INSTITUT NATIONAL DE L'ENVIRONNEMENT INDUSTRIEL ET DES RISQUES

DOAS monitoring campaign at Rotterdam Overschie

Final Test Report

DCMR Milieudienst Rijnmond

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1. ABSTRACT

In cooperation with DCMR, INERIS conducted an air quality monitoring campaign using a UV-DOAS instrument. The instrument was set up on a 90 meter long path length, 10 meter over an urban motorway in Rotterdam, district of Overschie. The path length was approximately perpendicular to the roadway.

A poor availability of the instrument was observed, as a result of the problems encountered with the platform supporting the emitter of the instrument.

On the remaining time period, where the emitter platform was stabilised enough, DOAS instrument provided an on time continuous monitoring of NO_2, SO_2, O_3, and NO with a satisfactory reliability. NO_2 and NO results are coherent with the usual characteristics of kerbsite stations. Particularly, the ratio of the 98 percentiles NO and NO_2 is far over 2.

As expected, the results for benzene and toluene are less reliable, with a poor repeatability and a noise as high as 20 $\mu g/m^3$ on quarter averages. Despite taht, the overall results are coherent with those observed with reference technics (chromatography, adsoption…) on similiar locations near a roadway. Particularly, the ratio of toluene on benzene is around 2,5.

For NO, NO_2 and NO_x (=NO+NO_2), an additional statistical data processing was performed, comparing the data of DOAS with those of a chemiluminescence point monitor located nearby the spectrometer of the DOAS. The comparison shows that the results of the two instruments are closely linked, and that they exhibit similar variations.

For NO_x and NO_2, the results of DOAS and point monitor are equivalent with a null or constant systematic difference, over the entire range of concentration. For NO, the difference between DOAS and point monitor is a linear function of the concentrations. Those two latter observations should be studied further on, using numerical simulation.

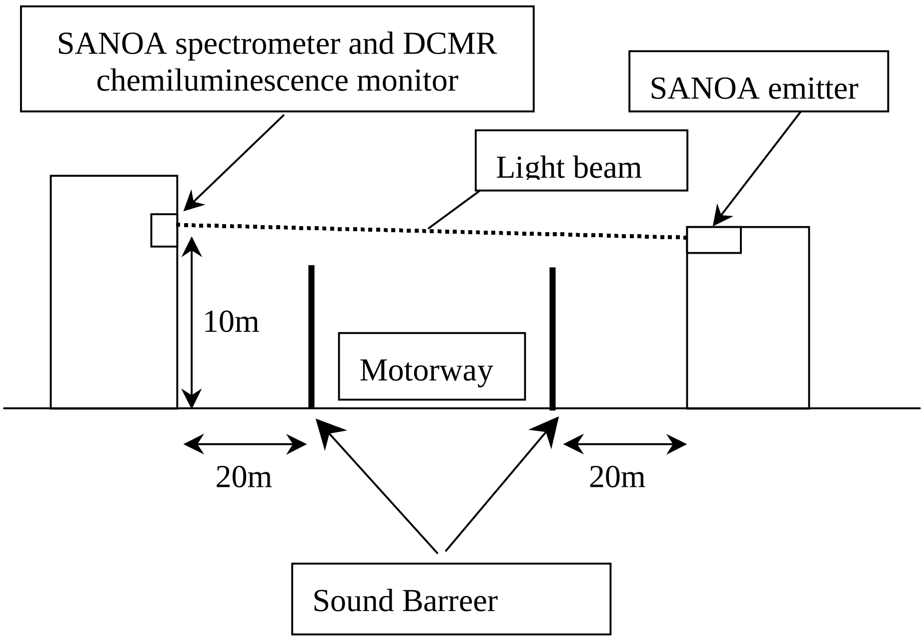
2. INTRODUCTION

This report presents the main results obtained by INERIS during an air quality monitoring campaign, held from october 31st 2001 to december 13th 2001 at Overschie, district of Rotterdam. A Differential Optical Absorption Spectrometer (DOAS) was set on a 90 meter long path length, over a motorway, providing a continuous on time monitoring.

