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MEMORANDUM

TO: TOWN BOARD
FROM: AIR QUALITY REVIEW COMMITTEE; PETER DUDA, CHAIRMAN
SUBJECT: **IN-DEPTH ANALYSIS OF PHASE II TRC TESTING DATA**
DATE: MAY 22, 2018
CC:

Tracing the impact of Aluf's emissions on surrounding neighborhoods by linking area and rooftop data

This report looks in depth at chemical data from TRC's Phase II area sampling conducted in January and February and its rooftop emissions (odor) sampling of 3/19/18.

Findings:

1. We can draw meaningful connections between Phase II area and rooftop measurements for compounds that were measured in both campaigns.
2. There is good evidence from this combined approach that area levels of four compounds measured in Phase II – Cyclohexane, Ethanol, Ethyl Acetate, and Isopropyl Alcohol – were impacted by emissions from Aluf.
3. Many compounds are much higher in Aluf emissions than in ambient air.
4. Aluf emissions from stacks with carbon filter treatment are not noticably lower than emissions from untreated vents and blowers. The 3/19/18 rooftop data indicates that the carbon filter treatment on the stacks is not effective.
5. There are many odorous compounds released by Aluf.
6. It is very unfortunate that Acrolein was not measured quantitatively in the 3/19/18 rooftop emissions samples. Acrolein exceed the AGC in at least 83% of the Phase II area samples. Acrolein's co-variance with Isopropyl Alcohol in Phase II - a chemical whose area levels appear to have been impacted by Aluf - suggests that area Acrolein levels may also be impacted by Aluf.

Caveats:

1. Some of these findings are weakened because the rooftop and Phase II samples were snapshots of different points in time. We have to assume that factory emissions caught on 3/19/18 were representative of emissions during Phase II. But we really don't know this.

2. As always, conclusions from TRC's sampling are weakened by the lack of QC data – blanks, duplicates, and background samples.

Still to do:

It is worthwhile to do these things, which I will try to get to:

1. Get a list of all the AGCs of the compounds in question. I believe Acrolein is the one most likely to be in exceedence but it's good to check.
2. Get a list of odor thresholds of all the odorous chemicals seen on the rooftop.
3. Investigate spatial variability of Phase I (late summer 2017) data. See if it's similar to Phase II – if there is a consistent story.
4. Check the chemical modeling in TRC's Odor Report (rooftop) to see if calculated area impacts of the four compounds they investigated (Benzene, Ethylbenzene, Hexane, and Xylene) compare to area concentrations actually measured in Phase II.

1. Possible Aluf impacts seen in Phase II sampling.

We note that there were no odor complaints during any of the Phase II sampling periods. Nevertheless, there are two pieces evidence that some of these measurements were impacted by Aluf emissions. I will go over these two here and then relate them to the rooftop data.

1A. 2/1/18 elevated levels at Murphy Court. Phase II featured three sets of four samples taken simultaneously at different locations around Aluf. The 2/1/18 Murphy Court sample is notable because levels of several compounds were much higher than the other 2/1/18 samples. Also, weather records show that there was a gentle south wind for much of this sampling period, which is ideal for bringing emissions to this site. Table 1 shows these elevated levels. In this table, a ratio of >1 means the compound is elevated at Murphy Court, while a ratio <1 means the other sites are elevated relative to Murphy Court. These are all the Phase II compounds that were detectable.

Table 1: Elevated levels on 2/1/18 at Murphy Court

Ratio of Murphy Court to average of other three sites on 2/1/18 (enrichment factor)

Ethyl Acetate	24.4	Tetrachloroethylene	1.8
Cyclohexane	23.8	Benzene	1.4
Methylene Chloride	13.0	2-Butanone (MEK)	1.3
Hexane	7.8	1,3-Butadiene	1.3
Ethanol	6.7	2-Hexanone (MBK)	1.2
Toluene	3.1	Chloromethane	1.1
Styrene	2.6	Trichlorofluoromethane (Freon 11)	1.1
Acetone	2.5	Carbon Tetrachloride	1.1
1,2,4-Trimethylbenzene	2.4	Dichlorodifluoromethane (Freon 12)	1.0
o-Xylene	2.4	Acrolein	1.0
Heptane	2.4	1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	1.0
m&p-Xylene	2.3	Chloroform	0.8
Ethylbenzene	2.2		
Isopropanol	2.2		

The compounds most highly elevated in this spike are Ethyl Acetate, Cyclohexane, Methylene Chloride, Hexane, and Ethanol (enrichment factors 6.7 – 24.4). Modestly elevated compounds (enrichment factors of 1.8 – 3.1) include Toluene and other aromatics, Styrene, Acetone, Heptane, Isopropanol, and Tetrachloroethylene. Barely or non-elevated compounds include the freons, other Chlorinated compounds, two ketones, 1,3-Butadiene, Benzene, and Acrolein.

