Concentration of nitrite in respirable particulate matter of ambient air in Vadodara, Gujarat, India

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Abstract: Water extract of respirable particulate matter (RPM) was analyzed by ion chromatography technique to investigate the presence of nitrite (NO_2^-) as secondary aerosol in ambient environment. The nitrite particulates undergo photo hydroxyl radical reaction in environment produce nitrous acid, which reacts with metal and absorbs on RPM as water-soluble metal salt. The mean concentration of nitrite was 20.86 µg m^-3 in ambient environment. Regression analysis showed that the relationship for respirable particulate matter and nitrite (RPM-NO_2^-, R^2=0.742) was positively significant. We are reporting the presence of nitrite as an aerosol in ambient environment.

Key words: Nitrite, Ion chromatography, Ambient environment

Introduction

Ambient air pollution in urban areas is continuously increasing and is closely related with adverse health effects like mortality (Borja-Aburto et al., 1997), heart disease (Edney et al., 2000), asthma and incidence of respiratory function and lung function (Forstner et al., 1997; Jang and Kamens, 2001; Kleindienst et al., 1999; Salve et al., 2007; Singh et al., 2008). Aromatic hydrocarbons contribute to ambient PM_{2.5} concentrations through formation of oxidation products that can undergo nucleation or condense on pre-existing aerosols (Koenig et al., 1993; Lee and Chung, 1999; Ostro et al., 1991) and examined aerosol products from several irradiated aromatic hydrocarbons/ NOX systems including toluene, m-, p-xylene, ethylbenzene, 1,2,4-trimethylbenzene and m-, p-ethyltoluene. Particulate Matter is a composition of primary aerosols and secondary aerosols such as sulfate, nitrate, organic sulfur dioxide (SO_2) and NO_2 which affect the respiratory tract causing irritation and increasing airway resistance (Tsai and Cheng et al., 2003). Several workers (Keeler et al., 1990; Pope et al., 2002; Schwartz et al., 1996) reported the atmospheric chemical composition of aerosols in different parts of India. Sulfate is a single component of the fine particles and it was reported that there was a association of 2.2 percentage increase in mortality per 10 µg m^-3 increase in sulfate concentration (Schwartz et al., 1996). The concentration of PM_{10^{*}} NOx and CO has been reported earlier (Sinha et al., 2003). It was found that the nitrate and nitrite are precursors in the vivo formation of N-nitroso compounds, potent animal carcinogens. Ganoderma lucidum inhibits inducible nitric oxide synthase expression in macrophages were reported by Woo et al. (2005). The recent study indicated that there is high accumulation of PM_{2.5} generated due to fireworks on Diwali festival which remains suspended in the air for up to 20 hr. During this period, extra mass burden of 289 mg m^-3 equivalent to 1.9 normal days was imposed in the environment (Barman et al., 2009). The short-term high accumulation of PM_{2.5} is a matter of serious concern for Lucknow, city dwellers as it can penetrate deep into the lungs and cause many respiratory and cardiovascular diseases.

The recent study showed a significant effect of nitrite concentrations, pulses and post-exposure times on the mortality of E. toletanus. The cumulative mortality at the end of pulse and that at the end of post-exposure time (delayed mortality) were different. Due to the high frequency of intermittent pollution in aquatic ecosystems it is necessary to incorporate the post-exposure effects into the traditional toxicological parameters to achieve a more realistic assessment of toxicants, especially at very short-term exposures (Alonso and Camargo 2009). Nitrite has been recognized as one of the considerable inhibitors of biological phosphorus removal on inhibitory effect of nitrite. These results strongly suggest that unstable nitrite inhibition of aerobic phosphate uptake is caused by widely distributed anoxic activity (Toshiaki Saito et al., 2008). McElroy et al. (2008) reported the cancer risk for rural women in Wisconsin, USA due to nitrogen-nitrate exposure. An exponential relationship between nitrite concentrations and specific growth rate as reported by Voslarova et al. (2008).

