



Supplement of

Hyphenation of a EC / OC thermal–optical carbon analyzer to photoionization time-of-flight mass spectrometry: an off-line aerosol mass spectrometric approach for characterization of primary and secondary particulate matter

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Supplemental material

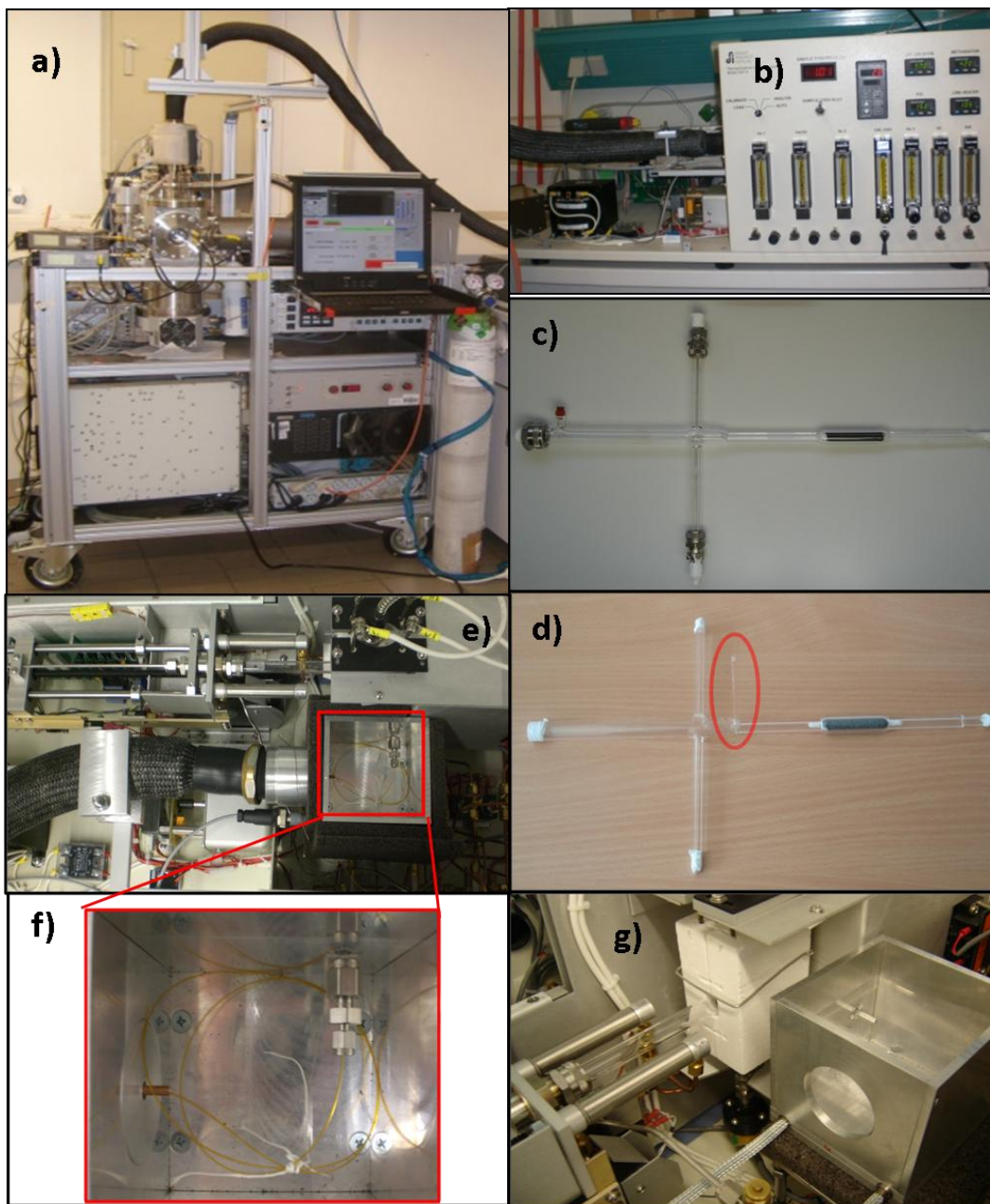


Figure S 1: Pictures of the coupling and assembling (a- PI-TOF-MS, b – carbon analyzer, c - the original quartz tubing system, d – the modified quartz tubing system, e – the whole connecting unit with aluminum box and heating hose, f - zoom into the aluminum box with quartz tube, Swagelok connector and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

Table S1: Experimental conditions of the chamber experiments

sample	Precursor concentration [ppm]	Ozone concentration [ppm]	Temperature [°C]	chamber volume [m ³]	Experiment duration [min]	PM on filter [µg/cm ²]
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

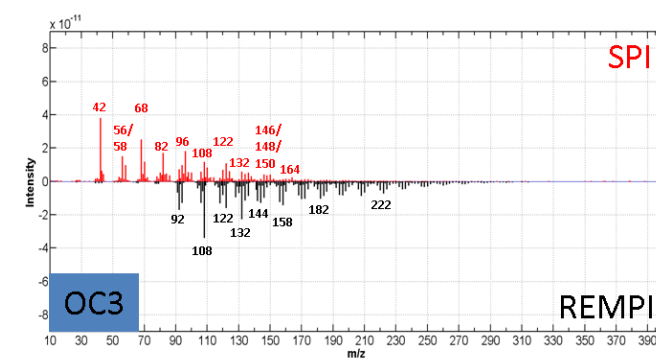
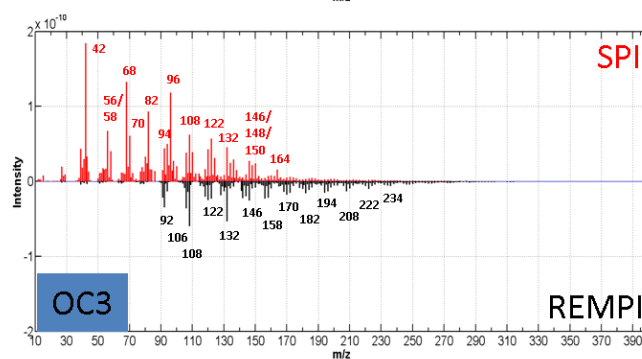
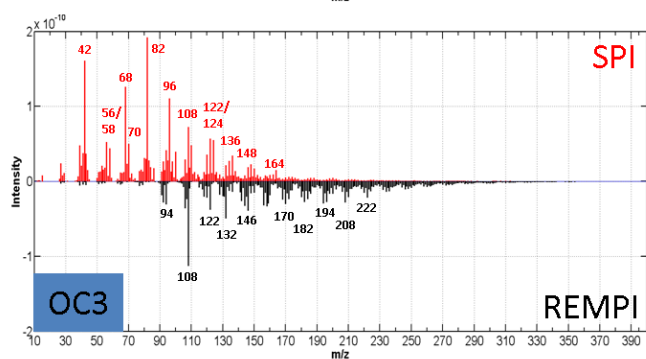
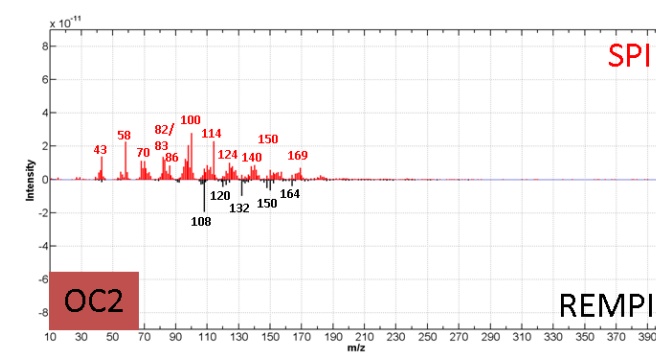
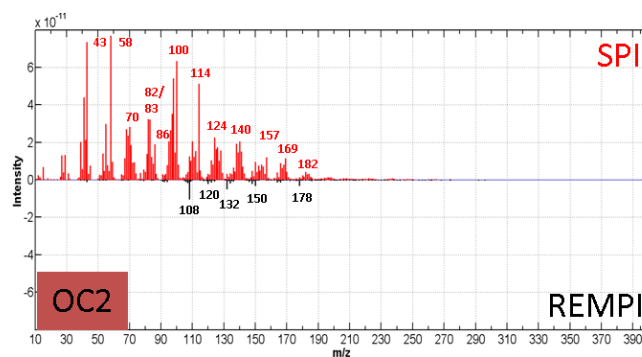
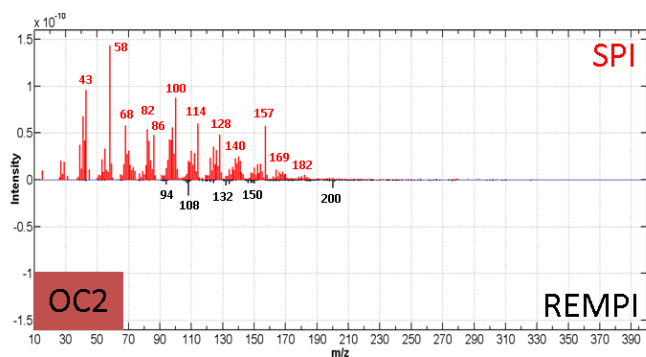
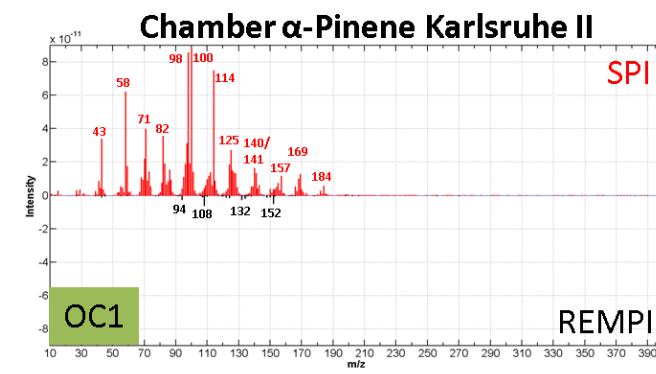
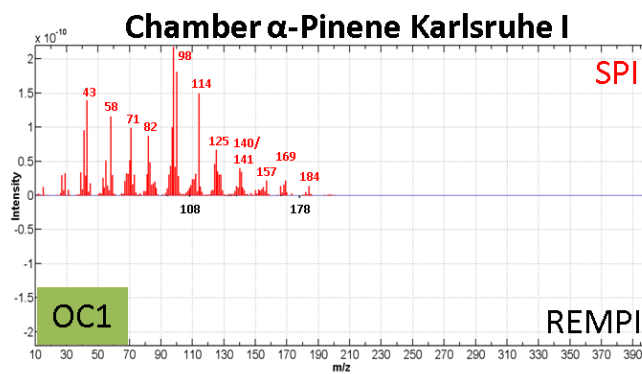
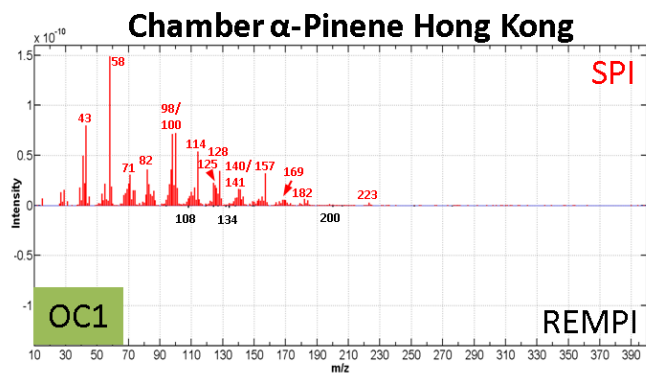


