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Five-Year Vapor Monitoring for Risk Management at a Hydrocarbon-Polluted Site

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ABSTRACT: Soil remediation (excavation and off-site disposal) was partially carried out in 2005 at a site in Milan (Italy), leaving a residual volume of soil polluted with petroleum-derived hydrocarbons. Indoor air, outdoor air, crawl-space air and soil gas samplings have been carried out since January 2009. In March 2011 the monitoring network was upgraded to its final configuration (18 indoor, 7 outdoor and 4 crawl-space sampling locations, 60 soil gas probes at four different depths from ground surface); after that, one monitoring campaign a season was performed until November 2013, fractionating hydrocarbons according to a modified version of the Massachusetts Department of Environmental Protection approach. In order to permanently keep risk below acceptable levels, a mitigation system of the contaminated source was installed in December 2013, and it is still working. Three monitoring campaigns of ambient air have been performed since then. Although not strictly necessary in terms of time-averaged health risk, the mitigation system allowed to extract significant amounts of mono- and light poly-cyclic aromatic hydrocarbons. This has helped manage concerns about future uncontrolled exposure for people working at the site.

INTRODUCTION

Risk assessment is a procedure frequently used at contaminated sites to evaluate if pollution in soil or groundwater may cause unacceptable risks for human health, resulting in the need of remediation activities or pollution confinement. Analytical models are included in the most common tools used to estimate risk, which allow for the calculation of the pollutant concentrations at the exposure point (ITRC, 2008).

The impact of vapor inhalation is directly proportional to the pollutant concentration in the air inhaled indoors or outdoors. Due to the uncertainty associated with models for the volatilization pathway, field samplings of a vapor phase (e.g., soil gas, ambient air) can be suggested or required to check model predictions (Hers et al., 2001; Ohio EPA, 2010).

Soil gas measurements allow to exclude the partitioning model in the secondary source, but the results are strongly affected by soil properties at the monitoring point/depth, soil moisture, temperature, and atmospheric pressure (Hutchinson et al., 2002; DTSC, 2004; MDNR, 2005). Ambient air sampling allow to bypass completely the modeling tools, but results may be affected by background values, local sources not ascribable to the secondary sources below ground surface, wind speed (for outdoor measurements), and air conditioning/heating (for indoor measurements) (Schmidt et al., 1998b; Hers et al., 2003; McHugh et al., 2004).

This work reports the approach adopted and the lesson learned in the risk assessment procedure and risk management at a site in Milan (Italy), where soil remediation (excavation and off-site disposal) was partially carried out in 2005, leaving a residual volume of soil polluted with petroleum-derived hydrocarbons.

MATERIALS & METHODS

The site covers approximately 24000 m², and it is part of a more extended service-sector area of the city (Figure 1). The southern zone of the site is used as a parking area, whereas the northern zone has a recreational use; a building ("A" in Figure 1) is located and already used in the central zone of the site. Between the existing building and the parking area, another building ("B" in Figure 1) is under construction; in order to prevent vapor intrusion from the residual pollution in the soil beneath, a drainage system covered by a vapor-tight membrane was placed under and around its basement.

