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# Rainwater toxicity and contamination study from São Paulo Metropolitan Region, Brazil

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**Abstract** Wet deposition is an important process that removes pollutants from the atmosphere and transfers them to waters and soil. The goal of this study was to assess the biological effects of the atmospheric contamination of rainwater in the metropolitan area of São Paulo (MASP) using *Daphnia similis*, *Ceriodaphnia dubia,* and *Vibrio fischeri*. Experimental assays were carried out according to standard toxicity methodology. Twenty-three rainwater samples were collected from October 2007 to December 2008, at the Nuclear Research Institute (IPEN), in MASP. Major ions were determined by ionic chromatography, which showed $NH_4^+$ and $NO_3^-$ as prevalent ions. Ecotoxicological results confirmed toxic potential of rainwater, as all samples were toxic to *D. similis* and *C. dubia*. The *V. fischeri* luminescence reduction confirmed those negative effects of rainwater and percentage inhibition of relative luminescence ranged from 0.2 to 0.9 for 16 samples. Worse conditions were observed during the rainy season, suggesting convective rains are more effective in transferring contaminants and toxicity from atmosphere to surface.

**Keywords** Air pollution · Urban area · Rainwater · Toxicity · Wet deposition

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## Introduction

Atmosphere has been recognized as an important pathway for transferring contaminants and nutrients to surface waters through wet and dry depositions (Karthikeyan et al. 2009). Contaminants and re-suspended particles may be transported throughout the atmosphere, where they can be subjected to a variety of physical and chemical processes. Depending on the atmospheric conditions, contaminants and particles can simply settle back to the ground due to gravity forces, depositing themselves on land and onto water bodies (dry deposition). On the other hand, they can also be subjected to physical and chemical processes, which cause their combination to atmospheric waters and vapors, and their further return to the ground diluted with rainwater (wet deposition).

The hydrochemistry of atmospheric precipitation is determined by the general conditions of the atmosphere, including in-cloud and below-cloud atmospheric chemical

reactions (Singh et al. 2007) and other atmospheric processes (Seinfeld and Pandis 1998), as well as by the type of pollutants emitted by natural and anthropogenic sources (Polkowska et al. 2005). In this sense, local sources largely influence the chemical composition of wet precipitation, which varies from site to site and region to region (Kulshrestha et al. 2003; Singh et al. 2007). Thus, pesticides tend to be more relevant to rural areas (Scheyer et al. 2007), whereas ions, metals, and carboxylic acids are more common in urban areas (Santos et al. 2007; Leal et al. 2004; Polkowska et al. 2005; Rouvalis et al. 2009).

Wet atmospheric precipitation is one of the most effective mechanisms for removal of both the particulate as well as gaseous pollutants from the atmosphere (Singh et al. 2007). Despite rainwater being considered as a route of contamination from atmosphere to aquatic ecosystems (Leal et al. 2004; Polkowska et al. 2005), a relatively small number of studies have been dedicated to assess the potential effects of rainwater on living organisms and ecosystems (Hamers et al. 2001; Rouvalis et al. 2009; Sakai 2006). Nevertheless, most of those studies were conducted in rural environments and focused on the presence of pesticides and their toxicity to aquatic invertebrates.

However, there is no doubt that atmospheric contamination in urban areas may also affect associated aquatic ecosystems. Recently, some studies have demonstrated biological effects of air pollution in urban regions. Silva et al. (2007) found genotoxicity in mollusks *Cantareus asperses,* from Southern Brazil (Canoas, Rio Grande do Sul State), and related the effects to atmospheric contamination. Also, in São Paulo, epiphytic lichens were used as a biological index for chemical quantification of pollutants concentrated by the *Canoparmelia texana* lichenized fungi (Fuga et al. 2008).

The metropolitan area of São Paulo (MASP) comprises one of the largest megalopolis of the world; with a population of over 19 million people (CETESB 2012) and a huge and increasing automotive fleet, this presents many environmental problems, including atmospheric pollution (Leal et al. 2004; Lin et al. 2004; Miraglia et al. 2005; Santos et al. 2007).

As a response to environmental problems, since the 1970s, the São Paulo State Environmental Protection Agency (CETESB) has created a series of enforcements and programs for controlling air pollution, especially at the MASP (CETESB 2009). Such programs include several tasks, as the enforcement of National Ambient Air Quality Standards; the identification, listing, assessment, and control of emission sources; and the establishment of a wide system for monitoring air quality, including quantification of carbon monoxide (CO), nitrogen oxides (NO + $NO_2$), sulfur dioxide ($SO_2$), particle material ($PM_{10}$), and tropospheric ozone ($O_3$), among others.

Despite the implementation of pollution control programs, the monitoring results show that air quality has not been improving, and, for some parameters, air in MASP quality has worsened if World Health Organization Air Quality Guidelines (WHO 2005). According to Ribeiro and Cardoso (2003), pollution control programs were neutralized by an increasing car fleet, as those programs were based on the control of single pollutants. In fact, such programs did not consider the complexity of atmospheric contamination in urban areas or the emergence of new contaminants.

