Ceylon Journal of Science : Physical Sciences, 9(1), 54-61 (2002)

MONITORING AIR POLLUTION LEVELS IN KANDY USING PASSIVE AND ACTIVE GAS SAMPLING TECHNIQUES

OLIVER A.ILEPERUMA[a,*] AND VILANI D.K.ABEYRATNE[b]

[a]*Department of Chemistry, University of Peradeniya, Peradeniya, Sri Lanka*
[b]*Postgraduate Institute of Science, University of Peradeniya, Peradeniya, Sri Lanka.*

ABSTRACT

The technique of passive gas sampling was employed to monitor air pollution in Kandy, the second largest city in Sri Lanka. This technique was developed to analyze sulphur dioxide, nitrogen dioxide and ozone in the ambient air at two locations within the city with a heavy concentration of traffic. Exposure of samplers in the field for 4-6 days and subsequent development were found to be satisfactory. In addition, active sampling was carried out using air samplers to determine the hourly variation of the pollutant levels. The analytical method was validated by comparing results obtained with those from a fixed monitoring station using automatic samplers. Results show that the air pollution standards in ambient air was exceeded on about 44% occasions.

Key words: *Air pollution, active and passive sampling*

1. INTRODUCTION

Air pollution has become a serious environmental problem resulting in adverse health problems in most big cities of developing countries in Asia [1]. Monitoring of air pollution using fixed stations is restricted due to the high costs involved. In Sri Lanka, two fixed monitoring stations measure the air quality of its capital city, Colombo. The city of Kandy, which is the second largest in Sri Lanka, is situated in a valley between two mountain ranges and is expected to experience a high degree of air pollution within the city limits. Around 20,000 vehicles enter the city from its suburbs on a daily basis and most of these vehicles emit noxious exhaust fumes. Concentrations of pollutants specially under calm weather can rise to alarming proportions. There has been no monitoring done in Kandy and unlike in Colombo where the sea breeze effectively disperses pollutants, the situation here could be much worse. The technique of passive sampling has been developed to monitor air pollution in places, which have no electricity such as forests or remote areas and where small, silent lightweight samplers are required for personal use to determine the level of exposure of individuals to specific pollutants [2]. Another use of this method particularly for developing countries is to monitor air pollutant levels in cities where there are no fixed monitoring stations. We have developed this passive gas sampling technique as an inexpensive method for the determination of average values of three key pollutants. This method has been used in Asia [3] and other countries in Europe to monitor air quality specially in remote areas. This paper describes some data obtained over a period of about two years on the air pollution levels in the city of Kandy where the ambient concentrations of sulphur dioxide, nitrogen dioxide and ozone have been determined. In addition, active sampling has been carried out to determine the hourly variation of some of the pollutants. Some preliminary data obtained from passive sampling have already been published [4].

---

[*] oliveri@pdn.ac.lk

2. EXPERIMENTAL

2.1 Passive gas sampling technique

Passive gas samplers were fabricated locally using 25 mm diameter Teflon rods. A schematic diagram of a sampler is given in figure 1. It consists of a Teflon ring, which is 25 mm in diameter and 10 mm in length. An impregnated filter (Whatman 1 filter paper which is 25 mm in diameter) was placed on top of the sampler and was fixed using a Teflon snap-on cap. A Teflon filter (25 mm diameter, 175 µm thickness, pore size 1.0 µm) was placed on the punched snap-on cap of the sampler to prevent deposition of aerosols. A stainless steel net (0.125 mm mesh size) was placed over the Teflon ring in order to prevent mechanical destruction and also to prevent effects of wind on the diffusion path. The filter and the net are attached by another snap-on cap, which has a 21 mm centered hole.

