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Hyphenation of a EC ⁄ OC thermal-optical carbon analyzer to photo ionization time-of-flight mass spectrometry: a new off-line aerosol mass spectrometric approach for characterization of primary and secondary particulate matter

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Correspondence to: R. Zimmermann (ralf.zimmermann@uni-rostock.de)

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Supplemental material

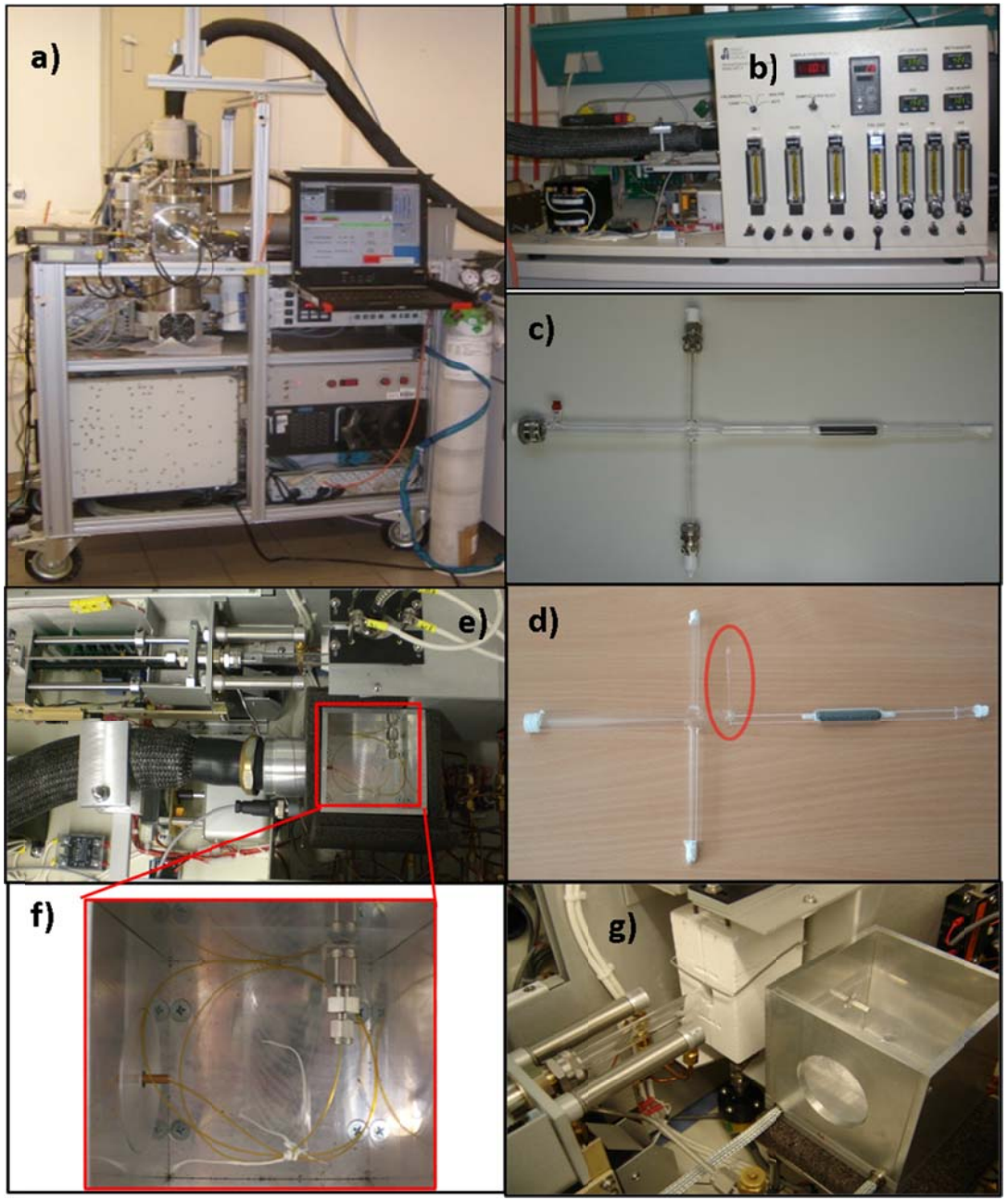

Figure S 1: pictures of the coupling and assembling (a- PI-TOF-MS, b – carbon analyzer, c - the original quartz tubing system, d – the modified quartz tubing system, e – the whole connecting unit with aluminum box and heating hose, f - zoom into the aluminum box with quartz tube, Swagelok connector and transfer capillary, g - quartz tube reaching into the aluminum box with heating cartridges)

Table S1: experiment conditions of the chamber experiments

sample	Precursor concentration [ppm]	Ozone concentration [ppm]	Temperature [°C]	chamber volume [m³]	Experiment duration [min]	PM on filter [µg/cm²]
Filter Samples Hong Kong						
α-pinene	500	0.069	23	18.26	135	51.8
β-pinene	200	0.157	23	18.26	135	15.2
Isoprene	100	0.17	23	18.26	240	12.9
Filter samples Karlsruhe						
α-pinene I	2.2	25	22	3.7	55	n.a.
α-pinene II	2.215	6	24	3.7	30	n.a.

Table S2: Carbon contents [µg/filter] of all samples corrected with laser transmittance (with regular split)

sample	TC [µg/filter]	OC [µg/filter]	EC [µg/filter]	OC/EC	OC/TC [%]	EC/TC [%]
diesel	24.18	12.47	11.71	1.07	52	48
gasoline	33.54	8.06	25.49	0.32	24	76
wood combustion I	130.56	122.63	7.92	15.48	94	6
wood combustion II	67.75	51.25	16.50	3.11	76	24
Ispra winter	25.18	18.61	6.57	2.83	74	26
Ispra summer	4.25	3.62	0.63	5.75	85	15
β-pinene HK	3.27	3.27	0.00	∞	100	0
α-pinene HK	12.66	12.65	0.01	1264.50	100	0
α-pinene KR	28.01	27.98	0.03	932.67	100	0
isoprene HK	0.56	0.55	0.01	55.00	98	2

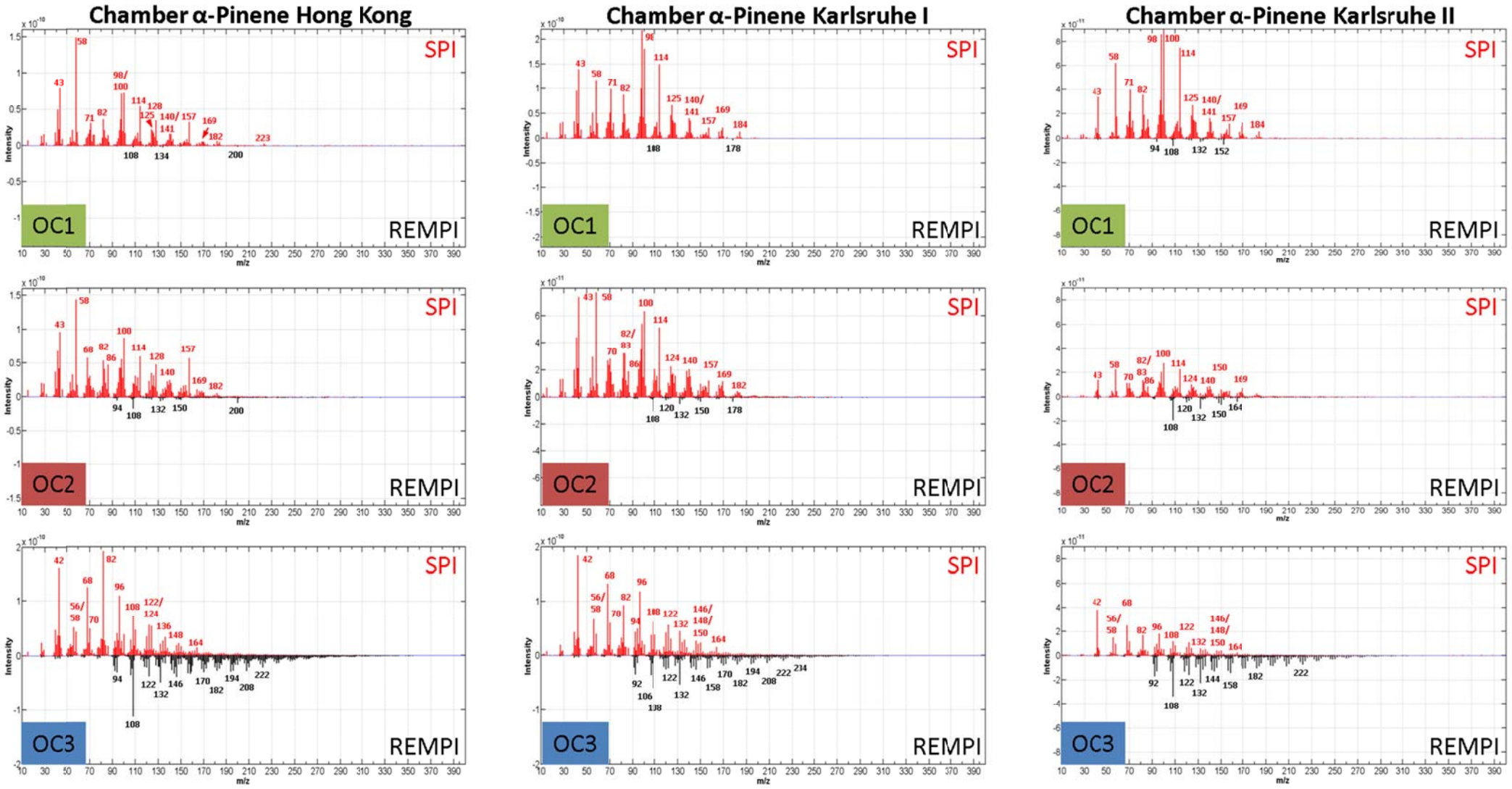

Figure S 2: Comparison of the mass spectra obtained by the measurement of the filter samples from the three different chamber experiments using α-pinene as a precursor.

