Comparison of Several Methods for Nitrogen Dioxide and Sulfur Dioxide in Metro Manila Air

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Date submitted: September 7, 2005; Date accepted: June 23, 2006

ABSTRACT

The pollutant gases nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) are two of the commonly monitored parameters for air quality assessment in the Philippines. In this study, several active and passive sampling methods for the analysis of the two gases were tested. Of the methods for NO_2 first tested indoors, the NaI sorbent passive sampling method was found most promising and was tested for ambient air NO_2 (using both Ferm and Korean passive samplers) against a collocated automated chemiluminiscence sampler. For SO_2, ambient levels were simultaneously measured using NaOH sorbent in a Ferm passive sampler and a collocated automated fluorescence sampler. Correlation and t testing indicate a positive bias for the NO2 Ferm method and a negative one for the SO_2 Ferm method in comparison with their corresponding automated methods. The results of the study support the 1997 annual average SO_2 and NO2 findings of a UP Natural Sciences Research Institute (NSRI) study (Quirit et al, 1999) which used Ferm passive samplers in various Department of Environment and Natural Resources (DENR) Metro Manila air sampling stations.

Key words: NO_2, SO_2, passive samplers, chemiluminiscence sampler, fluorescence sampler

INTRODUCTION

Nitrogen dioxide (NO_2) and sulfur dioxide (SO_2) play important roles in ecosystem acidification (Nishikawa, 2004). These gases are two of the air pollutants commonly monitored to assess air quality in the Philippines. The others are Total Suspended Particulates (TSP), Particulate Matter less than 10 um diameter (PM10), ozone, carbon monoxide and lead (Environmental Management Bureau (EMB), 1990).

Metro Manila (MM) data for ambient air pollutants are usually presented as levels versus time to show annual trends. For NO_2 and SO_2, data from 1975 to the present have been reported. However, the methods used for sampling and analysis of these two gases differ within this time period, introducing an uncertainty when trends are analyzed. Table 1 enumerates these different methods and the corresponding year(s) each was used, together with the institutions that did the sampling and analysis.

This study compared different sampling and analysis methods for NO_2 and SO_2, using both passive and active samplers and indoor and ambient sites. In 1998, a similar study was done with a fewer number of

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methods and samples, for NO_2 in an indoor site and SO_2 in a vehicular loading and unloading campus site (Quirit et. al., 2002). The availability of automated monitoring samplers in 2003 made possible the collection of a greater number of samples in an ambient sampling site for both gases. Four general methods used for past and present MM NO_2 and SO_2 data collection were used in this study. These are: passive sampling, manual active sampling to a sorbent, and automated active chemiluminiscence and fluorescence methods. The results could provide a significant basis for relating some of the past and present MM data for NO_2 and SO_2 in ambient air.

MATERIALS AND METHODS

A variety of active and passive sampling methods for NO_2 were first tested in the indoor laboratory air of the UP NSRI Room 238. Past studies have shown that indoor and outdoor NO_2 levels were generally comparable (Quirit et. al 2002, Quirit et. al. 1999). These methods were compared to the standard manual active method accepted by DENR, the Griess-Saltzman Method (Lodge, 1989a). All NO_2 methods tested for indoor air resulted in the same colored Griess-Saltzman analyte which was measured by visible light absorption at 540 nm. The best method was chosen for ambient air sampling and the results compared with the automated chemiluminiscence sampler results for NO_2. For SO_2, indoor levels were generally lower than ambient levels (Quirit et. al. 2002, Quirit et. al. 1999) so only ambient samples were taken, using the Ferm method for SO_2 (Ferm, 1991). The results were compared with the automated fluorescence sampler results for SO_2. The sampling site for ambient samples was the Manila Observatory grounds, situated at the Ateneo de Manila University Campus, Loyola Heights, Quezon City.

Period (Institution)	NO₂ Method	SO₂ Method
1975 - 1983 (NPCC)	automated air sampler from Japan (EMB 1990, EMP 1996)	automated air sampler from Japan (EMB 1990, EMB 1996)
1986-1996 (DENR-NCR)		manual sampler (TCM bubblers) (EMB, 2003)
1991-1992 (ADB and EMB-DENR)	automated chemiluminiscence monitor (ADB, 1992)	
1996-1998 (UP NSRI and DENR-NCR)	passive (Ferm) sampler with NaOH/NaI sorbent (Quirit et. al. 2002, Quirit et. al. 1999, Ferm 1991)	passive (Ferm) sampler w/ NaOH sorbent (Quirit et. al. 2002, Quirit et. al. 1999, Ferm 1991)
1996-2002 (JSPS and JICA w/ NCTS)	Japanese passive sampler w/ Griess-Saltzman sorbent (ICA 1999, JSPS 1998, Teodoro 1996)	
2003 (KFEM)	Korean passive sampler w/ TEA sorbent (Lee, 2002)	Korean passive sampler w/ sorbent[a] (Lee 2002)
2004-2005 (*DENR-NCR)	automated chemiluminiscence monitor (USEPA, 1996)	automated fluorescence monitor (USEPA, 1993)

