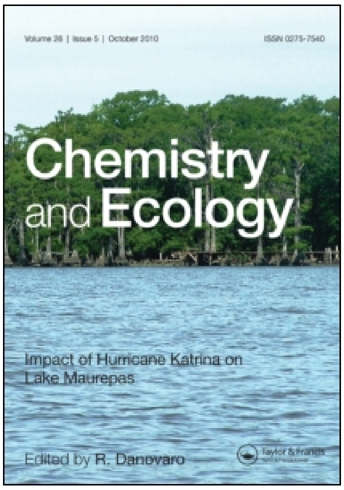

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Total peroxides in rainwater at two mountainous sites and in Mexico City, Mexico

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Rainwater samples were collected in the western sector of Mexico City (MC) and at Rancho Viejo (RV), 80 km west-south-west of MC, from 2001 to 2005, and Orizaba City (OC), about 90 km from the Gulf of Mexico, where rainwater collections were only possible on some weekends in 2001. Rainwater samples were treated in the field, and analysed by fluorescence at the laboratory. The volume-weighted mean concentration (VWMC) of H_2O_2 was 13.2 μM at RV, and 11.2 μM in MC, for the period 2001–2005. The highest VWMC was observed in OC (21.6 μM). The VWMCs for each year were 9.5, 14.4, 11.5, 16.7, and 14.3 μM at RV, and 12.2, 12.2, 14.3, 11.8, and 9.9 μM in MC, for 2001–2005, respectively. Hydrogen peroxide in rainwater correlated significantly and negatively with sulfate in both MC and RV, but not, however, in OC. This study confirmed that H_2O_2 concentration in rainwater is controlled by a complex combination of rain intensity, washout processes and in-cloud formation of H_2O_2, acting simultaneously. This was suggested by the fact that rain intensity seemed to predominate in certain rain fractions of a rain event, while washout processes seemed to predominate in other fractions of the same rain event.

Keywords: Hydrogen peroxide; Total peroxides; Sulfates; Rainwater

1. Introduction

The oxidation of sulfur dioxide to sulfuric acid is efficiently promoted by hydrogen peroxide [1–4]. Therefore, due to the importance that hydrogen peroxide (H_2O_2) has in the oxidation process of sulfur(IV) in the aqueous phase, the study of its concentration in air, in cloud droplets, and in rainwater is becoming increasingly important. Furthermore, according to some studies, H_2O_2 has adverse environmental effects. Masuch *et al.* [5] exposed young spruces and beeches to acid fog and H_2O_2 for 3 h per day. After 6 weeks, serious effects on leaves and needles were observed; causing a decreased resistance to drought and a decreased ability to transport assimilates. Möller [6] suggested that H_2O_2 is a key species in the yellowing of needles and magnesium deficiency, known as the 'Waldschäden syndrome'. Hewitt *et al.* [7] proposed that the reaction of ozone with biogenic alkenes to produce toxic peroxides could be one mechanism by which ozone damages plants, especially under acidic deposition that

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enhances the stability of peroxides. Simonaitis *et al.* [8] and Hewitt and Kok [9] also depicted the production of H_2O_2 and other peroxides from the reaction of ozone with natural alkenes. Polle and Junkermann [10] suggested a synergetic effect of H_2O_2 and other air pollutants in the damage to spruce trees.

The H_2O_2 concentrations in continental rainwater vary by more than four orders of magnitude (from 10 nM to 199 μM) [11]. However, the most widely observed concentrations vary from a few micromoles to several tens of micromoles [4, 11–13]. On the other hand, H_2O_2 concentrations in coastal and oceanic rain micromoles by only approximately one order of magnitude (3–82 μM). This small variation appears to be related to the washout process and the hour of the day in which the sample was collected [14–19].

The peroxide of greatest abundance in the atmosphere is H_2O_2, which is a key component in photochemical reactions taking place there [14]. The hydroperoxy radical, is the most important precursor of H_2O_2 in the gas and aqueous phases. Lee *et al.* [20] clearly delineated the chain of photochemical reactions that leads to the formation of hydrogen peroxide:

$$O_3 + h\nu(\lambda = 320\,\text{nm}) \longrightarrow O(^1D)O_2$$

$$O(^1D) + H2O \longrightarrow 2HO$$

$$HO + CO(+O_2) \longrightarrow HO_2 + CO_2,$$

where $O(^1D)$ denotes electrically excited oxygen atom.

