

Effect of humidity on vegetation

Jahangir Payamara*

Shahed University, Science Faculty, Tehran,Iran.

*Corres.author: jahangirpayamara@yahoo.com

Abstract: Fog and dew are not in list of pollutants. The chemistry of fog and dew is discussed in relation to the potential hazard for vegetation, depending on the local chemical regime, the water layer formed on plant surfaces by the deposition of cloud, fog or dew water can contain high concentrations up to $100 \mu\text{mol/L}$ of oxidizing or reducing species. Relatively high concentrations up to several tens of $\mu\text{mol/L}$ of Mn are found in dew water sampled from plants. This Mn, that is Leached from the plant itself, results in significant catalytic oxidation of S (IV).

Keywords: Fog and dew, vegetation, potential hazard.

1-INTRODUCTION

The main pathways for deposition of pollutants generally are wet and dry deposition. As a result, the research into the effects that pollutants have on vegetation is focused on the same pathways, that is, acidification of the soil and uptake of gases via the stomata. However, in addition to these gross deposition processes, effects on vegetation can also be caused by uptake of pollutants in dew water or by deposition of highly polluted fog droplets. Depending on various parameters such as distance to sources, type of sources as well as meteorology, the chemistry involved differs from that of the gross deposition. The forests that are located on mountain slopes are frequently enveloped in clouds. These clouds are formed at the interface of the boundary layer and the oxidant-rich free troposphere. As a result, cloud water often contains large amounts of hydrogen peroxide. The effect of H_2O_2 on vegetation was investigated [1]. In the study, young spruces and beeches were exposed to H_2O_2 -containing fog. At concentrations that are frequently found in clouds, H_2O_2 was proven to cause severe damage to the tissue of the exposed plants.

In valleys or in flat countries like Iran thin water

layers may form on vegetation due to the process of dew formation, or by deposition of fog droplets. Formation of (radiation-) fog occurs during calm nights in which the dispersion of pollutants is at a minimum. Therefore, the pollutant levels in meteorological situations that favor fog formation are quite high. Even if H_2O_2 would be formed under these conditions, the fog water is not likely to contain H_2O_2 as a result of the rapid reaction with SO_2 that takes place, in the droplets. Fog water often is in a reducing state due to the presence of sulfite. This sulfite predominantly is present as hydroxymethane sulfonic acid (HMSA), that is formed when formaldehyde is present. In the form of HMSA, large amounts of sulfite can be present even if the very high acidity of fog water inhibits the presence of free sulfite. Although total pollutant concentrations in dew water generally are low, individual components can be present in phyto-toxic concentrations. Typically, in Iran, this is the case for sulfite. The high emission levels of NH_3 in the Iran create a chemical regime in which the dissolution of SO_2 in water layers deposited on plants is no longer a process that is limited by the concurring drop in pH. As a result, the sulfite concentrations are frequently at a level

at which laboratory experiments clearly show effects on the photosynthesis of spruces. Dew water samples were taken from artificial surfaces as well as natural surfaces (vegetation). The artificial surface used is a plastic plate. The plate was cleaned daily, to remove dry deposition. Part of the 'natural' dew samples was taken from grass that grows on the sand dunes at Bibalan near sea site in north. Other samples were taken from a small lawn grown on a CaCO_3 rich soil at the same site. The dew water bulk ion concentrations are given in Table 1. In addition to this analysis, the Mn concentrations were determined; Table 2 shows concentrations of Mn found in dew water sampled from various substrates, and in rain water. The bulk component analysis shows that sulfite concentrations in dew water can be quite high. As stated before, the presence of NH_3 enables these high concentrations. Part of the sulfite is present in the form of HMSA.

The concentrations of major ions present in the two types of dew water samples cannot be compared easily. The difference in surface structure may result in different deposition rates. Also, no attempts were made to rinse the dry deposition off the vegetation. The dew plate however, was cleaned daily. In addition to the differences in dew water composition introduced by these different treatments, plants will interact with the water layer. Nevertheless the following

qualitative explanation for the differences observed in bulk ion concentrations of the two types of dew water can be given.

