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Volatile Organic Compounds (VOCs) in the smoke emanating from the fire at the Kagghamra waste storage facility

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Analysis report UiO/KI/ATM 01/2021 (25.02.2021)

1 Introduction

The Department of Chemistry of the University of Oslo (UiO) was commissioned to measure volatile organic compounds (VOCs) in the smoke emanating from the fire at the Kagghamra waste storage facility in the municipality of Botkyrka (Sweden). The fuel of the fire was described as unsorted construction waste, mainly consisting of wood, metal and plastics. Due to the poorly characterized nature of the waste, it was considered necessary to screen the smoke for toxic VOCs and to determine exposure levels in the nearby residential areas hit by the smoke.

2 Experimental

Figure 1: UiO's mobile laboratory with the PTR-TOF 1000 QB analyzer.

VOCs were measured by proton-transfer-reaction mass spectrometry (PTR-MS). This chemical-analytical technique has been extensively reviewed in the literature (Lindinger et al., 1998; de Gouw and Warneke, 2007; Yuan et al., 2017). A simple description can be found here[1]. PTR-MS is the state-of-the-art technique for online measurements of VOCs in fire plumes (Stockwell et al., 2015; Müller et al., 2016; Bruns et al., 2017; Koss et al., 2018). For the measurements reported herein, a proton-transfer-reaction time of flight mass spectrometry (PTR-ToF-MS) instrument (model PTR-TOF 1000 QB[2], Ionicon Analytik, Austria) was used. The analyzer was installed on UiO's mobile laboratory (Figure 1) and performed both mobile measurements (*i.e.*, it measured while the car was moving) and stationary measurements (*i.e.*, it measured while the car was parked with the analyzer being powered from the car battery). Measurements were carried out on the evening of Sunday, January 31, 2021 and during the first half of Monday, February 1, 2021. The PTR-MS instrument was calibrated using a dynamically diluted VOC standard (Apel-Riemer Environmental Inc., Miami, U.S.A. – see Appendix). For VOCs not present in the standard, we used the calibration factors reported by Koss et al. (2018).

3 Results and Discussion

3.1 VOCs in smoke emanating from the fire at the Kagghamra waste storage facility

Smoke contains hundreds of VOCs (*e.g.*, Hatch et al., 2017) and our automated data analysis detected 131 mass spectrometric signals with enhanced intensities in the smoke emanating from the fire at the Kagghamra waste storage facility. For reducing the complexity of the data, we only investigated compounds with concentrations > 1 µg m^{-3} measured at Tegelvretsvägen[3] on Monday, February 1, 2021, which is where and when the highest VOC concentrations were observed in a residential area (worst-case condition). Table 1 lists the compounds and concentrations measured at i) Tegelvretsvägen, ii) Söderängstorp (in proximity of SLB-analys' measurement station), and 3) directly at the fire. We note that that for safety reasons, the plume in the immediate vicinity of the fire was only sampled for 20 seconds at its outer edge. The reported concentrations may thus not be representative for the fire in its entirety.

[1] https://en.wikipedia.org/wiki/Proton-transfer-reaction_mass_spectrometry
[2] https://www.ionicon.com/products/details/mobile-voc-monitor-ptr-tof-qb
[3] see Figures 3a and 3b for locating the sections of Tegelvretsvägen where VOC levels peaked

Table 1: Major VOCs detected in the smoke emanating from the fire at the Kagghamra waste storage facility in the municipality of Botkyrka.

