TOXIC HAZARDS OF THE INDUSTRIAL ATMOSPHERIC POLLUTANT, SO_2 , on tree crops

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THESIS

submitted in partial fulfilment of the requirement for the degree MASTER OF SCIENCE IN AGRICULTURE Faculty of Agriculture

Kerala Agricultural University

1.

Department of Soil Science and Agricultural Chemistry COLLEGE OF AGRICULTURE Vellayani – Thiruvananthapuram

DECLARATION

I hereby declare that this thesis entitled "Toxic hazards of the industrial atmospheric pollutant, SO₂, on tree crops" is a bonafide record of research work done by me during the course of research and that the thesis has not previously formed the basis for the award to me of any degree, diploma, associateship, fellowship, or other similar title, of any other University or Society.

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20-05-1993

CERTIFICATE

Certified that this thesis, entitled "Toxic hazards of the industrial atmospheric pollutant, SO₂, on tree crops" is a record of research work done independently by Kumari Rani, B. under my guidance and supervision and that it has not previously formed the basis for the award of any degree, fellowship, or associateship to her.

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INTRODUCTION

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1. INTRODUCTION

Advances in Science and Technology have brought about progress in many spheres of development, but in the process, also contributed to pollution of air, land and water so much so that development has become synonymous with deforestation and desertification, and progress with pollution. The significant and sometimes devastating effects of air pollutants on vegetation have long been recognized. In fact, much of our concern with air pollution has revolved around these effects on vegetation. While urban smoke was sufficiently unpleasant to be classed as a nuisance in early ordinances, the failure of crops and the death of trees gave dramatic proof of the adverse effects of air pollution. The harmful effects of pollution have been experienced both in the geological times owing to lava and ash from volcanoes, and in historical times since the middle ages, particularly from the beginning of the fourteenth century, when coal began to be used. Brick kiln disease of mango in Uttar Pradesh has been traced to sulphur dioxide emitted from the brick kilns, However, in recent years there has been considerable resurgence of interest in the subject owing to widespread and alarming reports of the damage caused by air pollution.

major sources of air pollution are The transportation, industry and power generation. The air pollutant causing the maximum damage, is sulphur dioxide, the others being ozone, peroxy acetyl nitrate (PAN), nitrogen dioxide, fluoride, particulates. While in the world 300 million tonnes of pollutants are emitted annually in air. India contributes about 10 million tonnes in the form of particulates, sulphur dioxide, carbon monoxide and hydro carbons (Khoshoo, 1989).

The combustion of fossil fuels for domestic and industrial purposes, coupled with rapid industrial growth over the past 150 years, has resulted in sulphur dioxide (SO_2) becoming an integral part of the environment. Extensive research into the effects of sulphur dioxide on vegetation began in the 1920's and is testimony to the fact that twentieth century industrialisation has resulted in a steady increase in the rate of this pollutant's emission. Over the years, sulphur dioxide emission in India is on the increase and the projections are that by the year 2000 it would be reaching around 13.19 million tonnes as against 6.67 million tonnes in 1979 (Kumar and Sharma, 1981).

After emission, sulphur dioxide disperses and reacts with other substances of sinks, such as land , water and vegetation. Sulphur dioxide may cause adverse effects on

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vegetation where industry and forests are close together. It adversely affects serious physiological and biochemical processes which may lead to growth and yield reductions in plants (Last, 1982; Malhotra and Khan, 1984). It may bring about indirect effects in the environment by acidifying precipitation and consequently bringing about changes in the soil reaction even in areas distant from industrial centres.

Sulphur dioxide is a reducing gas and is 2.7 times heavier than air. The phytotoxicity of sulphur dioxide is ascribed to its oxidation-reduction potential. It undergoes a rapid hydration and one volume of water can dissolve 80 volumes of sulphur dioxide (228 g/litre). When damp air is polluted with oxides of sulphur droplets of water containing sulphurous and sulphuric acids are also present, causing a complex pattern of pollution. The increase in H⁺ ion concentration decreases the pH of leaf tissues which upsets plasma membrane functions and under extreme conditions, causes degradation of chlorophyll 'a' by displacing the Mg²⁺ ion from the chlorophyll molecule (Rao and Le Blanc, 1966). A fundamentally more serious mode of attack of sulphur dioxide is the ability to cleave disulphide linkages. Since the tertiary structure of many enzymes are dependent on the integrity of their disulphide bonds, destruction of this would deactivte them.

Sulphur dioxide itself tends to be more toxic to plants than sulphuric acid aerosols, which is in contrast to the situation in vertebrates. Some higher plants are damaged by concentrations of 0.02 ppm sulphur dioxide and higher, the magnitude of the effect depending on the period of exposure.

Kerala, though atmospheric pollution is not IΠ a widespread problem, it is becoming a matter of great concern in areas of industrial activity. The gases emitted by the D.C.D.A. Sulphuric acid plant of Titanium Complex (Kochuveli, Thiruvananthapuram), are suspected to contain toxic levels of sulphur dioxide. The acid mist of the plant also is a source of sulphur dioxide pollution. The Travancore Titanium Products at Kochu Veli. Thiruvananthapuram, is concerned with the manufacture of dioxide, using the locally available mineral sand Titanium and concentrated sulphuric acid ilmenite through the sulphate process.

In and around the factory, coconut is the major tree crop. It is the most important perennial tree crop of Kerala and plays a major role in its economy. By virtue of its geographical distribution, covering the whole of the intertropical zone of the globe, the coconut interests a

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large section of the world population, for wham it represents the sole source of fats. With the use of modern growing techniques, coconut has become an oil crop whose per hectare production is approaching that of oil palm. In view of this, the present study was designed to assess the effect of the industrial atmospheric pollutant, sulphurdioxide, on tree crops such as coconut. The study envisages , the changes in the sulphate content of the foliage and chlorophyll content in relation to severity of necrosis and leaf damage in coconut trees. The study aims at elucidating the effects of sulphur dioxide pollution on the various leaf constituents and nut characters of the coconut palm, like:

- a) sulphate sulphur
- b) potassium, calcium and magensium
- c) micronutrients
- d) chlorophyll and other pigments
- e) glucose and ascorbic acid content
- f) catalase activity, and also
- g) the copra and oil content of nuts.

REVIEW OF LITERATURE

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2. REVIEW OF LITERATURE

Though environmental pollution by natural sources has been known to mankind from time immemorial, pollution of our surrounding atmosphere due to industrial activity is of recent origin. The present century has witnessed environhazards causing damage to vegetation, land, water mental and the atmosphere. Among the pollutants causing plant injury, sulphur dioxide is most potent. The phytotoxic effects of the sulphur dioxide emitted from smelters, were first investigated in Europe, primarily in Germany, about the middle of the nineteenth century. These studies related to forest productivity and yield of agronomic crops, and were made with reference to point sources of pollution (Schroeder, 1873; Haselhoff and Lindau, 1903). Since then; considerable work on the effects of sulphur dioxide has ben done throughout the world. In India, sulphur dioxide on vegetation have been recognized as a major air pollutant in urban and industrial areas (Chakraborty and Rao, 1962; Yennwar et al. 1970). But research into the effects of sulphur dioxide on vegetation in these polluted areas were started only recently. (Chaphekar, 1972; Pandey, 1983). Majority of the work on the effect of sulphur dioxide on vegetation were related to growth parameters rather than the biochemical

effects. A brief review of the literatures on the effects of sulphur dioxide on plants is given in the following pages.

2.1 Effect of sulphur dioxide on the sulphur content of plants

Sulphur is necessary for the general metabolism of plants since it is a major constituent of aminoacids, proteins, and some vitamins. In healthy leaves sulphur content ranges from 500 to 14,000 ppm by dry weight (0.5 to 14 mg g^{-1}) depending on species (Treshow, 1970). In areas where the atmosphere is polluted with sulphur dioxide, the plants were reported to accumulate sulphur in various forms.

2.1.1 Total sulphur

Giudice (1975), in a study on the alterations attributable to scorching by sulphur dioxide on lemon plants found the leaves and fruits damaged. When healthy and affected parts were analysed for various elements, a much higher sulphur content was found in the damaged organs.

Rates of absorption of sulphur dioxide and translocation of absorbed sulphur were determined in sugar maple (<u>Acer saccharum</u>), big tooth aspen (<u>Populus grandidentata</u>), white ash (<u>Fraxinus americans</u>) and yellow birch (<u>Betula</u> <u>alleghanienses</u>). The foliar sulphur contents of all species

were increased with sulphur dioxide fumigation (Jensen and Kozlowski, 1975).

Farrar <u>et al</u>. (1977 a) observed that the occurrance of <u>Pinus sylvestris</u> was negatively correlated with needle sulphur content and that the needle sulphur content was positively correlated with sulphur dioxide levels.

Farrar <u>et al</u>. (1977 b) reported that the leaf sulphur content increased in trees of <u>Pinus sylvestris</u> exposed to about 5 pphm sulphur dioxide.

Jäger and Klein (1977) found a greater accumulation of inorganic sulphur in pea plants exposed to 0.1 to 0.25 ppm sulphur dioxide than in untreated controls.

Sidhu and Singh (1977) conducted a survey for sulphur dioxide damage near a liner board mill. It was found that most of the damage was restricted to within 0.8 km of the source of pollution. The incidence and intensity of the damage varied between species and between sites. About 48 to 157 per cent increase in total sulphur was noticed in the sampled trees.

Materna (1978) reported increased sulphur content in needles of norway spruce plants exposed to concentrations of sulphur dioxide between 0.24 and 0.4 mg m⁻³ air during the growing season for six successive years.

Kim <u>et al</u>. (1979) reported an increased sulphur content in soyabeans treated with sulphur dioxide.

Accumulation of sulphur from the air and soil by leaves of many woody plants were studied by Sergeichik (1979). It was observed that many plants absorbed sulphur from the air.

Fumigation of lu = erne, oats, rice, soyabean etc. with 0.3 to 0.9 ppm. sulphur dioxide was conducted by Ichikawa <u>et al</u>. (1980). They reported that the sulphur content of all species were increased.

An increase in total sulphur content of nine rice cultivars treated with 1 mg/litre hour sulphur dioxide was reported by Kim and Han, 1980.

Mishra (1980) observed an increased accumulation of sulphur when <u>Arachis hypoqaea</u>L. was exposed to fumigation concentrations of sulphur dioxide ranging from 0.06 to 1.00 ppm for six weeks. The sulphur accumulation increased with increasing concentrations of sulphur dioxide.

Biggs and Davis (1981 a) reported an increase in leaf sulphur content when two year old seedlings of <u>Betula</u> <u>spp</u> were exposed to 2358 μ g m⁻³ sulphur dioxide.

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Biggs and Davis (1981 b) further reported a higher sulphur content of the abscised foliage of hybrid poplar clone 'NE-388' (0.9 to 1.7 per cent dry weight) exposed to suplhur dioxide when compared to the untreated controls (0.24 to 0.32 per cent dry weight).

Elkiey and Ormrod (1981 a) reported an increase in sulphur content of certain grass species fumigated with sulphur dioxide.

An accumulation of total suplhur in leaves of Petunia plants exposed to 80 pphm sulphur dioxide was reported by Elkiey and Ormrod (1981 b).

Keller (1981 a) reported that leaves of maple, larch, elm and aspen exposed to sulphur dioxide fumigation upto 0.225 ppm absorbed the gaseous pollutant directly from air.

Keller (1981 b) fumigated grafts of <u>Picea excelsa</u> clones with 0.025, 0.075 or 0.225 ppm sulphur dioxide for three months. Soon after fumigation an increase in sulphur content was observed.

Milchunas <u>et al</u>. (1981) exposed western wheat grass to three levels of sulphur dioxide (55, 100 and 170 μ g m⁻³). Significant increases in plant suplhur content were observed, both with time and level of sulphur dioxide exposure.

Maly (1982) reported increased sulphur content of wheat, rye and oats when subjected to long term exposure of sulphur dioxide at 90 mg m⁻³.

Prasad and Rao (1982) observed an increase in the sulphur content of soybean and wheat exposed to 1 ppm sulphur dioxide for 2 hours/day.

Sulphur dioxide fumigations of upto 0.4 ppm, increased the sulphur concentrations in the leaves of soybean (Pratt <u>et al</u>. 1983).

Saxe, 1983, reported that the total sulphur content of <u>Phaseolus vulgaris</u> grown in water culture with separate air supply to roots, for 4-5 weeks, at five sulphur dioxide levels of 10-950 μ g m⁻³ was increased with time and concentrations of sulphur dioxide.

L'Hirondelle and Addison (1985) observed an increase in sulphur levels in <u>Pinus banksiana</u> seedlings exposed to 0.1 to 1.0 ppm sulphur dioxide for 0-96 hours. As sulphur dioxide concentration and duration increased the sulphur levels increased significantly.

Lockyer (1985) exposed plants of <u>Lolium</u> spp, <u>Dactylis</u> <u>olomerata</u> and <u>Phleum</u> <u>pratense</u> to mean sulphur dioxide concentrations of 0, 87 or 448 μ g m⁻³. It was observed that the total shoot sulphur concentration was increased almost linearly with increasing sulphur dioxide concentration.

Stratigakos and Ormrod (1985) found a significant increase in total sulphur content when tomato plants grown with 1.6, 16 or 80 ppm sulphate sulphur in nutrient solution were exposed to 0.1 or 0.4 ppm sulphur dioxide.

Krishnamurthy <u>et al</u>. (1986) observed a 30 per cent increase in sulphur in the leaves of <u>Eucalyptus longifolia</u> and <u>Peltophorum ferrugineum</u> and 70 per cent more sulphur in <u>Bauhinia tomentosa</u> when compared with unpolluted controls.

Lorenzini and Panattoni (1986) reported an increase in total sulphur content of sunflower, maize and soybeans exposed to sulphur dioxide.

Increased sulphur levels were reported in needles of <u>Pinus sylvestris</u> fumigated with high levels of sulphur dioxide by Schulz (1986).

Hasebe <u>et</u> <u>al</u>. (1987) reported an increase in the sulphur content of leaves of pear, peach, grapevine and apple with an increase in fumigation time or sulphur dioxide concentration.

Niedzwiecki and Madej (1988) conducted studies on Scotspine, planted in 1977-'79 and 1.0 and 2.5 km away from

a power station. It was found that only 50 per cent of the trees survived. The data when compared with unpolluted sites 100 km away showed that the sulphur content of the needles were higher than that of the controls.

Pierre and Queiroz (1988) reported an increased sulphur accumulation in spruce needles due to sulphur dioxide air pollution.

Lorenzini <u>et al</u>. (1990) subjected cultivars of wheat, barley and maize to long term fumigation of 68 ppb sulphur dioxide. The increase in sulphur content of plants ranged from 190.7 to 276 per cent.

Schätzle <u>et</u> <u>al</u>. (1990) reported an increased sulphur level in needles of fir seedlings and spruce, fumigated with sulphur dioxide.

2.1.2 Sulphate sulphur

Many researchers have reported an increase in sulphate sulphur contents of plants, where the atmosphere contained sulphur dioxide concentrations higher than normal.

Markowski <u>et al</u>. (1974) studied the effect of sulphur dioxide on sunflower, tobacco, maize, bean and barley. They found an increase in the sulphate sulphur content which was much higher when treated under optimum soil moisture conditions than under drought. Legge <u>et al</u>. (1977) subjected pine and aspen to sulphur dioxide and hydrogen sulphide exposures from a natural gas processing plant near White court, Alberta, Canada. Levels of 300-700 ppm sulphate sulphur occured in the leaves, with the older foliage showing slightly higher values. The ambient sulphur dioxide concentrations were generally less than 0.05 ppm.

Accumulations of sulphate sulphur in leaves of petunia exposed to 80 pphm sulphur dioxide were reported by Elkiey and Ormrod (1981 b).

Lockyer (1985) observed accumulated sulphate sulphur in lolium plants exposed to sulphur dioxide.

A significant increase in sulphate sulphur was reported by Stratigakos and Ormrod (1985) in tomato plants exposed to 0.1 or 0.4 ppm sulphur dioxide. The ratio of sulphate sulphur to total sulphur increased after the 0.4ppm exposure.

Kok <u>et al</u>. (1987) reported a rapid accumulation of sulphate in soybean, spinach and <u>Trifolium pratense</u> due to sulphur dioxide exposure.