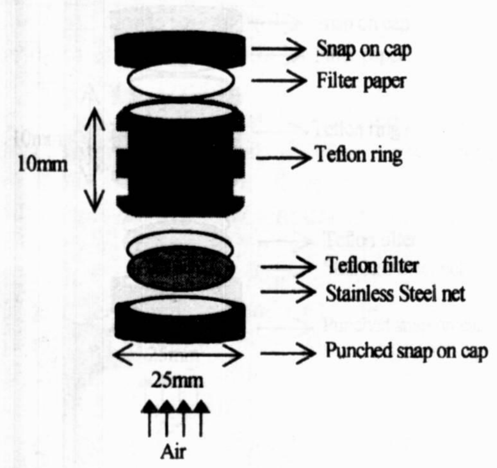

Fig. 1 A schematic diagram of the air sampler used

The sampler was stored in a polypropylene vial until the time of exposure. The samplers were first cleaned by sonication in de-ionized water and then dried in an oven at 40° C and stored in a desiccator. The filter papers used for coating were washed four times with deionized water, twice with methanol and dried in a desiccator.

2.2 Coating solutions to trap pollutants:

All chemicals were analytical reagent grade and deionized water was used to prepare solutions. The coating solution for NO_2 was prepared by dissolving 0.44 g NaOH and 3.95 g of NaI in 10 ml of water and diluting to 50 ml with methanol. For sulphur dioxide determination, the coating solution was prepared by dissolving 0.5 g NaOH in the minimum of water followed by dilution to 50 ml with methanol. For the ozone determination, the filter was soaked in a solution prepared by mixing 1 g $NaNO_2$ and 1 g K_2CO_3 with 2 ml of glycerol and diluting to 100 ml with a 70:30 water-methanol mixture. The filters were soaked in these solutions by spreading 100 µl aliquots and the end cap was immediately fixed and placed inside the polypropylene storage vials.

2.3 Sampler exposure in the field

Samplers were placed at a height of 1.5 m from the ground protected from rain and stuck on with the help of double glued tape. The sampler was exposed for 4 - 6 days in the field. Sampling was typically carried out at two high traffic zones in the Kandy city.

2.4 Rainfall measurements

Rainfall data for the entire period were obtained from the Gannoruwa research station of the Department of Agriculture (fig 5).

2.5 Determination of pollutant concentrations

The filter paper containing the trapped pollutants was handled with the extreme care to avoid contamination. The filter paper was transferred to a beaker containing 5 ml of deionized water and sonicated for 10 minutes. The analysis for NO_2 depends on its reaction with I^- to produce NO_2^- according to the following reaction.

$$NO_2 (g) + 3I^- \rightarrow NO_2^- + I_3^-$$

The NO_2^- produced was determined colorimetrically by diazotizing with sulphanilimide and coupling with N-(1-napthyl)-ethylenediamine dihydrochloride. The reaction to trap sulphur dioxide can be expressed as follows;

$$2SO_2\,(g) + 4OH^- + O_2 \rightarrow 2H_2O + 2SO_4^{2-}$$

The sulphate thus formed was determined turbidimetrically. Twenty milliliters of the solution was filtered using a sintered glass fiber filter (porosity 4) and 4 ml of the buffer solution [prepared by dissolving $MgCl_2.6H_2O$ (0.3 g), $CH_3COONa.3H_2O$ (0.5 g), KNO_3 (0.1 g), Na_2SO_4 (0.011 g) and acetic acid (2.0 ml) in 100 ml of water] was added. After stirring with $BaCl_2$ (1.0 g) the turbidity developed was measured using a Hatch DRT-15CE model turbidimeter. A calibration curve was constructed using the standards provided with this instrument.

The reaction to trap ozone can be expressed as follows:

$$O_3 + NO_2^- \rightarrow NO_3^- + O_2$$

When ozone is trapped using a nitrite solution an equivalent amount of NO_3^- is formed which is determined colorimetrically using the same procedure described in 2.5 after reduction using a Cu/Cd column. This gives the total NO_3^- and NO_2^- in the sample and the direct coupling reaction gives only NO_2^-. From the difference it is possible to calculate the NO_3^- concentration and hence the amount of ozone trapped by the filter.The filter paper with trapped ozone was transformed to a clean glass vial containing 5 ml of deionized water and then diluted to 20 ml with deionized water. One sample containing 5 ml of the above solution was used to estimate nitrite and the remaining 15 ml of the solution was passed through a Cu/Cd column to determine the nitrate formed.

