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# Volatile and persistent emissions from traffic and power production on Svalbard

## VETAPOS

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**Scientific report**

Measurements of indicator pollutions for the evaluation of environmental impact of fossil fuel combustion on Svalbard environments.  
A collaborative field study (2010)



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# **Final report**

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## 1 Scientific background

Recently published scientific studies on Svalbard local pollution issues (i.e., Reimann et al. 2009) identified considerable pollution risk and environmental impact on the Svalbard environment caused by emissions from fossil fuel combustion. Black carbon emissions (BC) have shown to have considerable local impact on the local atmospheric composition as well as on the snow surfaces around Longyearbyen, Barentsburg and Svea (Aamaas et al. 2011). In addition, combustion of gasoline related fuels both for transportation but also for energy production purposes is contributing significantly to increased emission of aromatic hydrocarbons which may have a considerably long half-life under Arctic environmental conditions as documented for middle latitude regions. This assumption is also supported by a recently finalised survey on soil samples collected at Kinnvika (Nord-Austlandet) in 2008, a former research station abandoned since more the 50 years. This study revealed, that very high levels of polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCB) were still present in the surface soils around the station, more than 50 years after the initial release of these pollutants into the Svalbard environment (Harris 2009).

Based upon a three-month monitoring campaign in 2007, Reimann et al. (2009) concluded that atmospheric levels of benzene- toluene-xylene (BTX) related emissions are extremely elevated during daytime along the main snowmobile routes in Longyearbyen during the late winter season (main tourist season) in 2007. Total emissions of about 81 t/year were estimated for 2007 solely for snowmobile activities. 2-stroke engine driven vehicles are estimated to stand for around 92 % (74 t/a) of the hydrocarbon emissions alone although it is estimated that only 360 of the 1802 snowmobiles driven in 2007 on Svalbard are equipped with 2-stroke engine technology (Vestreng et al 2009). The study by Reimann et al (2009) also concluded that around 51 % of the fuel leaves the 2-stroke engine unburned via the exhaust pipe. Thus, assuming an annual average consumption of around 900 L per 2-stroke snowmobile (Vestreng et al 2009) and estimating around 360 2-stroke snowmobiles registered at Svalbard, it can be expected that around 166 000 L (around 120 t) unburned gasoline was spread into the Svalbard environment in 2007 alone along the major snowmobile tracks. Even larger annual emission rates can be assumed for earlier years. Thus, considerable amounts of fuel residues can be expected as deposits in surface soils and ice surfaces on glaciers along the snowmobile tracks on Svalbard.

It is expected that persons driving snowmobiles on a regular basis or professional snowmobile guides could be exposed to considerable amounts of this complex chemical mixture with the potential for effects on health and well being of the respective persons.

Based upon the above-described facts, a science based survey on fuel residues (ie, polycyclic aromatic hydrocarbons = PAH, volatile organic carbons =VOC) in surface soil along the major snowmobile tracks on Nordenskiöld-landet (Longyeardalen, Adventdalen, Sassendalen) into selected shore lines has been performed during early summer of 2010. In addition, the local input of heavy duty vehicles (HTV) on the local hydrocarbon emission as well as the emission composition of the major power stations with respect to BTX levels (Longyearbyen), has been monitored as repetition (after 2007) in order to investigate whether the increased number of registered four-stroke engine snowmobiles in the past three years has a visible effect on the emission values for Benzene-Toluene-Xylene (BTX) emissions along the snowmobile tracks in and out of Longyearbyen.

## 2 Methods and materials

As the central part of the VETAPOS fieldwork, surface (PAH and VOC) samples were collected in the vicinity of Longyearbyen and Adventdalen (figure 2) and as reference site, Sassendalen (near Fredheim) was selected (figure 3). In addition, a continuously measuring monitoring device for the quantitative determination of Benzene-Toluene-Xylene (BTX) components in ambient air was installed at the Research Park (UNIS), Longyearbyen, Laboratory facilities in 2010. The following form was used for registration of samples during the field work (figure 1).

<b>Sample Location</b>		<b>Date/Time</b>		<b>Coordinates</b>	Lat:	Long:
<b>Sample Location Nr.</b>		<b>Further specification/description of sampling spot</b>				
<b>Sample ID/ nr of samples</b>		(distance from water)				
		(elevation)				
<b>Sample Type</b>						
<b>Sample Collection Type</b>						
<b>Estimated distance from middle of track</b>						
<b>other:</b>						
<b>Weather:</b>		<b>Sample Characteristics:</b>				
<b>Temperature:</b>		soil: grain size, colour, vegetation, material, humidity, sieved(?)				
		snow: age, density, wettness, colour				
<b>Wind:</b>						
<b>Precipitation/Humidity:</b>						
<b>Pressure:</b>						
<b>Clouds:</b>						
<b>other:</b>						
					Picture?	
					GPS-Position?	

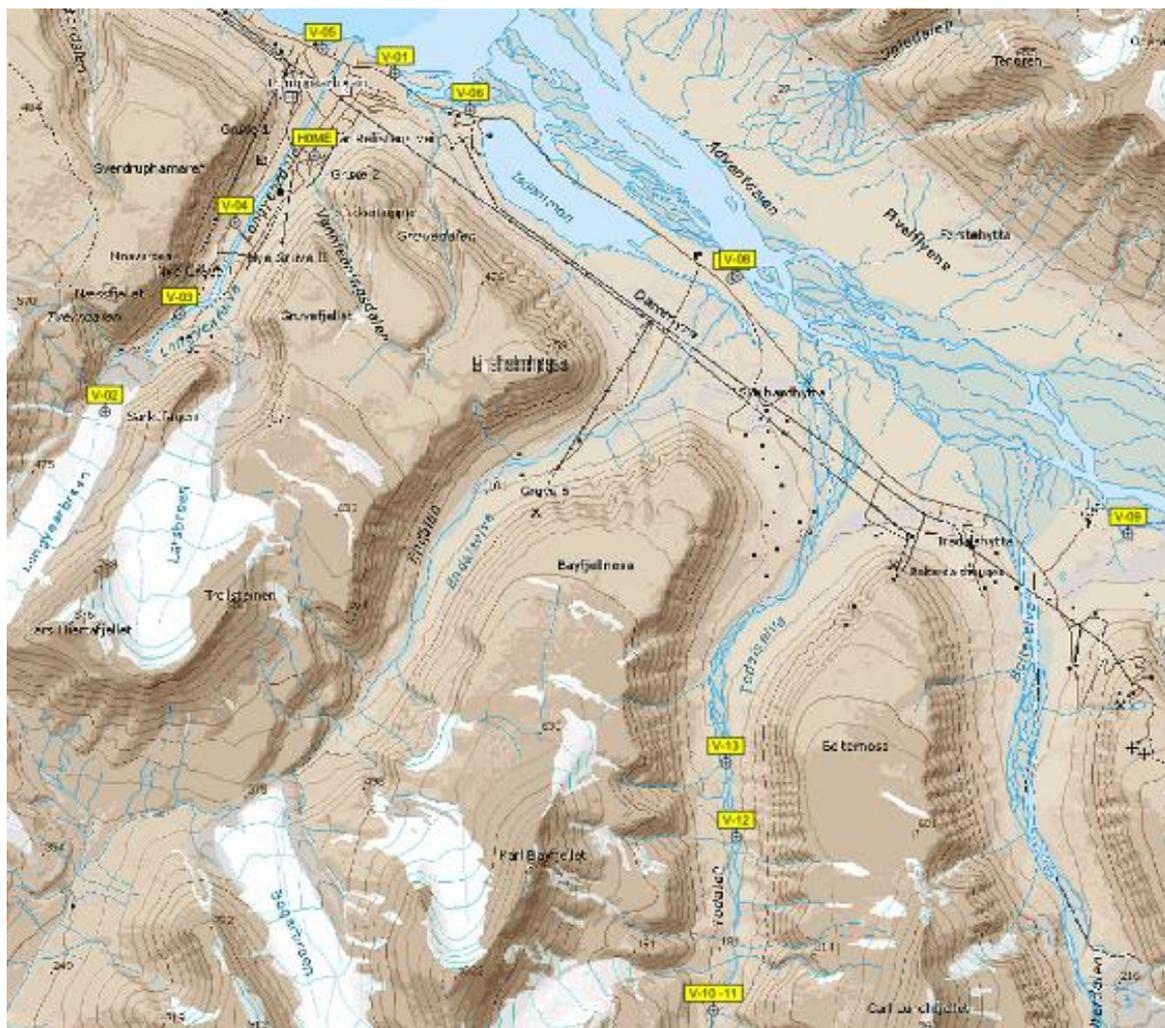
*Figure 1: field registration form for samples collected during the VETAPOS field campaign June/July 2010.*

### 2.1 Sampling locations

A summer field campaign was conducted in the period from 25.06. – 02.07.2010 in order to evaluate potential long-term effects on surface soil and associated vegetation originated from potential fossil fuel burning as well as direct release of fuel due to incomplete combustion.

