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REPORT ON PASSIVE SAMPLERS for ATMOSPHERIC CHEMISTRY MEASUREMENTS and their ROLE in GAW

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FOREWORD

This report addresses passive samplers and their possible uses within the GAW programme. This report was prepared by Professor Gregory R. Carmichael, from the University of Iowa, USA, during his stay at WMO from January through July, 1997. The discussion draws heavily on the work of Dr. Martin Ferm, IVL, Sweden, one of the pioneers in the use of passive samplers for ambient monitoring. Passive samplers provide a simple and cost effective way of monitoring specific species at urban, regional and global scales, and offer broad capacity building opportunities. Current developments and studies indicate that passive samplers are now a viable option for many monitoring applications. There appears to be a valuable role for the use of passive samplers in the GAW programme, and this is the focus of this discussion paper.

PASSIVE SAMPLERS FOR ATMOSPHERIC CHEMISTRY MEASUREMENTS AND THEIR ROLE IN GAW

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1. BACKGROUND

GAW is a co-ordinated network of observing stations and related facilities whose purpose and long-term goals are to provide data, scientific assessments, and other information on changes in the chemical composition and related physical characteristics of the background atmosphere from all parts of the globe. This information is required to improve understanding of the behaviour of the atmosphere and its interactions with the oceans and the biosphere and to enable prediction of future states of the earth-atmosphere system.

The GAW programme began in 1989 as a consolidation of the former WMO atmospheric chemistry monitoring programmes started in the 1950s. The implementation of GAW has been very successful. So far the programme has established over 20 new regional and global stations in areas where data was sparse or non-existent, strengthened its calibration activities, data archival capabilities, and the quality of its data through the establishment of three Quality Assurance/Science Activity Centres and six World Data Centres, and improved the technical expertise within the programme through technology transfer and capacity building efforts including sponsored workshops and training classes. Presently, - 80 member countries are participating in GAW's measurement programme. A quarter of them are establishing or operating global stations (partly with support from other members or international organisations), which comprise a global network of precise and long term measurements.

However, the GAW programme faces many challenges. GAW represents an effort of unprecedented complexity in the field of environmental measurement and assessment. It is trying to make state-of-the-science measurements of a large number of mostly low concentration chemical and physical constituents of the atmosphere at levels extending from the surface to the stratosphere and at some of the most difficult locations on Earth. GAW also finds itself being asked to take on larger roles in other important activities such as transboundary pollution, accidental release, and air quality and urban pollution.

Clearly, monitoring activities are at the heart of the GAW programme. However the realities are that monitoring activities, regardless of whether they are in developed or developing countries, are expensive and face various pressures. In developed countries the monitoring needs and priorities are constantly changing, making it difficult to both maintain long term measurement programmes and to expand activities.

The developing countries face a somewhat different problem. Often times efforts to develop and implement environmental management strategies in the developing regions are severely hampered by the lack of information on the present condition of the atmospheric environment. Countries throughout the developing world are faced with severe local air pollution problems while at the same time asked to respond to global and regional environmental problems such as global warming, stratospheric ozone destruction, and acid deposition. Often times these countries address these issues in the absence of the requisite observational data on air quality and emissions that would enable them, based on the present situation and observed country-specific trends, to prioritise their environmental programs.

One of the main challenges for GAW is to balance the needs of global-scale issues, with regional and urban concerns. Another major challenge is how to accomplish the desires to expand GAW monitoring activities to include measurements for each principal climatic zone and each major biome (some 30 global stations), and to add important species to the measurement list at GAW stations (e.g., NMHCs, aerosols, etc.).

Passive samplers present a means of addressing many of these issues in atmospheric chemistry monitoring, in that they provide a simple and cost effective way of monitoring specific species at urban, regional and global scales, and offer broad capacity building opportunities. While the appropriateness of the use of passive samplers has been questioned in the past due to concerns related to reliability and accuracy, current developments and studies indicate that passive samplers are now a viable option for many species and many applications.

There appears to be a valuable role for the use of passive samplers in GAW, and this is the focus of .this discussion paper. This paper begins with a general discussion of the basic principals behind passive samplers (Section 2). Specific details are then presented for a variety of species, including filter preparation, analysis and performance (Section 3). The use of passive samplers in various monitoring programmes is discussed in Section 4. The report concludes with a discussion of the potential uses of passive samplers in GAW (Section 5) and a set of proposed activities (Section 6).

2. BASIC PRINCIPLES

The sampling technique is based on the property of molecular diffusion of gases, hence the term passive (also referred to as diffusive) sampling. The gas molecules diffuse into the sampler where they are quantitatively collected on an impregnated filter or an absorbent material. Thus they achieve a time-integrated (or average) concentration. No electricity, pumps or other supporting equipment are needed.

Inorganic gases are absorbed by chemical reaction on a filter, impregnated with a solution specific to each pollutant measured. The reaction product, which is washed out of the filter prior to analysis, is specific to the particular gas in question. When species do not react sufficiently fast with other chemicals (e.g., organics) they are instead trapped on an absorbent material. Such gases are then desorbed from the adsorbent during analysis.

A passive sampler is a very simple device consisting of an impregnated filter or molecular sieve which preferentially sorbs the gas to be analysed, and a diffusion barrier (usually an entrapped air volume) that keeps the sampling rate constant. If the sampling efficiency is sufficiently high, then the sampling rate can be calculated using Fick's first law of diffusion from the cross sectional area perpendicular to the transport direction and the distance that the gas has to diffuse.

To work properly (and quantitatively) it is essential that the transport occurs solely by molecular diffusion and that no gas is lost to the walls of the sampler. Under these conditions then the sampling rate, and thus the concentration range of the sampler, is directly proportional to its cross sectional area and inversely proportional to its length. Furthermore, since the rate of molecular diffusion depends on temperature (through the temperature dependency of the molecular diffusivity), the average sampling rate (sorbed amount per unit time divided by the ambient concentration) is a temperature dependent constant for a given species and sampler.

Passive samplers take a variety of forms. Typical samplers in use in Sweden are presented in Figure 1. Small diameter and long (e.g., diameter 10 mm and length 50 mm) samplers (referred to as high-dose samplers) provide a higher detection limit, while wider and shorter samplers (typically, diameter of 20 mm and length of 10 mm) referred to as low-dose samplers, provide a lower detection limit. (For the same ambient concentrations the latter sampler has a 20 fold increase in sampling rate.)

Care must be taken to ensure that the gas is transported to the filter by molecular diffusion. If the inlet end of the tube is left open then convective transport can occur, resulting in a higher sampling rate and thereby an overestimation of the concentration (Ferm and Svanberg (1997), Gair and Penkett (1995) and Campbell et al. (1994)). Experiments by Ferm and Svanberg (1997) showed that covering the inlet region of the sampler with a fine mesh (stainless steel mesh with a thread diameter of 0.08 mm and mesh aperture of 0.125 mm) can minimise these errors for high-dose samplers. Low-dose samplers are more sensitive to wind effects, and porous membranes supported by steel mesh are commonly used to cover the sample inlet (Ferm and Svanberg, 1997).

Principle of Measurement

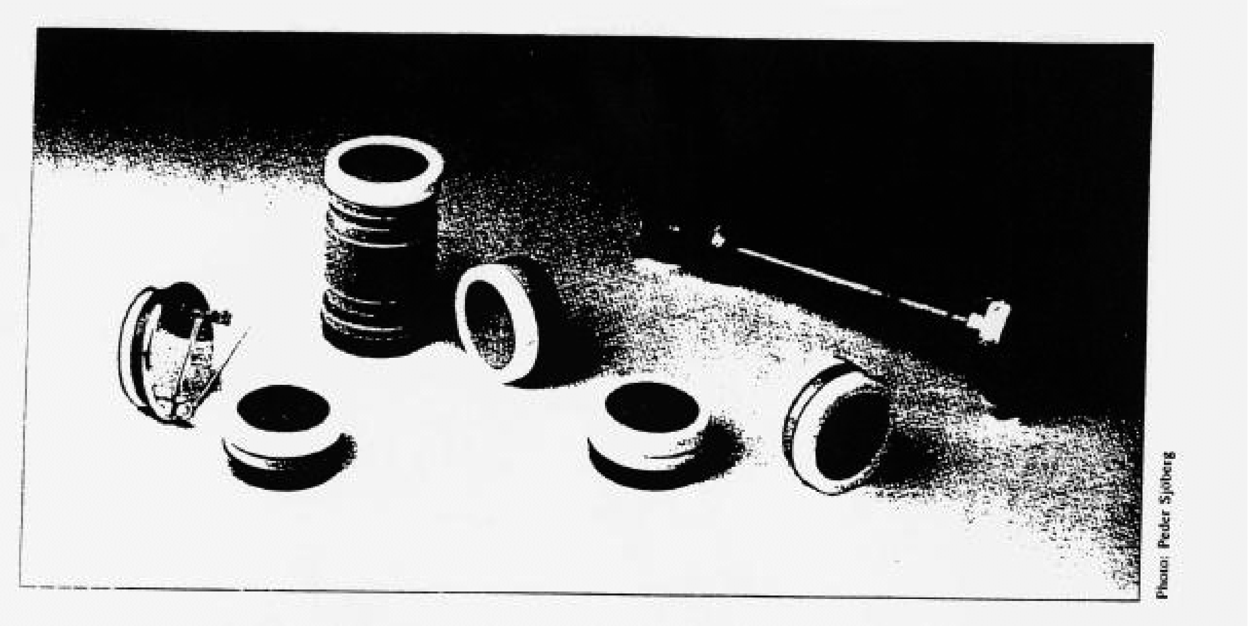


Photo: Peder Sjöberg

Figure 1. Types of passive samplers currently in use. The samplers above are for measurements of (left to right) SO_2 (two samplers), NO, NO_2, 0_3, NH_3 and NMHC. (From IVL, brochure on diffusive samplers.)

