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Comparative analyses of urban air quality monitoring systems: passive sampling and continuous monitoring stations.

Lanzafame Rosario, Monforte Pietro, Scandura Pier Francesco*

University of Catania, Viale A. Doria 6, 95125 Catania, Italy

Abstract

Indicative methods of measurement are an economical and efficient way of preliminarily evaluating urban air quality. In November and December 2012, there was a campaign to measure NO₂, C₆H₆ and O₃ around the city of Catania (Italy) using diffusive samplers (Passam model). Placing the samplers at the fixed sampling sites of the city's monitoring network allowed for a comparison of the concentration values measured by continuous samplers (reference method) with those obtained from passive samplers. For the comparison, the time data of the continuous samplers were mediated as a function of the number of hours of diffusive sampler exposure. With the help of meteorological data from the Sicilian Information Agrometeorological Service (SIAS), it was possible to verify and evaluate any uncertainties associated with the passive samples, since the sample amounts are a function of meteorological variables given they are collected by diffusion. Finally, a statistical analysis based on linear regression highlighted a good correlation between the passive samplers and the fixed monitoring stations.

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1. Introduction

Urban air pollution profoundly undermines man's quality of life. European norms from directive 96/62/CE to the latest 2008/50/CE relating to "environmental air quality and cleaner air in Europe" require air quality monitoring networks for urban conurbations of more than 250,000 people. The European Environmental Agency's (EEA) annual report on air quality reports on the current state of air quality in the European countries which not only impacts human health but also the entire socio-economic system. The main air quality pollutants of 2014 were PM, O₃, NO₂ and benzene. The World Health Organization (WHO) imposes much more restrictive legal limits on certain pollutants compared to the EU. In Europe, the latest evolutions of the diesel engine have promoted greater sales of them compared to petrol engines which has increased NO₂ emissions by 18 % over 2003–2012. Benzene emissions

* Corresponding author. Tel.: +39 095 7382455;
E-mail address: psscandu@dii.unict.it

have also increased by 21 % for the same period. However, the trend of O₃ concentrations has been decreasing in most EU countries with the exception of Italy and Spain. Managing and maintaining monitoring networks are fairly costly so, through directive 2008/50/CE, the EU stipulates that the number of fixed monitoring stations can be reduced by 50 % in those areas and conurbations where there is supplementary monitoring such as modelling or indicative measurements. Diffusive sampling is the most common type of indicative measurement. The use of passive sampling has become widespread in the EU. The Joint Research Centre [1] has carried an in-depth review into sampling NO₂, which samples are validated by calibrating with a reference method [2][3]. Various authors have analysed passive sampling in the Mediterranean area to evaluate how the climate influences measurement quality[4][5]. The impacts of O₃ and NO₂ on the ecosystem have been widely studied by various authors through passive sampling [6][7][8].

The city of Catania has been equipped with a network of air quality monitoring devices since 1992. The network is managed by the Ecology and Environment Office which has allowed the municipality to effectively identify pollutants and monitor the city's air quality [9][10]. The most suitable monitoring stations in the Catania network were identified to compare reference measurements with indicative ones (2008/50/CE). The selection was made by considering the most basic parameters which influence urban pollutant emissions: traffic flow distribution, rush hour congestion, work-base distribution and habitation density [11]. The pollutants monitored at the end of the following analysis are NO₂, C₆H₆ and O₃. The sample exposure times (the time between opening and closing the device) are on average one week (± 1 day) over which measurement uncertainty might affect the real value. The sampling campaign was carried out over eight weeks.

2. The general characteristics and functioning principles of continuous analysers

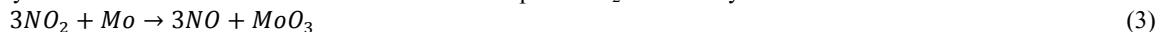
The samplers in Catania's monitoring network are certified by EU norms. Below, there is a description of the physical principle behind the measurements of the pollutants NO₂, C₆H₆ and O₃.

