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# Analysis of Volatile Organic Compounds in Aerosol Filters from Beijing using Proton-Transfer-Reaction Mass-Spectrometry

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## Abstract

Aerosols are colloids of fine solid particles or liquid droplets, in air or another gas. Aerosols in the atmosphere have several important effects on the environment and on the human health. Organic compounds are found in ambient aerosols. They include compounds from both biogenic and anthropogenic sources. Aerosols are important in the climate system and organics constitute a significant fraction of aerosols ( $\sim 50\%$ ) of which some are hazardous to the human health. Aerosols filters have been collected from a rural area close to Beijing to see what pollutants are present. The samples cover a time period of two weeks in the fall of 2013. Proton-Transfer-Reaction Mass-Spectrometry coupled with thermal desorption is used to measure the concentrations of the compounds on the filters, from which the original concentrations in the air can be calculated. The measurements are done at different settings to get a complete overview of the chemical composition of the organic aerosols. The concentrations in the air vary between 0.5 micrograms per cubic meter up to 6.5 micrograms per cubic meter. Some compounds show statistical differences between day and night and between weekdays and weekends. Almost all the compounds showed lower concentrations during the weekend. Biogenic emissions are not expected to change during the weekend, meaning that the change is to be found in anthropogenic resources.

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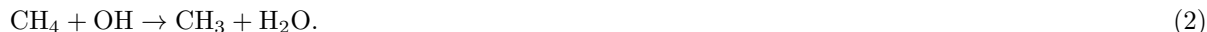
## 1 Introduction

### 1.1 Chemical reactions in the atmosphere

The atmosphere has its own way in cleaning up compounds that could be harmful to the environment. An important constituent of ambient air is the hydroxyl radical (OH). For example, it removes carbon monoxide from the atmosphere via the following oxidation reaction:



Most of the organic compounds are also oxidized by the hydroxyl radicals. Methane, for example, undergoes the following reaction:



The hydroxyl radicals thus play an important role in the composition of particles in the atmosphere. The concentrations of the hydroxyl radicals show a diurnal and seasonal variation, which indirectly affects the composition of other particles. The concentrations at daytime in summer are  $5\text{-}10 \cdot 10^6$  molecules per cubic centimeter and in the winter the concentrations are  $1\text{-}5 \cdot 10^6$  molecules per cubic centimeter while at night the concentrations are lower than  $2 \cdot 10^5$  molecules per cubic centimeter, which is an order of magnitude lower than the average concentration during daytime [3]. Bigger hydrocarbon compounds and other organic material in the atmosphere can be oxidized in a similar way, converting the more volatile compounds into compounds that are less volatile, and then able to condensate on the surface of liquid droplets or solid particles, called aerosols. Once condensed, the organic compounds can still react with other particles and change composition, or break down into smaller particles due to collisions, causes a wide range of different particles in the atmosphere. [4]

### 1.2 Aerosols

An aerosol is a colloid of fine solid particles or liquid droplets, in air or another gas [5]. Aerosols in the atmosphere have several important effects on the environment and on the human health. The latter is primarily the case in urban environments where the concentrations are high. Atmospheric aerosols can be divided into three subcategories: fine aerosol particles, which have a radius of less than  $1 \mu\text{m}$  and originate only from condensation of precursor gas; coarse particles,  $1\text{-}10 \mu\text{m}$  in radius and coming mainly from mechanical action of the wind on the surface of earth, emitting sea salt, soil dust and vegetation debris; ultrafine aerosols, which are typically in the  $10^{-3}\text{-}10^{-2} \mu\text{m}$  size range. Ultrafine aerosols originate from the clustering (nucleation) of gas molecules and these can grow rapidly to the  $0.01\text{-}1 \mu\text{m}$  (fine aerosol) size range by condensation of gases and by collisions between particles (coagulation). The coarse particles are removed from the atmosphere by rainout (Figure 1). Sulfate and organic carbon are the biggest constituents in aerosols (37% and 24% respectively). Organic carbon is mainly contributed by condensation of large hydrocarbons, which can be either of biogenic or anthropogenic origin. The main precursor gas contributing to the sulfates is sulfuric acid ( $\text{H}_2\text{SO}_4$ ) which is produced by oxidation of sulfur dioxide ( $\text{SO}_2$ ). A typical source of  $\text{SO}_2$  is fossil fuel combustion.  $\text{H}_2\text{SO}_4$  has a low vapor pressure and will condense under all atmospheric conditions to form aqueous sulfate particles ( $\text{H}_2\text{SO}_4\text{-H}_2\text{O}$ ). Thereafter, other compounds with a low vapor pressure like  $\text{NH}_3$ ,  $\text{HNO}_3$ , and organic compounds can modify the composition of these sulfate particles by condensation [6]. Aerosols that are the direct result of particles emitted into the atmosphere are called primary aerosols, aerosols that are produced via interaction of sunlight with volatile organic compounds (VOCs) and other particles (both of biogenic and anthropogenic sources) are called secondary organic aerosols (Section 1.3).

Aerosols play an important role in the environment. One important effect of aerosols is the scattering of radiation. An aerosol can alter the path of a beam of radiation without absorption taking place. The result of this scattering is the reduction of visibility, scattering of solar radiation is the main process that limits visibility in the troposphere. Scattering of solar radiation also causes the Earth's albedo to increase since a fraction of the radiation is reflected back in space. Volcano eruptions, which emit a large amount of aerosol into the atmosphere, are known to result in a cooling of the Earth's surface due to a decrease in the albedo [6]. Aerosols also interact with clouds, changing the concentration and size of air droplets, which in turn lead to a change in the albedo of the clouds, its lifetime and thereby influence the precipitation [7].

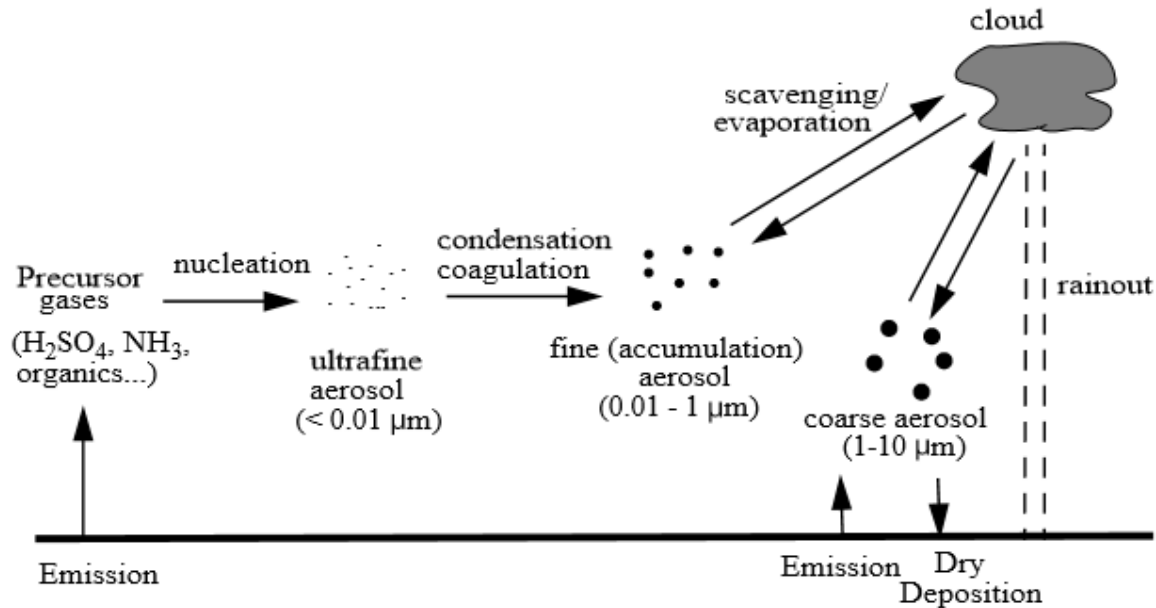


Figure 1: The different types of aerosols arise in different ways [5].

### 1.3 Secondary Organic Aerosols

Secondary organic aerosols (SOAs) are aerosols that are not directly emitted into the atmosphere but formed by collisions, reactions, and oxidation of compounds already present in the atmosphere. A big constituent of these SOAs is volatile organic compounds. Most of these compounds are too volatile to directly condensate on the surface of aerosols. Photo-oxidation and interaction with the hydroxyl radical, leading to the addition of an OH-group, can reduce the saturation vapor pressure by approximately 2 orders of magnitude. Once the volatility is lowered, the compounds can condensate on the surface of liquid or solid particles and form aerosols. [8]

VOCs come in all shapes and sizes. Their origin can be biogenic (naturally, produced by life processes) as well as anthropogenic (caused by humans). VOCs play an important role in communication between plants and messages from plants to animals [9]. VOCs contribute to two of the most serious air quality problems: the formation of photochemical smog and ground level ozone. Several VOCs are known to directly effect the human health as some VOCs found in urban air are classified as carcinogenic [10].

Anthropogenic sources of VOCs primarily include emissions from the transport section and the industrial section (solvent use, production and combustion processes). Vehicle emission in urban regions is often the main source of VOCs in air [11]. The ozone formation in the lower troposphere is due to the presence of nitrogen oxides and happens via the following reaction:



where "other products" refers to gaseous carbonyls and organic acids [12].

Beijing's air is heavily polluted and urban areas show concentrations ranging from  $60 \mu\text{g}/\text{m}^3$  (in spring) to  $160 \mu\text{g}/\text{m}^3$  (in autumn) and compared to other big Chinese cities, Beijing showed by far the highest concentrations of VOCs in air [13]. For this research air samples from a rural area close to Beijing have been collected and analyzed.

## 2 Method

### 2.1 Aerosol filter samples from China

A total of 28 samples has been taken, covering two weeks of sampling. The filters have been measured at a rural area approximately 50 kilometers southeast of Beijing. The coordinates for the exact location where the measurements have been made are 39.80 °N, 116.96 °E. The first measurements was started on the 27<sup>th</sup> of July 2013 at 6:00 and the last one was started on the 9<sup>th</sup> of August 18:00. Collecting one sample took 12 hours during which a constant airflow of 100 liters per minute has been pulled through the filters. Beside the 28 filters through which air has been pulled, 2 blank filters (zero sampling volume) will be analyzed to compensate for possible compounds being desorbed from the filters itself (Table 1). A total of 6 aliquots (pieces cut from the original sample with a diameter of 5 mm) has been taken from every sampled filter and 20 aliquots of each blank filter. The diameter of the original filters is 90 mm.

No.	Start sampling	End sampling	Sampled volume (L)	Diameter filter (mm)	Diameter aliquot (mm)
1	27-7-2013 6:00	27-7-2013 18:00	71998	90	5
2	27-7-2013 18:00	28-7-2013 6:00	72010	90	5
3	28-7-2013 6:00	28-7-2013 18:00	72000	90	5
4	28-7-2013 18:00	29-7-2013 6:00	72013	90	5
5	29-7-2013 6:00	29-7-2013 18:00	72001	90	5
6	29-7-2013 18:00	30-7-2013 6:00	72010	90	5
7	30-7-2013 6:00	30-7-2013 18:00	72001	90	5
8	30-7-2013 18:00	31-7-2013 6:00	72007	90	5
9	31-7-2013 6:00	31-7-2013 18:00	72002	90	5
10	31-7-2013 18:00	1-8-2013 6:00	72003	90	5
11	1-8-2013 6:00	1-8-2013 18:00	72003	90	5
12	1-8-2013 18:00	2-8-2013 6:00	72015	90	5
13	2-8-2013 6:00	2-8-2013 18:00	72002	90	5
14	2-8-2013 18:00	3-8-2013 6:00	72010	90	5
15	3-8-2013 6:00	3-8-2013 18:00	72003	90	5
16	3-8-2013 18:00	4-8-2013 6:00	72012	90	5
17	4-8-2013 6:00	4-8-2013 18:00	71998	90	5
18	4-8-2013 18:00	5-8-2013 6:00	72014	90	5
19	5-8-2013 6:00	5-8-2013 18:00	72001	90	5
20	5-8-2013 18:00	6-8-2013 6:00	72010	90	5
21	6-8-2013 6:00	6-8-2013 18:00	71998	90	5
22	6-8-2013 18:00	7-8-2013 6:00	72005	90	5
23	7-8-2013 6:00	7-8-2013 18:00	72002	90	5
24	7-8-2013 18:00	8-8-2013 6:00	72012	90	5
25	8-8-2013 6:00	8-8-2013 18:00	72003	90	5
26	8-8-2013 18:00	9-8-2013 6:00	72011	90	5
27	9-8-2013 6:00	9-8-2013 18:00	71998	90	5
28	9-8-2013 18:00	10-8-2013 6:00	72001	90	5
29	24-7-2013 7:30	24-7-2013 19:00	0 (blank)	90	5
30	24-7-2013 20:00	25-7-2013 9:00	0 (blank)	90	5

Table 1: Information of all the filters. The given sizes are the diameters of the filters and aliquots. The sampled volume is the total volume of air that has been pulled through the filters in liters.

## 2.2 The TD-PTR-MS Setup

The total setup consists of several parts: the PTR-MS; the desorption system (linked to a nitrogen tank) and a computer to run the systems. This section will shed light on the basic aspects of these systems and how they work together to create a whole.

