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

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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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Keywords: Air pollution, passive samplers, NO_2,O_3,C_6H_6

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, O_3, NO_2 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 NO_2 emissions by 18 % over 2003–2012. Benzene emissions

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have also increased by 21 % for the same period. However, the trend of O_3 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 NO_2, 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 O_3 and NO_2 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 NO_2, C_6H_6 and O_3. 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 NO_2, C_6H_6 and O_3.

2.1. Continuous NO_x, NO, NO_2 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.

$$NO + O_3 \rightarrow NO_2^* + O_2 \quad (1)$$
$$NO_2^* \rightarrow NO_2 + h\upsilon \quad (2)$$

The air sample air flow rate is about 500 cm^3/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 NO_2 into NO by reaction 3

$$3NO_2 + Mo \rightarrow 3NO + MoO_3 \quad (3)$$

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 NO_2/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 O_3 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 NO_2 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.