Supplement of

A technique for rapid source apportionment applied to ambient organic aerosol measurements from the Thermal desorption Aerosol Gas chromatograph (TAG)

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1 Calculating TAG MDL of each mass spectrum ion peak from a field study

Figure 1S shows how to calculate MDL, using the TAG GC mass spectra from a field study. The data format used here is similar to the data format used for the binning data matrix for source apportionment in Figure 1. The only difference is that the columns of matrix are chromatography scan numbers instead of bin numbers, as in Figure 1. We want to retrieve the instrument's MDL from the raw data. The chromatogram (sample) number is represented by n, the chromatography scan number is b, and the m/z index is from 1 to m. For each chromatography scan number and m/z values, the standard deviation among all samples is calculated from each column of the top matrix in Figure 1S. Then we rearrange the standard deviation matrix (the second matrix in Figure 1S) to form a matrix with dimensions $b \times m$ (the third matrix in Figure 1S). The distribution of standard deviations for each column (each m/z) in the third matrix is expressed in the form of a histogram, the number found in certain chosen intervals of the standard deviation. If this histogram distribution of standard deviations is a normal distribution, then the mean of data points in each column of third matrix is assumed as MDL of ion peak; otherwise there is no MDL retrieved from the measurement data. The missing MDL is assigned an artificial value from linear interpolation with existing MDL retrieved from the measurement data. Note the assumption, that the histogram distribution of the standard deviations is a normal distribution, is very important. If this assumption is true, then the standard deviations calculated here are distributed in a small range, and the mean of these standard deviations in this small range is considered as the TAG MDL for each ion.

Table 1S: The correlation coefficient R of factors' time series of PMF six-factor solution between AMS and TAG-Bin. The TAG-Bin indicates the TAG binning method for chromatogram deconvolution. The bin width of 5 scan points without retention time shift correction is used here.   Retention time shift is not required when using the binning method for chromatogram deconvolution.

Pearson R		AMS 6 components					
		cLV-OOA	LOA-AC	LOA2	SV-OOA	MV-OOA	HOA
TAG-Bin 6 factors	F1	.75	.12	-.12	-.15	.71	-.10
	F2	.57	-.12	-.24	-.13	.77	.14
	F3	.08	.02	-.29	-.08	.20	.75
	F4	.44	-.15	-.28	-.12	.70	.22
	F5	.04	-.06	-.24	-.11	.19	.74
	F6	-.06	-.02	-.21	.45	.14	.26
Maximum		.75	.12	–	.45	.77	.75

Table 2S: The correlation coefficient R of factors' time series of PMF 20-factor solution between AMS and TAG-Bin. The TAG-Bin indicates the TAG binning method for chromatogram deconvolution. The bin width of 5 scan points without retention time shift correction is used here.

Pearson R		AMS 6 components					
		cLV-OOA	LOA-AC	LOA2	SV-OOA	MV-OOA	HOA
TAG-Bin 20 factors of deconvolution chromatogram	F1	0.66	0.13	-0.19	0	0.64	0.1
	F2	0.48	0.03	-0.33	0.05	0.61	0.31
	F3	0.73	0.4	-0.05	0.19	0.44	0.15
	F4	0.37	0.09	-0.17	0.02	0.5	0.25
	F5	0.49	0.05	-0.29	0.02	0.63	0.14
	F6	0.3	0.09	-0.33	0.03	0.52	0.36
	F7	0.66	0.22	-0.19	0.23	0.89	0.17
	F8	0.2	0	-0.34	0.13	0.33	0.7
	F9	0.29	0.06	-0.2	0.21	0.44	0.41
	F10	0.08	0.03	-0.31	-0.1	0.17	0.78
	F11	0.08	-0.01	-0.28	-0.1	0.19	0.77
	F12	0.02	0.01	-0.3	0.03	0.15	0.73
	F13	0.41	-0.02	-0.32	0.23	0.58	0.45
	F14	0.64	0.08	-0.24	0.28	0.77	0.14
	F15	0.18	0.16	-0.36	0.03	0.48	0.42
	F16	0.01	0.03	-0.26	0.12	0.12	0.79
	F17	0.08	0.09	-0.28	0.13	0.25	0.72
	F18	0.35	0.07	-0.1	0.02	0.4	0.2
	F19	0.45	0.48	-0.4	0.04	0.26	0.03
	F20	-0.01	0.05	-0.24	0.08	0.11	0.73

Table 3S: The correlation coefficient R of factors' time series of PMF 20-factor solution between AMS and TAG-Bin. The TAG-Bin indicates the TAG binning method for source apportionment. The bin width of 5 scan points with retention time shift correction is used here.