The success of a diffusion sampler rests critically on the collection efficiency of the impregnated filter. A solid and stable reagent which selectively and quantitatively chemisorbs the targeted species, and transforms it into another stable form in which other pollutants do not interfere is needed for passive samplers. This is the key factor which determines which species are suitable for passive sampling. This will be discussed in more detail later.

The average concentration at the measurement site over the time period that the sampler is exposed to ambient conditions is determined by chemical analysis of the filter. Analysis consists of removing the impregnated filter and leaching the reaction product, typically using de-ionised water. The leachate is then analysed using an appropriate analytical technique. The highest concentration that can be measured depends on the amount of sorbent on the impregnated filter. This is typically estimated by the stoiciometric amount of the impregnate reduced by a safety factor (typically a factor of 2).

The lower detection limit of the samplers is determined by the use of blanks. As soon as a filter is impregnated it will begin to measure ambient levels. A filter kept in the laboratory will measure laboratory levels, while field blanks will measure the integrated exposure during the transport and storage periods. Just before the samplers are sent to the field, the filters are impregnated, samplers labelled for batch number, a few filters checked immediately, and then filters identified for lab and field blanks. The laboratory blanks are stored in the lab and periodically tested. The field blanks are kept in their containers and accompany the samplers to the field and are returned after the filters are exposed, and are analysed along with the exposed samples. The concentrations determined from the exposed filters are then corrected using the blanks. The lower detection limit is commonly defined as 2 to 3 times the standard deviation of the blanks. Thus, procedures/improvements which reduce the standard deviation of the blanks result in significant improvements in the lower detection limits of the samplers. The repeatability of the results is quantified and checked by use of duplicate samples.

The samplers are very easy to manufacture. For example, samplers used in Sweden are produced from commercially available 50 mm long polypropylene tubes. The tubes are cut to the desired length and then fitted with a solid cap containing the impregnated filter at one end, and an open cap containing the anti-convection mesh/membrane at the inlet end (as shown in Figure 1). They are also very cheap to manufacture and all components, except the impregnated filter can be reused. They have many other advantages as well for use in the field. For example they are small, light (~2 g) , and require no electricity.

It should be emphasised that they provide time integrated concentrations with continuous time coverage, with the averaging time determined by the period they are exposed to ambient air (which can be daily, weekly, monthly, etc.). They are obviously not well suited for monitoring temporal variations over short time intervals, or for detection of individual peak values, or when real-time measurements are needed.

3 . SPECIES SPECIFIC INFORMATION

Passive samplers are being used for a variety of applications and for a variety of species. The most experience is based upon their use in the measurement of ambient SO_2, NO_2, NH_3, and NMHCs concentrations.

3.1 SO_2

The measurement of SO_2 using passive samplers utilises a NaOH impregnated cellulose filter. On the filter sulphite is oxidised to sulphate during sampling and the sulphate amount is analysed using suppressed ion chromatography. In previous measurements in Asia it was found that an extra peak close to the sulphate peak often complicated the analysis. This problem has never been observed in samples from Europe. The cellulose filters also were found to have a sulphate blank that could not be completely reduced. It was discovered that the use of a very fine stainless steel net in parallel with the impregnated cellulose filters, eliminated this .extra peak. Thus a steel net placed in the outer cap is recommended both to insure molecular diffusion, and to reduce chemical interferences. The short samplers have a measurement range of ~0.05 to 40 ppb for a sampling time of 2 months (or 0.1 to 80 ppb for monthly sampling).

The measurements made using SO_2 passive samplers have been compared with those taken using active methods (gas wash bottle, and filter pack) at both urban and regional locations as described in Ferm and Svanberg (1997). The results for a comparison of SO_2 measurements using the filter pack method and passive samplers at five EMEP stations from May '93 to January '96 are presented in Figure 2. The dynamic range of the measurements went from below detection limit to 12 $\mu g/m^3$, and the monthly mean temperatures varied from -15 to + 16°C.

Passive samplers for SO_2 have also been compared in the field during the winter of 199394 at the Virolahti (EMEP) background station in southeastern Finland (Makkonen and Juntto, 1997), where sulphur dioxide was measured using: passive samplers; a ThermoEnvironmental Instruments Inc. 43S monitor; two- and three- stage filter packs; and an absorption solution system. The passive samplers were those designed by Ferm and discussed above. The passive samplers were operated with two week and with one month exposure times, and using single (for the monthly exposures) and duplicate (for the two-week exposure) filters. The passive sampler results were found to be in good agreement with the other methods tested (median standard deviation between all the methods was 6%), and consistent with the findings of the studies by Ferm and his co-workers.

The repeatability of the measurements is checked by always taking duplicate samples. An example of the repeatability determined from a monitoring program in Asia is shown in Figure 3, where results from duplicate samples at 45 stations using a monthly exposure are presented (Ferm, 1995). The standard deviation between duplicates was 17.6%. Repeatability of 8% and 11% were reported in Ferm and Rodhe (1997) for samples in Asia and for urban sampling in Sweden (Ferm and Svanberg, 1997), respectively.

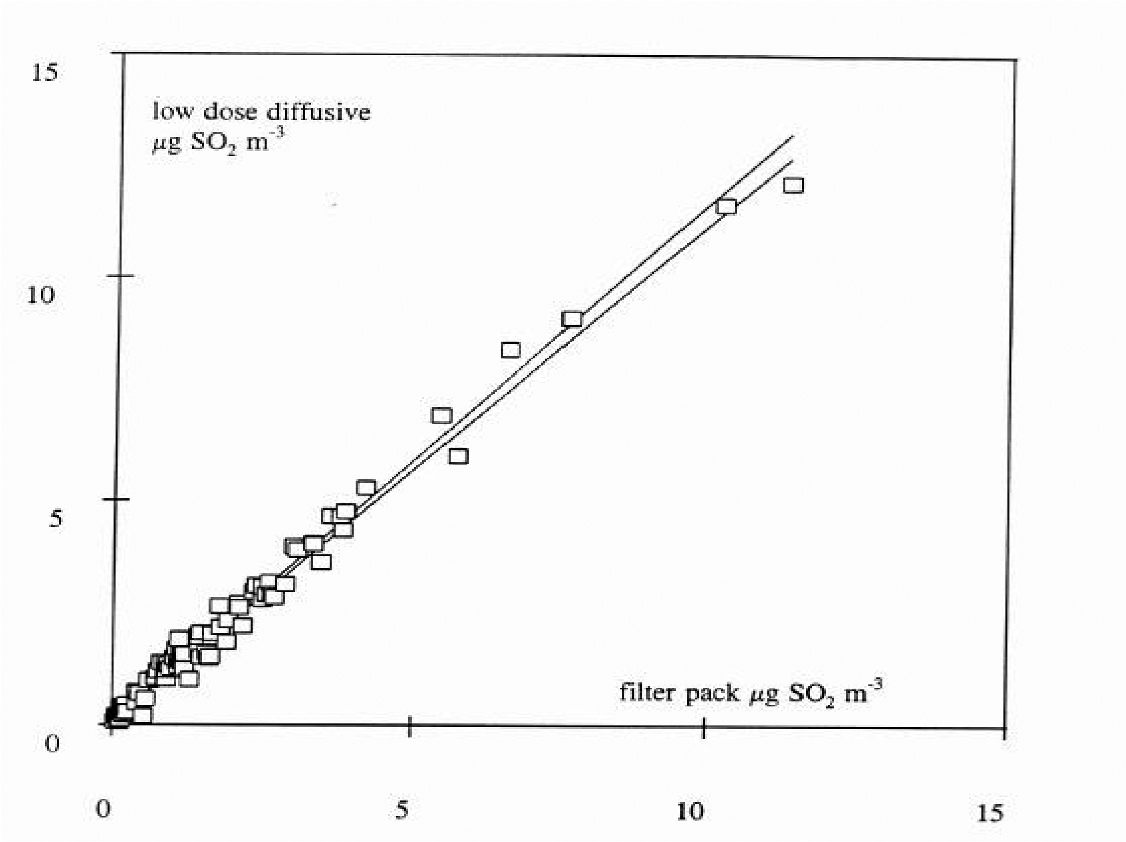


Figure 2. *Active Vs passive measurements of SO_2 at 5 EMEP stations. Mean passive and active are 2.2 and 1.8 µg/m^3 , respectively, slope is 1.13 ± 0.03, with an intercept of 0.14 ± 0.08.*

