Author comment in response to the comments provided by the Editor and Referee #2, second round of revision

We thank the Editor and Referee #2 for their effort in reading and commenting our manuscript carefully again and giving helpful feedback. In the following, we repeat the **referee's comments in bold typeface**, and give point-by-point answers in normal typeface; extracts from the *original manuscript are presented in red italic*, and from the *revised manuscript in blue italic*. Line numbers are referring to the updated manuscript version.

General Comments:

Dear Authors,

I received the reviews for your revised manuscript. Reviewer #2 still has some criticism how single mass spectrometer peaks are related to particle types (given below). As it is presented in the manuscript, I agree that this can be confusing and ambiguous.

Clearly, a specific particle type cannot be identified by a single mass peak. Looking at Schmidt et al. (2017) and Shen et al. (2018), several positive and negative peaks are applied to identify the particle type.

However, the text on page 7 (lines 258-272) states in several places that the focus is on single ions and either the fraction or relative intensity of a single ion is used for particle identification. This is somehow confusing.

In Fig. 5, bottom (c), several mass peaks are indicated for identification of the particle type. However, the correlation analysis shown in (a) and (b) focused on single ions (at least it appears like this)? As pointed out by the reviewer, a single mass peak is not sufficient, sometimes present in several different particle types, and thus renders analysis ambiguous.

Could you please elaborate on this point?

With kindest regards,

Daniel Knopf

Reviewer #2:

Overall, the authors have addressed my comments; however, I still disagree with their statements regarding Figure 5. Specifically, the authors have not addressed that single peaks often do not correlate to specific particle types. For example, in ALABAMA negative spectra, m/z 12 can be found in almost all of the particle types in Figure S9. The authors, however, interpret an ALABAMA anion with a high m/z 12 r_pos as "carbon," which the authors sometimes interpret as elemental carbon. Similarly, in the LAAPTOF positive spectra in Figure S10, many particle types contain large m/z 44 and 46 peaks, but Figure 5 suggests that these are mineral dust and sea spray, respectively. This reviewer suggests that this ambiguity makes this analysis much less useful that the authors suggest.

Perhaps more useful to this reviewer are the plots with black and pink markers in Figure S9. Here, the authors can correlate known particle types with INP, not just single peaks. This reviewer strongly suggests that the analysis in Figure 5 be revisited, and, if it remains in the paper, that the authors build a stronger case for assigning particles types to single m/z values (i.e., assigning colors to each m/z), or remove that analysis altogether.

We agree with the editor and the reviewer that single ion peaks cannot be used to identify specific particle types. We would like to point out that this is not the way we analyzed our data and realize that our explanation was not clear enough. We therefore changed the way our analysis is presented in the manuscript. Now, we first present the m/z correlation analysis (from previous Fig. 5, panel a and b) and turn this into Tab. 1. The assignment of ions to the m/z values and the use of selected ions as markers for particle types (formerly Fig. 5, panel c) is now presented separately in a new Tab. S1. As such we separate the discussion about the single ion correlation analysis and the ion assignment to m/z values and to particle types. From the new Tab. S1 it becomes clear that we are aware of the different possible ions contributing to one m/z and the occurrence of certain ions in several particle types.

Table1: Ranked correlation coefficients for [INP]$_{-31}$ and respective n_s (both determined > LOD) with m/z values for LAAPTOF (panel a) and ALABAMA (panel b), for method 1 and 2, respectively. The assignment of potential ions to m/z values can be found in the supporting information (Table S1).

