Supplemental information for:

Formation of Particulate Matter from the Oxidation of Evaporated Hydraulic Fracturing Wastewater

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S1. Additional details on sample origin, collection and storage

All samples were collected from the Wolfcamp shale formation in the Permian Basin: Samples 1-6 were collected in Ward County (Wolfcamp A Geology Zone); samples 7-9 were collected in Reeves County (Wolfcamp B Geology Zone) and samples 10-12 were collected in Reeves County (Wolfcamp A Geology Zone). All samples were collected from wells that produced both oil and gas during the flowback process before the first state reported well test date. Samples 1-3 were collected 5 days after fracturing, samples 4-6 were collected 8 days after fracturing the well, samples 7-9 were collected 11 days after fracturing the well and samples 10-12 were collected 1 day after fracturing the well. Samples 1, 4, 7 and 10 were collected directly from a separator during flowback; the other samples were collected from open-top flowback tanks. The samples were collected in cleaned amber 8 oz bottles purchased from Fisher Scientific (manufacturer: Qorpak™ GLC01948); bottles were filled completely and capped immediately

after collection. The bottles were shipped via Fedex first to Sugarland, TX and then to Austin, TX. Samples were stored in the amber bottles at room temperature.

S2. TVC measurement comparison, 1 year apart

Table S1 shows TVC measurements taken of all samples 1 year apart. Overall the data show that TVC did decrease over time; the reason for an increase observed in sample 12 is unclear. The 2015 TVC measurement of sample 4 was conducted in triplicate and resulted in measurements of 109.1, 116.2, and 103.0. Thus, observed changes in TVC content over time cannot be explained by measurement uncertainty / variability.

Table S1. Comparison of TVC measurements taken 1 year apart. Units are in mgC L^{-1}

	2015	2016	% decrease
sample 1	89.2	41.8	53%
sample 2	27.3	23.2	15%
sample 3	1.0	0.0	100%
sample 4	103.0	91.6	11%
sample 5	0.0	0.0	0%
sample 6	21.8	14.8	32%
sample 7	58.2	39.7	32%
sample 8	52.4	38.2	27%
sample 9	114.5	42.8	63%
sample 10	24.2	20.6	15%
sample 11	28.5	19.7	31%
sample 12	10.9	19.4	-79%

S3. Molecular formulae of most abundant ions identified in gas and particle phases

Table S2 below lists the 20 most abundant ions identified in the gas and particle phases during Expt. 1 as summarized in Figure 2. Molecules are ionized by H^+, H_3O^+ or H_3O^+ - water clusters. The ion formulae provided in Table S2 are as measured: the molecular formulae of the analytes are ambiguous to within multiples of H_2O. Double bond equivalency (DBE) is calculated assuming H^+ - ionization. However, since the identity of the reagent cluster is unknown, DBE is not discussed here or in the main text, and the discussion in the main text is focused on carbon number.

The~~Most~~ time series of most gas-phase species exhibit a monotonic increase for the duration of the photo-oxidation period shown in Figure 2. One ion ($C_6H_9O_2$) exhibits increases quickly and then decreases. We speculate that this trend is due to the formation of dimers from this C6 compound, as we detected several C12 compounds in the particle phase, as well as an overall indication of the importance of oligomerization reactions.

Table S2: Molecular formulae and double bond equivalency (DBE) of major ions shown in Figure 2

Gas phase (Fig 2a)	DBE		Particle phase (Fig 2b)	DBE
C5H9O2+	2		C11H19O8+	3
C5H9O3+	2		C12H21O8+	3
C6H9O2+	3		C12H22NO10+	3
C6H11O+	2		C13H24NO5+	3
C6H11O2+	2		C14H17O5+	7
C6H11O3+	2		C14H24NO5+	4

Gas phase (Fig 2a)	DBE		Particle phase (Fig 2b)	DBE
C7H13O+	2		C14H25O8+	3
C7H13O2+	2		C14H26NO9+	3
C8H13O2+	3		C14H28NO9+	2
C8H13O3+	3		C14H30NO9+	1
C8H15O+	2		C15H19O6+	7
C8H15O2+	2		C15H30NO9+	2
C9H15O2+	3		C16H29O8+	3
C9H17O+	2		C16H30NO10+	3
C9H17O2+	2		C17H23O4+	7
C10H17O2+	3		C18H28NO7+	6
C10H19O+	2		C19H27O6+	7
C10H19O2+	2		C19H28NO7+	7
C11H21O+	2		C20H27O5+	8
C11H21O2+	2		C23H25O2+	12

S4. NO_x and HONO concentrations at the beginning and end of each experiment

Table S3 lists NO_x concentrations at the beginning and end of each experiment, and an estimate of HONO concentrations at the beginning of every experiment. Total NO_x decreased by approximately 40% in each experiment due to the formation of HNO_3 and organic nitrates. High levels of NO_x were used in all experiments – the effects of these high NO_x levels on predicted ammonium nitrate formation are evaluated via box modeling as discussed in the main text.

Table S3. NO_x and HONO concentrations at the beginning and end of each experiment

Exp. #	$[NO_x]_0$ (ppb)	$[NO]_0$ (ppb)	$[NO_2]_0$ (ppb)	*$[HONO]_0$ (ppb)	$[NO_x]_f$ (ppb)	$[NO_x]_f$ - $[NO_x]_0$
1	744	160	146	438	517	39%
2	411	100	80	231	291	39%
3	457	47	44	366	317	34%
4	754	96	88	570	507	38%
5	642	126	125	391	449	37%
6	732	114	114	504	478	41%
7	351	38	32	281	228	39%
8	790	58	95	637	522	37%
9	493	63	78	352	330	38%
10	440	143	97	200	320	40%
11	210	18	13	179	137	38%
12	818	136	142	540	569	37%

* estimated using the difference of initial NO_2 measured by the chemiluminescent NOx monitor and the CAPS NO_2 monitor