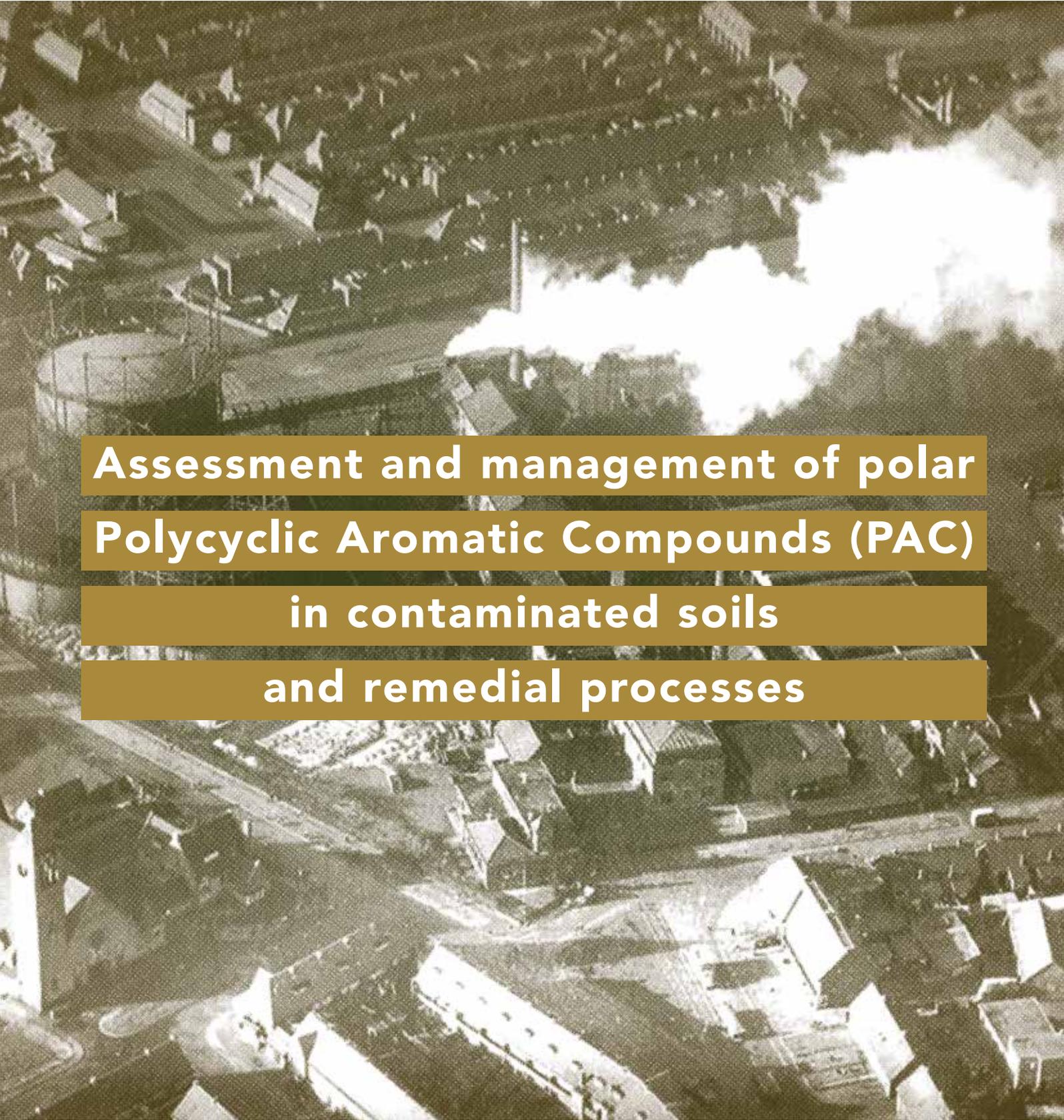




SNOWMAN NETWORK

Knowledge for sustainable soils



**Assessment and management of polar
Polycyclic Aromatic Compounds (PAC)
in contaminated soils
and remedial processes**

Introduction

It has been recently recognized by European Environment Agency (EEA) that soils contaminated with Polycyclic Aromatic Hydrocarbons (PAHs) may contain significant amounts of other Polycyclic Aromatic Compounds (PACs) as well. PAC contamination is a frequently occurring environmental problem in Europe: 200.000 sites may contain these pollutants [EEA, 2008]. Among the PACs, the polar compounds such as oxygenated PAHs (oxy-PAHs), hydroxy-PAHs, nitro-PAHs and nitrogen heterocyclic PACs (N-PACs) are shown to be considerably toxic for both humans (toxic, mutagenic and carcinogenic) and environment (leachable and bioavailable). However, only a small subset of 16 PAHs is generally monitored during risk assessment of the sites, in spite of the fact that many other contaminants also may be present. This may lead to a miscalculation of the risk induced by these sites, as well as of the remediation efficiency.