(a) LAAPTOF																
	Method 1 cations								Method 1 anions							
	r_pos				r_neg				r_pos				r_neg			
Rank	m/z	r([INP]$_{-31}$)	m/z	r(n_s)	m/z	r([INP]$_{-31}$)	m/z	r(n_s)	m/z	r([INP]$_{-31}$)	m/z	r(n_s)	m/z	r([INP]$_{-31}$)	m/z	r(n_s)
1	46	0.51	56	0.36	29	-0.42	13	-0.30	60	0.59	60	0.39				
2	45	0.50	46	0.34					76	0.55	76	0.36				
3	44	0.47	96	0.34					77	0.53	35	0.35				
4	57	0.47	74	0.32					37	0.51	77	0.35				
5	56	0.46	57	0.31					35	0.49	72	0.32				
6	74	0.44	45	0.30					59	0.47	37	0.32				
7	96	0.43	44	0.30					120	0.46	120	0.32				
8	58	0.42	41	0.29					50	0.45	50	0.32				
9	75	0.42							43	0.44	16	0.31				
10	76	0.41							28	0.44						
11	81	0.37							16	0.44						
12	82	0.36							17	0.43						
13	83	0.35							72	0.43						
14									42	0.43						
15									36	0.41						
	Method 2 cations								Method 2 anions							
	r_pos				r_neg				r_pos				r_neg			
Rank	m/z	r([INP]$_{-31}$)	m/z	r(n_s)	m/z	r([INP]$_{-31}$)	m/z	r(n_s)	m/z	r([INP]$_{-31}$)	m/z	r(n_s)	m/z	r([INP]$_{-31}$)	m/z	r(n_s)
1	44	0.57	44	0.37	13	-0.37	30	-0.33	60	0.60	60	0.38				
2	46	0.50	56	0.33					76	0.55	35	0.36				
3	45	0.47	46	0.33					77	0.54	76	0.35				
4	56	0.46	96	0.32					37	0.52	77	0.34				
5	96	0.44	41	0.32					35	0.52	72	0.32				
6	75	0.43	74	0.30					36	0.47	120	0.31				
7	76	0.43							120	0.47	73	0.31				
8	74	0.43							59	0.46	19	0.30				
9	57	0.41							50	0.44						
10	81	0.41							72	0.44						
11	58	0.40							28	0.42						
12	82	0.38							43	0.42						
13	40	0.37							29	0.42						
14	83	0.37							73	0.409						

(b) ALABAMA

	Method 1 cations								Method 1 anions							
	r_pos				r_neg				r_pos				r_neg			
Rank	m/z	r([INP]$_{-31}$)	m/z	r(ns)	m/z	r([INP]$_{-31}$)	m/z	r(ns)	m/z	r([INP]$_{-31}$)	m/z	r(ns)	m/z	r([INP]$_{-31}$)	m/z	r(ns)
1	165	0.47	78	0.44					12	0.48	42	0.47	141	-0.53	97	-0.39
2	78	0.46	144	0.42					18	0.45	43	0.43	99	-0.51	195	-0.37
3	7	0.44	165	0.41					37	0.44	12	0.42	97	-0.49		
4	35	0.43	62	0.39					35	0.44	27	0.40	155	-0.46		
5	62	0.41	63	0.37					4	0.44	37	0.39	96	-0.45		
6	22	0.40	222	0.37					9	0.43	35	0.37	217	-0.42		
7	23	0.39	224	0.37					23	0.43	9	0.37	115	-0.40		
8	133	0.38	132	0.36					34	0.43	40	0.34	101	-0.40		
9	164	0.38	23	0.36					50	0.39						
10	144	0.37	151	0.36					3	0.39						
11	224	0.35	108	0.35												
12	132	0.35	202	0.35												
13	222	0.34	217	0.35												
14	118	0.34	240	0.34												
15	20	0.34	181	0.34												
16	151	0.34	118	0.34												
17			180	0.34												
18			223	0.33												
19			231	0.33												
20			213	0.33												
21			133	0.32												

	Method 2 cations								Method 2 anions							
	r_pos				r_neg				r_pos				r_neg			
Rank	m/z	r(INP)	m/z	r(ns)	m/z	r(INP)	m/z	r(ns)	m/z	r(INP)	m/z	r(ns)	m/z	r(INP)	m/z	r(ns)
1	60	0.61	60	0.55					76	0.54	42	0.40	155	-0.51	97	-0.36
2	51	0.61	132	0.52					12	0.50	76	0.39	97	-0.51	177	-0.35
3	24	0.61	39	0.47					35	0.49	12	0.38	141	-0.50	195	-0.34
4	12	0.57	78	0.44					37	0.46	9	0.37	106	-0.44		
5	62	0.57	63	0.44					19	0.45	43	0.37	99	-0.44		
6	36	0.57	84	0.44					32	0.44	35	0.34	233	-0.41		
7	23	0.55	108	0.43					18	0.44	78	0.34				
8	40	0.55	62	0.43					4	0.44	37	0.33				
9	78	0.54	36	0.42					77	0.44	19	0.33				
10	165	0.54	120	0.41					9	0.43						
11	84	0.53	240	0.39												
12	63	0.52	23	0.38												
13	132	0.52	91	0.38												
14	35	0.50	165	0.38												
15	67	0.49	24	0.38												
16	22	0.46	76	0.38												
17	133	0.45	41	0.37												
18	17	0.43	138	0.37												
19	120	0.43														