### 2.2.1 The PTR-MS [2]

Proton-Transfer-Reaction Mass-Spectrometry (PTR-MS) is a technique that uses hydronium ( $\text{H}_3\text{O}^+$ ) ions to ionize trace constituents in air or nitrogen with a precision up to the order of 1 ppb. When  $\text{H}_3\text{O}^+$  is used as proton donor, most of the organic trace components in air are ionized by the following process:



where M is a combination of C, O, N and S atoms.  $\text{H}_2\text{O}$  has a proton affinity of 7,22 eV and most organic compounds have a proton affinity between 7 and 9 eV, causing most of the reactions to be exothermic. The natural constituents of ambient air ( $\text{N}_2$ ,  $\text{O}_2$ , Ar,  $\text{CO}_2$ ...) have a lower proton affinity than water so there will be no loss of  $\text{H}_3\text{O}^+$  ions due to reactions with these constituents. However, some  $\text{H}_3\text{O}^+$  might be lost due to the following ternary reaction:



where M is a neutral partner performing collision stabilization of the cluster  $\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O}$  formed in a binary collision between  $\text{H}_3\text{O}^+$  and  $\text{H}_2\text{O}$ . To reduce this loss problem, E/N (where E is the electric field strength and N the number density of the buffer gas i.e. how much energy is available per particle) should be kept elevated in the drift tube. If E/N is high enough, collisions with hydronium ions will break up the formed clusters into hydronium and water. At the transition to the ion detection system, the concentration of protonated ions  $[\text{MH}^+]$  is given by:

$$[\text{MH}^+] = [\text{H}_3\text{O}^+]_0(1 - e^{-k[\text{M}]t}) \approx [\text{H}_3\text{O}^+]_0[\text{M}]kt \quad (6)$$

where  $[\text{H}_3\text{O}^+]_0$  is the density of  $\text{H}_3\text{O}^+$  ions in the drift tube in absence of the gas to be analyzed and k is the reaction rate constant for the proton transfer reaction. t is the average time the ions spend in the drift tube and [M] denotes small densities of trace constituents. When  $[\text{MH}^+] \ll [\text{H}_3\text{O}^+] \approx [\text{H}_3\text{O}^+]_0$  is constant. The ion detection system measures the incoming number of ions per time unit, which is proportional to their densities. By keeping the density  $[\text{H}_3\text{O}^+]$  high enough, a high sensitivity can be achieved.

The hollow cathode acts as an ion source to provide a high enough density of primary ions ( $\text{H}_3\text{O}^+$ ). The incoming water vapor collides with high energetic electrons (a few hundred electronvolts) producing a high density plasma ( $10^{10}$ - $10^{11}$   $\text{cm}^{-3}$ ). The region is limited by an anode with a hole with a diameter of 1.0 mm through which the ions leave towards the source drift region. When  $\text{H}_2\text{O}$  is used as a discharge gas in the hollow cathode, most of the ions entering the source drift region are already in the form of the primary ions. All the ions produced by electron impact in the hollow cathode will finally end up as  $\text{H}_3\text{O}^+$  due to reaction with  $\text{H}_2\text{O}$  in the source drift region. This method provides  $\text{H}_3\text{O}^+$  ions with a purity of about 99.5% and has two advantages: high concentrations of primary ions are obtained and because of the high purity there is no need for a quadrupole system to preselect the primary ions before sending them to the drift tube.

The reaction time t is needed in order to calculate the density [M]. It can be either measured directly, by pulsing the ions at the beginning and end of the drift tube and monitoring the time spectrum, or by calculating it from the mobility of  $\text{H}_3\text{O}^+$  ions reported in literature.

Finally, the ions arrive in the Time of Flight (TOF) chamber. The ions are accelerated towards a pulser one by one. The pulser shortly generates an electric field, causing the ions to accelerate downward towards a mirroring surface causing them to travel back. The heavier the ions are, the longer it takes them to reach the detector. The total time of flight is then converted to the mass-to-charge ratio of the ions. See Figure 2 for a schematic overview of the setup.



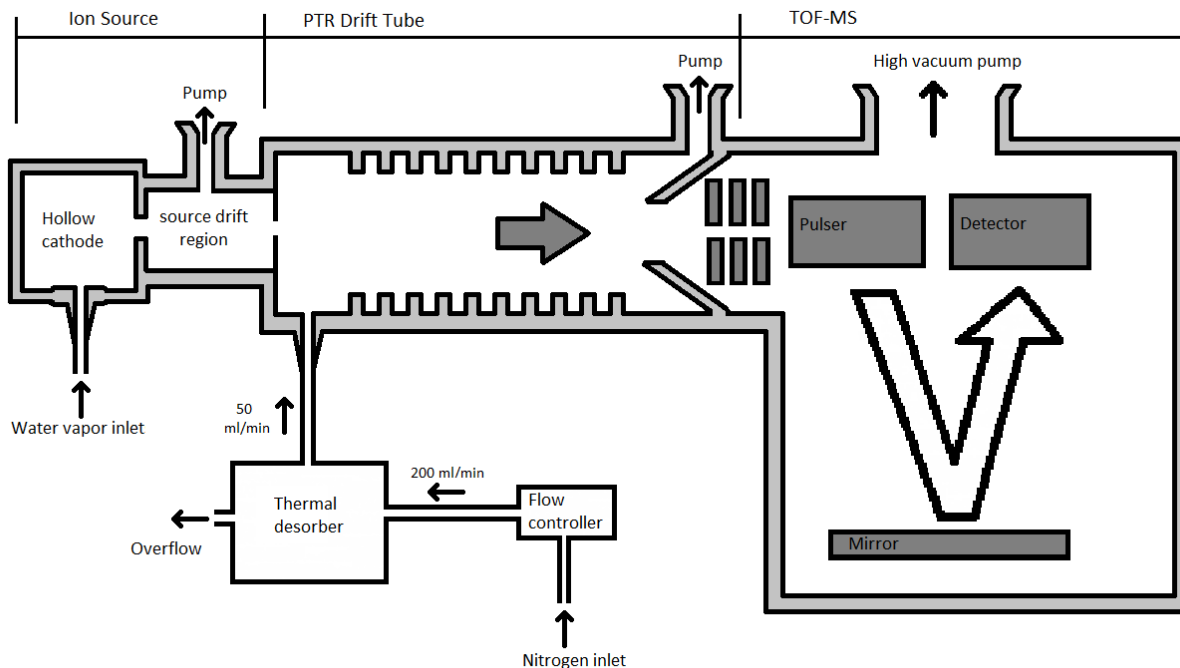


Figure 2: Schematic overview of the experimental setup. Left side: ion source consisting of a hollow cathode and a source drift region where the hydronium ions are formed. Middle: drift tube where the hydronium ions meet the gaseous compounds desorbed from the filters in the thermal desorption system. Right side: the time of flight mass spectrometer which uses the total flight time of the compounds to determine the mass-to-charge ratio. Heavier ions have a longer flight time than lighter ions.

### 2.2.2 The Thermal Desorption System

The filters are inserted in a small oven that is connected to the drift tube. Once the measurement is started, the filters are being heated up from 50 °C to 350 °C in six equal steps of three minutes. The compounds are released from the filters due to the heat and are transported to the PTR-MS using nitrogen as a buffer gas. The nitrogen flow is set to 200 ml per minute by the flow controller throughout the whole experiment, however, only 50 ml is transported towards the PTR-MS and the rest is released into the lab via the overflow. Diluting the gas too much might lead to a drop of sensitivity. [14]

### 2.3 Measurement plan

Six aliquots of each filter are being processed to be able to statistically analyze the outcome. Three of them are being measured on  $E/N = 125$  Td (Townsend,  $1 \text{ Td} = 10^{-17} \text{ V} \cdot \text{cm}^2$ ) and another three on  $E/N = 85$  Td. The energy and thus the velocity of the particles is higher for 125 Td, resulting in more fragmentation than on 85 Td. For 85 Td, the clusters do not break down as much as on 125 Td, so there is a lower concentration of hydronium ions, and thus less fraction of particles that is ionized decreases. The order of measurements of the aliquots is being randomized to minimize the influence of carryover (Table 2). A fraction of the compounds could get stuck somewhere inside the system and get loose during another measurement. By measuring three replicas of one filter in a row these compounds can accumulate and influence the data of the filters that follow. By randomizing the order this effect is minimized. The blanks have been measured at the beginning of the day and at the end of the day, this is also done to minimize the effect of carryover (Table 3). The following tables show the date and time of the measurements.

Filter	First replica (125)	Second replica (125)	Third replica (125)	First replica (85)	Second replica (85)	Third replica (85)
1	15-2-2017 11:40:04	28-3-2017 14:20:34	3-4-2017 13:01:22	27-2-2017 14:20:49	28-2-2017 13:34:37	20-3-2017 15:17:37
2	21-2-2017 13:21:23	15-2-2017 11:15:42	29-3-2017 11:47:47	28-2-2017 12:20:07	9-3-2017 11:32:09	21-3-2017 13:24:22
3	20-2-2017 13:31:25	16-2-2017 11:47:01	29-3-2017 12:17:56	27-2-2017 11:47:55	13-3-2017 12:02:59	16-3-2017 14:17:24
4	20-2-2017 13:54:50	16-2-2017 14:10:59	29-3-2017 12:41:01	1-3-2017 11:09:04	7-3-2017 11:35:32	20-3-2017 13:39:57
5	21-2-2017 14:32:55	15-2-2017 13:04:52	27-3-2017 15:15:20	27-2-2017 14:51:53	7-3-2017 13:30:54	16-3-2017 10:45:53
6	14-2-2017 15:26:04	16-2-2017 10:11:04	27-3-2017 15:56:43	1-3-2017 10:45:47	13-3-2017 11:17:14	20-3-2017 11:14:32
7	21-2-2017 14:09:06	16-2-2017 12:58:49	3-4-2017 11:53:41	28-2-2017 09:45:09	13-3-2017 10:52:43	16-3-2017 13:32:14
8	21-2-2017 11:33:14	15-2-2017 12:04:37	27-3-2017 14:29:51	27-2-2017 15:32:39	28-2-2017 11:10:03	16-3-2017 11:08:40
9	21-2-2017 15:22:07	16-2-2017 10:34:47	28-3-2017 12:32:47	1-3-2017 12:50:58	7-3-2017 12:21:28	21-3-2017 12:55:49
10	22-2-2017 09:47:46	15-2-2017 10:02:18	29-3-2017 10:32:55	28-2-2017 15:07:15	7-3-2017 11:13:14	20-3-2017 12:32:07
11	22-2-2017 10:11:14	22-2-2017 12:12:31	29-3-2017 11:16:25	28-2-2017 14:40:50	9-3-2017 12:47:05	21-3-2017 12:33:23
12	21-2-2017 12:56:12	22-2-2017 11:44:04	3-4-2017 10:48:18	28-2-2017 11:33:22	13-3-2017 12:51:52	20-3-2017 11:46:57
13	14-2-2017 15:51:01	22-2-2017 11:21:11	28-3-2017 14:43:37	27-2-2017 12:58:38	9-3-2017 13:14:52	20-3-2017 13:17:17
14	20-2-2017 15:02:06	15-5-2017 13:28:57	29-3-2017 13:03:58	28-2-2017 15:47:51	7-3-2017 11:58:32	16-3-2017 13:05:46
15	16-2-2017 12:32:56	28-3-2017 13:41:54	4-4-2017 10:52:29	13-3-2017 11:40:11	13-3-2017 12:28:07	20-3-2017 14:02:17
16	22-2-2017 10:58:08	3-4-2017 10:26:05	4-4-2017 12:29:40	28-2-2017 12:49:04	13-3-2017 10:07:21	21-3-2017 12:11:02
17	15-2-2017 12:28:49	28-3-2017 13:19:23	4-4-2017 12:06:35	27-2-2017 12:34:43	1-3-2017 12:04:50	20-3-2017 14:33:16
18	16-2-2017 13:47:06	29-3-2017 13:25:39	4-4-2017 11:44:49	7-3-2017 15:19:59	9-3-2017 14:00:16	16-3-2017 12:20:54
19	21-2-2017 13:45:22	16-2-2017 12:09:59	3-4-2017 11:10:27	28-2-2017 13:11:48	9-3-2017 11:55:02	20-3-2017 09:30:21
20	21-2-2017 11:56:56	29-3-2017 13:47:29	3-4-2017 13:45:44	28-2-2017 13:57:44	1-3-2017 12:28:09	20-3-2017 15:39:52
21	20-2-2017 13:04:40	21-2-2017 14:56:58	28-3-2017 12:56:45	1-3-2017 10:22:29	9-3-2017 10:46:09	21-3-2017 11:25:40
22	20-2-2017 15:26:40	22-2-2017 10:34:37	3-4-2017 12:15:23	7-3-2017 13:07:54	7-3-2017 14:22:18	16-3-2017 10:22:35
23	15-2-2017 10:26:39	16-2-2017 11:22:51	29-3-2017 10:54:44	1-3-2017 11:32:13	9-3-2017 00:00:00	21-3-2017 11:48:09
24	20-2-2017 15:50:00	16-2-2017 13:22:32	27-3-2017 14:06:57	1-3-2017 13:14:32	9-3-2017 11:09:01	20-3-2017 12:09:29
25	21-2-2017 12:25:25	3-4-2017 11:32:04	3-4-2017 13:22:59	27-2-2017 12:11:21	1-3-2017 13:37:33	20-3-2017 12:54:44
26	20-2-2017 14:18:22	15-2-2017 11:58:20	29-3-2017 14:09:13	9-3-2017 13:37:33	13-3-2017 10:29:52	16-3-2017 11:55:38
27	20-2-2017 12:38:07	15-2-2017 13:55:34	27-3-2017 14:52:59	27-2-2017 13:55:24	28-2-2017 11:56:34	16-3-2017 11:32:51
28	21-2-2017 15:47:20	3-4-2017 12:37:19	4-4-2017 11:22:50	7-3-2017 12:45:07	7-3-2017 13:59:07	16-3-2017 13:54:49

Table 2: Date and time of the measurements. The first column gives the filter numbers, the following three give the aliquots measured on E/N = 125 Td and the last three the aliquots measured on E/N = 85 Td.

