

Supplementary information

For the first time, one of the authors of this paper came across the discussed problem in the late autumn of 1976 while determining VOCs content in the urban atmosphere. Six monoterpene hydrocarbons were identified by GC-MS in the air samples collected in the sorption tube in the park zone of Leningrad. Because the sampling was conducted after the growing season, it was concluded that the most probable source of these compounds were fallen poplar leaves remaining at the testing site (Ioffe, B.V., Isidorov, V.A. and Zenkevich, I.G.: Gas chromatographic–mass spectrometric determination of volatile organic compounds in an urban atmosphere, *J. Chromatogr.*, 142, 787–795, 1977).

I. HS-SPME/GC-MS analysis of VOCs emitted from pine and spruce litter into the gas phase

Figure 1S presents some of the HS-SPME chromatograms of VOCs emitted from pine litter during its decomposition in natural conditions. Despite numerous advantages of the HS-SPME method over conventional methods of VOCs concentration in sorption tubes, including thermodesorption and cryofocusing of analytes, in some aspects it cannot rival especially the latter of the two mentioned. Primarily, this is related to the possibilities of simultaneous quantitative determination of the most and the least volatile VOCs. For instance, the registered traces of 2-butanone is not tantamount to extremely low emission of this substance, because small surface under the peaks on the chromatogram is a consequence of the low value of the substance's air-to-fiber partition coefficient ($K_{fg} = 251$ at 22°C, whereas for limonene the same coefficient at the same temperature $K_{fg} = 10,965$) (Isidorov and Vinogorova, 2005). On the other hand, HS-SPME is not appropriate for quantitative determination of sesquiterpenes, because the equilibrium distribution between air and PMDS phase requires several dozen hours. For this reason, in that stage of the experiment, the task was limited to evaluation of the emission rate of monoterpenes from pine and spruce litter.

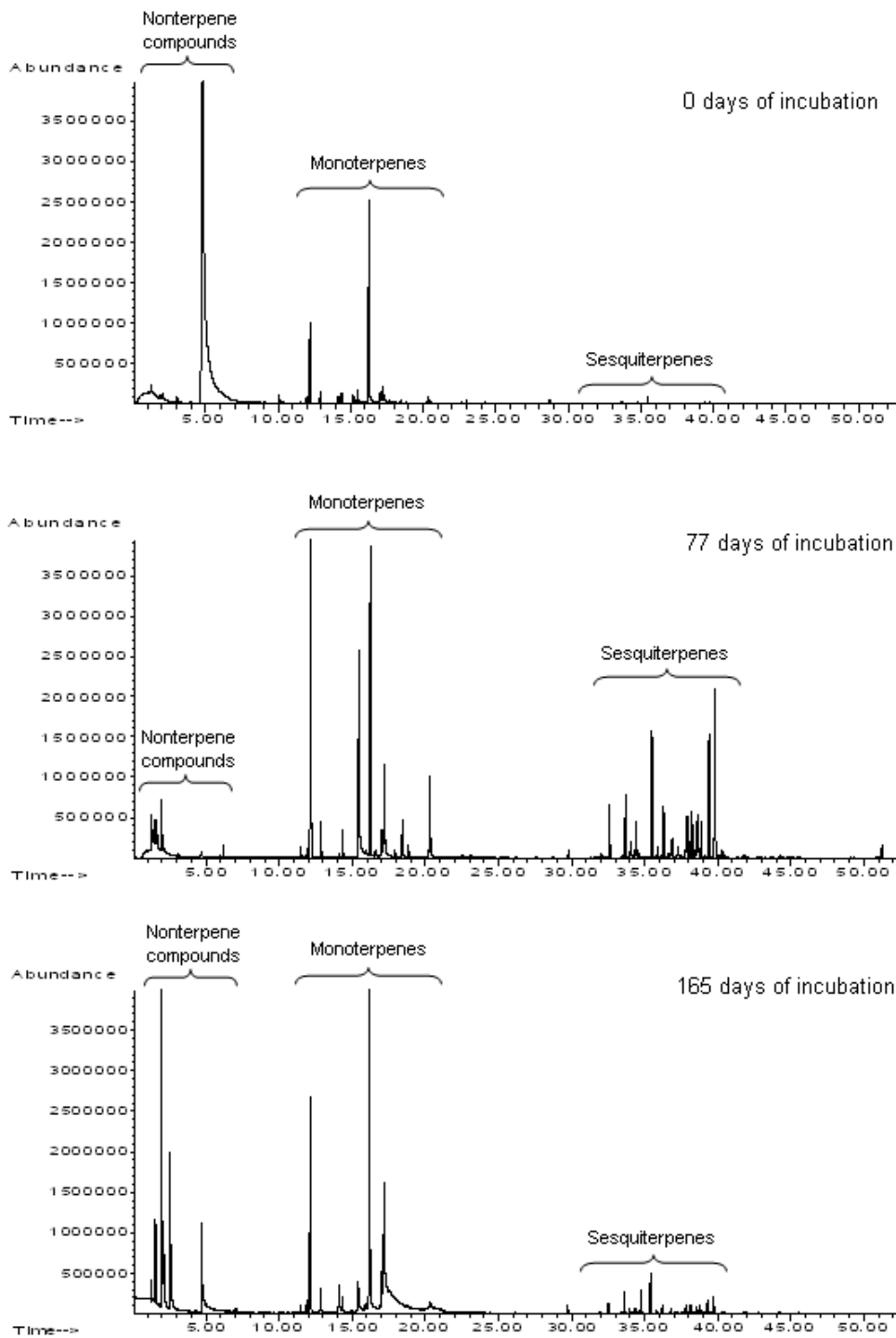


Fig. 1S. Typical HS-SPME/GC-MS chromatograms from pine needle litter emissions concentrated on PDMS (100 μ m) fiber.

Tables 1S–4S present the total the results of semi-quantitative GC-MS analysis. The ion current depends on the chemical structure of analyte and it is not a true quantification.

Table 1S. VOCs composition pine and spruce needle litter emissions (%) according to HS-SPME/GC-MS analysis with using of Carboxen/PDMS fiber coating

Compound	LTPRI	Pine litter					Spruce litter				
		Days of incubation									
		0	77	165	282	490	0	77	165	282	490
Ethanol	482	– ¹	–	–	0.3	0.3	–	1.2	–	4.9	0.3
Acetone	500	–	–	2.3	12.6	9.6	–	3.9	5.7	24.9	13.0
Ethyl formate	507	–	2.1	3.3	1.1	0.1	2.4	–	–	0.2	trace ²
Dichloromethane	527	–	1.3	1.7	trace	–	–	–	–	–	–
Methylene chloride	531	–	–	–	0.4	0.1	–	2.2	1.8	2.3	3.7
Methyl acroleine	562	–	–	–	–	–	–	–	2.3	trace	trace
2-Butanone	595	–	–	–	0.2	trace	–	–	–	trace	trace
Hexane	600	0.5	2.9	7.8	6.7	16.0	3.5	4.5	4.0	14.3	32.2
2-Methyl furan	602	–	–	–	0.9	–	–	–	2.3	1.0	–
Ethyl acetate	612	–	–	9.5	19.8	0.6	–	–	–	0.3	trace
3-Methylfuran	612	1.0	–	–	–	0.2	–	–	–	trace	trace
Trichloromethane	617	–	–	–	–	–	–	–	–	3.1	11.9
Benzene	653	–	–	5.7	3.0	0.2	–	–	0.5	0.9	4.4
Pentanal	701	–	–	–	–	–	–	0.5	0.2	0.3	0.5
2-Pentanone	687	–	–	0.3	0.4	0.3	–	–	–	–	–
Trichloroethylene	700	–	0.1	–	trace	0.6	–	–	–	–	trace
Pyridine	732	–	–	7.6	trace	trace	–	–	–	–	–
Toluene	760	78.4	0.2	0.3	1.8	2.8	66.9	0.2	0.4	3.0	6.6
3-Hexanone	784	–	–	0.2	0.5	0.2	–	–	–	–	–
Octane	800	–	–	0.3	–	–	–	0.1	0.1	trace	–
Hexanal	802	–	0.1	0.5	–	0.1	1.5	0.7	0.1	0.6	trace
Ethyl butanoate	805	–	–	0.2	0.5	–	–	–	–	0.3	0.4
Butyl acetate	815	–	–	–	0.5	0.1	–	–	–	0.3	trace
Ethyl benzene	854	–	–	–	–	trace	–	–	0.1	–	–
Santene	879	–	–	–	–	–	–	0.1	–	–	–
Tricyclene	916	0.1	0.4	0.2	0.1	0.3	0.2	0.5	0.5	0.9	6.0
α -Thujene	924	0.2	0.3	0.1	0.3	0.2	trace	0.2	0.4	trace	–
α -Pinene	928	2.8	13.4	5.1	12.6	31.9	1.6	4.2	3.1	5.0	11.2
Camphene	942	0.4	1.3	0.7	0.9	2.0	2.2	4.5	4.7	9.0	3.3
Benzaldehyde	956	–	–	–	–	–	0.2	–	–	trace	–
Verbenene	966	0.3	0.1	0.5	1.4	–	–	trace	0.1	0.3	–
Sabinene	970	–	–	0.3	0.3	–	–	1.2	1.3	0.9	–
4-Octanone	973	–	–	4.5	2.0	0.2	–	–	–	–	–
β -Pinene	969	0.5	1.0	2.0	–	1.4	1.0	–	–	–	trace
Phenol	985	0.4	–	–	–	–	0.3	–	–	–	–
3-Octanone	984	–	–	–	0.9	0.7	–	–	–	–	trace
6-Methyl-5-hepten-2-one	988	–	–	–	trace	–	–	0.1	–	trace	trace
Myrcene	989	0.8	10.2	trace	trace	–	2.6	30.0	15.1	13.2	trace
α -Phellandrene	998	–	0.4	–	–	–	–	–	0.9	–	–