2.6 Active gas sampling technique

Gilian air sampling pump connected to polypropylene tubes was used to pump air into the absorbing reagent contained in the glass fritted midget impinger. The pump has an automatic constant flow in the range of 0.2 to 3.0 litres per minute. The rechargeable Ni/Cd battery provides approximately 10-12 hours of reliable operation on a single charge. The two-piece impinger has a capacity of 25 ml and a graduated scale along the side in 5 ml increments. The tip is precisely spaced in relation to the bottom of the impinger.

The NO_2 was determined by employing the Greiss- Saltzman reaction while SO_2 was determined using the West-Gaecke method [5]. The absorbing reagent to trap NO_2 was prepared by dissolving 5 g of sulphanilic acid in almost a litre of water containing 140 ml of glacial acetic acid, 20 ml of 0.1% N-(1-naphthyl ethylenediamine dihydrochlo -ride and 10 ml of acetone and diluted to 1 litre.

For sulphur dioxide determination the absorbing reagent was prepared by dissolving 10.86 g $HgCl_2$, 5.96 g KCl and 0.066 g EDTA in 1 litre of distilled water and the pH was adjusted to 4.00 using 6M KOH. For ozone determination, the absorbing reagent was prepared by dissolving 0.25 g $NaNO_2$ and 0.3 g K_2CO_3 in 250 ml of water at a pH of 11.5.Ten millilitres of the absorbing reagent was pipetted into the impinger and the air was drawn though it for a one hour period at the rate of 0.4 litres per minute. This was continued for 5-7 hours during daytime for several days at the two sites, Bogamabara and on the Kandy lake road.

In the determination of NO_2 the red-violet colour of the azo dye formed was measured at a wavelength of 550 nm using a Shimadzu UV 101 model spectrophotmeter. The calibration curve was constructed using standards prepared using $NaNO_2$. For SO_2 determination, it is absorbed in tetrachloromercurate solution resulting in the formation of a dichlorosulphitomercurate complex. The solution obtained was first treated with 1 ml of 0.6% sulphamic acid to destroy the nitrite ion formed from the absorption of nitrogen oxides in the atmosphere. It was next treated with 2 ml of 0.2% formaldehyde and 2 ml of pararosaniline and after 30 minutes the violet colour developed was measured spectrophotmetrically at a wavelength of 548 nm.

Ozone concentration was measured using the same procedure as described under the passive sampling method and the nitrite formed was determined spectrophotmetrically at 550 nm.

3. RESULTS AND DISCUSSION

3.1 Passive gas sampling technique

The rates at which gaseous pollutants in ambient air diffuses into the sampler are controlled by the diffusion coefficients of the respective gases. At the end of the sampler the

Gases impinge on a paper disk impregnated with a reagent with which it reacts specifically and almost quantitatively. A static air layer may form at the entrance to the sampler in which laminar diffusion rather than turbulent motion predominates. For outdoor sampling locations, the thickness of the static air layer has been found [6] to be an average of 1.5 mm. The thickness of this laminar boundary depends on wind speed and turbulence of the ambient air and during sampling, the fluxes of gases through all sections are considered as equal and that nothing is adsorbed on the walls of the sampler. The sampler body can be lengthened as in many of the older versions of passive gas samplers but these types gave lower pollutant uptake rates.

Fick's first law states that the flux of the gas (the net amount transported per unit time and area) due to diffusion in the direction of mass flow is proportional to the concentration gradient of the gas and the proportionality constant is the diffusion coefficient. This governs the sampling rate and the ambient concentrations of pollutants in nm m^{-3} were determined from the following equation,

$$\text{Pollutant (g)} = L \times E_v \times [X] / T \times D_c$$

where, L= total air resistance(41.2 m^{-1}), E_v = extraction volume (ml), D_c = diffusion coefficient ($m^2\ s^{-1}$), T = sampling time (seconds) and [X] = pollutant anion concentration (μmol L^{-1}). This figure can be converted to ppbv using,

$$p = nRT / V$$

where, n = number of moles in 1 m^3 of air , R = gas constant, T = temperature (Kelvin) and V = air volume (1000 L).

