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The pH Dependence of SO_2 Damage to Lichens

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Summary. In order to determine the influence of the hydrogen-ion concentration on the damage exerted to lichens by sulfur dioxide gas, thalli of the species *Hypogymnia physodes* and *Xanthoria parietina* were submerged in buffer solutions of pH 2 to pH 8 and subsequently exposed to SO_2 gas. Net photosynthesis was employed as a criterion of vitality.

The degree of damage to the lichens after exposure to 4 mg of SO_2/m^3 air for 14 hrs is dependent on the pH of the buffer solutions. *Hypogymnia physodes* shows the least damage at pH 7, *Xanthoria parietina* at pH 5 to pH 7. The degree of damage increases with increasing acidity. After exposure to SO_2 gas at pH 3 no apparent photosynthesis is achieved.

The different degrees of impairment are due to the fact that the concentration of the toxic products, resulting from the reaction of SO_2 and water, is dependent on the pH value.

The mere shift of the pH into the strong acid range of pH 3 and pH 2 damages the lichens with *Xanthoria parietina* being more seriously damaged than *Hypogymnia physodes*. Basicity, however, is already harmful to the lichens under test in the low range of pH 8. Here *Xanthoria parietina* is less affected than *Hypogymnia physodes*.

Introduction

Lichens react very species-specifically to SO_2 stress. Aside from physiological and morphological properties of the thallus the physico-chemical factors of the substratum play a part in the growth and survival of lichens in emission-loaded areas. Of importance are the buffer capacity and the hydrogen-ion concentration of the thalli and substrata. Numerous field observations (for instance, Brightman, 1959; Pišút, 1962; Gilbert, 1965, 1970; Rao and LeBlanc, 1967; Coker, 1967; Skye, 1968; Johnsen and Søchting, 1973) have revealed that lichens growing on substrata with a high buffer capacity and low acidity are able to advance farther into SO_2-loaded areas. Experiments with aqueous SO_2 or $Na_2S_2O_5$ -solutions that were set on different pH values (Gilbert, 1968; Hill, 1971; Baddeley *et al.*, 1971; Puckett *et al.*, 1973; Türk *et al.*, 1974) proved that the noxious effect of SO_2 is worse in the acid than in the neutral and basic range.

The model experiments dealt with in this paper were aimed at clarifying the question of what influence is exerted by the pH on SO_2-fumigation of lichens and of how harmful an effect is brought about by merely changing the pH value. As a criterion of vitality the CO_2 gas exchange was employed.

Materials and Methods

Hypogymnia physodes (L.) Nyl., from *Malus domestica*, Lauda, Baden, 280 m above mean sealevel.

Xanthoria parietina (L.) Th. Fr., from *Populus* spp. growing alongside of a highway, Lauda, Baden, 195 m above mean sealevel.

For the special purpose of the experiment *Hypogymnia physodes* was chosen as an acidophytic, and *Xanthoria parietina* as a subneutrophytic species.

The pre- and post-culture of the lichens, the measurement of the CO_2gas exchange and the calculation of the net photosynthesis were carried out as described by Türk *et al.* (1974). The treatment with buffer solutions and the gassing with SO_2 were conducted as follows:

After the first measurement of CO_2gas exchange the air-dried lichens (weight 0.5 g) were soaked in Erlenmeyer flasks filled with 50 ml of buffer solution; the reference samples were placed in distilled water. For the different pH steps we used the following buffer solutions at a concentration of 20 mM:

pH 2.0 and 3.0: sodium citrate+HCl;
pH 4.0: potassium hydrogen phthalate+HCl;
pH 5.0: potassium hydrogen phthalate+NaOH;
pH 6.0: sodium dihydrogenphosphate+di-sodium hydrogen phosphate 2-hydrate;
pH 7.0 and 8.0: tris(hydroxymethyl)-aminomethane+HCl.

For pH 2 and 3 we initially had used potassium hydrogen phthalate+HCl as buffer solutions. Under these circumstances, however, the lichens were damaged severely, whereas damage to lichens soaked for 24 hrs in a highly diluted HCl solution of pH 2 was considerably less severe. This supports the assumption that potassium hydrogen phthalate +HCl at a strongly acidic pH is a detrimental medium for lichens. Therefore, in the following experiments potassium hydrogen phthalate was exchanged for sodium citrate, which, as a mere buffer solution is harmless.

