Sulphur content of Red pine (*Pinus brutia*) needles and bark as indicator of atmospheric pollution in Southwest Turkey

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Abstract. One-, two- and three-year-old red pine (*Pinus brutia* var. *brutia*) needles and tree bark samples were collected and analyzed for their sulphur content from localities where dead trees were observed. The results indicate that the sulphur content has increased in localities exposed to high levels of SO_2 emission. The highest increase was observed in two-year-old needles. We thus conclude that the sulphur content of two-year-old needles can be a bioindicator of some importance if the cause of tree death is known to be SO_2. The sulphur content of bark samples was found to be lower in less polluted areas.

Key words: *Pinus brutia*, red pine, Southwest Turkey, sulphur dioxide pollution, thermal power plant, tree death

Introduction

The study area

Our study area in Muğla includes the Bodrum peninsula (Fig. 1). Major streams are the Kanlı Dere and Kemer around Ören, and the Sarıçay in the vicinity of Milas. The other streams are dry outside the rainy season. The relief is quite varied, with mountainous terrain, high and low plateaux, plains, depressions, faults and deep valleys gouged out by erosion. The eastern part of the area rises from the sea level with steep escarpments and near-vertical slopes. High ranges and mountain passes extend east of the valleys, visible to travellers along the Milas-Ören highway. The maximum altitude in these areas is 1370 m, the average altitude of the high plateaux between 1000–1200 m and that of the low plateaux 100–500 m. Schist and gneiss are the dominant metamorphic rocks and for carbonated rock, limestone and marble. Magmatic rocks such as andesite and serpentine also occur. Gneiss rich in feldbas is prominent along the Sarıçay; karstic limestone predominates in other areas. The east side of the Milas-Ören highway, the area south of Milas and large areas of the Bodrum peninsula are of limestone. The lower soil layers near Milas have large amounts of schist and gneiss, ophiolitic gabbro and serpentine.

Climate

Data obtained from the nearest meteorological stations in Muğla (Milas, Yatağan and Bodrum) were evaluated. The total annual rainfall is 704.7 mm in Milas, 634.8 mm in Yatağan and 683.7 mm in Bodrum. More than half of it falls during the winter months and also in autumn and spring. There is hardly any precipitation in summer. Since 1980 we have observed a distinct decrease in the total rainfall of the region. This can be related to the greenhouse effect. The most important factor affecting the plant-cli-

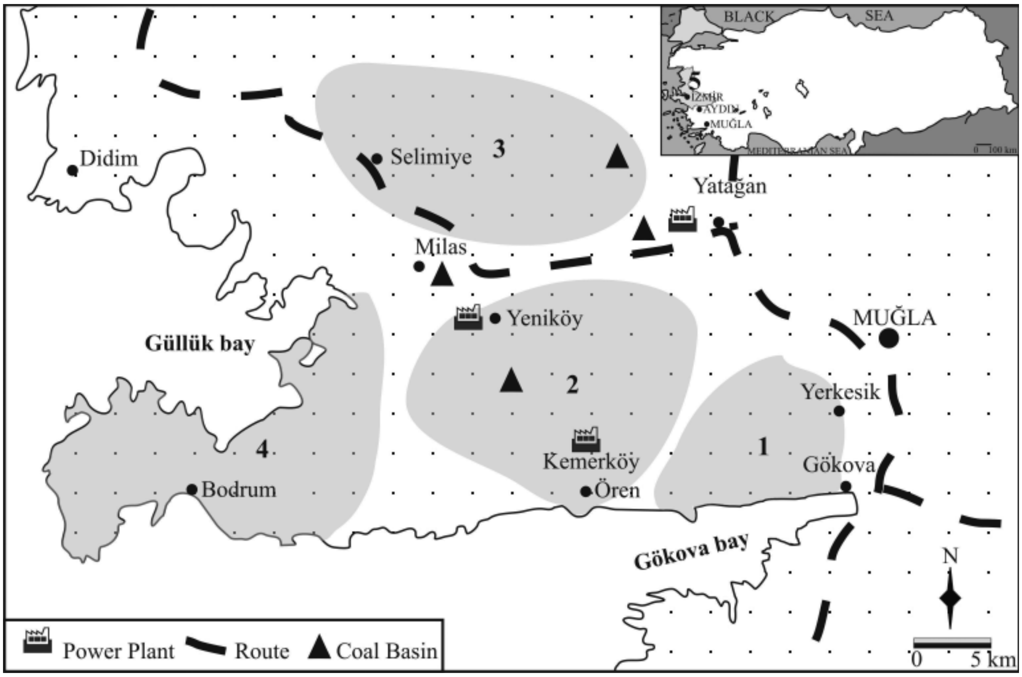

Fig. 1. Study area showing localities sampled (1-4).

mate relationships is that during the growing season rainfall is much under the desired levels and karstic terrain cannot hold rainwater, which percolates swiftly.