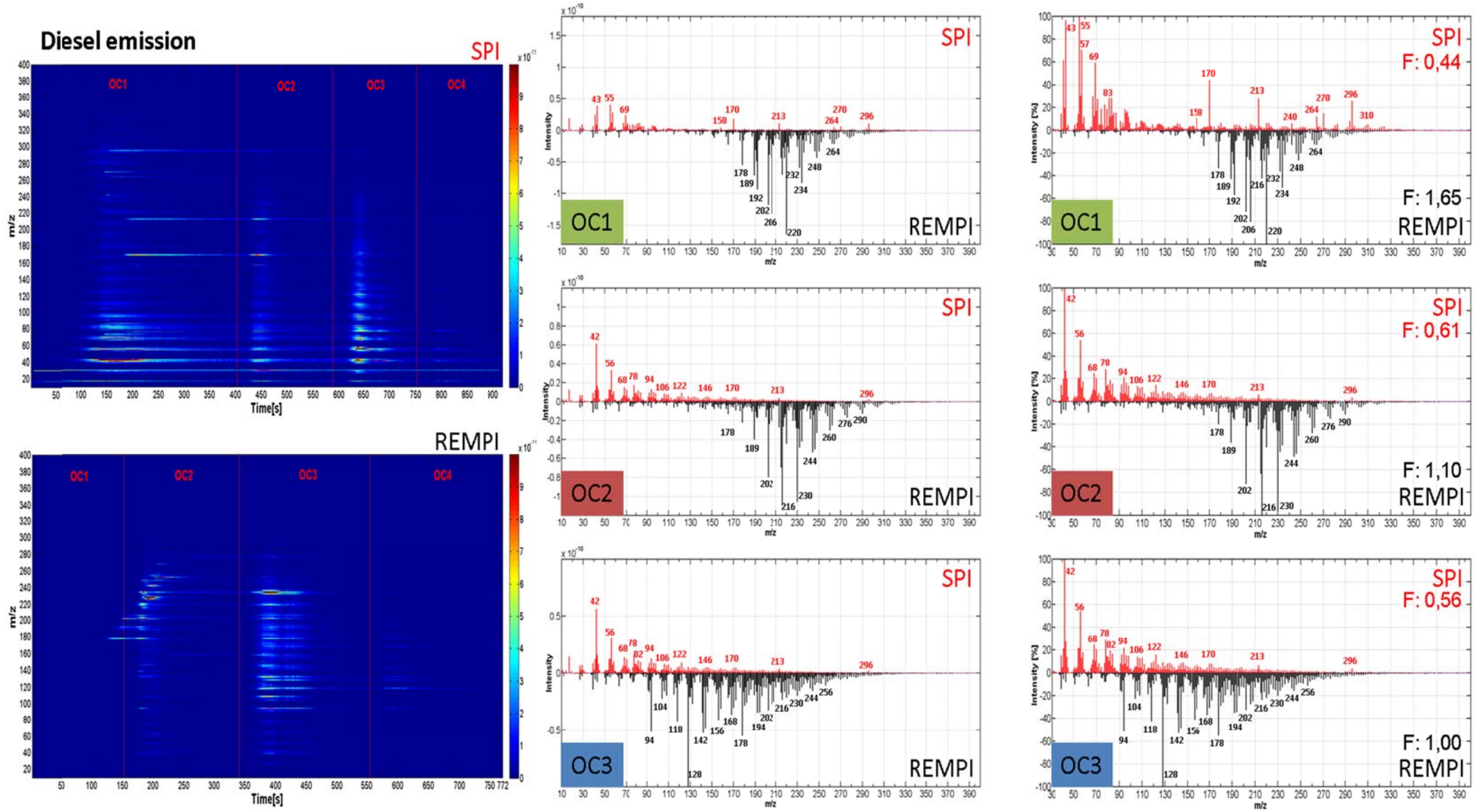

Figure S3: Two-dimensional mass spectrum of the course of signals (m/z) over the four OC-steps (left) for SPI (top) and REMPI (bottom), mass spectra for the first three OC-steps (SPI-red, REMPI-black) (middle), mass spectra for the first three OC-steps normalized to 100 % (right) of the diesel emission sample . Measured with the IMPROVE protocol.

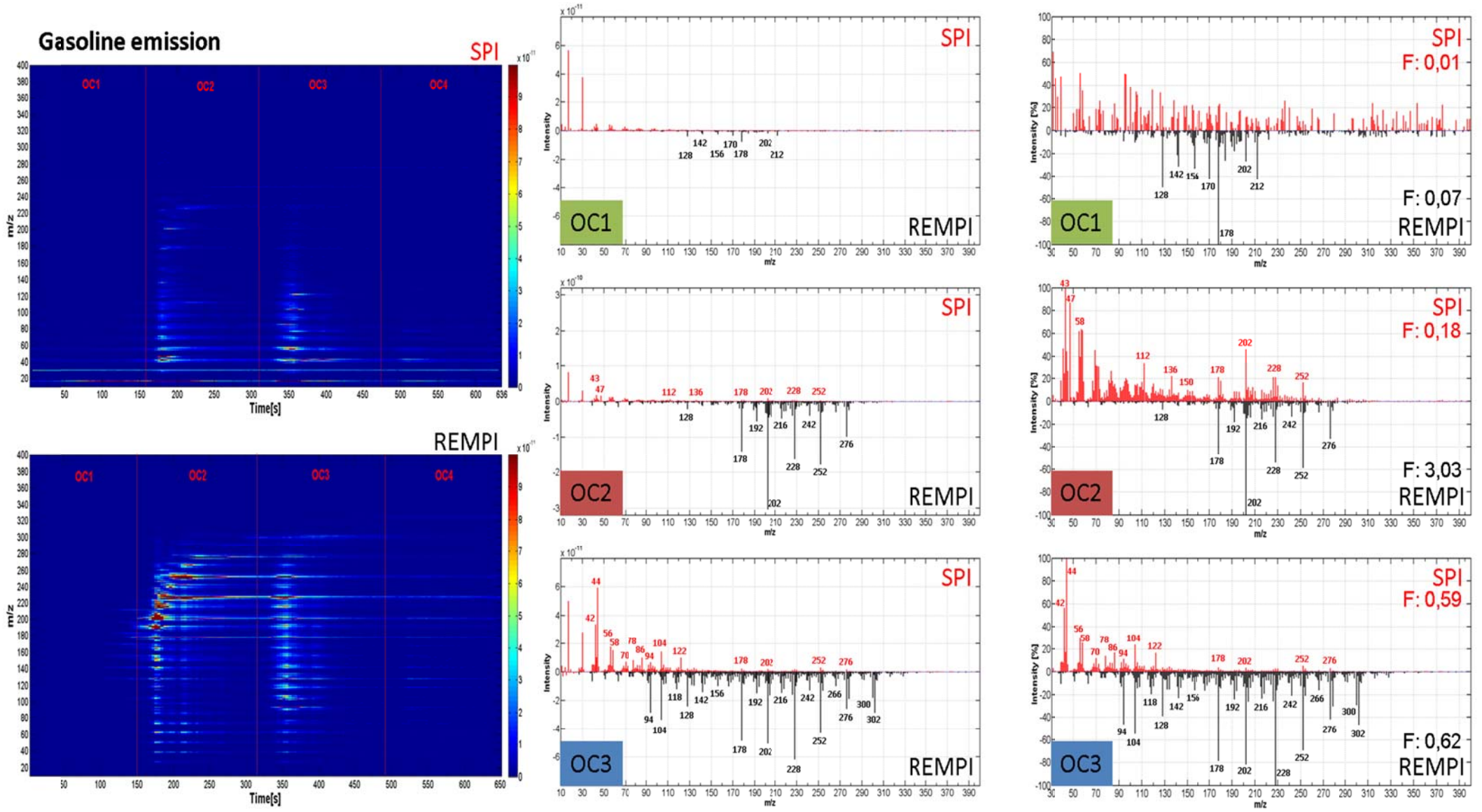

Figure S4: Two-dimensional mass spectrum of the course of signals (m/z) over the four OC-steps (left) for SPI (top) and REMPI (bottom), mass spectra for the first three OC-steps (SPI-red, REMPI-black) (middle), mass spectra for the first three OC-steps normalized to 100 % (right) of the gasoline emission sample . Measured with the IMPROVE protocol.

