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LABORATORY AND FIELD TESTING OF NEW DESIGN NITROGEN DIOXIDE DIFFUSIVE SAMPLERS

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Abstract. Nitrogen dioxide is one of the most monitored pollutants in ambient air because of this effect on the human respiratory system, his contributions to the acidification of the ecosystems and his role in the formation of photochemical oxidants. The level of nitrogen dioxide in rural and suburban areas is governed by imported air-pollution, and elevated NO_2 concentrations due to local traffic and increased industrial activity. The passive diffusive samplers have been used for many years to measure outdoor concentrations of nitrogen dioxide (NO_2) across rural and urban area. Passive sampling is based on the principle of passive diffusive of a pollutant through an air layer to an absorbing medium. The mean concentration of pollutant is calculated from the collected amount integrated over the sampling time. Neither pumping of air nor electricity is needed in passive sampling. The present study is directed to investigate new design diffusive samplers impregnated with 10 % and 20 % triethanolamine (TEA) solution diluted with water. Investigation was carried out in laboratory chamber and under field conditions. During investigation was obtained good agreement with chemiluminescence measurements (correlation coeficient r = 0.99) or control diffusive samplers (r = 0.94). Results indicate that the accuracy of this device when compared to co-located continuous NOx analyzer during chamber research is 10 % with precision of 8 % (relative standard deviation). However during field testing new diffusive samplers showed less accuracy 23 % and worse precision 12 %. But nevertheless, the new device complies with the Directive 2008/50/EC requirement for uncertainty (precision and bias) < 25 %.

Keywords: nitrogen dioxide, passive sampler, diffusive sampler, triethanolamine, air monitoring, chamber investigation.

1. Introduction

Nitrogen dioxide (NO_2) is common combustion-related pollutant that is mostly formed from oxidation of nitric oxide (NO) which is produced during high temperature burning of fuel in cars and other road vehicles, heaters and cookers (Heal *et al.* 1999; Ozden *et al.* 2005, Baltrėnas *et al.* 2008).

Nitrogen dioxide is considered to be an important atmospheric trace gas pollutant not only because of its effects on health (Ozden and Degeroglu 2008) but also because it absorbs visible solar radiation and contributes to impaired atmospheric visibility; as an absorber of visible radiation it could play a potentially direct role in the change in the global climate if its concentrations were to become high enough (WHO 2000; Delgado-Sabori and Esteve-cano 2006). It is one of the major sources of acid rain (Tang *et al.* 1999) and it is, along with nitric oxide (NO), a chief regulator of the oxidizing capacity of the free troposphere by controlling the build-up and fate of radical species, including hydroxyl radicals; and it plays a critical role in determining concentrations of ozone (O_3), nitric acid (HNO_3), nitrous acid (HNO_2), organic nitrates such as PAN ($CH_3C(O)O_2NO_2$), nitrate aerosols and other species in the troposphere because the photolysis of nitrogen dioxide in the presence of volatile compounds is the only key initiator of the photochemical formation of ozone (Atkins and Lee 1995) and photochemical smog, whether in polluted or unpolluted atmospheres (WHO 2000; Varshney and Singh 2003; Delgado-Sabori and Esteve-cano 2006). Therefore, monitoring of NO_2 levels is required by law in European Union countries.

Generally NOx monitoring is carried out using high volume samplers, handy samplers or through a chemiluminescence analyser. Such instruments require on site power source, apart from being capital intensive, involving complex operations and requiring specialist maintenance. In view of these limitations, extensive air quality monitoring over wide geographical areas presents serious difficulty. Passive samplers provide a convenient alternative for measuring ambient NO_2 in a highly cost effective manner (Varshney and Singn 2003). Currently, passive samplers are being used to determine the air quality in the work place, the living environment; and the ambient, out-

door environment including regional-scale air quality (Krupa and Lagge 2000, Valuntaitė *et al*. 2009).

The passive sampler is based on the principle of diffusion of air. The atmospheric NO_2 diffuses up the tube where it gets absorbed on the triethanolamine (TEA) coated mesh. This establishes a NO_2 concentration gradient along the length of tube, consequently NO_2 diffuses up the tube where it is absorbed on TEA coated meshes. The reaction product of TEA and NO_2 has been studied. The identification of the reaction product is still a subject of controversy (Varshney and Singn 2003).