The campaign was commissioned and partially funded by DCMR Milieudienst Rijnmond for INERIS travel costs from Verneuil en Halatte (F-60) to Rotterdam. Additional costs supported by INERIS (staff, instrument paying off….) were funded by the French Ministry of Environment, within a research programme on DOAS of the Central Laboratory for Air Quality Monitoring.

3. MONITORING CONDITIONS

The characteristics of the UV-DOAS used for this study are shown in Appendix A. The spectrometer was installed in a flat rented by DCMR and supported by a three-legged device. The emitter was set up on a wood platform, located alongside the wall of a building on the opposite side of the motorway. Both the emitter and the receiver were located approximately 20 meters alongside from a motorway. The light beam was nearly perpendicular to the motorway.



The instrument showed a poor availability, during the monitoring campaign, mainly due to the poor stability of the wood platform supporting the emitter. That poor stability led to a misalignment of the light beam. The effect was observed especially during the first two weeks, from october 31st to november 11th.

The overall availability is thus only 44% but rise up to more than 90% if only those periods with a good alignment of the light beam are taken into account. The remaining 10% unavailability was due to a malfunction of the emitter light bulb, from december 7th to december 13th.

Table 1 hereafter shows the pollutants monitored by the instrument, and the status of the results. The status takes into account the detection limit, the repeatabilty and the availability of a calibration function, obtained during preliminary laboratory tests performed at INERIS.

	Status of the results	Calibration function available	Detection limit	Reproducibility (as 95% confidence interval) houly average
Nitrogen dioxyde	Valid results	y	5	10%
Sulfur dioxyde		y	2	10%
Ozone		y	5	10%
Nitrogen Oxyde	Indicative results	y	20	not available
Toluene		y	10	not available
Benzene		y	10	not available
M-xylene	Unreliable results	n		
P-xylene		n		
Phenanthrene		n		
Styrene		n		
Nitrous acid (HNO2)		n		
Naphtalene		n		
Formaldehyd (CH2O)	poor availability			
Ammonia				

Table 1

Originally, it was planned to gauge the instrument on site with ozone, SO_2, NO_2, NO, benzene and toluene. Due to the problems encountered with the alignment of the beam and with the light bulb, that gauging was not possible. We therefore use the calibration functions as determined at INERIS in our underground galery.

4. RESULTS

The whole set of data is available as a MS Excel file attached to the present report. That Excel file comprises five sheets : raw quarter average results, calibration data, validated quarter averages, hourly averages and dayly averages. All values are expressed as µg/m^3, uncorrected with temperature and pressure. The path length parametrised in the software of the instrument was 100 meters, and an additional correction has to be performed using formlua 1.

$$c_{corr} = c_{uncorr} \frac{100 \text{ meters}}{\text{actual path length (90 meters)}} \text{ x span + offset}$$

Formula 1

The time curves of hourly average values corrected with the actual path way, and with calibration span and offset are shown in Appendix B, for the 6 polluants monitored with a sufficient reliability. A spot on a shorter period, from november 22nd to november 30th is also provided. Dayly averages data are shown in Appendix C.

As expected, NO and NO_2 curves show a dayly cycle related to traffic intensity, and O_3 is anti-correlated with NO_2, as it is usual.

Table 2 hereafter show the statistics associated with the overall results.

	Percentile 98 (hourly average)	Maximum hourly average	Maximum dayly average
SO_2	47	110	33
O_3	67	97	unrelevant
NO_2	84	100	86
NO	312	385	340

Table 2

Benzene and toluene results show a somehow less reliable figure, with many values below zero. The repeatability seems to be poor, considering the concentration fluctuations from one to next quarter. Those disappointing results could arise from too short a path length (90 meters to be compared with SANOA manufacturer requirements of 180 to 350 meters).

Therefore, the extremum dayly and hourly averages that are shown in table 3 hereafter for benzene and toluene, should be handled cautiously.

	Min. hourly average	Max. hourly average	Centile 98 Hourly average	Min. dayly average	Max. dayly average
Benzene	-19	52	31	-7	21
Toluene	-40	93	65	-25	55

Table 3

5. COMPARISON BETWEEN DOAS AND POINT ANALYSER

Parallel to the measurements performed by INERIS's DOAS, DCMR ran a Thermo Environmental chimiluminescence analyser, whose sampling point was located nearby the spectrometer of the DOAS. Ambient air from outside the buiding was sampled.