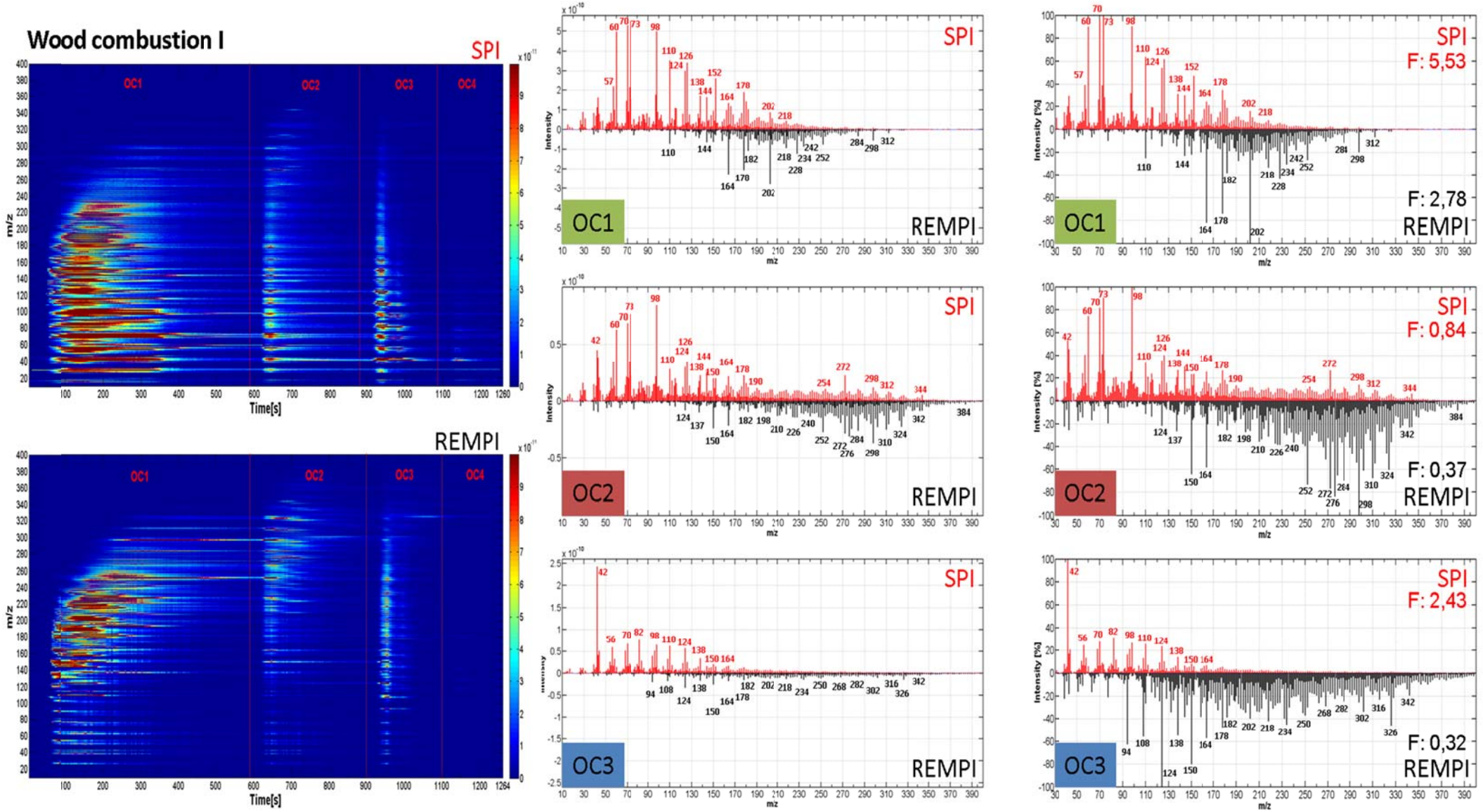

Figure S5: Two-dimensional mass spectrum of the course of signals (m/z) over the four OC-steps (left) for SPI (top) and REMPI (bottom), mass spectra for the first three OC-steps (SPI-red, REMPI-black) (middle), mass spectra for the first three OC-steps normalized to 100 % (right) of the wood combustion emission sample from the starting phase. Measured with the IMPROVE protocol.

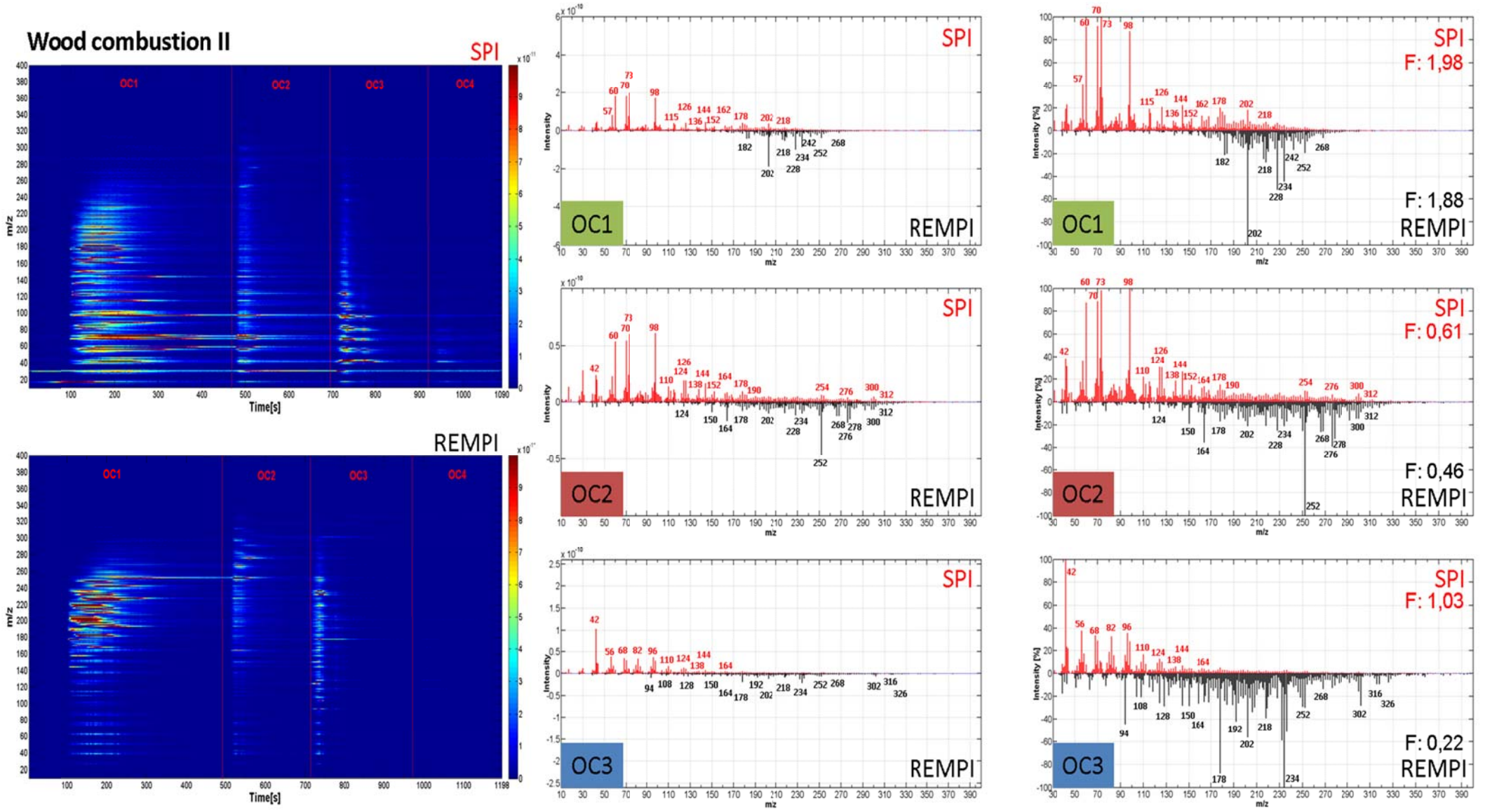

Figure S6: Two-dimensional mass spectrum of the course of signals (m/z) over the four OC-steps (left) for SPI (top) and REMPI (bottom), mass spectra for the first three OC-steps (SPI-red, REMPI-black) (middle), mass spectra for the first three OC-steps normalized to 100 % (right) of the wood combustion emission sample from the nominal load phase. Measured with the IMPROVE protocol.