Photolysis can also contribute to HO_2 formation:

$$CH_2O + h\nu(\lambda = 370\,\text{nm})(+2O_2) \longrightarrow 2HO_2 + CO.$$

Hydrogen peroxide is produced by the bimolecular combination of HO_2:

$$HO_2 + HO_2(+H_2O) \longrightarrow H_2O_2 + O_2.$$

Hydrogen peroxide formation should be enhanced at higher solar radiation, water, vapor and radical precursor levels [21]. Becker *et al.* and Das and Aneja [22, 23] studied the formation of H_2O_2 in the ozonolysis of alkenes, isoprene and some terpenes. Chameides and Davis, Schwartz, and McElroy [24–26] demonstrated that heterogeneous scavenging of OH and HO_2 from the gas phase, by cloud droplets in the presence of midday solar flux, can represent a major source of free radicals for cloud water. Zuo and Hoigné and Anastasio *et al.* [27, 28] concluded that aqueous-phase photochemistry is an important source of H_2O_2 for cloud droplets.

Other authors have reported other sources of H_2O_2. The production of nitrogen oxides in thunderstorms is well known, so it is possible that H_2O_2 can be formed in a similar way [13, 29].

Knowledge of H_2O_2 concentration in the environment is necessary to better understand H_2O_2 sources and sinks, and its contribution to the transformation of trace constituents in the atmosphere. Unfortunately, most reported H_2O_2 concentrations are not accurate or reliable due to peroxide's rapid decomposition in the aqueous phase and the interference inherent in its sampling in air. For this reason, it is necessary that monitoring methodologies be developed, in order to minimize inaccuracies in the measured concentrations of H_2O_2 in rainwater. One of the objectives of this research was to develop and propose a rainwater collection strategy for obtaining more representative concentrations of H_2O_2 in rainwater that can be applied in remote regions lacking electricity and chemical laboratories.

2. Material and methods

2.1 *Sampling sites*

Three sampling sites were chosen (figure 1): a residential area in the western sector of Mexico City (MC), at 2300 masl; Rancho Viejo (RV), in the State of Mexico, located in a mountainous wooded region, about 80 km west-south-west of Mexico City, at 2700 masl; and Orizaba City (OC), in Veracruz state, on the eastern foothills of the Sierra Madre Oriental, at 1300 masl. This site was included because of its high atmospheric humidity and its relatively short distance (about 90 km) from the Gulf of Mexico.

2.2 *Rainwater sampling procedures*

The high instability of H_2O_2 in rain samples represents a major impediment to obtaining reliable data on total peroxides concentration in rainwater, given that the concentration of