			Söderängstorp (SLB-analys station)		Tegelvretsvägen		At fire	
		time:	09:40:57 - 10:00:11		11:11:40 - 11:12:57		12:00:31 - 12:00:51	
		LAT:	59.0907		59.1005		59.0979	
		LON:	17.7780		17.8090		17.7884	
m/z	ion sum formula	compound assignment	VMR [ppbV]	Concentration [µg m^{-3}]	VMR [ppbV]	Concentration [µg m^{-3}]	VMR [ppbV]	Concentration [µg m^{-3}]
31.02	C1H3O1	formaldehyde	21.3	26.1	24.8	30.4	159.3	195.4
33.03	C1H5O1	methanol	52.1	68.2	57.3	75.1	854.7	1119.3
41.04	C3H5	unspecific hydrocarbon signal (fragment)	*	*	*	*	*	*
42.03	C2H4N1	acetonitrile (=methyl cyanide)	3.5	5.9	4.1	6.9	26.2	43.9
43.05	C3H7	unspecific hydrocarbon signal (fragment)	*	*	*	*	*	*
44.01	C1H2N1O1	isocyanic acid	1.0	1.8	1.2	2.1	16.0	28.1
45.03	C2H5O1	acetaldehyde	11.1	20.0	13.3	24.0	98.9	178.0
55.06	C4H7	1,3-butadiene	1.4	3.1	1.4	3.2	6.2	13.6
56.05	C3H6N1	propionitrile (=ethyl cyanide)	0.5	1.1	0.6	1.3	4.3	9.8
57.03	C3H5O1	acrolein	1.7	3.8	2.1	4.9	17.6	40.3
57.07	C4H9	unspecific hydrocarbon signal (fragment)	*	*	*	*	*	*
59.05	C3H7O1	acetone + propanal	12.0	28.4	14.4	34.1	122.9	291.6
60.05	C2H6N1O1	acetamide	1.4	3.4	1.6	4.0	18.8	45.4
61.03	C2H5O2	acetic acid + glycolaldehyde	16.2	39.7	15.5	37.9	246.5	604.9
69.03	C4H5O1	furan	2.5	7.1	2.9	8.1	49.8	138.5
71.05	C4H7O1	methylvinylketone + methacrolein + crotonaldehyde	1.2	3.4	1.4	4.1	14.5	41.6
71.08	C5H11	pentenes, methylbutenes, HC fragment	*	*	*	*	*	*
73.06	C4H9O1	methylethylketone + butanal + 2-methylpropanal	2.8	8.3	3.3	9.7	29.1	85.7
75.04	C3H7O2	propanoic acid + methyl acetate + ethyl formate + hydroxyacetone	6.3	19.0	6.7	20.4	73.8	223.5
79.06	C6H7	benzene	15.4	49.2	18.9	60.2	133.2	424.9
80.05	C5H6N1	pyridine + pentadienenitriles	0.9	2.8	1.1	3.5	19.6	63.4
83.05	C5H7O1	methylfurans	6.3	21.1	6.9	23.2	76.5	256.6
83.09	C6H11	unspecific hydrocarbon signal (fragment)	*	*	*	*	*	*
85.03	C4H5O2	2(3H)-furanone	0.7	2.3	1.0	3.3	30.2	103.8
85.07	C5H9O1	3-methyl-3-butene-2-one + cyclopentanone + isomers	1.4	4.9	1.7	5.7	13.4	46.2
85.10	C6H13	unspecific hydrocarbon signal (fragment)	*	*	*	*	*	*
87.04	C4H7O2	2,3-butanedione + methyl acrylate + isomers	1.5	5.3	1.6	5.5	29.6	104.1
87.08	C5H11O1	C5-ketones/aledhydes	0.8	2.7	0.9	3.3	2.8	9.9
89.06	C4H9O2	methyl propanoate + isomers	0.8	2.9	0.8	2.8	9.6	34.7
93.07	C7H9	toluene	8.3	31.3	10.1	38.0	58.2	218.9
95.05	C6H7O1	phenol	4.6	17.8	5.1	19.4	53.8	206.8
97.03	C5H5O2	furfural	1.8	7.1	1.8	7.2	33.5	131.4
97.08	C5H9N2	dimethylpyrazole	1.0	3.8	1.2	4.7	11.4	44.9
101.04	C5H9S	not identified	0.6	2.5	0.7	2.9	10.0	41.1
104.05	C7H6N1	benzonitrile (=phenyl cyanide)	1.0	4.3	1.3	5.5	9.5	40.1
105.07	C8H9	styrene	5.4	22.8	6.6	28.0	40.4	172.0
107.08	C8H11	xylenes / ethylbenzene	7.3	31.8	8.6	37.2	64.1	278.1
109.07	C7H9O1	methylphenols (=cresols) + anisol	2.8	12.5	3.0	13.3	16.2	71.7
119.08	C9H11	methyl styrenes + indane + propenyl benzenes	1.7	8.0	1.9	9.3	20.1	97.1
121.10	C9H13	C3-benzenes	1.4	6.8	1.5	7.3	12.0	58.7
123.07	C8H11O1	C2-phenols + methyl anisol	1.4	7.0	1.4	6.8	22.1	110.4
129.07	C10H9	napthalene	1.2	6.5	1.6	8.3	8.6	44.9

