

Results from the Swedish National Screening Programme 2004

Subreport 3: Limonene

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Title and subtitle of the report Results from the Swedish National Screening Programme 2004 Subreport 3: Limonene	
Summary Measurements of the terpene limonene were performed in 223 samples of air, sediment, sludge, water and biota from background and urban sites and from point sources. Both of the two optical isomers, d-limonene and l-limonene, were analyzed in all media. Since limonene is emitted from several plants, such as pine, it occurs naturally in the environment but is also used in household products and industrially. Air samples from industrial point sources indicated local emissions but limonene degrades quickly in the atmosphere. None of the background sediments and only two of the background water samples contained detectable concentrations of limonene. No limonene was detected in biota (fish) and the conclusion of the screening is that accumulation of limonene in the environment is of minor importance.	
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Sammanfattning

IVL har på uppdrag av Naturvårdsverket utfört en screening av limonen i Sverige. Limonen är en terpen som finns naturligt i vår omgivning där den avges från växtlighet, t. ex. barrskogar. Limonen förekommer som två optiska isomerer: d och l. I Sverige är det framför allt l-limonen som emitteras naturligt då den avges bl.a. från tall. Limonen används som smak- och lukttillsats till många livsmedel, hushållsprodukter, hygienprodukter och parfym. Dessutom används limonen som lösningsmedel inom t. ex. färgindustrin.

I troposfären bidrar limonen, tillsammans med andra volatila kolväten, till den fotokemiska bildningen av ozon. Limonen har visat sig vara toxisk för fisk och zooplankton. Flera oxidationsprodukter av limonen kan orsaka skador på vegetation. Den mänskliga hälsan kan påverkas bl.a. genom att limonen kan orsaka överkänslighet.

I screeningstudien ingick provtagning och analys av d- och l-limonen i både luft och vatten från två bakgrundsstationer, den ena placerad vid havet, den andra i ett skogsområde. Sedimentprover från tre bakgrundslokaler i Östersjön har analyserats. Luftprov från en urban mätplats i Göteborg. och tre slamprover från reningsverk inkluderades. Två punktkällor, en massaindustri och en juicefabrik, har också undersökts.

Länsstyrelserna har också haft möjlighet att skicka in prover för analys. Totalt fem länsstyrelser deltog och bidrog med 34 prov varav 19 slamprov, nio vattenprov, två fiskprov och fyra sedimentprov.

Resultaten från luftmätningarna visade inte på några ökade limonenkoncentrationer i Göteborg jämfört med bakgrundsstationerna. Inte heller fördelningen mellan d- och l-limonen visade på någon skillnad i ursprunget av limonen i staden jämfört med bakgrundsstationerna. Halterna av främst d-limonen, ökade med stigande omgivningstemperatur i skogsområdet, vilket visar att en biogen emission från barrträden förekommer.

Endast två vattenprover från bakgrundsstationerna hade koncentrationer som översteg detektionsgränserna. Båda dessa var provtagna i skogsområdet under den senare delen av maj när den biogena aktiviteten troligen är hög. Inget av sedimentproverna i det nationella programmet hade koncentrationer överstigande detektionsgränserna.

Luftproverna från de två punktkällorna visade på en viss lokal påverkan kring dessa. Nära massaindustrin uppmättes förhöjda lufthalter av l-limonen och kring juicefabriken av d-limonen.

De analyserade reningsverksslammarna visade mycket varierande halter. Förhållandet mellan d- och l-limonen varierade också dem emellan vilket tyder på skillnader i antropogen påverkan. Tre prover av utgående vatten från reningsverk analyserades utan att några koncentrationer över detektionsgränsen återfanns.

Summary

As an assignment from the Swedish Environmental Protection Agency, IVL has performed a screening study of limonene. Limonene is a terpene that exists naturally in the environment. It is emitted from vegetation such as conifer forests. Limonene exists as two optical isomers: d and l. l-Limonene is the naturally occurring isomer in Sweden since it is emitted from pine trees. Limonene is used as a flavour and odour additive in several house hold and hygiene products as well as in perfumes. In addition limonene is used as a solvent in e. g. the paint industry.

In the troposphere limonene promotes, along with other volatile hydrocarbons, photochemical production of ozone. It has been shown toxic to fish and zooplankton. Several of its oxidation products can cause damage to vegetation. Limonene can also induce hypersensability in humans.

The screening study includes sampling and analysis of d- and l-limonene in air and water from two background stations, one situated by the sea and the other in a forest area. Sediment samples from three background locations in the Baltic Sea were analysed. Air samples from an urban sampling location in Göteborg and three sludge samples from sewage treatment plants were also included. Two point sources, one pulp production plant and one juice factory were investigated.

The administrative county boards had the possibility to participate with extra samples for analysis. Five counties contributed 34 samples: 19 sludge samples, nine water samples, two fish samples and four sediments.

The results did not show any elevated limonene concentration in air in Göteborg compared to background stations. Neither did the ratio of d- to l-limonene show any difference in origin between the urban area and background stations. Concentrations of limonene, in particular d-limonene, increased with increasing temperatur in the forest area which implies a biogene emission from pine trees.

Only two water samples showed concentrations above detection limits. Both were taken in the forest area during the later part of May when the biogenic activity presumably was high. None of the sediments in the national programme showed concentrations above the detection limit.

Air samples from both point sources indicated local emissions. In the proximity of the pulp production plant, elevated concentrations of l-limonene were measured while in the proximity of the juice factory there were elevated concentrations of d-limonene.

The analysed sludge samples showed a great variation in concentration, as did the ratio d- to l-limonene. This implies differences in antropogenic influence between the different STPs. Three samples of effluent water were also analysed but were all below detection limits.

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1 Introduction

As an assignment from the Swedish Environmental Protection Agency, IVL has performed a "Screening Study". This screening, which was carried out during 2004/2005, includes the following substances: adipates, octachlorostyrene, limonene, siloxanes, mirex, endosulfan and isocyanates. The different substances or groups of substances are emitted to and spread in the environment via a variety of sources, e.g. point sources and use in products. Some of the chemicals are commonly used internationally and/or in Sweden.

The seven chemicals or chemical groups studied have been identified as potentially toxic, bioaccumulative and/or persistent. Some are also included on different international/national priority lists. Table 1 shows an overview of the chemicals included and the major reasons for their concern.

Table 1. Overview of chemicals included in the screening 2004 and the reason for their concern (Loh et al., 2003; Andersson, 2004; OSPAR, 2005; UNEP, 2005) The chemicals considered in the current report are written in bold/italic letters.

Chemical	Chemical type	Banned/ Restricted	HPV ^a	Indications of toxicity	Evidence for B/P ^b	International Priority List
Adipates	Additive	No	X	X		
Octachlorostyrene	Unintentional by-product	PRIO- substance ^c		X	X	Candidate for the Stockholm convention
<i>Limonene</i>	<i>Cleaning agent (also naturally occurring)</i>			X		
Siloxanes	Lubricant, industrial raw material, chemical additive	PRIO- substance ^c	X	X	X	OSPAR (HMDS)
Mirex	Pesticide	Banned		X	X	Stockholm convention
Endosulfan	Pesticide	Banned		X	X	WFD, OSPAR, Candidate for the Stockholm convention
Isocyanates	Industrial raw material	Regulated	X	X		OSPAR ^d

^{a)} High Production Volume

^{b)} Bioaccumulation/Persistence

^{c)} The chemical is included on Swedish Chemicals Inspectorate's PRIO-list, and is identified as a "phase-out-chemical"

^{d)} Concerns 3,3'-(ureylenedimethylene)-bis-(3,5,5-trimethylcyclohexyl) diisocyanate

The overall objectives of the screening were to determine concentrations in a variety of media in the Swedish environment, to highlight important transport pathways, and to assess the possibility of current emissions in Sweden. A further aim was to investigate the likelihood of atmospheric

transport and uptake in biota. The outcome of the study is aimed to serve as a basis for decision-making regarding monitoring activities of these chemicals.

Due to the variety in emission sources and use as well as differences in chemical properties, the screening has been carried out in seven sub-projects. This report considers the results of **limonene**. Results for the other chemicals are presented in subreports 1-2 & 4-6.

2 Chemical properties, fate and toxicity

Limonene is a highly volatile colourless liquid with a slight odour of citrus. It occurs as the two optical isomers l-limonene and d-limonene, as well as in the racemic mixture named dipentene. Its physical-chemical properties are listed in Table 2 and the chemical structure is shown in Figure 1. Limonene has a high K_{OC} , which indicates low mobility in soil. However, the high vapour pressure and Henry's Law's constant show that vaporisation from dry and wet soils and from water may take place (HSDB, 2004).

Table 2. Physical-chemical properties of limonene

MW (g/mol)	MP (°C)	W_{SOL} (mg/L)	V_p (Pa) (25°C)	H (Pa) m^3/mol	$\log K_{ow}$	K_{oc}	BCF	Half-lives (h) ^c
136	-95 ^a	13.8 ^a	206 ^a	3232 ^a	4.57 ^a	1030- 4780 ^b	246- 262 ^b	Air: 0.3 Water: 360 Soil: 720 Sediment: 3240

^aSRC database, 2005 ^bWHO, 1998 ^cEPIWIN (Meylan, 1999)

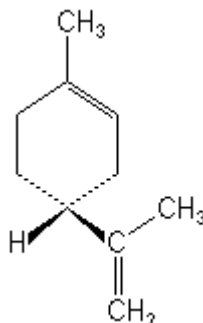


Figure 1. Chemical structure of limonene (CAS no 138-86-3, d-limonene: 5989-27-5, l-limonene: 5989-54-8)

In a simulated aerobic sewage water treatment process, limonene disappeared almost entirely during 14 days, which may be due to biological degradation (WHO, 1998). However, the decrease of limonene could also be a result of vaporisation. Stability tests of limonene during anaerobic conditions did not show any degradation (WHO, 1998). Data on degradation half-lives of limonene has not been possible to obtain.

The vaporisation of limonene from water has been estimated using a river model, which showed that the concentration decreased to 50% after 3.4 hours (depth 1m, flow 1 m/s, wind speed 3 m/s) (WHO, 1998).

A modelling exercise was performed using the Equilibrium Criterion (EQC) model (Mackay et al., 1996) in order to highlight likely fate and partitioning behaviour of limonene. Physical-chemical

properties were taken from Table 2. Emission rates were set to 1000 kg/h, for illustrative purposes. Limonene was only modelled with air as emission medium.

The outcome of the modelling exercise is shown in Table 3. The results are indicative, as the partitioning behaviour is dependent on model structure as well as chemical property data. It is evident, however, that the persistence (overall residence time) of limonene is low (estimated to <1 month). The modelling exercise also confirmed major transport of limonene from water and soil to air, where it is quickly degraded. Thus, despite slow biodegradation and hydrolysis, the volatility of limonene still enables a fairly quick system removal due to atmospheric breakdown.

When emitted only to air, which is the most likely emission route for limonene (see chapter 3), almost all of the chemical that is not degraded will remain in the atmosphere, and thus be available for advection out of the system.