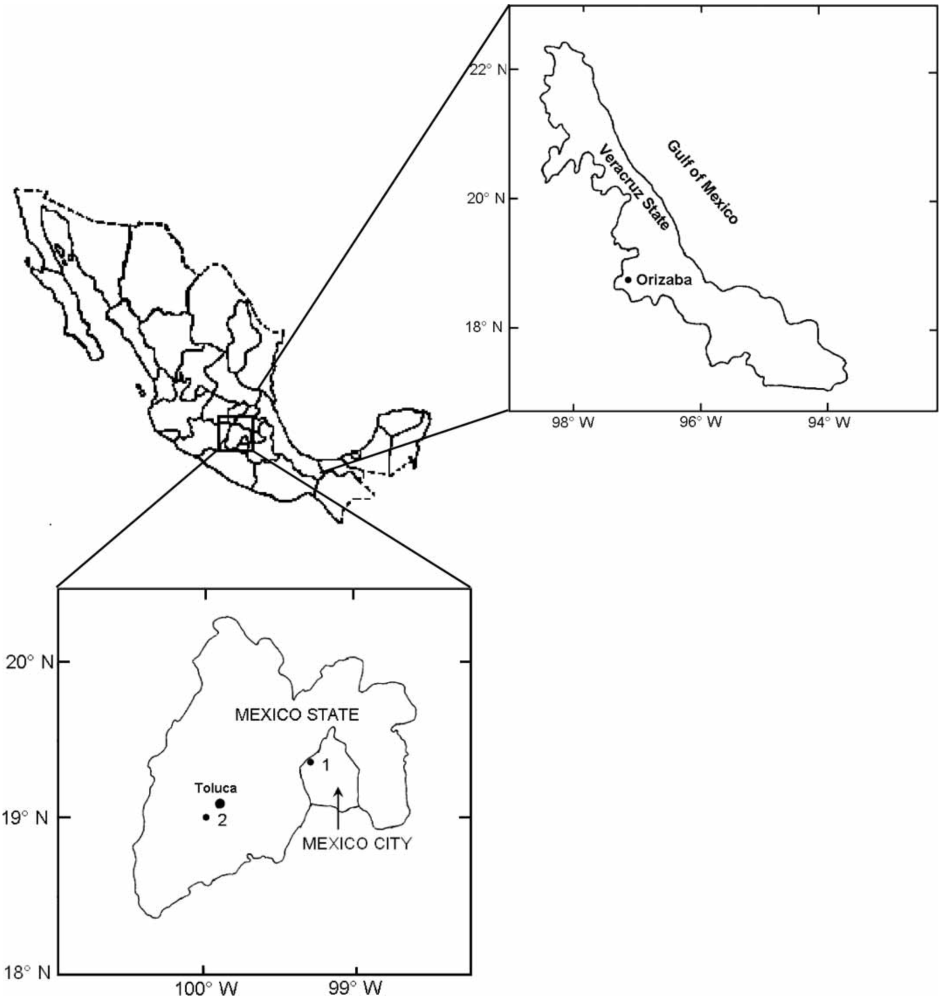

Figure 1. Sampling-site locations: (1) residential area in the western sector of Mexico City; (2) Rancho Viejo in the State of Mexico, and Orizaba City in Veracruz State.

H_2O_2 represents more than 95% of the total peroxides in a sample [3, 21]. Ortiz *et al.* [30] showed that it is difficult to calculate H_2O_2 concentrations in real time, due to the rapid H_2O_2 decomposition in the time elapsing between sample collection and analysis. For this reason, rain samples are treated as soon as rain events end (see sample field treatment). Nevertheless, this treatment is still not enough to overcome the problem of H_2O_2 decomposition in rainwater, since the peroxide starts decomposing immediately, and rapidly, the moment the collection of the sample begins, as a laboratory test to study the rate of H_2O_2 decay in an actual rain sample indicated. To perform this test, a rain sample was collected in less than 1 min during the onset of a heavy rain shower. An aliquot of this rain sample was treated immediately as described in sample field treatment (section 2.3), and several additional aliquots of the same sample were treated 0.5, 1, and 4 h after its collection. In brief, the results indicated that H_2O_2 concentrations decreased 11, 20, and 46%, at 0.5, 1, and 4 h, respectively. This test showed that H_2O_2 concentration data uncertainty is still significant, even when rain samples are treated as soon as rain events end. This becomes especially critical for long-lasting rain events. Consequently, we decided to perform sequential samplings every 15–30 min during rain events, so that H_2O_2 decay would be reasonably slight, while, at the same time, sample numbers would be kept to manageable proportions. Kok [31] collected rain samples at hourly intervals during daylight hours and on a less frequent basis at night. In this study, shorter sampling periods were performed only in 2001 and 2002 because of safety reasons, since the samplings were made manually to obtain samples of rain fractions during the frequent short periods of heavy lightning activity.

2.3 *Sample field treatment*

In brief, in order to analyse total peroxides (TP), the dimer of *p*-hydroxiphenilacetic acid, which is detected by fluorescence at 320–410 nm, must be formed in the rain sample. This dimer is obtained by the reaction of *p*-hydroxiphenilacetic acid with peroxides, in the presence of peroxidase acting as a catalyser [12, 32]. Chemical reagents and analytical procedures used in this work are described by Lazrus *et al.* [12]. Specifically, H_2O_2 is determined by the procedure based on the fact that catalase destroys that particular peroxide much faster than it does organic peroxides.

2.4 *Chemical analysis*

Treated samples were analysed by fluorescence, using the SpectraSYSTEM FL3000 (Thermo Separation Products) fluorescence meter, within 1 week of rainwater collection. Treated samples remain stable for several days under ambient conditions [12, 21, 33, 34]. The contribution of H_2O_2 and organic peroxides to TP can be estimated by the following procedure.

First, TP are determined by fluorescence of the dimer of *p*-hydroxiphenilacetic acid, formed directly in one untreated aliquot of the sample. Second, organic peroxides are determined by adding catalase to another aliquot of the same sample, followed by the formation of the dimer of *p*-hydroxiphenilacetic acid. Hydrogen peroxide is determined by subtracting organic peroxides from total peroxides [34, 35]. This procedure was applied to only five rainwater samples collected in MC in different days due to reagent limitations, showing that H_2O_2 represents more than 95% of the TP. These results concur with those obtained by other researchers, such as Olszyna *et al.* [21], who indicated that organic peroxides accounted for less than 5% of the TP at Whitetop Mountain in Virginia, USA, and Sakugawa *et al.* [3], who reported that organic peroxides accounted for less than 2% of the TP in rain samples in California. Since H_2O_2 represents more than 95% of the TP, the variations in TP concentration are due basically to those in H_2O_2 concentration. Therefore, in this work, TP are referred to as H_2O_2. The method of detection limit was 0.4 μM.

Sulfate was also analysed because the oxidation of SO_2 by H_2O_2 is the main source of non-sea-salt or non-marine sulfate in rainwater. Sulfate was analysed by non-suppressed ion chromatography, using a Perkin Elmer instrument, equipped with an Isocratic LC pump 250 and a conductivity detector ConductoMonitor III. The detection limit was 0.22 mg l^{-1}.

