Research article

Evaluation of atmospheric gaseous passive samplers through comparison with active *in situ* measurements

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Abstract

In order to assess compositional changes within the atmosphere it is crucial to measure concentrations of atmospheric trace gas species, which include the criteria pollutants sulphur dioxide (SO_2), nitrogen dioxide (NO_2) and ozone (O_3). Measurement of these species with passive samplers is a generally acknowledged and frequently utilised method, which offers a cost-efficient sampling method to monitor these atmospheric species, especially, in data-scarce regions with logistical restraints. However, the performance of these passive samplers must be evaluated regularly, which include comparison to measurements conducted with active in situ samplers that are frequently quality checked and calibrated. In this manner, correction- or scaling factors are determined, which improves the accuracy and precision of passive samplers. Therefore, the aim of this study was to reevaluate passive samplers used to measure SO_2, NO_2 and O_3 in relation to active in situ measurements of these species conducted at the Welgegund atmospheric monitoring station for approximately six years. Scaling factors of 0.9, 1.7 and 1.4 were determined for SO_2, NO_2 and O_3, respectively measured with passive samplers in relation to active measurements. Concentrations of these species determined with the type of passive samplers used in this study should be multiplied by these factors. These newly derived scaling factors were in the same range as previously determined correction factors. However, statistical analysis revealed that these newly determined scaling factors should be used in future studies utilising these passive samplers.

Keywords

Sulphur dioxide; Nitrogen dioxide; Ozone; Air quality; Atmospheric deposition; Welgegund; DEBITS

Introduction

The atmosphere of earth can be described as a vital mixture of gases forming a thin layer around the globe, which is essential for sustaining life (Török and Dransfield, 2018). Gaseous and particulate species are emitted into the atmosphere through natural and anthropogenic activities. Significant emissions of these species, especially, associated with increased human activity, can lead to air pollution if concentrations accumulate to harmful levels, which can impact plants, animals, ecosystems, and human health (Monks and Hey, 2009). Increased emissions associated with anthropogenic activities are of global and regional concern, particularly, within developing countries such as South Africa. Recent studies have indicated the impacts of increased energy consumption and rapid population growth within this region on elevated levels of atmospheric pollutant species (Laban et el, 2018; Swartz et al., 2019; Swartz et al., 2020).

The troposphere contains various trace gas species that can undergo chemical and physical transformations (Monks and Hey, 2009). The atmospheric concentrations of these trace gaseous species can be quantified through various sampling techniques, which include active *in situ* measurements and/or passive sampling. Active *in situ* measurements utilize photolytic processes such as fluorescence, chemiluminescence, and absorption, to determine the atmospheric concentration of trace species. If well maintained and calibrated, these

measurements are generally considered to provide precise and accurate data. However, these sampling techniques can be expensive and must be logistically feasible (Skoog et al., 1963, Martins et al., 2007). Although passive sampling has limitations with regard to temporal resolution and accuracy, these samplers are more cost-effective, mobile and require simpler field logistics (Ferm and Rodhe, 1997, Vardoulakis et al., 2009). However, the performance of these passive samplers must be evaluated regularly, which include comparison to high-quality measurements conducted with active *in situ* samplers that are frequently quality checked and calibrated.

Passive samplers developed in-house in South Africa were deployed at various remote monitoring sites within South Africa in several projects such as the Deposition of Biogeochemical Important Trace Species (DEBITS) program of the International and Global Atmospheric Chemistry (IGAC) project (Swartz et al., 2020, Swartz et al, 2021, Ngoasheng et al., 2021). These passive samplers will also be used in new research infrastructure projects in South Africa, e.g. the Expanded Freshwater and Terrestrial Environmental Observation Network (EFTEON). The design of these passive samplers is based on the Swedish Environmental Research Institute (IVL) passive sampler and are utilised to measure atmospheric concentrations of sulphur dioxide (SO_2), nitrogen dioxide (NO_2), ozone (O_3), ammonia (NH_3) and nitric acid (HNO_3). Previous comparisons between these passive samplers and active *in situ* measurements have indicated the necessity for species specific scaling- or correction factors to ensure the accuracy of these passive samplers (Dhammapala, 1996, Martins, 2009). Participation in international inter-comparison studies has confirmed the reliability, accuracy and precision of concentrations of these gaseous species determined with these passive samplers when applying scaling factors (He and Bala, 2008). However, as mentioned above, the performance of passive samplers must be assessed continuously, which is an important quality control and -assurance measure. Therefore, the aim of this study was to conduct an updated assessment of the performance of SO_2, NO_2, and O_3 passive samplers in relation to active *in situ* measurements of these species conducted at the Welgegund atmospheric monitoring site in the South African interior, as well as provide, if required, updated correction factors to utilise in the calculation of atmospheric concentrations of gaseous species measured with these passive samplers.

Method

Site description

The Welgegund atmospheric measurement site (Figure 1) is located approximately 30 km north of Potchefstroom in the

Figure 1: *Map of the North West province of South Africa with the red star indicating the location of Welgegund atmospheric monitoring station. A map of South Africa, showing its provinces, is present at the bottom right.*

North West Province of South Africa at an elevation of 1480 m above sea level (26°34'10"S, 26°56'21"E). Detailed description of this site has been presented in various other studies (e.g. Jaars et al., 2014, Vakkari et al., 2015, Booyens et al., 2015, Räsänen et al., 2017, Jaars et al., 2018). The station is situated on a commercial farm with no large point sources within proximity of the site. However, the site is a regional station impacted by the major pollutant source regions in the north-eastern interior of South Africa, which includes the Mpumalanga Highveld, Vaal Triangle, western Bushveld Igneous Complex and the Johannesburg-Pretoria megacity (e.g. Tiitta et al., 2014). In addition, Welgegund is also impacted by a relatively clean region to the west of the site (Tiitta et al., 2014, Jaars et al., 2016). The region experienced an average temperature of 17°C during the sampling period with summer temperatures maximums in the range of ~30°C, while winter minimum temperatures were in the order <0°C. This region is characterised by a distinct wet and dry season with precipitation mainly occurring during the warmer months, typically from mid-October to mid-May. The station is surrounded by grassland savannah (Jaars et al., 2016).