This method requires no field calibration and the concentrations of pollutants of interest is integrated over the time of exposure which in our experiments ranged from 4 - 6 days. For intercomparison purposes samples were exposed close to the fixed air quality monitoring station located in the capital city of Colombo. It was found that there was general agreement between the values obtained by the two methods provided that the sampling period is at least four days. At shorter sampling periods there were some discrepancies owing to the fact that the diffusive sampler's collection rates are slow.

3.1.2 Ambient concentration of NO_2

Figure 2 shows the variation of NO_2 levels during the period of study from October 26th, 2000 to March 31st, 2001 (sample numbers 1-17) and from 15th February 2002 to 27th June 2002 (sample numbers 18-30).

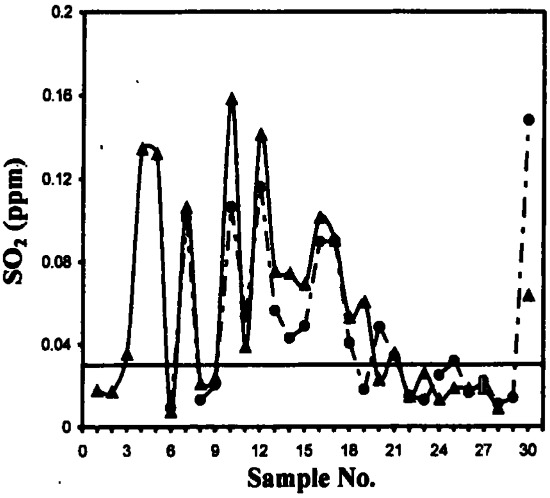

Fig. 2 Ambient concentration of NO_2 at two sites in Kandy city. (Solid line indicates the gazetted Sri Lanka ambient air quality standard for NO_2)

It was found that the NO_2 level was slightly lower during school holidays when the traffic volume was relatively lower and the highest average value of 0.17 ppm was observed during the first week of commencing the school term. Thereafter the values remain at consistently higher levels throughout the period from January 1st to March 31st, 2001. The NO_2 levels during 2002 were found to be slightly lower than those observed in 2001. This may be due to much better vehicular traffic arrangements in the

Kandy city limits than during the previous year and also due to the removal of restrictions on travel on certain roads of the city. The Sri Lanka standard for the 24 h average of NO_2 in ambient air is 0.03 ppm and the concentration obtained during the entire period from October 26th to March 31st showed that this standard is exceeded 38% of the time. Nitrogen dioxide is known to cause respiratory problems and asthmatics, specially young children are particularly sensitive. Recently, there have been increasing hospital admissions due to asthma, bronchitis and other respiratory illnesses. The NO_2 concentration was low at times of high rainfall as evident from fig.5, which gives rainfall patterns for the sampling occasions.

3.1.3 Ambient concentration of sulphur dioxide

Sulphur dioxide levels in the Kandy city exceeded the Sri Lanka standards on 53% of the occasions (fig. 3). Here too, the peaks for NO_2 (fig. 2) correspond to the same peaks observed for SO_2 concentrations, indicating that the same sources are responsible for this type of pollution. Fig. 3 gives the ambient levels of sulphur dioxide at the two locations studied. It is clear that the pollutant levels reached highest values just before the New Year festival season and during the wesak season. There is an inverse relationship between rainfall intensity and the concentration of sulphur dioxide as expected since SO_2 is removed from the atmosphere by dissolving in water. A similar correlation was also found to be the case with the NO_2 concentration with rainfall indicating that SO_2 is more likely get oxidized more rapidly under moist weather conditions forming SO_3 which rapidly reacts with water.