The ability of plants to take up nitrate via the leaves would introduce a lower concentration of the nitrate ion in the dew water collected from the vegetation with respect to that in the dew water taken from the artificial substrate. Indeed, such a difference exists in the mean values for the nitrate concentrations, but there is a large spread in the individual values. It is much less likely that the higher sulfate concentration found in the dew taken from grass surfaces can be explained by loss of sulfate from the plant [2]. In view of the rather high Mn concentrations found in this type of dew water samples (Table 2), it is much more plausible that catalytic oxidation of S(IV) by Mn is the responsible mechanism.

Fog water samples were obtained with a polyethylene cyclone. The sampling rate of this cyclone is 2 m³ per minute. A peristaltic pump is used to remove the sample from the cyclone. The collected water is stored in a collector. The blower that is used to draw air through the cyclone is activated by an optical fog detector [3]. Laboratory tests have shown that no substantial evaporation of the collected fog water takes place in the cyclone [4]. Generally, the fog water in north is highly polluted, and pH values are low. Most of the S(IV) in fog water is present in the form of HMSA.

TABLE 1 Major ions in dew concentrations in $\mu\text{mol/liter}$.

| | | N | mean | Std. Dev. | max |
|--------------------|-------|----|------|-----------|------|
| pH | grass | 30 | 5.33 | .45 | 6.15 |
| | plate | 35 | 5.16 | .59 | 6.30 |
| SO_4^{2-} | grass | 29 | 1190 | 790 | 2940 |
| | plate | 35 | 200 | 315 | 1900 |
| NO_3^- | grass | 29 | 145 | 340 | 1790 |
| | plate | 35 | 268 | 690 | 4030 |
| NH_4^+ | grass | 30 | 436 | 344 | 1650 |
| | plate | 34 | 362 | 465 | 2280 |
| S(IV) | grass | 7 | 41 | 45 | 130 |
| | plate | 27 | 19 | 15 | 75 |

TABLE Concentrations of Mn in $\mu\text{mol/l}$.

| | |
|--------------------------------|-------|
| grass grown on sandy soil | 20-70 |
| grass grown on calcareous soil | 1-20 |
| plate | 1-3 |
| rain (typical) | 0.04 |

2- EXPERIMENTAL

Exposure of plants to polluted water layers comparable to those that form when dew or fog water is deposited on plants, is done in fog chambers in Bibalan. A more detailed description of the technique is given earlier [5]. At present five chambers are in use. The damaging action caused by the presence of a specific chemical component is studied by adding this component to water containing sulfate, nitrate and chloride in concentrations of several hundreds of $\mu\text{mol/l}$ [6]. The plants in each of the five chambers are exposed to different concentrations of the component. In at least one of the chambers, this concentration is zero. The plants from this chamber are used as a reference.

A study into the effect on plants of S(IV) in water layers was done by dissolving Na_2SO_3 in water. The pH of the fog was 6. In this experiment the bushes of tea were exposed during three hours per day, for 5 days per week, for 6 weeks. The effects were studied by means of an in-vivo chlorophyll fluorescence technique [7]. This technique produces a vast amount of information concerning the process of photosynthesis and the ability of the plant to effectively convert actinic light into assimilates [8].

The experiments in which the bushes of tea were exposed to fog containing 62 $\mu\text{mol/l}$ of S(IV) showed a clear effect of the exposure. During the first 15 minutes after a transition from dark to light (20 $\mu\text{mol.m}^{-2}.\text{s}^{-1}$, $\lambda=650\text{nm}$) conditions, the fluorescence of the exposed bush is diminished due to enhanced non-photochemical quenching with respect to that measured for the plants in the reference series. The steady-state fluorescence of both series of plants is equal. The conclusion therefore must be that the S(IV) exposed plants have difficulties in adapting to changing illumination conditions. The high Mn and