Maas <u>et al</u>. (1987a) observed an increase in the content of sulphate sulphur in the shoots and roots of spinach plants exposed to sulphur dioxide when compared to normal plants. Nutrient analysis of the foliage of a pine hybrid was done by Amundson <u>et al</u>. 1990, to determine whether chronic exposure to sulphur gas emissions had affected nutrient status of trees. Significant inverse linear relationship was found between foliar sulphate sulphur and distance from the sulphur source. Sulphate sulphur increased with increasing age of foliage at sites near the source and decreased at sites not frequently exposed to sulphur dioxide.

2.2 Effect of sulphur dioxide pollution on plant nutrients

2.2.1 Effect on macro nutrients

2.2.1.1 Nitrogen `

Mishra (1980) noted a decrease in nitrogen content in <u>Arachis hypogaea</u> L. exposed to fumigation concentrations of sulphur dioxide ranging from 0.06 to 1.00 ppm for 4 hours daily for 6 weeks, with increasing concentraions of the pollutant.

Elkiey and Ormrod (1981 a) reported that the nitrogen levels may sometimes be raised in Kentucky blue grass cv. Cheri, Mercori and Touchdown fumigated with sulphur dioxide.

A reduction in nitrogen content was observed in wheat cv. Mironoskaya, rye cv. Kustro, spring barley cv. Amethyst, Dats cv. Tiger, red clover, lucerne, silage maize and potato which were subjected to long term exposure to sulphur dioxide at 90 mg m⁻³ (Maly, 1982).

Martinez <u>et al</u>. (1983) noted a decrease in nitrogen levels in tomato plants with increasing sulphate concentraion in the growing medium.

2.2.1.2 Effect on phosphorus content

A decrease in the phosphorus content was reported in <u>Arachis hypoqaea</u> L. exposed to sulphur dioxide by Mishra (1980).

Flagler and Youngner (1985) reported a reduction in the phosphorus concentration of the forage, tall fescue due to sulphur dioxide fumigation. The weight per plant of phosphorus was also reduced . Significant pollutant interactions occured with total phosphorus contents of forage.

2.2.1.3 Effect on potassium content

Tomassini <u>et al</u>. (1977) found a release of potassium ions from the lichen <u>Cladina</u> <u>rangiferina</u> (L) due to treatment with aqueous sulphur dioxide. Materna (1978) noted an increase in potassium content in the needles of norway spruce plants exposed to sulphur dioxide.

An increased potassium content was reported by Saxe (1983) in <u>Phaseolus vulgaris</u> exposed to sulphur dioxide concentration of 950 μ g m⁻³.

Jurat and Schaub (1988) fumigated shoots of <u>Picea</u> <u>abies</u> seedlings grown in nutrient solution with sulphur dioxide for 60 days. The uptake rate of K^+ by fumigated seedlings increased at first but later decreased when compared with control plants.

Decreased potassium content was reported by Niedzwiecki and Medej (1988) in scots pine in a polluted area when compared with unpolluted controls.

2.2.1.4 Effect of sulphur dioxide on the calcium content of plants

Martinez <u>et al</u>. (1983) reported a decrease in calcium levels in tomato plants with increasing sulphate concentration in the growing medium.

Bender <u>et al</u>. (1986) fumigated 8 - year - old norway spruce, silver fir and beech trees with sulphur dioxide together with simulated acid rain (pH 4.0). He noticed a decreased calcium content in the foliage. Jurat and Schaub (1988) fumigated shoots of <u>Picea</u> <u>abies</u> seedlings grown in nutrient solution with sulphur dioxide for 60 days. The uptake rates of Ca^{2+} by fumigated seedlings increased at first but later decreased when compared with control.

Niedzwiecki and Madej (1988) reported decreased calcium content in needles of scotspine (<u>Pinus sylvestris</u>) in a polluted area when compared with unpolluted sites 100 km away.

A decreased calcium content was observed by Schätzle <u>et al</u>. (1990) in needles of fir seedlings and spruce, fumigated with sulphur dioxide and simulated acid rain as background stress.

Seufert (1990) reported a leaching of calcium ions from canopies of spruce, fir and beech subjected to low level exposure of sulphur dioxide and simulated acid rain.

There are contradictory reports also on the effect of sulphur dioxide pollution on the plant content of calcium.

Materna (1978) reported an increased calcium content in norway spruce exposed to sulphur dioxide.

Saxe (1983) reported an increased calcium content in <u>Phaseolus vulgaris</u> (beans) exposed to 950 μ g m⁻³ sulphur dioxide.

2.2.1.5 Effect on magnesium

Malhotra (1977) found a loss of Mg²⁺ ions from needles of <u>Pinus contorta</u> treated with aqueous sulphur dioxide concentrations of 100-500 ppm.

A reduction in weight per plant of magnesium by sulphur dioxide was reported by Flagler and Youngner (1985) in tall fescue forage. Significant pollutant interactions occured for total magnesium contents of forage.

A decreased magnesium content of forage was reported in silver fir, norway spruce and beech trees fumigated with sulphur dioxide together with acid rain (pH 4.0) by Bender <u>et al</u>. (1986).

Jurat and Schaub (1988) noted that the uptake rates of Mg^{2+} by seedlings of <u>Picea</u> <u>abies</u> fumigated with sulphur dioxide increased at first but later decreased compared with control.

Seufert (1990) observed leaching of magnesium ions in spruce, fir and beech subjected to low level exposure to sulphur dioxide for long periods. An increased magnesium level was reported by Materna (1978) in needles of 4 - year - old norway spruce exposed to sulphur dioxide.

2.2.1.6 Effect of sulphur dioxide pollution on micronutrients

Results of a study on sulphur accumulation on beech and spruce stands in the Solling mountains by Rehfuess (1981) indicate that toxic rates of aluminium and manganese may eventually develop.

Saxe (1983) found that bromine, chlorine, manganese and zinc increased when <u>Phaseolus</u> <u>vulgaris</u> (beans) grown in water culture was exposed to sulphur dioxide levels of 10 to 950 μ g m⁻³.

Bender <u>et al</u>. (1986) noted an increased magnesium level in 8-year-old norway spruce, silver fir and beech trees fumigated with sulphur dioxide.

The contents of zinc in needles of <u>Pinus niora</u> from a polluted area averaged 84 ppm and was almost twice as high as that found in needles of control (Oleksyn et al., 1987)

Niedzwiecki and Madej (1988) observed an increase in the contents of aluminium and manganese in scotspine in a

polluted area when compared with controls in an unpolluted area 100 km away.

Bender and Jäger (1989) reported increased manganese levels in the foliage of <u>Abies</u> <u>alba</u>, <u>Picea</u> <u>abies</u> and <u>Fagus</u> <u>sylvatica</u> exposed to sulphur dioxide.

Amundson <u>et al</u>. (1990) conducted nutrient analysis of foliage from a naturally occuring hybrid of <u>Pinus contor-</u> <u>ta</u> and <u>Pinus banksiana</u> to determine whether chronic exposures to sulphur gas emissions had affected nutrient status of trees. The manganese concentrations in foliage from sites near the source was significantly higher than that of foliage from sites away from the source.

Schätzle <u>et</u> <u>al</u>. (1990) reported an increased manganese level in needles of fir seedlings (<u>Abies alba</u>) and spruce (<u>Picea abies</u>) fumigated with sulphur dioxide in open top chambers.

Seufert (1990) observed a leaching of manganese and zinc from canopies of spruce, fir and beech seedlings subjected to low exposure to sulphur dioxide.

2.3 Effect of sulphur dioxide pollution on the ascorbic acid content of plants

Keller and Schwager (1977) studied the changes in ascorbic acid content of the forest trees, larch and pine due to sulphur dioxide fumigation. They found that ascorbic acid was highly susceptible to sulphur dioxide with the content dropping drastically both under darkness and under light.

A decrease in the ascorbic acid content was noted in norway spruce plants exposed to concentrations of sulphur dioxide between 0.24 to 0.4 mg m⁻³ air (Materna, 1978).

Keller (1981 b) found a decrease in the ascorbic acid content of grafts of <u>Picea excelsa</u> (<u>P.abies</u>) clones fumigated with sulphur dioxide concentrations of 0.025, 0.05 and 0.225 ppm continuously for three months in open air fumigation chambers.

Prasad and Rao (1982) reported a reduction in ascorbic acid content in soybean and wheat exposed to sulphur dioxide.

Lotstein <u>et al</u>. (1983) noticed a slight but significant decrease in ascorbic acid content of potted tomato plants exposed to sulphur dioxide at 288 to 314 µg m⁻³. A multiple regression analysis indicated a weak and indirect but significant association between plant sulphur content and ascorbic acid content of fruits.

A decrease in ascorbic acid content was reported by Nandi <u>et al</u>. (1984 a) when field grown rice plants were exposed to either 0.25 or 0.5 ppm sulphur dioxide for 1.5 hours daily for 40 days.

Krishnamurthy <u>et al</u>. (1986) reported a decrease in ascorbic acid content in leaf samples of Eucalyptus and Peltophorum in polluted areas of Baroda where there were low concentrations of sulphur dioxide from a petrochemical plant, when compared to unpolluted plants.

Agrawal <u>et al</u>. (1987) observed that the development of visible injury symptoms were preceded by a decrease in ascorbic acid content in 45-days-old rice plants treated four times at 7 days intervals with 0.5 ppm sulphur dioxide for one hour.

2.4 Effect of sulphur dioxide on the sugar content of plants

There are varying reports regarding the effect of sulphur dioxide on the sugar content of plants.

Materna (1978) observed a decrease in glucose, fructose and sucrose content in norway spruce plants exposed to sulphur dioxide concentrations at a rate of 0.24 to 0.4 mg m⁻³ during the growing season for six successive years.

A reduction in carbohydrate content was reported in soybean and wheat exposed to 1 ppm sulphur dioxide for 2 hours/day by Prasad and Rao (1982).

Farooq <u>et al</u>. (1985) reported an increase in free sugar accumulation, especially reducing sugars, in tissues, associated with depletion of starch in <u>Holoptelea</u> <u>integrifolia</u> plants (Chilbil tree) exposed to 0.06, 0.1 and 0.8 μ L L⁻¹ sulphur dioxide for four hours in a continuous flow chamber.

L'Hirondelle and Addison (1985) found a decrease in fructose levels in ten weeks old <u>Pinus banksiana</u> seedlings exposed to 0.1 to 1 ppm sulphur dioxide for 0 to 96 hours, as the concentration of pollutant and duration of exposure increased. The changes in fructose levels were small and gradual.

Bender and Jäger (1989) reported changes in sugar content in young <u>Abies alba</u>, <u>Picea</u> <u>abies</u>, and <u>Fagus</u> <u>sylvatica</u> exposed to realistic concentrations of sulphur dioxide and acid rain (pH 4) for four years in open top chambers.

2.5 Effect of sulphur dioxide pollution on lipid concentration

Malhotra and Khan (1978) treated excised needles of <u>Pinus banksiana and Pinus contorta</u> Dougl var. latifolia Englim with either gaseous or aqueous sulphur dioxide. They noted a decreased lipid biosynthesis due to sulphur dioxide treatment and the effect was found to be more pronounced in the developing than in the fully developed needles.

A decrease in lipid concentration was reported by Constantinidou and Kozlowski (1979) in <u>Ulmus</u> <u>americana</u> seedlings due to sulphur dioxide exposure at 2 ppm for 6 hours.

2.6 Effect of sulphur dioxide on catalase activity

Nandi <u>et al</u>. (1980) exposed germinating seeds of <u>Phaseolus</u> <u>aureus</u> to 0.25 ppm sulphur dioxide in air tight closed exposure chambers for 1 hour. The catalase activity of the seedlings, when compared with the control, 72 hours after exposure, were found decreased.

Field grown rice plants were exposed to either 0.25 or 0.5 ppm sulphur dioxide for 1.5 hours daily for 40 days by Nandi <u>et</u> <u>al</u>. (1984a). The catalase activity was decreased due to exposure and the effect was dose dependent.

2.7 Effect of sulphur dioxide on plant pigments

The adverse effects of sulphur dioxide on the chemical composition and the contents of plant pigments is 'well establised.

2.7.1 Total chlorophyll

Studies with hinger plants exposed to sulphur dioxide have shown decreases in total chlorophyll content.

Markowski <u>et al</u>. (1974) reported a decrease in chlorophyll content in sunflower, barley and maize and an increase in chlorophyll content was observed in tobacco, broad bean and bean when exposed to sulphur dioxide.

Malhotra (1977) found that aqueous sulphur dioxide concentrations of 100 to 500 ppm resulted in a sharp decrease in total chlorophyll content of pine needles and that the breakdown of chlorophyll molecules by sulphur dioxide as measured by the loss of Mg^{2+} ions and total chlorophyll, was accompanied by a decreased ability of pine needles to photosynthesize $H^{14}CO_3$.

Suwannapinunt and Kozlowski (1980) reported a reduction in chlorophyll content in black locust seedlings fumigated <u>in situ</u> with sulphur dioxide at 0.75 ppm.

Liu <u>et al</u>. (1980) observed a decomposition of chlorophyll in wheat seedlings exposed to 0.5 to 100 mM NaHSO₃ concentration. It was suggested that as the response of segments to NaHSO₃ was the same as the response of plants to sulphur dioxide, the system could be used a model for investigation of sulphur dioxide injury.

Significantly lower chlorophyll contents were found in Arctic forage lichens fumigated with sulphur dioxide by Moser <u>et al</u>. (1980).

Henriksson and Pearson (1981) noticed a progressive decrease in chlorophyll content in the lichen <u>Pettiqera canina</u> exposed to increasing concentrations (0.1⁻¹ to 50 ppm) of sulphur dioxide.

Prasad and Rao (1982) observed a reduction in chlorophyll content in soybean and wheat exposed to 1 ppm sulphur dioxide for 2 hours per day.

Murray (1984) reported that many eucalyptus species were sensitive to continuous exposure to low concentrations of sulphur dioxide.

Nandi <u>et al</u>. (1984 b) exposed field grown cowpea plants to 0.25 ppm sulphur dioxide for 1.5 h daily for 40 days, within polythene chambers. They observed a significant reduction in total chlorophyll. A reduction in the chlorophyll contents of norway spruce, silver fir and beech trees fumigated with sulphur dioxide was reported by Bender <u>et al</u>. (1986).

Kumar (1986) studied the changes in the chlorophyll content of <u>Viqna radiata</u> plants exposed to 0.25 ppm sulphur dioxide. A drastic reduction was noted in the total chlorophyll content of the exposed plants.

Exposure of <u>Oryza</u> <u>sativa</u> plants to 670 and 1330 μ g m⁻³ sulphur dioxide revealed that the chlorophyll content of the treated plants remained below that of the control (Nandi <u>et al.</u>, 1986).

A decrease in the chlorophyll content of sunflower was reported by Lorenzini and Panattoni (1986) when the plants were exposed to 74 ppb sulphur dioxide.

Ayer and Bedi (1990) reported a reduction of chlorophyll content due to artificial fumigation of <u>Zea mays</u> L.var. American Sweet corn to sulphur dioxide.

2.7.2 Chlorophyll `a'

Malhotra (1977) reported a conversion of chlorophyll 'a' into phaeophytin a in <u>Pinus contorta</u> treated with aqueous sulphur dioxide concentrations of 100 to 500 ppm.

Destruction of chlorophyll 'a' of spinach 2 to 3 hours after fumigation with 2 ppm sulphur dioxide under light was observed by Shimazaki <u>et al</u>. (1980). Chlorophyll 'a' destruction by sulphur dioxide in leaf disks did not occur in darkness or under nitrogen.

Lauenroth and Dodd (1981) conducted field trials in South East Montana where exposure of western wheat grass to 60 to 175 μ g SO₂ per m³ decreased the concentration of chlorophyll 'a' without causing any visible plant necrosis. The sensitivity also increased with the time of exposure.

A reduction in chlorophyll 'a' was observed by Saxe (1983) in <u>Phaseolus vulgaris</u> (bean) exposed to five sulphur dioxide levels of 10 to 950 μ g m⁻³ for 4 to 5 weeks.

Karolewski (1985) reported a statistically significant reduction in chlorophyll 'a' in leaves of poplar CV Robusta cuttings with increasing length of exposure to 0.75 ppm sulphur dioxide.

Stratigakos and Ormrod (1985) found a reduction in chlorophyll 'a' content when tomato plants were exposed to sulphur dioxide concentrations of 0.1 ppm.

Nandi <u>et al</u>. (1986) noticed a reduction in chlorophyll 'a' in rice plants exposed to 670 and 1330 μ gm⁻³ sulphur dioxide during tillering and flowering stages. 2.7.3 Chlorophyll 'b'

Malhotra (1977) reported a destruction of chlorophyll 'b' due to aqueous sulphur dioxide treatment of <u>Pinus contorta</u> at 10 to 50 ppm.