Table 3. Results from EQC modelling of limonene, using the emission rate of 1000 kg/h. The table shows the percentage distribution of limonene in a generic environment at steady state.

Emission medium	Percentage in air	Percentage in water	Percentage in soil	Percentage in sediment	Persistence (h)
Air	99	<0.5	1	<0.5	0.44

The high log K_{ow} and high bioconcentration factor of limonene (Table 2) indicate potential for bioconcentration in fish and aquatic organisms (HSDB, 2004). However, due to the high volatility of limonene and thus high vaporisation from water, bioconcentration is probably limited in the environment.

D-limonene has a high partition constant between blood and air ($\lambda_{blood/air} = 42$) and is thus easily absorbed by alveoli in lungs, as a result of exposure from air. When exposed orally limonene is absorbed almost instantly in the gastrointestinal tract both in humans and animals. In experiments with rats, limonene has shown to be absorbed dermally. Limonene is quickly distributed between different organs in the body and easily metabolised. (WHO, 1998). Limonene shows no indices of enrichment with trophic level. The primary exposure route of limonene for humans is supposed to be via food. An acceptable daily intake for d-limonene was calculated to 0-1,5 mg/kg bodyweight /day (JEFCA, 1993). Calculated amounts of limonene that are ingested through food do not exceed critical levels for humans. Daily intake of limonene through food was estimated to 0,27 mg/kg bodyweight in the USA (WHO, 1998).

Limonene is toxic to fish and daphnia (zooplankton) (HSDB, 2004). However, concentrations found in biota are generally 250 to 20 000 times lower than the lowest EC_{50} -value (Table 4). There is no data on chronic exposure (WHO, 1998). Several oxidation products have known toxic effects on forests and plants.

Table 4. Ecotoxicological data for limonene

	Daphnia (zoo plankton) mg/L	Fathead minnow (fish) mg/l	Reference
Limonene	EC_{50} 0.4	LC_{50} 0.702	WHO (1998)

3 Emission sources, production, use and regulation

Limonene occurs naturally in several plants and natural oils such as orange, lemon, grapefruit, berries, leaves etc (HSDB, 2004). Thus, there are numerous biogenic sources from where emissions may arise. The global annual emissions of biogenic monoterpenes such as limonene range from 147 to 827 million tonnes (WHO, 1998). The biogenic emissions may well exceed the anthropogenic. The latter have been identified to mainly occur to air from industrial point sources such as paper mills, production of wood chips and landfills. Limonene may also be emitted with effluent water from such industries (Loh et al, 2003).

As the optical isomers of limonene have different origin, with l-limonene mainly occurring in pine forests and d-limonene in citrus fruits, the choice of manufacturing process has a large impact on the character of the emissions. The ratio l/d-limonene in the atmosphere can thus be used as an indication of the origin.

Two methods are widely used for manufacturing d-limonene from orange oils: vacuum distillation or washing of cold pressed oil. L-Limonene is generally produced by purification of isolated monoterpenes from pine needle oils, or synthetically from pinene by acid catalysis (NICNAS, 2002). In Sweden a limonene-containing fraction is produced at a pine oil distillery.

In 1992, Boström *et al* estimated the emissions of volatile organic hydrocarbons (VOC) to air from the Swedish pulp and paper industry to 16 000-32 000 tonnes/year, which was about 4% of the total anthropogenic VOC emission in Sweden (Boström et al., 1992). The terpene emissions were approximately 30% of the total VOC-emissions and limonene 2-4% of the terpene emissions (Berg et al. 1993). Based on this, the annual emission of limonene to air from Swedish pulp and paper industry 1992 was estimated to about 200 metric tonnes. Thus, pulp and paper production sites are important sources for limonene.

The majority of the limonene emissions from the pulp and paper industry arise from the chopping and storage of pine and spruce. In pine wood l-limonene is the dominant enantiomer and thereby it should also be the dominant form of limonene in the emissions from pulp- and paper mills.

Limonene degrades quickly in the atmosphere, thus long-range transport of limonene should be limited and the concentrations should be highest close to point sources. In the atmosphere, oxidation of terpenes, e.g. limonene, may contribute to formation of aerosols and photochemical smog. Emissions of limonene may lead to lower ozone levels if the concentration of nitrogen oxides are low and the opposite if levels of nitrogen oxides are high (WHO, 1998).

Limonene is used industrially as a solvent for metal degreasing prior to industrial painting, for cleaning electronics and in printing industries as well as in paint. Besides this, limonene is used as a flavouring agent and odour additive in food, household products and perfumes as well as a substitute for fluorinated and chlorinated hydrocarbons (WHO, 1998; HSDB, 2004). There is a slight tendency towards decreasing usage within Sweden (Figure 2).

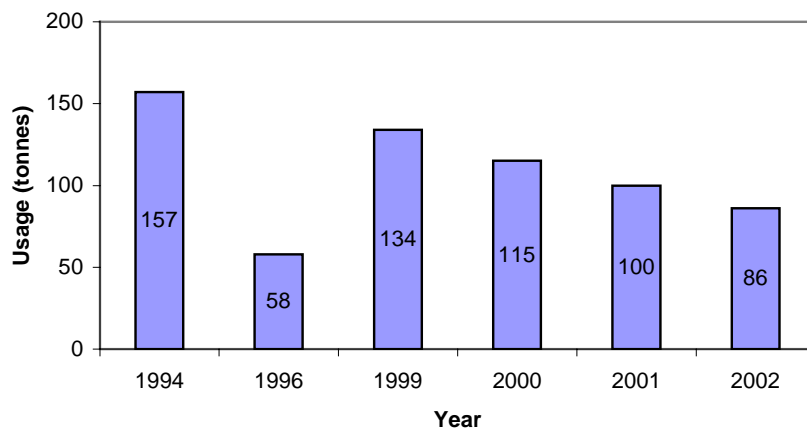


Figure 2. Use of limonene (l and d) in Sweden excluding export (SPIN, 2005)

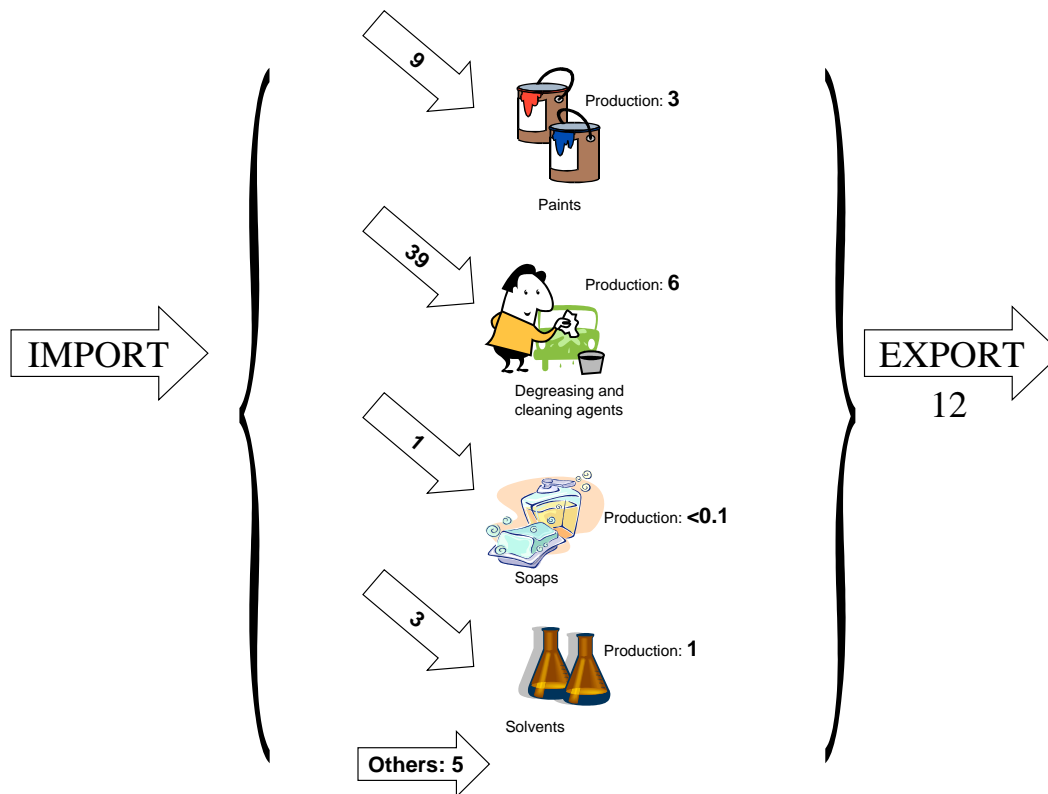


Figure 3. Flows of limonene in chemical products in Sweden in 1999 (tonnes; KemI, 2004b)

Limonene is present in a large number of different products (171 in 1999). The flows of limonene in chemical products in Sweden are illustrated in Figure 3. Both l-limonene and d-limonene, as well as the racemic mixture, are present in the products. Because of long-term effects and allergenic properties, limonene is listed as a risk reduction substance in the Swedish Chemicals Inspectorate's database for prioritisation (PRIO). This means that the risk should be evaluated based on the use (KemI, 2004a). The wide use of limonene in different products may result in important diffuse emissions to the environment, which may take place during the whole life cycle of the product.

4 Previous measurements in the environment

Limonene has previously been detected in gas from landfills in Great Britain and in indoor air. It has also been detected in surface water, ground water and ice both close to and far from sources. A summary of measured concentrations is given in Table 5.

Table 5. Measured concentrations of limonene

Matrix	Concentration	Unit	Site	Year	Reference
Ambient air	0.036	µg/m ³	Whitaker´s Forest, USA	June 1990	WHO (1998)
Forest air	0.49	µg/m ³	Monte Cimini, Italy	1992	WHO (1998)
Forest air	0.6-12	µg/m ³	North West Qubec, Canada	1989	WHO (1998)
Forest air	Night 1.3-7.7	µg/m ³	Jönköping	June-July 1983	WHO (1998)
Ambient air	Average day 0.17	µg/m ³	Rocky Mountains USA	July-Dec.1982	WHO (1998)
Ambient air	Average night 0.40	µg/m ³	Rocky Mountains USA	July-Dec.1982	WHO (1998)
Urban air	<1-11	µg/m ³	Northern Italy	1983-1984	WHO (1998)
Suburban	0.14	µg/m ³	Montelibretti, Italy	1992	WHO (1998)
Urban air	0-32	µg/m ³	Houston, USA	1974	WHO (1998)
Indoor air	10-480	µg/m ³	Italy	1986	WHO (1998)
Indoor air	40	µg/m ³	Los Angeles	1991	WHO (1998)
Indoor air	1.6-78	µg/m ³	Washington, USA	1989	WHO (1998)
Indoor air	9-30	µg/m ³	Canada	1993	WHO (1998)
Lake water	0.47 and 84	ng/l	Resurrection bay ,USA	1986	WHO (1998)
River water	590-1 600	ng/l	Spain	1991	WHO (1998)
Sea water	2-40	ng/l	Mexican Gulf, USA	1981	WHO (1998)
Ground water	10000	ng/l	Netherlands	1981	HSDB (2004)
Ground water	1000 -130 000	ng/l	Gainesville, Florida	1983	HSDB (2004)
Antarctic Ice	15 and 20	ng/l	Terra Nova Bay, Antarctica	1991	WHO (1998)
Antarctic water	5.4	ng/l	Terra Nova Bay, Antarctica	1991	WHO (1998)
Waste water, influent, sewage treatment plant	nd - 20 000	ng/l	Göteborg	1989-1991	WHO (1998)
Sediment	105-807	ng/kg	Southhampton estuary, UK	1991	WHO (1998)

5 Sampling strategy and study sites

5.1 National programme

A national sampling strategy was developed in order to determine the environmental concentrations of limonene in different environmental matrices in Sweden. The aim of the measurements was also to identify major emission sources as well as important transport pathways. The sampling programme was based on the identified possible sources and use of limonene as well as on the behaviour of the substances in the environment. The programme included both measurements in background areas and close to point sources. Measurements of diffuse pathways from the society included sewage treatment plants.