2.1. Continuous NO_x, NO, NO₂ sampler

It works through the oxidation of nitric oxide by ozone (reaction 1) which can then produce a characteristic luminescence (reaction 2) whose intensity is proportional to the NO concentration in the sample.



The air sample air flow rate is about 500 cm³/min at ambient temperature and pressure. The final data is normalised to 293K at a pressure of 101.3 kPa. The analysis is carried out every 10 seconds and the concentration values are expressed as hourly averages. The analyser conforms to UNI EN 14211:2005; calibration is automatic every 24 hours. In reaction 2, the nitrogen dioxide must be converted into nitric oxide in order to be measured so a molybdenum converter at 325 °C converts all the sample's NO₂ into NO by reaction 3



The air sample is sucked in by a sampling head (fig.1), hot filtered to remove any humidity, sent to the analyser by a control capillary and then on to a solenoid valve. The valve sends the sample to the NO₂/NO converter from where it goes to the reaction chamber when set to NO_x, or bypassing the converter if set to NO. When the sample flows through the converter, the luminescence measured in the reaction chamber is directly proportional to NO_x concentration. If the converter is bypassed, the luminescence represents NO concentration.

The reaction chamber, which pumps in O₃ to react with NO, produces a luminescence measured by the optical filter of a photomultiplier which is proportional to NO content and, depending on the solenoid setting, measures either NO or NO_x which then provides the relative NO₂ content. The digital-analogue converter converts the 3 recorded values into analogue signals which are displayed at the back of the instrument. The analysed sample is sucked in by a pump and then blown across an activated carbon filter to remove any ozone residue.

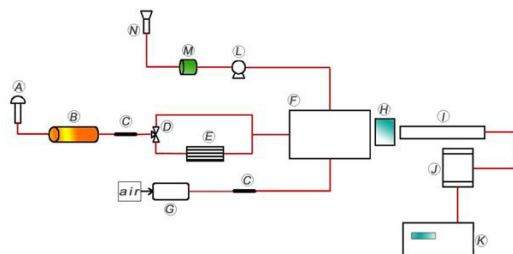


Fig. 1. Block diagram of NO_x-NO-NO₂ analyser: A) sampling head; B) heated filter; C) control capillary; D) solenoid valve; E) NO₂/NO converter; F) reaction chamber; G) O₃ generator; H) optical filter; I) photomultiplier; J) D/A converter; K) display; L) pump; M) activated carbon filter; N) outlet.

2.2. BTX CHROMATOTEC continuous analyser

The analyser is designed for BTX compounds (benzene, toluene, ethylbenzene, MP-xylene, O-xylene). It works automatically with a CPU board that interfaces with a PC. It works on the gas chromatography principle with a photo-ionisation (PID) sensor. The air is sampled by sucking in about 15 cm³/min every 30 minutes at ambient temperature and pressure. The final data is normalised to 293K at a pressure of 101.3 kPa. Calibration is automatic every 24 hours using purified air. To check chemical zero, a span gas calibration is carried out via a certified permeation tube with a known concentration of benzene. The analyser conforms to UNI EN 14662:2005 parts 1, 2 and 3. Figure 2 shows the block diagram of the AIR TOXIC analyser.

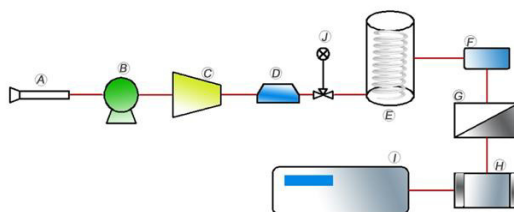


Fig. 2. BTX analyser block diagram: A) sample input; B) suction pump; C) activated carbon trap; D) desorption zone; E) analysis column; F) PID sensor; G) A/D converter; H) microprocessor; I) display; J) carrier gas input.