Two major collection locations were chosen for the sampling campaign.

- 1.) Longyear valley (Longyeardalen) / Advent valley (Adventdalen), see figure 2
- 2.) Sassenvally (Sassendalen) and Fredheim, see figure 3)



*Figure 2: Sample locations in Longyear valley (Longyeardalen), To-valley (Todalen) and Advent valley (Adventdalen) for soil and snow/ melt water samples. Twelve (12) samples were collected.*

Surface soil samples were collected along known and frequently used snowmobile tracks in/out of Longyearbyen. In Sassendalen, reference samples were collected close to the trapper cabin along shore. In addition four surface soil samples were collected as transect across the frequently used snowmobile track towards Fredheim (sample 17, 18, 19 and 20).

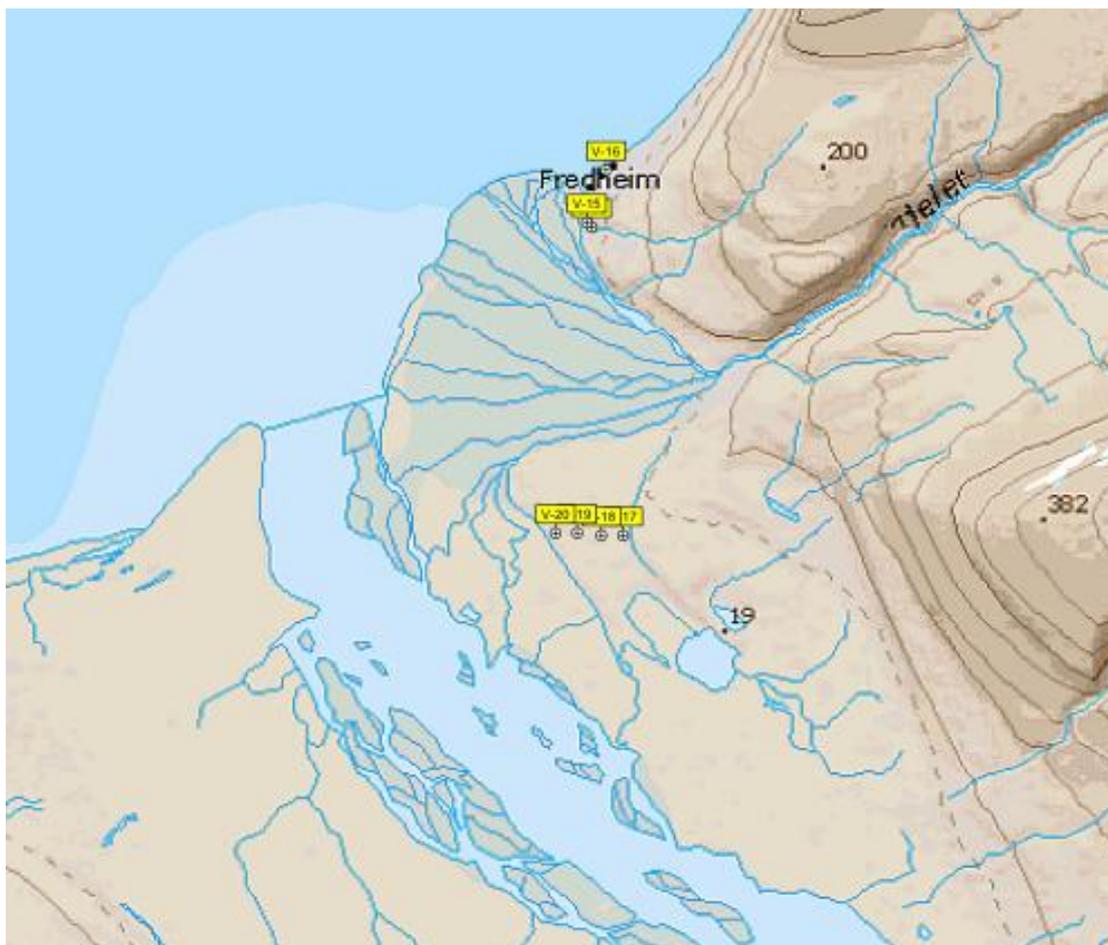


Figure 3: Sample locations in Sassendalen (Sassendalen) for soil and snow/ melt water samples. Six (6) samples were collected.

## 2.2 Monitoring of Benzene-Toluene-Xylene (BTX) components in Longyearbyen air

As integrated monitoring activities for the determination of BTX compounds, a measuring campaign was conducted from the UNIS-laboratory (Forskningsparken, Longyearbyen). A continuously measuring monitoring device for the quantitative determination of Benzene-Toluene-Xylene (BTX) components in ambient air was installed and conducted in the UNIS Laboratory facilities in 2010 during two measuring periods in spring 2010 (07 April to 11 May) and in autumn 2010 (05 September to 25 October). The monitoring device was jointly maintained by Empa and UNIS personnel during the campaigns (figure 4). For detailed method descriptions, see below.



Figure 4: For monitoring of Benzene-Toluene-Xylene (BTX) components a Syntech Spectras GC-855 (Synspec, Groningen, The Netherlands) monitoring device was used. Figure reproduced with courtesy of Synspec, Groningen, NL

As representative volatile organic pollutants, Benzene-Toluene-Xylene (BTX) were also analysed in/ above soil samples, collected in parallel with the soil material dedicated for PAH analysis (see above). All soil samples were, thus, collected in duplicate.

### **2.2.1 Sample selection criteria**

Based on literature information, polycyclic aromatic hydrocarbons as well as Benzene-Toluene-Xylene (VOC) components were identified as priority indicator chemicals for the identification of environmental risks associated with emissions from fossil fuel combustion processes.

The sample locations were selected based upon a two major criteria, important to ensure representative results for the planned assessment.

- 1.) **Representativeness for the purpose:** All soil samples were collected in proximity of the main scooter tracks (during winter) as well as along the routes used for truck-based transportation of coal from the mine (No. 7) to the shipping areas in the harbor.
- 2.) **Accessibility:** The sampling sites were easily accessible for repeated sample collection (Adventdalen as well as in Sassendalen).

Specific infrastructures were identified (gasoline stations and snowmobile maintenance facilities) where elevated levels of PAH/VOCs are expected. Here several parallel samples were collected. Background sites were selected in Longyeardalen, Todalen as well as Sassendalen in order to illustrate the distribution properties for the selected pollutants. In this context, a representative transect (figure 3: V-17, V-18, V-19, V-20) across a heavily frequented snowmobile track was sampled (soil samples) for PAH and VOC in order to identify possible gradients with respect to soils contamination (PAH/VOC).

In total 180 surface soil samples were collected for PAH and VOC analysis respectively.

As a part of the quality control protocol of the project a total of 10 field blank samples were collected for all four sub-locations (Longyeardalen, Adventdalen, Todalen and Tempelfjord/Sassendalen, see table 1) by exposing pre-cleaned sodium sulphate during sample collection and transportation.

