0.26 | 0.10 | -2.09 | -10.50 |
| 2010-09-23 21:35 | 1 | 80 | 79.99 | 79.33 | 0.11 | 0.15 | -0.66 | -0.80 |
| 2010-09-23 21:55 | 1 | 10 | 10.01 | 8.41 | 0.25 | 0.09 | -1.60 | -16.00 |
| 2010-09-23 22:15 | 1 | 30 | 29.98 | 28.63 | 0.12 | 0.13 | -1.35 | -4.50 |
| 2010-09-23 22:35 | 1 | 70 | 70.01 | 70.92 | 0.09 | 0.09 | 0.91 | 1.30 |
| 2010-09-23 22:55 | 2 | 0 | 0.33 | 0.99 | 0.18 | 0.07 | 0.66 | NA |
| 2010-09-23 23:15 | 2 | 20 | 20.03 | 21.52 | 0.16 | 0.11 | 1.49 | 7.40 |
| 2010-09-23 23:35 | 2 | 40 | 40.03 | 41.32 | 0.18 | 0.11 | 1.29 | 3.20 |
| 2010-09-23 23:55 | 2 | 90 | 89.97 | 92.64 | 0.12 | 0.12 | 2.67 | 3.00 |
| 2010-09-24 00:15 | 2 | 60 | 60.01 | 60.77 | 0.12 | 0.13 | 0.76 | 1.30 |
| 2010-09-24 00:35 | 2 | 10 | 10.52 | 9.55 | 0.57 | 0.18 | -0.97 | -9.20 |
| 2010-09-24 00:55 | 2 | 30 | 30.02 | 28.81 | 0.09 | 0.11 | -1.21 | -4.00 |
| 2010-09-24 01:15 | 2 | 50 | 49.97 | 49.96 | 0.10 | 0.09 | -0.01 | 0.00 |
| 2010-09-24 01:35 | 2 | 70 | 70.02 | 70.26 | 0.07 | 0.14 | 0.24 | 0.30 |
| 2010-09-24 01:55 | 2 | 80 | 80.00 | 81.88 | 0.12 | 0.10 | 1.88 | 2.40 |
| 2010-09-24 02:15 | 3 | 0 | 0.32 | 0.13 | 0.21 | 0.04 | -0.19 | NA |
| 2010-09-24 02:35 | 3 | 30 | 30.00 | 29.82 | 0.19 | 0.15 | -0.18 | -0.60 |
| 2010-09-24 02:55 | 3 | 50 | 49.96 | 49.99 | 0.10 | 0.20 | 0.03 | 0.10 |
| 2010-09-24 03:15 | 3 | 10 | 10.03 | 8.53 | 0.14 | 0.12 | -1.50 | -15.00 |
| 2010-09-24 03:35 | 3 | 90 | 90.03 | 92.13 | 0.08 | 0.19 | 2.10 | 2.30 |
| 2010-09-24 03:55 | 3 | 60 | 59.97 | 61.27 | 0.15 | 0.15 | 1.30 | 2.20 |
| 2010-09-24 04:15 | 3 | 20 | 19.96 | 19.55 | 0.19 | 0.10 | -0.41 | -2.10 |
| 2010-09-24 04:35 | 3 | 80 | 80.01 | 83.55 | 0.17 | 0.17 | 3.54 | 4.40 |
| 2010-09-24 04:55 | 3 | 70 | 70.03 | 73.03 | 0.16 | 0.12 | 3.00 | 4.30 |
| 2010-09-24 05:15 | 3 | 40 | 40.03 | 41.81 | 0.18 | 0.16 | 1.78 | 4.40 |
| 2010-09-24 05:35 | 4 | 0 | 0.24 | 3.02 | 0.20 | 0.18 | 2.78 | NA |
| 2010-09-24 05:55 | 4 | 40 | 40.02 | 44.23 | 0.14 | 0.22 | 4.21 | 10.50 |
| 2010-09-24 06:15 | 4 | 90 | 89.99 | 96.31 | 0.13 | 0.18 | 6.32 | 7.00 |
| 2010-09-24 06:35 | 4 | 60 | 60.01 | 63.19 | 0.14 | 0.14 | 3.18 | 5.30 |
| 2010-09-24 06:55 | 4 | 50 | 50.00 | 52.20 | 0.11 | 0.22 | 2.20 | 4.40 |
| 2010-09-24 07:15 | 4 | 20 | 19.98 | 19.90 | 0.10 | 0.24 | -0.08 | -0.40 |
| 2010-09-24 07:35 | 4 | 80 | 80.02 | 83.14 | 0.15 | 0.15 | 3.12 | 3.90 |
| 2010-09-24 07:55 | 4 | 10 | 10.07 | 8.00 | 0.19 | 0.21 | -2.07 | -20.60 |
| 2010-09-24 08:15 | 4 | 30 | 29.95 | 30.03 | 0.17 | 0.12 | 0.08 | 0.30 |
| 2010-09-24 08:35 | 4 | 70 | 70.02 | 74.04 | 0.13 | 0.17 | 4.02 | 5.70 |

Table 15. Results of the La Quiaca ozone analyzer (OA) TEI 49 #54577-300 compared to the WCC-Empa transfer standard (TS).

| DateTime | Run # | Level (ppb) | TS (ppb) | OA (ppb) | sdTS (ppb) | sdOA (ppb) | OA-TS (ppb) | OA-TS (%) |
|------------------|--------------|--------------------|-----------------|-----------------|-------------------|-------------------|--------------------|------------------|
| 2010-09-23 11:50 | 1 | 0 | -0.01 | -0.09 | 0.32 | 0.04 | -0.08 | NA |
| 2010-09-23 12:05 | 1 | 15 | 15.14 | 14.80 | 0.52 | 0.14 | -0.34 | -2.20 |
| 2010-09-23 12:20 | 1 | 45 | 44.99 | 45.31 | 0.17 | 0.10 | 0.32 | 0.70 |
| 2010-09-23 12:35 | 1 | 60 | 60.01 | 60.53 | 0.12 | 0.12 | 0.52 | 0.90 |
| 2010-09-23 12:50 | 1 | 75 | 75.02 | 75.77 | 0.08 | 0.08 | 0.75 | 1.00 |
| 2010-09-23 13:05 | 1 | 90 | 90.01 | 91.34 | 0.15 | 0.12 | 1.33 | 1.50 |
| 2010-09-23 13:20 | 1 | 30 | 30.00 | 30.21 | 0.08 | 0.11 | 0.21 | 0.70 |
| 2010-09-23 13:35 | 2 | 0 | 0.25 | -0.04 | 0.26 | 0.04 | -0.29 | NA |
| 2010-09-23 13:50 | 2 | 30 | 29.98 | 30.21 | 0.28 | 0.09 | 0.23 | 0.80 |
| 2010-09-23 14:05 | 2 | 90 | 89.99 | 91.08 | 0.13 | 0.10 | 1.09 | 1.20 |
| 2010-09-23 14:20 | 2 | 60 | 59.99 | 60.40 | 0.15 | 0.12 | 0.41 | 0.70 |
| 2010-09-23 14:35 | 2 | 15 | 15.02 | 14.51 | 0.15 | 0.08 | -0.51 | -3.40 |
| 2010-09-23 14:50 | 2 | 45 | 45.02 | 45.29 | 0.13 | 0.06 | 0.27 | 0.60 |
| 2010-09-23 15:05 | 2 | 75 | 75.02 | 75.88 | 0.07 | 0.13 | 0.86 | 1.10 |
| 2010-09-23 15:20 | 3 | 0 | 0.15 | -0.18 | 0.16 | 0.07 | -0.33 | NA |
| 2010-09-23 15:35 | 3 | 15 | 15.02 | 14.45 | 0.15 | 0.09 | -0.57 | -3.80 |
| 2010-09-23 15:50 | 3 | 30 | 29.97 | 29.85 | 0.15 | 0.14 | -0.12 | -0.40 |
| 2010-09-23 16:05 | 3 | 90 | 90.03 | 91.07 | 0.13 | 0.16 | 1.04 | 1.20 |
| 2010-09-23 16:20 | 3 | 45 | 45.02 | 45.28 | 0.18 | 0.13 | 0.26 | 0.60 |
| 2010-09-23 16:35 | 3 | 60 | 60.02 | 60.72 | 0.12 | 0.09 | 0.70 | 1.20 |
| 2010-09-23 16:50 | 3 | 75 | 75.01 | 75.77 | 0.11 | 0.16 | 0.76 | 1.00 |