Table 6. Samples included in the national screening programme of limonene.

	Air	Water	Sediment	Sludge	Total
Background					
Råö	36	5			41
Gårdsjön	57	5			62
Various			3		3
Point source					
Pulp industry	23	12	1		36
Juice plant	23	1			24
Diffusive Source					
WTP Henriksdal				1	1
WTP Eslöv				1	1
WTP Floda				1	1
Göteborg	20				20

5.1.1 Background and urban areas

Air, water and sediment samples were collected in order to determine background levels of limonene and to investigate the importance of biogenic sources as well as possible long-range transport. Diffuse sources were investigated by collecting air samples in an urban area. Sludge samples were used to identify diffusive emissions from the society. The location of the sampling sites is shown in Figure 4.

Air and water samples were collected at two background sites at the Swedish West Coast, Råö and Gårdsjön. Råö is a sampling station used within the national monitoring programme for air pollutants. It is situated close to the sea with almost no forest, traffic or industrial complexes in the vicinity. Gårdsjön is a forest lake north-east of Göteborg. The air samples at this site were sampled at 10 meters distance from the edge of a conifer forest. This forest mainly consists of a mixture of pine and spruce.

A monitoring site at rooftop level in central Göteborg was used as urban background station for diffuse sources of limonene. The Environmental Department, City of Göteborg, uses this site for measurements of other air pollutants, such as ozone and nitrous oxides. Meteorological parameters,

such as wind speed, wind direction, temperature and global radiation, are also measured at this station. (Data from the Environmental Department, City of Göteborg.)

During the winter and spring 2005 eight measurement occasions were carried out at Råö, six at Gårdsjön and five in central Göteborg. Several samples were taken at each occasion.

The three marine background sampling sites (Ö Gotlandsdjupet, Ö Öland, Norrköpingsdjupet) were chosen from areas with continuous deposition of fine-grained sediment. These sites were identified with hydroacoustic methods (shallow seismic, sub-bottom profiler and chirp side-scan sonar). Prior to sampling, the bottom at the sampling site was inspected with a submarine video camera. Furthermore, a sediment-core from the site was X-rayed with a sediment-scanner (Cato et al. 2000) in order to detect unwanted physical disturbances as strong bioturbation, anchoring, trawling, etc. Sites, which fulfilled the sedimentological demands set up, were then sampled with a Gemini corer and the cores were sliced in vertical position with a core-cutter onboard. Surface sediments (0-1 cm) from four cores taken at each site were mixed in order to neutralise sediment inhomogenities. The samples collected were stored dark and frozen in pre-cleaned and burned glass bottles.

Sludge from three different sewage treatment plants (STP) in Sweden were collected and analysed to indicate diffusive spreading of limonene. The STPs chosen were Henriksdal, Eslöv and Floda, which also are included in the Swedish Environmental Protection Agency's monitoring for environmental pollutants in sludge.

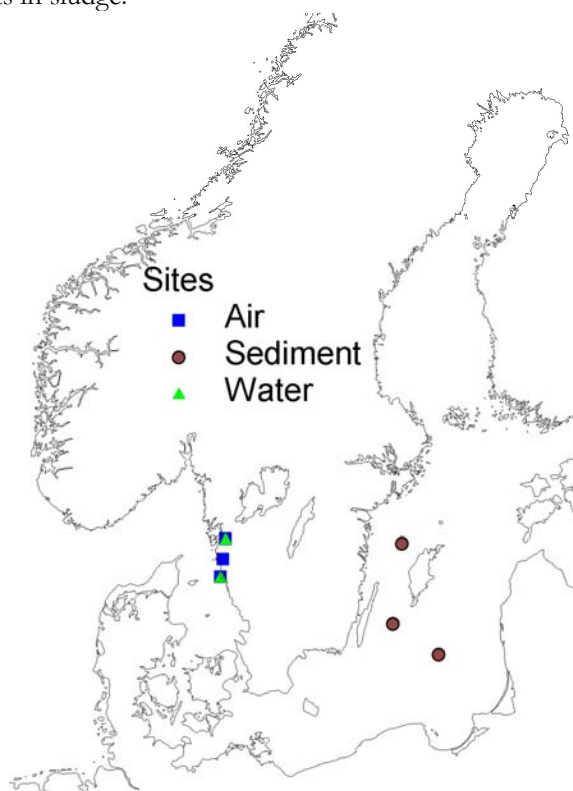


Figure 4. Geographic distribution of background and urban sampling stations.

5.1.2 Pulp and paper production plant

Due to the fact that terpenes are emitted from wood chipping, storage of the chopped wood and from the manufacturing process a pulp and paper mill was chosen as the first point source, namely Billeruds AB Gruvöns Bruk in Grums. The sampling was undertaken on the 18th and 19th of May 2005.

Air samples were collected both in- and outside the factory area. The sampling points for air are shown in Figure 5. The red stars represent samples from the 18th and the blue from the 19th of May. The samples were collected at the following locations inside the factory area:

1. At the mixing pond, where different wastewaters are mixed before entering the aerated lagoon.
2. At both the south side of and the inlet to the aerated lagoon.
3. Close to the lake, downwind the pulp- and paper mill.
4. At the piles of wood chips and bark.

Sampling outside the factory area was carried out both up- and downwind from the mill (Figure 5).

Additional air samples with high "time resolution" were collected at an exposed location in the factory area. A semiautomatic sampling device was used (see chapter 6). In this case, sampling was carried out both the 18th and the 19th. The sample duration using this sampling device was 30 minutes and in total 6 measurements were performed.

Four **wastewater samples** were collected:

1. The fibre sedimentation pond of the paper mill.
2. Mixture of wastewater that is led to the aerated lagoon.
3. The cooling water that is led back into the lake Vänern.
4. The outlet from the aerated lagoon into the lake Vänern.

One **sediment sample** from the aerated lagoon was also collected. This sediment is circulated and returned to the pond.

Recipient water samples were collected just outside the factory area (1), at different locations inside the bay (2-4), just outside the aerated lagoon (5) and at different distances from the aerated lagoon outlet and the factory area (6-8). The sampling points are shown in Figure 5. The natural water flow is in the direction from point 2 towards point 5. The outlet from the aerated lagoon is located about 100 metres west of the pond (Figure 6).



Figure 5. The red stars are the locations of air measurements from the first sampling day, 18th of May, and the blue stars are the locations of the air measurements of the second day, 19th of May. The arrows in corresponding colours show the wind direction of each sampling day.

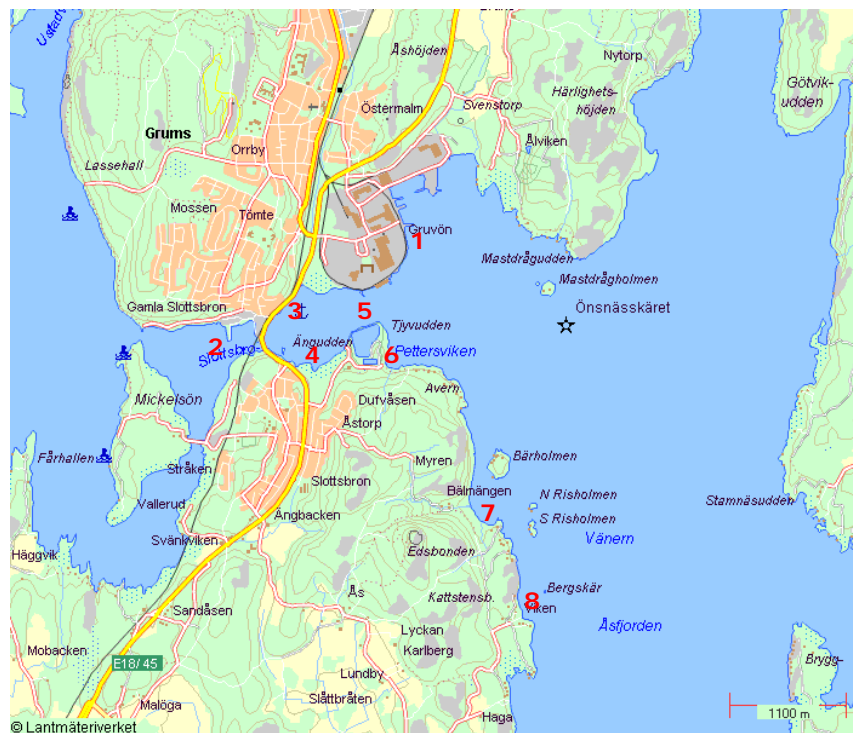


Figure 6. Location of water sampling sites around the pulp- and paper mill point source.

5.1.3 Juice pressing factory

A juice-pressing factory in Brämhult was chosen as the second point source. Brämhult is situated outside Borås and Brämhults Juice is the only factory of this type in Sweden. The citrus fruits mainly contain d-limonene, thus the distribution between the l- and d- form of limonene differs from that in pine trees.

The measurements were carried out the 31st of May, a rainy day with almost no wind. The pressing of citrus fruit was carried out after 2 p.m. and **air samples** were collected both before and after this procedure.

Some of the air samples were collected with the semiautomatic sampling device (see chapter 6.1.1) just outside the open door to the fruit storage room. The sample duration time was 30 minutes and seven samples were collected between 09:45 a.m. and 12:15 p.m.

During the pressing of oranges in the afternoon four air samples were taken just outside the open door to the processing room and four samples about 10 metres from the door which was close to the highway. There was an odour of lemon around the air conditioner of the storage room and two measurements were performed at this location. Discarded fruit is put in an open container on the yard before it is sent away for disposal. One air sample was collected just above the container top. Reference samples were taken outside the factory area where no obvious citrus smell occurred.

At the juice plant, the industrial wastewater is isolated in a tank where the acidic water is treated with sodium hydroxide to increase the pH-value. The wastewater is then led to the local sewage treatment plant in Borås. One **water sample** was collected from the tank.

