



SNOWMAN NETWORK
Knowledge for sustainable soils

PACMAN

Project No. SN-03-11

PACMAN

Assessment and Management of polar PACs in Contaminated Soils and Remedial Processes



Final report

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1 Project partners and funders

PACMAN is a consortium between Umeå University in Sweden (UmU) and the French research institutes Bureau de Recherches Géologiques et Minières (BRGM) and National Center for Scientific Research (CNRS), the latter with the sub-units GeoRessources and LIEC in Nancy. The project is funded by the Swedish Environmental Protection Agency (Naturvårdsverket) and the French Environment and Energy Management Agency (ADEME), via the SNOWMAN network.

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Partners



Funders



2 Table of contents

1	Project partners and funders	1
2	Table of contents	2
3	Executive summary	3
4	Glossary and list of abbreviations	7
5	Background	9
6	Objectives and selected methodology	11
7	Project Management and Co-ordination - WP1	12
7.1	Project status and deliverables.....	12
8	Dissemination and exploitation – WP2.....	13
8.1	Public and scientific dissemination	13
8.2	Policy dissemination	13
8.3	Project status and deliverables.....	17
9	Polar PACs at contaminated sites – WP3.....	18
9.1	Inventory of PAC-contaminated sites	18
9.2	Existing data on the occurrence of polar PAC at contaminated sites	19
9.3	New data on the occurrence of polar PAC	21
9.4	Polar PACs at a Swedish wood preservation site – Holmsund, Umeå	24
9.5	Project status and deliverables.....	30
10	Assessment of remediation methods for PAC-contaminated soils – WP4.....	31
10.1	Report on existing technologies for PAC remediation.....	31
10.2	Degradation experiments performed on PAC-contaminated soils	33
10.3	Project status and deliverables.....	36
11	Leaching behavior of polar PACs – WP5.....	38
11.1	Leaching tests in the laboratory.....	38
11.2	Leaching studies in the field using lysimeters	40
11.3	Project status and deliverables.....	43
12	Toxicity and risk assessment of polar PACs – WP6	44
12.1	Review on the toxicity of polar PACs.....	44
12.2	Project synthesis.....	45
12.3	Project status and deliverables.....	48
13	Conclusions	50
14	References	51
	Appendix 1: Cost Benefit Analysis.....	56

3 Executive summary

PACMAN or 'Assessment and Management of polar PACs in Contaminated Soils and Remedial Processes' is a project within the third research call of the SNOWMAN Network. The overall objectives of PACMAN have been to elucidate to what extent compounds belonging to the group polar PACs, i.e. oxy-PAHs, N-PACs, hydroxy-PAHs and nitro-PAHs, contribute to the risk at PAH contaminated sites, and also to find ways to manage and reduce this risk. Research have been carried out within four work packages with the specific objectives to: investigate the potential dimension of the polar PAC problem by collecting data on their occurrence and distribution at various contaminated sites (WP3), evaluate various remediation technologies regarding the risk for polar PAC formation (WP4), investigate the leaching behavior of polar PACs in comparison to that of PAHs (WP5), assess the overall risk posed by polar PACs by making a synthesis of all the knowledge gained within the project, also including knowledge on the toxicity of polar PACs (WP6).

A general objective for all SNOWMAN projects is also to efficiently disseminate information and knowledge gained within the project to all interested parties in the society (WP2). For PACMAN, information and project outcomes has been spread via websites, various seminars and personal contacts. The latter include other researchers, persons in authority, consultants and entrepreneurs, among others, and have to a large extent been carried out during the data collection phase of the project. PACMAN has also been represented at several conferences and meetings, including AquaConsoil 2013 in Spain, ISPAC 2013 in USA, CSME 2013 in the Netherlands, ICEM 2013 in Brazil, Nordrocs 2014 in Sweden, a meeting for ADEME in France 2014 and SETAC North America 2014 in Canada. During AquaConsoil 2013, PACMAN had its own session with several invited speakers, which was very successful and beneficial for the project. In terms of publications, the PACMAN group have so far published one report (besides the internal Snowman reports) and 17 articles in scientific journals.

The data collected and produced within PACMAN confirms that polar PACs, like other PACs, are highly relevant contaminants in the environment in general, and at certain contaminated sites in particular. The inventories performed within the project show that Sweden and France most likely house more than 1000 PAC contaminated sites each, and an even larger number of sites that may be PAC contaminated. The sites identified are mainly connected to similar industries in the two countries, i.e. former and active gasworks, coke oven plants, wood preservation facilities and asphalt industries, but some differences were also observed. For example, gasworks and coke ovens seem to have been more important industries in France, while wood preservation and wood tar production have been more important in Sweden. In fact, wood tar production has been practically inexistent in France, while it has been a widely spread industry/activity in Sweden. These differences are most likely connected to differences in the availability of natural resources and the demands from other industries within the two countries. Anyhow, severe PAC contamination is, as expected, a frequently occurring environmental problem in both Sweden and France, and there is no indications that these two countries are unique in this sense, not in Europe nor compared to countries in the rest of the world.

The existing data on the occurrence of polar PACs at PAC contaminated sites were, as expected, scarce, but the data that did exist indicated that these compounds generally are present in significant concentrations. The highest absolute concentrations seem to be found at severely PAC contaminated sites, where also the PAH levels are very high, while the highest relative levels (or proportions) of polar PACs seem to be found at urban sites where the absolute levels are lower. This could be due to a larger influence of PACs from exhaust gases and atmospherically transformed compounds. Some previous studies also indicate that various N-PACs are present at relative high concentrations in groundwater at and downstream of PAC-contaminated sites.

The new data generated within PACMAN confirms many of the previous indications, e.g. that the polar PACs constitute a significant fraction of the PAC-load at many sites, that the highest polar PAC levels are found where the highest PAHs levels are found, and that groundwater usually become enriched in low molecular weight (LMW) PACs. However, some additional findings have also been made based on the new data. For example, the proportions and profiles of polar PACs at typical PAC-contaminated sites may (like for PAHs) vary considerably from site to site, but show at least some correlation with the activities carried out at the sites. The soil at gasworks and coke oven sites thus contain more of the high molecular weight (HMW) PACs, while soil from wood preservation sites seem to be more enriched in medium molecular weight (MMW) compounds, including pyrene, fluoranthene and 4H-cyclopenta[def]-phenathrene. Furthermore, the highest proportion of total polar PACs were, at least in these studies, found at wood tar production sites, while some individual polar PACs stood out at other sites, e.g. 9-fluorenone at coke oven sites and 4H-cyclopenta[def]phenathrene at wood preservation sites.