The complete analysis cycle occurs in two steps: the sampling phase and analysis phase. The former concentrates the volatile organic compounds (VOC) in the ambient air or carrier gas (N). By means of an external suction pump, the gas sample flows through a slender tube containing a porous substance (activated carbon) which can extract C₆ - C₁₀, without interfering with permanent gases or water vapour. Sample flow is regulated by a 50 μm orifice from between 10 – 25ml/min. Gas sample volume is measured downstream of the adsorption section. At the end of sampling, a relay directs the sample outward. During the analysis phase, the trapped VOCs are injected into an analysis column by thermal desorption fixed at 380 °C for 60 seconds. The gas sample is injected into the analysis column via the carrier gas. The sample components elute at a characteristic velocity which depends on their boiling points and how they interact with the column's stationary phase. A PID sensor on the column outputs a signal proportional to the sample component concentrations during elution.

The PID is based on ionising compounds by the UV radiation produced by Kr, Xe or H₂ gas discharge lamps. The lamp emits photons from 10.0 eV to 10.6 eV which pass through an ionisation chamber where some photons are absorbed by the eluents. The compounds whose ionisation energy is lower than the photon energy become ionised and as a consequence the ion current in the ionisation chamber is proportional to the compound concentrations. This current is then digitalised and transferred to the CPU where the microprocessor processes the data and transfers it to the RS232 output to be visualised.

2.3. Continuous O₃ analyser

The analyser works by spectrophotometry to determine ozone concentrations in samples. It works on the principle of UV wave absorption according to the Lambert-Beer law (equation 4) which defines how much light for a specific wavelength is absorbed by a particular gas molecule at a certain distance and a given temperature and pressure. The equation for these three parameters for gas at a standard temperature and pressure (STP) is:

$$I = I_0 e^{-\alpha LC} \quad (4)$$

from which

$$C = \ln\left(\frac{I_0}{I}\right) \cdot \left(\frac{1}{\alpha L}\right) \quad (5)$$

where I_0 is light intensity without absorption, I is light intensity with absorption, L is the distance travelled by the light during absorption, C is the concentration of the absorbed gas, and α is the coefficient of absorption. Since both the ambient temperature and pressure influence the density of the gas sample in the absorption tube, the quantity of light absorbed is subject to variation. To represent this effect, a correction factor is added to equation 5:

$$C = \ln\left(\frac{I_0}{I}\right) \cdot \left(\frac{1}{\alpha L}\right) \cdot \left(\frac{T}{273} \cdot \frac{29,92 \text{ in Hg}}{P}\right) \quad (6)$$

where T is Kelvin temperature and P is pressure in inches of mercury. Air sampling is by suction flow of about 2000cm³/min at ambient temperature and pressure. The final data is normalised by the acquisition system to a temperature of 293K and a pressure of 101.3 kPa. The analysis is carried out continuously every 10 seconds with the concentration value expressed as an hourly average. The ozone analyser conforms to UNI EN 14625:2005. Figure 3 shows the analyser's block diagram.

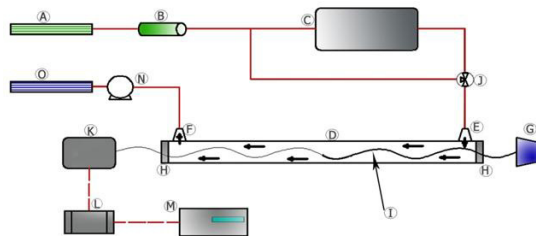


Fig.3. O₃ analyser block diagram: A) sample input; B) particulate filter; C) ozone scrubber; D) absorption tube; E) absorption tube inflow; F) absorption tube outflow; G) gas discharge lamp; H) filtered opening; I) light strip; J) valve switch; K) detector; L) microprocessor; M) display; N) exhaust gas suction pump; O) sample gas outlet

The gas sample from the air goes through a particulate filter before going into the absorption tube into which ambient air and scrubbed air are alternatingly pumped. A high energy gas discharge lamp close to the tube sample inlet emits UV light of wavelength 254 nm. The light passes through a filtered window which does not react with ozone and is transparent to 254 nm UV radiation, runs the whole length of the absorption tube which is full of sample to an analogous window at the other extreme of the tube where radiation very close to 254 nm wavelength is detected. Depending on how much radiation is detected, a voltage is produced which is digitalised and sent to the CPU which works out the ozone concentration in the absorption tube. Since resolving the Lambert-Beer equation requires knowing the light intensity during its absorption both in and out of ozone, the sample's path is deviated about every 3 seconds to the scrubber, then back again inside the tube. From the alternating measurements with and without ozone together with the calibration values and the current temperature and pressure data, the CPU can work out the final concentration of ozone. All these values are stored as well as displayed.