There are several issues that must be considered a priori, before passive absorption samplers can be used to collect data on ambient pollutant concentrations. Such issues include: (1) linearity in the reaction response of the sampler to varying pollutant concentrations (Bush *et al.* 2001); (2) specificity of the reaction response of the absorbent to the pollutant of interest, without interferences from other chemical constituents in the atmosphere; (3) effects of air turbulence on the sampler collection efficiency; and (4) correlation or comparison of the values obtained by passive sampling to the corresponding continuous or active measurement or sampling method as appropriate (Ayers *et al.* 1998; Krupa and Legge 2000). These issues are not a problem or their influence can be minimized if an already proven passive sampling system is being used. But if a new passive sampling system is being considered, then such a system must be thoroughly tested both under laboratory and field conditions (Krupa and Legge 2000).

In this study a new structure and composition of diffusive samplers were investigated under laboratory and field conditions.

2. Experimental

Diffusive tube preparation and analysis

The diffusive tube samplers applied in this study consists of the polypropylene tube approximately 34 mm long and 21 mm inner diameter and closely fitting cap. In one end of the diffusive tube is placed one stainless steel mesh.

For the preparation of diffusive tubes stainless steel mashes were impregnated with 10 % and 20 % solutions of TEA and water. After exposure samplers were analyzed in the laboratory spectrophotometrically using Saltzman reagent. Ten minutes are required for full coloured development before optical absorbance of the coloured solution is measured spectrophotometrically at 542 nm. The amount of nitrite ion in the sample is obtained with the help of calibration plot derived from standard nitrite solutions. The amount of extracted nitrite for samplers is used to calculate ambient NO_2 concentrations.

Firstly all samplers were examined in chamber test, then in the field conditions.

Laboratory - chamber experiments

The laboratory experiments were performed in an exposure chamber that allowed controlling of concentrations level, temperature and relative humidity.

The exposure chamber size was 1.5 m lengthy, by 1.5 m width and by 1.8 m height with a volume of 4.05 m^3. The chamber was constructed from the polyethylene. The nitrogen oxides in the chamber were obtained by means of the reaction between sulphuric acid and sodium nitrite. During the chemical reaction between sulphuric acid and sodium nitrite there are released nitrogen oxides into the air. 0.1 N sulphuric acid was dripped from burette into the glass with 20 % aqueous solution of sodium nitrite to obtain expected NO_2 concentration. Nitrogen oxides concentrations were measured using a chemiluminescent (Environnement S. A.) nitrogen oxides analyzer AC32M. Its detectable limit is 0,4 $\mu g/m^3$. To accelerate mixing of air in the chamber, the fan was used (Fig 1).

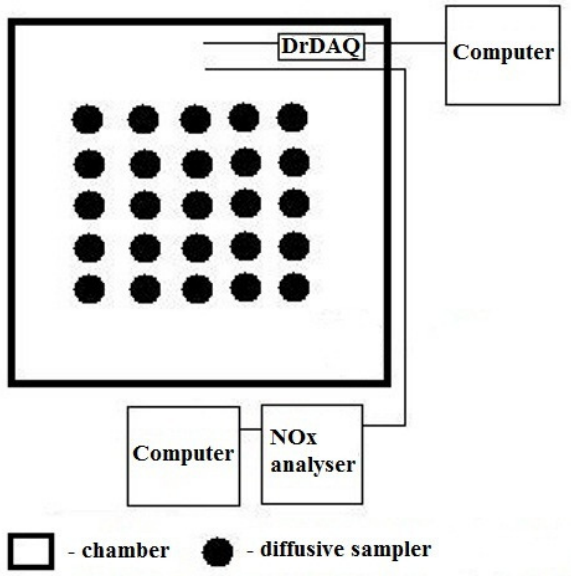

Fig 1. Scheme of experimental chamber

The parameters of microclimate were measured in the chamber during experiment with datalogger DrDAQ: temperature and relative humidity. Data were recorded automatically in the computer. The sensors for temperature and relative humidity were placed at the 1 m height, in the same place were diffusive samplers are placed (Fig 1). During laboratory experiments in the chamber was generated and maintained for 2 weeks three different NO_2 concentrations: approximately 3 $\mu g/m^3$, 45 $\mu g/m^3$ and 70 $\mu g/m^3$. Samplers were exposed for 2 weeks.