2.5 *Statistical analysis*

The Shapiro–Wilk W test was applied to assess the normality of the data for the entire period under study. The null hypothesis, establishing that the data corresponded to a normal distribution, was rejected at the 5% significance level, and so non-parametric statistical methods were used. The Kruskal–Wallis test was used to compare the concentrations of H_2O_2 across the three sampling sites. The Wilcoxon–Mann–Whitney U test was applied whenever significant differences were observed using the Kruskal–Wallis test. Spearman's rank correlation was applied to compute the correlation between H_2O_2 concentrations with SO_4^{2-} concentrations, rain amount, and rain rate.

3. Results and discussion

Eighty rain samples were collected in MC, and 141 at RV, from 2001 to 2005. At OC, 16 samples were collected during weekends from May to October 2001.

3.1 *Annual variations*

Annual volume-weighted mean concentrations (VWMC) and standard deviations of the VWMC (SDVWMC), of H_2O_2 and SO_4^{2-}, are shown in figures 2 and 3, for MC and RV sampling sites, respectively. Small variations in H_2O_2 concentrations were observed at both sites. The Mann–Whitney test showed that there were no significant differences in H_2O_2 concentration between RV and MC for the whole sampling period 2001–2005. It is interesting to note that there were no significant differences in sulfate concentration between these locations either. The VWMCs of H_2O_2 were 13.3 and 11.2 μM, in RV and MC, respectively. Hydrogen peroxide concentrations in rainwater collected in MC from 2001 to 2005 correlated significantly and negatively with rain intensity, rain amount, and SO_4^{2-} (−0.335, −0.223, and −0.364 at $p < 0.05$, respectively). At RV, they did not correlate with rain intensity but did correlate significantly and negatively with rain amount and SO_4^{2-} (−0.258 and −0.373 at $p < 0.05$, respectively). Since rainwater was collected in OC only in 2001, the Mann–Whitney test for OC-RV, OC-MC, and RV-MC was also applied for that year. Again, there was no significant difference in H_2O_2 concentration between RV and MC, but there were significant differences between OC and RV, and between OC and MC, at $p < 0.05$. This corresponds with the fact that the VWMC of H_2O_2 observed in OC was 21.6 μM, whereas the VWMC were 9.5 and 12.2 μM, in RV and MC, respectively. The VWMC were 9.5, 14.4, 11.5, 16.7, and 14.3 μM, at RV, for 2001–2005, and 12.2, 12.2, 11.3, 11.8, and 9.9 μM, in MC, for the same years. All these values are noticeably lower than the 21.6 μM observed in OC in 2001. It is possible that the high air pollution in Mexico City depleted the formation of hydrogen peroxide, due to competing reactions, in that city and in RV, which is situated downwind of Mexico City. It is also possible that the high atmospheric humidity in OC favoured the formation of H_2O_2. Becker *et al.* [36] found that the production of H_2O_2 is enhanced when water vapour is present.

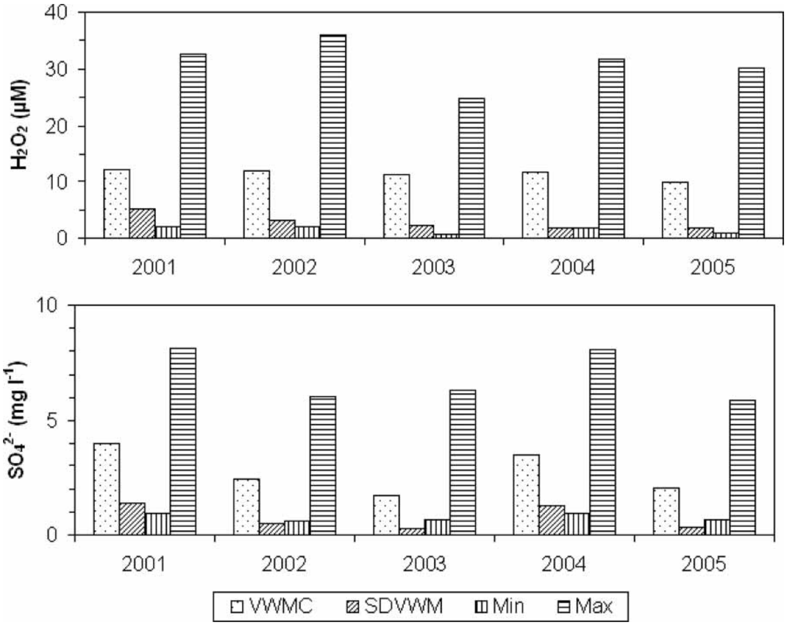

Figure 2. Hydrogen peroxide concentration for Mexico City from 2001 to 2005.

