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# Terpenes Emitted to Air from Forestry and the Forest Industry

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1992

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# Terpenes Emitted to Air From Forestry and the Forest Industry

by

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# ABSTRACT

A major environmental concern with respect to hydrocarbon emissions is the formation of phytotoxic photooxidants. The work reported in this thesis focusses on the poorly studied anthropogenic terpene emissions from the industrial use of softwood. The advanced analytical determinations were made by adsorption sampling followed by thermal desorption and gas chromatography in the laboratory.

Monoterpenes from forestry were analyzed for Scots pine (*Pinus sylvestris*) and Norway spruce (*Picea abies*) (I). Near to a harvester, the total monoterpene concentrations reached ~1000 $\mu g/m^3$, whereas the background level was ~1 $\mu g/m^3$. Prominent monoterpenes were α-pinene, β-pinene, 3-carene, camphene, limonene, β-phellandrene, myrcene and terpinolene. Local formation of phytotoxic photooxidants may occur because of the short lifetimes of terpenes in air.

Terpenes in process emissions and plumes from kraft pulp industries were found to have a uniform composition similar to that of pulpwood and of recovered sulphate turpentine (II). Predominant monoterpenes were α-pinene and 3-carene from Scots pine. The emitted terpenes give rise to photooxidants and to oxidation of co-emitted sulphur and nitrogen oxides.

The monoterpenes in emissions from industries producing stone groundwood (III) and thermomechanical pulp (IV) were similar in composition to that of the processed pulpwood from Norway spruce. The major monoterpenes were α-pinene (>50%) and β-pinene (~25%). The process emissions from a sulphite mill consisted mainly of *p*-cymene, formed from spruce monoterpenes by acid rearrangements (IV). The terpene emissions from the barking of timber and pulpwood differed somewhat in composition from that of the wood (V). Increased proportions of β-phellandrene and myrcene were observed for Norway spruce.

Oxidative decomposition and acid rearrangements of monoterpenes in the sampling cartridges were studied as major analytical difficulties (VI). Pretreatment with thiosulphate and hydrogencarbonate prevented unwanted reactions of the terpenes.

*Keywords:* Norway spruce, Scots pine, logging, barking, pulp mills, monoterpenes, adsorbent sampling, gas chromatography, photooxidants

## LIST OF PUBLICATIONS

This thesis is based on the following papers, as referred to in the text by Roman numerals (**I-VI**).

**I.** **Conifer Monoterpenes Emitted to Air by Logging Operations**
Strömvall, A.-M. and Petersson, G. (1991)
*Scandinavian Journal of Forest Research* **6**, 253-258

**II.** **Photooxidant-forming Monoterpenes in Air Plumes from Kraft Pulp Industries**
Strömvall, A.-M. and Petersson, G. (1992)
Accepted for publication in *Environmental Pollution*

**III.** **Ambient Monoterpenes from Stone Groundwood Pulp Production**
Strömvall, A.-M. and Petersson, G. (1990)
*Holzforschung* **44**, No. 6, 449-452

**IV.** **Terpenes Emitted to Air from TMP and Sulphite Pulp Mills**
Strömvall, A.-M. and Petersson, G. (1992)
*Holzforschung* **46**, No. 2, 99-102

**V.** **Monoterpenes Emitted to Air from Industrial Barking of Scandinavian Conifers**
Strömvall, A.-M. and Petersson, G. (1992)
Accepted for publication in *Environmental Pollution*

**VI.** **Protection of Terpenes Against Oxidative and Acid Decomposition on Adsorbent Cartridges**
Strömvall, A.-M. and Petersson, G. (1992)
*Journal of Chromatography* **589**, 385-389

# CONTENTS

# INTRODUCTION

The work behind this thesis was carried out at the department of Chemical Environmental Science during the years 1988-1992. The main reason for starting the project was the potential importance of anthropogenic terpene emissions for the formation of phytotoxic photooxidants. Related research is carried out at the department on volatile petroleum hydrocarbons. These hydrocarbons have long been recognized as major precursors of photooxidants, and great efforts are being made to decrease emissions from traffic, industry and other sources. Man-made emissions of terpene hydrocarbons turn out to be of a similar size in conifer areas but have been little studied. Therefore, this work brings up several new facts and problems which may be of great importance to the environment as well as the forest industry.