| Pearson R		AMS 6 components					
		cLV-OOA	LOA-AC	LOA2	SV-OOA	MV-OOA	HOA
TAG-Bin 20 factors of source apportionment	F1	0.34	0.02	-0.11	-0.18	0.39	-0.13
	F2	0.09	0.48	-0.1	0.22	-0.19	-0.13
	F3	0.04	-0.18	0.08	-0.17	0.07	-0.37
	F4	0.13	0.57	-0.22	0.35	-0.14	0.33
	F5	0.53	-0.15	-0.16	-0.3	0.71	-0.14
	F6	-0.03	-0.16	-0.07	0.18	0.18	-0.05
	F7	0.73	-0.1	-0.11	-0.47	0.76	-0.06
	F8	-0.27	-0.17	0.45	0.38	-0.34	-0.03
	F9	0.32	-0.09	-0.06	-0.04	0.45	-0.09
	F10	-0.27	-0.1	0.26	-0.22	-0.4	-0.16
	F11	0.14	-0.04	-0.22	-0.22	0.23	-0.14
	F12	-0.27	-0.22	0.32	0.32	-0.18	0.03
	F13	0.34	-0.12	-0.12	-0.3	0.55	0.02
	F14	0	0.23	0.07	-0.15	-0.13	0.11
	F15	0.04	0.07	-0.31	-0.04	0.12	0.52
	F16	-0.37	-0.14	-0.25	0.44	-0.13	0.16
	F17	0.16	-0.12	-0.23	-0.06	0.02	0.36
	F18	0.11	-0.14	0.06	0.09	0.19	0.11
	F19	-0.08	-0.17	-0.17	-0.03	0.18	-0.04
	F20	-0.16	-0.04	0.1	-0.08	-0.12	0.8
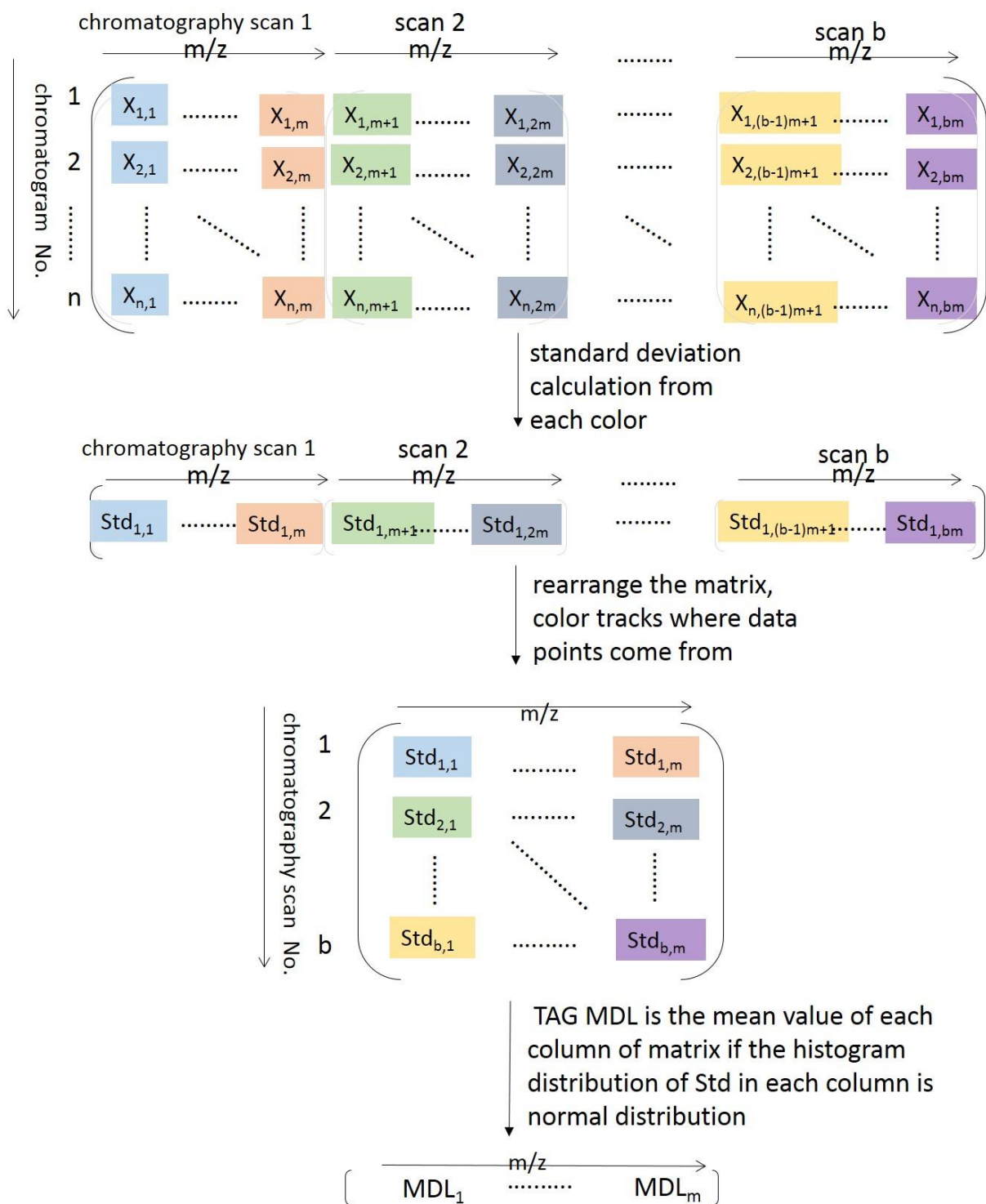
Figure 1S: Flow chart on how to calculate TAG MDL of each mass spectrum ion peak from a TAG field study dataset.
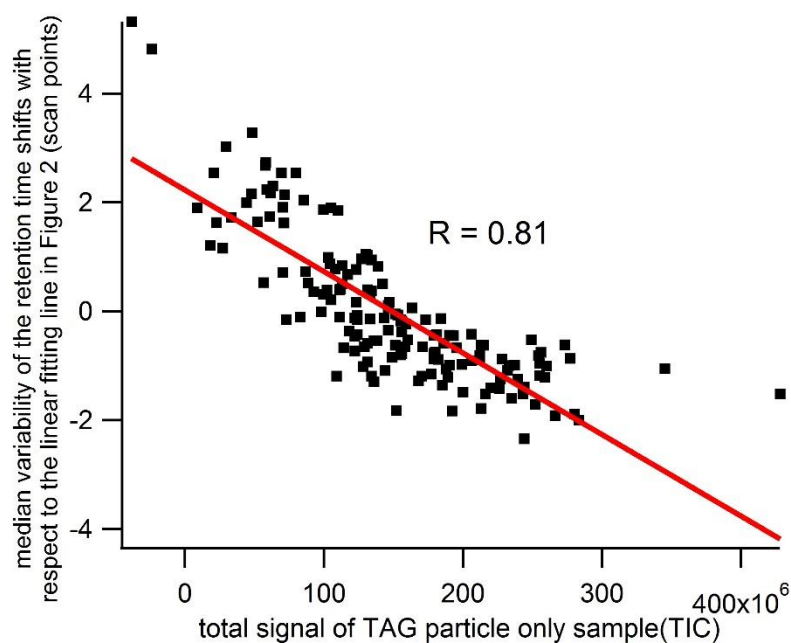
A.
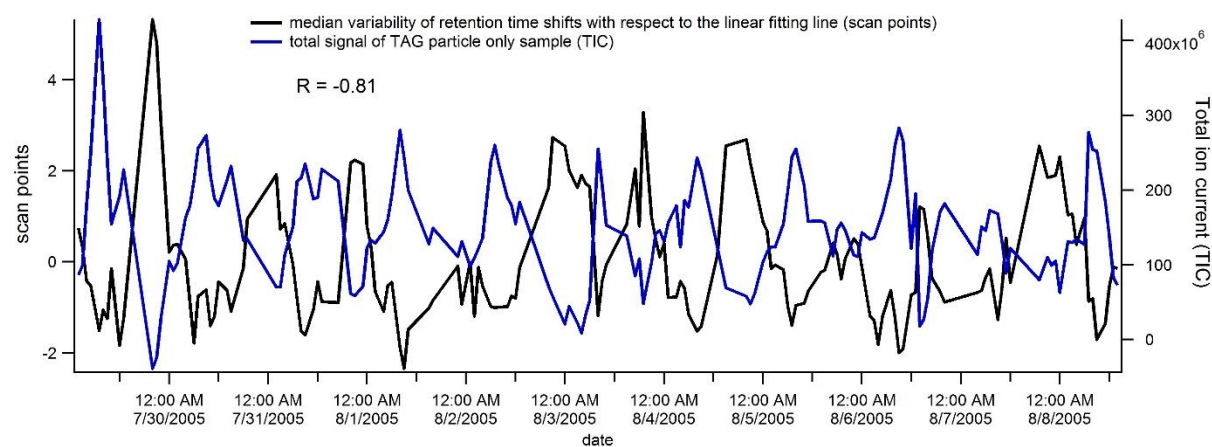
B.