Figure S 2: Comparison of the mass spectra obtained by the measurement of the filter samples from the three different chamber experiments using α -pinene as a precursor.

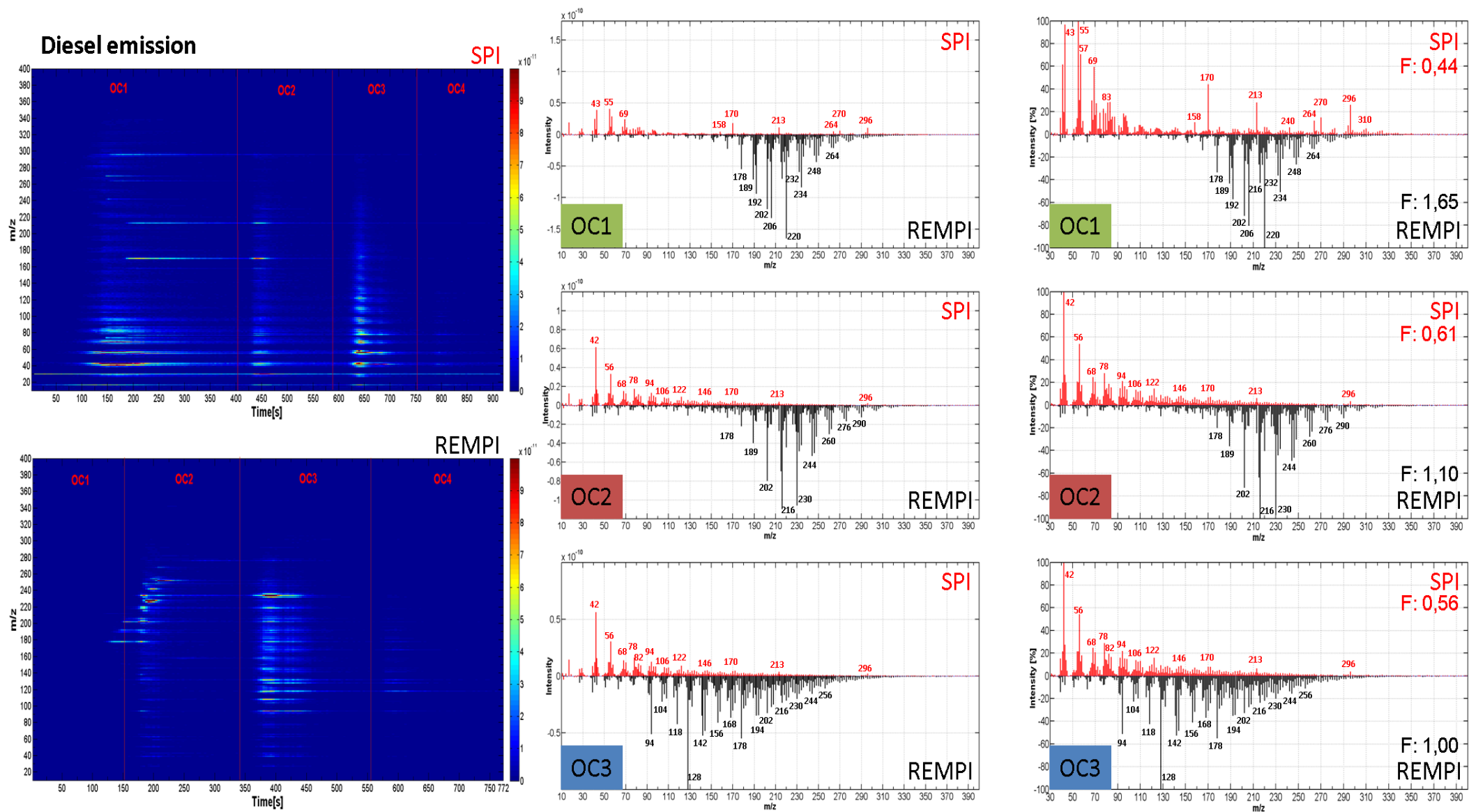


Figure S3: Two-dimensional mass spectrum of the course of signals (m/z) over the four OC-steps (left) for SPI (top) and REMPI (bottom), mass spectra for the first three OC-steps (SPI-red, REMPI-black) (middle), mass spectra for the first three OC-steps normalized to 100 % (right) of the diesel emission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