Table 16. Results of the San Lorenzo ozone analyzer (OA) TEI 49 #54501-300 compared to the WCC-Empa transfer standard (TS).

| Date/Time | Run # | Level (ppb) | TS (ppb) | OA (ppb) | sdTS (ppb) | sdOA (ppb) | OA-TS (ppb) | OA-TS (%) |
|------------------|-------|-------------|----------|----------|------------|------------|-------------|-----------|
| 2010-09-22 17:52 | 1 | 0 | 0.14 | 0.73 | 0.14 | 0.04 | 0.59 | NA |
| 2010-09-22 18:12 | 1 | 40 | 39.97 | 41.92 | 0.12 | 0.08 | 1.95 | 4.90 |
| 2010-09-22 18:32 | 1 | 90 | 90.03 | 94.13 | 0.15 | 0.11 | 4.10 | 4.60 |
| 2010-09-22 18:52 | 1 | 60 | 60.01 | 62.98 | 0.15 | 0.08 | 2.97 | 4.90 |
| 2010-09-22 19:12 | 1 | 50 | 50.01 | 52.37 | 0.12 | 0.08 | 2.36 | 4.70 |
| 2010-09-22 19:32 | 1 | 20 | 19.99 | 20.96 | 0.20 | 0.10 | 0.97 | 4.90 |
| 2010-09-22 19:52 | 1 | 80 | 80.01 | 83.57 | 0.09 | 0.10 | 3.56 | 4.40 |
| 2010-09-22 20:12 | 1 | 10 | 10.19 | 10.31 | 0.32 | 0.07 | 0.12 | 1.20 |
| 2010-09-22 20:32 | 1 | 30 | 30.00 | 31.47 | 0.17 | 0.06 | 1.47 | 4.90 |
| 2010-09-22 20:52 | 1 | 70 | 69.98 | 73.65 | 0.12 | 0.15 | 3.67 | 5.20 |
| 2010-09-22 21:12 | 2 | 0 | 0.35 | 0.46 | 0.19 | 0.08 | 0.11 | NA |
| 2010-09-22 21:32 | 2 | 20 | 19.97 | 21.50 | 0.15 | 0.10 | 1.53 | 7.70 |
| 2010-09-22 21:52 | 2 | 40 | 40.00 | 42.19 | 0.18 | 0.17 | 2.19 | 5.50 |
| 2010-09-22 22:12 | 2 | 90 | 89.97 | 94.35 | 0.14 | 0.10 | 4.38 | 4.90 |
| 2010-09-22 22:32 | 2 | 60 | 59.97 | 63.05 | 0.15 | 0.11 | 3.08 | 5.10 |
| 2010-09-22 22:52 | 2 | 10 | 10.24 | 10.56 | 0.37 | 0.10 | 0.32 | 3.10 |
| 2010-09-22 23:12 | 2 | 30 | 29.99 | 31.36 | 0.18 | 0.09 | 1.37 | 4.60 |
| 2010-09-22 23:32 | 2 | 50 | 49.99 | 52.20 | 0.14 | 0.12 | 2.21 | 4.40 |
| 2010-09-22 23:52 | 2 | 70 | 70.01 | 73.59 | 0.13 | 0.11 | 3.58 | 5.10 |
| 2010-09-23 00:12 | 2 | 80 | 80.01 | 83.82 | 0.15 | 0.17 | 3.81 | 4.80 |
| 2010-09-23 00:32 | 3 | 0 | 0.02 | 0.43 | 0.15 | 0.06 | 0.41 | NA |
| 2010-09-23 00:52 | 3 | 30 | 30.02 | 31.40 | 0.12 | 0.06 | 1.38 | 4.60 |
| 2010-09-23 01:12 | 3 | 50 | 49.99 | 52.64 | 0.24 | 0.11 | 2.65 | 5.30 |
| 2010-09-23 01:32 | 3 | 10 | 9.99 | 10.33 | 0.17 | 0.09 | 0.34 | 3.40 |
| 2010-09-23 01:52 | 3 | 90 | 89.97 | 94.26 | 0.14 | 0.12 | 4.29 | 4.80 |
| 2010-09-23 02:12 | 3 | 60 | 59.98 | 62.86 | 0.13 | 0.11 | 2.88 | 4.80 |
| 2010-09-23 02:32 | 3 | 20 | 19.98 | 20.93 | 0.22 | 0.11 | 0.95 | 4.80 |
| 2010-09-23 02:52 | 3 | 80 | 80.05 | 83.66 | 0.09 | 0.15 | 3.61 | 4.50 |
| 2010-09-23 03:12 | 3 | 70 | 70.01 | 73.04 | 0.12 | 0.05 | 3.03 | 4.30 |
| 2010-09-23 03:32 | 3 | 40 | 40.01 | 41.87 | 0.12 | 0.08 | 1.86 | 4.60 |
| 2010-09-23 03:52 | 4 | 0 | 0.36 | 0.66 | 0.17 | 0.07 | 0.30 | NA |
| 2010-09-23 04:12 | 4 | 40 | 40.04 | 41.86 | 0.13 | 0.10 | 1.82 | 4.50 |
| 2010-09-23 04:32 | 4 | 90 | 89.97 | 94.39 | 0.16 | 0.12 | 4.42 | 4.90 |
| 2010-09-23 04:52 | 4 | 60 | 60.02 | 63.02 | 0.09 | 0.09 | 3.00 | 5.00 |
| 2010-09-23 05:12 | 4 | 50 | 50.04 | 52.42 | 0.11 | 0.08 | 2.38 | 4.80 |
| 2010-09-23 05:32 | 4 | 20 | 20.01 | 21.10 | 0.16 | 0.07 | 1.09 | 5.40 |
| 2010-09-23 05:52 | 4 | 80 | 79.98 | 83.66 | 0.09 | 0.13 | 3.68 | 4.60 |
| 2010-09-23 06:12 | 4 | 10 | 10.01 | 10.42 | 0.16 | 0.12 | 0.41 | 4.10 |
| 2010-09-23 06:32 | 4 | 30 | 30.04 | 31.35 | 0.08 | 0.10 | 1.31 | 4.40 |
| 2010-09-23 06:52 | 4 | 70 | 70.05 | 73.71 | 0.11 | 0.14 | 3.66 | 5.20 |

Table 17. Results of the El Tololo ozone analyzer (OA) TEI 49 #49978-285 compared to the WCC-Empa transfer standard (TS).

