



Seasonal and diurnal variations of atmospheric concentrations of phenols and nitrophenols measured in the Strasbourg area, France

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ABSTRACT

Atmospheric sampling (gas and particle-phases) of phenols and nitrophenols (PNP) were performed between 2002 and 2004 in Strasbourg (east of France) and its vicinity. Sites were chosen to be representative of urban (Strasbourg), suburban (Schiltigheim) and rural (Erstein) conditions. Field campaigns were undertaken simultaneously in urban and suburban and urban and rural sites during three seasons on glass fibre filters and XAD-2 resin by using high volume samplers. Concentrations of compounds were determined by analysis with gas chromatography- mass spectrometry (GC-MS) after a silylation step using N-methyl-N-tert-butyl-dimethylsilyl-trifluoroacetamide (MTBSTFA) reagent.

Mean total concentrations varied between 21.1 ng m⁻³ for the rural site, 23.5 ng m⁻³ for the suburban site, and 25.2 ng m⁻³ for the urban site. At the three sites, the most abundant compounds of those measured were phenol, followed by 4-methyl-2-nitrophenol for the rural site and by 2,4-dinitrophenol for the urban and suburban sites. In terms of concentrations, there was negligible difference between the three sites, independently of the seasons considered. On the other hand, a difference in concentrations has been observed between the three sites according to the periods of sampling, especially during the spring. The observed diurnal variations of compounds in warm period (spring) were essentially dependent of the vehicle circulation. In cold period (fall and winter), it seemed that the contribution of domestic heating influence the diurnal variations of some compounds in rural site while for the two other sites (urban and suburban), the intensity of the vehicle circulation seemed predominant.

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1. Introduction

Nitrophenols are compounds of environmental concern, because of their high phytotoxic activity enhanced by long-term chemical and photochemical stability (Grosjean, 1991). Indeed, it has been suggested that nitrophenols could be one factor responsible for forest decline in Central and Northern Europe and in other parts of the world (Rippen et al., 1987). Due to their toxicological potential and ubiquitous environmental occurrence, different phenols were classified as “priority pollutants” by the US environmental protection agency (EPA, 1981).

As a result, nitrophenols have gained more attention and have been analyzed in the air (Herterich and Herrmann, 1990; Nishioka and Lewtas, 1992; Luttko et al., 1997; Belloli et al., 1999; Cecinato et al., 2005), rain (Rippen et al., 1987; Leuenberger et al., 1988; Levsen et al., 1990; Schussler and Nitschke, 2001; Schummer et al., 2009), water (Geissler and Scholer, 1994), fog (Herterich, 1991; Richartz et al., 1990), snow (Kawamura and Kaplan, 1986; Alber et al., 1989) and plant leaves (Hinkel et al., 1989; Natangelo et al., 1999). In general, nitrophenols have been detected in the ng m⁻³ range in clear air and in the µg L⁻¹ range in rain and cloud water (Leuenberger et al., 1985). However, these figures are only approximate as concentrations vary considerably with location.

The origins of PNP in the atmosphere can be very different. They can be emitted directly from combustion processes in vehicles (Trempe et al., 1993; Nojima and Isogami, 1994) and also indirectly formed in the atmosphere by photochemical reactions of precursors (benzene, toluene, phenols, and cresols) with OH radicals and NO₂ (Nojima et al., 1975; Atkinson et al., 1980;

Grosjean, 1984). Some other sources, in particular for nitrophenols, can give rise to their introduction into the atmosphere, like the combustion of coal and wood, the biodegradation of organophosphorus insecticides such as parathion and methyl-parathion (Laplanche et al., 1981) and the use of nitrophenols as herbicides (dinitro-ortho-cresol, dinoseb or dinoterb) (Leuenberger et al., 1988). Phenols are used in large quantities in chemical production of plastics, drugs, colors, explosives, pesticides, detergents and antioxidants (Heberer and Stan, 1997).

In this study, 4 phenols (phenol, o-cresol, m-cresol and p-cresol), 11 nitrophenols (3-methyl-2-nitrophenol, 3-nitrophenol, 4-methyl-2-nitrophenol, 5-methyl-2-nitrophenol, 2-methyl-3-nitrophenol, 3-methyl-4-nitrophenol, 2,6-dinitrophenol, 2,5-dinitrophenol, 2,6-dinitro-p-cresol, 2,4-dinitrophenol and 3,4-dinitrophenol), 4 herbicides (bromoxynil, dinoseb, dinitro-ortho-cresol and ioxynil) and pentachlorophenol were monitored in atmospheric samples (gas and particle-phases). Sampling campaigns have been performed between 2002 and 2004 in spring, autumn, and winter seasons simultaneously at two sites (rural and urban; urban and suburban) during 4 hour time intervals (06:00-10:00; 11:30-15:30; 17:00-21:00) in order to compare the seasonal and geographical variations of concentrations.