Table 1. Metro Manila NO₂ and SO₂ Methods (Quirit et. al., 2005)
[a]sorbent not given in reference
NPCC - National Air Pollution Control Commission, DENR-NCR - DENR National Capital Region, ADB - Asian Development Bank, JSPS - Japan Society for the Promotion of Science, JICA - Japan International Cooperation Agency, NCTS - National Center for Transportation Studies, KFEM - Korean Federation for Environmental Movement

NO$_2$ Determination Methods

Standard Active Sampler Griess-Saltzman Method (Lodge, 1989a)

Ten mL of the Griess-Saltzman absorbing solution was pipetted into a dry fritted impinger (SKC 4225) attached to an air sampling pump (SKC 224-PCXR4). Flow rate was set to 0.4 L/minute (LPM), with the sampling duration varied from at least about 8 h to at most 24 h. At the end of the sampling period, the resultant pink-colored solution was transferred to a vial and analyzed immediately.

Calibration standards of NaNO$_2$ equivalent to 0, 0.08, 0.16, 0.24, 0.40 and 0.56 μL NO$_2$/mL absorbing solution were used to determine the NO$_2$ level in the samples. The absorbances were read in a UV-VIS spectrophotometer at a wavelength of 540 nm.

NaI-Ferm Passive Sampler Method (Quirit et. al. 2002, Ferm 1991)

NaI-NaOH-methanol coating solutions were made fresh for each batch preparation of Ferm samplers. Fifty μL of this coating solution were pipetted onto paper filters (Whatman 40) loaded in the partially assembled samplers. The samplers are described in the reference for the method (Ferm, 1991) and in a previous publication (Quirit et. al, 2002).

The assembled samplers were then kept in a refrigerator inside polythene storage containers before and after exposure. Sampling durations ranged from at least 1 week to at most 1 month (4 weeks), wherein the samplers were taken out of storage and attached to frisbees secured on top of 1.83 m (6 ft) poles.

Prior to analysis, the paper filters were transferred into vials and extracted with 5 mL ultrapure water. Five-mL standards (0, 5, 10, 20, 40, 60, 80 μM NaNO2) were prepared and equal volumes (5 mL) of Griess-Saltzman solution were added to both standards and samples. Absorbances were read in a UV-VIS spectrophotometer (? = 540 nm) after 15 minutes.

TEA-Ferm Passive Sampler Method (Ferm 1991, Lodge 1989b)

The TEA (triethanolamine) liquid absorber solution was prepared and used to coat paper filters, as described in the Intersociety Committee Methods of Air Sampling and Analysis (Lodge, 1989b). Samplers used were the same as those described in the NaI-Ferm Method (Ferm, 1991), except the paper filters were first dried using lint-free tissue to absorb the excess coating solution and further dried by N2 stream prior to loading into the samplers.

Five-mL standards having concentrations of 0, 0.08, 0.16, 0.24, 0.40 and 0.56 μL NO$_2$/mL were prepared. Samples were extracted with 5 mL ultrapure water and equal volumes of the Griess-Saltzman absorbing solution were added to both standards and samples. Absorbances were measured at a wavelength of 540 nm.

TEA-Korean Passive Sampler Method (Lee, 2002)

Basically the same procedures as the TEA-Ferm Sampler Method were followed for the TEA-Korean method, except for the different sampler used. The Korean sampler is made up of a small clear plastic tube (internal diameter: 10.016 mm, outer diameter 12.092 mm, height: 43.176 mm) covered by a white plastic (probably Teflon) on one end, and removable rubber caps on both ends. Whatman 40 paper filters (cut to fit inside the tube) were coated with a liquid absorber solution prepared with five times as much TEA (triethanolamine) but the same amount of butanol and ultrapure water as that used in the TEA-Ferm method. Samples were extracted with 2.0 mL ultrapure water and standards were prepared as described previously.

NaI-Korean Passive Sampler Method (Quirit et. al. 2002, Ferm 1991, Lee 2002)

Basically the same procedures as the NaI-Ferm Sampler Method were followed, except that the sampler used was the Korean passive sampler described above.

TEA-Glass Fiber Filter Active Sampler Method (Lodge 1989b, Sickles et. al. 1990)

Glass fiber filters (Sickles et. al., 1990) were soaked in liquid TEA absorbing solution (Lodge, 1989b), pressed between sheets of lint-free tissue and dried in a N_2 stream to remove any excess coating solution. Filters were then placed inside sampling cassettes (SKC 225-45). NO_2 was absorbed by pulling air with an SKC 224-PCXR4 sampling pump at 1 LPM.

After exposure, the filters were transferred into vials. Five-mL calibration standards (0, 0.2, 0.6, 1, 1.4 µg NO_2/mL) were prepared from a stock standard of 2 µg NO_2/mL and the liquid absorber solution. Samples were likewise extracted with 5 mL of the liquid absorber solution. Then, to both standards and samples, Griess-Saltzman reagents were added and the resulting pink-colored solutions were measured for their absorbances at 540 nm.