29 (125)	30 (125)	29 (85)	30 (85)
15-2-2017 14:19:38	4-4-2017 10:30:44	27-2-2017 11:24:47	28-2-2017 09:26:49
16-2-2017 14:34:25	4-4-2017 13:19:46	27-2-2017 16:12:23	28-2-2017 16:13:00
21-2-2017 16:10:25	15-2-2017 09:38:07	1-3-2017 09:58:14	9-3-2017 10:23:22
22-2-2017 09:24:01	16-2-2017 09:47:26	1-3-2017 14:00:37	9-3-2017 14:22:57
22-2-2017 12:35:57	20-2-2017 12:14:49	7-3-2017 10:50:10	13-3-2017 09:44:05
27-3-2017 16:19:16	20-2-2017 16:13:17	7-3-2017 15:53:54	20-3-2017 09:01:21
28-3-2017 12:10:08	21-2-2017 11:09:45	13-3-2017 13:19:02	20-3-2017 16:02:59
28-3-2017 15:08:20	27-3-2017 10:09:47	16-3-2017 09:59:34	21-3-2017 11:02:26
29-3-2017 10:10:02	29-3-2017 14:30:58	16-3-2017 14:40:10	21-3-2017 13:46:56
3-4-2017 14:52:26	3-4-2017 10:03:56		

Table 3: Measurement date and times of the blank filters. The first two columns give the measurements made on E/N = 125 Td and the last two on E/N = 85 Td.

## 2.4 Analysis

The raw output from the PTR-MS is extracted resulting in a file for every filter containing the number of ions detected in ppb for every ion per second. This data can be plotted to visualize the concentration desorbed per temperature step (Figure 3). After that, the concentrations are averaged over the temperature steps, resulting in only six values per ion per filter. Two blank filters have been measured each day as background concentrations. The background is subtracted from the filters measured that specific day. The values are averaged over the three replicas with the standard deviation as the error, calculated as follows:

$$\sigma = \frac{\sqrt{(x_1 - \mu)^2 + (x_2 - \mu)^2 + (x_3 - \mu)^2}}{3} \quad (7)$$

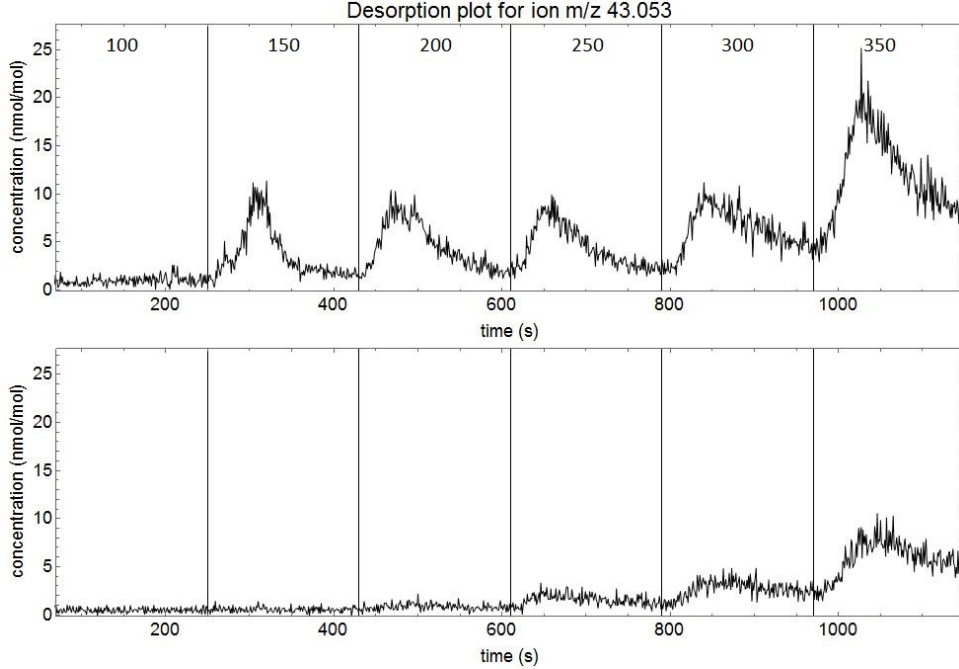


Figure 3: The desorption spectrum for the ion a with mass-to-charge ratio of 43.053 Da. Above: the mass desorbed from a dirty filter. Below: the same mass but desorbed from a blank filter. The temperature steps are given at the top of the top figure.

with  $x_i$  the concentration of the specific ion of replica  $i$  and  $\mu$  the mean of the replicas of this ion. The limit of detection (LOD) is set to three standard deviations of all the measured blanks. Every value below the limit of detection is set to zero.

The values are given in parts per billion, which is the same as nanomole per mole carrier gas. These can be converted into actual concentrations present in the air at the location of measuring. The flow controller converts the nitrogen to standard pressure so one mole has a volume of 22.4 liters, according to the ideal gas law. The total volume of nitrogen can be converted into the total mole of nitrogen, to calculate the number of nanomoles desorbed from the filter. Then the total mass per square centimeter released from the filters ( $M_f$ ) is:

$$M_f = \frac{ppb \cdot t \cdot F_{N_2} \cdot M}{A_{aliquot}} \cdot 10^3 \frac{\mu g}{cm^2} \quad (8)$$

where  $t$  is the duration of the measurement in minutes (3 minutes per temperature step),  $F_{N_2}$  the nitrogen flow in moles per minute,  $M$  is the molecular weight of the specific ion in Daltons (1 Da = 1g/mol) and  $A$  is the surface of the analyzed aliquot in  $cm^2$ . Multiplying this value with the total surface of the filter will give the total mass desorbed from the filter. The air pulled through the filters is known so the conversion to the concentration in micrograms per cubic meter ( $C$ ) is easily made by dividing by the volume in cubic meters:

$$C = \frac{M_f \cdot A_{filter}}{V_{sample}} \frac{\mu g}{m^3} \quad (9)$$

where  $M_f$  is given by Equation 8.  $A_{filter}$  is the total surface of the filter in  $cm^2$  and  $V_{sample}$  is the total sampled volume in liters.

The compound with a mass-to-charge ratio lower than forty have been removed from the mass list, as they are mostly inorganic compounds, except for 28.018 ( $CHNH^+$ ), 31.017 ( $CH_2OH^+$ ) and 33.034 ( $CH_4OH^+$ ). Some heavier inorganic ions have been removed too. We are only interested in organic compounds for the purpose of this thesis, the inorganic ions often show deviating behavior that could influence the analysis and are thus removed. Furthermore, most of the organic compounds with a mass-to-charge ratio ( $m/z$ ) below

140 Da are products of thermal instability of heavier compounds or products from fragmentation in the drift tube, they are not found in this form in aerosols. As all the compounds are only protonated one time, their charge is 1+ so their  $m/z$  equals their mass. From now on I will use mass to indicate the mass-to-charge ratio of the compounds.

## 2.5 Precision

To see if the errors of the single ions are proportionally small ( $\sim 20\%$ ) their mean is divided by the corresponding standard deviation for every ion and every filter. Then this value is averaged over every filter for which the corresponding ion gave a signal. Figure 4 shows this value for every ion that is detected.

The average value in the plot is given by the gridline with the corresponding value: 4.05 for high E/N and 6.89 on low E/N. For E/N = 125 Td the mean is on average 4.05 times higher than the standard deviation, meaning that the error is approximately 25 % on average. For E/N = 85 Td the average value in the figure is almost 7, meaning that the average error is around 15 % of the mean values. The values in the figure have been calculated via the following formula:

$$\frac{1}{n} \sum_i^n \frac{x_1 + x_2 + x_3}{3 \sigma}. \quad (10)$$

The denominator is the standard deviation for the three replicas (Equation 7) in the nominator is the mean of the three concentrations measured. The sum runs over all the filters, from 1 to 28 in this case.

For both E/N settings, the bulk lies around the value 5, with the values of the lower graph a little more elevated, meaning their uncertainties are lower. There is a clear distinction for low E/N between ions with an accuracy below one and above one. For high E/N this is a bit more unclear, there are a lot more ions below two of which some have a value below one.

A calibration gas was used to check the PTR-MS sensitivity. This gas contains compounds for which the concentrations are known. The result shows the PTR-MS is sensitive for compound with a mass up to 300 Da. The number of different compounds decreases rapidly above 200 Da (Figure 10) which may suggest the PTR-MS is not sensitive to compounds with a mass above 200 Da. The calibration gas showed this is not the case.

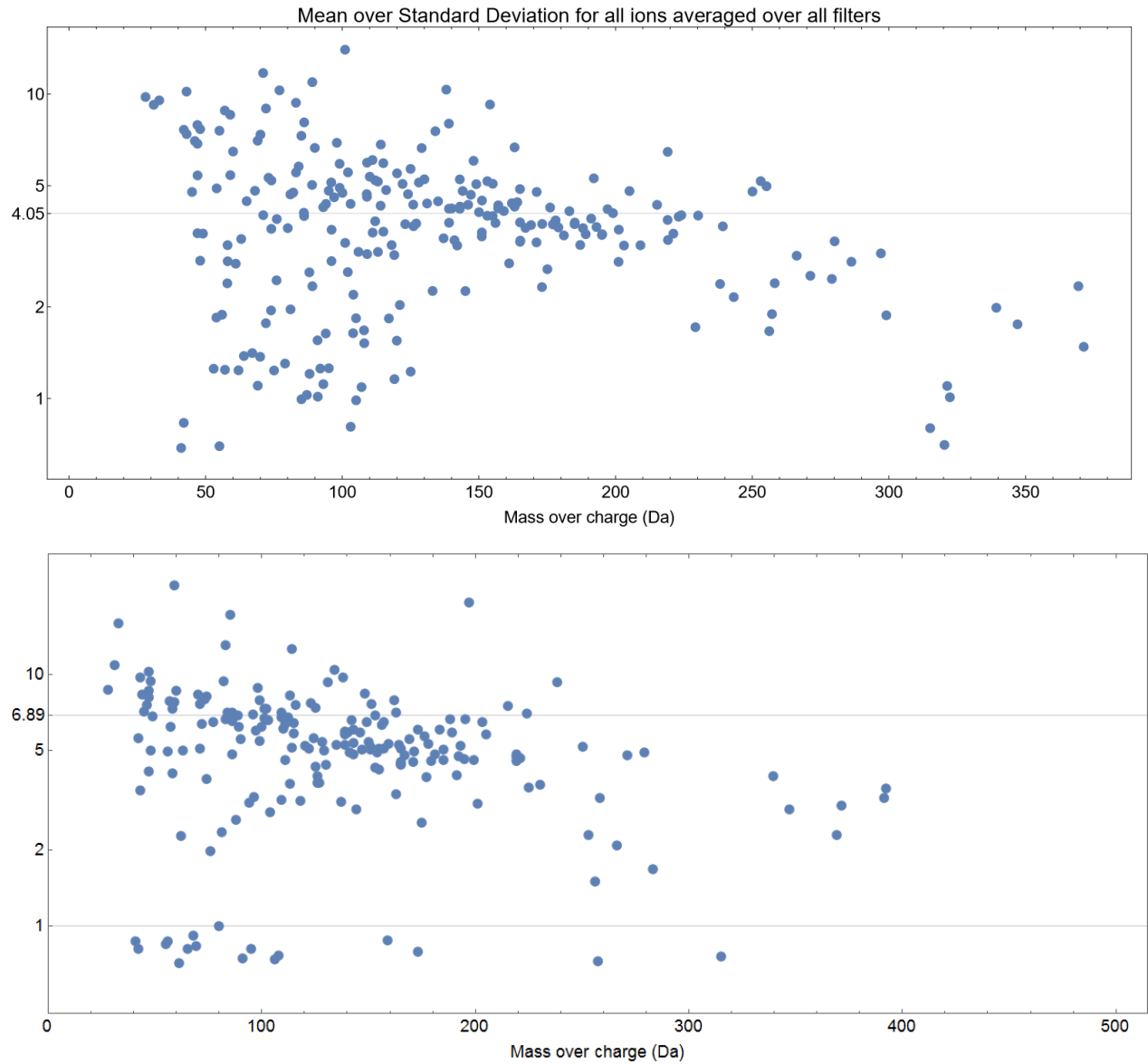


Figure 4: The mean over the standard deviation of all detected ions, calculated as in Equation 10 on a log scale. Values above ten have an error of less than ten percent and values below one have an error higher than the corresponding average. The top figure is for high  $E/N$  and the figure below is for low  $E/N$ .

### 3 Results and Discussion

Before looking in detail at a specific filter or specific compounds that exhibit interesting properties, some basic analysis will be shown. This includes graphs like total mass desorbed per filter, the volatility of the compounds (more volatile compounds are expected to be released at a lower temperature than less volatile compounds) and how the masses of the compounds are distributed. Further on in this chapter will be looked at which compound exhibit a day and night difference and if there is a difference between weekdays and weekends.

Figure 5 shows the total compounds (every temperature step summed up) released from the filters in micrograms per cubic meter, measured on  $E/N = 125$  Td. There is a clear variation in the total concentration found in the filters, some show concentrations higher than  $6 \mu g/m^3$  and some filters show concentrations below  $1 \mu g/m^3$ . As shown in Table 1, the odd numbered filters are measured during daytime and the even numbered filters are measured at night. The errorbars give the error in the total mass per filter (Equation 11) and they seem to be around the typical errors for measurements with the PTR-MS, which are 20% [2]. The errors for the single ions are also around the 20% (Figure 4).