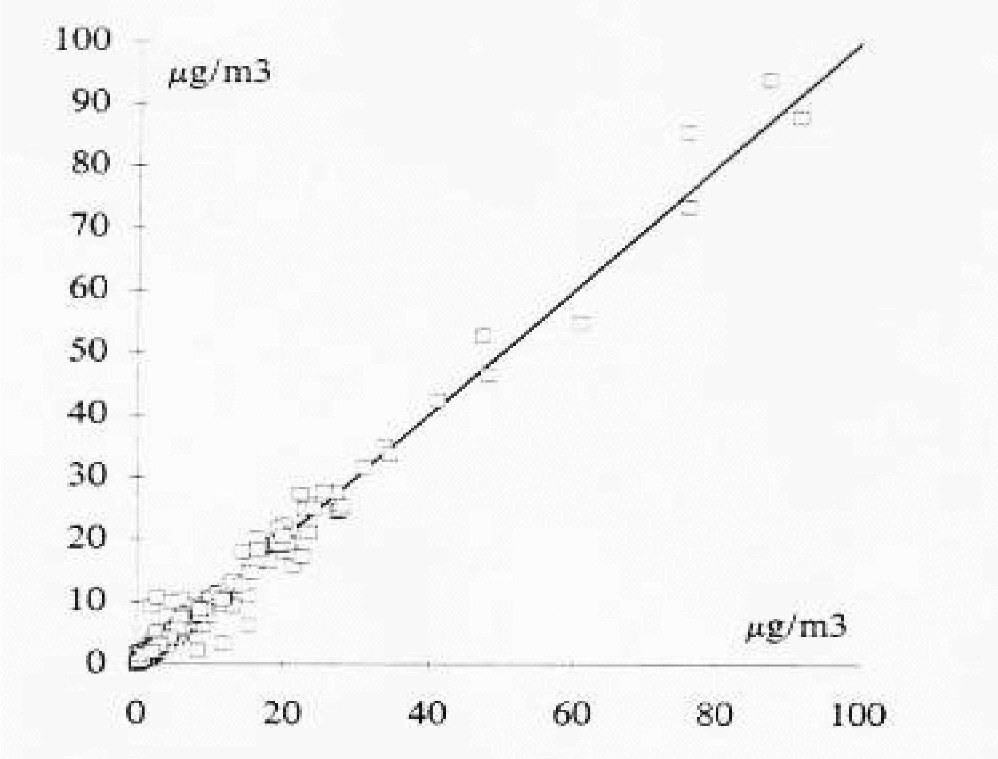


Figure 3. *Repeatability of SO_2 in the Asia network (Ferm 1995).*

3.2 NO_2

The most commonly used sorbent for NO_2 sampling is triethanolamine, but stability problems have been encountered with its use. Ferm and his group have tested several impregnations including an iron (II) salt, diphenyl amine, and a mixture of iodide, arsenite and ethylene glycol. The last mixture performed the best and is the one recommended for use. It also has the added benefit of being insensitive to light and thus the impregnated filters can be stored for several months before as well as after sampling. On the filters NO_2 is converted to nitrite and then analysed spectrophotometrically using FIA (flow injection analysis).

NO_2 measurements using this impregnation method in an active-filter mode have been compared to those using a standard chemiluminescent technique and the results are shown in Figure 4. The circles represent measurements at a background site (Aspvreten, January - March, 1988) and the squares an urban site (Gothenburg, October 1986). The results agree very well for both low and high concentration conditions.

The NO_2 passive samplers have also been compared with active measurements in urban environments using weekly exposures and regional environments using monthly exposures (Ferm and Svanberg, 1997) and the results are presented in Figure 5. The repeatability of the NO_2 sampler based on the measurements in Asia was ~8% (Ferm and Rhode, 1997), while the repeatability from the comparisons in Figure 5 were ~4%. The measurement range of the short passive NO_2 samplers is 0.05 - 200 ppb (0.1 - 400 ppb for monthly sampling).

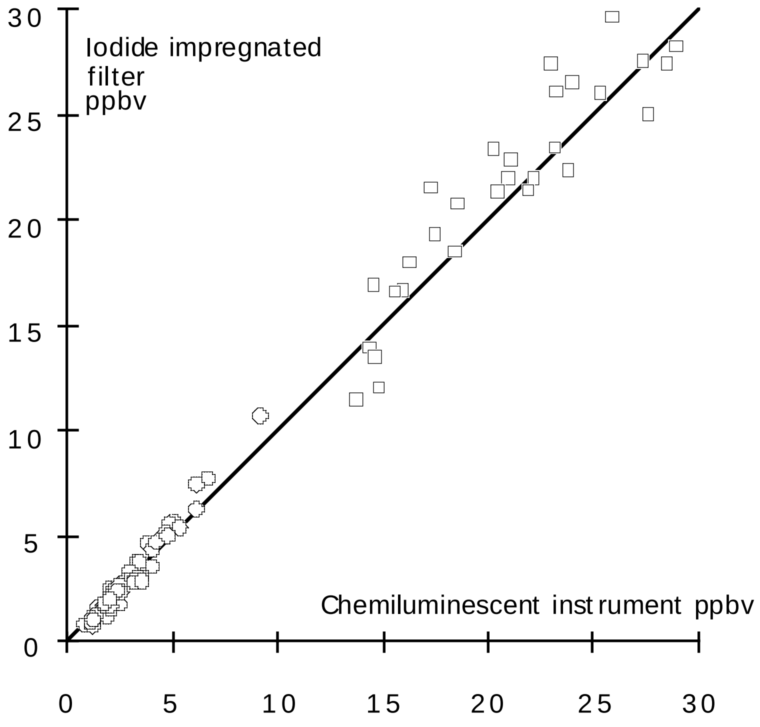


Figure 4. *Comparison between active filter measurement of* NO_2 *(iodide-technique) and the chemiluminescent technique. The circles represent measurements at a background site (Aspvreten, January-March 1988) and the squares an urban site (Gothenburg, October 1986).*

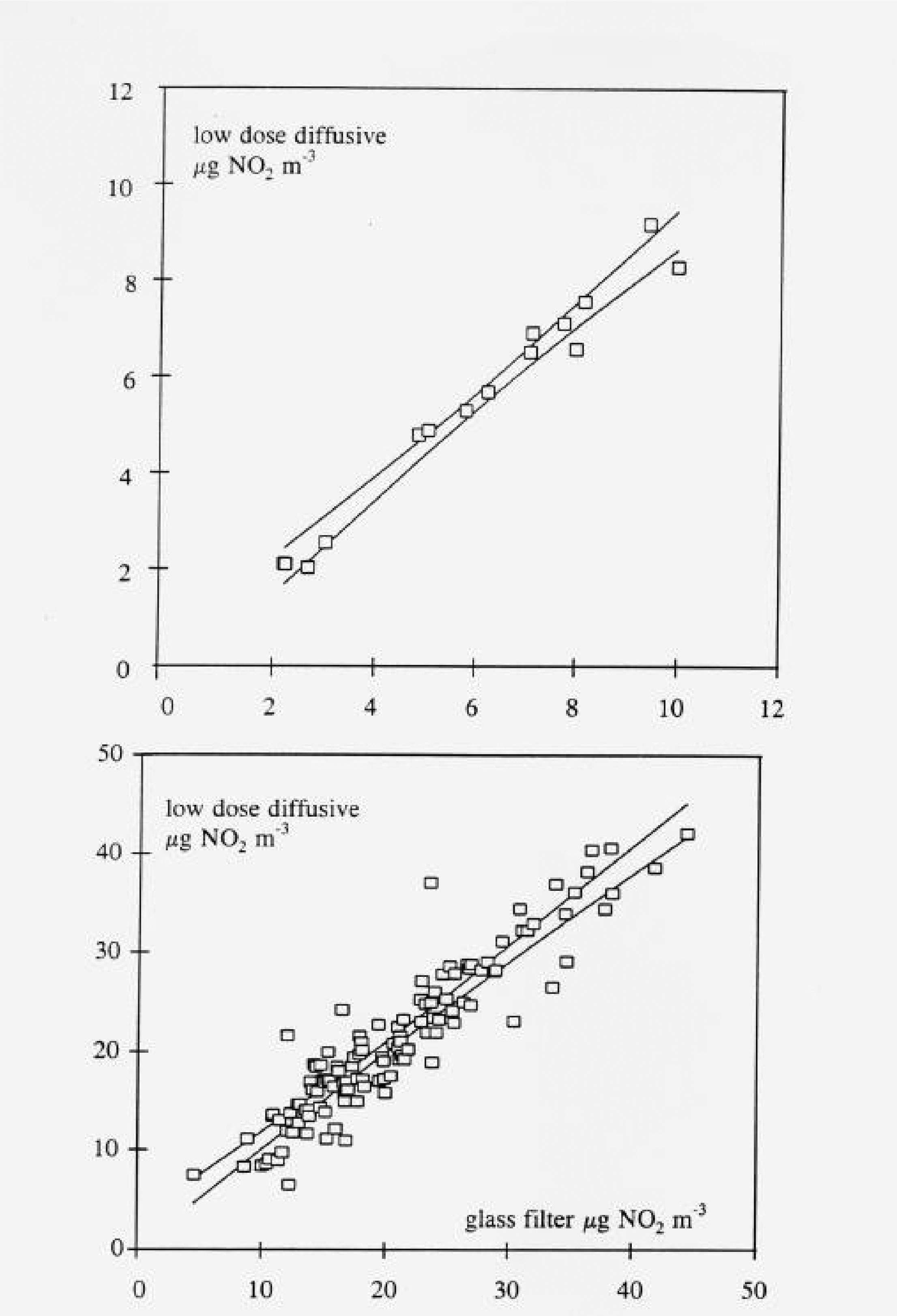


Figure 5. *Comparison of NO2 measurements using a passive sampler and those using an active-sampler. Top is for 5 urban sites from October '94 to March '95 using a weekly exposure, bottom is for two regional sites from May '93 to April '94, using monthly exposure. For the urban sites the mean values for the passive and active methods are 5.5 and 6 µg/m^3, with a regression slope of 0.95 ±0.07, and an intercept 7.5 ± 5; For the regional sites the* mean *value for the passive and active methods are 2.2 and 1.8 µg/m^3 ,respectively, with a regression slope of 0.90 ±0.09 and intercept of 0.06±0.006. (From Form Svenberg, 1997.*

3.3 NH_3

Citric acid is used to impregnate the NH_3 samplers. The NH_4^+ in the exposed filters is analysed after separation through a gas diffusion membrane using FIA. The concentration range of a short passive sampler is ~0.1 - 15 ppb (0.2 - 30 ppb for monthly sampling).