Measurements

Passive samplers

SO_2, NO_2 and O_3 passive samplers were monthly deployed at the Welgegund atmospheric measurement station between August 2012 and June 2018. Detailed description of the theory and functioning, which is based on chemical reactions and laminar diffusion, as well as the assembly of the passive samplers utilised in this study, have been presented in literature (Ferm, 1991, Koutrakis et al., 1993, Ferm et al., 1994, Ferm, 2001, Carmichael et al., 2003, Aiuppa et al., 2004, Adon et al., 2010, Swartz, 2020, Ngoasheng et al., 2021). In brief, these samplers comprise an ash-less paper filter impregnated with an appropriate absorbing solution, a PTFE filter and a stainless-steel mesh, which are housed in top and bottom assembly caps connected with a polypropylene support ring (Adon et al., 2010, Ngoasheng, et al. 2021; Swartz et al., 2020). The PTFE filter and stainless-steel mesh serve to prevent active air movement through turbulent diffusion (Carmichael et al., 2003). Passive samplers were prepared and deployed in duplicate, while blank samplers were also prepared for each month of sampling. The prepared passive samplers were placed in airtight containers, stored in airtight bags, and kept in a freezer until the day of exposure.

Passive samplers were removed from the bags and placed in the housing unit on the day of deployment. These enclosures were located approximately 3 m above the ground on top of one of the containers at Welgegund and comprised of rails specifically designed to accommodate the passive samplers. The samplers were inserted in the rails, with the top assembly oriented downward, exposing the stainless-steel mesh. After the one-month sampling period, passive samplers were removed, placed in airtight bags and containers, and stored in the freezer until analysis. Prior to analysis, the hardened ash-less paper filters were removed from the passive samplers (and blanks) used to measure SO_2, NO_2 and O_3 and placed in 5 mL, 10 mL and 25 mL deionised water, respectively for 30-minute sonication in an ultrasonic bath. Analyses of all extracted samples from passive samplers were conducted with a Dionex ICS-3000 IC system (Swartz et al., 2020).

Active *in situ* measurements

Active *in situ* sampling of SO_2, NO_2 and O_3 at Welgegund were conducted with a Thermo Model 43S analyser, a Teledyne 200AU analyser and an Environnement S.A. O341M ozone analyser, respectively (Petäjä et al, 2013). Measurements were recorded in intervals of 1 min from which monthly concentrations of these species were calculated in order to compare to the passive samplers.

Quality assurance

Maintaining optimal laboratory cleanliness is crucial when quantifying concentrations of atmospheric trace elements. Passive samplers were prepared and analysed in laboratories equipped with air filtration systems, which ensured a clean laboratory environment by maintaining positive pressure and eradicating exposure to dust particles. Prior to preparing the passive sampler, all components were cleaned to prevent contamination. This included immersion in a 0.2% (v/v) o-H_3PO_4 solution, washing and rinsing with an 3% (v/v) EXTRAN MA O2 solution, and sonication. All glassware, containers and tools utilised in this study were also cleaned using the same method. The ash-less paper filters were rinsed through sonication with methanol (MeOH) for 30 minutes to eliminate any potential impurities and particles. The process was repeated four times after which the filters were allowed to dry and sealed-off in airtight bags for storage until deployment. Blanks were also prepared for each batch of passive samplers deployed. The IC analytical techniques utilised in this study, as well as the pH and conductivity measurements, were also verified by participating in the bi-annual Laboratory Inter Comparison Study of the World Meteorological Organisation (WMO LIS) (Conradie et al., 2016; Swartz et al., 2020).

The reliability and quality of the data obtained from the active *in situ* measurements of SO_2, NO_2, and O_3 were ensured through regular checks and calibrations. The performance of these instruments was verified daily, while site visits were conducted weekly. These instruments were calibrated three to four times per year with the analysers typically showing small span drifts, i.e. <1%. The one-minute readings of the gaseous species were adjusted for calibration drift assuming that the response of the analyser varied in a linear manner over time (Laakso et al., 2008). The dataset was evaluated and processed in order to remove any errors and uncertainties associated with the dataset due to e.g. power cuts. Prior to calculating the monthly average concentrations of SO_2, NO_2, and O_3, 15-minute mean values were derived from the one-minute recorded data. Only 15-minute averages that included 66.7% data coverage during the 15-minute sampling period were considered in the calculation of 30-minute mean concentrations.

Data processing, statistical analysis and calculations

Active *in situ* measurements were plotted against the monthly concentrations determined for SO_2, NO_2 and O_3 with passive

samplers. Large outliers were removed by utilising Cook's distance (D) equation (Chatterjee and Hadi, 2012), which quantifies the influence of omitting an observation in the correlation plot, while incorporating both the residual and leverage of an observation (Neter et al., 1996, Chatterjee and Hadi, 2012). The potential outlier identified by Cook's distance equation was assessed in relation to other datapoints in the dataset and concentrations determined for a specific species for the same months in other years during the sampling period. In addition, passive data was also removed from the dataset in the absence of any active *in situ* measurements for a specific month.

Since the data was found to be non-normally distributed, non-parametric analytical tests, i.e. Spearman's correlation, Kruskal-Wallis, and Bland-Altman analyses were performed to determine and evaluate scaling factors in the calculation of SO_2, NO_2, and O_3 concentrations measured with passive samplers. Furthermore, the statistical significance of scaling factors determined in this study in relation to previously used scaling factors for passive samplers was also established. Correction factors for the passive samplers were derived from Spearman's correlations between active *in situ* data and passive measurements similarly to previous comparison studies conducted by Dhammapala (1996) and Martins (2009). The r_s and the p-value derived from the Spearman test also provided insight into the correlation between the active data and the uncorrected passive data. The Kruskal-Wallis test was employed to compare SO_2, NO_2, and O_3 concentrations determined with active *in situ* measurements to levels determined with passive samplers derived from the previously used and newly determined scaling factors. This post hoc analysis utilised a pairwise Dunn's test after establishing statistically significant differences, with p-values corrected through the Benjamini-Hochberg correction for multiple comparisons. Concurrently, ε^2 was employed to evaluate the effect magnitude. The degree of agreement between the two sampling techniques was evaluated through Bland-Altman analysis, which entails plotting the discrepancies between the data acquired from both sampling techniques on the y-axis against the mean of the measurements on the x-axis. This analysis could provide essential insights into systematic differences between sampling techniques, which enables assessment of the reliability, accuracy, precision and reliability of different methods in relation to each other.