## 2.3 Sample collection

Location	Sampling time	Location description (see figure 2 and 3)	PAHs Soil (sample no)	VOCs Soil (sample no.)
<b>Longyeardalen</b>				
V-01; Svalbard Scooter Utleie	25.06.2010	Gasoline station	2+1Bl	2+2Bl
V-03; „Brygge“	27.06.2010	Connection between mines, narrowing of river bed	3+1Bl	2+2Bl
V-04; Huset	27.06.2010	Scooter track, 20 m from road	3	2
V-05; Statoil Bensinstasjon	28.06.2010	Snowmobile departure site into Adventdalen	3+1Bl	2+2Bl
V-06; Dog Yard	28.06.2010	Close to road	3	2
<b>Adventdalen</b>				
V-07; Nordlysstasjon	29.06.2010	in 100-150 m distance, close to road	3	2
V-08; Nordlysstasjon	29.06.2010	in 100-150 m distance, away from road	3+1Bl	2+2Bl
V-09; Gruve 7	29.06.2010	parallel/below	3	2
<b>Todalen</b>				
V-13; lower	30.06.2010	(Former) riverbed, western margin	3	2
V-12; middle	30.06.2010	(Former) riverbed, elevated	3+1Bl	2+1Bl
V-10; upper	30.06.2010	(Former) riverbed, elevated	3+1Bl	2+2Bl
V-11; upper	30.06.2010	Western Side, above riverbed	3	2
<b>Tempelfjord</b>				
V-15; lower Sassendalen	01.07.2010	close to Fredheim-cabin (ca 150 m), soil	3+1Bl	2+2Bl
V-16; Fredheim cabin	01.07.2010	Narrowing behind cabins towards Pyramiden	3+1Bl	2+1Bl
V-17; Light-Pole, up valley	01.07.2010	“Corner” along main-scootertrack	3	2
V-18; Transect 1-into valley	01.07.2010	Into valley from V-17	2	2
V-19; Transect 2-into valley	01.07.2010	Into valley from V-17	2	2
V-20; Transect 3-into valley	01.07.2010	Into valley from V-17	2	2

*Table 1: Samples (location and numbering) collected for the here-performed study in Nordenskjold land (Spitsbergen, Svalbard). June/ July 2010. Explanations: Bl = Blank samples. For locations see figure 1 and 2.*

## **2.4 Quantitative determination of polycyclic aromatic hydrocarbons (PAH) in surface soil.**

### **2.4.1 Preparation of soil samples**

Approximately 14 g of wet soil were ultra sonic bath extracted with 3x 50 mL of Dichloromethane (DCM) and Methanol (MeOH) 3:1 (Merck, Darmstadt SupraSolv quality). The joined extracts were collected in a separation funnel and cleaned with 50 ml of milliQ water by constant manual shaking. Afterwards, the organic phase was transferred into a separate vial and the volume reduced to 500  $\mu$ L (Turbovap, Zymark). The heavy asphaltene content was removed by filtering the concentrated extract through dry and pre-cleaned sodium sulphate ( $\text{Na}_2\text{SO}_4$  = preconditioned at 450°C, 6 hrs, Merck, Darmstadt) and rinsed with small amounts of n-hexane (PA quality, Merck, Darmstadt). For further clean-up, silica gel fractionation was performed. The glass columns were packed wet with 2.2 g of silica gel (pre-cleaned: 450 °C, 6 hrs, deactivated with 5 % milliQ; Merck, 60, (63-200 $\mu$ m) eluted in 40 ml of n-hexane and sodium sulphate was added on top as 0.5 cm thick layer for moist removal. Two fractions were taken by eluting the columns with 25 mL of n-hexane:DCM 2:1 and 20 ml DCM, resulting in fraction F1 and F2 respectively. In order to further remove potentially interfering compounds an aliquot of fraction F1 was cleaned on preconditioned Alumina (neutral, 850 °C , 2h and deactivated with 5%-w MilliQ water). For column protection a 0.5 cm thick layer of sodium sulphate was added on top of the column. The samples were eluted with 5 ml of n-hexane:DCM 2:1, followed by 30 ml of DCM. While fraction 1 was discarded, the DCM fraction was evaporated under a gentle nitrogen stream (nitrogen 5.0, Hydro, Porsgrunn, Norway) to a volume of approximately 500  $\mu$ L. The samples were transferred into injection-vials for gas chromatographic separation and quantification.

As to the amount of asphaltenes present in sample the final volume was adjusted to 0.5, 1.0 or 1.5 ml and a defined amount of OCN (octachloronaphthalene) as recovery standard was added accordingly. In order to determine the dry weight of the samples, 3 small aliquots were separated and used for dry weight determination prior to extraction. The dry weight was determined by gently drying the aliquot in an oven at 100 °C for 12 hours.

### **2.5 Sample preparation for VOC analysis in soil samples**

The 5-10 g soil samples/ 100mL melt water) for VOC analysis were collected in gas tight 100 mL glass containers and shipped to the Norwegian institute for Air Research (NILU) for quantitative analysis. The samples were flushed with 200 ml of pre cleaned Helium at 90 ° onto a sorbent material (TENAX<sup>®</sup>TA tubes). The TENAX tubes were thermally desorbed using a Markes Ultra/Unity automated Thermodesorber coupled to a Agilent 7890A GCxGC system and a Time of Flight mass spectrometer (LECO Pegasus TOFMS, Saint Joseph, MI, USA). Quantitative analyses

## 2.6 Quantification of PAH in surface soil

Analyses were performed on a gas chromatograph coupled to a mass selective detector (GC/MS = Trace GC, PolarisQ low resolution ion trap mass spectrometer, Thermo Fisher, USA) A 10m of uncoated fused silica guard column was mounted in front of a DB-5MS + 10m Duraguard capillary column (30m x 0.25 mm x 0.25  $\mu$ m, J&W Scientific). The ion source and MS transfer line temperatures were set to 200 and 280 °C respectively. The samples were injected on-column and the mass selective detector was operated in electron impact/ full scan mode. The following GC temperature program was used for separation of PAHs. Starting temperature was 70°C (2 min isotherm) followed by ramping with 10°C/min to 150°C (4 min isotherm) and continued with 4°C/min to 300°C (10 min isotherm). Helium (6.0, Hydro gas, Porsgrunn, Norway) was used as carrier gas and the injection volume was adjusted according to the expected concentration of the samples (based on asphaltene content) and varied between 1 – 3  $\mu$ l. A standard series of a solution of 16 EPA priority PAHs (Chiron) was run before the first sample to insure instrument conditions and linearity. Internal Standard ( $d_{10}$ -naphthalene and  $d_{12}$ -perylene) were used for the quantitative determination of PAH concentrations and OCN (octachloronaphthalene) was applied as recovery standard.

## 2.7 Quantitative determination of BTX compounds in Longyearbyen air

Continuous measurements of the aromatic hydrocarbons benzene ( $C_6H_6$ ), toluene ( $C_7H_8$ ), and  $C_2$ -benzenes ( $C_8H_{10}$ ) were conducted during two periods in spring 2010 (07 April to 11 May) and in autumn 2010 (05 September to 25 October) in Longyearbyen, Spitsbergen (78° 13' N, 15° 38' E). The measurements were performed at the University of Svalbard (UNIS) using an inlet which was placed about 5 m above the ground and which was connected with a 1/8" x 2 m stainless steel inlet, which was protected from icing by a protecting plastic cup. Every 15 min 200 mL of air was sampled. Subsequently, samples were analysed by gas chromatography (Syntech Spectras GC-855, Synspec, Groningen, The Netherlands, see instrument description, figure 4) using an apolar fused-silica capillary column (BGB 2.5, 0.25 mm x 30 m; BGB, Adliswil, Switzerland) and a photo ionisation detector (PID). The initial oven temperature of 50 °C was held for 3 min and was then raised to 75 °C in 3 min, where it was held constant for 5 min. Calibration was performed using an NPL standard (National Physics Laboratory, Teddington, United Kingdom) in the lower ppb range. The detection limit was 0.004 ppb and precision 10% ( $\sigma$ ) for all measured compounds. Ethyl benzene, m/p-xylene and o-xylene were measured individually and were lumped together as xylenes afterwards.

### 3 Results

#### 3.1 Polycyclic Aromatic Hydrocarbons (PAH) in surface soil

A total of 15 representative polycyclic aromatic hydrocarbons (PAHs) were determined in 18 soil samples (June/July 2010). The selected compounds are listed in table 2.

*Table 2: Selected polycyclic aromatic hydrocarbons (PAH) in VETAPOS soil samples.*

Name	Abbreviation
Fluorene	Fl
Phenanthrene	Phe
Anthracene	Anth
Fluoranthene	Flu
Pyrene	Pyr
Benz(a)anthracene	BaA
Triphenylene	Tri
Chrysene	Chr
Benzo(b)Fluoranthene	BbF
Benzo(k)Fluoranthene	BkF
Benzo(e)Pyrene	BeF
Benzo(a)pyrene	BaP
Indeno(123cd)pyrene	IP
Dibenzo(ah)anthracene	DahA
Benzo(ghi)perylene	BgP

##### 3.1.1 Quality Control

Field blank (6) and laboratory blank samples (2) were analysed for the determination of unintended PAH contamination during sampling. Sample transport and sample treatment.