This *Policy brief* provides a synthesis of the research project PACMAN (2011-2014), funded by the SNOWMAN network. The overall objectives of this project have been to elucidate to what extent compounds belonging to the polar PACs contribute to the risk at PAH contaminated sites, and also to find ways to manage and reduce this risk.

Main findings

- Polar PACs are highly relevant contaminants in the environment in general and at certain contaminated sites in particular: former and active gasworks, coke oven plants, wood tar production, wood preservation and asphalt industries.
- Levels of polar PACs in many cases are correlated to the PAH-levels and their risks can be assessed together. But for several situations, the risk caused by polar PACs may be overlooked if not specifically considered.
- Remediation processes applied (oxidation, biodegradation) indicate that the polar PACs will be degraded if the process degrades PAHs, even though the oxy-PAH depletion may be a bit delayed. During harsh oxidation, process needs to be conducted to its term (run long enough) to avoid any accumulation of polar PACs (oxy-PAHs and other transformation products).

Key policy recommendations

- ▶ Encourage to monitor polar PACs during investigation and remediation in probable PACs contaminated sites. According to the necessity to embrace the whole range of polar PAC's physicochemical properties, a suggested selection of 12 compounds to monitor is included in PACMAN's conclusions. Price for each sample in which also polar PACs are analysed may be doubled. So to save money and resources, prioritization of samples is possible, focussing on relevant situations listed hereafter.
- ▶ Include polar PACs in risk assessment for the following situations, otherwise the risk may be underestimated:
 - if surface or groundwater may have been contaminated
 - if the contamination has had the possibility to leach vertically in a homogenous and undisturbed soil
 - if the contamination has spread horizontally to a large extent, by dusting and evaporation for instance
 - if a powerful oxidation technique is used to remediate the PACs.

Polycyclic Aromatic Hydrocarbons (PAHs) are common pollutants at contaminated sites of gasworks, wood preservation and tar production sites, coke oven plants, and asphalt production sites.

In Sweden 8 % (1.200 sites) of the PAH-contaminated sites identified in the highest risk classes are estimated to be contaminated with Polycyclic Aromatic Compounds (PACs) and in France the corresponding figure is 17 % (1.046 sites).

PAHs compounds are transformed into polar PACs compounds either by chemical and photochemical oxidation in air and water or chemical and microbial oxidation in soil and water. The structure of polar PACs and PAHs are similar. However, polar PACs contain an atom or a radical of oxygen, nitrogen, nitrogen dioxide or hydroxyl (Figure 2).



Figure 1. Rennes gas plant site (50's)

