EUROPEAN COMMISSION
DIRECTORATE-GENERAL
Joint Research Centre

Institute for Environment and Sustainability
Emissions and Health Unit
I-21020 Ispra (VA) Italy

Laboratory and Field Inter-Comparisons of NO_2 Diffusive Samplers

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2003 **EUR 20860 EN**

EUR 20860 EN

Printed in Italy

SUMMARY

The objective of this study is the evaluation of the extent of differences between NO_2 measurements performed by diffusive samplers and NO_2 measurements performed using the chemiluminescence method under extreme conditions of influencing factors and according to the EN protocol of validation of diffusive samplers.

In recent years, many diffusive sampler designs have been developed and implemented for the determination of NO_2 in ambient air (tube-type sampler, badge-type sampler and radial sampler). Ten leading European laboratories were invited to participate. The selected participants were responsible for the preparation and analysis of the samplers. The whole range of diffusive samplers commercially available on the market was included in the study.

The inter-comparison consisted of laboratory and field experiments. The laboratory tests took place in the exposure chamber developed by ERLAP, which can control the exposure environment while ensuring consistent conditions for all the samplers. The reference value is fully traceable to SI units by use of primary system for generation and monitoring of NO_2 concentrations in the exposure chamber.

The field experiments were carried out at two monitoring stations of the AIRPARIF monitoring network, an accredited laboratory for 'on site' determination of NO_2 ambient level, one was an urban site and one was a background site. The field experiments were undertaken in order to check the results of the laboratory experiments and to identify sources of uncertainty related to real environmental conditions

The results of the laboratory experiments showed that most of the diffusive samplers were affected by extreme exposure conditions. The field tests showed better agreement between the reference value and the samplers than the laboratory tests. The correction of the uptake rate according to the conditions of the experiment using a model equation gave an improved agreement between the diffusive sampler and the reference method. Using the results of the laboratory experiments it is possible to evaluate the contribution to the uncertainty of factors influencing the diffusive sampler. However the exposure chamber must be able to accommodate the whole sampling system, i.e. samplers and shelter or rain shield.

ACKNOWLEDGMENT

The participation of the following laboratories to the inter-comparison is acknowledged:

Surveillance de la Qualité de l'air en Ile-de-France, (F)	Mme Esthel Le Bronnec
Consiglio Nazionale della Ricerca (I)	M. Franco De Santis
Ecole des Mines de Douai (F)	M. Hervé Plaisance
Fondazione Salvatore Maugeri (I)	Mr. Paolo Sacco
Gradko Ltd. (UK)	Mr. Gerry Stuchburry
Instituto Carlos III (S)	Mrs Rosalia Fernandez Patier
IVL Swedish Environmental Research Institute (S)	Mr. Martin Ferm
Laboratoire d'Hygiène de la ville de Paris (F)	Mr. Yvon Le Moullec
Passam A.G. (CH)	Mr. Markus Hangartner

The authors would like to acknowledge the support of Mrs Hélène Marfaing, Mr. Patrick Garnoussi, Laurent Gauvin et Christophe Ampe, of the laboratory *Surveillance de la Qualité de l'air en Ile-de-France (AIRPARIF)* for the installation of diffusive samplers and for providing reference measurements of the monitoring stations of the automatic network of AIRPARIF.

The authors wish to honor the memory of Dr. Vincenzo Cocheo, who passed away in May 2003 during this inter-comparison. Over many years, the collaboration with Dr. Vincenzo Cocheo has resulted in scientific and technical progress for monitoring air pollution using diffusive samplers.

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1 Objective of the inter comparison

The objective of this study is the evaluation of the extent of differences between NO_2 measurements performed by diffusive samplers and NO_2 measurements performed using the chemiluminescence method under extreme conditions of influencing factors and according to the EN protocol of validation of diffusive samplers[1].

First, experiments were carried out in an exposure chamber so that the parameters affecting the performance of diffusive samplers could be controlled. Second, field inter-comparisons were performed in order to evaluate the consistency of the results of the laboratory tests.

2 Inter-comparison protocol

The laboratory experiments consisted of 2 expositions under controlled atmosphere into the ERLAP exposure chamber. Two sets of extreme conditions were applied so that one low diffusive uptake rate and one high diffusive uptake rate could be expected (see Table 1). The condition ranges were also chosen in order to match real ambient meteorological conditions and the yearly limit value of the European Daughter Directive for NO_2 (40 $\mu g/m^3$).

Table 1: Conditions for the laboratory inter-comparisons.

NO_2 diffusive samplers	High level High uptake rate	Low level Low uptake rate
Averaging time	7 days	14 days
Level of concentration	80 µg/m³	40 µg/m³
Wind Speed	2.5 m/s	1.0 m/s
Temperature	25 °C	5 °C
Relative humidity	75 %	30 %

Two field tests of all diffusive samplers, one urban site at Genevilliers, and one rural site at Fontainebleau (see Figure 6 and Figure 7), were also performed at two monitoring stations of the automatic network of AIRPARIF in Paris. AIRPARIF is accredited under ISO 17025 for the measurement of several pollutants including nitrogen oxides at the automatic stations of its monitoring network.

Each participant was requested to use 6 replicate samplers and one blank sampler per exposition. All samplers were analysed by the participants. Small protective boxes used to limit the effect of air velocity on the response of diffusive sampler gathering six samplers were installed in the exposure chamber, while larger rain shields and shelters could no fit in (see Table 2). For the field

test, all protective boxes, shelters and rain shields requested by the participants were installed for sampling.

Table 2: Participants to the laboratory experiments.

Participants	Sampler type	Preparation and supplier	Shelter/rain shield/protective box	
			Laboratory	Field
Lab. M	Passam diffusion tube	Passam	Grey Passam protective box	
Lab. L	Ogawa sampler	Ogawa	None	Ogawa shelter for NO_2
Lab. K	Badge IVL	IVL	None	IVL Rain shield
Lab. J	Ogawa sampler	Ogawa and Lab. J	None	Ogawa shelter for O_3
Lab. I	Gradko diffusion tube	Gradko	None	
Lab. H	Radiello sampler	Fondazione S. Maugeri	None	Radiello Shelter
Lab. G	Gradko diffusion tube with a membrane	Coated by Lab. D Gradko	None	
Lab. F	Gradko diffusion tube	Coated by Lab. F Gradko	Grey Passam protective box	
Lab. E	Gradko diffusion tube	Coated by Lab. E Gradko	None	
Lab. D	Radiello sampler	Fondazione S. Maugeri	None	Radiello Shelter
Lab. C	Gradko diffusion tube	Coated by Lab. C Gradko	Grey Passam protective box	
Lab. B	Analyst sampler	CNR	None	CNR Rain shield
Lab. A	Passam diffusion tube	Passam	White Passam protective box	

3 Experiments

Exposure chamber

All diffusive samplers were exposed in the ERLAP exposure chamber, which allowed the simultaneous exposition of 72 sensors on the wall of the chamber and installation of a certain number of other ones inside it. It was possible to control concentration level, temperature, relative humidity and wind velocity inside the exposure chamber. The schematic of the whole system is presented in Figure 1. The system was composed of the following parts:

Air zero generator. This generator was capable of generating pollutant mixtures up to 100 *l/min.* It consisted of a compressor that fills a tank. Then the air was dried and chemically filtered.

Permeation system. A prototype of gas standard generation system was composed of 9 permeation ovens filled with permeation tubes and periodically weighed.

Humidifier. The humidifier system worked based on the saturation method. It was flushed with zero air. The relative humidity of the flow could be regulated from 0 to 80 % according to the balance of dry/humid air and the controlled temperature of the liquid in the humidifier.

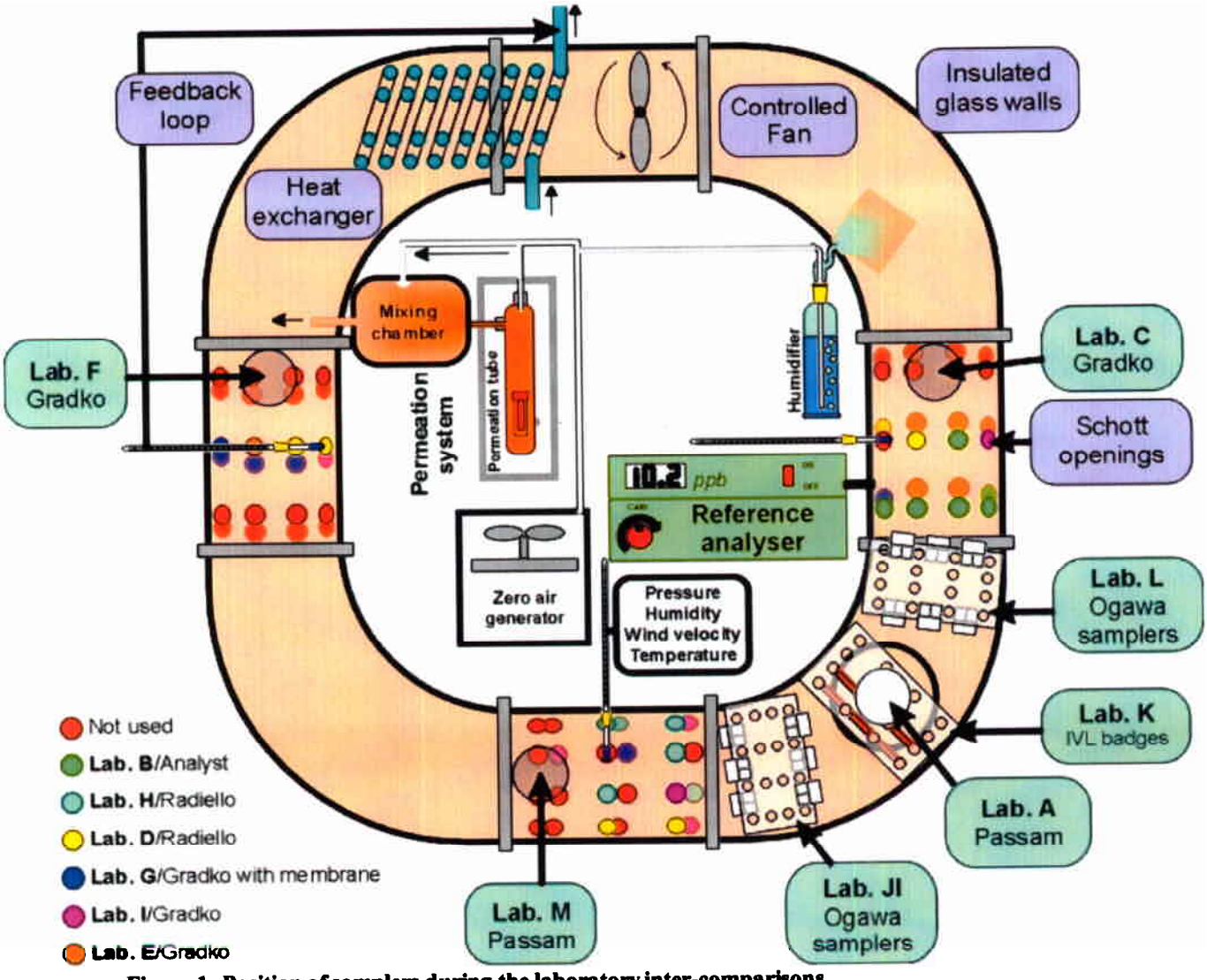

Figure 1: Position of samplers during the laboratory inter-comparisons

Exposure chamber. The exposure chamber was a ring tube system shaped "O" (size including support, 130 x 110 x 140 cm). The tube was insulated with dark insulation material to limit photo dissociation of NO_2 and to improve the thermal insulation. The wind speed was controlled by a fan installed inside the chamber that allowed air velocities speed from 0.4 to 4 *m/s*. Sensors and samplers could be introduced or removed through 72 Scott 32GL entrances and a wider opening