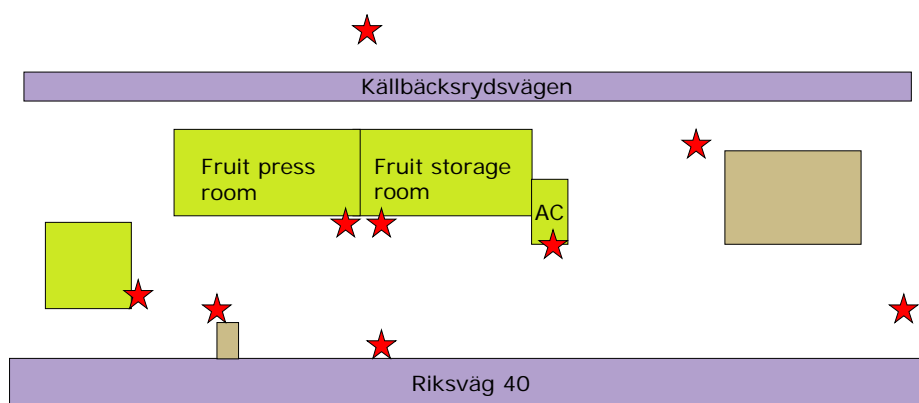


Figure 7. The stars indicate where air measurements were performed at Brämhults Juice factory.

5.2 Regional programme

Swedish county administrative board had the possibility to add regional samples to the sampling programme. Different counties have chosen different strategies for their sampling scheme. One way of selecting was to increase the number of samples for substances connected to the environmental programs i.e. substances that have been regulated or included in the national priority database. Another strategy was to choose substances where environmental levels were expected to differ from national levels because of intense use within the county, i.e. local industrial areas or because of geographic proximity to European industrial areas.

Five county administrative boards participated in the regional sampling programme of limonene with 34 extra samples: 2 fish samples, 4 sediment samples, 19 sludge samples and 9 water samples (Table 7).

Table 7. Limonene samples within the regional sampling programme.

County	City	Location	Water	Sediment	Sludge	Fish
Blekinge	Karlshamn	Karlshamn STP			1	
Blekinge	Karlshamn	Mörrum deponi	1			
Blekinge	Karlskrona	Karlskrona STP			1	
Blekinge	Olofström	Volvo personvagnar			1	
Blekinge	Ronneby	Angelskogstippen	2			
Blekinge	Ronneby	Ronneby STP			1	
Blekinge	Sölvesborg	Sölvesborg STP			1	
Jämtland	Berg	Myrviken STP			1	
Jämtland	Bräcke	Bräcke STP			1	
Jämtland	Härjedalen	Björnrike STP*			1	
Jämtland	Krokom	Hissmofors STP			1	
Jämtland	Ragunda	Överammer STP			1	
Jämtland	Strömsund	Strömsund STP			1	
Jämtland	Åre	Åre STP*			1	
Jämtland	Östersund	Gövik STP			1	
Stockholm	Botkyrka	Himmerfjärdsverket	1		1	
Stockholm	Södertälje	St Envättern		1		1
Stockholm		Himmerfjärden		1		1
Västernorrland	Timrå	SCA Östrand	1	1		
Västernorrland	Örnsköldsvik	Bodum STP			1	
Västernorrland	Örnsköldsvik	Husum, massaind	2	1		
Västernorrland	Sundsvall	Tivoliverket			1	
Västra Götaland	Lidköping	Lidköping STP	1		1	
Västra Götaland	Vara	Vara STP			1	
Västra Götaland	Åmål	Åmål STP	1		1	
sum			9	4	19	2

* Mun.sample taken during tourist season not according to sampling instructions.

6 Methods

6.1 Sampling

As a guideline for adequate and consistent sampling, a manual for the sampling personnel was developed. Detailed instructions for sampling, storing and transport were given. Sampling protocols for all sample types were included in the sampling manual.

The overall aim of the sampling protocols was to:

1. Guide the personnel, responsible for sampling on how to avoid contamination when sampling
2. Ensure documentation of the sampling procedure, quality of the sample and environmental and physical circumstances during the sampling.

All samples from the regional county administrative boards were sent to IVL for analysis.

6.1.1 Air

Limonene was collected on sorbent cartridges containing Tenax TA. Each sorbent tube was mounted in a specially manufactured stainless steel holder with a back-up tube connected in series to control that no breakthrough occurred. Strömvall et al. (1992) and Calogirou et al. (1996) have shown that ozone and other reactive components in air degrade terpenes trapped on adsorbent cartridges. Field studies in urban air, carried out within the current study, showed that about 65% of the limonene were degraded with a sampling volume of 3 litres. With an ozone filter mounted in the airflow prior to the sorbent tube decomposition and rearrangements of adsorbed limonene were avoided. Staff from IVL carried out all air sampling.

At the urban, forest and the background sites one hour sampling time with a flow of 50 ml/min was used. In order to study diurnal variations with "high time resolution" a semiautomatic sampler was also used, see Figure 8. In this sampling device, a pump created a flow through a glass manifold connected by magnetic valves to eight different sampling channels. At each sampling channel two adsorbent tubes were mounted in series. A mass flow control unit controlled the sampling flow.

At the point sources, the measurements were partly performed by the semiautomatic sampler, using a sampling time of 30 minutes and a flow of 50 ml/min. The other air measurements at the point sources were carried out with various sampling durations that were based on expected limonene concentrations. The flow was 50-150 ml/min.

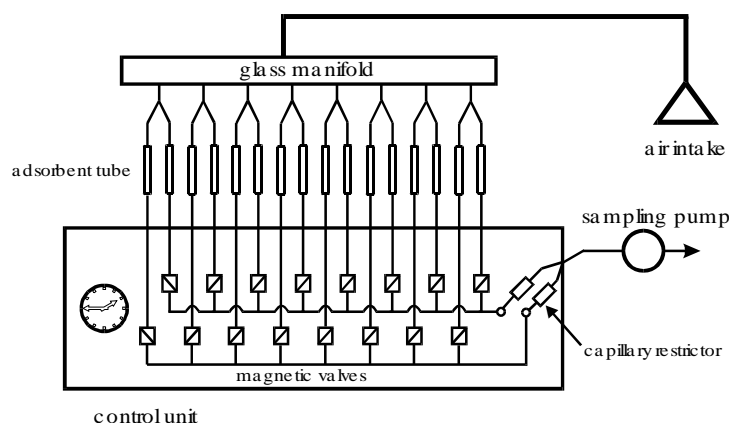


Figure 8. Semiautomatic sampler used in limonene measurements.

6.1.2 Sediment

Sediment samples from lakes or sites close to the coast were collected by means of a Kajak sampler. The sediment core was sliced and transferred into pre-heated (400°C) glass jars fitted with aluminium foil lined screw caps and stored in a freezer (-18°C) until analysed.

The four marine sampling sites (Ö Gotlandsdjupet, Ö Öland, Norrköpingsdjupet, Ö Landsortsdjupet) were chosen from areas with continuous deposition of fine-grained sediment. These sites were identified with hydroacoustic methods (shallow seismic, sub-bottom profiler and chirp side-scan sonar). Prior to sampling, the bottom at the sampling site was inspected with a submarine video camera. Furthermore, a sediment-core from the site was X-rayed with a sediment-scanner (Cato et al. 2000) in order to detect unwanted physical disturbances as strong bioturbation, anchoring, trawling, etc. Sites, which fulfilled the sedimentological demands set up, were then sampled with a Gemini corer and the cores were sliced in vertical position with a core-cutter onboard. Surface sediments (0-2 cm) from four cores taken at each site were mixed in order to neutralise sediment inhomogeneities. The samples collected were stored dark and frozen in pre-cleaned and burned glass bottles.

6.1.3 Sludge

The staff at the different treatment plants collected the sludge samples from the anaerobic chambers. The sludge was transferred into pre-heated (400°C) glass jars fitted with aluminium foil lined screw caps and stored at 4°C or -18°C until analysed. A glass jar filled with modified diatomaceous earth was used as field blank.

6.1.4 Water

Water samples were collected in 125 ml Teflon bottles fitted with screw caps and stored in a refrigerator until analysed. A bottle with Milli-Q water, which was exposed to the surrounding environment during the sampling time, was used as a field blank. The bottles have passed a cleaning procedure at IVL's laboratory prior to sampling.

6.2 Analysis

6.2.1 Air

The air samples, which were collected on Tenax tubes, were analysed according to chapter 6.2.4.

6.2.2 Water

Purge and trap technique was used in order to extract the limonene from the sampling matrices. Ten millilitres of water were thermostated at 70°C and purged with helium at a flow of 50 ml/min for 30 minutes. The purge gas first passed through an “ozone-filter” and then a sorbent cartridge with Tenax TA, where the limonene was adsorbed. The Tenax adsorbent tubes were analysed according to chapter 6.2.4.

6.2.3 Sludge, sediment and biota

Purge and trap technique was used in order to extract the limonene from the sampling matrices. About 2 g of the sample was placed in a test tube and 20 millilitres pre-boiled milli-Q water was added. The mixture was then homogenised with a mixer (Ultraturrax). About 1 g of the mixture was transferred to a new test tube to which additional water was added to a volume of 10 ml.

The mixture was thermostated at 70°C and purged with helium at a flow of 50 ml/min for 30 minutes. The purge gas first passed through an “ozone-filter” and then a sorbent cartridge with Tenax TA, where the limonene was adsorbed. The Tenax adsorbent tubes were analysed according to chapter 6.2.4.

6.2.4 Adsorbent tube analysis

The limonene analysis of the Tenax TA adsorbent tubes was carried out on an automated thermal desorption instrument (ATD-400, Perkin-Elmer) attached to a gas chromatograph equipped with a flame ionisation detector (GC-FID). During the desorption stage the adsorbent tubes were heated to 250°C for 5 minutes under a flow of helium. The desorbed components were refocused on a cold trap packed with Tenax-GR cooled to -30°C. The trap was then heated rapidly to 250°C in order to inject the retained analytes into the capillary column as a highly concentrated band of vapour.

The analysis column (CP Chirasil-DEX CB, Varian) was chosen because of its ability to separate the two enantiomers of limonene from each other. A part of a chromatogram is showed in Figure 9 below.

