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A Simple Technique for Measurements of SO_2 and NO_2 in Alexandria and Delta Region, Egypt

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Abstract: A simple analysis technique of atmospheric NO_2 and SO_2 by passive sampler was investigated and applied to the analysis of air pollutants in Alexandria and Delta region. The passive is based on the principle of molecular diffusion from the sampled medium to a collecting medium according to Fick's law. The samplers were setup in four locations in Alexandria and five locations in Delta region. NO_2 and SO_2 were monitored at different area characteristics (urban, residential and industrial) during 2005. The sampling period were taken once per month for two weeks. The results of NO_2 and SO_2 showed a seasonal variation as the highest were winter. NO_2 concentrations in Alexandria stations ranged from 3.8 to 80.5 μg m^{-3}, while SO_2 ranged from 21 to 250 μg m^{-3}. NO_2 concentrations ranged from 1.1 to 119.8 μg m^{-3} at Delta stations, while SO_2 concentrations ranged from 2.4 to 71.2 μg m^{-3}. The highest levels of SO_2 were recorded at the industrial areas (Kafr Zayate and Nahda), while the highest levels of NO_2 were recorded at the stations in the urban areas, heavy traffic such as IGSR in Alexandria and Damanhour in Delta. The advantages of passive samplers are cheap and efficient and the samplers require no maintenance or power supply.

Key words: Passive sampler · fick's law · molecular diffusion · NO_2 and SO_2 levels

INTRODUCTION

Air pollution is a major problem facing all nations of the world. Exposure to an airborne pollutant may be defined as the contact with the pollutant for a given time period [1, 2]. There are several techniques are used in the measurement of air pollutants, but the passive sampler is the simplest one. Passive samplers are devices capable of taking samples of gas or vapor pollutants from the atmosphere, without involving air active movement through them. The fixation rate is controlled by a physical process, which can be diffusion through a static air layer or permeation through a membrane [3]. It is cheap and efficient and the samplers require no maintenance or power supply [4]. The low cost and flexibility of placement for passive sampling systems also make them attractive alternatives for assessing exposures at locations that are difficult to access [5]. Several passive samplers have been developed since Palmes and Gunnison [6] published the principles of passive sampling. Several types of SO_2 passive samplers have been described with variations regarding dimensions, diffusion barriers and pollutant trapping reagents. Ferm and Svanberg [7] carried out comparisons between SO_2 passive samplers and active techniques at both urban and remote sites in Sweden. The results demonstrated close agreement between the two methods (within 71.5%). Nevertheless, it lacks validation for tropical environments, where high temperatures and relative humidity are present at all times. Recent advancements have led to the development of a new generation of diffusive samplers which present high uptake rates for NO_2 (exceeding 50 cm^3 min^{-1}). This is the case of Radiello, a radial diffusive sampler developed by Fundazione Salvatore Maugeri and also of an Ecole des Mines de Douai (EMD) sampler recently developed by their own laboratory [8]. Cair *et al*. [4] carried out in detail the improvement of passive sampling technique for the measurement of nitrogen dioxide in the remote continental atmosphere and reduction in contamination of unexposed samplers.

Extensive monitoring and characterization of gaseous air-pollutant exposure of forest health plots or spatial extension of forest exposure over the landscape will only be achieved by the use of relatively inexpensive passive

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samplers. These should be deployed at the sampling sites, with some co-located with available continuous monitors for cross-correlation and calibration purposes [9, 10]. Deploying a large number of passive samplers can also provide data on small-scale variations in pollutant exposures, a valuable tool in mechanistic studies of air-pollution impacts on forest plants [11, 12]. Air quality objectives and standards established for the protection of crops and other plants, are now being exceeded over large forested areas in North America [13, 14]. NO_2 and SO_2 are gases that contribute to acidic deposition in terrestrial ecosystems as dry-deposited gases or in dissolved form in precipitation, fog and cloud [5].

Aims of this paper are (1) to discuss physical processing of the passive sampler and (2) to use passive samplers for determining the variation in SO_2 and NO_2 at different sites in Egypt.

