EVALUATION OF ENVIRONMENTAL OZONE IMPACTS BY USING THREE COMPLEMENTARY TECHNICS IN AN INDUSTRIAL AREA IN NORTHERN FRANCE.

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ABSTRACT

Ozone is one of the most problematic pollutant also for health than environment. Bioindication has enable us to show that a deacrease in precursors emission could lead, in some cases, to an increase of ozone impacts, especially downtown and in industrial area. We've studied this pollution in Dunkerque area. The aim of this study was to evaluate environmental impacts of ozone during some summers. Environmental impacts were evaluated using 13 biostations equipped with sensitive tobacco plants. Atmospheric concentrations were determined using four automatic stations from Opal'Air network, whose results were completed with passive samplers displayed on biostations. Data from the different methods were correlated. Necrosis on tobacco leaves were clearly linked with ozone concentrations, which are influenced by climatic conditions and proximity of local sources of pollution. This work has enabled us to put in advance ozone in particular situation as downtown or in industrial area. In a second way, those experiments conduced us to associate three complementary techniques for ozone monitoring. With tobacco, we've obtained a more precise picture of the ozone impacts and we've observed that the combination of tobacco and passive samplers could be a good alternative of automatic network in areas which are not equipped with.

INTRODUCTION

Ozone is one of the most problematic pollutant also for health than environment. This pollutant is now well studied in a large panel of situations e.g. for impacts on cultivated plants [1], on rural areas [2] as well as a large scale [3] or for a city [4]. Meanwhile data on particular locations (for instance near industrial complex) are still not well documented.
In the case of Dunkerque, atmospheric pollution survey was mainly oriented on industrial pollutants as SO_2, Particulate Matter, NOx and more recently VOC. In this context, we've developed a multidisciplinary approach using tobacco sensitive plants as bioindicator [5-6] and physico-chemical techniques, for a first evaluation of environmental impacts caused by ozone pollution. This strategy, which is not frequently used (see [7-8] 2002 for review), is a

good alternative method for ozone pollution evaluation for areas without automatic apparatus [9].

