



Phenol and nitrophenols in the air and dew waters of Santiago de Chile

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ABSTRACT

Phenol, nitrophenols and dinitrophenols were measured in air and dews in downtown Santiago de Chile. In both systems, phenol, 2-nitrophenol (2-NP), and 4-nitrophenol (4-NP) were the compounds found in higher concentrations and with major frequency. Temporal profiles in air were compatible with a significant direct incorporation from mobile sources. The data can be explained in terms of a faster removal of 2-NP than 4-NP, with the former predominating in fresh air masses and 4-NP in more aged samples. All these compounds, as well as dinitrophenols, were found in dew waters. Simultaneous measurements in air and dew indicate that phenol present in dew exceeds that expected in equilibrated samples, while the opposite occurs with 4-NP. This last result is associated to mass transfer limitations for the highly water soluble nitroderivative.

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1. Introduction

Nitrophenols constitute a family of important pollutants due to their high phytotoxicity coupled to relatively long thermal and photochemical lifetimes (Grosjean, 1991). Due to their toxicological potential, several phenols and nitrophenols have been considered as “priority pollutants” by the US Environmental Protection Agency (EPA, 1981).

Nitrophenols concentrations in the atmosphere have been reviewed by Harrison et al. (2005a). They have been detected and quantified in air (Cecinato et al., 2005; Morville et al., 2006; Bishop and Mitra, 2007; Delhomme et al., 2010), clouds (Luettke et al., 1999), rain (Leuenberger et al., 1988; Schuessler and Nitschke, 2001; Schummer et al., 2009), water (Geissler and Scholer, 1994), fog (Richartz et al., 1990), snow (Alber et al., 1989) and plant leaves (Natangelo et al., 1999). In air, they are partitioned between the gas phase and the atmospheric particles (Schwarzenbach et al., 1988; Cecinato et al., 2005). This distribution between particles or hydrometeors and gas phase is a very complex phenomenon that can hardly be depicted by simple gas/liquid equilibrium (Luettke et al., 1999).

2-Nitrophenol (2NP) and 4-nitrophenol (4NP) are two of the most ubiquitous and abundant nitrophenols (Harrison et al., 2005a). They are both primary and secondary pollutants. They are introduced to the atmosphere in combustion processes (Nojima et al., 1983; Tremp et al., 1993), and direct traffic emission is likely to be an important source of these compounds in urban areas (Luettke et al., 1999; Bolzacchini et al., 2004). Also, they are formed

in the nitration (thermal and photochemical) of phenols both in gas phase (Bolzacchini et al., 2001; Olariu et al., 2002) and in solution (Vione et al., 2002a, 2002b; Harrison et al., 2005b; Heal et al., 2007). In aqueous solutions they can be formed (and decomposed) in thermal (Patnaik and Khoury, 2004; Heal et al., 2007) and photochemical processes (Vione et al., 2002a, 2002b; Patnaik and Khoury, 2004).

Nitrophenols are cause of concern mostly because of their phytotoxicity (Shea et al., 1983) and their ability to penetrate into plant tissues (Schoenherr and Riederer, 1988; Sabljic et al., 1990; Natangelo et al., 1999), and they can substantially contribute to forest decline in polluted areas (Blank, 1985). Dew is formed most of autumn and winter days and could contribute significantly to the deposit and incorporation of damaging compounds in leaves (Shafer and Schoenherr, 1985), since they can be absorbed directly by diffusion through the cuticles of the leaves (Sabljic et al., 1990). It is then surprising that, at the best of our knowledge, there are not estimations of nitrophenols concentrations in dew waters and the amounts of these toxic compounds deposited in leaves. Even more, data regarding incorporation of phenols to dew waters are very scarce. Polkowska et al. (2008) reported total phenols concentrations in different regions of Poland. Phenols were detected in 95% of dew samples, with event concentrations ranging from 0.005 to 2.43 meq L⁻¹, and mean concentrations ranging from 0.08 (rural inland) to 0.89 meq L⁻¹ (urban coastal). Klimaszewska et al. (2009) measured the concentrations of total phenols in 162 dew waters collected in Poland, reporting values between 0.01 and 103 meq L⁻¹. On the other hand, Muselli et al. (2006) reported less than 0.01 meq L⁻¹ of total phenols in dew waters collected in Ajaccio, Corsica Island. In these works, no speciation of the phenols was attempted.

Simultaneous measurements in the atmosphere and in dew can provide a direct estimation of the nitrophenols distribution (Rubio

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et al., 2006). In spite that this distribution can be influenced by the presence of particles, it should be controlled by the Henry's coefficients and/or the solubility of the compounds in water solutions. To this regard it must be noted that 2-NP is much more hydrophobic than 4-NP (Mueller and Heal, 2001), a difference that must displace the former compound towards the gas phase, with the less volatile 4-NP being preferentially present in the aqueous phase and particles (Cecinato et al., 2005; Harrison et al., 2005a). This distribution determines nitrophenols reactions and atmospheric lifetimes (Leyssens et al., 2005; Vione et al., 2009).

In the present work we report the concentration of phenol and the main nitrophenols present in Santiago de Chile atmosphere and in dew waters collected downtown during autumn and winter periods.

2. Materials and methods

Air and dew samples were collected during 2010 (June to September) and 2011 (June and July) at the University of Santiago de Chile campus, located at the west side of downtown (Central Station). Samplers were located on the roof of the chemistry and Biology building at ca. 5 m height and far from any known pollution source. Air samples were collected using a SiOH cartridge (rinsed and dried) with a flux of 3.2 L min⁻¹ provided by a Dryfast 210 C-02 Welch vacuum Tech pump (Belloli et al., 1999; Harrison et al., 2005a). After 4 h, it was eluted with 1 mL of acetic acid.