At each pH step two samples (in several experiments) were kept in the buffer solutions for 3 hrs, so as to impregnate the thalli completely with the buffer solution. After removal of the residual fluid which was still adhering to the surface, the content of buffer solution in the fully permeated thalli of *Hypogymnia physodes* was approximately 310% of the weight of the thallus in the air dried state; for *Xanthoria parietina* it was (approx.) 370%.

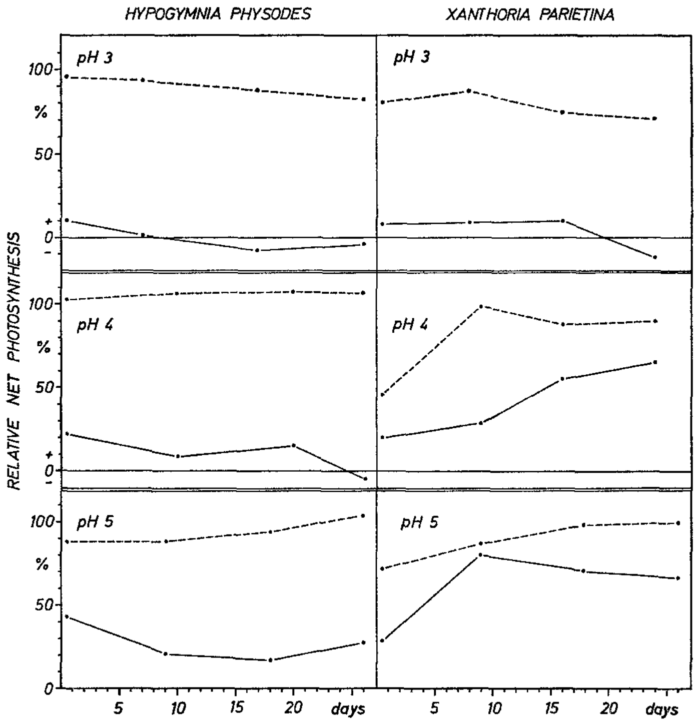
Then one of the two samples from each species was exposed to gas for 14 hrs in the dark at 10°C. The other sample, which was to serve the purpose of detecting the effect of the pH alone, was kept under the same conditions without being exposed to gas. The concentration of the gas-air mixture was 4 mg of SO_2/m^3 of air and the flow rate in the gas cuvette amounted to 100 l/hr, by means of which the loss of SO_2 in the cuvette due to SO_2 uptake by the thallus could be kept at a negligible rate (*cf.* Türk *et al.*, 1974).

After exposure to gas both samples, the gassed one as well as the un-gassed, were washed in distilled water for 10 min, then dried superficially by pressing the surface lightly against filter paper and finally placed in the CO_2-measuring cuvettes parallel with the reference samples. The rates of CO_2gas exchange of the samples treated with buffer solution and those of the additionally SO_2-gassed samples were related in percent to those of the samples that had been treated only with distilled water instead of buffer solution. In an additional experimental series samples were submerged for 24 hrs in buffer solutions at pH 2.

Results

The effect of gaseous SO_2 at different pH steps (solid line) and of different hydrogen-ion concentrations (no SO_2 exposure, dotted line) on the net photosynthesis of *Hypogymnia physodes* and of *Xanthoria parietina* are described in Fig. 1a and b. Treatment of the thalli of *Hypogymnia physodes* with buffer solutions at pH 4–6 has only negligible influence on net photosynthesis. Initially at pH 7 a slight stimulation of the net photosynthesis occurs, but in the course of the experiment photosynthetic activity decreases slowly to 90%. At pH 3 net photosynthesis is depressed slightly immediately after treatment with the buffer

Fig. 1. (a) Relative net photosynthesis (in percent of the normal values) after treatment of *Hypogymnia physodes* and *Xanthoria parietina* with buffer solutions and subsequent gassing with SO_2 (solid line) and after mere treatment with buffer solutions (dotted line) at pH 3 to 5. (b) The same as (a), but at pH 6 to 8