Field tests

To test the performance of new passive sampler, Passam diffusion tubes were also used for the comparison.

In the field measurements all samplers were placed in special shelters to protect them from rain and minimize the wind influence during exposure. Special care was taken at all times when handling the passive samplers. All samplers were kept in airtight bags during transportation to and from field. After exposure samplers were kept in the refrigerator until preparation for analysis.

All passive samplers (new sampler and Passam tube) were exposed at all sampling sites for two week sampling period in different seasons: in spring, summer and autumn.

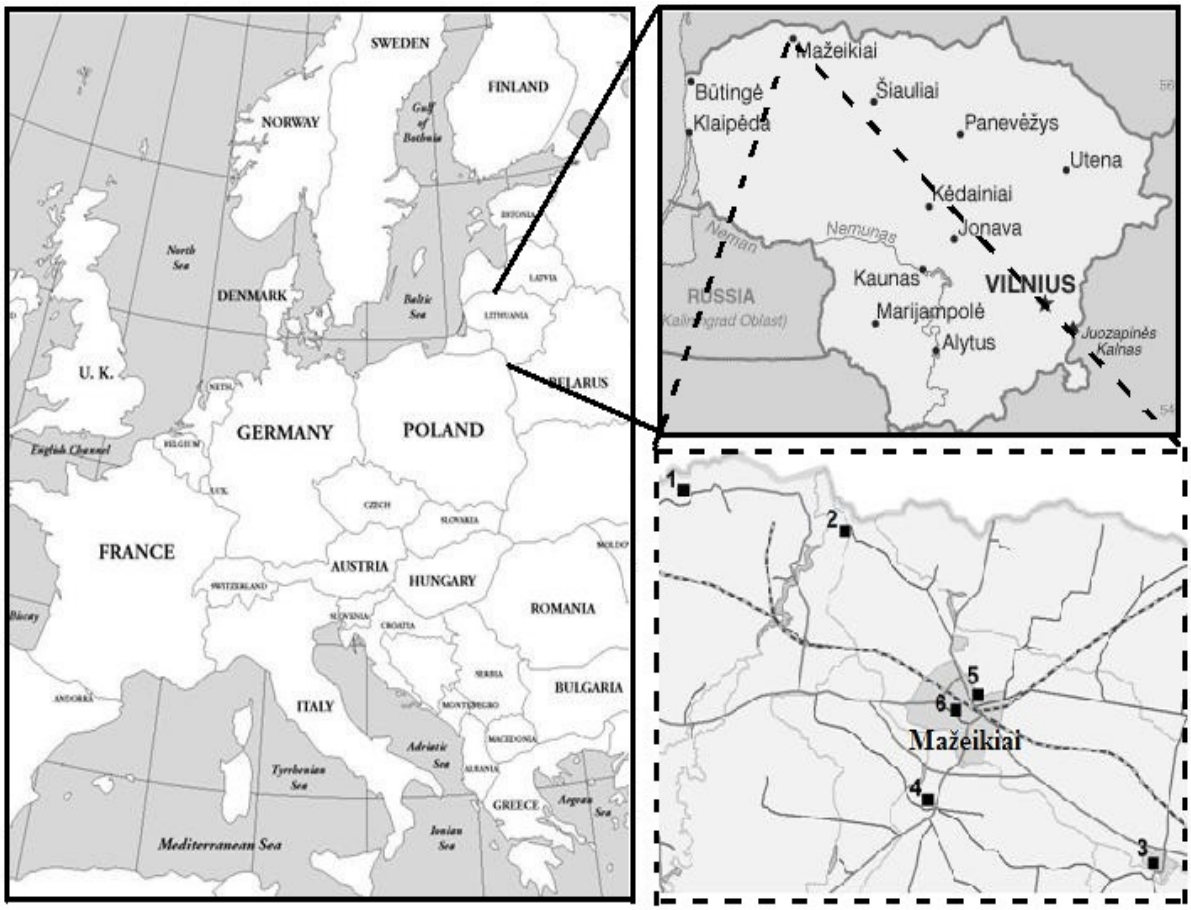

Fig 2. Six sampling sites in Lithuania in Mažeikiai region during field measurements