in the ring-tube. Temperature, relative humidity, pressure and wind velocity were continuously controlled and recorded.

Heat exchanger: The temperature of the exposure chamber was controlled using a cryostat supplying cold or hot liquid to a heat exchanger (area of exchange 1 m^2) into the chamber. A feed back loop consisting of a Pt 100 sensor giving feedback order to the cryostat allowed the temperature control inside the exposure chamber.

NO_2 monitor. The NO_2 concentration was monitored at the exit of the chamber by a *NOx* analyser based on the chemiluminescence method. This monitor was periodically checked with a *NO* in N_2 cylinder, certified against permeation system and crosschecked with the static volumetric method.

Once during each laboratory exposition, a check of homogeneity of temperature, air velocity, relative humidity and *NO/NOx* concentration was performed by measuring these parameters at all the free openings of the exposure chamber over a small period of time. Results are shown in Table 7 and Table 8.

Reference value for NO_2 during laboratory exposition

During the 1st exposition (22 - 29 November), the analyser gave raw average concentrations of [*NOx*] of 40.4 *ppb* and 0.2 *ppb* for [*NO*]. During this period, the analyser was submitted to several calibration checks and one adjustment. Figure 8 and Table 3 show that the response of analyser linearly increased between 22 to 29 November. Further to the results of these calibration checks, the reference values for *NO* and *NOx* were corrected and become 41.4 *ppb* for [*NOx*] (1.2 % and 0.5 *ppb* were added) and 0.7 *ppb* for [*NO*] (+0.5 *ppb* was added). No correction for humidity was applied since a naflion dryer was installed at the inlet of analyser so that the absolute humidity was very low. A second analyser without naflion dryer gave 37.3 *ppb* for [*NOx*]. An absolute humidity of 20 g/Nm^3 gives a signal decrease of about 10 % leading to a corrected [*NOx*] = 41.0 *ppb*, in agreement with the concentration obtained by the analyser with a naflion dryer. The efficiency of the analyser was evaluated and found to be better than 99.6 % at a concentration of 40 *ppb*. Finally, [NO_2] was 40.8 *ppb* equivalent to 76.8 $\mu g/m^3$ at the temperature of the experiment 25 °C (see Figure 10).

During the 2nd exposition (2 - 14 December), the average concentrations were 21.5 *ppb* for [*NOx*] and 0.2 *ppb* for [*NO*]. During this period, the analyser was submitted to several calibration checks and one adjustment (see Table 3). Figure 9 and Table 3 show that the response of analyser increased linearly until 13 December when it was adjusted. Then it remained stable. Further to the results of these checks [*NOx*] became 22.5 *ppb* (2.3 % and 0.5 *ppb* were added) and [*NO*] became

0.7 *ppb* (+0.5 *ppb* was added). No correction for humidity was applied since a naflion dryer was installed at the inlet of analyser and anyhow the absolute humidity was very small. This absolute humidity would not anyhow create a significant interference: a humidity of less than 3 g/Nm^3 gives a decrease lower than 1 %). The efficiency of the analyser was evaluated and found to be better than 99.6 % at a concentration of 20 *ppb*. Finally [NO_2] was 21.9 *ppb* equivalent to 43.5 $\mu g/m^3$ at the temperature of the experiment (9.5 °C see Figure 11) .

Table 3: Calibration checks of the *NO* analyser

Date	Span Drift	Adjustment	Zero
20 Nov	0 %	No	- 0.5 ppb
25 Nov	1.4 %	No	- 0.5 ppb
29 Nov	1.9%	No	- 0.5 ppb
9 Dec	2.9%	No	- 0.5 ppb
13 Dec	3.7%	Yes	- 0.5 ppb
18 Dec	0%	No	- 0.5 ppb

The expanded uncertainty of the NO_2 measurement was evaluated using the GUM method[2]. Conversion efficiency, repeatability and linearity of the analyser, uncertainty of standard and zero air for calibration and zero/span drift were the factor taken into account in the calculation. The evaluation gave a relative expanded uncertainty of 6.7 % for the first exposition and 11 % for the second experiment.

Comparison between chemiluminescence and permeation value

It is not possible to foresee the NO_2 concentration in the exposure chamber by dividing the NO_2 permeation rate by the air flow in the chamber because exposed samplers absorb a part of the NO_2 molecules in the chamber. However when no samplers are installed in the chamber, the concentration of NO_2 in the exposure chamber depends only on the permeation rate of the permeation system and the sum of all dilution and complementary flows. Then, it is possible to compare the chemiluminescence method and permeation method before and after exposition. The average of the last 4 permeation rates determined by gravimetry was 574.2 ng/min ± 4 ng/min over a period of 3 months. The total flow in the chamber is the sum of the flow of permeation oven, flow for dilution, flow of humidifier and water vapour flow. For the 1st experiment, the total flow was 4.532 *Nl/min* or 4.95 *l/min* at 25 °C. Using the permeation method, the concentration of NO_2 should be 116 $\mu g/m^3$ while chemiluminescence method gives a value of 108 $\mu g/m^3$. For the second exposition the total flow was 11.5 *Nl/min* or 12.0 l/min at 9.5 °C leading to a concentration 47.9 $\mu g/m^3$ while the measurement by chemiluminescence was 43.8 $\mu g/m^3$.

Differences between the permeation method and the chemiluminescence method are due to NO_2 absorption on the chamber walls and NO_2 photo-dissociation in the generation system.

Field tests in Paris (Feb. 27th until Mar. 13th)

At the urban site, a *NOx* analyser manufactured by Environnement s.a model AC32M was used. Over the period, the average temperature, relative humidity and wind speed were 10.3 *°C* (from 3.7 to 17.5 *°C*), 73.8 *%* (from 36 to 96 *%*) and 2.8 *m/s* (from 1 to 7 *m/s* at the top of a meteorological mast) and about 11 mm of rain were recorded (see Figure 14). The *NOx* measurements were corrected for the exact value of the NO_2-to-*NO* converter efficiency. During this period, the analyser was submitted to 3 calibration checks and adjustments (see Table 4). The measurements were corrected according to the calibration checks and for humidity. An absolute humidity of 7 g/Nm^3 (corresponding to a temperature of 10 *°C* and a relative humidity of 78 *%*) gave a signal decrease about 3 % for both *NO* and *NOx*. Losses in the sampling line of the monitoring station were found to be less than 2 *%* during the yearly check. Finally the raw value for NO_2 was 44.6 $\mu g/m^3$ (NO = 18.4 *ppb* and NOx = 39.8 *ppb*). After correcting *NO* and *NOx* for zero/span drift and humidity interference, the reference value for $[NO_2]$ is 41.6 $\mu g/m^3$. Figure 12 shows the profile of NO_2 concentration over the exposition period.

In Fontainebleau, a *NOx* analyser manufactured by Thermo Environment model 42C was used. Over the period, the average temperature and relative humidity were 9.2 *°C* and 79 *%* respectively and about 7 mm of rain were recorded (see Figure 15). The *NOx* measurements were corrected for the exact value of the NO_2-to-*NO* converter efficiency. During this period, the analyser was submitted to 3 calibration checks and adjustments (see Table 5). The same correction for humidity as the one of Genevilliers was applied for both *NO* and *NOx*. Losses in the sampling line of the monitoring station were found to be less than 2 *%* during the yearly check. Finally the raw value for NO_2 was 14.5 $\mu g/m^3$ (NO = 1.0 *ppb* and NOx = 8.1 *ppb*). After correcting *NO* and *NOx* for zero/span drift and humidity interference, the reference value for $[NO_2]$ is 14.1 $\mu g/m^3$. Figure 13 shows the profile of NO_2 concentration over the exposition period.

All samplers were installed in their protective box, at 1 meter high above the roof of the monitoring stations at 1 to 2 meter high far from the sampling inlet.

Table 4: Calibration checks of the *NOx* analyser in Genevilliers

Date	NO				NOx			
	Span Drift	Adjustment	Zero	Adjustment	Span Drift	Adjustment	Zero	Adjustment
18 Feb	1.5 %	Yes	0 ppb	No	2.5 %	Yes	2 ppb	No
4 Mar	0 %	Yes	0 ppb	No	-0.5 %	Yes	2 ppb	No
18 Mar	1.5 %	Yes	0 ppb	No	1.5 %	Yes	1 ppb	No

Table 5: Calibration checks of the *NOx* analyser in Fontainebleau

Date	NO				NOx			
	Span Drift	Adjustment	Zero	Adjustment	Span Drift	Adjustment	Zero	Adjustment
27 Feb	-1 %	Yes	0.7 ppb	No	-1 %	Yes	0.7 ppb	No
11 Mar	-0.5 %	Yes	0 ppb	No	-1 %	Yes	0.4 ppb	No
25 Mar	-1 %	Yes	0.2 ppb	No	-1 %	Yes	1.5 ppb	No

4 Results of experiments

The results are presented in Figure 2, Figure 3, Figure 4 and Figure 5. In these figures, the NO_2 reference values measured by the analysers are indicated by a bold line. The errors bars indicate the standard deviation of the replicate measurements by each participant. All values are given in µg/m³ and at the conditionsof the experiment for ambient temperature and pressure.