Furthermore, the results obtained during a detailed study on a Swedish wood preservation site, show that the proportions of polar PACs, like the total PAC levels, may vary significantly even within a site. Although, the overall data show that the more water soluble LMW PACs were more distributed in the groundwater and to some extent also in deeper soil layers at the site, no clear such difference could be observed between oxy-PAHs and PAHs for instance. Hence, it looks like the effect of the oxy-PAHs' larger water solubility was concealed by other processes in the ground, e.g. dissolved organic carbon (DOC) and colloid facilitated transport of hydrophobic compounds, selective interactions between oxy-PAHs and soil, or more efficient degradation of oxy-PAHs in solution. The importance of these processes may however vary from soil to soils and from situation to situation, considering that enhanced leachability of oxy-PAHs, compare to PAHs, have been observed during previous leaching experiment in the lab. The N-PACs studied were more clearly enriched in the groundwater at the site, which might be due to a higher persistency of the N-PACs, as compared to the oxy-PAHs, and a lower influence of specific interactions between the N-PACs and the soil.

Molluscs collected from the bay adjacent to the wood preservation site, show that water living organisms are, or at least have been, highly exposed to the PACs from the site. The contaminant profile found in the molluscs were like a mix of those found in the soil and the groundwater, with a dominance of MMW PAHs (like in the soil) and LMW oxy-PAHs (like in the water). The N-PACs were found in proportions similar to the soil, except carbazole that was found in higher proportions, although lower than in the groundwater. The water treatment plant that was in operation during remediation of the site removed all PACs efficiently from the drainage water, although LMW compounds were removed somewhat less efficiently than the more hydrophobic compounds. This was most likely because the purification in the plant was based mainly on particle removal. The more soluble PACs could therefore escape through the plant to a larger degree than the less soluble PACs. The differences between the compound classes were however small.

In WP4, four promising soil remediation technologies, i.e. three chemical oxidation technologies and one bioslurry technique, were investigated in detail regarding their overall PAC removal efficiency, with a special focus on their potential to form polar PACs. The degradation result was found to be highly influenced by the availability of the contaminants, which varied between the soils. The PACs were thus most strongly sorbed (least available) in a coke oven soil (containing relatively large amounts of carbonaceous material) and least strongly sorbed in a soil from a wood preservation site. As a consequence, the PAC degradation was least efficient in the coke oven soil, which on the other hand was most strongly affected by a pre-treatment subjected to the soils. Surprisingly, the largest PAC degradation was not seen in the wood treatment soil, but in a gasworks soil showing intermediate contaminant availability. However, this was probably because of the relatively low oxidant dose applied on the wood treatment soil, containing very high levels of PACs, emphasizing the importance of such factors as well.

Overall, the KMnO_4 -oxidant was most efficient in oxidising the original PACs in the soils, but it was also most efficient in producing transformation products in the form of oxy-PAHs. This was seen as slower depletion of oxy-PAHs compared to PAHs originally present in the soils, and as an actual increase of some individual oxy-PAHs, i.e. 9-fluorenone and anthracene-9,10-dione, during the first hours of the treatment. A similar slower depletion of oxy-PAHs was also seen in the other two chemical treatments and in the biological treatment, indicating that some polar PACs were formed in these processes as well, at least temporarily.

To investigate the proposed enhanced leaching and mobility of the polar PACs, several column leaching experiments were performed on a selection of the PAC contaminated soils sampled within the project. The results showed a strong influence of DOC and colloids in the leachate that reduced the difference in leachability between different compounds and compound classes, i.e. LMW PACs vs. HMW PACs and PAHs vs. polar PACs, also resulting in smaller differences than expected in the determined soil-water partitioning coefficients (K_{TOC}). The more hydrophobic compounds were thus leached to a larger degree than what would be predicted from their water solubilities and octanol-water partitioning coefficients (K_{OW}), while the polar PACs generally leached only slightly more. These results might be considered as overestimations of the water solubilities and leachabilities of the more hydrophobic compounds, but are probably representing a realistic leaching scenario in the field where DOC and colloid facilitated transport certainly occur, at least in some situations. However, when it comes to uptake and (bio)availability estimations the column experiments probably give misleading results, because generally only dissolved contaminants are available for uptake in living organism.

To further investigate this difference between leachable and bioavailable fraction, a passive sampler based method (POM) was also applied on the soils used in the column tests. This POM-method only measures the truly dissolved fraction of the contaminants, and should therefore generate larger K_{TOC} -values for all PACs, and particularly for the most hydrophobic compounds. This is also what the results showed and it led to a much better correlation between the determined K_{TOC} and the literature based water solubilities / K_{OW} . This means that, when it comes to the dissolved phase, there is a clear enrichment of LMW PACs in general but also of polar PACs as compared to PAHs of similar size and molecular structure. However, this may be of most importance for the bioavailability and uptake of the contaminants, since leaching is influenced by other factors as well.

Leaching was also investigated in the field, using lysimeters, during various in situ oxidative treatments of a coke oven soil. However, no increased leaching of polar PACs was observed during the two years the experiment was carried out. The overall degradation of the original PACs was very limited though, which probably was due to the low availability of the contaminants in the studied soil. The relative levels of polar PACs were on average rather decreasing than increasing in the soil, which indicate that the polar PACs generally are degraded more efficiently than PAHs when the overall degradation rate is low. However, when similar experiments were performed in the lab under harsher oxidation conditions, a clear increase of oxy-PAH levels were observed in both soil and percolating water. In the water, the relative levels of polar PACs, in relation to total PACs, were also clearly increasing.

The information collected regarding the toxicity of polar PACs show that they may cause a variety of negative effects in both humans and the environment. In some cases the effects are weaker than the effects caused by PAHs but in other cases the effects are even stronger. Overall, the polar PACs seem to contribute significantly to the toxicity and risk posed by many contaminated sites, and the question is rather whether they have to be considered, assessed and managed separated from the PAHs. The data collected and generated within PACMAN show that the levels of polar PACs in many cases are correlated to the PAH-levels, which would indicate that they can be assessed together. However, there are situations when the risk caused by polar PACs may be overlooked if they are not specifically considered, these situations are:

- 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.

The PACMAN project has not come up with any alarming results, in terms of extremely elevated polar PAC levels, for any of these situations, but indications of potential problems have been observed for all of them. A certain enrichment of N-PACs has thus been observed in surface- and groundwater as well as in deeper soil layers in the investigations performed within PACMAN, and even if no such enrichment was seen for oxy-PAHs in this project it has been observed in previous studies. Previously it has also been observed that soils highly influenced by exhaust gases and soils in which the PACs have been subjected to atmospheric transformation processes to a large extent, contain larger proportions of oxy-PAHs than heavily contaminated soils. This can at least partly be explained by an atmospheric transformation of PAHs into oxy-PAHs, while being airborne, and can be relevant also for the PAC profiles found at the outskirts of a contaminated area to which the contaminants mainly have come via dusting and evaporation/condensation processes.

Furthermore, the results produced within PACMAN show, like some previous studies, that there is a clear risk for oxy-PAH formation and accumulation if remediation techniques based on PAC degradation are used. This risk is probably maximized if a powerful oxidation technique is used that will accelerate the PAH depletion significantly, but the risks exists for other degradation techniques as well, e.g. biodegradation. Although the oxy-PAHs most often will be degraded as well if the process is run long enough, it is important to verify that this actually happens and to make sure when the process can be safely terminated.