Figure 2S: (A) Time variability of median variability of the retention time shifts with respect to the linear fitting line in Figure 2, and total signal of TAG particle only samples. (B) The scatter plot of time variability of median variability of the retention time shifts with respect to the linear fitting line in Figure 2 and total signal of TAG particle only samples.
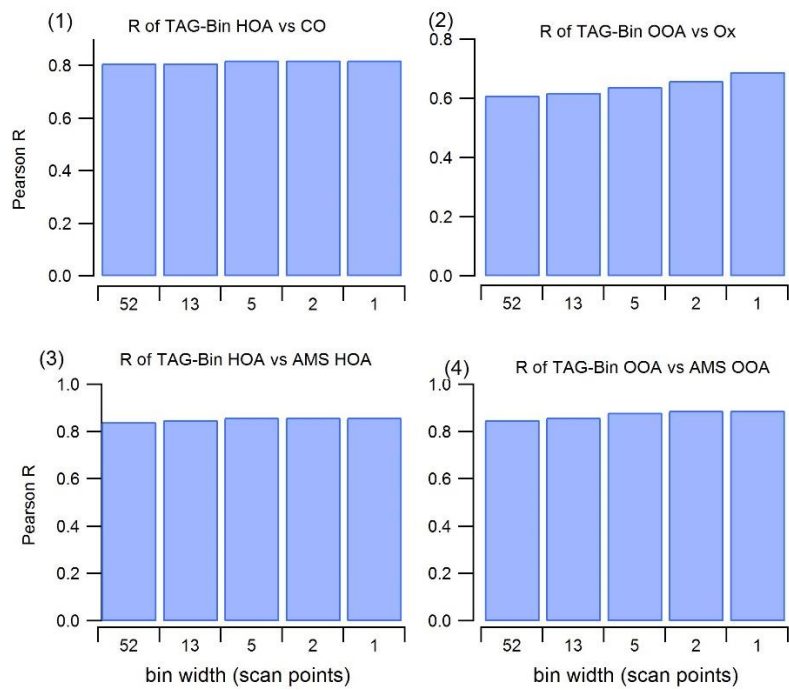
