Nitrite in rain and dew in Santiago city, Chile. Its possible impact on the early morning start of the photochemical smog

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Abstract

Cations (pH, potassium, sodium, calcium, magnesium, and ammonium) and anions (sulfate, nitrate, nitrite, and chloride) concentrations were measured in Santiago city rain and dew waters collected during the 1995 to 1999. Concentrations measured in dews are considerably higher than those measured in rains. The high ionic concentration present in dew waters could contribute to their corrosion potential. Natural dust makes an important contribution to the ions present in dews, but the presence of rather high sulfate concentrations (up to 900 μeq/l) indicate a significant contribution of anthropogenic sources.

A peculiar characteristic of dew waters is the relatively high nitrite concentrations (up to 180 μeq/l). This nitrite can be resuspended into the boundary layer after dew water evaporation, possibly due to the relatively high volatily of ammonium nitrite. This upward flux could constitute an important source of hydroxyl radicals in the early morning, contributing so to the initial steps of the observed photochemical smog. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

Nitrous acid is a secondary pollutant that presents a notorious daily cycle, with higher concentrations during night, where it can reach levels as high as tens of ppb (Febo et al., 1996). The steady state concentration during daytime is very low due to its high rate of photolysis. The photolysis implies molecule cleavage, according to

$$HONO + hv \rightarrow HO* + NO. \qquad (1)$$

This process, that takes place with a high quantum yield, can be a predominant source of hydroxyl radicals (Demerjian et al., 1974), particularly early in the morning when the concentrations of other hydroxyl radicals sources, such as formaldehyde and ozone, are low (Sjödin and Ferm, 1985; Harris et al., 1982; Kitto and Harrison, 1992; Winer, 1985). Harris et al. (1982)

have carried out estimations of HONO impact on Los Angeles ozone isoplets, and Jenkins et al. (1988) have estimated that the presence of 1 ppb at night could increase the photochemical ozone production by 16% the next day. Given the importance of hydroxyl radicals in the chemistry of the urban atmosphere, both in the generation of the oxidants associated to the photochemical smog and in the transformation of PAH in more toxic substituted compounds, it is important to evaluate the levels, sources and sinks of nitrous acid in the polluted urban atmosphere.

During daytime, the main sink of HONO can be represented by reaction (1). During nighttime, it can be captured by the ground, particularly in the presence of dew, given its high solubility in water, in particular at relatively high pHs as those generally found in dew waters (Ryaboshapko et al., 1998; Ortiz et al., 2000). The sources of nitrous acid are not so clear. It can be significatively emitted directly in the combustion, both in vehicles (Kirchestetter et al., 1996) and in biomass burning (Rondon and Sanhueza, 1989; Pitts et al., 1985).

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It can also be formed as a secondary pollutant in the reactions of NO with hydroxyl radicals (Sjödin, 1988). Also, it has been reported that the decomposition of pernitric acid and PAN (Lammel et al., 1990; Grosjean et al., 1984) could contribute to the HONO budget. Also, it can be produced in heterogeneous reactions in aerosols. In particular, a reaction such as

$$2NO_2 + H_2O \rightarrow HONO + HONO_2, \qquad (2)$$

could take place at interfaces and contribute to nitrous acid formation (Harrison and Kitto, 1994; Lammer and Pernel, 1988). The nitrous acid in the aerosols and hydrometeors is rapidly equilibrated with the gaseous compound. This distribution is strongly influenced by the pH. Notholt et al. (1992), reported that HONO(g) is rapidly produced in brumous episodes, presenting evidence that wet aerosols could participate in the oxidation of NO_x to HONO. Lammel and Pernel (1988), have pointed out that atmospheric aerosols could be an important source of gaseous HONO in the atmosphere.