TEA-Molecular Sieve Active Sampler Method (Lodge, 1989b)

The solid absorber was prepared by soaking molecular sieve in TEA absorber solution for 30 minutes then drying in a vacuum oven at 70º C. These were then packed in a glass tube (measuring 55 cm in length and 5 mm in diameter) through which air was pumped into for 8 h using an SKC 224-PCXR4 sampling pump at a rate of 0.4 LPM.

Ten-mL calibration standards were prepared similarly to those in the Glass Fiber method while the absorbed NO2 was extracted using 50 mL of the liquid TEA absorbing solution. One mL of 0.02% (v/v) hydrogen peroxide, 10 mL sulphanilamide solution and 1.4 mL of 0.1% (w/v) (1-Naphtyl ethylenediamine dihydrochloride) NEDA solution were then added to the calibration standards and to a 10-mL aliquot of the extract, after which absorbance readings were measured at 540 nm.

Chemiluminiscence Automated Sampler Method (USEPA, 1996)

NO_x levels were measured using a Horiba APNA-360CE. NO_x is the sum of nitric oxide (NO) and nitrogen dioxide (NO_2) in a gaseous sample. Two fractions of ambient air are sampled - one has all of its NO_2 converted to NO, with the NO then made to react with ozone (O_3) to form $NO_2 + O_2$ + light. The chemiluminescence generated is therefore proportional to the NOx level. On the other hand, the other fraction is reacted with O3 immediately (without reducing NO_2 to NO) and since NO_2 is unreactive towards O_3, only the NO reacts, giving the NO level. The difference between the values from fraction 1 and 2 therefore gives the NO_2 level.

SO_2 Determination Methods

NaOH-Ferm Passive Sampler Method (Quirit et. al. 2002, Ferm 1991)

The same procedures as those for the NaI-Ferm method for NO_2 determination were followed in preparing the SO_2 samplers, except that a different coating solution, NaOH-methanol, was used. The absorbed SO_2, in the form of SO_4^{2-} ion, was analyzed by ion chromatography.

Prior to analysis, the paper filters were transferred into vials and extracted with 2.5 mL of degassed ultrapure water. Sample solutions were filtered with 0.45 µm Millipore filters to remove particles that might clog or damage the column.

Standard solutions containing 0.5, 2, 5, 10 and 20 ppm of SO_4^{2-} were prepared using degassed ultrapure water and, along with the samples, were analyzed using an ion chromatograph (Dionex Ion Chromatograph 2000i). 12.5 mM H_2SO_4 was used as a regenerant and 1.36 mM $NaHCO_3$/1.44 mM Na_2CO_3 as eluant. Eluant flow rate was set to 2 mL/minute and sensitivity to 30 µS.

Fluorescence Automated Sampler Method (USEPA, 1993)

SO_2 levels were obtained using a TEI 43C SO_2 analyzer, which gives SO_2 levels in ambient air by measuring the fluorescent electromagnetic radiation emitted by the SO_2 molecules when excited with ultraviolet light. The fluorescence emitted is proportional to the SO_2 mixing ratio in the sampled ambient air.

RESULTS AND DISCUSSION

Comparison of Methods (Indoor Air NO$_2$)

Figure 1 shows how the different methods compared with the standard Griess-Saltzman Method for NO$_2$, and with each other. The assumption for the comparison is 100 % NO$_2$ collection efficiency for the standard method.

sieve active method had the lowest average collection efficiency.

Comparison of Methods (Ambient Air NO$_2$)

For ambient NO$_2$, the NaI-Ferm passive sampling method was chosen on the basis of its performance in the indoor sampling comparison. The Korean passive sampler was also tried, but with the sorbent changed
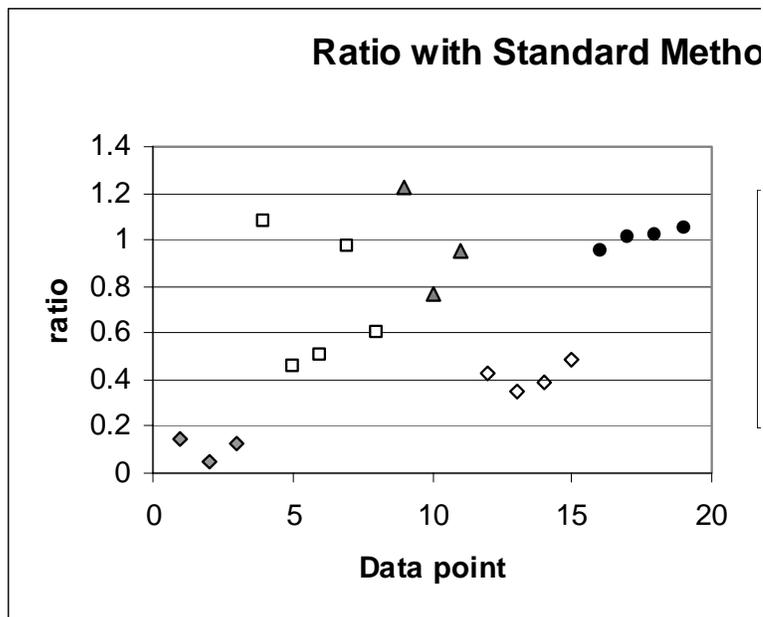
Figure 1. Comparison of Methods for Indoor Air NO$_2$ (using ratio of Method NO$_2$ level with Standard Griess-Saltzman Method NO$_2$ level) (Quirit et. al., 2005)