Table S1: Possible ions contributing to the best correlating m/z values from Tab. 1, along with their occurrence in different particle types and the use of selected ions as markers for certain particle types for ALABAMA and LAAPTOF, for cations (panel a) and anions (panel b).

(a)	cations	observed in these particle types				marker ions	
m/z	potential ions	mineral dust	sea spray	EC	sulfate containing	ALA	LAAP
7	Li^+	Li^+	-	-	-	🟧	
12	C_1^+, Mg^{2+}	Mg^{2+}	Mg^{2+}	C_1^+	C_1^+	⬛	
13	C_1H^+	-	-	-	-		
17	NH_3^+	-	-	-	-		
20	$^{40}Ca^{2+}$	$^{40}Ca^{2+}$	$^{40}Ca^{2+}$	-	-		
22	$^{44}Ca^{2+}$	$^{44}Ca^{2+}$	$^{44}Ca^{2+}$	-	-		
23	Na^+	Na^+	Na^+	Na^+	Na^+	🟦	
24	C_2^+, Mg^+	Mg^+	Mg^+	C_2^+	C_2^+		
29	$C_2H_5^+$, CHO^+, CH_2NH^+	-	-	-	-		
35	$NH_4NH_3^+$	-	-	-	-		
36	C_3^+	-	-	C_3^+	-	⬛	
39	$^{39}K^+$, $C_3H_3^+$	$^{39}K^+$	$^{39}K^+$	$^{39}K^+$	$^{39}K^+$		
40	$^{40}Ca^+$, MgO^+	$^{40}Ca^+$	$^{40}Ca^+$, MgO^+	-	-	🟧	🟧
41	$^{41}K^+$, $MgOH^+$, $Na(H_2O)^+$	$^{41}K^+$	$^{41}K^+$	$^{41}K^+$	$^{41}K^+$		
44	$^{44}Ca^+$, SiO^+	$^{44}Ca^+$, SiO^+	$^{44}Ca^+$	-	-		🟧
45	$COOH^+$, CHS^+, CH_3CHOH^+, $CH_3OCH_2^+$	-	-	-	-		
46	Na_2^+, $(CH_3)_2NH_2^+$, CH_2S^+	-	Na_2^+	-	-		🟦
51	V^+,$C_4H_3^+$	-	-	-	-		
56	CaO^+, Fe^+, Si_2^+, KOH^+	CaO^+, Fe^+, Si_2^+	CaO^+	-	KOH^+		🟧
57	$CaOH^+$,$C_4H_9^+$, $C_2O_2H^+$, $C_3H_5O^+$	$CaOH^+$	$CaOH^+$	-	-		🟧
58	$(CH_2)C_2H_5NH^+$	-	-	-	-		
60	C_5^+, AlO_2H^+	-	-	C_5^+	-	⬛	
62	Na_2O^+, $(CH_3)_2NHOH$	-	Na_2O^+	-	-	🟦	
63	Na_2OH^+, $C_5H_3^+$,Cu^+	-	Na_2OH^+	-	-	🟦	
67	VO^+, $CaAl^+$, $C_3H_3N_2^+$,$NaSiO^+$	-	-	-	-		
74	$C_3H_6O_2^+$, $(C_2H_5)_2NH_2^+$, $N(CH_3)_4^+$	-	-	-	-		
75	$CaCl^+$	$CaCl^+$	-	-	-		🟧
76	$(CH_3)_3NOH^+$	-	-	-	-		
78	K_2^+	-	K_2^+	-	-	🟦	
81	$Na_2{}^{35}Cl^+$	-	$Na_2{}^{35}Cl^+$	-	-		🟦
82	$CaCNO^+$, HBr^+	-	-	-	-		
83	$Na_2{}^{37}Cl^+$, VO_2^+,$CaAlO^+$	$CaAlO^+$	$Na_2{}^{37}Cl^+$	-	-		🟦
84	C_7^+, VHO_2^+, Si_3^+, $C_5NH_{10}^+$	-	-	C_7^+	-	⬛	
91	$C_7H_7^+$, $C_6H_3O^+$, $C_4H_8Cl^+$, $(CH_3)_2NHNO_2^+$	-	-	-	-		
96	Ca_2O^+,C_8^+	Ca_2O^+	-	C_8^+	-		🟧
108	C_9^+, $Na_2NO_3^+$	-	$Na_2NO_3^+$	C_9^+	-	⬛	
118	$(C_2H_5)_3NOH^+$	-	-	-	-		
120	C_{10}^+, $CaSO_3^+$, $MgSO_4^+$	$CaSO_3^+$, $MgSO_4^+$	-	C_{10}^+	-	⬛	
132	C_{11}^+	-	-	C_{11}^+	-	⬛	
133	Cs^+	Cs^+	-	-	-	🟧	
138	Ba^+	Ba^+	-	-	-	🟧	
144	C_{12}^+, $Fe_2O_2^+$	-	-	C_{12}^+	-	⬛	
151	$C_{12}H_7^+$	-	-	-	-		
164	K_3PO^+	-	-	-	-		
165	$Na_3SO_4^+$	-	$Na_3SO_4^+$	-	-	🟦	
180	C_{15}^+, $K_3PO_2^+$	-	-	C_{15}^+	-		
181	$KNa_2SO_4^+$	-	$KNa_2SO_4^+$	-	-		
202	-	-	-	-	-		
213	$K_3SO_4^+$	$K_3SO_4^+$	$K_3SO_4^+$	$K_3SO_4^+$	$K_3SO_4^+$		
217	-	-	-	-	-		
222	-	-	-	-	-		
223	-	-	-	-	-		
224	$(CaO)_4^+$,PbO^+	-	-	-	-		
231	-	-	-	-	-		
240	PbO_2^+	-	-	-	-		