There are few studies regarding HONO levels in polluted atmospheres (Lammel and Cape, 1996). Reported gaseous HONO levels in western Europe and USA range from 0.02 to 8 ppb, but levels as high as 14 ppb have been reported in Los Angeles city (Kitto and Harrison, 1992). Reports regarding HONO and/or nitrite levels in rains, fog and dews are even more scarce. Nitrite levels in rain between 0.0022 and 0.6 μM have been reported (Kieber et al., 1999) On the other hand, there are no reports of nitrites in fogs or dews. In the present communication, we present data obtained in events of rain and dew that have taken place at Santiago city, Chile city during the years 1995–1999. Santiago city constitutes an example of air pollution where important levels of primary contaminants and particulate material have been reported (Artaxo et al., 1999) and that, at the same time, presents high levels of oxidants associated to hydroxyl mediated photochemical oxidation (Gamboa and Rubio, 1997; Rappenglück et al., 2000). During autumn, winter and part of spring, there is extensive dew formation. This dew could then be a sink and/or source of HONO. In the present communication, we have evaluated nitrite levels both in rain and dew waters. The results obtained would indicate that re-evaporation from dew waters could contribute significantly to the free hydroxyl radical generation in early hours of the morning. This should have to be considered in the modeling of the urban photochemical smog.

2. Experimental

Waters from rains and dews were collected at the University of Santiago, located near the center of Santiago city. Water collection was carried out during the years 1995–1999. Rains were collected in an automatic Rain Only equipment, equipped with a 12 cm diameter funnel and a 2 l plastic bottle. Rain for the whole event was collected. Most rainy episodes took place in late autumn, winter and early spring, that correspond to the rainy season. Dew waters were manually collected daily by employing a Teflon film (1 m², 0.4 mm width), bent at the center at an angle of ca. 90°. The deposited waters drained towards a plastic bottle of 0.5 l. Collection was carried out between 7 p.m. and 7 a.m. the next day. The samples were obtained during autumn, winter and spring, the period in which there are significative dews over all the city. After collection, all samples were measured, stabilized and cooled to 5°C until analysis.

Cations concentrations were determined by flame emission and absorption spectroscopy. Ammonium concentration was determined spectrophotometrically by the indophenol methodology. Anions concentrations were measured by capillary electrophoresis by employing a Water-Quanta 400E equipment. Nitrite was determined with Griess reagent. The absorbance at 540 nm was measured in a Zhimadzu UV-160 spectrophotometer.

3. Results

Average volume-weighted concentrations of the collected rains and dews are shown in Table 1. In this table, the highest and lowest measured values are also included.

In order to estimate the amount of nitrite (or nitrous acid) recycled to the atmosphere, the pH of dew samples and the remaining nitrite concentration were evaluated as a function of the fraction of evaporated water. Evaporations were carried out in a rotavapor kept at 21°C or 30°C under moderate vacuum. The evaporated water was collected in cooled traps in order to evaluate the amount of resuspended nitrite. Standard solutions of nitrite at different pHs were also evaporated in order to assess the behavior of the system under different experimental conditions. At 80% water evaporation, all the nitrite remains in the residual water. This is compatible with the fact that the pH of the solution always remains above the pK_a (3.3) of the nitrous acid. There is a significant evaporation of the nitrous acid only when the samples are acidified to pH 3. On the other hand, significant loss of nitrite takes place, particularly in dews, when the samples are taken to dryness (see Table 2). It is interesting to note that most of the nitrite remains in the residue when solutions prepared in pure water at the same pH were employed. Typical results are given in Table 2.

In order to evaluate the source of the different behavior observed in dew waters and nitrite solutions prepared in pure water, ammonium sulfate was added to

Table 1
Mean, lowest and highest values of ions concentrations measured in rain and dew waters (years 1995–1999) (concentration in μeq/l)

Type of event	pH	Nitrite	Nitrate	Sulfate	Chloride	Ammonium	Calcium	Sodium	Potassium	Magnesium
Dew										
Mean	6	106	132	458	68	569	468	59	28	61
Low	5.4	47	93	177	28	419	284	15	7	25
Highest	6.6	177	238	901	86	748	703	128	80	103
Rain										
Mean	5	1	34	72	17	59	47	10	3	11
Low	3.7	0.9	15	31	8	17	28	2	1	3
Highest	5.8	2	40	134	24	106	54	21	4	26

Table 2
Percentage of nitrite remaining in the residue after total evaporation of the sample