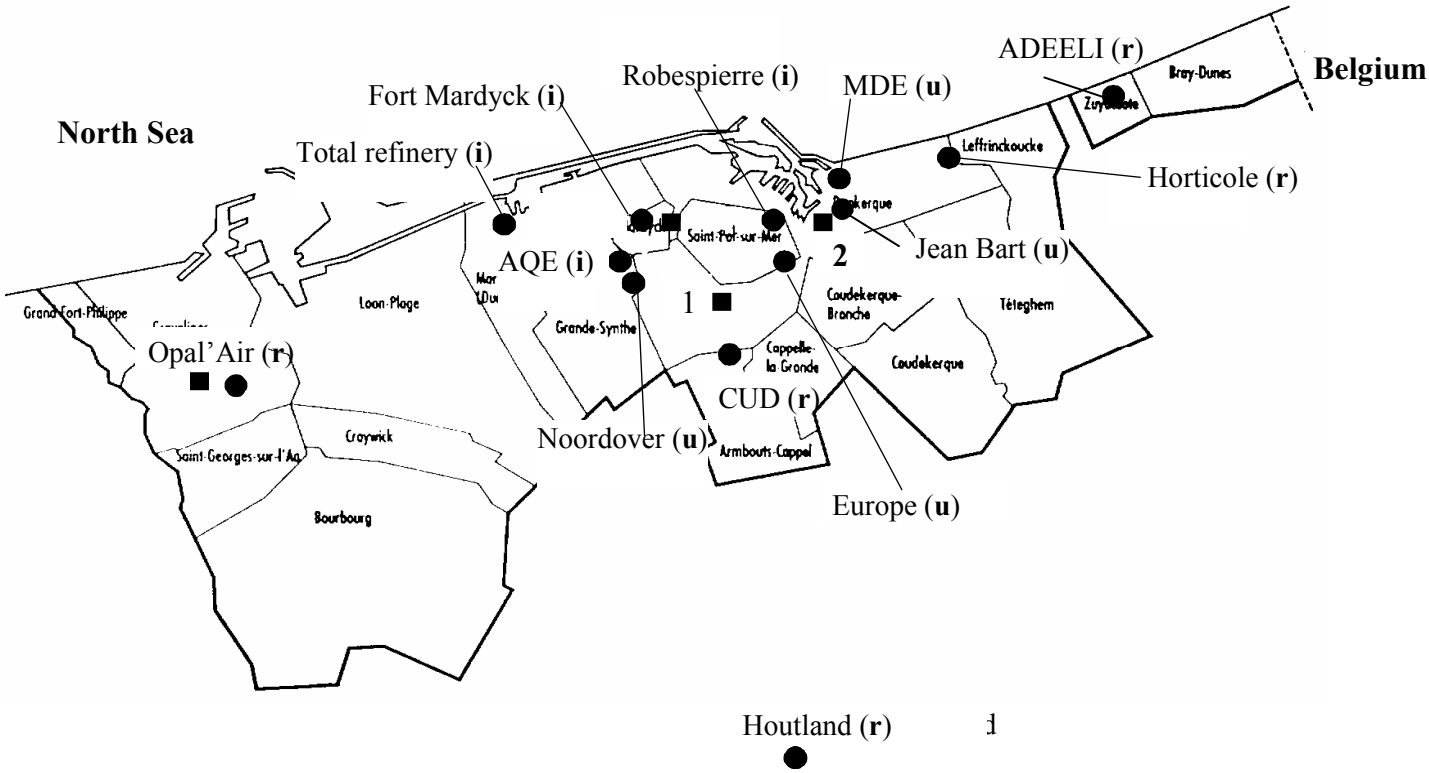
OBJECTIVE

Main objective of this study was to obtain data about ozone impacts on environment; in a large industrial area where ozone had increased in the last years.

MATERIAL AND METHODS

Dunkerque is located in the North coast of France, near Belgium and Great Britain (Fig. 1).

Figure 1: presentation of the studied stations.



Black square represent localisation of ozone automatic apparatus: in addition to Opal'Air (rural site) and Fort Mardyck (industrial site) station, 1: Petite Synthe station (near a busy street) and 2: Dunkerque Centre (downtown Dunkerque) station.
(**i**) : industrial station, (**r**) : rural station and (**u**) : urban station.

This area is a fairly flat region characterized by an oceanic climate with mean precipitation around 800 mm per year. Winds, predominantly from southwest, favour pollution dispersion to the North Sea. Dunkerque area is composed of an important industrial complex located along the sea surrounded by a dense urban zone mixed with agricultural surfaces. The studied area includes 20 districts, that is to say 220 000 inhabitants. Main sources of atmospheric pollutants are industries and transports. Industrial complex is 10 kilometres long and located

along the sea. Main activities producing atmospheric pollutants are: petrochemistry, chemistry, metallurgy, energy production. Environmental impacts were evaluated using 13 biostations equipped with sensitive tobacco plants: 4 near industrial complexes, 5 in rural areas and 4 in urban areas (Fig. 1).. We used *Nicotiana tabacum* plants (Bel B and Bel W3 cultivars, seeds were provided by J.P. Garrec INRA – Nancy, France and Altadis Company). Three Bel W3 and two Bel B were placed in each station during 1 month. Plants were protected from the sun with special shadow linen, which avoided direct sun damage, hydric stress (in addition with a water tank) and favoured a good opening of stomata. Percentage of necrotic leaf surface was determined each week using reference pictures as for Eurobionet program [10]. This study lasted 6 months (May – October) during three years (2001 - 2003).
The study was completed with passive samplers displayed (Radiello®, Fondazione S. Maugeri, Padova, Italy) on some biostations in June, July and August. Tubes were replaced each week. They were analysed following a standardized protocol using Radiello procedure.
An automatic network, Opal'Air, makes atmospheric pollution survey. Twelve stations are present on the studied area, 4 equipped with ozone analysers (Environnement S.A., Poissy).
All data were interpreted using statistical analysis (using Statistica® software).

RESULTS

During the experiment, wind orientation was from Southwest as classically observed in this region. Mean temperatures were between 16 and 18°C with maximum around 35°C (Tab. 1, data from Meteo France). Usually ends of experimental periods were characterized by climatic conditions less favourable for ozone formation with clouds and rainy episodes.

	Temperature (°C)	Wind speed (m/s)	Rain (mm/ hour)
2001	(20) 16,34 +/- 2,37	(20) 5,82 +/- 1,37	(20) 0,08 +/- 0,07
2002	(19) 16,70 +/- 1,73	(19) 5,49 +/- 0,77	(19) 0,08 +/- 0,08
2003	(19) 17,89 +/- 2,19	(19) 4,87 +/- 0,85	(19), 0.07 +/- 0.02

Table 1: variation of meteorological data (data from Météo France).
(Number of weeks) Mean +/-SD.