The NaI-Ferm passive sampler gave the best results, with all sample levels having ratios (with simultaneous standard method sample levels) close to 1, indicating approximately 100 % collection efficiency. Correlation with standard method levels gave an R = 0.9954. The TEA- Korean passive sampler method had the next average ratio value closest to 1, but had significantly lower precision for the collection efficiencies, compared to the NaI-Ferm passive sampler method. The same poor precision for the ratios is true for the TEA-Glass Fiber filter method.

TEA was also tried as a sorbent for the Ferm passive sampler. Although ratio precision and correlation with the standard method (R = 0.9644) were good, sampling efficiency (around 40 %) was low. The TEA-molecular

to the NaI-Ferm coating solution. Therefore, what was tried was the same sorbent, but in different passive sampler configurations. Sampling (one week to one month duration per sample) was from February to December, 2004. Figures 2 and 3 show how these two passive sampler types compare with the automated chemiluminiscence method for NO$_2$ in ambient air.

The regression equation for the NaI-Ferm Method, when correlated with the Chemiluminiscence Method (without forcing the intercept to zero), gives a slope of 0.9763 and an intercept, 0.0015 ppm, which is about twice the average standard deviation, 0.0007 ppm, for the data points. This indicates an overall positive bias of the NaI-Ferm Method relative to the automated method. When the intercept of the correlation line is

Ambient NO$_2$
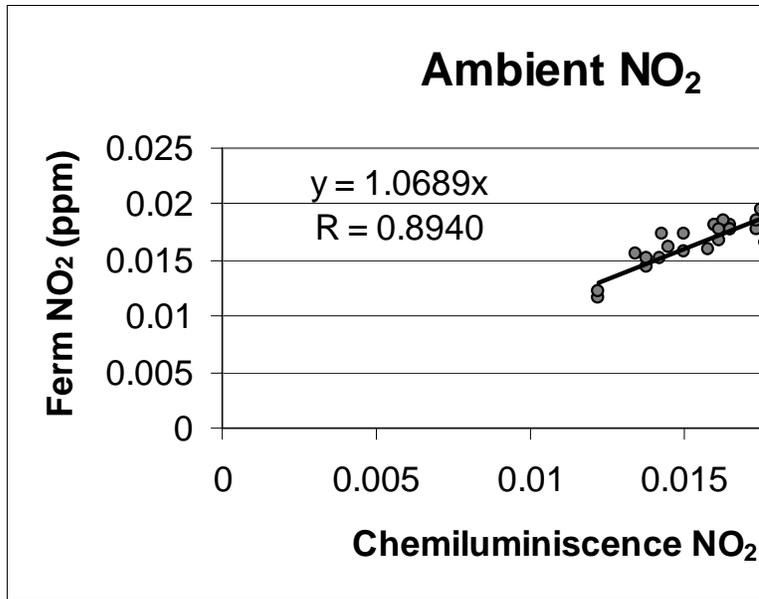
Figure 2. Comparison of NaI-Ferm Method with Automated Chemiluminiscence Method for Ambient Air NO$_2$ (N = 30 duplicate data points, Ferm sampler 4% average RSD, Chemiluminiscence Method, 2% RSD) (Quirit et. al., 2005)

forced to zero, the slope became 1.0689, as shown in Figure 2. Assuming 100% collection efficiency for the automated method, the collection efficiency of the NaI-Ferm method for NO$_2$, based on this slope, is around 107%. The correlation coefficients, 0.8981 and 0.8940

respectively, for the non-zero and zero intercept equations, are similar.