| DateTime | Run # | Level (ppb) | TS (ppb) | OA (ppb) | sdTS (ppb) | sdOA (ppb) | OA-TS (ppb) | OA-TS (%) |
|------------------|-------|-------------|----------|----------|------------|------------|-------------|-----------|
| 2010-09-22 17:52 | 1 | 0 | 0.14 | 0.88 | 0.14 | 0.06 | 0.74 | NA |
| 2010-09-22 18:12 | 1 | 40 | 39.97 | 39.81 | 0.12 | 0.11 | -0.16 | -0.40 |
| 2010-09-22 18:32 | 1 | 90 | 90.03 | 89.83 | 0.15 | 0.11 | -0.20 | -0.20 |
| 2010-09-22 18:52 | 1 | 60 | 60.01 | 60.06 | 0.15 | 0.14 | 0.05 | 0.10 |
| 2010-09-22 19:12 | 1 | 50 | 50.01 | 49.98 | 0.12 | 0.09 | -0.03 | -0.10 |
| 2010-09-22 19:32 | 1 | 20 | 19.99 | 20.36 | 0.20 | 0.14 | 0.37 | 1.90 |
| 2010-09-22 19:52 | 1 | 80 | 80.01 | 79.86 | 0.09 | 0.13 | -0.15 | -0.20 |
| 2010-09-22 20:12 | 1 | 10 | 10.19 | 10.32 | 0.32 | 0.08 | 0.13 | 1.30 |
| 2010-09-22 20:32 | 1 | 30 | 30.00 | 30.44 | 0.17 | 0.10 | 0.44 | 1.50 |
| 2010-09-22 20:52 | 1 | 70 | 69.98 | 70.31 | 0.12 | 0.12 | 0.33 | 0.50 |
| 2010-09-22 21:12 | 2 | 0 | 0.35 | 0.83 | 0.19 | 0.06 | 0.48 | NA |
| 2010-09-22 21:32 | 2 | 20 | 19.97 | 20.32 | 0.15 | 0.11 | 0.35 | 1.80 |
| 2010-09-22 21:52 | 2 | 40 | 40.00 | 40.24 | 0.18 | 0.14 | 0.24 | 0.60 |
| 2010-09-22 22:12 | 2 | 90 | 89.97 | 89.68 | 0.14 | 0.07 | -0.29 | -0.30 |
| 2010-09-22 22:32 | 2 | 60 | 59.97 | 60.01 | 0.15 | 0.10 | 0.04 | 0.10 |
| 2010-09-22 22:52 | 2 | 10 | 10.24 | 10.62 | 0.37 | 0.13 | 0.38 | 3.70 |
| 2010-09-22 23:12 | 2 | 30 | 29.99 | 30.21 | 0.18 | 0.10 | 0.22 | 0.70 |
| 2010-09-22 23:32 | 2 | 50 | 49.99 | 50.14 | 0.14 | 0.09 | 0.15 | 0.30 |
| 2010-09-22 23:52 | 2 | 70 | 70.01 | 70.40 | 0.13 | 0.10 | 0.39 | 0.60 |
| 2010-09-23 00:12 | 2 | 80 | 80.01 | 80.13 | 0.15 | 0.16 | 0.12 | 0.10 |
| 2010-09-23 00:32 | 3 | 0 | 0.02 | 0.81 | 0.15 | 0.05 | 0.79 | NA |
| 2010-09-23 00:52 | 3 | 30 | 30.02 | 30.25 | 0.12 | 0.11 | 0.23 | 0.80 |
| 2010-09-23 01:12 | 3 | 50 | 49.99 | 50.56 | 0.24 | 0.11 | 0.57 | 1.10 |
| 2010-09-23 01:32 | 3 | 10 | 9.99 | 10.19 | 0.17 | 0.08 | 0.20 | 2.00 |
| 2010-09-23 01:52 | 3 | 90 | 89.97 | 89.65 | 0.14 | 0.11 | -0.32 | -0.40 |
| 2010-09-23 02:12 | 3 | 60 | 59.98 | 59.86 | 0.13 | 0.05 | -0.12 | -0.20 |
| 2010-09-23 02:32 | 3 | 20 | 19.98 | 20.43 | 0.22 | 0.11 | 0.45 | 2.30 |
| 2010-09-23 02:52 | 3 | 80 | 80.05 | 80.01 | 0.09 | 0.11 | -0.04 | 0.00 |
| 2010-09-23 03:12 | 3 | 70 | 70.01 | 69.97 | 0.12 | 0.11 | -0.04 | -0.10 |
| 2010-09-23 03:32 | 3 | 40 | 40.01 | 39.92 | 0.12 | 0.07 | -0.09 | -0.20 |
| 2010-09-23 03:52 | 4 | 0 | 0.36 | 0.83 | 0.17 | 0.08 | 0.47 | NA |
| 2010-09-23 04:12 | 4 | 40 | 40.04 | 39.76 | 0.13 | 0.08 | -0.28 | -0.70 |
| 2010-09-23 04:32 | 4 | 90 | 89.97 | 89.51 | 0.16 | 0.11 | -0.46 | -0.50 |
| 2010-09-23 04:52 | 4 | 60 | 60.02 | 59.77 | 0.09 | 0.11 | -0.25 | -0.40 |
| 2010-09-23 05:12 | 4 | 50 | 50.04 | 49.95 | 0.11 | 0.11 | -0.09 | -0.20 |
| 2010-09-23 05:32 | 4 | 20 | 20.01 | 20.39 | 0.16 | 0.06 | 0.38 | 1.90 |
| 2010-09-23 05:52 | 4 | 80 | 79.98 | 79.92 | 0.09 | 0.14 | -0.06 | -0.10 |
| 2010-09-23 06:12 | 4 | 10 | 10.01 | 10.14 | 0.16 | 0.07 | 0.13 | 1.30 |
| 2010-09-23 06:32 | 4 | 30 | 30.04 | 30.36 | 0.08 | 0.10 | 0.32 | 1.10 |
| 2010-09-23 06:52 | 4 | 70 | 70.05 | 70.23 | 0.11 | 0.09 | 0.18 | 0.30 |
| 2010-09-23 07:12 | 5 | 0 | 0.37 | 0.83 | 0.19 | 0.06 | 0.46 | NA |
| 2010-09-23 07:32 | 5 | 20 | 20.02 | 20.51 | 0.10 | 0.10 | 0.49 | 2.40 |
| 2010-09-23 07:52 | 5 | 40 | 40.02 | 39.95 | 0.10 | 0.09 | -0.07 | -0.20 |
| 2010-09-23 08:12 | 5 | 90 | 90.00 | 89.61 | 0.10 | 0.10 | -0.39 | -0.40 |
| 2010-09-23 08:32 | 5 | 60 | 59.96 | 59.77 | 0.10 | 0.07 | -0.19 | -0.30 |
| 2010-09-23 08:52 | 5 | 10 | 10.22 | 10.17 | 0.31 | 0.16 | -0.05 | -0.50 |

Table 18. Results of the Natal ozone analyzer (OA) TEI 49C #62170-334 compared to the WCC-Empa transfer standard (TS) before repair.

| Date/Time | Run # | Level (ppb) | TS (ppb) | OA (ppb) | sdTS (ppb) | sdOA (ppb) | OA-TS (ppb) | OA-TS (%) |
|------------------|-------|-------------|----------|----------|------------|------------|-------------|-----------|
| 2010-09-23 19:35 | 1 | 0 | 0.29 | 9.39 | 0.16 | 0.58 | 9.10 | NA |
| 2010-09-23 19:55 | 1 | 40 | 39.98 | 37.65 | 0.14 | 0.60 | -2.33 | -5.80 |
| 2010-09-23 20:17 | 1 | 90 | 90.00 | 74.79 | 0.12 | 0.29 | -15.21 | -16.90 |
| 2010-09-23 20:35 | 1 | 60 | 60.01 | 53.14 | 0.15 | 0.78 | -6.87 | -11.40 |
| 2010-09-23 20:55 | 1 | 50 | 50.01 | 43.17 | 0.18 | 0.23 | -6.84 | -13.70 |
| 2010-09-23 21:15 | 1 | 20 | 19.99 | 20.17 | 0.26 | 0.10 | 0.18 | 0.90 |
| 2010-09-23 21:35 | 1 | 80 | 79.99 | 64.64 | 0.11 | 0.39 | -15.35 | -19.20 |
| 2010-09-23 21:55 | 1 | 10 | 10.01 | 11.28 | 0.25 | 0.13 | 1.27 | 12.70 |
| 2010-09-23 22:15 | 1 | 30 | 29.98 | 24.98 | 0.12 | 0.26 | -5.00 | -16.70 |
| 2010-09-23 22:35 | 1 | 70 | 70.01 | 55.79 | 0.09 | 0.21 | -14.22 | -20.30 |
| 2010-09-23 22:55 | 2 | 0 | 0.33 | 2.87 | 0.18 | 0.23 | 2.54 | NA |
| 2010-09-23 23:15 | 2 | 20 | 20.03 | 17.37 | 0.16 | 0.34 | -2.66 | -13.30 |
| 2010-09-23 23:35 | 2 | 40 | 40.03 | 32.75 | 0.18 | 0.13 | -7.28 | -18.20 |
| 2010-09-23 23:55 | 2 | 90 | 89.97 | 70.00 | 0.12 | 1.13 | -19.97 | -22.20 |
| 2010-09-24 00:15 | 2 | 60 | 60.01 | 47.20 | 0.12 | 0.16 | -12.81 | -21.30 |
| 2010-09-24 00:35 | 2 | 10 | 10.52 | 9.58 | 0.57 | 0.12 | -0.94 | -8.90 |
| 2010-09-24 00:55 | 2 | 30 | 30.02 | 24.05 | 0.09 | 0.09 | -5.97 | -19.90 |
| 2010-09-24 01:15 | 2 | 50 | 49.97 | 38.96 | 0.10 | 0.12 | -11.01 | -22.00 |
| 2010-09-24 01:35 | 2 | 70 | 70.02 | 53.70 | 0.07 | 0.25 | -16.32 | -23.30 |
| 2010-09-24 01:55 | 2 | 80 | 80.00 | 60.65 | 0.12 | 0.11 | -19.35 | -24.20 |
| 2010-09-24 02:15 | 3 | 0 | 0.32 | 0.06 | 0.21 | 0.07 | -0.26 | NA |
| 2010-09-24 02:35 | 3 | 30 | 30.00 | 22.10 | 0.19 | 0.12 | -7.90 | -26.30 |
| 2010-09-24 02:55 | 3 | 50 | 49.96 | 37.43 | 0.10 | 0.16 | -12.53 | -25.10 |
| 2010-09-24 03:15 | 3 | 10 | 10.03 | 6.71 | 0.14 | 0.12 | -3.32 | -33.10 |
| 2010-09-24 03:35 | 3 | 90 | 90.03 | 67.96 | 0.08 | 0.11 | -22.07 | -24.50 |
| 2010-09-24 03:55 | 3 | 60 | 59.97 | 44.60 | 0.15 | 0.08 | -15.37 | -25.60 |
| 2010-09-24 04:15 | 3 | 20 | 19.96 | 14.47 | 0.19 | 0.10 | -5.49 | -27.50 |
| 2010-09-24 04:35 | 3 | 80 | 80.01 | 60.37 | 0.17 | 0.10 | -19.64 | -24.50 |
| 2010-09-24 04:55 | 3 | 70 | 70.03 | 52.20 | 0.16 | 0.11 | -17.83 | -25.50 |
| 2010-09-24 05:15 | 3 | 40 | 40.03 | 29.32 | 0.18 | 0.10 | -10.71 | -26.80 |
| 2010-09-24 05:35 | 4 | 0 | 0.24 | -0.74 | 0.20 | 0.10 | -0.98 | NA |
| 2010-09-24 05:55 | 4 | 40 | 40.02 | 29.79 | 0.14 | 0.10 | -10.23 | -25.60 |
| 2010-09-24 06:15 | 4 | 90 | 89.99 | 67.72 | 0.13 | 0.13 | -22.27 | -24.70 |
| 2010-09-24 07:15 | 4 | 20 | 19.98 | 12.71 | 0.10 | 1.04 | -7.27 | -36.40 |
| 2010-09-24 07:35 | 4 | 80 | 80.02 | 59.96 | 0.15 | 0.10 | -20.06 | -25.10 |
| 2010-09-24 07:55 | 4 | 10 | 10.07 | 6.54 | 0.19 | 0.08 | -3.53 | -35.10 |
| 2010-09-24 08:15 | 4 | 30 | 29.95 | 22.22 | 0.17 | 0.12 | -7.73 | -25.80 |
| 2010-09-24 08:35 | 4 | 70 | 70.02 | 53.09 | 0.13 | 0.08 | -16.93 | -24.20 |
| 2010-09-24 08:55 | 5 | 0 | 0.50 | -0.58 | 0.19 | 0.08 | -1.08 | NA |
| 2010-09-24 09:17 | 5 | 20 | 20.02 | 16.40 | 0.25 | 0.16 | -3.62 | -18.10 |
| 2010-09-24 09:32 | 5 | 40 | 40.07 | 30.29 | 0.01 | 0.04 | -9.78 | -24.40 |