The results have been published internationally in six articles (**I-VI**). One article (**I**) deals with emissions from logging operations, whereas four articles (**II-V**) deal with industrial emissions. Important analytical aspects are treated in a separate article (**VI**). The monoterpenes studied and a comparison of their occurrence in different emissions are given in Table I.

**Table 1.** Monoterpenes emitted from the industrial use of Scandinavian conifers[a].

| | Logging Spruce (I) | Logging Pine (I) | Sulphate pulp mill (II) | SGW and TMP pulp mills (III,IV) | Barking Spruce (V) | Lifetime in air (hours) | Main reactants day, summer |
|---|---|---|---|---|---|---|---|
| bicyclic (1=) | | | | | | | |
| α-pinene | +++ | +++ | +++ | +++ | +++ | 2 | OH,$O_3$ |
| β-pinene | +++ | ++ | ++ | +++ | +++ | 2 | OH |
| 3-carene | ++ | +++ | +++ | ++ | ++ | 1 | OH,$O_3$ |
| camphene | ++ | ++ | ++ | ++ | ++ | 2 | OH |
| α-thujene | + | + | + | + | + | 1 | OH,$O_3$ |
| monocyclic (2=) | | | | | | | |
| limonene | ++ | ++ | ++ | ++ | ++ | 0.5 | OH,$O_3$ |
| β-phellandrene | ++ | ++ | ++ | ++ | ++ | 1 | OH,$O_3$ |
| terpinolene | + | ++ | ++ | + | + | 0.1 | $O_3$ |
| γ-terpinene | + | + | + | + | + | 0.5 | OH,$O_3$ |
| α-phellandrene | + | + | + | + | + | 0.1 | $O_3$ |
| α-terpinene | + | + | + | + | + | 0.02 | $O_3$ |
| acyclic (3=) | | | | | | | |
| myrcene | ++ | ++ | ++ | ++ | ++ | 0.2 | $O_3$,OH |
| tricyclic (0=) | | | | | | | |
| tricyclene | + | + | + | + | + | 5 | OH |
| aromatic | | | | | | | |
| *p*-cymene | + | + | + | + | + | 2 | OH |

[a] Major (>10%), prominent (1-10%) and minor (<1%) components are marked with three, two and one asterisk, respectively.

# NATURAL OCCURRENCE OF TERPENES

Terpenes are biogenic hydrocarbons present in large amounts in conifers and in smaller amounts in a large variety of other plants. Structurally, the terpenes may be regarded as polymers of isoprene (2-methylbutadiene). Monoterpenes ($C_{10}H_{16}$) predominate among the volatile terpenes. Sesquiterpenes ($C_{15}H_{24}$), diterpenes ($C_{20}H_{32}$) and triterpenes ($C_{30}H_{48}$) have been identified in large numbers in plant material. The chemical properties of the terpenes depend much on the presence of one or more olefinic double bonds in the structure. The monoterpenes may be grouped as bicyclic, monocyclic and acyclic with one, two and three double bonds, respectively (Table 1).

## Terpenes in conifers

This study is focussed on the Scandinavian conifers Norway spruce (*Picea abies*) and Scots pine (*Pinus sylvestris*), although the principles apply to other conifers as well.

The composition of monoterpenes and related biogenic compounds varies much between different parts of the tree as demonstrated for Norway spruce (Bufler et al., 1990). This is also evident from studies of specific tissues of Norway spruce, such as wood (Kimland and Norin, 1972; Schuck and Schütt, 1975), bark (Heeman and Francke, 1977), needles (Jüttner, 1988a) and female flowers (Borg-Karlsson et al., 1985). Conifer monoterpenes are often studied by analyzing the cortical oleoresin released when the tree is deliberately wounded, i. e. by cutting off shoot buds. Such studies have demonstrated large differences between genetic varieties of Norway spruce (Thorin and Nommik, 1974; Esteban et al., 1976).

The content of volatile biogenic compounds in wood of Scots pine (Flodin and Andersson, 1977) from Sweden is very different not only from that of Norway spruce but also from that of other pine species and other varieties of Scots pine (Hafizoglu, 1983). The monoterpene composition of cortical oleoresin from Scots pine varies considerably even within Sweden (Yazdani and Nilsson, 1986). It has also been demonstrated that non-genetic factors, such as fertilization, have an impact on the monoterpene composition (Hiltunen et al., 1975).

