Ambient monoterpenes from stone groundwood pulp production

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Subsequent studies of terpene emissions were made for:
TMP and sulphite pulp mills
Barking of logs and pulpwood
Kraft pulp mills

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Summary

Composition and ambient concentrations in air were
studied for monoterpenes from stone groundwood
production at a Swedish plant using exclusively pulp
wood from Norwegian spruce. Field samples were taken
on Tenax adsorption cartridges and analyzed by
thermal desorption combined with temperature
programmed capillary gas chromatography. The major
monoterpenes emitted from the process were α-pinene
(54-59%) and β-pinene (24-28%). Limonene, 3-carene,
β-phellandrene, camphene and myrcene (1-10% each)
followed in decreasing relative proportions. Total
ambient monoterpene concentrations above 500 μ g/m^3
were assessed at ground level downwind from the
emissions. Photo-oxidants formed in the monoterpene
plumes are discussed with respect to forest damage
and health hazards.

Introduction

Ozone and other photo-oxidants are now regarded as a major factor behind the widespread forest decline not only in the US, but also in Europe. It is also recognized that emissions of hydrocarbons rather than nitrogen oxides give rise to enhanced ozone levels in local and regional anthropogenic emission plumes (Guderian Ed. 1985). The role of reactive biogenic hydrocarbons like terpenes in the formation of photo-oxidants has been studied and debated for a long time (Bufalini and Arnts Eds. 1981). Ambient monoterpenes from anthropogenic emissions have escaped similar attention. The present study is part of a program for the study of terpenes from forestry and the forest industry and of their environmental impact.

Stone groundwood pulp (Casey Ed. 1980) has long been and is still produced in million ton quantities, partly because of the high yield (up to 97%) compared to chemical pulps. Technically, the terpenes are released in the grinding process at elevated temperatures. The wood in the grinding zone is heated to 100-200°C when the revolving water-cooled grindstone sets the wood fibres free. In Sweden, stone groundwood is made from Norwegian spruce only, which facilitates a stringent characterization of the terpene emissions.

Experimental

Industrial plant. The industry studied was Papyrus Mölndal AB in the centre of the town of Mölndal south of Göteborg. More than 30 000 tons yearly of dry groundwood pulp are produced from two adjacent stones (Great Northern - Tampella) which are normally operated both day and night. Terpene-containing steam is emitted through one pipe from each of the enclosed stones at a height of 5-10 metres. The pulp is used for cardboard production in another section of the plant. Farther away, paper is produced from chemical pulp inside the industrial complex.

Approximately 100 000 m^3 (solid volume) of pulp wood is required yearly. The softwood species used is exclusively Norwegian spruce (Picea abies) taken mostly from southern Sweden. Several thousand cubic metres of almost fresh unbarked and debarked pulp wood is stored in a wood-yard just south of the plant. Dry debarking is performed inside this wood-yard.

Sampling and analysis. Field sampling by adsorption was made on specially designed Tenax glass cartridges coupled to portable air sampling pumps. Samples were taken at ground level downwind from the emissions of monoterpenes. Sampling volumes were from 200 to 800 ml and sampling times from 20 to 80 minutes.

In the laboratory, thermal desorption was accomplished in the injector of a Carlo Erba gas chromatograph by the heated helium carrier gas. The fused silica capillary column (25 m x 0.33 mm i.d.) acted first as a cold trap and then as an analytical column. The stationary phase was a cross-linked BP-1 methyl silicone and the temperature was raised 2^{O}C min^{-1} linearly from 0°C. Detection was by flame ionization and the response factor of monoterpenes was set equal to that determined for n-heptane.

Further experimental details were given in a methodological study (Mattsson and Petersson 1982) with urban air pollutant applications. A modified application to monoterpenes in air was described in a recent study of biogenic terpenes in Scots pine forests (Petersson 1988).

Results and discussion

The results are summarized in Tables 1 and 2 and in Figure 1, which also illustrates the chromatographic separation of the monoterpenes.

Plume concentrations. In Table 1 results are given for samples selected as representative of ground-level downwind concentrations. As anticipated, the highest concentrations of more than 600 μg/m^{3} of total monoterpenes were recorded near the process emissions.