Figure 3S: Correlation coefficient R of TAG-Bin HOA (OOA) with retention time shift correction, (1-2) vs CO (Ox), and (3-4) vs AMS HOA (OOA) time series.
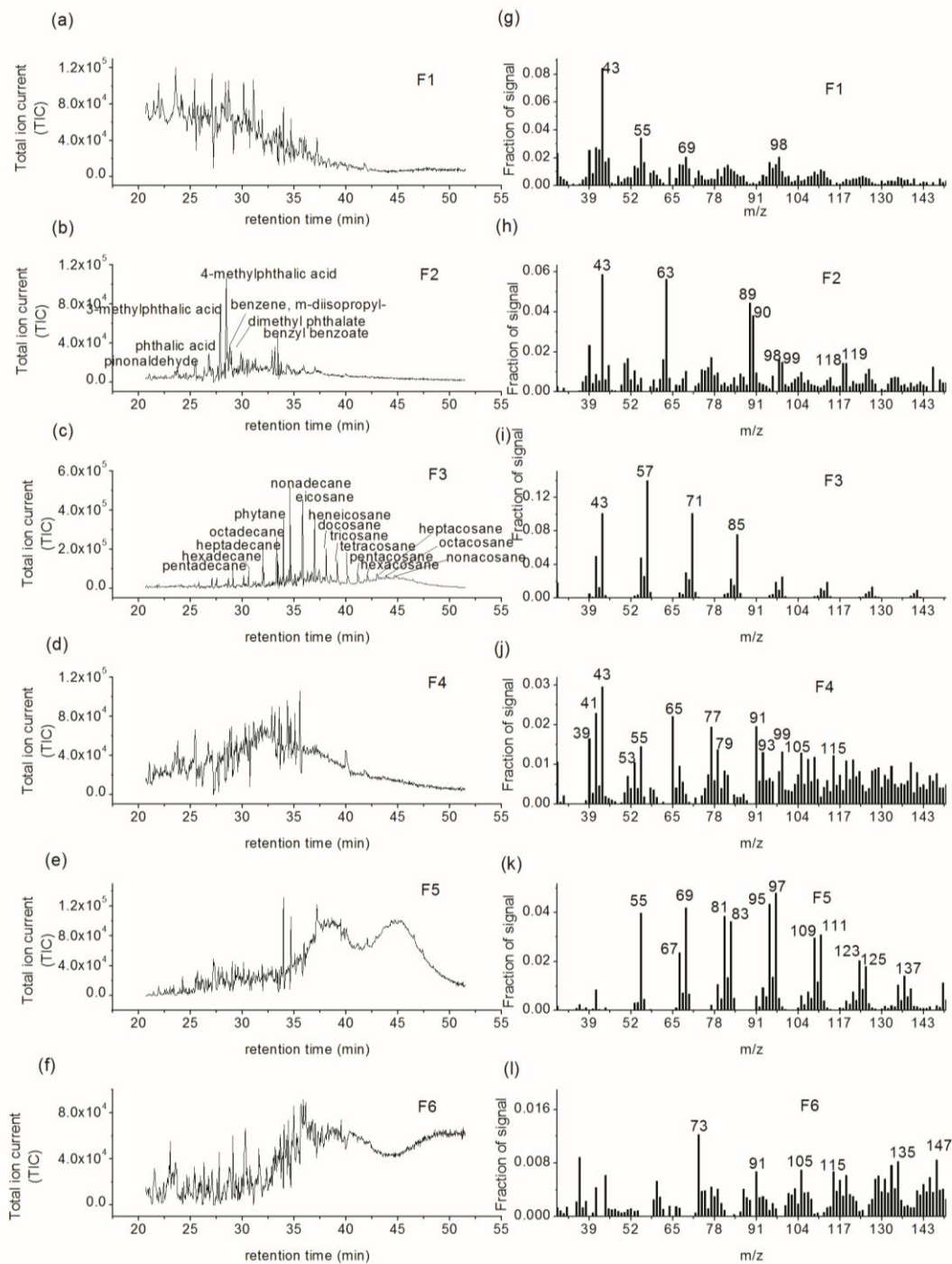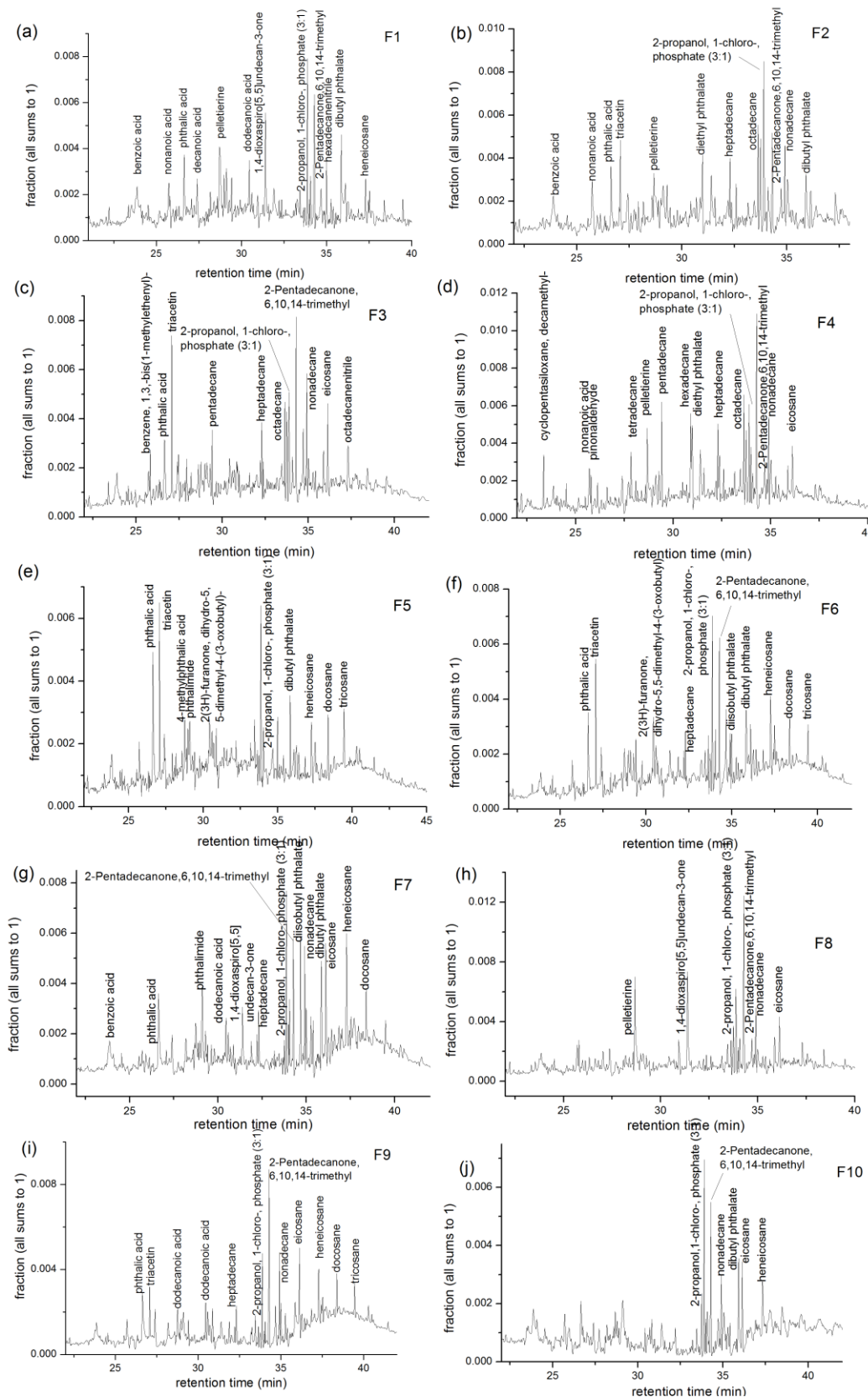
Figure 4S: The factor chromatograms and mass spectra of six-factor solution of TAG-Bin for the chromatogram deconvolution method. Bin widths of 5 scan points are used here.