Clearly, the differences in composition between parts of the tree, individual trees and tree populations should be considered when anthropogenic terpene emissions are studied. This work reports average emissions from a large number of trees and the industries studied receive wood from large regions.

## Ecological aspects on conifer terpenes

Basically, the terpenes act as a solvent in the conifer oleoresin. When a tree is wounded, oleoresin flows to the wound and the volatile terpenes are emitted to air. Non-volatile components of the oleoresin are left as a hydrophobic cover, protecting the tree physically and chemically against attacks from insects, fungi and other organisms. The content of oleoresin is normally highest in vulnerable parts of the tree.

The complex interactions between insects and Scandinavian conifers are studied by several research groups. For Norway spruce, attack by bark beetles has been shown to induce the release of terpenes and terpene-related compounds from the tree (Birgersson and Bergström, 1989). Bark beetles convert monoterpenes stereospecifically and even produce pheromones from them. Recent determinations of the enantiomeric composition of monoterpenes are therefore of great ecological interest (Lindström et al., 1989). For Scots pine, specific monoterpenes are important for the attraction and orientation of insects studied (Schroeder and Lindelöw, 1989; Nordlander, 1991). It is concluded that anthropogenic emissions of monoterpenes may also be of interest with respect to insects and other organisms.

## Terpenes in the air of conifer forests

The atmospheric chemistry and the photooxidant problems cannot be properly understood without knowledge of natural terpenes in the air. Worldwide efforts have therefore been made to determine concentrations of mainly monoterpenes in forest air. Results are available from many regions with different conifer species, i. e. the USA (Roberts et al.,1985), Japan (Yokouchi et al., 1983), Russia (Isidorov et al., 1985), Italy (Ciccioli et al., 1984), France (Riba et al., 1987), Germany (Jüttner

1988b), Norway (Hov et al., 1983) and Sweden (Janson et al., 1992). The recorded concentrations depend on many factors, such as conifer species and varieties, geographic region, topography, age and density of conifer stand, sampling point, temperature, air humidity, air stratification, time of the day and time of the year. In an early study at this department, total monoterpene concentrations of ~ 100 μg/m$^3$ were recorded in a stand of Scots pine during conditions chosen to favour high concentrations (Petersson, 1988). Typical concentrations reported in conifer forests are 1-10 μg/m$^3$, but the variations are large.

Recently, the annual natural emissions of monoterpenes to air from Swedish conifer forests were determined to be ~ 400 000 tons (Janson, 1992). It is emphasized that these emissions give rise to ecologically sound concentration levels in forest air. Only terpenes from anthropogenic emissions should be regarded as air pollutants. The parallels with biogenic and anthropogenic emissions of compounds such as ethene and sulphur dioxide are evident.

## TERPENES AND PHOTOOXIDANTS

Hydrocarbons are decomposed in complicated reactions in air, and a wide range of the products have oxidative properties. These products are called photooxidants because certain key reactions are photochemical, i. e. mediated by light.

### Phytotoxic photooxidants

A wide range of photooxidants are phytotoxic because of reactions with essential biological molecules. Conifers are particularly vulnerable because their needles are exposed during several years. Photooxidants formed from anthropogenic emissions of hydrocarbons are now recognized as a major cause of widespread forest decline both in the United States and in western Europe. In Figure 1, structures are given for some of the best-known types of photooxidants.

| | | |
|---|---|---|
| $O_3$ | HOOH, ROOH, ROOR | HO•, RO•, HOO•, ROO• |
| Ozone | Peroxides | Odd-electron radicals |
| $RONO_2$ | $R(CO)OONO_2$ | RC-O-O• |
| Alkylnitrates | Peroxyacylnitrates | Criegee biradicals |

**Figure 1.** Important classes of phytotoxic photooxidants.

For a long time, the effects of photooxidants on forest decline were blamed almost exclusively on ozone (Ashmore et al., 1985). Recent studies emphasize effects of less easily studied photooxidants, such as hydrogen peroxide (Möller, 1989), organic peroxides (Hellpointner and Gäb, 1989) and oxygen radicals (Möller, 1988). Similarly, interest has shifted from the classical phytotoxic peroxyacetylnitrate (PAN) to a wider range of organic nitrates and other nitrogen-containing photooxidants (Jay and Stieglitz, 1989).