In general, no significant blank contamination was detected. Minor contamination (low ng/g dw range) was determined for Phe (2 ng/g dw), BbF (1.9 ng/g dw) and BeP (3 pg/g dw). The instrumental limit of detection was determined between 0,3-0.5 g/g dw for all quantified compounds. The Limit of quantification (LOQ) was calculated as 5x average blank concentration (field and laboratory blank).

All samples were quantified in duplicate in order to monitor the method/instrument variability. In general, variations between 10 and 30% for all PAH measurements were determined. Usually, only quantification “No 1” was used for further data interpretation (no average was determined).

#### 3.2 Spatial level distribution for PAH in soil

PAHs were determined and quantified in all samples analysed ranging between 21 ng/g dw (gasoline station, near road, Longyearbyen) up to 1883 ng/g dw (= 1.83 µg/g dw) collected in ADventdaeln close to themine 7 road towards mountain (Adventdalen). Based upon the sum PAH levels determined (table 3), several hot spot contamination sites have been identified.

Table 3: Sum PAH (15 compounds) determined in 18 soil samples in Svalbard

Samples	conc. [ng/g dw]
V-1-1	1495.2
V-3-1	1382.8
V-4-1	1662.6
V-5-1	21.4
V-6-1	304.4
V-7-1	528.5
V-8-1	1883.1
V-9-1	368.6
V-10-1	138.9
V-11-1	336.8
V-12-1	176.4
V-13-1	360.4
V-14-1	70.2
V-16-1	536.4
V-17-1	95.6
V-18-1	104.2
V-19-1	286.4
V-20-1	126.8

The concentration levels for all individual PAH compounds are summarized in Table A1 (Appendix A).

Samples site V1, V3, V4 and V8 are characterized by PAH Sum levels above 1300 ng/g dw. (Hot spots) All “hot spot” samples are characterized by predominant Phe and Chr concentration (ratio 1:1). Except for sample V-3-1 (Longyearbreen moraine), where Phe is the overall predominant PAH compound (Figure 5: 42% of the total PAH burden).

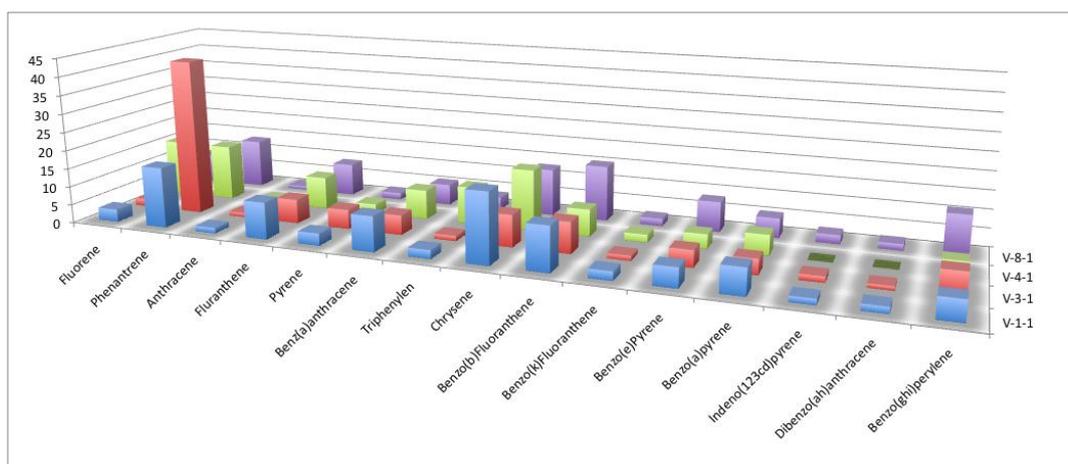


Figure 5: Percentage distribution (Sum 15 PAH = 100%) for the high contaminated “Hot spot” soil samples collected during the VETAPOS campaign June/July 2010.

The hot-spot contaminated locations (figure 5) are characterized with high levels of PAHs originated over-average emissions from fossil fuel driven technologies (coal combustion, gasoline drive driven engines) or direct spilling of fossil fuel products (gasoline, diesel, petroleum products).

Medium-level Sum PAH concentrations with levels in the concentration range 300 – 1300 ng/g dw (dry weight) were found in samples V6, V7, V9, V11, V13 and 16 (figure 6). These samples represent locations with over-average PAH contamination representative for areas with considerable human activities and frequent usage of fuel combustion engine driven technology (transportation, electric power generator).

Low-level Sum PAH concentrations (Sum PAH: 21 – 300 ng/g dw) were identified in samples V5, V10, V12, 15, 17, V18, 19 and V20 (figure 7). These samples represent locations with below average PAH contamination (in the VETAPOS study) at ca. background PAH concentration levels.

Only few soil samples were analysed in Svalbard for PAH levels earlier. Harris (2009) determined PAH in surface soil from Kinnvika (Nord-Austlandet). Background levels of around 200 ng/g dw (Sum 15 PAH) were determined at this long-term exposed site (with considerable anthropogenic impact during the past 50 years). Yunker et al. (2002) determined general background levels for Sum PAH in Arctic soils of around 100 ng/g dw dependent also on the geology of the respective regions.

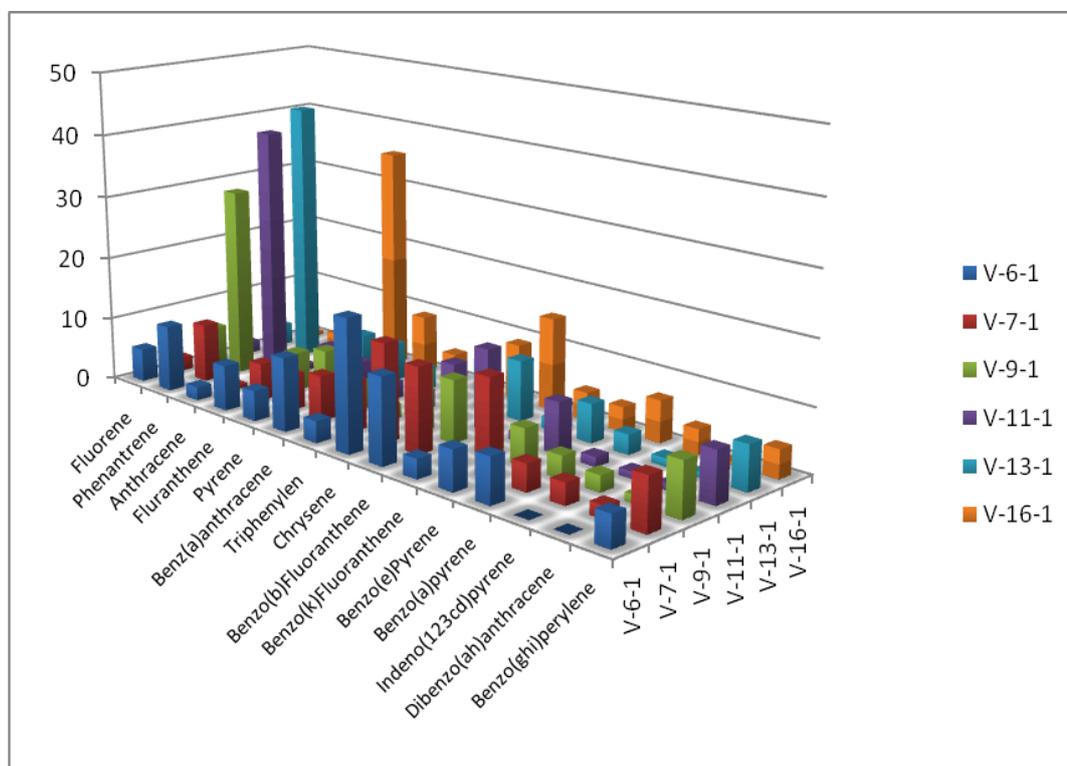


Figure 6: Percentage PAH distribution (Sum 15 PAH=100%) in medium level PAH contaminated surface oil samples (300 – 1300 ng/g dw).