The Korean passive sampler (using TEA as coating solution) was used by a Korean Non-Government

Ambient NO$_2$
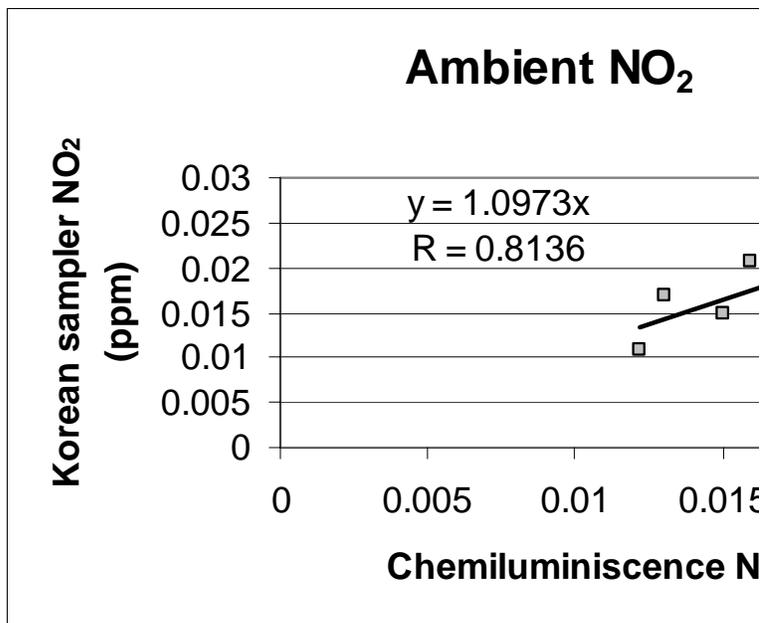
Figure 3. Comparison of NaI-Korean Sampler Method with Automated Chemiluminiscence Method for Ambient Air NO$_2$ (N = 6 data points) (Quirit et. al., 2005)

Organization (NGO), the Korean Federation for Environmental Movement (KFEM), in cooperation with a Philippine NGO, the Concerned Citizens Against Pollution (COCAP), plus students and teachers, grass-root NGO activists and some local government officials (Lee, 2002). They collected 24 h NO_2 air samples in various locations in Metro Manila from January 18 to January 19, 2002. The authors of this study used the sampler, but with a different coating solution (NaI/NaOH) as mentioned in the methodology above. Interest in the sampler was due to its simple configuration, plus its use for recently collected data by KFEM.

Data points were considerably less for the NaI-Korean Sampler Method, since the authors procured only one sampler from the local NGO, Concerned Citizens Against Pollution (COCAP), which participated in the above mentioned exercise. Duplicate data points could not be acquired, hence the absence of an average RSD. KFEM reports the sampler's precision as 9.6 % RSD. The regression equation for the NaI-Korean sampler, when correlated with the chemiluminiscence method (without forcing the intercept to zero), gives a slope of 1.2032 and an intercept of -0.0017 ppm, which is similar

in magnitude to the NaI-Ferm intercept. Results shown in Figure 3, when the intercept is forced to zero, indicates approximately 110% NO_2 collection efficiency, relative to the chemiluminiscence method. The correlation coefficients, 0.8168 and 0.8136 respectively, for the non-zero and zero intercept equations, are similar.

Comparison of Methods (Ambient Air SO_2)

For ambient SO_2, the NaOH-Ferm passive sampling method was compared to the automated fluorescence method, and the results are shown in Figure 4. Sampling (one week to one month duration per sample) was from February to December, 2004. Only 21 duplicate data points are shown, since some of the samples were analyzed by $BaSO_4$ turbidimetry (instead of by ion chromatography). The turbidimetric method performed poorly, in terms of precision, compared to ion chromatography. The standard active manual method accepted by DENR uses a mercury compound (tetrachloromercurate or TCM) in the sorbent. This method was not used due to its being both cumbersome and toxic.