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Table 1. Concentration levels (µg/m³) of monoterpenes in ambient
air downwind from stone groundwood production.

	grinding plume near plant[a] 5/10/89	6/28/89	grinding plume housing area[b] 6/09/89	plume from woodyard[c] 5/30/89
α-pinene	350	360	92	32
camphene	13	15	3.1	1.5
β-pinene	160	160	46	19
myrcene	3.7	6.5	–	2.3
3-carene	24	32	6.7	4.5
β-phellandrene	13	19	2.9	4.3
limonene	22	39	4.2	3.8
p-cymene	3.9	3.5	0.9	0.5

[a]Samples taken on local street 50 m from the emissions 16³⁰-
17⁰⁰(10°C) and 23¹⁰-23⁵⁰(15°C).
[b]Sample taken in uphill area 150 m from the emissions 09³⁰-
10³⁰(15°C).
[c]Sample taken outside wood-yard during debarking 10⁵⁰-11³⁰(10°C).

Although the samples were taken along a street with
local traffic, the concentration of the most abundant
monoterpene (α-pinene) was approximately 100 times
higher than that of the most abundant alkylbenzene
(toluene) from traffic emissions. The concentrations
in the housing area should reflect the downwind
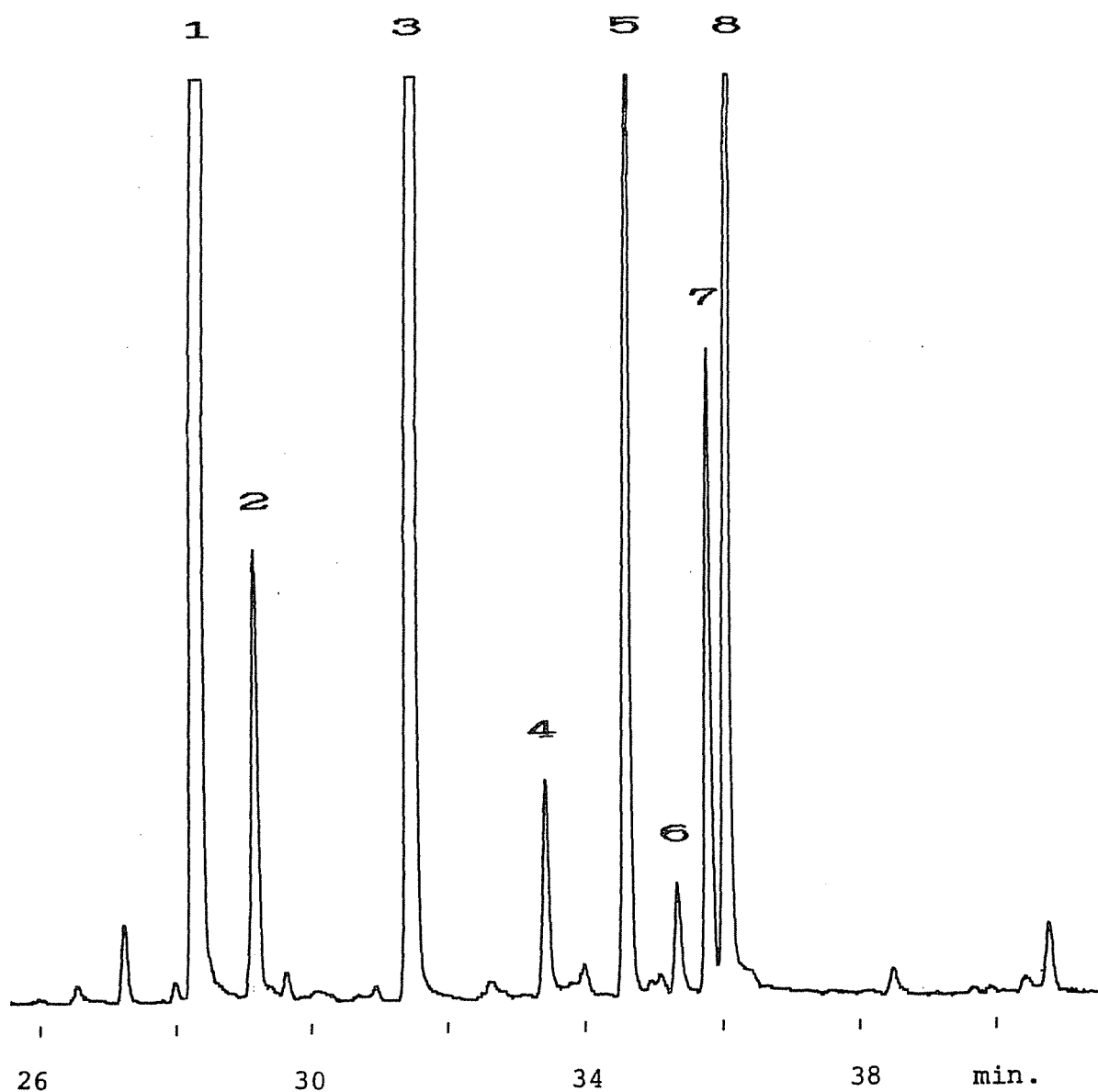exposure of the inhabitants from the grinding plume.
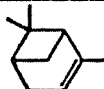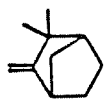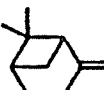
Figure 1.
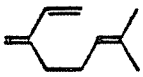
Gas chromatographic separation of monoterpenes in the near-plant plume from stone groundwood pulp production (1. α-pinene; 2. camphene; 3. β-pinene; 4. myrcene; 5. 3-carene; 6. p-cymene; 7. β-phellandrene; 8. limonene). Sample taken 6/28/89 23^{10}-23^{50}.
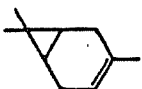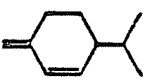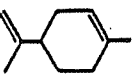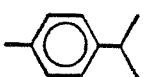
The samples were taken under conditions with turbulent air at positions where the smell of terpenes was strong. The fluctuating wind caused the sampling point to be not only below, but also often beside, the grindning plume centre. Consequently the concentrations in the centre of the plume are expected to be much higher than those given.