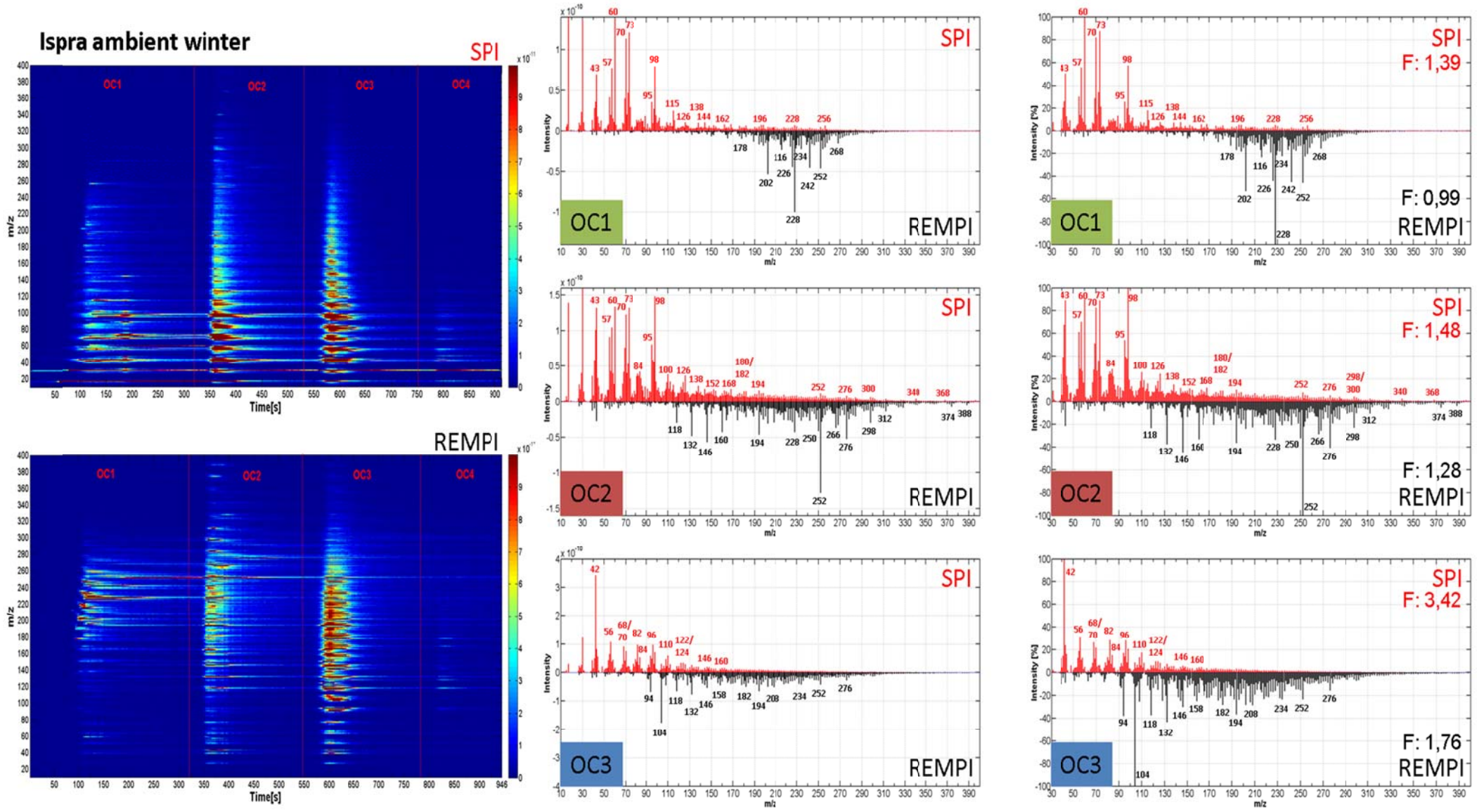

Figure S7: Two-dimensional mass spectrum of the course of signals (m/z) over the four OC-steps (left) for SPI (top) and REMPI (bottom), mass spectra for the first three OC-steps (SPI-red, REMPI-black) (middle), mass spectra for the first three OC-steps normalized to 100 % (right) of the ambient winter sample from the rural background site in Ispra, Italy. Measured with the IMPROVE-A protocol.

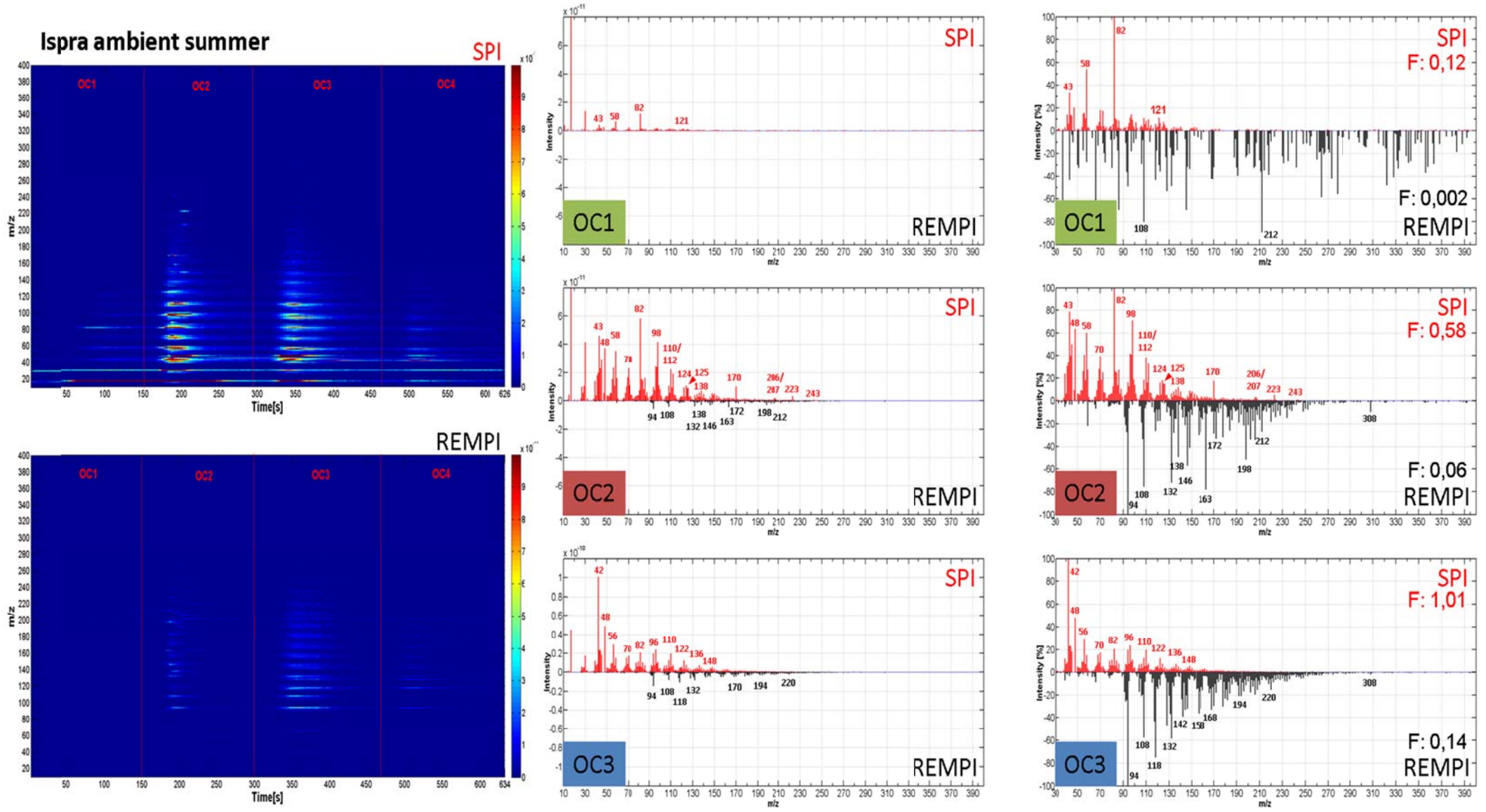

Figure S8: Two-dimensional mass spectrum of the course of signals (m/z) over the four OC-steps (left) for SPI (top) and REMPI (bottom), mass spectra for the first three OC-steps (SPI-red, REMPI-black) (middle), mass spectra for the first three OC-steps normalized to 100 % (right) of the ambient summer sample from the rural background site in Ispra, Italy. Measured with the IMPROVE-A protocol.

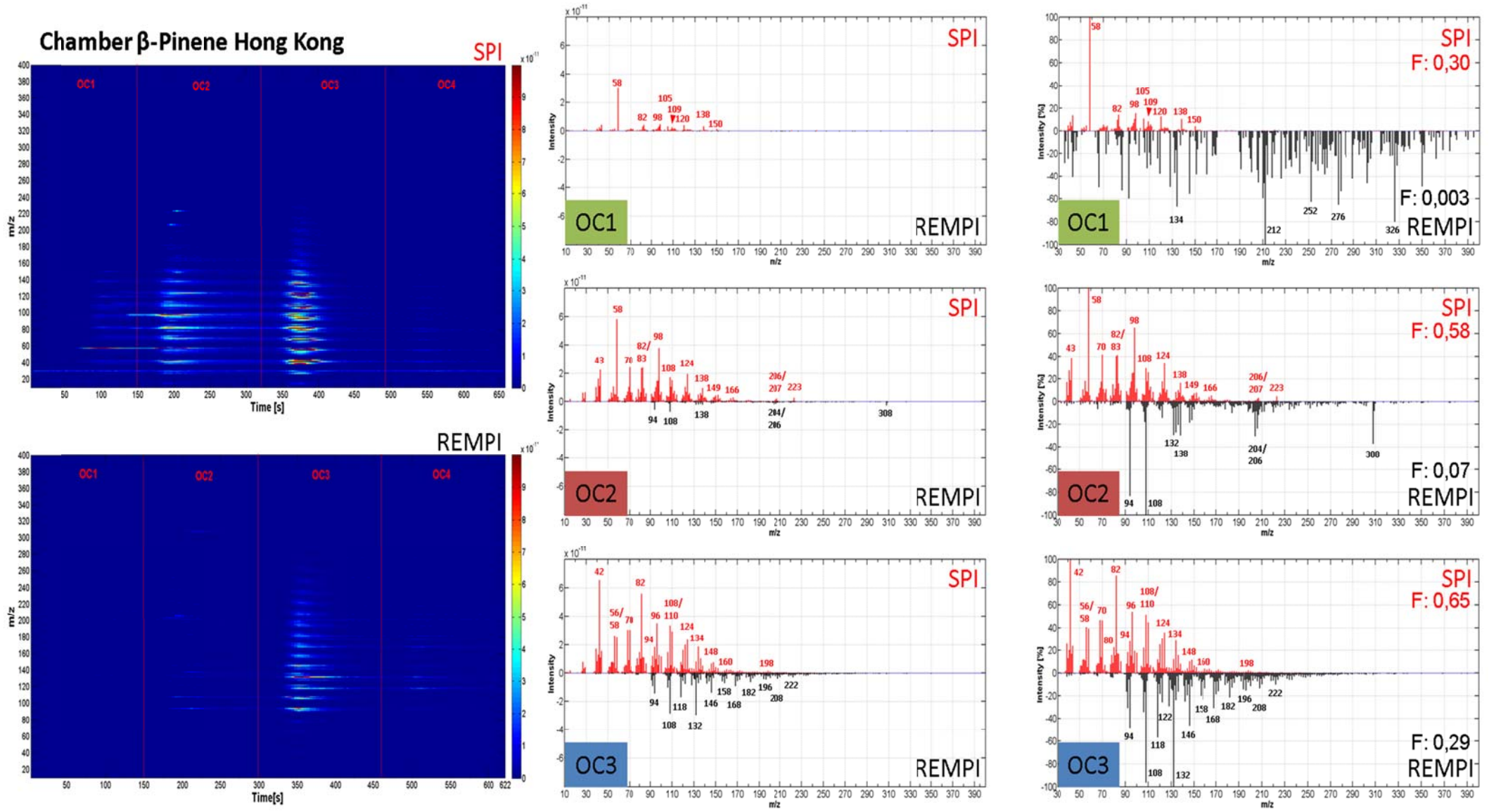

Figure S9: Two-dimensional mass spectrum of the course of signals (m/z) over the four OC-steps (left) for SPI (top) and REMPI (bottom), mass spectra for the first three OC-steps (SPI-red, REMPI-black) (middle), mass spectra for the first three OC-steps normalized to 100 % (right) of the chamber experiment performed in Hong Kong with β-Pinene as a precursor. Measured with the IMPROVE-A protocol.