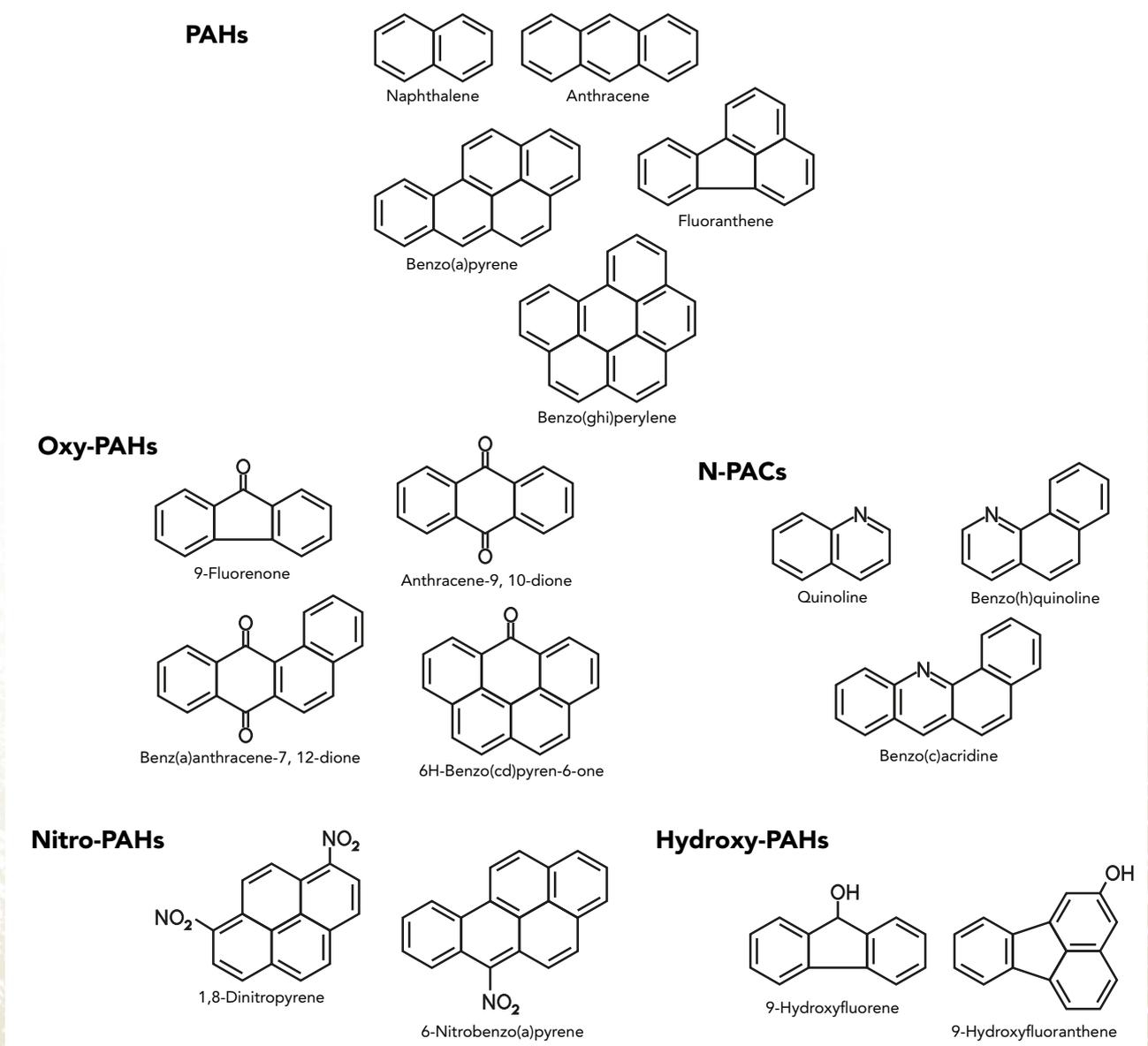


Figure 2. Molecular structures for selected unsubstituted PAHs and polar PACs including oxy-PAHs, N-PACs, nitro-PAHs and hydroxy-PAHs

Studies have shown that the structure of polar PACs play an important role in their physicochemical and toxicological properties. Due to their polar group, the polar PACs have a relatively high solubility in water. This implies that **they may have higher tendency to spread via ground- and surface waters in the environment, as compared to the unsubstituted PAHs**. The data collected so far show that polar PACs (as individual compound or in mixtures) may cause a variety of toxic effects in humans and other organisms (such as effect on growth and reproduction, endocrine disruption, oxidative stress or mutagenicity¹). **Polar PACs are also considerably more toxic than PAHs** because they don't always require a metabolic activation to induce a mutagenic response.

To assess and manage PAC-contaminated sites, the PACMAN project used existing data on polar PACs from 20 sites in Sweden (gasworks, coke production, wood preservation) and 2 sites in France (coke production).

New data on polar PACs data have also been generated on 15 Swedish sites, 7 French sites and 1 Belgian site in order to understand the distribution of polar PACs in the soil, the groundwater and the biota. In addition, the investigations focused on one Swedish wood preservation site and its surroundings.

Issue: polar PACs are practically never included in the risk assessment of PAC-contaminated sites as well as in their remediation monitoring in spite of their toxicity and their bioavailability.