Moreover, there is no concern of monitoring dry and wet atmospheric depositions in MASP. The literature reports a decreasing trend of rainwater free acidity from 1983 until 2003, and, since 1995, no monthly volume weight mean pH values below 4.5 have been observed (Fornaro and Gutz 2006). Regarding the MASP rainwater composition, literature reports that, besides the major ions (sulfate, nitrate, chloride, sodium, ammonium, potassium, and calcium), organic acids and hydrogen peroxide also occur as by-products of the photochemical reactions in the liquid phase (Fontenele et al. 2009; Gonçalves et al. 2010; Santos et al. 2007; Castanho and Artaxo 2001).

Additionally, MASP presents a large number of water bodies, which comprise urban polluted rivers, some ponds and lagoons and several water reservoirs (many of them located in protected areas) that provide good quality drinkable water to the population.

Considering that many substances found in MASP rainwater may be toxic to the aquatic biota along with the scarcity of research examining related aquatic environmental effects, the present study aimed to evaluate the potential of rainwater from São Paulo, Brazil, to negatively affect biodiversity due to the presence of toxic contaminants.

## Material and methods

### Site sampling

The MASP is the main economic center of Brazil, which comprises São Paulo City and other 38 surrounding

cities and serves as home to almost 20 million inhabitants (Fig. 1). It is located in the southeastern portion of the São Paulo State (23°S and 46°W), Brazil, with an extension of 8,000 km$^2$, covering a predominantly hilly topography with heights between 650 and 1,200 m.

Pluviometric historical data (1933–2002) showed that MASP has characteristic rainy seasons from October through early April (mid-spring and summer), reaching 1,022 mm of mean rainfall during this interval. Moreover, São Paulo has a drier period from April to September (autumn to early spring), with 350 mm of mean rainfall along this period (IAG/USP Meteorological Station). The rainy season is associated with the continental heating that, together with tropical convection, extra-tropical systems (cold fronts) and instability areas of continental origin, favors copious rainfalls. The dry season is dominated by high-pressure stability, with generally rapid passage of cold fronts. During this season, diminished rainfall volumes, lower mean temperatures, and periods of atmospheric stability are also common, which allows the occurrence of frequent thermal inversions when unfavorable conditions to the dispersion of air pollutants arise (CETESB 2009).

Historically, MASP has presented problems of air pollution and, according to CETESB (2009), the air quality degradation is associated with atmospheric emissions by industries and, mainly, by the large fleet of light and heavy vehicles (more than nine million). Still, according to the State Environmental Agency, the total emission, in 2008, was estimated in 1.5 million ton year$^{-1}$ of CO, 365,000 t year$^{-1}$ of hydrocarbons (HC), 339,000 t year$^{-1}$ of nitrogen oxides ($NO_x$), 29,500 t year$^{-1}$ of inhalable $PM_{10}$, and 8,200 t year$^{-1}$ of $SO_2$. The vehicular fleet is the main factor for the emissions of atmospheric pollutants in MASP: 98 % CO, 97 % HC, 96 % $NO_x$, 33 % $SO_2$, and 40 % $PM_{10}$.

## Rainwater sampling

A set of 23 rainwater samples was collected between October 2007 and December 2008 at the Nuclear Research Institute (IPEN) (23°33′58″S and 46°44′14″W), located in São Paulo City, Brazil (Fig. 1). The collection vials were made of polycarbonate, with a 0.05 m$^2$ collecting area. They were exposed in the beginning of rain events and were removed after the rain had finished. The samplers were rinsed three times with deionized water before use.

The total volumes of precipitated rainwater retained in the containers during each of the rain episodes were measured and aliquots were immediately taken to the laboratory. Further, the monthly register of accumulated rain from IPEN pluviometer was consulted, allowing estimations of magnitude for each rain episode relative to the respective month pluviosity. In the laboratory, electric conductivity and pH were measured by a Hach conductivity meter (HQ40d) and a Micronal pH-meter (B474), respectively. Afterwards,

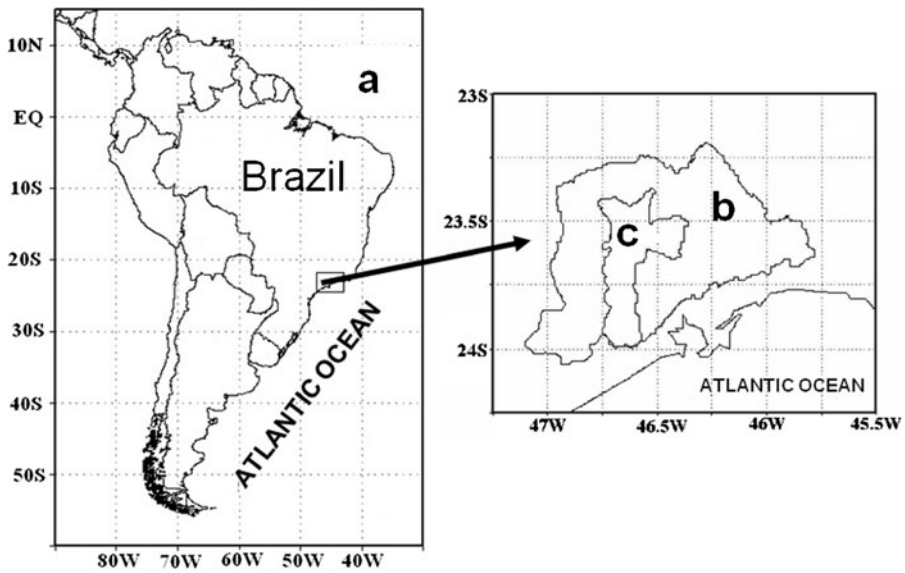


**Fig. 1** Localization of MASP in Southeastern Brazil: *a* South America and Brazil, *b* MASP and *c* sampling area in São Paulo city

additional aliquots were transferred to polyethylene flasks and stored at −20 °C for use in the ecotoxicological assays and chemical analyses.