## Reactivity of terpenes in air

The rate-limiting step in the decomposition of hydrocarbons in air during daylight is normally an initial reaction with the OH radical. For certain alkenes, reaction with ozone may compete. Reactions and rate constants for various hydrocarbons have recently been reviewed (Atkinson, 1990).

The monoterpenes are alkenes and react more rapidly with both the OH radical and $O_3$ than most other volatile hydrocarbons. Recent studies of rate constants with $O_3$ (Atkinson et al., 1990) report lower values than previous determinations. Terpenes which are highly branched at the double bonds have high rate constants and are thought to react preferentially with ozone (Table 1). The prominent bicyclic monoterpenes normally react with the OH radical during the day. In terpene emission plumes, strongly diverging concentration ratios between ozone and the OH radical may change the reaction paths and lifetimes given in Table 1. During the night, the OH radical almost disappears from the air, and reactions with ozone and the $NO_3$ radical take over and give different lifetimes for the monoterpenes (Corchnoy and Atkinson, 1990).

## Photooxidants from terpenes

Smog-chamber experiments for α-pinene demonstrate that monoterpenes like other alkenes give rise to ozone formation (Nolting and Zetzsch, 1988). Other photooxidants from terpenes may well be more phytotoxic, however. Much research is therefore now done to clarify the reaction paths of and reaction products from terpenes in air.

Studies of monoterpene reactions with the OH radical (Arey et al., 1990; Hatakeyama et al., 1991) and with ozone (Yokouchi and Ambe, 1985; Hatakeyama et al., 1989) demonstrate the formation of a wide range of aldehydes and other carbonyl compounds from intermediate radicals. Aldehydes act as oxidants and may accelerate radical formation by photolytic cleavage.

Criegee biradicals formed from monoterpenes are thought to be involved in the formation of phytotoxic hydrogen peroxide (Becker et al., 1990) as well as phytotoxic organic peroxides (Gäb et al., 1985). The Criegee radicals are formed by decomposition of ozonides resulting from the addition of ozone to a double bond. The ability of terpenes and other alkenes to lower the concentration of ozone in air in an initial reaction phase may therefore turn out to be a disadvantage with respect to the total phytotoxicity of terpene emission plumes.

## Man-made emission plumes

The terpene concentrations in industrial and other man-made emission plumes are typically 10-1000 times higher than in those resulting from natural conifer forest emissions. This in itself is the main reason for the occurrence of phytotoxic levels of photooxidants. Because of the short lifetimes of the monoterpenes (Table 1), the highest photooxidant concentrations are to be expected within 5 hours on the time scale and within 50 km on the distance scale, given favourable day-time conditions for photooxidant formation.

Especially for industrial emissions of terpenes, it is important to consider interactions with other emissions. Emissions of gaseous chlorine greatly accelerate photochemical reactions by the rapid formation of Cl radicals (Hov, 1985). Nitrogen dioxide increases the reaction rate of monoterpenes in the presence of ozone and leads to the formation of organic nitrates (Kotzias et al., 1990). Sulphur dioxide in the presence of ozone is oxidized much more rapidly if monoterpenes are present (Stangl et al., 1988). An increased concentration of OH radicals speeds up the oxidation of $NO_2$ to $HNO_3$. From these facts it is concluded that terpenes co-emitted with $SO_2$ and $NO_x$ may increase local acid deposition and soil acidification.

Photooxidants are also of concern with respect to health hazards. An irradiated mixture of propene and $NO_x$ gives rise to a variety of mutagenic products (Kleindienst et al., 1985). The products from terpenes are similar in nature. Nitrogen oxides from combustion engines and stationary combustion are normally co-emitted with terpenes in both forestry and the forest industry.

# TERPENES FROM FORESTRY

The study of terpene emissions from forestry (I) was focussed on modern logging operations. These are likely to cause the highest concentrations and the largest man-made emissions from forestry. Apparently, this is the first systematic investigation of terpenes from forestry. Emphasis was put primarily on determinations of the composition and concentrations of monoterpenes.

## The impact of logging on the ecosystem

Logging in itself is a most dramatic transition of the conifer ecosystem. The recorded concentration increases of up to 1000 times for a wide range of different monoterpenes demonstrate a similar striking change in the chemical composition of the air. This is likely to influence the function of the ecosystem and the relations between its organisms. The reported results may therefore be of interest in several ways beyond the environmental aspects discussed.