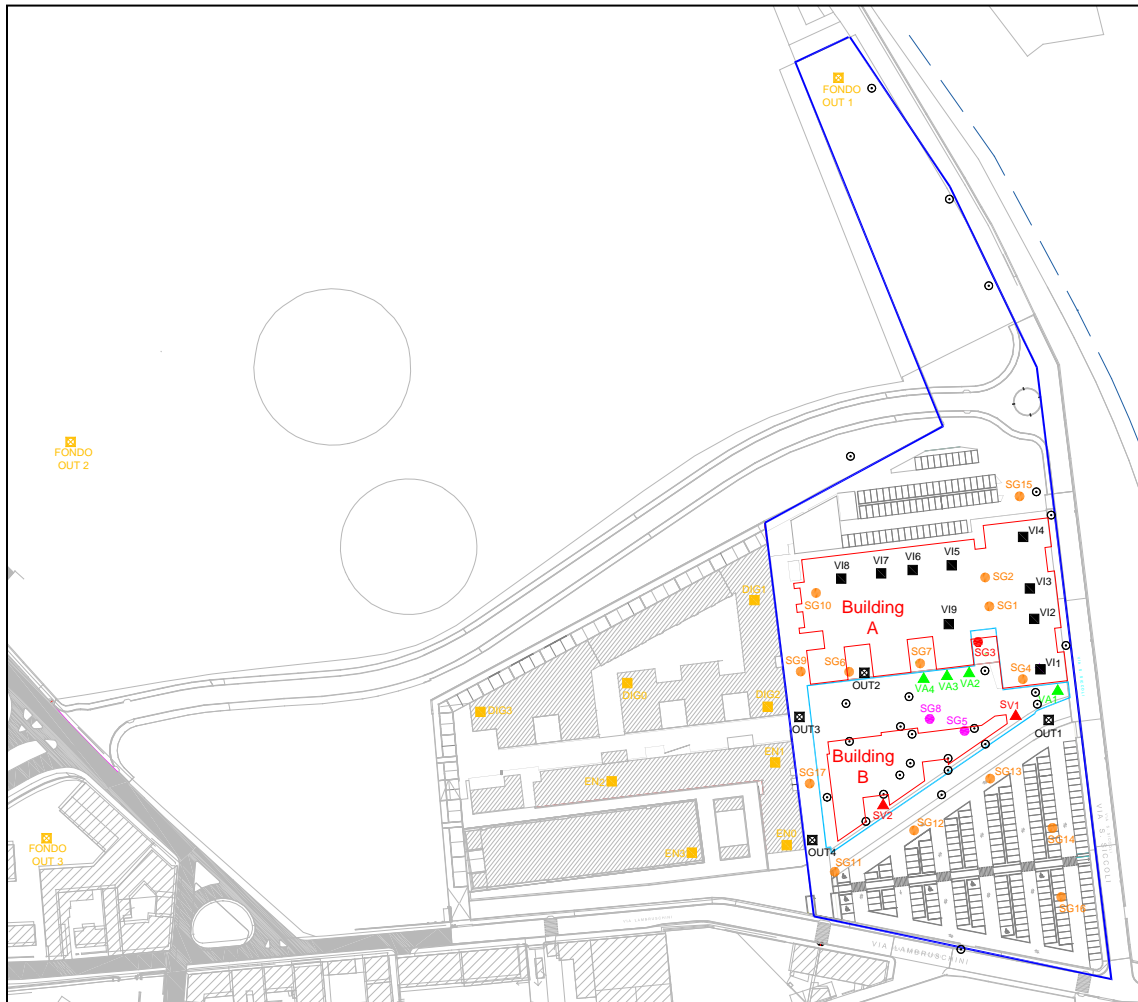


FIGURE 1. Site map. —: site boundary; —: vapor-tight membrane boundary;
 ●: soil gas probes at 1, 4, 10 and 15 m bgs; ●: soil gas probes at 1 and 4 m bgs;
 ●: soil gas probes at 4 m bgs; ■: indoor monitoring locations at the site; □: outdoor monitoring locations at the site; ▲: crawl-space monitoring locations;
 ■: indoor background monitoring locations; □: outdoor background monitoring locations; ○: additional boreholes for soil investigation;
 ▲: soil vapor extraction wells.

More than 30 boreholes with a maximum depth between 4 and 25 m below ground surface (bgs.) allowed to assess the local geology of the site, resulting in the following stratigraphy: (1) pavement, with an average thickness of about 0.5 m; (2) sandy silt with pebbles, down to a depth between 1.5 and 7.5 m bgs.; (3) gravelly sand or sand with gravel (autochthonous materials), in the remaining thickness investigated. The groundwater level fluctuates between 16 and 20 m bgs.

Potential contamination in soil was evaluated with reference to the table values of the Ministry Decree (1999) and the Italian Health Institute guidelines (ISS, 2012) for green/residential use. After partial remediation, monoaromatic hydrocarbons (BTEX: benzene, toluene, ethylbenzene, xylenes), polyaromatic compounds (PAHs: benzo(a)-anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)-perylene, chrysene, dibenz(a,e)pyrene, dibenz(a,h)anthracene, indeno(1,2,3-cd)pyrene, pyrene and mostly acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, naphthalene) and total petroleum hydrocarbons were left variously distributed in soil between 0.8 and 22 m bgs. The highest concentration values of the residual pollution were located beneath building B.