5 Description and comments on implementation of diffusive samplers

In the following, $[NO_2]$ were calculated using the general equation where m is the mass of nitrite, Sr is the uptake rate and t is the exposure time: $[NO_2]_{ppb} = \frac{m(NO_2)_{ng}}{Sr_{ng\ ppb^{-1}\ min^{-1}}\ t_{min}}$ *(1)*

Lab. M, Passam diffusion tube

The sampler is based on the design of Palmes (see Figure 16). It collects NO_2 by molecular diffusion along an inert tube to an absorbent, in this case triethanolamine. The sampler consists of a polypropylene tube; the collected NO_2 is determined spectrophotometricallyby the Saltzmann method. During laboratory experiments, samplers were placed in the grey-type shelter (see Figure 17) to minimize the wind influence while during the field experiments white-type shelters (see Figure 18) were used. Initially, Lab. M gave its results using an uptake rate of 0.9047 *ml/min*, the one estimated at 20 °C. However, since lab. M is monitoring NO_2 since 1986 using an uptake rate of 0.8536 *ml/min*, to be consistent over time both results from laboratory and field measurements were calculated using 0.8536 *ml/min* the uptake rate estimated at 9°C. It is the policy of Lab. M to keep this uptake rate unchanged in order to have the possibilityto evaluate long-term trend of air pollution level and not to influence the evolution of air pollution by sudden correction of the value of the uptake rate. As expected, the modification of value from 0.9047 *ml/min* to 0.8536 *ml/min*, has worsened the agreement of the 1st laboratory experiment (the one at 25 °C). It also improved the one of the 2nd experiment (the one at 10°C) so that it is shown that with an uptake rate determined in the conditions of experiment, the response of the sampler better fits reference values. The uptake rate of the Passam sampler has been determined[3] under different exposure conditions,and users can decide which uptake rate to choose.

Participants	A	B	C	D	E	F	G	H	I	J	K	L	M
	85.4	105.9	93.2	50.6	154.8	84.3	69.3	53.4	147.3	246.9	76.8	130	87.6
	65.2	101.6	88.3	54.8	138.6	87.1	72.4	53.4	110.4	231.2	76.7	132	90.2
	89.6	109.8	106.1	58.3	126.7	112.6	69.3	59.6	117.3	192.0	79.1	108	89.4
	82.4	108.9	109.4	56.2	143.0	105.2	72.6	48.9	140.3	137.2	77.4	157	92.5
	95.3	101.3	90.8	54.4	125.3	100.3	74.0	56.8	105.8	164.6	75.5	150	118.6
	102.5	135.9	91.1	71.5	142.6	92.2	71.5	52.4	133.4	156.8	78.3	116	104.8
Average	86.7	110.6	96.5	57.7	138.5	97.0	71.5	54.1	125.8	188.1	77.3	132.2	97.2
Standard deviation	12.8	12.9	8.9	7.2	11.1	11.0	1.9	3.7	16.9	43.5	1.3	18.7	12.2
Reference	76.8	76.8	76.8	76.8	76.8	76.8	76.8	76.8	76.8	76.8	76.8	76.8	76.8

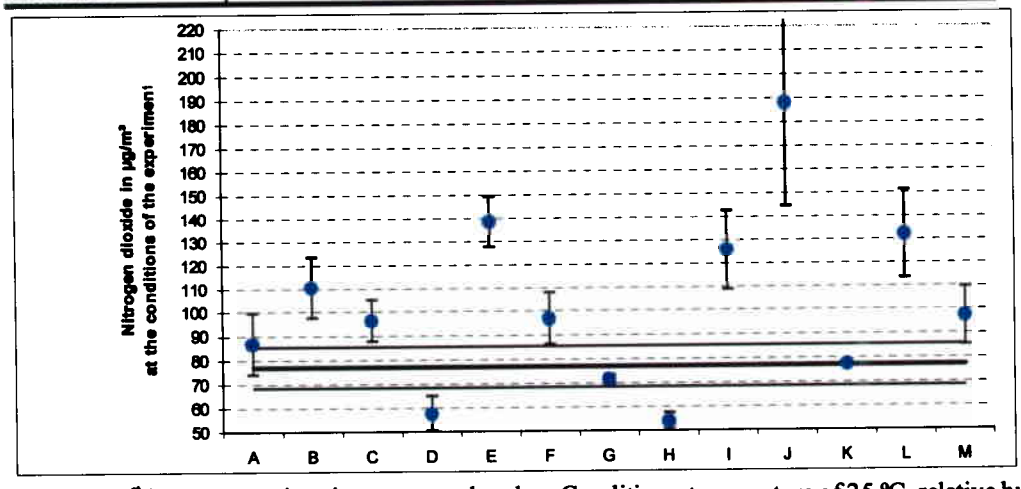

Figure 2: 1st inter-comparison in exposure chamber. Conditions: temperature of 25 °C, relative humidity of 75 % and wind speed of 2.8 m/s. The solid line indicates the NO_2 reference value ± 6.7 % (U). The error bars represent the standard deviation of the 6 replicate measurements for each participant.

Participants	A	B	C	D	E	F	G	H	I	J	K	L	M
	35.2	40.9	31.0	29.0	36.9	34.4	41.0	28.9	49.3	41.9	31.7	44	37.7
	36.0	46	32.2	25.9	35.6	34.6	37.3	28.5	38.7	41.9	31.4	45	38.5
	37.9	43.9	34.8	26.0	35.0	34.7	42.7	27.3	48.1	41.9	30.3	47	42.5
	38.1	40.3	31.1	27.0	36.7	36.9	40.7	29.5	46.9	45.9	31.4	45	39.6
	38.2	45.9	35.0	24.6	40.9	34.3	40.5	33.5	43.4	45.9	30.4	47	39.8
	37.1	42.7	31.7	26.4	38.2	40.0	40.1	32.4	49.3	43.9	32.6	51	38.9
Average	37.1	43.3	32.6	26.5	37.2	35.8	40.4	30.0	45.9	43.6	31.3	46.4	39.5
Standard deviation	1.3	2.4	1.8	1.5	2.1	2.3	1.7	2.4	4.2	2.0	0.8	2.6	1.7
Reference	43.5	43.5	43.5	43.5	43.5	43.5	43.5	43.5	43.5	43.5	43.5	43.5	43.5

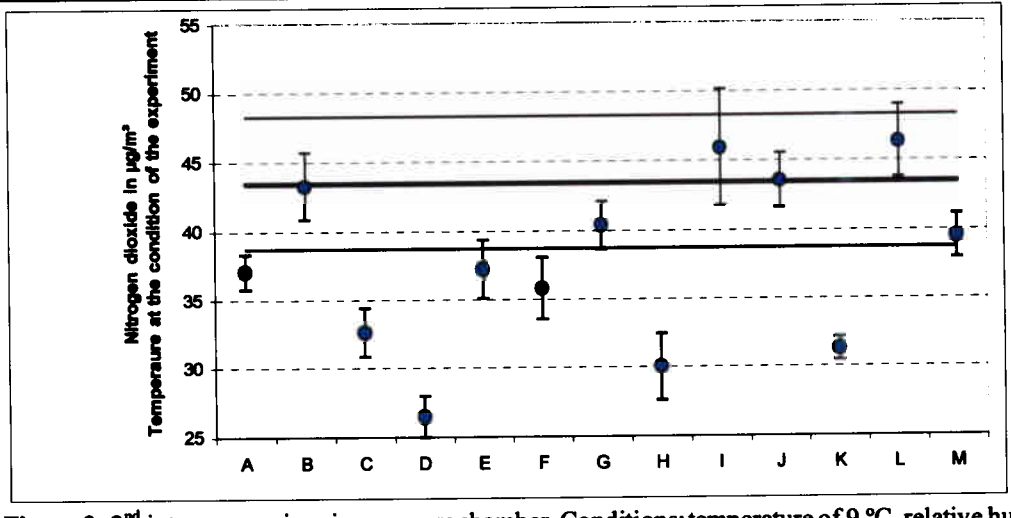

Figure 3: 2nd inter-comparison in exposure chamber. Conditions: temperature of 9 °C, relative humidity of 30 % and wind speed of 1 m/s. The solid line indicates the NO_2 reference value ± *11 % (U)*. The error bars represent the standard deviation of the 6 replicate measurements for each participant.

Participants	A	B	C	D	E	F	G	H	I	J	K	L	M
	45	54.8	45.2	36.6	44.5	41	39.1	42.1	46.1	66.9	66.4	39.8	53.4
	47	59.4	44.1	43.4	43.0	41	40.1	47.2	43.8	66.9	70.3	41.3	52.4
	47	51.0	46.9	44.7	42.1	41	39.7	43.8	41.5	70.8	66.2	42.0	53.7
	48	54.2	48.4	41.2	41.3	38	40.6	40.3	48.5	70.8	73.9	41.7	52.3
	45	60.4	48.1	41.8	42.0	41	41.2	46.7	43.8	64.9	64.7	42.3	53.6
	48	55.7	50.6	40.0	41.9	41	42.3	48.3	47.3	66.9	50.6	41.2	53.4
Average	46.7	55.9	47.2	41.3	42.5	40.5	40.5	44.7	45.2	67.8	65.3	41.4	53.1
Standard deviation	1.3	3.5	2.3	2.8	1.1	1.3	1.1	3.2	2.6	2.4	8.0	0.9	0.6
Reference	41.6	41.6	41.6	41.6	41.6	41.6	41.6	41.6	41.6	41.6	41.6	41.6	41.6

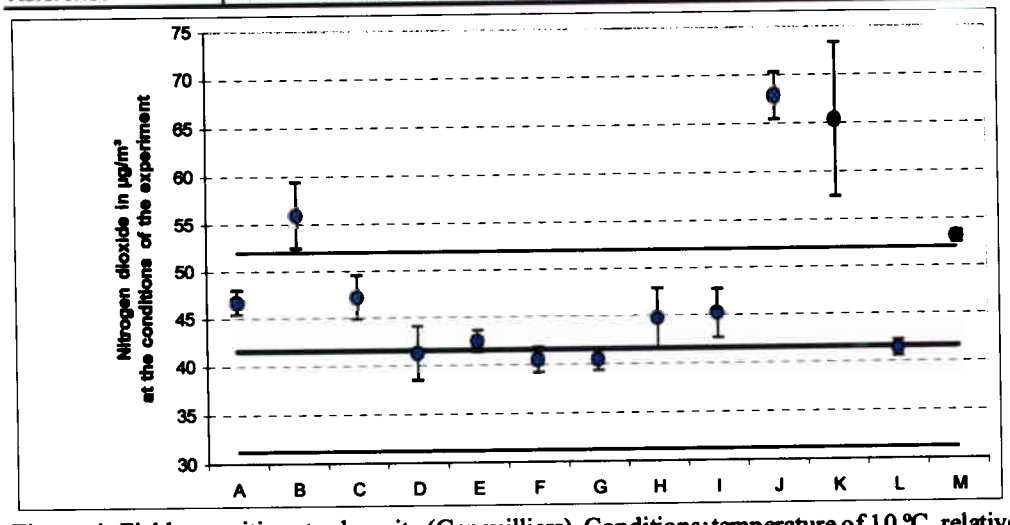

Figure 4: Field exposition at urban site (Genevilliers). Conditions: temperature of 10 °C, relative humidity of 74 % and wind speed of 2.8 m/s. The solid line indicates the NO_2 reference value ± 25 %. The error bars represent the standard deviation of the 6 replicate measurements for each participant.