3-Carene	1005	9.1	13.9	13.1	15.9	24.5	0.8	1.6	1.2	0.9	trace
α -Terpinene	1013	–	0.4	0.4	0.2	0.1	trace	0.3	0.3	trace	–
<i>p</i> -Cymene	1020	0.6	1.3	1.1	0.6	0.8	1.0	1.8	1.4	1.9	0.1
D-Limonene	1025	1.4	4.7	11.5	8.8	2.3	47.9	32.9	42.9	5.9	3.2
Benzyl alcohol	1031	0.4	–	–	trace	–	1.6	–	–	–	–
2-Ethyl-1-hexanol	1032	–	–	0.9	0.3	1.3	–	–	3.2	0.9	trace
β -(Z)-Ocimene	1036	0.2	0.2	0.2	–	–	–	0.1	–	–	–
β -(E)-Ocimene	1046	–	1.4	–	–	–	–	0.3	–	–	–
γ -Terpinene	1056	0.1	0.5	0.6	0.3	0.2	0.4	0.6	0.2	–	–
Isopentyl butanoate	1059	–	–	0.2	0.4	0.3	–	–	–	–	–
<i>p</i> -Mentha-2,4(8)-diene	1083	0.3	0.3	–	trace	–	–	–	–	–	–
Terpinolene	1085	6.5	3.5	1.8	0.2	0.2	2.3	trace	0.2	trace	–
Nonanal	1102	–	–	0.1	0.3	–	–	–	–	0.2	0.1
Camphor	1135	0.2	trace	0.1	trace	–	0.3	0.3	0.6	0.5	trace
Camphene hydrate	1140	–	–	–	–	–	0.2	0.2	0.2	0.1	–
Borneol	1160	–	–	trace	trace	–	0.5	0.2	0.5	0.3	–
α -Terpineol	1171	–	trace	trace	–	–	–	0.1	trace	–	–
Myrtenol	1190	trace	–	–	trace	–	0.2	–	–	–	–
2-Decanone	1195	–	–	trace	0.2	trace	–	–	–	–	–
Verbenone	1203	trace	trace	–	0.5	1.4	–	–	–	0.1	0.3
Thymol, methyl ether	1230	–	trace	trace	0.3	–	–	–	–	–	–
Bornyl acetate	1278	trace	0.2	0.2	0.4	0.3	2.0	3.9	2.8	1.9	trace
α -Longipinene	1341	–	–	–	–	–	0.1	0.1	0.3	0.3	–
Cubebene	1341	trace	2.0	1.1	0.2	0.2	0.1	0.2	0.1	trace	–
α -Terpinyl acetate	1344	–	trace	–	0.1	0.1	–	0.3	0.1	0.1	–
Ylangene	1362	–	0.1	0.1	–	trace	–	–	–	–	–
Copaene	1366	0.1	2.4	1.3	–	trace	0.1	0.2	0.2	–	–
β -Bourbonene	1374	trace	0.7	0.4	–	–	–	trace	trace	–	–
β -Cubebene	1381	–	0.3	0.1	0.1	–	–	–	–	–	–
β -Elemene	1383	trace	1.4	0.4	–	–	0.1	0.2	0.2	0.1	–
Sesquiterpene	1386	trace	0.3	0.1	–	–	–	–	–	–	–
D-Longifolene	1392	–	–	0.1	trace	–	0.2	0.3	0.4	0.1	–
β -(E)-Caryophyllene	1408	0.3	4.9	2.1	0.9	trace	0.3	0.4	0.4	0.3	trace
Aromadendrene	1428	trace	0.2	0.8	0.2	0.4	–	trace	–	trace	–
α -Humulene	1445	trace	0.7	0.2	0.6	trace	0.2	0.2	0.2	trace	–
γ -Muurolole	1467	trace	1.9	0.7	0.2	–	–	0.1	0.1	–	–
Germacrene D	1470	–	0.6	0.1	trace	–	–	–	–	–	–
β -Selinene	1475	trace	2.0	0.6	trace	–	–	–	–	–	–
α -Selinene	1484	–	2.8	0.6	0.2	–	–	0.1	–	–	–
α -Muurolole	1491	trace	1.6	0.5	0.2	–	0.2	0.1	0.1	–	–
γ -Cadinene	1504	0.1	4.9	2.5	0.6	0.2	0.1	0.4	0.5	0.3	–
δ -Cadinene	1514	0.1	7.2	1.8	0.4	0.2	0.2	0.4	0.1	0.2	–
Cadina-1,4-diene	1525	–	0.1	–	0.2	trace	–	trace	trace	0.2	–
α -Cadinene	1528	–	0.3	0.1	0.1	–	–	–	–	–	–
α -Calacorene	1533	–	0.1	0.1	0.2	–	–	trace	–	–	–
Caryophyllene oxide	1574	–	0.1	–	0.1	–	–	–	–	–	–
τ -Cadinol	1634	–	0.1	0.1	–	–	–	–	–	–	–
α -Cadinol	1645	–	0.1	trace	–	–	–	–	–	–	–

¹ not registered; ² below 0.1 % of TIC.

II. Changes in the chemical composition of the extractive organics in the litter

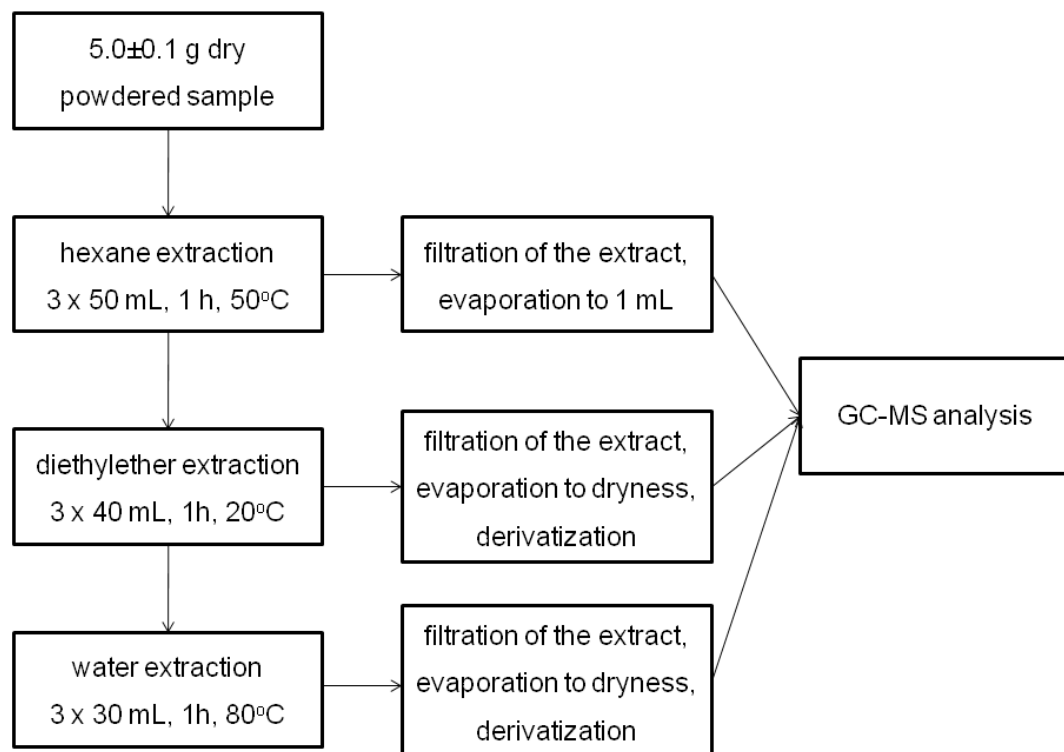


Fig. 2S. Analysis flow chart

On the chromatograms of each of the extracts (hexane, ether and water extracts) one could observe peaks representing hundreds of substances of various classes, and for some of them it was impossible for us to find either the value of retention index in literature or their mass spectra in the available databases. In such cases individual identification is extremely difficult, if at all possible. As a result, in the presented tables there are different levels of structure specification for the analytes: chemical name (individual identification), homologous series (e.g. sesquiterpene alcohol $C_{15}H_{24}O$; resin acid; etc.), or substance class (e.g. sesquiterpenes, diterpenes, disaccharides).