## Character of the emissions

For a better understanding of various aspects on the emitted terpenes, comparisons with traffic-emitted hydrocarbons may be helpful. The recorded monoterpene concentrations near to a harvester (~1000 $\mu g/m^3$) are higher than the hydrocarbon concentrations in a street with dense traffic. Virtually all the monoterpenes are highly reactive in air with short lifetimes. Equally reactive $C_4$-$C_6$ alkenes constitute only a few per cent of the total hydrocarbons from vehicle emissions (Löfgren and Petersson, 1992). This means that photooxidants from terpenes are formed more rapidly and within shorter distances than photooxidants from traffic emissions. The formation of ozone from vehicle emissions is favoured by the co-emissions of $CH_x$ and $NO_x$. Similarly, the formation of ozone, organic nitrates and other nitrogen-containing photooxidants from terpenes is favoured by co-emissions of $NO_x$ from harvesters and other diesel machines used in forestry. Power saws contribute with considerable emissions of exhaust hydrocarbons. After-logging emissions of terpenes, without co-emission of $NO_x$, favour the formation of phytotoxic peroxides.

The distribution of emissions during the year is important because the photooxidant problems arise mainly during the spring and summer. Unfortunately, branch wood left from winter logging is likely to emit terpenes to air mainly during sunny and warm spring days. However, the emissions from logging operations during critical spring and summer periods are likely to give rise to worse problems. This is explained by the higher terpene concentrations and by co-emissions of nitrogen oxides.

## Prevention of photooxidant problems

The environmental consequences of terpene emissions from forestry are far from fully understood, but consideration of prevention measures at an early stage may offer great advantages. It is emphasized that potential photooxidant problems may be decreased in several widely different ways such as the following:

- Avoiding logging during the critical spring and summer high-pressure periods.
- Decreasing terpene emissions during logging by improved tools and logging methods.
- Decreasing $NO_x$ emissions from logging machines.

# TERPENES FROM CHEMICAL PULP MILLS

Chemical pulp includes sulphate (kraft) pulp and sulphite pulp. Terpenes were studied in the emissions from both sulphate (II) and sulphite (IV) mills. In principle, the terpenes pass the alkaline sulphate process unchanged, whereas extensive chemical conversions occur in the acid sulphite process. The total Swedish pulp production in 1989 included 61% sulphate pulp and 7% sulphite pulp.

## Turpentine

Recovery of terpenes as liquid turpentine is closely linked to pulp mill emissions. The more of the wood terpenes that can be recovered as turpentine, the less remains to be emitted to air. Sulphate turpentine is normally recovered in varying amounts at sulphate pulp mills. The monoterpene content in pulpwood of Swedish conifers has been studied from turpentine (Groth, 1958). The total monoterpene content is estimated to be ~ 0.6% (Scots pine) and ~ 0.1% (Norway spruce) of the dry wood. A study of potential turpentine recovery from American and Canadian conifers (Drew and Pylant 1966) demonstrated large differences in the monoterpene composition and the total monoterpene content in chips from different species.

Turpentine should be regarded as a valuable by-product from pulp mills which can be used for a wide range of purposes (Drew, 1971; Pearl, 1982). The environmental aspect on terpene emissions adds to other arguments for increased recovery.

## Emissions from storage of roundwood and chips

Terpenes are present in conifer wood resin, which often causes problems in the pulping process (Back, 1960). During storage of roundwood, terpenes are slowly released to air. Chipping and particularly long storage of wood chips increase terpene losses markedly (Thornburg, 1963; Drew et al., 1971). More than half of the terpene content may be lost during chip pile storage for a few weeks. The losses occur mainly by evaporation to air. Microbial activity increases losses primarily by increasing the chip pile temperature, and the composition of the remaining terpenes is not much changed (Drew et al., 1971).

The terpene losses from chip storage can be efficiently decreased by using fresh chips in the kraft pulping process (Tate, 1967; Springer, 1978). Chemical treatment can also decrease losses (Springer and Zinkel, 1987) but may be environmentally questionable. Chips for the sulphite process are seasoned for process reasons (Dillner et al., 1981) but contain less terpenes when spruce wood is used. Terpene losses from roundwood can be decreased by short storage times and by wet storage.