Figure 3. A wood preservation site (nowadays)

KEY RESULTS

Study case on a Swedish wood preservation site:

The wood preservation sites (Figure 3) are among the most probable PAC-contaminated sites in Sweden (44 % of total PAC-contaminated sites), before asphalt production sites (32 % of total PAC-contaminated sites) and wood tar production (15 % of total PAC-contaminated sites).

Distribution of polar PACs in soil, groundwater and biota

	In soil (n = 3)	In groundwater (n = 8)
Σ PAH16	2 100 - 14 000 µg/g	22 - 426 µg/L
Σ Oxy-PAH11	219 - 420 µg/g	0.82 - 17 µg/L
Σ N-PAC4	5.2 - 139 µg/g	0.86 - 32 µg/L
Fraction Oxy-PAH (%)	9.0 % (2 - 17 %)	2.4 % (0.56 - 4.4 %)
Fraction N-PAH (%)	0.39 % (0.05 - 0.93 %)	8.7 % (1.2 - 20 %)

Table 1. Levels of PAHs, oxy-PAHs and N-PACs found in soil and groundwater at the former wood preservation site. The relative levels of oxy-PAHs and N-PACs (fractions of total PACs) are also given ; n = number of samples

The results of soil and groundwater sampling at a former wood preservation site showed that contaminants were distributed over the whole site, in both matrices (Table 1). Moreover, polar PAC levels showed a high spatial heterogeneity.

The data collected show that the polar PACs constitute a small but significant fraction of the total PAC-load in soil and in groundwater.

The groundwater is enriched in polar PACs, especially in N-PACs. Indeed, higher proportions of N-PACs were observed in the groundwater at the former wood preservation site. However, no clear enrichment of oxy-PAHs compared to PAHs was observed, despite the higher oxy-PAHs water solubilities.

The distribution of polar PACs in the soil and in the groundwater could be a combination of:

- the adsorption of PACs in the groundwater onto small particles (colloids) and dissolved organic carbon (DOC), which increase the water concentration of the less soluble compounds,
- the selective interactions that may absorb some oxy-PAHs,
- the more likely degradation of dissolved oxy-PAHs than PAHs.

¹ Mutagenicity refers to a chemical or physical agent's capacity to change genetic material, usually DNA, of an organism and thus increases the frequency of mutations above the natural background level.

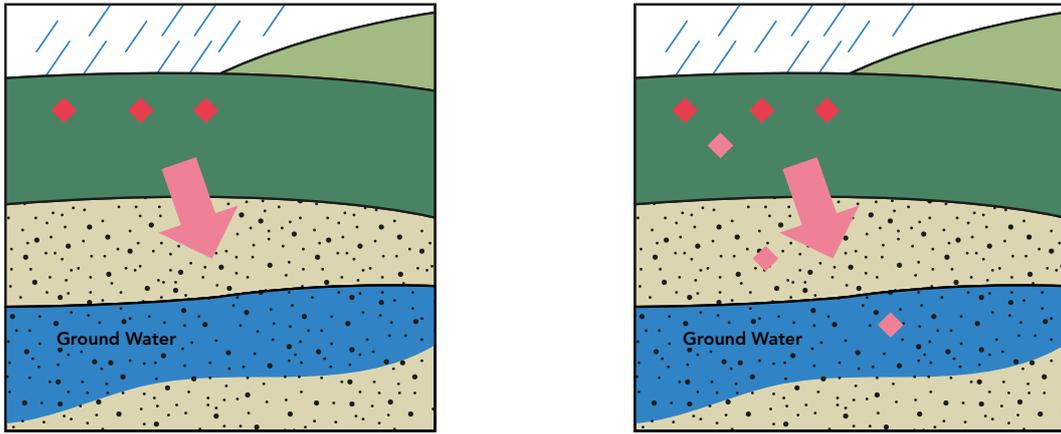


Figure 4. Diagram of soil contamination by PAHs (l), by PAHs and polar PACs with infiltration (r)

Moreover, the results from sample to sample indicate that the spatial heterogeneity of polar PACs and PACs is high; the whole site was more or less severely contaminated. No clear fluctuations between different profiles of soils for the different compound classes were identified: the fluctuations of PAHs and polar PACs were more or less correlated down

through the profiles. This can most likely be explained by colloids, DOC and specific interactions that are reducing the differences in leachability between compound classes, and by degradation processes that are more active on the polar PACs than on PAHs.