Lauenroth and Dodd (1981) noted a reduction in chlorophyll 'b' concentration in western wheat grass exposed to sulphur dioxide.

A reduction in chlorophyll 'b' in <u>Phaseolus</u> <u>vulgaris</u> exposed to sulphur dioxide, was observed by Saxe (1983).

Karolewski (1985) reported a statistically significant reduction in chlorophyll 'b' in leaves of poplar with increasing length of exposure to sulphur dioxide.

Stratigakos and Ormrod (1985) observed a reduction chlorophyll 'b' content of tomato plants exposed to sulphur dioxide.

Nandi <u>et</u> <u>al</u>. (1986) noted a reduction in chlorophyll 'b' in rice plants exposed to sulphur dioxide.

Singh <u>et al</u>. (1988) found that seedlings of <u>Dahlia</u> <u>rosea</u> planted in the field and fumigated under polytheme covers with sulphur dioxide at 1 or 2 ppm for 2 hours on alternate days, showed a decrease in the chlorophyll 'b' content. There are also contradictory reports on the effect of sulphur dioxide on chlorophyll 'b' content.

Beckerson and Hofstra (1979) treated leaves of <u>Phaseolus</u> <u>vulgaris</u> (White bean) with 0.15 ppm sulphur dioxide. They noted a sudden increase in chlorophyll 'b' content.

Shimazaki <u>et al</u>. (1980) reported that chlorophyll 'b' was undamaged when spinach leaves were fumigated with sulphur dioxide (2 ppm) under light.

Anbazhagan and Bhagwat (1992), in a study of the response of 21-day-old rice plants to sulphur dioxide fumigation, reported a degradation of chlorophyll 'b' contents in all the three cultivars tested.

2.7.4 Carotenoids

A reduction in carotenoid contents was reported by Shimazaki <u>et al</u>. (1980) in spinach leaves fumigated with sulphur dioxide.

Prasad and Rao (1982) reported a reduction in carotenoid content in soybean and wheat exposed sulphur dioxide at 1 ppm for 2 hours per day.

Nandi <u>et</u> <u>al</u>. (1986) observed a reduction in carotenoid content in rice plants exposed to sulphur

dioxide. A similar reduction was noted by Singh and Rao (1986) in <u>Phaseolus aureus</u>.

A decreased carotenoid content was reported by Singh <u>et al</u>. (1988) in field planted <u>Dahlia</u> <u>rosea</u> seedlings exposed to sulphur dioxide at 1 or 2 ppm for 2 hours on alternate days.

MATERIALS AND METHODS

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3. MATERIALS AND METHODS

The present study was undertaken to assess the effect of sulphur dioxide pollution on tree crops such as coconut. The toxic effects of sulphur dioxide on plant nutrients, leaf pigments and nut characters of coconut palm were investigated.

3.1 Experimental site

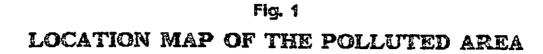
The study was confined to the Veli area of Thiruvananthapuram district where sulphur dioxide toxicity is high due to the working of the Titanium complex.

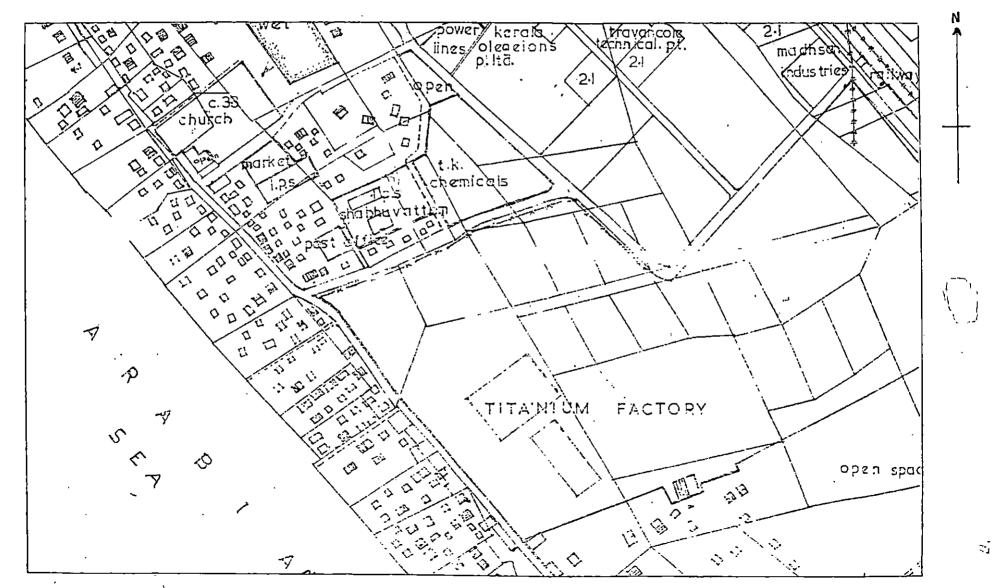
3.2 Experimental material

Leaves and nuts of the affected and healthy coconut palms were taken to have a comparative study of the toxic effects of the industrial atmospheric pollutant, sulphur dioxide.

3.3 Selection of samples

Plant samples were collected from coconut palms of about the same age, around the Titanium factory at Kochuveli in Thiruvananthapuram district.





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The samples were collected from five radial distances taking the factory as the focal point at 250, 500, 1000, 1500 and 2000 metres. Control samples from palms of the same age were also collected from a distance of 5000 m, from the same radii around the factory. Two palms were sampled from each distance in a radius. The soil of the area from where palms were selected for sampling was texturally sandy.

3.4 Collection of leaf samples

The fourteenth leaf was sampled from the selected palms at each distance, for analysis. This leaf is regarded as one which has reached physiological maturity but has not entered the phase of senescence (Zillar and Prevot, 1962). The procedure adopted for collection and preparation of leaf samples were according to the specifications described by I.R.H.D. The fourteenth leaf was selected from each palm and five leaflets each, from either side of the middle of the frond were removed. The central 15 cm portions from each leaflet were taken for analysis.

3.5 Preparation of leaf samples

The leaflets collected were rinsed in distilled water to remove the adhering soil particles. The cleaned leaflets were dried at 70° C until constant weight was

* Institut de Recherches pour les Huiles et Oleagineux

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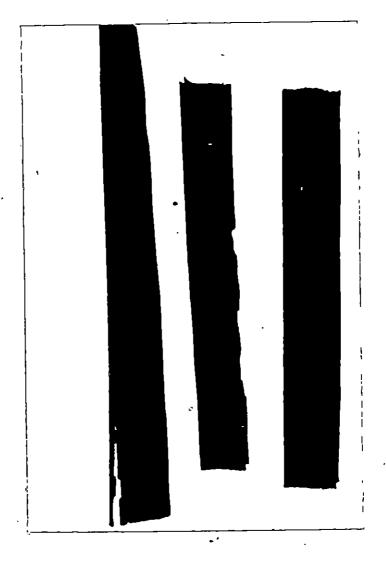


PLATE 1

Leaflets affected by sulphur diaxide pollution

obtained. The dried samples were then powdered and stored in airtight polythene bottles for nutrient analysis. Fresh samples without drying were used for estimating the catalase activity, vitamin C content and chlorophyll contents.

3.6 Sampling of nuts

Two mature nuts were collected at random from each , palm selected for leaf analysis, for recording the nut characters.

3.7 Leaf sample analysis

The estimation of leaf nutrients were done by the following methods.

3.7.1 Nitrogen

The nitrogen content of the leaf samples were estimated by the microkjeldahl method (Jackson, 1973).

3.7.2 Phosphorus

The triple acid digest was prepared by digesting the powdered leaf samples with a triacid mixture consisting of nitric, perchloric, and sulphuric acids in the ratio of 10:4:1. Phosphorus content of leaf samples were estimated from the triple acid digest by the vanadomolybdate method (Jackson, 1973).

3.7.3 Potassium

Potassium was estimated from the triple acid digest by employing Atomic Absorption Spectrometry using a Perkin-Elmer (Model No.3030) Atomic Absorption Spectrophotometer.

3.7.4 Calcium and Magnesium

Calcium and magnesium in the leaf samples were also estimated from the triacid mixture by Direct Flame Absorption Spectrometry using a Perkin-Elmer Atomic Absorption Spectrophotometer (Model No.3030).

3.7.5 Total sulphur

Sulphur was estimated in an aliquot prepared by the wet oxidation of leaf by the diacid mixture (Jackson, 1973). Sulphur in the aliquot was determined turbidimetrically as per the procedure outlined by Chesnin and Yien (1951).

3.7.6 Sulphate sulphur

Fresh leaf samples were homogenized in water for the estimation of sulphate sulphur. The homogenized mixture was filtered and an aliquot was taken for the estimation of sulphate sulphur by the same turbidimetric method of Chesnin and Yien (1951) as described above. samples.

3.7.8 Boron

The boron content of the plant samples were estimated by the curcumin method (Jackson, 1973).

3.7.9 Molybdenum

Total molybdenum of the dried leaf samples were determined by the thiocyanate method of Jackson (1973).

3.7.10 Chlorine

The chlorine content of plant samples were determined by digestion with nitric acid and potassium permanganate in the presence of excess silver nitrate to precipitate chloride as silver chloride. The excess silver was titrated with potassium thiocyanate in the presence of acetone using ferric iron as indicator (Anon, 1972).

3.7.11 Other micronutrients

Other micronutrients like manganese, zinc, and copper were estimated from the triacid digest using an Atomic Absorption Spectrophotometer (Perkin-Elmer Model No.3030).

3.7.12 Beneficial elements

Aluminium and sodium concentrations in the samples were also determined using the Perkin-Elmer Atomic Absorption Spectrophotometer (Model No.3030).

3.7.13 Glucose

For the estimation of glucose, the dried, ground, plant samples were extracted with 80 per cent ethyl alcohol. The extract was clarified using sodium oxalate and lead acetate and the glucose content of the clear extract was estimated by the copper reduction method using Fehling's solution (ADAC, 1975).

3.7.14 Ascorbic acid

The ascorbic acid content of the fresh leaf samples were estimated by titrating the oxalic acid extract of the same with 2,6 dichlorophenol indophenol, a redox indicator dye (Gyorgy and Pearson, 1967).

3.7.15 Catalase activity

The method as outlined by the ADAC (1975) was followed for the estimation of catalase activity in the leaf samples.

3.7.16 Leaf pigments

The representative leaf samples were homogenized in cold 85 per cent acetone and centrifuged to get the clear extract. The optical densities of the extracts were measured at wavelengths of 480 and 510 nm for carotenoids and at 645 and 663 nm for chlorophyll 'a' and 'b' in a Spectronic 2000 Spectrophotometer. The amounts of carotenoids were calculated using the formulae of Richards and Thompson (1952), and those of total chlorophyll, chlorophyll 'a' and 'b', by the formulae of Starnes and Hadley (1965).

3.8 Nut characters

The various nut characters were recorded by the following methods:

3.8.1 Weight of husked nut

The nuts collected from the palms were dehusked and the average weight was recorded.

3.8.2 Weight of shell per nut

The average weight of shell per nut was recorded after removing the kernel from the nuts.

3.8.3 Weight of fresh meat per nut

The weight of fresh meat was obtained by subtracting the weight of shell from the weights of husked and split nuts.

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3.8.4 Weight of copra / nut

The split nuts were sundried uniformly for seven days to get copra. The total weight of copra obtained at each distance was taken and the average weight recorded.

3.8.5 Copra content

The percent copra in relation to the weight of fresh meat was calculated and the average value recorded.

3.8.6 Fresh meat to copra ratio

The ratio of the average weights of fresh meat and copra of the two nuts sampled at a distance in a radius was recorded to obtain the ratio of fresh meat to copra.

3.8.7 Husked nut to fresh meat ratio

The ratio of the average weights of husked nut and copra of the two nuts sampled at a distance in a radius was recorded to obtain the ratio of husked nut to fresh meat.

3.8.8 Husked nut to shell ratio

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The average weights of husked nut and shell of the two nuts sampled at a distance in a radius was recorded and their ratios calculated.

3.8.9 Dil content

The oil content was estimated by solvent extraction with carbon tetrachloride by the cold percolation method developed by Kartha and Sethi (1957).

3.9 Statistical analysis

The data pertaining to the various characters were analysed statistically by applying the technique of analysis of variance. Correlation and regression studies were also made to determine the interrelation of leaf constituents and nut characters with total sulphur and sulphate sulphur (Panse and Sukhatme, 1967).

RESULTS

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4. RESULTS

The results of the study conducted to assess the impact of sulphur dioxide as an air pollutant on coconut palms are summarised in the following pages. The palms in the polluted area showed a high degree of chlorosis and necrosis of leaves with increased degree of leaf necrosis accompanied by malformation of young leaves in palms closer to the factory. Chemical analyses of such leaves and nuts were made to assess the extent of damage caused by sulphur dioxide injury. The results of the chemical analyses are given in Tables 1 to 10.2. The data obtained were statistically analysed to test the significance of the results.

4.1 Nutrient status of the fourteenth leaf of coconut

The contents of macro and micro nutrients of the sampled coconut palms are given below.

4.1.1 Nitrogen

The results showed that the nitrogen content in the fourteenth leaf varied widely as distance from the factory increased (Table 1.). The nitrogen content of palms near the factory were significantly lower than that of the control palms at 5000m, the values being 1.360, 1.704, 1.944, 2.130, 2.256 and 2.584 per cent corresponding to 250, 500, 1000, 1500 and 2000 and 5000m. A clear increase in the nitrogen content was observed with increasing distance, the maximum being shown by the control palms. Up to 500m the N level was highly reduced and no significant difference was observed in values within this distance. Palms at 500m did not show significant difference from palms at 1000 and 1500m, but those at 250m differed significantly from palms It was also observed that significant beyond 500m. difference did not exist among palms from 1000 to 2000 m, though within that distance, only palms at 1000 m had nitrogen values significantly different from that of control palms at 5000m.

4.1.2 Phosphorus

As distance from the factory increased, the phosphorus content also showed a significant increase (Table 1.), with the values at 0.25 and 0.50 km highly decreased and on par (0.024 per cent). At 1.0, 1.5, 2.0 and 5.0 km the contents of phosphorus were 0.029, 0.034, 0.036 and 0.047 per cent respectively, the control palms at 5.0 km showing a highly significant increase when compared to that of the affected palms upto 2.0 km. Within 1.0 km no significant difference was noticed among palms, the values being significantly lower than that of palms at 1.5 and 2.0km.

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Table 1.

Distance from the factory (m)	N (%)	P (%)	К (%)	Ca (%)	Mg (%)
250	1.360	0.024	0.235	1.100	0.156
500	1.704	0.024	0.268	1.298	0.253
1000	1.944	0.029	0.428	1.439	0.266
1500	2,130	0.034	0.522	1.516	0.285
2000	2,256	0.036	0.644	1.735	0.287
5000	2.584	0.047	0.846	2.009	0.311
F	7.200**	* 28,550**	19.210**	⁺ 18.993 ^{**}	2,108 ^{n ≤}
SE	0.160	0.002	0.053	0.074	0.037
CD	0.468	0.005	0.155	0.215	
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****** Significant at 1% level

ns Not significant

palms at 250, 500, 1000, 1500 and 2000 m away from the factory were 0.235, 0.268, 0.428, 0.522 and 0.644 per cent respectively (Table 1.), the control palms at 5000 m recording the highest value (0.846 per cent). Sulphur dioxide had significantly reduced the potassium content of palms upto 2000 m when compared to control palms at 5000 m. Upto 500 m, the potassium contents were significantly reduced with palms within this distance being affected with equal intensities. Only slight difference in potassium was observed between 1000 and 2000 m. A clear significant increase in values were observed in leaves with increase in distance from the source of pollutant.

4.1.4 Calcium

The calcium content of palms at 250, 500, 1000, 1500, 2000 and 5000 m were 1.100, 1.298, 1.439, 1.516, 1.735 and 2.019 per cent respectively (Table 1.). There was a clear increase in values with decreased exposure to sulphur dioxide, the control palms at 5000 m registering the highest value. Calcium in palms at 250 m was the lowest and upto 1500 m, the values were significantly lower than that of p ns beyond 1500 m. At 2000 m also significant reduction in calcium content was observed.