The performance of the passive samplers for ammonia was found not to be as good as that for SO_2 and NO_2 in the study by Ferm and Rodhe (1997) for Asian conditions. The repeatability was initially never better than 27% but improved to 16% after replacing the inlet screen with a solid cap after sampling to minimise volatilisation (equilibrium) with a solid phase which deposits on the inlet screen. An intercomparison using the ammonia passive sampler will be performed this summer ('97) outside Munich.

3.4 NMHCs

Passive samplers have recently been extended for use in monitoring non-methane hydrocarbons (NMHCs). Presently these samplers are being used to measure C_6 to C_9 hydrocarbons from a single sample in urban air quality monitoring networks in Europe. The samplers are shown in Figure 6, and consist of tubes filled with adsorbent packing. The tubes are fitted with a swagelock cap so that they can be used directly in a gas chromatography instrument. The chemical analysis is done via thermal desorption and gas chromatography with a flame ionisation detector (FID).

The performance of the passive sampler for NMHCs depends upon the choice of a suitable packing material and on conditioning and packing of the tubes. (It is necessary that these be consistent between samplers.) Presently Tenax TA, a 35-60 mesh, porous polymer based on 2,6 diphenylene oxide is the packing of choice, and tubes are 89 mm x 5 mm (id). Based on feasibility studies a one week sampling period is used to ensure concentrations at least one order of magnitude above the detection limit. The lower detection limit is ~ 0.1 $\mu g/m^3$ for most species. Complete details are presented in Mowrer et al., (1996). There is a problem with sampling benzene because it can desorb during sampling. Presently this is handled by using empirically determined uptake rates.

Measurements using passive samplers (for benzene, toluene, ethylbenzene, p-, o- and m-xylene, octane, and nonane) have been compared with active measurements using a BTX Analyzer (sampling every 30 minutes) in Copenhagen, Denmark. The differences in the weekly averaged values varied from a low of ~2% for benzene, to a high of ~ 20% for ethylbenzene. The repeatability for the aromatic hydrocarbons is typically 3 to 5%. The stability of the samples has also been tested for periods up to one year. Laboratory studies showed that the samples are stable up to ± 5% over a one year period, while field experience indicates errors of less than 10% with up to a 5 week storage period.

These samplers are now used at 30 urban sites within Sweden. It should be emphasised that these samplers have been optimised for Swedish conditions. Further testing is needed to establish the validity of the method over a wider range of sampling conditions.

The use of new packings may allow the technique to be extended to NMHCs lighter than C_6.

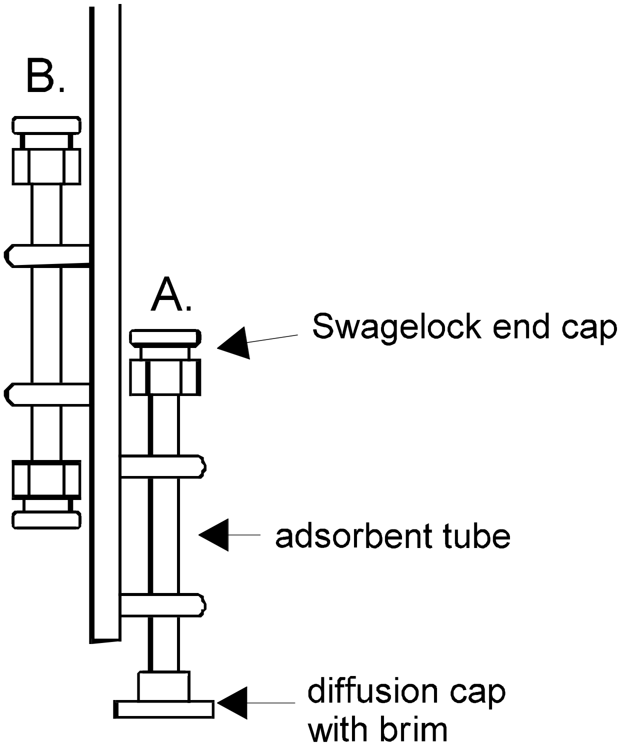


Figure 6. *Diffusive sampler for NMHCs with diffusion cap mounted on bottom end; and B, sample blank. (From Mowrer et aL, 1996).*

3.5 Ozone

Passive samplers for ozone have also been developed and Martin Ferm feels that these are now ready for widespread use. The ozone sampler was developed internally at IVL-Sweden and details can not be disclosed at this time. Typical test results are presented in Figure 7 where results from passive samplers are compared with those using a UV-absorption instrument. Based on a series of such tests it is found that the relative standard deviation between the ozone passive sampler and UV-instruments is less than 4%, the lowest value for any species measured passively. The repeatability is also -4%. These samplers are now being used in a project in Argentina where 20 passive ozone sites, in and around Buenos Aires, have been established in co-operation with a Swedish company and with funding from The World Bank. Greg Ayers has also developed an ozone sampler and he has reached similar conclusions about their use.

4. PREVIOUS MONITORING EXPERIENCES WITH PASSIVE SAMPLERS

4.1 Sweden's Experience

As discussed above passive samplers are used widely in Sweden. In the Swedish monitoring network passive sampling activities are an integral component and are used in conjunction with active sampling.

4.2 RAINS-Asia

As part of the *RAINS-ASIA* project funded by the World Bank and the Asian Development Bank a pilot monitoring program was conducted using passive samplers. (This aspect of the project was funded by the Asian Development Bank.) The objective of this monitoring activity was to obtain base-level data for future model evaluation.

Sulphur dioxide was monitored at the surface at forty-five locations, for a 12-month period. The first sites began monitoring in December 1993, and others in February 1994. Sulphur dioxide was monitored using the passive samplers developed by Martin Ferm at the Swedish Environment Research Institute (IVL) at a cost of ~$35 US/sample (including manufacturing, mailing and analysis).

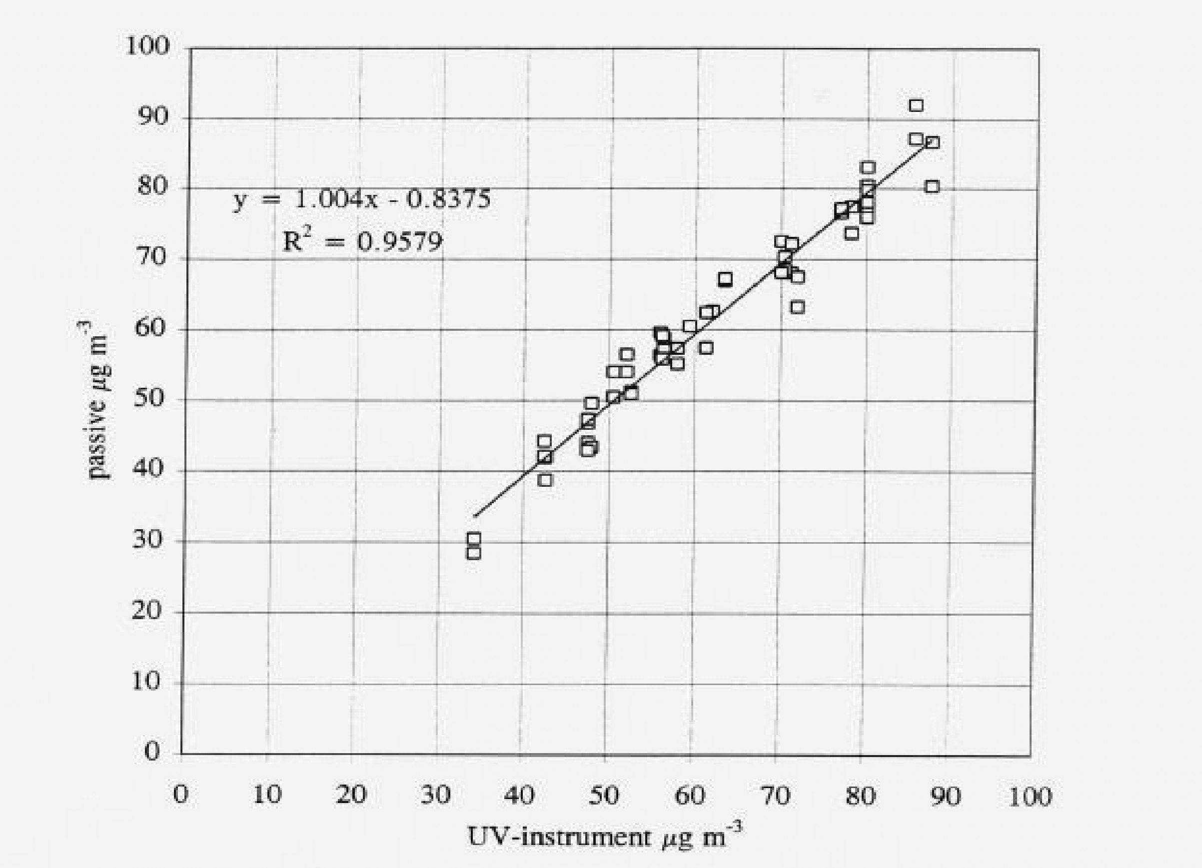


Figure 7. *Ozone results from passive and active (UV-absorption) measurements.*

The measurement sites were selected to provide information on the regional aspects of sulphur in Asia. Thus sites were chosen to be away from major local sources and to be distributed in highly sensitive regions as determined from maps of ecosystem sensitivity developed as part of the *RAINS-ASIA* project. The location of the monitoring sites are shown in Figure 8. The distribution of sites was determined by a variety of considerations. For example, five sites were selected for China to complement monitoring programs already in existence. In China, four of the five sites were located in the south in highly sensitive areas. Practical considerations of security, access, etc., also played an important role in the final selection of sites. The final distribution of sites span a latitude range from 10^{o}S to 40^{o}N, a longitude range of 70°E to 130°E, and an altitude range from sea level to above 4000m.