Sample	% of initial nitrite remaining in the dry residue
Nitrite in pure water, pH 5.5	83
Nitrite in pure water, pH 5.6, plus 20 ppm Ammonium sulfate	22
Nitrite in pure water, pH 5.6, plus 40 ppm Ammonium sulfate	7
Dew water, pH 5.6, 70 μS conductivity	42
Dew water, pH 5.6, 170 μS conductivity	5
Dew water, pH 6,5, 190 μS conductivity	19

the prepared solutions. The results show a noticeable decrease in the amount of nitrite present in the residue in the presence of ammonium sulfate. This is compatible with the high volatility of ammonium nitrate, and can explain the different behavior of dew waters and pure nitrite solutions. Most of the initial nitrite is recovered in the cold traps. In fact, up to 60% of the initial nitrite was recovered as titriable nitrite, showing that the original nitrite goes to the gas phase as HONO and/or $(NH_4)ONO$.

4. Discussion

Ions concentration in dews are considerably higher than in rains. It is interesting to note that the rather high ionic concentration of dew waters could contribute to their corrosion potential. This could be particularly relevant given the high number of dew events and the fact that dew is present at the surfaces nearly 10 h/day. The high amount of salts dissolved in dew can be due to the presence of natural dust. This is supported by high Ca^{2+} concentrations. Furthermore, the excess of cations evidenced in dew waters can be due to the presence of

carbonates and silicates, present in natural dust, and not evaluated in the present work. However, the very high concentrations of sulfate, nitrate and nitrite present in the collected waters indicate that anthropogenic sources must also contribute significantly. It is interesting to note that, in spite of the very high sulfate concentrations, the presence of Ca^{2+} and ammonium ions in the solution increase the pH above the normal 5.6 value.

Nitrites and nitrates arise mainly from NO_x gases (Lammel and Cape, 1996). However, it is interesting to note that both the absolute and relative values are significantly different in rains and dews. In particular, while nitrites in rains are barely detectable and sometimes below our detection limit (0.06 μM), the values in dews are considerably higher and of the same order than nitrates. It is important to note that the nitrites measured in dew waters cannot be due to the deposition of particulate matter. In fact, the data of Table 1 show that nitrites in dew are usually higher than nitrates. On the other hand, it has been reported (CONAMA, 2000) that the nighttime particulate matter in Santiago city has nearly 20 times more nitrate than nitrite. This implies that a substantial fraction of the nitrite measured in dews must arise from the dissolution of gaseous HONO and/or be produced in the aqueous droplets by a process like that represented by Eq. (2).

It is difficult to establish the source of the nitrites in dews. Practically throughout all the year, but predominantly in autumn, winter and spring, low inversions in Santiago city renders high levels of particulate matter. Furthermore, in the city, there is significant formation of photochemical oxidants, the PAN levels being extremely high (Rappenglcük et al., 2000). Both the particulate material and the PANs (Lammel and Cape, 1996) could contribute to the high levels of nitrites observed in the collected dews. The relationship between atmospheric pollution and amounts of nitrites in dew waters is evidenced by the fact that the highest levels are measured in winter time and, particularly, in days of very high levels of particles in the atmosphere of the city (data not shown).

The recycling of the nitrites present in dew could constitute an important early source of hydroxyl radicals. Our experiments with respect to the fate of the nitrite during the evaporation of dew waters show that a significant amount goes to the gas phase. The results obtained in artificial samples comprising nitrites and ammonium sulfate would indicate that it goes to the atmosphere as ammonium nitrite. This compound readily decomposes to re-generate nitrous acid and ammonia. This will be favored, in dews, due to the rather high amounts of ammonium ions present in these waters (see Table 1). This early incorporation of nitrous acid into the atmosphere could be relevant in the starting of the photochemical smog process. This could be potentiated by the fact that temperature inversion takes place at ground level most of the days in Santiago, at least during autumn, winter and spring times. In Santiago, high levels of ozone are found, in the direction of the winds leaving the center of the city. Some representative data are collected in Table 3.