## Emissions from the sulphate process

Sulphate pulp is produced in process systems based either on batch digesters or on continuous digesters. Terpenes are released mainly during different phases of the digesting process. Turpentine recovery systems (Drew et al., 1971; Landry and Stillwell, 1984) are used for both processes. In practice, the highest recovery is usually obtained for the batch process. Critical process points with respect to turpentine recovery were early discussed for both the batch process (Tate, 1967) and the continuous process (Jansson,1967). More recent studies discuss further methods of improving turpentine recovery (Tinnis and Kinnula, 1981; Foran, 1992).

The terpene quantities released in the process depend first of all on the terpene content in the conifer species used. In Swedish kraft pulp mills, Scots pine is used together with Norway spruce, but pine terpenes predominate in emissions (Table 1) as well as in turpentine because of the much higher terpene content in pine. The terpene quantities entering the process also depend on the degree of terpene losses from wood and chip storage. With efficient turpentine recovery, the use of fresh wood chips should be advantageous with respect to total terpene emissions. Terpene emissions which are difficult to recover as turpentine may be burnt together with the commonly burnt malodorous sulphur compounds. In summary, however, increased turpentine recovery to the level of the best industries appears to be the most efficient and advantageous way of decreasing terpene emissions.

## Emissions from the sulphite process

Sulphite pulp from conifers is produced in batch digesters under acid conditions. The monoterpenes released from the wood are converted by acid rearrangements with formation mainly of *p*-cymene. The *p*-cymene oil can be recovered (Pearl, 1982), and recovery has been practised in Sweden (Waller, 1941). The amounts of terpenes released in the process are smaller than in the kraft process because pine cannot easily be used. A large proportion of the spruce wood monoterpenes are lost already during the required seasoning of the chips (Dillner et al.,1981).

Among prominent anthropogenic emissions to air of alkylbenzenes, those of *p*-cymene from sulphite mills appear to be the most reactive in forming photooxidants. Recovery of *p*-cymene and efforts to decrease emissions for environmental reasons may well be required both in Scandinavia and in central Europe where forest decline is severe and the proportion of sulphite mills is high. A German study of the composition of *p*-cymene oil from sulphite processing of Norway spruce was recently published (Pörschmann et al., 1990) with these aspects in mind.

# TERPENES FROM MECHANICAL PULP MILLS

Mechanical pulp is produced by several different methods. Terpene emissions were studied for a stone groundwood (SGW) mill (III) and a thermo-mechanical pulp (TMP) mill (IV). The terpene emissions from the production of chemical thermo-mechanical pulp (CTMP) are vented to air in the same way as those from TMP mills, but may be similar in composition to those from sulphate or sulphite mills depending on the wood material and pretreatment chemicals. The proportion of mechanical pulp tends to increase and now exceeds 30% of the total pulp production in Sweden.

## Character of terpene emissions

Norway spruce is the only Scandinavian conifer suitable for the production of mechanical pulp. This means that the terpene content of the fresh wood is normally lower than for the kraft process. On the other hand, fresh wood is normally processed, meaning that storage losses are avoided.

In the traditional stone groundwood process, barked roundwood is ground on rotating stones. A large proportion of the monoterpenes are vented to air in high concentrations, bur recovery is not yet applied.

In the TMP process, wood chips are disintegrated in refiners. The terpenes are still often vented to air with steam after use of the steam for preheating chips and water. Fortunately, efficient turpentine recovery can be profitably combined with heat recovery, as demonstrated for an American TMP plant (Rockhill and Hostetter, 1982). Furthermore, the turpentine does not contain the unwanted sulphur contaminants present in sulphate turpentine. Considering the large TMP production volumes, installing turpentine recovery systems in TMP plants is likely to be given a high priority in efforts to decrease terpene emissions to air.

## TERPENES FROM BARKING

Almost all timber and pulpwood are barked before use in pulp mills and saw mills. Consequently, large monoterpene emissions result from barking. These emissions are also of special interest because they might be expected to differ in composition compared to monoterpenes from wood processing. Monoterpenes from industrial barking were therefore studied for Scots pine and Norway spruce (V).