## Ecotoxicological assays

The toxicity of rainwater samples was measured using the freshwater cladocerans *Daphnia similis* and *Ceriodaphnia dubia*, and the marine bacteria *Vibrio fischeri*, according to the Brazilian Association of Technical Standards Methods (ABNT), protocols 12713, 13373, and 15411–2, respectively (ABNT 2004, 2005 and 2006).

### *Daphnia similis toxicity test*

The organisms were taken daily from cultures maintained in the laboratory. Four rainwater dilutions were tested as follows: 100, 75, 50, and 25 %, using natural freshwater as a dilution vehicle; this water was also used to cultured the organisms. The test system consisted of four replicates of each dilution, prepared in glass test tubes containing 20 ml of test solution. Five organisms were introduced into each test chamber. The test system was kept at 20 °C±2, without light for 48 h, in an incubation chamber. The control group consisted of organisms exposed to clean dilution water. After 48 h of exposure, test organisms were observed for immobility and this aspect was recorded. Test results were accepted only when mortality in the control group did not exceed 10 %. The results were expressed as $EC_{50}$ 48 h (percentage values) and were analyzed by the Trimmed Spearman–Karber method (Hamilton et al. 1977).

### *Vibrio fischeri toxicity test*

*V. fischeri* luminescence was determined using Microtox 500® (Microbics), without sample dilution. The bacteria were purchased as freeze-dried product from Unwelt®. After rehydration with a reconstitution solution, the light emission of a bacterial suspension was measured in a luminometer (15 °C constant temperature). The results were expressed in percentage inhibition of relative luminescence values, after 15-min exposure.

### *Ceriodaphnia dubia chronic toxicity test*

All the organisms were taken from cultures maintained in the laboratory. Rainwater samples were diluted in natural freshwater (dilution water) to obtain 100, 75, 50, and 25 % concentrations. Test chambers were filled up to 20 mL with test solution and the respective controls. Ten replicates were used per concentration and one organism was introduced in each test chamber. The test system remained in an incubation chamber at 24 °C (±2) with controlled photoperiod (16-h light) for 8 days. Daily, test solutions were renewed. Reproduction and survival of exposed organisms were recorded. *F* test and Student's *t* test were performed in order to verify the differences among samples and the control group.

## Chemical analyses

Each rainwater sample was filtered through a 0.22-μm pore size (Millex) filter for the analyses of ions, which were performed using a Metrohm 761 Compact ionic chromatograph with an electrical conductivity detector. Anion and cation determinations were handled using the following Metrohm accessories: an A-Supp 5 (250×4 mm) separator column with an anion micromembrane suppressor for anions and a C2-150 (150×4 mm) separator column for cations. The analytical determination of each major ion was carried out using a calibration plot with a concentration range from 5 to 50 μmol $L^{-1}$. As majoritarian cations and anions in rainwater were identified and quantified, the ionic balance was calculated.

## Statistical analyses

Results of each individual toxicological test were compared to their respective controls using Student's *t* test to determine the presence of toxicity in the samples. An analysis of variance, followed by Tukey's multiple comparison was carried out to observe seasonal differences among the rainwater samples.

Environmental, chemical, and ecotoxicological data were integrated by the use of multiple Pearson correlations. A cluster analysis (correlation similarity and weighted paired group algorithm) was applied to chemistry data aiming to observe associations among contaminants.

## Results

Evidences of the potential biological effects of rainwater contamination on aquatic organisms are shown in the results presented in Figs. 2 and 3, and in Table 1. Values of percentage inhibition of relative luminescence above 0.2 were assumed as toxic effects to *V. fischeri* (Wang et al. 2002), as shown in Fig. 2. From the 20 tested samples, 16 exhibited some degree of toxicity, except for SP2, SP10, SP15, and SP16 samples. To *V. fischeri* bacteria, the worst effects were measured at SP18, SP19, SP20, and SP22 samples, all collected during the wet season (summer). In a general term, rainy season (summer) samples tended to be more toxic to *V. fischeri.*

The acute toxicity bioassays using *D. similis* showed significant reduction in the survival of exposed organisms in all rainwater samples. The $EC_{50}$ (48 h) values to *D. similis* are shown in Fig. 3, and ranged from 50 to 90.86 %. Toxicity also tended to be higher during the summer 2008/2009.

In addition to the chronic effects (reproduction), all rainwater samples tested for chronic toxicity caused mortality to *C. dubia*, thus they were considered acutely toxic as well; moreover most of them produced significant negative effects on reproduction even when diluted (Table 1).