The results obtained with DOAS and point monitor for NO, NO_2 and NO_x (= NO+NO_2) are closely linked, as shown in Figure 1 hereafter.

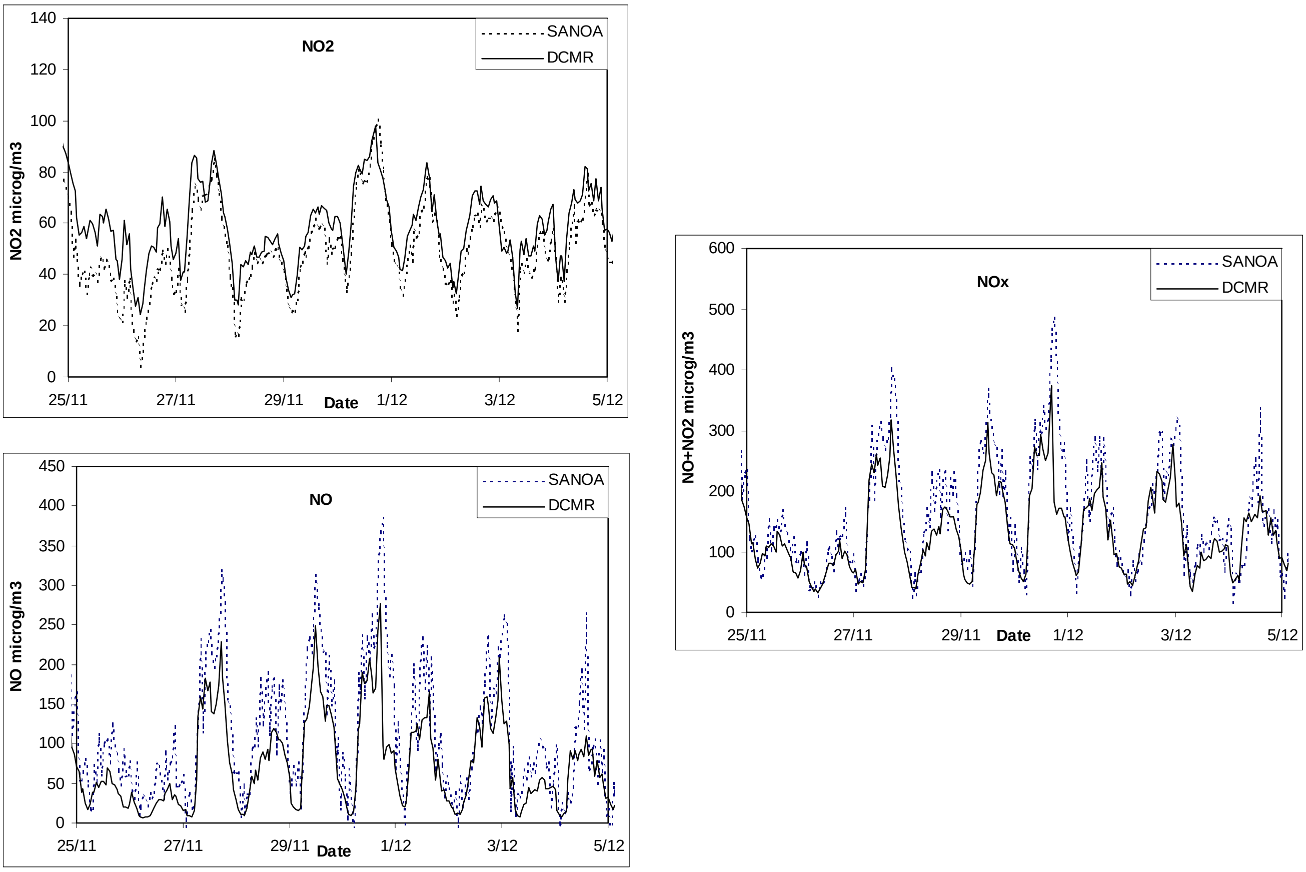


Figure 1 Time plot of the results obtaines with DOAS and with point monitor for NO, NO2 and NOx (NO+NO2)

INERIS performed some statistical calculations on the results obtained by those two instruments, applying french standard NF AFNOR XP X 43-331 to the concentrations of NO, NO_2 and NO_x (NO+NO_2) monitored over the entire period. The charts summarizing those calculations are shown in Appendix D.