Ambient SO_2

$y = 0.8404x$
$R = 0.8477$
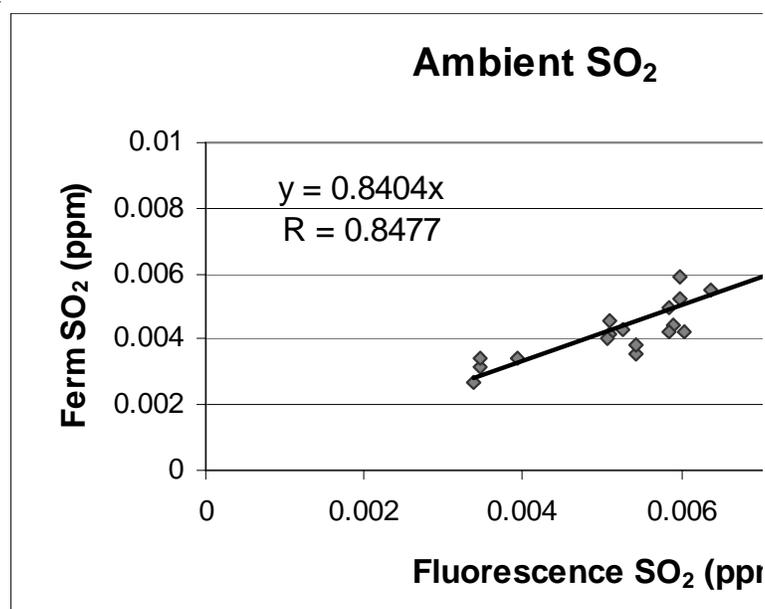
Figure 4. Comparison of NaOH-Ferm Method with Automated Fluorescence Method for Ambient Air SO_2 (N = 21 duplicate data points, Ferm sampler 8% average RSD, Fluorescence Method 1% RSD) (Quirit et. al., 2005)
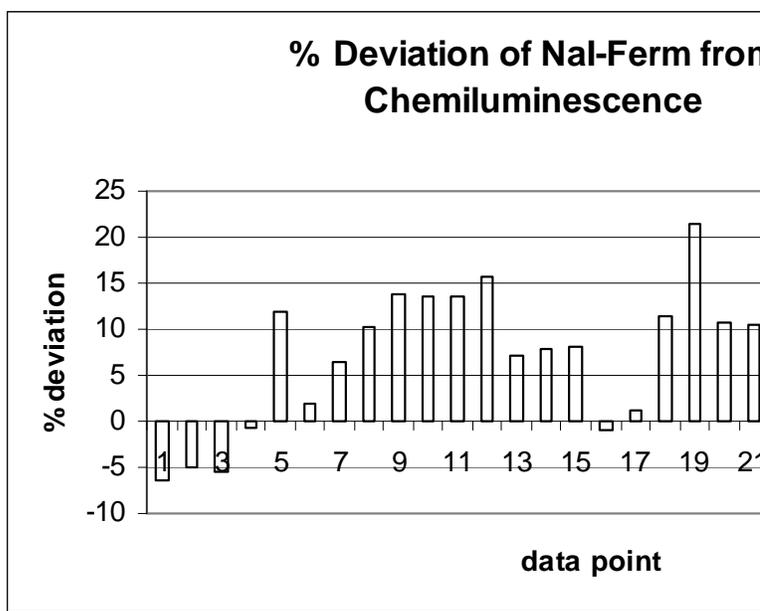
Figure 5. % Deviation for NO_2 [[(NaI-Ferm data - chemiluminiscence data)*100/chemiluminiscence data)] (Quirit et. al., 2005)

The regression equation for the NaOH-Ferm Method, when correlated with the fluorescence method (without forcing the intercept to zero), gives a slope of 0.8479 and an intercept, -0.1008 ppm, the absolute magnitude of which is higher than the average standard deviation, 0.0019 ppm, for the data points. This indicates an overall negative bias of the NaOH-Ferm Method relative to the automated method. When the intercept of the correlation line is forced to zero, the slope became 0.8404, as shown in Figure 4. Assuming 100% collection efficiency for the automated method, the collection efficiency of the NaOH-Ferm method for SO2, based on this slope, is around 84%. The correlation coefficients, 0.8479 and 0.8477 respectively, for the non-zero and zero intercept equations, are similar.

t Test

Aside from correlation with the automated methods, the t test was also used to find out if there is a statistical difference between the results obtained using the passive sampler and the automated methods (Christian, 2004). For both NO_2 and SO_2, the passive sampler method was considered the *test* method, and the automated method was the *accepted* method. The two automated methods use calibration gases (USEPA 1996, USEPA 1993), while passive sampler levels were calculated from the dimensions of the sampler and

Fick's first law, a theoretical diffusion equation (Quirit et. al. 2002, Ferm 1991). The results are shown in Table 2. The number of degrees of freedom, other than 8, in the t table was only up to 25, so the calculated *t* was done overall (30 data points or 29 degrees of freedom) and per set of 6 data points (5 degrees of freedom) for NaI-Ferm NO_2. This was also to compare with the 6 data points of the NaI-Korean sampler.

The *t* test results (magnitude of $t_{calculated}$ > magnitude of t_{table}) confirm the positive bias (107% collection efficiency) for the NaI-Ferm method for NO_2, and the negative bias (84% collection efficiecy) for the NaOH-Ferm method for SO_2, compared to the automated methods. The opposite result (magnitude of tcalculated < magnitude of *t*table), indicating no statistical difference between the NaI-Korean sampler results and the chemiluminiscence method for NO_2 at the 95% confidence level, is true for the small number of data points collected. This is also true, however for the first 6 data points of the NaI-Ferm method for NO_2.

Figures 5 and 6 further illustrate the biases for the Ferm passive sampler methods, using % deviations from the automated sampler results. The results were compared to deviations of the Ferm passive samplers (one month samplings) from parallel 24 h active sampler data in Sweden (Ferm, 1991).

In this study, around 77 % of the data points have NO_2 levels greater than the automated chemiluminiscence levels, 10 % have levels close to the automated method levels, and 3 % have levels lower than chemiluminiscence levels, as seen in Figure 5. This is similar to the Sweden results, where 67 % of the approximately 48 data points had levels above the active sampler levels, and the rest of the data points were about equally distributed between those close to and those below active sampler levels (Ferm, 1991).

Figure 6 shows that around 80 % of the data points have SO_2 levels below the automated fluorescence levels, 10 % have levels close to the automated method levels, and 10 % have levels higher than fluorescence levels. This is again similar to the Sweden results, where 65 % of the approximately 46 data points had levels below the active sampler levels, 11 % close to and 24 % above active sampler levels (Ferm, 1991).