A qualitative comparison of results from the ecotoxicological assays is summarized in Table 2, according to sampling date. The results evidenced the presence of toxicity in most samples, as well as a sturdy agreement between the different approaches. Data also showed worse conditions during summer, as toxicity tended to be higher along the wet season.

Figure 4 shows the ionic balance in rainwater samples, indicating a good correlation between cations and anions ($r^2$=0.85; $p$<0.05). Figure 5 shows pH values for rainwater collected during the studied periods; pH ranged from 4.81 to 7.80 and values above 5.6 were prevalent. However, five samples collected during summer (wet season) exhibited pH below 5.6, which is considered acid rain. Ion concentration and rainfall data are shown in Fig. 6, indicating ionized ammonia (NH4+) as the predominant ion, followed by $NO_3^-$.

In terms of ion association, results showed correlations between formate and glycolate ($r$=0.64; $p$=0.003) and between acetate and oxalate ($r$=0.58; $p$=0.01). Fluorides, chlorides, nitrates, sulfates, ammonia, potassium, magnesium, and calcium presented positive correlations among each other (Table 3). Association among contaminants is shown in Fig. 7, evidencing the influence of different sources on contamination of MASP rainwater, such as direct emission by ethanol-fueled cars (acetic and formic acids), local emissions by gasoline and diesel fueled cars (nitrates, sulfates, and ammonium), marine salts ($Na^+$ and $Cl^-$) and soil dust ($K^+$, $Mg^{2+}$, $Ca^{2+}$, fluorides).

Furthermore, pH values correlated positively to contents of fluorides ($r$=0.61; $p$=0.03), $K^+$ ($r$=0.61; $p$=0.04), $Ca^{2+}$ ($r$=0.68; $p$=0.03), and $Mg^{2+}$ ($r$=0.56; $p$=0.04) and

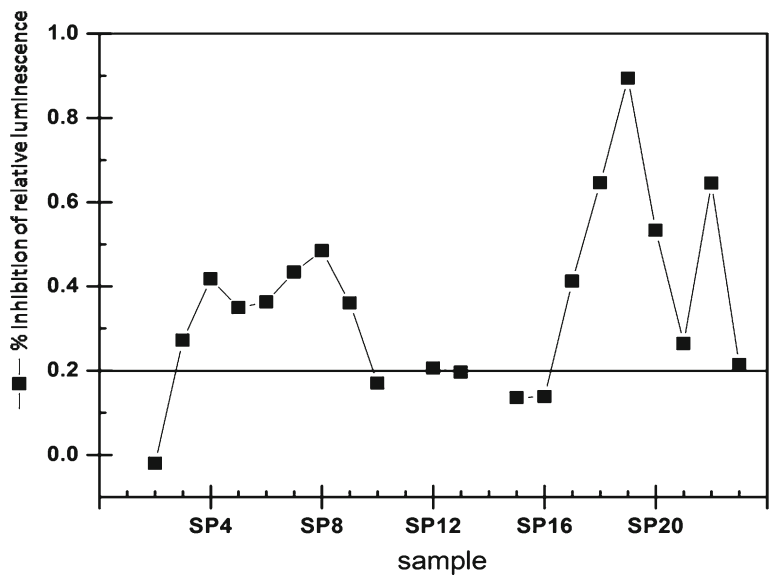


**Fig. 2** Values of percentage inhibition of relative luminescence of *V. fischeri* exposed to rainwater samples. (Values >0.2 were considered toxicity indicative)