For NO_2 field measurements were selected 6 places in Mažeikiai region (Fig 2). Five of the same type diffusive samplers were placed in each sampling site. This six sampling places represents different NO_2 concentrations ranging from about 4 µg/m^3 till 30 µg/m^3. First two sampling places represent low NO_2 concentrations (4 µg/m^3). A secondand third sampling site represents average NO_2 concentrations (10 µg/m^3). The last two places (fifth and sixth) are located in the Mažeikiai city, near a busy crossroad there are the biggest NO_2 concentrations (30 µg/m^3).

3. Results

New design diffusive samplers were verified in the experimental chamber.

Linearity of response (i.e. the extent to which response is directly proportional to input) was evaluated by exposure to known concentration of NO_2.

During chamber experiments individual NO_2 diffusive tubes were generally in very good agreement with chemiluminescence measurements. The performance of the tubes did not appear to be significantly affected by ambient concentration levels. However, there was a slight tendency of the diffusive tubes to underestimate the NO_2 concentrations recorded with the chemiluminescence analysers, although the correlation between measurements obtained with the two methods was very strong (Fig 3). This figure indicates that the samplers exhibit very good linearity characteristics. The values lie on straight lines with a correlation coefficient (R_2) equal to 0.99 for both samplers, with 10 % and 20 % TEA/ water impregnating solutions. It should be stressed that the issue of linearity is one of the most important aspects that must be considered when evaluating a new passive sampler.

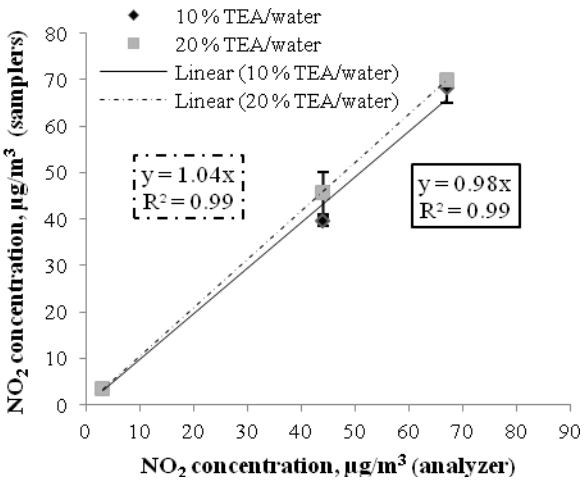

Fig 3. Diffusive tubes vs. chemiluminescence analysers in chamber test

Table 1. Results of new design diffusive samplerslaboratory and field measurements precision and accuracy

	Laboratory research		Field research	
	Diffusion sampler with 10 % TEA/water solution	Diffusion sampler with 20 % TEA/water solution	Diffusion sampler with 10 % TEA/water solution	Diffusion sampler with 20 % TEA/water solution
Accuracy (RE, %)	10.5	9.6	24.2	21.3
Precision (RSD, %)	6.7	9.7	12.5	10.6

Precision is a measure of the variability of response expected at any given concentration. The relative standard deviation (RSD, %) is a common indicator of precision. Precision of diffusive samplers with 10 % and 20 % TEA/water impregnating solutions were 7 % and 10 %, respectively. The accuracy of the passive samplers in comparison to chemiluminescence technique expressed as percent relative error (RE, %) was found to be 10 % (Table 1).

During chamber test was examined new design diffusive samplers linearity of response in different NO_2 concentrations also precision and accuracy. The objective of the field-testing was to identify estimates of bias and precision under normal field operating conditions. Under the Daughter Directive the data quality objective for diffusive monitoring for NO_2 has been set at ±25%.

The same composition diffusive samplers were tested under field conditions. High degree of linearity was found between new design diffusive sampler and *Passam* diffusive tubes (Fig 4). Correlation coefficient (R_2) equal to 0.87 and 0.91 respectively for samplers, with 10 % and 20 % TEA/ water impregnating solutions.