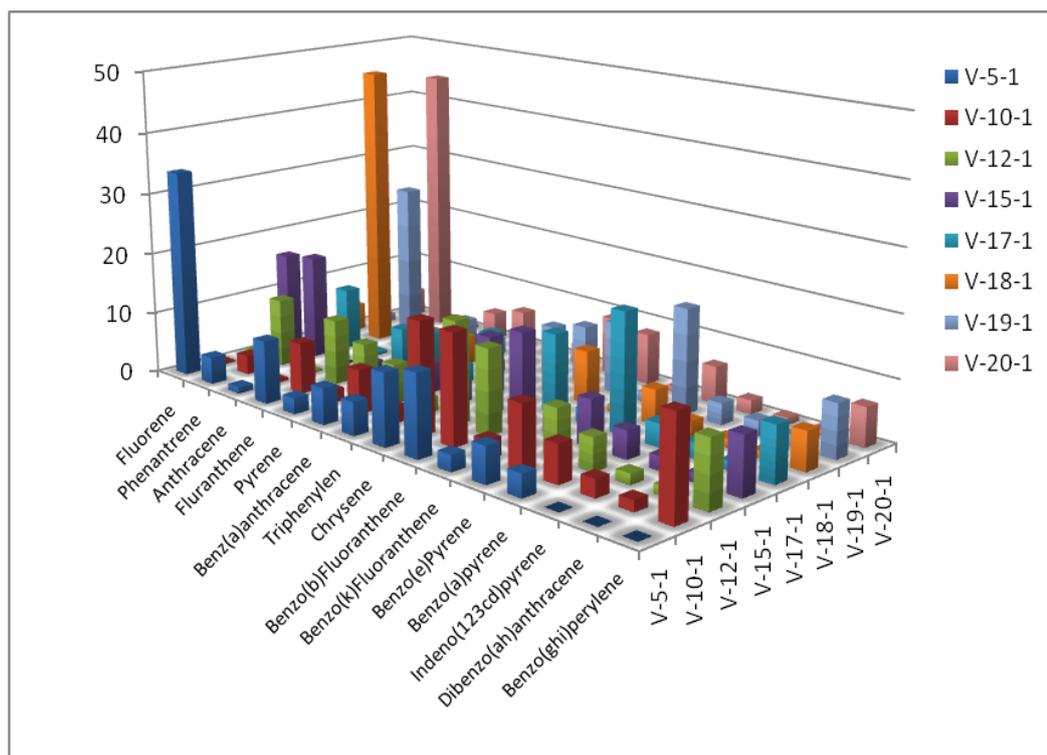


Figure 7: Percentage PAH distribution (Sum 15 PAH=100%) in low/ background level PAH contaminated surface oil samples (21 - 300 ng/g dw).

According to Yunker et al (1995), PAH compounds like Phenanthrene, Pyrene, Triphenylene and Benzo(ghi)perylene belong to the most environmentally stable PAH constituents and are, thus, indicators for a PAH pattern after long term exposure and considerable weathering processes. The absence of two-ring PAHs (i.e., naphthalene), usually representing freshly emitted PAH mixtures, is also a clear indication for weathered PAH mixtures in the analysed soil samples during the VETAPOS study.

Usually the Phenanthrene/ Anthracene (P/A) as well as the Fluoranthene/ Pyrene (F/P) ratios allows a good evaluation and discrimination between petrogenic (natural fossil based emissions), photogenic and pyrogenic (combustion) source. Pyrogenic sources predominate when F/P ratios approach and pass 0.9. Pyrogenic sources predominate also when P/A ratios are higher than 3 (>3; Stein et al. 2006). The predominance of compounds like Phenanthrene and Retene are an indication for unburned oil-release (petrogenic sources). Perylene, a pentacyclic hydrocarbon, is reported to be predominantly of diagenic origin and thus an indicator for fuel combustion from fuel driven engines or coal pyrolysis. The above described P/A and F/P ratios are calculated and presented in figure 8a and b.

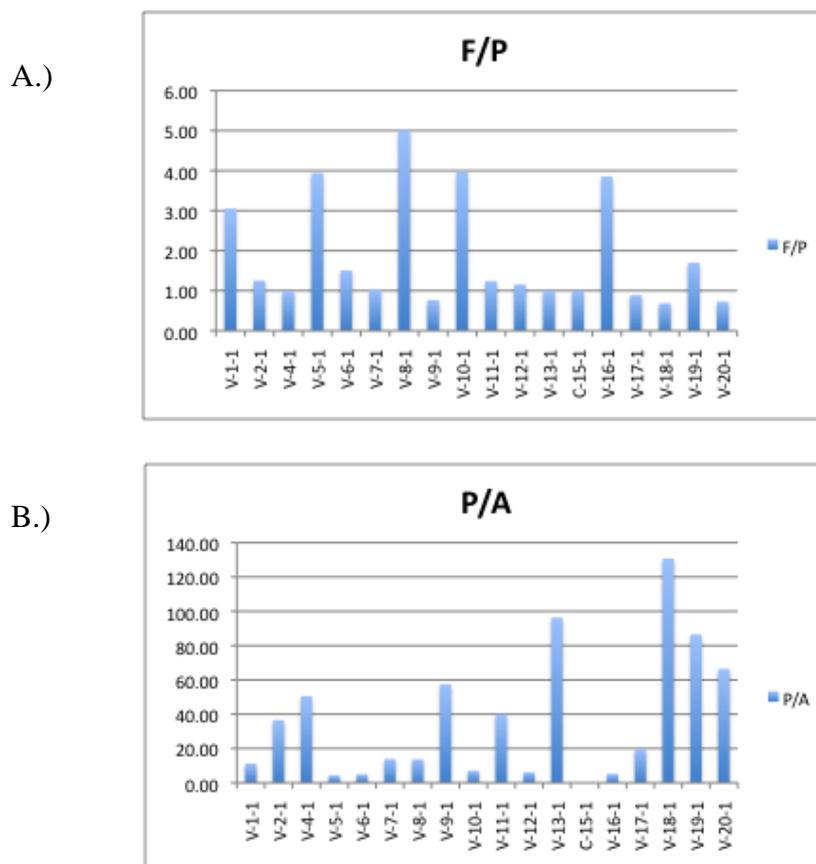


Figure 8: Concentration ratios (y-axis) for (A): Fluoranthene/ Pyrene (F/P) and (B) Phenanthrene/ Anthracene (P/A) in the VETAPOS surface soil samples

Except for samples V9, V18, and V 20 all samples are characterized by a F/P Ratio above/or equal with 0.9. All samples without exception are found with P/A ratios above 3 (max. 131). Thus, for all samples a predominant pyrolytic origin must be assumed.

### 3.2.1 Volatile organic compounds (VOC)

Benzene, Toluene and Xylene related chemicals (BTX) were analysed in soil and atmospheric samples.

### 3.2.2 Volatile organic compounds in soil

Parallel samples for the analysis of Benzene-Toluene-Xylene (BTX) related compounds were collected for the quantitative analysis in air above the respective soil samples (see method description). After shipping to the NILU lab, the samples were analysed and BTX was quantified using highly sensitive GC/ToF quantification methods. None of the soil samples contained levels of BTX compounds above the Limit of Detection (LOD). Due to weathering of the original emissions from gasoline/ diesel combustion and the subsequent deposition on snow and soil surfaces, the BTX related compounds are readily

evaporated and re-emitted into the atmosphere. Even in soil samples from the gasoline filling station there are no BTX compounds adsorbed to the soil.

### 3.2.3 *Volatile organic compounds in ambient air*

In earlier studies, surprisingly high levels of BTX-related chemicals were found in ambient air collected at the Research Park (UNIS laboratories) in 2007 (Reimann et al. 2009). Direct emissions from the passing traffic (snowmobiles and heavy trucks) were identified as major emission sources during the sampling period. As follow up, a new BTX monitoring campaign was initiated as an integrated part of the VETAPOS field study. Two separate sampling campaigns were conducted in 2010.