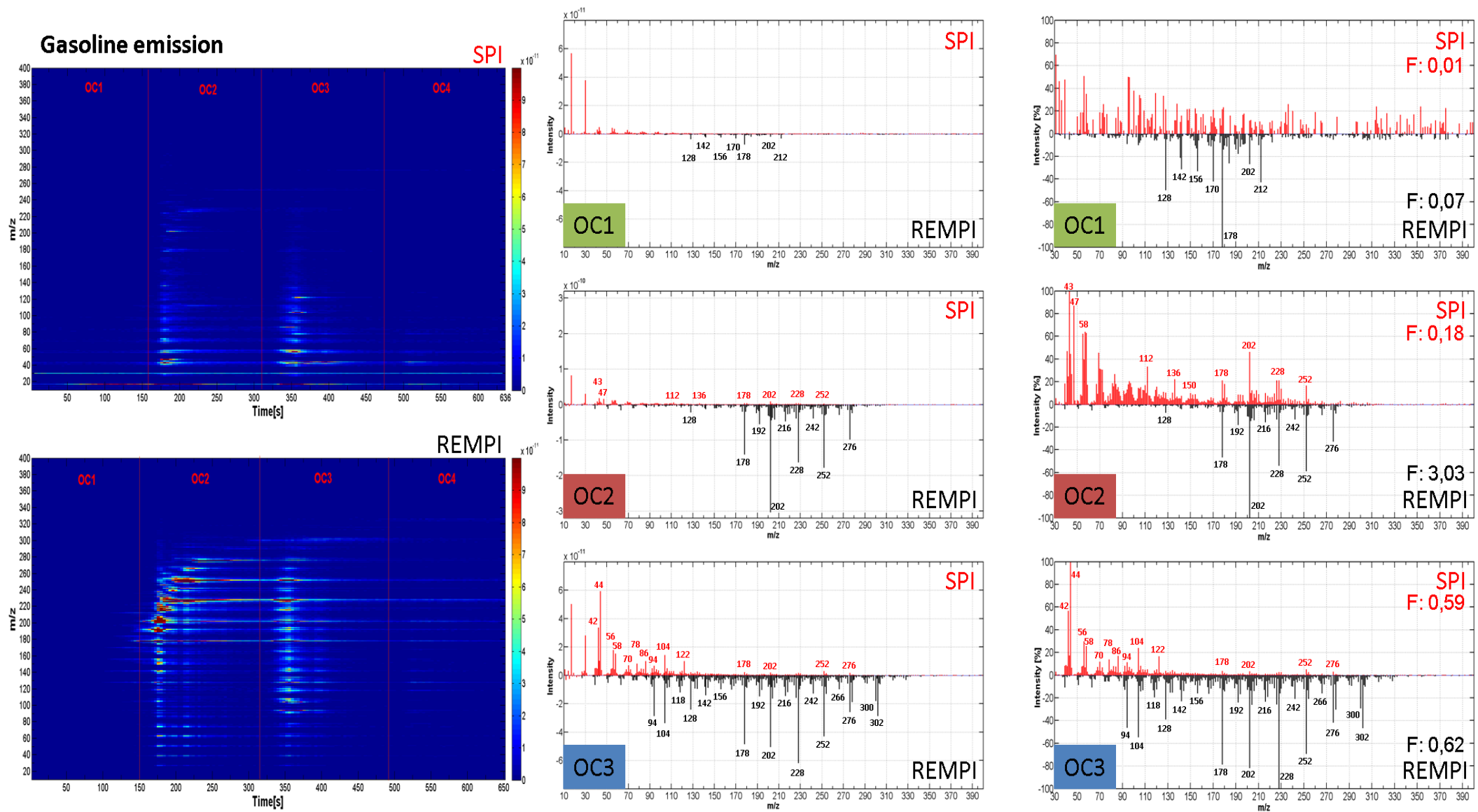


Figure S4: Two-dimensional mass spectrum of the course of signals (m/z) over the four OC-steps (left) for SPI (top) and REMPI (bottom), mass spectra for the first three OC-steps (SPI-red, REMPI-black) (middle), mass spectra for the first three OC-steps normalized to 100 % (right) of the gasoline emission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

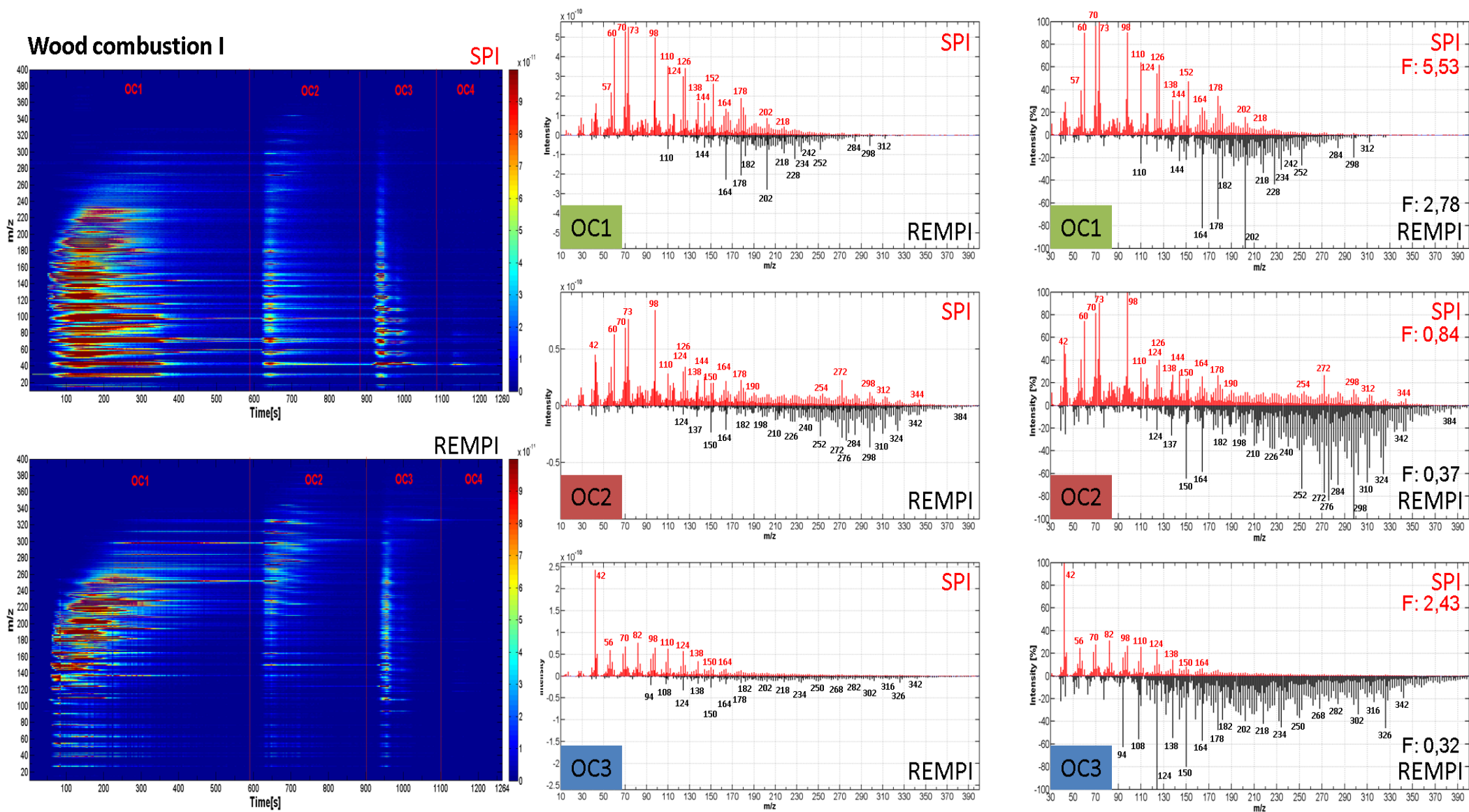


Figure S5: Two-dimensional mass spectrum of the course of signals (m/z) over the four OC-steps (left) for SPI (top) and REMPI (bottom), mass spectra for the first three OC-steps (SPI-red, REMPI-black) (middle), mass spectra for the first three OC-steps normalized to 100 % (right) of the wood combustion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