An upward flux of HONO, as that arising from dew evaporation, is compatible with the very high HONO/NO$_2$ ratios reported in wintertime in Santiago city. In fact, values of this ratio as high as 0.3 have been reported (CONAMA, 2000). These values are considerably higher than those expected and clearly indicate that a heterogeneous process must be responsible for the HONO formation.

Nitrous acid levels in the atmosphere, due to recycling of dew nitrite, can be easily predicted by

$$[HNO_2]\,(ppb) = 0.02\,[ONO^-]\,V/H,$$

where $[ONO^-]$ is the nitrite concentration (μM) in the water, V is the collected volume (ml)/m^2 of surface, and H is the mixing layer (m).

Table 3
Ozone episodes in Santiago city during 1998 and 1999. Data correspond to measurements carried out at a sampling site located in the direction of the winds leaving the center of the city. The number of days indicated that the measured level was above the norm of 160 μg/m^3 (data provided by CONAMA, RM)

Period	Number of episodes	Maximum measured value
1998		
Autumn	25	408
Winter	9	204
Spring	58	280
1999		
Autumn	22	245
Winter	8	227
Spring	46	351

Taking H as 100 m, and considering the average volume (100 ml) and nitrite concentration (100 μM) of the collected dews, it can be obtained an initial nitrite concentration of ca. 2 ppb or 7×10^{10} molecules/ml. This could make a significant contribution to the gaseous HONO of Santiago city, where values of ca. 5 ppb are frequently measured in the early hours of the morning (CONAMA, 2000). This re-introduced HONO could be a significant source of free radicals. In fact, the calculations of Harris et al. (1982) indicate that, early in the morning, 2 ppb of HONO leads to an effective hydroxyl radical production rate of ca. 1×10^7 radicals/s/ml. This value is compatible with the high photolytic rate constant of HONO (Heicklen, 1976). The hydroxyl radical production rate associated with HONO photolysis is then considerably larger than that estimated by Rappenglück et al. (2000) from the photolysis of ozone in Santiago city in conditions of maximum light intensity (summer time, noon). Furthermore, it is interesting to note that the time integrated hydroxyl radical potential of the recycled HONO (7×10^{10} radicals/ml) is considerably higher than the total production of hydroxyl radicals estimated for a day of high photochemical smog formation in Santiago (ca. 10^{10} radicals/ml) (Rappenglück et al., 2000). This total amount of radicals will be produced in a rather short (ca. 1 h) time, due to the high photolytic rate of HONO even at rather high zenith angle values. This hydroxyl radical production is, early in the morning, more relevant than that due to formaldehyde photolysis (Winer, 1985). The level of formaldehyde in Santiago is generally below 13 ppm (Oyola, unpublished results). If the differences in the photolytic rate constants values between both compounds are considered (Demerjian et al., 1974), in particular at high zenith angles (Finlayson-Pitts and Pitts, 1986; Harris et al., 1982), it can be concluded that after surnrise, HONO is the dominant hydroxyl radicals source and that dew re-evaporation can significantly contributed to the total rate of hydroxyl radical production. These simple calculations show that, even if only a fraction of the nitrite is recycled, the contribution of dew derived nitrite cannot be disregarded and should be considered in any modeling of the photochemical smog carried out in days were dew is present prior to sunrise. It is difficult to evaluate what fraction of the dew incorporated nitrite is going to be recycled into the atmosphere when it is deposited on real surfaces. Most of the flat surface in Santiago city are building roofs that will be driven to dryness during the early morning hours. Evidently, depending on the type of surface and the ambient conditions, dew formation can be a net sink and/or source of HONO (Lammel and Cape, 1996; Harrison and Kitto, 1994).

The above discussion indicates that, in spite of the rather high pH of dew waters, most of the nitrite

deposited and/or formed at the surface can be recycled into the mixing layer, favored by the relatively high volatility of ammonium nitrite. In this sense, the wet surface can be considered to be a particularly active sink during the night and a source of nitrite during early morning hours. However, we consider that even if the efficiency of the process depends upon the characteristics of the surface (Lammel and Cape, 1996), this process must be taken into consideration in the evaluation of HONO fluxes during the night and sunrise, and could be an important factor in hydroxyl radical production during early morning hours.

Acknowledgements

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