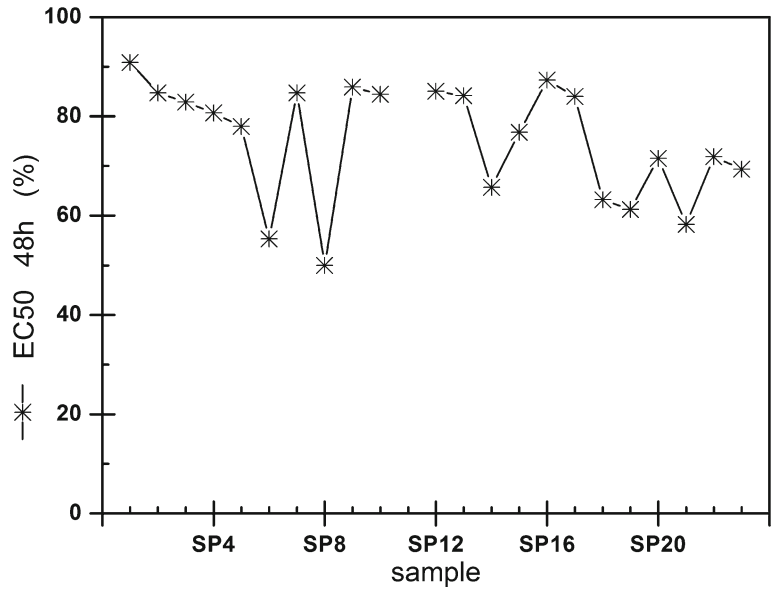


**Fig. 3** $EC_{50}$ 48-h values (percentage) for *Daphnia similis*

negatively to nitrates ($r$=−0.54; $p$=0.04), whereas conductivity presented positive correlation to most of measured ions, such as fluorides ($r$=0.81; $p$=0.006), chlorides ($r$=0.67; $p$=0.02), nitrates ($r$=0.97; $p$=0.0004), sulfates ($r$=0.92; $p$=0.006), $Na^+$ ($r$=0.59; $p$=0.04), $NH_4^+$ ($r$=0.72; $p$=0.02), $K^+$ ($r$=0.77; $p$=0.02), $Ca^{2+}$ ($r$=0.64; $p$=0.03) , and $Mg^{2+}$ ($r$=0.90; $p$=0.01). Immobility rates of *D. similis* presented negative correlation to oxalate ($r$=−0.53; $f$=0.05) and $Ca^{2+}$ ($r$=−0.52; $p$=0.05) concentrations, but $EC_{50}$ values correlated negatively to $NH_4^+$ levels ($r$=−0.70, $p$=0.02). Toxicity to *V. fischeri* presented positive correlation to nitrate ($r$=0.51; $p$=0.05), and ammonia ($r$=0.53; $p$=0.05) levels, whereas toxicity to *C. dubia* (lowest observed effect concentration (LOEC) values) correlated negatively to nitrate ($r$=−0.57, $p$=0.04) and $NH_4^+$ ($r$=−0.59; $p$=0.04) concentrations.

**Table 1** Chronic toxicity to *C. dubia* exposed to rainwater samples from MASP

| | Endpoint | | Qualitative classification |
|---|---|---|---|
| Sample | NOEC (%) | LOEC (%) | |
| SP3 | 75 | 100 | Toxic* |
| SP4 | 75 | 100 | Toxic* |
| SP5 | 75 | 100 | Toxic* |
| SP7 | 25 | 50 | Toxic* |
| SP10 | 75 | 100 | Toxic* |
| SP12 | 75 | 100 | Toxic* |
| SP13 | 50 | 75 | Toxic* |
| SP15 | 0 | 25 | Toxic* |
| SP16 | 75 | 100 | Toxic* |
| SP17 | 50 | 75 | Toxic* |
| SP18 | 0 | 25 | Toxic* |
| SP20 | 0 | 25 | Toxic* |
| SP21 | 25 | 50 | Toxic* |
| SP22 | 50 | 75 | Toxic* |
| SP23 | 25 | 50 | Toxic* |

*Acute effect

## Discussion

There are many studies that analyzed the chemical composition of rainwater focusing, mainly, on the alkalinity/acidity and ionic composition of samples (Fornaro and Gutz 2006; Zhang et al. 2007a; Anatolaki and Tsitouridou 2009). The approach adopted by such studies is useful to the understanding of local and regional sources of pollution, especially concerning urban sites with large population and rapid economic growth associated with systems of energy production (Mouli et al. 2005).

The pH of rainwater samples presented values around 6.0 (Fig. 5), while the acid samples (pH <5.6) occurred during the summer season, which may be due to the short time of residence for the soluble species in the air (Zhang et al. 2007b). These results are in agreement with data previously obtained for MASP (Leal

**Table 2** Qualitative effect of rainwater samples of MASP on aquatic organisms

| Sample | Collection date (mm/dd/year) | Ecotoxicological assays—organisms | | |
|---|---|---|---|---|
| | | *D. similis* | *V. fischeri* | *C. dubia* |
| **SP1** | **10/31/2007** | **T** | **ND** | **ND** |
| **SP2** | **12/12/2007** | **T** | **NT** | **ND** |
| **SP3** | **12/19/2007** | **T** | **T** | **T** |
| **SP4** | **12/20/2007** | **T** | **T** | **T** |
| **SP5** | **01/29/2008** | **T** | **T** | **T** |
| **SP6** | **02/18/2008** | **T** | **T** | **ND** |
| **SP7** | **02/24/2008** | **T** | **T** | **T** |
| **SP8** | **03/12/2008** | **T** | **T** | **ND** |
| **SP9** | **03/13/2008** | **T** | **T** | **ND** |
| *SP10* | *04/03/2008* | *T* | *NT* | *T* |
| *SP11* | *04/10/2008* | *T* | *ND* | *ND* |
| *SP12* | *06/01/2008* | *T* | *T* | *T* |
| *SP13* | *06/04/2008* | *T* | *T* | *T* |
| *SP14* | *06/22/2008* | *T* | *ND* | *ND* |
| *SP15* | *08/03/2008* | *T* | *NT* | *T* |
| *SP16* | *08/10/2008* | *T* | *NT* | *T* |
| *SP17* | *09/14/2008* | *T* | *T* | *T* |
| **SP18** | **10/01/2008** | **T** | **T** | **T** |
| **SP19** | **11/24/2008** | **T** | **T** | **T** |
| **SP20** | **12/02/2008** | **T** | **T** | **T** |
| **SP21** | **12/10/2008** | **T** | **T** | **T** |
| **SP22** | **12/11/2008** | **T** | **T** | **T** |
| **SP23** | **21/12/2008** | **T** | **T** | **T** |

Wet season = in bold; dry season = in italics

*T* toxic, *NT* nontoxic, *ND* no data

et al. 2004; Santos et al. 2007). According to such authors, several ions and organic acids in rainwater