Passive sampler and its operating principles: Dispersion is the process of distributing or spreading out of concentration (or saturation) profiles due to mechanisms in which the flux is proportional to the concentration (saturation) gradient. Diffusion is a special case of dispersion when the velocity of the fluid is zero. Passive samplers (sometimes called diffusive samplers) have been defined by the European Committee for Standardization as: ''A device that is capable of taking samples of gases or vapors from the atmosphere at a rate controlled by a physical process such as gaseous diffusion through a static air layer or a porous material and/or permeation through a membrane, but which does not involve active movement of air through the device''[15]. In a truly diffusive sampler, the external wind speed will not affect the sampling rate because the gas molecules are transported only by molecular diffusion, which is a function of air temperature and pressure. This independence allows the time-weighted average ambient concentration to be calculated using Fick's laws of diffusion [15]. Rate of pollutant gas absorption for a simple diffusion tube sampler is controlled by the diffusion path length and the internal cross-sectional area of the sampler.

Theory of passive diffusion samplers: Air pollutants at the entrance of the tube and inside the cylinder move towards the collection medium by diffusion. The quantity of contaminants sampled by the passive sampler is determined in applying Fick's first law [16, 17].

$$N = AD\frac{dC}{dX} \quad (1)$$

Where N is the air pollutant transfer rate (g min^{-1}), A is the internal cross-sectional area of the diffusion tube (cm^2), D is the diffusion coefficient of air pollutant (cm^2 min^{-1}), C is the concentration in air (g cm^{-3}) and X is the distance from the collection area (cm). The equation describing the concentration of pollutant within the passive sampler is given by Fick's second law

$$\frac{dC}{dT} = D\frac{d^2C}{dX^2} \quad (2)$$

where t is the average time in the sampling period. If the concentration profile in the diffusion tube is not modified with time, that is, the steady state, $\frac{dC}{dT}$ is equal to zero and Eq. (2) is simplified as

$$\frac{d^2C}{dX^2} = 0 \quad (3)$$

Under the boundary conditions of C=C° at X=L and C=0 at X=0; a solution of Eq. (3) can be found as

$$C = C°\frac{X}{L} \quad (4)$$

where L is the length of the diffusion tube and C° is the concentration in air surrounding the passive sampler. In this case, C° is a constant parameter. Eq. (4) shows that a linear concentration profile settles in the diffusion tube. By substituting Eq. (4) into Eq. (1):

$$N = C°\frac{AD}{L} \quad (5)$$

The sampled mass of pollutant, m (g), is given by

$$m = Nt_s \quad (6)$$

where t_s is the sampling time.

By substituting Eq. (6) into Eq. (5), the ambient concentration C° is calculated as

$$C° = \frac{N}{AD}L = \frac{mL}{DtA} \quad (7)$$

This last expression is generally used to determine the concentration in air (C°) from the mass collected by the passive sampler. Nevertheless, Eq. (7) is set up for the steady state, a constant concentration in air during the

sampling period. L/A is the term depends of the geometry of the sampler and resistances in the diffusion path. For the Ferm [18], sampler this may be expressed by:

$$\frac{L}{A}=\frac{L_R}{A_R}+\frac{L_F}{A_F}+\frac{L_N}{A_N}+\frac{L_{BL}}{A_R} \quad (8)$$

where L_R is the length of the stagnant tube (1.2 cm), A_R is the cross sectional area of the tube (3.46 cm^2 in our case), L_F is the thickness of the filter (0.0175 cm), A_F is the total area of pores in the filter (calculated from the exposed area, A_R and the filter porosity 3.46*0.85 = 2.94 cm) and A_N is the area of the steel net porosity of 0.13 (0.403 cm^2), while L_{BL} is the thickness of the laminar boundary layer that exists in contact with the external force of the sampler (0.15 cm).

Experimental

Study area: Nine sites have been selected to represent various area characteristics, such as urban areas, industrial areas and residential areas as shown in Table 1. Four sites at Alexandria city are IGSR, Shouhada, Abu-Qir and Nahda; while five sites at Delta region are Kafr Dawar, Damanhour, Kafr Zayat, Tanta and Damietta.

Sampling: Passive samplers are generally protected from the rain, sun and mechanical damage during field deployment by a shelter. The sampling period were taken once per month for two weeks in most sites were selected during the study period. The sampler was developed by the Swedish Environmental Research Institute. The sampler consists of a cylindrical polyethylene tube (internal diameter 21 mm, length 12 mm). The sample includes an impregnated filter inside a polyethylene tube. To avoid internal turbulent diffusion and particle interference the inlet is covered by a thin porous membrane filter. The membrane was protected from mechanical damage by a stainless steel screen. Gases are transported and collected by molecular diffusion. The uptake rate is only dependent upon the diffusion rate of the gas. The collection rate is 31 L/24 h for SO_2 and 36 L/24 h for NO_2 [19].