The barking emissions may be regarded as a mixture of several monoterpene pools in certain proportions. Important pools are those of exuded oleoresin and of bark, phloem and sapwood. The proportions vary somewhat according to barking technique and type of roundwood. For spruce, significant differences in composition were demonstrated compared to wood processing. It should be noted that terpenes from barking in forests may have an impact on various insects.

With respect to photooxidant formation, it is essential that the terpene emissions from barking can be regulated as to time and place. Thus emissions can be decreased in the photooxidant season and in places with unfavourable co-emissions of other air pollutants from forest industries and urban areas.

## ANALYTICAL DETERMINATION OF TERPENES IN AIR

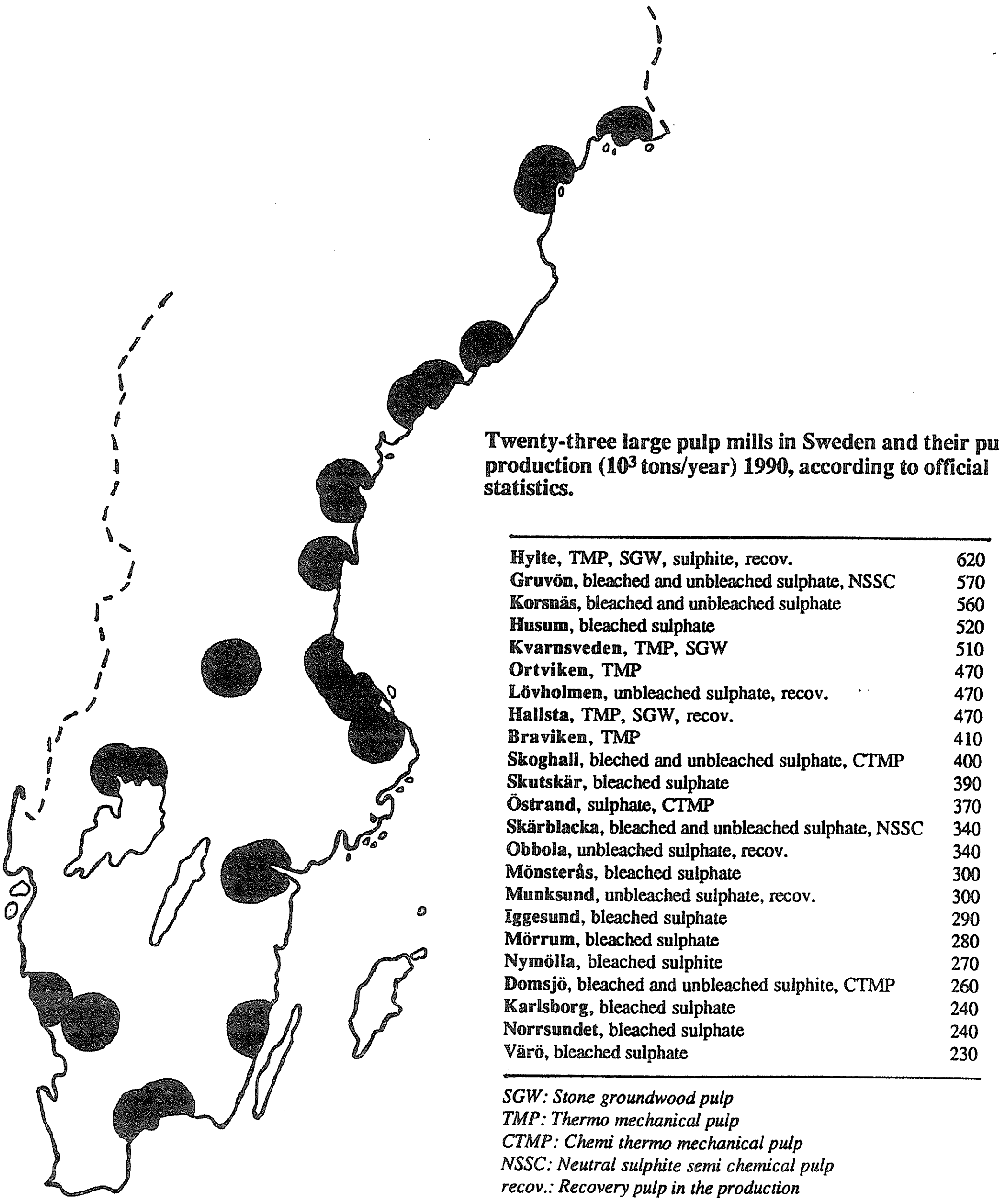
Adsorbent sampling followed by thermal desorption and gas chromatography has long been a common technique for advanced determinations of volatile hydrocarbons in air. The Tenax porous polymer is usually preferred for hydrocarbons with 5-15 carbon atoms. The determination of monoterpenes in air is challenging because of the high resolution needed and especially because of the high reactivity of the monoterpenes. Oxidative and acid sampling reactions which may give erroneous results were demonstrated and discusssed in a separate study (VI). These problems are of wide interest, and more or less subtle errors are likely to occur in the international literature because they have been disregarded.