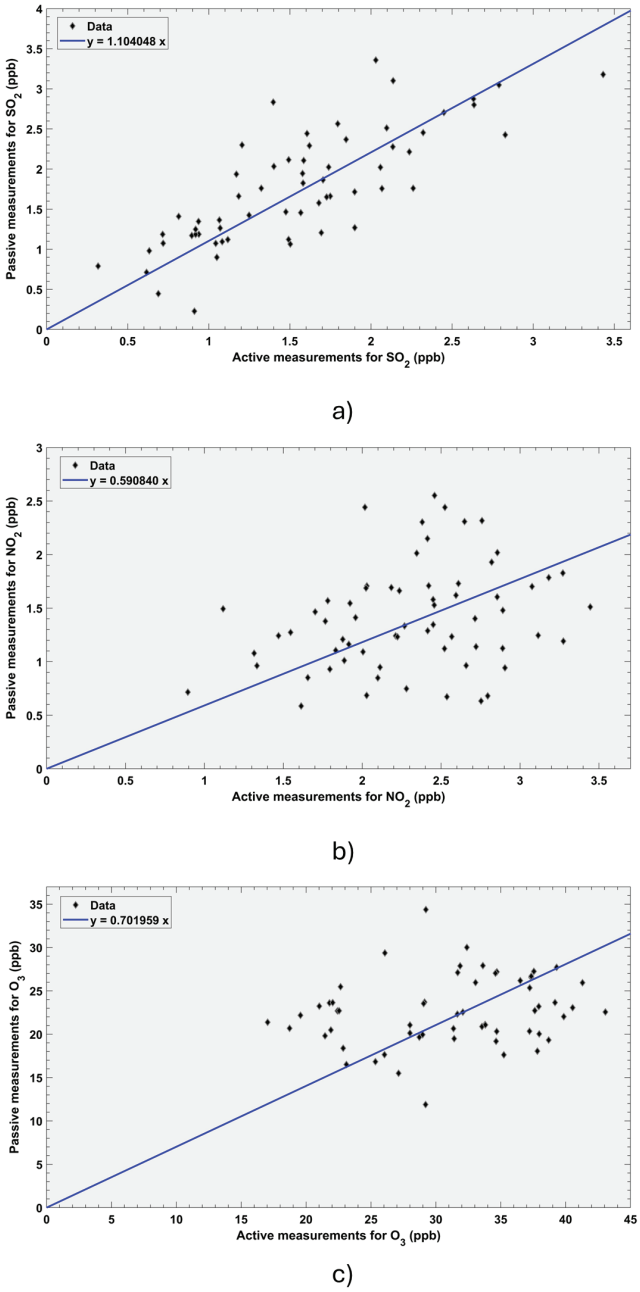

Figure 2: *Comparison of active in situ measurements with the uncorrected passive measurements for a) SO_2 b) NO_2 and c) O_3 sampled at Welgegund between August 2012 to June 2018.map of South Africa, showing its provinces, is present at the bottom right.*

Results and discussion

Data availability

In Figure A1, Cook's distance calculated for monthly concentrations of SO_2, NO_2 and O_3 determined with passive and active samplers during the sampling period are presented. Observations exceeding the heuristic threshold, i.e. more than three times the mean Cook's distance (Neter et al., 1996) were considered to be outliers and removed from the dataset. Observations that were in proximity of the heuristic threshold were also inspected and removed if necessary. A summary of the data availability used in the subsequent statistical analysis in this study is presented in Table A1. It is evident that >80% of the data collected for the three gaseous species could be utilised for further analysis, which can be considered very good for the six-year sampling period.

Spearman's correlation

Spearman's correlation between the SO_2, NO_2 and O_3 concentrations determined with the unscaled passive samplers and the active *in situ* measurements in order to derive scaling factors for the passive samplers are presented in Figure 2. Strong correlation between uncorrected passive and active *in situ* measurements is evident for SO_2, while weaker relationships

are observed for NO_2 and O_3 concentrations determined with the two sampling techniques. The r_{s-} and p-values determined in these correlations are summarised in Table A2. The r_{s-} and p-values calculated for SO_2 (0.792 and 0.00, respectively) confirms a statistically significant correlation between uncorrected passive and active data (Fowler et al., 2013, Ali Abd Al-Hameed, 2022), while $r_{s-}$and p-values determined for NO_2 (0.2837 and 0.022, respectively) and O_3 (0.2198 and 0.0945, respectively) reflects weaker correlation between unscaled passive and *in situ* data. The average ratios between SO_2, NO_2, and O_3 concentrations determined with passive samplers in relation to active *in situ* measurements were 1:1.1, 1:0.6 and 1:0.7, respectively. Therefore, the scaling factors for SO_2, NO_2, and O_3 passive samplers derived in this study are 0.9, 1.7 and 1.4, respectively, i.e. concentrations of these species determined with passive samplers used in this study should be multiplied by these respective factors.

Previous studies by Dhammapala (1996) and Martins (2009) calculated ratios of 1:1 for SO_2, 1:0.6 and 1:0.7 for NO_2, and 1:08 for O_3 with scaling factors of 1, 1.5 and 1.3 for SO_2, NO_2, and O_3 respectively, when comparing passive data with active measurements. Therefore, it is evident that the correlations between SO_2, NO_2, and O_3 levels determined with passive samplers in relation to active *in situ* measurements at Welgegund in this study, are in the same order as ratios determined in previous studies. It has to be mentioned that similar correlations between unscaled passive measurements and active *in situ* data were also observed in these previous comparisons. However, as indicated in subsequent sections, it is suggested that these newly derived scaling factors determined for SO_2, NO_2, and O_3 passive samplers in this study should be used in future research when utilising these specific passive samplers.