4.1.5 Magnesium

The magnesium content in the fourteenth index leaf of coconut palms were 0.156, 0.253, 0.266, 0.285, 0.287 and 0.311 per cent at distances of 250, 500, 1000, 1500, 2000, and 5000 m respectively from the point of sulphur dioxide pollution (Table 1.). A gradual increase was observed in the values as distance from the pollution source increased, though not significant.

4.1.6 Total sulphur

The total sulphur content of leaves, presented in Table 2., showed significant result, since the values decreased with increase in distance from the factory. At 250 m the sulphur content was 1.731 per cent, the corresponding values for 500, 1000, 1500, 2000 and 5000 m (control) being 0.964, 0.681, 0.604, 0.439 and 0.202 respectively. The mean value of 1.731 per cent recorded by palms at 250 m was significantly higher than those at a distance of 500 to 5000 m. Palms at 500 m also had significantly higher sulphur levels than those beyond that distance, but at 250 and 500 m, statistically significant difference was not noticed.

4.1.7 Sulphate sulphur

The contents of sulphate sulphur in leaves of palms at 250, 500, 1000, 1500, 2000 and 5000 m from the

Table 2.

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Total sulphur, sulphate sulphur and their ratio at different distances

Distance from the factory(m)	Total sulphur(%)	Sulphate sulphur(%)	Sulphate sulphur: total sulphur
250	1.731	0.364	0.210
500	0.964	0.196	0.204
1000	0.681	0.129	0.190
1500	0.604	0.111	0.183
2000	0.439	0.079	0.180
5000	0.202	0.037	0.181
 F	15.573**	17.971**	9.179 **
SE	0.132	0.027	0.004
CD	0.386	0.079	0.012

****** Significant at 1% level

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factory were 0.364, 0.196, 0.129, 0.111, 0.079 and 0.37 per cent respectively (Table 2.). Palms closer to the factory had significantly higher values than those away from the pollution source. At 250 m, sulphate sulphur was significantly higher than that of palms at longer distances. At 500 and 1000 m, the contents were not significantly different from each other. The difference in sulphate suplhur contents were negligible in palms from 1000 m onwards though a decrease could be observed as the intensity of sulphur dioxide pollution decreased.

4.1.8 Sulphate sulphur to total sulphur ratios

The ratio of sulphate sulphur to total sulphur was found to decrease significantly as distance from the pollution source increased (Table 2.). At a distance of 250 m, the ratio was found to be the highest (0.210), the values at 500, 1000, 1500, 2000 and 5000 m being 0.204, 0.190, 0.183, 0.180 and 0.181 respectively. Beyond 1000 m, the difference in the ratios were not detectable, the palms at 2000 and 5000 m, showing almost equal values.

4.1.9 Iron

The iron content showed a highly significant decrease in concentration as the distance from the sulphur dioxide source increased (Table 3.). At 250 m, nearest to the pollution source, the concentration was maximum with 943.4 ppm, the minimum being recorded in control palms at 5000 m (563.4 ppm). At 500, 1000, 1500 and 2000 m the leaf iron contents were 851.6, 718.0, 626.0, and 626.2 ppm respectively. Upto 1000 m the values were on par though an increase was observed in palms near the factory.

4.1.10 Manganese

Palms closer to the pollution source was found to have increased manganese concentration, the trend decreasing with increasing distance (Table 3.). At 250 m, the manganese content was highest with 397.4 ppm and at 5000 m the content was lowest with 70.6 ppm. The values at 500, 1000, 1500 and 2000 m were 316.2, 135.0, 117.0 and 110.8 ppm, respectively. Palms at 250 and 500 m did not show significant difference in manganese from each other. But the values were statistically significant from those of the control palms at 5000 m.

4.1.11 Copper

The copper status of the palms decreased considerably with increase in distance from the factory (Table 3.). At 250, 500, 1000, 1500, 2000 and 5000 m, the values were 17.96, 12.40, 9.60, 8.52, 7.74 and 7.80 ppm respectively. At 250 m, the leaf copper content was the

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highest and showed significant difference from the copper values in palms farther from the factory. The control palms at 5000 m showed the lowest level of copper.

4.1.12 Zinc

The contents of zinc in the fourteenth index leaf of coconut at 250, 500, 1000, 1500, 2000 and 5000 m from the factory were 46.2, 64.0, 54.8, 30.6, 36.8 and 29.0 ppm respectively (Table 3.). There was no significant variation in concentration as distance from the pollution source increased though a gradual reduction was observed in the values.

4.1.13 Boron

An increase in boron content was observed in palms with increase in distance from the pollution source (Table 3.), the values at 250, 500, 1000, 1500, 2000 and 5000 m being 14.10 , 14.08 , 16.61- 20.53 , 20.10 $^{\circ}$ and 23.41 .ppm respectively. Upto 1000 m, the boron contents were on par but showed significant difference when compared with values obtained for control palms at 5000 m.

4.1.14 Molybdenum

The molybdenum contents of the sampled palms are presented in Table 3. The concentrations did not vary



Table 3,

Micronutrient content of the 14th leaf of coconut

Distance from the factory (m)	Fe (ppm)	Mn (ppm)	Շս (ppm)	Zn (ppa)	8 (ppm)	Mo (ppm)
250	943.40	397.40	17.96	46.20	14.10	0.24
500	851.60	316,20	12.40	64.00	14.08	0.08
1,000	718.00	135.00	9.60	54.80	16.61	0.08
1500	626.00	117.00	8.52	30.60	20.53	0.11
2000	626.20	110.80	7.74	36.80	20.10	0.09
5000	563.40	70.60	7.80	29.00	23.41	0.14
F	3.10*	2,43 ^{ns}	4.84**	0.57 ^{ns}	5.93**	2.06 ^{ns}
SE	84.06	84.96	1,80	18.50	1.56	0.04
CD	245.35		5.27		4.56	
* Signifi ** Signifi	245.35 cant at 5% cant at 1% nificant		5.27		4.56	

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significantly at different locations from the factory except at 250 m, where the palms had a higher concentration (0.24 ppm) than those beyond that distance . At 500, 1000, 1500, 2000 and 5000 m, the molybdenum contents were 0.08 , 0.08 , 0.11 , 0.09 and 0.14 ppm respectively.

4.1.15 Sodium

As distance increased, the sodium contents also showed a significant increase (Table 4.). The level of sodium in leaves were 0.22;, 0.26;, 0.30, 0.32, 0.36 and 0.47 per cent respectively at distances of 250, 500, 1000, 1500, 2000 and 5000 m. The values upto 1500 m were on par and significantly lower than that of palms beyond that distance. At 2000 and 5000 m the palms did not show any significant difference in the sodium concentrations from one another.

4.1.16 Chlorine

Palms at 250, 500, 1000, 1500 and 2000 m showed chlorine values of 0.18, 0.31, 0.32, 0.39, and 0.49 per cent respectively (Table 4.), the control palms at 5000 m showing the highest value of 0.62 per cent. A significant difference was observed in chlorine content of palms between each distance except between 500 and 1000 m. As distance from the factory increased, the chlorine contents also

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Table 4.

Contents of Na, Cl and Al at different distances

Distance from the factory (m)	Na (%)	Cl (%)	Al (ppm)
250	0.22	0.18	401.80
500	0.26	0.31	225.00
1000	0.30	0.32	188,80
1500	0.32	0.39	140.40
2000	0.36	0.49	116.60
5000	0.47	0.62	79.60
F	4,56**	87.13**	11.49**
SE	0.04	0.02	33.92
CD	0.12	0.05 99.0	

****** Significant at 1% level

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showed a significant increase. At 250 m, palms had a highly reduced chlorine level, statistically significant from the control palms at 5000 m.

4.1.17 Aluminium

A highly significant decrease was observed in aluminium contents with decreasing intensity of pollution (Table 4.). The highest aluminium concentration observed was at 250 m (401.8 ppm), significantly different from the values beyond that distance. The contents at 500, 1000, 1500 and 2000 m were 225.0, 188.8, 140.4, 116.6 and 79.6 ppm respectively, control palms at 5000 m registering the least value.

4.2 Catalase activity

The activity of catalase enzyme as measured by kf was minimum in palms at 250 m (0.054) (Table 5.). At 500, 1000, 1500, 2000 and 5000 m the values of kf were 0.079, 0.094, 0.284, 0.297 and 0.150 respectively. No significant difference was obtained in the activities of catalase enzyme at different distances from the factory.

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4.3 Ascorbic acid content

The leaf content of ascorbic acid decreased significantly as distance from the factory increased

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(Table 5.). At 250 m, the ascorbic acid content was the lowest (0.592 mg g^{-1} fresh leaf) which is significantly lower than that of palms at other distances studied around the factory. The ascorbic acid contents were 0.705, 0.720, 0.897, 0.943 and 1.041 mg g^{-1} fresh leaf at distances of 500, 1000, 1500, 2000 and 5000 m respectively. At 500 m and 1000 m, the values were significantly lower than that of palms beyond 1000 m. Ascorbic acid levels of palms at 1500, 2000 and 5000 m were on par with apparantly no effect of sulphur dioxide.

4.4 Glucose content

The glucose contents of the palms presented in (Table 5.), show highly significant reduction in values near the pollution source. Palms at 250 m from the factory had the lowest value (1.190 per cent) the highest being 3.668 per cent for the control plams at 5000 m distance. At 500, 1000, 1500 and 2000m, the glucose contents were 1.416, 1.856, 2.390 and 3.078 per cent respectively. The values upto a distance of 500 m showed no significant difference from each other. Table 5.

Catalase activity, ascorbic acid and glucose contents of coconut palms at different distances.

Distance from the factory (m)	Catalase activity (kf)	Ascorbic acid (mg g ⁻¹ fresh leaf)	Glucose (%)
250	0.054	0.592	1.190
500	0.079	0.705	1.416
1000	0.094	0.720	1.856
1500	0.284	0.899	2.390
2000	0.297	0.943	3.078
5000	0.150	1.041	3,668
F	1,193 ^{ns}	22.551**	45.695**
SE	0.097	0.036	0.143
CD		0.105	0.418

****** Significant at 1% level

ns Not significant

4.5 Pigment concentration of the coconut leaf

4.5.1 Total chlorophyll

With increase in distance from the factory, the total chlorophyll contents showed a significant increase (Table 6.). The control palms at 5000 m showed the highest chlorophyll content (1.492 mg g^{-1} fresh leaf) and those at 250 m, registered the lowest value (0.187 mg g^{-1} fresh leaf). Up to 2000 m, the total chlorophyll contents were significantly reduced, the values at 500, 1000, 1500 and 2000 m being 0.348, 0.569, 0.773 and 0.972 mg g^{-1} fresh leaf

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4.5.2 Chlorophyll `a'

There was a significant increase in the chlorophyll 'a' content of leaves as distance from the factory increased (Table 6.). At 250, 500, 1000, 1500, 2000 and 5000 m, the values were 0.101, 0.222, 0.392, 0.530, 0.699 and 1.051 mg g^{-1} fresh leaf respectively. The chlorophyll 'a' contents upto 1000 m were on par and differed significantly from palms at 5000 m. Beyond 1000 m, the chlorophyll 'a' contents seem to be unaffected by sulphur dioxide pollution, with the values on par with those of control palms.

Table 6.

Leaf	pigment	concentration	of	the	coconut	palm	(mg	9 ⁻¹	fresh	leaf)

Distance	Total carote-	Total chloro-	Chloro- phyll 'a'	Chloro-	Ratio of chlorophyll
factory (m)	noids MSPU/ml	phy11	hull a	U	'a' to 'b'
250	0.051	0.187	0.101	0.086	1.141
500	0.091	0.348	0,222	0.126	1.801
1000	0.135	0.569	0.392	0.177	2.221
1500	0.207	0.773	0.530	0.243	2.165
2000	0.221	0.972	0.699	0.273	2.526
5000	0.270	1,492	1.051	0.441	2.383
F	17.003**	18,846**	6,705**	14.284**	17.383**
SE	0.020	0.108	0.110	0,032	0.125
CD	0.059	0.316	0.321	0.094	0.365

** Significant at 1% level

4.5.3 Chlorophyll 'b'

A highly significant increase was observed in the chlorophyll 'b' contents of coconut leaves with progressive increase in distance from the factory (Table 6.). The control palms at 5000 m had a chlorophyll 'b' content of 0.441 mg g^{-1} fresh leaf which was significantly higher than that of palms upto 2000 m. At 250m, the chlorophyll 'b' content showed the minimum value (0.086 mg g^{-1} fresh leaf), the concentration being 0.126, 0.177, 0.243 and 0.273 at 500, 1000, 1500 and 2000 m away from the sulphur dioxide source. Upto 1000m, difference in chlorophyll 'b' content of leaves were not detectable though there was a slight increase in the values within this distance.

4.5.4 Chlorophyll 'a' to 'b' ratio

The ratio of chlorophyll 'a' to 'b' was found to increase significantly with increase in distance from the source of sulphur dioxide pollution (Table 6.). At 250m, the ratio showed the lowest value (1.141) which was significantly different from that of palms beyond 250m. The chlorophyll 'a' to 'b' ratios were 1.801, 2.221, 2.165, 2.526 and 2.383 at distances of 500, 1000, 1500, 2000 and 5000 m respectively from the factory. The ratios beyond 500m did not show any significant difference.

4.5.5 Total carotenoids

A regular and significant increase in carotenoid contents from 0.051 to 0.270 MSPU/ml, was observed as disincreased from 250 to 5000 m from the source of tance pollution (Table 6.). Upto 500 m, the palms did not vary significantly in their carotenoid levels. The control palms at 5000m showed the highest carotenoid content with the palms at 250 m showing the least value, the intermediate values being 0.091, 0.135, 0.207 and 0.221 at distances of 500, 1000, 1500 and 2000 m. Beyond 1500 m, the palms did show any significant increase in the carotenoid not contents.

4.6 Nut characters of the coconut palm

4.6.1 Weight of husked nut

No significant difference could be observed in the weight of husked nut with increase in distance from the factory. At 250, 500, 1000, 1500, 2000 and 5000m, the values were 415.6, 455.2, 396.5, 403.2, 420.8 and 462.1 g respectively (Table 7.).

4.6.2 Weight of shell per nut

At 250 m, the weight of shell per nut was 119.8 g and the corresponding value at 5000 m was higher, being

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Table 7.

Nut characters of the coconut palm.

Weight of husked nut (g)	Weight of shell/ nut (g)	Weight of fresh meat/ nut (g)	Weight of copra / nut (g)	Copra content (%)	Fresh meat: copra	Husked nut:fresh meat	Husked nut: shell	Oil content (%)
415.60	117.80	208.70	104.80	47.81	2.02	2.02	3.58	54.22
455.20	127.30	226.20	125.20	55.59	1.81	2.00	3.66	56.48
396.50	108.10	202.70	110.30	54.29	1.86	1.95	3.77	55.50
403.20	115.60	216.80	124.60	57.31	1.75	1.86	3.49	60.64
420.80	118.20	229.40	135.90	59.18	1.70	1.84	3.55	66.46
462.10	134.70	255.00	170.70	66.60	1.52	1.82	3.86	71.86
0.57 ^{ns}	0.61 ^{ns}	0.98 ^{ns}	3.46**	5.79**	5.19**	3.25*	0.42 ^{ns}	6.55**
35.94	11.86	18.80	12.61	2.34	0.07	0.05	0.21	2.73
			36.82	6.8 2	0.21	0.14		7.97
	husked nut (g) 415.60 455.20 396.50 403.20 420.80 462.10 0.57 ^{ns}	husked af shell/ nut nut (g) (g) 415.60 117.80 455.20 127.30 396.50 108.10 403.20 115.60 420.80 118.20 462.10 134.70 0.57 ^{ns} 0.61 ^{ns}	huskedof shell/ nutfresh meat/ nutnutnutnut(g)(g)(g)415.60117.80208.70455.20127.30226.20396.50108.10202.70403.20115.60216.80420.80118.20229.40462.10134.70255.00 0.57^{ns} 0.61^{ns} 0.78^{ns}	husked nutof shell/ nutfresh meat/ nutcopra / nut(g)(g)(g)(g)415.60117.80208.70104.80455.20127.30226.20125.20396.50108.10202.70110.30403.20115.60216.80124.60420.80118.20229.40135.90 462.10 134.70255.00170.70 0.57^{ns} 0.61^{ns} 0.98^{ns} 3.46^{**} 35.94 11.8618.8012.61	husked nut nut (g)of shell/ nut (g)fresh meat/ nut nut (g)copra / nut (%)content (%)415.60117.80208.70104.8049.81455.20127.30226.20125.2055.57396.50108.10202.70110.3054.29403.20115.60216.80124.6057.31420.80118.20229.40135.7059.18462.10134.70255.00170.7066.600.57 ^{ns} 0.61 ^{ns} 0.98 ^{ns} 3.46**5.79**35.7411.8618.8012.612.34	husked nut nut (g)of shell/ nut (g)fresh meat/ nut (g)copra / nut (g)content (%)meat: copra415.60117.80208.70104.8047.812.02455.20127.30226.20125.2055.571.81396.50108.10202.70110.3054.291.86403.20115.60216.80124.6057.311.75420.80118.20229.40135.9059.181.70462.10134.70255.00170.7066.601.520.57 ^{ns} 0.61 ^{ns} 0.98 ^{ns} 3.46**5.79**5.19**35.9411.8618.8012.612.340.07	husked nutof shell/ nutfresh meat/ nutcopra / nutcontent (%)meat: nut resh meat(g)(g)(g)(g)(g)415.60117.80208.70104.8047.812.022.02455.20127.30226.20125.2055.571.812.00376.50108.10202.70110.3054.291.861.75403.20115.60216.80124.6057.311.751.86420.80118.20229.40135.9059.181.701.84462.10134.70255.00170.7066.601.521.82 0.57^{ns} 0.61^{ns} 0.78^{ns} 3.46^{**} 5.79^{**} 5.19^{**} 3.25^{*} 35.9411.8618.8012.612.34 0.07 0.05	husked nut (g)of shell/ nut (g)fresh meat/ nut (g)copra / nut (%)content meat:nut:fresh meatnut: shell415.60117.80208.70104.8049.812.022.023.58455.20127.30226.20125.2055.571.812.003.66396.50108.10202.70110.3054.291.861.953.77403.20115.60216.80124.6057.311.751.863.49420.80118.20229.40135.9059.181.701.843.55462.10134.70255.00170.7066.601.521.823.860.57 ^{ns} 0.61 ^{ns} 0.98 ^{ns} 3.46**5.79**5.19**3.25*0.42 ^{ns} 35.9411.8618.8012.612.340.070.050.21

134.7 g (Table 7.), but no significant difference was observed in values of affected and healthy palms. The weight of shell per nut were 127.3, 108.1, 115.6 and 118.2 respectively at 500, 1000, 1500 and 2000 m.