- 1.) Winter/ spring period: 07.04.2010 – 11.05.2010
- 2.) Autumn period: 01.09.2010 – 25.10.2010

As major indicator for the anthropogenic emissions from fossil fuel engine driven vehicles (snow mobiles and trucks), benzene ( $C_6H_6$ ) was chosen. Compared to the 2007 emission data, a significant reduction of the benzene levels was identified (30% of the 2007 levels observed). The comparison is presented in figure 9.

Although a considerable reduction is registered (to about 30% of the levels determined in 2007) elevated levels are still reported for the winter/ spring period 2010 (max. level 20.04.2010 = 0.65 ppb). Background concentrations (around 0,01 ppb) were found for the autumn 2010 period.

As already seen in the 2007 data, also for winter/spring 2010, an expressed daily pattern distribution with elevated levels in morning and evening was observed.

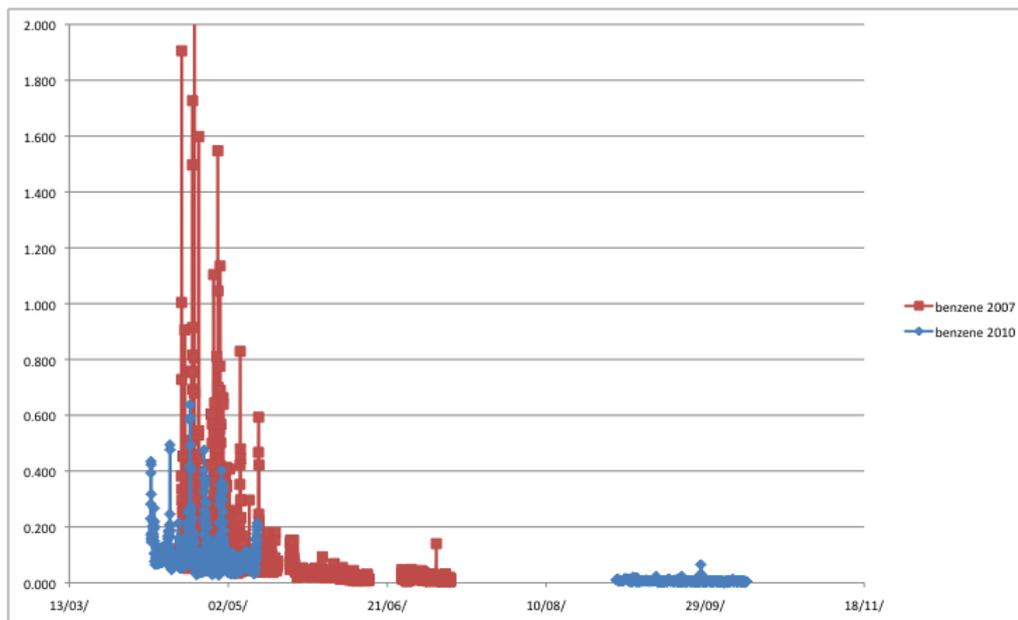


Figure 9: Benzene level (parts per billions =ppb) comparison between the 2007 (red) and 2010 (blue) sampling campaign (ca.  $3.19 \mu\text{g}/\text{m}^3$ )

### 3.3 Discussions and implications

Combustion processes specifically related to fossil fuel types (coal and petroleum oil products) are identified as major pollutant source for Arctic environments including Svalbard (Vestreng et al 2009). Based upon the above described considerations, virtually all soil samples analysed (18 soil samples) were dominated by a pyrogenic PAH pattern (see figure 8a,b). In addition the absence of volatile indicator compounds proved that the pollutant mixtures in the soil samples underwent continuous and effective weathering in the month/years before sampling took place. Thus combustion sources (i.e., gasoline/ diesel consuming engines) are obviously the main source for the observed contamination in the soil. According to White and Carrol (Table 14; 1998), PAH patterns from two-stroke snowmobile engines were dominated by fluoranthene and pyrene (figure 10, around 40%). Also fluorine, benzo(ghi)pyrene and phenanthrene contribute significantly to the overall PAH pattern (12%, 12% and 15%). In total, these 4 components stand for around 83% of the total PAH emissions from two-stroke snowmobile engines. This, above described, pattern still resembles closely the PAH distribution identified in most of the 18 VETAPOS soil samples, taking into account, that combination of long-term weathering and freshly emitted PAH (just about six weeks after the snowmobile season has been finalized) contribute mainly to the soil contamination patterns.

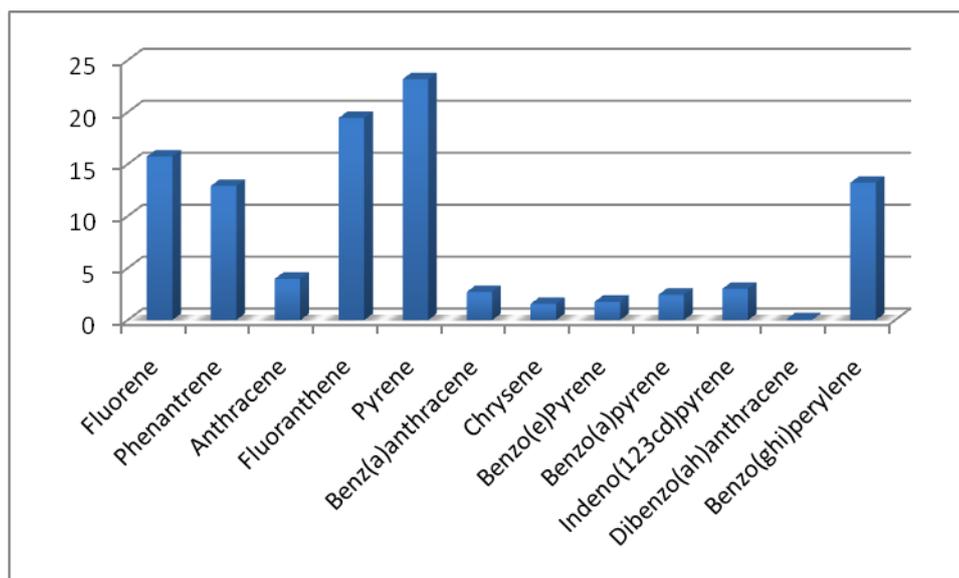


Figure 10: Percentage distribution of relevant PAH components (total PAH concentration = 100%) from running two-stroke snowmobile engines using bio-based gasoline types.

The highest contaminated samples were identified with Sum PAH levels between 1500 and 1800 ng/dw (table 3) with predominant phenanthrene, chrysene and Benzo(b) fluoranthene in the PAH pattern (15 PAHJ compounds identified). The four highest contaminated soil samples were V-1-1, V-3-1, V-4-1 and V-8-1.

Sample V-1-1 (78 ° 13' N and 15° 48' E) was collected from surface soil at the gasoline station close to the Svalbard snowmobile rental station (Svalbard scooterutleie). A combination of gasoline/ lubricant spillage and emissions from running engines (from snowmobiles and other off-road vehicles) must be assumed as main pollutant source (Sum PAH: 1495 ng/g dw).

Sample V-3-1 (Sum PAH 1382 ng/g dw) has been collected on the slope of the Glacier Longyearbreen, where the winter snowmobile track moves along a narrow slope onto the glacier on the way to Fardalen and Coles bay (sampling location 78° 11' N and 15° 33' E, see figure). The soil sample (for PAH and VOC analysis) was collected directly on the main snowmobile track. Due to the narrow slope, during the winter season, the snowmobiles are usually forced to move along a very narrow track onto the glacier. Thus, the emissions from a large number of snowmobiles, using this track as main route to Barentsburg and even to Svea (van Mijenfjord) during winter, are concentrating along a narrow track and thus are deposited in the surface soil after the snow melt. The narrow accumulation zone for PAHs along this section may be the main reason for the high PAH levels identified. Especially high Phenanthrene concentrations were found, twice as high as four the other three "hot spot" locations (583 ng/g dw).

Soil sample V-4-1-1 was collected from the snowmobile track (20m from the road) south of the restaurant "Huset" (78°12' N and 15° 35' E). Snowmobile traffic as well as historical deposition remaining from many decades with mining activities (including heavy duty equipment) are considered as the major PAH contamination source (Sum PAH: 1630 ng/g dw).