The minor differences in the scaling factors determined in this study compared to previous studies may be attributed to various factors. Martins (2009) attributed observed differences between passive and active O_3 measurements to the indirect passive sampling of O_3, which measures the overall oxidation potential of the atmosphere with lower O_3 attributed to wall effects (Adon et al., 2010). Moreover, the discrepancies in NO_2 and SO_2 ratios can be attributed to several factors, with the chemistry of the sorbent being a significant contributor. Multiple decomposition and reverse processes for NO_2-have been identified, leading to the unreliable and inconsistent estimation of NO_2 utilising a passive sampler (Martins et al., 2007, Martins, 2009).

Kruskal-Wallis test

In Figure 3 to 5, the Kruskal-Wallis tests for SO_2, NO_2, and O_3, respectively are presented. In these tests, SO_2, NO_2, and O_3 concentrations determined with active *in situ* measurements (Active) are compared to levels determined for these species with passive samplers derived from the previously used scaling factor (Old CF) (Dhammapala, 1996, Martins, 2009), and newly determined scaling factors (New CF). These figures combine violin, box and jittered plots, while the inferential statistics, as well as the estimation of impact size together with the uncertainty levels and pairwise comparisons, are indicated.

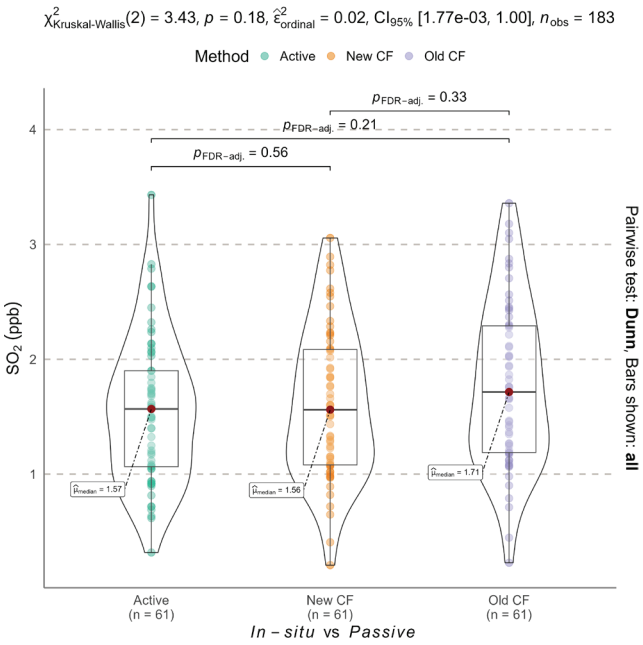

Figure 3: *A combination of a violin, box and jittered plot of the monthly average SO_2 concentrations determined with the active in situ sampler, as well as passive samplers utilising the previously used and new scaling factors determined in this study. Top and bottom line shows the 25th and 75th percentile of concentration, and the middle line and red dot show the median. Whiskers on the boxplots show 95% coverage of the data; the axis is broken along the line to show outliers. The inferential statistics, an estimate of effect size and uncertain, and pairwise comparisons are also known.*

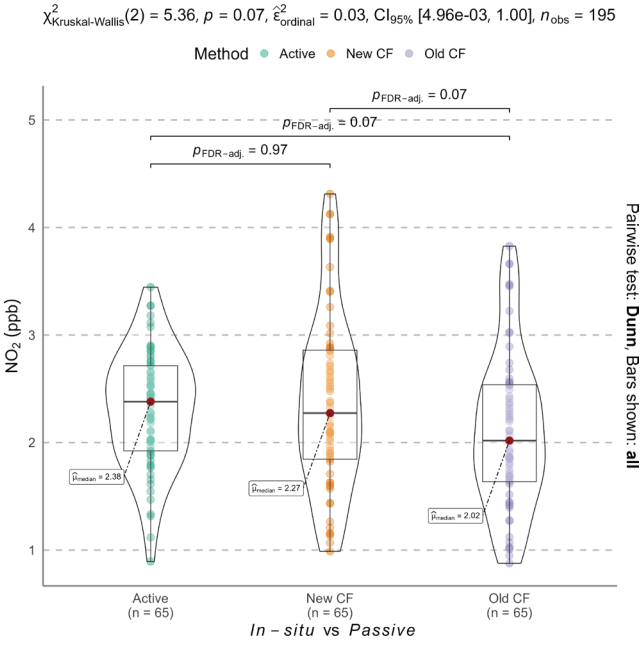

Figure 4: *A combination of a violin, box and jittered plot of the monthly average NO_2 concentrations determined with the active in situ sampler, as well as passive samplers utilising the previously used and new scaling factors determined in this study. Top and bottom line shows the 25th and 75th percentile of concentration, and the middle line and red dot show the median. Whiskers on the boxplots show 95% coverage of the data; the axis is broken along the line to show outliers. The inferential statistics, an estimate of effect size and uncertainty, and pairwise comparisons are also shown.*

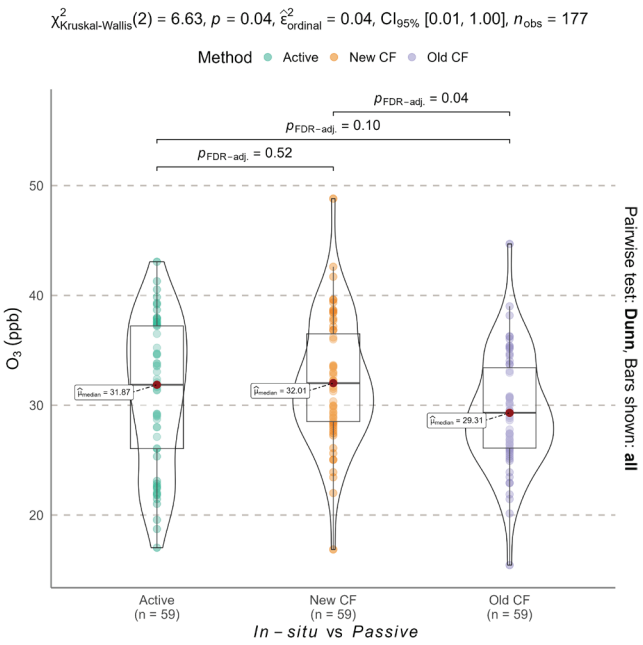

Figure 5: *A combination of a violin, box and jittered plot of the monthly average O_3 concentrations determined with the active in situ sampler, as well as passive samplers utilising the previously used and new scaling factors determined in this study. Top and bottom line shows the 25th and 75th percentile of concentration, and the middle line and red dot show the median. Whiskers on the boxplots show 95% coverage of the data; the axis is broken along the line to show outliers. The inferential statistics, an estimate of effect size and uncertainty, and pairwise comparisons are also shown.*