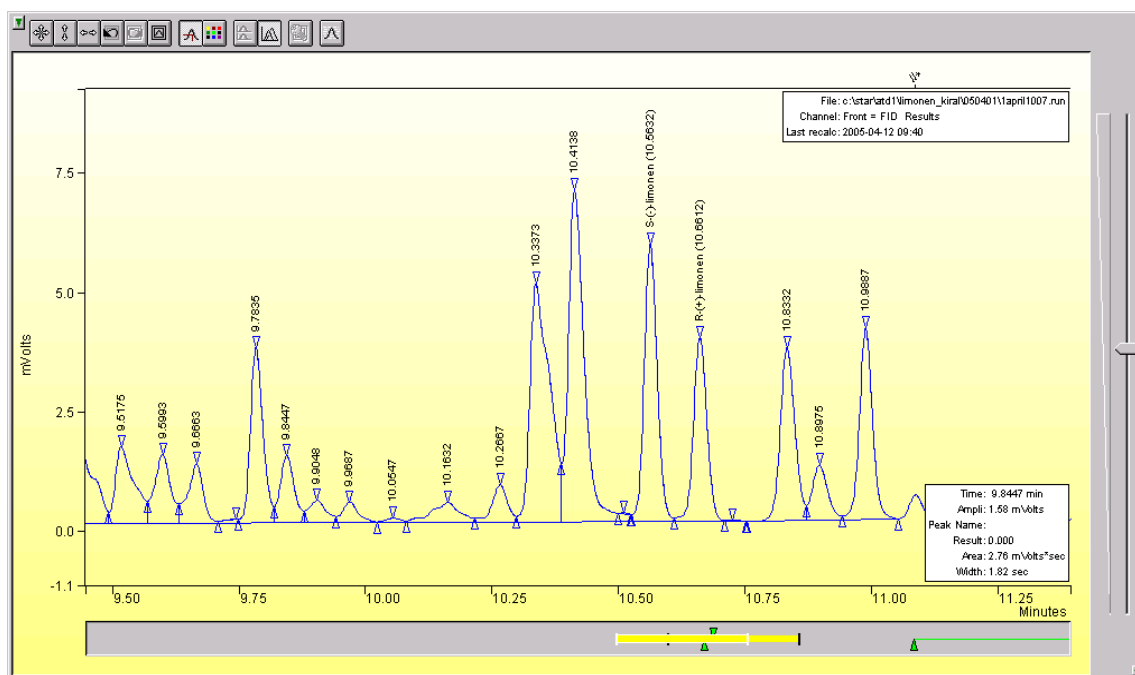


Figure 9. Part of a chromatogram showing the separation of the limonene enantiomeres.

7 Results and discussion

7.1 National programme, background and urban areas

The concentrations of limonene from background and urban sites are presented in Appendix 1, 2 and 3.

7.1.1 Air at Råö, Gårdsjön and Göteborg

The variation in the concentrations of l- and d-limonene found at the different sampling locations, Råö, Gårdsjön and Göteborg are shown in Figure 10 a-d. The average of the total limonene concentrations at each site together with the maximum and minimum concentrations are summarised in Table 8. The concentrations of limonene measured the 3rd of June were excluded in the average values.

The concentrations of d-limonene varied between 0.5 and 1 $\mu\text{g}/\text{m}^3$ and l-limonene between 1 and 2 $\mu\text{g}/\text{m}^3$ at all three sites. Thus, there were no great variations in the concentrations among the three different sampling locations. In the last week of April, when the weather was sunny and the ambient temperature higher, increased concentrations of d- and l-limonene occurred at all three sampling sites, especially at the coastal station. The ratio between l- and d-limonene was generally about 2 at all the three sites.

In order to investigate the temperature dependence of the air concentrations of limonene, an additional sample was collected at Gårdsjön in June. As shown in figure 10d the concentrations of l-limonene on 3rd of June was much higher compared to the other occasions. Thus a significant natural emission of limonene occurred in the forest in connection with high ambient air temperature.

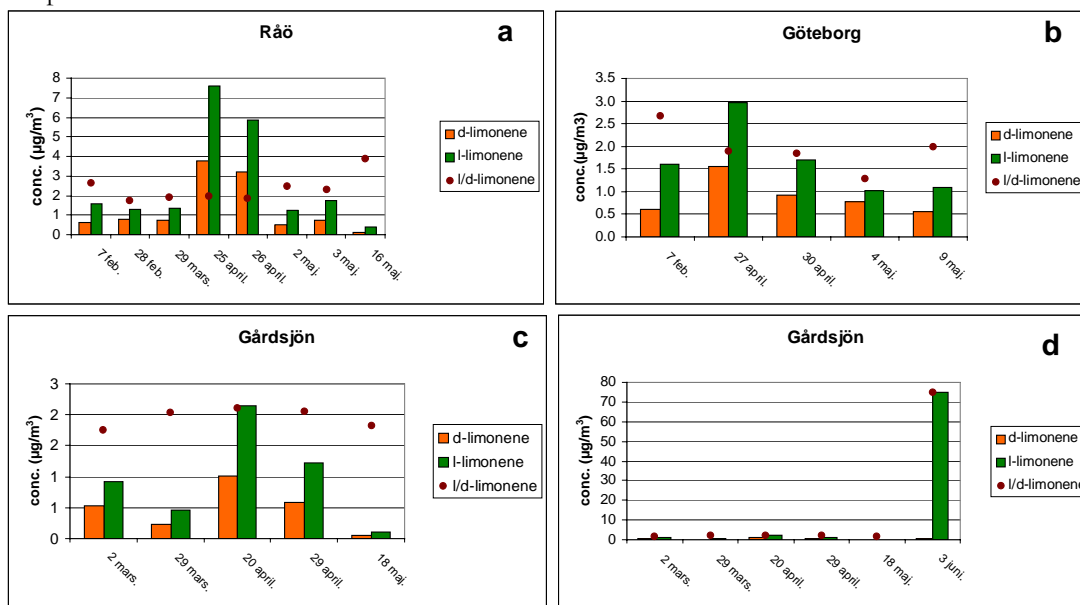


Figure 10. The variation of limonene concentrations in air at Råö, central Göteborg and Gårdsjön at the different sapling occasions.

Table 8. Total concentration of limonene in air at background and urban stations. The high concentration from 3rd of June is excluded.

	Göteborg	Gårdsjön	Råö
Average conc. ($\mu\text{g}/\text{m}^3$)	2.8	2.1	2.1
Max conc. ($\mu\text{g}/\text{m}^3$)	7.2	5.9	6.6
Min. conc. ($\mu\text{g}/\text{m}^3$)	1.2	0.01	0.01
Number of samples	20	51	36

The concentrations found at the background stations Gårdsjön and Råö were in the same range as previously reported concentrations from forest sites in Northwest Quebec (1989) (chapter 4, table 5). The measured concentrations in Göteborg were in the same range as in urban areas in northern Italy (1983-1984) and in Houston, USA (1974) (chapter 4, table 5).

Only small diurnal variations of limonene from morning until late afternoon was observed, see Figure 11. The diurnal variations were higher at the forest site Gårdsjön than at Råö and Göteborg. In Göteborg and Råö, there was almost no daily variation in the ratio between l/d-limonene whereas at Gårdsjön higher l/d-ratios was observed in the evening 28th April 2005.

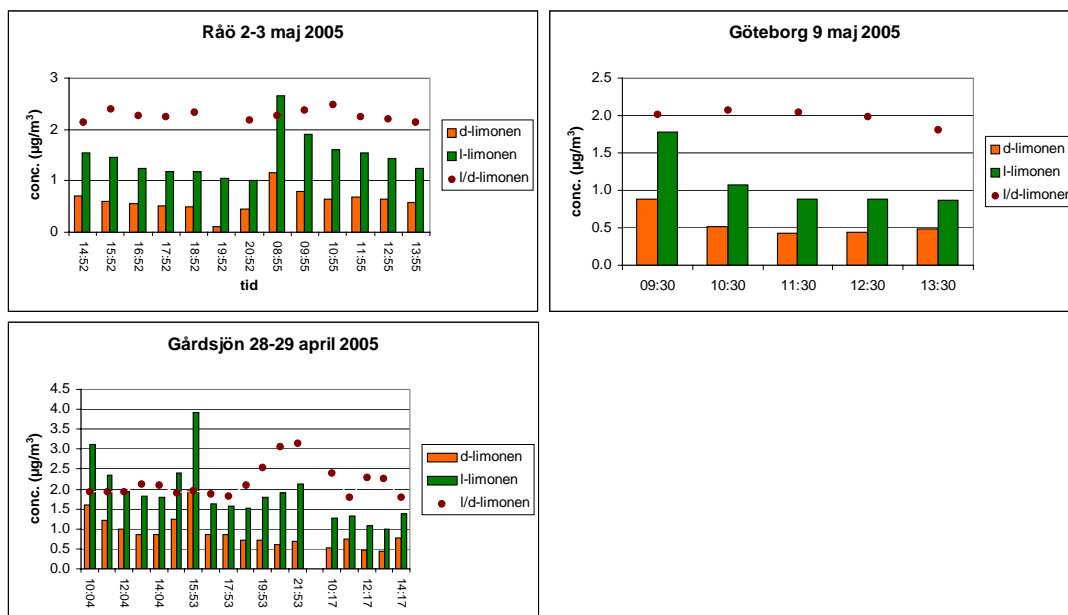


Figure 11. Diurnal variation in the air concentration of limonene at Råö, central Göteborg and Gårdsjön.

The results of the air measurements did not show any increased concentrations of limonene in Göteborg compared to the background stations. Nor did the distribution indicate any difference in the origin of limonene in the urban area. Thus no significant diffuse emissions affect the air concentrations in the urban area.

A significant natural emission of limonene occurred in the forest in connection with high ambient air temperature in June.

7.1.2 Water and sediment at background sites.

The concentrations of limonene in water are given in Appendix 4.

No detectable amounts of limonene were found in the samples collected outside Råö. The detection limits were $0.1 \mu\text{g}/\text{l}$ for d-limonene and $0.2 \mu\text{g}/\text{l}$ for l-limonene. Limonene was detected in two of the five samples. The measured concentrations in the water sample, collected 20th May were $0.17 \mu\text{g}/\text{l}$ for d-limonene and $0.46 \mu\text{g}/\text{l}$ for l-limonene.

All the water samples from Gårdsjön, except the one from 31st May, were taken at the outflow of the lake. The sample from 31st May which contained somewhat higher concentrations of limonene, $0.20 \mu\text{g}/\text{l}$ for d-limonene and $0.57 \mu\text{g}/\text{l}$ for l-limonene, was collected below a draining area in a part of the forest where several trees had fallen down during a winter storm. Limonene may have washed off fallen trees during rain events and been transported to the lake. The l-/d- ratios were 2.7 and 2.8 in the two water samples respectively, which was slightly higher than the ratio in the air samples collected at the same location.

The concentrations of limonene found in Lake Gårdsjön were in the same concentration range as measured levels in lake water from Resurrection Bay, USA (see Table 5).

No detectable amounts of limonene were found in the sediment samples, which were collected from background areas at offshore stations in the Baltic Sea. The detection limits are shown in Appendix 5.

7.1.3 Sludge

The results are presented in Appendix 6. The concentrations of limonene varied between 150 and 870 ng/g dw. At the large sewage treatment plant, Henriksdal, in Stockholm the ratio between l- and d-limonene was different compared to the corresponding ratios from Eslöv and Floda. At Henriksdal l-limonene dominated while at Eslöv and Floda d-limonene was the dominating enantiomer. Low l- / d- ratios indicate an anthropogenic influence on the limonene levels.