Participants	A	B	C	D	E	F	G	H	I	J	K	L	M
	13.2	13.8	10.9	10.7	12.3	11.4	12.9	11.5	12.7	31.5	14.3	12.7	17.3
	14.2	15.5	10.9	13.6	12.3		12.1	14.5	12.7	29.5	17.6	13.1	15.6
	16.3	16.3	13.0	12.8	13.1	11.6	12.2	10.9	12.7	35.4	12.4	12.5	15.3
	14.9	16.4	11.4	14.7	12.5	12.1	12.9	14.1	13.8	29.5	13.0	12.5	14.8
	14.3	14.3	10.8	12.6	12.1	12.1	12.1	8.6	12.7	25.6	12.0	12.9	15.8
	14.8	13.7	12.3	13.9	11.8	11.6		12.2	13.8	39.4	19.5	12.2	15.2
Average	14.6	15.0	11.5	13.1	12.4	11.8	12.4	11.9	13.1	31.8	14.8	12.7	15.7
Standard deviation	1.0	1.2	0.9	1.4	0.4	0.3	0.4	2.2	0.6	4.9	3.1	0.3	0.9
Reference	14.1	14.1	14.1	14.1	14.1	14.1	14.1	14.1	14.1	14.1	14.1	14.1	14.1

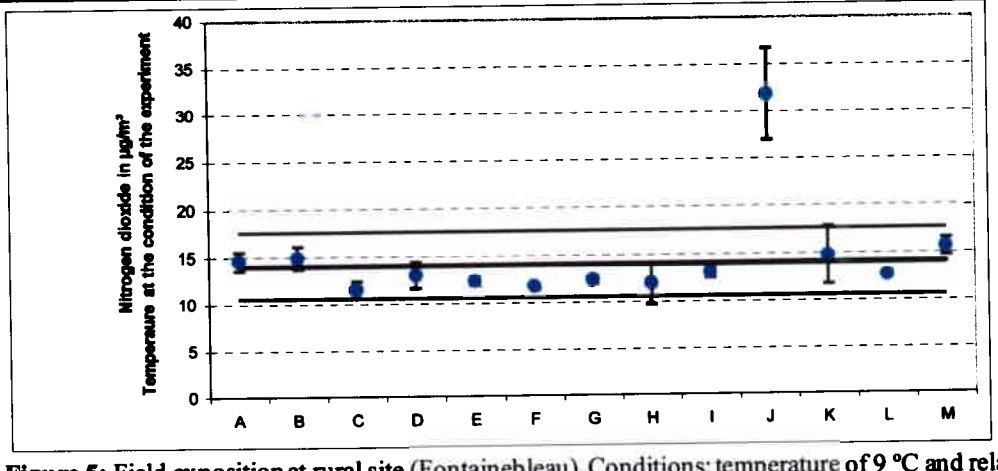

Figure 5: Field exposition at rural site (Fontainebleau). Conditions: temperature of 9 °C and relative humidity of 79 %. The solid line indicates the NO_2 reference value ± 25 %. The error bars represent the standard deviation of the 6 replicate measurements for each participant.

Lab. L, Ogawa sampler

Lab. L used the sampler prepared and manufactured by OGAWA (see Figure 30). The sampler was implemented according to the operational procedure laid down by OGAWA[4], in particular for the determination of the uptake rate. During the laboratory experiments the samplers were not protected by a shelter. It must be mentioned that this is not in agreement with the instruction of the manufacturer who requires that a shelter is used for outdoor environmental monitoring. The difference between sampler response and the reference value for the first experiment in exposure chamber could be explained by the lack of rain shield, which must be used when the wind velocity is high. For the laboratory expositions, the samplers were maintained as shown in Figure 1 on a teflon plate like for the IVL samplers and in such a position that the sampler cylinder was parallel to the ground and the two end caps parallel to the air flow. For the field experiments NO_2 shelters manufactured by Ogawa were used (see Figure 19).

For the first laboratory exposition, the uptake rate was 0.0192 ng.ppb-1.min-1 at a temperature of 25°C and relative humidity of 75%. For the second exposition , the uptake rate was 0.0130 $ng.ppb^{-1}.min^{-1}$ 1 at a temperature of 9.5°C and relative humidity of 30%. For the field exposition at the urban site, the uptake rate was 0.01695 ng.ppb-1.min-1 at a temperature of 10°C and relative humidity of 75%. For the field exposition at the rural site, the uptake rate was 0.01754 ng.ppb-1.min-1 at a temperature of 9°C and relative humidity of 80.6 %. Lab. L always placed two filters in each Ogawa samplers on which [NO_2] was determined and averaged.

Lab. K, badge IVL

The sampler is of the badge type[5] and fully based on the theory for calculation of the concentration[6] . During outdoor sampling a rain shield is used. This rain shield was not used in the chamber since rain was not simulated there. The samplers were mounted perpendicular to the wind as shown in Figure 20. During field exposure, samplers were placed under a rain shield (see Figure 21). The laboratory reported that, during the analyses of the NO_2 samplers from the field tests, an error in the analytical instrument occurred, which could not be detected at once and it was not possible to repeat the analyses afterwards.

Lab. J, Ogawa sampler

Lab. J used the sampler manufactured by OGAWA (see Figure 19). Lab. J did not follow the operational procedure established by OGAWA, in particular for the determination of uptake rate. For the field experiment, Ogawa prepared all samplers. On the opposite, for the laboratory experiments, the samplers were partly coated by CARLOS III and partly by OGAWA. No

significant difference coming from the two preparation procedures was evidenced. As for Lab. L, the other participant using OGAWA sampler, during the laboratory experiments, the samplers were not protected by a shelter and this is not in agreement with the instruction of the manufacturer. The samplers were maintained as shown in Figure 1 on a teflon plate as for Lab. L. For the field experiments shelters were used (see Figure 22).

All results were obtained by using an uptake rate of 0.031 $ng.ppb^{-1}.min^{-1}$. This uptake rate was determined by the Lab. J by means of experiments in exposition chamber. It must be noted that this uptake rate was estimated for use with the nitrite mass collected on two filters placed in one OGAWA sampler. Further to some new experiments, Lab. J decided to use a new uptake rate of 0.050 ± 0.004 $ng.ppb^{-1}.min^{-1}$. The results corrected using the new uptake rate are given in Table 6.

Table 6: Results of Lab. J corrected with the uptake rate of 0.050 $ng.ppb^{-1}.min^{-1}$

	Uptake rate: 0.031 $ng.ppb^{-1}.min^{-1}$	Uptake rate: 0.050 $ng.ppb^{-1}.min^{-1}$	Reference value $\mu g/m^3$
1st laboratory test	188.6 ± 43.5 $\mu g/m^3$	116.6 ± 27 $\mu g/m^3$	76.8 $\mu g/m^3$
2nd laboratory test	43.6 ± 2.0 $\mu g/m^3$	27.0 ± 1.2 $\mu g/m^3$	43.5 $\mu g/m^3$
Field test: Urban site	67.8 ± 2.4 $\mu g/m^3$	42.0 ± 1.5 $\mu g/m^3$	41.6 $\mu g/m^3$
Field test: Rural site	31.8 ± 4.9 $\mu g/m^3$	19.7 ± 3.0 $\mu g/m^3$	14.1 $\mu g/m^3$

Lab. I, Gradko diffusion tube

Lab. I use a sampler of the Palmes type (see Figure 23). It collects NO_2 by molecular diffusion along an inert tube to an absorbent (triethanolamine). The sampler consists of an acrylic tube; the collected NO_2 is determined spectrophotometrically by the Saltzmann method. During experiments and as requested by the manufacturer, samplers were never exposed inside a protective box or shelter. They were just kept in position using a clip. The uptake rate for all the experiments was 72 $cm^3.hr^{-1}$.

Lab H, Radiello sampler

The sampler is of the radial type and it was supplied by Fondazione S. Maugeri. During the laboratory experiments, the samplers were not protected by a shelter but a holder was used (see Figure 24). For the field experiments shelters were used (see Figure 25).

For the laboratory expositions, $[NO_2]$ have been calculated using the uptake rate equation available in November 2002: $Q_t = Q_r (T_K/298)^{5.83}$ where Q_t was the uptake rate in $ng\ ppb^{-1}\ min^{-1}$ at temperature T_K in Kelvin and Q_r (0,189 $ng\ ppb^{-1}\ min^{-1}$) was the uptake rate at the reference

temperature (298 °K). For the first experiment the uptake rate was 0.189 $ng\ ppb^{-1}\ min^{-1}$ and 0.138 $ng\ ppb^{-1}\ min^{-1}$ for the second exposition.

For the field exposition in Paris, the uptake rate was calculated according to the Radiello operational manual version of 01/2003. $[NO_2]$ has been calculated using equation $Q_t = Q_r (T_K/298)^7$ where Q_t was the uptake rate in $ng\ ppb^{-1}\ min^{-1}$ at temperature T_K in Kelvin and Q_r (0,141 $ng\ ppb^{-1}\ min^{-1}$) was the uptake rate at the reference temperature (298 °K). For the two field expositionsthe uptake rate is 0.098 $ng\ ppb^{-1}\ min^{-1}$.