Impregnation solution: The impregnation solution for SO_2 was 5.6 g KOH dissolved in methanol using ultrasonic shaking add 10 ml glycerol and dilute to volume 100 ml by methanol, while for NO_2 was 7.9 g NaI and 0.88 g NaOH dissolved in methanol using ultrasonic shaking and ailuted to 100 ml by methanol [18].

Table 1: Sites selected and its characteristics

Location	Station	Area characteristics
Alexandria	IGSR	Urban
	Shouhada square	Urban
	Abu Qir	Industrial
	Nahda	Industrial
Delta region	Kafr Dawar	Residential
	Damanhour	Residential
	Kafr Zayat	Industrial/Residential
	Tanta	Urban
	Damietta	Residential/Urban

Impregnation of filter: The impregnation is performed by placing the filter paper into the cap of the passive sampler. 50 µl of the impregnation solution is carefully added to the filter with a micropipette. Make sure that the whole filter is wetted with the impregnation solution. Let the impregnated filter dry on the cap for maximum 10 minuets and mount then the passive samplers place the mounted sampler in a transport box which is properly closed [18].

Extraction of passive samplers: The composition of the extraction solutions for NO_2 are 133 µl of triethanolamine added to 1000 ml of deionized water, while for SO_2 are 10 ml 30% H_2O_2 added to 1000 ml deionized water. After exposure the sample filters were extracted in 5 ml extraction solution in sealed plastic bags. The filter extracts were analyzed for SO_2 as sulphate, while for NO_2 as nitrate by ion chromatography, Dionex, AS4A, USA [18].

RESULTS AND DISCUSSIONS

Seasonal variation: The seasonal variation was studded for NO_2 and SO_2 at Alexandria and Delta in Egypt during 2005.

Nitrogen dioxide (NO_2): Monthly average concentration of NO_2 during 2005 at IGSR, Shouhada, Abu Qir, Nahda, Kafr Zayat, Tanta, Kafr Dawar, Damietta and Damanhour were graphed in Fig. 1. The results of NO_2 showed a seasonal variation as the highest were winter. The general meteorology of the region during the winter is dominated by low wind speed which increased atmospheric stability. Stagnant air masses allow more accumulation of air pollutants in given area. During the winter, atmospheric dispersion is typically at a minimum and therefore, the NO_2 pollutant will not be as wind dispersed throughout the Planetary Boundary Layer (PBL).

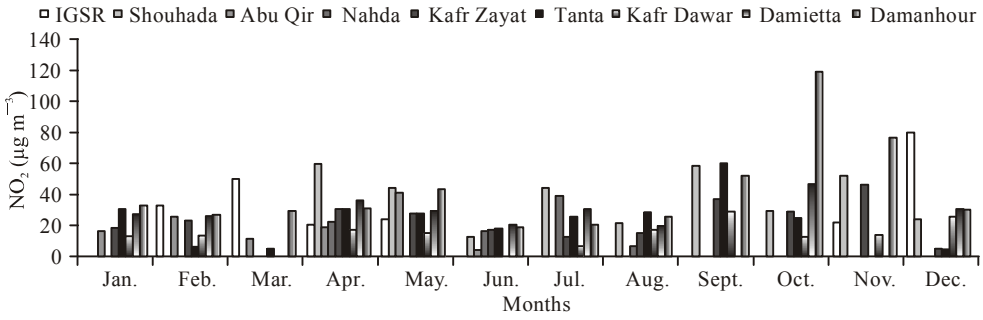

Fig. 1: Monthly average concentration of NO_2 (µg m^{-3}) at Alexandria and Delta during 2005

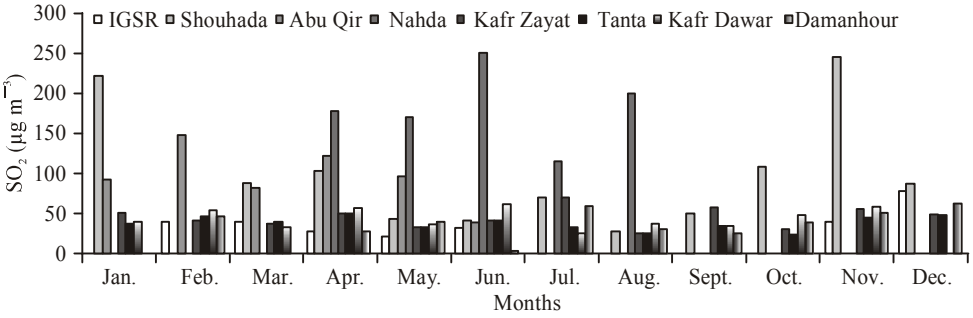

Fig. 2: Monthly average concentration of SO_2 (µg m^{-3}) at Alexandria and Delta during 2005

Conversely, during the summer months the average PBL height is typically as its greatest, resulting in increased mixing through a greater volume of the troposphere and hence lower pollutant concentrations. Moreover, the availability, of enhanced OH during summer months may also act to consume NO. Moreover, the summer season enhance NO_2 photolysis to give NO that react with volatile organic compounds and results in peroxy radicals and ozone formation [20].