4.6.3 Weight of fresh meat per nut

The weights of fresh meat per nut were 208.7, 226.2, 202.7, 216.8, 229.4 and 255.0 g respectively at distances of 250, 500, 1000, 1500, 2000 and 5000 m from the source of sulphur dioxide emission (Table 7.). It was observed that no significant difference existed in the weight of fresh meat per nut with increasing distance from the factory.

4.6.4 Weight of copra per nut

The palms at 250 m showed the lowest copra weight per nut (104.8 g), which was significantly lower than the highest value observed in palms at 5000 m (170.7 g). At 500, 1000, 1500 and 2000 m the mean weights of copra were significantly lower than that of the control palms at 500m, the difference in values of palms at 2000 m and 5000 m not showing any significance (Table 7.).

4.6.5 Copra content

A highly significant increase in copra content was observed as distance from the factory increased (Table 7.). The highest value was recorded by nuts of control palms at 5000 m (66.60 per cent) and the lowest by palms at 250 m (47.81 per cent) from the factory. The corresponding values were 55.57, 54.27, 57.31 and 57.18 per cent at distances of 500, 1000, 1500 and 2000m respectively. The difference in the content of copra per nut of palms at distances of 500, 1000, 1500 and 2000 m were not significant.

4.6.6 Ratio of fresh meat to copra

The difference in the ratios of the weight of fresh meat to copra per nut of palms at different distances were significant (Table 7.). The ratio showed a decrease as distance from the factory increased with the highest value being recorded in palms at 250 m (2.02) and the lowest at 5000 m (1.52). The values for 500, 1000, 1500 and 2000 m were 1.81, 1.86, 1.75 and 1.70 respectively, comparable values being recorded upto 1000 m.

4.6.7 Ratio of husked nut to fresh meat

A significant decrease was observed in the ratios of husked nut to fresh meat as distance from the factory increased (Table 7.), the highest ratio being at 250 m (2.02) and the least at 5000 m (1.82). At 500, 1000, 1500 and 2000 m, the values were 2.00, 1.95, 1.86 and 1.84 respectively.

4.6.8 Ratio of husked nut to shell

The ratio of husked nut to shell weights at 250, 500, 1000, 1500, 2000 and 5000m from the pollution source were 3.58, 3.66, 3.77, 3.49, 3.55 and 3.86 respectively (Table 7.). No significant difference was observed in the ratios as distance from the factory increased.

4.6.9 Dil content

The oil content of nuts showed a highly significant increase with increase in distance from the factory (Tables 7.). The lowest value for oil content was registered at 250 m (54.22 per cent) and the highest was for the control palms at 5000m (71.86 per cent). At 500, 1000, 1500 and 2000 m, the values were 56.48, 55.50, 60.64 and 66.46 per cent respectively. Upto 1500 m the oil contents did not show any significant difference. No significant difference in values were obtained between palms at 2000 and 5000 m.

4.7 Inter-relationship between total sulphur and sulphate sulphur

A highly significant positive correlation existed between total sulphur and sulphate sulphur (0.9952 **). The ratio of sulphate sulphur to total sulphur in the plant also showed a positive and significant correlation with both total sulphur (0.6817**) and sulphate sulphur (0.7331**).

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4.8 Inter-relationship between leaf constituents and the two forms of sulphur

4.8.1 Macro nutrients

Both forms of sulphur were negatively correlated with the macro nutrients like nitrogen, phosphorus, potassium, calcium and magnesium. Nitrogen had a highly significant negative correlation with total sulphur $(-0.6765 \ ^{**})$ and sulphate sulphur $(-0.6935 \ ^{**})$. Phosphorus $(-0.5513 \ ^{**})$, potassium $(-0.6101 \ ^{**})$, calcium $(-0.5714 \ ^{**})$ and magnesium $(-0.5267 \ ^{**})$ also showed significant negative correlation with total sulphur. Highly significant negative correlation also existed between sulphate sulphur and phosphorus $(-0.5548 \ ^{**})$, potassium $(-0.6218 \ ^{**})$, calcium $(-0.5863 \ ^{**})$ and magnesium $(-0.5530 \ ^{**})$.

4.8.2 Micronutrients

The micronutrients like chlorine, and boron exhibited significant negative correlation with both total sulphur (-0.7125^{**} , and -0.5445^{**} respectively) and sulphate sulphur (-0.7216^{**} , and -0.5495^{**} respectively). Significant positive correlation were noticed between total sulphur and iron (0.4812^{**}), copper (0.6412^{**}) and manganese (0.4168_{*}) and also between sulphate sulphur and iron (0.4966^{**}), copper (0.6247^{**}) and manganese (0.4333^{*}). Sodium was significantly and negatively correlated with total sulphur and sulphate sulphur (-0.4382^{*} and -0.4314^{*} respectively) while aluminium showed a significant positive correlation (0.7279^{**} and 0.7465^{**} respectively).

Zinc and molybdenum did not show any significant correlation with either total sulphur or sulphate sulphur.

4.8.3 Catalase activity, ascorbic acid and glucose contents

Catalase activity of palms did not show any significant correlation with either sulphate sulphur or total sulphur.

The ascorbic acid content of palms also showed negative and highly significant correlation with both total sulphur (-0.6978^{**}) and sulphate sulphur (-0.6931^{**}).

Glucose was negatively correlated with both total sulphur (-0.6706^{**}) and sulphate sulphur (-0.6716^{**}).

4.8.4 Plant pigments

All plant pigments showed negative correlation with both forms of sulphur. Highly significant negative correlation existed between total sulphur and total chlorophyll (-0.5127^{**}), chlorophyll `a' (-0.4643^{**}), chlorophyll a/b (-0.8161^{**}) and carotenoids (-0.6135^{**}). Chlorophyll `b' also showed significant negative correlation with total sulphur (-0.4603^{*}).

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Г Leaf constituents Total sulphur Sulphate sulphur 0.9952** Sulphate sulphur 0.7331** 0.6817** Sulphate S:total S -0.6765** -0.6935** Nitrogen -0.5513** -0.5548** Phosphorus -0.6101** -0.6218** Potassium -0.5714** -0.5863** Calcium -0.5267** -0.5530** Magnesium 0.4812** 0.4966** Iron 0.4333* 0.4168* Manganese 0.6247** 0.6412** Copper 0.0852^{ns} 0.0920^{ns} Zinc -0.5445** -0.5495** Boron 0.3024^{ns} 0.3280^{ns} Molybdenum -0.4382* -0.4314* Sodium -0,7216** -0.7125** Chlorine 0.7279** 0.7465** Aluminium -0.2570^{ns} -0.2660^{ns} Catalase activity -0.6998** -0.6931** Ascorbic acid -0.6706** -0.6716** Glucose -0.6135** -0.6255** Carotenoids -0.5127** -0.5256** Total chlorophyll -0.4643** -0.4786** Chlorophyll 'a' -0.4603* -0.4712** Chlorophyll 'b' -0.8244** ~0.8161** Chlorophyll a/b

Significant at 5% level
Significant at 1% level
Not significant

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total

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Coefficient of simple linear correlation between sulphur, sulphate sulphur and leaf constituents.

Table 8.1.

Table 8.2.

Coefficient of simple linear correlation between total sulphur, sulphate sulphur and nut characters

Nut characters	٦					
	Total sulphur	Sulphate sulphur				
Wt. of husked nut	0.0258 ^{ns}	0.0318 ^{ns}				
Wt. of shell/nut	0.0146 ^{ns}	0.0114 ^{ns}				
Wt. of fresh meat/nut	-0.0981 ^{ns}	-0.0822 ^{ns}				
Wt. of copra/nut	-0.2866 ^{ns}	-0.2730 ^{ns}				
Copra content	-0.4738 ^{**}	-0.4648 ^{**}				
Fresh meat : copra	0.5079**	0.4944 ^{**}				
Husked nut : fresh meat	0.4318 [*]	0.4058*				
Husked nut : shell	0.0057 ^{ns}	0.0134 ^{ns}				
Oil content	-0.5006**	-0.4827 ^{**}				

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Significant at 5% level
Significant at 1% level
Not significant.

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Sulphate sulphur was also negatively and significantly correlated with total chlorophyll, (-0.5256^{**}) chlorophyll 'a' (-0.4786^{**}) , chlorophyll 'b' (-0.4712^{**}) , chlorophyll a/b (-0.8244^{**}) and carotenoids (-0.6255^{**}) .

4.9 Inter-relationship between nut characters and the two forms of sulphur.

The weights of husked nut, shell, fresh meat and copra per nut did not show any significant correlation with either total or sulphate sulphur. The ratio of the weight of husked nut to shell also did not show significant correlation with both forms of sulphur. But the copra and oil contents exhibited significant negative correlation with total sulphur (-0.4738^{**} and -0.5006^{**} respectively) and sulphate sulphur (-0.4648^{**} and -0.4827^{**} respectively). The ratios of the weight of husked nut to fresh meat and fresh meat to copra showed significant positive correlation with total sulphur (0.4318^{*} and 0.5079^{**} respectively) and sulphate sulphur (0.4058^{*} and 0.4944^{**} respectively).

4.10 Linear regression of leaf constituents and nut characters on total sulphur

The linear regression of leaf constituents and nut characters on total sulphur are given in Tables 9.1 and 9.2 respectively.

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Table 9.1,

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Linear regression of leaf constituents (y) on total sulphur (x)

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Dependent variable, y	Regress	ion ec	quation	Coefficient of determina- tion, R ² (%)
Sulphate sulphur	$y_1 = -0.0$	023 +	0.230x**	99.0
Sulphate S:total S	$y_2 = 0$.	170 +	0.030x ^{**}	46.5
Nitrogen	$y_3 = 2.4$	481 -	0.629× ^{**}	45.8
Phosphorus	y ₄ = 0.	039 -	0.009× ^{**}	30.4
Potassium	$y_5 = 0.4$	695 -	0.265× ^{**}	37.2
Calcium	$y_6 = 1.$	781 -	0.345× ^{**}	32.7
Magnesium	$y_7 = 0.3$	327 -	0.087× ^{**}	27.7
Iron	y ₈ =574.	774 +	190.393× ^{**}	23.2
Manganese	y ₉ = 68.1	278 +	159.530× [*]	17.4
Copper	$y_{10} = 6.0$	035 +	6.017× ^{**}	41.1
Zinc	$y_{11} = 38.2$	850 +	6.120x ^{ns}	0.7
Baron	$y_{12} = 21$.	720 -	4.660× ^{**}	29.7
Molybdenum	$y_{13} = 0.0$	080 +	0.060x ^{ns}	9.1
Sodium	$y_{14} = 0.1$	389 -	0.089× [*]	50.8
Chlorine	$y_{15} = 0.3$	527 -	0.187× ^{**}	17.2
Aluminium	$y_{16} = 63.$	434 +	166.950x ^{**}	53.0
Catalase activity	$y_{17} = 0.$	238 -	0.102× ^{ns}	6.6
Ascorbic acid	$y_{18} = 0.$	986 -	0.220× ^{**}	49.0
Glucase	$y_{19} = 3.$	140 -	1.140× ^{**}	45.0
Carotenoids	$y_{20} = 0.$	240 -	0.100x ^{**}	37.6
Total chlorophyll'	$y_{21} = 1$.	072 -	0.453x ^{**}	26.3
Chlorophyll `a'	y ₂₂ = 0.	690 -	0.290x ^{**}	21.5
Chlorophyll `b'	$y_{23} = 0.1$	310 -	0.110× [*]	21.2
Chlorophyll a/b	y ₂₄ = 2.	680 -	0.810× ^{**}	66.6

Significant at 5% level Significant at 1% level Not significant *

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Table 9.2.

Linear regression of nut characters (y) on total sulphur (x)

Dependent variable,y	Regression equation	Coefficient of determination,R ⁴ (%)	
Wt. of husked nut	y ₂₅ = 422.80 + 3.40 x ^{ns}	0.1	
Wt. of shell/nut	y ₂₆ = 120.10 + 0.68 x ^{ns}	0.0	
Wt. of fresh meat/nut	y ₂₇ = 228.86 − 7.43 x ^{ns}	1.0	
Wt. of copra/nut	y ₂₈ = 141.99 - 17.41 x ^{ns}	8.2	
Copra content	y ₂₉ = 61.78 - 6.03 x**	22.5	
Fresh meat: copra	$y_{30} = 1.62 + 0.20 x^{**}$	25.8	
Husked nut: fresh meat	$y_{31} = 1.84 + 0.10 \times^*$	18.7	
Husked nut: shell	y ₃₂ = 3.65 + 0.01 x ^{n⊆}	0.0	
Oil content	y ₃₃ = 66.81 - 7.72 x**	25.1	

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Significant at 5% level Significant at 1% level *

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Not significant กร

The rate of change of sulphate sulphur, sulphate sulphur to total sulphur ratios, nitrogen, phosphorus, potassium, calcium and magnesium with unit change in total highly significant were found to be • sulphur Micronutrients like iron, copper and boron also showed a significant change with a change in total sulphur of palms. Regression analysis revealed that zinc and molybdenum did not vary significantly with unit change in total sulphur. Leaf metabolites like glucose, ascorbic acid and leaf pigments also showed a significat decrease with increase in total sulphur.

Among the nut characters studied, only the fresh meat to copra and husked nut to fresh meat ratios, and the contents of copra and oil, showed a significant variation with the fresh meat to copra and husked nut to fresh meat ratios increasing with increased sulphur contents and the copra and oil contents decreasing significantly.

4.11 Linear regression of leaf constituents and nut characters on sulphate sulphur

Total sulphur, sulphate sulphur to total sulphur ratios, nitrogen, phosphorus, potassium, clacium, magnesium iron, copper, boron, aluminium and chlorine showed significant rate of change with unit change in sulphate sulphur (Table 10.1).

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Table 10.1.