Based on these facts it would first of all be suggested to include a number polar PACs among the compounds that are analysed during risk assessment and remediation of PAC contaminated sites. This is of particular importance for surface- and groundwater samples, samples from environments that may have been contaminated by such waters (e.g. sediments, biota etc.), samples of deeper soil layers, samples from the outskirts of a contaminated area, and not least samples from remediation process that involve PAC degradation. Depending on the results of these analyses and the following risk assessment, this may then, in the worst case, lead to an expansion of the remediation plan, which may include a more extensive excavation of the site, a more extensive water treatment program and longer treatment times for remediation methods based on PAC degradation. This will of course increase the costs for risk assessment and remediation of the site, but it will also ensure that risks connected to polar PACs are considered and properly taken care of. As a general judgement it will seldom be necessary to expand the remediation plan because of the polar PACs, but it is still important to make sure that this is the case in each individual situation.

4 Glossary and list of abbreviations

ADEME	French Environment and Energy Management Agency (PACMAN funder)
Ah receptor	Aryl hydrocarbon receptor
APHA	American Public Health Organization
AquaConsoil	International UFZ-Deltares Conference on Sustainable Use and Management of Soil, Sediment and Water Resources
ASTM	Formerly known as American Society for Testing and Materials
BASOL	Database on French polluted sites and soils
BRGM	The French Geological Survey (PACMAN partner)
CABERNET	Concerted Action on Brownfield and Economic Regeneration Network
CaO ₂	Calcium peroxide
CLU-IN	US-EPA's Contaminated Site Clean-up Information
CNRS	National Center for Scientific Research (PACMAN partner)
CSME	Contaminated Site Management in Europe
CYP	Cytochrome P450 monooxygenases
DG Research	EC's Directorate General for Research
DNA	Deoxyribonucleic acid
DOC	Dissolved organic carbon
EC	European Commission
EOM	Extractable organic matter
EPI Suite	Estimation Program Interface Suite,
ER-H	Equilibrium Recirculation column test for hydrophobic organic compounds
EU	European Union
EUGRIS	Web portal for information on soil and water management in Europe
EURODEMO+	European Platform for Demonstration of Efficient Soil and Groundwater Remediation
Fe ²⁺	Ferrous iron
Fe ₃ O ₄	Iron oxide, magnetite
H ₂ O ₂	Hydrogen peroxide
GISFI	Experimental station on brownfield revitalization in Nancy, France
HMW	High molecular weight
Hydroxy-PAHs	Hydroxylated PAHs (a type of polar PACs)
IBRACS	The SNOWMAN project: Integrating Bioavailability in Risk Assessment of Contaminated Soils: opportunities and feasibilities
ICCL	International Committee on Contaminated Land
ICEM	International Conference on Environmental Mutagens
IMPEL	EU Network for the Implementation and Enforcement of Environmental Law
INERIS	French establishment for controlling risks for sustainable development.
ISCO	In Situ Chemical Oxidation
ISO	International Standards Organisation
ISPAC	International Society for Polycyclic Aromatic Compounds
JRC	EC's Joint Research Centre
K _d	Soil-water partitioning coefficient
K _{OW}	Octanol-water partitioning coefficient
K _{TOC}	Total organic carbon normalized soil-water partitioning coefficient
KMnO ₄	Potassium permanganate
LIEC	The Interdisciplinary Laboratory for Continental Environments, Sub-unit of CNRS

LMW	Low molecular weight
MCN	The Northern Sweden Soil Remediation Network
MEDDE	The Ministry of Ecology, Sustainable Development and Energy in France
MgO ₂	Magnesium peroxide
MMW	Medium molecular weight
NAC	N-acetyl cysteine
Na ₂ CO ₃ x 1.5 H ₂ O ₂	Sodium carbonate peroxyhydrate
Naturvårdsverket	Swedish Environmental Protection Agency (PACMAN funder)
NICOLE	Network for Industrially Contaminated Land in Europe
N ₂	Nitrogen gas
Nitro-PAHs	Nitro substituted PAHs (a type of polar PACs)
Nordrocs	Nordic Joint Meeting on Remediation of Contaminated Sites
N-PAC	Heterocyclic PACs containing nitrogen (a type of polar PACs), synonymous to azaarenes
Σ N-PAC ₄	Sum of the four N-PACs analysed within PACMAN
OH-	Hydroxyl-
ONEMA	French National Agency for Water and Aquatic Environments
ORC	Oxygen releasing compound
Oxy-PAHs	Oxygenated PAHs (a type of polar PACs)
Σ Oxy-PAH ₁₁	Sum of the eleven oxy-PAHs analysed within PACMAN
PAC	Polycyclic aromatic compound
PACMAN	The SNOWMAN project: Assessment and Management of polar PACs in Contaminated Soils and Remedial Processes
PAH	Polycyclic aromatic hydrocarbon (a sub-group of the PACs)
Σ PAH ₁₆	Sum of the 16 (US-EPA) PAHs analysed within PACMAN
PCA	Principal component analysis
POM	Polyoxymethylene membrane (passive sampler)
REACH	EC regulation on Registration, Evaluation, Authorization and Restriction of Chemicals
ROS	Reactive oxygen species
SDAGE	French management plans of the Water Framework Directive
SEDNET	European Sediment Network
SETAC	Society of Environmental Toxicology and Chemistry
SFE	Supercritical fluid extraction
SGI	The Swedish Geotechnical Institute
SNOWMAN	Transnational group of research funding organizations and administrations in the field of soil and groundwater in Europe
SURF	Sustainable Remediation Forum
TCDD	2,3,7,8-tetrachlorinated dibenzo-p-dioxin (most toxic dioxin)
UBA (DE)	Umweltbundesamt (Germany)
UmU	Umeå University (PACMAN partner, coordinating organization)
UPDS	Union of Remediation Professionals in France
US-EPA	United States Environmental Protection Agency
UV	Ultra violet
WFD	EC's Water Framework Directive
WG groundwater	Working group on groundwater within the WFD
WP	Work package

5 Background

Polycyclic aromatic compounds (PAC), of which the polycyclic aromatic hydrocarbons (PAH) are most widely known, are common pollutants at contaminated sites, e.g. at those of former gasworks, wood preservation facilities and coke oven plants [Howsam and Jones 1998]. In fact, according to the European Environment Agency more than 13 % of all 1.5 million contaminated sites in Europe may house these pollutants [EEA 2008], which would correspond to around 200 000 sites in total. In Sweden, 8% of the contaminated sites identified in the highest risk classes are estimated to be contaminated with PAC/PAH [SEPA 2010], and in France the corresponding figure is 17% [Basol 2010]. The PAC-contaminated sites are of environmental concern because many PACs are known to be toxic, mutagenic and carcinogenic [Delistraty 1997, Howsam and Jones 1998]. However, during risk assessment of the sites only a small subset of 16 PAHs, often referred to as “the priority PAHs”, are generally monitored, in spite of the fact that many other contaminants also may be present [Lundstedt et al. 2003]. This may lead to a miscalculation of the risk posed by these sites, as well as of the detoxification result during remedial treatments of the sites.