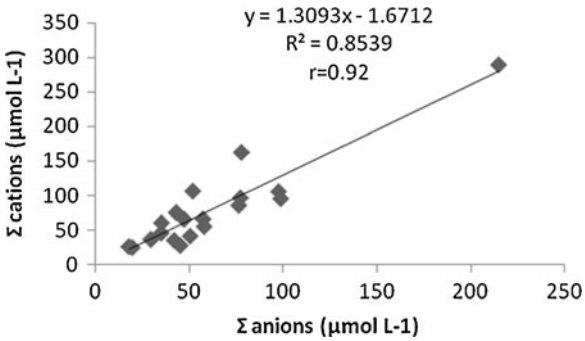


**Fig. 4** Ionic balance in rainwater samples from MASP

contribute to the acidic equilibrium, maintaining pH values around 6.0. Moreover, lower pH values observed in rainwater may increase metals reactivity, with repercussions on toxicity, and may change the potential toxicity due to ammonia, as $H^+$ ions alter the balance between unionized ammonia and ionized ammonia ($NH_4^+$). It is worth mentioning that the respective ion registered the highest concentration among all measured ions, reinforcing the results of previous studies on MASP rainwater ionic composition (Fontenele et al. 2009; Fornaro and Gutz 2006; Bourotte et al. 2006; Castanho and Artaxo 2001). Furthermore, the volume and frequency of rainwater are important parameters that influence the ionic concentrations. Notably, the SP14 sample presented the highest ion concentration and the lowest rainwater volume, as can be observed in Fig. 6.

Regarding the toxicity of rainwater, the effects on *V. fischeri* bacteria were expressed in percentage inhibition of relative luminescence, and the results showed that most rainwater samples were toxic. These findings differ from results obtained by Hamers et al. (2001) for an agricultural zone where rainwater is frequently contaminated by pesticides but not always toxic to *V. fischeri*.

The toxicity tests conducted with *D. similis* and *C. dubia* showed that all samples were significantly toxic (Fig. 3; Table 1). These findings were similar to those obtained by Rouvalis et al. (2009), who observed the toxicity of rainwater samples from urban areas to *Daphnia pulex*. Lower $EC_{50}$ values were obtained for samples SP6 (55.33 %) and SP8 (50 %), both collected during rainy season. Moreover, the average $EC_{50}$ values calculated for the set of samples collected in rainy seasons (65.9 %±5.78) was significantly different from the values obtained for samples collected during dry seasons (80.56 %±7.09) ($p<0.05$). The overall analysis of rainwater toxicity showed that such waters are capable of affecting the environment, especially the aquatic systems.

The majority of ecotoxicological studies about rainwater imply that the consequences are due to pesticides (Rouvalis et al. 2009; Hamers et al. 2001). In Japan, Sakai (2006) observed decreased toxicity of rainwater to *Daphnia magna* after removing nonpolar compounds, such as pesticides. However, for an urban area such as MASP, the combination of low pH and ion-like $NH_4^+$ may be related to the observed toxicity, especially during the rainy season. In fact, toxicities correlated to ammonia, nitrates, and sulfates levels, suggest that such substances may have contributed to the observed

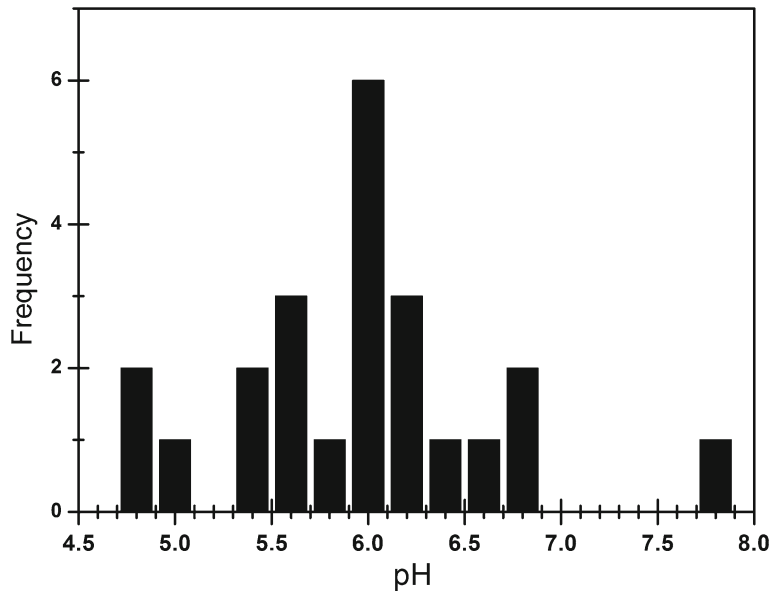


**Fig. 5** Frequency of pH values to rainwater samples from MASP

effects. However, it is possible that other substances that were not measured have also influenced the toxicity of rainwater samples. Notably, oxidants, such as $H_2O_2$ in rainwater and $O_3$ in gaseous phase, have been historically observed in the MASP atmosphere during spring and summer, which are the rainy seasons (CETESB 2009; Fontenele et al. 2009; Gonçalves et al. 2010), and, as oxidants are highly reactive, their contribution to toxicity cannot be neglected. In addition, considering the large automotive fleet in MASP (Miraglia et al. 2005), hydrocarbons, aldehydes, and some metals, together with $SO_x$, $NO_x$, and other ions, are emitted by such sources (Bourotte et al. 2006; Castanho and Artaxo 2001; Fornaro and Gutz 2006) and may possibly contributed to the observed toxicity. Still, as such pollutants were not measured in the present, further studies are needed to provide complete chemical profiles of MASP rainwater and to identify the main compounds related to toxicity.