The concentrations just outside and above the wood-yard were much lower than those downwind of the grinding emissions. The wood-yard plume differs from the process plume not only by being approximately 100 m broad but also by reaching the sampling point all the time. The concentration ratios therefore do not necessarily reflect the emission ratios. In contrast to the grinding emissions, the wood-yard emissions are also expected to be strongly dependent on ambient parameters like temperature.

<u>Composition of monoterpenes</u>. In Table 2 the percentual composition of monoterpenes is given for samples taken downwind and near the process emissions. The individual night-time sample corresponds to the chromatogram of Figure 1 and is thought to be well representative. The narrow intervals for the five samples taken under somewhat differing conditions demonstrate a uniform composition of the emissions.

Table 2. Monoterpenes emitted to air from the grinding process; reaction rates with ozone, and composition(%).

	relative reaction rate (O$_3$)[a]	grinding plume 6/28/89 23^{10}-23^{50}	grinding plume interval for 5 samples[b]
α-pinene	8.4	56	54 — 59
camphene	1	2.2	1.7 - 3.1
β-pinene	2.1	25	24 - 28
myrcene	120	1.0	0.4 - 1.2
3-carene	12	5.0	4.0 - 7.4
β-phellandrene	18	2.9	2.1 - 3.3
limonene	64	6.0	3.6 - 7.4
p-cymene	0.001	0.5	0.4 - 0.7

[a]Rate constant for α-pinene $8.4 \times 10^{-17} cm^3$ molecule^{-1}s^{-1}; data from Atkinson et al. 1986.
[b]5/10/89, 16^{30}-17^{00}; 5/30/89, 10^{50}-11^{30} (two samples); 6/28/89, 23^{10}-23^{50} (two samples)

The content of the two predominant monoterpenes in the process plume was 54-59% for α-pinene and 24-28% for β-pinene in all samples. The low content of 3-carene contrasts with the very high content of this terpene in the terpene-rich Scots pine (Pinus sylvestris) which is the other major Scandinavian softwood species. A limited portion of Scots pine in the pulp wood may be used in certain groundwood plants and should then increase the content of 3-carene considerably. Limonene, β-phellandrene,

camphene and myrcene were present in proportions decreasing in this order. It is notable that the percentual content in needles of _Picea_ _abies_ is much higher for camphene, limonene and myrcene and lower for α- and β-pinene (Jüttner 1988 a). Retention data indicate that the compound eluting before α-pinene (Fig.1) is the saturated monoterpene tricyclene shown to be present in needles. The content of this species was similar to that of the monoterpene-related alkylbenzene p-cymene. The small components appearing after limonene in the chromatogram are γ-terpinene and terpinolene. A study of emissions from plywood veneer drying (Crown et al. 1983) reports almost the same monoterpenes from wood of American softwood species but in varying proportions.