By correcting the results of the laboratory expositions using the equation of operational manual version 1/2003, the uptake rate become 0.141 instead of 0.189 $ng\ ppb^{-1}\ min^{-1}$ for the first experiment and 0.098 instead of 0.138 $ng\ ppb^{-1}\ min^{-1}$ for the second exposition.Consequently,the estimated concentrations are changed from 54.1 to 72.5 μg/m³ for the first exposition (the reference value is 76.8 $\mu g/m^3$) and from 30.0 to 42.8 $\mu g/m^3$ for the second exposition (the reference value is 43.5 $\mu g/m^3$). In both cases the corrected concentrations are more similar to the reference values than the ones calculated with the previous model of uptake rate. It must be outlined that the radiello samplers supplied for the two laboratory experiments were of the same type as those supplied for the field experiment. The extraction procedure before analysis was the same too. The equation for the determination of the uptake rate can be found in the "Instruction manual for Radiello sampler" of Fondazione S. Maugeri version 1/2003[7].

Lab. G, Gradko diffusion tube with membrane

The sampler is based on the one of Palmes[8,9] but with a membrane inserted at the open end (see Figure 29). The uptake rate is calculated using a model established in previous laboratory experiments by Lab. G[10]. In the laboratory, for the first experiment the uptake rate is 0.00227 $ng\ ppb^{-1}\ min^{-1}$ while for the second expositionthe uptake rate is 0.00184 $ng\ ppb^{-1}\ min^{-1}$. The uptake rate for the rural field test is 0.00207 $ng\ ppb^{-1}\ min^{-1}$ while for the urban test 0.00204 $ng\ ppb^{-1}\ min^{-1}$

Lab. F, Gradko diffusion tube (open tube) with protective box

The sampler, based on the one of Palmes is the same as the one used by Gradko (see Figure 23). During all expositions,samplers were placed in a grey-type shelter manufactured by Passam (see Figure 17). The theoretical uptake rate[11] of 1.22 ml/min is used for the calculation.

Lab. E, Gradko diffusion tube (open tube) without protective box

The sampler, based on the one of Palmes is the same as the one used by Gradko (see Figure 23). No shelter was used for all exposition. The theoretical uptake rate[11] of 1.22 ml/min is used for the calculation.

Lab. D, Radiello sampler

The sampler is of the radial type and it was supplied by Fondazione S.Maugeri. During the laboratory experiments, the samplers were not protected by a shelter but a holder was used (see Figure 24). For the field experiments shelters were used (see Figure 25).

For the laboratory expositions, $[NO_2]$ have been calculated using the uptake rate equation available in November 2002: $Q_k = Q_r (T_K/298)^{5.83}$ where Q_k was the uptake rate in $ng\ ppb^{-1}\ min^{-1}$ at temperature T_K in Kelvin and Q_r (0,189 $ng\ ppb^{-1}\ min^{-1}$) was the uptake rate at the reference temperature (298 ^oK). For the first experiment the uptake rate was 0.138 $ng\ ppb^{-1}\ min^{-1}$ and 0.189 $ng\ ppb^{-1}\ min^{-1}$ for the second exposition.

For the field exposition in Paris, the uptake rate was calculated according to the Radiello operational manual version of 01/2003. $[NO_2]$ have been calculated using equation $Q_k = Q_r (T_K/298)^7$ where Q_k is the uptake rate in $ng\ ppb^{-1}\ min^{-1}$ at temperature T_K in Kelvin and Q_r (0,141 $ng\ ppb^{-1}\ min^{-1}$) is the uptake rate at the reference temperature (298 ^oK). For the exposition in Genevilliers the uptake rate is 0.0986 $ng\ ppb^{-1}\ min^{-1}$ (49.9 *ml/min*) and 0.0967 $ng\ ppb^{-1}\ min^{-1}$ (48.8 *ml/min*) for the exposition in Fontainebleau. Extraction of nitrite of the Radiello cartridge using a shaker for 1 minute at 2500 *rot/min* was found not to be sufficient and needed 1 or 2 repetitions before complete extraction. Another extraction method by sonication for 25 *min* of the cartridge placed in a glass container with 10 ml of Millipore water gave full satisfaction.

By correcting the results of the laboratory expositions using the equation of operational manual version 1/2003, the uptake rate becomes 0.141 instead of 0.189 $ng\ ppb^{-1}\ min^{-1}$ for the first experiment and 0.097 instead of 0.138 $ng\ ppb^{-1}\ min^{-1}$ for the second exposition. Consequently, the estimated concentrations are changed from 57.7 to 77.3 µg/m³ for the first exposition (reference value: 76.8 $\mu g/m^3$) and from 26.5 to 37.7 $\mu g/m^3$ (reference value: 43.5 $\mu g/m^3$). In both cases the corrected concentrations are more similar to the reference values than the ones calculated with the previous model of uptake rate.

Lab. C, Gradko diffusion tube

The sampler, based on the design of Palmes tube is the same as the one used by Gradko (see Figure 23). During all expositions, samplers were placed in a grey-type shelter manufactured by

Passam (see Figure 17). The concentrations given for the laboratory experiments have been calculated using the theoretical uptake rate of 72.8 ml/h. However a model able to foresee the uptake rate of the Gradko sampler was developed[12] by performing some tests in exposure chamber in order to evaluate the influence of temperature and relative humidity on the uptake rate. When this empirical model is applied, the values of uptake rate are 80.2 and 65.6 ml/h for the first and the second experiments in laboratory, respectively. Consequently, the estimated concentrations are changed from 96.5 to 87.6 ± 7.4 $\mu g/m^3$ for the first exposition and from 32.6 to 36.2 ± 1.8 $\mu g/m^3$. In both cases the corrected concentrations are more similar to the reference values than the ones calculated with the nominal uptake rate. For the field experiments, the uptakes rates estimated using the same model are similar to the theoretical value: 69.2 and 67.9 ml respectively instead of 72.8 ml/h. Applying this correction, the results at the urban site becomes 49.2 instead of 47.2 $\mu g/m^3$ and the ones at the rural site become 12.3 $\mu g/m^3$ instead of 11.5 $\mu g/m^3$. The correction using the model is especially necessary for the expositions in extreme conditions as shown by the experiments in exposure chamber.

Lab. B, Analyst sampler

Lab. B used the Analyst sampler, which is a modification of the open-tube design (see Figure 26). As expected for this type of diffusive sampler overestimation can occur at high flow-rates. In the laboratory experiment the device was exposed without using any shelter while the manufacturer requires to use a simple rain shield (see Figure 27) to protect the sampler. The difference between sampler response and the reference value for the 1st experiment in exposure chamber may be explained by the lack of rain shield, which must be used when the wind velocity is high. For harsh conditions, when a strong influence of wind is expected it is recommended to use the shelter shown in Figure 28. The laboratory experiment was conducted in condition of turbulent flow and therefore the 44% higher value obtained in this experiment for the Analyst may be due to convective transport and not to diffusion. On the basis of previous experiments carried out by Lab. B, an overestimation of 30 % may occur at wind velocity of 3 m/sec.

De Santis *et al.* showed in several monitoring studies and inter-comparison exercises performed in Italy and abroad that a rain and wind shield (see Figure 27) is sufficient for an effective protection of the Analyst sampler[13,14,15,16]. When a strong influence of wind is expected it is recommended to use a shelter as shown in Figure 28. A thorough validation of the sampler was carried out at an urban background site (Villa Ada, Rome, Italy), side-by-side with a reference chemiluminescence analyser[15]. All results were obtained by using an uptake rate of 0.0232 $ng \cdot ppb^{-1} \cdot min^{-1}$.

Lab. A, Passam diffusion tube

Lab. A implemented the Passam sampler supplied by Passam a. g. (see Figure 16). Samplers were placed in the white Passam shelter during all expositions (see Figure 18). Both results from laboratory and field measurements were calculated using the nominal uptake rate of 0.9017 *ml/min* which was evaluated for a temperature of 20 °C. Lab. M, the other participant using the Passam sampler decided to use an uptake rate of 0.8536 *ml/min* estimated for 9°C (see Lab. M, Passam).

No correction for the conditions of exposition was applied to the results. However by correcting the uptake rate for temperature (from 54 cm^3/hr at 20 °C to 55.5 cm^3/hr at 25 °C and 50 cm^3/hr at 5 °C), the estimated concentrations are changed from 86.7 to 84.6 $\mu g/m^3$ for the first exposition and from 37.1 to 40.1 $\mu g/m^3$. In both cases the corrected concentrations are more similar to the reference values than the ones calculated with the nominal uptake rate.

6 Discussion and conclusions

The majority of diffusive samplers overestimate the reference value of the laboratory experiment when [NO_2], temperature, humidity and wind speed are set to the highest level (see Figure 2). On the contrary when [NO_2], temperature, humidity and wind speed are set to the lowest level, the majority of diffusive samplers underestimate the reference value of the laboratory experiment (see Figure 3).

The objective of the inter-comparison was to evaluate the contribution of extreme conditions to the uncertainty of NO_2 measurement by diffusive samplers according to the EN protocol of validation of diffusive samplers. Chapter 8.3 and appendix C of the part 2 of the protocol suggests calculation assuming a rectangular distribution between the relative deviations to the reference value for both laboratory tests, thereby adding the relative standard deviation determined for the two laboratories experiments. Since the combination of influencing factors leading to a low uptake rate and high uptake rate have a small probability to occur a triangular distribution may be more appropriate to use than a rectangular one. Furthermore this would reduce the evaluation of standard uncertainty of the uptake rate.

Using the results of the two laboratory experiments, it is then possible to evaluate the contribution of the influencing factors on the uncertainty for the Passam tube, the Palmes tubes with membrane and with protective box. However, for the IVL badge, OGAWA sampler and Analyst sampler it was not possible to fit the shelters and rain shields necessary for sampling in the exposition chamber. The lack of these shelters and rain shields may be responsible for the bias

between the response of some of these samplers and the reference values of the laboratory experiments. In the 1st laboratory experiment, high wind velocities combined with protective boxes blocking air flow in the chamber may have created turbulence (see Table 7), adding convection to the process of diffusion and hence creating bias. For the IVL badge, OGAWA sampler, Radiello sampler and Analyst sampler and for the Gradko diffusion tube with an open end, conclusions about measurement uncertainty should not be drawn based on the results of the two laboratory experiments. Among the samplers that could not be installed with shelter, the Radiello sampler and the Gradko diffusion tube with membrane seem not to have suffered from this absence in the laboratory experiments. It is thought that by using a thick membrane, samplers could remain unaffected by the conditions in the exposition chamber in particular by wind velocities.