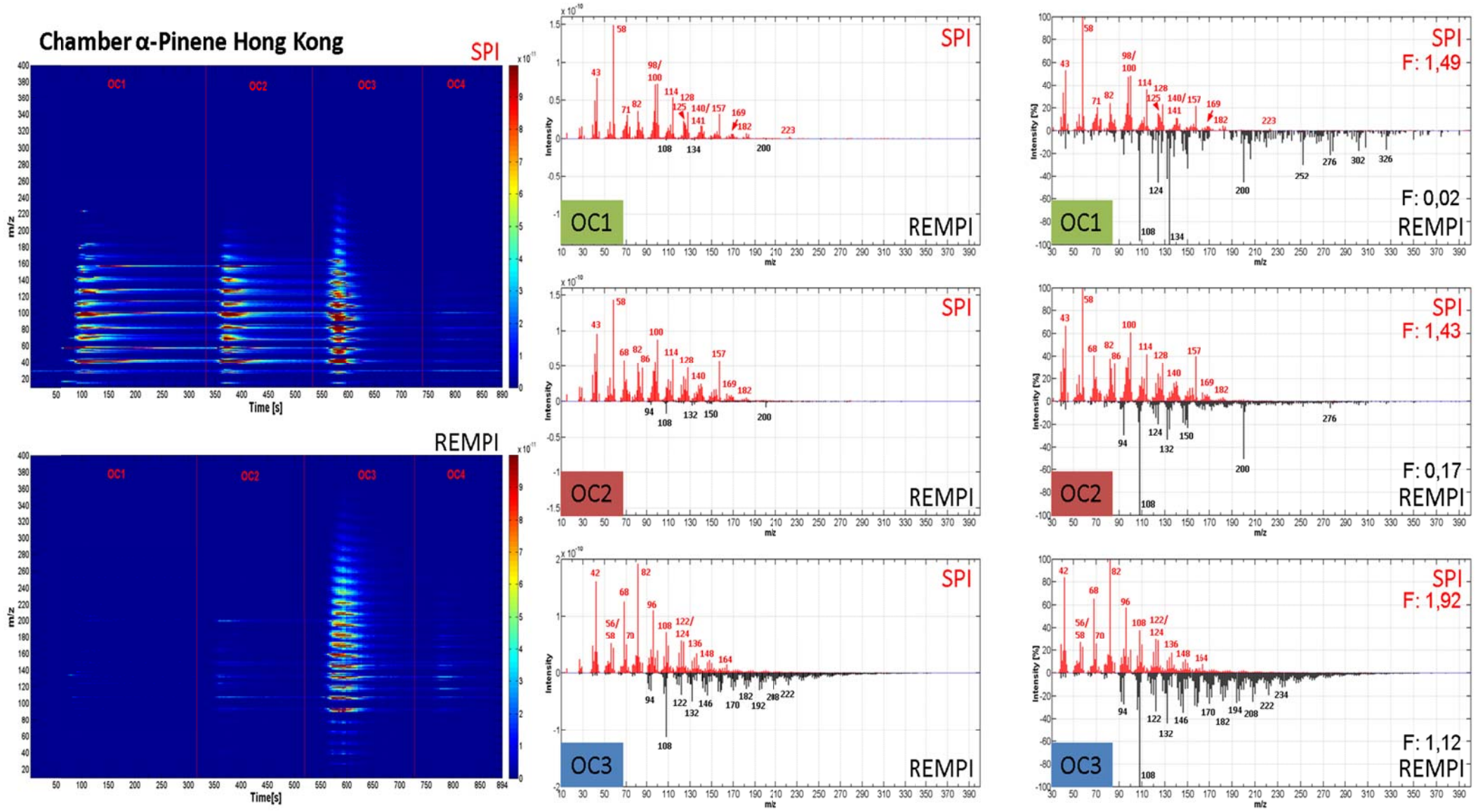

Figure S10: Two-dimensional mass spectrum of the course of signals (m/z) over the four OC-steps (left) for SPI (top) and REMPI (bottom), mass spectra for the first three OC-steps (SPI-red, REMPI-black) (middle), mass spectra for the first three OC-steps normalized to 100 % (right) of the chamber experiment performed in Hong Kong with α-Pinene as a precursor. Measured with the IMPROVE-A protocol.

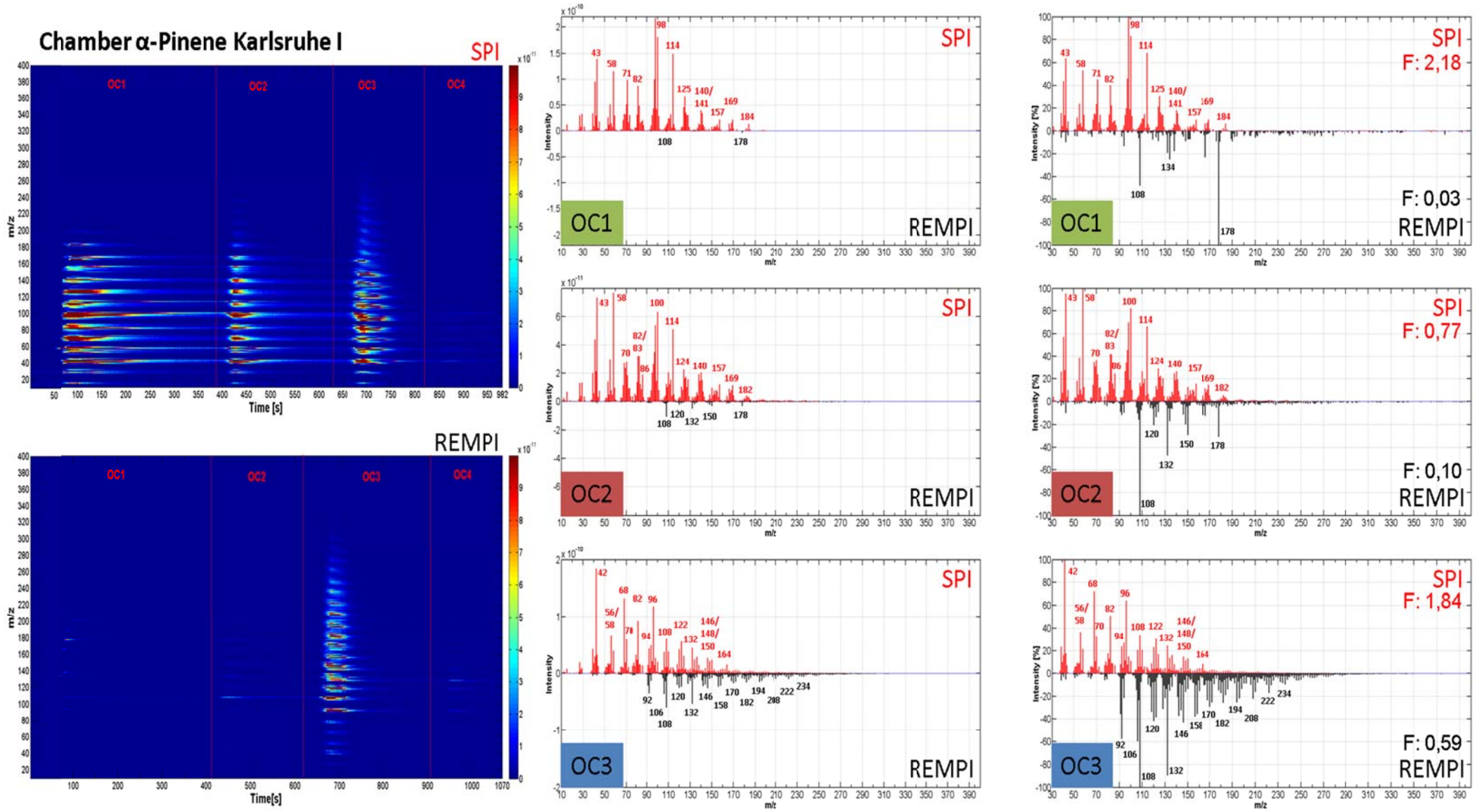

Figure S11: Two-dimensional mass spectrum of the course of signals (m/z) over the four OC-steps (left) for SPI (top) and REMPI (bottom), mass spectra for the first three OC-steps (SPI-red, REMPI-black) (middle), mass spectra for the first three OC-steps normalized to 100 % (right) of the chamber experiment performed in Karlsruhe with α-Pinene as a precursor. Measured with the IMPROVE-A protocol.