Table 19. Results of the Natal ozone analyzer (OA) TEI 49C #62170-334 compared to the WCC-Empa ozone reference (SRP) after repair at Empa.

| Date/Time | Run # | Level (ppb) | SRP (ppb) | OA (ppb) | sdSRP (ppb) | sdOA (ppb) | OA-TS (ppb) | OA-SRP (%) |
|------------------|-------|-------------|-----------|----------|-------------|------------|-------------|------------|
| 2011-05-05 17:52 | 1 | 0 | -0.04 | -0.03 | 0.22 | 0.08 | 0.01 | -25.00 |
| 2011-05-05 18:01 | 1 | 180 | 175.92 | 176.25 | 0.23 | 0.04 | 0.33 | 0.20 |
| 2011-05-05 18:11 | 1 | 140 | 142.05 | 142.04 | 0.27 | 0.04 | -0.01 | 0.00 |
| 2011-05-05 18:21 | 1 | 240 | 238.45 | 237.97 | 0.27 | 0.09 | -0.48 | -0.20 |
| 2011-05-05 18:30 | 1 | 100 | 106.59 | 106.79 | 0.21 | 0.02 | 0.20 | 0.20 |
| 2011-05-05 18:40 | 1 | 40 | 43.03 | 43.24 | 0.25 | 0.04 | 0.21 | 0.50 |
| 2011-05-05 18:49 | 1 | 80 | 71.46 | 71.10 | 0.25 | 0.06 | -0.36 | -0.50 |
| 2011-05-05 18:59 | 1 | 20 | 17.10 | 17.11 | 0.25 | 0.07 | 0.01 | 0.10 |
| 2011-05-05 19:09 | 1 | 200 | 206.82 | 207.57 | 0.21 | 0.08 | 0.75 | 0.40 |
| 2011-05-05 19:24 | 2 | 0 | 0.12 | -0.06 | 0.27 | 0.03 | -0.18 | NA |
| 2011-05-05 19:40 | 2 | 80 | 71.73 | 71.54 | 0.21 | 0.07 | -0.19 | -0.30 |
| 2011-05-05 19:49 | 2 | 140 | 142.33 | 143.10 | 0.24 | 0.08 | 0.77 | 0.50 |
| 2011-05-05 19:59 | 2 | 20 | 17.12 | 17.39 | 0.22 | 0.06 | 0.27 | 1.60 |
| 2011-05-05 20:08 | 2 | 40 | 43.38 | 43.58 | 0.20 | 0.03 | 0.20 | 0.50 |
| 2011-05-05 20:18 | 2 | 100 | 107.62 | 107.38 | 0.18 | 0.04 | -0.24 | -0.20 |
| 2011-05-05 20:28 | 2 | 180 | 174.92 | 175.85 | 0.22 | 0.05 | 0.93 | 0.50 |
| 2011-05-05 20:38 | 2 | 240 | 238.14 | 238.75 | 0.53 | 0.07 | 0.61 | 0.30 |
| 2011-05-05 20:49 | 2 | 200 | 206.52 | 207.32 | 0.42 | 0.06 | 0.80 | 0.40 |
| 2011-05-05 21:04 | 3 | 0 | 0.06 | -0.12 | 0.29 | 0.06 | -0.18 | NA |
| 2011-05-05 21:19 | 3 | 200 | 208.64 | 208.50 | 0.18 | 0.06 | -0.14 | -0.10 |
| 2011-05-05 21:29 | 3 | 20 | 17.24 | 17.06 | 0.34 | 0.05 | -0.18 | -1.00 |
| 2011-05-05 21:39 | 3 | 140 | 142.34 | 142.30 | 0.21 | 0.06 | -0.04 | 0.00 |
| 2011-05-05 21:48 | 3 | 180 | 174.84 | 175.60 | 0.24 | 0.08 | 0.76 | 0.40 |
| 2011-05-05 21:58 | 3 | 240 | 238.51 | 238.31 | 0.31 | 0.06 | -0.20 | -0.10 |
| 2011-05-05 22:07 | 3 | 100 | 107.13 | 107.12 | 0.20 | 0.06 | -0.01 | 0.00 |
| 2011-05-05 22:17 | 3 | 40 | 43.55 | 43.25 | 0.20 | 0.06 | -0.30 | -0.70 |
| 2011-05-05 22:27 | 3 | 80 | 71.28 | 71.61 | 0.27 | 0.04 | 0.33 | 0.50 |
| 2011-05-05 22:42 | 4 | 0 | -0.14 | 0.08 | 0.28 | 0.03 | 0.22 | NA |
| 2011-05-05 22:58 | 4 | 240 | 240.87 | 241.10 | 0.47 | 0.06 | 0.23 | 0.10 |
| 2011-05-05 23:07 | 4 | 140 | 142.35 | 142.69 | 0.23 | 0.05 | 0.34 | 0.20 |
| 2011-05-05 23:17 | 4 | 80 | 71.39 | 71.69 | 0.29 | 0.06 | 0.30 | 0.40 |
| 2011-05-05 23:26 | 4 | 20 | 17.41 | 17.10 | 0.38 | 0.03 | -0.31 | -1.80 |
| 2011-05-05 23:36 | 4 | 200 | 207.80 | 207.87 | 0.36 | 0.11 | 0.07 | 0.00 |
| 2011-05-05 23:46 | 4 | 100 | 107.25 | 107.04 | 0.24 | 0.04 | -0.21 | -0.20 |
| 2011-05-05 23:55 | 4 | 40 | 43.10 | 43.30 | 0.24 | 0.02 | 0.20 | 0.50 |
| 2011-05-06 00:05 | 4 | 180 | 175.68 | 175.64 | 0.34 | 0.05 | -0.04 | 0.00 |
| 2011-05-06 00:22 | 5 | 0 | 0.00 | -0.08 | 0.23 | 0.03 | -0.08 | NA |
| 2011-05-06 00:40 | 5 | 40 | 43.48 | 43.46 | 0.20 | 0.05 | -0.02 | 0.00 |
| 2011-05-06 00:50 | 5 | 180 | 176.65 | 176.11 | 0.14 | 0.04 | -0.54 | -0.30 |
| 2011-05-06 00:59 | 5 | 240 | 238.97 | 238.81 | 0.24 | 0.04 | -0.16 | -0.10 |
| 2011-05-06 01:09 | 5 | 80 | 71.44 | 71.40 | 0.17 | 0.03 | -0.04 | -0.10 |
| 2011-05-06 01:18 | 5 | 140 | 141.97 | 142.33 | 0.20 | 0.06 | 0.36 | 0.30 |
| 2011-05-06 01:28 | 5 | 20 | 17.13 | 16.90 | 0.22 | 0.04 | -0.23 | -1.30 |
| 2011-05-06 01:38 | 5 | 100 | 107.58 | 107.67 | 0.12 | 0.06 | 0.09 | 0.10 |
| 2011-05-06 01:47 | 5 | 200 | 206.88 | 208.09 | 0.29 | 0.05 | 1.21 | 0.60 |
| 2011-05-06 02:02 | 6 | 0 | 0.04 | -0.02 | 0.48 | 0.02 | -0.06 | NA |
| 2011-05-06 02:18 | 6 | 240 | 239.81 | 241.14 | 0.34 | 0.07 | 1.33 | 0.60 |