Several studies, in which chemical separation techniques have been combined with biological toxicity assays (i.e. effect directed chemical fractionation), have thus shown that the fractions of the soil extracts containing the polar and semi-polar PACs, in many cases are even more toxic or at least as toxic as the fraction containing the commonly analyzed PAHs [Lundstedt et al. 2007, Lemieux et al. 2008]. These polar fractions are often predominated by oxygenated PAHs (oxy-PAHs) and heterocyclic PACs containing nitrogen (N-PACs), but may also contain hydroxy-PAHs and nitro-PAHs for instance (Figure 1). The levels of oxy-PAHs and N-PACs are very often comparable to the PAH-levels, and sometimes they are even higher [Lundstedt et al. 2007, Bandowe and Wilcke 2010]. For example, in a study by Lundstedt et al. [2006a] in which 17 oxy-PAHs were quantified in seven typical PAC-contaminated soils, viz. four wood preservation sites, one gasworks site, and one coke oven site in Sweden, and a superfund site in US, the total oxy-PAH-levels were found to be in the range of 10-66% of the total PAH-levels (sum of 16 US-EPA PAHs). In addition, some individual oxy-PAHs were found at even higher concentrations than their corresponding PAHs (e.g. 9-fluorenone vs fluorene, and anthracene-9,10-dione vs anthracene). Preceding this study, both Meyer et al. [1999], Eriksson et al. [2000] and Lundstedt et al. [2003] had found similar levels and proportions of several individual oxy-PAHs at two German wood preservation site and a Swedish gasworks site. In two of these studies, viz. Meyer et al. and Lundstedt et al., several N-PACs were also found at similar levels. In a more recent study, Bandowe and Wilcke [2010] measured the concentration of seven oxy-PAHs in a gasworks soil and an urban soil from Germany, and they found the total levels to correspond to 18% and 5 %, respectively, of the total PAH-levels (sum of 16 US-EPA PAHs) in the soils. Even in these cases some individual oxy-PAHs (e.g. 9-fluorenone and anthracene-9,10-dione) were found at higher concentrations than their corresponding PAHs.

In addition to these high original levels of polar PACs at contaminated sites, some of these compounds, i.e. oxy-PAHs and hydroxy-PAHs, may also be formed via secondary transformation of PAHs. This may happen through chemical as well as biological processes and may potentially lead to accumulation of the polar PACs formed [Cerniglia 1992, Kochany and Maguire 1994, Lundstedt et al. 2007, Ghislain et al. 2010], which is of particular concern when PAHs are remediated with methods based on PAH-degradation. This have, for instance, been observed during fungal degradation of PAHs in spiked soil [Andersson et al. 2003], as well as during chemical oxidation (using Fenton's reagent) [Lundstedt et al. 2006b] and bioslurry treatment of real PAH-contaminated gasworks soils [Lundstedt et al. 2003, Lemieux et al. 2009]. In all these studies, the concentrations of some oxy-PAHs were observed to increase at the same time as the PAH-levels decreased.

Many of the polar PACs have indeed been highlighted as individual toxicants, mutagens and probable carcinogens [Bleeker et al. 2002, Lundstedt et al. 2007], but the polar PACs are also of concern because of their relatively high solubility in water, which implies that they may have higher tendency to

spread via ground- and surface waters in the environment, as compared to the unsubstituted PAHs. Polar PACs, such as oxy-PAHs and N-PACs, have thus been found to leach faster than PAHs in various leaching experiments [Weigand et al. 2002, Benhabib et al 2009, Lundstedt et al. 2007], and also to be abundant in groundwater and deeper soil layers at PAC contaminated sites [Schlanges et al. 2008, Bandowe et al. 2010]. Despite these facts, polar PACs are practically never included in the risk assessment of PAC-contaminated sites, and neither are they monitored during remediation of the sites.

The reason for this low interest in considering the polar PACs are first of all that they are fairly unknown to the public, and also to the environmental authorities in general. Most site owners and regulators do not even know that the polar PACs exist, and even fewer know that they actually may constitute a problem. Neither are there any regulations or guidelines values available for the polar PACs, meaning that the incentives to include them in monitoring programs are very low. As a result, the polar PACs are, so far, only included in research oriented projects. Another aggravating factor is that the polar PACs are quite complicated to analyse, and that there are no standardized analytical methods available from internationally recognised institutions such as ISO, ASTM, US-EPA or APHA. Consequently, polar PAC analysis is still very much limited to well equipped research laboratories with experienced staff, while commercial offers for these compounds are almost inexistent.