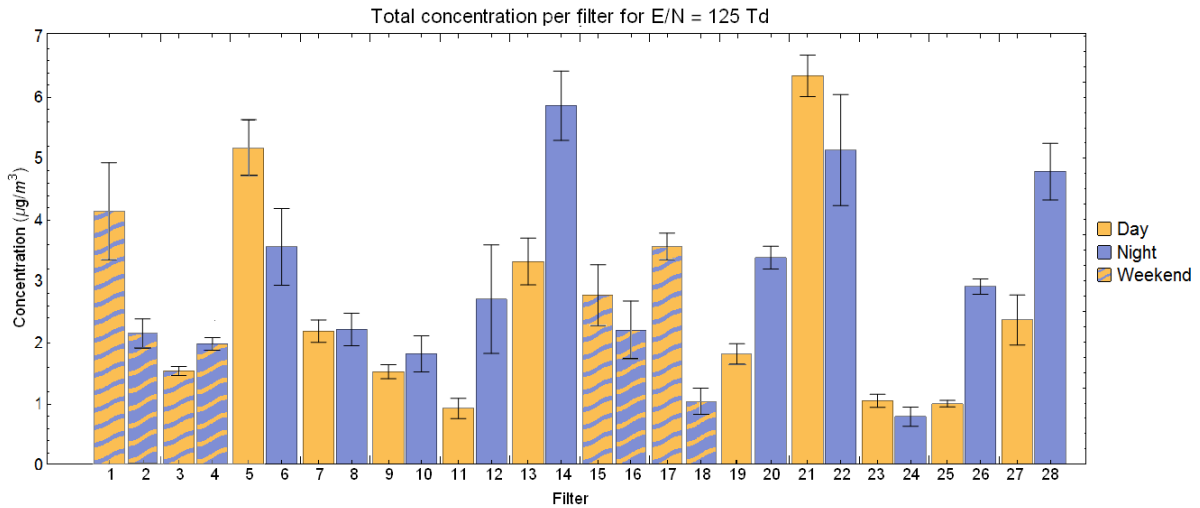


Figure 5: Total organic aerosol concentrations measured per filter with corresponding errors. The concentrations are summed over all temperature steps. Samples taking during daytime are represented by orange bars and nighttime samples by blue bars. The hatched bars indicate the weekends.

To obtain the total concentration of detected compounds in a filter, the concentrations of the individual compounds have been added up. The errorbars (Figure 5) have been calculated the following way:

$$\sigma_{filter} = \sqrt{\sigma_1^2 + \sigma_2^2 + \sigma_3^2 + \dots + \sigma_n^2} = \sqrt{\sum_{i=1}^n \sigma_i^2} \quad (11)$$

where  $\sigma_{filter}$  is the total uncertainty that is used in the figure and  $\sigma_i$  the uncertainty in the  $i^{th}$  compound detected in the filter.

Figure 6 shows the concentrations for all the filters in both  $E/N$  settings to compare them. The concentrations measured on  $E/N = 85$  Td are shown on the vertical axis and the concentrations on  $E/N = 125$  Td on the horizontal axis. Filter 6 has been excluded from the figure because it is most likely an outlier. One of the three replicas of filter 6 showed concentrations ten times higher than the other replicas on  $E/N = 85$  Td, resulting in an average concentration of  $23 \mu g/m^3$  while on  $E/N = 125$  Td the total concentration is  $3.6 \mu g/m^3$ . The gray broken line represents the line of equal concentrations and the black line shows the linear fit through the data points. The corresponding fit is given by:

$$y = 0.91 + 0.85x, \quad (12)$$

where  $y$  is the concentration measured on  $E/N = 85$  Td and  $x$  is the concentration on  $E/N = 125$  Td. The fit goes toward the line of equal concentrations until  $6.5 \mu\text{g}/\text{m}^3$ , where it goes underneath the line. When filter 6 is included in the fit, it takes another form:

$$y = 0.97 + 1.07x. \quad (13)$$

The slope is almost equal to the gray dashed line ( $y = x$ ) but the 0.97 causes the line to be lifted above the gray line at all times, meaning that the concentrations on  $E/N = 85$  Td are consistently higher with at least  $0.97 \mu\text{g}/\text{m}^3$ . The correlation coefficient tells how good the fit matches the data. The correlation coefficient of the fit is  $r^2 = 0.51$  when filter 6 is discarded and  $r^2 = 0.16$  when filter 6 is not discarded, meaning the fit matched the data better when filter 6 is removed.

The number of the filters have been indicated with the corresponding number in the plot. More points are situated above the gray line rather than below the line, so a slightly higher concentration has been measured on low  $E/N$ . Some compounds could have been fragmented on the high  $E/N$  measurements into compound with a mass lower than 40 Da, which have been excluded from the list, while the same compound have not been fragmented during the measurements on low  $E/N$ , resulting in the fact that this mass is lost in the measurements on high  $E/N$ .

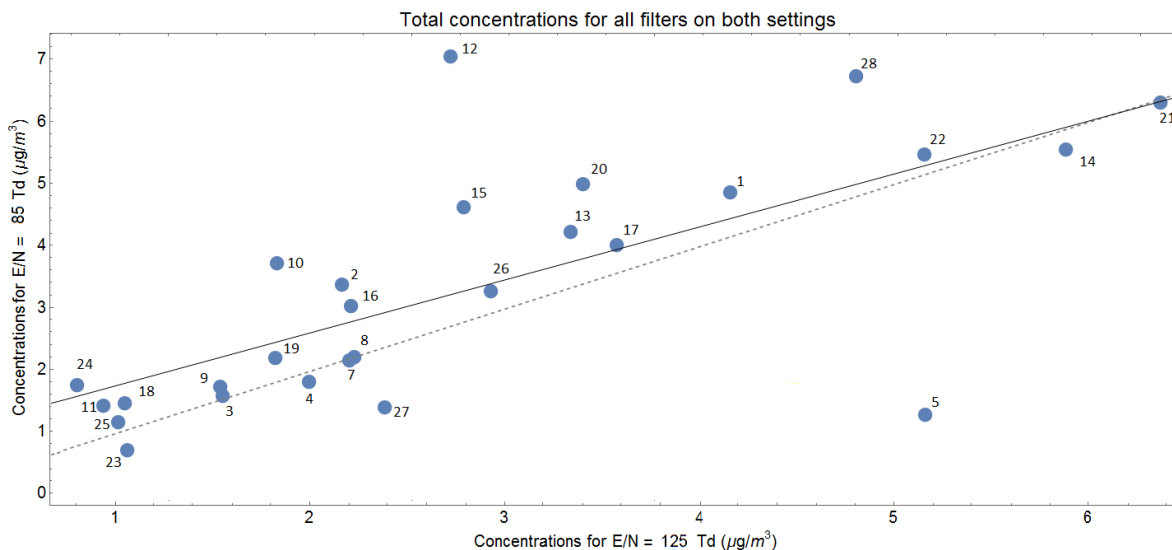


Figure 6: Total concentrations on high  $E/N$  plotted against total concentrations on low  $E/N$ . The gray line is the line of equal concentrations and the black line represents the fit through the data points.

### 3.1 Spectra for two filters

The following figure (Figure 7) show the spectra for two filters. The figures show every compound detected (after LOD) with the corresponding error. The top figure is the spectra of filter 21, which has a total concentration of about  $6.4 \mu\text{g}/\text{m}^3$ , the dirtiest filter of all. The graph below shows the spectra of filter 23, which is the second cleanest filter with a total concentration of  $1.0 \mu\text{g}/\text{m}^3$ .

Most of the detected compound have a mass to charge ratio between 50 and 200 Da and very few have a ratio above 200 Da, which may suggest the PTR-MS has a lower sensitivity above this range. However, a calibration gas (mentioned earlier in the method section) was used which showed that the PTR-MS was sufficiently sensitive for higher masses. Conclusively, the PTR-MS is sensitive for these ions and thus there are not many ions with a mass higher than 200 present in the filters.

For both filters, the compounds in the bulk have concentrations roughly around  $0.01 \mu\text{g}/\text{m}^3$ . There are more different compounds detected in the dirtier filters than in the cleaner one. Filter 21 contains a total of 221 compounds, whereas filter 23 only contains 96 compounds. Furthermore, the dirtier filter contains a lot more compounds (20) with a concentration above  $0.05 \mu\text{g}/\text{m}^3$  whereas the cleaner filter contains only

4 of such compounds. Filter 21 also shows 9 compounds with concentrations higher than  $0.1 \mu\text{g}/\text{m}^3$  from which the most abundant shows a concentration of  $1.6 \mu\text{g}/\text{m}^3$ , while the second most abundant compound in filter 23 only showed a concentration of  $0.06 \mu\text{g}/\text{m}^3$  (the most abundant is the only one with a concentration above  $0.1 \mu\text{g}/\text{m}^3$  with  $0.12 \mu\text{g}/\text{m}^3$ ). A combination of higher concentrations of the present compounds and a higher number of different compounds lead to a difference of more than  $5 \mu\text{g}/\text{m}^3$ .

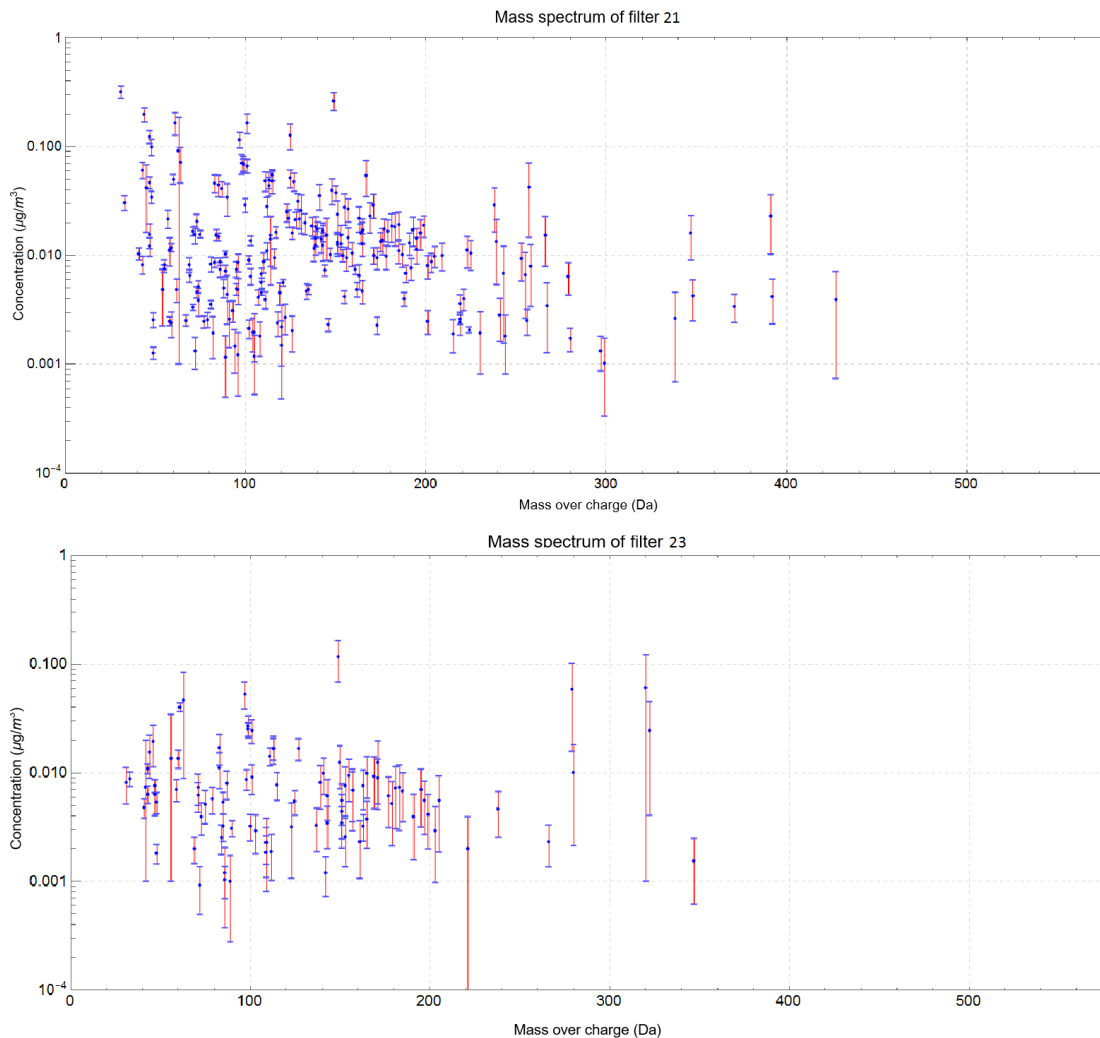


Figure 7: Mass spectra for two filters. Above: filter 21 with the highest measured concentration of all the filters. Below: filter 23 which has one of the lowest concentrations.

### 3.2 Mass of the compounds

The ions vary in mass from in the twenty Da up to almost six hundred Da. Heavier compounds are often less stable against fragmentation than lighter and smaller compounds. Processes in the atmosphere also play a role in the decomposition of certain elements, as we have seen in the introduction. It is expected to find more mass in the lower mass ranges, i.e 20-100 Da. However, these ions are primarily formed in the drift tube due to fragmentation and thermal decomposition of bigger compounds. These compounds are often too volatile and remain in the gas phase in ambient air. Figure 8 shows how much mass is desorbed from each filter in the specified mass ranges for the measurement on  $E/N = 125 \text{ Td}$ . The masses are normalized to the total mass in the filter. For almost every filter, at least 50% of the mass that is desorbed consist of ions with a mass below 100 Da.