The Kruskal-Wallis test conducted for SO_2 (Figure 3) indicates no statistically significant difference (p = 0.18) between the active *in situ* measurements and SO_2 levels determined with passive samplers utilising the two scaling factors ($\chi^2_{Kruskal-Wallis}$ (2,N = 183) = 3.43, p = 0.18; ε^2 = 0.02). Post hoc analysis was also employed to evaluate whether the newly derived scaling factor was an improvement on the previously derived correction factor in relation to active *in situ* measurements. Although no significant difference was determined, a smaller difference between SO_2 concentrations derived from the passive samplers utilising the newly derived scaling factors and the active *in situ* measurements was evident compared to SO_2 levels determined with passive samplers using the previous correction factor. This is also reflected through comparison of the median SO_2 concentrations determined with the different sampling techniques. The median determined for active measurements was 1.57 ppb, compared to the median values of 1.56 ppb and 1.71 ppb calculated with the new and previously used scaling factors, respectively. Comparison of the SO_2 concentrations derived from passive samplers with the two scaling factors also indicate no significant differences (p = 0.33).

The Kruskal-Wallis test reveals no statistically significant differences between the NO_2 levels determined with active *in situ* and passive sampler measurements using the two scaling factors when considering an α value of 0.05 ($\chi^2_{Kruskal-Wallis}$ (2,N = 195) = 5.36, p = 0.07; ε^2 = 0.03), which is also confirmed by post hoc analysis However, the newly derived scaling factor does show a small improvement when comparing active and passive data. This is also evident when comparing the median values, i.e. 2.38 ppb measured with the active sampler, and 2.27 ppb and 2.02 ppb derived from passive samplers utilising the new and the previously used scaling factor, respectively.

The Kruskal-Wallis tests performed for O_3 measurements are presented in Figure 5, which indicate statistically significant differences (p = 0.04) between the active *in situ* measurements and O_3 levels derived from passive samplers with the previously used and the newly determined scaling factors ($\chi^2_{Kruskal-Wallis}$ (2,N = 177) = 6.63, p = 0.04; ε^2 = 0.04). Pairwise differences in concentrations determined with the active and passive samplers were also further assessed through post hoc analyses. No significant difference is observed for O_3 concentrations determined with passive samplers utilising the new or previous scaling factors compared to active *in situ* measurements. The higher p-value (0.52) between the active measurements and the passive samplers corrected with the new scaling factor reflects better comparison between the O_3 concentrations derived from the passive samplers using the new correction factor compared to the previously used scaling factor. Furthermore, comparison of the O_3 levels derived from passive samplers with the two scaling factors indicates a statistically significant difference (p = 0.33). Comparison of the median concentrations derived with the new (32.01 ppb) and previous (29.31 ppb) correction factors to the median determined for the active data (31.87 ppb) also reveals an improvement.

Bland-Altman analysis

In Figure 6 and 7 the Bland-Altman analysis evaluating SO_2 concentrations determined with the active sampler in relation to SO_2 levels derived from passive samplers with previously used and new scaling factors, respectively, are presented. The (0,0) point representing perfect agreement in the accuracy plots resides outside the 95% confidence intervals of [0.0947, 0.3423] for active *in situ* measurments in relation to SO_2 levels determined with the previously used scaling factors, while the 95% confidence interval of [-0.0535, 0.1719] determined with the new scaling factor resides within the 95% confidence interval. This suggests a statistically significant positive bias when using the previously used scaling factor, indicating that the concentrations derived from passive samplers appear to overestimate SO_2 levels in comparison to the active method. However, there is no significant bias when using the new scaling factor. It is also important to note that no consistent overestimation or underestimation is evident when comparing passive to the active measurements. The precision tests (Figure 6b and Figure 7b) depicted for SO_2 levels derived with the previously used scaling factor indicated that the horizontal precision (x, 0) lines were beyond the 95% confidence ranges, hence rejecting the null hypothesis of precision equivalency. However, the precision of passive SO_2 concentrations determined with the new scaling factor resided inside the 95% confidence ranges, indicating that these levels are statistically equivalent to active measurements of this species. The reliability of the SO_2 passive measurements adjusted according to the previously used scaling factor (Figure 6c) and the passive SO_2 levels

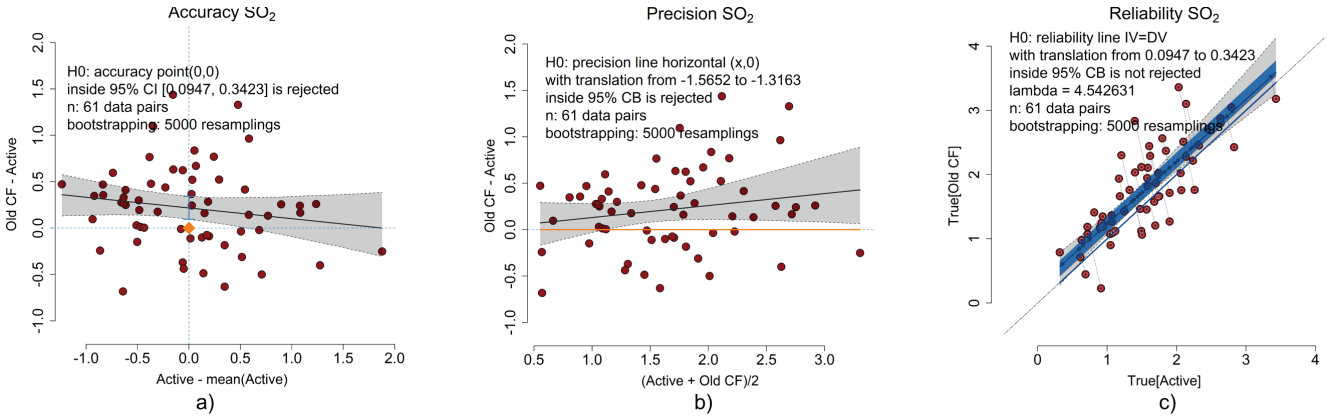

Figure 6: *Similarity of a) accuracy, b) precision, and c) reliability for active in situ SO_2 measurements in relation to SO_2 concentrations determined with passive samplers utilising the previously used scaling factor obtained using 5×10^3 bootstrap iterations.*