The same monoterpenes were also recorded in the emissions from the wood-yard but the composition was found to be less uniform. The results given in the fourth column of Table 1 correspond to an elevated proportion of myrcene and β-phellandrene compared to the process emissions. On other occasions only minor deviations in composition were found between the pulp wood plume and the process plume. The terpenes from the wood-yard are expected to be emitted from bark, debarked surfaces, and sawed cross-sections of the pulp wood. In contrast, the process emissions correspond to the monoterpene content in bark-free whole spruce wood.

Photo-oxidant aspects. The rate-limiting initial reaction step during the day-light formation of photo-oxidants from monoterpenes involves reaction with the hydroxide radical (Atkinson et al. 1986) or with ozone (Atkinson and Carter 1984). With the bicyclic monoterpenes, the two reactions compete, whereas the attack by ozone is normally more rapid for most monocyclic and for noncyclic monoterpenes (Table 2). During the spring and summer days critical with respect to formation of ozone and other photo-oxidants, the atmospheric lifetimes of the bicyclic monoterpenes may be less than one hour and that of myrcene less than 10 minutes. This means that elevated concentrations of photo-oxidants are obtained within shorter times and distances in monoterpene plumes than in most other types of hydrocarbon plumes. As a consequence, potential contributions to forest damage by the photo-oxidants formed are also expected to be found more locally and probably primarily within 0-50 km from the emissions.

Before net ozone production occurs in a monoterpene plume, the most reactive monoterpenes are expected to decrease ambient ozone concentrations in the plume by the initial reaction with ozone. The samples were taken under conditions not favouring ozone formation and in winds containing ozone-reducing NO from traffic. Nevertheless, myrcene, and to some extent limonene, were lost from several samples taken in the housing area farther away from the emissions. This is

probably partially explained by reaction with ambient ozone in the sampling cartridge (Jüttner 1988 b) and not only by rapid decomposition in the plume.

Under stagnant anticyclonic spring and summer periods, the reactive monoterpenes are expected to react to an appreciable extent within one or two kilometres from the emissions. Genotoxic reaction products obtained when nitrogen oxides are present in the air may then constitute a health hazard. A high mutagenic activity has been reported for gaseous products formed from alkenes in reaction-chamber experiments (Kleindienst et al. 1985).

The urban position of the industrial complex studied is particularly unfavourable with respect to potential health hazards. Nitrogen oxides are emitted both from the industry and from extensive traffic around the industrial area. The position of the monoterpene plume inside the much wider town plume may also be unfavourable with respect to air pollution outside the town. Photo-oxidant formation should be promoted by nitrogen oxides being continuously mixed into the central monoterpene plume.

Prevention of emissions. The Swedish monoterpene emissions to air from the stone groundwood process are approximately 1000 tons yearly assuming that 0.1% of the dry spruce wood is lost as monoterpenes. A

similar estimate of the process emissions from the particular plant studied indicates 40 tons yearly. Considering the photochemical reactivity of the monoterpenes, these large point source emissions of monoterpenes are not likely to be acceptable with respect to environmental protection.

The most environmentally attractive method to eliminate the emissions appears to be recovery of turpentine. The non-chemical groundwood process would give a different and more well-defined quality than the kraft pulping process from which large quantities of turpentine are recovered. The recovery of turpentine is facilitated by concentrated emission streams. Alternatively, the terpene emissions can be eliminated by a proper technique for combustion.

The emissions from storage and debarking of pulp wood are apparently more difficult to eliminate. On the other hand most of these emissions can easily be kept away from large emissions of nitrogen oxides and from densely populated areas. The reasons for debarking and storage outside urban and industrial areas are strongest during the spring and summer periods which are critical with respect to elevated emission levels as well as photo-oxidant formation.

ACKNOWLEDGEMENTS

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