

## Investigation of interactive effects of acid fog and ozone on spruce seedlings\*

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**Abstract**—Ozone and acidic fog are considered as two important factors to cause forest decline. In this study, laboratory experiment was carried out to simulate the effects of mountainous air pollution on spruce seedlings at high altitude with high content of ozone and high acidity of fog. Three aspects of analysis were performed: nutrient contents in needles; nutrient contents in washout solutions; epicuticular wax structure before and after exposure. All the results of three aspects were combined to interpret the effects of ozone and acid fog.

**Keywords:** air pollutant; forest decline; acidic fog; ozone; spruce.

### 1 Introduction

Serious incidences of forest decline were observed in many parts of the world and much effort has been placed in research to elucidate the major causes of the various decline phenomena. Possible causes have been discussed very controversially under most divergent aspects in the past. It is difficult to find out a general reason explaining forest decline in different regions of the world because of its complexity and diversity. Nevertheless, acidic precipitation and ambient ozone were considered widely as important factors (Prinz, 1989). The high ozone concentration and frequent, long-lasting acid fog occurrences were among the important pollution characteristics at higher altitudes of mountainous areas, where the more severe forest decline incidences were found. In China, with the 60% occurrence of acid fog and 40-50 ppb O<sub>3</sub> content as usual, Mt. Emei represents such a situation. This paper focussed on possible combinatory effects of different fog acidities and ozone concentrations with respect to needle nutrient content and nutrient leaching as well as the relationship between the two pollution factors. Furthermore, the impact of ozone and acidic fog on epicuticular wax structure of spruce needles was investigated.

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## 2 Materials and methods

Five year old Norway spruce seedlings (*Picea abies* (L.) Karst.) were grown in a standardized soil substrate for 2 years at the Experimental Station of the Landesanstalt für Immissionsschutz in Essen - Kettwig. Plants were fertilized and watered according to general procedures before fumigation. The nutrient content of the soil used, was (mg/L soil): N 247;  $P_2O_5$  205;  $K_2O$  357; Mg 91. Two plants were transferred to each of three van Haut chambers (Van, 1972), placed in a fully air conditioned greenhouse after three weeks of adaptation.

Trees were selected in such a way that the difference of total needle surface varied less than 10%, in order to make the leaching amount from the needles comparable.

Chambers (1m×1.2m×1.8m) were ventilated by charcoal filtered air at a rate of 250 air changes per hour. Ozone was produced from charcoal filtered air passing over a Sander ozone generator and fed to the air inlets of the chambers. Concentration measurements were executed continuously in plant height using a Datsibi ozone monitor. Monitor calibrations were executed to the specifications of the manufacturer. Fog water was prepared from distilled water and sulfuric acid and sprayed on plants via a high pressure air flow through special nozzles, forming droplets of about 10µm in diameter.

Fog droplets dripping of trees were collected with a funnel-shaped collector made from PVC-foilage for each tree. Volumes of sampled fog-water were determined and nutrient element contents of K, Ca, Mg and Mn analyzed. Representative samples of needles were taken at the beginning, middle and end of the experiment respectively, dried at 60° for 48 h before they were analyzed by standard procedures such as AAS and ICP. Simultaneously, needles were examined by scanning electron microscope (Zeiss DSM 950 with X-ray microprobe) and sputtered with gold directly after harvest, for further details of general methods of such experiments (Krause, 1989).

In present research, the experimental parameters were selected according to climatic situation and air pollution condition in mountainous areas at high altitude (Mohnen, 1988). The situation in Mt Emei, based on our investigation is: fog occurrence rate: 80% approx.; acid fog frequency 60% approx.; pH value 3.2 at lowest; 4.35 on average;  $O_3$  content 30-60 ppb. In order to obtain an obvious dose-effect results. The higher  $O_3$  content and stronger fog acidity than real situation were used in this short-term experiment, to speed up the processes.

Two major experiments were carried out;

(1) Effect of acid fog alone.

Experimental parameters: fog pH 2.8 (Chamber 1); 4.0 (Chamber 2); 5.0 (Chamber 3).

For each day, the exposure schedule was: from 9 pm to 3 am (18 hours) filtered air without acid fog; from 3 am to 9 am (6 hours) filtered air with acid fog.

Exposure period; 3 months.

(2) Interactive effects of acid fog and ozone.