For each country there was a principal contact person with responsibility to oversee all the measurements. In many cases (e.g., Bangladesh, Nepal, Vietnam), this data represent some of the first monitoring activity outside of the major urban centres. The annual averaged observed SO_2 concentrations are summarised in Figure 9. The annual mean values range from less than 0.3 $\mu g/m^3$ at Tana Rata, located at 1545 m on the Malaysia Peninsula, Lawa Mandau, (Borneo) Malaysia, and Dhankuta, Nepal, to values greater than 20 $\mu g/m^3$ at Luchongguan (Guiyang) China, Babar Mahal, Nepal, and Hanoi, Vietnam.

This data provided important insights into the seasonal cycle of surface SO_2. The seasonal cycles of the observed SO_2 concentrations at four sites are presented in Figure 10. Shown are stations in Bangladesh, Korea, Malaysia and Nepal. All four stations show distinct seasonal cycles. For example, the seasonal cycle for station at Jahangimagar (station B1) in Bangladesh. exhibits dry season concentrations exceeding 10 µg/m^3, falling to ~2 µg/m^3 during the monsoon season (May through October). This cycle is influenced both by the large wet removal of SO_2 during the monsoon season and also by the change in wind direction. During the monsoon season flows in this region are southerly from the Bay of Bengal area and are expected to have lower concentrations than those coming from the west and north during the dry periods. The station in Nepal shows a similar minimum value during the rainy season, followed by high concentrations during the winter inversion periods. Yangyang (station K2), S. Korea, located on the Northeast region of South Korea, shows a rainy season minimum in July and August and maxima in early winter and spring. In this region the flows in the winter are largely northerly, and those in the spring are west-north-westerly. The stations in Malaysia show interesting seasonal cycles. The 2 stations on the Malaysia peninsula (M1 & M2) show similar seasonal cycles. For example, Mersing, Malaysia, located on the southern part of the Malaysia peninsula, experiences minimum values during the NE monsoons (November to March), and maximum values during the SW monsoon. During the NE monsoon air comes from the South China Sea, while the SW monsoon brings air from the major SO2 emissions regions, e.g., Singapore, industrial regions around Kuala Lumpur, and the major shipping lane along the Straits of Malacca. The station at Lawa Mandau (M4) located on the island of Borneo shows an opposite seasonal cycle (not shown), with peak values in February to May (0.6 µg/m^3) and minimum values ~0.2 µg/m^3) during the SW monsoon.

Also shown in Figure 10 are model predictions. These results are obtained from a trajectory model developed and used as part of the *RAINS-ASIA* project. Details regarding the model are presented in (Arndt and Carmichael, 1995). At these four locations the model tends to overpredict the concentrations but does capture many of the important features in the observations. The model is being used to help explain seasonal variations in the transport and removal processes, and to estimate the contributions of various sources to selected receptor regions. For example, at Mersing we find that emissions from Kuala Lampur contribute ~ 15%, emissions from the rest of the Malaysia Peninsula contribute ~20%, and emissions from Singapore and the ship lanes accounting 50% and 5%, respectively. At Yangyang, South Korea, emissions from Seoul area contribute 20%, while emissions from the remaining northern and southern regions of S. Korea contribute 25% and 5%, respectively. Emissions from N. Korea and China account for 30% and 20%, respectively.

The above points out a valuable use of passive samplers. Atmospheric chemistry models on global and regional scales, because of their formulation and spatial and temporal resolution, are best used for analysis of time averaged behaviour. They are often tested against time integrated data (e.g., daily, weekly, monthly means). Passive samplers operated at weekly to monthly exposure times, provide continuous measurements which can be used directly for these purposes.

4.3 Other Activities

Dr. Greg Ayers (CSIRO) -- is using passive samplers extensively in some of his studies in Indonesia and Malaysia. He is working directly with the National Meteorological Service (NMS) in Malaysia, where they are using passive samplers, low-volume aerosol collectors, and precipitation chemistry collectors to characterise urban and regional pollution sources. These activities are taking place at (at least) one GAW regional station. Passive samplers are also being used at the new background station in Indonesia.

He and his group have conducted a number of experiments designed to confirm and characterise the performance of passive samplers. They found that variations in the tube geometry can significantly influence the repeatability of the measurements. For example a difference in tube length of ±1 mm can account for a ±10% difference in the calculated concentration. Similar biases occur if machining tolerances on the sampler body diameter are not tight, or if the backing filter or inlet filter are not perpendicular to the diffusion direction. While the samplers are simple, accurate and repeatible results require that the sampler geometry be manufactured with tight tolerances. They have also found that the choice of filter material is also important. They were able to improve the blanks by a factor of 5 for HCHO passive samplers by changing from a filter which required washing to another that did not.

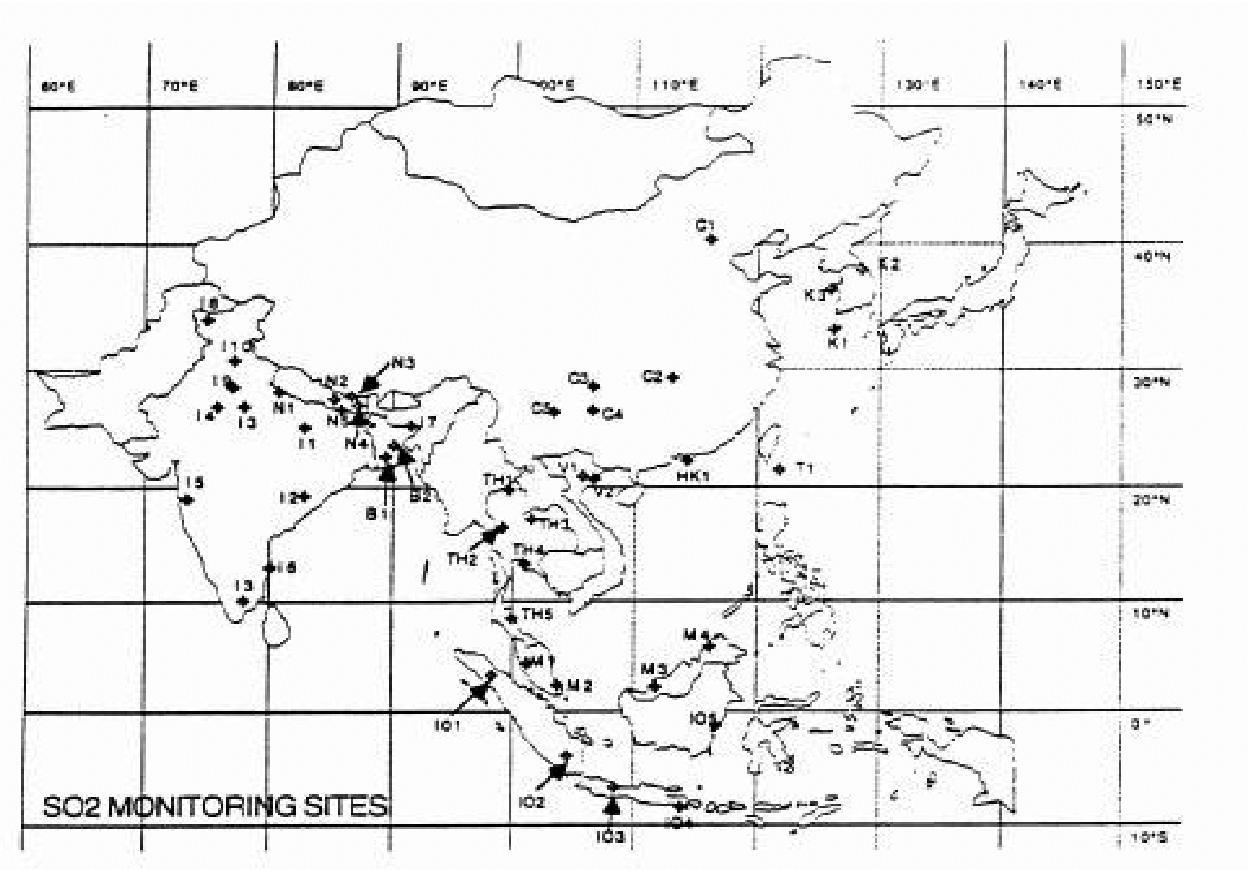


Figure 8. *Location of S02 passive sampler sites in the RAINS-Asia study. The name of sites are presented in Figure 9.*