The difference frequency distribution curves were plotted on the same charts in Appendix D. One notices that those distribution curves are broad and of multi-modal shape. That situation could be compared to the results obtained previously by INERIS, during a comparison between two DOAS monitors (SANOA and OPSIS). In that latter case, the distribution curves were sharper and of mono-modal shape. The comparison between the two kind of distribution curves are shown in Figure 2 and in Figure 3 hereafter. It is presumable that the departure from mono-modal (gaussian) distribution curve arise from varying mixing ratio between point monitor location and DOAS location. The variation of the mixing ratio is liable to come from meteorological parameters (wind direction and velocity). That point could be studied further with numerical simulation.

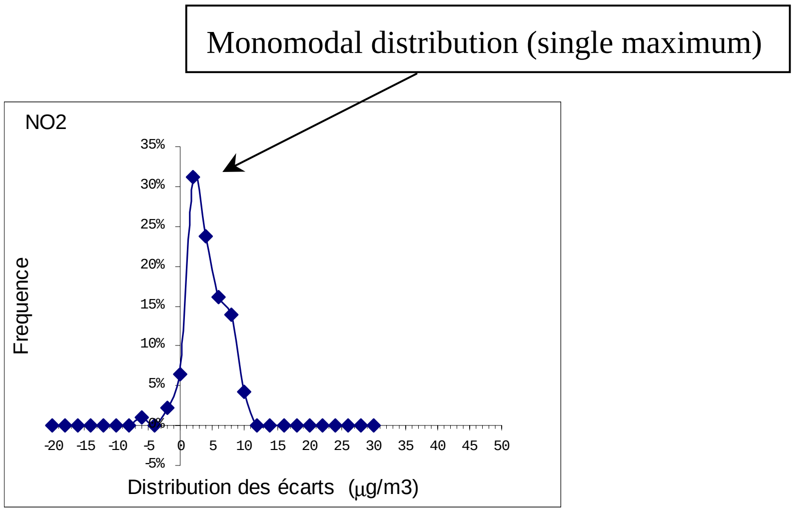


Figure 2 example of a frequency distribution curve of the differences between two DOAS monitors run parallel over the same path length

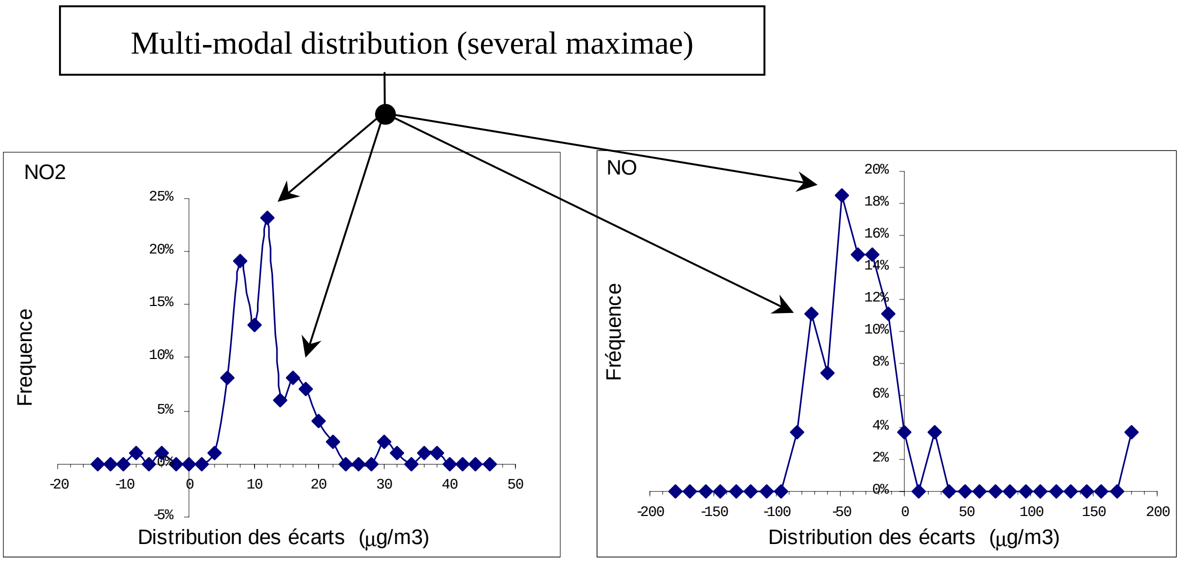


Figure 3 Example of frequency distribution curves of the differences between DOAS and point monitors for this campaign (all results and curves in annex 6)