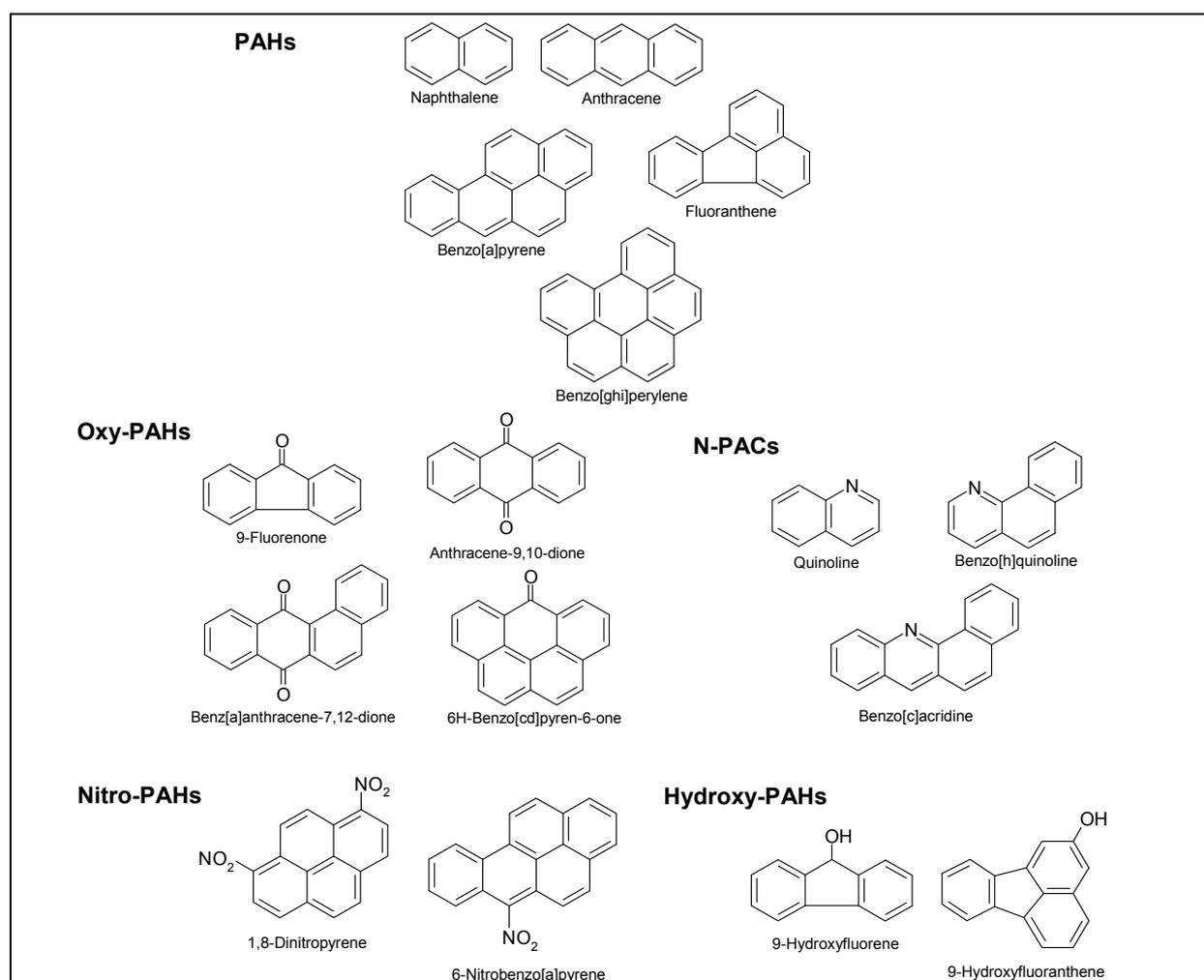


Figure 1. Molecular structures for selected unsubstituted PAHs and polar PACs including oxy-PAHs, N-PACs, nitro-PAHs and hydroxy-PAHs

6 Objectives and selected methodology

The overall objectives of PACMAN have been to increase the knowledge pertaining to polar PACs in order to elucidate to what extent these compounds add extra risk to contaminated sites, and to provide suggestions how this risk can be managed and reduced. The problems have been approached by a combination of review activities, i.e. collection and compilation of existing data, and experimental studies generating new data. More specifically, data have been collected on the occurrence and distribution of polar PACs at contaminated sites, their potential formation in remediation processes and regarding their negative effects on human health and the environment. These data have then been supplemented by sampling campaigns at selected contaminated sites, measuring levels and distribution of polar PACs, and by laboratory studies concerning the leachability of polar PACs and their possible formation in various remediation processes. The work has been carried out within six work packages (WPs) according to the list below and the sketch in Figure 2.

- **WP 1: Project Management and Co-ordination**
- **WP 2: Dissemination and exploitation**
- **WP3: Polar PACs at contaminated sites**, with the objectives to demonstrate the dimension of the polar PAC problem at contaminated sites, including the determination of levels and distribution of polar PACs in relation to PAHs at various types of sites.
- **WP 4: Assessment of remediation methods for PAC-contaminated soils with respect to PAH removal and polar PAC formation**, with the objectives to evaluate remediation technologies applied or applicable to PAC-contaminated sites, and to identify those that constitute the greatest and lowest risk in terms of polar PAC formation.
- **WP 5: Leaching behavior of Polar PACs**, with the objectives to determine soil-water partitioning coefficients for a number of polar PACs that later can be used in risk assessment models for contaminated sites, and also to investigate in what way various scenarios and remedial treatments will influence the mobility of the polar PACs.
- **WP 6: Toxicity and risk assessment of polar PACs**, with the objectives to make a synthesis of all the knowledge gained within the project focusing on knowledge gaps that have been filled and those that remains to be filled in order to perform a proper risk assessment of PAC-contaminated sites, and to assess the usefulness and risk of different remediation technologies. This work package will also include a literature review of the toxicological aspects of polar PACs.

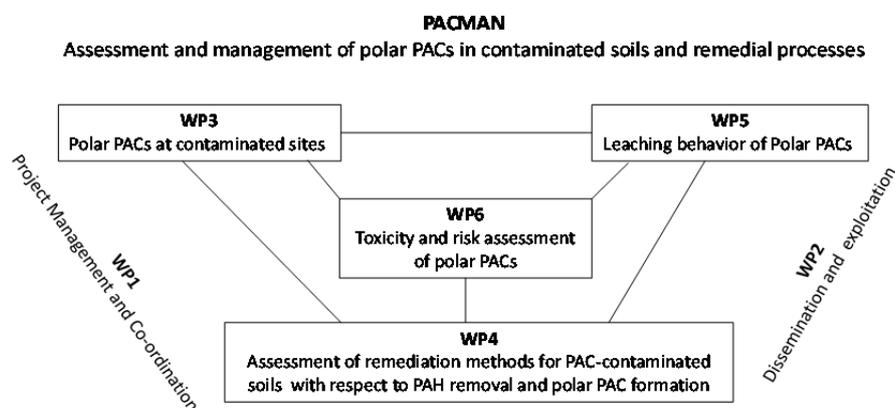


Figure 2. The structure of the PACMAN project, showing the six work packages and how they are connected

7 Project Management and Co-ordination - WP1

The project has run smoothly during the whole project period. The activities have been coordinated through a coordination committee with one person from each partner organization. All in all the coordination committee have had 12 meetings, including three face-to-face meetings (during conferences) and nine telephone meetings, in which various project issues and joint activities have been discussed. Project members (Table 1) have also met at several other conferences and meetings, which have provided possibilities for further discussions and planning of project issues. Current matters have usually been solved through e-mail contacts which have been used regularly. During the two joint SNOWMAN meetings in Paris in November 2011 and November 2013, the project coordinator Staffan Lundstedt had meetings with the project board members Kerstin Jansbo and Frédérique Cadere discussing outcomes of the project and plans for the coming periods.

The composition of the PACMAN group has changed slightly during the project time. Halfway through the project Christophe Mouvet decreased his activities within project, and because of that Bruno Lemière replaced Christophe as the BRGM representative in the coordination committee. At about the same time, Elke Fries joined the PACMAN group within BRGM.

Table 1: Partners within the PACMAN project, with the Coordination Committee underlined.

<p>Umeå University (UmU), Sweden <u>Staffan Lundstedt (PhD), Coordinator</u> Mats Tysklind (PhD, Prof.)</p> <p>Bureau de Recherches Géologiques et Minières (BRGM), France <u>Bruno Lemière (PhD)</u> Christophe Mouvet (PhD) Stéfan Colombano (MSc) Alain Saada (PhD) Elke Fries (PhD)</p> <p>National Center for Scientific Research (CNRS – UMR G2R), France <u>Pierre Faure (PhD)</u> Laurence Mansuy (PhD) Catherine Lorgeoux (MSc)</p>

7.1 Project status and deliverables

All deliverables within this WP have been fulfilled (Table 2).

Table 2. Deliverables for WP1 within PACMAN

	Deliverables	Fulfilment and comments
DL1.1	A well-coordinated project.	Fulfilled
DL1.2	Initial coordination to establish national agreements and contracts.	Fulfilled
DL1.3	Consortium agreement.	Fulfilled
DL1.4	An all project-kick-off meeting and an initial meeting with the Chairman of the project board.	Fulfilled
DL1.5	Two annual progress reports, a draft final report and a final report.	Fulfilled

8 Dissemination and exploitation – WP2

8.1 Public and scientific dissemination

Information about the project has been disseminated nationally in Sweden and France at various seminars and meetings. Information has also been spread to authorities, research collaborators and companies during the collection of information on contaminated sites in Sweden and France, and during sampling campaigns in the two countries. This has, among others, resulted in many new contacts with interests in the field and also to an expansion of the existing contact network “Polar PAC Network” (www.mcnio.com/projects/the-polar-pac-network). Information about the project has also been posted on the SNOWMAN website and the EUGRIS web portal. Furthermore, outcomes of the project have been presented at various international conferences (Table 3), which also include the three SNOWMAN meetings in Paris in 2011, 2013 and 2015.