The active sampler NO_2 method done in Sweden used sintered glass filters impregnated with the same sorbent (KI) for NO_2 as the passive samplers, while the active impinger method (with 0.03% H_2O_2) was used for comparison with the SO_2 Ferm passive samplers (coating solution is K_2CO_3). The coating solutions used in Sweden are chemically similar to those used in this study (NaOH is quickly transformed to Na_2CO_3 when exposed to CO_2 in air) for the passive samplers. It is interesting to note that even for the same NO_2 sorbent used in the active and passive samplers in Sweden, the positive bias was observed for NO2 in ambient air, for the passive relative to the active samplers. Precisions of the Ferm samplers in this study, 4% and 8% RSD respectively for NO_2 and SO_2, are similar to precisions (5% and 10% RSD respectively for NO_2 and SO_2) of the Ferm sampler in the Sweden study.

No explanation, as of now, could be offered for the higher levels predominantly observed for NO_2 passive samplers, relative to the active automated chemiluminiscence method levels. A passive sampler reported in NIOSH 6700 method for NO_2 (NIOSH, 1984) gave results for a field study (ambient air) where the passive sampler levels were $109 \pm 9\%$ of the reference method (Jones et. al., 1979). This is similar to the $107 \pm 5\%$ results for the Ferm NO_2 sampler in this study. For SO_2, it is postulated that part of the sorbed SO_2 was not transformed to SO_4^{2-}, but remained as SO_3^{2-}, hence the seemingly lower collection efficiency of the passive sampler compared to the automated fluorescence sampler. The corresponding author is currently part of a research where SO_3^{2-} ions are analyzed by a method called pervaporation.
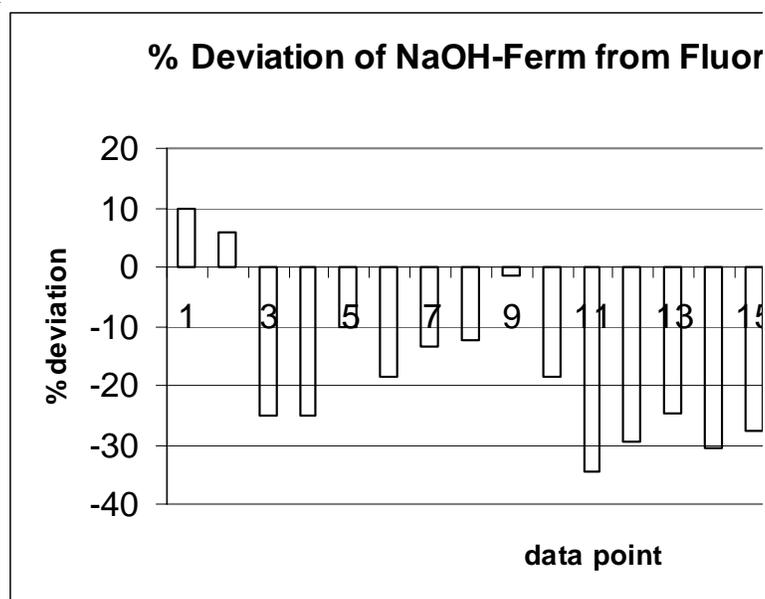
Figure 6. % Deviation for SO_2 [[(NaOH-Ferm data - fluorescence data)*100/fluorescence data)] (Quirit et. al., 2005)

Preliminary results using this method on the NaOH-Ferm sampler extracts show the presence of SO_3^{2-} ions in the samplers exposed to ambient air.

CONCLUSION

Ferm Passive sampler NO_2 and SO_2 levels in ambient air of the Manila Observatory were found to be positively and negatively biased, respectively, relative to automated chemiluminiscence NO_2 and automated fluorescence SO_2 levels. No explanation, as of now, could be found for the positive NO_2 bias. Incomplete oxidation of the sorbed SO_2 in the basic sorbent of the Ferm passive sampler is postulated to be the reason for the sampler's negative SO_2 bias. This is due to the nature of the analytical method used for oxidized SO_2, which analyzes the fully oxidized form (SO_4^{2-}), but not the the partially oxidized SO_3^{2-} form. This systematic error can be remedied by fully oxidizing the sorbed SO_2 prior to analysis by addition of H_2O_2. An alternative remedy is analyzing the sampler extract for both SO_3^{2-} and SO_4^{2-} ions.

The results of the study support the 1997 annual average SO_2 and NO_2 findings in a UP NSRI study using Ferm passive samplers in various DENR Metro Manila air sampling stations (Quirit et al, 1999). Two sites (Taft and Valenzuela) exceeded annual average SO_2 standards (84 and 86 ug/m³ respectively compared to the annual SO_2 national standard of 77 ug/m³). The 1997 average levels would even be higher if the negative bias of the Ferm SO_2 sampler is true. On the other hand, all sites were found to have 1997 annual NO_2 average levels below the national annual standard (150 ug/m³). The average levels would be even lower if the Ferm NO_2 sampler positive bias is considered.