A remarkable aspect highlighted in this investigation is the fact that, during wet season (summer), contaminant concentrations and toxicities tended to be higher, which was not expected. Both literature and reports from the State Environmental Agency regularly inform that air pollution is worse during winter, that is, the dry season (Castanho and Artaxo 2001; CETESB 2009; Lin et al. 2004; Orsini et al. 1986; Sharovski et al. 2004), and so, a worse condition in rainwater would be

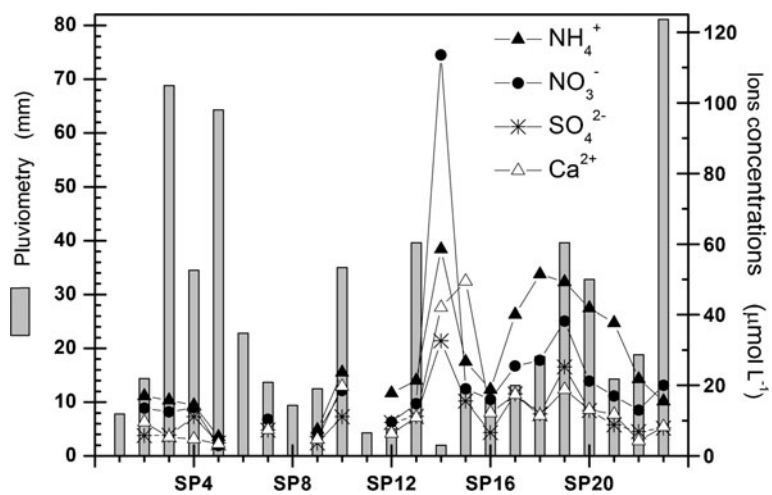


**Fig. 6** Rainfall data (millimeter) and ion concentration (micromole per liter) in rainwater samples from MASP

**Table 3** Pearson correlations among contaminants in rainwater samples from MASP between 2007–2008 (Pearsons' *r*/*p*)

| | Fluoride | Glycolate | Acetate | Formate | Chloride | Nitrate | Sulfate | Oxalate | Sodium | Ammonia | Potassium | Calcium | Magnesium |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Fluoride | | 0.18 | 0.43 | 0.22 | ***0.01*** | ***0.00*** | ***0.00*** | 0.42 | 0.08 | ***0.00*** | ***0.00*** | ***0.00*** | ***0.00*** |
| Glycolate | −0.32 | | 0.72 | ***0.00*** | 0.17 | 0.32 | 0.24 | 0.71 | 0.45 | 0.11 | 0.28 | 0.16 | 0.14 |
| Acetate | −0.19 | 0.09 | | 0.95 | 0.23 | 0.73 | 0.49 | ***0.01*** | 0.33 | 0.94 | 0.93 | 0.57 | 0.54 |
| Formate | −0.30 | ***0.64*** | −0.02 | | 0.31 | 0.41 | 0.27 | 0.96 | 0.92 | 0.34 | 0.81 | 0.39 | 0.40 |
| Chloride | ***0.56*** | −0.33 | −0.29 | −0.24 | | ***0.00*** | ***0.01*** | 0.60 | ***0.01*** | ***0.01*** | ***0.04*** | 0.06 | ***0.00*** |
| Nitrate | ***0.74*** | −0.24 | −0.08 | −0.20 | ***0.66*** | | ***1.2E-06*** | 0.08 | ***0.02*** | ***4.8E-04*** | ***8.5E-04*** | ***0.00*** | ***0.00*** |
| Sulfate | ***0.72*** | −0.28 | −0.17 | −0.27 | ***0.60*** | ***0.87*** | | 0.78 | 0.06 | ***0.00*** | ***0.00*** | ***0.00*** | ***0.00*** |
| Oxalate | 0.19 | −0.09 | ***0.58*** | 0.01 | −0.13 | −0.05 | 0.07 | | 0.54 | 0.57 | 0.08 | 0.06 | 0.43 |
| Sodium | 0.41 | −0.19 | −0.23 | −0.03 | ***0.59*** | 0.52 | 0.44 | −0.15 | | 0.35 | ***0.05*** | 0.12 | ***0.01*** |
| Ammonia | ***0.65*** | −0.38 | −0.02 | −0.23 | ***0.60*** | ***0.72*** | ***0.82*** | 0.14 | 0.23 | | ***0.02*** | ***0.02*** | ***0.01*** |
| Potassium | ***0.78*** | −0.26 | 0.02 | −0.06 | 0.47 | ***0.70*** | ***0.64*** | 0.42 | 0.45 | 0.53 | | 0.00 | 0.00 |
| Calcium | ***0.84*** | −0.34 | −0.14 | −0.21 | 0.43 | ***0.64*** | ***0.72*** | 0.44 | 0.37 | 0.54 | 0.78 | | 0.00 |
| Magnesium | ***0.87*** | −0.35 | −0.15 | −0.20 | ***0.70*** | ***0.87*** | ***0.79*** | 0.19 | ***0.55*** | ***0.61*** | ***0.88*** | 0.84 | |