Experimental parameters: fog pH 3.2 (Chamber 1); 3.2 (Chamber 2); no fog (Chamber 3); ozone 70 ppb (Chamber 1); 130 ppb (Chamber 2); 130 ppb (Chambers 3).

For each day, the exposure schedules was; from 9 pm to 3 am (18 hours) filtered air with ozone; from 3 am to 9 am (6 hours) filtered air with acid fog.

Exposure period; 1 month

### 3 Results

#### 3.1 Influence of acid fog

##### 3.1.1 Nutrient leaching form needles

Fig. 1 shows that the wash - out amounts of Ca, Mg and Mn increase with the increase of fog acidity. This change is very apparent; the wash - out amounts of Ca, Mg and Mn exposed to 2.8 pH fog are approximately 3-5 times as high as those exposed to pH 5.0 fog.

Potassium in the wash - out water shows no regularity and its wash - out behavior may depend on unknown factors.

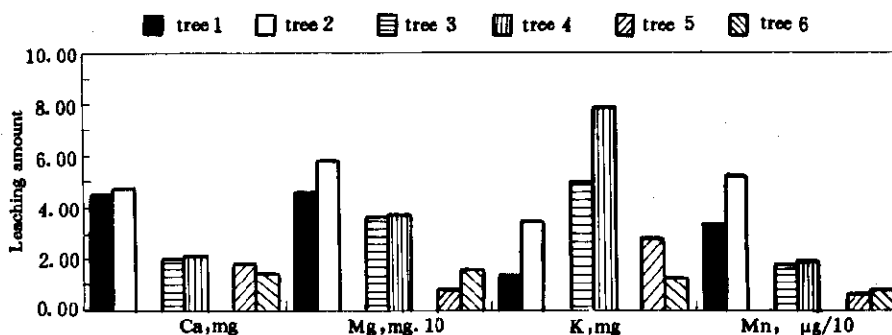


Fig. 1 Nutrient leaching with different fog acidity

Treatments: trees 1,2(pH 2.8); trees 3,4(pH 3.4); trees 5,6(pH 5.0)

##### 3.1.2 Nutrient content of needles

After about 3 months of exposure in experiment 1 and 1 month in experiment 2 nutrient contents of most elements in needles have increased but to a different extent (Fig. 2 and Fig. 4), although a considerable amount of nutrients were leached from the needles (Fig. 1 and Fig. 3). This phenomenon will be discussed later on. The relative change of nutrients between different treatments are considered as more important than their absolute change. To describe the nutrient changes and make them more comparable among the different treatments, the so - called change rate is used for discussion, which is the difference between needle content before and after the experiment related to the value before the experiment, and expressed as percent. As Fig. 2 shows, the change rates of Ca and Mg contents in the needles apparently get higher as the fog acidity decreases. As for Ca, it shows a distinct linear relationship with respect to fog pH. The increase rates at pH 5.0 are about 3 times as much as those at pH 2.8. The result agrees well with the result of the Ca, Mg leaching amount (Fig. 1). Similar to Fig. 1, potassium concentration in nee-

dles shows no regularity.

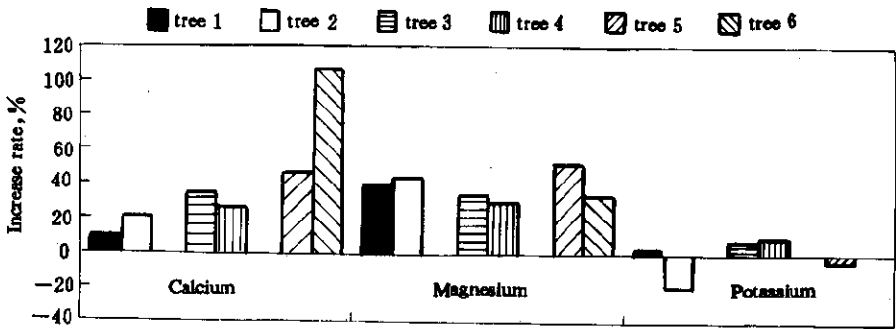


Fig. 2 Relative change of needle content before and after exposure to acid fog  
Treatments: trees 1,2 (pH 2.8); trees 3,4 (pH 3.8); trees 5,6 (pH 5.0)