Evolution of mean ozone concentrations measured by automatic device is presented in table 2.

Dunkerque Centre	Fort Mardyck	Petite Synthe	Opal'Air
2001(20) 49,91+/-8,64	(20) 48,6 +/- 7,06	(20) 45,91 +/- 8,65	(20) 52,21 +/- 6,32
2002(19) 52,21 +/- 8,48 **a**	(19) 36,20 +/- 5,46 **a, b**	(19) 44,24 +/- 8,50 **a, b**	(19) 54,4 +/- 8,09 **b**
2003(19) 52,38 +/- 10,15 **a, b**	(19) 33,14 +/- 5,46 **a, c**	(19) 34,77 +/- 8,50 **b, d**	(18) 50,28 +/- 8,09 **c, d**

Table 2: results of ANOVA on automatic network data ((number of weeks) Mean +/- SD).
Data from station with the same letter are significantly different
(Newman-Keuls test, $p<0.05$).

ANOVA results show that pollution periods are not the same during experiment. In 2001, ozone pollution was very homogenous in the whole studied area. In 2002, ozone concentrations observed in Dunkerque Centre and Opal'Air stations were significantly higher

than in Fort Mardyck and Petite Synthe. Those differences were confirmed in 2003. Fort Mardyck is influenced by local industrial sources as refineries and metallurgic plant. Petite Synthe station is located near a road and influenced by traffic emissions.
Table 3 presents results obtained with ozone passive samplers. Tubes were placed during the three months when ozone concentrations are higher. Differences for ozone concentrations between sites are not significant. During those three months, influence of local sources where less important than during the beginning and the end of the experiment (this was the same for each year). We have to take into account that, during summer holidays, industrial activity and consecutively pollutants emissions decrease.

Lac	Opal'Air	Fort-Mardyck	Total	Europe	MDE
2001 (14) 58,21 +/- 10,21	(13) 60,08 +/- 13,17	(14) 58,93 +/- 9,50		(14) 59 +/- 13,07	(13) 59,77 +/- 12,11
2002 (15) 52,27 +/- 12,45	(15) 59,47 +/- 13,40	(16) 56,88 +/- 12,97	(15) 62,07 +/- 24,85	(14) 57,86 +/- 12,13	(16) 54,88 +/- 13,51
2003 (15) 52,13 +/- 15,66	(15) 56,93 +/- 13,04	(15) 59,13 +/- 13,14	(16) 65,31 +/- 15,35	(15) 58,67 +/- 16,01	(15) 53,93 +/- 12,57

Table 3: results of ANOVA on passive samplers data ((number of weeks) Mean +/- SD).
Differences for ozone concentrations between sites are not significant.
(Newman-Keuls test, $p<0.05$).

Results presented table 4 show that there are different situations between exposure periods for ozone impacts on tobacco.

Houtland	Lac	Opal'air	AQE	Noordover	Fort-Mardyck	Total
2001 (20) 1,59 +/- 1,18 **a**	(20) 1,99 +/- 2,07	(20) 3,37 +/- 3,01	(20) 1,51 +/- 0,66 **b**		(20) 2,05 +/- 1,82	
2002 (19) 2,4 +/- 1,40	(16) 3,11 +/- 2,02	(19) 3,98 +/- 2,49 **a**	(19) 2,40 +/- 0,96	(19) 5,44 +/- 2,71 *	(19) 2,72 +/- 1,73	(19) 1,92 +/- 1,34
2003 (18) 5,89 +/- 3,40	(18) 5,25 +/- 3,32	(15) 3,33 +/- 2,34	(15) 4,06 +/- 3,15	(17) 3,92 +/- 3,68	(18) 3,28 +/- 2,31	(18) 3,91 +/- 3,80

Robespierre	Europe	Jean Bart	MDE	Horticole	Adeeli
2001 (20) 2,31 +/- 2,02	(20) 2,23 +/- 1,22	(18) 1,81 +/- 0,83	(20) 3,69 +/- 4,59 **a,b**	(20) 1,85 +/- 1,13	(20) 2,15 +/- 1,52
2002 (19) 2,30 +/- 1,59	(19) 2,51 +/- 1,72	(19) 1,57 +/- 0,71 **a**	(19) 6,18 +/- 4,58 *	(15) 3,22+ /- 1,37	(19) 3,49 +/- 2,08
2003 (15) 2,50 +/- 2,32 **a**	(15) 3,03 +/- 2,11 **b**	(8) 4,28 +/- 1,18	(18) 6,58 +/- 4,26 **a,b,c**	(15) 3,39 +/- 3,29	(15) 2,73 +/- 1,82 **c**

Table 4: results of ANOVA on tobacco data ((number of weeks) Mean +/- SD).
In 2002, data with * are significantly different from the others but Nordoover and MDE are not significantly different. In 2001 and 2003, data from station with the same letter are significantly different
(Newman-Keuls test, $p<0.05$).