(a)

F1

benzoic acid
nonanoic acid
phthalic acid
decanoic acid
pelletierine
dodecanoic acid
1,4-dioxaspiro[5,5]undecan-3-one
2-propanol, 1-chloro-, phosphate (3:1)
2-Pentadecanone,6,10,14-trimethyl
hexadecanenitrile
dibutyl phthalate
heneicosane

(b)

F2

2-propanol, 1-chloro-, phosphate (3:1)
2-Pentadecanone,6,10,14-trimethyl
benzoic acid
nonanoic acid
phthalic acid
triacetin
pelletierine
diethyl phthalate
heptadecane
octadecane
nonadecane
dibutyl phthalate

(c)

F3

2-Pentadecanone, 6,10,14-trimethyl
benzene, 1,3,-bis(1-methylethenyl)-
triacetin
2-propanol, 1-chloro-, phosphate (3:1)
phthalic acid
pentadecane
heptadecane
octadecane
nonadecane
eicosane
octadecanenitrile

(d)

F4

cyclopentasiloxane, decamethyl-
2-propanol, 1-chloro-, phosphate (3:1)
2-Pentadecanone,6,10,14-trimethyl
nonanoic acid
pinonaldehyde
tetradecane
pelletierine
pentadecane
hexadecane
diethyl phthalate
heptadecane
octadecane
nonadecane
eicosane

(e)

F5

phthalic acid
triacetin
phthalimide
4-methylphthalic acid
2(3H)-furanone, dihydro-5,
5-dimethyl-4-(3-oxobutyl)-
2-propanol, 1-chloro-, phosphate (3:1)
dibutyl phthalate
heneicosane
docosane
tricosane

(f)

F6

2-Pentadecanone, 6,10,14-trimethyl
phthalic acid
triacetin
2(3H)-furanone,
dihydro-5,5-dimethyl-4-(3-oxobutyl)
heptadecane
2-propanol, 1-chloro-, phosphate (3:1)
diisobutyl phthalate
dibutyl phthalate
heneicosane
docosane
tricosane

(g)

F7

2-Pentadecanone,6,10,14-trimethyl
2-propanol, 1-chloro-, phosphate (3:1)
diisobutyl phthalate
benzoic acid
phthalic acid
phthalimide
dodecanoic acid
1,4-dioxaspiro[5,5]
undecan-3-one
heptadecane
nonadecane
dibutyl phthalate
eicosane
heneicosane
docosane

(h)

F8

pelletierine
1,4-dioxaspiro[5,5]undecan-3-one
2-propanol, 1-chloro-, phosphate (3:1)
2-Pentadecanone,6,10,14-trimethyl
nonadecane
eicosane

(i)

F9

2-Pentadecanone,
6,10,14-trimethyl
phthalic acid
triacetin
dodecanoic acid
dodecanoic acid
heptadecane
2-propanol, 1-chloro-, phosphate (3:1)
nonadecane
eicosane
heneicosane
docosane
tricosane

(j)

F10

2-Pentadecanone,
6,10,14-trimethyl
2-propanol,1-chloro-, phosphate (3:1)
nonadecane
dibutyl phthalate
eicosane
heneicosane