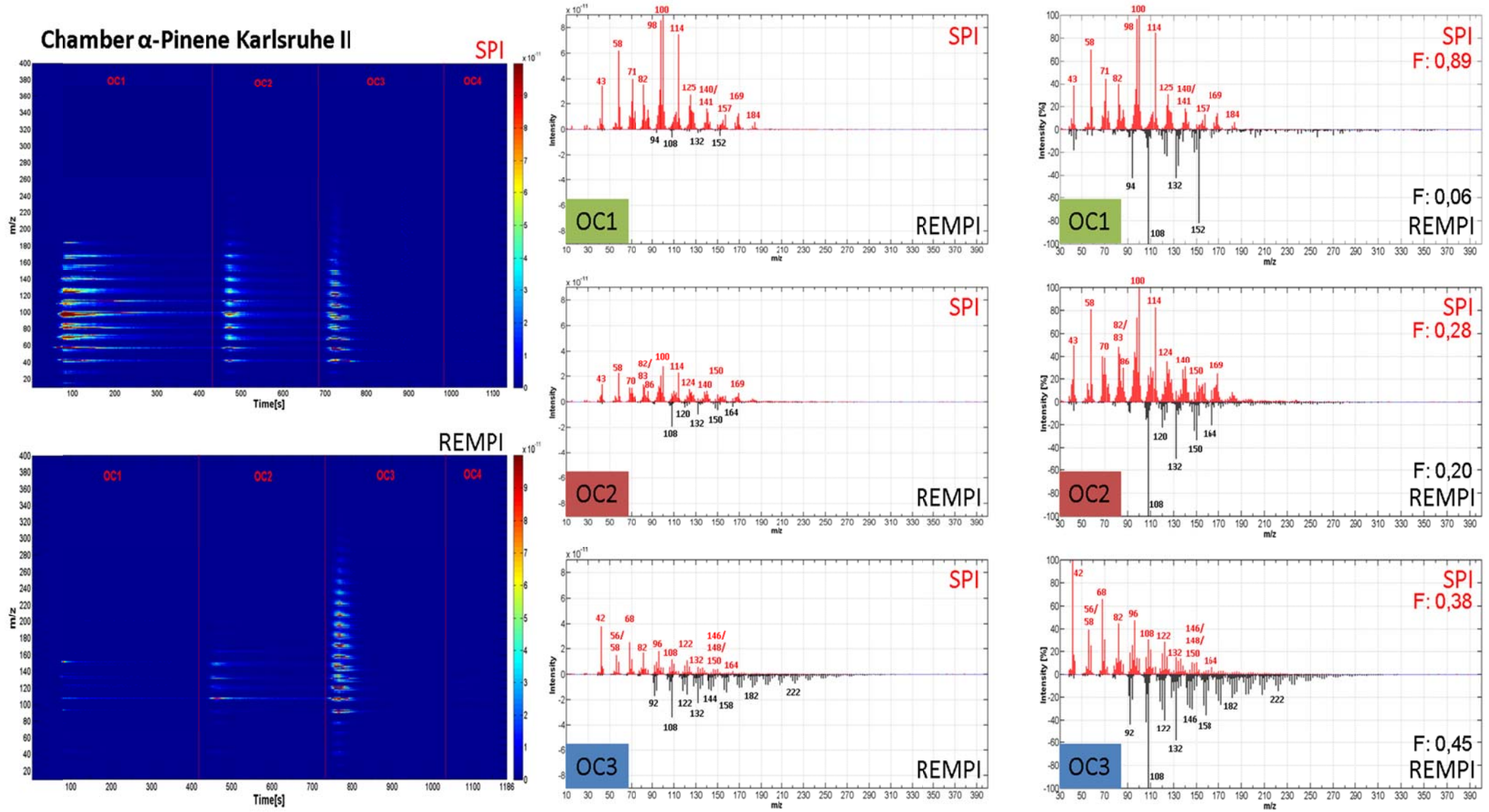

Figure S12: Two-dimensional mass spectrum of the course of signals (m/z) over the four OC-steps (left) for SPI (top) and REMPI (bottom), mass spectra for the first three OC-steps (SPI-red, REMPI-black) (middle), mass spectra for the first three OC-steps normalized to 100 % (right) of the chamber experiment performed in Karlsruhe with α-Pinene as a precursor. Measured with the IMPROVE-A protocol.

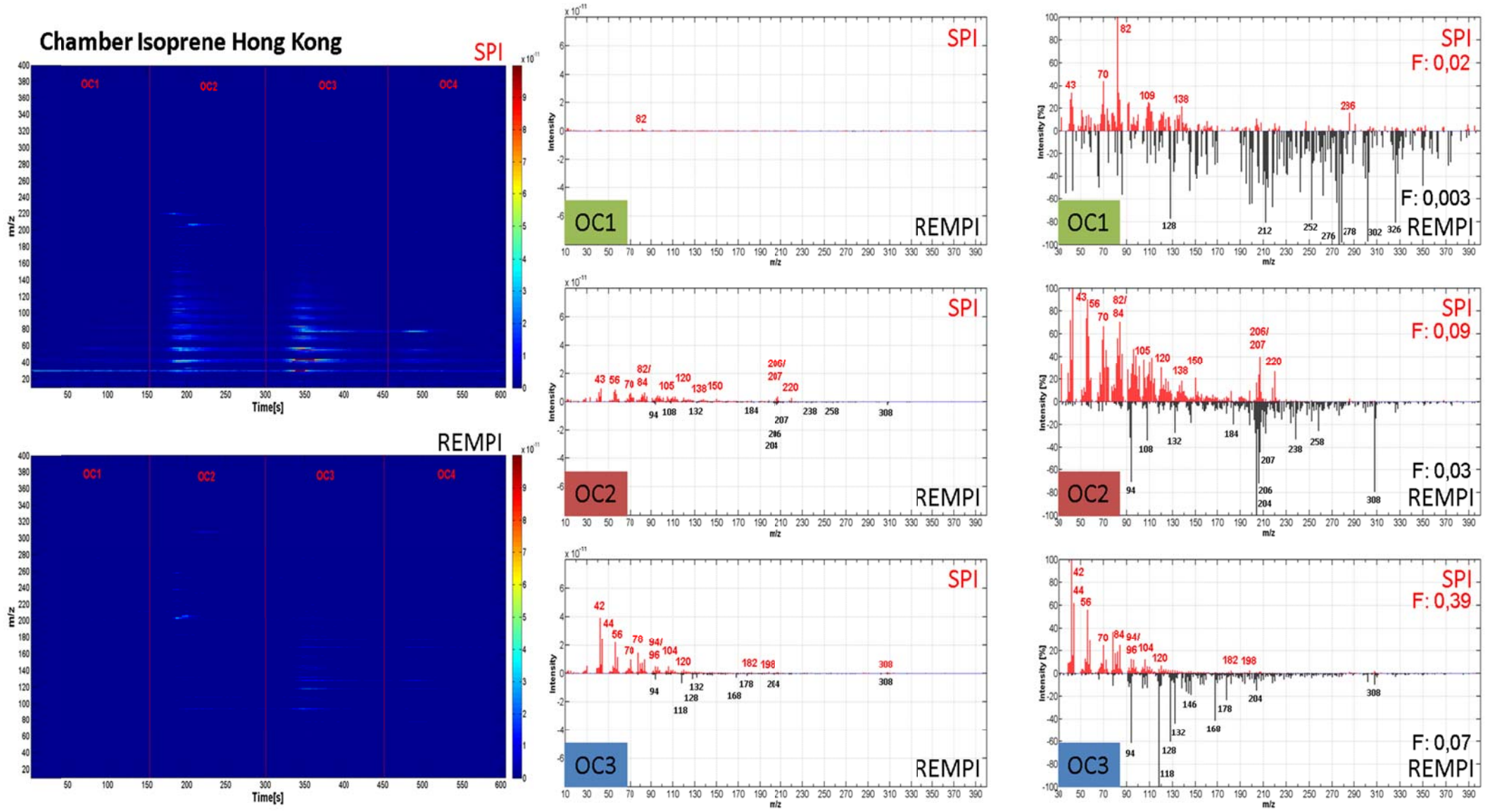

Figure S13: Two-dimensional mass spectrum of the course of signals (m/z) over the four OC-steps (left) for SPI (top) and REMPI (bottom), mass spectra for the first three OC-steps (SPI-red, REMPI-black) (middle), mass spectra for the first three OC-steps normalized to 100 % (right) of the chamber experiment performed in Hong Kong with Isoprene as a precursor. Measured with the IMPROVE-A protocol.