In spite of limited results, the simplicity of the Korean passive sampler makes it a good candidate for relatively cheap local fabrication. The Ferm sampler configuration is more complicated (Quirit et. al. 2002, Ferm 1991) and local plastic mold manufacturers have quoted quite a steep price for its fabrication (> P200,000.00 for the mold). The Korean NGO have not replied as to the material of their sampler, but the configuration does not have the stainless steel mesh nor the precisely molded parts of the Ferm sampler, hence the preliminary

assessment of its cheaper fabrication, compared to the Ferm sampler. Once the molds are made, however, production of the samplers is projected to be relatively cheap, according to the plastics mold manufacturers (they did not quote actual prices, but projected less than P100 per sampler). Passive samplers are lightweight, convenient to use and does not need expensive pumps and electricity. Imported passive samplers, however, are also quite expensive (around four times projected local price, once the mold is made). It would be good to be able to fabricate and study various configurations of locally produced passive samplers.

ACKNOWLEDGEMENTS

REFERENCES

Asian Development Bank, 1992. Vehicular Emission Control Planning in Metro Manila Final Report.

Christian G.D., 2004. Analytical Chemistry, 6th ed. USA, John Wiley & Sons: 90-97pp.

Environmental Management Bureau, 2003. 2002 National Air Quality Status Report.

Environmental Management Bureau, 1990. The Philippine Environment in the Eighties.

Environmental Management Bureau, 1996. The Philippine Environmental Quality Report, 1990-1995.

Ferm M., 1991. A Sensitive Diffusional Sampler. Goteborg 1991-03-13. Swedish Environmental Research Institute, pp. 1-27.

Japan International Cooperation Agency, 1999. Metro Manila Urban Transportation Integration Study (MMUTIS) Final Report.

Japan Society for the Promotion of Science, 1998. JSPS-NCTS Air Pollution Survey Using Filter Badge in Metro Manila.

Jones W., E.D. Palmes, C. Tomczyk & M. Millson, 1979. Field Comparison of Two Methods for the Determination of NO_2 Concentration in Air. Am. Ind. Hyg. Assoc. J. 40:437-438.

Lee J-H., 2002. A Fundamental Survey Using Passive Samplers for the Establishment of Air Pollution Monitoring System in Metro Manila, Philippines. Korean Federation for Environmental Movement (KFEM), pp. 64.

Lodge J.P. (ed.), 1989a. Method 406: Determination of the Nitrogen Dioxide Content of theAtmosphere (Griess-Saltzman Reaction). In Methods of Air Sampling and Analysis, 3rd ed. Intersociety Committee (APCA, ACS, AIChE, APWA, ASME, AOAC, HPS, ISA). Michigan, USA, Lewis Publishers Inc.: 389-393pp.

Lodge J.P. (ed.), 1989b. Method 818: Determination of Nitrogen Dioxide in Air.). In Methods of Air Sampling and Analysis, 3rd ed. Intersociety Committee (APCA, ACS, AIChE, APWA, ASME, AOAC, HPS, ISA). Michigan, USA, Lewis Publishers Inc.: 601-603pp.

National Institute for Occupational Safety and Health, 1984. Nitrogen Dioxide: Method 6700. NIOSH Manual of Analytical Methods, 3rd ed. Vol. 2. Cincinnati, Ohio: US Dept. of Health & Human Services.

Nishikawa, Y., 2004. Simultaneous Measurement of Nitric Acid, Sulfur Dioxide and Ammonia in Air using a Passive Sampling Polyamide Filter. *J Envi Chem* 14(2):351-355.

Quirit L.L., E.C. Llaguno, P.C.B. Pabroa, F.B.B. Bello, B.P. Gonzales, 2002. Comparison of Methods for Ambient Air Sulfur Dioxide and Nitrogen Dioxide. Kimika 18(1):19-22.

Quirit L.L., E.C. Llaguno, B.P. Gonzales, F.B.B. Bello, P.C.B. Pabroa, 1999. Acid Gases and Acidic Particulate Species in Metro Manila Air. *Proceedings of the 15th Phil Chem Congress,* pp. 130-133.

Sickles J.E., P.M. Grohse, L.L. Hodson, C.A. Salmons, K.W. Cox, A.R. Turner & E.D. Estes, 1990. Development of a Method for the Sampling and Analysis of SO_2 and NO_2 from Ambient Air. Anal Chem 62:338-346.

Teodoro R.V., 1996. Empirical Analysis on the Relationship Between Air Pollution and Traffic Flow Parameters, M.S.C.E. Thesis, College of Engineering, University of the Philippines.

USEPA, 1996. Automated Reference Method #RFNA-0196-111. *Federal Register* 61:11404.

USEPA, 1993. Automated Equivalent Method #EQSA-0193-092. *Federal Register* 58:6984.