2. Materials and Methods

2.1. Chemicals

Acetonitrile, n-hexane and methylene chloride of high pressure liquid chromatographic (HPLC) grade were purchased

from VWR International (Fontenay-sous-Bois, France). Ultrapure water was obtained from a Milli-Q water system (Millipore, St. Quentin en Yvelines, France). MtBSTFA was purchased from Macherey Nagel (MN, Hoerth, France).

The PNP standards were supplied by Sigma-Aldrich (St Quentin Fallavier, France) and Dr. Ehrenstorfer (Augsburg, Germany). The levels of purity were higher than 99% for phenol, m-cresol, o-cresol, p-cresol, 2-chlorophenol-3,4,5,6-d4, 3-methyl-2-nitrophenol (3-Me-2-NP), 4-methyl-2-nitrophenol (4-Me-2-NP), pentachlorophenol (PCP), ioxynil, dinitro-ortho-cresol (DNOC), and dinoseb. The levels of purity were higher than 98% for 3-nitrophenol (3-NP), 2-methyl-3-nitrophenol (2-Me-3-NP), 3-methyl-4-nitrophenol (3-Me-4-NP), bromoxynil, 2,5-dinitrophenol (2,5-DNP), 2,6-dinitro-p-cresol (2,6-DNPc) and higher than 97% for 5-methyl-2-nitrophenol (5-Me-2-NP), 2,6-dinitrophenol (2,6-DNP), 2,4-dinitrophenol (2,4-DNP), 3,4-dinitrophenol (3,4-DNP). A stock solution of each PNP was prepared at 1 g L⁻¹ in acetonitrile.

2.2. Sampling method and sites

Samples were collected using a Digitel DA-80 high volume sampler (Digitel, Switzerland), equipped with a glass fiber filter ($\phi = 150$ mm) and 20 grams of XAD-2 resin at a flow rate of 60 m³ h⁻¹ for 4 hours between 06:00 and 10:00, 11:30 and 15:30 and 17:00 and 21:00, permitting the pumping of 240 m³ of air into traps. Sampling flow rate was controlled to be constant during the sampling period and for each time intervals.

Prior to sampling, the filter and resin were cleaned by Soxhlet extraction for 24 hours with a mixture of n-hexane/methylene chloride (50:50, v/v). After cleaning, the traps were hermetically stored in new plastic bags and glass bottles in the freezer (-18 °C). After sampling, the samples were stored in the freezer and were separately (gas and particle) extracted as fast as possible (no later than one week afterwards) for 12 hours in a Soxhlet apparatus with the same solvent mixtures used for cleaning. The liquid extract was concentrated by using a rotary evaporator and evaporated to dryness under a gentle flux of nitrogen. Then 1 mL of acetonitrile and 2-chlorophenol-3,4,5,6-d4 (internal standard) at 1 mg L⁻¹ were added. Extracts were derivatized according to the Heberer and Stan (1997) method. Recoveries of the 20 PNP studied after extraction, evaporation to dryness, refilling in acetonitrile, and derivatization varied between 38% (phenol) and 107% (2-methyl-3-nitrophenol) with about 8% of uncertainty as previously validated by Morville et al. (2004). These results were taken into account in the calculation of concentrations.

The sites have been chosen in order to be representative of urban, suburban and rural conditions. The urban site was situated in downtown Strasbourg (250 000 inhabitants) far from direct emissions (about 2 km of an industrial area and about 1 km of several heavy roads) and the DA-80 sampler was located on the roof of the Botanical Institute of the University of Strasbourg (30 m above ground). The suburban site was situated in Schiltigheim (29 000 inhabitants), a direct neighboring city, northwest of Strasbourg and the DA-80 was installed on the roof (10 m above ground) of the technological school of the University of Strasbourg. The rural site was situated in Erstein (small sized town of 8 000 inhabitants), situated 20 km in the south-east of Strasbourg. The DA-80 sampler was installed at ground level in a closed area.