Figure 5S: The chromatogram profiles of TAG-Bin 20-factor solution for source apportionment. The bin width of five scan points and retention time shift correction are used here.
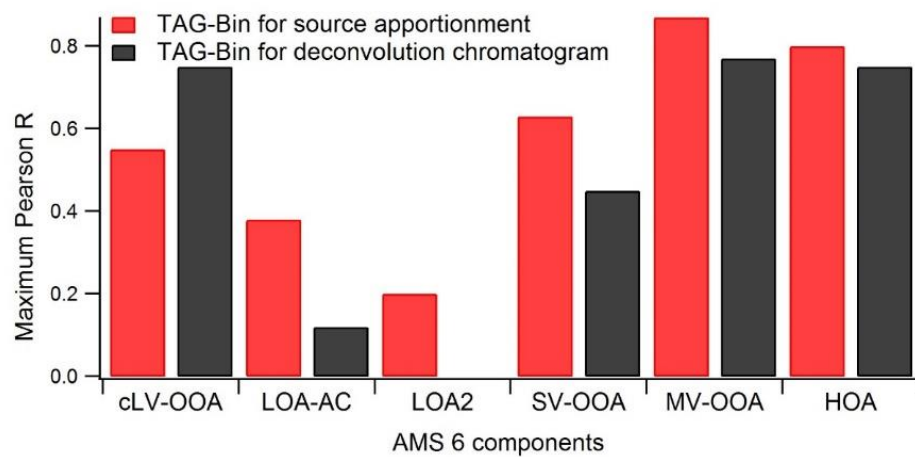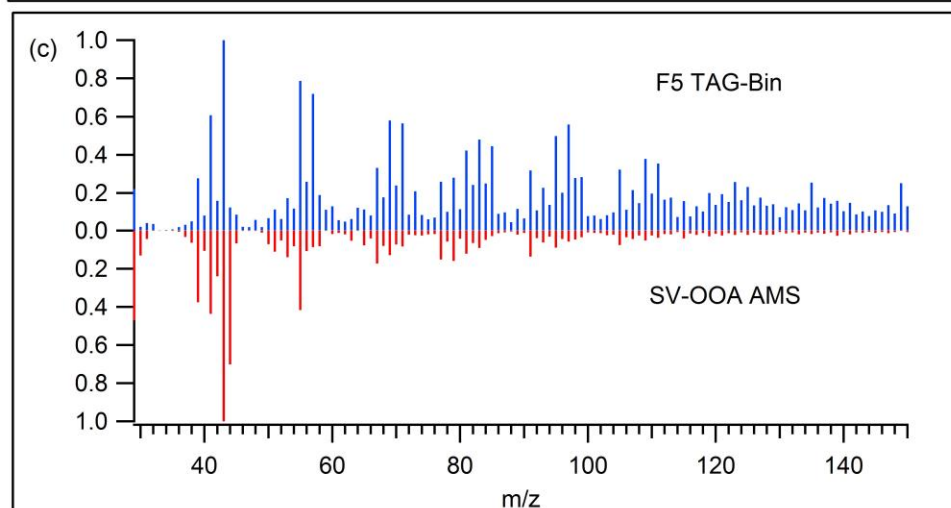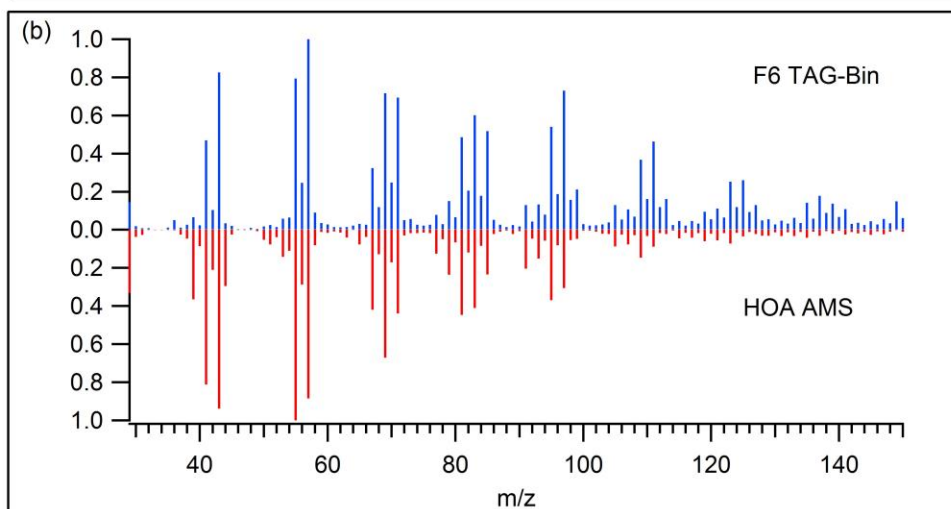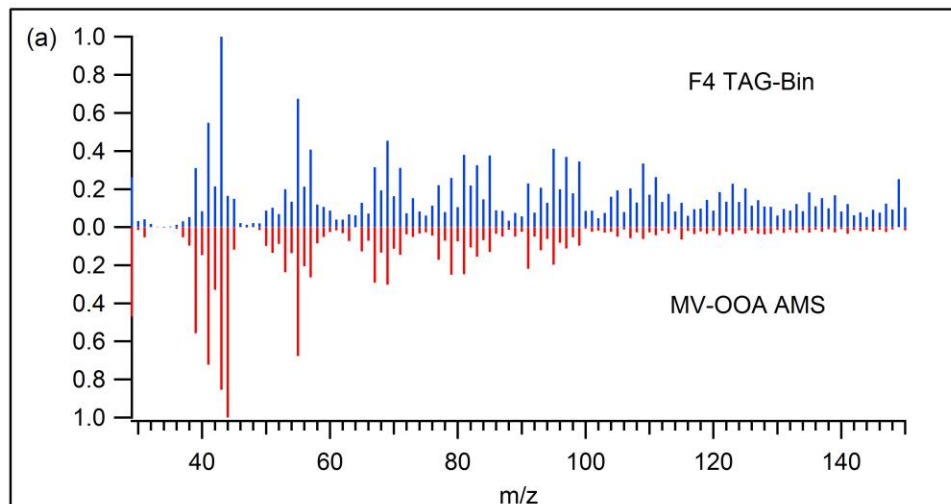
Figure 6S: The maximum correlation coefficient R from Table 2 and 1S for the comparison of TAG-Bin for source apportionment and deconvolution chromatogram.