Dependent variable, y	Regressi	on equation	Coefficient of determination, R ² (%)
,		······	
Total sulphur	y ₁ = 0.0		99.0
Sulphate S:total S	y ₂ = 0.1		53.7
Nitrogen	y ₃ = 2.4		48.1
Phosphorus	y ₄ = 0.4	3- 0.18× ^{**}	30.8
Potassium	y ₅ = 0.7	0- 1.40× ^{**}	38.7
Calcium	y ₆ = 1.7	2- 1.40× ^{**}	34.4
Magnesium	y ₇ = 0.3	7- 0.70× ^{**}	30.6
Iron	y ₈ =582.4	0+ 910.50× ^{**}	24.7
Manganese	y ₉ ≓ 73.8	2+ 768.50× [*]	18.8
Copper	y ₁₀ = 6.5	1+ 27.27× ^{**}	39.0
Zinc	y ₁₁ = 38.8	7+ 30.77x ^{ns}	0.9
Boron	$y_{12} = 21.4$	5- 21.68× ^{**}	30.2
Molybdenum		1+ 0.07x ^{ns}	
Sodium	$y_{14} = 0.4$	3- 0.70x*	18.6
Chlorine	$y_{15} = 0.4$	9~ 0.70× ^{**}	52.1
Aluminium	y ₁₆ = 70.9	4- 793.01× ^{**}	55.7
Catalase activity	y ₁₇ = 0.2	7- 0.70x ^{ns}	7.1
Ascorbic acid	y ₁₈ = 0.9	2- 0.70× ^{**}	48.0
Glucose	y ₁₉ = 3.1	2- 5.59× ^{**}	45.1
Carotenoids	y ₂₀ = 0.2	7- 0.70x ^{**}	39.1
Total chlorophyll	y ₂₁ = 1.0	4- 2.10× ^{**}	27.6
Chlorophyll `a'	y ₂₂ = 0.6	8- 1.40× ^{**}	22.9
Chlorophyll `b'	y ₂₃ = 0.3	3- 0.70×**	22.2
Chlorophyll a/b	y ₂₄ = 2.5	9- 3.50x ^{**}	68.0

Linear regression of leaf constituents (y) on sulphate sulphur (x)

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* Significant at 5% level
** Significant at 1% level
ns Not significant

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Table 10.2.

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Linear regression o sulphur (x)	f nut characters (y) on sulphate
Dependent variable, y	Regression equation	Coefficient of determination, R ² (%)
Wt. of husked nut	y ₂₅ =422.47 + 2.28× ^{ns}	0.1
Wt. of shell/nut	y ₂₆ =120.30 + 2.10x ^{n⊊}	0.0
Wt. of fresh meat/nut	y ₂₇ =227.51 -28.61x ^{n⊆}	0.7
Wt. of copra/nut	y ₂₈ ≈140.33 -76.92x ^{ns}	7.5
Copra content	y ₂₉ = 61.30 -27.27× ^{**}	21.6
Fresh meat:copra	y ₃₀ = 1.67 + 0.70x**	24.4
Husked nut:fresh meat	$y_{31} = 1.80 + 0.70x^*$	16.5
Husked nut:shell	y ₃₂ = 3.64 + 0.07x ^{n⊆}	0.0
Oil content	y ₃₃ = 66.09 -37.27× ^{**}	23.3

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Significant at 5% level Significant at 1% level Not significant * ¥¥

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Glucose, ascorbic acid and leaf pigments decreased significantly with unit increase in total sulphur contents.

The ratios of fresh meat to copra, and husked nut to fresh meat, and the contents of copra and oil, showed significant change in rate with change in sulphate sulphur contents (Table 10.2.).

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DISCUSSION

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5. DISCUSSION

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Coconut is recognized 85 the most important perennial tree crop of Kerala from time immemorial. Though it is a source of food and oil to a vast majority of the people of this state, its productivity has been decreasing continuously for the past two decades. There have been many factors affecting its productivity, which include poor fertility, water deficiency during summer months, and the attack of pests and diseases. But environmental factors like pollution of the atmosphere, contributing to the decrease in coconut productivity is of recent origin. Dwing to the rapid rate of industrialization, the toxic gases emitted by the industries pollute the surrounding atmosphere. These gases include sulphur dioxide, oxides of nitrogen and hydrogen chloride fumes,which are capable of inflicting injury to plants and animals.

It has been suspected that the fumes emitted by the Titanium factory at Kochuveli, Thiruvananthapuram, contain toxic levels of the atmospheric pollutant, sulphur dioxide. This sulphur dioxide can pollute the surrounding atmosphere, which can injure the native and cultivated plants in that area in addition to the injury inflicted to

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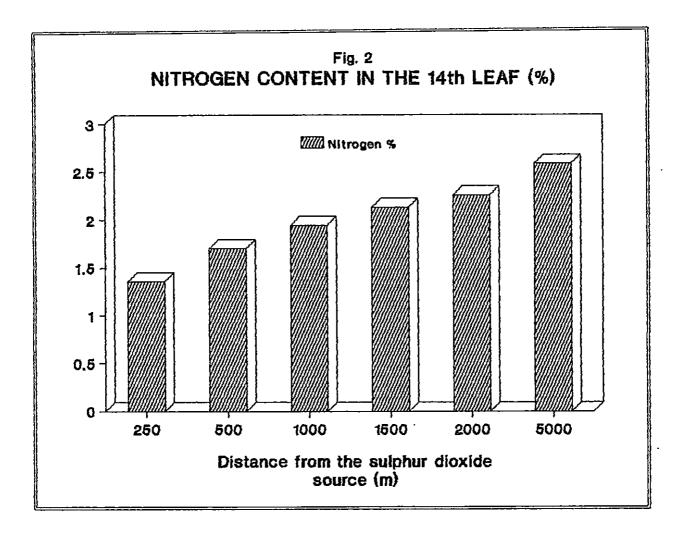
by determining the changes in the nutrient contents of plant tissue as compared to healthy plants. Since coconut is the major tree crop in the area and due to its importance as an oilseed, the study was conducted on coconut palms near the factory. Sulphur dioxide, though reported to influence plant growth and yield, has not been studied in detail under Kerala conditions. The results of such a study with the objectives enumerated above are discussed in the succeeding paragraphs.

5.1 Nutrient content of the coconut palm

5.1.1 Nitrogen

The data in Table 1. shows the percentage nitrogen in palms at selected distances from the factory. The nitrogen content of palms upto 500m did not differ significantly among themselves. Upto 1000m the nitrogen contents were significantly lower than the control palms at This indicates that the effect of sulphur dioxide 5000m. pollution in reducing the nitrogen content of palms exists upto 1000m from the source of pollution. Beyond 1000m, sulphur dioxide pollution had little effect on the nitrogen content. Correlation studies revealed a negative and highly significant relationship between total nitrogen content and total sulphur in palms.

The critical level of nitrogen, in the 14th index leaf for the tall varieties of coconut as fixed by I.R.H.O. is 1.80 to 2.00 per cent of the dry matter yield. In the present study, the control palms at 5000 m had a nitrogen content of 2.584 per cent and those at 1000 m and beyond had a value more than 1.80 per cent while in palms near the factory the values were less than 1.80 per cent. Thus it is evident from the present study that the palms at 250 and 500 m are having a leaf nitrogen content much below the critical This can be attributed to the accumulation of level. sulphur in the leaves of palms. An increase in respiration of plants resulting from sulphur dioxide exposure (Turk et al. 1974) results in decreased adenosine tri phosphate (ATP)levels (Harvey and Legge, 1979) which invariably leads to a build up of adenosine di phosphate (ADP). Thus, as ATP levels fall and ADP levels rise in a cell, cessation of nitrogenase activity occurs, resulting in decreased nitrogen fixation (Conn and Stumpf, 1976). Similar results were reported by Mishra (1980) who observed a decrease îп nitrogen content of Arachis hypogaea L. exposed tofumigation concentrations of sulphur dioxide ranging from 0.06 to 1.00 ppm, with increasing concentrations of the pollutant.



5.1.2 Phosphorus

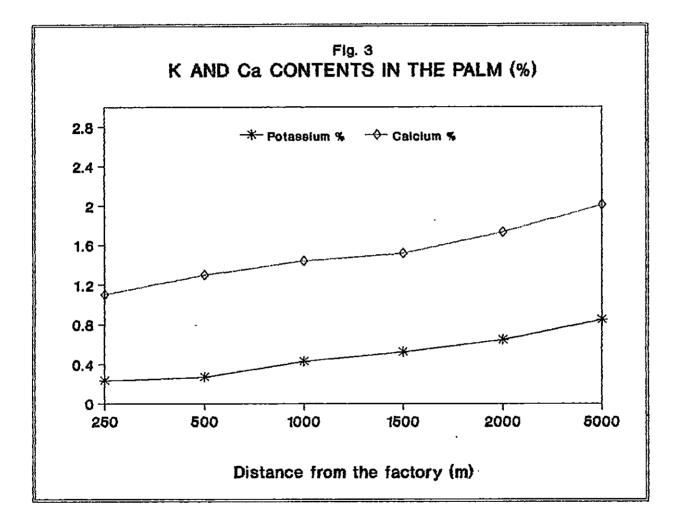
from the factory increased, the Δs distance phosphorus content was also found to increase (Table 1.). However, upto 2000 m, the values were much lower than the values obtained for control palms at 5000 m. The effect of sulphur dioxide in reducing the phosphorus content of palms was thus found to be significant. Upto 500 m, sulphur dioxide pollution showed significant diminishing effect on the phosphorus content. The negative and significant linear correlation of total sulphur and sulphate sulphur with phosphorus also indicates the adverse effect of accumulated sulphur. Similar results were obtained by Mishra (1980) who recorded reduced phosphorus levels in sulphur dioxide treated plants.

The critical level of phosphorus in the 14th index leaf of the tall varieties of coconut as fixed by the I.R.H.D. is 0.12 percent of the dry matter yield. In the present study, it was observed that the phosphorus content of the affected and control palms were below the critical But as distance from the pollution source level. phosphorus content also was increased. the found to The reduction in phosphorus content in palms increase. exposed to sulphur dioxide could due to sulphur be accumulation and its interference in mineral absorption and other physiological and biochemical processes (Agrawal et al. 1989).

5.1.3 Potassium

A study of the data in Table 1. reveals the depressing effect of sulphur dioxide on the plant potassium content. Since the healthy palms at 5000 m showed significantly higher potassium percentage than palms upto 2000 m, it may be inferred that the effect of sulphur dioxide pollution in decreasing the potassium content of palms existed beyond 2000 m.

For the fourteenth index leaf, the critical level of potassium was fixed at 0.80-1.00 per cent of dry matter yield for Tall varieties by I.R.H.O. Only the control palms at 5000 m had a potassium content higher than 0.80 per Other palms near the source of pollution showed cent. potassium contents below the critical level. Potassium found increasing as the intensity of deficiency was pollution increased, which proves the effect of increased sulphur content in inducing deficiency. This deficiency can be attributed to a release of K⁺ from leaves (Tomassini et al. 1977) or due to a reduction in the uptake of potassium (Jurat and Schaub, 1988). Correlation studies linear relationship showed significant negative between potassium content and plant sulphur. Regression studies indicated that upto 34 per cent decrease in potassiun content was related to an increase in sulphur content of the



palm. The reduction in potassium content can be attributed to a leakage of the element from the protoplast or to the reduction in potassium uptake induced by sulphur accumulation (Agrawal <u>et al.</u> 1989).

5.1.4 Calcium

As distance from the pollution source increased, the calcium content also exhibited an increasing trend (Table.1). Correlation studies revealed a significant negative relationship between calcium content and the plant contents of both total and sulphate sulphur. The depressing effect of sulphur dioxide pollution on the calcium content of palms was higher upto 500 m though a reduction was noticed upto 2000 m. All palms upto 2000 m significantly differed from palms at 5000 m in their calcium contents.

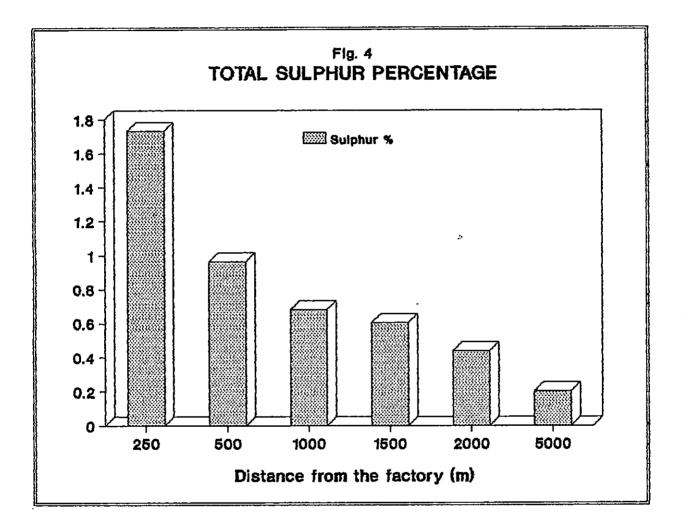
Though the calcium content of all the palms studied were above the critical level fixed by I.R.H.O. (0.50 per cent), a significant decrease was observed in palms exposed to sulphur dioxide pollution. Similar results were obtained by Agrawal <u>et al</u>. (1989) in different cultivated plants. But the results of the present study were at variance with the results obtained by Materna (1978) and Saxe (1983), who reported an increase in plant calcium content due to sulphur dioxide exposure. The decrease in calcium content could be due to its leakage from the protoplast (Agrawal <u>et al</u>.1989).

5.1.5 Magnesium

Magnesium content of palms at 250, 500, 1000, 1500, 2000 and 5000m from the pollution source are presented in Table 1. No significant decrease in magnesium content was found near the factory when compared to the healthy palms at 5000m,though a slight increase in values was observed with anincrease in distance. Flagler and Youngner (1985) had reported a reduction in magnesium level in plants exposed to sulphur dioxide. The critical level of magnesium fixed by I.R.H.D. is 0.24 per cent of dry matter yield in the fourteenth index leaf of coconut. From the table, it can be observed that the magnesium level of palms near the factory were below the critical level suggested by I.R.H.O.

5.1.6 Total sulphur

Atmospheric sulphur dioxide may enter plants through stomata as gaseous sulphur dioxide or as sulphite ions $(SD_3^{2^-})$ which may diffuse through the cell wall and penetrate the outer cell membrane, disturbing its permeability (Hallgren, 1978). Both forms can be utilized by plants through normal sulphur metabolism. It is the amount of these ions in excess of normal requirement that is injurious to plant metabolism (Malhotra and Hocking, 1976).



An analysis of the data in Table 2. reveals that sulphur dioxide pollution caused an increase in the sulphur content of palms near the factory. The values were highest in palms at 250 m and decreased with increasing distance. From 2000m, the sulphur content did not vary significantly. Thus it can be inferred that the effect of sulphur dioxide existed upto a distance of 2000m. A positive and significant correlation also existed between total sulphur and sulphate sulphur.

The critical level of sulphur in the fourteenth index leaf of coconut was observed as 0.15 to 0.20 per cent by I.R.H.O. The sulphur contents of the 14th leaf upto a distance of 2000 m from the factory were found to be much higher than the critical level. The palms near the factory had the highest sulphur content which could be attributed to the absorption of sulphur gas from the atmosphere. The control palms at 5000 m had a sulphur content of 0.202 per cent indicating that those palms were unaffected.

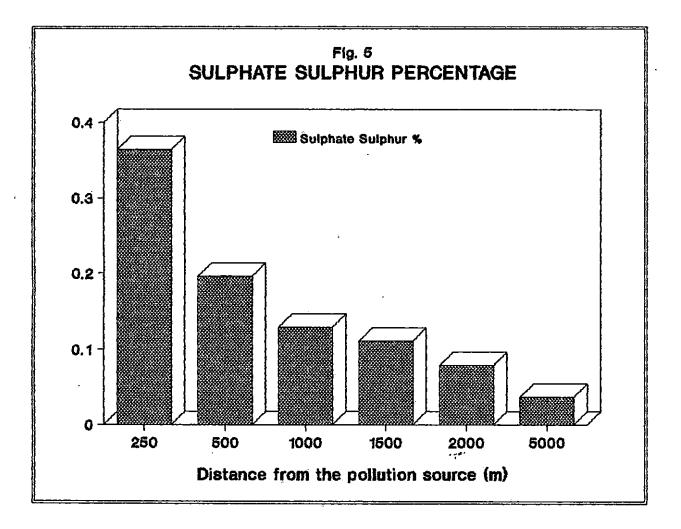
Similar results were obtained by Agrawal <u>et al</u>. (1989) who studied the responses of four species of plants after exposing them at selected phenological stages of their active growth period to 0.5 ppm sulphur dioxide. The plants included gram, rice, broom corn millet and broad bean. They found an increase in sulphur content in the exposed plants by 2.79, 7.64, 7.64 and 14.83 per cent respectively. The present study confirms that when plants are exposed to sulphur dioxide, they absorb sulphur through the foliage to toxic levels.