Table 2S. Relative composition (%) of the hexane extracts from the pine and spruce litter on various stages of decomposition

Compound (TMS derivative)	LTPRI	Pine litter					Spruce litter				
		Days of incubation									
		0	77	165	282	490	0	77	165	282	490
Toluene	777	–	–	–	0.1	0.2	trace	trace	–	–	–
3-Hexanone	788	trace	–	–	trace	trace	–	–	–	–	–
2-Hexanone	791	trace	–	–	0.1	0.1	–	trace	–	–	–
3-Hexanol	795	trace	–	–	0.1	0.2	trace	trace	trace	–	–
2-Hexanol	799	trace	–	–	trace	trace	–	–	–	–	–
Hexanal	798	–	trace	–	–	–	trace	trace	trace	0.1	–
Santene	880	–	–	–	–	–	trace	trace	trace	–	–
Heptanal	899	–	–	–	–	–	–	–	trace	0.1	0.2
Tricyclene	914	0.2	0.1	trace	trace	trace	0.1	trace	0.1	trace	trace
α -Thujene	921	0.1	0.1	0.1	–	–	trace	trace	trace	–	–
α -Pinene	926	4.2	3.2	1.0	0.7	1.8	0.7	0.2	0.3	0.7	0.5
Camphene	940	0.6	0.4	0.3	trace	0.1	1.3	0.4	0.6	0.9	0.9
Thuja-2,4(10)-diene	946	–	trace	trace	–	–	–	–	–	–	–
α -Fenchene	953	–	–	trace	–	–	trace	–	–	–	–
Benzaldehyde	956	–	–	–	trace	0.2	trace	–	–	trace	trace
Verbenene	963	–	trace	trace	0.1	0.4	–	–	trace	0.3	0.6
Sabinene	966	0.1	trace	0.1	0.1	0.1	0.1	trace	trace	trace	–
β -Pinene	968	0.5	0.3	0.1	0.3	0.9	0.1	trace	0.1	0.1	0.3
6-Methyl-5-hepten-2-one	983	–	trace	trace	–	–	–	trace	trace	–	–
β -Myrcene	986	0.2	0.1	trace	–	–	0.4	0.1	0.1	0.2	0.2
α -Phellandrene	999	–	–	–	–	–	trace	–	trace	trace	–
Octanal	1000	–	–	–	–	–	–	–	trace	trace	trace
3-Carene	1004	2.8	1.6	0.6	0.6	1.2	trace	trace	trace	trace	–
α -Terpinene	1011	trace	trace	0.1	0.1	0.1	trace	trace	trace	–	–
p-Cymene	1019	trace	trace	trace	0.2	0.5	trace	trace	trace	0.1	0.3
Limonene	1022	0.3	0.2	0.1	0.2	0.6	1.4	0.2	0.5	0.7	0.6
Eucalyptol	1024	–	–	–	–	–	1.4	0.4	0.4	0.4	0.4
β -(Z)-Ocimene	1044	0.1	trace	trace	–	–	trace	–	trace	trace	–
γ -Terpinene	1053	0.1	0.1	trace	0.1	trace	trace	trace	trace	–	–
cis-Sabinenehydrate	1062	–	–	–	–	–	0.1	0.1	–	–	–
Terpinolene	1082	0.3	0.1	trace	trace	trace	0.1	–	trace	–	–
α -Pinene oxide	1090	–	–	trace	trace	0.1	–	–	–	–	–
trans-Sabinenehydrate	1092	–	–	–	–	–	0.1	trace	trace	–	–
Linalool	1096	–	–	–	–	–	0.1	trace	trace	–	–
Terpenoid	1099	–	–	0.1	trace	trace	–	–	–	–	–
Nonanal	1100	–	–	–	–	–	–	trace	trace	0.1	trace
endo-Fenchol	1107	–	–	–	–	–	trace	trace	trace	–	–
α -Campholenal	1120	trace	trace	trace	–	–	trace	trace	trace	–	–
trans-Pinocarveol	1131	trace	trace	trace	trace	–	trace	trace	trace	–	–
Camphor	1136	0.1	trace	trace	–	–	0.7	0.2	0.3	0.7	0.5
cis-Verbenol	1138	0.1	trace	0.1	trace	0.1	–	–	–	–	–
Camphenehydrate	1140	–	–	–	–	–	1.0	0.5	0.5	0.4	0.7
Isoborneol	1149	–	–	–	–	–	trace	trace	trace	–	–

Pinocarpone	1155	–	–	trace	trace	trace	–	–	trace	trace	–
Borneol	1159	trace	trace	trace	trace	–	1.5	0.9	1.0	1.3	1.5
<i>cis</i> -Pinocamphone	1166	–	trace	trace	trace	–	–	–	trace	trace	–
4-Terpineol	1171	trace	trace	trace	0.1	0.1	trace	trace	trace	–	–
<i>m</i> -Cymene-8-ol	1178	trace	trace	trace	–	–	–	–	trace	–	–
<i>p</i> -Cymene-8-ol	1181	trace	0.1	0.1	0.2	0.6	trace	trace	trace	0.3	0.5
α -Terpineol	1185	0.1	trace	trace	trace	–	0.5	0.4	0.2	0.4	0.3
Myrtenal	1189	–	–	trace	trace	–	–	–	trace	–	–
Myrtenol	1191	trace	trace	trace	–	–	–	–	trace	–	–
Verbenone	1202	0.1	0.1	0.1	0.2	trace	trace	trace	trace	0.1	0.1
Fenchyl acetate	1214	–	–	–	–	–	trace	–	trace	–	–
Citronellol	1226	–	–	–	–	–	0.1	0.1	trace	–	–
Thymol, methyl ether	1232	trace	trace	–	–	–	trace	–	–	–	–
Piperitone	1247	–	–	–	–	–	0.1	0.1	trace	trace	–
Linalool acetate	1252	–	–	–	–	–	–	trace	trace	–	–
2-(E)-Decenal	1258	–	–	–	–	–	–	trace	trace	–	–
2,5-Bornanedione	1258	0.4	trace	–	trace	–	–	–	–	–	–
Bornyl acetate	1281	0.2	0.1	trace	trace	0.1	5.9	2.7	3.4	5.2	4.8
2-Undecanone	1290	trace	trace	–	–	–	trace	trace	trace	–	–
Tridecane	1300	0.1	trace	trace	–	trace	0.1	trace	trace	–	–
(E,E)-2,4-Decadienal	1312	–	–	trace	trace	–	–	trace	trace	–	–
δ -Elemene	1330	0.5	0.1	0.1	trace	0.2	trace	trace	trace	–	–
α -Terpenyl acetate	1334	trace	–	trace	–	–	0.4	0.3	0.4	0.3	0.4
<i>exo</i> -2-Hydroxycineole acetate	1336	–	–	–	–	–	0.1	0.1	trace	–	–
α -Longipinene	1341	–	–	–	–	–	0.1	–	trace	trace	–
α -Cubebene	1343	0.6	0.8	0.9	0.7	0.7	–	–	–	–	–
Citronellyl acetate	1350	–	–	–	–	–	trace	trace	trace	–	–
Ylangene	1363	0.1	trace	0.1	trace	–	–	–	trace	–	–
α -Copaene	1368	0.7	0.6	0.7	0.1	0.7	0.1	trace	0.1	0.3	0.2
β -Bourbonene	1376	0.3	0.2	0.3	trace	0.1	–	–	trace	trace	–
β -Cubebene	1383	0.6	0.3	0.5	0.8	0.5	–	–	trace	–	–
β -Elemene	1385	0.5	0.3	0.5	0.4	0.4	0.2	0.1	0.1	0.1	0.2
Sesquiterpene	1388	–	0.1	0.2	0.1	0.3	–	–	–	–	–
Isolongifolene	1391	0.1	–	–	–	–	–	–	–	–	–
Longifolene	1394	–	–	–	0.1	trace	0.2	0.1	0.2	0.2	0.1
Methyl eugenol	1401	–	–	–	–	–	–	trace	trace	–	–
β -(E)-Caryophyllene	1415	3.0	2.0	2.4	1.9	3.4	0.3	0.2	0.3	0.4	0.6
Sesquiterpene	1420	0.3	0.2	0.3	trace	–	–	trace	trace	–	–
Sesquiterpene	1428	–	trace	–	–	0.2	–	trace	trace	–	–
Aromadendrene	1431	0.7	0.9	1.0	trace	–	–	–	–	–	–
Sesquiterpene	1438	–	0.1	0.1	–	–	–	–	trace	trace	–
α -Humulene	1444	0.5	0.5	0.4	0.2	0.3	0.3	0.2	0.2	0.3	0.3
Geranyl acetone	1448	–	–	–	–	–	trace	trace	trace	–	–
β -Farnesene	1452	–	–	–	–	–	0.1	trace	trace	0.1	0.1
Sesquiterpene	1454	–	0.3	0.3	trace	–	–	–	0.1	–	–