Dew samples were manually collected on a Teflon film (1 square meter) from 7 pm to 8 am. Once collected, the pH and conductivity of the samples were determined. Dew solution were filtered through a 0.45 µm pore size membrane and pre-concentrated using cartridges for solid phase extraction (Licrolut EN, 200 mg, Merck) (Harrison et al., 2005a).

Phenols were quantified using a chromatograph HPLC, 600 waters with detector PDA and Column C-18 Symmetry RPC-18, 4.6 × 250 mm. The mobile phase used in isocratic mode was 5 mM Buffer phosphate, pH 4.5 and acetonitrile (82/12). Phenol, 2-NP, 3-NP, 4-NP, 2,3-DNP, and 2,5-DNP were identified by their retention times. Retention times under our experimental conditions range from 4.46 min (2,6-DNP and 2,4-DNP) to 12.54 min (2-NP). Detection limits were: Phenol 1.6 ng/mL; 4-NP 2.7 ng/mL, 2-NP 1.9 ng/mL; 3-NP 1.7 ng/mL; 2,3-DNP 8 ng/mL; 2,5-DNP 1 ng/mL and 2,6-DNP 1.1 ng/mL. The identity of the main phenols was confirmed by HPLC MS (Agilent 1200 Series, followed by ionization electrospray (ESI) in positive way and detection by means of mass spectrometry (6410 Agilent Triple quadrupole).

Recovery efficiency from the cartridges after SPE procedure was estimated employing standard solutions ranging from 75% to 105%. These values are similar to the previously reported employing similar procedures (Belloli et al., 1999).

3. Results and discussion

The methodology employed in the present work is similar to that applied previously for air samples (Belloli et al., 1999; Harrison et al., 2005a). Evaluations in dews were performed by procedures similar to the employed in water samples. These procedures were validated by recovering assays on standard samples. This recovery amounts to more than 75% of the original phenols.

3.1. Nitrophenols in the atmosphere

Phenol, 2-nitrophenol, 3-nitrophenol, 4-nitrophenol, 2,3-dinitrophenol and 2,5-dinitrophenol were detected in air samples. 2-NP and 4-NP were the most abundant nitrophenols and were present in all analyzed samples. Averages and minimum and

maximum values are given in Table 1, where have been included data obtained in other urban atmospheres.

From this table we can conclude that:

- (i) 4-NP is the most abundant phenol present in the whole air of Santiago, where it can reach concentrations higher than 1 µg m⁻³. Similar results have been reported for an urban site in Switzerland (Leuenberger et al., 1988),
- (ii) 4-NP/2-NP ratios are higher than one, reaching a value of ca. 12 in Santiago. This high ratio is rather surprising since vehicle emissions are richer in 2-NP (Nojima et al., 1983; Tremp et al., 1993; Harrison et al., 2005a). This prevalence of 4-NP in gas samples has been observed in other polluted atmospheres (Luettke et al., 1999; Gramatica et al., 2001) and could be explained in terms of a faster removal rate of the 2-substituted compound (Harrison et al., 2005a). This is supported by a comparison of the daily profiles shown in Fig. 1.

Fig. 1 shows that, for the three compounds (phenol, 2-NP and 4-NP) there is an early morning noticeable increase in concentrations that can be associated to the emissions from vehicles at the rush hour (data for the 8.00–12.00 period). This is the behavior expected for pollutants for which traffic emission is an important source, such as nitrophenols (Luettke et al., 1999; Bolzacchini et al., 2004; Harrison et al., 2005a).

The data obtained for the time period 8.00–12.00 h mostly reflect concentrations in fresh air masses polluted by emissions of vehicles at the rush time. In this air samples 2-NP concentrations are higher than those evaluated for 4-NP, in agreement with the relative emission factors.

After the morning, there is a fast concentration decrease. This decrease is larger for phenol, a result that could be related to its much faster removal by hydroxyl radicals, both in gas and liquid phases. Regarding 2-NP and 4-NP the data of Fig. 1 show that this decay is considerably larger for 2-NP. This indicates a faster removal rate of 2-NP and/or other (secondary) sources of 4-NP. The contribution of these processes can then explain the average higher concentrations of 4-NP reported in Table 1.

A puzzling feature of the data shown in Fig. 1A is the decay in atmospheric nitrophenols levels in the 4.00–8.00 h period. A similar decay is observed for phenol in Fig. 1B. It is interesting to note that this period corresponds to that of dew formation (Rubio et al., 2003). A plausible explanation of the observed decay could be removal of the phenols by dew, either by their solubilization and/or reaction in the liquid phase (Harrison et al., 2005a). Re-evaporation of the phenols after sunrise could contribute to the burst observed in gas phase concentrations after 8.00 h. However, the fact that in this period 2-NP gas phase concentrations are larger than those measured by 4-NP would imply that other factors, such

Table 1

Atmospheric concentrations (ng m⁻³) of phenol, 2-NP, 4-NP, and dinitrophenols in urban atmospheres.

Sampling place	Phenol	2-NP	4-NP	2,5-DNP	2,3-DNP	2,4-DNP
Santiago: average	114	37	462	55	169	
Minimum	42	8.3	40	13	135	
Maximum	220	106	1400	91	192	
England	14–71	0.8–6.4	1.2–35			0.1–8.5
Oregon	320	24				
Switzerland	40	350				
Milan	400		300			
Strasbourg	10.4					
Rome			3.9			

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