During the AquaConsoil conference in Barcelona, PACMAN organized a thematic session entitled “Polar Polycyclic Aromatic Compounds” to which several collaborators in the field was invited. Five oral presentations, of which PACMAN members held two (see Table 3), were given in the session, and they were followed by joint discussions. The session was very successful and provided a great opportunity to disseminate the project issues from different angles. A meeting was also held after the session with the presenters and other interested parties to discuss and coordinate future activities in the field.

Furthermore, additional dissemination activities are currently being planned, although after the actual project closure. In connection to the joint SNOWMAN meeting in Paris in March 2015, PACMAN is planning to run a half-day seminar summarizing the outcomes of the project. This seminar will be open to everybody but key-persons in the field will be specifically invited. In addition, a proposal has been submitted to the organizers of the ISPAC conference in Bordeaux in September 2015, to allow the PACMAN group to organize a special session at the conference. This session will be similar to the session at the previous AquaConsoil conference, but with updated information.

In December 2013, the coordinator of PACMAN examined a PhD-thesis in the polar PAC field, written by Esther Boll at the University of Copenhagen. The thesis and the discussions at the defence provided interesting knowledge for PACMAN, but the event also gave opportunities for spreading information about PACMAN. Among others, a presentation was held at Esther's department.

In terms of publications, the PACMAN group have so far published one report (besides the internal Snowman reports) and 17 articles in scientific journals. There are also five manuscripts that are in preparation or in the peer-review process. These will be published in the near future (Table 4).

8.2 Policy dissemination

In order to illustrate the potential problem constituted by polar PACs and to influence policy makers and legislators to consider these compounds for regulations, a plan for policy dissemination has been set-up.

The target organisations and dissemination channels on EU- and global levels are:

- REACH – UBA (DE), which have already shown interest for the project results
- WG groundwater of the Water Framework Directive (WFD), which will have activities around emerging pollutants in groundwater. PACMAN could for example be presented at a WG meeting.
- EUGRIS web portal, on which PACMAN already is present. However, the project could be even more visible there. www.eugris.info

- International Committee on Contaminated Land (ICCL), which is an informal international forum where issues related to contaminated land and groundwater can be discussed. www.iccl.ch
- Common Forum network and other networks such as NICOLE, SEDNET, SNOWMAN, EURODEMO+, CABERNET, IMPEL. A summary of the project and its results can be announced in their e-newsletters.
- European Commission – DG Research, JRC
- US-EPA and their CLU-IN Newsletter
- Sustainable remediation forum (SURF) and its global network.

The national target organisations and dissemination channels in Sweden are:

- The Swedish Environmental Protection Agency (Naturvårdsverket) and their unit for contaminated sites
- The county administrative boards of Sweden (Länsstyrelsen) and their national coordinator.
- The Swedish Geotechnical Institute (SGI)
- The Clean Soil Network, (Nätverket Renare Mark), for which PACMAN already has been presented several times.
- The Northern Sweden Soil Remediation Centre (MCN)

The national target organisations and dissemination channels in France are:

- The Ministry of Ecology, Sustainable Development and Energy (MEDDE) who has the responsibility of the French policies on potential pollutants, contaminated sites and water protection.
- The French Environment and Energy Management Agency (ADEME), which is a public agency under the joint authority of the Ministry for Ecology, Sustainable Development and Energy and the Ministry for Higher Education and Research. Its mission is to encourage, supervise, coordinate, facilitate and undertake operations with the aim to protect the environment and manage energy. Its priority areas are energy, air, noise, transport, waste, polluted soil and sites, and environmental management. The agency contributes to implementing European policy and developing the European research centre in the energy and environmental sectors.
- INERIS, which is a public research body under the aegis of the French Ministry for Ecology. It carries out or commissions studies and research programs aimed at preventing the risks brought about by economic activities on health, the safety of persons and property and on the environment, and to provide any services intended to facilitate the adaptation of companies with this objective in mind. Its activities include risk mitigation and ecotoxicology. It supports also the French government in the selection process of priority substances. Some polar PACs, such as anthraquinone, were identified by INERIS among the substances that should be watched in the ambient air, and followed through the SIN (Substitute It Now!) list (REACH).
- Water resources, in France, that are managed by several agencies with specific areas of competence:
 - six regional Water Agencies are in charge of the Water Development and Management Master Plans (SDAGE, French management plans of the Water Framework Directive)
 - ONEMA, the French National Agency for Water and Aquatic Environments, which aim is to preserve water quality and good ecological status of aquatic systems,
 - BRGM, more specifically in charge of groundwater resources and protection. Monitoring emerging pollutants in groundwater, and developing analysis methods and standards, is a part of public missions of BRGM. It depends on public policies for each substance or group.
- The Union of Remediation Professionals (UPDS) in France is the main gateway for knowledge transfer to remediation companies. It cooperates with ADEME in linking technology objectives, policy, standards and regulations. It may provide an efficient dissemination vector for the project's outcome on PACs production during PAH remediation, and how to mitigate it.

Table 3. Conferences at which PACMAN activities have been presented.