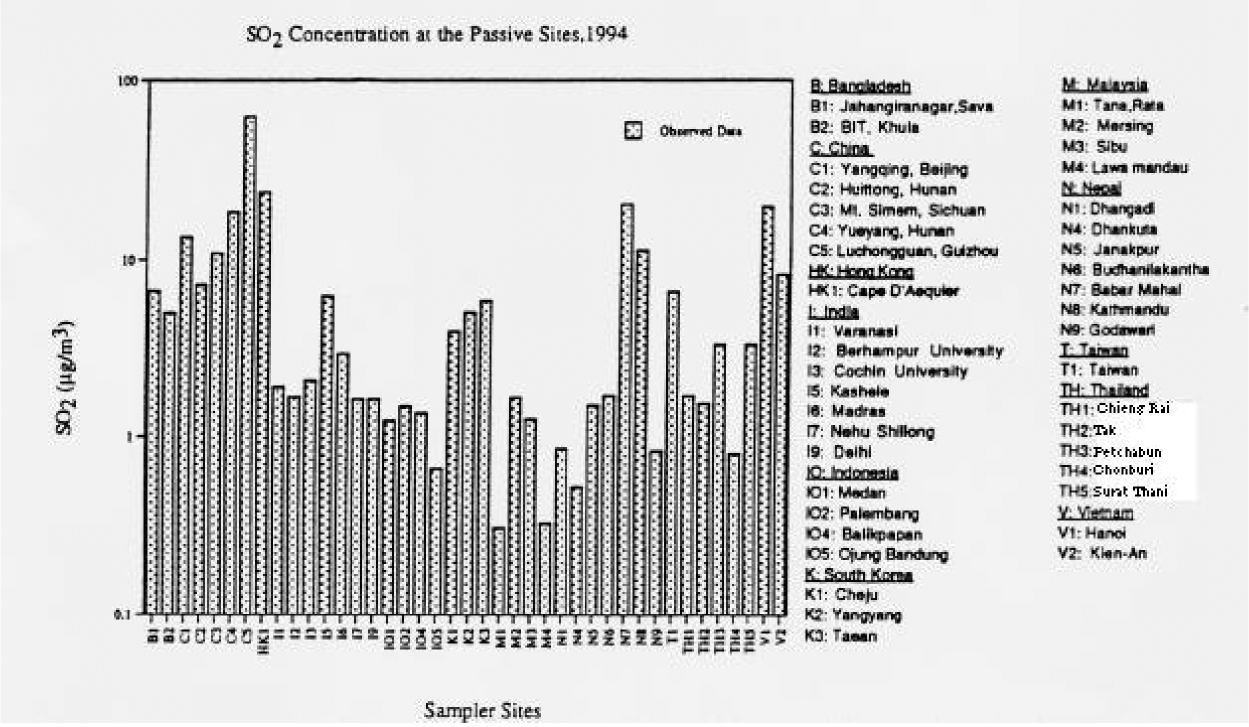


Figure 9. *Annual averaged S0$_2$ surface concentrations (as S0$_2$) observed using the passive samplers.Each point is the average of duplicate samples exposed for month long periods.*

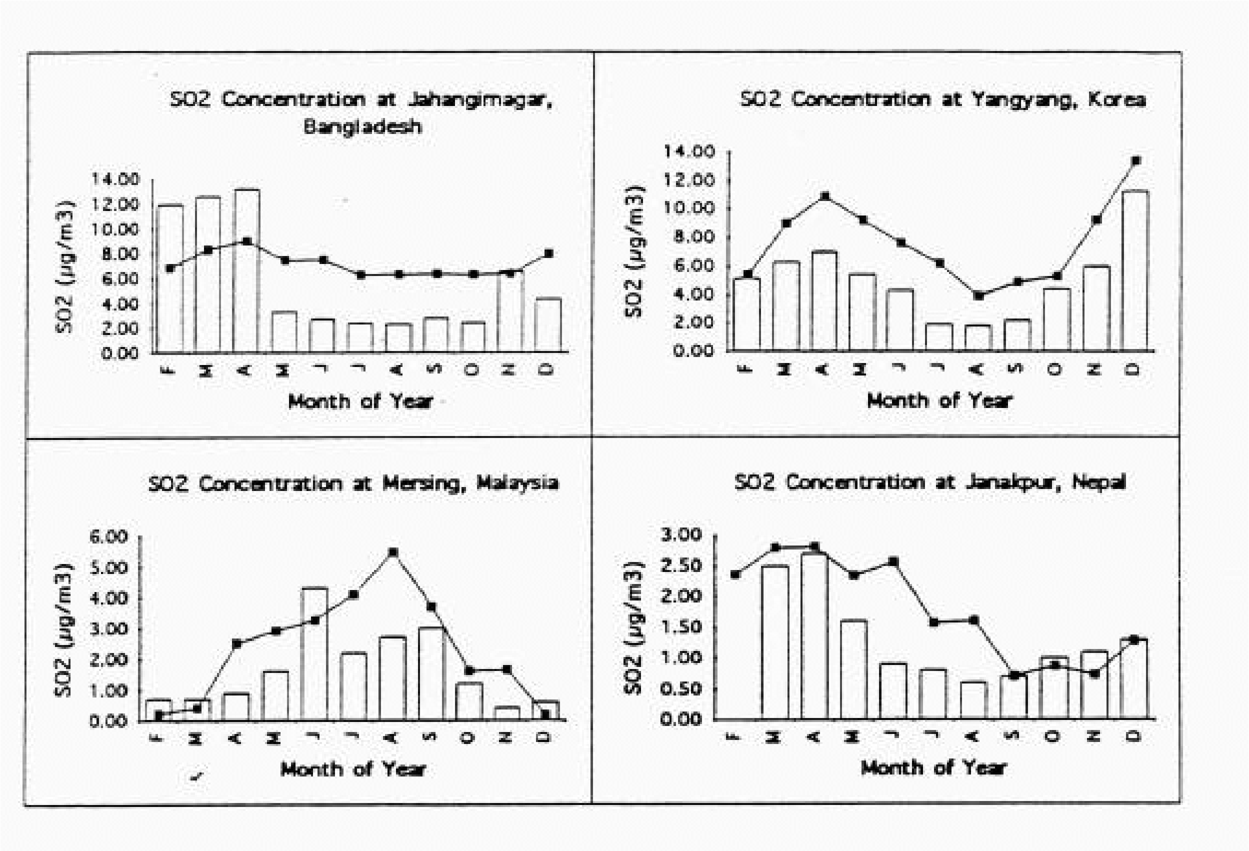


Figure 10. *Seasonal cycle of observed surface-level $S0_2$ concentrations. Also shown are model predicted values. Details regarding the location of the site and the annual average are found in Figures 8 & 9.*

Based on these studies as well as "plenty" of active/passive comparisons and comparisons with tubes of different length, he concludes that passive samplers are excellent for SO_2 and NO_2, and apparently fine for 0_3 and HCHO, and good for NH_3 (but there remain problems with the blanks). He is also now beginning to test the new NMHC passive samplers.

Rodhe and Ferm -- performed the first tests of passive samplers at background locations in Asia as described above and in Ferm and Rodhe (1997).

RAiNS-Asia -- Phase-II of this project has recently been funded by the Japan Fund within The World Bank. As part of Phase-II a second pilot study will be conducted using passive samplers in Asia. An additional proposal for the use of passive samplers in urban/regional environments has recently been awarded to Martin Ferm by the Swedish Consultancy Fund at The World Bank.

Dr. Bruce Hicks (NOAA) -- and his group are working on a passive sampler for NH3 with the intent of deploying them at a large number of sites in the US. No further details are available at this time.

IUPAC Commission on Atmospheric Chemistry -- has established a subcommittee on diffusive sampling chaired by Dr. R. H. Brown, with members Professors H. Akimoto, X. Tang, J. Slanina, and Dr. T. Tavares. The subcommittee has the objective to optimise the performance of diffusive samplers for use in air quality studies. This IUPAC activity is closely aligned with EU programrues and Directives and supports the IUPAC Divisional focus on solving environmental problems by developing appropriate analytical methodologies.

This activity is centred at the Health and Safety Laboratory, Sheffield, UK, under the direction of Dr. R. H. Brown. The primary focus has been on the measurement of benzene, toluene and xylene (BTX). Passive samplers are being compared with active measurements based on conventional monitoring instrumentation for sampling periods of 1, 2 and 4 weeks. The results indicate that these devices are promising. The work to date is summarised in Health and safety laboratory reports (Brown et al., 1996). Further activities will entail the study of the effect of environmental factors (temperature, etc.) on the performance of passive samplers under controlled test conditions. There is also a pilot project using these samplers to survey BTX levels throughout UK and world-wide (on a one time - one sample basis).

European Commission -- has several activities on-going related to the use of passive samplers for ambient air measurements. There is a working group, chaired by of Dr. R. H. Brown, Health and Safety Laboratory, Sheffield, UK, that is developing guidelines, requirements and test methods for ambient air quality measurements using passive samplers for the European Committee for Standardisation. These documents will comprise the European Standard for the use of passive samplers to measure air quality, and contain details regarding device requirements including unambiguity, selectivity, and uncertainty for minimum specified measuring ranges and averaging times, desorption efficiency, diffusive uptake rates and sensitivity to air velocity, as well as guidance on selection, use and maintenance.

There is a new project within the EC *Life-Environment* Programme titled European Diffusive sampling Initiative (EDSI) which brings together seven institutions in Europe involved in passive sampling, with the focus on validation and demonstration of the use of passive samplers for monitoring and assessing ambient air quality. The multi-year project has three components: development of performance criteria and test protocols for passive sampling; testing of selected samplers for key pollutants against the proposed protocols; and interlaboratory comparisons to demonstrate the applicability of passive samplers for air quality monitoring in Europe. The project involves both laboratory and field experiments. The field experiments will be conducted in rural and urban environments in northern, central and southern Europe.