VMR: volume mixing ratio, 1 ppbV = 10^{-9} v/v

*: signal produced from different saturated and unsaturated linear hydrocarbons (including fragments for larger hydrocarbons), cannot be quantified

Table 1 is still difficult to interpret for the non-expert and we thus give a simplified interpretation:

1. The main VOC classes found in the smoke include:
   a. small linear hydrocarbons (*lin.*-C_xH_y, including saturated and unsaturated hydrocarbons)[4]
   b. small oxygenated VOCs ($C_xH_yO_z$, including methanol, formaldehyde, acetaldehyde, acetic acid, furans, phenols, etc.)
   c. aromatic hydrocarbons (*arom.*-C_xH_y, including benzene, toluene, xylenes/ethylbenzene, styrene, and naphthalene)
2. The major VOCs found in smoke emanating from the fire at the Kagghamra waste storage facility qualitatively resemble those typically found in smoke from forest fires (*e.g.*, Koss et al., 2018).
3. Known air toxics such as formaldehyde, 1,3-butadiene, and benzene were among the detected VOCs.
4. The concentration of isocyanic acid was low (≤ 2 µg m^{-3}) in residential areas. Methyl isocyanate was not detected. Isocyanates are formed in the thermal breakdown of nitrogen containing plastics (polyurethane, nylon, etc.)
5. No chlorinated VOCs were among the major VOCs detected. Chlorinated organics are formed as minor products (HCl being the main product[5]) during the thermal breakdown of polyvinyl chloride (PVC).
6. Concentrations of nitriles (= organic cyanides) were within the range of concentrations typically observed in smoke from forest fires.
7. The relative abundances of benzene, toluene, xylenes and in particular of styrene were significantly higher in the smoke from the Kagghamra fire as compared to smoke derived from wildfires. Table 2 lists the concentrations of selected oxygenated VOCs and aromatic VOCs as measured at Tegelvretsvägen along with their emissions factors from fires in temperate forests (Andreae, 2019). It is immediately evident that, while oxygenated VOCs dominate in wildfire smoke, aromatics were of comparable quantity in the smoke from the Kagghamra fire. The high concentration of styrene (and methylstyrene) indicates that polystyrene was among the fire fuels. Polystyrene is known to emit large amounts of monomeric styrene upon thermal breakdown. It is noted that aromatic fuels typically have higher yields of smoke particles (Purser, 2016). The higher fraction of aromatics (benzene and styrene in particular) must be taken into account when using results from wildfire exposure studies for assessing potential health outcomes of exposure to smoke from the Kagghamra fire.

Table 2: Concentration of oxygenated and aromatic VOCs measured at Tegelvretsvägen and emission factors (in g kg^{-1} of dry fuel burned) from forest fires in temperate regions (*e.g.*, California).

	Tegelvretsvägen Concentration (µg m^{-3})	Andreae, 2019 Emission factors - temperate forest (g kg^{-1})
methanol	68.2	2.2 ± 0.9
acetaldehyde	24.0	1.21 ± 0.56
acetone	28.4	0.76 ± 0.50
benzene	60.2	0.42 ± 0.17
toluene	38.0	0.27 ± 0.15
xylenes	37.2	0.16 ± 0.09
styrene	28.0	0.066 ± 0.019

[4] Note that these compounds cannot be selectively identified and quantified by PTR-MS.
[5] HCl cannot be detected by PTR-MS.

3.2 Spatial extension of the fire plume

We use benzene as a tracer for the fire plume. Figure 2 shows the distribution of benzene as observed during the measurements on Sunday, January 31, 2021. Maximum benzene concentrations were 121 µg cm^{-3} on road 225. Benzene was significantly elevated in Tegelvreten (5-40 µg cm^{-3}), while it remained at background levels over most of the study area.