The interpretation here is that the highly elevated compounds were much higher in factory emissions 2/1/18 than ambient air, the modestly elevated ones somewhat higher, and non-elevated ones not higher by much or at all.

One thing to note here is that Acrolein was not elevated, indicating that it was not released by the factory in this event.

Below I will compare these observations to the rooftop measurement, which bolsters the conclusion that the elevated compounds noted here come from the factory.

1B. Spatial Variablity in Phase II (and Phase I) as an indicator of factory emissions.

I looked as spatial variability in phase II with the following logic: Compounds with no source or sink in the study area should show LOW spatial variablity. Compounds with a source or sink in the study are should show HIGHER spatial variability. By “spatial variability” I mean how different from each other are measurements taken at the same time at different locations. Since Phase II consisted of three sets of four simultaneous measurements this analysis is possible.

I characterized spatial variability by taking the average of the percent relative standard deviation (%RSD – the standard deviation divided by the average) of each 24-hour set of four measurments. This is the

average %RSD. These results are shown in Table 2A (highest spatial variability) and 2B (lowest). Compounds with intermediate variability are not shown.

Compounds with highest spatial variability in Phase II are the five with highest enrichment on 2/1/18 at Murphy Court (Ethyl Acetate, Cyclohexane, Methylene Chloride, Hexane, and Ethanol – shown in yellow) and four others – Chloroform, 2-Hexanone (MBK), Isopropanol, and Acrolein, shown in red.

Table 2A: High Spatial Variablity, Phase II

compound	Average %RSD
Acrolein	47%
Hexane	48%
Ethanol	50%
Methylene Chloride	65%
Cyclohexane	69%
Isopropanol	72%
2-Hexanone (MBK)	75%
Chloroform	86%
Ethyl Acetate	93%

Table 2B: Low Spatial Variability. Phase II

compound	Average %RSD
Trichlorofluoromethane (Freon 11)	4%
Carbon Tetrachloride	5%
Chloromethane	5%
Dichlorodifluoromethane (Freon 12)	6%
Benzene	12%

In addition to sharing high spatial variability, the four compounds in red also correlate reasonably well with one another over the Phase II sampling (R generally > 0.6), and do not correlate well with any other compounds. A possible interpretation of these observations is that the four compounds in red were co-released from Aluf at various times (but not 2/1/18), and the other set (yellow) was co-released specifically on 2/1/18. It may be these two sets of compounds come from different processes. Again, the rooftop data (below) strengthens the conclusion that at least Isopropanol comes from the factory.

The low spatial variability of the freons is expected and gives confidence that this data is corrected. These compounds are well-mixed in the air (they were released decades ago) and thus the same at each sampling location.

2. Observations from Rooftop Sampling of 3/19

TRC's sampling of 3/19/18 was primarily targeted at testing odors. However, they did analyze air concentrations of a number of compounds from six points on the rooftop. This suite of analytes was different for Phase II, though there is some overlap.

Table 3 shows the rooftop data of all compounds in common with the Phase II data set, as well as other compounds with high variablity among the six rooftop sampling locations. (Compounds with low variability or below the detection limit were not included here.) In addition, for the compounds in common between the two sampling efforts, the Phase II median value is included as an estimate for ambient concentration (concentration in the air coming into the factory). Ambient concentrations were not measured 3/19/18, but an estimate of them is useful to understand how factory emissions compare to ambient air and thus how much of an impact the emissions could have.

Several points are apparent:

1. Levels in exhaust air measured on the roof are much higher than ambient, by a factor of as high as 700.
2. Levels in the six rooftop sampling points vary widely, indicating that a) the different processes exhausted at the six points produce different emissions, or b) the factory's emissions over the course of the day (I believe the rooftop locations were done sequentially, not simultaneously) varied widely. Probably it's the former.
3. We were told that the exhaust from Stacks 2, 4, and 5 was treated, and exhaust from the other exhaust sampling ports was not treated. However, the levels from the stacks are not obviously lower than at the other locations – in fact, Stack 2 levels are often highest. Thus it appears the air treatment was not effective.

As in the area sampling, high spatial variability among the six sites on the roof indicates that the source is the factory, not the inlet air into the factory.

Five of the nine compounds ID'd in Phase II as being possibly from Aluf (Table 2A, pink & yellow). Four of those (Cyclohexane, Ethanol, Ethyl Acetate, and Isopropyl Alcohol) were both elevated above background and highly variable on the rooftop, supporting that conclusion. Hexane was elevated above background, but not as dramatically as the others, nor was it highly variable.