Alloaromadendrene	1457	0.5	–	–	–	–	–	–	–	–	–	–
γ -Muurolene	1469	2.2	1.6	1.9	0.6	1.1	0.1	0.1	0.1	0.1	0.3	0.1
Germacrene D	1472	1.3	0.4	0.7	0.9	trace	0.2	0.1	0.1	trace	0.1	0.1
ar-Curcumene	1479	–	–	–	–	–	trace	trace	–	trace	0.1	–
β -Selinene	1479	1.5	1.2	1.7	0.6	0.7	–	–	–	–	–	–
Sesquiterpene	1487	–	–	–	–	–	0.1	–	0.1	trace	–	–
α -Selinene	1488	3.4	1.9	2.4	0.4	1.1	–	–	–	–	–	–
Valencene	1489	–	–	–	–	–	–	0.1	–	trace	trace	–
2-Tridecanone	1493	–	–	–	–	–	0.1	–	–	–	–	–
α -Muurolene	1493	1.3	1.2	1.6	1.7	1.5	0.1	0.2	0.2	0.3	0.2	0.2
γ -Cadinene	1506	7.5	5.2	6.9	1.2	1.9	0.5	0.6	0.6	1.0	0.6	0.6
δ -Cadinene	1516	8.4	7.1	8.0	0.8	1.6	0.5	0.5	0.5	0.8	0.8	0.8
NN	1525	–	–	–	–	–	–	0.2	0.2	0.3	0.1	–
Cadina-1,4-diene	1526	–	0.4	0.5	0.2	0.5	–	–	–	–	–	–
Sesquiterpenoid C ₁₅ H ₂₆ O	1527	0.3	–	–	0.3	0.2	–	–	–	–	–	–
α -Cadinene	1529	0.5	0.5	0.6	0.3	0.3	–	0.1	0.1	0.2	0.2	–
α -Calacorene	1535	0.2	0.2	0.4	trace	trace	–	trace	0.1	0.1	trace	trace
β -Calacorene	1555	–	–	0.3	trace	0.2	–	–	–	trace	trace	–
(E)-Nerolidol	1559	–	–	–	–	–	0.2	0.1	0.1	0.2	0.2	–
Germacrene D-4-ol	1569	5.4	–	0.4	1.0	1.6	4.2	2.7	2.2	0.9	1.5	–
Spathulenol	1571	0.8	1.8	2.1	0.4	0.6	–	–	–	–	–	–
Caryophyllene oxide	1573	0.5	0.4	0.9	0.2	0.8	0.1	0.1	0.1	0.3	0.3	–
Humulene epoxide II	1602	–	–	0.2	0.4	0.6	–	0.1	0.1	0.1	0.1	–
1,10-di- <i>epi</i> -Cubenol	1608	–	0.1	0.2	–	–	0.2	0.2	0.1	–	–	–
Cubenol	1622	–	0.3	–	–	–	–	trace	–	–	trace	–
τ -Cadinol	1634	–	2.1	1.8	0.2	1.2	0.2	0.2	0.2	0.1	0.3	–
τ -Muurolol	1637	–	–	0.9	0.1	0.2	–	–	–	trace	–	–
α -Muurolol (δ -cadinol)	1639	–	–	0.4	0.1	0.3	–	–	trace	–	trace	–
α -Cadinol	1648	1.7	1.4	1.8	0.3	0.5	0.2	0.2	0.2	0.2	0.2	–
Sesquiterpene alcohol	1666	–	0.2	0.4	–	–	–	–	0.1	0.3	–	–
Cadalene	1668	–	0.2	0.5	0.1	0.6	–	–	–	trace	trace	–
Pentadecanal	1714	–	–	–	–	–	0.1	–	–	–	–	–
11-(Z)-Tetradecenoic acid	1720	0.2	0.1	0.2	1.2	0.4	0.2	0.2	0.2	0.4	0.6	–
Oplopanone	1734	0.5	0.4	0.8	–	–	2.6	2.4	1.9	–	–	–
Tetradecanoic acid	1774	0.4	0.4	–	–	–	0.3	–	–	–	–	–
Sesquiterpenoid C ₁₅ H ₂₄ O	1805	–	–	–	–	–	0.3	0.3	–	trace	–	–
Khusinol acetate	1816	–	–	0.2	–	–	1.0	0.8	0.8	–	–	–
Neophytadiene	1835	0.6	0.4	0.5	trace	0.1	0.5	0.5	0.2	0.2	0.2	–
Hexahydrofarnesyl acetone	1842	0.2	0.2	0.4	0.1	0.1	0.3	0.6	0.4	0.4	trace	–
(E)-2-Hexadecenal	1877	0.3	0.2	0.2	trace	–	0.3	0.2	0.1	–	–	–
11-(Z)-Hexadecenoic acid	1921	0.9	0.5	0.7	7.8	7.0	0.4	0.5	0.6	0.7	0.7	–
Manoyl oxide	1980	0.7	0.4	0.5	0.5	0.8	0.2	0.1	0.1	0.3	0.1	–
13- <i>epi</i> -Manoyl oxide	2002	0.2	0.1	0.1	trace	0.2	–	–	0.2	0.4	0.2	–
NN	2007	–	0.1	0.3	–	–	–	–	–	–	–	–
Diterpenoid	2033	0.5	0.2	0.3	–	–	–	–	–	–	–	–
NN	2041	–	–	–	–	–	–	1.1	–	0.3	0.4	–

Manool	2055	–	0.3	–	–	–	14.0	13.0	12.7	11.9	10.0
NN	2080	0.6	0.2	–	–	–	–	–	–	–	–
<i>epi</i> -Manool	2090	1.4	0.6	–	1.5	1.2	–	–	–	0.3	0.1
NN	2104	21.0	8.9	–	–	–	–	–	–	–	–
Phytol	2111	0.6	0.2	1.1	trace	–	0.7	0.4	0.9	0.4	0.5
Sterol	2146	–	0.1	–	–	–	–	0.2	–	trace	–
NN	2174	–	–	0.2	–	–	–	–	0.4	–	–
Diterpenoid	2177	–	–	–	–	–	–	0.3	–	0.1	–
2-Oxomanoyl oxide?	2190	0.7	0.3	–	–	–	–	–	–	–	–
Sclareol	2226	–	–	–	1.5	1.9	–	–	0.5	0.1	0.1
Diterpenoid	2255	0.6	0.5	2.3	trace	–	2.5	–	–	–	–
Verticiol?	2259	–	–	–	–	–	–	–	2.9	0.6	0.5
Dehydroabietal	2261	–	0.4	–	0.1	0.2	–	–	–	–	–
Diterpenoid	2262	–	–	–	–	–	–	2.4	–	0.4	0.4
Diterpenoid	2286	–	–	–	–	–	0.4	0.4	–	trace	trace
Larixol	2297	–	–	–	–	–	–	–	0.8	trace	trace
Diterpenoid	2298	–	–	–	–	–	0.8	0.8	–	trace	trace
Diterpenoid	2323	–	–	–	–	–	0.7	0.6	–	–	–
Methyldehydroabietate	2332	–	–	0.6	0.3	0.1	–	–	0.1	trace	–
Toruloso?	2356	–	–	–	–	–	9.6	9.2	11.0	9.3	4.0
NN	2403	–	–	–	–	–	–	1.7	–	0.6	0.8
Methyl neoabietate	2425	–	0.6	–	–	trace	0.9	–	–	–	trace
NN	2432	–	1.4	2.0	0.7	1.1	–	–	–	–	–
Diterpenoid	2435	–	–	–	–	–	–	1.2	1.2	0.9	1.4
NN(retinoic acid, methyl ester?)	2494	–	2.3	3.3	0.5	1.1	–	–	–	–	–
NN	2526	–	2.3	2.9	0.4	0.2	–	–	–	–	–
Hexacosane	2600	–	–	–	–	–	–	0.3	0.2	–	–
Tetracosanal	2629	–	–	–	–	–	–	0.4	0.3	0.3	trace
Heptacosane	2700	–	–	–	0.2	0.4	–	–	0.3	0.4	0.1
Lanost-7-en-3-one?	2759	–	–	2.7	3.0	2.9	–	–	–	0.4	0.9
All- <i>trans</i> -squalene?	2778	–	–	1.6	0.1	0.1	–	0.6	0.5	trace	–
Tetracosanol acetate	2821	–	1.5	–	0.1	0.6	–	–	–	–	–
Squalene	2826	–	–	1.1	0.2	0.9	–	0.7	0.5	0.3	0.3
NN	2851	–	0.8	–	–	–	–	0.8	0.8	trace	0.2
Nonacosane	2900	–	–	1.0	0.6	0.8	–	0.6	0.5	0.7	1.0
NN	2944	–	–	0.8	–	–	–	–	0.7	trace	trace
NN	3006	–	–	–	–	–	1.7	1.2	1.1	1.8	1.3
Sterol	3037	–	0.7	–	0.3	0.9	0.5	0.5	0.6	0.9	1.0
Sterol	3052	–	–	1.6	1.6	1.9	–	0.9	1.1	2.2	1.0
γ -Sitosterol	3072	1.4	1.2	–	1.1	1.9	0.7	1.9	0.7	0.9	0.9
Sterol	3086	–	–	1.2	0.9	1.4	0.7	–	1.0	1.5	0.7
NN	3089	–	–	–	–	–	0.6	1.0	–	0.6	trace
1-Octacosanal	3090	–	0.8	–	0.2	trace	–	–	–	–	–
Sitostenone	3114	–	1.9	trace	1.1	0.9	–	3.9	–	0.2	0.1
Nonacosanal	3105	–	–	3.1	1.6	0.9	5.7	–	4.6	0.9	0.3