For NO_x, the two instruments show equivalent results without systematic errors on the whole range of concentrations, from 0 to 200 µg/m^3. A departure from equivalence was however observed at value over 200 µg/m^3. Figure 4 hereafter shows the difference D (D = DCMR - DOAS) between DOAS and point monitor as a function of concentration. On the plot, D is surrounded by the curves $D \pm \sigma_{exp}$, where σ_{exp} is the experimental standard deviation.

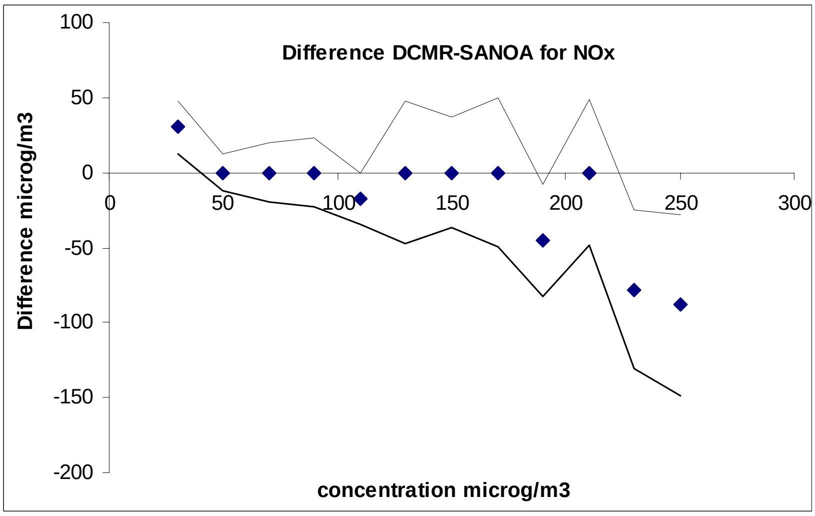


Figure 4 Difference between DOAS and point monitor as a function of the concentration for NOx

For NO_2, the results are also equivalent, with a systematic difference of approximately 10 µg/m^3, point monitor results being higher than DOAS. That difference is nearly constant over the whole range from 0 to 100 µg/m^3. One should notice that a good reproducibility of SANOA versus point monitor has been achieved during the campaign, with a 95% confidence interval on the hourly averages, of approximately 20 µg/m^3 on the whole range.

Figure 5 hereafter shows the difference D (D = DCMR - DOAS) between DOAS and point monitor as a function of concentration. On the plot, D is surrounded by the curves $D \pm \sigma_{exp}$, where σ_{exp} is the experimental standard deviation.

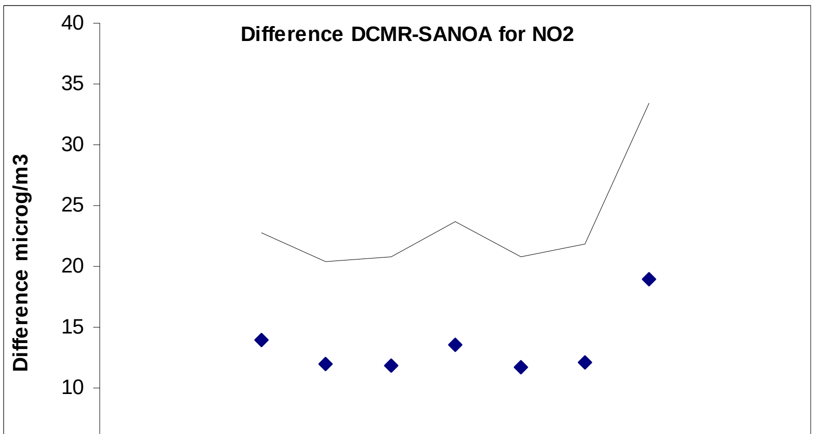


Figure 5 Difference between DOAS and point monitor as a function of the concentration for NO_2

That observed equivalency should be studied further with numerical modelisation, taking into account the background levels of NO_2 for the city of Rotterdam, the distance of the point monitor to the motorway, the site specific configuration (sound barreer..), the kinetics of oxydation of NO to NO2 and the dispersion conditions (meteorology…).