Indoor air, outdoor air, crawl-space air and soil gas samplings had been carried out since January 2009; however, in March 2011 the monitoring network was upgraded to its final configuration (Figure 1) composed of 60 soil gas probes (15 at 1 m bgs, 17 at 4 m bgs, 14 at 10 m bgs and 14 at 15 m bgs), 18 indoor, 7 outdoor and 4 crawl-space sampling locations, including background monitoring points ("Fondo OUTn" for outdoor air, "DIGn" and "ENn" for indoor air). Seasonal monitoring campaigns were carried out for 15 months after the upgrade, in order to perform risk assessment (March, July, and October 2011, and January 2012) and confirm the procedure results over time (April and July 2012). From October 2012, the ambient air and the crawl-space air were monitored three times a year (October 2012; January, May, and October 2013; March, July, and November 2014; February 2015).

Active sampling of the vapor phase was performed at the flow rate of 1 l/min for 4 to 7 h. Hydrocarbons were fractionated with a modified Massachusetts Department of Environmental Protection (MADEP) approach (MADEP, 2002, 2004a, b). Activated carbon sorbent tubes (ORBO 32, 400/200 mg, Sigma Aldrich) and XAD-2 (ORBO 609, 400/200 mg, Sigma-Aldrich) were used in parallel to capture volatile organic compounds (VOCs: benzene, toluene, ethylbenzene, xylenes, Aliphatics C6-C8 and C9-C10, Aromatics C9-C10) and semi-volatile organic compounds (SVOCs: PAHs, Aliphatics C>10-C18), respectively. A PTFE filter (37 mm diameter, 0.5 µm pore size) was placed in the sampling line to remove aqueous vapor. VOCs were extracted from the sorbent cartridges with 2 ml carbon disulfide, whereas SVOCs were extracted with 2 ml dichloromethane. VOCs were separated chromatographically with a Petrocol DH column (50 m x 0.2 mm i.d., 1.5 µm film thickness) and quantified by gas chromatography-mass spectrometry - GC/MS (Trace DSQ, Thermo Corporation) operating in selected ion monitoring mode with the following instrumental conditions: 220°C split injector temperature, 35°C initial oven temperature (held for 5 min), 220°C final oven temperature (held for 15 min), oven temperature ramp 8 °C/min. SVOCs were separated with a Equity-5 column (30 m x 0.25 mm i.d., 0.25 µm film thickness) and quantified by GC/MS in selected ion monitoring mode with the following instrumental conditions: 280°C split/splitless injector temperature, 50 °C initial oven temperature (held for 1 min), 50°C to 150°C at 12°C/min, 150°C to 290°C at 7°C/min, 290°C final oven temperature (held for 15 min). The Aromatic C9-C10 fraction did not include benzene, toluene, ethylbenzene, xylenes and polyaromatic compounds.

Risk assessment was performed taking into consideration the following set of pollutants: benzene, toluene, ethylbenzene, xylenes, naphthalene, Aliphatics C6-C8,

Aliphatics C9-C18 and Aromatics C9-C10. Values for the physical-chemical and toxicological properties were taken from the Italian Health Institute database (ISS-ISPEL, 2009a, b) or from RISC 5.0 database (Spence, 2011) whenever not reported in ISS-ISPEL (2009a, b). For each monitoring campaign, carcinogenic risks and hazard indexes were estimated using RISC 4.0 from the representative soil gas concentrations at the different depths, which were calculated with ProUCL 4.00.02 as the Upper Confidence Limit 95% of the pollutant concentrations measured in (1) SG1 to SG10, SG13 and SG15, for indoor exposure in building "A"; (2) SG1 to SG14, for indoor exposure in building "B"; (3) SG1 to SG17, for outdoor exposure. Soil was assumed as homogeneous sandy gravel (0.25 total porosity, 0.10 water-filled porosity). Wind velocity (0.8 m/s) was calculated as the average value over a ten-year period of measurements at the nearest public meteorological station. Building foundation parameters affecting vapor intrusion and exposure parameters were assigned the default values reported in APAT (2008).

After soil vapor extraction (SVE) pilot tests, a full-scale plant was designed and installed in December 2013. The plant is still working in order to reduce the contaminant mass in the residual pollution source. It consists of four extraction wells, SV1A and SV1B (next to each other) and SV2A and SV2B (next to each other), located as shown in Figure 1. SV1A and SV2A are screened between 1 and 8 m bgs, while SV1B and SV2B are screened between 8 and 15 m bgs. Each couple "A" and "B" of extraction wells is connected to a moisture separator and a blower. Until March 2015, the off-gas treatment was performed by catalytic oxidation and activated carbon adsorption; since then, the catalytic burner has been bypassed, due to a significant decrease in the pollutant concentrations in the extracted flow.