α -Tocopherol	3130	2.1	1.4	1.9	0.7	1.7	3.0	2.0	1.7	2.8	2.7
Ergosterol	3151	–	–	0.7	1.5	1.8	–	–	–	0.3	0.4
Squalene derivative	3198	–	–	0.7	0.5	0.2	–	0.7	0.7	trace	–
NN	3210	–	1.2	2.0	–	–	–	1.0	1.1	–	–
Squalene oxide?	3242	–	–	0.7	trace	trace	–	–	0.6	trace	–
Ergosta-4,22-dien-3-one	3279	–	–	–	0.5	0.6	–	–	0.8	0.4	0.4
Sarsasagenone	3312	1.7	2.3	2.6	4.8	1.9	6.1	3.4	3.3	2.4	2.5
Stigmastan-7-one?	3356	–	0.7	–	0.9	0.3	1.1	1.1	1.5	1.8	2.2
Sterol	3364	–	1.2	1.2	3.2	4.1	–	–	–	trace	trace
β -Saccharostenone?	3398	–	1.1	1.2	0.9	0.8	–	0.9	1.0	0.8	1.3
Sterol	3406	1.0	–	–	–	–	1.0	–	–	–	–
24-Methylenecycloartan-3-one	3424	–	–	–	–	–	–	1.1	1.5	1.8	2.0
Sterol (sitostenone?)	3441	–	1.6	4.0	25.5	15.8	8.9	9.4	15.0	15.5	8.1
Fucostenone?	3463	–	–	0.6	2.3	1.9	0.8	1.2	0.8	1.0	1.9
Triterpenoid	3473	–	–	0.7	0.1	0.3	0.9	1.1	1.2	0.8	1.1
Sterol	3513	–	–	0.8	0.9	0.4	–	1.4	0.9	1.6	1.9
Triterpenoid	3550	–	–	–	–	–	0.9	1.2	0.8	1.6	1.3
Phytol derivative?	3558	–	–	2.1	3.3	0.7	–	–	0.8	1.2	0.4
Stigmastane-3,6-dione?	3603	–	1.0	1.1	1.0	1.6	1.6	2.7	2.5	2.4	1.0
NN	3615	–	1.4	1.1	0.4	0.6	–	–	–	–	–
Squalene derivative	3620	–	–	–	–	–	–	1.3	–	–	trace
NN	3629	–	0.8	–	–	–	–	1.1	–	–	–
Triterpenoid (betulin?)	3637	–	–	0.5	2.0	0.8	–	–	–	–	–
NN	3640	–	0.8	–	trace	trace	–	2.3	–	–	–
NN	3732	–	1.7	1.4	trace	0.2	–	–	–	–	–
Octadecyl oleate?	3738	–	0.9	0.8	4.6	3.8	–	–	0.8	0.7	1.1

Table 3S. Relative composition (%) of the ether extracts from the pine and spruce litter on various stages of decomposition

Compound (TMS derivatives)	LTPRI	Pine litter					Spruce litter				
		Days of incubation									
		0	77	165	282	490	0	77	165	282	490
Ethylene glycol	994	–	–	–	–	–	0.2	–	–	0.1	0.2
1,2-Propylene glycol	1009	–	–	0.1	trace	trace	–	–	trace	trace	trace
Cadaverine	1061	trace	trace	trace	trace	trace	0.1	0.1	0.1	trace	trace
Lactic acid	1071	0.1	trace	0.1	trace	0.2	0.3	0.2	0.1	0.1	0.2
Hexanoic acid	1077	0.1	trace	trace	trace	–	trace	0.1	trace	trace	0.1
Glycolic acid	1086	0.1	trace	trace	trace	–	trace	trace	trace	0.1	0.1
Pyruvic acid	1097	trace	trace	trace	–	–	trace	trace	trace	–	–
<i>n</i> -Butylamine	1108	0.1	–	trace	–	–	trace	trace	trace	–	–
Levulinic acid	1138	trace	trace	trace	0.1	0.1	0.1	0.1	0.1	–	–
2-Methyl-2-hydroxy butyric acid	1142	–	–	–	–	–	0.1	0.1	–	–	–
3-Hydroxypropanoic acid	1154	trace	trace	trace	–	–	–	trace	trace	–	–

3-Hydroxybutyric acid	1168	trace	trace	trace	–	–	–	–	–	–	–
1-Octanol	1185	–	0.1	trace	0.1	0.2	–	trace	0.1	0.2	0.1
Dithioerythritol?	1206	–	trace	–	–	–	–	trace	0.1	–	–
NN	1227	trace	trace	–	–	–	0.2	0.1	–	–	–
Benzoic acid	1245	0.1	trace	trace	trace	0.1	0.1	trace	trace	0.1	0.1
Octanoic acid	1267	–	trace	trace	0.1	0.2	–	0.1	0.1	trace	0.1
Phosphoric acid	1288	0.3	trace	trace	0.1	0.2	–	0.1	trace	0.1	trace
Glycerol	1292	0.3	trace	trace	0.1	0.2	1.5	0.2	0.1	0.1	0.1
Succinic acid	1320	0.1	trace	0.1	0.1	trace	0.1	–	–	–	–
Methylsuccinic acid	1333	–	trace	trace	–	–	–	–	–	–	–
Fumaric acid	1356	trace	trace	–	–	–	trace	0.1	–	–	–
Nonanoic acid	1363	trace	trace	trace	–	–	trace	trace	trace	–	–
4-Hydroxybenzaldehyde	1369	–	trace	–	–	–	0.1	trace	0.1	0.2	0.2
Hydroquinone	1406	–	trace	trace	–	–	–	trace	trace	trace	–
Glutaric acid	1411	–	trace	–	–	–	–	–	trace	trace	–
3-Methylglutaric acid	1432	–	trace	trace	–	–	–	–	–	–	–
Decanoic acid	1459	–	–	–	–	–	trace	0.1	–	–	–
4-Hydroxyacetophenone	1467	–	–	–	–	–	0.6	0.6	–	0.3	trace
NN	1468	0.3	0.2	–	–	–	–	–	–	–	–
NN	1470	–	–	–	–	–	–	0.1	0.1	trace	–
NN	1511	0.3	0.1	–	–	–	–	0.1	–	–	–
Vanillin	1533	0.1	0.1	0.1	0.2	0.4	0.2	0.1	0.1	0.2	0.2
Cinnamic acid	1539	trace	–	trace	–	trace	–	–	–	–	–
NN	1551	0.2	0.2	–	0.1	–	–	0.4	–	–	–
1-Dodecanol	1568	–	–	–	–	–	–	–	0.1	–	–
3-Hydroxybenzoic acid	1570	–	–	–	–	–	0.2	0.2	–	trace	–
4-Hydroxybenzoic acid	1631	0.1	0.1	0.1	0.2	0.4	0.2	0.2	0.1	0.3	0.4
Vanillyl alcohol	1649	–	–	–	–	–	0.1	0.1	–	0.3	0.5
Dodecanoic acid	1656	0.3	0.2	0.2	0.3	trace	0.2	0.3	0.4	trace	trace
NN	1671	0.3	–	–	–	–	0.5	–	–	–	–
1-Tridecanol	1675	0.1	–	0.1	–	–	–	–	–	–	–
NN	1702	0.3	0.2	–	–	–	–	0.6	0.5	–	–
Octanedioic acid	1708	0.1	0.1	trace	0.1	trace	–	–	0.1	–	–
NN	1715	–	–	–	–	–	0.2	0.2	–	trace	–
11-(Z)-Tetradecenoic acid	1723	–	0.1	0.1	0.4	trace	–	0.3	0.6	trace	–
Arabinitol	1760	0.3	0.1	–	0.1	–	0.3	0.1	–	trace	0.1
4-Hydroxyhydrocinnamic acid	1768	–	0.1	–	0.2	0.5	–	0.2	–	0.3	0.3
Vanillic acid	1776	0.2	0.1	0.1	0.5	0.7	0.2	0.2	0.2	0.5	0.2
NN	1778	–	0.1	0.1	–	–	–	–	–	–	–
Azelaic acid	1807	0.2	0.1	0.1	0.1	trace	0.1	0.3	0.3	trace	trace
3-Vanilpropanol	1831	–	–	–	0.3	0.4	0.3	0.2	–	0.3	0.4
Methylphosphonic acid?	1836	0.3	0.2	0.2	–	–	1.2	0.8	0.8	–	–
Shikimic acid	1848	–	trace	trace	13.5	6.8	–	–	–	–	–
Tetradecanoic acid	1855	1.0	0.5	0.5	1.2	0.7	1.5	1.4	1.7	1.4	1.1
<i>myo</i> -Inositol, penta-TMS	1870	0.7	0.1	–	–	–	0.6	0.2	–	–	–