3. General characteristics and working principles of passive samplers

A passive sampler is a device capable of determining pollutant concentrations in the atmosphere without using pumps. They consist of polypropylene or glass vials generally closed at one end. A compound is placed within the vial which reacts with the target pollutant. Sampling begins when the vial is unplugged and the pollutant diffuses within the vial. The vial is re-plugged at the end of exposure. Once the reaction starts, a concentration differential is created between the inside and outside of the vial. This is the passive diffusion of a gas towards something absorbent according to Fick's law (7):

$$F = -D \frac{dc}{dL} \quad (7)$$

where F is molar flow, D is the diffusion coefficient, C is concentration and L is diffusion progression [12]. Considering that the diffusion conditions depend on the length of the diffusion's progression, L [cm] and the tube's cross section [cm^3], the average concentration of the ambient gas is given by:

$$C = \frac{Q \cdot L}{D \cdot A \cdot t} \quad (8)$$

with t [min] the exposure period and Q [μg] the total gas absorbed by the filter (obtained from spectrophotometric analysis). The samplers are placed in specific devices for exposure (fig. 4) so they are protected from rain, excessive sun and wind, are integral part of the measurement method. The vial holders must be placed at between 2 – 2.5 m above ground and because of the reactivity of the sampler compounds the holders must also be placed where the air can circulate freely without obstacles. As regards exposure time, days are required to collect enough pollutant which provides an average value for the whole sampling period. Any alterations in reliability may occur if pollutant concentrations exceed the samplers' range limits. Furthermore, the uncertainties of the weather can influence the efficacy of the sampling.



Fig. 4. A passive sampler holder in situ in Viale V. Veneto (note the yellow square).

3.1 The NO_2 and NO_x samplers

The NO_x sampler can identify oxides of nitrogen, in particular nitrogen oxide (NO). At one end of the sampler there is a filter impregnated with an oxidising compound, $\text{C}_{14}\text{H}_{16}\text{N}_2\text{NaO}_4$, known as carboxy-PTIO which reacts with NO to produce NO_2 identified through a second filter impregnated with a solution of triethanolamine, $\text{C}_6\text{H}_{15}\text{NO}_3$ (TEA). The NO_2 sampler has only one filter at one end impregnated with a solution of TEA. NO_2 is measured at the same time as that of NO_x (fig.5a). What drives the absorption is the concentration gradient between the outside air and the absorbent surface in which the pollutant concentration is almost zero at the opening of the vial. The diffusion velocity follows Fick's law. After exposure, the total gas absorbed by the filter is obtained by spectrophotometry, identifying and quantifying the rose colouration formed on the filter after the reaction between pollutant and TEA as per the Palmes method. Working range is 1–200 $\mu\text{g}/\text{m}^3$ while sampling time 1–4 weeks. No influence for temperature between 5 to 40 °C and humidity between 20 to 80 %. Influence of wind speed < 10% up to 4.5 m/sec using protection shelters; overall uncertainty is about 19.0%.

3.2. The BTX samplers

The passive sampler for measuring benzene consists of a glass tube open at both ends and inside which there is activated carbon (fig.5b, 5c). Both ends are blocked by a diffusive barrier of cellulose acetate. Benzene, toluene and xylene (BTX) are absorbed by the carbon, the analysis of which includes a desorption phase using a solution of carbon disulphide (CS_2) followed by gas-chromatography analysis. Working range is $0.5\text{--}500\ \mu\text{g}/\text{m}^3$ while sampling time 1–4 weeks. No influence for temperature between 10 to 30 °C and humidity between 20 to 80%. Influence of wind speed < 10% up to 4.5 m/sec using protection shelters; overall uncertainty is about 26.0%.