RESULTS AND DISCUSSION

Figure 2 shows the cumulative carcinogenic risk and the cumulative hazard index for indoor exposure in building "A" and outdoor exposure at the site, resulting from the risk assessment procedure based on soil gas concentrations at the different depths; results for building "B" are not shown as similar to those of building "A". Data collected 1 m bgs resulted in calculated risks lower than those based on data from soil gas probes deeper in soil; the estimates differed by up to about two orders of magnitude for indoor exposure. This result was ascribed to the variation with depth of soil lithology, which was considered very permeable to vapors in calculations, though soil contained a certain amount of fine material toward ground surface. Another point is that the transport model in soil did not consider biodegradation, which is actually going on as suggested by the low O₂ and the high CO₂ concentrations measured at 10 and 15 m bgs in many monitoring probes below or near the building footprints (data not reported).

Comparison between the different monitoring campaigns at a specific depth highlighted that the estimated risks differed by up to one order of magnitude without a systematic seasonal effect. The two monitoring campaigns performed in April and July 2012 confirmed full compliance of the calculated risks to the regulatory limits (individual carcinogenic risk: 10⁻⁶; cumulative carcinogenic risk: 10⁻⁵; cumulative hazard index: 1).

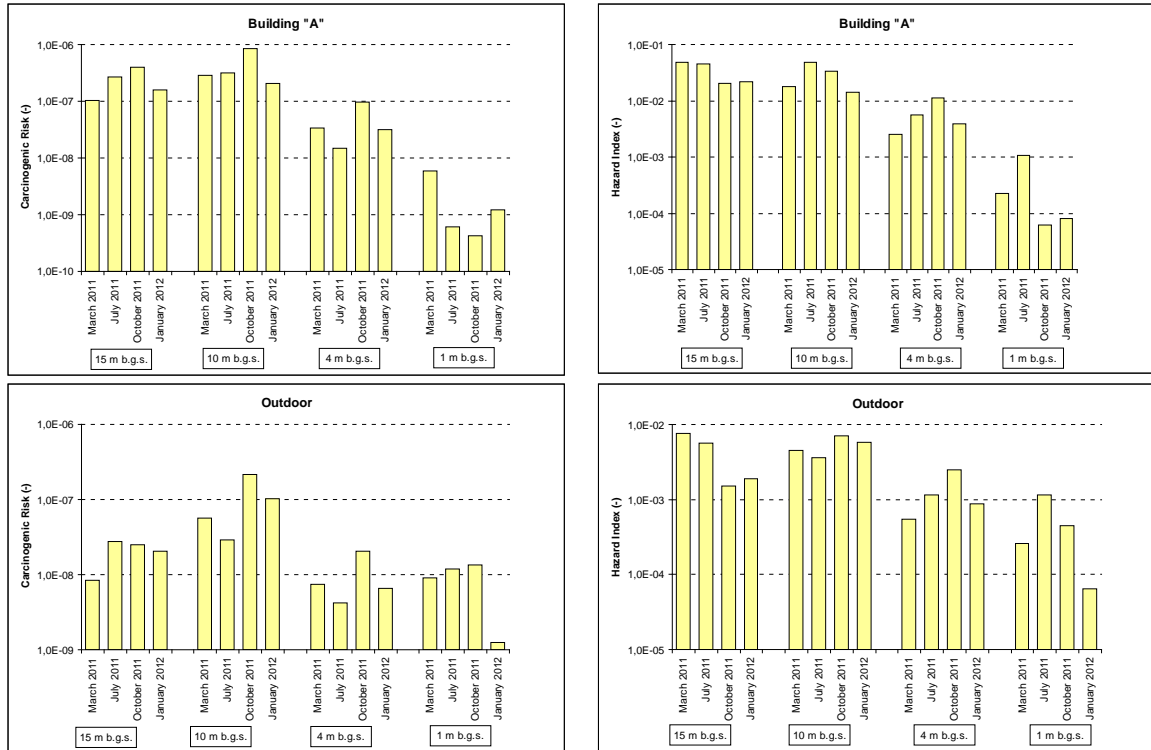


FIGURE 2. Cumulative carcinogenic risk and cumulative hazard index for indoor exposure in building "A" and outdoor exposure, resulting from the risk assessment procedure based on soil gas concentrations at the different depths.