11-(Z)-Hexadecenoic acid	1925	0.5	–	0.3	0.5	trace	–	0.6	1.9	0.9	0.7
NN	1928	–	–	–	–	–	0.3	0.3	–	–	–
NN	1931	–	–	0.1	–	–	–	–	0.9	–	–
NN	1934	–	0.1	–	–	–	0.6	0.6	–	–	–
<i>p</i> -Coumaric acid	1947	0.4	0.2	0.2	0.3	0.3	0.9	0.6	0.6	0.2	trace
Pentadecanoic acid	1953	–	0.1	0.1	0.1	–	0.3	0.3	0.3	trace	trace
1-Hexadecanol	1967	–	–	0.1	0.3	trace	–	0.2	0.2	0.3	0.1
Undecanedioic acid	2017	0.9	0.4	0.6	1.6	trace	0.5	0.5	0.8	0.2	–
2,3-Dimethyl-3-hydroxyglutaric acid	2020	2.3	0.9	0.5	–	–	–	–	–	–	–
Palmitelaidic acid	2024	–	–	–	–	–	0.4	0.3	–	trace	–
Hexadecanoic acid	2050	1.6	1.2	1.0	0.7	1.9	3.2	2.1	1.8	2.2	2.0
Ferulic acid	2103	0.5	–	0.1	1.2	1.4	0.9	0.7	–	0.9	0.9
<i>i</i> -Heptadecanoic acid	2122	0.2	–	–	–	–	0.8	0.4	0.3	–	–
NN	2127	0.3	0.2	–	–	–	–	0.3	0.4	–	–
NN	2136	0.6	0.3	–	–	–	–	–	–	–	–
Heptadecanoic acid	2151	–	0.2	0.2	0.4	trace	0.2	0.2	0.2	–	–
Caffeic acid	2155	0.3	–	–	1.1	0.8	–	–	–	trace	trace
1-Octadecanol	2161	–	0.2	0.2	0.4	0.2	–	–	0.3	0.2	0.3
Phytol	2180	1.4	0.8	1.4	trace	–	0.9	–	0.5	trace	trace
NN	2189	0.4	0.3	–	–	–	–	–	–	–	–
Linolenic acid	2194	–	–	–	–	–	0.3	0.2	–	0.3	0.1
NN	2210	0.6	–	0.5	1.2	0.8	3.3	–	4.0	1.3	1.6
Linoleic acid	2217	–	0.6	0.3	0.4	0.8	3.4	1.5	0.2	0.8	1.2
Oleic acid	2224	0.7	0.8	0.7	0.5	1.0	5.7	2.6	1.5	2.1	3.2
NN	2224	0.4	0.3	0.4	0.3	–	–	–	–	–	–
8-Octadecenoic acid	2227	–	–	–	–	–	0.4	–	0.3	trace	trace
Octadecanoic acid	2250	0.6	0.4	0.5	0.6	1.7	0.4	0.4	0.5	0.7	0.7
Resin acid	2258	–	0.3	0.5	0.8	0.4	–	–	–	–	–
Resin acid	2293	2.1	1.4	1.4	1.5	0.7	–	–	–	–	–
Tetradecanedioic acid	2296	–	–	–	–	–	0.2	–	–	–	–
Pimaric acid	2310	0.5	0.4	0.4	0.7	1.1	0.3	–	0.4	0.6	0.3
Isopimaric acid	2327	0.4	0.3	0.4	1.4	1.9	0.1	–	0.4	0.7	0.7
NN	2337	–	–	–	–	–	0.6	0.5	0.7	0.3	trace
Palustric acid	2347	2.9	1.9	1.6	2.1	1.9	–	–	–	–	–
Isopimara-8,15-dienoic acid	2372	4.9	3.2	2.8	7.2	5.4	0.2	0.3	0.3	trace	trace
NN	2376	–	–	–	–	–	–	0.3	0.5	0.2	0.1
Dehydroabietic acid	2388	3.0	2.7	3.4	10.0	12.9	7.5	4.4	7.6	8.7	9.2
Labda-8(20),13-dien-15-oic acid	2400	–	–	–	–	–	5.8	4.0	4.9	1.9	3.2
Abietic acid	2403	0.6	0.4	0.7	1.3	2.3	0.6	0.6	0.7	1.6	1.9
NN	2408	2.3	1.4	1.8	3.6	1.2	5.0	3.5	6.8	5.3	2.2
Resin acid	2439	–	–	–	–	–	–	0.8	1.0	1.2	2.1
Eicosanoic acid	2448	–	–	1.2	0.5	trace	0.2	0.4	0.5	trace	0.1
Resin acid	2462	4.5	4.4	3.6	6.2	5.4	–	–	–	–	–
Diterpenoid	2480	–	2.6	2.0	1.3	0.8	–	–	0.8	0.6	0.8

Neobietic acid	2502	–	1.3	1.6	1.7	2.3	–	–	–	–	–
Diterpenoid	2530	2.6	2.7	2.9	1.4	0.7	–	–	–	–	–
Diterpenoid	2533	–	–	–	–	–	–	1.3	1.2	0.8	0.9
Diterpenoid	2539	–	1.3	–	6.1	5.4	–	1.1	1.6	0.8	0.9
Pinocembrin	2549	2.5	2.2	–	–	–	–	2.7	–	–	–
NN	2563	–	–	–	–	–	–	1.5	1.8	2.1	0.9
Diterpenoid	2569	10.8	8.9	–	11.4	6.8	–	–	–	–	–
7-Oxodehydroabietic acid?	2591	–	–	–	0.1	0.4	2.8	–	–	2.2	1.9
15-Hydroxydehydroabietic acid	2594	–	–	–	0.5	0.9	–	3.4	4.1	4.5	4.1
NN	2633	–	–	–	–	–	–	1.9	2.2	0.9	trace
Docosanoic acid	2646	–	–	–	–	–	–	1.7	–	0.3	0.1
Diterpenoid	2731	3.6	3.1	3.1	10.6	7.4	–	–	–	–	–
NN	2747	–	2.8	–	–	–	–	1.3	–	–	–
NN	2769	3.3	3.2	–	–	–	–	–	–	–	–
Diterpenoid	2795	–	2.8	2.7	0.2	0.8	–	1.0	1.1	0.9	1.3
NN	2830	–	–	–	–	–	–	3.0	2.5	2.9	2.9
Tetracosanoic acid	2846	–	–	0.9	0.6	0.2	–	0.6	0.8	0.7	trace
NN	2854	–	–	–	–	–	–	3.0	3.2	2.5	trace
α -Hydroxytetracosanoic acid, methyl ester	2998	–	–	0.6	trace	trace	–	1.0	1.2	0.8	0.9
Catechin	3023	1.7	1.3	1.5	1.8	1.2	–	–	–	–	–
NN	3052	2.6	–	1.5	–	–	–	–	–	–	–
β -Tocopherol	3055	–	1.7	0.9	–	–	–	0.7	0.7	–	–
NN	3078	3.7	–	2.1	–	–	2.9	–	4.9	1.7	trace
NN	3081	–	2.1	–	–	–	–	5.0	–	–	–
α -Tocopherol	3153	8.3	–	4.6	1.2	0.8	6.3	–	2.9	1.9	0.8
NN	3153	–	5.3	–	–	–	–	2.6	–	–	–
Triterpenoid	3172	3.0	2.2	2.1	0.2	1.6	–	–	–	–	–
Matairesinol	3182	9.2	6.5	6.6	3.2	7.1	5.0	2.5	3.0	4.5	5.1
Triterpenoid	3234	–	1.6	2.1	0.9	1.3	5.6	2.0	1.9	0.9	2.1
NN	3261	1.6	–	1.0	–	–	–	1.1	1.3	0.8	trace
β -Sitosterol	3349	2.7	1.6	1.9	4.5	3.0	7.1	3.5	4.3	4.3	5.1
NN	3353	1.6	1.1	1.1	trace	–	–	–	–	–	–
Sterol (β -saccharostenone?)	3400	2.1	1.3	1.3	2.8	0.9	–	1.5	1.5	0.6	0.8
Sterol (sitostenone?)	3442	–	–	1.4	0.8	0.9	2.7	2.3	4.5	2.1	2.6
NN	3475	1.0	–	–	–	–	–	–	1.1	–	–
NN	3489	–	–	–	–	–	–	1.1	1.3	0.8	0.9
Glucoside	3549	–	1.1	1.3	0.8	1.2	–	–	–	–	–
NN	3578	–	1.2	–	–	–	–	1.6	–	–	–

Table 4S. Relative composition (%) of the water extracts from the pine and spruce litter on various stages of decomposition