In order to compare concentrations between sites, two kinds of sampling campaigns were performed: between urban and suburban sites and between urban and rural sites. Samplings at the three sites were performed: between 06:00 and 10:00, between 17:00 and 21:00 (two time intervals with high vehicle circulation) and between 11:30 and 15:30 (time interval with less vehicle circulation). Five campaigns were undertaken along three different seasons: spring 2002 (April and May), fall 2002 (November), fall 2003 (October/November) and winter 2004 (January/February).

2.3. Apparatus and analysis

All measurements were performed using a Thermo Quest GC 2000 coupled to a Thermo Finnigan Trace MS detector. Chromatographic conditions and detection limits of the method were presented elsewhere in detail (Morville et al., 2004). Detection limits for atmospheric samples varied between 20 pg m⁻³ to 40 pg m⁻³ for 240 m³ of air sampled. The samples were analyzed by electron impact ionization (EI) at 70 eV in selected ion monitoring mode by selecting two or three characteristic ions.

3. Results and Discussion

3.1. Mean concentrations

PNP were analyzed between 2002 and 2004 during five sampling campaigns at the three sites. Mean total concentrations (gas and particle-phases) obtained for the three sites are presented in Table 1. As a first observation, it could be seen that bromoxynil, 2,5-DNP, ioxynil and 3,4-DNP were never detected in samples independent from the sites. Mean total concentrations varied between 21.1 ng m⁻³ for the rural site (Erstein), 23.5 ng m⁻³ for the suburban site (Schiltigheim) and 25.2 ng m⁻³ for the urban site (Strasbourg). It could be assumed that a few spatial variations of the compounds between the three sites occurred. In urban and suburban sites, the most abundant compounds were phenol (>6.5 ng m⁻³), 2,4-DNP (>4.7 ng m⁻³), p-cresol (>2.6 ng m⁻³), m-cresol (>2.2 ng m⁻³), 4-Me-2-NP (>1.6 ng m⁻³) and o-cresol (>1.2 ng m⁻³). In rural site, the most important compounds were also phenol (>9.6 ng m⁻³), but followed by 4-Me-2-NP (>2.7 ng m⁻³) and the three cresols.

Atmospheric levels of PNP measured at the three sites were generally much lower than those recorded by other studies. In urban areas, the concentration of phenol was 320 ng m⁻³ in Portland (Leuenberger et al., 1985), 40 ng m⁻³ in Dübendorf (Leuenberger et al., 1988) and 400 ng m⁻³ in Milan (Belloli et al., 1999). Cecinato et al. (2005) have observed a concentration of 9.8 ng m⁻³ for 4-Me-2-NP and 6.5 ng m⁻³ for 5-Me-2-NP in Rome. Even if these two last results were higher than those obtained in the present study, they remained nevertheless in the same order of magnitude. In a rural area, Lüttke et al. (1997) have observed in Great Dun Fell (United Kingdom), some values between 13.8 and 47.4 ng m⁻³ for phenol in the ambient air. For PCP, Cessna et al. (1997) recorded average concentrations varying between 0.23 and 1.53 ng m⁻³ for various sites in Canada, and these were comparable to the levels observed in the present study. Lastly, for dinitrophenols, Lüttke et al. (1997) observed values between 0.1 and 0.5 ng m⁻³ for 2,4-DNP, and from 0.2 to 1.4 ng m⁻³ for DNOC.

3.2. Seasonal variability

Mean total concentrations of the sum of the different PNP at the three sites were summarized for all campaigns on Table 2. A moderate variation of these average concentrations on the same site according to the seasons could be observed. For example, the total average concentrations of the rural site were 19.5 ng m⁻³ during the spring (warm period) and 22.7 ng m⁻³ during the winter (cold period). The average temperatures at the Strasbourg site were 17.0 °C during the spring, 7.7 °C during the fall and 4.9 °C during the winter (the average temperature were similar for the three sites, ± 0.7 °C, regardless of the season). So, we had considered two periods according to this temperature difference: the sampling realized taking the warm period (spring) and the sampling realized taking the cold period (fall and winter).