Figure 3 shows the average outdoor, crawl-space and indoor air concentrations for some selected pollutants (benzene, naphthalene) and hydrocarbons fractions (Aliphatics C6-C8, Aliphatics C9-C18) as an example. A few measurements resulted in episodic high values for benzene (OUT1 and OUT3 in January 2012), naphthalene (VA1 in March 2011, OUT1 in October 2011, and OUT3 in February 2015), and Aliphatics C9-C18 (crawl-space VA1 in March 2011 and VA4 in October 2011). However, the average outdoor and indoor concentrations were not significantly higher than the outdoor background and the indoor background respectively, with the exception of the Aliphatics C6-C8 outdoor value in July 2011 and the indoor value in October 2013. Indoor and crawl-space concentrations were not significantly higher than outdoor background, except for Aliphatics C6-C8 in January 2012 (indoor and crawl-space) and October 2012 and 2013 (indoor), Aliphatics C9-C18 in October 2013 (indoor) and March 2014 (crawl-space), and benzene in July 2014 (indoor).

Throughout the years, only for BTEX it was possible to identify July as the systematic month with the lowest average concentrations. As a general trend, for all pollutants the highest average values were measured from October to March. These results suggest that, though the temperature in July is higher than in the other monitoring periods and might enhance emission from soil, the worst air quality is found during the cold seasons, when the atmospheric conditions promote stagnation and sources other than pollution in soil (vehicular traffic, heating systems) are active.