Sulfur dioxide (SO_2): Monthly average concentration of SO_2 during 2005 at IGSR, Shouhada, Abu Qir, Nahda, Kafr Zayat, Tanta Kafr Dawar and Damanhour were graphed in Fig. 2. Generally, the highest values of SO_2 concentration were found in the winter, whereas the lowest concentrations were detected in the summer season. At IGSR station (Alexandria), the study revealed that, in spite of relatively high SO_2 emissions, the ambient air SO_2 levels were low. It was suggested that, this is due to the possibility of chemical transformation of SO_2 to SO_4 [21]. This finding is explainable by the fact that, corresponding SO_4 levels are high at the same time. The atmospheric conditions in this study are characterized by (i) high particulate matter less than 10 micron (PM_{10}) concentrations, (ii) high pH of aerosols (alkaline soil), (iii) high water content and (iv) high Ca content [21]. These conditions are conductive environment for conversion of SO_2 to SO_4.

Table 2: Minimum, maximum, average and standard deviation of NO_2 concentration µgm^{-3} during 2005 at Alexandria and Delta stations

Location	Station	Minimum	Maximum	Average	SD
Alexandria	IGSR	21.20	80.50	38.70	23.20
	Shouhada square	12.30	59.10	38.30	17.10
	Abu Qir	3.35	76.10	23.95	20.20
	Nahda	6.77	36.49	20.95	12.43
Delta region	Kafr Dawar	1.10	29.99	15.30	7.93
	Damanhour	2.37	119.80	42.55	29.10
	Kafr Zayat	5.10	46.40	24.30	11.80
	Tanta	4.40	59.00	23.90	15.90

In the summer, the physical parameters such as, higher sunlight, wind speed and mixing heights are all likely causes that lead lower SO_2 concentrations. The greater solar flux would promote the efficiency of atmospheric chemical reactions, leading to greater conversion of SO_2 to SO_4. This would reduce the concentrations of gaseous pollutants, but could increase the relative amount of particulate matter formed [22].

Yearly average concentration: Yearly average data are presented in Table 2 and 3, where IGSR, Shouhada and Damanhour had the highest levels in Alexandria and Delta for NO_2 gas, these stations represent the urban and heavy traffic area. In case of SO_2 the stations which represent the industrial area had the highest yearly average levels in Alexandria. In Delta there are no big

Table 3: Minimum, maximum, average and standard deviation of SO_2 concentration μgm^{-3} during 2005 at Alexandria and Delta stations

Location	Station	Minimum	Maximum	Average	SD
Alexandria	IGSR	20.9	77.6	38.5	17.3
	Shouhada square	27.6	243.4	98.5	71.1
	Abu Qir	7.8	173.8	98.5	48.5
	Nahda	118.0	250.8	187.0	55.0
Delta region	Kafr Dawar	23.5	62.7	44.6	12.0
	Damanhour	2.37	62.4	38.4	17.8
	Kafr Zayat	24.5	71.17	45.2	12.7
	Tanta	23.9	49.3	38.6	8.3

variations in the yearly average concentration of SO_2 among the all types of stations. The comparison of the yearly average levels with the AQL established by WHO in case of NO_2 (50 $\mu g\ m^{-3}$) [23] revealed that all recorded averages were lower than the AQL. In contrary to that SO_2 annual average exceeded the AQL for both WHO and EEAA (60 $\mu g\ m^{-3}$) [23, 24] at three stations in Alexandria city. The station which represent the urban area (heavy traffic) Shouhada had annually average nearly two times the WHO AQL, while Abu Qir and Nahda staions which represent the industrial area had annual average from 2 to 3.5 times respectively the WHO AQL.

CONCLUSION

The passive diffusion samplers have the potential to provide a cheap and effective means for determining atmospheric trace gas concentrations in the remote areas. The results from passive diffusion samplers could be considered reliable.

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