| DateTime | Run # | Level (ppb) | SRP (ppb) | OA (ppb) | sdSRP (ppb) | sdOA (ppb) | OA-TS (ppb) | OA-SRP (%) |
|------------------|--------------|--------------------|------------------|-----------------|--------------------|-------------------|--------------------|-------------------|
| 2011-05-06 02:27 | 6 | 140 | 142.26 | 142.84 | 0.29 | 0.09 | 0.58 | 0.40 |
| 2011-05-06 02:37 | 6 | 40 | 43.19 | 43.46 | 0.24 | 0.03 | 0.27 | 0.60 |
| 2011-05-06 02:47 | 6 | 180 | 175.65 | 175.88 | 0.35 | 0.03 | 0.23 | 0.10 |
| 2011-05-06 02:56 | 6 | 20 | 17.10 | 17.03 | 0.16 | 0.08 | -0.07 | -0.40 |
| 2011-05-06 03:06 | 6 | 200 | 207.87 | 207.80 | 0.45 | 0.13 | -0.07 | 0.00 |
| 2011-05-06 03:16 | 6 | 80 | 71.60 | 71.29 | 0.32 | 0.06 | -0.31 | -0.40 |
| 2011-05-06 03:25 | 6 | 100 | 107.02 | 107.06 | 0.38 | 0.04 | 0.04 | 0.00 |
| 2011-05-06 03:41 | 7 | 0 | 0.10 | -0.21 | 0.23 | 0.05 | -0.31 | NA |
| 2011-05-06 03:56 | 7 | 100 | 107.23 | 107.63 | 0.17 | 0.08 | 0.40 | 0.40 |
| 2011-05-06 04:06 | 7 | 40 | 43.41 | 43.36 | 0.14 | 0.06 | -0.05 | -0.10 |
| 2011-05-06 04:16 | 7 | 180 | 175.86 | 175.98 | 0.22 | 0.06 | 0.12 | 0.10 |
| 2011-05-06 04:27 | 7 | 200 | 206.91 | 207.78 | 0.35 | 0.05 | 0.87 | 0.40 |
| 2011-05-06 04:37 | 7 | 140 | 142.36 | 142.57 | 0.17 | 0.08 | 0.21 | 0.10 |
| 2011-05-06 04:46 | 7 | 240 | 238.32 | 239.03 | 0.19 | 0.11 | 0.71 | 0.30 |
| 2011-05-06 04:56 | 7 | 20 | 16.98 | 17.14 | 0.21 | 0.10 | 0.16 | 0.90 |
| 2011-05-06 05:06 | 7 | 80 | 71.52 | 71.63 | 0.29 | 0.03 | 0.11 | 0.20 |
| 2011-05-06 05:21 | 8 | 0 | -0.09 | 0.02 | 0.34 | 0.02 | 0.11 | NA |
| 2011-05-06 05:37 | 8 | 200 | 209.42 | 209.18 | 0.43 | 0.08 | -0.24 | -0.10 |
| 2011-05-06 05:46 | 8 | 180 | 175.06 | 176.10 | 0.24 | 0.04 | 1.04 | 0.60 |
| 2011-05-06 05:56 | 8 | 20 | 17.13 | 16.98 | 0.29 | 0.08 | -0.15 | -0.90 |
| 2011-05-06 06:05 | 8 | 140 | 142.52 | 142.72 | 0.23 | 0.10 | 0.20 | 0.10 |
| 2011-05-06 06:15 | 8 | 80 | 71.58 | 71.57 | 0.23 | 0.04 | -0.01 | 0.00 |
| 2011-05-06 06:25 | 8 | 100 | 106.79 | 107.27 | 0.20 | 0.05 | 0.48 | 0.40 |
| 2011-05-06 06:34 | 8 | 40 | 43.26 | 43.26 | 0.26 | 0.07 | 0.00 | 0.00 |
| 2011-05-06 06:44 | 8 | 240 | 238.26 | 238.39 | 0.49 | 0.06 | 0.13 | 0.10 |
| 2011-05-06 06:59 | 9 | 0 | -0.20 | -0.11 | 0.33 | 0.03 | 0.09 | NA |
| 2011-05-06 07:15 | 9 | 180 | 176.06 | 176.51 | 0.36 | 0.06 | 0.45 | 0.30 |
| 2011-05-06 07:24 | 9 | 240 | 238.12 | 238.62 | 0.22 | 0.02 | 0.50 | 0.20 |
| 2011-05-06 07:34 | 9 | 20 | 17.26 | 17.01 | 0.14 | 0.04 | -0.25 | -1.40 |
| 2011-05-06 07:43 | 9 | 40 | 43.50 | 43.46 | 0.19 | 0.03 | -0.04 | -0.10 |
| 2011-05-06 07:53 | 9 | 140 | 142.15 | 142.57 | 0.32 | 0.05 | 0.42 | 0.30 |
| 2011-05-06 08:03 | 9 | 100 | 106.82 | 107.30 | 0.34 | 0.04 | 0.48 | 0.40 |
| 2011-05-06 08:14 | 9 | 80 | 71.12 | 71.63 | 0.22 | 0.03 | 0.51 | 0.70 |
| 2011-05-06 08:23 | 9 | 200 | 207.29 | 208.11 | 0.24 | 0.07 | 0.82 | 0.40 |

Table 20. Results of the Salto ozone analyzer (OA) TEI 49 #54947-302 compared to the WCC-Empa transfer standard (TS).