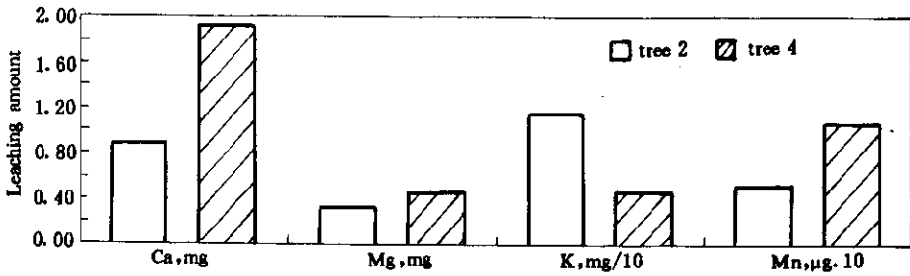


Fig. 3 Nutrient leaching for different fog acidities and ozone concentration  
Treatments: tree 2 (fog pH3.2, O<sub>3</sub>70 ppb); tree 4 (fog pH 3.2, O<sub>3</sub>130 ppb)

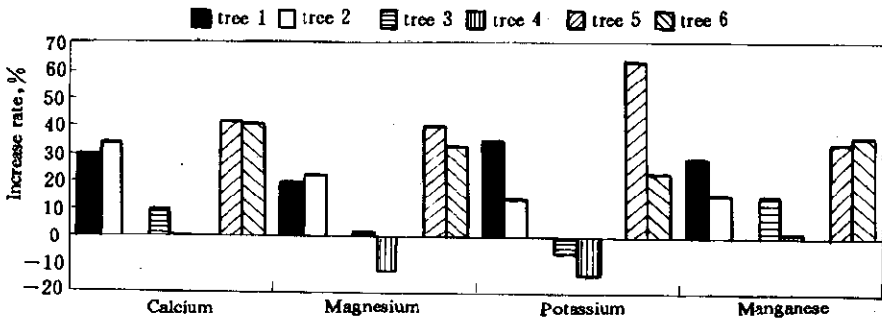


Fig. 4 Relative changes of needle contents effected by acid fog and ozone  
Treatments: trees 1,2(pH 3.2, O<sub>3</sub>70 ppb); trees 3,4 (pH 3.2, O<sub>3</sub>130 ppb); trees 5,6 (no fog, O<sub>3</sub>130 ppb)

3.2 Interactive effects of acid fog and ozone

3.2.1 Nutrient leaching from needles

It is clearly that acidic precipitation affects the forest growth with several ways, such as nutrients leaching from the needles; root damage caused by acidification of soils; pathogenic diseases. Present paper only focuses on the first one as, in mountainous areas at high altitude, the long-lasting acid fog plays a relatively important role for the forest decline.

The wash-out water samples from two trees were collected and analyzed for possible differences caused by the different ozone treatments, while pH was kept constant at 3.2 in the fog water. The result shows that the wash-out of Ca, Mg and Mn increased with increasing ozone concentrations (Fig. 3).

### 3.2.2 Nutrient content of needles

There are great differences in nutrient change between the trees exposed to the lower ozone concentration (70 ppb) and those exposed to the higher ozone concentration (130 ppb) for over all examined elements.

In Fig. 4, the difference between tree 3,4 and tree 5,6 represents the reduction of the nutrients caused by acid fog wash-out. The difference between tree 1, 2 and tree 3,4 represents the change caused by the two ozone regimes (70 and 130 ppb).

During the period of exposure, some new needles were budding. Those new needles were also sampled respectively and compared with the old needles of the same trees. The results are shown in Fig. 5. It is indicated that the Ca and Mn contents in new needles only have one-fourth and one-half respectively of those in old needles, while the Mg and K contents in the new needles are more than 1.5 times as high as those in old ones.

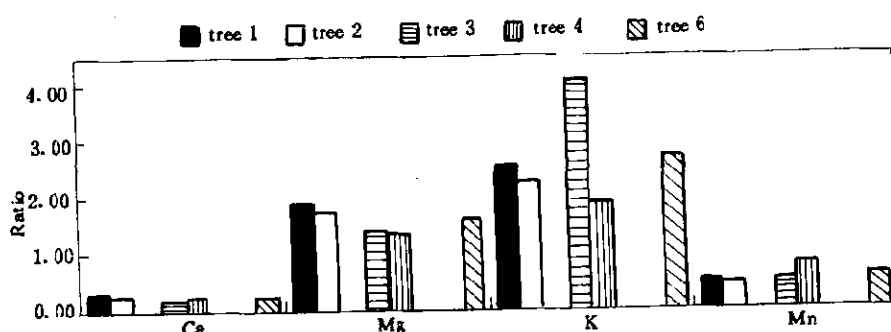


Fig. 5 Content ratio of new needles to old ones

Treatments: trees 1,2 (pH 3.2,  $O_3$  70 ppb); trees 3,4 (pH 3.2,  $O_3$  130 ppb); trees 5,6 (no fog,  $O_3$  130 ppb)