The field tests, carried out under conditions of expositions which were a mixture of the laboratory experiments (low concentration and temperature, high humidity and a wind velocity estimated at 1 m/s) show better agreement between the reference values and response of samplers.

For some samplers, the uptake rate can be computed using a model equation according to the exposition conditions, mainly temperature and humidity. Subsequent calculation of the uptake rate was applied by Lab. A for the Passam sampler, Lab. C on Gradko diffusion tube, Lab. D and H for Radiello sampler, Lab. L and lab J on a OGAWA sampler. The corrected values of Lab. A on Passam sampler show relative deviations between reference values and sampler measurements of about 10 %. The correction using a model developed by Lab. C on the Gradko diffusion tube with open end placed in a protective box allowed to limit the relative deviation between reference values and Gradko measurements to about 15 %, a smaller value than the one of uncorrected results of Lab. F using the same sampler. The correction of the Radiello sampler by Lab. D and H using a model established by the Fondazione S. Maugeri gave an agreement within 10 %. Although showing an improvement, the correction of Lab. J on OGAWA results still gave a relative deviation between reference values and sampler responses of about 35 %. However, applying the model equation developed by OGAWA, Lab. L obtained better agreement. All these calculations show that it is possible to improve the agreement between the diffusive sampler response and the reference method by calculating an uptake rate for each condition of exposition. However, as stated Lab. M using a Passam sampler, modifying the uptake rate may artificially create a trend in air pollution level.

The Gradko diffusion tubes are implemented by several laboratories (C, E, F, G, I) with and without protective box and membrane. Like the majority of samplers, all the implementations of

Gradko diffusion tubes gave satisfactory results in the field experiments. In fact, using the model equation developed by Lab. C, it was shown that the uptake rates calculated for the conditions of exposition agree with the theoretical value normally used. In the laboratory experiments, it is shown that under high wind velocities a protective box is able to improve the agreement between sampler response and the reference value.

In the future, a solution must be found in order to accommodate several diffusive samplers using large shelters and rain shields in exposition chamber to run inter-comparison. The number of inter-comparison proposed to participants should be extended in order to draw conclusions based on a higher number of exposure conditions, reflecting more accurately the range of values expected for the influencing factor all the year long.

Appendix: Figures and tables

Figure 6: Monitoring station at rural site (Fontainebleau)

Figure 7: Monitoring station at urban site (Genevilliers)

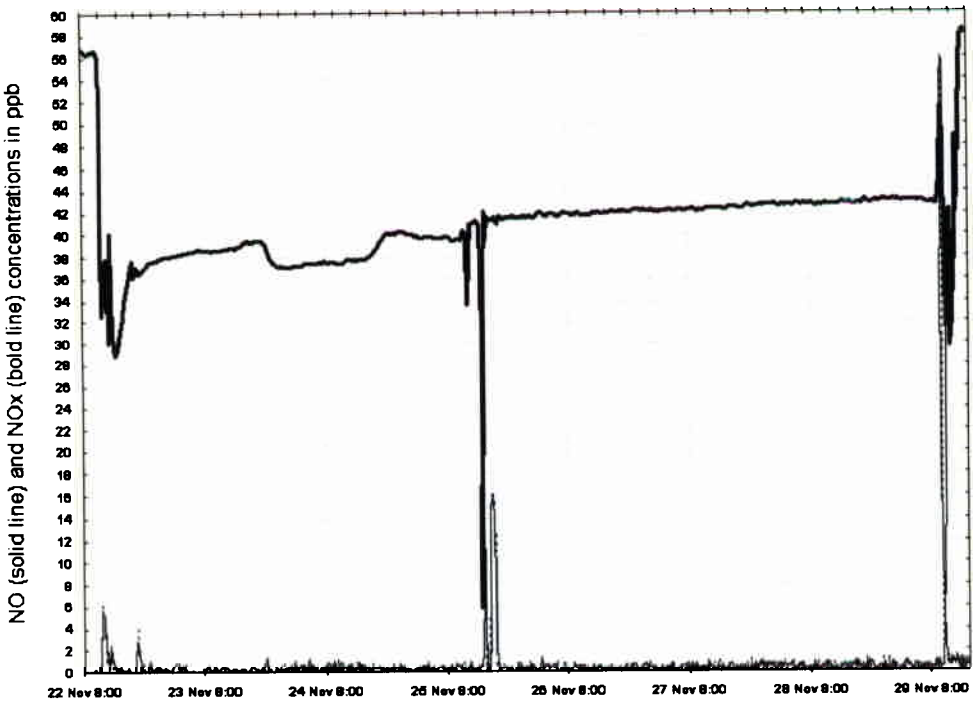

Figure 8: NO/NOx profile during the first exposition period.

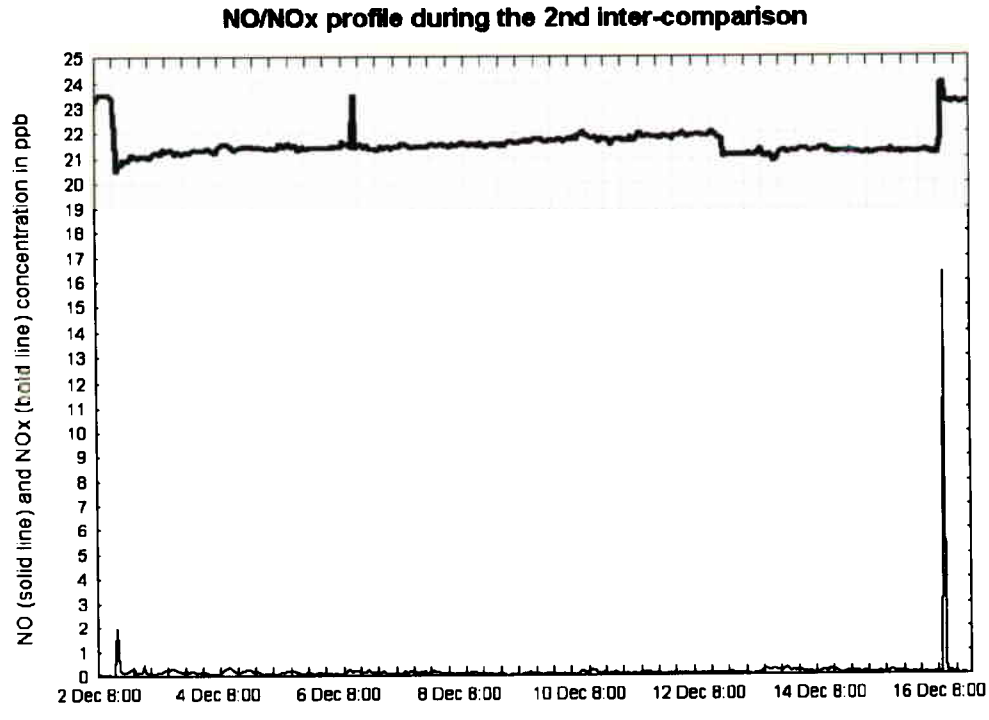

Figure 9: *NO/NOx* profile during the second exposition period.

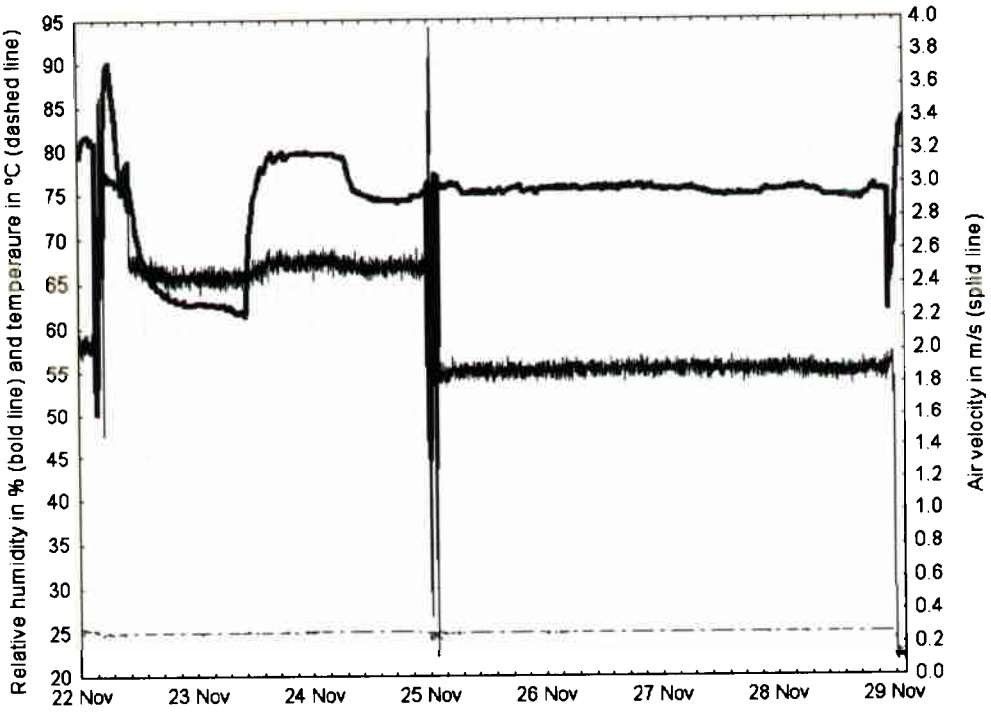

Figure 10: Temperature and humidity during the 1st exposition.