Therefore the objective of the present study is to characterize, estimate and find out any association of Respirable Particulate Matters (RPM) with nitrite in ambient air. In this paper we are reporting the presence of nitrite as a secondary aerosol in ambient environment.
**Materials and Methods**

**Stock solution:** Stock solution of standards [procured from National Institute of Standard and Technology (NIST) USA] of nitrite, nitrate and sulfate (100 ppm each) were prepared in distilled water while water-soluble salt for analysis of nitrite was extracted in double distilled water from Respirable Particulate Matter (RPM). The working standard was prepared in three different concentrations (10, 5, 2 ppm) of nitrite, nitrate and sulfate for study. The analytical reagent of lithium hydroxide and phthallic acid was purchased from Loba Chemie Pvt. Ltd. Mumbai, India.

**Sampling:** On the basis of meteorological records of wind direction, population area registered vehicles, four sampling stations at heavy and medium traffic junctions were identified for the collection of RPM and NOx. The RPM was collected at ST Bus Stand and Kala Ghoda (heavy traffic junctions) and Nayay Mandir and Khande Rav Market (medium traffic junctions) of Vadodara city of Gujarat (Sinha et al. 2005). The eight samples of RPM and NOx have been collected at ST Bus Stand, Kala Ghoda (heavy traffic), Nayay Mandir and Khande Rav Market (medium traffic) of Vadodara city in Gujarat as per the reported method earlier (Sinha et al., 2005). The NOx was absorbed in sodium hydroxide solution for analysis. The samples were collected from monitoring sites on glass fiber filters (Whatman EPM 2000 glass fiber) using a Respirable Dust Sampler (Envireotech model APM 451) at a fixed flow rate 1 m³ min⁻¹ during early in the morning at 9 AM to 1 PM (peak hr). The detail process of sampling, number of samples, sampling location, duration of sampling has been reported our earlier study (Sinha et al., 2005).

**Instrumentation:** The ion chromatography method was used to separate the nitrite, nitrate and sulfate as per our earlier study (Sinha et al., 2005). The ion Chromatography (Perkin Elmer, USA) consisted of Isocratic LC pump 250 injector, LC 21 conductive detector and integrator. The mobile phase phthalic acid (4 mM, pH 4.25 adjusted with LiOH buffer in water) was used at a flow-rate of 1.0 ml min⁻¹ though a Allsep™ anion column at ambient temperature for the separation of anions. The mobile phase was filtered and ultrasonicated before use.

**Results and Discussion**

Mobile phase of different pH were used for the separation of sulfate, nitrate and nitrite using ion chromatography method. It was found that the separation was best achieved using phthalic acid (4 mM, pH 4.25) pumped at a flow-rate of 1.0 ml min⁻¹ through Allsep™ anion column. The retention time of nitrite, nitrate and sulfate were obtained at 4.00, 5.60 and 10.21 min. respectively. The mean concentration of nitrite (NO₂) particulate in ambient environment was 20.86 µg m⁻³ (SD ± 17.48) with a range of 5.07-49.76 µg m⁻³. While the mean concentration of RPM was 645.82 µg m⁻³ (SD ± 656.75) and nitrate (NO₃) were 28.79 µg m⁻³ (SD ± 15.92) with range 100.30-1724.24 µg m⁻³ and 8.72-54.37 µg m⁻³ respectively. Similarly the average concentration of NOx was 69.23 µg m⁻³ (SD ± 22.53) with range 30.4-93.6 µg m⁻³. The regression equation, correlation coefficient and significant level have shown in Table 1.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Regression equation</th>
<th>Correlation coefficient (r)</th>
<th>Coefficient of determination(r²)</th>
<th>Significance(p value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrite</td>
<td>6.05×0.02*RPM</td>
<td>0.8618</td>
<td>0.7428</td>
<td>0.003</td>
</tr>
<tr>
<td>Sulphate</td>
<td>24.56×0.03*RPM</td>
<td>0.8733</td>
<td>0.7626</td>
<td>0.002</td>
</tr>
<tr>
<td>Nitrate</td>
<td>21.78×0.01*RPM</td>
<td>0.4476</td>
<td>0.2004</td>
<td>0.227</td>
</tr>
<tr>
<td>NOx</td>
<td>64.34×0.01*RPM</td>
<td>0.2209</td>
<td>0.0488</td>
<td>0.568</td>
</tr>
</tbody>
</table>