The surface soil sample V-08-01 (78° 12' N and 15° 30' E) was collected in the proximity (around 150 m distance) of the former Northern Light observatory

(Nordlysstasjonen) and around 100 m from the main route (Longyearbyen – Mine 7). The soil sample was collected in the middle of the main snowmobile track (tracks still visible from the snowmobiles from the previous season). Thus, snowmobile emissions are considered as the major pollution source (Sum PAH: 1883 ng/g dw).

All high-contaminated sites (“Hot spots”) could be associated with over average usage of snowmobile (driving and maintenance).

However, also the medium contaminated locations (6 sites) were characterized by predominant phenanthrene, triphenylene and chrysene, identified as clear signals from snowmobile/ car emissions (figure 6). However the contribution of the other PAH constituents are more pronounced (2-10 % per compound) as seen for the “hot spot” samples. These samples represent obviously the average PAH contamination along the major snowmobile tracks on Spitsbergen

This trend is also continuing in the low contaminated sites (figure 7: 8 soil samples). A more even distribution of all measured PAH components are obvious. However, also here phenanthrene, benzo(ghi)perylene and chrysene are the predominant constituents in the surface soil. These levels represent background concentrations in surface soil on Svalbard.

Sample V-5-1 (21 pg/g dw), however, seems unusual due to a special PAH pattern deviating considerably from the overall distribution shown for the other low-contaminated samples. Fluorene is the predominant PAH compound whereas fluoranthene, chrysene and benzo(b)fluoranthene are following. This sampling site is represented by the lowest contaminated surface soil sample measured during the VETAPOS campaign (table 3), collected at the drive-in area near the main Longyearbyen gas station (“Svalbard Auto”). The pattern may be mainly influenced by direct and fresh emissions from 4-stroke engines (diesel/ gasoline). However, it is evident that no major leakage from storage facilities or from fuelling is evident for this sampling site.

### **3.3.1 *Transect across a snowmobile track***

As an indication of a cross-sectional PAH concentration gradient, the soil samples V-17, V-18, V-19 and V-20 were collected along a typical transect across the major snowmobile track close to the Tempelfjord in Sassendalen towards Fredheim was chosen for surface soil sampling (figure 3). As expected a significant gradient of PAH concentrations were identified along the transect reaching from background (V-17-1: 96 ng/g dw) to medium level contamination (286 ng/g dw) and a subsequent concentration reduction (V-20-1: 127 ng/g dw) toward the opposite rim of the snowmobile track. Sample V-19-1 is representing the centre of the snowmobile track and thus, the accumulation zone for emissions from snowmobile traffic to/ from Fredheim cabin as important goal/ relay station for day tips towards the Tempelfjord/ Billefjord region (Figure 11).

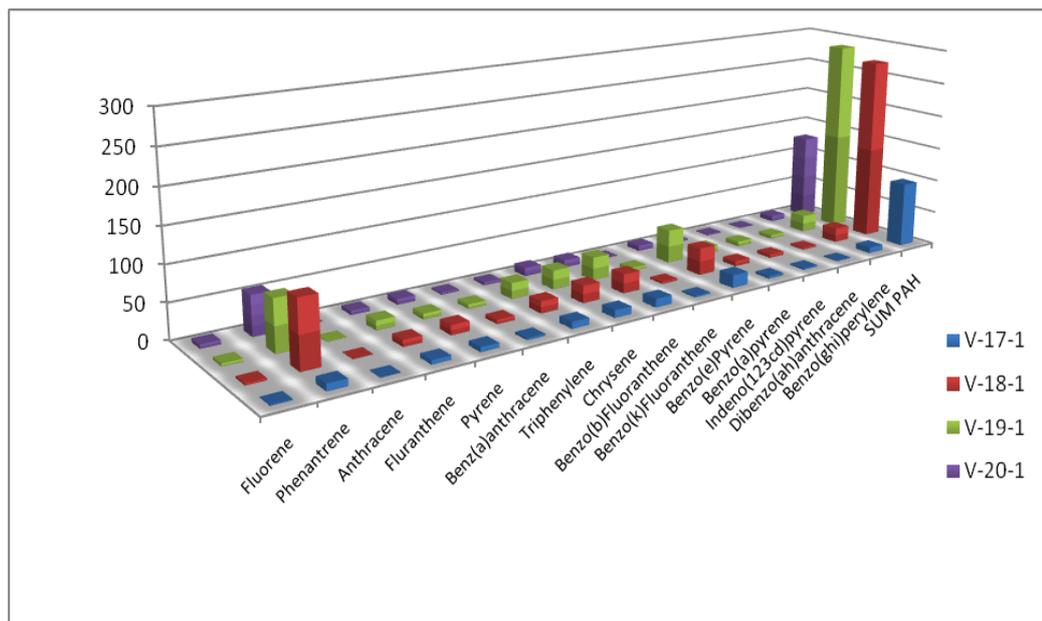


Figure 11: PAH concentrations (ng/g dw) along a transect crossing the snowmobile track near Fredheim (Sassendalen, Tempelfjord: 78° 20' N and 16° 55' E).

Also here, phenanthrene is the predominant PAH compound (indicator for fuel combustion i.e., snowmobile emissions). Soil samples V-16-1 has been collected in close vicinity of the Fredheim cabins, at the parking and recreational areas south of the cabin (150 m from the cabin: Sum PAH=536 ng/g dw; table 3). The intensive human activities around the Fredheim cabin is reflected in the medium range PAH levels found (the only possible source for these elevated levels are winter snowmobile activities and diesel generators for electric power supply).

It is, thus, obvious that fuel combustion processes (snowmobiles, generators, etc) will lead to elevation of PAH levels in the receiving soil surface. Elevated PAH concentrations in the soil may be consequently accumulated in biota (vegetation and organisms) and may finally cause hazardous effects in the sensitive local Arctic habitats/ ecosystems.

### 3.3.2 Volatile organic compounds (VOC) in soil

All soil samples were collected in parallel. Aside the soil samples analysed for PAH concentrations, a dedicated set of samples (18 soil samples) was collected in gas tight glass containers for the analysis of Benzene-Toluene-Xylene related compounds (BTX). However, the levels of BTX related contaminants in the headspace above all the soil samples were below the limit of detection (LOD). These findings demonstrate clearly that weathering processes (incl. evaporation, microbial- and photochemical transformation as well as selective adsorption on surfaces) is an effective remediation process for a selection of contaminants incl. BTX related chemicals. Just about 6 weeks after the snowmobile season 2010 was effectively finalised, volatile BTX related residues have been effectively removed from the contaminant cocktail in the surface soil, presumably by direct evaporation and photochemical transformation.

### 3.3.3 Volatile organic compounds (VOC) in air

As a follow up of an earlier study conducted in Longyearbyen in 2007 (Reimann et al 2009) a follow up study was performed during the VETAPOS campaign in 2010 on the distribution and concentration of BTX related compounds in Longyearbyen air (figure 9).

The considerable reduction of the benzene (toluene and xylene is not presented here) is obviously caused by a combination of two major factors.

- 1.) Due to “no mining activity” at mine no. 7 (the mine was not operated during the BTX monitoring period in 2010), no significant “heavy duty” transportation activities were registered along the road to/from Mine No. 7. Therefore the contribution from heavy-duty vehicles (contributed to the 2007 BTX levels) on the overall BTX emission was absent during the 2010 monitoring campaign.
- 2.) A continuous replacement of 2-stroke snowmobiles with more efficient 4-stroke engine driven snowmobile is evident for the past 5 years. 4-stroke engine driven snowmobiles are emitting less BTX related pollutants into the environment and thus a continuous reduction of BTX emissions is expected (Vestreng et al. 2009).

Overall, it can be concluded that for spring/autumn 2010 a significant reduction of BTX-related pollution into ambient air is observed in the local area around the Research Park Longyearbyen (Forskningsparken) compared with the published results from the 2007 campaign (Reimann et al. 2009).

### 3.3.4 Literature comparison

According to the reported monitoring data from Zeppelin mountain (Ny-Ålesund) from 1999 ([www.emep.org](http://www.emep.org)), the benzene (representative for BTX) background levels are in the concentration range 0.01 – 0.05 ppb in Svalbard. Thus, although considerably reduced, the 2010 benzene levels are still significantly above the expected background levels for Svalbard (VETAPOS data: max. 0.7 ppb benzene in 2010). Benzene-Toluene-Xylene (BTX) related compounds are today considered as suitable markers for fresh and direct emissions from fossil fuel combustion and, thus, should be continued to be monitored in Longyearbyen, Svea, Ny-Ålesund and Barentsburg as essential part of a continuous local air quality monitoring program organized by the Governors office.