7.2 National programme, point sources

7.2.1 Pulp and paper production plant

7.2.1.1 *Water and sediment*

The results for water and sediments are given in Appendix 7. The sample locations at Billeruds AB Guvöns Bruk in Grums have been described previously (chapter 5.1.2).

Limonene was not detected in any of the water samples despite the fact that there were wood chips in the shallow water at some locations. This is possibly a reflection of the high volatility of limonene, leading to quick volatilisation from the water compartment. The detection limits for l- and d-limonene were 0.08 and 0.18 µg/l respectively. Limonene occurred in the sediment sample that was collected in the aerated lagoon. This sediment is circulated and returned to the pond. The ratio of l- to d-limonene was 2.2.

7.2.1.2 *Air*

The locations where air samples were taken are shown in chapter 5, Figure 5, where also the wind direction during the sampling is given. The results from the air samples collected with the semiautomatic sampling device at an exposed location in centre of the mill are shown in Figure 12 as well as in Appendix 8.

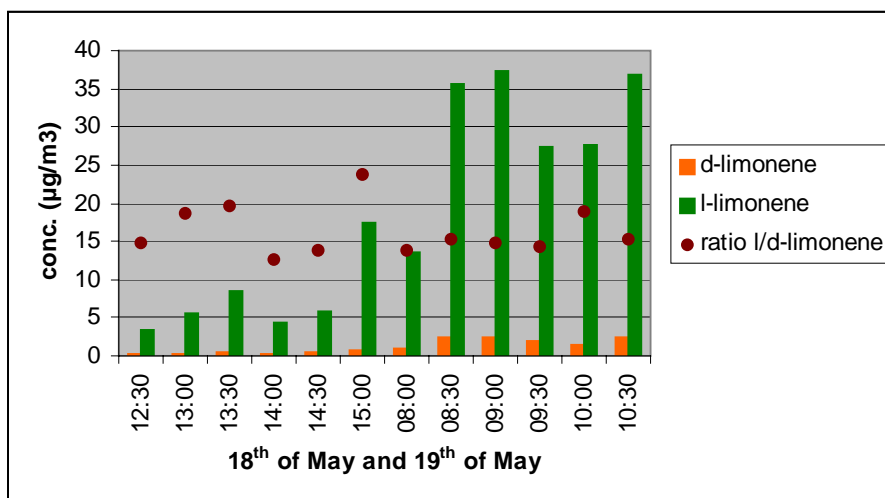


Figure 12. Limonene concentrations in air collected with semiautomatic sampler at Gruvön.

The air concentration of limonene at this "exposed area" varied from 7.9 to 32 µg/m³ with higher concentrations during the second day, 19th May. The ratio between l- and d-limonene at this sampling point was 15-24 which is significantly higher than the ratio of about 2 which were found in ambient air measured at Råö, Gårdsjön and in Göteborg. An increased ratio was also expected since pinewood mainly contains l-limonene.

The air samples, which were collected at the same point as the wastewater samples contained higher limonene concentrations than the ambient air samples. The highest concentration occurred in the sample collected about 1 meter above the mixing pond for the wastewater, where the concentration was 16 µg/m³. The ratio between l- and d-limonene in this sample was 9 indicating that emission from the water takes place. The concentration of limonene in the other air samples, collected at locations close to the aerated lagoon was only somewhat higher than ambient air concentrations with ratios between l-/d- limonene of 2.4 and 2.8.

The air sample collected about 30 cm above the piles of chopped wood showed increased concentrations of limonene. The concentrations above the coniferous wood, 79 µg/m³, were as expected substantially higher than the concentrations of 4.6 µg/m³ above the birch wood. The ratio between l- and d-limonene was 19 in both these samples.

The air concentrations of limonene found in the surroundings of the paper mill were 0.12 µg/m³ (1 km south) and 0.24 µg/m³ (1 km north). This were in the same range or lower than at the background stations at the Swedish West Coast. Thus the paper mill did not cause any increased concentration of limonene 1 km from the factory.

A small increase of the l-limonene concentration was observed north, downwind of the mill, compared to the south. The ratio between l- and d-limonene was 1.6 south of the factory compared to 3.7 north of the factory, which indicates a minor influence from the pulp- and paper mill on the limonene concentrations at a distance of 1 km. However, this effect was not of any quantitative importance.

7.2.2 Juice factory

High concentration of limonene, 420 $\mu\text{g}/\text{l}$, was found in the waste water sample collected at Brämhults juice factory (Appendix 9). This was expected since the sample contained orange peels. However, the ratio between l- and d-limonene was 5, which is about twice the ratio from ambient air measurements. Since citrus fruit mainly contain the enantiomer d-limonene this was not expected. A change from d- to l-limonene or a degradation of d-limonene when the water is neutralised with sodium hydroxide may take place.

The limonene concentrations in air measured at Brämhults are shown in Appendix 9. High concentrations of d-limonene were found in the air at the factory area with great differences between different sampling occasions, which are shown in Figure 13.

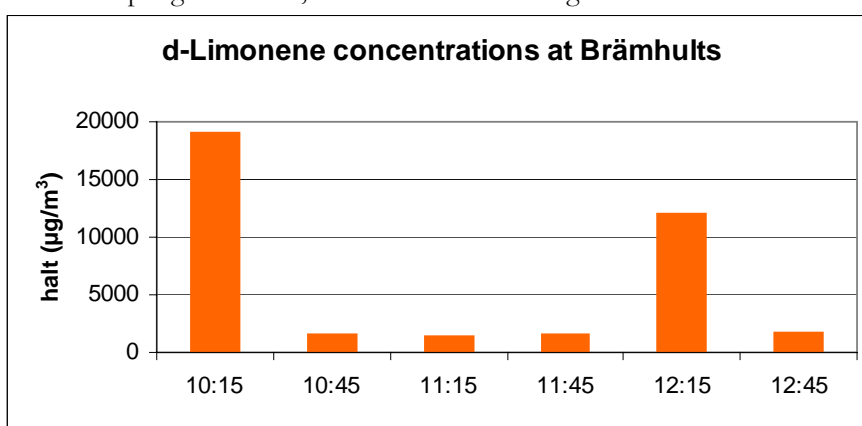


Figure 13. d-Limonene concentrations outside open door to fruit storage room at different occasions.

Samples were taken at the same location in the factory, outside an open door to the fruit storage room. The sampling was carried out at different periods during the day. The limonene concentrations found at this sampling point were above 1000 $\mu\text{g}/\text{m}^3$ for all samples, while the concentrations were below 1 $\mu\text{g}/\text{m}^3$ at 25 and 50 meters upwind from the factory area.

The ratio between l- and d-limonene in samples collected close to the fruit storage room were 0.01. Thus these samples contained almost exclusively d-limonene. The corresponding ratio in the samples collected upwind the factory area where 0.6, which were somewhat lower compared to the ambient air samples from Göteborg.

Additional air samples were collected just outside an open door to the processing room, during the orange pressing procedure. Limonene was found in the same concentration range, 5 000-20 000 $\mu\text{g}/\text{m}^3$, as outside the fruit storage room. The limonene concentration decreased to 200 and 700 $\mu\text{g}/\text{m}^3$ at distance of 10 metres from that point

During the pressing procedure, two samples were collected 25 and 75 metres upwind from the factory. The limonene concentrations in these samples were 30 and 3.4 $\mu\text{g}/\text{m}^3$, which were higher compared to the samples collected at the same point during the morning. This indicates a greater influence on the limonene concentrations from the juice factory during the pressing procedure. The “factory background” site also showed higher concentration during the pressing in the afternoon, 560 compared to 22 $\mu\text{g}/\text{m}^3$ during the morning. The l/d-limonene ratios of 0.01 compared to 0.05

also indicated a greater influence on the concentrations from the juice factory during the pressing process.

A conclusion from the measurements at the juice factory is that d-limonene concentrations are elevated close to the factory especially during the pressing of citrus fruits.

7.3 Regional programme

Results from the regional limonene screening are shown in Appendix 10.

The concentrations of limonene in the sludge samples from different sewage treatment plants from the regional as well as the national screening are shown in Table 9. The concentrations and the ratios between the enantiomers varied at different locations. The sewage treatment plants with the highest l-limonene concentrations in this study were Sölvesborg, Åre, Myrviken (Berg), Åmål and Lidköping. These locations also had the highest ratios between l- and d-limonene.

The highest concentrations of d-limonene were found at Tivoliverket (Sundsvall), Överammer (Ragunda), Vara, Bräcke, Eslöv and Hissmofors (Krokom). These plants had ratios between l- and d-limonene of 1 and below. The high concentrations and low ratios indicate that diffuse emissions of limonene to the environment occur.

Effluent water from the sewage treatment plants Himmerfjärdsverket, Åmål and Lidköping were analysed but the limonene concentrations were below the detection limit in all these samples. Detection limits are given in Appendix 10. At all these three plants the limonene concentrations in the sludge were relatively high. This is in agreement with the high K_{oc} of the substance. Thus, no considerable emissions of limonene occur via effluent water from these plants.

Fish and sediment from Himmerfjärden and St Envättern in Stockholm County were analysed. The results are given in Appendix 10 and Table 10. The limonene concentrations were higher in sediment from St Envättern than from Himmerfjärden, while no detectable concentrations were found in the fish at either location.

Table 9. Limonene content in sludge samples from sewage treatment plants.

County	Location	d-Limonene	I-Limonene	I/d-Limonene
		ng/g dw	ng/g dw	
Blekinge	Karlshamn STP	<28	250	>9
Blekinge	Sölvesborg STP	<39	2900	>70
Blekinge	Ronneby STP	<42	<95	
Blekinge	Karlskrona STP	<45	<100	
Jämtland	Åre STP*	<39	16000	>400
Jämtland	Björnrike STP*	<12	35	>3
Jämtland	Gövikens STP	<26	<60	
Jämtland	Hissmofors STP	450	430	1.0
Jämtland	Överammer STP	1600	380	0.24
Jämtland	Bräcke STP	820	310	0.38
Jämtland	Strömsund STP	53	930	18
Jämtland	Myrviken STP	<34	3700	>100
Skåne	Eslöv	560	310	0.55
Stockholm	Himmerfjärdsverket	<31	320	>11
Stockholm	Henriksdal	150	350	2.3
Västernorrland	Bodum STP	<0.79	<1.8	
Västernorrland	Tivoliverket	2600	760	0.29
Västra Götaland	Floda	82	70	0.85
Västra Götaland	Åmål STP	100	1300	13
Västra Götaland	Lidköping STP	77	2600	34
Västra Götaland	Vara STP	1200	640	0.53

* Mun.sample taken during tourist season not according to sampling instructions.

Table 10. Limonene in fish and sediments from the regional sampling programme

County	Location	Fish			Sediment		
		d-Limonene	I-Limonene	I+d-Limonene	d-Limonene	I-Limonene	I+d-Limonene
		ng/g dw	ng/g dw	ng/g dw	ng/g dw	ng/g dw	ng/g dw
Stockholm	St Envättern	<8.3	<19	<27	100	260	360
Stockholm	Himmerfjärden	<5.1	<12	<17	<30	15	15

8 Conclusions

The results of the air measurement did not show any increased concentrations of limonene in Göteborg compared to the background stations. Nor did the I-/d- -ratio indicate any difference in the origin of limonene at the different sites. No significant diffuse emission to air was indicated in the urban area.