Figure 5. Lymnaea stagnalis

To investigate the transport of PACs from the site to the nearby bay and their accumulation in water living biota, molluscs were collected (Figure 5). The results showed that the molluscs in the whole bay contained elevated levels of both PAHs and polar PACs (Figure 6).

The PAC profile in the molluscs is a mix of the profiles found in the soil and the groundwater with a PAH pattern similar to that in the soil and an oxy-PAH or N-PAC pattern more like that in the groundwater.

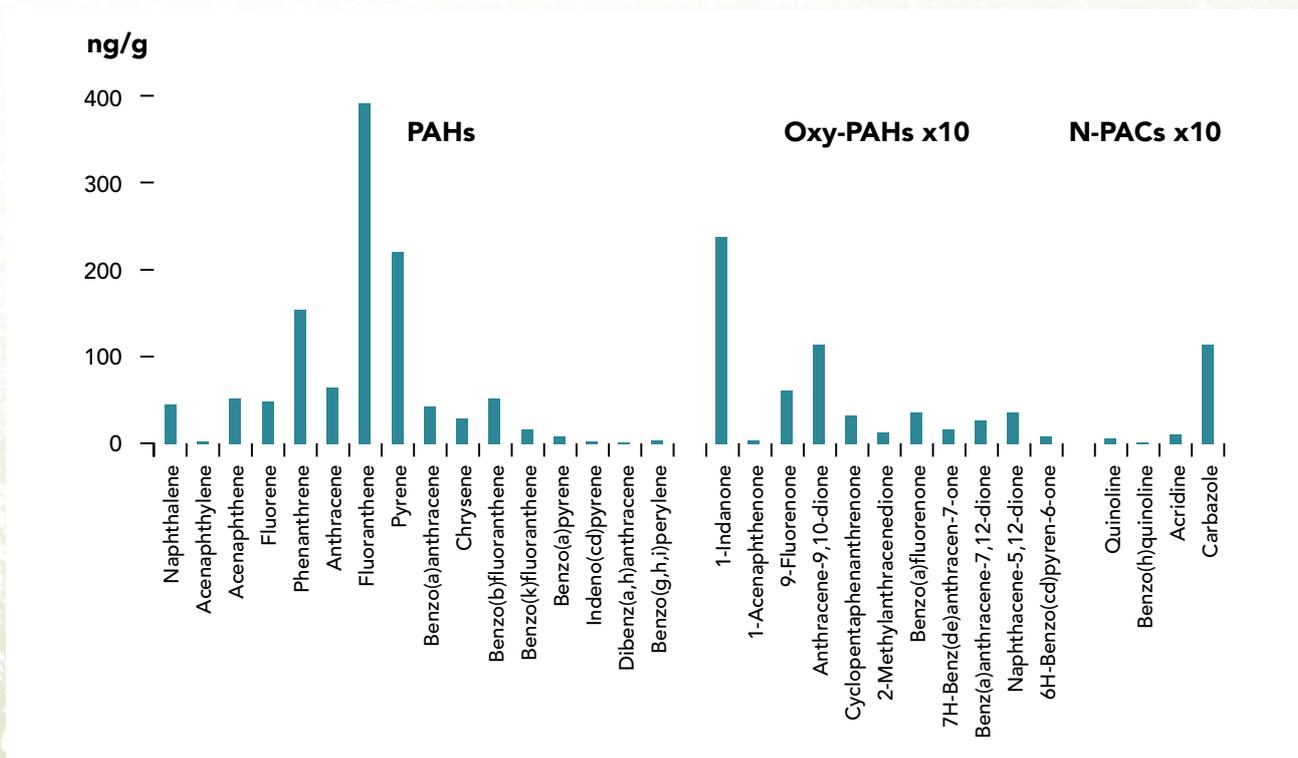


Figure 6. Distribution of selected PAHs, oxy-PAHs and N-PACs in the molluscs

The PAC level in the molluscs is a combination of what the molluscs take up and what they accumulate. N-PACs would be more available for uptake, but they would also be more easily metabolized and excreted. Overall, this might

lead to an optimal uptake/accumulation of the oxy-PAHs and PAHs. For the oxy-PAHs and N-PACs, other processes might be involved as well, such as enhanced metabolism and excretion of specific compounds.