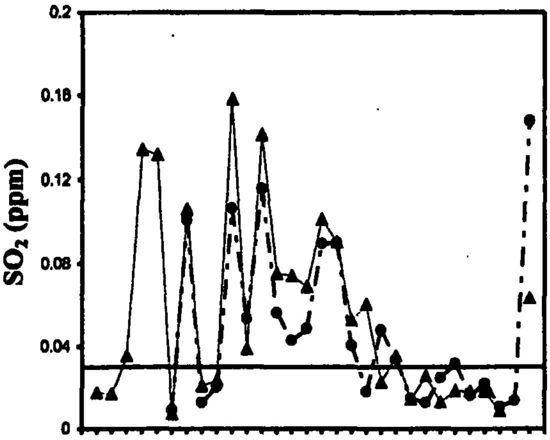

Fig. 3 Ambient SO_2 concentrations at the two locations in the Kandy city.
(Solid line indicates the gazetted Sri Lanka ambient air quality standard for SO_2)

3.1.4 Ambient concentration of ozone

The ambient concentrations of ozone levels in the Kandy city exceeded the Sri Lanka standards on 40% of the occasions monitored during this study (fig. 4). Generally only short term standards are available for ozone and we have used the US-EPA 8 hour guideline of 0.06ppm as the basis for exceedance. The observed ozone levels were found to be significantly higher than this 8 hour standard on many occasions. There was a significantly low level of ozone during the rainy days (sampling occasions 10-13) and higher levels can be correlated to the intensity of sunlight as expected. The lower levels of

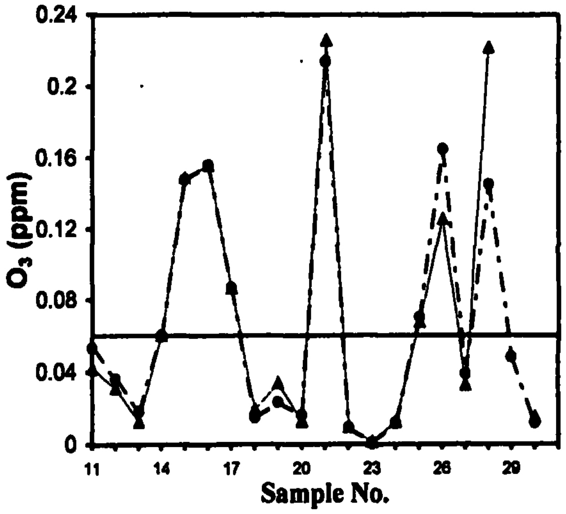

Fig. 4 Ambient O_3 concentrations at the two locations in the Kandy city.
(Solid line indicates the US-EPA 8 hour standard for ambient ozone concentration.)

ozone observed for the sampling occasions when there was relatively high rainfall may be due to the fact that the precursors required for ozone formation such as NO_2 and SO_2 levels were low during high rainfall events.

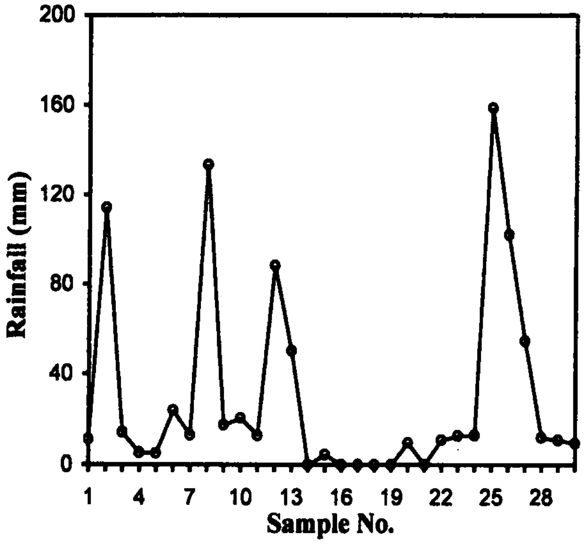

Fig. 5 Rainfall during sampling occasions in the city of Kandy.