Compound (TMS derivative)	LTPRI	Days of incubation	
		Pine litter	Spruce litter

		0	77	165	282	490	0	77	165	282	490
Carbodiimide	977	–	0.1	0.1	trace	–	–	0.2	0.2	trace	trace
Ethylene glycol	996	–	0.1	0.1	0.2	–	0.1	0.1	0.1	trace	–
1,2-Propylene glycol	1011	0.1	0.1	0.1	–	–	0.1	0.1	0.1	–	–
2,3-Butanediol	1047	0.1	0.4	0.4	0.2	–	0.1	0.2	0.3	trace	–
Cadaverine	1061	trace	0.1	0.1	trace	–	trace	0.1	0.1	2.9	trace
Lactic acid	1071	0.1	0.2	0.2	0.3	0.4	0.1	0.4	0.3	2.1	1.1
2-Hydroxyisobutyric acid	1072	trace	–	–	–	–	–	–	–	trace	–
Glycolic acid	1086	0.1	0.2	0.1	0.3	0.4	0.1	0.1	0.2	1.1	2.6
Valine, mono-TMS	1092	–	–	–	0.2	–	–	trace	–	trace	–
Pyruvic acid	1098	0.1	0.1	0.1	0.1	–	0.1	0.1	0.1	0.1	–
<i>n</i> -Butylamine	1108	–	trace	trace	–	–	–	–	trace	–	–
Alanine	1116	trace	trace	0.1	0.1	trace	trace	0.1	0.2	0.2	–
Glycine	1128	–	–	–	–	–	–	–	trace	4.0	–
Laevulic acid ?	1139	–	–	0.1	–	–	trace	0.1	0.1	–	–
Butanoic acid, 2-methyl-2-hydroxy-	1143	trace	0.1	–	–	–	0.1	0.1	–	–	–
Oxalic acid	1146	trace	0.2	0.1	trace	0.2	trace	0.1	0.1	0.2	trace
3-Hydroxypropanoic acid	1154	trace	0.1	0.1	0.1	–	trace	0.1	0.1	0.1	–
Leucine, mono-TMS	1155	–	–	–	0.2	–	–	–	–	–	–
3-Hydroxybutyric acid	1161	trace	trace	trace	0.1	–	trace	trace	trace	0.1	–
3-Hydroxyisobutyric acid	1171	–	0.1	0.1	–	–	–	trace	trace	–	–
Isoleucine, mono-TMS	1174	–	–	–	0.1	–	–	–	–	trace	–
Octanol	1183	–	–	0.1	–	trace	–	–	trace	trace	–
Dithioerythritol?	1206	–	0.1	0.2	trace	–	–	0.1	0.1	trace	–
Malonic acid	1215	trace	trace	0.1	0.1	–	0.1	0.1	0.2	0.2	–
Butanoic acid, 3-methyl-3-hydroxy-	1219	trace	–	–	trace	–	trace	–	–	–	–
Valine, di-TMS	1225	trace	–	–	0.1	–	trace	0.1	0.1	trace	–
Benzoic acid	1245	0.1	0.1	0.1	0.1	trace	trace	trace	trace	0.5	0.1
Urea	1255	–	–	trace	0.1	–	–	trace	–	trace	trace
Serine, di-TMS	1265	–	0.1	–	0.4	trace	–	0.1	0.1	0.3	–
Leucine, di-TMS	1283	trace	–	0.1	0.1	–	trace	0.1	0.1	0.1	–
Phosphoric acid	1288	0.2	0.3	0.3	1.6	1.8	2.3	2.1	3.9	4.0	3.9
Glycerol	1292	3.1	0.9	0.9	4.3	3.7	3.5	1.0	0.8	3.9	4.2
Benzeneacetic acid	1296	trace	trace	–	–	–	–	–	–	–	–
Threonine, di-TMS	1299	–	–	–	0.3	–	–	–	–	–	–
Proline	1301	trace	–	trace	0.2	0.1	–	trace	trace	trace	–
Isoleucine, di-TMS	1303	trace	–	trace	0.2	–	trace	0.1	0.1	–	–
Maleic acid	1313	0.2	0.5	0.1	trace	–	–	0.4	0.3	trace	–
Succinic acid	1322	0.1	0.2	0.1	0.2	0.3	0.4	0.1	0.2	0.1	0.2
Methylsuccinic acid	1335	–	0.1	trace	–	–	trace	trace	trace	–	–
Glyceric acid	1345	0.1	0.1	0.1	0.2	0.3	0.2	0.1	0.1	0.4	0.6
Fumaric acid	1356	0.3	0.7	0.3	0.1	–	1.2	1.1	0.9	0.1	trace
4-Hydroxybenzaldehyde	1369	–	0.1	trace	–	–	–	–	–	0.3	0.5

Serine, tri-TMS	1370	–	–	trace	0.1	trace	–	0.1	0.1	trace	–
2(3H)-Furanone, dihydro-3,4-	1382	trace	0.1	0.1	–	–	–	trace	0.1	–	–
NN	1387	0.1	–	–	–	–	–	0.1	–	–	–
NN	1393	0.1	–	–	–	–	–	0.1	–	–	–
Threonine, tri-TMS	1404	–	–	–	trace	–	–	0.1	0.1	trace	–
Hydroquinone	1405	–	0.1	0.1	–	–	–	–	–	–	0.3
NN	1407	0.3	–	–	–	–	–	–	0.1	–	–
Methionine	1420	–	–	–	0.3	–	–	–	–	–	–
NN	1437	0.4	0.2	–	–	–	–	0.1	–	–	–
α -Pinene, 3-hydroxy-?	1453	0.5	0.4	0.2	–	–	–	0.1	0.1	0.1	–
4-Hydroxyacetophenone	1466	–	–	trace	–	–	–	0.6	0.5	0.2	0.4
NN	1478	–	–	–	–	–	–	0.1	0.1	0.1	trace
Homoserine, tri-TMS	1486	–	–	–	0.2	–	–	–	–	–	–
Malic acid	1509	3.4	2.5	1.5	0.4	0.6	5.2	3.3	2.9	0.6	1.2
Salicylic acid	1514	–	0.2	–	–	–	–	–	–	–	–
Pyroglutamic acid	1528	0.2	0.3	0.2	0.5	0.5	0.7	0.4	0.6	0.3	trace
Vaniline	1532	–	0.1	0.1	trace	trace	–	–	0.1	0.3	0.1
Threitol	1537	–	0.1	0.1	trace	trace	0.5	0.2	0.1	trace	–
Glycine, tri-TMS	1538	–	–	–	2.1	trace	–	–	–	–	–
NN	1557	0.4	0.1	–	–	–	0.2	0.2	–	–	–
Erythronic acid	1572	0.2	–	–	0.1	–	0.2	0.1	–	–	–
NN	1577	0.3	–	–	–	–	0.4	0.3	–	–	–
Threonic acid	1590	0.4	0.1	0.1	0.2	–	–	0.2	0.2	0.1	0.3
Asparagine	1600	–	–	–	0.2	trace	–	–	–	–	–
NN	1612	–	0.1	–	–	–	0.3	0.2	–	–	–
3-Hydroxybenzoic acid	1617	–	0.1	0.1	–	–	–	–	0.1	–	–
4-Hydroxybenzoic acid	1630	0.9	0.4	0.3	0.3	0.6	0.9	–	0.5	0.5	0.5
Phenylalanine, di-TMS	1633	–	–	–	–	0.1	–	0.1	–	–	–
Glutamic acid	1639	–	–	0.3	0.4	trace	–	0.5	0.9	0.1	–
α -Arabinofuranose	1644	0.6	0.3	–	trace	–	–	0.2	0.2	trace	trace
β -Arabinopyranose	1647	–	0.6	–	trace	–	0.3	0.4	0.4	trace	–
Arabinonic acid, γ -lactone	1652	–	0.1	–	–	–	0.1	0.1	–	–	–
Dodecanoic acid	1653	–	–	0.1	trace	trace	–	–	0.1	trace	–
Rhamnose	1661	0.7	0.5	0.4	–	–	0.1	0.2	0.2	–	–
α -Ribofuranose	1665	–	–	0.2	–	–	–	0.1	0.1	0.1	–
NN	1670	–	–	–	–	–	0.3	0.3	–	–	trace
Xylonic acid, γ -lactone	1670	0.2	0.1	0.1	–	–	–	–	–	–	–
β -Ribopyranose	1679	0.8	1.0	0.4	0.2	0.2	0.2	0.5	0.5	0.2	0.3
Carbohydrate (pentose)	1681	–	–	0.3	0.2	0.1	–	0.2	0.2	trace	–
α -Ribopyranose	1684	–	0.1	0.2	0.1	–	–	–	0.3	0.7	0.6
Carbohydrate	1691	–	0.1	0.1	–	–	–	–	–	0.3	0.1
Carbohydrate	1707	0.2	0.3	0.1	–	–	–	0.2	0.3	–	–
Suberic acid	1709	–	–	–	0.1	0.3	–	–	–	–	0.2
NN	1715	–	0.2	–	–	–	–	0.3	–	–	–

Carbohydrate	1723	0.5	0.7	0.4	–	–	0.1	0.4	0.4	–	–
Carbohydrate	1730	–	0.8	–	–	–	0.1	–	0.2	–	–
Xylitol	1734	0.4	–	–	–	–	0.3	0.2	–	–	–
D-Xylose	1739	0.4	0.2	0.1	–	–	–	0.2	0.2	–	–
Carbohydrate acid	1748	–	–	–	0.2	0.4	0.2	0.3	6.7	2.0	0.9
NN	1750	–	0.3	0.3	–	–	–	–	–	–	–
Arabinitol	1759	–	–	4.5	3.1	0.1	–	–	0.5	0.2	–
Ribitol	1762	10.8	2.1	0.2	0.1	–	16.1	6.1	–	–	–
Vanillic acid	1776	0.5	0.6	0.3	0.3	0.6	0.4	0.3	–	0.5	0.4
Carbohydrate acid	1779	0.4	–	–	–	–	0.3	0.2	–	–	–
Gentisic acid	1793	–	–	–	0.2	trace	–	–	–	–	–
β -Xylopyranose	1795	–	0.2	–	–	–	–	–	0.4	–	–
Carbohydrate acid	1796	–	–	0.2	0.4	trace	–	0.6	–	–	0.2
Glycerophosphoric acid	1800	–	–	–	–	–	0.6	0.5	0.6	trace	–
Carbohydrate	1802	1.3	0.8	0.7	–	–	0.6	–	–	–	–
NN	1803	–	–	–	–	–	–	0.5	0.6	–	–
Arabinoic acid	1807	–	0.2	–	–	–	0.4	0.3	–	–	–
Azelaic acid	1810	–	0.3	0.3	0.3	0.1	–	–	0.3	0.2	trace
Ribonic acid	1823	0.3	–	–	0.1	–	0.6	0.2	–	–	–
3-Vanilpropanol	1831	0.5	0.4	0.2	trace	–	0.4	0.3	0.4	–	–
Protocatechuic acid	1837	–	1.2	1.0	0.4	–	0.7	0.9	1.3	0.4	0.1
Carbohydrate	1841	1.8	–	–	–	–	–	–	–	–	–
α -D-Fructofuranose	1844	–	–	0.8	–	–	–	–	–	–	–
Shikimic acid	1845	–	–	–	–	–	–	–	0.7	0.2	–
α -D-Mannopyranose	1849	0.5	1.5	–	trace	–	6.0	4.1	–	–	–
β -D-Fructofuranose	1849	1.5	–	–	–	–	–	–	–	–	–
Tetradecanoic acid	1852	–	–	–	–	–	–	–	–	2.2	0.8
Citric acid	1855	1.4	0.5	0.9	1.5	–	1.6	1.1	1.7	–	–
<i>myo</i> -Inositol, penta-TMS	1871	12.3	2.5	0.5	0.3	–	7.1	5.0	0.7	0.1	0.4
Adenine	1875	–	0.2	–	–	–	–	0.3	0.7	trace	–
NN	1882	–	–	–	–	–	0.9	0.7	0.8	trace	0.6
β -D-Glucofuranose	1891	1.2	0.8	0.8	1.0	0.1	0.8	1.0	0.9	trace	trace
NN	1896	–	0.4	–	–	–	–	0.7	–	0.2	0.9
Quinic acid	1901	1.2	0.8	0.7	0.8	0.4	3.2	2.1	0.8	–	–
Carbohydrate acid	1917	–	0.2	–	0.9	0.6	–	0.3	–	0.6	0.3
Gluconic acid, δ -lactone	1919	–	–	–	–	–	–	–	0.3	0.4	trace
Galactonic acid, γ -lactone	1922	–	0.2	0.4	trace	trace	–	0.4	–	–	–
NN	1929	–	0.3	–	–	0.1	–	0.5	–	–	–
α -D-Glucopyranose	1933	6.3	1.1	4.1	3.9	10.8	4.9	6.0	3.7	1.9	14.3
Glucaric acid, γ -lactone	1944	–	0.6	0.6	0.3	0.4	0.6	0.9	0.7	1.1	1.0
<i>p</i> -Coumaric acid	1947	–	0.6	0.8	0.8	1.1	0.5	0.9	0.9	0.4	0.2
NN	1961	–	1.1	1.0	1.2	1.3	–	0.8	–	–	–
L-Ascorbic acid	1979	–	–	0.4	–	–	–	–	–	–	–
Glucitol	1981	6.6	0.3	9.9	3.6	4.6	4.4	0.1	17.5	8.5	2.7