### 3.3 Epicuticular structure of the needles

Using an enlargement of 1000 times, the wax structures around stomata of spruce needles were investigated by scanning electron microscopy. For each tree, the samples were divided into three groups: group 1, needles older than 2 years (before exposure); group 2, needles older than

2 years (after exposure) and group 3 current year needles (after exposure, part 2). The results showed that group 2 needle wax structures from trees receiving 70 ppb ozone and fog treatments at pH 3.2 (tree 1 and 2) changed from granular structure into a solid one, and that the wax structures of current year needles were more or less unaffected. Similar effects were observed for older and current year needles of trees receiving 130 ppb ozone and fog treatments at pH 3.0 (tree 4 and 5). Only a slight change towards a wax solidification was observed in those needles of trees (tree 5 and 6) receiving just ozone (130 ppb).

## 4 Discussion

### 4.1 Effect of acid fog

Based on this experiment and considering both results of nutrient changes in needles as well as the results from leaching experiments by acid fog, it is quite evident that nutrient loss, especially for calcium depends on fog acidity ( $H^+$ -ion concentration). Supposing that the difference of calcium - needle content, shown in Fig. 2 is caused completely by washout, Ca - needle content was reduced by about 50% in comparison to controlled needles in the pH 2.8 treatment. Potassium leaching seems not to be influenced by pH, which agrees with other results (Krause, 1989; Guderian, 1987).

### 4.2 The interactive effect of ozone and acid fog

There are some contradictory conclusions on the effects of ozone and acid fog on needles. Saxe *et al.* (Saxe, 1990) who investigated one day short-term effects with high dose ozone and acid rain on spruce trees, suggested that there was little or no effects on epicuticular wax of needles. However, Elstner and Osswald (Elstner, 1985) as well as Karhu and Huttunen (Karhu, 1986) found ambient levels of ozone to change the epicuticular wax structure, with the consequence of increased fungal and insect attack. The present experiment shows a considerable effect of ozone and acid fog on spruce needles. All the three aspects show that there was the following clear interactive influence of ozone and acid fog:

(a) Nutrient change in needles (Fig. 4) is greatly different between different treatments.

(b) The wash-out amounts of the nutrients increase with the increase of ozone and fog acidity (Fig. 3).

(c) The epicuticular wax structure is damaged more seriously at the higher concentration of ozone and stronger acidity (The photos are omitted).

In recent investigation on Mt. Emei, a great forest death zone has been found around "Shuang shuijing", which coincides with its high frequency (>40%), low pH (<4.0) of acid fog and high  $O_3$  content (50 ppb). These suggest that the acid fog and  $O_3$  make great contribution to the forest death.

### 4.3 Compensation of high nutrient soil for leaching loss

In most cases of all the investigations, despite the increased leaching by acid fog and ozone, the nutrient contents in spruce needles still increase, but to a different extent. Similar results were also observed by Krause and Prinz (Krause, 1989), Guderian *et al.* (Guderian, 1987) as well as Turner and Tingey (Turner, 1989). The results shown in Fig. 2 and 4 can be ex-

plained as the comprehensive effects combining the increase of nutrients caused by time - dependent uptake from the soil and the decrease caused by acid fog wash - out. It is suggested by this assumption that, to some degrees, fertilizing of poor soils may help to compensate nutrient losses caused by wash - out of acidic precipitation in combination with ambient ozone concentrations.

## 5 Conclusions

The nutrient leaching from needles, caused by acid fog and ozone is recognized as quite a considerable effect on needle nutrients status. Furthermore, marked influences on the epicuticular wax structure of spruce needles due to the impact of acid fog and ozone could be demonstrated. However, plants growing in nutrient sufficient soils may well compensate the nutrient loss caused by wash - out and ozone (Tuckey, 1970). But, long term effects of both pollutant types under adverse soil conditions are important factors for reducing tree vitality so increasing the predisposition to other stress factors such as drought or pests (Krause, 1986).

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