Italic bold numbers indicate significant correlations

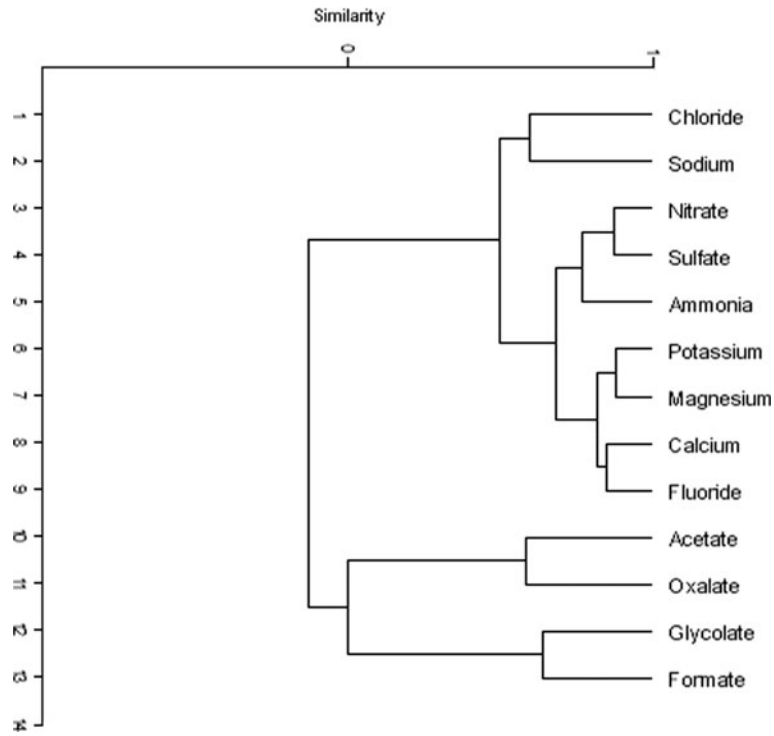


**Fig. 7** Similarity in contaminants occurrence in rainwater from MASP during 2007–2008 (correlation index; WPGMA)

expected during dry season. Besides, it has been stated that better atmospheric conditions in wet seasons are a result of washing process produced by frequent rains (Castanho and Artaxo 2001; Lin et al. 2004; Saldiva et al. 1995), as demonstrated to other areas of the world (Singh et al. 2007). Nevertheless, our data corroborate the evidences that convective rainstorm episodes are more effective in removing contaminants from the atmosphere. However, based on the washing capacity of summer convective rainstorms, we assumed that it would be expected that the first rainstorm episodes of the wet seasons would find worse atmospheric conditions and, thus, present more contaminated waters. Yet, with the continuation of rain episodes, rainwater would show a decrease in contaminants concentration and toxicity, which seems to not be occurring at MASP. Assuming that emission rates do not present seasonality (Castanho and Artaxo 2001; Orsini et al. 1984, 1986; Miranda and Andrade 2000), further investigations should be made focusing on the possibility of secondary compounds from photochemical reactions affect rainwater quality during wet season. Castanho and Artaxo (2001) observed the secondary production of organic carbon at MASP during the summer as a result of reactions between Volatile Organic Compounds from motor vehicle emissions and light radiation. Likewise, inputs from external regions should be investigated, as winds are stronger during spring and summer. Moreover, the presence of marine salts in aerosols from MASP was evidenced only during summer (Miranda and Andrade 2000), showing that influence of external areas may occur at MASP. Removal of atmospheric contamination by dry deposition should be considered as well as Miranda and Andrade (2000) showed that, during wintertime, due to climatic stability, contaminants tend to remain for longer periods in the atmosphere, causing the formation of agglomerates which precipitate without action of rain. In this case, the possibility of contaminants transference to water bodies should be considered (Huston et al. 2009). Further studies should also care to identify the substances responsible for rainwater toxicity in MASP.

In addition, since toxicity was high and frequent, rainwater should be considered an additional source of pollution to water bodies and soils, as observed by Huston et al. (2009) in Australia. Further implications involve problems to re-use rainwater due to their toxicity and contamination, and since some episodes of acid rain were detected, it is possible that corrosion of urban structures be increased. In this context, there is no official protocol in MASP, or even in Brazil, for monitoring the chemical composition of rainwater or its effects on soil

and water bodies. Therefore, the results herein suggest that rainwater should be monitored, as they constitute a pollution source to soil and aquatic environments.

## Conclusions

Rainwater from MASP is frequently toxic and present high levels of some contaminants during the year. Toxicity probably occurs as synergistic effects involving chemical contamination, low pH, ammonia, and oxygen reactive species. Worse conditions occurred during rainy months, suggesting that convective rain episodes are more effective in transferring contaminants (and toxicity) from atmosphere to surface soils and aquatic environments, while showing that the transfer of contaminants to water bodies appeared to be more problematic during the aforementioned season.

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