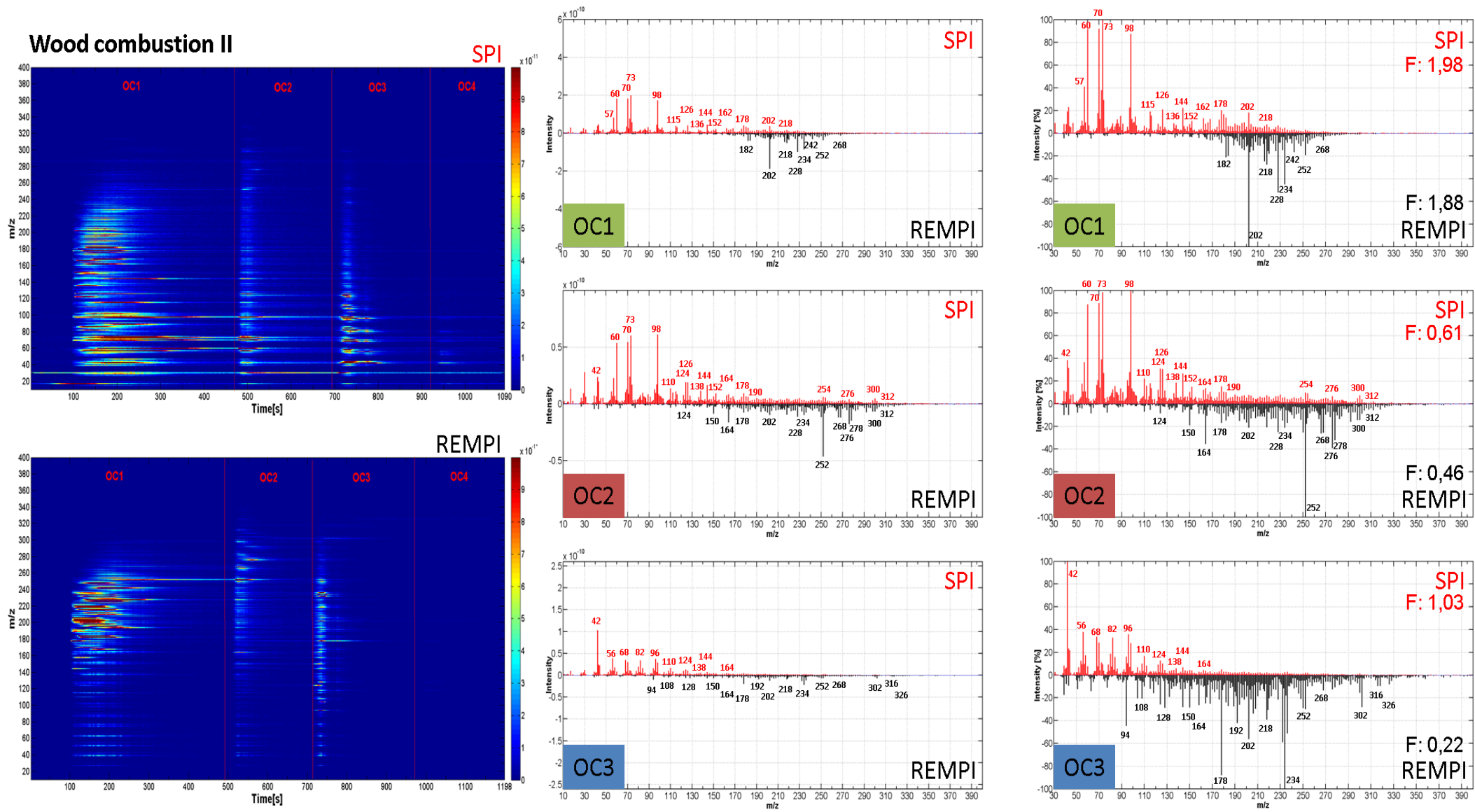


Figure S6: Two-dimensional mass spectrum of the course of signals (m/z) over the four OC-steps (left) for SPI (top) and REMPI (bottom), mass spectra for the first three OC-steps (SPI-red, REMPI-black) (middle), mass spectra for the first three OC-steps normalized to 100 % (right) of the wood combustion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

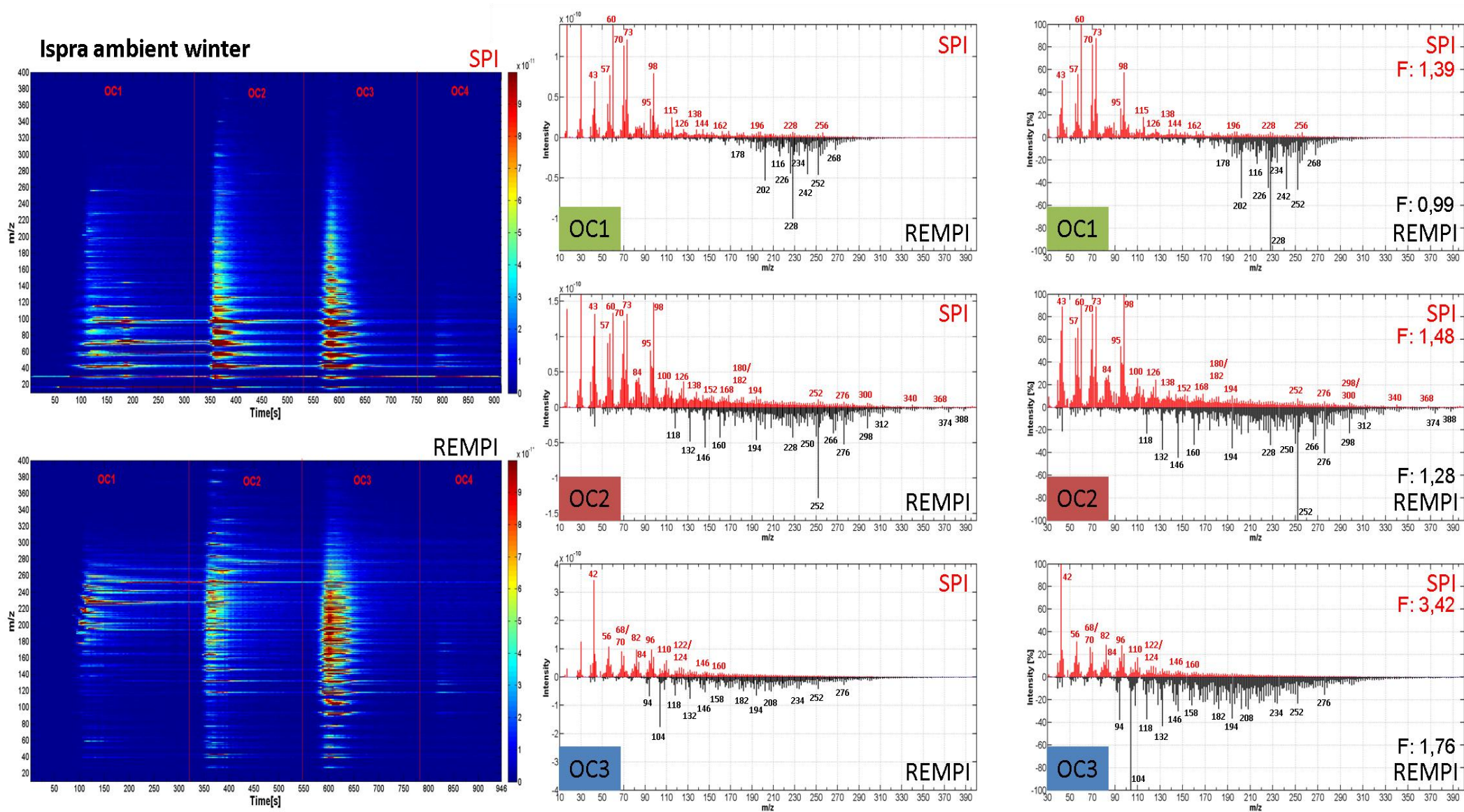


Figure S7: Two-dimensional mass spectrum of the course of signals (m/z) over the four OC-steps (left) for SPI (top) and REMPI (bottom), mass spectra for the first three OC-steps (SPI-red, REMPI-black) (middle), mass spectra for the first three OC-steps normalized to 100 % (right) of the ambient winter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