HYPOGYMNIA PHYSODES
XANTHORIA PARIETINA
RELATIVE NET PHOTOSYNTHESIS
pH 3
pH 4
pH 5
100
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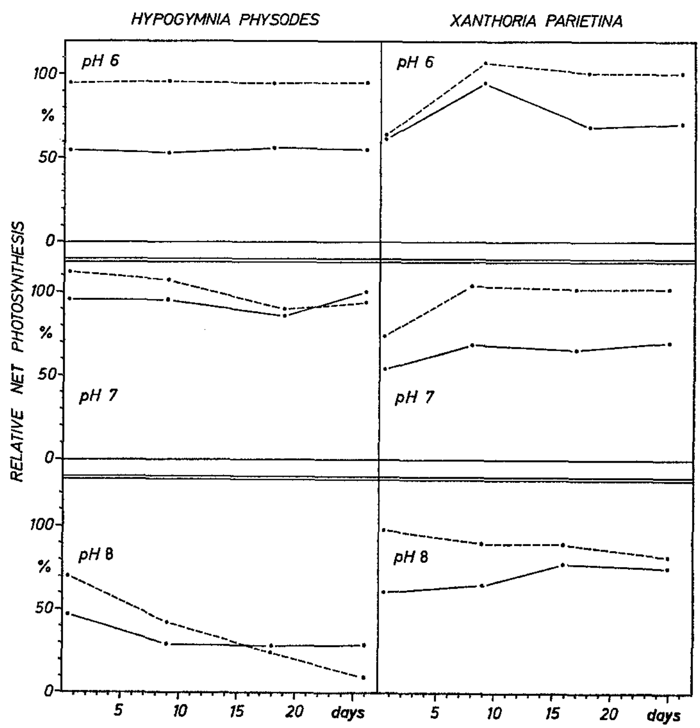
HYPOGYMNIA PHYSODES
XANTHORIA PARIETINA
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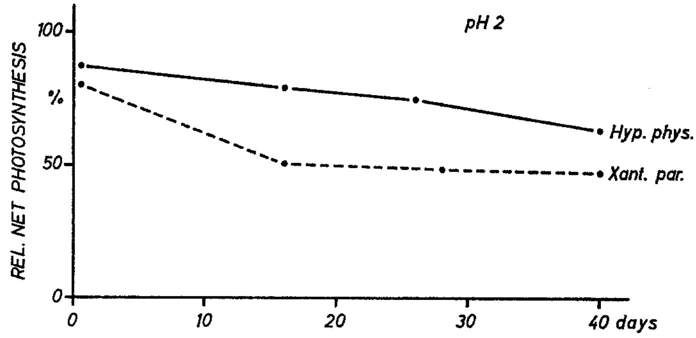

Fig. 2. Relative net photosynthesis (in percent of the normal values) after treatment of *Hypogymnia physodes* and *Xanthoria parietina* with buffer solutions at pH 2

solution. In the sequel, however, it keeps on decreasing steadily, which indicates a minor impairment.

The initially occuring minor reduction of CO_2 uptake at pH 7 is, after 14 hrs of gas-exposure, fully reversible. Net photosynthesis reaches even slightly higher values than with the sample treated only with buffer solutions. With declining pH the noxious effect of SO_2 increases. At pH 3 photosynthesis is very severely impaired and finally, about one week after gassing, the poor photosynthetic activity ceases completely.

Submersion in the basic range (pH 8) without subsequent exposure has a highly injurious effect. Immediately after submersion of the thalli the photosynthetic rate is reduced to 70% and keeps falling during the whole period of the experiment. Finally, after approximately 4 weeks, it reaches as little as 19% of the original capacity. The other sample, which has been exposed to SO_2 gas, initially suffers from a worse depression of apparent photosynthesis than the un-gassed sample. Then, however, the photosynthetic rate stays constant at about 30% for the entire length of the experiment and is in the end higher than the rates of the sample which had not been gassed.

With *Xanthoria parietina* the photosynthetic rate is decreased considerably immediately after treatment with buffer solutions of pH 4, 5, 6 and 7. In the subsequent course of the experiment, however, a pronounced recovery can be observed, which is complete at pH 5–7, and only slightly less at pH 4. The gassed samples also show a certain ability to recover, but the lasting lowering of the photosynthetic rate—also in the neutral range—indicates an irreversible impairment. At pH 3 *Xanthoria parietina* is damaged by the effect of the buffer solution slightly worse than *Hypogymnia physodes*. After exposure to SO_2 gas there is initially still some evidence of apparent photosynthetic activity, later on, however, CO_2 gas exchange falls below the compensation point. At all pH steps, except for pH 7 and pH 3, the gassed samples of *Xanthoria parietina* are less injured than those of *Hypogymnia physodes*.

As seen with *Hypogymnia physodes*, a shift of the pH into the basic region is also detrimental to *Xanthoria parietina*. The rate of photosynthesis at pH 8 is diminished in comparison with the rate at pH 7.