(b)	**anions**	observed in these particle types				marker ions	
m/z	**potential ions**	**mineral dust**	**sea spray**	**EC**	**sulfate containing**	**ALA**	**LAAP**
3	-	-	-	-	-		
4	-	-	-	-	-		
9	-	-	-	-	-		
12	C_1^-	C_1^-	C_1^-	C_1^-	-	▨	
16	O^-	O^-	O^-	O^-	O^-		
17	OH^-	OH^-	OH^-	OH^-	OH^-		
18	-	-	-	-	-		
19	F^-	F^-	-	-	-		
23	Na^-	-	Na^-	-	-	🟦	
27	-	-	-	-	-		
28	CO^-, H_2CN^-	-	-	-	-		
29	-	-	-	-	-		
32	$^{32}S^-$, $^{16}O_2^-$	$^{16}O_2^-$	$^{16}O_2^-$		$^{32}S^-$, $^{16}O_2^-$		
34	$^{34}S^-$, $^{18}O_2^-$	$^{18}O_2^-$	$^{18}O_2^-$	-	$^{34}S^-$, $^{18}O_2^-$		
35	$^{35}Cl^-$	$^{35}Cl^-$	$^{35}Cl^-$	-	-	🟦	🟦
36	C_3^-	C_3^-	C_3^-	C_3^-	-		▨
37	$^{37}Cl^-$	$^{37}Cl^-$	$^{37}Cl^-$	-	-	🟦	🟦
40	-	-	-	-	-		
42	CNO^-	CNO^-	CNO^-	CNO^-	CNO^-		
43	AlO^-, $HCNO^-$	AlO^-, $HCNO^-$	$HCNO^-$	-	$HCNO^-$	🟧	🟧
50	C_3N^-	-	-	-	-		
60	SiO_2^-, C_5^-	SiO_2^-	-	C_5^-	-	🟧	🟧
72	C_6^-, FeO^-, $(CaO)O^-$	FeO^-, $(CaO)O^-$	-	C_6^-	-		▨
76	SiO_3^-, $AlO_2(OH)^-$	SiO_3^-, $AlO_2(OH)^-$	-	-	-	🟧	🟧
77	$HSiO_3^-$	$HSiO_3^-$	-	-	-	🟧	🟧
78	-	-	-	-	-		
96	SO_4^-, C_8^-	SO_4^-	SO_4^-	SO_4^-, C_8^-	SO_4^-	🟩	
97	$H^{32}SO_4^-$, C_8H^-, $H_2PO_4^-$	$H^{32}SO_4^-$	$H^{32}SO_4^-$	$H^{32}SO_4^-$	$H^{32}SO_4^-$	🟩	
99	$H^{34}SO_4^-$, SiO_3Na^-	$H^{34}SO_4^-$, SiO_3Na^-	$H^{34}SO_4^-$	$H^{34}SO_4^-$	$H^{34}SO_4^-$	🟩	
101	-	-	-	-	-		
106	-	-	-	-	-		
115	$HSO_4(H_2O)^-$, $Na(NO_2)_2^-$	-	$Na(NO_2)_2^-$	-	$HSO_4(H_2O)^-$		
120	C_{10}^-, $(SiO_2)_2^-$, $NaHSO_4^-$, $(NaCl)NO_3^-$	-	$NaHSO_4^-$, $(NaCl)NO_3^-$	C_{10}^-	-		🟦
141	$CHO_2SO_4^-$, $C_2H_5OSO_4^-$	-	-	-	$CHO_2SO_4^-$, $C_2H_5OSO_4^-$	🟩	
155	$C_2H_3O_2SO_4^-$, $C_3H_7OSO_4^-$	-	-	-	$C_2H_3O_2SO_4^-$, $C_3H_7OSO_4^-$	🟩	
177	$HSO_4SO_3^-$, $CH_3(HSO_3)_2^-$	$HSO_4SO_3^-$, $CH_3(HSO_3)_2^-$	$HSO_4SO_3^-$, $CH_3(HSO_3)_2^-$	-	$HSO_4SO_3^-$, $CH_3(HSO_3)_2^-$	🟩	
195	$H(HSO_4)_2^-$, $NH_4HSO_4SO_3^-$	$H(HSO_4)_2^-$, $NH_4HSO_4SO_3^-$	-	-	$H(HSO_4)_2^-$, $NH_4HSO_4SO_3^-$	🟩	
217	$MgH(SO_4)_2^-$, $Na(HSO_4)_2^-$, $NH4NaSO_4SO_3^-$	-	-	-	$MgH(SO_4)_2^-$, $Na(HSO_4)_2^-$, $NH4NaSO_4SO_3^-$	🟩	
233	$KSO_4H_2SO_4$-	-	-	-	$KSO_4H_2SO_4^-$	🟩	