3.2 Active gas sampling technique

Pollutant concentration of the NO_2 in ppm was calculated using the following equation,

$$NO_2\,(ppm) = [A \times K \times v \times 0.532/V]\,D$$

where A= Absorbance at 550 nm, K= Standardization factor, v= Volume of absorbing reagent (ml), V= Volume of air sampled (L) D= Dilution factor. Pollutant concentration of the SO_2 in ppm was calculated using the following equation,

$$SO_2\,(ppm) = [C \times v \times 0.382/V]\,D$$

where C= Concentration of SO_2 in Solution) µg/ml, v= Volume of absorbing reagent (ml), V= Volume of air sampled (L), D= Dilution factor. Pollutant concentration of the O_3 in ppm was calculated using the following equation;

$$O_3\,(ppm) = [C \times v \times 0.509/V]\,D$$

where C= Concentration of O_3 in Solution(µg/ml), v= Volume of absorbing reagent (ml), V= Volume of air sampled (L), D= Dilution factor.

3.2.1. Ambient concentration of NO_2

Figure 6 shows the hourly variation of NO_2 levels during the daytime at the Bogambara site collected on three different days. The variation pattern of the concentration with time is the same on all three days of observation. The highest values were observed during the period between 7 a.m. to 8 a.m. perhaps owing to the heavy school traffic. A similar observation has been reported on the diurnal variation of the pollutants from the city of Los Angeles [7] where the NO_2 peaks at the rush hour between 6 to 8 a.m. Lower concentrations were observed for data collected on a rainy day and there was ample sunshine on the other two sampling occasions.

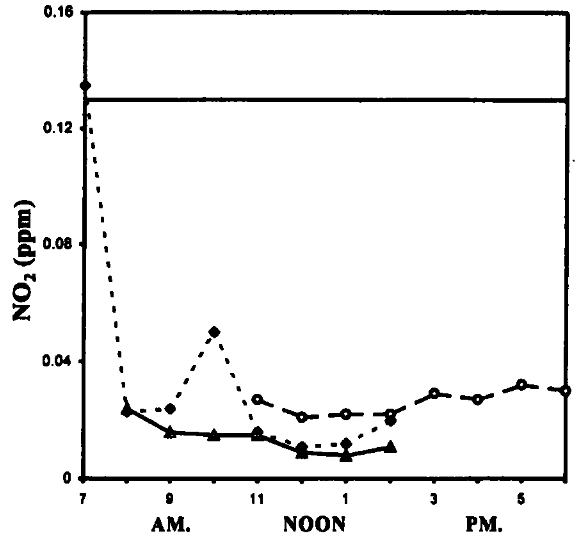

Fig. 6. Hourly variations of the day time ambient NO_2 concentration in the Kandy city.

This is the usual pattern observed for NO_2 variation in other parts of the world. The maximum NO_2 concentration was observed during the 7 – 8 hours in the morning rush hour, but the values come down sharply as the NO_2 formed undergoes photolysis due to sunny weather. Solid line indicates the Sri Lanka standard for NO_2 in ambient air for one hour average which is 0.13 ppm and this is exceeded during the morning hours and hence a matter of serious concern for the health of the population.

3.2.2 Ambient concentration of sulphur dioxide:

Hourly variations of Sulphur dioxide levels during the daytime at the Bogambara site with high traffic were recorded during five days (fig.7). Lower line indicates the data collected on a rainy day and the upper four lines show the data collected on sunny days.

There are only limited data available here owing to experimental limitations. It is clear that at least on one of the occasions, the SO_2 levels have exceeded the Sri Lanka standards considerably. Solid line indicates the Sri Lanka standard for SO_2 in ambient air for one-hour average, which is 0.08 ppm. It is also seen that there is an inverse relationship between the rainfall intensity and the concentration of sulphur dioxide.