During 2001, all results are in the same range. There are no differences between rural, urban and industrial stations. Those observations are confirmed by ANOVA analysis. MDE station is significantly different from two stations, which are influenced by local sources of pollution. It remains difficult to interpret results from MDE because of the situation on the platform more than 5 meters above the soil. Jean Bart Station, located at less than 1 kilometre, never gave comparable results. Ozone impacts on tobacco were still important on this station during 2002 and 2003. In 2002, results obtained in Nordoover show a similar pattern than in MDE.
For the other, we found results in accordance with the typology of the site. Results from stations influenced by industrial sources are lower than stations far from local source of pollutants (which are more exposed to ozone). Surprisingly, tobaccos placed in some rural

stations as Houtland and ADEELI were not more affected by ozone than the others despite more favourable conditions for ozone formation. Standard deviations are generally more important in 2003. This is due to some episodes more favourable for ozone formation and characterized by more important impacts on tobacco. Paradoxically, we have not observed important ozone impacts during heat wave in august. It seems that during this episode, temperature impacts were more predominant. Ozone exposure was lower because high temperature has cause a closure of foliar stomata.

DISCUSSION

Despite of favourable conditions, for ozone formation such as climatic conditions and coastal localisation (favourable conditions found also in other parts in North West of France, for instance in Normandy) we've observed that ozone concentrations were relatively low. This means that variations of ozone pollution were quite homogenous in the entire zone. Using an automatic network, we've observed that those concentrations are affected by local sources as industries or traffic. Despite a fairly good repartition of those four automatic apparatus, they're still insufficient to give precise data about ozone pollution impacts over a large area. This has to be completed with other data such as those from passive samplers and tobacco, which enable us to investigate more various situations. Excepted for MDE, we've observed that there's no significant difference as well as for ozone concentrations as for impact on tobacco leaves among stations. As previously described, MDE station was placed on the top of a platform; we could suggest that, in this situation, tobacco plants were more exposed to ozone. This could be due to the higher distance from the main street and, consequently, a situation more favourable to ozone formation. Data obtained during heat wave indicate that, in a high temperature and ozone pollution period, temperature is a predominant parameter causing stomata opening regulation and decreasing foliar ozone exposure. As previously mentioned, industrial and urban areas are mainly located near the sea. The predominant wind direction is from southwest, and favours pollutants dispersion to the sea. Meanwhile, we have to take into account the sea breeze, especially from April to September. In Dunkerque area, we don't know exactly the distance covered by pollutant transported by this breeze. Those pollutants include ozone precursors as NOx and VOC, which can disturb ozone's formation. Relatively low ozone concentrations and damage obtained, even in rural area (as Houtland), could be related to this phenomenon. In this condition we can assume that effects of ozone precursors is significant at more than 10 kilometres from the sea. This is only an evaluation, which is certainly underestimated, but we don't have station far enough to precise it. Houtland station located at 25 kilometres from the sea could be affected by more local sources of VOC as a perfume production company. Moreover, first results from a study in Dunkerque area about the evolution of epiphytic lichen flora, show a large influence of NOx emitted as well by industries as by traffic [9]. This is in accordance with our present hypothesis.

CONCLUSION

This was the first time that this kind of investigation, associating 3 different techniques, was done in Dunkerque area. Those 3 techniques gave us complementary results. At first, it enables to have more information about atmospheric pollution caused by ozone. We observed that this pollution was present, but despite favourable geographic and climatic conditions ozone formation was limited. We didn't find constant differences between stations. Pollutants

emitted by local sources cover a large area including rural sites, and limit ozone formation. Wind from the sea transports them from the coast to the continent. We still don't have precise data on the distance of this penetration. Our results suggest that the effects are still significant 10 km from the sea. In a quite difficult context, with a low level of automatic equipment, we observed that the use of tobacco together with passive samplers is a very good alternative for a better understanding of ozone pollution. As a matter of fact, passive samplers give a good integration of weekly ozone concentration, and tobacco a good picture of the environmental impacts of high concentration.

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