Remediation of the site

The formation and the accumulation of oxy-PAHs seem mainly to be a problem during harsh oxidation (H_2O_2 oxidation, KMnO_4 oxidation, Fenton like oxidation) conditions when the degradation rate is strongly enhanced: PAH depletion is combined with oxy-PAH formation. When the degradation is running more slowly, the oxy-PAHs will usually be degraded accordingly. Consequently, during more enhanced degradation conditions it is important to make sure that the process is not terminated too early, so that oxy-PAHs and other transformation products will have time to degrade as well.

The processes investigated in this project do not point towards any long term accumulation of polar PACs as a result of the remediation processes applied, but are instead indicating that the polar PACs will be degraded if the process degrades PAHs, even though the oxy-PAH depletion may be a bit delayed.

Recommendations

The PACMAN project showed that polar PACs are highly relevant environmental contaminants and they are particularly abundant at certain industrial sites. They are

considerably toxic and may constitute a hazard to humans and other biota.

Monitoring polar PAC compounds

The polar PACs could add extra risk to the sites, despite a large part of them will probably be degraded. They should be considered even if the risk assessment and remediation is based on PAH data only. Indeed there are some circumstances where risks caused by polar PACs have to be analyzed:

- If surface- or groundwater may have been contaminated ;
- If the contamination has had the possibility to leach vertically in a homogenous and undisturbed soil ;
- If the contamination has spread horizontally to a large extent, by dusting and evaporation for instance.

Moreover, if a powerful oxidation technique is used to remediate soil, water or other contaminated material, some polar PACs (oxy-PAHs in particular) may be depleted more slowly than the PAHs. They may even accumulate in the process due to a simultaneous formation of oxy-PAHs via oxidation of PAHs.

Consequently, it appears necessary to monitor polar PACs during investigation and remediation in probable PACs contaminated-sites.

Including polar PACs among the analyzed compounds as PACs contaminated sites

Although, no alarming results, in terms of extremely elevated polar PAC levels, have been obtained for any of these situations within the PACMAN project, results pointing in this direction have been observed for all of them. As a consequence, it would be wise to include a number of polar PACs among the analyzed compounds as PAC-contaminated sites are risk assessed and remediated. The polar PACs to monitor could be those studied within PACMAN, but it could also be a selection of these. In that case, it is important to select compounds of different molecular weights and size, in order to embrace the whole range of the polar PAC's physicochemical properties. Likewise, it would also be suggested to include one or two high molecular weight (HMW) N-PACs among the selected compounds. A suggested selection would be

As a rough estimate the price for each sample in which also polar PACs are analyzed may be doubled. But if polar PACs aren't analyzed, the subsequent remediation might be somewhat more costly, depending on the extra measures that need to be taken.

These compounds could either be analyzed in all samples collected at the sites, but to save money and resources it could be limited to samples connected to the situations mentioned above, i.e. to water samples, to samples at the fringes (horizontally and vertically) of the contaminated area, and to samples collected from degradation processes applied on the contaminated material. It would also be suggested to include polar PACs when analyzing samples that may have been exposed to drainage water or other material with potentially elevated polar PAC levels, e.g. sediments and water living biota.

Oxy-PAHs

1-indanone
 9-fluorenone
 anthracene-9,10-dione
 4H-cyclopenta[def]phenanthrenone
 7H-benz[de]anthracen-7-one
 benz[a]anthracene-7,12-dione
 6H-benzo[cd]pyren-6-one

N-PACs

Quinoline
 Benzo[h]quinoline
 Carbazole
 Benzoacridine
(not include in PACMAN)
 Dibenzoacridine
(not include in PACMAN)



About the SNOWMAN network

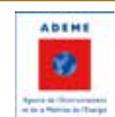


The SNOWMAN Network is a transnational group of research funding organizations and administrations in the field of sustainable management of soil in Europe. Acting as a Science-Policy-Practice interface, it aims to bridge the gap between knowledge demand and supply.

This policy brief is part of a series presenting the main results of the 17 European research project funded from 2006 to 2013 by the network.



More information on www.snowmannetwork.com.



SNOWMAN Projects

PACMAN: Lundstedt, S. et al (2015) Assessment and Management of polar PACs in Contaminated Soils and remedial processes.

Full reports available at

http://snowmannetwork.com/?page_id=286

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