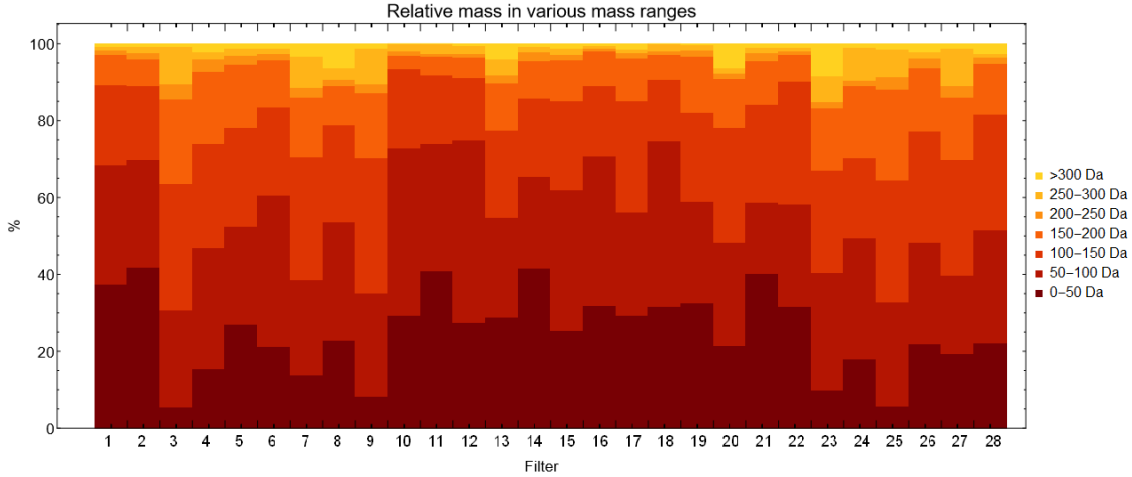


Figure 8: Relative mass desorbed per filter categorized in various mass ranges.

A lot of mass that is desorbed consists of ions with a mass below 50 Da. Looking at Figure 9, which gives the relative number of ions desorbed in a specific mass range, we see that only a small fraction of the detected ions have a mass below 50 Da. Since their mass is low, it means that these ions must have been present in high concentrations in order to get such high percentages of the total mass. It seems that the relative number of ions desorbed in the three mass steps between 50 Da and 200 Da are roughly the same, while the relative desorbed mass is getting smaller with every temperature step, as can be seen in Figure 8. This can mean that in general the concentrations of the detected ions are decreasing for increasing mass. This does not have to be true for every ion, as the mass per ion is also increasing. For filter 21 (Figure 7) this seems to be true. Filter 23, however, shows some higher masses with relatively high concentrations but overall the lower masses seem to be more abundant.

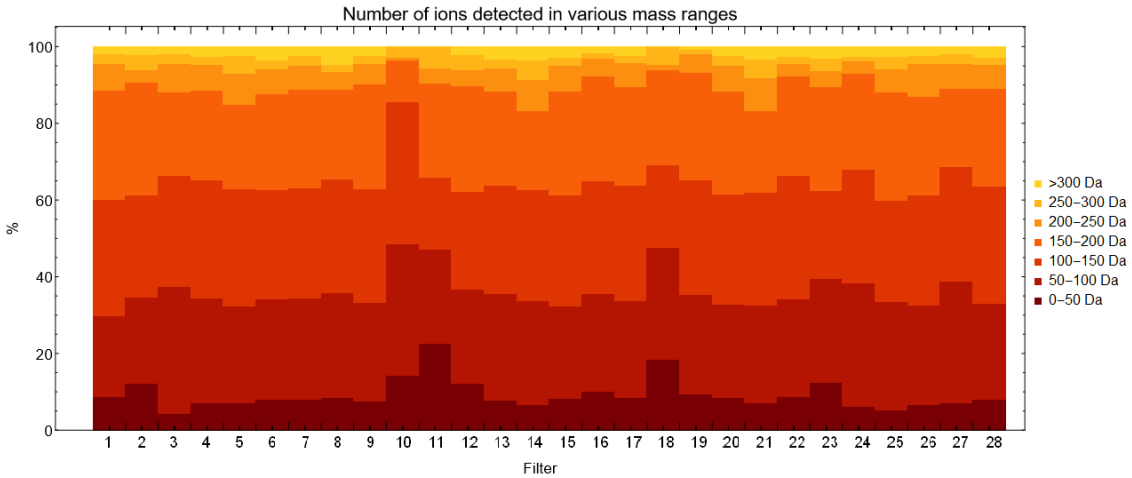


Figure 9: Relative number of ions that is desorbed per filter categorized in various mass ranges.

### 3.3 Volatility

The total mass that is desorbed in a particular temperature step tells something about the volatility of the compounds: the more volatile they are, the sooner they release from the filters. Figure 10 shows the relative mass desorbed per temperature step for each filter on  $E/N = 125$  Td. The mass desorbed in each temperature step is normalized to the total mass desorbed in that filter which makes comparisons between the different

filters easier. As the figure shows, there are some highly volatile compounds (desorbed at  $T = 100\text{ }^{\circ}\text{C}$ ) but they account only for a small fraction of the mass. The compounds that are semi-volatile account for most the mass that is released and the less volatile compounds (released above  $T = 250\text{ }^{\circ}\text{C}$ ) take up only a small fraction of the mass.

Some filters show a higher concentration of compounds that were released in the last temperature step, filter 2, 10, 12 and 22. These filters were the only filters that contained the compound with a mass of 97.028 Da. The molecular formula belonging to this mass is  $\text{C}_5\text{H}_4\text{O}_2\text{H}^+$ , which is protonated furfural. The mass of furfural is relatively low and it is very volatile. It is expected to desorb at temperatures around  $100\text{ }^{\circ}\text{C}$ , so what is seen here could be a fragment of another (heavier) compound that was present in these filters. On  $E/N = 85\text{ Td}$ , this compounds is not seen, what proves that is is indeed a fragmentation product, which is stable against fragmentation on  $85\text{ Td}$ .

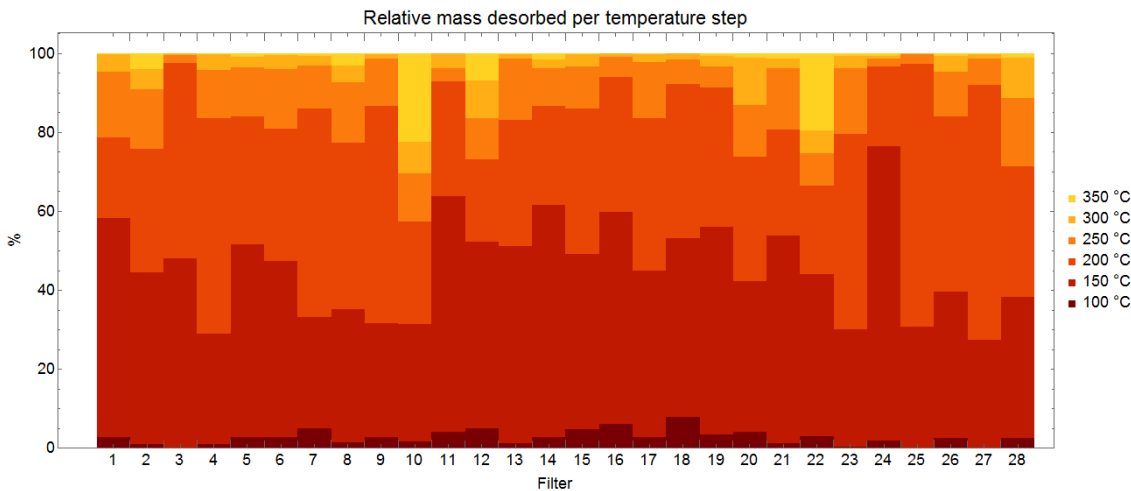


Figure 10: Total mass desorbed in each temperature step normalized to the total mass that is released from the filters. Most of the mass is desorbed at  $T = 150\text{ }^{\circ}\text{C}$  and  $T = 200\text{ }^{\circ}\text{C}$  and only little mass is desorbed at the first and last temperature step.

### 3.4 Mass defect

Another way to gain some insight into the structure of the compounds is by looking at the mass defect. The mass defect is defined by the difference between the predicted mass of a molecule and the actual mass of it, caused by the nuclear binding energy, which would be needed to disassemble a nucleus into its constituents. For the purposes of this research, we look to the mass defect of the compounds relative of the alkanes. The alkanes are molecules only consisting of carbon and hydrogen with the following formula:  $\text{C}_n\text{H}_{2n+2}$ . Alkanes have a very low mass defect due to the high number of hydrogen atoms. Organic compounds consisting of carbon, hydrogen, and atoms like oxygen and nitrogen will have a mass defect higher than that of the alkanes. Compounds with a mass defect close to that of alkanes are then alkane-like compounds (i.e. mostly existing of carbon and hydrogen atoms). The more oxygen a compound has, the bigger the difference to the alkanes will be. Figure 11 shows all the detected compounds with their corresponding mass defect. The gray line represents the mass defects of the alkanes, calculated using a fit through several calculated points.

The green squares (Figure 11) represent compounds that are only detected on  $E/N = 85\text{ Td}$  and they are roughly scattered between 200 and 400 Da, meaning these compound were probably also present at high  $E/N$  but fragmented in the drift tube. The fragments of these ions pop up as yellow stars in the lower left corner of the figure with a mass below 120 Da, meaning they are only detected at high  $E/N$ . These compounds are probably the fragmentation products of those that were only detected on  $85\text{ Td}$ . They do not show up on  $85\text{ Td}$  because the energy was not high enough to fragment these compounds.

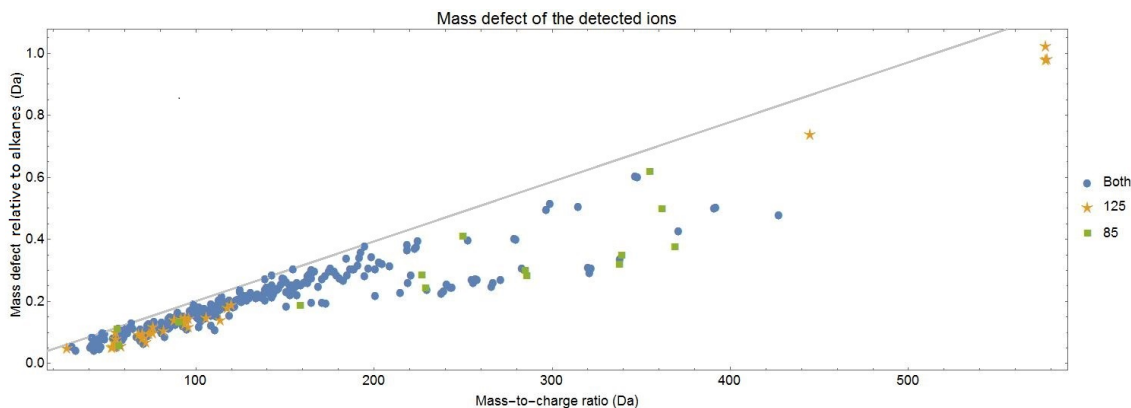


Figure 11: The detected components with their mass defect. The blue dots represent compounds that have been detected at both E/N settings, the green squares are compounds detected only at E/N = 85 Td and the yellow stars have only been detected at E/N = 125 Td

### 3.5 Differences day and night

Half of the filters (the odd numbered filters) are measured during daytime while the other half is measured during nighttime, which gives a good opportunity to see if there are any difference in the filters between day and night. Typical work hours in Beijing are 9 am to 6 pm [15] so more emission of traffic and industry is expected during these hours. At night fewer oxidation processes occur than during daytime thus heavier ions are expected to be more abundant during night. The values in the figure are calculated as follows:

$$\frac{[\text{Day}]}{\frac{1}{2}([\text{Day}] + [\text{Night}])} \quad (14)$$

where the square brackets denote the average concentration of the ion for all the filters in the group. If the value is one it means that the concentrations were the same for day and night. Ions with values higher than one showed higher concentrations during the day. For high E/N, most of the ions seem to be close to one, meaning the concentrations are not very different for day and night. However, for low E/N, almost all the ions are below the line, meaning they were more abundant during the night than during daytime (Figure 12). For the following analysis, all zeros have been excluded from the datasets. The datasets of the samples

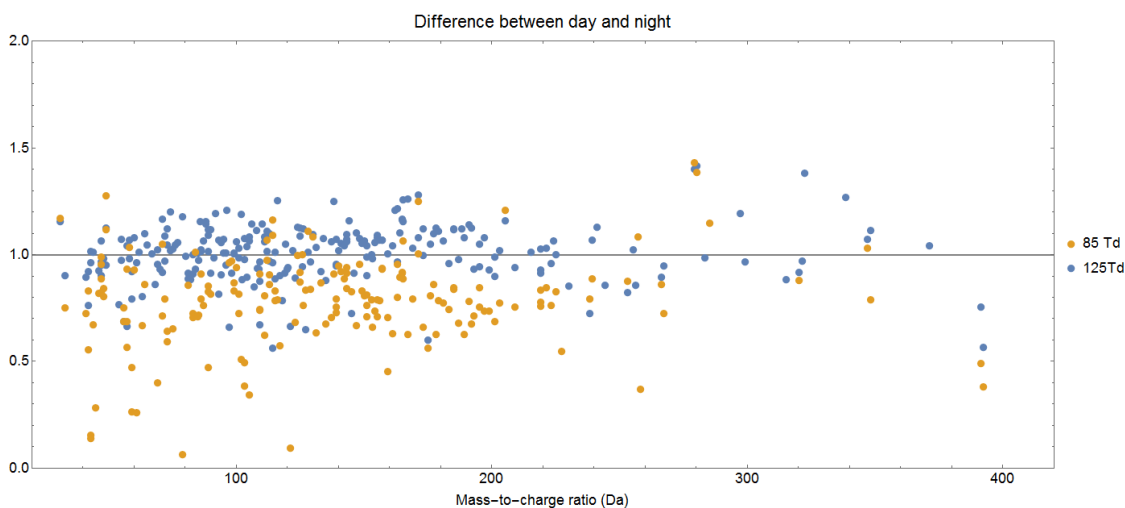


Figure 12: Difference between day and night concentrations for all ions. The yellow dots represent ions measured on E/N = 85 Td and the blue ones E/N = 125 Td.

taken during daytime are compared to those that were taken during nighttime. After applying the limit of detection, not all compounds show the same number of data points for the two datasets that survived this limit. Keeping the zeros in the dataset will highly influence statistical analysis, as an ion that was detected 14 times during day could be only detected 3 times during night and setting the other 11 values to zero will automatically cause statistical differences. It is hard to tell if the actual value of the concentration is 0, as the blanks could get polluted somewhere in the process.