<p>SNOWMAN kick-off meeting in Paris, France, November 2011</p> <ul style="list-style-type: none"> • <i>Assessment and Management of polar PACs in Contaminated Soils and Remedial Processes (PACMAN)</i> – oral presentation by Staffan Lundstedt
<p>AquaConsoil 2013 in Barcelona, Spain, April 2013</p> <ul style="list-style-type: none"> • <i>Chemical remediation treatments on PAH contaminated soils: consequences on polycyclic aromatic compounds (PACs)</i> - oral presentation by Pierre Faure. • <i>Leaching behaviour of polar polycyclic aromatic compounds at contaminated sites</i>- oral presentation by Staffan Lundstedt
<p>ISPAC 2013 in Corvallis, Oregon, USA, September 2013</p> <ul style="list-style-type: none"> • <i>Impact of chemical remediation treatments on Polycyclic Aromatic Compounds (PAC) applied to different contaminated soils</i> – oral presentation by Catherine Lorgeoux • <i>Chemical remediation treatments on Polycyclic Aromatic Compound (PAC) contaminated soils: Consequences on mobilization of the remaining PAC by water</i> – oral presentation by Pierre Faure • <i>Influence of mineral phases on PAH transformation during oxidation of contaminated soils</i> – oral presentation by Coralie Biache (PACMAN associated at CNRS) • <i>Oxygenated Polycyclic Aromatic Compounds (Oxy-PACs) occurrence at French sites: Known issues and strategy for investigations</i> – poster presentation by Bruno Lemiere
<p>CSME, Amsterdam, The Netherlands, October 2013</p> <ul style="list-style-type: none"> • <i>Remediation of PAH contaminated soils by chemical oxidation and bioremediation: Consequences on polar polycyclic aromatic compounds (Degradation, formation and mobility)</i> – oral presentation by Pierre Faure • <i>Enhancement of PAH availability by using thermal pretreatment to improve chemical oxidation of PAHs in contaminated soils</i> – oral presentation by Pierre Faure
<p>ICEM 2013 in Iguassu falls, Brazil, November 2013</p> <ul style="list-style-type: none"> • <i>Toxic hazards of Polar Polycyclic Aromatic Compounds in Environmental Samples</i> – oral presentation by Staffan Lundstedt • <i>Identification of polar Polycyclic Aromatic Compounds in complex PAH-contaminated environmental matrices</i> – oral presentation by Staffan Lundstedt
<p>SNOWMAN mid-term meeting in Paris, France, November 2013</p> <ul style="list-style-type: none"> • <i>Assessment and Management of polar PACs in Contaminated Soils and Remedial Processes (PACMAN)</i> – oral presentation by Staffan Lundstedt
<p>ADEME meeting “3ème Rencontre nationale sur les sites et sols pollués” in Paris, France, November 2014</p> <ul style="list-style-type: none"> • <i>Les composés aromatiques polycycliques (CAP) polaires : dégradation – formation – mobilization</i> – oral presentation by Pierre Faure
<p>NORDROCS 2014 in Stockholm, Sweden, September 2014</p> <ul style="list-style-type: none"> • <i>Occurrence of polar Polycyclic Aromatic Compounds at Contaminated Sites</i> – poster presentation by Staffan Lundstedt • <i>Assessment of soil-water partitioning of Polycyclic Aromatic Compounds using passive samplers and leaching tests</i> – Oral presentation by Anja Enell (collaborator within IBRACS)
<p>SETAC North America in Vancouver, Canada, November 2014</p> <ul style="list-style-type: none"> • <i>Using POM to assess partitioning, bioavailability, bioaccumulation and toxicity of PAHs, oxy-PAHs and N-PACs in historically contaminated soil</i> – Poster presentation by Hans Peter Arp (collaborator within IBRACS)
<p>SNOWMAN network meeting and final meeting for PACMAN, Paris, France, March 2015</p> <ul style="list-style-type: none"> • <i>Assessment and Management of polar PACs in Contaminated Soils and Remedial Processes (PACMAN)</i> – oral presentation by Staffan Lundstedt

Table 4. Publications produced within PACMAN.

<p>Reports</p> <ol style="list-style-type: none"> 1. Colombano and Mouvet 2012, <i>Remediation technologies for PAH contaminated soils</i>, PACMAN report,
<p>Peer-reviewed articles</p> <ol style="list-style-type: none"> 1. Ghislain T., Faure P., Michels R. (2012) <i>Detection and Monitoring of PAHs and Oxy-PAHs by High Resolution Mass Spectrometry: Comparison of ESI, APCI and APPI source detection</i>. Journal of the American Society for Mass Spectrometry 23: 530-536. 2. Usman M., Faure P., Rubya C., Hannaet K. (2012) <i>Remediation of PAH-contaminated soils by magnetite catalyzed Fenton-like oxidation</i>. Applied.Catalysis.B: Environmental 117-118: 10-17. 3. Usman M., Faure P., Rubya C., Hannaet K. (2012) <i>Application of magnetite-activated persulfate oxidation for the degradation of PAHs in contaminated soils</i>. Chemosphere 87:234-240. 4. Niziolek-Kierecka M., Dreij K., Lundstedt S., Stenius U. (2012) <i>γH2AX, pChk1 and Wip1 as potential markers of persistent DNA damage derived from Dibenzo[a,l]pyrene and PAH-containing extracts from contaminated soils</i>. Chemical Research in Toxicology 25: 862-872. 5. Biache C., Faure P., Mansuy-Huault L., Cébron A., Beguiristain T., Leyval C. (2013) <i>Biodegradation of the organic matter in a coking plant soil and its main constituents</i>. Organic geochemistry 56: 10-18. 6. Cébron A., Faure P., Lorgeoux C., Ouvrard S., Leyval C. (2013) <i>Experimental increase in availability of a PAH complex organic contamination from an aged contaminated soil: Consequences on biodegradation</i>. Environmental pollution 177:98-105 7. Biache C., Mansuy-Huault L., Faure P. (2014). <i>Impact of oxidation and biodegradation on the most commonly used polycyclic aromatic hydrocarbon (PAH) diagnostic ratios: Implications for the source identifications</i>. Journal of Hazardous Materials., 267, 31-39. 8. Lundstedt S., Bandowe B.A.M., Wilcke W., Boll E., Christensen J.H., Vila J., Grifoll M., Faure P., Biache C., Lorgeoux C., Larsson M., Frech Irgum K., Ivarsson P., Ricci M. (2014) <i>First intercomparison study on the analysis of oxygenated polycyclic aromatic hydrocarbons (oxy-PAHs) and nitrogen heterocyclic polycyclic aromatic compounds (N-PACs) in contaminated soil</i>. Trends in Analytical Chemistry 57: 83-92. 9. Arp HP.H., Lundstedt S., Josefsson S., Cornelissen G., Enell A., Allard A-S., Berggren Kleja D. (2014) <i>Native Oxy-PAHs, N-PACs and PAHs in historically contaminated soils from Sweden, Belgium and France: Their soil-porewater partitioning behavior, bioaccumulation in Enchytraeus crypticus and bioavailability</i>. Environmental Science & Technology 48:11187-11195. 10. Biache C., Kouadio O., Lorgeoux C., Faure P. (2014) <i>Impact of clay mineral on air oxidation of PAH-contaminated soils</i>. Environmental Science and Pollution Research 21: 11017-11026 11. Biache C., Kouadio O., Hanna K., Lorgeoux C., Faure P. (2014) <i>Role of goethite during air oxidation of PAH contaminated soils</i>. Chemosphere 117, 823-829. 12. Hanser O., Biache C., Boulangé M., Parant S., Lorgeoux C., Billet D., Michels R., Faure P. (2015) <i>Evolution of dissolved organic matter during abiotic oxidation of coal tar - comparison with contaminated soils under natural attenuation</i>. Environmental Science and Pollution Research 22: 1431-1443. 13. Josefsson S., Arp HP.H., Berggren Kleja D., Enell A., Lundstedt S. (2015) <i>Determination of polyoxymethylene (POM) – water partitioning coefficients for oxy-PAHs and PAHs</i>. Chemosphere 119:1268-1274. 14. Lemieux C.L., Long A.S., Lambert I.B., Lundstedt S., Tysklind M., White P.A. (2015) <i>In Vitro mammalian mutagenicity of complex polycyclic aromatic hydrocarbon mixtures in contaminated soils</i>. Environmental Science & Technology 49: 1787-1796. 15. Lemieux C.L., Long A.S., Lambert I.B., Lundstedt S., Tysklind M., White P.A. (2015) <i>Cancer risk assessment of polycyclic aromatic hydrocarbon contaminated soils determined using bioassay-derived levels of benzo[a]pyrene equivalents</i>. Environmental Science & Technology 49:1797-1805. 16. Wincent E., Jönsson M.E., Bottai M., Lundstedt S., Dreij K. (2015) <i>Aryl hydrocarbon receptor activation and development toxicity in zebrafish in response to soil extracts containing unsubstituted and oxygenated PAHs</i>. Environmental Science & Technology 49: 3869-3877. 17. Biache C., Lorgeoux C., Anadriatsihoarana S., Colombano S., Faure P. (2015) <i>Effect of pre-heating on the chemical oxidation efficiency: implications for the PAH availability measurement in contaminated soils</i>. Journal of Hazardous Materials 286: 55-63.