The average annual relative humidity in all three stations is ca. 60%. The average annual temperatures are 17.5°C in Milas, 15.9°C in Yatağan, and 18.6°C in Bodrum. Thus the study area is typically Mediterranean, with a winter rain regime. The general nature of such climate is arid in the dry months and slightly humid in the others.

Wind direction and force are influenced by topography. Since the study area is closed on the east side, winds blowing from this direction are very rare. Winds from the southeast are dominant in Muğla (frequency 23.1%), from the south in Milas (19.5%), and from the north in Yatağan and Bodrum (22.3% for Bodrum). The wind force in all three meteorological stations is either low (1.6–3.3 m/sec) or moderate (3.4–7.9 m/sec), and strong and very strong winds are quite infrequent. In addition to wind, one should not ignore the air movements created along the valleys. If wind directions play any role, chimney gas emissions from the Yatağan Thermal Power Plant are expected to move southwards, while emissions from the Yeniköy and Kemerköy power plants are expected to move northwards.

Thermal power plants

One of the largest coal basins in Turkey is located in the Muğla province, to the southwest. The coal mined in this basin has a low calorific level (an average 2241 Kcal/kg), with an ash content of 18.54%, sulphur content of 3.15% and water content of 37.75% (Gökmen & al. 1993). In a study conducted by Karayiğit & al. (2000) on Turkey's lignites, the sulphur content was found to range between 0.4% and 4.8%, which is relatively high. Three thermal power plants were built in the region in order to make use of the coal resources (Fig. 1). The first units in the Yatağan Thermal Power Plant were operational by 1982, in the Yeniköy Plant by 1986, and in the Kemerköy Plant by 1993. Two more units were later set up in the Yatağan and the Kemerköy plants. A total of 12 million tons of lignite coal is burned annually in these three plants. Although all plants have devices for desulphuration and are supplied with electric filters, the systems are not always functional and there are frequent breakdowns. The chimney gas emission (SO_2 production) in Yatağan was 5657 mg/NM^3, in Yeniköy 9196 mg/NM^3 and in Kemerköy 13103 mg/NM^3 prior to installation of the desulphuration systems. Post-installation values were noted to have decreased to 283 mg/NM^3, 460 mg/NM^3 and 650 mg/NM^3 respectively (*fide* Republic of Turkey Electricity Production Joint-Stock Company 2002, unpubl. report).

Power plants have been long pending on the problems agenda of the Turkish environmental protection laws owing to the pollution they are supposed to cause. After 1996, tree deaths in the red pine (*Pinus brutia* Ten. var. *brutia*) forests rekindled genuine attempts to solve the problem. The blame was placed on acid rain. The mountainous relief of the region and the existence of meteorological stations only in the larger towns have further affected the creation of a predictive model. Direct chimney gas measurements were not carried out in the areas suffering tree death.

Kantarcı (2003), who examined the effect of the three power plants on the forest vegetation located along the Yerkesik-Denizova strip (Fig. 1, locality 1) to the southeast of our study area, reported that these forests have started to dry up since 1998 and seem to be affected by the Yatağan and Yeniköy power plants. According to his studies, c. 1650 ha of forest area were damaged by the increased amounts of gaseous pollution, SO_2 in particular. It was reported between 1996 and 2002 that chlorophyll destruction, as well as narrowing of the annual rings width were linked to strong emissions of SO_2. Emissions from the three thermal power plants in the region were found to have caused an imbalance in ecological sensitivity which, in turn, in the long run has aggravated the economic losses in the area. Tree deaths were subject to court proceedings filed out by the Turkish Ministry of Forestry and Environment, and large amounts were demanded in compensation. In addition to the reports drawn up by Kantarcı and submitted to court, it was also found that the amount of sulphur in the needles of trees of different ages, which appear green or brown, varied between 4218–6674 ppm (Gemici 2003, unpubl. report).