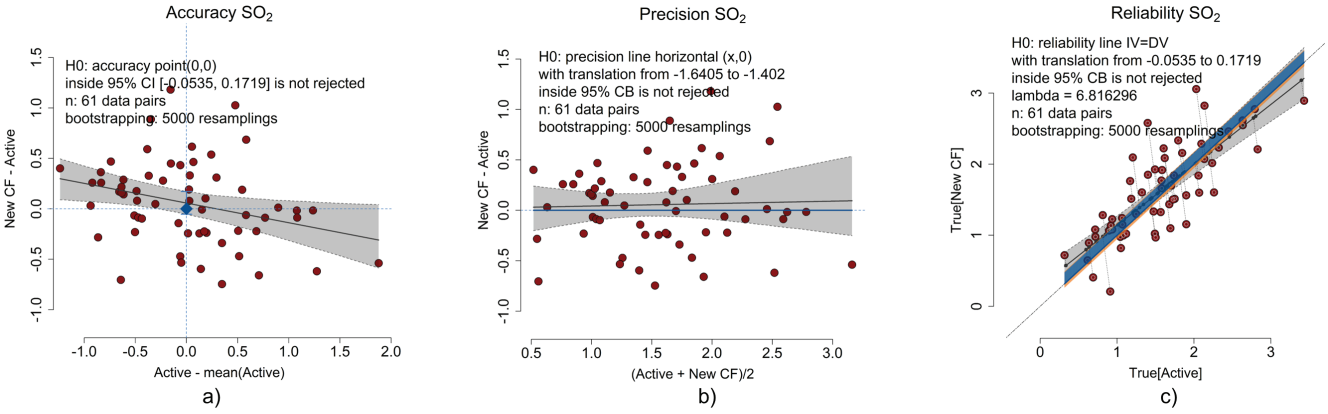

Figure 7: *Similarity of a) accuracy, b) precision, and c) reliability for active in situ SO_2 measurements in relation to SO_2 concentrations determined with passive samplers utilising the new scaling factor obtained using 5×10^3 bootstrap iterations.*

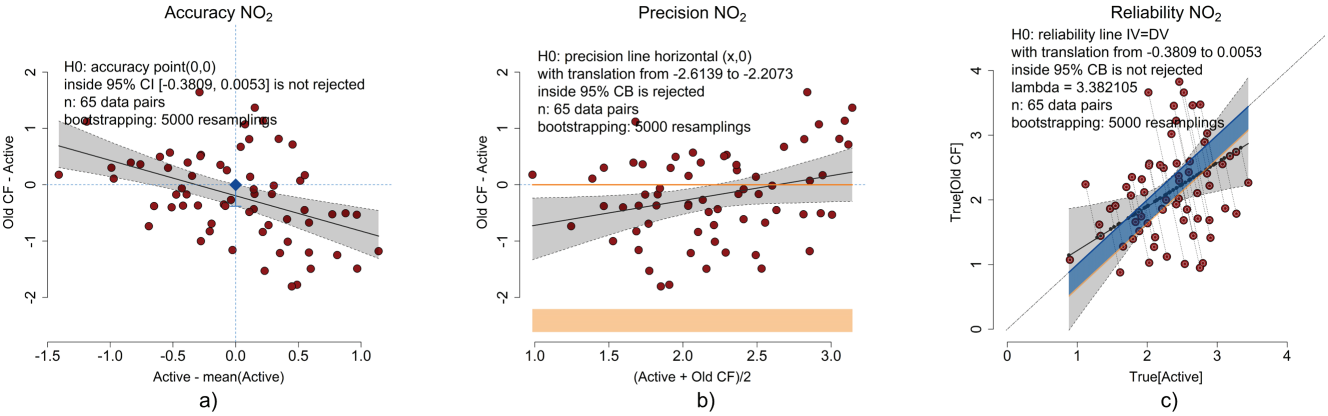

Figure 8: *Similarity of a) accuracy, b) precision, and c) reliability for active in situ NO_2 measurements in relation to NO_2 concentrations determined with passive samplers utilising the previously used scaling factor obtained using 5×10^3 bootstrap iterations.*

derived with the new scaling factor (Figure 7c), is statistically significant. For both instances, the bisector line that represents perfect agreement, resides within the 95% confidence intervals, reflecting a high degree of reliability and statistical significance between the SO_2 concentrations derived from passive samplers utilising the previously used and newly determined scaling factors in relation to active *in situ* measurements.

The Bland-Altman analysis performed for NO_2 measurements are presented in Figure 8 and Figure 9. The (0,0) point in the accuracy analysis for both passive sampling calculations resides within the 95% confidence range, which was determined to be [-0.137, 0.2982] when comparing active *in situ* measurements to NO_2 concentrations determined with passive samplers utlising the previous scaling factor and [-0.137, 0.2982] when relating active measurements to NO_2 concentrations determined with the new scaling factor for passive samplers. This suggests no substantial statistical bias between the measurements, while no consistent overestimation or underestimation is evident. The precision tests for NO_2 levels derived with the previously used