| Date/Time | Run # | Level (ppb) | TS (ppb) | OA (ppb) | sdTS (ppb) | sdOA (ppb) | OA-TS (ppb) | OA-TS (%) |
|------------------|-------|-------------|----------|----------|------------|------------|-------------|-----------|
| 2010-09-22 17:52 | 1 | 0 | 0.14 | 0.59 | 0.14 | 0.07 | 0.45 | NA |
| 2010-09-22 18:12 | 1 | 40 | 39.97 | 41.59 | 0.12 | 0.10 | 1.62 | 4.10 |
| 2010-09-22 18:32 | 1 | 90 | 90.03 | 93.64 | 0.15 | 0.11 | 3.61 | 4.00 |
| 2010-09-22 18:52 | 1 | 60 | 60.01 | 62.44 | 0.15 | 0.12 | 2.43 | 4.00 |
| 2010-09-22 19:12 | 1 | 50 | 50.01 | 51.68 | 0.12 | 0.08 | 1.67 | 3.30 |
| 2010-09-22 19:32 | 1 | 20 | 19.99 | 20.98 | 0.20 | 0.10 | 0.99 | 5.00 |
| 2010-09-22 19:52 | 1 | 80 | 80.01 | 82.81 | 0.09 | 0.10 | 2.80 | 3.50 |
| 2010-09-22 20:12 | 1 | 10 | 10.19 | 10.30 | 0.32 | 0.09 | 0.11 | 1.10 |
| 2010-09-22 20:32 | 1 | 30 | 30.00 | 31.32 | 0.17 | 0.11 | 1.32 | 4.40 |
| 2010-09-22 20:52 | 1 | 70 | 69.98 | 72.97 | 0.12 | 0.12 | 2.99 | 4.30 |
| 2010-09-22 21:12 | 2 | 0 | 0.35 | 0.53 | 0.19 | 0.06 | 0.18 | NA |
| 2010-09-22 21:32 | 2 | 20 | 19.97 | 21.08 | 0.15 | 0.08 | 1.11 | 5.60 |
| 2010-09-22 21:52 | 2 | 40 | 40.00 | 41.72 | 0.18 | 0.18 | 1.72 | 4.30 |
| 2010-09-22 22:12 | 2 | 90 | 89.97 | 93.69 | 0.14 | 0.12 | 3.72 | 4.10 |
| 2010-09-22 22:32 | 2 | 60 | 59.97 | 62.79 | 0.15 | 0.17 | 2.82 | 4.70 |
| 2010-09-22 22:52 | 2 | 10 | 10.24 | 10.73 | 0.37 | 0.15 | 0.49 | 4.80 |
| 2010-09-22 23:12 | 2 | 30 | 29.99 | 31.07 | 0.18 | 0.07 | 1.08 | 3.60 |
| 2010-09-22 23:32 | 2 | 50 | 49.99 | 51.97 | 0.14 | 0.09 | 1.98 | 4.00 |
| 2010-09-22 23:52 | 2 | 70 | 70.01 | 73.03 | 0.13 | 0.10 | 3.02 | 4.30 |
| 2010-09-23 00:12 | 2 | 80 | 80.01 | 83.39 | 0.15 | 0.15 | 3.38 | 4.20 |
| 2010-09-23 00:32 | 3 | 0 | 0.02 | 0.53 | 0.15 | 0.05 | 0.51 | NA |
| 2010-09-23 00:52 | 3 | 30 | 30.02 | 31.20 | 0.12 | 0.11 | 1.18 | 3.90 |
| 2010-09-23 01:12 | 3 | 50 | 49.99 | 52.33 | 0.24 | 0.15 | 2.34 | 4.70 |
| 2010-09-23 01:32 | 3 | 10 | 9.99 | 10.21 | 0.17 | 0.07 | 0.22 | 2.20 |
| 2010-09-23 01:52 | 3 | 90 | 89.97 | 93.86 | 0.14 | 0.15 | 3.89 | 4.30 |
| 2010-09-23 02:12 | 3 | 60 | 59.98 | 62.54 | 0.13 | 0.13 | 2.56 | 4.30 |
| 2010-09-23 02:32 | 3 | 20 | 19.98 | 20.81 | 0.22 | 0.09 | 0.83 | 4.20 |
| 2010-09-23 02:52 | 3 | 80 | 80.05 | 83.07 | 0.09 | 0.13 | 3.02 | 3.80 |
| 2010-09-23 03:12 | 3 | 70 | 70.01 | 72.61 | 0.12 | 0.14 | 2.60 | 3.70 |
| 2010-09-23 03:32 | 3 | 40 | 40.01 | 41.61 | 0.12 | 0.10 | 1.60 | 4.00 |
| 2010-09-23 03:52 | 4 | 0 | 0.36 | 0.35 | 0.17 | 0.09 | -0.01 | NA |
| 2010-09-23 04:12 | 4 | 40 | 40.04 | 41.43 | 0.13 | 0.21 | 1.39 | 3.50 |
| 2010-09-23 04:32 | 4 | 90 | 89.97 | 93.63 | 0.16 | 0.13 | 3.66 | 4.10 |
| 2010-09-23 04:52 | 4 | 60 | 60.02 | 62.49 | 0.09 | 0.14 | 2.47 | 4.10 |
| 2010-09-23 05:12 | 4 | 50 | 50.04 | 51.79 | 0.11 | 0.10 | 1.75 | 3.50 |
| 2010-09-23 05:32 | 4 | 20 | 20.01 | 20.83 | 0.16 | 0.13 | 0.82 | 4.10 |
| 2010-09-23 05:52 | 4 | 80 | 79.98 | 83.04 | 0.09 | 0.13 | 3.06 | 3.80 |
| 2010-09-23 06:12 | 4 | 10 | 10.01 | 10.26 | 0.16 | 0.06 | 0.25 | 2.50 |
| 2010-09-23 06:32 | 4 | 30 | 30.04 | 31.14 | 0.08 | 0.10 | 1.10 | 3.70 |
| 2010-09-23 06:52 | 4 | 70 | 70.05 | 73.04 | 0.11 | 0.11 | 2.99 | 4.30 |

APPENDIX III - WCC-EMPA TRAVELING STANDARD

The WCC-Empa traveling standard (TS) was compared with the Standard Reference Photometer before and after the workshop. Details of these comparisons at the Empa calibration laboratory are summarized in Table 21, the comparison data is given in Table 22.

Table 21. Experimental details of the comparison of traveling standard (TS) and Standard Reference Photometer (SRP).

| Standard Reference Photometer | NIST SRP#15 (WCC-Empa) |
|--------------------------------|---|
| Traveling standard (TS) | Model, S/N |
| | TEI 49i-PS #0810-153 (WCC-Empa) |
| Settings | BKG = -0.2; COEFF = 1.009 |
| Ozone source | Internal generator of SRP |
| Zero air supply | Pressurized air - zero air generator (Purafil, charcoal, filter) (WCC-Empa) |
| Connection between instruments | Ca. 1 meter of 1/4" PFA tubing between SRP manifold and TS inlet |
| Data acquisition | SRP data acquisition system, 1-minute averages with standard deviations |
| Levels (ppb) | 0, 30, 60, 90, 140, 200 |
| Duration per level (min) | Variable based on standard deviation criterion, the last 10 30-second readings are aggregated |
| Sequence of Levels | Repeated runs of randomized sequence |
| Runs | 3 runs before shipment of TS (2010-07-20) 3 runs after return of TS (31 2010-10-28) |

Table 22. Five-minute aggregates computed from 10 valid 30-second values for the comparison of the Standard Reference Photometer (SRP) with the WCC-Empa traveling standard (TS).