A significant natural emission of limonene occurred in the forest in connection with high ambient air temperature as high concentration of I-limonene was measured.

Limonene was only detected in two water samples from background stations, which were collected in the end of May in Lake Gårdsjön. No detectable amounts of limonene were found in the sediment samples from background areas.

There was a great variation in concentrations of limonene in sludge from different STPs. The high concentrations found at some of the plants as well as the variation in the ratios between l/d-limonene indicated an influence of limonene from different sources. However, no considerable emissions of limonene occurred via outgoing water.

The measurements of limonene at the point sources showed that high air concentrations of Limonene occurred at exposed sites in the industrial areas. However, the air concentrations decreased to background levels at a distance of 1 km from the point source. Limonene was not detected in recipient water samples, collected close to the paper mill. The differences in the ratio between l/d-limonene at the two different point sources, representing citrus and pine, were well illustrated.

The general conclusion of this screening is that accumulation of limonene in the environment is of minor importance. In the air, limonene mostly occurred at background levels. Limonene degrades quickly in the atmosphere and the concentrations should be highest close to point sources, which is in agreement with the findings. However, the importance of limonene as a precursor in photochemical reactions has not been included in this study.

9 Acknowledgements

Thanks to all staff at the county administrative boards and different municipalities that have contributed to the sampling. Especially thanks to Anders Bignert, NRM and personnel at point source industry for contributing with samples for the national program.

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Appendix 1. Limonene in air at Råö

Limonene air measurements at Råö						
date	starttime	endtime	d-limonene µg/m ³	l-limonene µg/m ³	d+l-limonene µg/m ³	l/d-limonene µg/m ³
2005-02-07	13:40	14:40	0.60	1.6	2.2	2.6
2005-02-28	13:40	14:40	0.76	1.3	2.1	1.7
2005-03-29	13:22	14:22	0.92	1.8	2.7	2.0
2005-03-29	14:25	15:24	0.50	0.94	1.4	1.9
2005-04-25	11:05	12:05	8.1	16	24	2.0
2005-04-25	12:05	13:05	5.1	10	15	2.0
2005-04-25	13:05	14:05	4.3	8.4	13	2.0
2005-04-25	14:05	15:05	3.1	6.6	9.7	2.2
2005-04-25	15:05	16:05	3.3	6.3	9.6	1.9
2005-04-25	16:05	17:05	3.1	6.0	9.1	1.9
2005-04-25	17:05	18:05	2.9	5.4	8.3	1.8
2005-04-26	09:20	10:20	5.3	10	15	1.9
2005-04-26	10:20	11:20	2.9	5.4	8.3	1.8
2005-04-26	11:20	12:20	2.5	4.4	6.9	1.8
2005-04-26	12:20	13:20	2.0	3.5	5.5	1.8
2005-05-02	14:52	15:52	0.72	1.5	2.3	2.1
2005-05-02	15:52	16:52	0.61	1.5	2.1	2.4
2005-05-02	16:52	17:52	0.55	1.2	1.8	2.3
2005-05-02	17:52	18:52	0.52	1.2	1.7	2.2
2005-05-02	18:52	19:52	0.50	1.2	1.7	2.3
2005-05-02	19:52	20:52	0.10	1.0	1.1	10
2005-05-02	20:52	21:52	0.46	1.0	1.5	2.2
2005-05-03	08:55	09:55	1.2	2.7	3.8	2.3
2005-05-03	09:55	10:55	0.80	1.9	2.7	2.4
2005-05-03	10:55	11:55	0.65	1.6	2.3	2.5
2005-05-03	11:55	12:55	0.68	1.5	2.2	2.3
2005-05-03	12:55	13:55	0.64	1.4	2.1	2.2
2005-05-03	13:55	14:55	0.58	1.3	1.8	2.1
2005-05-03	14:55	15:15	0.77	1.8	2.6	2.3
2005-05-16	09:50	10:50	0.18	0.50	0.67	2.8
2005-05-16	10:50	11:50	0.12	0.41	0.53	3.3
2005-05-16	11:50	12:50	0.10	0.37	0.48	3.7
2005-05-16	12:50	13:50	0.08	0.40	0.48	5.1
2005-05-16	13:50	14:50	0.06	0.37	0.43	6.1
2005-05-16	14:50	15:50	0.06	0.25	0.31	4.4
2005-05-16	15:50	16:50	0.06	0.27	0.34	4.3

Appendix 2. Limonene in air at Gårdsjön

Limonene air measurements at Gårdsjön						
date	starttime	endtime	d-limonene µg/m ³	l-limonene µg/m ³	d+l-limonene µg/m ³	l/d-limonene µg/m ³
2005-02-07	13:20	14:25	2.7	1.7	4.4	0.61
2005-03-02	12:40	13:38	0.52	0.92	1.4	1.7
2005-03-29	12:44	13:45	0.22	0.46	0.68	2.0
2005-04-28	10:04	11:04	1.6	3.1	4.7	1.9
2005-04-28	11:04	12:04	1.2	2.3	3.5	1.9
2005-04-28	12:04	13:04	1.0	1.9	2.9	1.9
2005-04-28	13:04	14:04	0.86	1.8	2.7	2.1
2005-04-28	14:04	15:04	0.86	1.8	2.7	2.1
2005-04-28	15:04	15:48	1.3	2.4	3.6	1.9
2005-04-28	15:53	16:53	2.0	3.9	5.9	2.0
2005-04-28	16:53	17:53	0.87	1.6	2.5	1.9
2005-04-28	17:53	18:53	0.86	1.6	2.4	1.8
2005-04-28	18:53	19:53	0.72	1.5	2.2	2.1
2005-04-28	19:53	20:53	0.71	1.8	2.5	2.5
2005-04-28	20:53	21:53	0.62	1.9	2.5	3.1
2005-04-28	21:53	22:53	0.68	2.1	2.8	3.1
2005-04-29	10:17	11:17	0.53	1.3	1.8	2.4
2005-04-29	11:17	12:17	0.74	1.3	2.1	1.8
2005-04-29	12:17	13:17	0.48	1.1	1.6	2.3
2005-04-29	13:17	14:17	0.45	1.0	1.5	2.3
2005-04-29	14:17	14:43	0.78	1.4	2.2	1.8
2005-05-18	11:15	12:15	0.22	0.53	0.75	2.4
2005-05-18	12:15	13:15	0.05	0.04	0.09	0.87
2005-05-18	13:15	14:15	0.02	0.02	0.04	0.93
2005-05-18	14:15	15:15	0.03	0.01	0.04	0.17
2005-05-18	15:15	16:15	0.01	0.01	0.02	1.7
2005-05-18	16:15	17:15	0.005	0.002	0.01	0.39
2005-04-28	10:04	11:04	1.6	3.1	4.7	1.9
2005-04-28	11:04	12:04	1.2	2.3	3.5	1.9
2005-04-28	12:04	13:04	1.0	1.9	2.9	1.9
2005-04-28	13:04	14:04	0.86	1.8	2.7	2.1
2005-04-28	14:04	15:04	0.86	1.8	2.7	2.1
2005-04-28	15:04	15:48	1.3	2.4	3.6	1.9
2005-04-28	15:53	16:53	2.0	3.9	5.9	2.0
2005-04-28	16:53	17:53	0.87	1.6	2.5	1.9
2005-04-28	17:53	18:53	0.86	1.6	2.4	1.8
2005-04-28	18:53	19:53	0.72	1.5	2.2	2.1
2005-04-28	19:53	20:53	0.71	1.8	2.5	2.5
2005-04-28	20:53	21:53	0.62	1.9	2.5	3.1
2005-04-28	21:53	22:53	0.68	2.1	2.8	3.1
2005-04-29	10:17	11:17	0.53	1.3	1.8	2.4
2005-04-29	11:17	12:17	0.74	1.3	2.1	1.8
2005-04-29	12:17	13:17	0.48	1.1	1.6	2.3
2005-04-29	13:17	14:17	0.45	1.0	1.5	2.3
2005-04-29	14:17	14:43	0.78	1.4	2.2	1.8
2005-05-18	11:15	12:15	0.22	0.53	0.75	2.4
2005-05-18	12:15	13:15	0.05	0.04	0.09	0.87
2005-05-18	13:15	14:15	0.02	0.02	0.04	0.93
2005-05-18	14:15	15:15	0.03	0.01	0.04	0.17
2005-05-18	15:15	16:15	0.01	0.01	0.02	1.7
2005-05-18	16:15	17:15	0.005	0.002	0.01	0.39
2005-06-03	09:00	10:00	<1	66	66	66
2005-06-03	10:00	11:00	<1	42	42	42
2005-06-03	11:00	12:00	<1	36	36	36
2005-06-03	12:00	13:00	<1	57	57	57
2005-06-03	13:00	14:00	<1	140	140	140
2005-06-03	14:00	15:00	<1	110	110	110

Appendix 3. Limonene in air at Göteborg

Limonene air measurements at Göteborg						
date	starttime	endtime	d-limonene µg/m ³	l-limonene µg/m ³	d+l-limonene µg/m ³	l/d-limonene µg/m ³
2005-02-07			0.60	1.6	2.2	2.7
2005-04-27	04:00	05:00	2.6	4.6	7.2	1.8
2005-04-27	05:00	06:00	2.1	3.8	5.8	1.8
2005-04-27	06:00	07:00	1.5	3.0	4.5	2.0
2005-04-27	07:00	08:00	1.3	2.5	3.8	2.0
2005-04-27	08:00	09:00	1.2	2.4	3.6	2.0
2005-04-27	09:00	10:00	1.1	2.1	3.2	2.0
2005-04-27	10:00	11:00	1.2	2.3	3.5	1.9
2005-04-30			0.92	1.7	2.6	1.8
2005-05-04	11:16	12:16	1.1	1.6	2.7	1.4
2005-05-04	12:16	13:16	0.75	1.0	1.8	1.4
2005-05-04	13:16	14:16	0.63	0.92	1.5	1.5
2005-05-04	14:16	15:16	0.67	0.79	1.5	1.2
2005-05-04	15:16	16:16	0.72	0.81	1.5	1.1
2005-05-04	16:16	17:00	1.5	1.0	2.5	0.65
2005-05-09	08:30	09:30	0.89	1.8	2.7	2.0
2005-05-09	09:30	10:30	0.52	1.1	1.6	2.1
2005-05-09	10:30	11:30	0.43	0.88	1.3	2.0
2005-05-09	11:30	12:30	0.45	0.89	1.3	2.0
2005-05-09	12:30	13:30	0.48	0.87	1.4	1.8

Appendix 4. Limonene in water at Råö and Gårdsjön.