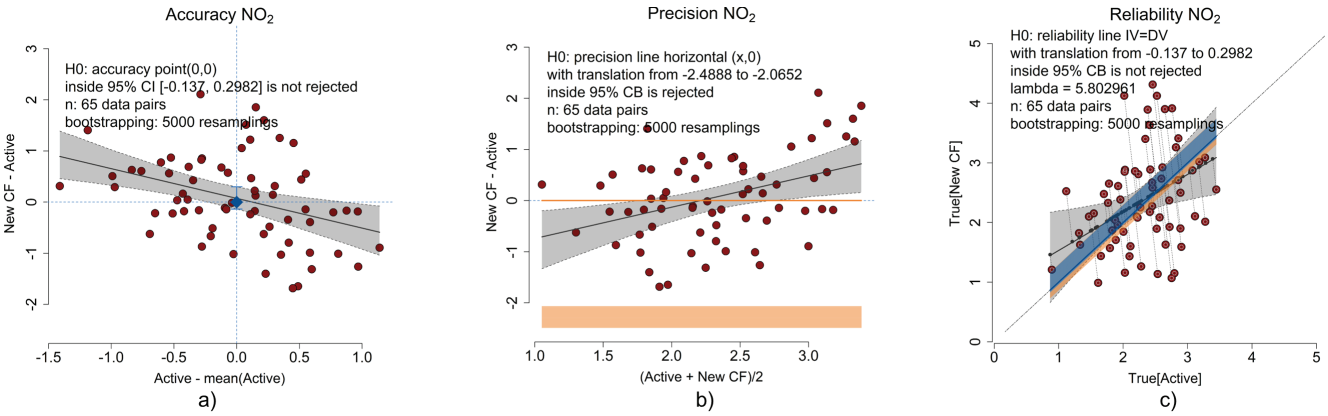

Figure 9: *Similarity of a) accuracy, b) precision, and c) reliability for active in situ NO_2 measurements in relation to NO_2 concentrations determined with passive samplers utilising the new scaling factor obtained using 5×10^3 bootstrap iterations.*

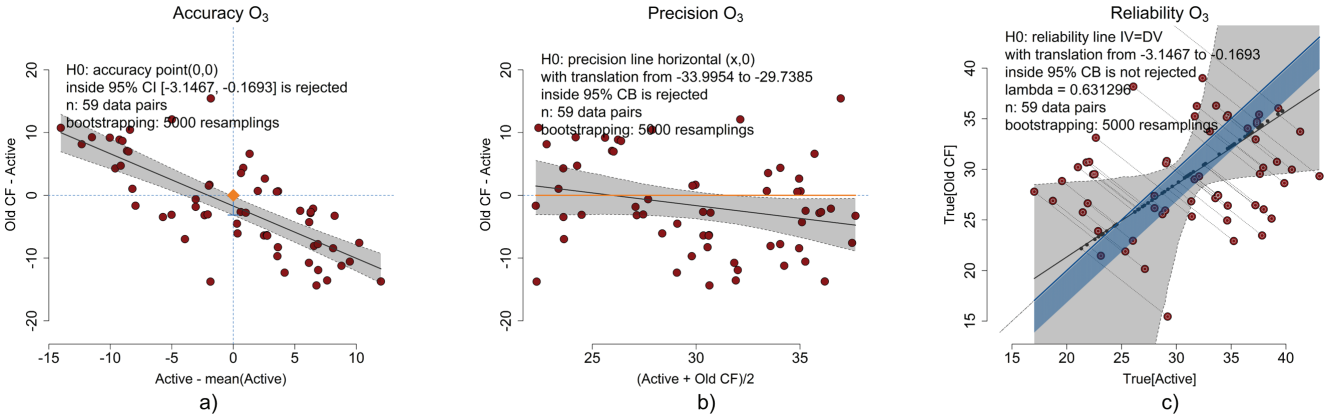

Figure 10: *Similarity of a) accuracy, b) precision, and c) reliability for active in situ O_3 measurements in relation to O_3 concentrations determined with passive samplers utilising the previously used scaling factor obtained using 5×10^3 bootstrap iterations.*

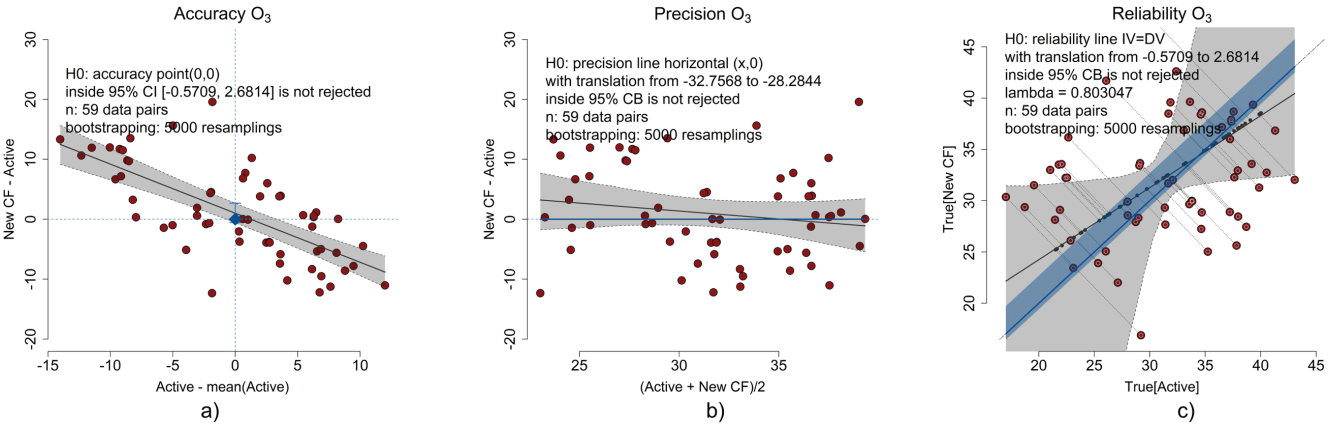

Figure 11: *Similarity of a) accuracy, b) precision, and c) reliability for active in situ O_3 measurements in relation to O_3 concentrations determined with passive samplers utilising the new scaling factor obtained using 5×10^3 bootstrap iterations.*

scaling factor (Figure 8b) and the new scaling factor (Figure 9b) indicated that the horizontal precision (x, 0) lines were outside the 95% confidence ranges, which therefore also rejects the null hypothesis of precision equivalency. Signifiicant reliability is evident when relating active NO_2 data to NO_2 concentrations derived from passive samplers utilising both scaling factors, as is evident from Figure 8c and Figure 9c. The bisector line resides within the 95% confidence intervals, which is indicative of strong reliability and statistical significance between the NO_2 concentrations derived from passive samplers utlising the previously used and newly determined scaling factors compared to active *in situ* measurements.