On the contrary, the difference between DOAS and point monitor for NO and the corresponding confidence interval increased quite linearly with concentrations. Figure 6 hereafter shows the difference D (D = DCMR - DOAS) between DOAS and point monitor as a function of concentration. On the plot, D is surrounded by the curves $D \pm \sigma_{exp}$, where σ_{exp} is the experimental standard deviation.

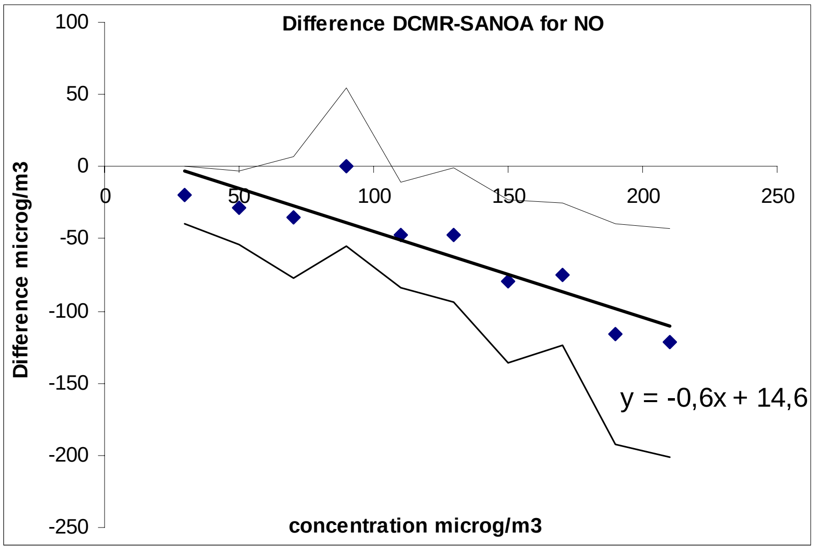


Figure 6 Difference between DOAS and point monitor as a function of the concentration for NO

Therefore, it is presumable that NO emitted on the motorway is unevenly distributed in the atmosphere, due to its dispersion and its oxydation to NO_2, as shown diagrammmatically in Figure 7 hereafter.