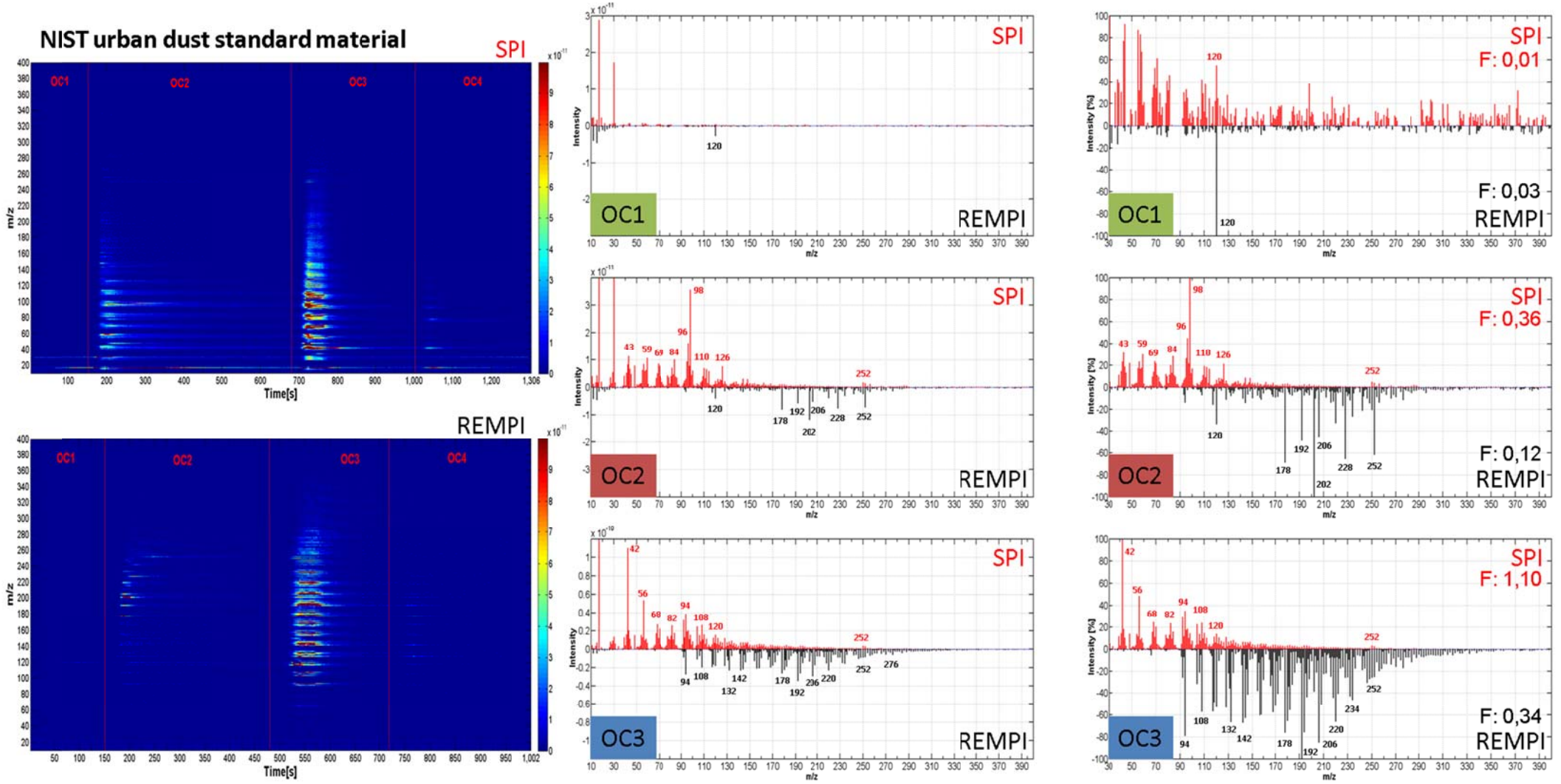

Figure S14: Two-dimensional mass spectrum of the course of signals (m/z) over the four OC-steps (left) for SPI (top) and REMPI (bottom), mass spectra for the first three OC-steps (SPI-red, REMPI-black) (middle), mass spectra for the first three OC-steps normalized to 100 % (right) of the NIST urban dust standard material. Measured with the IMPROVE-A protocol.

Table S3: proposals of the most likely compounds for the signals found in the samples analyzed, whereby (?) means that no suitable compound was found in the literature, (-) mean: not present in the sample, (+) present, (++) dominant signal.

m/z	structure proposals	samples															
		gasoline		diesel		wood combustion		Italy winter		Italy summer		β-Pinene HK		α-Pinene HK		α-Pinene KR	
		SPI	REMPI	SPI	REMPI	SPI	REMPI	SPI	REMPI	SPI	REMPI	SPI	REMPI	SPI	REMPI	SPI	REMPI
41	alkyl fragment	-	-	+	-	-	-	-	-	-	-	+	-	-	-	+	-
42	propene	++	-	++	-	++	-	++	-	++	-	++	-	++	-	++	-
43	alkyl fragment	+	-	+	-	-	-	++	-	++	-	+	-	++	-	++	-
44	acetaldehyde	++	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
47	?	+	-	-	-	-	-	-	-		-	-	-	-	-	-	-
48	methylsulfide	-	-	-	-	-	-	-	-	++	-	-	-	-	-	-	-
55	alkene fragment	+	-	+	-	-	-	++	-	-	-	-	-	-	-	-	-
56	butene, propenal, acrolein	+	-	++	-	++	-	++	-	+	-	++	-	+	-	+	-
57	alkyl fragment	-	-	+	-	+	-	++	-	-	-	-	-	-	-	-	-
58	acetone, propanal, glyoxal, …	+	-	-	-	-	-	-	-	++	-	++	-	++	-	++	-
60	wood combustion fragment (C2H4O2+), glycolaldehyde	-	-	-	-	++	-	++	-	-	-	-	-	-	-	-	-
68	isoprene, furan, pentadiene, …	-	-	+	-	++	-	++	-	+	-	++	-	++	-	++	-
70	pentene, methylbutene, methacrolein, methyl vynil ketone, …	+	-	+	-	++	-	++	-	+	-	++	-	+	-	+	-
73	wood combustion fragment (C3H5O2+), butylamine	-	-	-	-	++	-	++	-	-	-	-	-	-	-	-	-
78	benzene, ?	+	-	+	-	-	-	-	-	-	-	-	-	-	-	-	-
82	Methylfuran, methylpyrazole, …	-	-	+	-	++	-	++	-	++	-	++	-	++	-	++	-
83	?	-	-	-	-	-	-	+	-	-	-	+	-	+	-	+	-
84	cyclohexane, methylbutenal, hexene , …	-	-	+	-	-	-	+	-	+	-	-	-	-	-	-	-
86	hexane, methylbutanal, …	+	-	-	-	-	-	-	-	+	-	-	-	+	-	+	-
92	toluene	-	-	-	-	-	-	-	-	-	-	-	-	-	+	-	+
94	phenol,vinylfuran, methylpyrazine, …	+	++	+	++	+	+	+	++	+	+	+	+	+	+	-	+
95	dimethylpyrrole, formylpyrrole, …	-	-	-	-	-	-	++	-	-	-	-	-	+	-	-	-
96	diemthylfuran, furfural, dimethylpyrazole, …	-	-	+	-	+	-	++	-	+	-	++	-	++	-	++	-

98	methylfuranone, 4-oxo-pent-2-enal, heptene, …	-	-	+	-	++	-	++	-	++	-	++	-	++	-	++	-
100	heptane, methylhexane, dihydro-furandione, …	-	-	-	-	-	-	-	-	-	-	-	-	++	-	++	-
104	styrene, malonic acid	+	++	-	+	-	-	-	++	-	-	-	-	-	-	-	-
106	xylene, benzaldehyde, ethylbenzene, …	-	+	+	+	-	-	-	-	-	-	-	-	-	-	+	+
108	anisol, methylphenol, benzylalcohol, …	-	+	+	+	-	+	-	+	+	+	++	++	++	++	++	++
110	methylfurfural, acetylfuran, heptadienal, …	-	-	+	-	++	++	+	-	+	-	++	-	+	-	+	-
112	methyl-furandione, ethyl- or dimethyl-furanone, …	+	-	-	-	-	-	-	-	+	-	-	-	+	-	-	-
114	octane, methylheptane, dihydro-ethyl-furanone, …	-	-	-	-	-	-	-	-	-	-	-	-	++	-	++	-
115	?	-	-	-	-	-	-	+	-	-	-	-	-	-	-	-	-
118	methylstyrene, benzofuran, succinic acid, indane …	-	+	-	++	-	-	-	++	-	+	-	+	-	-	-	+
120	phenylacetaldehyde, 1,3,5-trimethylbenzene, acetophenone, …	-	-	-	-	-	-	-	-	-	-	+	+	+	+	+	+
122	benzoic acid, hydroxybenzaldehyde, trimethylpyrazine, …	+	-	+	-	-	-	-	-	+	-	+	+	++	+	++	+
124	guaiacol, acetyl-methylfuran, dihydroxymethylbenzene, …	-	-	-	-	++	++	+	-	+	-	+	-	++	-	+	-
125	?	-	-	-	-	-	-	-	-	-	-	-	-	+	-	+	-
126	hydroxymethylfurfural, levoglucosenone, trimethylfuranone, …	-	-	-	-	++	-	+	-	-	-	-	-	+	-	+	-
128	naphthalene, 3-acetyldihydro-2(3H)-furanone, …	-	++	+	++	-	-	-	+	-	+	-	+	+	-	+	-
132	methylbenzofuran, ethylstyrole, methylsuccinic acid, ...	-	-	-	-	-	-	+	++	-	+	-	++	+	+	+	+
134	malic acid, dimethylbenzaldehyde, methylacetophenone, …	-	-	-	-	-	-	-	-	+	-	+	+	+	+	+	-
136	2-methylerythritol, 2-methylthreitol, methoxybenzaldehyde, toluic acid, tetramethylpyrazine, phenylacetic acid, ...	-	-	-	-	-	-	-	-	+	-	+	-	+	-	+	-
137	Nitrotoluene	-	-	-	-	-	+	-	-	-	-	-	-	-	-	-	-
138	methylguaiacol, hydroxybenzoic acid, acetylfuraldehyde, pinaketone, nopinone …	-	-	-	-	++	+	+	-	+	+	+	+	+	-	+	-
140	2,2-Dimethyl-cyclobutyl-1,3-diethanal, Trimethyl-cyclohex-2-en-1-ol	-	-	-	-	-	-	-	-	-	-	-	-	+	-	+	-
142	2-methylnaphthalene, nonanal, …	-	+	-	++	-	-	-	-	-	-	-	+	-	-	-	+
144	octanoic acid, phenylfuran, naphthol, …	-	+	-	++	++	+	+	-	-	-	-	+	-	+	-	+
146	methylpentanedioic acid, hexanedioic acid, methylindanone, …	-	-	+	-	-	-	-	++	-	+	+	+	+	+	+	+