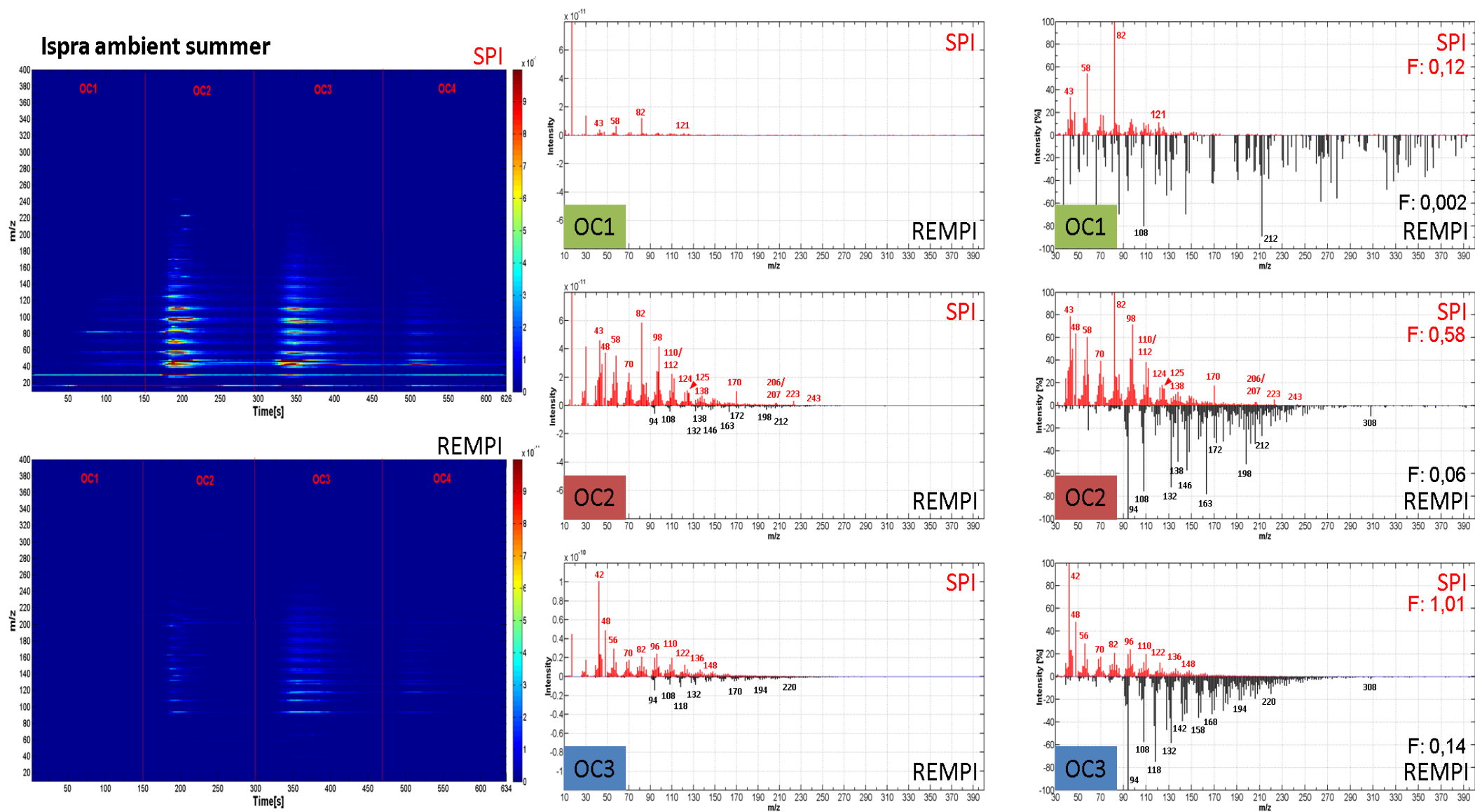


Figure S8: Two-dimensional mass spectrum of the course of signals (m/z) over the four OC-steps (left) for SPI (top) and REMPI (bottom), mass spectra for the first three OC-steps (SPI-red, REMPI-black) (middle), mass spectra for the first three OC-steps normalized to 100 % (right) of the ambient summer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

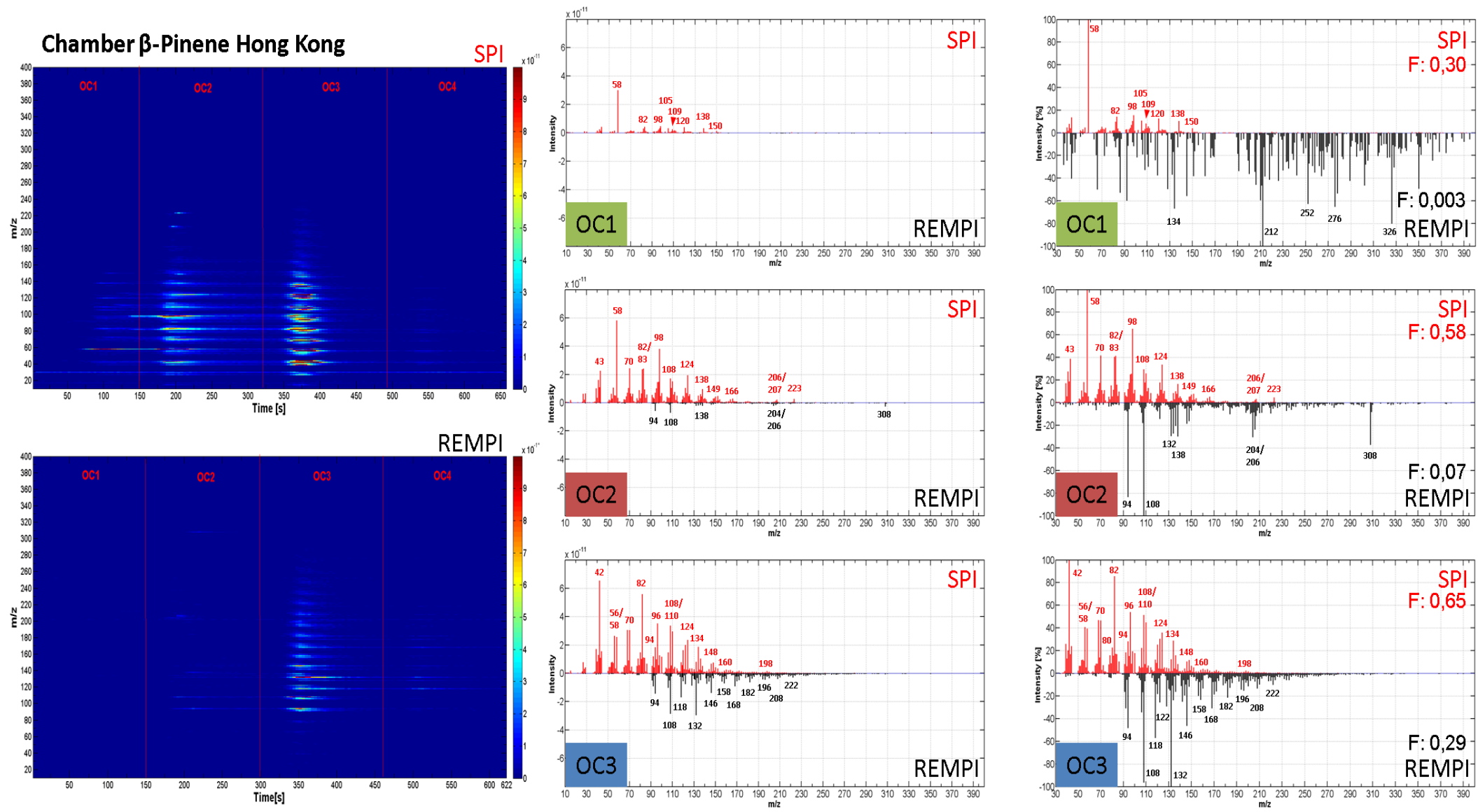


Figure S9: Two-dimensional mass spectrum of the course of signals (m/z) over the four OC-steps (left) for SPI (top) and REMPI (bottom), mass spectra for the first three OC-steps (SPI-red, REMPI-black) (middle), mass spectra for the first three OC-steps normalized to 100 % (right) of the chamber experiment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