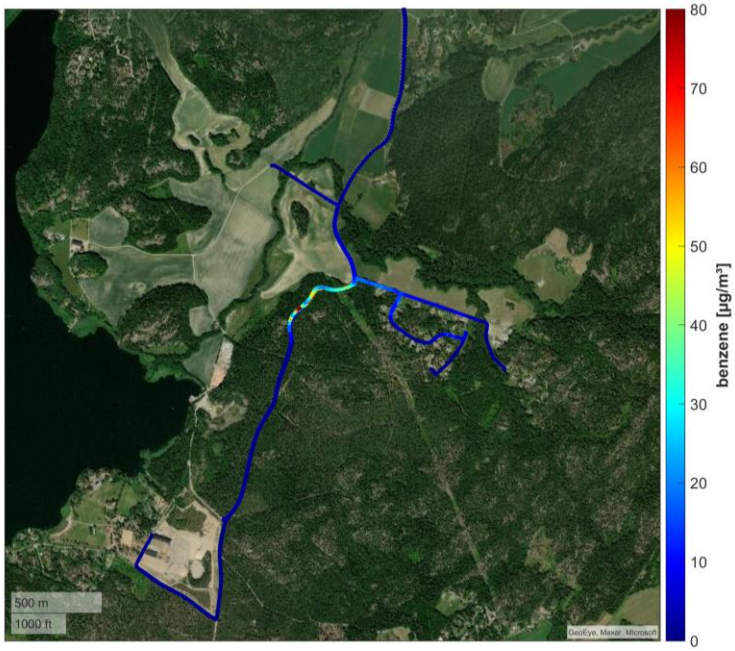

Figure 2: Benzene concentrations as measured on Sunday, January 31, 2021, 20:18-21:43h.

Figures 3a-d show benzene concentrations as measured on Monday, February 1, 2021. Notably, during the early morning hours (Figure 3a) elevated benzene concentrations were not only observed downwind of the fire (*i.e.*, to the northeast), but also in Söderängstorp, in proximity of SLB-analys' measurement station (24-93 µg m^{-3}). Figure 4 shows that smoke had accumulated in the lower topographic area over the lake under the prevailing meteorological conditions (strong temperature inversion and low wind speed). One important conclusion from the spatial survey is thus that under certain meteorological conditions exposure did not only occur downwind of the fire. Later in the morning, the entire lower topographical area to the northeast of the fire was filled with smoke (Figures 3b-d). Benzene concentrations on Tegelvretsvägen were in the range between 4 to 129 µg m^{-3}.

Table 3: Air Guidance Values (AGVs) for benzene given by the Minnesota Department of Health.

Exposure Duration	Value (µg/m^3)	Health Endpoint(s)
Acute	30	Hematotoxicity
Short-term	10	Hematotoxicity
Subchronic	8	Hematotoxicity
Chronic	3	Hematotoxcity

Acute = 24 hours or less
Short-term = >24 hours - 30 days
Subchronic = >30 days - 8 years
Chronic = >8 years - lifetime

The European Union has set a limit value for benzene for the protection of human health: the annual mean benzene concentration may not exceed 5 µg/m^3 (Directive 2008/50/EC). Obviously, an annual mean value cannot be used for a condition persisting over several weeks. Guidelines and recommendations for short-term exposures to benzene are sparse. The Minnesota Department of Health (MDH) has developed health-based Air Guidance Values (AGVs) to evaluate potential human health risks from exposures to chemicals in ambient air. Table 3 summarizes the AGVs for benzene. Our measurements indicate that the acute and short-term AGVs may have been exceeded under certain meteorological conditions at Tegelvreten and Söderängstorp.