A T-test is used to compare the two groups, which determines if the two datasets significantly differ from each other. A significance level of 5% is used to compare the groups, meaning that the ions have a 5% change, or lower, to be part of the other group. If the distribution of the ions was completely randomized, 5% of the total ions would be significant different. As the total detected number of ions is 286, about 6 ions could pop up for this significance level purely by chance. Table 4 give the ions for which the p-value is the lowest, for both E/N settings. The corresponding boxplots are given in Appendix A, these show how the day and night concentrations are distributed. Only a few ions seem to be statistically different for a significance level of 5% and we expect 6 to be significantly different just by chance, so it is hard to tell which of these compounds really show significant differences between their day- and night concentrations. The T-test is also done without excluding the zeros and with the concentrations before applying the limit of detection, both cases showed unrealistically low p-values of below 0.1%. These low p-values often show up when one of the datasets contain a lot of zeros. Excluding the zeros seems to be the most conservative method.

m/z	E/N	Molecular formula	Mean concentration daytime (ng/m <sup>3</sup> )	Mean concentration nighttime (ng/m <sup>3</sup> )	p-value	No. of day filters	No. of night filters
71.084	125	C <sub>5</sub> H <sub>10</sub> H <sup>+</sup>	5.73	4.10	0.045	13	9
93.068	125	C <sub>7</sub> H <sub>8</sub> H <sup>+</sup>	3.27	4.75	0.047	8	10
121.062	125	C <sub>8</sub> H <sub>8</sub> OH <sup>+</sup>	4.90	9.87	0.016	11	11
171.14	125	C <sub>10</sub> H <sub>18</sub> O <sub>2</sub> H <sup>+</sup>	13.79	7.76	0.013	14	12
175.049	125	C <sub>9</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub> H <sup>+</sup>	9.50	22.09	0.026	13	12
238.293	125	C <sub>16</sub> H <sub>31</sub> NH <sup>+</sup>	10.51	18.52	0.042	13	11
279.141	125	C <sub>12</sub> H <sub>22</sub> O <sub>7</sub> H <sup>+</sup>	65.45	28.03	0.028	14	14
280.144	125	<sup>13</sup> CC <sub>11</sub> H <sub>22</sub> O <sub>7</sub> H <sup>+</sup>	11.41	4.71	0.032	14	13
57.033	85	C <sub>3</sub> H <sub>4</sub> OH <sup>+</sup>	20.93	53.05	0.008	14	14
83.049	85	C <sub>5</sub> H <sub>6</sub> OH <sup>+</sup>	12.85	23.59	0.035	13	13
126.054	85	C <sub>6</sub> H <sub>7</sub> O <sub>2</sub> NH <sup>+</sup>	5.12	8.34	0.047	7	5
131.034	85	C <sub>5</sub> H <sub>6</sub> O <sub>4</sub> H <sup>+</sup>	9.85	21.32	0.041	10	11
153.083	85	C <sub>9</sub> H <sub>12</sub> O <sub>2</sub> H <sup>+</sup>	5.41	10.97	0.034	12	14
167.032	85	<sup>13</sup> CC <sub>3</sub> H <sub>7</sub> O <sub>6</sub> NH <sup>+</sup>	13.63	29.93	0.043	12	12
279.141	85	C <sub>12</sub> H <sub>22</sub> O <sub>7</sub> H <sup>+</sup>	69.95	27.83	0.011	13	14
280.144	85	<sup>13</sup> CC <sub>11</sub> H <sub>22</sub> O <sub>7</sub> H <sup>+</sup>	15.40	6.85	0.016	9	7

Table 4: The ions for which the statistical difference between day and night is the biggest. A lower p-value means a higher difference. The most probable molecular formula is given in column 3. Column 2 gives the E/N on which the measurement was made. The last two columns show in how many filters the compounds is detected.

Only a few ions show a significance level below 5%, of which some could be based on random chance. On both E/N settings, however, there are two compounds that look interesting. Both settings show high concentrations of the compound with mass ratio 279.141 Da, with C<sub>12</sub>H<sub>22</sub>O<sub>7</sub>H<sup>+</sup> as molecular formula, and 280.144, which is an isotope of 279.141 in which one of the carbon atoms has an extra neutron: <sup>13</sup>CC<sub>11</sub>H<sub>22</sub>O<sub>7</sub>H<sup>+</sup>. The concentrations during day are almost twice as high as during night. The abundance of this isotope is about 15 % compared to the original compound, which roughly matches the detected concentrations [16]. Furthermore, these ions show a striking resemblance in the overview (Figure 12), the four points are very close to each other, meaning that their differences between day and night are practically equal for both E/N settings. This compound could thus either be a tracer for anthropogenic emissions or biogenic emissions that are likely to happen during day and less likely during night.

Another interesting ion with a low p-value is C<sub>10</sub>H<sub>18</sub>O<sub>2</sub>H<sup>+</sup> with a mass of 171.14, which could be protonated citronellic acid. Citronellic acid is an oxidation product of citronellal. Citronellal is a monoterpene, a form of isoprene that is released into the environment mainly from plants. The concentrations are higher during day as the oxidation process is more likely to happen during daytime [17].

m/z	E/N	Possible molecular formula	Mean concentration daytime (ng/m <sup>3</sup> )	Mean concentration nighttime (ng/m <sup>3</sup> )	p-value	No. of day filters	No. of night filters
280.144	125	<sup>13</sup> CC <sub>11</sub> H <sub>22</sub> O <sub>7</sub> H <sup>+</sup>	11.41	4.65	0.032	14	13
279.141	125	C <sub>12</sub> H <sub>22</sub> O <sub>7</sub> H <sup>+</sup>	65.45	28.03	0.028	14	14
322.317	125		10.34	4.64	0.593	3	2
171.14	125	C <sub>10</sub> H <sub>18</sub> O <sub>2</sub> H <sup>+</sup>	13.79	7.76	0.013	14	12
167.032	125	<sup>13</sup> CC <sub>3</sub> H <sub>7</sub> O <sub>6</sub> NH <sup>+</sup>	48.15	28.15	0.204	2	6
280.144	85	<sup>13</sup> CC <sub>11</sub> H <sub>22</sub> O <sub>7</sub> H <sup>+</sup>	15.40	6.85	0.016	9	7
279.141	85	C <sub>12</sub> H <sub>22</sub> O <sub>7</sub> H <sup>+</sup>	69.95	27.83	0.011	13	14
171.14	85	C <sub>10</sub> H <sub>18</sub> O <sub>2</sub> H <sup>+</sup>	14.82	8.89	0.074	12	11
205.081	85	<sup>13</sup> CC <sub>7</sub> H <sub>13</sub> O <sub>5</sub> NH <sup>+</sup>	13.10	8.54	0.082	12	11
257.229	85	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub> H <sup>+</sup>	15.9	13.45	0.806	3	5

Table 5: The ions that were most abundant during day, giving in order of highest day-night difference, for both E/N settings.

The ions can also be selected on their difference between day and night. This means picking the ions with the highest value (higher concentrations during daytime) and the ions with the lowest value (highest concentrations during night) from Figure 12. The ions that are the most abundant during day are given in Table 5 and the ions that are most abundant during night are given in Table 6.

Between the ions that are most abundant during day we again see 279.141 and its isotope 280.144. The rest of the ions showing up have a rather high p-value, meaning the differences in the datasets are not big enough to say they statistically differ. Another compound that pops up again for both E/N setting is 171.14. We can safely say that these three compounds show the clearest statistical difference in abundance between day and night.

Most of the ions that are most abundant during night neither show a low p-value, except for the compound with a mass of 175.049 with the molecular formula: C<sub>9</sub>H<sub>6</sub>N<sub>2</sub>O<sub>2</sub>H<sup>+</sup>, better known as toluene diisocyanate.

m/z	E/N	Possible molecular formula	Mean concentration daytime (ng/m <sup>3</sup> )	Mean concentration nighttime (ng/m <sup>3</sup> )	p-value	No. of day filters	No. of night filters
114.025	125	C <sub>4</sub> H <sub>3</sub> O <sub>3</sub> NH <sup>+</sup>	7.63	19.62	0.411	3	2
392.225	125	<sup>13</sup> CC <sub>23</sub> H <sub>38</sub> O <sub>4</sub> H <sup>+</sup>	4.45	11.24	0.146	9	8
175.049	125	C <sub>9</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub> H <sup>+</sup>	9.50	22.09	0.026	13	12
127.038	125	C <sub>6</sub> H <sub>6</sub> O <sub>3</sub> H <sup>+</sup>	24.79	51.83	0.087	13	12
97.028	125	C <sub>5</sub> H <sub>4</sub> O <sub>2</sub> H <sup>+</sup>	92.85	188.4	0.059	14	14
79.053	85	C <sub>6</sub> H <sub>6</sub> H <sup>+</sup>	5.42	164.2	0.197	8	6
121.062	85	C <sub>8</sub> H <sub>8</sub> OH <sup>+</sup>	4.80	84.75	0.525	4	10
43.018	85	C <sub>2</sub> H <sub>2</sub> OH <sup>+</sup>	19.33	261.8	0.238	13	14
61.028	85	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> H <sup>+</sup>	87.85	584.5	0.122	13	14
45.034	85	C <sub>2</sub> H <sub>4</sub> OH <sup>+</sup>	12.73	77.9	0.319	12	14

Table 6: The ions that were most abundant during night, giving in order of highest day-night difference, for both E/N settings.

### 3.6 Differences week and weekend

Another interesting thing to look at would be the difference between the pollution during weekdays and during the weekend. A decrease in anthropogenic emissions is expected, as the industry is less active and there is less traffic in the weekend. The biogenic emissions are not expected to change during the weekend. The overview of the ions are given in Figure 13 and are calculated in the same way as the difference between day and night. Ions with a value higher than one showed higher concentrations in the weekday filters.

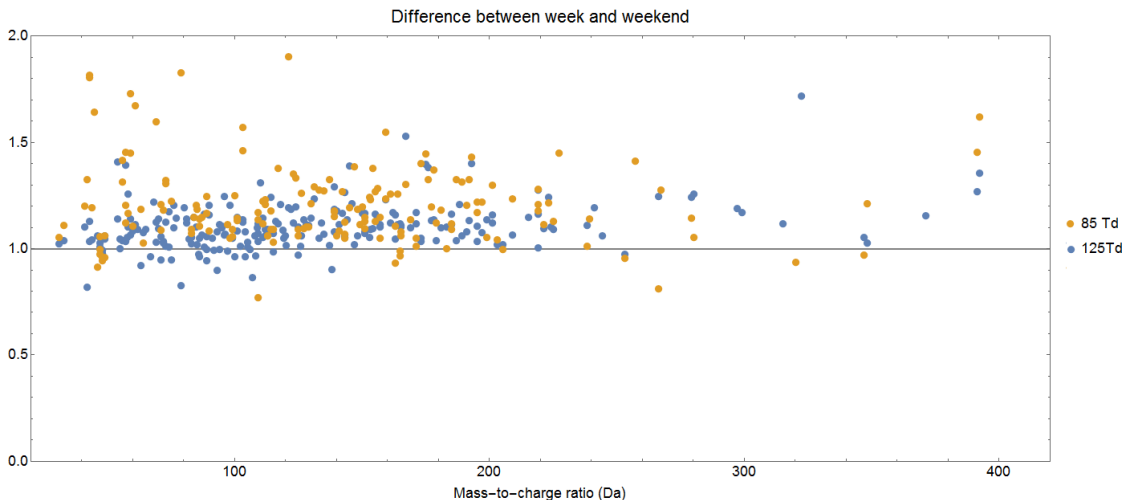


Figure 13: Difference between weekday and weekend concentrations for all ions. The yellow dots represent ions measured on  $E/N = 85 Td$  and the blue ones  $E/N = 125 Td$ .

From the figure it is clear that the week filters are more polluted than the weekend filters since almost all the ions show values above one. Some ions show values below one, meaning they were more abundant during the weekend. The difference between the two  $E/N$  setting seems to be less drastic than in Figure 12. However, the differences seem bigger again for the measurements on  $E/N = 85 Td$ .