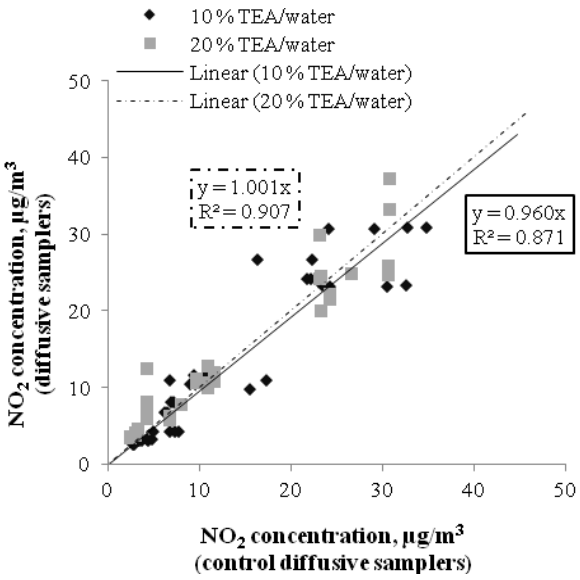

Fig 4. Diffusive tubes vs. chemiluminescence analyzer in field measurements

During field measurements was obtained less precision and accuracy of diffusive samplers (Table 1) compared with laboratory test results. Possible explanation could be that during laboratory experiments in the chamber the exposure conditions changed insignificantly: average temperature 19 °C, average relative humidity 30 %. But during field conditions environment conditions ranged significantly. Environmental factors, such as temperature, relatively humidity, and wind speed can affect the performance of passive samplers (Brown 2000; Varshney and Singn 2003; Delgado-Saborit and Estevecano 2006; Yu *et al.* 2008). Consideration of these environmental factors when selecting for field studies is important.

Field measurements were carried out during autumn, spring and summer seasons when average air temperature and relative humidity was 6 °C/88%, 10 °C/77% and 23°C/77% respectively. Figure represents during field measurements obtained accuracy and precision of new passive sampler comparison with control diffusive tubes (Fig 5).

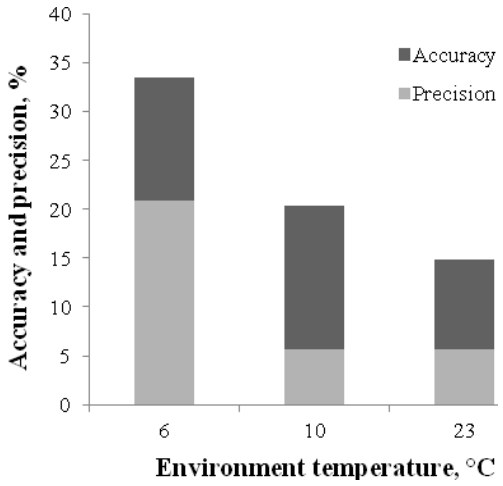

Fig 5. Accuracy and precision of diffusive samplers obtained during different seasonal field measurements

Worse accuracy (34 %) was obtained during autumn season measurements, when air temperature ranged from 1°C to 13 °C. New diffusive samplers showed better accuracy during spring and summer measurements, 20 % and 15 % respectively. The reason of that could have been higher air temperature: spring time ranged from 1°C to 23°C and summer time ranged from 14 °C to 23°C.

4. Conclusions

1. Passive diffusive samplers of 34 mm tube length and stainless steel meshes impregnated with 10 % and 20 % TEA/water solutions have been tested in laboratory chamber and in the field research.
2. Highly significant correlations were found between all diffusive tube exposure types and corresponding

chemiluminescent measurement (r = 0.99) data or control diffusive samplers (r = 0.94).

3. Results indicate that the accuracy of this device when compared to co-located continuous NOx analyzer during chamber research is 10 % with precision of 8 %. However during field testing new diffusive samplers showed less accuracy 23 % and worse precision 12 %. But nevertheless, the new device complies with the Directive 2008/50/EC requirement for uncertainty (precision and bias) < 25 %.

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