Oxidative reactions in the front of the adsorption cartridge occur first of all for the monoterpenes which react rapidly with ozone (Table 1). If the cartridges are not protected against oxidation, it is difficult to know if these terpenes are lost by oxidative reactions in the atmosphere or in the cartridge.

The rapid acid rearrangements of several monoterpenes may be of importance as soon as acid components are present in the sampled air. An interesting aspect is the possibility of acid rearrangements in the environment due to acidification. In studies of forest decline, the acidification of needle surfaces by deposition and acid mist has attracted a great deal of interest.

## AREAS INFLUENCED BY INDUSTRIAL EMISSIONS

Because of the rapid formation of photooxidants from terpenes, industrial emissions give rise to the highest photooxidant levels within short distances. This is illustrated in Figure 2 by the marked areas, expected to be most influenced by large industrial terpene emissions in Sweden.



**Twenty-three large pulp mills in Sweden and their pulp production ($10^3$ tons/year) 1990, according to official statistics.**

| | |
|---|---|
| **Hylte**, TMP, SGW, sulphite, recov. | 620 |
| **Gruvön**, bleached and unbleached sulphate, NSSC | 570 |
| **Korsnäs**, bleached and unbleached sulphate | 560 |
| **Husum**, bleached sulphate | 520 |
| **Kvarnsveden**, TMP, SGW | 510 |
| **Ortviken**, TMP | 470 |
| **Lövholmen**, unbleached sulphate, recov. | 470 |
| **Hallsta**, TMP, SGW, recov. | 470 |
| **Braviken**, TMP | 410 |
| **Skoghall**, bleched and unbleached sulphate, CTMP | 400 |
| **Skutskär**, bleached sulphate | 390 |
| **Östrand**, sulphate, CTMP | 370 |
| **Skärblacka**, bleached and unbleached sulphate, NSSC | 340 |
| **Obbola**, unbleached sulphate, recov. | 340 |
| **Mönsterås**, bleached sulphate | 300 |
| **Munksund**, unbleached sulphate, recov. | 300 |
| **Iggesund**, bleached sulphate | 290 |
| **Mörrum**, bleached sulphate | 280 |
| **Nymölla**, bleached sulphite | 270 |
| **Domsjö**, bleached and unbleached sulphite, CTMP | 260 |
| **Karlsborg**, bleached sulphate | 240 |
| **Norrsundet**, bleached sulphate | 240 |
| **Värö**, bleached sulphate | 230 |

*SGW: Stone groundwood pulp*
*TMP: Thermo mechanical pulp*
*CTMP: Chemi thermo mechanical pulp*
*NSSC: Neutral sulphite semi chemical pulp*
*recov.: Recovery pulp in the production*

**Figure 2.** Important pulp mills in Sweden, and local areas expected to be influenced by photooxidants from their terpene emissions.

The characteristic localization of pulp mills along coasts and large lakes markedly increases the formation of photooxidants during the critical high-pressure periods of spring and summer. This is due to the effect of circulation with land and sea breeze, which is known from many international studies of urban air pollution. The effect is increased by fjords, bays and narrow water passages, as demonstrated in a Scandinavian study (Hov, 1985). The sea breeze typically transports the photooxidants 20-40 km in over land.

The most serious effect to be feared from the photooxidants is increased forest decline in the areas around terpene-emitting industries, but contributions to effects on crops and human health cannot be excluded. It should be observed that the formation and effects of photooxidants from terpene emissions depend to a great extent on co-emitted other pollutants from industrial and urban sources. Hopefully, this thesis can contribute both to a better understanding of the character of terpene emissions and to efforts to decrease these emissions and their environmental effects.

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