Dense rain forests lie near OC, so the higher concentrations of H_2O_2 in OC could be important from the point of view of forest ecosystems, because H_2O_2 is considered as one of the possible agents in forest decline (see section 1).

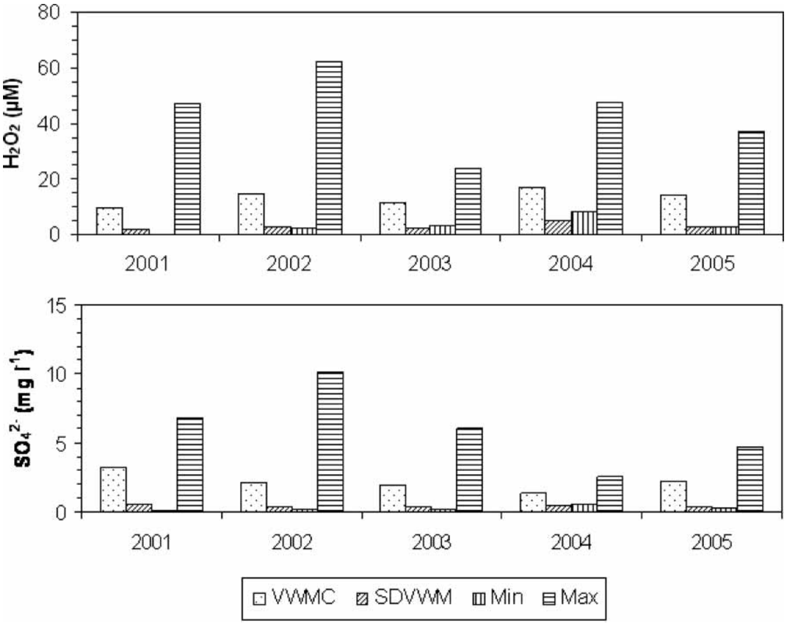

Figure 3. Hydrogen peroxide concentration for Rancho Viejo from 2001 to 2005.

The contribution of sea-spray aerosols ranged from only 1.7 to 7% of the total sulfate observed in rainwater collected in OC, which is the closest site to the coast (section 2.1). Therefore, almost all sulfate observed in rainwater in the three sampling sites comes from the oxidation of anthropogenic SO_2 by H_2O_2. In OC, H_2O_2 concentrations correlated neither with rain intensity, nor with rain amount, nor with SO_4^{2-} (–0.012, –0.096, and –0.188 at $p < 0.05$, respectively), although, in this case, the sample number was only 16.

The results of Zika *et al.* [14] could be due to the good dispersion conditions present in Miami, as the H_2O_2 levels they reported were higher than those reported in California, where air pollution is obviously much higher than in Florida. During two storms at midday, H_2O_2 concentrations remained fairly constant throughout the rain events, possibly, according to the researchers, because H_2O_2 was generated in cloud water by chemical processes. However, due to a small sample number, no explanation was found for a significant decrease in the H_2O_2 concentration during another storm in the early evening.

Hydrogen peroxide concentration was certainly the result of a complex interaction of rain rate and washout processes, with rain rate being the predominant factor in some cases, and washout processes being the predominant factors in other cases. Nevertheless, none of these parameters could easily explain H_2O_2 concentration variation in many other cases.

The negative and significant correlations of H_2O_2 with SO_4^{2-}, in MC and RV, evidenced the fact that H_2O_2 was depleted by SO_2. On the other hand, the non-significant correlation in OC could also indicate that a much longer sampling period would be needed, in order for definite explanations to be drawn.

Luria *et al.* [37] found that total peroxides concentrations were higher in the afternoon in all the rainwater samples they collected in Los Angeles. The regression analysis indicated that the concentrations of H_2O_2, H^+, organic acids and dissolved organic carbon are practically independent of precipitation volume, but that the total deposition is correlated with precipitation volume, indicating that the concentration of these species is controlled not by dilution but by other factors, such as chemical reaction of H_2O_2 with dissolved SO_2.