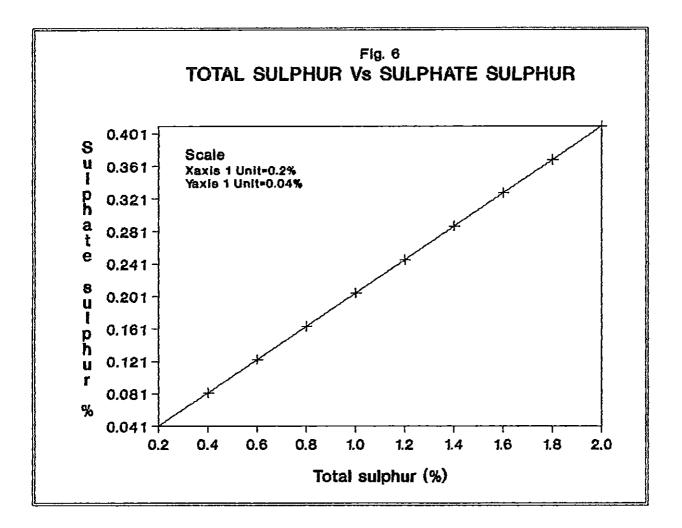
5.1.7 Sulphate sulphur

The sulphate sulphur contents in the sampled coconut palms are presented in Table 2. The values were maximum in palms at 250 m with the contents decreasing abruptly with increasing distance from the factory. From 1500 m, the palms did not show significant difference in sulphate sulphur content though a decrease was observed as distance from the pollution source increased. A significant positive linear relation between total sulphur and sulphate sulphur was also observed. Thus the increase in sulphate sulphur could be considered as due to the increased sulphur content of palms exposed to sulphur dioxide. At each distance, a corresponding change was noticed in the sulphate sulphur content in relation to the total sulphur content of the plant.

Similar results obtained by Amundson <u>et al</u>. (1990) reported a significant inverse relationship between foliar sulphate sulphur and distance from the pollution source in pine trees. Maas <u>et al</u>. (1987 b) reported that a major part of the sulphur dioxide entering the plant is converted to sulphate and stored in the vacuoles and a smaller portion is

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incorporated into organic compounds or may be emitted as hydrogen sulphide. Thus increase in sulphate sulphur may have resulted from the conversion of sulphur which was absorbed through the stomata, to sulphate. This inference is supported by the significant positive correlation between total sulphur and sulphate sulphur. Regression studies also showed that 99 per cent of the increase in sulphate was explained by the total sulphur content.

5.1.8 Ratio of sulphate sulphur to total sulphur

The ratio of sulphate sulphur to total sulphur was highest at 250 m and showed a significant decrease upto 500m (Table 2.). Beyond 500 m, no significant reduction could be detected. The significant positive correlation of the ratio with total sulphur and sulphate sulphur indicates an increase in sulphate sulphur or total sulphur as the total sulphur or sulphate sulphur content increased in the plant.

5.1.9 Iron

Table 3. presents the data on the content of iron in palms at selected distances from the factory. Control palms at 5000 m showed iron contents significantly lower than that of palms near the pollution source. Thus sulphur dioxide pollution induced the iron uptake of palms but this trend was observed to exist only upto 1000 m. Manciot <u>et</u> <u>al</u>. (1979) had reported that visible signs of iron deficiency in coconut occurred when the leaf concentrations of iron were below 50 ppm. Fremond <u>et al</u>. (1966) have also suggested 50 ppm iron as critical for tall palms. In the present study, all the selected palms showed an iron content above 50 ppm.

5.1.10 Mangamese

Palms at 250 m, which showed the highest total sulphur and sulphate sulphur content, had shown the highest concentrations of manganese also (Table 3). But there was no significant difference from the control palms at 5000 m. Though the increase in manganese content in palms near the factory was not significant, the data indicated an accumulation of manganese in plant tissue as the sulphur content increased. Similar results were obtained by Rehfuess (1981) who reported that toxic levels of manganese eventually develop in beech and spruce stands which have accumulated sulphur.

Pillai <u>et al</u> (1975) reported that the manganese content of coconut palms growing in Kerala ranged from 37.1 to 112.2 ppm. Palms near the pollution source, in the present study, showed much higher values.

5.1.11 Copper

According to Manciot <u>et al</u>. (1979), a copper level of 5 to 7 ppm in the 14th frond is sufficient for the coconut palm. All the sampled palms showed a copper content greater than this sufficiency level (Table 3.). Though a decreasing trend could be noticed with increase in distance from the pollution source. The high sulphur content of palms might have influenced the absorption of copper from soil by palms near the factory. Beyond 250 m copper content of palms were comparable indicating that sulphur dioxide pollution had not influenced the copper uptake of palms beyond this distance.

5.1.12 Zinc

The palms studied did not show any significant difference in the zinc content (Table 3.) indicating that sulphur dioxide pollution had not influenced the zinc uptake of palms though a gradual decrease was observed as the distance from the factory increased. Correlation and regression studies also did not reveal any influence of sulphur on the zinc content of palms.

5.1.13 Baran

The boron contents of palms presented in Table 3. showed a decreasing trend as proximity to the sulphur source increased. Palms upto 1000 m showed significant reduction in boron contents when compared to palms beyond 1000 m. Thus the effect of sulphur dioxide in reducing the boron content of palms existed upto 1000 m and the values beyond this distance were comparable with that of healthy palms at 5000 m.

Pillai <u>et al</u>. (1975) had reported a boron content of 10.9 to 14.6 ppm in coconut plams of Kerala. All palms in the present study showed higher values for boron.

5.1.14 Molybdenum

Table 3. presents the molybdenum contents of palms at varying distances from the Titanium factory. It was observed that sulphur dioxide pollution had no significant effect in altering the molybdenum content of palms. But the palms near the pollution source showed a slight increase in the values.

5.1.15 Sodium

The sodium contents of palms at different distances are presented in Table 4. A significant increase in concentration was noticed with increasing distance from the factory. The increased sulphur content of palms near the factory might have played a role in suppressing the uptake of sodium. 5.1.16 Chlorine

The data presented in Table 4 indicate that the control palms at 5000 m showed a significantly higher chlorine content than palms upto 2000 m. Thus though there was significant reduction in chlorine content near the pollution source, palms at 5000 m were not affected.

According to Ollagnier and Ochs (1971), for high yields, a chlorine content of 0.5 to 0.6 percent is necessary in the leaf. In this study, the palms at 250 m had a chlorine value which could be considered as deficient. As distance from the factory increased, the chlorine content of palms increased to the optimum level beyond a distance of 2000 m.

5.1.17 Aluminium

Table 4. presents data on the aluminium contents of palms at different distances from the source of sulphur dioxide pollution. Palms near the pollution source showed the highest value and decreased with increase in distance. The palms with the highest total sulphur and sulphate sulphur contentsshowed the highest concentrations with respect to aluminium. At 250 m the aluminium content was significantly higher than that of palms beyond 250 m. No significant difference in concentration was found in palms from 500 m and above. The significant increase in aluminium content of palms near the pollution source show the effect of sulphur dioxide pollution in altering the plant content of this element. Similar results were obtained by Niedzwiecki and Madej (1988) in scotspine, where aluminium accumulation was noticed in plants in a polluted area when compared to controls in an unpolluted area 100 km away.

5.2 Catalase activity

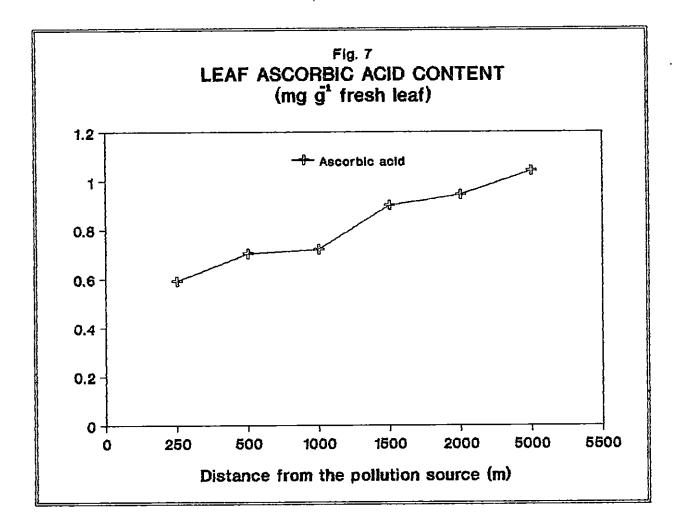
The catalase activity in the leaves of coconut palms presented in Table 5. indicates a gradual increase as distance from the factory increased, though no significant difference could be observed between affected and healthy palms. Thus the increased sulphur content had not affected the catalase activity.

Since sulphur dioxide enter the cell organelles and affect the membrane permeability, (Malhotra, 1976), it was suggested by Nandi <u>et al</u>. (1984 a) that the activity of the enzyme found in peroxisome was affected. Agrawal <u>et al</u>. (1989) had suggested that under stress conditions, the tetrameric catalase molecules may degrade into monomeric forms having peroxidase like activity. Dassler and Ranft (1967) had also reported an inhibition of catalase activity in plants exposed to sulphur dioxide. The present study indicated that sulphur dioxide had no significant influence in altering the activity of the catalase enzyme.

5.3 Ascorbic acid

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The leaf content of ascorbic acid in the selected palms are presented in Table 5. A significant increase was observed in the ascorbic acid content as distance from the factory increased. Thus the ascorbic acid contents of the palms near the factory were reduced significantly due to collution. The values at 1500, 2000 and 5000 m were comparable showing that the effect of sulphur dioxide in reducing ascorbic acid content existed only upto 1000 m. Since sulphur dioxide enter the cell organelles and affect membrane permeability (Malhotra, 1976), it was suggested by Nandi et al., (1984 a) that the ascorbic acid found in the chloroplast was affected. Ascorbic acid can reduce sulphur dioxide thereby helping in deto,xification of the affected plant thus resulting in its reduced concentration (Keller and Schwager, 1977). The decreased glucose content of palms could also result in reduced ascorbic acid levels (Conn and Stumpf. 1976). Thus it appears that the decrease in ascorbic acid content can be related to sulphur dioxide sensitivity of plants. In palms near the factory, the reduction in concentration were of higher magnitude. Agrawal et al., (1991) reported that the decrease in ascorbic acid content of plants in a sulphur dioxide polluted area were maximum in heavily polluted zone than in a less polluted zone.



A significantly negative relationship was obtained between ascorbic acid content and total sulphur. Regression studies also indicated that 48 to 49 percent of the decrease in ascorbic acid near the factory was due to sulphur dioxide pollution. Ascorbic acid is known to regulate various physiological and biochemical processes in plants and helps them to resist pollution. Thus, the decreased level of ascorbic acid in plants near the pollution source would increase their sensitivity.

5.4 Glucase

Table 5. presents the glucose percentage of plants at a distance of 250 to 5000 m from the pollution source. The glucose content increased significantly as distance from the factory increased. Upto a distance of 2000 m, the glucose content showed a significant reduction when compared to the healthy palms at 5000 m. Thus the effect of increased sulphur content of palms existed beyond 2000 m, but palms at 5000 m were unaffected. This result is in sharp contrast to the findings of Agrawal et al. (1989) who reported increased glucose contents in plants exposed to Koziol and Jordan (1978) observed that sulphur dioxide. there was an increase in free sugar when exposed to low concentrations of sulphur dioxide in red kidney beans and exhibited toxic symptoms when the concentrations increased.

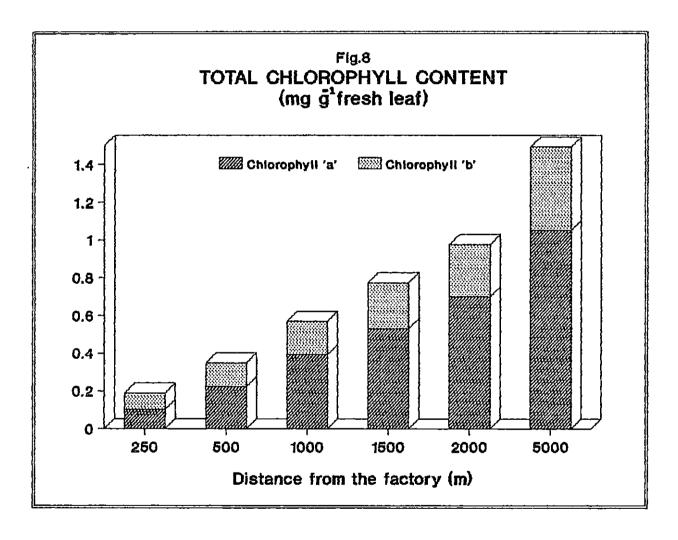
An increase in respiration rate was reported in sulphur dioxide exposed plants (Turk <u>et al</u>., 1974, Pandey, 1978). Since damage to plants increased with increase in concentrations of sulphur dioxide, greater amount of energy would be needed to correct this damage. Thus sugar and starch would be used in greater amounts for respiration when compared to healthy palms.

5.5 Plant pigments

5.5.1 Total chlorophyll

Table 6. presents the content of total chlorophyll at varying distances from the factory. The total chlorophyll content of healthy palms at 5000 m was significantly higher than that of palms upto 2000 m. Thus the effect of sulphur dioxide pollution in reducing the total chlorophyll content existed beyond 2000 m but not upto 5000 m.

Sulphur dioxide, at higher concentrations can interact with chlorophyll resulting in the loss of magnesium ions (Rao and Le Blanc, 1966). It was also observed that the excess free oxygen radicals formed due to sulphur dioxide exposure may affect cellular components including chlorophyll pigments (Shimazaki <u>et al</u>. 1980). The decrease in chlorophyll content was reported to be due to an



inhibition of chlorophyll synthesis (Spedding and Thomas, 1973) or due to its destruction (Malhotra, 1977, Shimazaki <u>et al</u>. 1980). In sulphur dioxide exposed plants, H_2O_2 dependent and peroxidase mediated oxidation of chlorophyll was reported to occur, (Nandi, 1984).

5.5.2 Chlorophyll 'a'

The chlorophyll 'a' content of leaves of palms showed significant reduction up to 1000 m (Table 6). Beyond 1000 m, sulphur dioxide pollution did not reduce significantly the chlorophyll 'a' content of palms. Rao and Le Blanc (1966) found that exposure of lichens to 5 ppm sulphur dioxide affected the decomposition of chlorophyll 'a' by displacing the magnesium atom from the chlorophyll molecule. The decrease in chlorophyll 'a' content of palms studied could be due to such a destruction of chlorophyll 'a' releasing magnesium ions.

5.5.3 Chlorophyll 'b'

Table 6. presents the chlorophyll 'b' content of palms at different distances from the factory. As distance from the factory increased, the chlorophyll 'b' content also showed a significant increase. The concentration in healthy palms at 5.0 km was significantly higher than that of palms upto 2.0 km. Thus sulphur dioxide pollution was seen to

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decrease the content of chlorophyll 'b' upto 2.0 km but palms at 5.0 km were unaffected. Similar results were obtained by Malhotra (1977) in pine needles treated with 10 to 50 ppm sulphur dioxide solution. He observed a decrease in chlorophyll 'b' following sulphur dioxide treatment which led him to suggest that the loss of chlorophyll 'b' was probably due to the splitting of the phytol chain by chlorophyllase enzyme.

5.5.4 Ratio of chlorophyll 'a' to 'b'

The ratio of chlorophyll 'a' to 'b' is presented in Table 6. As distance from the sulphur dioxide source increased, the ratio also showed a significant increase, the lowest value being shown by palms nearest to the factory, at This indicated that the effect of sulphur dioxide 250 л. pollution in decreasing the ratio was maximum at 250 m. The effect of sulphur dioxide pollution in reducing the ratio of chlorophyll 'a' to 'b' existed only upto a distance of 500 m since the ratio in palms beyond 500 m were comparable with that of healthy palms at 5000 m. It can be inferred that the toxic effect of sulphur dioxide pollution in lowering chlorophyll was more on chlorophyll 'a' than on chlorophyll Similar results were obtained by Williams et al. ъ. (1971) and Kondo <u>et</u> <u>al</u>. (1980).