S(IV) concentrations found in dew in combination with the relatively high pH make it very likely that the catalytic oxidation of S(IV) is a significant pathway for the production of sulfate. This is also indicated by the fact that sulfate concentrations found in dew water collected from grass are higher than those in dew collected from the plate. In earlier studies [9,10] into the Mn-catalyzed oxidation of S(IV), either the pH values or the Mn and S(IV) concentrations were different from those encountered in dew. Therefore, the kinetics for the oxidation under conditions typical for the dew sampled at Bibalan was studied. The studies were performed in a cloud chamber. The use of a cloud chamber for this type of experiments has the advantage that the surface-to-volume ratio of the water is large. Thus, the experiments are not easily influenced by transport limitations, except for very fast reactions. The volume of the chamber is 1 m^3 . In the cloud chamber, Mn-containing droplets are introduced in an atmosphere containing SO_2 . After a residence time of 3 minutes, the droplets are sampled and analyzed. In order to study the reaction at a constant pH of 5, a buffer (10^{-3} to 10^{-2} molar acetate) is added to the spray solution. A more detailed description of the cloud chamber is given earlier [11]. The amount of sulfate formed in the fog in the droplets in the cloud chamber as function of both the S(IV) and the Mn concentrations ; which given for three different Mn concentrations, at PH 5.

The curves drawn in the figure indicate a square root dependency of the S(IV) concentration. The kinetics that best describes the results of the experiments is:

$$\frac{d[\text{SO}_4^{2-}]}{dt} = k \cdot [\text{Mn}^{2+}] \cdot [\text{S(IV)}]^{0.5}$$

with: $k = 3.7 \pm 1.2 \text{ (mol/l)}^{-0.5} \text{ s}^{-1}$

A more detailed description of the experiments is given in [12].fig.1 concentrations of sulfate found in dew water sampled from grass plotted against those of manganese.

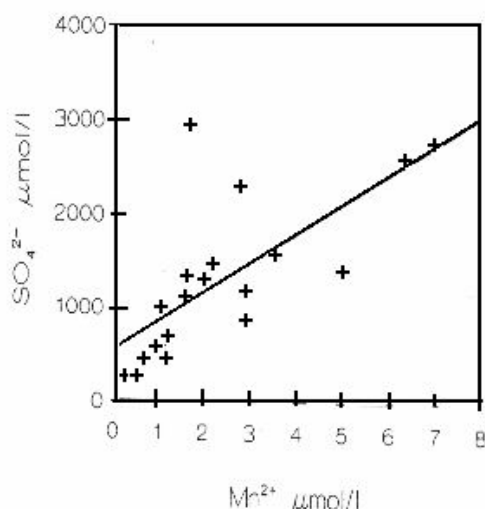


Figure 1. Concentrations of sulfate found in dew water.

3-CONCLUSIONS

Experiments spruces were exposed to H_2O_2 have shown that at concentrations comparable to those found in cloud water ($30 \mu\text{mol/l}$), H_2O_2 clearly effects plants [5,6,13]. The effects point towards a more rapid aging of the tissue, as well as to the occurrence of water stress.

The experiments described here show that the exposure to sulfite containing fog also leads to noticeable effects. Thus, it seems to be clear that components that are present in water layers deposited on plants in much lower concentrations than the major ions cannot be neglected in the contemplations regarding the processes that lead to plant damage. Formation of dew and deposition of fog water are of importance in these processes. The resulting water layer acts as a concentrating medium, as opposed to the layer that is formed during rain fall. The observed enhanced sulfate concentration found in dew sampled from

plants, the high Mn concentration, as well as the cloud chamber experiments indicate that the Mn that is leached from the plants increases the oxidation rate of S(IV). The positive correlation of the sulfate and Mn concentration in dew water, further more points in that direction. It is imaginable that radicals involved in the oxidation reaction in turn effect the leaf surface. The reported reaction rate for the Mn-catalyzed oxidation of S(IV) when applied to typical Bibalan night-time atmospheric conditions, leads to the conclusion that this catalytic oxidation is an important, possibly the most important, process for the formation of sulfate on plants during nights in which dew is formed. An important factor of course is that, the acidity of the dew is lowered by the relatively high NH_3 concentrations in the Iran.

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