3.3. The Ozone sampler

The sampler consists of a propylene vial (fig.5d). At one end there is a fibre-glass filter soaked in an acetic solution of DPE. The reaction between ozone and DPE is not stoichiometric. The passive sampler is based on the reaction between 1,2-Di(4pyridyl)ethylene (DPE) with ozone to form an aldehyde which is quantified by the MBTH method. Working range is $5\text{--}240\ \mu\text{g}/\text{m}^3$ while sampling time 1–2 weeks. No influence for temperature between 5 to 40 °C, humidity between 20 to 80%. Influence of wind speed < 10% up to 2 m/sec using protection shelters; overall uncertainty is about 25%.



Fig. 5. Passive samplers: A) for nitrogen dioxide and nitrogen oxide, B) and C) for BTX, D) for ozone.

4. DATA ANALYSIS

4.1. Meteorological parameters

Taking into account the variability of Catania's weather, it was considered opportune to monitor temperature, humidity and wind-speed trends (SIAS data) during the sampling period since these parameters affect measurement uncertainty should the optimum ranges overshoot[13]; for each parameter a minimum (min), a maximum (max) a mean were considered. Figure 6 show all the parameters relating to the sampling period.

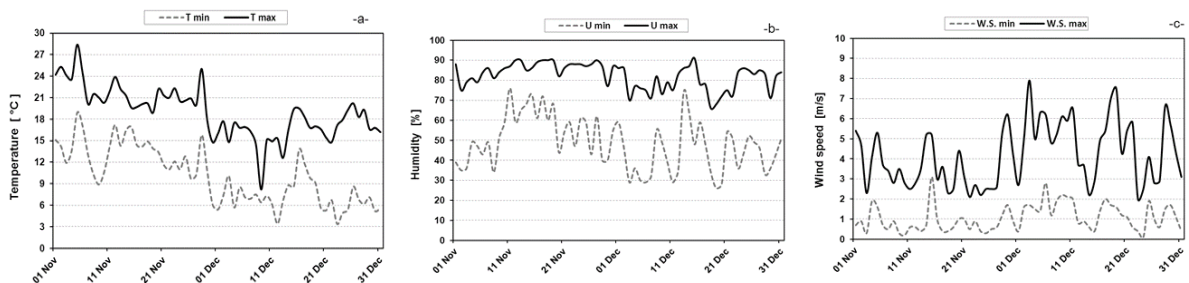


Fig. 6. Parameters relating to the sampling period: a) Temperature, b) Humidity, c) Wind speed.

It can be seen from analysing the weather data that the minimums and maximums of temperature do not show variations which could influence the sampling during that period; as for humidity, the maximum acceptable value is overshoot in the middle of the sampling period whereas the wind-speed maximums should not raise any uncertainties about the sampling except in sporadic cases.

4.2. Continuous analysers and passive samplers compared.

A statistical calculation was carried out to find the linear regression between measurements from the two systems relative to nitrogen dioxide (NO₂) followed by a calculation of the correlation coefficient (fig.7). Linear regression produces R²=0,81 with a correlation coefficient R= 0,90. In the case of benzene (C₆H₆), the statistical analysis highlights high correlations between the concentrations obtained by both systems. Linear regression produces R² =0,75 with a correlation coefficient R=0,87 (fig.8). Also in the case of ozone (O₃), the statistical analysis highlights high correlations between the concentrations obtained by both systems. Linear regression produces R² =0,71 with a correlation coefficient R=0,84 (fig.9).