Contrary to the findings of Kantarcı (2003) and Gemici (2003, unpubl. report), Günay (1985, unpubl. report) had analyzed earlier one-year-old needles in the study area, reporting that the sulphur content of the affected trees varied between 2600 ppm and 3400 ppm and that of healthy trees between 1100 ppm and 2100 ppm. On the other hand, Makineci (1997) determined a sulphur content of 2000 ppm in one-year-old needles in an area free of pollution. Tuna (2005) conducted studies on heavy metals in the study area and examined the sulphur contents of one-year-old needles over the seasons finding that the highest amount was 3500 ppm in spring and the lowest was 900 ppm in summer. According to him, the sulphur contents during the four seasons varied within the range of 900 ppm to 3500 ppm.

Drying out of pine needles exposed to SO_2, changes in needle anatomy, narrower tree rings, burning and damage of root tips in plants, and impoverishment of the flora, accompanied by disappearance of the endemic taxa, were all submitted as documentary evidence to the official court proceedings.

Plant susceptibility to sulphur dioxide damage varies according to the different plant categories and species. Cryptogams are known to be more susceptible than seed plants (Spermatophytes). The highest degree of susceptibility is known to occur in the following order: fungi, lichens, conifers, evergreen plants, deciduous plants. Lichens occurred in quantity in the study area; lichens and conifers are useful indicators due to their high susceptibility.

Sulphur dioxide primarily damages the protective waxy layer of the leaves. In broad-leaved plants damage occurs between the veins, visible as lesions. Strong toxicity first leads to the formation of red and orange-coloured spots at the leaf tips and circular lesions on the petioles. Leaf injury in conifers, however, starts with the formation of a yellowish-green colour at the needle apex, moving towards the base. The formation of greyish-green blisters in the parenchyma tissue is visible in leaf transverse sections. The chlorophyll is redistributed within the chloroplast and then transmitted to the cytoplasm. Another effect of sulphur dioxide acidity is the loss of root hairs at the root tips; this root burning is related to an increase in soil pH.

The sulphur content of soils in the region, wet and dry weights of the needles, chlorophyll analyses, pH measurements, relation not only with the pollutants but also with physical conditions, insect- and fungal-damage, were all investigated by the second author (Gemici 2003, unpubl. report). Parts of the report dealing with plant morphology, anatomy, physiology and ecophysiology were dealt with by the first author. Synthesizing all this in one article is beyond our present scope. However, we can report so far that our findings have failed to prove that SO_2 has a drastic killing effect.

Materials and methods

It is well known that tree bark is a bioindicator of atmospheric pollution (Odukaya & al. 2000). Five samples of tree bark as well as one, two and three-year-old red pine needles were collected from each of the four different localities in areas where tree drying was most evident during the months of December and January when vegetative growth of the red pine ceased.

Needles have been classified by the yearly growth of branches. Branch age was identified by the annual rings. One hundred samples of needle pairs were taken by the year 2002 towards the end of their growth period (November). The applied temperature for sample drying was 20–25 °C (room temperature) away from direct sunlight.

The selected trees were well-developed, firm and healthy, of comparable height (15 m), stem diameter (c. 40 cm) and age (c. 60 years). Control samples were taken from the Ege University Botanical Garden Applied Research Centre. The samples were pulverized, mixed and the mixture from each locality analyzed. The bark samples, c. 10 cm^2 in surface area and 3 cm thick, were collected from a stem height of 1.5 m and from the part facing the prevailing wind. Sulphur analyses were carried out at the soil laboratories of the Faculty of Agriculture. The 'wet digestion method' was used, whereby samples were treated with nitric and perchloric acid and the total amount of S (sulphur) determined by using an ICP (Inductively Coupled Plasma) spectrophotometer (Variant ICPAS). In that process nitrogen was used for conditioning the device and argon for obtaining the plasma.

The results were expressed in terms of ppm dry weight (Kacar 1984). The publications of Alpaslan & al. (1998) and Kacar & Katkat (1999) were referred to throughout our assay.