Table 1. Average, minimum and maximum of the total concentrations (ng m^{-3}) (gas and particle-phases) for the three sites studied

Compound	Urban site (n = 36)			Suburban site (n = 22)			Rural site (n = 14)		
	Avg	Min	Max	Avg	Min	Max	Avg	Min	Max
phenol	10.4	0.4	58.7	6.5	1.4	24.0	9.6	0.3	28.6
m-cresol	2.2	< LQ	17.7	2.8	0.03	14.5	2.1	n.d.	14.8
p-cresol	2.6	0.08	16.3	3.0	0.03	13.9	2.4	0.05	7.4
o-cresol	1.2	n.d.	12.8	1.4	n.d.	10.1	0.9	n.d.	6.8
3-Me-2-NP	0.5	n.d.	2.0	0.5	n.d.	2.1	0.6	n.d.	2.1
3-NP	0.1	n.d.	2.7	0.2	n.d.	2.2	0.01	n.d.	0.05
4-Me-2-NP	1.6	n.d.	10.8	2.1	n.d.	14.0	2.7	0.2	10.8
5-Me-2-NP	0.4	n.d.	1.6	0.4	n.d.	2.1	0.6	n.d.	2.1
2-Me-3-NP	0.1	n.d.	0.6	0.1	n.d.	0.3	0.04	n.d.	0.5
3-Me-4-NP	0.4	< LQ	5.0	0.3	0.06	0.8	0.2	n.d.	0.5
PCP	0.2	< LQ	1.3	0.2	0.05	1.7	0.1	0.02	0.2
2,6-DNP	0.2	n.d.	1.1	0.4	n.d.	1.7	0.3	n.d.	2.7
bromoxynil		n.d.	n.d.		n.d.	n.d.		n.d.	n.d.
2,5-DNP		n.d.	n.d.		n.d.	n.d.		n.d.	n.d.
2,6-DNpC	0.1	n.d.	0.3	0.2	n.d.	0.3	0.03	n.d.	0.1
2,4-DNP	4.7	0.1	42.1	5.0	0.2	53.5	1.1	0.05	4.8
ioxynil		n.d.	n.d.		n.d.	n.d.		n.d.	n.d.
DNOC	0.1	n.d.	0.3		n.d.	n.d.	0.1	n.d.	0.3
3,4-DNP		n.d.	n.d.		n.d.	n.d.		n.d.	n.d.
dinoseb	0.4	n.d.	2.1		n.d.	0.8	0.3	n.d.	1.1
Σ compounds	25.2			23.5			21.1		

n = number of samples

Avg : average ; Min : minimum ; Max : maximum

LQ : limit of quantification; n.d : not detected

The seasonal variations were not similar between the various compounds. Indeed, a significant increase of phenol concentrations during the warm period was observed, whereas for the majority of other compounds, this increase was recorded during the cold periods. Thus, results obtained for phenol will be discussed separately. For the urban site, in order to visualize the seasonal variations in more detail, the evolution of the total compound concentrations, except phenol, was plotted as a function of the ambient air temperature (Figure 1). It could be clearly seen that an increase of the compound concentrations was observed when the temperature decrease, since concentrations were lower during the two first campaigns (April and May 2002) performed in spring than during the three other campaigns (November 2002 and 2003, February 2004) performed in fall and winter.

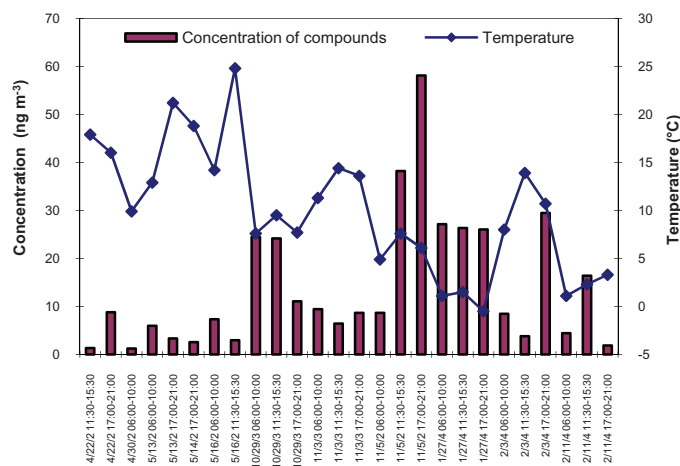
Table 2. Mean total compound concentrations (ng m^{-3}) during the five campaigns

Campaigns	Urban site	Suburban site	Rural site
April 2002 (1)	18.2	16.1	
May 2002 (2)	31.7		19.5
November 2002 (3)	28.4	29.6	
October/November 2003 (4)	26.1	24.8	
January/February 2004 (5)	21.6		22.7

The ratios of the total compound concentrations (without phenol) between cold period and warm period had some values largely higher than 1, which varied between 3.6 and 5.2 for the urban site, between 4.7 and 6.1 for the suburban site and had a value of 4.6 for the rural site. These higher ratios could be explained by:

- an increase of emissions from vehicles since (Bjorseth and Ramdahl, 1985) vehicles exhausts could be increased by a factor varied between 4 to 10 during low air temperature,

- an increase of nitrophenol emissions by domestic heating during the cold period (Hawthorne et al., 1992),
- a decrease of the degradation rate of these compounds during cold periods,
- an occurrence of thermal inversion in cold seasons, inducing a more stability of low air masses and consequently a limitation of the dispersion of pollutants.