Analysis results from background water samples				
date	location	d-limonene Conc. (µg/l)	l-limonene Conc. (µg/l)	Sum d+l-limonene
05-04-26	Råö	<0.08	<0.18	<0.26
05-05-02	Råö	<0.08	<0.18	<0.26
05-05-17	Råö	<0.08	<0.18	<0.26
05-05-25	Råö	<0.08	<0.18	<0.26
05-05-31	Råö	<0.08	<0.18	<0.26
05-04-28	Gårdsjön	<0.08	<0.18	<0.26
05-05-12	Gårdsjön	<0.08	<0.18	<0.26
05-05-17	Gårdsjön	<0.08	<0.18	<0.26
05-05-20	Gårdsjön	0.17	0.46	0.63
05-05-31*	Gårdsjön	0.20	0.57	0.77

* Sample collected close to inflow to lake from forest drainage area.

Appendix 5. Limonene in sediments from background sites.

Analysis results from background sediment samples					
Location	Depth (m)	Layer (cm)	d-limonene Conc. (ng/g TS)	l-limonene Conc. (ng/g TS)	d+l-limonene Conc. (ng/g TS)
Ö Gotlandsdjupet	121	0-2	<64	<140	<200
Ö Öland	77	0-2	<56	<130	<190
Norrköpingsdjupet	179	0-2	<93	<210	<300

Appendix 6. Limonene in sludge from sewage treatment plants.

location	Sample id.	d-limonene Conc. (ng/g TS)	l-limonene Conc. (ng/g TS)	d+l-limonene Conc. (ng/g TS)	Ratio l/d-limonene
Henriksdal	MR3760	150	350	500	2.3
Eslöv	MR3848	560	310	870	0.55
Floda	MR3701	82	70	150	0.85

Appendix 7 Limonene in water and sediments from Gruvön

Limonene concentrations in water samples from Gruvön.

date		location	d-limonene Conc. (µg/l)	l-limonene Conc. (µg/l)	Sum d+l-limonene
05-05-19	1	Vänern outside factory area	<0.08	<0.18	<0.26
05-05-18	2	Vänern Gamla Slottsbron	<0.08	<0.18	<0.26
05-05-18	3	Vänern ca 500 m south of mill	<0.08	<0.18	<0.26
05-05-18	4	Vänern, bay ca 1 km south of mill	<0.08	<0.18	<0.26
05-05-18	5	Vänern, outside aired waste water pond	<0.08	<0.18	<0.26
05-05-18	6	Vänern, bay close to aired waste water pond	<0.08	<0.18	<0.26
05-05-18	7	Vänern ca 2 km south of mill	<0.08	<0.18	<0.26
05-05-18	8	Vänern ca 3 km south of mill	<0.08	<0.18	<0.26
05-05-18	9	Waste water from fibres sedimentation, led to the aired waste water pond	<0.08	<0.18	<0.26
05-05-18	10	Mixture of different waste waters led to the aired waste water pond	<0.08	<0.18	<0.26
05-05-18	11	Outlet from wastewater pond into Vänern	<0.08	<0.18	<0.26
05-05-18	12	Cooling water led back to Vänern	<0.08	<0.18	<0.26

Limonene concentrations in sediment sample from Gruvön.

date		location	d-limonene Conc. (µg/l)	l-limonene Conc. (µg/l)	Sum d+l-limonene
05-05-18	1	Aired waste water pond	120	270	390

Appendix 8. Limonene in air at Gruvön.

date	location	starttime	endtime	d-limonene µg/m ³	l-limonene µg/m ³	d+l-limonene µg/m ³	l/d-limonene µg/m ³
2005-05-18	Central location at mill	12:30	13:00	0.23	3.4	3.6	15
2005-05-18	Central location at mill	13:00	13:30	0.30	5.6	5.9	19
2005-05-18	Central location at mill	13:30	14:00	0.43	8.4	8.8	20
2005-05-18	Central location at mill	14:00	14:30	0.35	4.4	4.7	13
2005-05-18	Central location at mill	14:30	15:00	0.41	5.7	6.1	14
2005-05-18	Central location at mill	15:00	15:30	0.73	17	18	24
2005-05-19	Central location at mill	08:00	08:30	0.98	14	15	14
2005-05-19	Central location at mill	08:30	09:00	2.3	36	38	15
2005-05-19	Central location at mill	09:00	09:30	2.5	37	40	15
2005-05-19	Central location at mill	09:30	10:00	1.9	27	29	14
2005-05-19	Central location at mill	10:00	10:30	1.5	28	29	19
2005-05-19	Central location at mill	10:30	11:00	2.4	37	39	15
2005-05-18	about 1 km south of mill	15:45		0.05	0.08	0.12	1.6
2005-05-18	about 1 km north of mill	17:00		0.05	0.18	0.23	3.7
2005-05-18	Exposed location at mill	14:30		0.38	3.4	3.7	9
2005-05-18	above aired wastewater pond, south side	13:00		0.52	1.5	2.0	2.8
2005-05-18	3 m from inlet to aired wastewater pond	13:15		0.22	0.54	0.8	2.4
2005-05-18	above mixing pond of waste waters	14:00		1.6	14	16	9.2
2005-05-19	above pile of wood chips, birch	08:50		0.23	4.4	4.6	19
2005-05-19	above pile of bark	09:10		0.22	5.3	5.5	24
2005-05-19	above pile of wood chips, conifer	08:30		4.0	75	79	19
2005-05-19	above pile of reject pulp	09:35		2.6	7.8	10	3.0
2005-05-19	At the edge of area against the lake	10:35		0.96	14	15	14

Appendix 9. Limonene in air and waste water from Brämhult. Limonene concentrations in air samples from Brämhults.

date	location	starttime	endtime	d-limonene µg/m ³	l-limonene µg/m ³	d+l-limonene µg/m ³	l/d-limonene µg/m ³
2005-05-31	At the A/C to the storage room	09:55		34	6.0	40	0.18
2005-05-31	At the A/C to the storage room	09:55		17	2.9	20	0.17
2005-05-31	Above container with bad fruit	10:20		2400	24	2400	0.01
2005-05-31	between the houses at the area	10:30		21	0.97	22	0.05
2005-05-31	between the houses at the area	16:10		550	5.3	560	0.01
2005-05-31	outside door to fruit press room	14:40		20000	79	20000	0.00
2005-05-31	outside door to fruit press room	15:50		5500	39	5500	0.01
2005-05-31	outside door to fruit press room	16:10		5000	35	5000	0.01
2005-05-31	outside door to fruit press room	16:37		18000	97	18000	0.01
2005-05-31	10m from door to fruit press room	14:20		690	7.5	700	0.01
2005-05-31	10m from door to fruit press room	14:40		>300			
2005-05-31	10m from door to fruit press room	15:50		670	7.2	680	0.01
2005-05-31	10m from door to fruit press room	16:35		230	2.1		
2005-05-31	outside door to storage room	10:15	10:45	19000	100		
2005-05-31	outside door to storage room	10:45	11:15	1600	13	1600	0.01
2005-05-31	outside door to storage room	11:15	11:45	1400	13	1400	0.01
2005-05-31	outside door to storage room	11:45	12:15	1500	13	1500	0.01
2005-05-31	outside door to storage room	12:15	12:45	12000	74	12000	0.01
2005-05-31	outside door to storage room	12:45	13:15	1700	14	1400	0.01
2005-05-31	outside factory area, north 25m	11:00		0.20	<0.10		
2005-05-31	outside factory area, north 50m	11:00		0.43	0.24	0.67	0.58
2005-05-31	outside factory area, north 25m	15:15		29	0.62	30	0.02
2005-05-31	outside factory area, north 75m	15:05		3.2	0.16	3.4	0.05

Limonene concentrations in wastewater sample from Brämhults.

location	d-limonene Conc. (µg/l)	l-limonene Conc. (µg/l)	d+l-limonene Conc. (µg/l)	Ratio l/d-limonene
Brämhult	70	350	420	5

Appendix 10. Regional screening of limonene in sediment, sludge and water.

County	Location	Sampling date	sludge	Sediment and sludge			Water		
				d-limonene ng/gTS	l-limonene ng/gTS	d+l-limonene ng/gTS	d-limonene ng/ml	l-limonene ng/ml	d+l-limonene ng/ml
Blekinge	Karlshamn STP	2004-09-28	X	<28.5	250	250			
Blekinge	Mörnum deponi	2004-09-23					<0.08	<0.18	<0.26
Blekinge	Karlskrona STP	2004-10-07	X	<45	<100	<140			
Blekinge	Volvo personvagnar	2004-10-06	X	<28	430	<460			
Blekinge	Angelskogstippen	2004-10-06					<0.08	<0.18	<0.26
Blekinge	Angelskogstippen						<0.08	<0.18	<0.26
Blekinge	Ronneby STP	2004-10-06	X	<42	<95	<140			
Blekinge	Sölvesborg STP	2004-09-29	X	<39	2900	2900			
Jämtland	Myrviken STP	2004-11-01	X	<34	3700	3700			
Jämtland	Bräcke STP	2004-10-19	X	820	310	1100			
Jämtland	Björnsjö STP *	2004-06-21	X	<12	35	35			
Jämtland	Hissmofors STP	2004-10-19	X	450	430	880			
Jämtland	Överammer STP	2004-10-19	X	1600	380	2000			
Jämtland	Strömsund STP	2004-10-27	X	53	930	980			
Jämtland	Åre STP *	2004-04-13	X	<39	16000	16000			
Jämtland	Gövikens STP	2004-09-29	X	<26	<60	<86			
Stockholm	Himmerfjärdsverket	2004-09-28	X	<31	320	320			
Stockholm	Himmerfjärdsverket						<0.08	<0.18	<0.26
Stockholm	St Envättern	2004-09-01		100	260	360			
Stockholm	Himmerfjärden	2004-09-01		<30	15	15			
Västernorrland	SCA Östrand			<28	<63	<91			
Västernorrland	SCA Östrand						<0.08	<0.18	<0.26
Västernorrland	Bodum STP	2004-11-10	X	<0.79	<1.8	<2.6			
Västernorrland	Husum	2004-10-20		<9.8	19	19			
Västernorrland	Husum, löv						1.9	<0.18	1.9
Västernorrland	Husum, barr						<0.08	<0.18	<0.26
Västernorrland	Tivoliverket		X	2600	760	3360			
Västra Götaland	Lidköping STP		X	77	2600	2677			
Västra Götaland	Lidköping STP						<0.08	<0.18	<0.26
Västra Götaland	Vara STP	2004-10-04	X	1200	640	1840			
Västra Götaland	Åmål STP	2004-09-29	X	100	1300	1400			
Västra Götaland	Åmål STP	2004-09-29					<0.08	<0.18	<0.26

* Mun.sample taken during tourist season not according to sampling instructions.

County	Location	Sampling date	Fish		
			d-limonene ng/gTS	l-limonene ng/gTS	d+l-limonene ng/gTS
Stockholm	St Envättern	2004-07-22	<8.3	<19	<27
Stockholm	Himmerfjärden	2004-09-01	<5.1	<12	<17