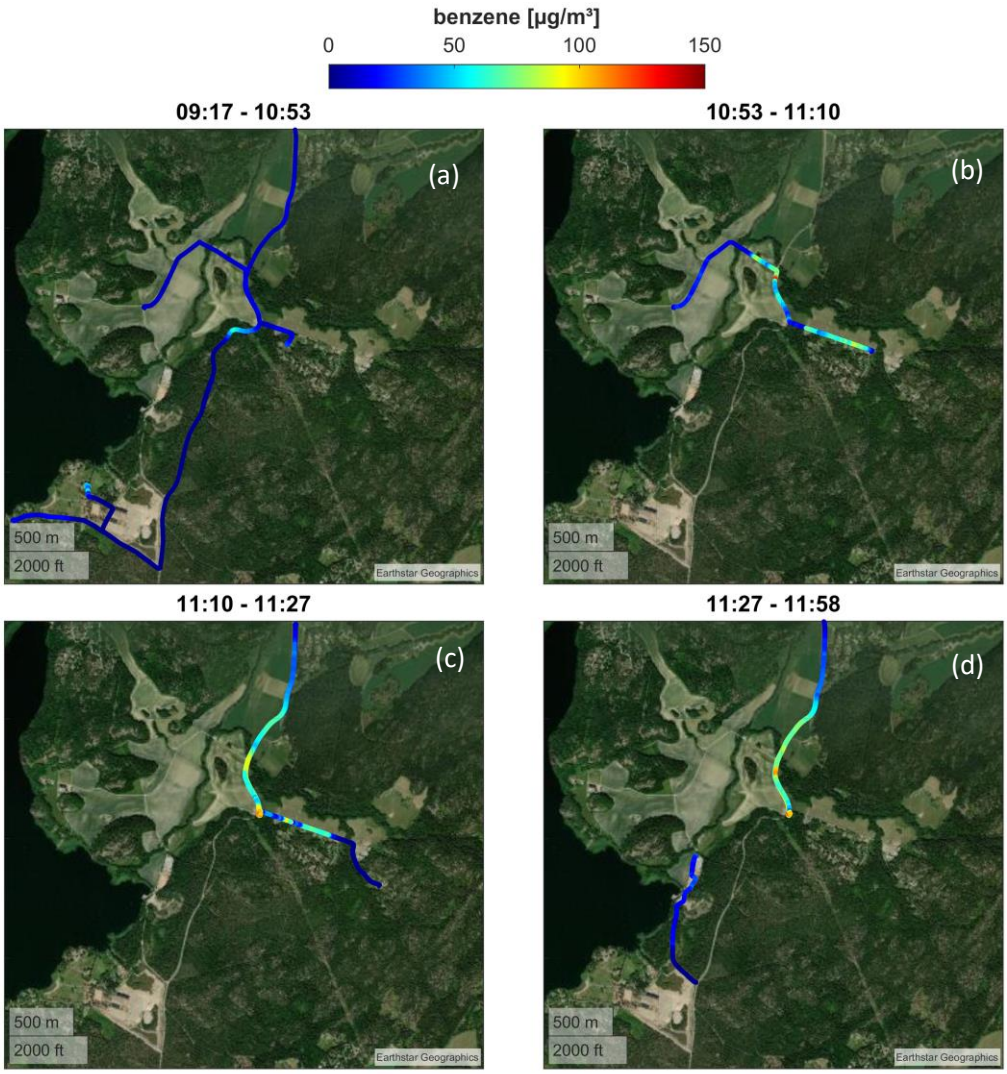

Figure 3: Benzene concentrations as measured on Sunday, January 31 2021, in the time periods between (a) 9:17-10:53h, (b) 10:53-11:10h, (c) 11:10-11:27h, and (d) 11:27-11:58h.

Figure 4: Photograph taken on the morning of Monday, February 1, 2021. Photo credit: M. Norman/ SLB-analys

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Appendix

Cylinder: D861310
Cylinder Date: 10/19
Valve: CGA350 SS 19/574565
Lot No.: 20248.1
Cylinder Pressure: 2000 psia
Analysis Date: October 15, 2020

Multi-component calibration mixture in nitrogen

Compound	CAS#	Concentration (ppb)	Uncertainty
Formaldehyde	50-00-0	10119	±5%
Propene	115-07-1	9560	±5%
Acetaldehyde	75-07-0	991	±5%
Methanol	67-56-1	1070	±5%
Acetonitrile	75-05-8	1008	±5%
Acetone	67-64-1	1037	±5%
Isoprene	78-79-5	944	±5%
DMS	75-18-3	1002	±5%
Methyl Ethyl Ketone	78-93-3	1013	±5%
Benzene	71-43-2	1002	±5%
Toluene	108-88-3	984	±5%
m-Xylene	108-38-3	995	±5%
α-Pinene	80-56-8	1004	±5%
1,3,5-Trimethylbenzene	108-67-8	999	±5%
Octamethylcyclotetrasiloxane (D4)	556-67-2	522	±5%
Decamethylcyclopentasiloxane (D5)	541-02-6	519	±5%
1,3,5-Triisopropylbenzene	717-74-8	533	±5%

Uncertainty is a conservative estimate of the combination of the uncertainties of the gravimetric preparation and analysis.