**Figure 1.** Variation of the total compound concentrations (except phenol) as a function of temperature for the urban site.

Nevertheless, evolution of the concentration with temperature was not identical for each compound. Indeed, for example, the cresols had high seasonal variations with ratio of about 10. These variations could be explained by the contribution of additional sources in cold period and/or by the strong reactivity of these compounds with the global radiation, more frequent in warm periods (Grosjean, 1984; Grosjean, 1991). On the other

hand, the ratios for the phenol were always lower than 1 and varied between 0.2 and 0.4 for the urban site, between 0.3 and 0.4 for the suburban site, and the rural site had a value of 0.3. These ratios lower than 1 was in contradiction with the concept of photochemical degradation of this compound and should be better explained by hypothesizing the presence of a direct source like organic matter combustion, unusual for the warm period or agricultural activities. It will be useful to undertake some experiments in order evaluate the source of phenol during the warm period by collecting air samples close to possible sources (i.e., combustion and agricultural activities).

Even if the distribution of the various compounds changed appreciably between the warm and the cold periods, the proportion of volatile compounds like phenol (the most abundant compound at the three sites independent of the seasons), the three cresols, 4-Me-2-NP and 3-Me-2-NP, dominated this distribution, independent from of the periods. It could be seen that the abundance of some other compounds such as 2,4-DNP, dinoseb, DNOC and PCP did not vary between the two periods.

In order to compare concentrations between the three sites regarding the seasons (warm or cold), the ratios of the total PNP concentration between the urban and the rural sites ($C_{\text{urban}}/C_{\text{rural}}$) or between the urban and the suburban sites ($C_{\text{urban}}/C_{\text{suburban}}$) were calculated. In warm period (Campaigns 1 and 2), the $C_{\text{urban}}/C_{\text{rural}}$ ratio was 1.6 especially due to the high concentration of phenol in urban site (ratio between concentrations of phenol in urban site and in rural site had a value of 1.8). When the phenol concentration was excluded from the calculation, the ratio $C_{\text{urban}}/C_{\text{rural}}$ presented a value of 1.2, practically similar to the $C_{\text{urban}}/C_{\text{suburban}}$ ratio (value of 1.1), showing in fact, a very slight increase of the total concentration for 19 other compounds in urban site. In cold period, the ratios $C_{\text{urban}}/C_{\text{rural}}$ and $C_{\text{urban}}/C_{\text{suburban}}$ (including phenol) had the same value of 1, indicating similar levels of contamination between all sites during this period. In terms of total concentrations, there was a negligible difference between the three sites, independently of the seasons.

3.3. Diurnal variations of concentration

As air sampling has been performed during 4 hour time intervals during the same day, the comparison of the variations of concentrations between the morning, the afternoon and the evening was possible. This comparison could also be performed between cold and warm periods.

For this investigation, 6 compounds (phenol, p-cresol, 4-methyl-2-nitrophenol, pentachlorophenol, 2,4-dinitrophenol and dinoseb) among the 20 studied have been selected as the more abundant compounds of their categories (i.e. 2,4-DNP for dinitrophenols and dinoseb for herbicides).

Warm period. The diurnal variation of the total concentration of compounds considered during Campaigns 1 and 2, was presented in Figures 2a and 2b, respectively for one specific day. This specific day has been chosen since the meteorological conditions between the two sites and between the three time intervals were comparable.

The nitrophenols as 4-Me-2-NP were largely emitted by the vehicles (Trempe et al., 1993). The concentration profile observed for 4-Me-2-NP was in accordance with the intensity of the vehicle circulation, with highest concentrations during the morning and the evening, the periods corresponding to an important flux of vehicles at the three sites. In fact, the urban and suburban sites were both heavily impacted by traffic due to their proximities to locations with busy city streets, and approximately 3 km of the intersections of several freeways. The rural site was less impacted by traffic than the two other sites but the presence of a very close

freeway to the sampling point (about 2 km) induced a high concentrations of 4-Me-2NP the morning.