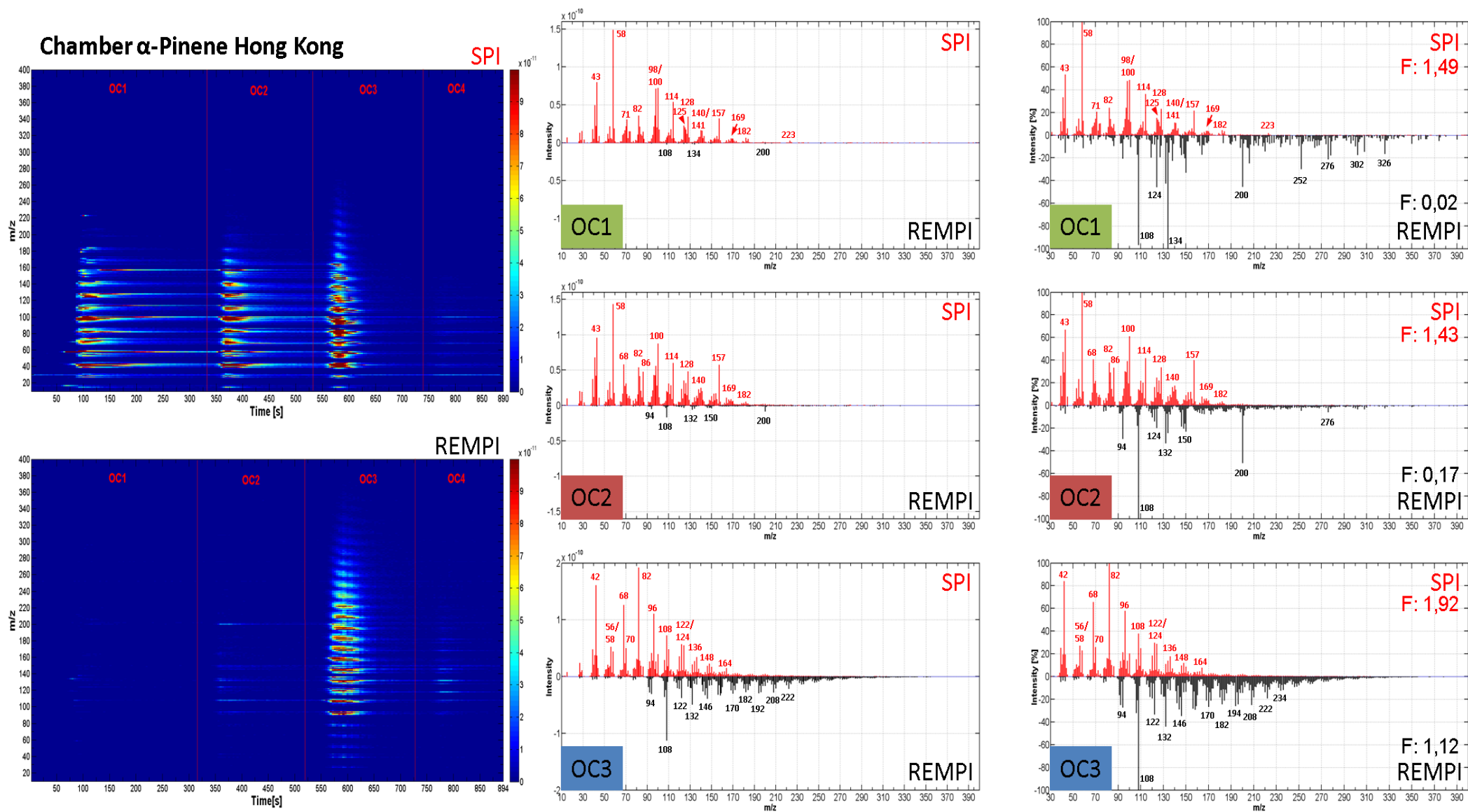


Figure S10: Two-dimensional mass spectrum of the course of signals (m/z) over the four OC-steps (left) for SPI (top) and REMPI (bottom), mass spectra for the first three OC-steps (SPI-red, REMPI-black) (middle), mass spectra for the first three OC-steps normalized to 100 % (right) of the chamber experiment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

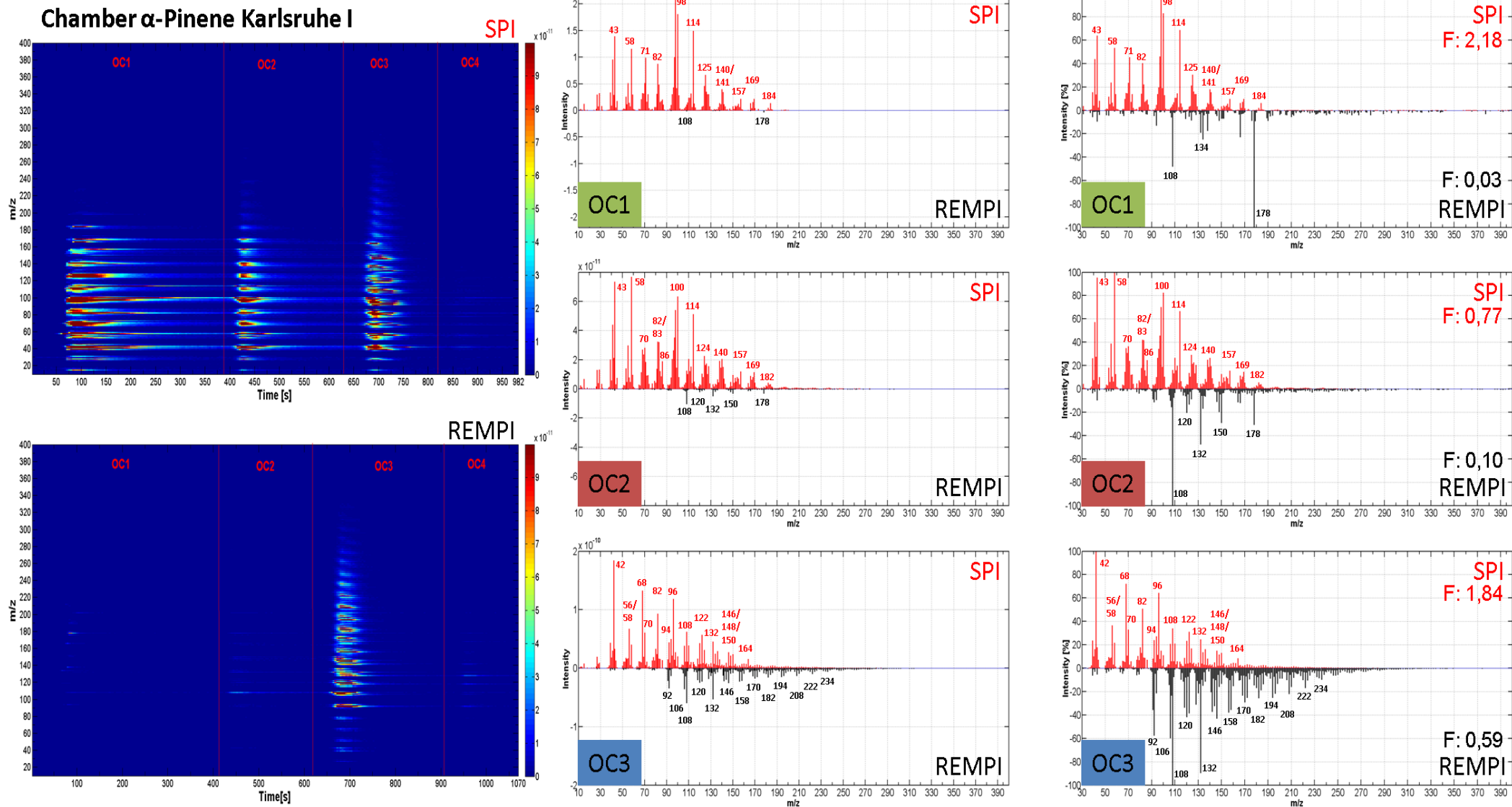


Figure S11: Two-dimensional mass spectrum of the course of signals (m/z) over the four OC-steps (left) for SPI (top) and REMPI (bottom), mass spectra for the first three OC-steps (SPI-red, REMPI-black) (middle), mass spectra for the first three OC-steps normalized to 100 % (right) of the chamber experiment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