| Date | Run | Level [#] | SRP (ppb) | sdSRP (ppb) | TS (ppb) | sdTS (ppb) |
|------------|-----|--------------------|-----------|-------------|----------|------------|
| 2010-07-20 | 1 | 0 | -0.12 | 0.60 | 0.01 | 0.34 |
| 2010-07-20 | 1 | 40 | 117.65 | 0.47 | 117.51 | 0.37 |
| 2010-07-20 | 1 | 200 | 198.08 | 0.21 | 198.02 | 0.20 |
| 2010-07-20 | 1 | 120 | 39.54 | 0.40 | 39.46 | 0.17 |
| 2010-07-20 | 1 | 160 | 157.04 | 0.33 | 156.95 | 0.31 |
| 2010-07-20 | 1 | 80 | 77.77 | 0.22 | 77.59 | 0.28 |
| 2010-07-20 | 1 | 0 | -0.22 | 0.48 | -0.03 | 0.38 |
| 2010-07-20 | 2 | 0 | -0.04 | 0.46 | 0.08 | 0.17 |
| 2010-07-20 | 2 | 120 | 118.49 | 0.36 | 118.42 | 0.30 |
| 2010-07-20 | 2 | 200 | 198.22 | 0.40 | 198.08 | 0.46 |
| 2010-07-20 | 2 | 40 | 39.71 | 0.45 | 39.77 | 0.22 |
| 2010-07-20 | 2 | 160 | 157.58 | 0.36 | 157.75 | 0.16 |
| 2010-07-20 | 2 | 80 | 77.98 | 0.34 | 77.85 | 0.24 |
| 2010-07-20 | 2 | 0 | -0.11 | 0.39 | 0.05 | 0.19 |
| 2010-07-20 | 3 | 0 | 0.05 | 0.41 | -0.04 | 0.26 |
| 2010-07-20 | 3 | 120 | 39.93 | 0.38 | 39.83 | 0.18 |
| 2010-07-20 | 3 | 200 | 159.14 | 0.49 | 158.74 | 0.19 |
| 2010-07-20 | 3 | 40 | 78.11 | 0.30 | 77.81 | 0.16 |
| 2010-07-20 | 3 | 160 | 117.79 | 0.26 | 117.95 | 0.18 |
| 2010-07-20 | 3 | 80 | 197.92 | 0.27 | 198.04 | 0.11 |
| 2010-07-20 | 3 | 0 | 0.23 | 0.26 | -0.11 | 0.23 |
| 2010-10-28 | 4 | 0 | 0.05 | 0.27 | 0.11 | 0.18 |
| 2010-10-28 | 4 | 80 | 79.85 | 0.18 | 80.01 | 0.14 |
| 2010-10-28 | 4 | 200 | 202.20 | 0.54 | 202.52 | 0.46 |
| 2010-10-28 | 4 | 120 | 120.14 | 0.63 | 120.41 | 0.13 |
| 2010-10-28 | 4 | 40 | 40.51 | 0.36 | 41.02 | 0.20 |
| 2010-10-28 | 4 | 160 | 160.44 | 0.63 | 160.99 | 0.25 |
| 2010-10-28 | 4 | 0 | -0.15 | 0.55 | -0.08 | 0.24 |
| 2010-10-28 | 5 | 0 | -0.10 | 0.33 | 0.02 | 0.17 |
| 2010-10-28 | 5 | 160 | 161.26 | 0.22 | 162.10 | 0.21 |
| 2010-10-28 | 5 | 200 | 201.89 | 0.84 | 201.93 | 0.44 |
| 2010-10-28 | 5 | 40 | 40.99 | 0.35 | 40.93 | 0.28 |
| 2010-10-28 | 5 | 80 | 79.65 | 0.35 | 79.86 | 0.16 |
| 2010-10-28 | 5 | 120 | 120.20 | 0.34 | 120.35 | 0.26 |
| 2010-10-28 | 5 | 0 | -0.07 | 0.23 | -0.04 | 0.15 |
| 2010-10-28 | 6 | 0 | 0.02 | 0.35 | -0.10 | 0.21 |
| 2010-10-28 | 6 | 40 | 40.86 | 0.28 | 41.10 | 0.21 |
| 2010-10-28 | 6 | 80 | 79.69 | 0.37 | 79.66 | 0.16 |
| 2010-10-28 | 6 | 200 | 200.86 | 0.44 | 201.54 | 0.48 |
| 2010-10-28 | 6 | 160 | 159.48 | 0.32 | 160.18 | 0.20 |
| 2010-10-28 | 6 | 120 | 119.12 | 0.31 | 119.54 | 0.16 |
| 2010-10-28 | 6 | 0 | 0.03 | 0.63 | 0.03 | 0.16 |

[#]the level is only indicative.

The traveling standard passed the assessment criteria defined for maximum acceptable bias before and after the audit [J. Klausen *et al.*, 2003] (cf. Figure 17). The data were pooled and evaluated by linear regression analysis, considering uncertainties in both instruments. From this, the unbiased ozone mixing ratio produced (and measured) by the TS can be computed (equation 3). The uncertainty of the TS was estimated previously (cf. equation 19 in [J. Klausen *et al.*, 2003]).

$$X_{TS} (\text{ppb}) = ([TS] + 0.01 \text{ ppb}) / 1.001$$

$$u_{TS} (\text{ppb}) = \text{sqrt} ((0.43 \text{ ppb})^2 + (0.0034 * X)^2) \quad (3)$$

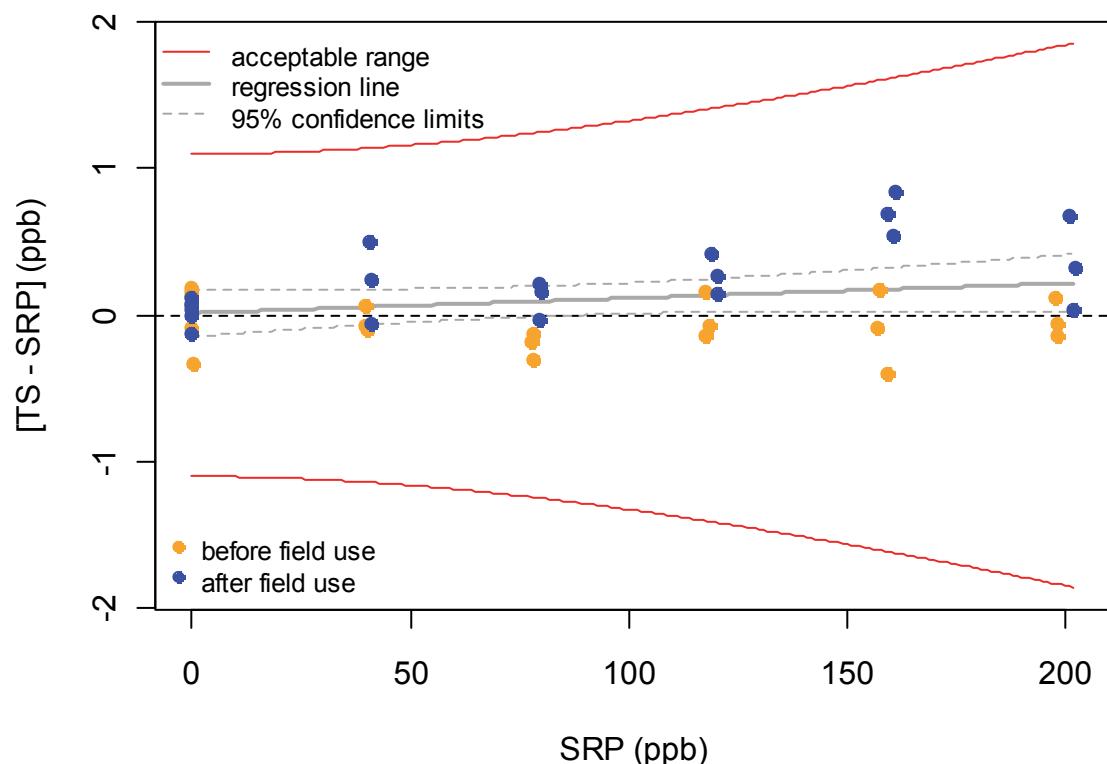


Figure 17. Deviations between traveling standard (TS) and Standard Reference Photometer (SRP) before and after use of the TS at the field site.

APPENDIX IV - LIST OF PARTICIPANTS

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APPENDIX V – WORKSHOP PROGRAMME

Workshop programme (http://www.smn.gov.ar/htms/intercomparacion_ingles.pdf)



**IV TROPOSPHERIC OZONE ANALYZERS
INTERCOMPARISON**
SERVICIO METEOROLÓGICO NACIONAL
OBSERVATORIO CENTRAL DE BUENOS AIRES
BUENOS AIRES, ARGENTINA.
20-24 September, 2010

Scope

The 4th intercomparison for surface ozone analyzers which will be held at the WMO-GAW Regional Calibration Centre Buenos Aires (RCC-BsAs) is open to participants operating surface ozone measurements within the framework of Global Atmosphere Watch in the WMO-GAW region III (South America).

Participating Countries: Brazil, Paraguay, Uruguay, Chile, Switzerland, and Argentina.

Participating Stations:

Regional GAW San Lorenzo (Paraguay),
Regional GAW Sao Paulo (Brazil),
Regional GAW El Tololo (Chile),
Regional GAW El Salto (Uruguay),
GAW RCC Buenos Aires (Argentina),
Regional GAW La Quiaca (Argentina),
Regional GAW Pilar (Argentina),
Regional GAW San Julian (Argentina),
Global GAW Ushuaia (Argentina).

IV TROPOSPHERIC OZONE ANALYZERS

SERVICIO METEOROLÓGICO NACIONAL
OBSERVATORIO CENTRAL DE BUENOS AIRES
BUENOS AIRES, ARGENTINA.

20-24 September, 2010

Organization:

Regional Calibration Centre for Surface Ozone (RCC-BsAs),
Servicio Meteorológico Nacional, Argentina,
Gerardo Carbajal Benítez, María Elena Barlasina, and Ricardo Sánchez.
In collaboration with the:

World Calibration Centre for Surface Ozone (WCC-Empa), Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland (Christoph Zellweger).