148	hydroxyglutaric acid, isopropyl-1,2dihydroxybutanol, …	-	-	-	-	-	-	-	-	+	-	+	-	+	-	+	-
150	vinylguaiacol, methyl-hydroxy-acetophenone, dimethylbenzoic acid, …	-	-	-	-	++	++	+	-	-	-	-	-	-	-	+	-
152	ethylguaiacol, vanillin, 3-oxo-pina ketone, …	-	-	-	-	++	-	+	-	-	-	-	-	-	-	-	-
156	Dimethylnaphthalene, …	-	+	-	++	-	-	-	+	-	+	-	+	-	+	-	+
157	?	-	-	-	-	-	-	-	-	-	-	-	-	++	-	+	-
158	nonanoic acid, naphthalenedione, methylnaphthol, …	-	-	+	+	-	-	-	+	-	+	-	+	-	+	-	+
160	Heptanedioic acid, methyl-furyl-pyrazine, …	-	-	-	-	-	-	-	+	-	-	+	-	-	-	-	-
162	Levoglucosan, nicotine, …	-	-	-	-	-	-	+	-	-	-	-	-	-	-	-	-
163	?	-	-	-	-	-	-	-	-	-	+	-	-	-	-	-	-
164	Allylguaiacol, eugenol	-	-	-	-	++	++	+	-	-	-	-	-	+	-	+	-
166	propylguaiacol, benzenedicarboxylic acid, ...	-	-	-	-	+	-	-	-	-	-	-	-	-	-	-	-
168	vanillic acid, trimethoxybenzene, …	-	-	-	++	-	-	+	-	-	-	-	+	-	+	-	+
169	4-isopropenyl-1-methyl-1hydroxy-2-oxocyclohexane, …	-	-	-	-	-	-	-	-	-	-	-	-	+	-	+	-
170	decenoic acid, dodecane, …	-	-	++	+	-	-	-	-	+	+	-	+	-	+	-	+
172	decanoic acid, nonanoic acid methyl ester, …	-	-	-	+	-	-	-	-	-	+	-	+	-	-	-	+
178	phenanthrene, anthracene, coniferyl aldehyde…	+	++	-	++	++	++	-	+	-	-	-	-	-	-	-	+
180	guaiacyl acetone, phenalenone, 3,5-dimethoxy-acetophenone, …	-	-	-	+	+	-	+	+	-	-	-	-	-	+	-	+
182	syringaldehyde, benzophenone, 4-Oxopononaldehyde, …	-	-	-	+	-	++	+	+	-	-	-	+	+	+	+	+
190	?	-	-	-	-	-	-	-	-	-	-	-	+	-	-	-	-
192	methylphenanthrene, methylanthracene	-	++	-	++	-	-	-	-	-	-	-	-	-	+	-	-
194	4-allyl-2,6-dimethoxyphenol	-	+	-	++	-	-	+	++	-	-	-	+	-	+	-	+
196	acetosyringone, propylsyringol, methyl homovanillate, …	-	-	-	-	-	-	+	-	-	-	-	+	-	-	-	+
198	oxo pinonic acid, 2-methyl-4,6-dinitrophenol, …	-	-	-	-	-	-	-	-	-	+	+	-	-	-	-	-
200	dibenzofuranol, 10-hydroxypinonic acid, dodecanoic acid	-	-	-	-	-	-	-	-	-	-	-	-	-	+	-	-
202	pyrene, flouranthene, …	+	++	-	++	+	++	-	++	-	-	-	-	-	-	-	-
204	phenylnaphthalene, …	-	-	-	-	-	-	-	-	-	-	-	+	-	-	-	-
206	dimethylphenanthrene	-	-	-	++	-	-	-	+	+	-	+	+	-	-	-	-
207	?	-	-	-	-	-	-	-	-	+	-	+	-	-	-	-	-
208	anthracenedione, phenathroquinone	-	-	-	+	-	-	-	+	-	-	-	+	-	+	-	+

210	?	-	-	-	-	-	+	-	-	-	-	-	-	-	+	-	+
212	trimethoxybenzoic acid, …	-	-	-	-	-	-	-	-	-	+	-	-	-	-	-	-
213	?	-	-	+	-	-	-	-	-	-	-	-	-	-	-	-	-
215	?	-	-	-	+	-	-	-	-	-	-	-	-	-	-	-	-
216	?	-	++	-	++	-	-	-	+	-	-	-	-	-	-	-	-
218	Benzofluorene, benzonaphthofuran	-	+	-	+	+	++	-	-	-	-	-	-	-	-	-	-
220	?	-	-	-	++	-	-	-	-	-	-	-	-	-	-	-	-
222	?	-	-	-	+	-	-	-	-	-	-	-	+	-	+	-	+
223	phthalatderivative	-	-	-	-	-	-	-	-	+	-	+	-	+	-	-	-
226	hexadecane, tetradecenoic acid, cyclopenta(cd)pyrene, benzo(ghi)fluoranthene, …	-	+	-	+	-	+	-	+	-	-	-	-	-	-	-	-
228	chrysene, benz[a]anthracene, triphenalene, myristinic acid, …	+	++	-	+	-	++	+	++	-	-	-	-	-	-	-	-
230	dimethylpyrene, 7H-Benz[de]anthracen-7-one, …	-	-	-	++	-	-	-	-	-	-	-	-	-	-	-	-
232	?	-	-	-	++	-	-	-	+	-	-	-	-	-	+	-	+
234	retene, di-tert-butyl-hydroxybenzaldehyde, …	-	-	-	++	-	++	-	+	-	-	-	-	-	+	-	+
240	pentadecanoic acid, heptadecane, …	-	-	-	-	-	+	-	-	-	-	-	-	-	-	-	-
242	methylchrysene, pentadecanoic acid, tetradecanoic acid methyl ester, …	-	++	-	-	-	+	-	+	-	-	-	-	-	-	-	-
244	tridecanedioic acid	-	-	-	++	-	-	-	-	-	-	-	-	-	-	-	-
246	?	-	-	-	++	-	-	-	-	-	-	-	-	-	-	-	-
248	?	-	-	-	++	-	-	-	-	-	-	-	-	-	-	-	-
250	octadidecen	-	-	-	-	-	-	-	+	-	-	-	-	-	-	-	-
252	benzo(a)pyrene, benzo(k)fluoranthene, …	+	++	-	-	-	++	+	++	-	-	-	-	-	-	-	-
254	octadecane, hexadecenoic acid, benzo(cd)pyren-6-one, …	-	-	-	-	+	+	+	-	-	-	-	-	-	-	-	-
256	palmitic acid, heptadecanol, dimethylchrysene, …	-	-	-	+	-	-	-	-	-	-	-	-	-	-	-	-
260	?	-	-	-	++	-	-	-	-	-	-	-	-	-	-	-	-
264	?	-	-	+	+	-	-	-	-	-	-	-	-	-	-	-	-
266	nonadecen	-	+	-	-	-	-	-	+	-	-	-	-	-	-	-	-
268	nonadecane, pristane, heptadecenoic acid, …	-	-	-	-	-	-	-	+	-	-	-	-	-	-	-	-
270	methyl palmitate, heptadecanoic acid, …	-	-	+	-	-	-	-	-	-	-	-	-	-	-	-	-
272	methylbis(phenylmethyl)-benzene, …	-	-	-	-	++	++	-	-	-	-	-	-	-	-	-	-

276	benzo(ghi)perylene, indeno(1,2,3-cd)pyrene, …	+	++	-	+	-	++	+	+	-	-	-	-	-	-	-	-
278	dibenz[a,h]anthracene	-	+	-	-	-	+	-	-	-	-	-	-	-	-	-	-
284	heptadecanoic acid methyl ester, stearic acid, …	-	-	-	-	-	++	-	-	-	-	-	-	-	-	-	-
296	heneicosane	-	-	+	-	-	-	-	-	-	-	-	-	-	-	-	-
298	abietatetraenoic acid, octadecanoic acid methyl ester, …	-	-	-	-	+	++	-	+	-	-	-	-	-	-	-	-
300	coronene, dehydroabietic acid	-	++	-	-	+	+	+	+	-	-	-	-	-	-	-	-
302	pimaric acid, abietic acid	-	++	-	-	+	-	+	-	-	-	-	-	-	-	-	-
308	?	-	-	-	-	-	-	-	-	-	-	-	+	-	-	-	-
310	ethyl oleate, docosane, …	-	-	-	-	-	+	-	-	-	-	-	-	-	-	-	-
312	methylabietatetraenoate, eicoscanoic acid, ethyl stearate, …	-	-	-	-	+	++	+	+	-	-	-	-	-	-	-	-
322	?	-	-	-	-	-	+	-	-	-	-	-	-	-	-	-	-
324	Tricosane, docosanal, …	-	-	-	-	-	+	-	-	-	-	-	-	-	-	-	-
326	?	-	-	-	-	-	+	-	-	-	-	-	-	-	-	-	-
340	docosanoic acid, tricosanol, …	-	-	-	-	+	-	+	-	-	-	-	-	-	-	-	-
342	tetramethoxyisoflavone	-	-	-	-	-	+	-	-	-	-	-	-	-	-	-	-
344	deoxomatairesinol	-	-	-	-	+	+	-	-	-	-	-	-	-	-	-	-
368	tetracosanoic acid	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
374	?	-	-	-	-	-	-	-	+	-	-	-	-	-	-	-	-
384	deisopropyldehydroabietic acid	-	-	-	-	-	+	-	-	-	-	-	-	-	-	-	-
388	?	-	-	-	-	-	-	-	+	-	-	-	-	-	-	-	-