Because there are two lines of evidence (Phase II and rooftop), we can be more confident saying that Aluf emissions of these four chemicals – Cyclohexane, Ethanol, Ethyl Acetate, and Isopropyl Alcohol – impact the ambient area in the neighborhood around the factory.

Conversely, Benzene did not vary much spatially in Phase II, nor was it highly variable or elevated on the roof. Based on these data, Benzene from Aluf has less impact on ambient levels than the other compounds do.

Of course, these conclusions are tempered by the fact that they are based on a few discrete sampling events. It may be that Aluf releases Benzene at other times or does not release Ethyl Acetate at other times.

Table 3: Rooftop data, 3/19/18, selected compounds

compound	median phase II ppbV	rooftop ppbV ->	#5 stack	stack #2	HB-4	stack 4	WF-1	HDF 3
cyclohexane	0.1		62	15	2.5	0.5	7.3	0.5
Styrene	0.0		0.3	0.3	0.5	0.5	0.3	0.5
Acetone	4.1		36	59	43	146	77	42
benzene	0.3		2.3	1.5	1.2	2.7	1.6	0.5
2-butanone (MBK)	0.5		53	1.8	13	62	0.5	0.5
Ethanol	7.2		46	21	80	48	69	22
ethyl acetate	0.3		206	2	64	14	3.6	0.5
ethyl benzene	0.1		3	2.9	3.1	2.4	3.3	1.3
hexane	0.2		2.3	1.5	1.2	2.7	1.6	0.5
isopropyl alcohol	1.2		900	65	23	64	9.7	4.9
Toluene	0.5		20	16	17	9.6	11	6.2
m-xylene	0.2		2.9	4.3	2.4	1.8	3.1	1
o,p-xylene	0.1		9.2	9.7	9.8	7.5	11	5.5
Heptane	0.1		0.1	4.4	4.6	0.5	0.5	0.5
methyl butane			35	54	179	46	2.5	14
pentane			34	56	193	226	14	21
2,3,4-trimethyl pentane			128	4.6	0.5	0.5	1.9	0.5
2,2,5-trimethyl hexane			261	0.5	0.5	0.5	0.5	0.5
Octane			0.5	0.5	0.5	0.5	0.5	38
N-Decane			0.5	4.5	0.5	0.5	0.5	59
ethyl methyl octane			3.2	5.5	0.5	1	29	1.7
Dodecane			0.5	29	2.2	0.5	0.5	8.8
methyl butanone			211	7.2	641	52	0.1	3.3
2-methyl-1-propanol			154	3.1	8.9	3.1	0.5	0.5
2-pentanone			101	0.5	0.5	0.1	0.5	0.5
3-methyl-1-Butanol			41	2.9	0.5	0.2	0.3	23
propanal			9	14	0.9	22	0.5	11
butanal			53	0.5	0.5	0.5	0.5	0.5
2-ethyl butanal			211	1.5	65	14	0.5	3.3
2-methyl butanal			44	3.4	2.5	0.6	3.1	0.5
1-pentanal			14	1.5	0.5	0.5	0.5	0.2
octanal			26	4.3	0.5	0.5	22	7.3
Limonene			70	18	13	13	41	18

2B – Chemicals from Aluf not measured in Phase II

The compounds in the lower part of Table 3 (starting with Methyl Butane) were measured on the rooftop but not in Phase II. These compounds were also highly variable among the six sampling points and thus almost certainly produced by the factory. The first eight are alkanes (name ends in *–ane*). The rest are ketones (*-one*), alcohols (*-ol*), aldehydes (*-al*), and one fragrance (limonene). All of these save the alkanes are odorous, described as smelling sweet, fruity, acrid, like acetone, etc., by internet sources. These probably contribute to the odors noted by neighbors.

George Swiekert (I believe it was him) has suggested that these aldehydes, ketones, and alcohols are an unwanted by-product of the "repro" process in which some other material is heated and then oxidized to these compounds.

Acrolein was the one aldehyde of interest that was not measured quantitatively on the rooftop, which is unfortunate. Like the others, it has a distinct odor. It also has a very low Annual Guideline Concentration (AGC, from NYSDEC) meaning it is more toxic and could possibly contribute to health impacts. The AGC was exceeded in all the detectable Phase II area samples (10 out of 12 total), even with the improved sampling techniques designed to address the issues raised in the 12/1/17 memo from TRC to Tom

Diviny. The lack of a rooftop measurement for Acrolein hinders our ability to assess the health impact of Aluf on the surrounding neighborhood.

The fact the Acrolien was both variable spatially and reasonably well-correlated (R = 0.65) with Isopropyl Alcohol in Phase II - whose ambient levels we believe are impacted by Aluf – suggests that the ambient Acrolein levels also (at least in part) come from Aluf.