![Fig. 1: The relationship of RPM-NO₂ drawn at 95% CI](image1.png)

![Fig. 2: The relationship of NO₂-SO₄ drawn at 95% CI](image2.png)
Regression analysis was carried with 95% CI and result showed that the relation ship between RPM-NO \(_2\) was significantly positive correlated (R\(^2\)=0.742, r=0.862 Fig. 1) at significance level (p) was 0.009. The relationship between NO\(_3\) - SO\(_4\) was positively significant (r=0.719 at p 0.029, Fig. 2). However, we did not find statistically significant positive relationship for NOx-NO\(_2\) (r=0.389). The NO\(_3\) was 3.32% in PM\(_{10}\) by weight in ambient environment. Atmospheric reactions of gaseous air pollutants give sulfate, nitrate and nitrite has shown in Fig. 3. Sinha et al. (2005) showed that the significant correlation was observed between RPM-NO\(_x\) (r=0.870) and NO\(_2\)-NO\(_3\) (r=0.389). The NO\(_2\) was 3.32% in PM\(_{10}\) by weight in ambient environment.

An ion chromatography method was used for the separation and identification of nitrite, nitrate and sulfate. The HPLC grade water was used as mobile phase. The base line separation between nitrite, nitrate and sulfate was achieved using phthalic acid (4 mM, pH 4.25). The concentration of nitrate is 34.03% higher as comparison to nitrite in the sample of RPM; it may be due to the fact that the nitrate is more stable than nitrite. The NOx represents the gaseous mixture of NO and NO\(_2\), this environmental free radical undergoes photohydroly radical reaction in environment, produce nitrous and nitric acids, which reacts with metal and adsorbs on RPM as a water-soluble metal salt of nitrite. The concentration of nitrate is higher than the nitrite may be due to the rate of conversion of nitrite in to nitrate is faster and also they different environmental geometry. Our earlier study (Sinha et al., 2005) showed that the RPM-SO\(_4\), RPM-NO\(_x\) and SO\(_4\)-NO\(_x\) were positively correlated. The relationship between RPM-SO\(_4\) was highly significant. The percentage of SO\(_4\) at Nayay Mandir is higher as compared to St. Bus Stand due to the different environmental geometry and also the rate of transformation of SO\(_2\) in to SO\(_4\) is high. Nitrite is potent carcinogen, which cause several health effects. Usyugora et al. (2002) reported the effect of nitrate nitrite on immune functions, i.e., human lymphocytes proliferation and cytokine production where nitrate had no effect on lymphocyte growth, but nitrite decreased proliferation. The nitrate and nitrite are precursors in the vivo formation of N-nitrosocompounds, potent animal carcinogens (Ward et al., 2006). A typical coal plant produces 10 200 tons Oxides of nitrogen in a year leads to formation of ozone (smog) that inflames the lung tissues, making people more susceptible to respiratory illness (Sinha and Nag, 2010).

These studies may also have important benefits in understanding the mechanism of formation nitrite and any adverse health effect associated with exposure to the ambient nitrite. The mean concentration of nitrite (NO\(_2\)) in ambient environment was 20.86 µg m\(^{-3}\) and the result showed that the relationship between RPM-NO\(_2\) was significantly positive correlated (R\(^2\)=0.742, Fig. 1). However, we did not find statistically significant positive relationship for NOx-NO\(_2\) and NO\(_2\)-NO\(_3\).

\[ \text{Metal nitrite} \]
\[ MNO_2 \]
\[ \begin{align*}
   &\text{M}^+ \\
   &\text{HNO}_2 \\
   &\text{NO} + \text{OH} \\
   &\text{NO}_x \\
   &\text{NO}_2 + \text{OH} \\
   &\text{HNO}_3 \\
   &\text{M}^+ \\
   &\text{MNO}_3 \\
\end{align*} \]

Metal nitrate

Fig. 3: Illustration of formation of nitrite in ambient environment

References


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