3.2 *Variations in sequential samplings*

Figures 4a–d and 5a–c show some examples of sequential samplings of single rain events collected in RV and MC, respectively. Rain rate or dilution effects appeared to influence H_2O_2 during the collection of the rain event of 16 June 2001 (figure 4a). The lowest H_2O_2 concentration occurred during the first rain fraction, when the rain rate was the highest, whereas the highest H_2O_2 concentration occurred during the fifth rain fraction, when the rain rate was the lowest. On 4 August 2001 (figure 4b), the first two rain fractions presented the highest H_2O_2 concentration, indicating that the high H_2O_2 concentration was due, probably to a high H_2O_2 concentration already in the air at the onset of rain. The fact that H_2O_2 concentration decreased between the first and second rain fractions, even though the rain rate remained constant, points to the washout of H_2O_2 as being the most important factor in controlling H_2O_2 concentration. From the third to the ninth rain fractions, rain rate was the predominant variable. A washout effect was apparent from the ninth to the eleventh rain fractions. The rain event occurring on 15 May 2002 (figure 4c) presents a major challenge as regards explaining H_2O_2 concentration variation. That is, some processes are important in certain portions of this rain event and others in other portions of the rain event. Both the H_2O_2 concentration and the rain rate decreased during the first two rain fractions. These variations seemed to indicate that the washout process was important during these rain fractions. A decrease in rain rate means that there is less water ‘available’ for dilution, so an increase and not a decrease in H_2O_2 concentration should have been observed, unless the washout of H_2O_2 compensated for this

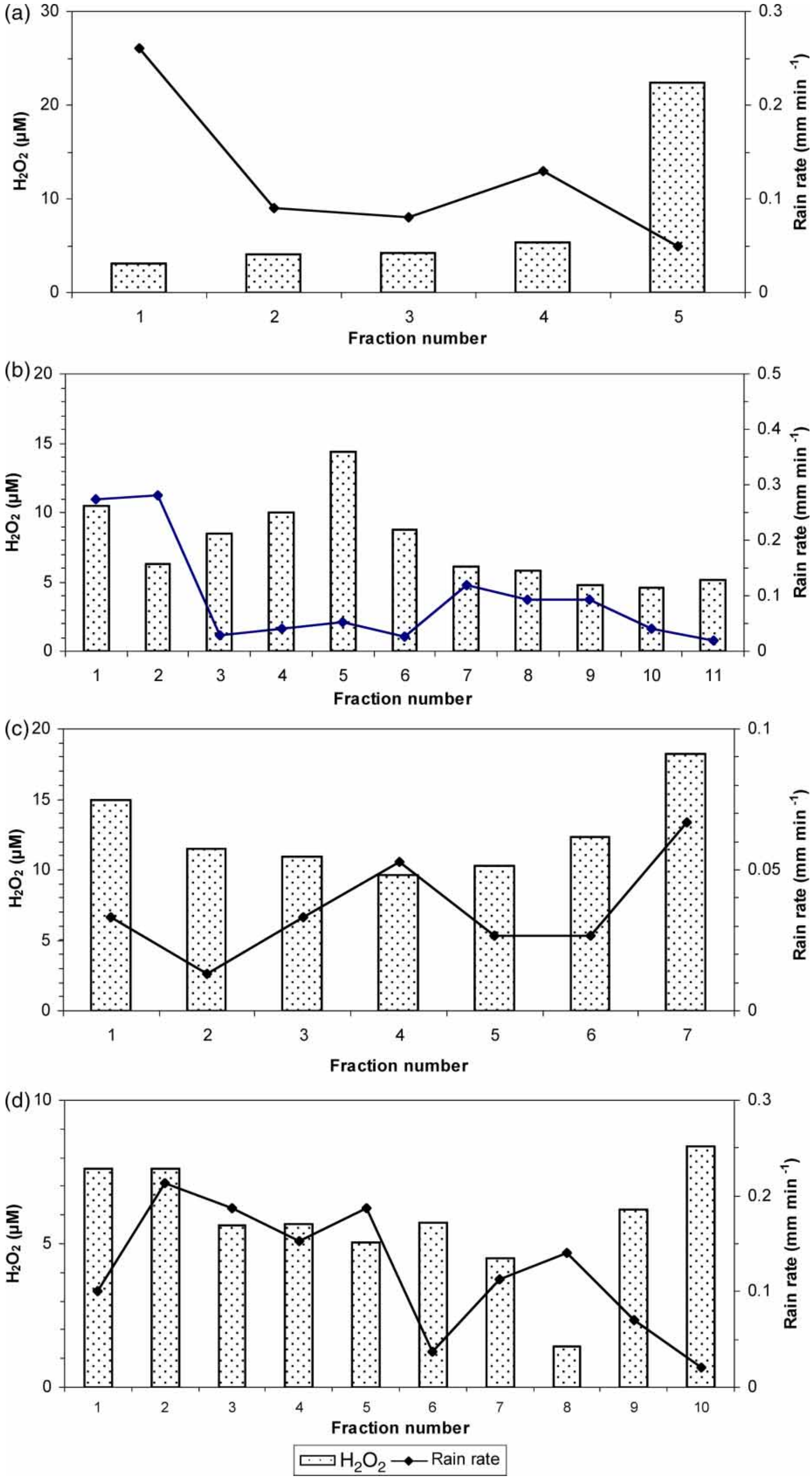

Figure 4. Hydrogen peroxide concentration in sequentially collected rainwater at Rancho Viejo in relation to rain rate: (a) 16 June 2001; (b) 4 August 2001; (c) 15 May 2002; (d) 20 July 2002.