The same behavior was observed for phenol and p-cresol. The decrease of the two compounds during 11:30-15:30 could be the consequence of a decrease in traffic or a more important degradation of these two compounds. Indeed, the 11:30-15:30 period was known to be a time interval with high photochemical activity (the value of the mean global irradiance could reach 269 joule cm^{-2} in the mid-day in comparison to a value of 73 joule cm^{-2} in the morning and a value of 98 joule cm^{-2} in the late afternoon). For 2,4-DNP, the concentrations have increased during the day with a minimum on the 06:00-10:00 time interval and a maximum in the evening. Although dinitrophenols such as 2,4-DNP have several origins, the observed concentration profile would be explained by the fact that the formation of dinitrophenols through atmospheric formation processes were their source (Rindone et al., 1999).

It could be noted that the concentrations of phenol, p-cresol, 4-Me-2-NP and 2,4-DNP were in general higher in urban site for the time intervals 11:30-15:30 and 17:00-21:00 respectively, while for the time interval 06:00-10:00, the concentrations of these compounds were higher in rural site (Figure 2b). The observation of higher concentrations in rural site during the morning time interval was surprising, in spite of the presence of a freeway close to this site with busys traffic during this time interval. This could be explained by the presence of emission sources very close to the rural sampling point that were not necessarily traffic related. On the other hand, the strongest concentration in urban site between 11:30 and 15:30 could be explained by a more intense traffic in downtown Strasbourg in contrary to the rural site during the same period.

At the three sites, concentrations of PCP and dinoseb were less important than those measured for phenol or 4-Me-2-NP. The concentrations of these two compounds were similar between the three sites and only few variations between the different time intervals could be noted. Consequently, the presence of PCP in the ambient air could be attributed only by its use as a fungicide for the treatment of wood, and not to its emission by fossil fuel combustion processes since in this case, an increase of PCP concentration at the end of day and/or the morning would be observed. No interpretation could be done for dinoseb pesticides.

Cold period. The diurnal variations of the total concentration of the six compounds selected were illustrated in Figure 3a for the Campaign 4 and in Figure 3b for the Campaign 5. These have been plotted according to the criteria used for the warm period.

For Campaigns 4 and 5, the profiles of 4-Me-2-NP were comparable to the profile described for warm periods, at the three sites. High concentrations corresponding to high automobile traffic, in particular in the morning for the Campaign 5, were observed. Concentrations measured during Campaigns 4 and 5 were higher than those observed in warm period and this observation could probably be attributed to a lower degradation processes and an increase of direct emissions, especially from vehicles. No more data or references were available to confirm this hypothesis. PCP and dinoseb have presented no diurnal variation at the three sites. For the 2,4-DNP only few variations between the different time intervals could be noted. The diurnal concentration profile determined for phenol and p-cresol have seemed to be the almost comparable to the ones observed during the warm period. In fact, in urban site, the maximum concentration for phenol was measured between 11:30 and 15:30. Moreover, the concentrations of compounds in urban and suburban sites were very similar during the three time intervals, except for phenol, with a maximum in urban site during the 11:30-15:30 time interval. It was very difficult

to explain this phenomenon but the multiple sources for phenol must be taken into account. In fact, the presence of an industrial area (about 2 km in the East) to the urban sampling point in contrary to the suburban sampling point could be the reason for the higher concentrations of phenol during the 11:30-15:30 time interval. The mean wind direction (East) during the campaign was in accordance with a possible contribution of source from the industrial area.

On the other hand, the compound concentrations between the urban site and the rural site were less similar. The concentrations of 4-Me-2-NP were always higher in rural site. The p-cresol was more important in urban site during the time interval 11:30-15:30 and the 2,4-DNP was more important in rural site between 11:30 and 21:00. Domestic heating could influence the diurnal variations of these compounds especially for the rural site, using more frequently the combustion of wood than the two other sites.