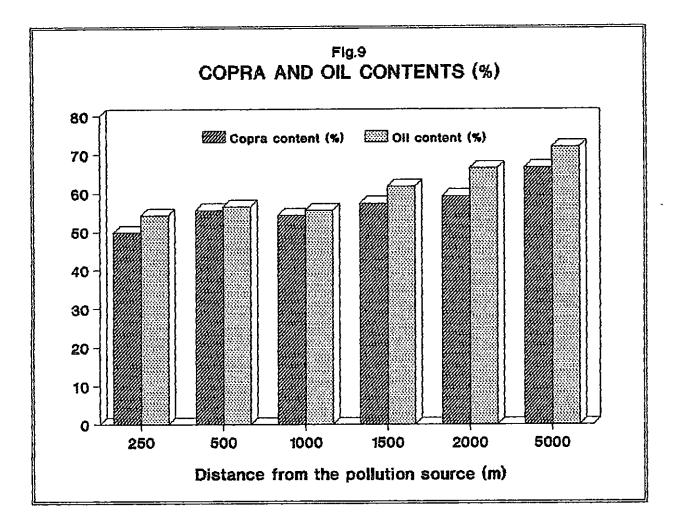
5.5.5 Total carotenoids

Table 6. presents the total carotenoid content of palms at varying distances from the factory. The sulphur in the atmosphere significantly decreased the dioxide carotenoid content of the coconut palms and the decrease was of the same magnitude upto 500 m. Beyond 500 m, the The decrease iп carotenoid contents were comparable. carotenoid content of palms exposed to sulphur dioxide was reported to be due to impaired synthesis of the pigments (Agrawal <u>et al</u>. 1989).

The carotenoid pigments of palms exposed to sulphur dioxide were less sensitive than chlorophyll. This was possibly because of the more resistant nature of carotenoids to destruction by sulphur dioxide pollution than chlorophyll (Kramer and Kozlowski, 1979).

5.6 Nut characters

The nut characters of the coconut palms are represented in Table 7. The weights of husked nut, shell per nut, fresh meat per nut and the weight of husked nut to shell ratios of palms at different distances from the pollution source showed no significant difference from healthy palms at 5000 m. But sulphur dioxide pollution significantly reduced the weight of husked nut to fresh meat



and weight of fresh meat to copra ratios, the oil content, weight of copra per nut and copra content.

The reduction in oil content may probably be due to the oxidation of lipids by sulphur dioxide. Shimazaki <u>et al.</u> (1980) suggested that sulphur dioxide fumigation produce singlet oxygen radicals (${}^{1}O_{2}$) which may oxidize lipid. Similar results were obtained by Constantinidou and Kozlowski (1979) who noticed that the total lipids decreased in <u>Ulmus americana</u> leaves exposed to 2 ppm sulphur dioxide.

SUMMARY

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6. SUMMARY

An experiment was conducted on coconut palms factory Kochuveli in Titanium near around the Thiruvananthapuram district to find out the toxic effects of the industrial atmospheric pollutant, sulphur dioxide, on tree crops. The different parameters studied were, the effect on plant pigment contents, mineral status, other metabolites and the copra and oil content of palms. Plant samples were collected around the pollution source, at distances of 250, 500, 1000, 1500, 2000 and 5000 m. The palms sampled at 5000 m were taken as control. Detailed chemical studies were conducted on the sampled palms and the data obtained were compared with that of the control. The salient findings of the study are enumerated below and the conclusions highlighted.

6.1 Visual observations

Visual observations of the palms showed a high degree of chlorosis and necrosis of the leaves with respect to control. In palms near the factory, a high degree of leaf necrosis accompanied by malformation of young leaves were seen.

6.2 Nutrient status of the fourteenth frond of coconut

6.2.1 Nitrogen

The nitrogen content of palms at different distances showed an increasing trend as the effect of sulphur dioxide pollution decreased. Thus the palms at 250 m contained the least nitrogen contents which could be attributed to increased sulphur content of the palms. Regression studies showed that 48 per cent of the decrease in nitrogen was due to sulphur dioxide pollution.

6.2.2 Phosphorus

Sulphur dioxide was found to reduce significantly the phosphorus content of palms near the Titanium factory. Correlation and regression studies also showed a significant negative relation between total sulphur and phosphorus content.

6.2.3 Potassium

Increased sulphur content was found to decrease the potassium content of palms probably by leaching the K^+ ions from the leaves or by affecting the absorption of potassium from the soil.

6.2.4 Calcium

The calcium contents of palms were also significantly affected by sulphur dioxide pollution. As the intensity of pollution decreased, the calcium content was also seen to be reduced.

6.2.5 Magnesium

Sulphur dioxide pollution had a significant effect in reducing the magnesium content of palms. Thus sulphur accumulation was found to decrease the magnesium content of coconut palms.

6.2.6 Total sulphur

Concentrations of sulphur dioxide in the atmosphere higher than normal was found to increase significantly the total sulphur content of the sampled palms.

6.2.7 Sulphate sulphur

The leaf content of sulphate sulphur was also found to increase in palms near the pollution source. A significant positive correlation was also obtained between total sulphur and sulphate sulphur. The rate of increase of sulphate sulphur was found to be more in the more polluted palms than in the less polluted ones.

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6.2.8 Iron

Sulphur dioxide pollution was found to cause an increased accumulation of iron in leaves of coconut palms. Thus sulphur accumulation could result in increased iron contents.

6.2.9 Manganese

The manganese content was found to increase in palms near the factory. But the increase in manganese levels were not significant when compared to control palms.

6.2.10 Sodium

The sodium content of palms also showed a significant reduction as the intensity of sulphur dioxide pollution increased. Regression studies showed that 18.6 per cent of the decrease in sodium content was explained by the increased sulphur content of palms.

6.2.11 Chlorine

Chlorine, which is considered as an essential element for coconut, also showed decreased values with increasing from the sulphur dioxide pollution.

6.2.12 Other micro nutrients

The copper content of palms were increased due to pollution. But sulphur dioxide seems to have no effect

on the content of zinc and molybdenum of coconut palms. Sulphur dioxide pollution had significantly reduced the content of boron in the affected coconut palms.

6.2.13 Aluminium

Sulphur dioxide pollution also had resulted in an accumulation of aluminium in exposed palms. The aluminium accumulation was found to be higher in palms near the factory than in palms less affected by sulphur dioxide pollution.

6.3 Other metabolites

The content of other metabolites like glucose and ascorbic acid had decreased owing to increased sulphur in palms. The decrease was more in palms near the source of pollution.

6.4 Catalase activity

Although the activities of catalase enzyme showed a decreasing trend with increased sulphur content, no significant difference was observed in values with increased pollution.

6.5 Plant pigments

All the studied plant pigments like total chlorophyll, chlorophyll 'a', chlorophyll 'b' and carotenoids were found to be affected by sulphur dioxide pollution, with their contents dropping significantly as distance from the factory decreased.

6.6 Nut characters

The nut characters were not affected by sulphur dioxide pollution, except the copra and oil contents, the ratios of the weight of husked nut to fresh meat and the weight of fresh meat to copra. The copra and oil contents showed a significant decrease with increased pollution, while the ratios of the weights of husked nut to fresh meat and the weights of fresh meat to copra showed significant increase in palms near the Titanium factory.

The following important conclusions were drawn from the above study.

- Sulphur dioxide pollution, though considered to be less toxic to tree crops, had affected the coconut palms near the Titanium factory significantly.
- 2. The pollution had caused visual damage to the affected palms and also altered their chemical composition.

- 3. The total sulphur and sulphate sulphur contents of the affected palms were highly increased.
- 4. All the macro nutrients except magnesium were affected significantly due to sulphur dioxide pollution.
- 5. The contents of iron and copper were increased while those of boron, sodium and chlorine were decreased with increased sulphur accumulation.
- The content of aluminium was increased significantly due to increase in sulphur accumulation.
- 7. Sulphur dioxide pollution had affected significantly the pigment content of leaves.
- 8. The minor elements like zinc, molybdenum and mangamese, and the activity of catalase enzyme were not significantly affected due to increased sulphur dioxide pollution.
- 9. The concentrations of other metabolites like glucose and ascorbic acid were significantly reduced in plants due to increased sulphur accumulation.
- 10. The adverse effects of sulphur dioxide did not exist upto 5.0 km from the source of sulphur dioxide emission.

These studies conducted on coconut palms are replicable on other tree crops and also on short duration crops. The effect of sulphur dioxide can be studied by subjecting the plants to high levels of sulphur dioxide in exposure chambers. Sulphur dioxide pollution is to be given due importance since the proposed Thermal Power Plant at Kayamkulam, Kerala, can cause high level of pollution in the surrounding area where coconut dominates the tree crops.

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* Originals not seen

APPENDICES

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APPENDIX - I

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ABSTRACT OF ANOVA

N, P, K, Ca and Mg content of palms

Source	df	Mean squares	F
Treatments	5	0.92376	7.199**
Error	24	0.12831	
Treatments	5	0.0003B	28.548**
Error	24	0.00001	
Treatments	5	0.26953	19.205**
Error	24	0.01403	
Treatments	5	0.51687	18,993**
Error	24	0.02721	
Treatments	5	0.01482	2.108 ^{ns}
Error	24	0.00703	
	Treatments Error Treatments Error Treatments Error Treatments Error Treatments	Treatments 5 Error 24 Treatments 5 Error 24 Treatments 5 Error 24 Treatments 5 Error 24 Treatments 5 Error 24	Treatments 5 0.92376 Error 24 0.12831 Treatments 5 0.00038 Error 24 0.00001 Treatments 5 0.26953 Error 24 0.01403 Treatments 5 0.51687 Error 24 0.02721 Treatments 5 0.01482

****** Significant at 1% level

ns Not significant

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APPENDIX - II

ABSTRACT OF ANOVA

Total sulphur, sulphate sulphur and their ratio at different distances

Parameter	Saurce	df	Mean squares	F
Total sulphur				
	Treatments	5	1.36174	15.573 ^{**}
	Error	24	0.08744	
Sulphate sulphur				
	Treatments	5	0.06544	17.971**
	Error	24	0.00364	,
Sulphate sulphur: total sulphur				
	Treatments	5	0.00079	9.179**
	Error	24	0.00009	

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Significant at 1% level **

APPENDIX - III

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ABSTRACT OF ANOVA

Micronutrient content of the palm

Parameter	Source	df	Mean squares	F
Iron				
	Treatments	5	109375.8	3.096*
	Error	24	35326.5	
Manganese				
	Treatments	5	87816.05	2.435 ^{ns}
	Error	24	36086.33	
Соррег				
	Treatments	5	78.726	4.836**
	Error	24	16.278	
Zinc				
	Treatments	5	976.753	0.571 ^{ns}
	Error	24	1711.483	
Boran				
	Treatments	5	72.464	5.934**
	Error	24	12.212	
Molybdenum				
	Treatments	5	0.1079	2.057 ^{ns}
	Error	24	0.0087	
	Significant a	at 5%]	level ns No	t significa
1	<u> </u>			

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APPENDIX - IV

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ABSTRACT OF ANOVA

Contents of Na, Cl and Al at different distances

				a
Parameter	Source	df	Mean squares	F
Sodium			, <u> </u>	
	Treatments	5	0.0358	4.555'
	Error	24	0.0078	
Chlorine				
	Treatments	5	0.1159	89.127**
	Error	24	0.0013	
Aluminium				
	Treatments	5	66096.7500	11.492**
	· Error	24	5751,3860	
*	Significant at 5%	level		
**	Significant at 1%	level		

APPENDIX - V

ABSTRACT OF ANOVA

Catalase activity, ascorbic acid T and glucose content

Parameter	Source	df	Mean squares	ج
Catalase activity				
	Treatments	5	0.0563	1.19 ^{ns}
	Error	24	0.0472	
Ascorbic acid				
	Treatments	5	0.1457	22.55**
	Error	24	0.0065	
Glucose				
	Treatments	5	4.6887	45.70**
	Error	24	0.1026	

****** Significant at 1% level

ns Not significant

APPENDIX - VI

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ABSTRACT OF ANOVA

Pigment concentration in the 14th leaf of coconut

Parameter	Source	df	Mean squares	F
Total carotenoids				
	Treatments	5	0.03518	17.003**
	Error	24	0.00207	
Total chlorophyll				
	Treatments	5	0.10628	18.846**
	Error	24	0.05870	
Chlorophyll `a'				
	Treatments	5	0.40512	6.705**
	Error	24	0.06042	
Chlorophyll `b'				
	Treatments	5	0.07439	14.284**
	Error	24	0.00521	
Chlorophylla/b'				
	Treatments	5	1.35781	17.383**
	Error	24	0.07811	

****** Significant at 1% level

APPENDIX -VII

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ABSTRACT OF ANOVA

Nut characters of the coconut palm

Parameter	Source	df	Mean squares	F
Weight of husked	nut			
	Treatments	5	3680.0	0.5697 ^{ns}
	Error	24	6459.2	
Weight of shell/n	цt			
	Treatments	5	431.35	0.6136 ^{ns}
	Error	24	702.96	
Weight of fresh m	eat/nut			
	Treatments	5	1730.13	0.9789 ^{ns}
	Error	24	1767.37	
Weight of copra/n	ut			
	Treatments	5	2754.59	3.4632*
	Error	24	795.40	
Copra content				
	Treatments	5	158.00	5.7921**
	Error	24	27.28	
Fresh meat : copr	a			
	Treatments	5	. 0.1390	5.1927 ^{**}
	Error	24	0.0268	
Husked nut : fres	h meat			
	Treatments	5	0.0382	3.2467*
	Error	24	0.0118	
Husked nut : shel	1			
	Treatments	5	0.0955	0.4192 ^{ns}
	Error	24	0.2279	
Oil content				
	Treatments	5	244.4109	6.5544 ^{**}
	Error	24	37.2897	

Significant at 5% level

****** Significant at 1% level

ns Not significant

TOXIC HAZARDS OF THE INDUSTRIAL ATMOSPHERIC POLLUTANT, SO_2 , ON TREE CROPS

By RANI, B.

ABSTRACT OF A THESIS submitted in partial fulfilment of the requirement for the degree **MASTER OF SCIENCE IN AGRICULTURE** Faculty of Agriculture Kerala Agricultural University

Department of Soil Science and Agricultural Chemistry COLLEGE OF AGRICULTURE Vellayani – Thiruvananthapuram

ABSTRACT

A study was conducted to assess the effects of the industrial atmospheric pollutant, sulphur dioxide, on tree crops. The Veli area in Thiruvananthapuram district, Kerala which has been established as a polluted zone, due to the working of the Travancore Titaninum products, was selected as the experimental site. Since coconut dominates the tree crops in the area, and due to its added importance as an oilseed, the study was conducted on coconut palms near the factory. Influence of sulphur dioxide pollution on plant like sulphur content of foliage, pigment parameters concentration, macro and micro nutrients, plant metabolites like glucose and ascorbic acid, catalase activity and the copra and oil contents of nuts were studied. Leaf and nut samples were taken at distances of 250, 500, 1000, 1500, 2000 and 5000 m, with the samples at 5000m taken as control. Visual observations, detailed chemical analyses of leaf samples and study of nut characters were conducted on the sampled palms.

Visual observations revealed a high degree of chlorosis and necrosis of palms near the factory. As distance from the pollution source increased, the intensity

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of damage decreased, with the control palms at 5000 m showing no signs of visible injury. Data from chemical analyses showed significantly higher concentration of total sulphur and sulphate sulphur in palms near the Titanium factory, (1.731 and 0.364 per cent respectively). Α drastic reduction was noticed in the plant nutrients like nitrogen, phosphorus, potassium and calcium in palms exposed to higher sulphur dioxide concentrations. Magnesium content was not affected significantly though in palms near the factory, there was a decrease in concentration. Among the micronutrients analysed, iron, copper and boron were affected, with the contents of iron and copper increasing with increased sulphur dioxide pollution and boron showing a decrease. Sulphur dioxide had no effect on the zinc. molybdenum and manganese contents while sodium and chlorine The contents of aluminium contents was reduced. was increased significantly in palms near the pollution source. Plant metabolites like ascorbic acid and glucose were decreased but the activity of catalase enzyme in leaf remained unaffected. The plant pigments like chlorophyll and carotenoids were also reduced in quantity, which may either be due to their degradation or decreased production. Among the nut characters studied, the contents of copra and oil were drastically reduced. The adverse effects of increased sulphur dioxide content in the atmosphere was high

upto 1 km from the source and gradually decreased with the effect not felt at 5 km.

These findings reveal that concentrations of sulphur dioxide higher than normal in the atmosphere can lead to plant injury in the surrounding area, in addition to the effects on human beings. The establishment of new industries and thermal power stations pose a new treat to the cultivated and native plants in that area. Since industrialization is the forerunner of development, the contribution of industries to toxic gases should be reduced by the adoption of suitable pollution control measures, if plant life in nature should proceed unhindered.

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