Results and discussion

A comparison of the sulphur content in one, two and three-year old needles from the four different localities is provided in Table 1. Locality 5 acted as the control group. Two-year-old needles had the highest internal sulphur values. In the 1st and 2nd localities, which were heaviest exposed to emission, the sulphur content of three-year-old needles was higher than the content of one-year-olds. No distinct differences were observed in one- and three-year-old needles from the other localities. The third locality was closest to Yatağan and Yeniköy thermal power plants, where the heaviest emission was measured. That is why the accumulation in samples was very high. Thus there was no significant correlation between one- and three-year-old needles in these localities. When expressed in percentage, the results showed a difference of 6.2 % between the one- and two-year-old needles in the first locality. In the second locality the difference was as high as 44 %. Completely opposite values were found in the needle samples from the third locality. Accordingly, the highest internal sulphur content (37 %) was measured in the one-year-old needles. In the 2nd, 3rd, and 5th localities, however, lower values were obtained. In the 4th locality, a decrease of 24 % was observed.

Table 1. Internal sulphur contents (ppm in dry weight) of red pine needles sampled from different localities.

	1-year-old needles	2-year-old needles	3-year-old needles	bark samples
Locality 1	1290*	1370*	1247*	606*
Locality 2	1340*	1930*	1655*	467
Locality 3	960*	1027*	823*	280
Locality 4	750*	935*	750*	450
Locality 5	680*	750*	690	400

*Mean difference significant at P< 0.05

Samples from Locality 2 (Sarıçay) were found to have the highest sulphur values (Fig. 2). This was followed by Locality 1 (Yerkesik). Both localities seem to be the strongest affected by the emissions. Locality 4 (Bodrum), however, seemed to have the lowest sulphur values. Sulphur values in it were quite comparable to those in the control group (Locality 5).

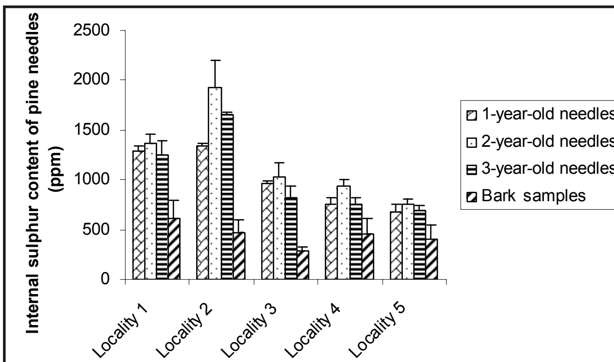

Fig. 2. Internal sulphur content of red pine needles sampled from different localities. Bars in columns show standard deviations.

Localities 1 and 2 witnessed the highest degree of needles drying-out related to high sulphur content, whereas in Localities 3 and 4 needles dried much less. Court records also contained references to the observed incidence of drying and tree deaths in Localities 3 and 4. We can confirm these observations as these regions were not so heavily exposed to emission. In fact, values obtained from Locality 4 were not much higher than in the control group. Locality 3, on the other hand, ranked third in the category of pollution, a finding corroborated by the sulphur content of the needles (Gemici 2003, unpubl. report). Although the values in Locality 4 were not much higher than in the controls, drying-out and tree death indicate that the threshold value is quite low, if caused by SO_2 emissions.

An examination of the sulphur contents of red pine bark revealed that the values were comparable to the findings obtained for the needles. The only difference between the first two localities was the rank in both cat-

Figs 3-4. Trees of red pine in the research area (between Ôren and Sarniç) affected by sulphur dioxide emission – the drying-out effect.

egories. The highest value was obtained in Locality 1, followed by Locality 2. The same was true for Localities 3 and 4. The fact that the sulphur content in bark samples from Locality 3 was even lower than that in the control group may be due to the fact that the trees selected for sampling were very healthy individuals.

The earlier studies conducted on red pine have failed to provide meaningful values, as there were significant differences and discrepancies in the sulphur values obtained. Thus for both the control area and the areas exposed to SO_2 emissions, values for one- and three-year-old needles were below 700 ppm and those for two-year-old needles were c. 750 ppm. The normal values for the bark samples were found to be c. 400 ppm, except from Locality 3. In Turkey, red pine is listed as a species with a moderate level of vulnerability. The sulphur content in the leaves of some other species growing in the same maquis has also been analysed (Gemici 2003, unpubl. report). It was found that *Olea europaea*, *Pistacia lentiscus* and *Lavandula stoechas* had comparatively high sulphur levels within the range of 2480, 2440 and 1790 ppm. On the other hand, there was no significant difference for *Cistus creticus* (average 1050 ppm in locality 1 and 1350 in control samples).