Accordingly, we update the discussion about our reasoning to choose single ions for correlation coefficient analysis in the method section, lines 282 - 284:

The advantage of the ion correlation method is that it looks at the correlation of chemical substances rather than whole particle types, which means that fewer initial assumptions have to be made and a cross-particle type approach can be taken.

Furthermore, we update the explanation of our approach in the results, lines 412 - 427:

In the following, we present the results of those correlations for the possible particle types inferred from assigning ions to the observed m/z values. A selection of possible ions for each meaningful correlator m/z value listed in Tab. 1 and the assignment to possible particle types can be found in Tab. S1. The interpretation of particle components and particles types was achieved by the comparison with existing reference mass spectra from both mass spectrometers (see Figs. S9 and S10, panel a), as well as a m/z-to-m/z correlation analysis. The latter method provides information about which ions show a similar time series and thus can either represent isotopes of one element or different molecular fragments of the same original substance. Finally, single meaningful correlators were only assigned to a particle type if other meaningful correlators also indicated the same particle type and if this could be confirmed by both single particle mass spectrometers. When assigning ions to m/z values, it must be taken into account that different ions can be assigned to an integer m/z value, which in turn means that a single m/z value can be assigned to several particle types. This may result, for example, in two different ions *of the same m/z value having increased correlations with the INP variables and thus appearing for the same polarity and m/z value for different particle types. Moreover, we also investigate ions with negative correlation coefficients. Furthermore, it should be noted that several particle types can be mixed internally due to long range transport. Therefore, it would not be surprising to find the marker ions in almost all the particle types.. At the end of this section, we also discuss the differences between the two single particle mass spectrometers, and the correlation methods.*