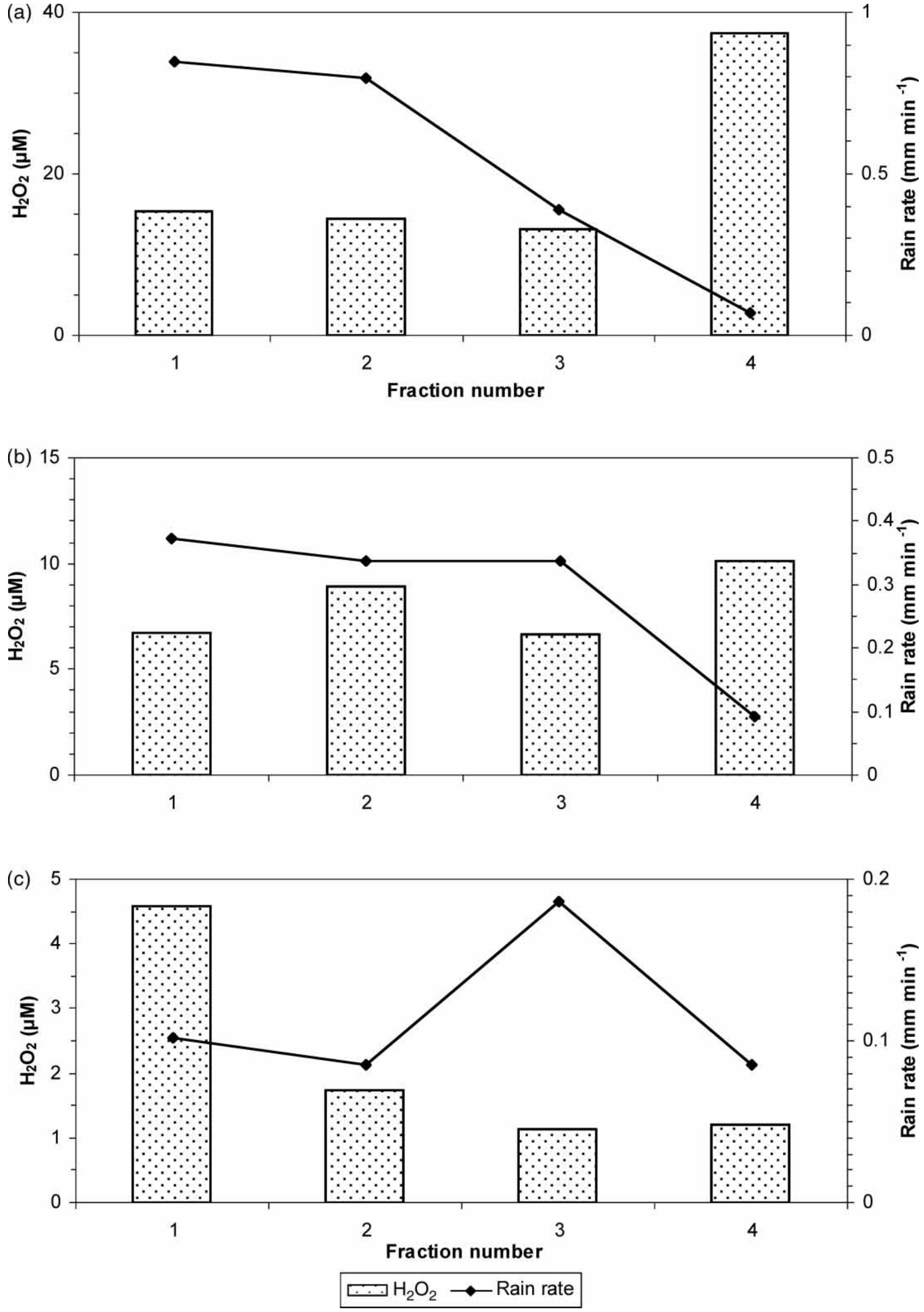

Figure 5. Hydrogen peroxide concentration in sequentially collected rainwater in Mexico City in relation to rain rate: (a) 26 July 2001; (b) 3 August 2001; (c) 27 June 2002.

effect. On the other side, the increase in rain rate and H_2O_2 concentration observed during the last two rain fractions seemed to indicate that the formation of H_2O_2 in cloud droplets compensated for the dilution effect produced by an increase in water available for dilution.