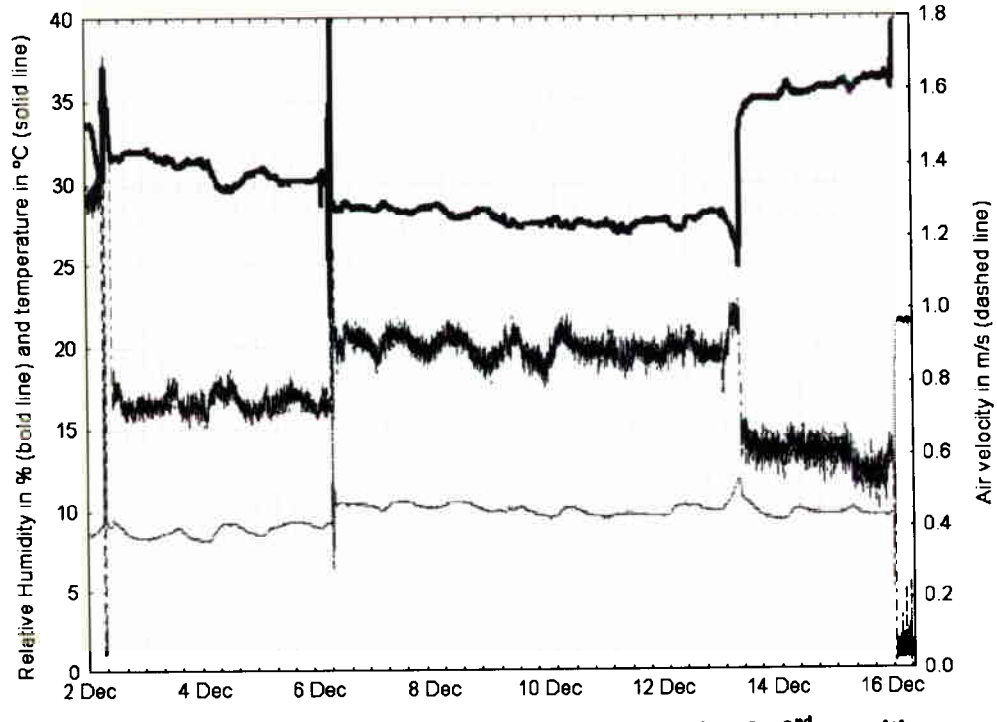

Figure 11: Temperature, relative humidity and air velocity during the 2nd exposition.

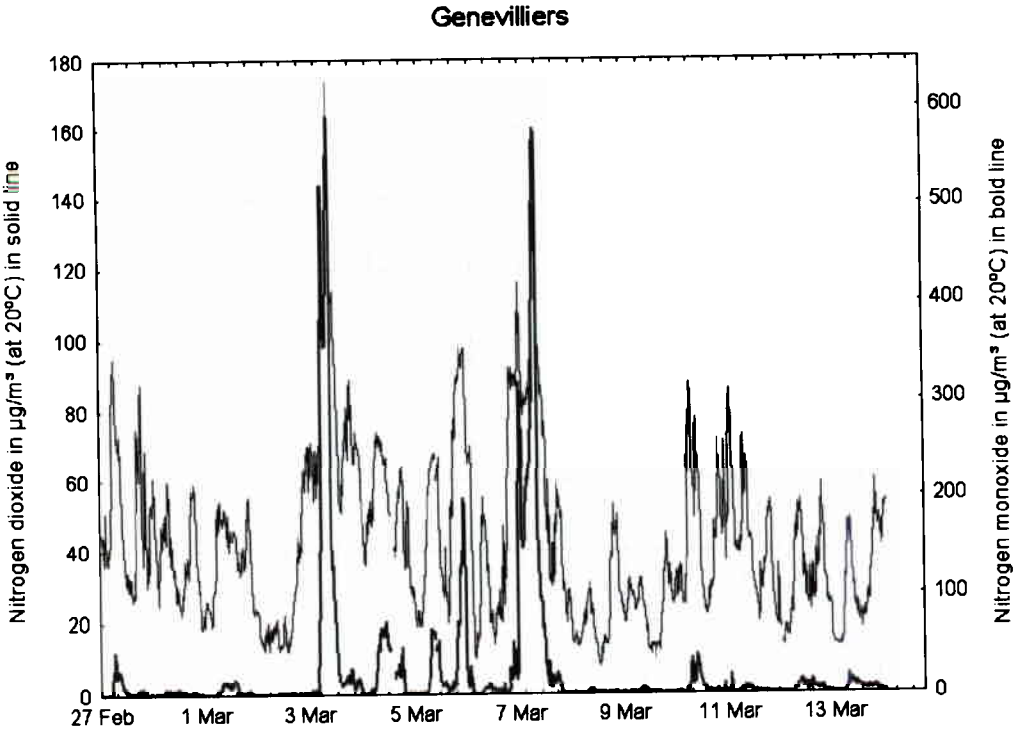

Figure 12: Nitrogen dioxide during the field exposition in Paris for the urban site

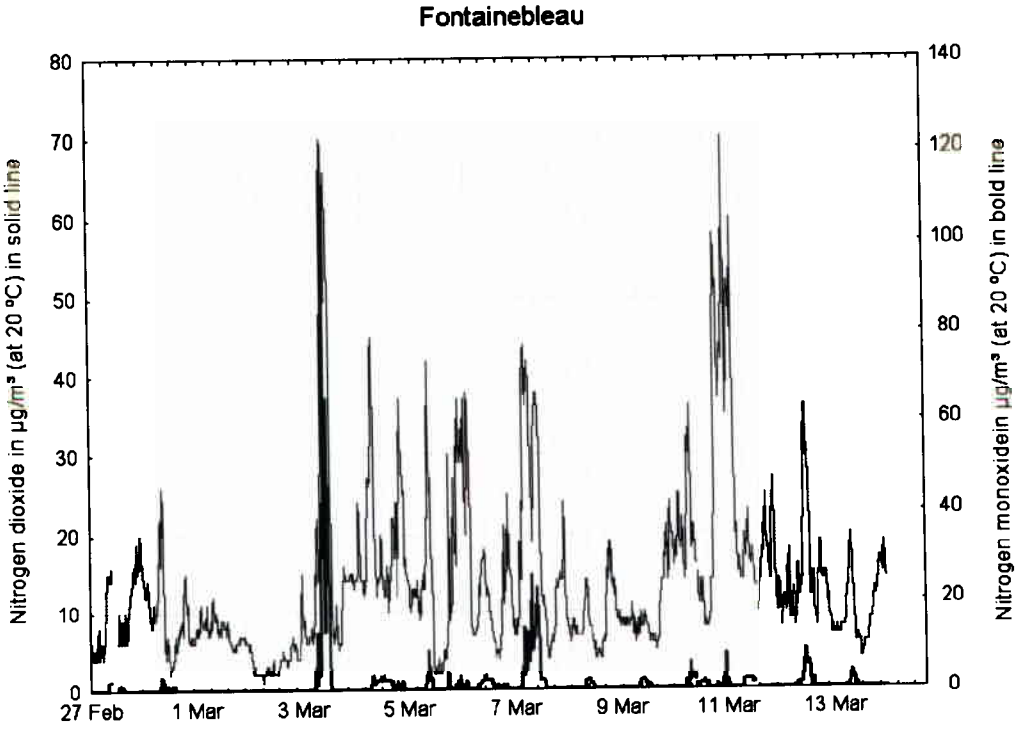

Figure 13: Nitrogen dioxide during the field exposition in Paris for the rural site

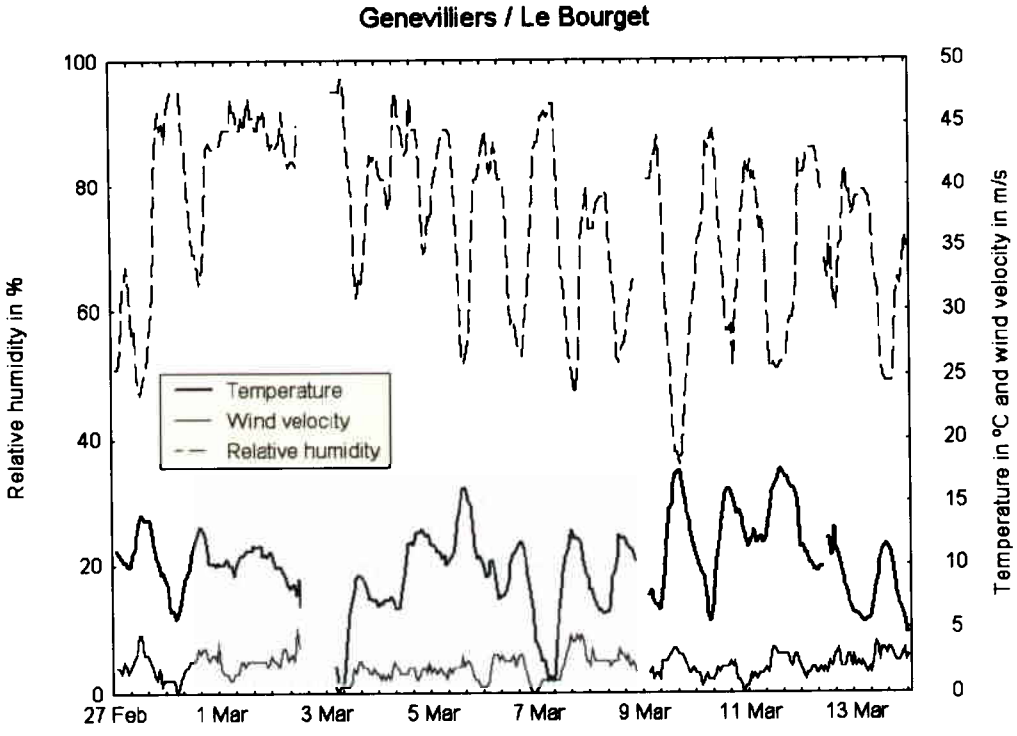

Figure 14: Temperature, relative humidity and air velocity at the urban site.