Information: Observatorio Central de Buenos Aires, Av. De los Constituyentes 3454 – C1427BLS – Buenos Aires Argentina. Tel. /Fax: +5411 51676767 int. 18306. Email: gcarbajal@smn.gov.ar, barlasina@smn.gov.ar, ozonio@smn.gov.ar.

Aim

The aim of the intercomparison at RCC-BsAs is to ensure traceability of ozone measurements carried out within the WMO-GAW region III against the WMO ozone standard maintained by the Central Calibration Laboratory (CCL) for Surface Ozone at the National Institute for Standard (NIST). It will focus on the following topics:



Central Calibration Laboratory

| | |
|----------|--|
| 9.00 am | Inspection and diagnostics of the ozone instruments Participants, Ricardo Sánchez and Christoph Zellweger. |
| 10.00 am | Coffee break. |
| 10.30 am | Continue with work on ozone instruments Participants, Ricardo Sánchez and Christoph Zellweger. |
| 12.30 pm | Lunch. |
| 1.30 pm | First intercomparisons (assessment of ozone analyzers) Participants, Ricardo Sánchez and Christoph Zellweger. |
| 3.30 pm | Lab course on instrument maintenance and repair Participants, Ricardo Sánchez and Christoph Zellweger. |
| 6.00 pm | End of workday. |

22nd September:

| | |
|----------|---|
| 9.00 am | Continue with intercomparisons (assessment of ozone analyzers) throughout the day. Participants, Ricardo Sánchez and Christoph Zellweger. |
| 10.00 am | Coffee break. |
| 10.30 am | Evaluation of intercomparison results Participants, Ricardo Sánchez and Christoph Zellweger. |
| 12.30 pm | Lunch. |
| 1.30 pm | Review of existing time series Participants present ozone time series from their stations. |
| 3.30 pm | Lab course on instrument maintenance and repair, adjustment of calibration factors, evaluation of intercomparison results Participants, Ricardo Sánchez and Christoph Zellweger. |
| 6.00 pm | End of workday. |

23rd September:

| | |
|----------|--|
| 9.00 am | Continue with intercomparisons (assessment of ozone analyzers) throughout the day Participants, Ricardo Sánchez and Christoph Zellweger. |
| 10.00 am | Coffee break |
| 10.30 am | Data handling and evaluation, measurement uncertainty, data submission, Christoph Zellweger. |
| 12.30 pm | Lunch |
| 1.30 pm | Group work depending on the needs of the participants. -Review and correction of existing time series. -Data evaluation and submission. -Instrument maintenance and repair. |
| 6.00pm | End of workday. |

24th September:

| | |
|----------|--|
| 9.00 am | End intercomparisons, evaluation of results Participants, Ricardo Sánchez and Christoph Zellweger. |
| 10.30 am | Conclusions and recommendations All. |
| 11.30 am | Handing in of attendance certificates |
| 12.00 pm | Lunch and end of the intercomparison |

- Assessment of surface ozone analyzers operated at global and regional stations of the WMO-GAW region III through inter-comparisons against NIST traceable ozone standards from RCC-BsAs and WCC-Empa. The assessment involves an initial intercomparison of the instruments in the current state, and a second inter-comparison for instruments that need to be repaired or to be adjusted according to the calibration factors.
- Diagnostics and repair of instruments.
- Review and validation of existing surface ozone data series from the WMO-GAW region III, with the aim to submit these data to the World Data Centre for Greenhouse Gases (WDGG).
- Operator training in surface ozone chemistry, measurement techniques, instrument maintenance and data handling.

Instruments corresponding to each station:

| | |
|-------------------------|---|
| Regional GAW Asuncion | 1 TEI 49 |
| Regional GAW El Tololo | 1 TEI 49 |
| Regional GAW El Salto | 1 TEI 49 |
| GAW RCC Buenos Aires | 2 TEI 49 and the Regional Stand 49C-PS. |
| Regional GAW La Quiaca | 1 TEI 49 |
| Regional GAW Pilar | 1 TEI 49 |
| Regional GAW San Julian | 1 TEI 49 |
| Global GAW Ushuaia | 3 TEI 49 (2 TEI49 1 TEI49C) |

Schedule:

20th September:

| | |
|-----------|---|
| 10.00 am | Welcome to the event, <i>IV Tropospheric Ozone Analyzers intercomparison.</i> |
| 10.15 am | Introduction of Participants. |
| 10.45 am | Coffee break. |
| 11.00 am | Ozone Chemistry - MSc. Gerardo Carabajal Benítez -SMN and Researcher of Universidad Católica Argentina. |
| 11.45 am. | Ozone and Climate Change. - MSc. Diana Melnický, Researcher of San Martín University. |
| 12.30 pm | Lunch. |
| 1.30 pm | Seminar for operators of surface ozone instruments.- Mr. Christoph Zellweger, <i>World Calibration Centre for Surface Ozone (WCC-Empa),</i> Intercomparison of ozone standards (RCC-BsAs and WCC-Empa). |
| 4.00 pm | Ricardo Sánchez and Christoph Zellweger. |
| 6.00 pm | End of workday. |

21st September:

| | |
|----------|--|
| 9.00 am | End intercomparisons, evaluation of results Participants, Ricardo Sánchez and Christoph Zellweger. |
| 10.30 am | Conclusions and recommendations All. |
| 11.30 am | Handing in of attendance certificates |
| 12.00 pm | Lunch and end of the intercomparison |

REFERENCES

- Hofer, P., B. Buchmann, and A. Herzog (2000), Traceability, Uncertainty and Assessment Criteria of Surface Ozone Measurements *Rep. 98/5*, 19 pp, WCC-EMPA Report 98/5, Swiss Federal Laboratories for Materials Testing and Research (EMPA), Dübendorf, Switzerland.
- Klausen, J., C. Zellweger, B. Buchmann, and P. Hofer (2003), Uncertainty and bias of surface ozone measurements at selected Global Atmosphere Watch sites, *Journal of Geophysical Research-Atmospheres*, 108(D19), 4622, doi:4610.1029/2003JD003710.
- Klausen, J., S. Henne, C. Zellweger, and B. Buchmann (2006), System and Performance Audit of Surface Ozone and Carbon Monoxide at the Global GAW Station Mt. Kenya, January 2006, Empa-WCC Report 06/1*Rep.*, 39 pp, Dübendorf, Switzerland.
- Viallon, J., P. Moussay, J. E. Norris, F. R. Guenther, and R. I. Wielgosz (2006), A study of systematic biases and measurement uncertainties in ozone mole fraction measurements with the NIST Standard Reference Photometer, *Metrologia*, 43(5), 441-450.
- WMO (2007), WMO Global Atmosphere Watch (GAW) Strategic Plan: 2008 – 2015, GAW Report No. 172*Rep. GAW Report # 172*, World Meteorological Organization, Geneva, Switzerland.
- WMO (in preparation), Standard Operating Procedure (SOP) for Performance Audits of Surface Ozone Measurements at WMO/GAW Sites, Draft Version 1.0, World Meteorological Organization, Scientific Advisory Group Reactive Gases, Geneva, Switzerland.
- Zellweger, C., J. Klausen, and B. Buchmann (2008), System and Performance Audit of Surface Ozone and Carbon Monoxide at the Global GAW Station Ushuaia, Argentina, November 2008, WCC-Empa Report 08/4*Rep.*, 42 pp, Dübendorf, Switzerland.

LIST OF ABBREVIATIONS

| | |
|----------|---|
| ABP | Arembepe |
| CCL | Central Calibration Laboratory |
| DAQ | Data Acquisition System |
| DQO | Data Quality Objective |
| GAW | Global Atmosphere Watch |
| NAT | Natal |
| NIST | National Institute of Standards and Technology |
| PMO | Paramaribo |
| OA | Ozone Analyzer |
| RCC-BsAs | Regional Calibration Centre for Surface Ozone, Buenos Aires |
| SAG | Salto |
| SMN | Servicio Meteorológico Nacional |
| SOP | Standard Operating Procedure |
| SRP | Standard Reference Photometer |
| TS | Traveling Standard |
| USH | Ushuaia |
| WCC-Empa | World Calibration Centre for Surface Ozone, Carbon Monoxide and Methane |
| WDCGG | World Data Centre for Greenhouse Gases |
| WMO | World Meteorological Organization |