We adjusted the descriptions in section 3.3.1 Sea spray (lines 429 - 433):

In the analysis of both instruments, we find that sea spray related ions have elevated correlation coefficients with both $[INP]_{-31}$ and n_s (Tab. 1, Tab. S1). The chlorine anions $^{35}Cl^-$ and $^{37}Cl^-$ as well as cations with m/z 46 (Na_2^+), 81 ($Na_2{}^{35}Cl^+$), 83 ($Na_2{}^{37}Cl^+$) in the LAAPTOF (Tab. 1, panel a) and $^{35}Cl^-$, $^{37}Cl^-$, 23 (Na^+), 62 (Na_2O^+), 63 (Na_2OH^+), 78 (K_2^+), 12 (Mg^{2+}), 108 ($Na_2NO_3^+$), 181 ($KNa_2SO_4^+$) and 165 ($Na_3SO_4^+$), in the ALABAMA show positive correlation coefficients (r) between 0.31 and 0.57 (Tab. 1, panel b).

In section 3.3.2 Mineral dust (lines 438 - 443):

Mineral dust (Tab. 1, Tab. S1) is certainly a particle type that is expected to act as an INP. In general, we find correlation coefficients between ions indicative of mineral dust with both $[INP]_{-31}$ and n_s in the range of 0.32 to 0.60.. For example, the cations m/z 44 (SiO^+), 56 (CaO^+), 57 ($CaOH^+$), 75 ($CaCl^+$) as well as the anions m/z 60 (SiO_2^-), 76 (SiO_3^-), and 77 ($HSiO_3^-$) appear in the LAAPTOF correlation table with correlation coefficients between 0.3 and 0.6, in the ALABAMA data set we find cations such as m/z 7 (Li^+), 12 (Mg^{2+}), 23 (Na^+), 24 (Mg^+), 39 (K^+), 41 (K^+), 40 (Ca^+), 133 (Cs^+), 138 (Ba^+) and anions with m/z 43 (AlO^+), 76 and 77 (SiO_3^- and $HSiO_3^-$) on the list with correlations coefficients above the threshold.

In particular, we address now the issue raised by the reviewer regarding elemental carbon in section 3.3.3 (lines 450 - 452):

However, it should be mentioned that C_1^- (m/z 12) in particular is not a unique feature for elemental carbon, but is also frequently observed in mass spectra of other particle types.

And update the description about the creation of time series of particle types in lines 523 - 532:

Similarly, we created a time series for sea spray also from LAAPTOF data, for mineral dust and for elemental carbon (ALABAMA and LAAPTOF), and for sulfate-containing particles (ALABAMA only) using the ions listed in Tab. 1, panel a and b and the color coded marker ions in Tab. S1 (bold marked). The signals at m/z +12, +24, +39, +41 were not considered for the sea spray and mineral dust time series, because these are very common signals across all particle types. The ions at m/z +12 and +24 can be attributed to both carbon and magnesium. Although m/z +12 clearly shows an increased intensity in the EC type compared to the other particle types listed, it is less clear for m/z +24. Therefore, m/z +24 was not used as a marker for any of the particle types. The signals at m/z +39 and +41 are mainly indicative of potassium, which is a common component of mass spectra due to its ionization energy. For example, potassium is occurring in biomass burning particles (e.g., Silva et al., 1999) but is also present in sea water and in mineral dust. Thus, the ions m/z +39 and +41 were not considered here in the analysis.

Our results are now summarized in the conclusions accordingly in lines 739 - 743:

Such correlation analysis allows to include also small ion signals which still might represent chemical substances rather than whole particle types, such that fewer assumptions have to be made initially, allowing a cross-particle type approach. Based on our analyses, sodium-, calcium-, silicon- and chlorine-containing ions in particular showed increased correlation with $[INP]_{-31}$ and n_s. We concluded that these ions originate from substances that are essentially due to mineral dust and sea salt particles.

References

Silva, P. J., Liu, D.-Y., Noble, C. A., and Prather, K. A.: Size and Chemical Characterization of Individual Particles Resulting from Biomass Burning of Local Southern California Species, Environmental Science & Technology, 33, 3068-3076, 10.1021/es980544p, 1999.