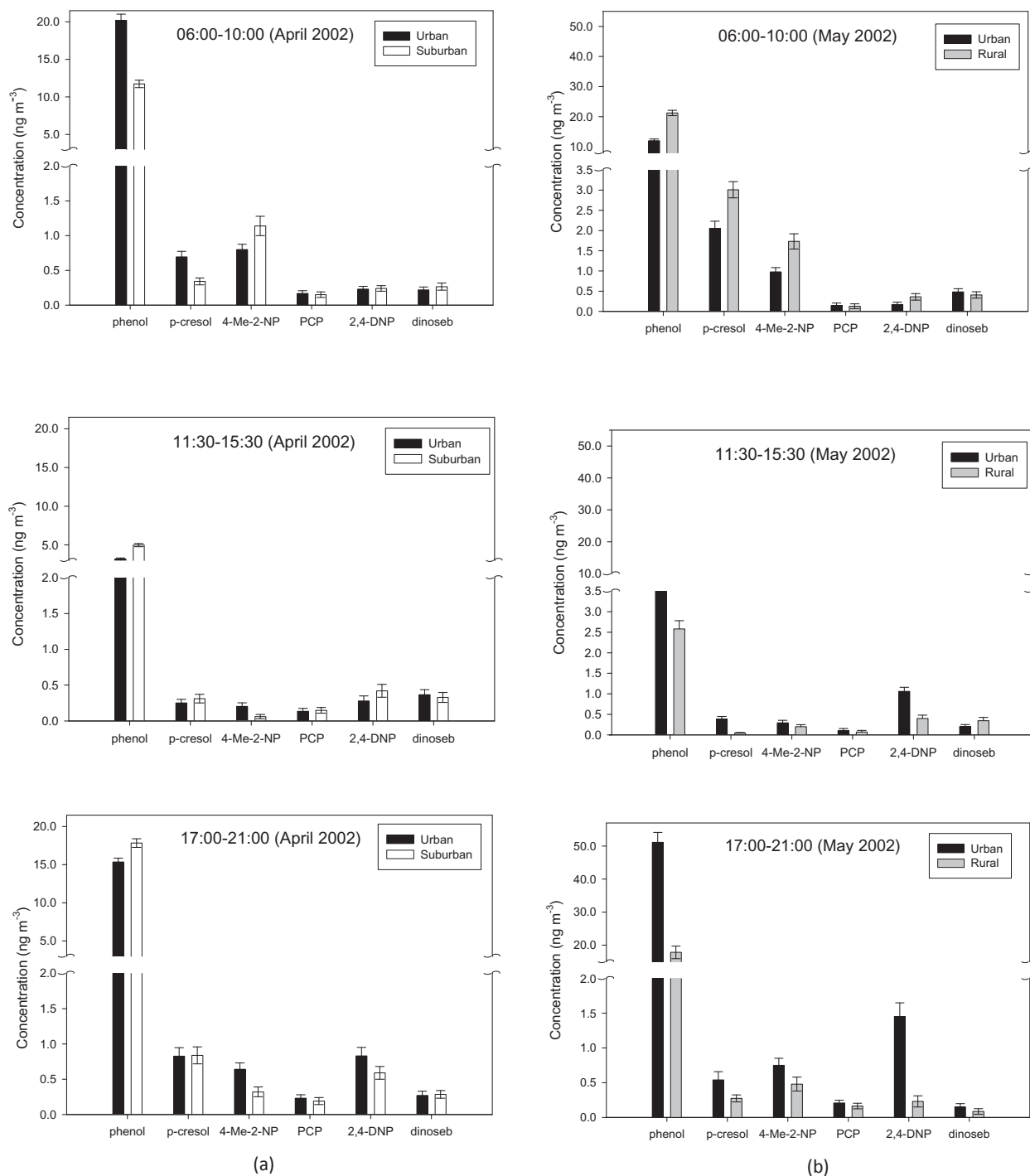


Figure 2. Diurnal variations of the total concentrations for the six compounds selected during (a) the Campaign 1 (warm period) and (b) the Campaign 2 (warm period). Errors bars correspond to the analytical uncertainty.