The case observed in MC on 27 June 2002 (figure 5c) again showed that several processes are involved in the variation of H_2O_2 concentration. The high concentration of H_2O_2 observed in the first fraction could possibly be explained by a high concentration of H_2O_2 being already present in the air when cloud droplets formed. The H_2O_2 concentration dropped noticeably from the first to the second rain fractions, while the rain rate remained nearly constant, as the result of washout processes, since dilution effects may be ruled out. The decrease in the concentration of H_2O_2 from the second to the third rain fractions was not as noticeable as would be expected from dilution alone, given the sharp increase in rain rate between these rain fractions, possibly because of a formation of H_2O_2 in cloud droplets, as it was also proposed in the rain event of 15 May 2002. Finally, washout and/or atmospheric dispersal could explain why the H_2O_2 concentration remained practically constant in the third and fourth rain fractions in spite of the noticeable decrease in rain rate; a factor which would normally be expected to increase the H_2O_2 concentration. On 20 July 2002 (figure 4d), although the rain rate increased nearly twofold from the first to the second rain fractions, the H_2O_2 concentration remained constant. Washout processes seemed to overcome the positive effects of a sharp decrease in rain rate. Hydrogen peroxide increased slightly from the fifth to sixth rain fractions. Only from the sixth to the tenth rain fractions could it be seen that the rain rate was, by far, the most important factor controlling H_2O_2 concentration. The variation in hydrogen peroxide concentration in other rain events during the present study could not be explained in a consistent manner either.

It is interesting to remark that the variation in H_2O_2 concentration was more consistently explained in other cases. For example, figures 5a and 5b show two such cases observed in MC. The hydrogen peroxide concentration variation observed on 26 July 2001 and 3 August 2001 seemed to depend mainly on rain rate.

Given the results of these cases, and others not shown, it can be stated that H_2O_2 concentration variation and rain intensity, associated with the first rain fraction of rain events collected on different dates, did not seem to be related. Additionally, the variability of the initial H_2O_2 concentration among rain events did not clearly depend on any specific characteristic present at the onset of a rain event. Rather, it was a complex function of meteorological conditions, storm characteristics, and air-pollution levels prior to the formation of rain clouds. Unfortunately, it was not possible to measure cloud base height along with simultaneous rainwater samplings just below cloud base and at the surface to estimate the contribution of below cloud and in-cloud scavenging to the concentration of H_2O_2 observed at ground level. Besides, H_2O_2 decomposes during rainwater collection, before sample treatment in the field, masking the effect of the above-mentioned parameters on H_2O_2 concentration. The scavenging of H_2O_2 by washout mechanisms appeared to be the most important factor responsible for the consistent decrease in its concentration throughout a single rain event. Kok [31] found that the decrease in H_2O_2 concentration during the course of a rain event suggests that washout mechanisms predominate during the uptake of H_2O_2 in rainwater. It is interesting to note that this statement differs from that of Zika *et al.* [14] in which they propose that a significant fraction of H_2O_2, observed in their rain samples, was generated in cloud water. Yuan and Shiller [19] stated that the washout effect and time of day of sample collection appear to explain why the concentration of H_2O_2 in rainwater over the Atlantic Ocean varied by more than an order of magnitude. The decrease in the concentration during a single rain event suggests a washout effect, and the slight increase at the end of the sample collection could have been the result of the increase in solar radiation at the end of the storm. Collections made during late afternoon or early evening rain events presented higher concentrations than collections made from midnight to early morning. The concentration of H_2O_2 in marine rainwater is higher, and less variable, than in continental rainwater.

4. Conclusions

The variability of the initial hydrogen peroxide concentration among different rain events and the variability observed in sequential rainwater samplings of single rain events did not clearly depend on any specific parameter observed at the onset of rain events. Rather, it is a complex function of rain rate, atmospheric humidity, washout processes, in-cloud formation of hydrogen peroxide and air-pollution levels prior to the formation of rain clouds, as was suggested by the negative and significant correlation found between hydrogen peroxide and sulfate concentrations.

The scavenging of hydrogen peroxide by washout mechanisms appeared to be the most important parameter responsible for the consistent decrease in the concentration of hydrogen peroxide during a single rain event.

The higher concentration of H_2O_2 in rainwater in the sampling site surrounded by rain forests means that more rainwater samplings must be performed in rain and tropical forests, which could be affected by high concentrations of H_2O_2.

The decomposition of hydrogen peroxide during the time elapsed between the onset of a rain event and the rainwater sample field treatment is a variable that introduces ‘noise’ in finding a relationship between the concentration of hydrogen peroxide in rainwater and atmospheric processes and photochemical reactions. More research projects to measure the degree of the decomposition of hydrogen peroxide under various atmospheric conditions during rainwater collection are needed, or at least the collection of rainwater should be made at fixed intervals throughout the whole rainy season so as to minimize the adverse effects of such decomposition as much as possible.

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