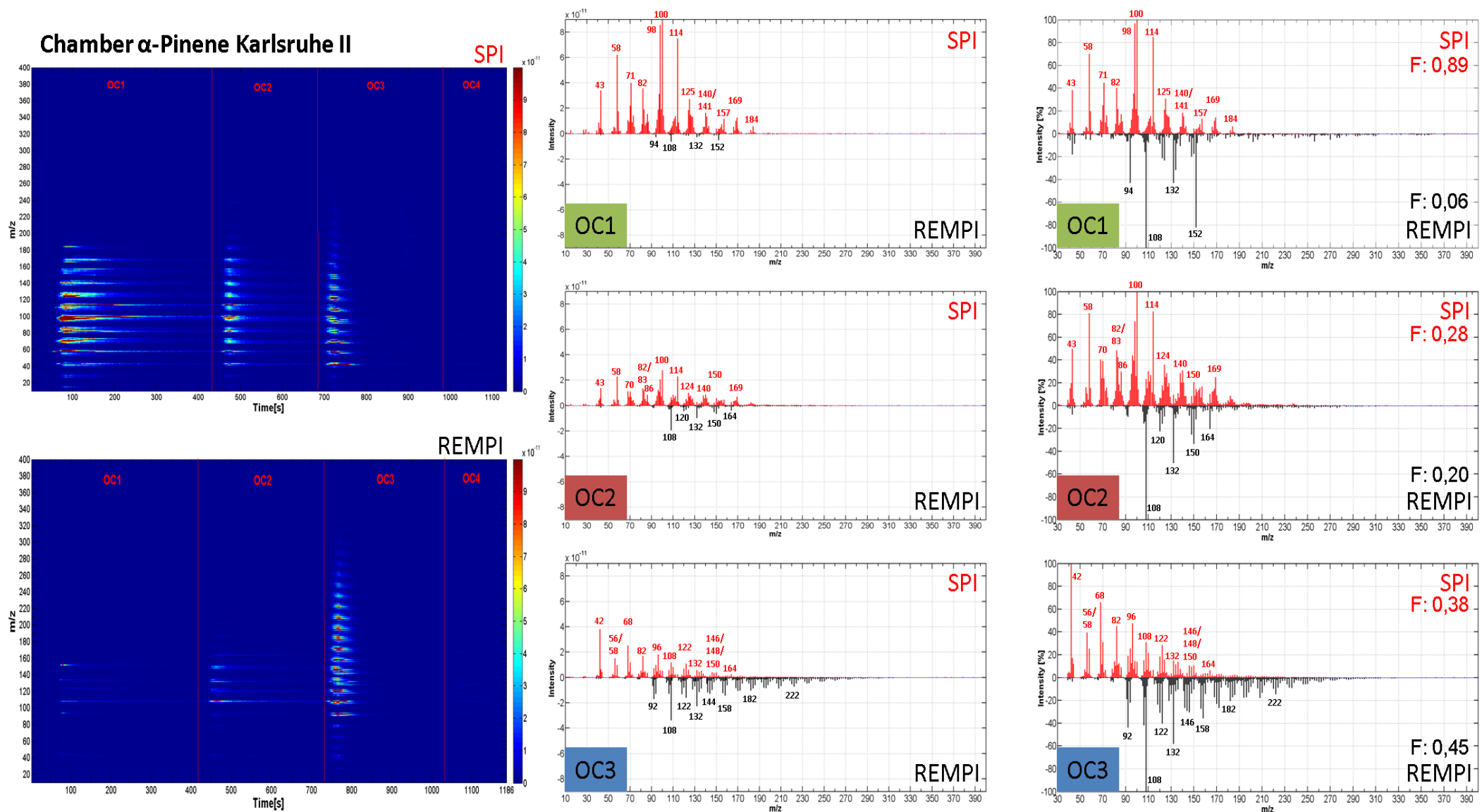


Figure S12: Two-dimensional mass spectrum of the course of signals (m/z) over the four OC-steps (left) for SPI (top) and REMPI (bottom), mass spectra for the first three OC-steps (SPI-red, REMPI-black) (middle), mass spectra for the first three OC-steps normalized to 100 % (right) of the chamber experiment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

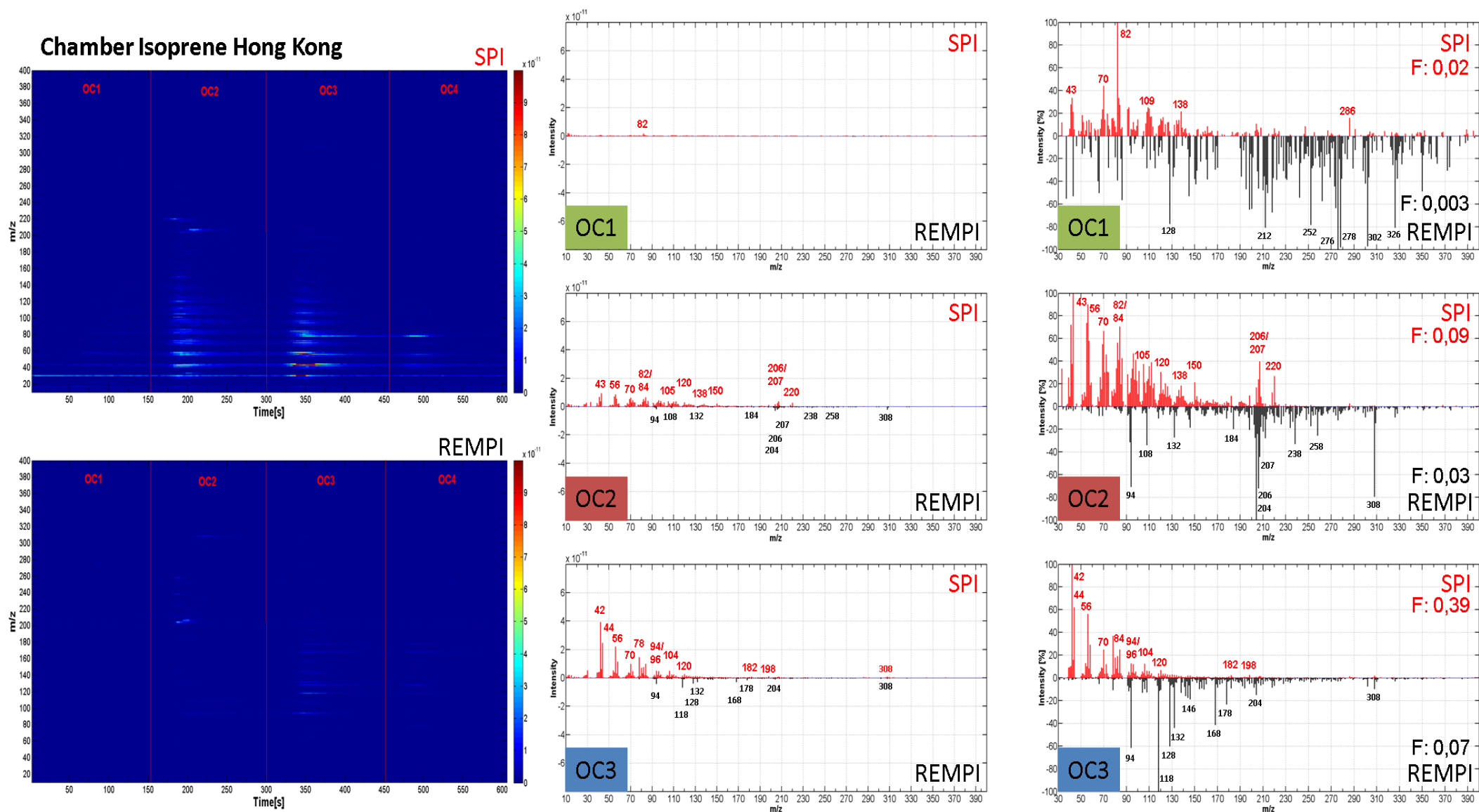


Figure S13: Two-dimensional mass spectrum of the course of signals (m/z) over the four OC-steps (left) for SPI (top) and REMPI (bottom), mass spectra for the first three OC-steps (SPI-red, REMPI-black) (middle), mass spectra for the first three OC-steps normalized to 100 % (right) of the chamber experiment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