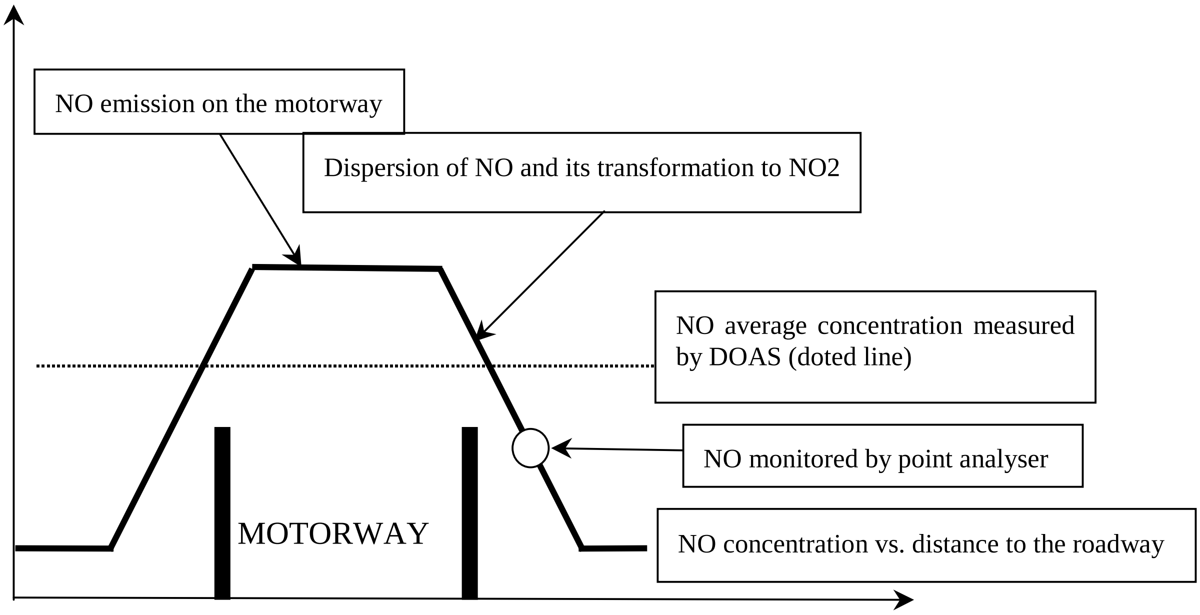


Figure 7 Presumed NO profile across the motorway

That difference between DOAS and point monitor resuts for NO should be studied further with a modelisation study .

6. LIST OF APPENDIXES

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APPENDIX A

Characteristics of the DOAS instrument used for this study

TECHNICAL CHARACTERISTICS OF SANOA DOAS

Manufacturer : Environnement SA, 111, bd Robespierre, F 78 300 POISSY

The instrument comprises an emitter and a receiver plus spectrometer.

Emitter :

High pressure Xenon lamp (OGR type), 150 Watt

Receiver and spectometer

Spectral range : 200 to 350 nm

Slit : 50 µm * 2 mm

Aperture : F/3

Spectral resolution : 0,34 nm

Detector : array of 512 diodes

Path length range : 100 to 500 m (best results 180 to 350 m)

Compounds monitored :

Nitrogen dioxyde NO2,

Sulfur dioxyde

Ozone

Nitrogen Oxyde

Toluene

Benzene

M-xylene

P-xylene

Phenanthrene

Styrene

Nitrous acid (HNO2)

Naphtalene

Formaldehyd

Ammonia

APPENDIX B

Time plot of hourly average results

APPENDIX C

Dayly average results

Tmesure	LightVis	NO2	SO2	O3	NO	Ben	Tol
31/10/00	25%	44	27	26	68	21	36
01/11/00	25%	40	16	41	86	13	34
06/11/00	23%	57	7	22	101	6	6
07/11/00	27%	59	7	26	170	-1	17
08/11/00	26%	46	20	27	95	2	9
09/11/00	28%	53	27	32	95	-6	24
10/11/00	31%	60	34	38	111	-4	23
11/11/00	34%	45	9	48	47	-7	28
12/11/00	21%	39	8	54	50	-1	26
13/11/00	18%	62	26	28	119	8	23
14/11/00	20%	74	20	0	255	19	-25
15/11/00	23%	57	21	11	149	11	-7
16/11/00	23%	54	19	16	128	5	-8
17/11/00	24%	68	29	20	173	6	7

18/11/00	24%	40	20	34	76	4	-2
19/11/00	21%	24	15	39	53	10	-8
20/11/00	23%	62	17	12	144	13	-7
21/11/00	25%	51	11	25	150	4	19
22/11/00	23%	49	16	32	87	5	14
23/11/00	24%	60	14	17	200	4	31
24/11/00	24%	68	31	23	139	8	45
25/11/00	24%	42	13	31	76	6	33
26/11/00	24%	31	19	53	52	6	26
27/11/00	24%	59	29	24	153	6	39
28/11/00	20%	40	20	12	110	16	18
29/11/00	22%	46	17	6	150	15	22
30/11/00	22%	70	24	19	182	9	45
01/12/00	22%	53	8	19	114	6	41
02/12/00	21%	50	11	25	105	9	48
03/12/00	20%	46	11	30	89	15	43
04/12/00	18%	56	8	28	82	6	44
05/12/00	22%	59	10	24	123	4	50
06/12/00	22%	61	13	23	158	4	50
07/12/00	21%	65	16	22	175	8	55

(all values in $\mu g/m^3$, actual pressure and temperature)

APPENDIX D

Statistical calculations on the difference between DOAS and point monitor