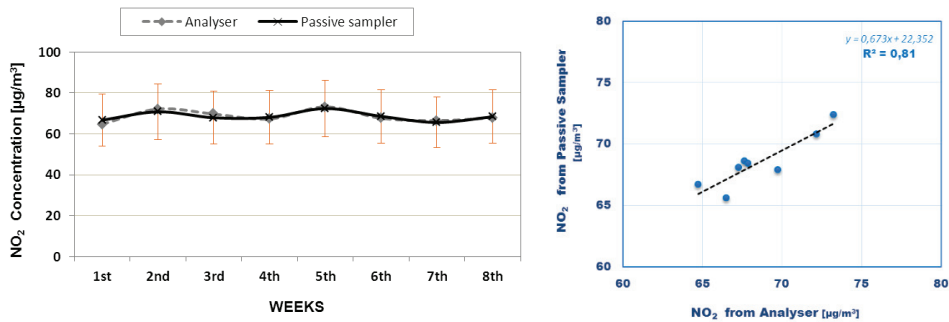


Fig. 7 Continuous analyser and passive sampler concentrations for NO₂ compared.

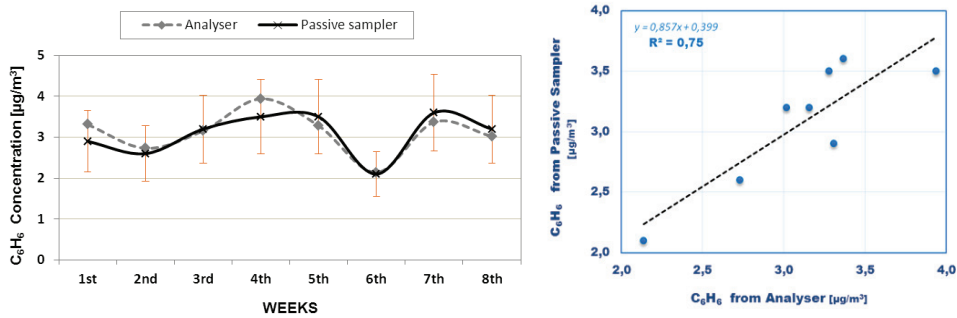


Fig. 8. Continuous analyser and passive sampler concentrations for C₆H₆ compared.

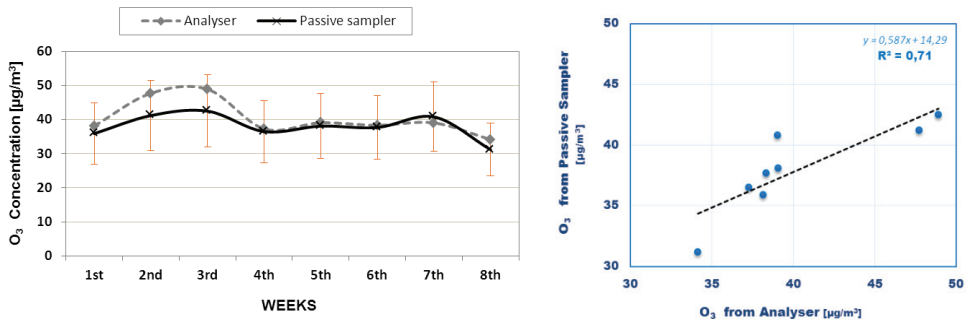


Fig. 9. Continuous analyser and passive sampler concentrations for O₃ compared.

5. CONCLUSIONS

Air quality is one of the principle threats to public health which is why the EU has set maximum pollution concentration limits for all human activity. Continuous measurement of air quality carries a high price. The legislative norm provides for the use of indicative measurements so as to cut down on the number of continuous monitoring stations. The analysis carried out in the city of Catania evaluated passive samplers (low cost and user-friendly) in zones without monitoring stations. So, a campaign was conducted to experimentally compare the data from passive samplers and certified monitoring stations. Following the first experiment, a statistical analysis was carried out. The resulting correlation coefficients show that the indicative measurements for NO_2 , O_3 and C_6H_6 could be validly integrated with the certified systems. To identify the criticality of the Catania area and as a consequence to mitigate against the impact of pollution on public health, future developments of this work would consist in collocating about fifty measurement points for mapping Catania's air quality.

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