Sulphur is one of ca. 10 essential macro elements. It is extremely important not only for plants but also for organ building in all living organisms. Sulphur deficiency can lead to serious growth disorders. However, excessive amounts of sulphur contribute to environmental problems. The increased rate of sulphur dioxide emission was one of the reasons to object against the existence of coal-burning power plants in the Muğla region. A large number of soil, plant and water samples had been collected in a study to determine the actual increase in sulphur dioxide (Gemici 2003, unpubl. report). Sulphur dioxide increases soil acidity as a consequence of acid rain. According to Ramade (1982), no plant can possibly tolerate the amount of sulphur dioxide in the atmosphere exceeding 1 ppm. The maximum level of sulphur dioxide in the atmosphere has been accepted as 0.1 ppm. Sulphur does not move freely within the plant but is fixed shortly and altered into sulphate. This situation can occasionally create problems when determining the total amount of sulphur in plants. In a study conducted on *Pinus sylvestris* L. needles of various ages, Rautio & al. (1988) stated that the levels of sulphur were often higher in young needles and the high total sulphur concentration in needles comprised particles deposited on the waxy layer. Sulphur concentration on the waxy layer can be double the internal sulphur content. According to Mirov (1967), shoots and young branches of pine trees are covered with waxy substances of different concentration. This corroborates the findings of Rautio & al. (1988) that the total sulphur content is higher in young branches. Far greater amounts of waxy substance are found on *Pinus sylvestris* needles as compared to red pine not only by virtue of different anatomical and physiological features but also by adaptation to colder climatic conditions. The highest internal sulphur values obtained in our present study were in two-year-old needles. These needles can be a valuable indicator of SO_2 emissions. Our data is in agreement with the findings of Rautio & al. (1988). The sulphur content was highest in the 1^{st} and 2^{nd} localities, which had the greatest number of dead trees as demonstrated by 100 % of needles drying-out (Iles 1998), followed by the 3^{rd} and 4^{th} localities, which had fewer dead trees. Sulphur content in the tree barks was also correlated, except for the 3^{rd} locality.

Correlation between climate characteristics and the levels of SO_2 in the different localities

The data obtained by us from the meteorological stations in the area were also considered. Northerly winds of high frequency are dominant in Yatağan and Bodrum and carry chimney gas emissions from the Yatağan Power Plant, depositing them in Locality 1. Thus tree deaths in that locality are correlated with the power plant emissions. The highest sulphur concentrations were found in that locality. Chimney gas emissions from the Yeniköy Power Plant in Milas are brought to the north by the southerly winds prevalent in that area. Locality 2 has the second highest degree of dead trees. Localities 3 and 4 have a lower sulphur concentration because the chimney gas emissions are not moving so much in their direction. Thus tree deaths in these two localities are much lower than as observed in Locality 1 and 2. Thus there is a proven direct relation between the wind direction and concentration of sulphur deposition in the needles and tree bark.

According to Kantarcı (2003), sulphur content ranges between 4218–6674 ppm in the 1st locality (with the greatest number of tree deaths). According to Tuna (2005), the sulphur content in old needles from healthy trees ranges between 800–2500 ppm, varying with the seasons. Our survey has indicated this amount to be between 1247–1370 ppm in healthy trees in the 1st locality and that the sulphur content in the research area in general was between 750–1930 ppm. Our findings for healthy trees support the values found by Günay (1985, unpubl. report) but are below the 2000 ppm level obtained by Makineci (1997).

The total annual rainfall has been also observed to have decreased in the area since 1980 and tree deaths have been associated with physiological decline of the trees due to drought.

Our results are compatible with those obtained by Matziris & Nakos (1978), Bussioti & Ferreti (1998), and Velissariou & al. (1992).

However, one should refrain from upholding that the increase in internal sulphur content of the needles is the direct cause of tree death in red pine. It is more likely that physiological weakness has been aggravated by increased atmospheric SO_2 pollution when the trees were already affected by water deficiency, dust or insect-attacks (the pest *Blastophagus minor* is quite common in the research area), and pollution has facilitated their decline. Grodzinska (1971, 1982) demonstrated that pH and conductivity differences in bark extracts can be used to estimate the level of air pollution and the mosses growing on tree bark are an important indicator. In a study carried out in W Anatolia, which includes our research area, Tuncel & Yenisoy-Karakas (2003) found that lichens were accumulators of air pollution. High levels of heavy metals were found in lichens in our research area.

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