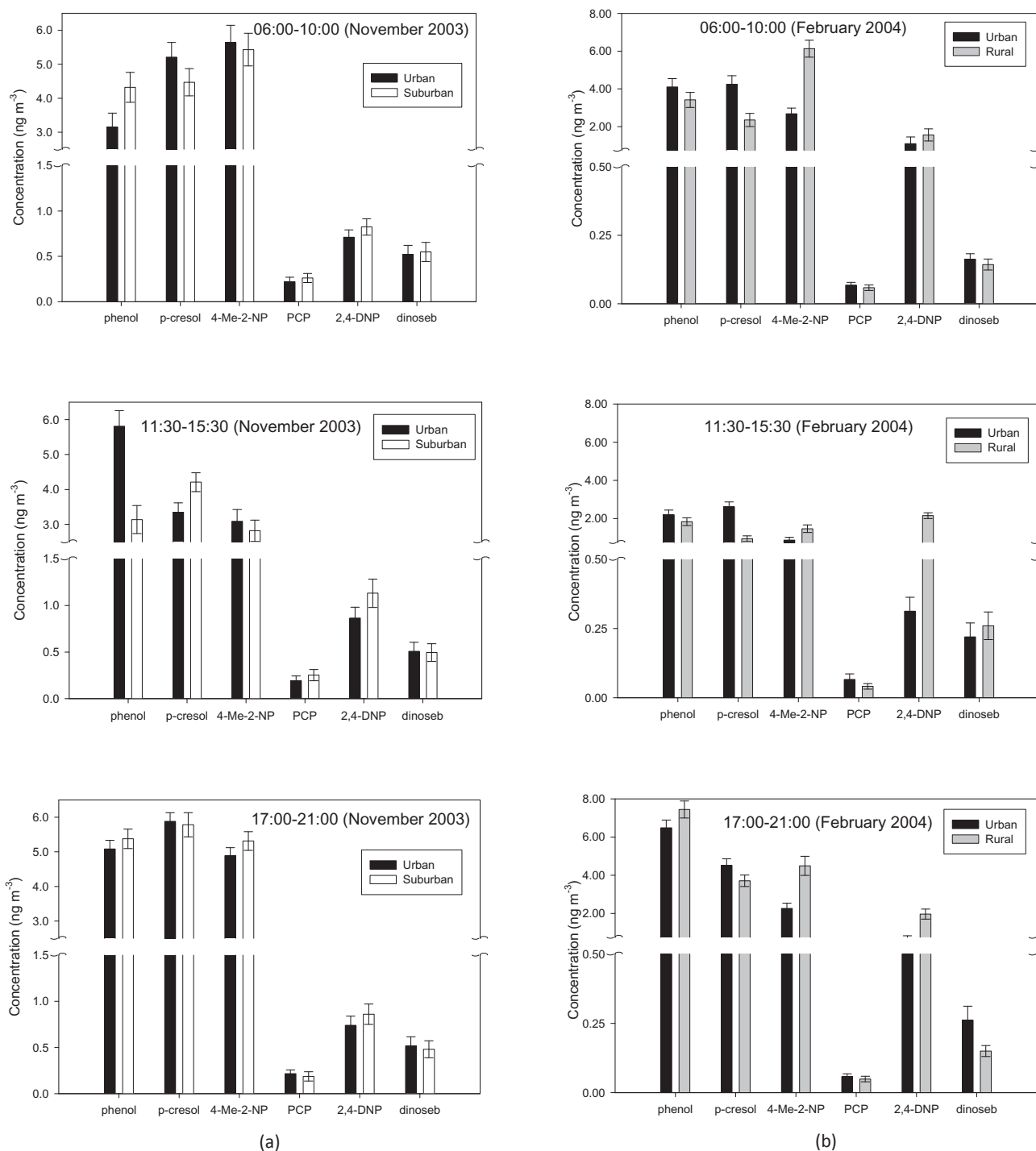


Figure 3. Diurnal variations of the total concentration for the six compounds selected during (a) the Campaign 4 (cold period) and (b) the campaign 5 (cold period). Errors bars correspond to the analytical uncertainty.

4. Conclusion

The analysis of atmospheric samples in both particulate and gas-phases have shown the presence of PNP at the three different studied sites. From 20 compounds that were monitored only three were never detected. At the three sites, independent of campaigns, the phenol was the most abundant compound. Atmospheric levels of PNP measured at the three sites were generally much lower than those recorded by other studies (until about 30% for phenol).

The seasonal variabilities of these compounds in urban, suburban and rural atmosphere have shown that the concentration increased when the temperature decreased, except for phenol which had a maximum concentration during the warm period. The predominance of phenol at all sites in the warm season, and its significant decrease in the cold period have seemed to confirm the presence of a phenol source in warm period, which became less important or disappeared in winter. Moreover, in terms of concentrations, there was negligible difference between the three sites, independent of the seasons considered.

The diurnal variation, in warm period, observed for 4-Me-2-NP was in accordance with the vehicle circulation, with highest concentrations during the morning and the evening hours. The decrease of phenol and p-cresol during 11:30-15:30 could be the consequence of a decrease in traffic or a more important degradation of these two compounds. For 2,4-DNP, the increase in concentrations during the day was in accordance with the formation of dinitrophenols in the atmosphere. The presence of PCP in the ambient air could be attributed to its use as fungicide for the treatment of wood. In cold period, the diurnal variation for 4-Me-2-NP was also in accordance with the vehicle circulation. PCP, dinoseb and 2,4-DNP presented no diurnal variation at the three sites. More similar diurnal concentration profiles have been observed between the urban and suburban sites than between the urban and rural sites, especially for the cold period. Domestic heating could influence the diurnal variations in rural site, being able to explain the bigger difference of concentration profile with the urban site, in cold period.

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