4.4 Laboratory Requirements

While passive samplers are inexpensive and easy to manufacture and deploy, the chemical analysis requires the use of modern analytical equipment. The recommended analysis technique depends on the species measured. Below are presented some typical costs of the major instruments (including sample injectors):

Table 1. *Typical analytical equipment used in conjunction with passive samplers.*

Gases	Instrument	Price ($ US)
NMHC	Gas Chromatography (GC)	62,500
NO_2, NH_3	Flow Injection Analysis (FIA) Spectrophotometry	37,500
SO_2	Ion Chromatography (IC)	25,000

4.5 Summary

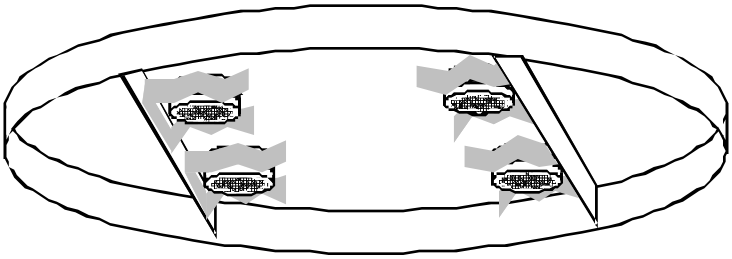
Passive samplers offer a wide variety of advantages for use in the field. There is no need for calibration and electricity, and thus are easy to deploy in the field. A typical deployment is shown in Figure 11. The passive samplers are simply fastened on the 'underside of a Frisbee (to avoid splashing from precipitation) attached to a pole which is typically ~

1 meter high. They are small inexpensive, and provide time-integrated, and continuous samples. They can be used to check spatial variability in pollution fields, they can be used to check the representativeness of locations of advanced sampling stations, used to measure background concentrations at places where other measurements are difficult, and can be used in urban environments.

Based on the above discussion of the state-of-the-science it is concluded that there are a number of species for which passive samplers offer a viable method for ambient measurements, and several species for which the success of passive sampling is highly probable, but require further testing:

Now: SO_2, NO_2, O_3, and NMHCs (> C_5)

Near future: NH_3 ,NO, HNO_3, HCHO, organic acids (formic, acetic and oxalic).



Four passive samplers mounted on rain shield.

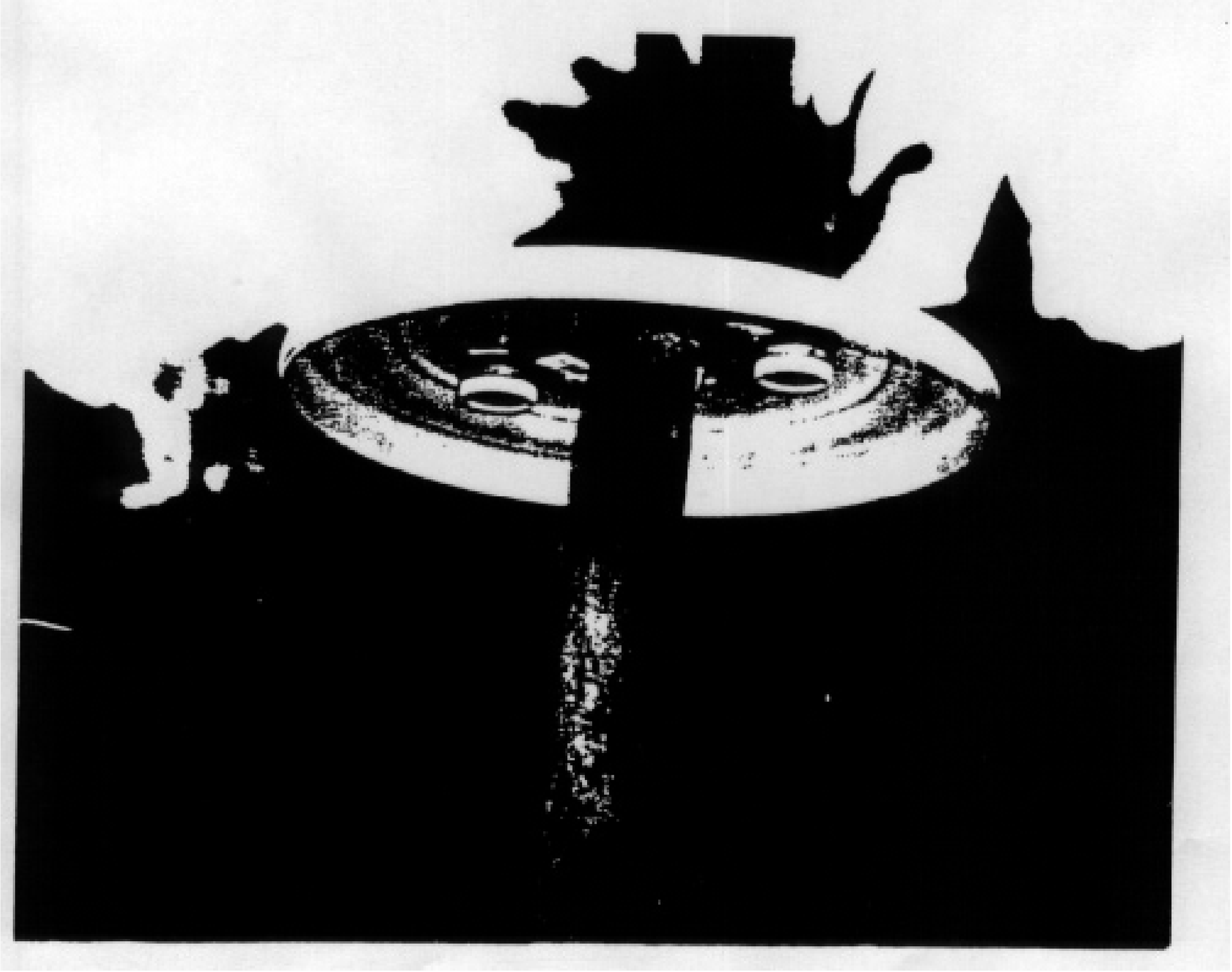


Figure 11. *Typical deployment of passive samplers in the field.*

5. POSSIBLE USES OF PASSIVE SAMPLERS WITHIN GAW

There are a variety of potential uses of passive samplers within the GAW programme. They can be used to:

(a) Increase the Spatial Resolution of GAW - By providing measurements of key species (say O_3) at locations (biomes) which are not presently covered by the global stations. GAW has a stated objective to expand its monitoring activities to include measurements for each principal climatic zone and each major biome (some 30 additional stations). Passive samplers could provide information on key species in areas that are not yet covered by present measurements.

(b) Add Species Coverage at GAW Stations - Passive samplers could be used to provide measurements of species that are not presently taken at a give site (say NMHCs, NO_x, NH_3, $S0_2$), and provide back-up (for the case where an instrument goes down) for other measurements, such as ozone, so that continuous records are obtained. In addition the growing interest in tropospheric ozone as a greenhouse gas and atmospheric oxidant has heightened GAW's need to document the global distribution of NMHCs and NO_x as precursors for ozone and other oxidants in the troposphere. Due to their short lifetime in the atmosphere, the global concentration of these species varies significantly from region to region, making it difficult for GAW to establish their global climatology with only a limited number of measurement sites. Passive samplers could augment the existing stations and provide increased species, as well as spatial and temporal, coverage.

(c) Augment Measurements at Precipitation Sampling Sites - At many stations precipitation samples are taken without companion measurements of gas phase species. The addition of gas phase measurements of key sulfur and nitrogen gaseous compounds at precipitation measurements sites would aid in the interpretation of the measurements and be particularly helpful to modelling studies.

(d) Enable the Expansion of GAW Activities to Urban-Scales - There are increasing interests in expanding GAW activities to include urban issues. Passive samplers offer a means upon which to do this in a manner which is both cost effective and with a technology which the local entities can easy build upon for local applications.

(e) Enhance Regional-Scale Studies - Passive samplers can provide valuable information for use in environmental studies that may be of interest to national and regional entities. Many risks to humans and ecosystems are caused by integrated exposures to ambient pollution levels above some threshold levels (also called critical levels). Passive samplers can be used in this way.

(f) Expand Measurement Capacity - The possible uses of passive samplers are many, and the appropriate use is determined by the objectives of the measurement programme. However, passive samplers, because of the low costs, and ease in deploying them, are a great way to get people involved in measurement activities. Once they are familiar with the strengths and weaknesses of the method, they will then be in a position to make use of the devices for national studies.

(g) Screening Studies to Evaluate **Monitoring Locations** - Because of their ease in use and low cost, passive samplers could be used in screening studies to help evaluate the suitability of proposed monitoring sites.

(h) Aid in Model Evaluation - Increasing the spatial resolution of the GAW network, adding measurements of key chemical species, and providing continuous time records, would be of great value to the modelling community in their efforts to evaluate model performance and to study trace gas cycles and trends.

(i)As a tool in QA/QC - Conceptually, it is also possible to use passive samplers as a routine way of checking the performance of the active instruments at GAW stations. Given that the performance of passive samplers have been characterised for a given climatic region, then the samplers could be used as part of a QA/QC programme. For example, the active sampler could be checked. against passive samplers at a much greater frequency than the more rigorous instrument calibrations or standard sample analysis, thus providing an option for earlier detection of instrument malfunction

(j) To Integrate Measurements Across Scales - Passive samplers provide the means to connect measurements made at global, regional and urban scales. The use of identical measurement technology and analysis at a large number of measurement sites would provide a unique and valuable data set, and reduce many of the current problems in merging data obtained from a wide variety of measurement methodologies.

6. PROPOSED ACTIVITIES

As discussed above there are a variety of potential uses of passive samplers within the GAW programme. While there is a rapidly growing body of knowledge and experience regarding passive samplers and their use in the field, it remains a fact that they are not yet widely used. It is strongly recommended that GAW take a closer look at what role they *should* play within the programme, and begin to make use of this technology. The following actions are recommended:

(I) Organise an expert meeting on the *Role of Passive Samplers in GAW*. The purpose of this meeting would be to more fully discuss the state-of-the-science and where it is headed, to formalise a strategy based on ideas put forth in this report as well as new ideas brought forth at the meeting, to offer ways to co-ordinate with other on-going or proposed activities using passive samplers, and to plan a GAW pilot study on passive samplers (as discussed below).