Gallic acid	1986	–	0.6	0.4	–	–	–	–	0.3	–	–	
Saccharic acid	1992	–	–	–	–	–	–	0.5	0.6	–	trace	0.2
Inositol. isomere	1996	1.7	0.5	0.4	–	–	–	–	–	–	–	–
Undecandioic acid	2017	0.4	0.3	0.6	2.1	0.3	–	–	0.3	0.5	0.2	–
β -D-Glucopyranose	2034	7.0	2.1	4.4	11.0	13.1	7.3	5.6	4.4	2.2	8.7	–
D-Gluconic acid	2046	0.5	0.2	0.3	0.7	2.2	0.7	0.8	0.3	0.2	1.9	–
Vanillylmandelic acid derivative	2051	0.9	0.8	1.2	0.5	–	1.0	0.9	–	–	–	–
Hexadecanoic acid	2052	–	–	–	0.1	0.4	–	–	–	–	5.2	2.1
Glucuronic acid-1	2066	–	0.1	–	–	–	–	0.3	–	–	trace	0.3
Glucaric acid	2072	–	–	–	–	–	–	0.3	–	–	–	–
NN	2078	–	–	–	–	–	1.4	0.3	0.5	–	trace	–
Glucuronic acid-2	2088	–	0.2	–	–	–	–	0.4	–	–	trace	0.4
Dodecanedioic acid	2099	–	–	–	0.3	trace	–	–	–	–	–	–
Ferulic acid	2103	–	0.3	–	0.3	–	–	0.2	0.3	0.4	–	–
Carbohydrate	2104	0.6	–	–	–	–	0.6	–	–	–	–	–
<i>myo</i> -Inositol, hexa-TMS	2127	1.4	0.1	0.4	trace	0.3	0.5	0.3	0.4	–	trace	–
<i>n</i> -Acetyl-D-glucosamine-1	2139	–	–	–	0.3	trace	–	–	–	–	–	–
<i>n</i> -Acetyl-D-glucosamine-2	2146	–	–	–	0.6	trace	–	–	–	–	–	–
Carbohydrate	2149	0.5	–	–	0.5	0.2	0.4	–	–	–	–	–
Uridine	2470	–	–	–	1.5	–	–	–	–	–	–	–
Thymol glucopyranoside	2182	–	0.3	0.4	0.5	–	–	–	–	–	–	–
NN	2189	1.6	1.3	1.2	–	3.5	–	–	–	–	–	–
NN	2190	–	–	–	–	–	4.5	0.6	–	–	–	–
Oleic acid	2222	–	–	0.5	0.3	0.2	–	0.1	0.4	1.2	0.4	–
NN	2227	–	0.4	0.4	–	0.7	–	–	–	–	–	–
Octadecanoic acid	2249	–	0.1	0.2	0.2	trace	–	–	0.2	2.2	1.0	–
Carbohydrate alcohol	2273	0.5	–	–	–	–	0.3	0.1	0.1	–	–	–
Disaccharide/glucoside	2396	–	–	–	–	–	0.3	0.2	0.4	–	–	–
NN	2404	–	–	0.6	–	0.9	–	–	0.4	–	–	–
Carbohydrate	2414	–	0.1	–	–	–	–	0.2	–	–	–	–
Carbohydrate	2424	–	0.2	–	–	–	0.4	0.2	0.3	–	–	–
NN	2442	–	0.8	1.2	–	0.3	–	–	–	–	–	–
NN	2452	0.5	0.7	0.9	–	0.1	–	–	–	–	–	–
Uridine, di-TMS	2465	–	–	0.7	–	–	–	–	–	–	–	–
Carbohydrate	2470	–	–	–	–	–	0.5	0.3	0.5	–	–	–
NN	2560	–	0.4	0.6	–	–	–	–	–	–	–	–
Disaccharide	2584	–	0.1	0.3	–	–	0.4	0.2	–	–	–	–
NN	2592	–	0.5	0.9	–	–	–	–	–	–	–	–
Disaccharide	2613	–	–	–	–	–	–	0.2	–	–	–	–
NN	2619	–	0.3	0.5	–	–	–	0.2	–	–	–	–
NN	2634	–	0.5	0.6	–	0.4	–	–	–	–	–	–
Adenosine	2672	–	–	–	–	–	–	0.3	0.3	–	trace	–
α -Lactulose	2683	–	–	0.7	–	–	–	0.2	–	–	–	–
β -Lactulose	2686	–	–	–	–	–	–	0.2	0.7	–	–	–

Sucrose	2714	–	–	–	–	–	–	–	–	–	0.8	0.1
NN	2727	0.6	0.6	1.9	–	–	–	–	–	–	–	–
α -Cellobiose	2768	–	–	–	–	–	0.4	0.3	–	–	–	–
Disaccharide	2773	0.6	0.6	1.0	0.9	0.8	–	0.2	0.4	–	–	–
NN	2777	–	–	0.7	–	–	–	–	0.5	–	–	–
Maltose	2804	0.8	0.5	2.5	0.6	0.2	–	0.4	1.5	0.5	0.2	–
Trehalose (mycose)	2816	2.7	3.3	8.9	19.0	19.7	3.3	5.5	15.1	28.6	30.0	–
Leucrose	2864	–	0.6	1.1	0.6	trace	–	–	0.6	–	–	–
Disaccharide	2897	–	–	–	–	–	–	0.6	0.6	–	–	–
Catechin, (+)-2.3- <i>trans</i> -	2939	–	0.6	–	trace	trace	–	0.5	–	trace	–	–
β -Melibiose?	2960	–	–	–	–	–	0.6	0.4	–	–	–	–
NN	2970	–	0.7	–	–	–	1.6	–	–	–	–	–
Gentibiose	2991	–	1.2	1.1	trace	–	2.1	0.6	–	–	–	–
NN	3022	1.9	–	1.1	–	–	–	–	0.6	–	–	–
Taxifolin	3023	1.2	1.3	0.9	0.2	–	–	–	–	–	–	–
Disaccharide	3043	–	–	–	–	–	0.8	0.5	–	–	–	–
NN	3054	–	1.2	0.9	–	–	–	0.5	0.6	–	–	–
NN	3077	2.4	4.0	2.3	–	–	–	0.9	1.1	trace	–	–
NN	3150	–	1.3	1.7	–	–	–	–	0.5	–	–	–
Matairesinol	3180	–	0.7	0.9	0.5	trace	–	0.2	0.4	trace	–	–
NN	3189	–	0.5	–	–	–	–	0.3	0.4	–	–	–
NN	3251	–	–	–	–	–	–	0.3	0.5	–	–	–
α -Tocopherol	3353	–	0.6	0.7	–	–	–	–	–	–	–	–
Trisaccharide	3361	–	–	–	–	–	–	0.5	0.4	0.1	–	–
Trisaccharide	3422	–	0.6	–	–	trace	–	–	0.8	–	–	–
Trisaccharide (cellotriase?)	3728	–	0.9	–	–	–	–	0.7	0.1	0.1	–	–
Tetrasaccharide	3934	1.4	2.0	–	–	trace	–	1.0	–	–	–	–
Tetrasaccharide	4324	–	15.5	14.4	0.9	trace	–	7.2	–	0.8	0.1	–