The accuracy, precision and reliability tests determined for O_3 levels determined with the different sampling techniques are presented in Figure 10 and 11. The (0,0) point for O_3 concentrations calculated with the previous scaling factors lies outside the 95% confidence interval of [-3.1467, -0.1693],

which suggests a statistically significant negative bias, i.e. underestimation of O_3 levels. compared to the active *in situ* method. O_3 levels determined with the new scaling factor showed strong agreement with active *in situ* measurements and resided within the 95% confidence interval of [-0.05709, 2.6814], which reveals no significant bias. No consistent overestimation or underestimation is also evident. The precision tests for O_3 concentrations calculated with the previously used scaling factor and indicated that the horizontal precision (x, 0) lines were outside the 95% confidence range, which therefore refuted the null hypothesis of precision equivalency. However, the precision of passive O_3 concentrations determined with the new scaling factor was within the 95% confidence range, i.e. statistically equivalent. The bisector line representing perfect agreement resides within the 95% confidence intervals in both instances, indicating strong reliability between the O_3 concentrations derived from passive samplers utilising the previously used and newly determined scaling factors in relation to active *in situ* measurements.

Conclusion

In this study the performance of SO_2, NO_2 and O_3 passive samplers were assessed through comparison with active *in situ* measurements of these species conducted at Welgegund from 2012 to 2018, as well as, if required, to update scaling factors used in the calculations of concentrations of these species determined with passive samplers. Excellent data coverage, i.e. 85.9%, 91.6% and 83.1%, for SO_2, NO_2, and O_3, respectively was achieved for the six-year sampling period given laboratory and field sampling procedures followed to ensure high-quality data, while statistical analyses successfully identified outliers. Scaling factors established in this study for SO_2, NO_2 and O_3 passive samplers in relation to active *in situ* measurements were 0.9, 1.7 and 1.4, respectively. These correlations were in the same order as previously determined correction factors with marginal differences. The Kruskal-Wallis test and post hoc analysis revealed improved correlation between passive data derived from the new scaling factors and active *in situ* measurements compared to the correlation between active data and levels determined with passive samplers with the previously used scaling factors. The Bland-Altman analysis also indicated improvements in terms of accuracy, precision and reliability when utilising the new scaling factors. It is recommended that future studies in which SO_2, NO_2 and O_3 are measured with these passive samplers use the new scaling factors derived in this work. It is also suggested that future comparison studies are conducted in other environments e.g. in regions with typically higher concentrations of these gaseous species.

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Author contributions

CXIG, PGvZ, KJ and SS were the main investigators in this study and wrote the manuscript. CXIG conducted this study as part of her PhD degree, as well as performed most of the experimental work and data processing. The project was led by PGvZ, KJ and SS, which were also study leaders of the PhD. SS assisted with analysis of passive samplers, while MJ and VV assisted with active *in situ* measurements. Conceptual contributions were made by GTF, MK and LL, while MK also gave financial support.

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Appendix

Table A1: *Data availability for the sampling period after removing outliers and data for months for which no active measurements were conducted.*

Gaseous species	Total number of samples collected	Total number of outliers	Total number of samples retained	Percentage of samples retained
SO_2	71	10	61	85.92%
NO_2	71	6	65	91.55%
O_3	71	12	59	83.10%

Table A2: *r_s and p-values determined from Spearman's correlations between uncorrected passive data and active in situ measurements.*

Gaseous species	r_s value	p-value
SO_2	0.792	0.000
NO_2	0.284	0.022
O_3	0.220	0.095

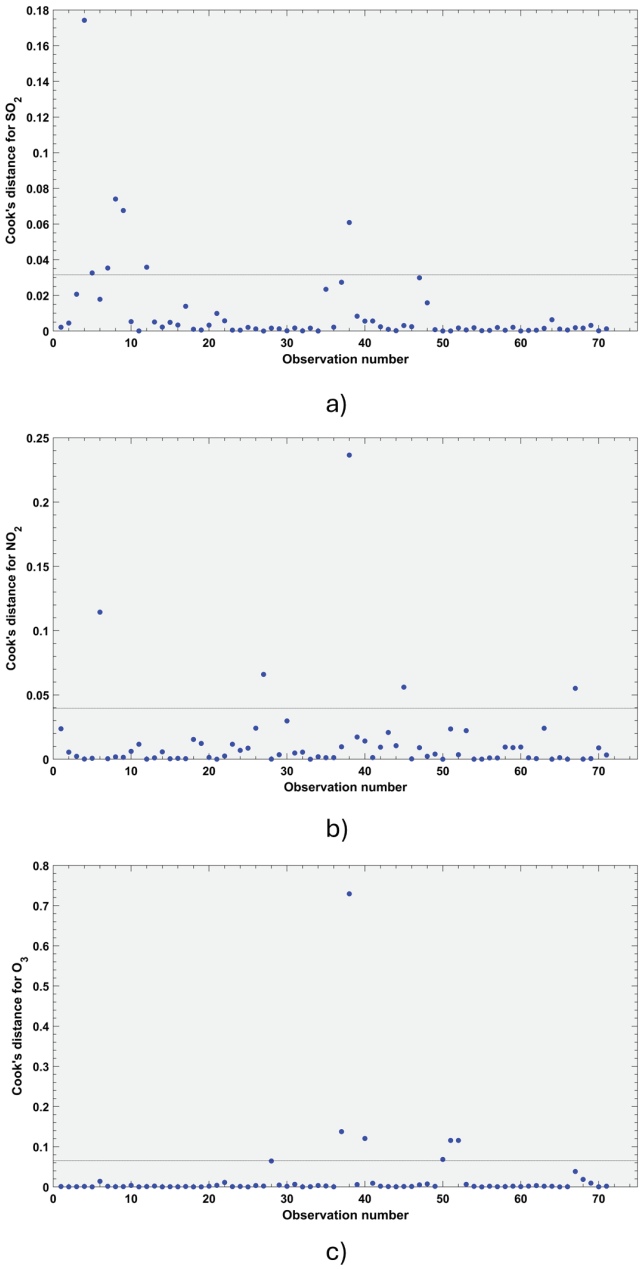

Figure A1: *Cook's distance calculated for concentrations determined for a) SO_2 b) NO_2 and c) O_3, with passive and active samplers together with the heuristic threshold indicated with a black dotted line.*