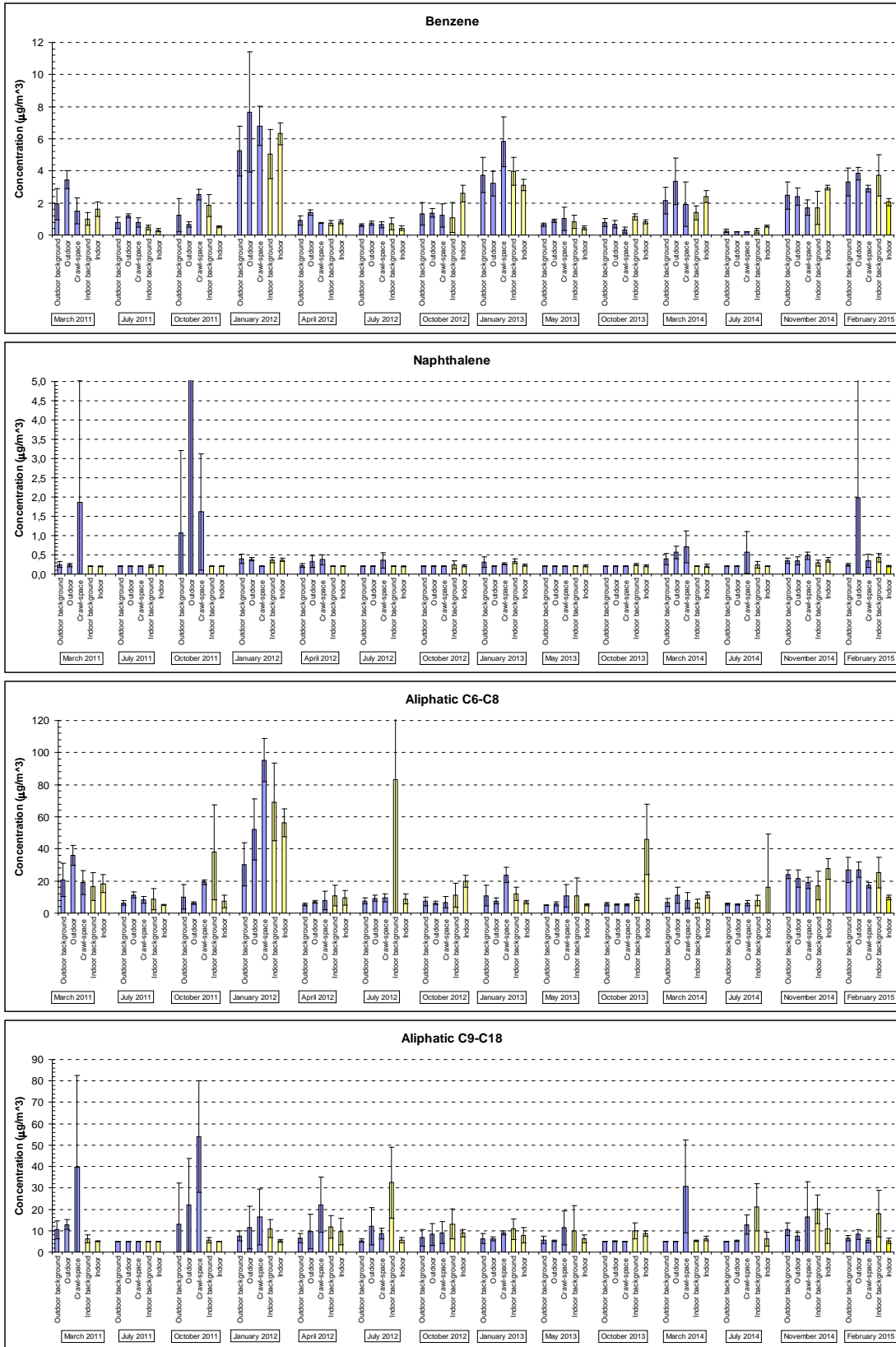


FIGURE 3. Average outdoor, crawl-space and indoor air concentrations for some selected pollutants. The error bars show the standard deviation of data.

Although the risk assessment procedure indicated that the residual pollution at the site was not dangerous to human receptors, workers attending the site were quite worried about the situation. In order to keep them calm and to exclude potential emissions from soil permanently, a soil vapor extraction plant was designed and installed in December 2013 as a mitigation system to reduce the pollutant concentrations below building B. Figure 4 shows the amount of contaminants extracted from January 2014, on a monthly basis (Figure 4a) and as the cumulative amount (Figure 4b). For all pollutants, one year operation resulted in a significant decrease (by two orders of magnitude) of the concentrations in the gas from well SV1B, which was the most impacted stream. Based on this abatement and the plateau of Figure 4b reached in 2015, a soil gas monitoring campaign has been scheduled in order to decide the shutdown of the plant.

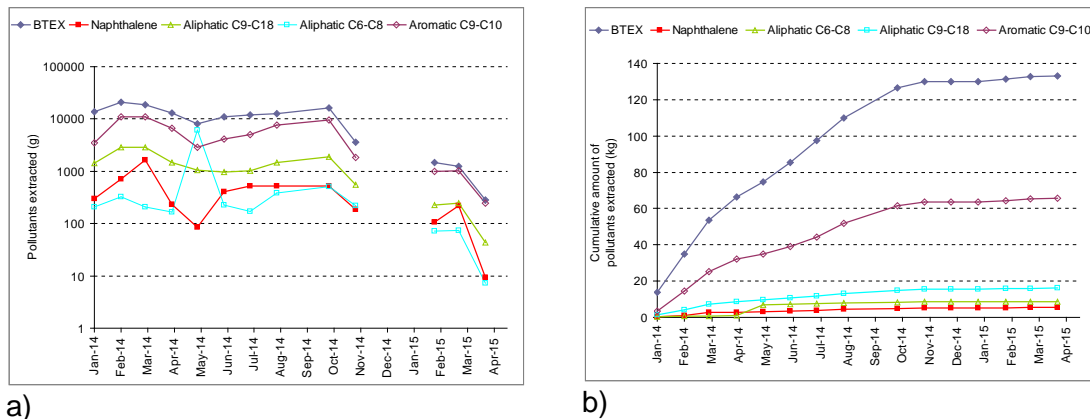


FIGURE 4. Contaminants extracted with the SVE system, on a monthly basis (a) and as the cumulative amount (b).

CONCLUSIONS

Health risk calculations at the site resulted in a cumulative carcinogenic risk up to $1.0 \cdot 10^{-6}$ (indoor exposure based on soil gas data at 10 m bgs in October 2011) and a cumulative hazard index up to about 0.05 (indoor exposure based on soil gas data at 15 m bgs in March 2011). Estimates lower by about two orders of magnitude were obtained when data at 1 m bgs were used for calculations.

A few outdoor air and crawl-space measurements resulted in episodic high values. However, as a general trend, the average outdoor and indoor concentrations did not differ significantly from the background values. The worst air quality was found in autumns and winters, when the atmospheric conditions promote stagnation and sources other than pollution in soil (vehicular traffic, heating systems) are active. Compared with background values, indoor and outdoor air concentrations at the site suggested that hydrocarbons were widely spread and sources other than pollution in soil were affecting the quality of the air inhaled at the site.

Although not strictly necessary in terms of time-averaged health risk, the mitigation system allowed to extract significant amounts of mono- and light poly-cyclic aromatic hydrocarbons. This has helped manage concerns about future uncontrolled exposure of people working at the site.

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