Relatively few data on PAH levels in Svalbard surface soil are reported in the Literature. Harris (2009) conducted a survey on around 60 surface soil samples collected from Kinnvika (Nord-Austlandet) as a significant part of her BSc thesis (a cooperative project between the University of Tasmania, Australia and the University Centre in Svalbard). Several very high contaminated samples were identified containing PAH levels up to 4780 ng/g dw. Background concentration between 140 and 200 ng/g dw were calculated. For Arctic surface soil samples calculated Yunker et al. (2002) general background levels for Sum PAH in Arctic soils of around 100 ng/g dw (average). However considerable variations must be considered and accounted for due to natural PAH in various geological formations including coal deposited (quite common on Svalbard) which may result in slightly elevated PAH levels, but characterized with petrogenic PAH patterns.

The highest PAH levels determined in the here presented VETAPOS study was found for soil sample V-8-1, collected about 100 m from the earlier Northern

Light observatory and close to the main road to/from Mine No 7 and the EISCAT research installations (Sum PAH = 1883 ng/g dw). Although this value is considerably lower than found for the hot-spot location at Kinnvika (factor 2.5), the elevated value is clearly caused by emission and subsequent deposition of PAH from fossil fuel driven engines and the subsequent deposition on the surface snow and finally on the underlying soil. The sample is dominated by a pyrogenic PAH patterns (figure 8a,b). However, as possible long-term exposure source and potential contribution, PAH remaining from technical installations/ spills at the former winter airfield, operated in this location on frozen ground until the early 1970s, cannot be excluded and should, thus, be explored in more detail during future research activities.

### 3.4 Conclusions and perspectives

Volatile organic compounds (VOC) including Benzene-Toluene-Xylene (BTX) related compounds were monitored in ambient air samples during Spring (April-Mai) and Autumn (October) 2010 as a follow-up of an earlier BTX ambient air monitoring program in 2007 (Reimann et al. 2007) at the Research park in Longyearbyen (Forskningsparken). In addition, BTX related compounds were measured in 18 “headspace” samples above collected surface soil along snowmobile tracks in Longyeardalen, Adventdalen, Todalen as well as Sassendalen (Fredheim). In addition, during the 2010 VETAPOS in a parallel surface soil sampling campaign, 18 samples were analysed for 15 priority PAH compounds.

In comparison to the 2007 BTX ambient air monitoring campaign a significant reduction of the BTX emissions was found for the snowmobile season (April/May 2010). Only max 30% of the 2007 concentrations were detected for Benzene in air. This significant concentration reduction is assumed to be caused by two major reasons: 1.) Lack of continuous heavy-duty vehicle related traffic on the road to/from Mine No. 7 since the coal-cleaning facilities in the harbor was decommissioned and the Mine No. 2 was not operated in the monitoring period. 2) Higher proportion of 4-stroke engine driven snowmobiles during the 2010 season and the associated reduced emission of BTX due to higher efficacy of the 4-stroke engines.

No BTX related contamination was found in the “headspace” samples of the 18 soil samples analysed. Although considerable emissions are reported (see above), the fresh deposits on the surface soil are obviously continuously removed due to effective weathering processes (re-evaporation and/or photochemical decomposition). Weathering processes seem to contribute significantly to the effective removal of volatile and labile contaminants in soil.

Polycyclic aromatic hydrocarbons (PAH) were determined in all 18 surface soil samples in the concentration range between 21 and 1883 ng/g dw (dry weight, SUM 15 PAH). All samples were characterized with pyrogenic PAH patterns obviously dominated by PAHs released from fossil fuel combustion (diesel/gasoline driven engines). The highest concentrations were found in a soil sample collected at the former winter airfield close to the old Northern Light observatory. Although the soil was collected directly from a frequently used snowmobile track, historical contamination from technical installations/ spillage associated with the former airfield cannot be excluded and should be investigated in more detail. Highly contaminated soil samples are clearly associated with point sources (i.e.,

gas station at the snowmobile rental facilities) and heavily trafficked snowmobile tracks (entrance into the Longyearbreen glacier and close to the restaurant “Huset”). In Sassendalen, a typical transect across the major snowmobile track close to Fredheim, revealed a PAH concentration gradient towards the center of the track as accumulation zone. PAHs are, thus, considered as valuable indicator compounds for human activities around Svalbard (recreation, transportation). Although effective weathering processes continuously reduce the deposited PAH concentration in the soil, the most recalcitrant compounds remain in the surface soil with the inherent potential to accumulate in biota (vegetation and organisms) and may even cause hazardous effects on the local low tropic levels in the terrestrial Arctic ecosystem.

The here-performed VETAPOS study revealed a few hot-spot contaminated locations in the vicinity of Longyearbyen. However, due to obvious contamination history, similar locations are expected also in Svea, Barentsburg and Ny-Ålesund. It is, therefore, recommended to initiate a follow-up study on identification of high-contaminated locations (PAH) in all settlements on Svalbard including abandoned locations (i.e., Pyramiden, Grumant, Coles bay, Hjorthamna). Such a study should also include the development of appropriate remediation actions and abatement strategies as recommendations for the regulatory authorities on Svalbard.

### **3.5 Acknowledgement**

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BTX measurements in ambient air were performed at UNIS, but concentration calculations were done at Empa, Switzerland.

The BTX measurements in soil “headspace” samples were done at NILU.

### 3.6 References

- Aamaas, B., Bøggild, C.E., Storda, F., Berntsen, T., Holmen, K., Ström, J. (2011) Elemental carbon deposition to Svalbard snow from Norwegian settlements and long-range transport. *Tellus*, DOI: 10.1111/j.1600-0889.2011.00531.x, in press.
- Reimann, S., Kallenborn, R., Schmidbauer, N. (2009) Severe aromatic hydrocarbon pollution in the arctic town of Longyearbyen (Svalbard) cause by snowmobile emissions. *Environ. Sci. Technol.*, 43, 4749-4795.
- Stein, E., Tiefenthaler, L.L., Schiff, K. (2006) Watershed based sources of polycyclic aromatic hydrocarbons in urban storm water. *Environ. Toxicol. Chem.*, 25, 373-385.
- Harris, E. (2009) Weathering processes and remediation options for polychlorinated biphenyl and polycyclic aromatic hydrocarbon contamination at Kinnvika Station, Svalbard. B. Ant. Sci. University of Tasmania, Hobart, Australia.
- Vestreng, V., Kallenborn, R., Økstad, E. (2009) Climate influencing emissions, scenario and mitigation options at Svalbard. Oslo, Klima- og forurensningsdirektoratet (TA-2552/2009).
- White, J.J., Carrol, J.N. (1998) Emissions from snowmobile engines using bio-based fuels and lubricants. San Antonio, Texas, SouthWest Research institute (Report SWRI 7383).
- Yunker, M.B., Macdonald, R.W. (1995) Composition and origins of polycyclic aromatic hydrocarbons in the Mackenzie River and on the Beaufort Sea Shelf. *Arctic*, 48, 118-129.
- Yunker, M.B., Macdonald, R.W., Vingarzan, R., Mitchell, R.H., Goyette, D., Sylvestre, S. (2002) PAHs in the Fraser River basin: a critical appraisal of PAH ratios as indicators of PAH source and composition. *Organic Geochem.*, 33, 489-515.

## **Appendix A**

### **Polycyclic Aromatic Hydrocarbons (PAH) in surface soil**





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for Air Research**

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ABSTRACT Volatile organic compounds (VOC) including Benzene-Toluene-Xylene (BTX) related compounds were monitored in ambient air samples during Spring (April-Mai) and Autumn (October) 2010 as a follow-up of an earlier BTX ambient air monitoring program in 2007 (Reimann et al 2007) at the Research park in Longyearbyen (Forskningsparken). In addition, BTX related compounds were measured in 18 "headspace" samples above collected surface soil along snowmobile tracks in Longyeardalen, Adventdalen, Todalen as well as Sassendalen (Fredheim). In addition, during the 2010 VETAPOS in a parallel surface soil sampling campaign 18 samples were analysed for 15 priority PAH compounds.			
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