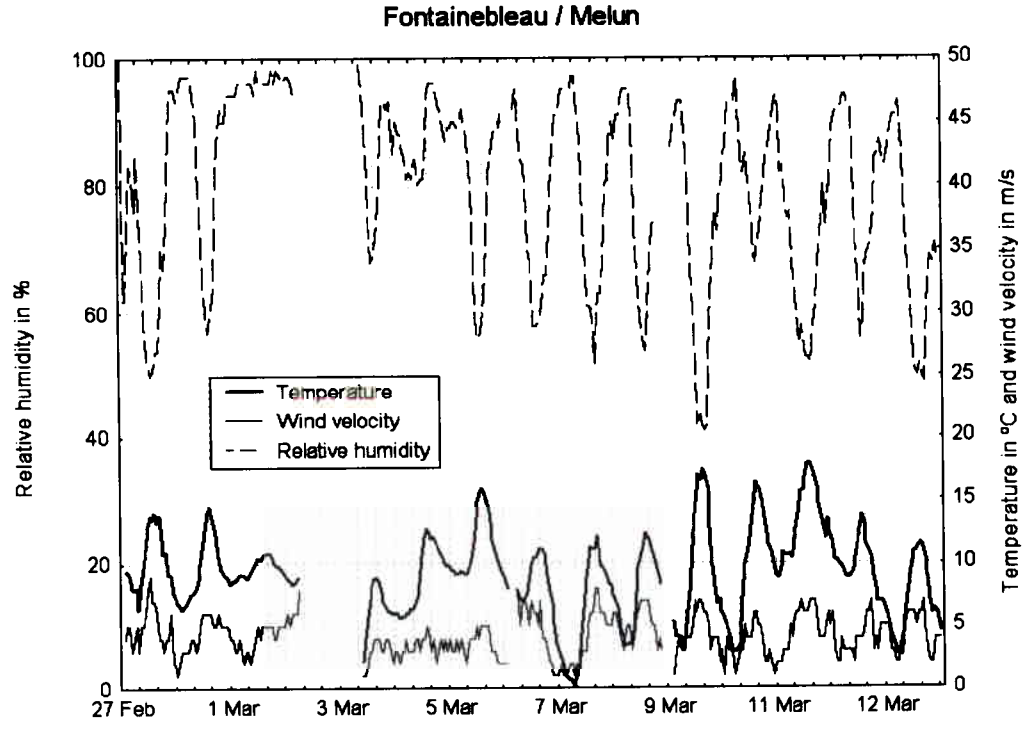

Figure 15: Temperature, relative humidity and air velocity at the rural site.

Table 7: Check of homogeneity of conditions on 25 November for the 1st exposition

Position	Air Velocity m/sec	Temperature °C	Relative humidity %	Time	NOX ppb	Time
2	3.24	25.4	74.6	12:02	41.3	17:50/18:00
6	2.80	25.1	76.2	12:06	41.6	17:35/45
7	3.12	25.1	75.2	12:04	41.7	17:45/17:50
17	2.05	25.1	76.2	12:14	41.5	17:10/15
18	2.16	25.2	76.3	12:16	41.5	17:00/17:10
22	2.50	25.1	76.9	12:10	41.8	17:25/35
23	1.92	25	78.5	12:12	41.4	17:15/25
25	2.04	25.1	74.8	11:54	41.3	16:25/35
26	2.02	25.2	74.8	11:52		
29	2.53	25.2	74.7	12:00	41.6	16:55/17:00
30	2.65	24.8	75.2	11:58	41.6	16:45/55
31	2.83	25.1	74.8	11:56	41.7	16:35/45
33	1.88	24.7	77	12:22	41.4	18:00/10
65	2.36	24.8	76.4	11:45	41.5	15:45/55
66	2.58	24.9	76.4	11:43	41.5	16:08/25
70	2.93	24.9	76.4	11:50	41.6	16:05/08
71	2.85	24.9	77.4	11:47	41.5	15:55/16:05

Table 8: Check of homogeneity of conditions on December 6th for the 2nd exposition

Position	Air Velocity m/sec	Temperature °C	Relative humidity %	Time	NOX ppb	Time
1	1.35	7.7	32.6	14:50	21.5	16:25
2	1.54	7.6	32.5	14:45	21.3	16:20
3	1.47	7.6	31.9	14:40		
6	1.43	9.2	29.4	15:00	21.4	16:40
7	1.35	9	30.7	14:55	21.5	16:30
18	0.96	8.7	26.2	14:30		
19	1.23	8.1	30.6	14:35		
25	1.38	10.3	24.8	14:05	21.4	15:35
26	1.03	10.3	21.8	14:00		
29	1.2	11.1	25.6	14:25	21.4	16:10
30	1.25	11.5	22.7	14:20	21.3	16:05
31	1.19	9.3	25.3	14:10	21.2	15:55
33	0.77	9.2	30	13:30	21.5	15:10
33	0.96	10.5	28.4	15:05		
37					21.5	15:05
65	1.18	10.2	26.4	13:45		
66	1.17	9.9	28.9	13:35		
69					21.6	
70	1.44	10.6	25.1	13:55	21.4	15:15
71	1.42	10.1	26.5	13:50	21.4	15:30

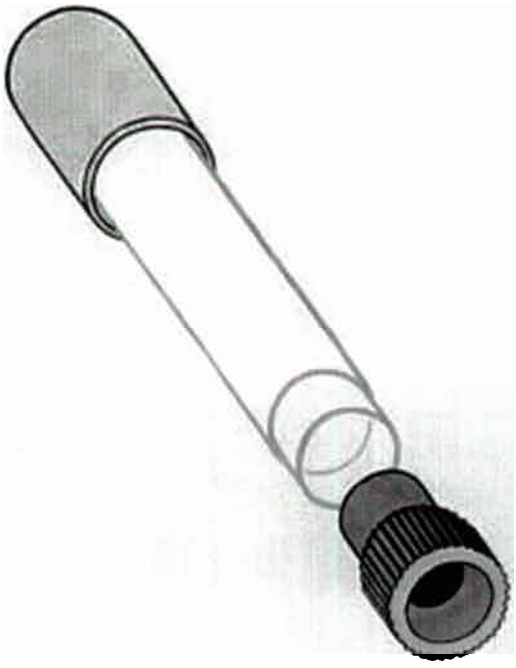

Figure 16: Passam's Diffusive sampler

Figure 17: Grey shelter for diffusive samplers manufactured by Passam a. g.

Figure 18: White shelter used for Passam samplers

Figure 19: Photo of Ogawa sampler with shelter

Figure 20: Ivl sampler holder used for laboratory exposition

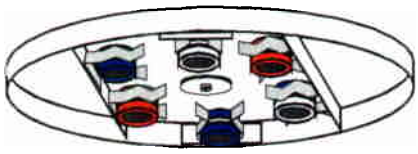

Figure 21: Rain shield for the ivl sampler

Figure 22: Shelter used by lab. J for the Ogawa samplers

Figure 23: Palmes tubes from Gradko

Figure 24: Radiello with holder for exposure chamber

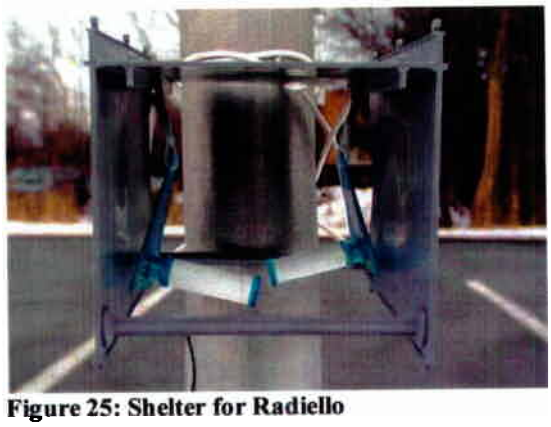

Figure 25: Shelter for Radiello

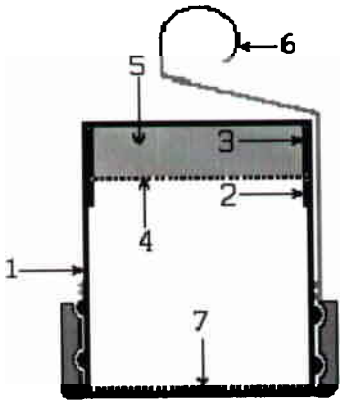

Figure 26: Structure of the Analyst sampler: 1 = glass cylinder (20 mm I.D. x 20 mm diffusive path length); 2 = retaining stainless steel (SS) ring; 3 = viewing SS ring; 4 = SS net; 5 = adsorbent bed; 6 = hook; 7 = removable aluminium and SS mesh shield (air barrier).

Figure 27: Rain shield for Analyst

Figure 28: Protective box for Analyst

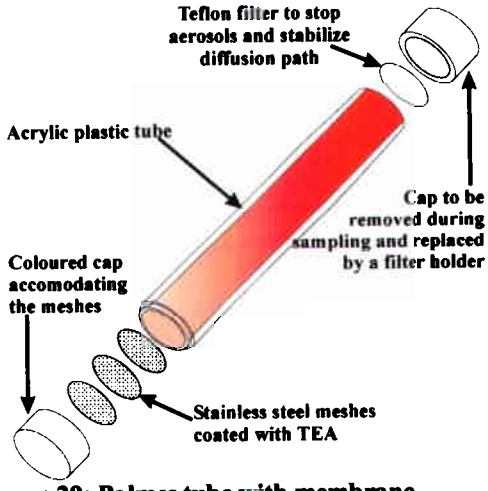

Figure 29: Palmes tube with membrane

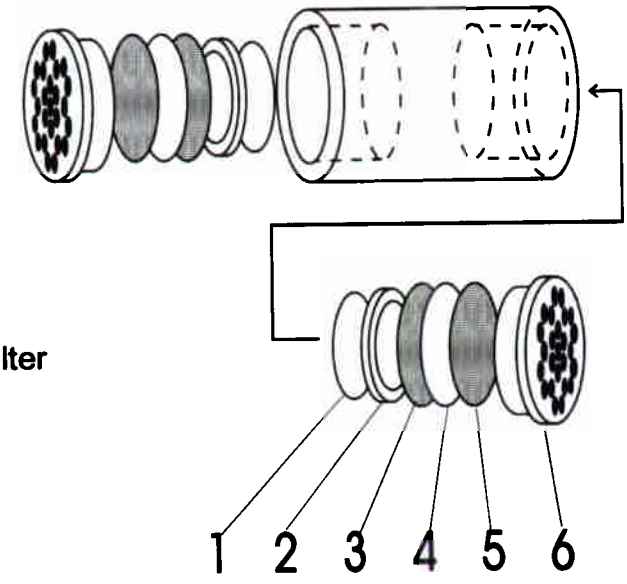

Figure 30: Structure of an Ogawa sampler The sampler body is 2 cm (outer diameter) x 3 cm (length) and has two independent cavities (1.4 cm inner diameter) each containing a diffusive-barrier end-cap, a reactive filter between an inner and outer stainless steel screen, and a retainer ring over a base pad. See ogawausa.com for additional design and deployment details.

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