The statistical differences between the weekdays and weekends are smaller than those between day and night and thus a significance level of 10 percent is used to compare these groups, whereas a significance level of 5 percent was used to compare day and night. Table 7 give the ions all the ions based on their p-value for both  $E/N$  setting. There are no differences for a significance level of 5 percent. The corresponding boxplots are found in Appendix B. There is a good reason why the statistical differences between week and weekend filters are much lower. The total concentration in the weekend filters is relatively low compared to the concentrations in the weekday filters (Figure 5) and the differences between weekend filters is much lower than between the weekday filters. The variance of the weekday filters is thus a lot bigger, causing the distribution of the ions during the week to overlap the distribution during the weekends, making statistical analysis a lot harder, which can be seen in the boxplots too (Appendix B). Nonetheless, looking at Figure 13, it is safe to assume the weekday filters are more polluted than the weekend filters.

One ion pops up in both  $E/N$  settings, that is, the one with a mass of 193.021 Da. The corresponding molecular formula is  $C_9H_4O_5H^+$ , which is believed to be protonated trimellitic anhydride. Trimellitic anhydride (TMA) is used in the production process of many chemicals and plastics. It is used in the production of cars, in paints and coatings and in inks and packing materials. It may be released in air and water from facilities producing or using it. There are believed to be no natural sources of the release of TMA into the environment [18]. The concentration of this compound is higher during weekdays, as the industry is more likely to be active during weekdays.

The ion with the lowest p-value is  $C_6H_5NO_2H^+$ , with a mass of 124.041. The corresponding compound is protonated nitrobenzene. The concentrations of nitrobenzene is during the weekdays almost twice as high as during the weekends. Nitrobenzene can be formed in the atmosphere from reactions of benzene with nitrogen oxides. The reaction is possibly initiated by hydroxyl radicals. Once formed, nitrobenzene reacts quite slowly in the atmosphere, what could be an indication for the levels during the weekends. It has not been

possible yet to quantify this source of nitrobenzene [19]. Benzene is a primary indicator of traffic emissions, as nitrobenzene is formed from atmospheric benzene, this can be an indirect indicator for traffic emissions.

m/z	E/N	Possible molecular formula	Mean concentration weekdays (ng/m <sup>3</sup> )	Mean concentration weekends (ng/m <sup>3</sup> )	p-value	No. weekday filters	No. weekend filters
43.053	125	C <sub>3</sub> H <sub>6</sub> H <sup>+</sup>	7.29	5.62	0.080	19	8
57.033	125	C <sub>3</sub> H <sub>4</sub> OH <sup>+</sup>	36.35	15.87	0.065	11	5
139.039	125	C <sub>7</sub> H <sub>6</sub> O <sub>3</sub> H <sup>+</sup>	6.72	3.68	0.068	14	7
193.021	125	C <sub>9</sub> H <sub>4</sub> O <sub>5</sub> H <sup>+</sup>	9.34	4.03	0.095	11	4
219.063	125	C <sub>15</sub> H <sub>6</sub> O <sub>2</sub> H <sup>+</sup>	3.00	1.70	0.057	10	5
124.041	85	C <sub>6</sub> H <sub>5</sub> NO <sub>2</sub> H <sup>+</sup>	9.88	4.96	0.052	6	3
126.054	85	C <sub>6</sub> H <sub>7</sub> O <sub>2</sub> NH <sup>+</sup>	7.49	4.40	0.073	8	4
142.05	85	<sup>13</sup> CCH <sub>8</sub> O <sub>5</sub> N <sub>2</sub> H <sup>+</sup>	7.66	4.40	0.079	4	2
173.059	85	C <sub>8</sub> H <sub>12</sub> O <sub>4</sub> H <sup>+</sup>	10.26	4.40	0.086	9	6
193.021	85	C <sub>9</sub> H <sub>4</sub> O <sub>5</sub> H <sup>+</sup>	11.59	4.62	0.085	9	5

Table 7: The ions for which the statistical difference between weekdays and weekends is the biggest. A lower p-value means a higher difference. The most probable molecular formula is given in column 3. Column 2 gives the E/N on which the measurement was made. The last two columns give the number of filters in with the compound was found for weekdays and weekends respectively.

The ions can also be selected based on their difference between weekdays and weekends, like in the previous section. Table 8 gives the ions that were most abundant during the weekdays and Table 9 gives the ions that were most abundant during the weekends. Note, however, that the points below one in Figure 13 are very close to one. Moreover, the p-values of the ions in Table 13 are very high, so no conclusions can be drawn from this.

Benzene is one of the ions that was most abundant during the weekdays. Protonated benzene has a mass of 79.053 and molecular formula C<sub>7</sub>H<sub>7</sub>H<sup>+</sup>. Benzene is too volatile and remains in the gas phase in the atmosphere, so it can not be detected directly. However, benzene is a common fragmentation product of toluene. Toluene, C<sub>7</sub>H<sub>8</sub>O, is an indicator for traffic emissions. The high concentrations of benzene could thus indirectly be an indicator for traffic emissions too. The high concentrations of benzene in the week filters are only seen for E/N = 85 Td, on E/N = 125 Td the concentrations of benzene are low for weekdays and weekends (Figure 9). The aromatic structure of benzene makes it too sturdy to fragment into other compounds, and if benzene is a fragmentation product it should also be seen for E/N = 125. This might suggest that we are seeing another form of C<sub>7</sub>H<sub>7</sub>, perhaps an aliphatic compound, which is safe against fragmentation on E/N = 85 Td but not strong enough to survive E/N = 125 Td.

m/z	E/N	Possible molecular formula	Mean concentration weekdays (ng/m <sup>3</sup> )	Mean concentration weekends (ng/m <sup>3</sup> )	p-value	No. weekday filters	No. weekend filters
322.317	125	C <sub>22</sub> H <sub>43</sub> NH <sup>+</sup>	9.68	1.60	-	4	1
167.032	125	<sup>13</sup> CC <sub>3</sub> H <sub>7</sub> O <sub>6</sub> NH <sup>+</sup>	36.28	11.21	-	7	1
54.034	125	C <sub>3</sub> H <sub>3</sub> NH <sup>+</sup>	4.12	1.73	-	4	1
193.021	125	C <sub>9</sub> H <sub>4</sub> O <sub>5</sub> H <sup>+</sup>	9.43	1.73	0.095	11	4
175.049	125	C <sub>9</sub> H <sub>6</sub> N <sub>2</sub> O <sub>2</sub> H <sup>+</sup>	18.49	7.97	0.102	18	7
121.062	85	C <sub>8</sub> H <sub>8</sub> OH <sup>+</sup>	99.68	5.03	0.527	10	4
79.053	85	C <sub>6</sub> H <sub>6</sub> H <sup>+</sup>	84.38	7.84	0.670	12	2
43.018	85	C <sub>2</sub> H <sub>2</sub> OH <sup>+</sup>	197.7	20.09	0.433	19	8
59.013	85	C <sub>2</sub> H <sub>2</sub> O <sub>2</sub> H <sup>+</sup>	29.55	4.65	0.527	5	2
61.028	85	C <sub>2</sub> H <sub>4</sub> O <sub>2</sub> H <sup>+</sup>	453.0	89.15	0.307	19	8

Table 8: The ions that were most abundant during the week, giving in order of highest week-weekend difference, for both E/N settings.

m/z	E/N	Possible molecular formula	Mean concentration weekdays (ng/m <sup>3</sup> )	Mean concentration weekends (ng/m <sup>3</sup> )	p-value	No. weekday filters	No. weekend filters
79.053	125	C <sub>6</sub> H <sub>6</sub> H <sup>+</sup>	3.94	5.59	0.178	17	4
107.05	125	C <sub>7</sub> H <sub>6</sub> OH <sup>+</sup>	3.86	5.08	0.346	14	2
93.068	125	C <sub>7</sub> H <sub>8</sub> H <sup>+</sup>	3.94	4.83	0.395	15	3
138.054	125	<sup>13</sup> CC <sub>2</sub> H <sub>8</sub> O <sub>4</sub> N <sub>2</sub> H <sup>+</sup>	3.83	4.67	0.616	15	4
63.019	125	C <sub>5</sub> H <sub>2</sub> H <sup>+</sup>	215.1	253.0	0.629	20	8
109.027	85	C <sub>6</sub> H <sub>4</sub> O <sub>2</sub> H <sup>+</sup>	13.48	21.47	-	4	1
266.27	85	C <sub>18</sub> H <sub>34</sub> OH <sup>+</sup>	4.83	7.06	0.268	11	2
163.039	85	C <sub>9</sub> H <sub>6</sub> O <sub>3</sub> H <sup>+</sup>	9.64	11.03	0.656	17	7
320.311	85	C <sub>22</sub> H <sub>41</sub> NH <sup>+</sup>	4.14	4.69	-	1	2
253.095	85		7.46	8.15	0.839	9	4

Table 9: The ions that were most abundant during the weekend, giving in order of highest week-weekend difference, for both E/N settings.



## 4 Conclusion

The concentrations of VOCs in the air near Beijing at the time of sampling vary from  $0.7 \mu\text{g}/\text{m}^3$  to  $6.5 \mu\text{g}/\text{m}^3$ . The errors lie roughly between 15% and 25% which is reasonable for measurements made with the PTR-MS.

The bulk of the ions is desorbed at 150 and 200 degrees Celsius, and a small part at the remaining temperature steps. At the last step, only a very small fraction of the mass is desorbed. Most compounds were volatile enough to desorb below 200 degrees Celsius.

The fragmentation pattern is not the same for the different E/N settings. On 85 Td we see several compounds with a mass between 200 and 400 Da that do not show up on 125 Td. On 125 Td some lighter compounds are detected that are not seen for 85 Td, meaning these are the fragments of the particles that only showed up on 85 Td.

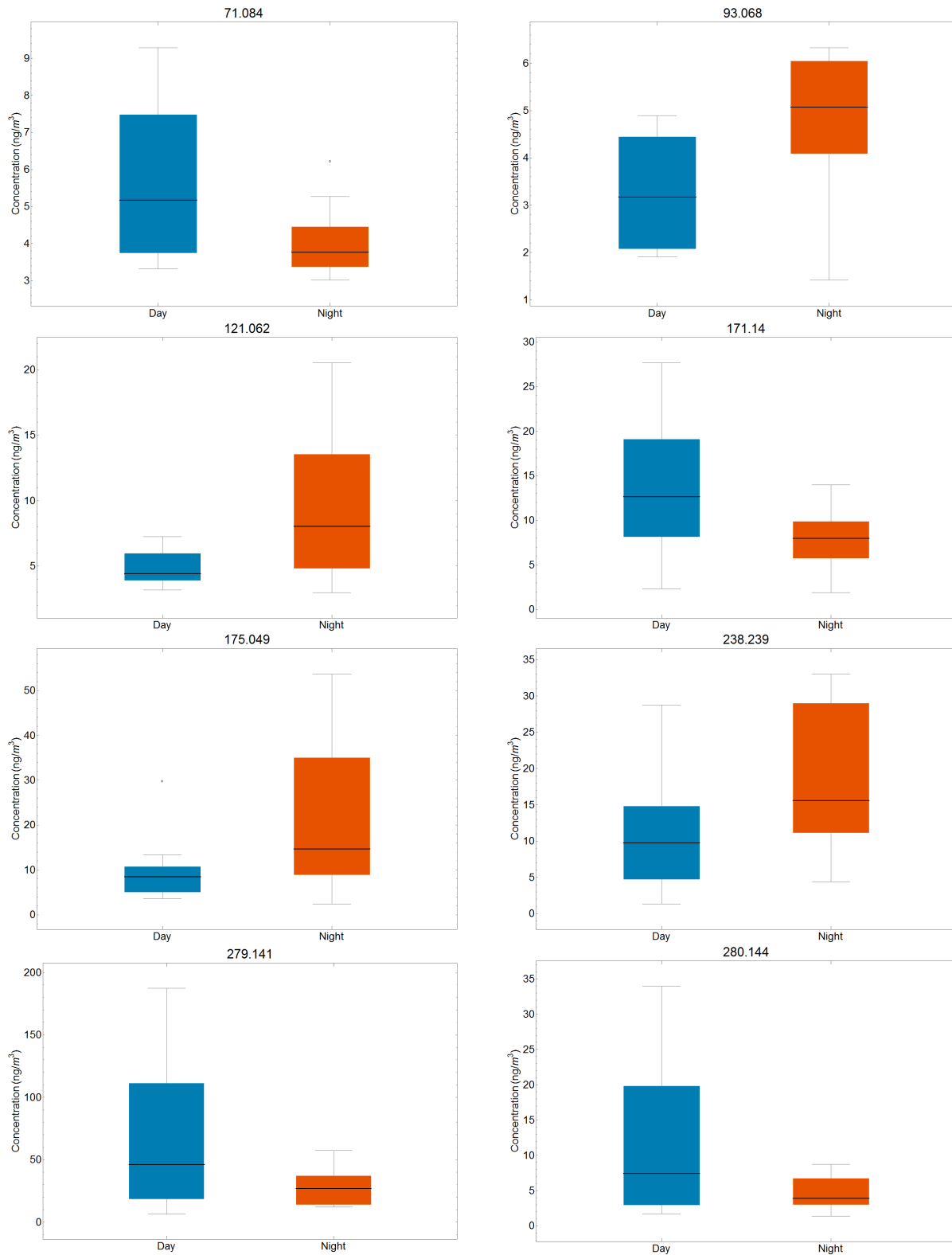
Surprising is the low number of ions with a mass above 200 Dalton. At first sight, it was expected that the PTR-MS was not sensitive enough to detect the higher masses, or limit of detection was too strict. However, use of a calibration gas showed that the PTR-MS achieved a good sensitivity for ions with a mass above 200 Dalton, meaning that these ions were just not abundant in the air at the location where the samples were taken.