(II) Embark upon a series of pilot studies aimed at: (a) gaining experience within GAW in the use of passive samplers; (b) evaluating and testing new and existing passive samplers under a variety of measurement conditions; and (c) embedding their use within GAW.

Specifically, it is recommended to *Establish GAW Passive Sampler Testing Site(s)* by designating sites within the GAW network where a wide variety of passive samplers could be evaluated against active measurements. Both existing and newly developed samplers could be evaluated. These sites should be selected to provide a range of environmental conditions so as to establish the robustness of the methodology. It is important to recognise that most of the experience to-date with passive samplers has been in the high latitude regions of the Northern Hemisphere. Studies which provide performance data in high temperature and high and low humidity regions is needed. There are many ways to organise such an activity, but one possibility would be to designate global, regional and urban sites. At these sites a variety of common testing activities would take place, but some tests and demonstrations would be geared towards characterising the most appropriate role of passive samplers at that scale. For example:

At the *Global Station(s)* ozone passive samplers could be intercompared with continuous measurements. The use of passive sampling for ozone could be used as a backup to ensure a continuous ozone measurement at the global stations. NO_2 and NMHC samplers could be used to determine levels of these species to aid in the design and implementation of NO_2 and NMHC measurements at the global stations as proposed in the GAW Strategic Plan.

At the *Regional Station(s)* evaluate as many species as possible by comparison with active techniques. Performing these tests within highly visible networks (e.g., EMEP) would maximise potential for acceptance of the techniques. In addition studies could be designed to evaluate how passive samplers could be used in conjunction with the GAW precipitation chemistry network. These activities should be done in co-operation with the EC-EDSI project.

At the *Urban sites(s),* in close collaboration with NMSs interested in expanding their activities in urban air quality, conduct tests and demonstrations on how passive samplers can be utilised in urban environments. Such an activity could be mounted rather quickly and would show a specific example of a GAW directive aimed at urban environments. This activity could be co-ordinated with WHO since they have advocated the use of passive samplers (GEMS/AIR Methodology. Review Handbook Series, Vol. 4).

(III) Stimulate further development of passive sampler technology. Because of their large potential value in atmospheric chemistry monitoring it is important to push for further developments and wider-spread application of passive sampler technology. For example Martin Ferm's group is developing and testing passive samplers for HCHO, organic acids, $HN0_3$, and NO, all species of interest and value to atmospheric chemistry studies and to GAW. In addition Martin Ferm has suggested that it is also possible to measure CO passively, but he has not begun to develop a CO passive sampler. CO is an important trace species, and the atmospheric chemistry community and GAW would greatly benefit from better defined CO distributions at urban, regional and global-scales. The GAW programme should consider ways to stimulate and encourage the development of passive samplers for CO and other important trace species.

(IV) Conduct a GAW-wide experiment. Passive samplers provide the means to obtain an unprecedented data set. It is possible and feasible to deploy passive samplers at *ALL* GAW stations and obtain monthly measurements of 0_3, SO_2, NH_3, NO_2 and HCHO (or some subset) for a one or two year period. The study would yield a data set containing measurements from over 200 stations and 80 countries, approximating global coverage, obtained using identical measurement technology and analysis, would engage and involve all the countries, and integrate the efforts of the global and regional/urban stations. This project would produce a unique and valuable data set that could be used for a wide variety of purposes including: as a data set to test and compare with satellite based measurements; global and regional modelling; and in studies and analysis which assess tropospheric chemistry.

The estimated costs of such an study are presented in the Annex. The cost per species for 200 stations in 80 countries taking monthly samples is ~ $200,000 per year.

7. CLOSING COMMENTS

The above activities related to the use of passive samplers in GAW should build upon experiences in passive sampling already in place within GAW (e.g., Greg Ayers, NMSs in Malaysia and Indonesia, etc.). In addition GAW activities should co-ordinate with, and make use of, on-going activities. For example the new ozone measurements in Buenos Aires, the two new World Bank initiatives in Asia, the ongoing IUPAC activities, and the new EC-EDIS project offer opportunities for GAW to implement some of the recommendations outlined above.

It is also important to note that while the sampling technique is simple, the chemical analysis relies on modern analytical chemical analysis techniques, and the quality of the data rests intimately on QA/QC considerations. Therefore it is important that any passive sampler studies be co-ordinated very carefully. The established organisational structure in GAW should be utilised. For the inorganic species the techniques are very similar to those used in precipitation chemistry analysis, and thus passive sampling could fit nicely within that QA/SAC.

Finally, it is clearly advantageous and recommended that GAW activities in passive sampling be done in close association with scientists actively working on the development and deployment of passive samplers. Possibilities include setting up an ad hoc working group on passive samplers within GAW and/or adding scientists involved in passive sampling to appropriate standing committees of GAW.

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ANNEX I

Estimated Costs of a GAW-Wide Passive Sampling Experiment.

Below is a summary of representative costs associated with the use of the techniques described in this report. They are taken from a proposed study, so they represent "actual" costs including mailing, analysis, and overhead charges.

Analysis costs for the different compounds

	US$
HCHO*	150
VOC*	200
NO_X	70
0_3	75
SO_2	50
organic acids	100
NH_3	50
sum for entire suit + extra 0_3	770

* = single analysis, for other species costs are based on duplicate samples.

As illustrative examples:

An urban pilot study where these species are measured at 11 towns on three occasions:
11 x 3 x 770 = **$25,410**

A GAW-wide integrated study at 200 sites and 80 countries (one blank per country) using a monthly exposure:

SO_2:200 stations and 80 blanks on 12 occasions = 3360 analysis equals	**$168,000**
0_3:200 stations and 80 blanks on 12 occasions = 3360 analysis equals	**$252,000**
NH_3:200 stations and 80 blanks on 12 occasions = 3360 analysis equals	**$168,000**
NO_X: 200 stations and 80 blanks on 12 occasions = 3360 analysis equals	**$235,000**

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102. Report of the Workshop on Precipitation Chemistry Laboratory Techniques, Hradec Kralove, Czech Republic, 17-21 October 1994

103. Report of the Meeting of Experts on the WMO World Data Centres, Toronto, Canada, 17-18 February 1995, (prepared by Edward Hare)

104. Report of the Fourth WMO Meeting of Experts on the Quality Assurance/Science Activity Centres (QA/SACs) of the Global Atmosphere Watch, jointly held with the First Meeting of the Coordinating Committees of IGAC-GLONET and IGACoACE, Garmisch-Partenkirchen, Germany, 13ol 7 March 1995

105. Report of the Fourth Session of the EC Panel of Experts/CAS Working Group on Environmental Pollution and Atmospheric Chemistry (Garmisch, Germany, 6-11 March 1995)

106. Report of the Global Acid Deposition Assessment (edited by D.M. Whelpdale and M-S. Kaiser)

107. Extended Abstracts of Papers Presented at the WMO-IGAC Conference on the Measurement and Assessment of Atmospheric Composition Change (Beijing, China, 9-14 October 1995).

108. Report of the Tenth WMO International Comparison of Dobson Spectrophotometers (Arosa, Switzerland, 24 July o 4 August 1995)

109. Report of an Expert Consultation on 85Kr and 222Rn: Measurements, Effects and Applications (Freiburg, Germany, 28-31 March 1995)

110. Report of the WMO-NOAA Expert Meeting on GAW Data Acquisition and Archiving (Asheville, NC, USA, 4-8 November 1995)

111. Report of the WMO-BMBF Workshop on VOC Establishment of a "World Calibration/Instrument Intercomparison Facility for VOC" to Serve the WMO Global Atmosphere Watch (GAW) Programme (Garmisch-Partenkirchen, Germany, 17-21 December 1995)

112. Report of the WMO/STUK Intercomparison of Erythemally-Weighted Solar UV Radiometers, Spring/Summer 1995, Helsinki, Finland

113. The Strategic Plan of the Global Atmosphere Watch (GAW)

114. Report of the Fifth WMO Meeting of Experts on the Quality Assurance/Science Activity Centres (QA/SACs) of the Global Atmosphere Watch, jointly held with the Second Meeting of the Coordinating Committees of IGAC-GLONET and IGAC-ACE^{Ed}, Garmisch-Partenkirchen, Germany, 15-19 July 1996

115. Report of the Meeting of Experts on Atmospheric Urban Pollution and the Role of NMSs (Geneva, 7-11 October 1996)

116. GAW Guide
117. Report and Proceedings of the Workshop on the Assessment of EMEP Activities Concerning Heavy Metals and Persistent Organic Pollutants and their Further Development (Moscow, Russian Federation, 24-26 September 1996) (Volumes I and II)

118. Report of the International Workshops on Ozone Observation in Asia and the Pacific Region (IWOAP, IWOAP-II), (IWOAP, 27 February-26 March 1996 and IWOAP-II, 20 August-18 September 1996)

119. Report on BoM/NOAA/WMO International Comparison of the Dobson Spectrophotometers (Perth Airport, Perth, Australia, 3-14 February 1997), (prepared by Robert Evans and James Casson)

120. UV Monitoring and WMO

121. Report of the Eighth WMO Meeting of Experts on Carbon Dioxide Concentration and Isotopic Measurement Techniques (prepared by Thomas Conway) (Boulder, CO, 6-11 July 1995)

122. Report of Passive Samplers for Atmospheric Chemistry Measurements and their Role in GAW (prepared by Greg Carmichael)