(a) F4 TAG-Bin / MV-OOA AMS

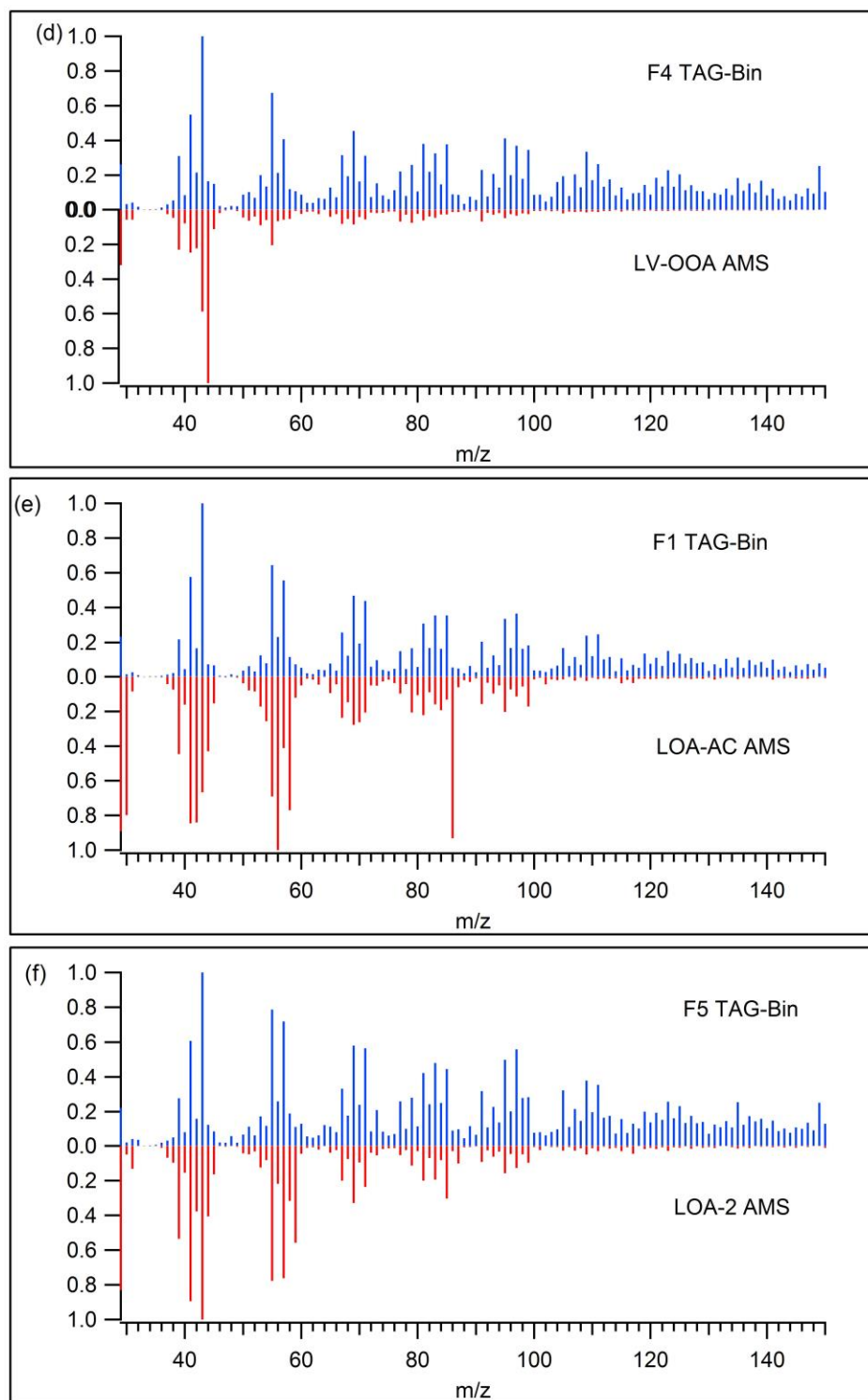(b) F6 TAG-Bin / HOA AMS

(c) F5 TAG-Bin / SV-OOA AMS

Figure 7S: The mass spectra comparison of the six pairs of TAG-Bin (assigned by factor number) vs. AMS – F4 vs. MV-OOA, F6 vs. HOA, F5 vs. SV-OOA, F4 vs. LV-OOA, F1 vs. LOA-AC, F5 vs. LOA2. Each pair shows the maximum Pearson R in Table 2. m/z is cut off at 150 to highlight smaller fragments. However, TAG has significant signal at m/z over 200.