At pH 3 damage to both species is comparatively minor. To achieve a stronger effect of the treatment with buffer solutions another experimental series was arranged, in which the thalli of these two lichen species were submerged in a solution of pH 2 for a period of 24 hrs. *Hypogymnia physodes* is definitely less affected by this treatment than *Xanthoria parietina* (Fig. 2). The edges of the thallus lobes of both species bleach out after this treatment and this irreversible defect apparently parallels signs of chlorophyll destruction. One fact generally noticed is that the noxious effect of the hydrogen-ion concentration alone increases gradually (in the acidic region), whereas after exposure to SO_2 gas it either reaches its full intensity at once or in some cases decreases slowly.

Discussion

The foregoing experiments reveal that the noxious effect exerted by gaseous SO_2 on lichens depends on the pH value of the buffer solutions. In the highly acidic, as well in the basic range, lichens are affected even without being exposed to sulfur dioxide, by the effect of the pH alone.

SO_2 is only effective in connection with water. Completely dry lichens cannot take up any SO_2 and are not damaged by it (Türk *et al.*, 1974). The resulting products of the reaction of SO_2 and water, such as H_2SO_3, HSO_3^-, SO_3^{--} and $S_2O_5^{--}$ (Schmidt, 1972), occur in considerably different concentrations, the equilibria of which are dependent on temperature and pH. In this connection the equation $HSO_3^- \rightleftharpoons H^+ + SO_3^{--}$ is of special importance because the concentration rates of HSO_3^-/SO_3^{--} ions are dependent on the pH value. According to Seel (1967) the pK_s value of $HSO_3^- \rightleftharpoons H^+ + SO_3^{--}$ equals 7. Accordingly the ratio of HSO_3^--ions and SO_3^{--}-ions at a pH 7 is 1:1, at pH 6 it is 10:1 and at pH 4 is 1000:1, for instance[1]. Since damage is particularly large in the strong acidic region the assumption seems justified that the HSO_3^--ion is the more toxic component. Additionally all forms of water-dissolved SO_2 solutions become stronger oxidizers, the more the pH value is reduced (Puckett *et al.*, 1973). The irreversible impairment of photosynthesis at low pH values by SO_2 is correlated with destruction of the chlorophyll in the lichen algae, which is also indicated by the gradual bleaching of the thallus lobes.

If we compare the reactions of *Hypogymnia physodes* to a mere shift of the pH with those of *Xanthoria parietina*, we find that in the strong acidic range of pH 2 and 3 the latter species is more sensitive than the first one. These experimental findings correspond to the ecological range of the two species: *Hypogymnia physodes* prefers acidic substrata, whereas *Xanthoria parietina* prefers lightly acidic or neutral ones. Since the pH value of aqueous thallus extracts of *Hypogymnia physodes* from a natural habitat is 3.4 to 3.7 (own measurements), no damage is liable to occur above this pH. On the other hand, *Xanthoria parietina*, the aqueous thallus extracts of which have a pH of 6.0 to 6.8 (own measurements) tolerates submersion in a basic medium better.

If we apply the findings of our investigations to lichens with a close contact to their substrata, *i.e.*, to crustose and foliose lichens, we realize the prominent role of the pH value of the substratum as an avoidance factor against the effect

1 In Türk *et al.* (1974) the ratio is mistakenly reversed.

exerted by SO_2. Investigations on the distribution of lichens (including epilithic species) in cities and industrial areas with a high SO_2 emission have revealed that crustose lichens growing on basic substrata such as lime, mortar, or asbestos are able to endure high SO_2immissions (Beschel, 1958; Brightman, 1959; Pišút, 1962; Gilbert, 1970). Uptake of buffering substances into the lichen thallus is rather easy for crustose lichens and, to a certain degree, also for foliose lichens. In investigations on the $CaCO_3$ content of lichens growing on calcareous substrata, Syers *et al.* (1967) detected a clear relation between the growth forms of lichens and their $CaCO_3$content. Crustose lichens had a higher $CaCO_3$content than the foliose ones. Several investigations on the heavy-metal content of lichens prove the high absorbing capacity of crustose lichens for substances from the substratum (*e.g.* Lange and Ziegler, 1963).

In regards to the SO_2 stress, dissolved and absorbed substances in the lichen thallus can be of special importance by increasing the pH and the buffer capacity. This is proved by the findings of the investigations reported here, *i.e.*, that lichen thalli soaked with buffer solutions at higher pH values around the neutral region are distinctly more resistant to SO_2 damage than at pH values in the acidic range.

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