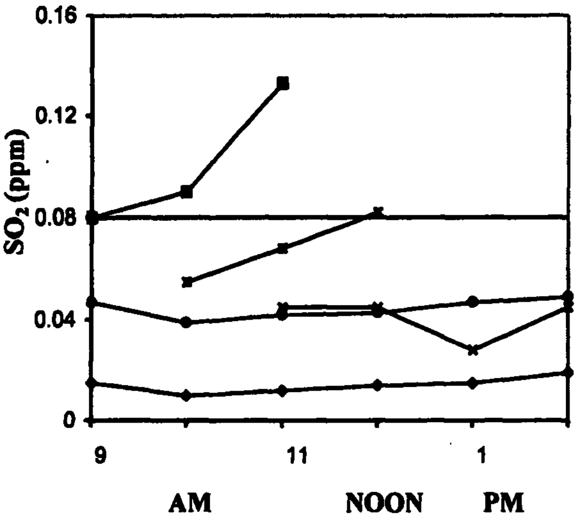

Fig. 7 Hourly variations of the day time ambient SO_2 concentration in the Kandy city.

3.2.3 Ambient concentration of ozone:

The ambient concentrations of ozone were monitored hourly, during 12 hours of a sunny day, was recorded (fig. 8). The observed ozone levels were found to be significantly higher during 10.00 am – 2.00 pm as is observed in the Los Angeles study. The NO_2 concentration decreases with the time of the day since a part of it undergoes atmospheric reactions leading to photochemical smog including ozone. Higher levels of ozone can be correlated to the intensity of sunlight and the temperature and such variations have been reported from studies elsewhere.

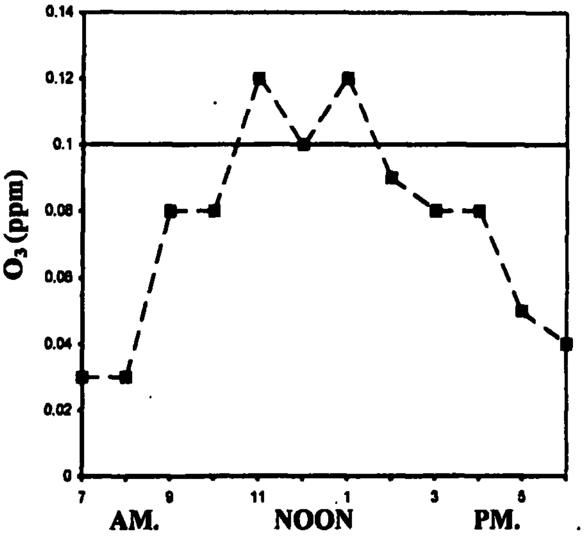

Fig. 8 Hourly variation of the ambient O_3 concentration in the Kandy city.

Solid line indicates the Sri Lanka standard for O_3 in ambient air for one-hour average, which is 0.1 ppm.

4. ACKNOWLEDGEMENT

Financial assistance from the National Science Foundation in the form of a research studentship (NSF/RSP/2001/PGIS/05 is gratefully acknowledged. The authors also wish to thank Dr. V.R. Punyawardana of the National Resources Management Center, Department of Agriculture for providing rainfall data during the course of this study.

REFERENCES

1. ADB *"Asian Development Outlook"*, Asian Development Bank, Manila (1991).
2. M. Ferm, *A Sensitive Diffusional Sampler* IVL publication B-1020, (1991) Swedish Environmental Research Institute Goteberg, Sweden.
3. M..Ferm and H. Rodhe, *J. Atmospheric Chemistry* **27** (1997) 17.
4. O.A.Ileperuma and VDK Abeyratne, *Analytical Sciences* (Japan) **17** (2001) 291.
5. Annual book of ASTM standards section II, Water and Environmental technology, Easton, MD,USA 11.03, (1983) 58.
6. M.Ferm and P.A. Svanberg, *Atmospheric Environment* **32** (1998) 13.
7. G.Baumbach, Air Quality Control, Springer, Berlin (1996) 101.