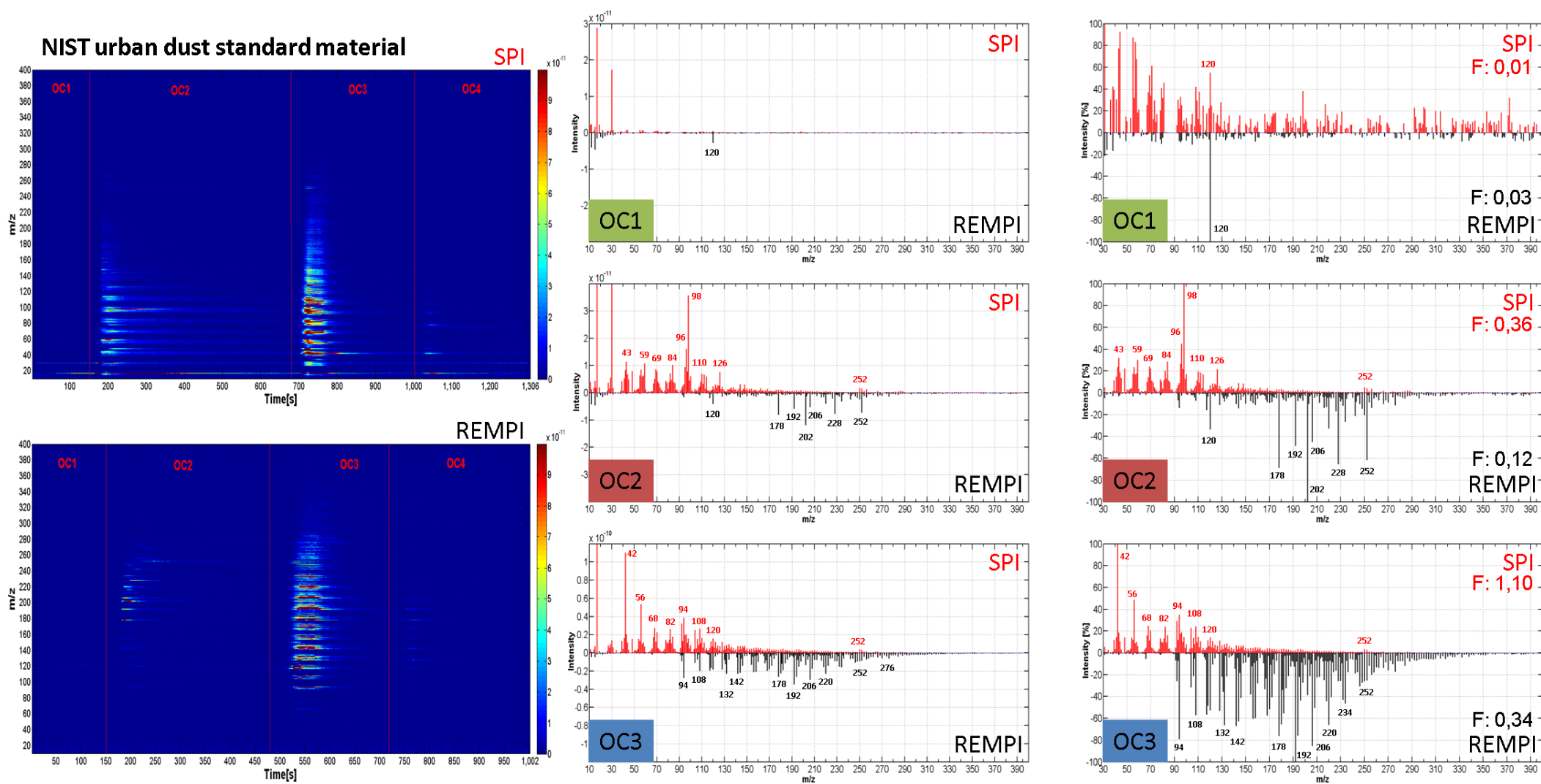


Figure S14: Two-dimensional mass spectrum of the course of signals (m/z) over the four OC-steps (left) for SPI (top) and REMPI (bottom), mass spectra for the first three OC-steps (SPI-red, REMPI-black) (middle), mass spectra for the first three OC-steps normalized to 100 % (right) of the NIST urban dust 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 vinyl 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	diethylfuran, 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	guaiaicol, 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	methylguaiaicol, 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	vinylguaiaicol, methyl-hydroxy-acetophenone, dimethylbenzoic acid, ...	-	-	-	-	++	++	+	-	-	-	-	-	-	-	+	-
152	ethylguaiaicol, vanillin, 3-oxo-pina ketone, ...	-	-	-	-	++	-	+	-	-	-	-	-	-	-	-	-
156	Dimethylnaphthalene, ...	-	+	-	++	-	-	-	+	-	+	-	+	-	+	-	+
157	?	-	-	-	-	-	-	-	-	-	-	-	-	++	-	+	-
158	nonanoic acid, naphthalenedione, methylnaphthol, ...	-	-	+	+	-	-	-	+	-	+	-	+	-	+	-	+
160	Heptanedioic acid, methyl-furyl-pyrazine, ...	-	-	-	-	-	-	-	+	-	-	+	-	-	-	-	-
162	Levoglucozan, nicotine, ...	-	-	-	-	-	-	+	-	-	-	-	-	-	-	-	-
163	?	-	-	-	-	-	-	-	-	-	+	-	-	-	-	-	-
164	Allylguaiacol, eugenol	-	-	-	-	++	++	+	-	-	-	-	-	+	-	+	-
166	propylguaiaicol, benzenedicarboxylic acid, ...	-	-	-	-	+	-	-	-	-	-	-	-	-	-	-	-
168	vanillic acid, trimethoxybenzene, ...	-	-	-	++	-	-	+	-	-	-	-	+	-	+	-	+
169	4-isopropenyl-1-methyl-1hydroxy-2-oxocyclohexane, ...	-	-	-	-	-	-	-	-	-	-	-	-	+	-	+	-
170	decanoic acid, dodecane, ...	-	-	++	+	-	-	-	-	+	+	-	+	-	+	-	+
172	decanoic acid, nonanoic acid methyl ester, ...	-	-	-	+	-	-	-	-	-	+	-	+	-	-	-	+
178	phenanthrene, anthracene, coniferyl aldehyde...	+	++	-	++	++	++	-	+	-	-	-	-	-	-	-	+
180	guaiaicyl 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	-	-	-	+	-	-	-	+	-	-	-	+	-	+	-	+

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, dehydroabiatic acid	-	++	-	-	+	+	+	+	-	-	-	-	-	-
302	pimaric acid, abiatic acid	-	++	-	-	+	-	+	-	-	-	-	-	-	-
308	?	-	-	-	-	-	-	-	-	-	-	+	-	-	-
310	ethyl oleate, docosane, ...	-	-	-	-	-	+	-	-	-	-	-	-	-	-
312	methylabietatetraenoate, eicosanoic acid, ethyl stearate, ...	-	-	-	-	+	++	+	+	-	-	-	-	-	-
322	?	-	-	-	-	-	+	-	-	-	-	-	-	-	-
324	Tricosane, docosanal, ...	-	-	-	-	-	+	-	-	-	-	-	-	-	-
326	?	-	-	-	-	-	+	-	-	-	-	-	-	-	-
340	docosanoic acid, tricosanol, ...	-	-	-	-	+	-	+	-	-	-	-	-	-	-
342	tetramethoxyisoflavone	-	-	-	-	-	+	-	-	-	-	-	-	-	-
344	deoxomatairesinol	-	-	-	-	+	+	-	-	-	-	-	-	-	-
368	tetracosanoic acid	-	-	-	-	-	-	-	-	-	-	-	-	-	-
374	?	-	-	-	-	-	-	-	+	-	-	-	-	-	-
384	deisopropyldehydroabiatic acid	-	-	-	-	-	+	-	-	-	-	-	-	-	-
388	?	-	-	-	-	-	-	-	+	-	-	-	-	-	-