The differences between day and night are not that clear at first sight, however, there are a few of ions which possess a statistical day and night difference but most of these could be statistically different pure by chance. However, some ions are very likely to be stastically different. This difference could be of anthropogenic cause or by a change of processes in the atmosphere during day and night. More oxidizing processes are expected during daytime, due to the sunlight and elevated hydroxyl radical concentrations. This would lead to the breakdown of VOCs and thus higher concentrations of smaller compounds. However, there is not a clear pattern found. Citronellic acid is found as a potential tracer of biogenic emissions of VOCs and  $\text{C}_{12}\text{H}_{22}\text{O}_7\text{H}^+$  is very likely to be a tracer of anthropogenic emissions happening during daytime.

The difference between weekdays and weekends is clearer, almost all the ions show higher concentrations during the weekdays than in the weekend. Biogenic emissions are expected to remain the same during weekdays and weekends, meaning these differences are most likely due to changes in anthropogenic emissions. There is more traffic during the weekdays and working hours are the same as in the Netherlands, meaning that industry is less active in the weekend. Due to the bigger variance in concentration in the week filters relative to the weekend filters, statistical differences are hard to spot. Likely tracers that are found for anthropogenic emissions are trimellitic anhydride and nitrobenzene. Elevated concentrations of benzene are also found for E/N = 85 Td, but not for higher E/N so it is hard to tell if we are actually dealing with benzene or with an aliphatic compound with the same molecular formula.

For further research, it could be interesting to take a closer look at single ions and what the source of these ions could be.

## A Boxplots day and night difference

Figure 14: Boxplots for the ions in table 4 measured on  $E/N = 125$  Td.

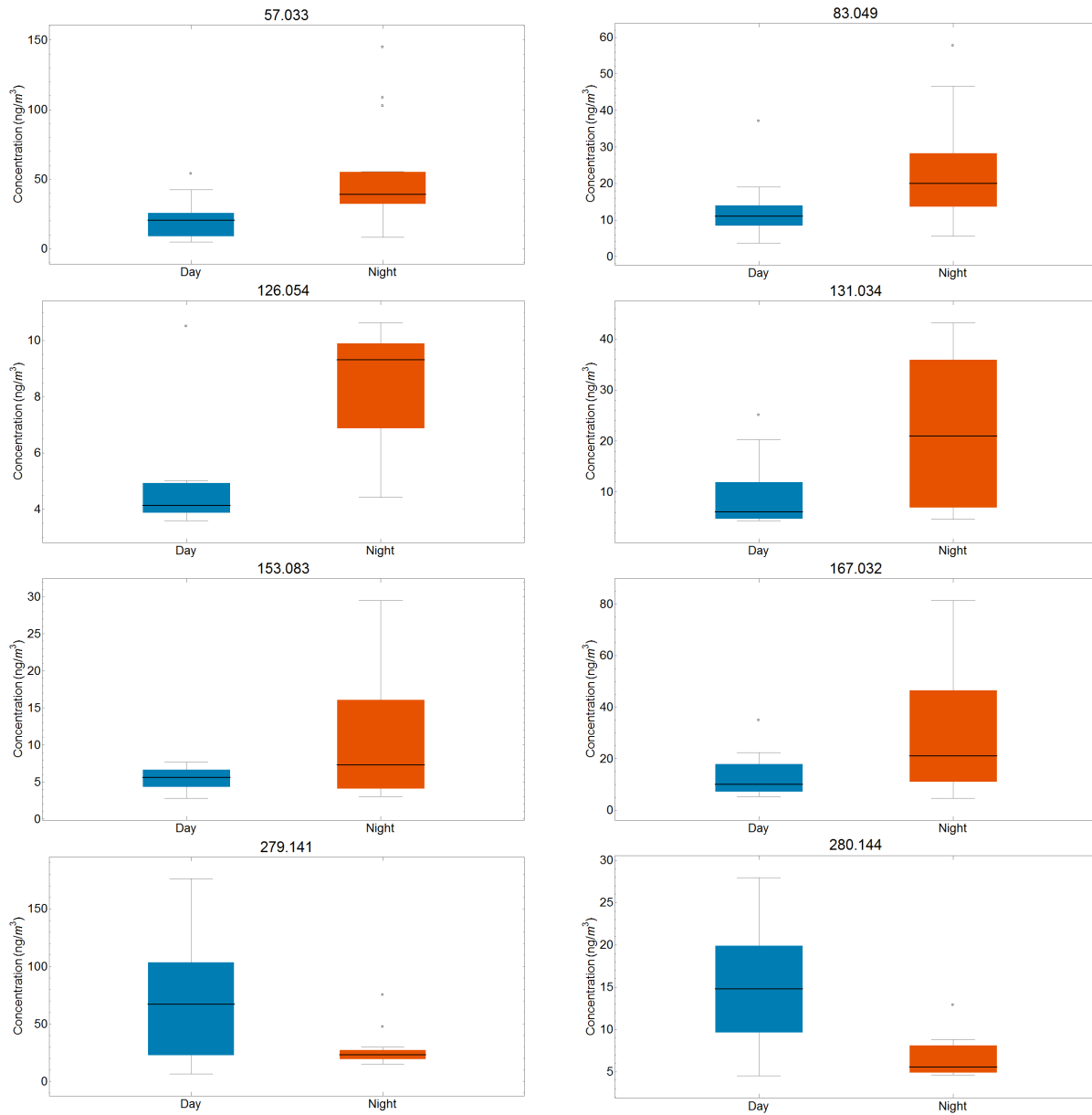
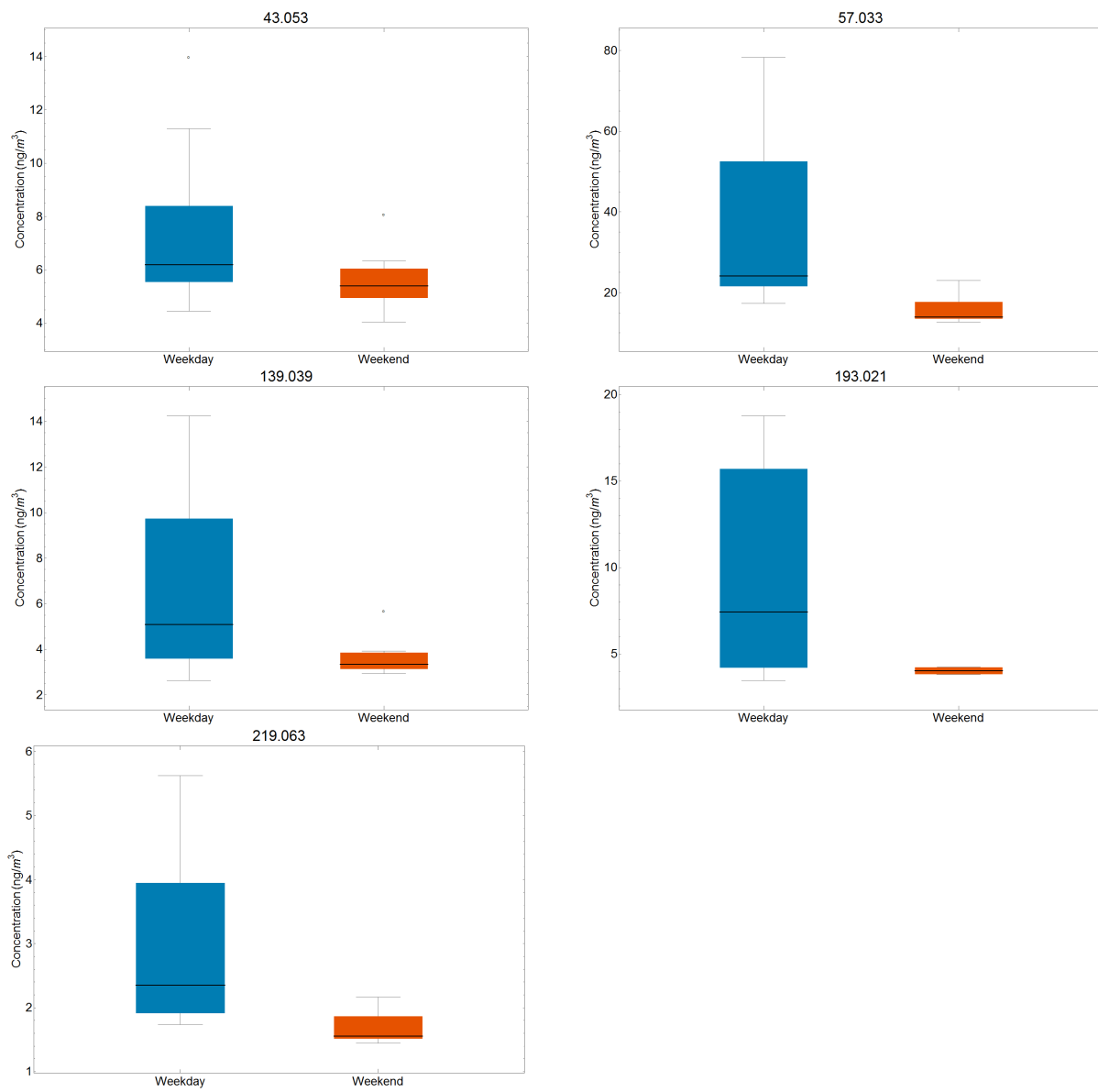


Figure 15: Boxplots for the ions in table 4 measured on  $E/N = 85$  Td.

## B Boxplots weekday and weekend difference

Figure 16: Boxplots for the ions in table 7 measured on  $E/N = 125$  Td.

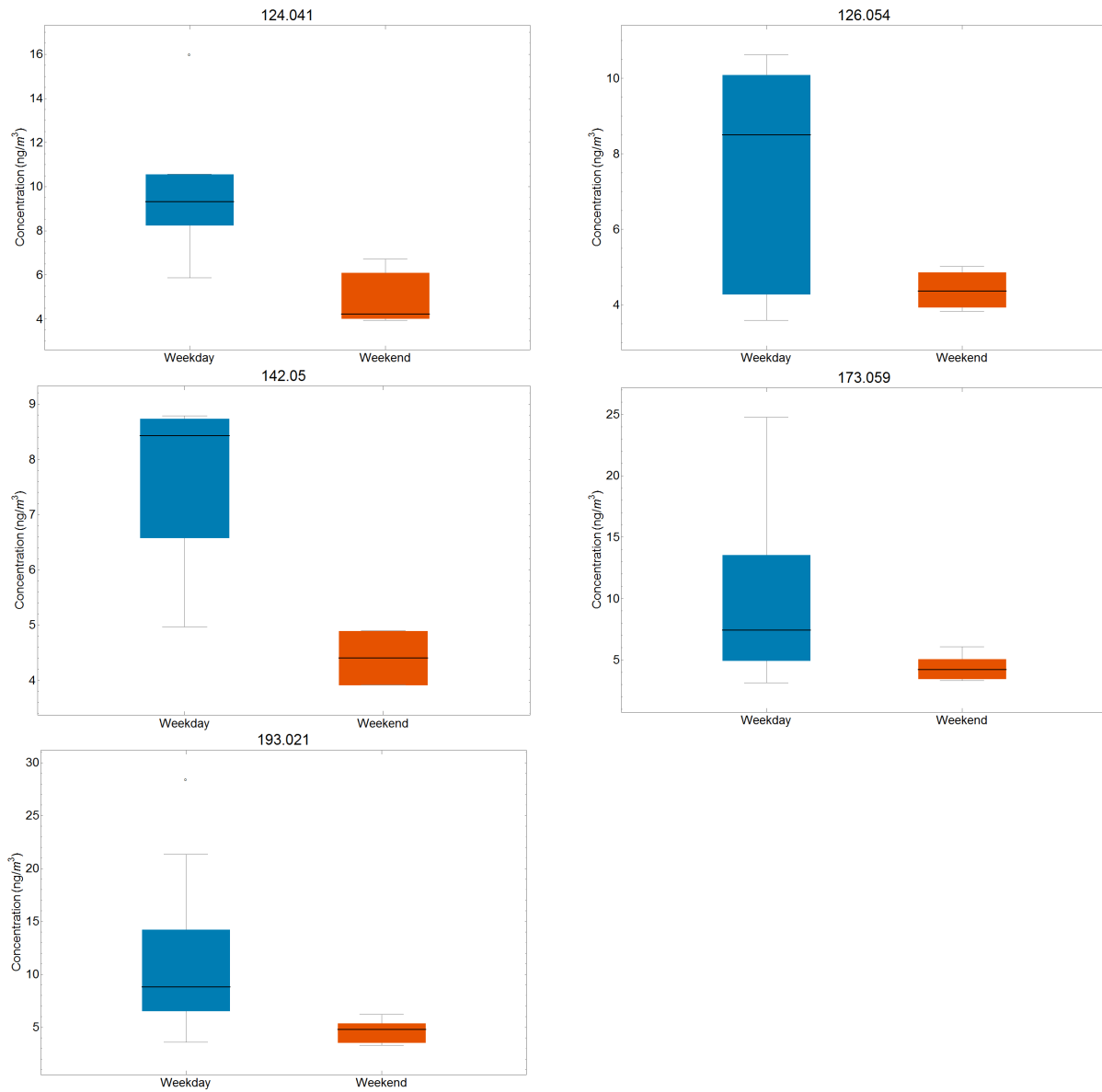


Figure 17: Boxplots for the ions in table 7 measured on  $E/N = 85$  Td.

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