Table 4. Publications produced within PACMAN, continued.

Submitted manuscript and manuscript in preparation
<ul style="list-style-type: none"> • Usman M., Chaudhary A., Biache C., Faure P., Hanna K. (2015) <i>Thermal pretreatment as a novel way to increase availability of PAHs for their successive chemical oxidation in contaminated soils</i> (submitted manuscript) • Enell A., Lundstedt S., Arp HP.H., Josefsson S., Cornelissen G., Berggren Kleja D., <i>Comparison of a column leaching test and a passive sampler test for assessment of mobility and partitioning of native oxy-PAHs, N-PACs and PAHs in historically contaminated soils</i> (manuscript in preparation) • Lundstedt et al., <i>Occurrence of polar Polycyclic Aromatic Compounds at Contaminated Sites</i> (manuscript in preparation) • Lundstedt et al. <i>Occurrence and distribution of polar PACs at a former wood preservation site</i> (manuscript in preparation) • Boulangé M. et al., <i>Consequences of chemical and biological remediation treatments on Polar PAC leachability</i> (manuscript in preparation).

8.3 Project status and deliverables

All deliverables, except the project specific website and the thematic day announced in the project plan, have been fulfilled (Table 5). The necessity of a project specific website was discussed during the kick-off meeting in 2011, after which PACMAN decided to abandon this activity. The SNOWMAN website was considered to be sufficient for the purpose. Regarding the thematic day, the issue has been discussed within the project group as well as with representatives from the project board. It was concluded that it was wiser and more efficient to use already existing meeting places in Sweden, France and Europe to disseminate the project. This has also been done throughout the project. It was also realized that some stakeholders might be easier to reach at national meetings as opposed to large international meetings. A half-day seminar focusing on the project outcomes will therefore be arranged in connection to the joint SNOWMAN meeting in Paris in the end of March 2015, as described above.

Table 5. Deliverables for WP2 within PACMAN

	Deliverables	Fulfilment and comments
DL2.1	Internet based dissemination, including information on EUGRIS and the SNOWMAN website, as well as a project specific website.	Fulfilled, except the project specific website, which have been discussed and dissuaded by Snowman
DL2.2	Participation and presentations at the joint SNOWMAN activities, i.e. the kick-off meeting, the all-projects-workshop, and the all-projects-final-meeting.	Fulfilled so far
DL2.3	A project meeting combined with a thematic day in Sweden.	Efforts put on other meetings instead
DL2.4	Participation and presentations at external, national and international conferences and workshops, including the organization of a project specific session at one of the international conferences.	Fulfilled.
DL2.5	Two annual progress reports, a draft final report and a final report, including project fact sheets and executive summaries.	Fulfilled

9 Polar PACs at contaminated sites – WP3

9.1 Inventory of PAC-contaminated sites

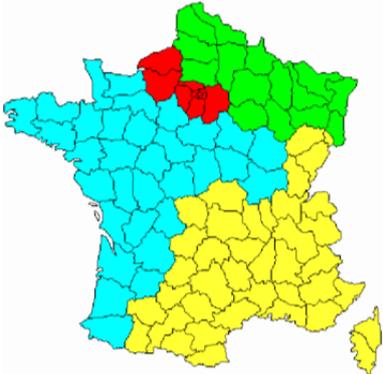
Inventories of verified and possible PAC-contaminated sites in Sweden and France have been carried out by UmU and BRGM, respectively. In Sweden, the information has mainly been collected via the country administrative boards and their contaminated-site-database. In this, the sites are categorized based on the activities and business carried out at the sites and not on verified contamination. The inventory presented here are therefore based on the assumption that the PAC contamination in Sweden mainly is connected to some certain industrial activities and, inversely, that these activities most often are causing PAC contamination. The inventory thus shows that the preliminary number of sites that most likely house a serious PAC-contamination is around 1200, which agrees well with the previous assumption that 8 % of the 14 000 sites in the highest risk classes house these contaminants. These 1200 sites can be subdivided into 82 gasworks sites (or related to this industry), 36 coke oven or coal tar production sites, 527 wood preservation sites, 178 wood tar production sites and 386 asphalt production sites (Table 6). There are also an even larger number of sites that might be PAC-contaminated, belonging to the categories; sawmills, railroad yards, gas stations, oil depots etc.

In France, the information has mainly been collected from the BASOL contaminated sites database (<http://basol.environnement.gouv.fr/>) containing information on 5014 contaminated sites. Among these, 1046 have been identified as PAC contaminated. Like in Sweden, gasworks, coke ovens and creosote based wood preservation facilities are important industries in this context, constituting 360, 57 and 58 of the identified sites, respectively (Table 7), while wood tar production have been a less common industry in France. Regarding asphalt production, this industry is not separated from other petrochemical or carbochemical industries in contaminated sites inventories in France, and is therefore included in the uncategorized 571 sites.

Table 6. Probable PAC-contaminated sites in Sweden divided into the five most relevant industrial categories and the 21 county regions of Sweden.

Swedish county	Gasworks and related sites	Coke ovens and coal tar prod.	Wood pres.	Wood tar prod.	Asphalt prod.
BD: Norrbotten	2	-	27	2	
AC: Västerbotten	-	-	31	8	12
Z: Jämtland	1	1	5	45	101
Y: Västernorrland	3	-	14	3	12
X: Gävleborg	4	-	30	36	11
W: Dalarna	2	-	24	17	
S: Värmland	3	-	14	8	7
T: Örebro	5	6	15	2	9
U: Västmanland	2	-	19	-	33
C: Uppsala	4	2	32	4	21
AB: Stockholm	3	-	58	17	49
D: Södermanland	6	-	17	5	13
E: Östergötland	4	1	6	2	43
O: Västra götaland	13	-	78	-	34
F: Jönköping	3	1	47	2	
N: Halland	1	4	27	-	10
G: Kronoberg	-	-	12	2	
H: Kalmar	7	2	22	9	7
I: Gotland	1	8	1	15	2
K: Blekinge	3	-	9	-	3
M: Skåne	15	11	39	1	19
Total	82	36	527	178	386

Table 7. Regional distribution of potentially PAC-contaminated sites in France divided into the three most relevant industrial categories

	Regions of France	History and climate	Gasworks	Coke ovens	Wood pres.
	Northern and Eastern	coal and iron industries	108	53	17
	Paris & Seine area	all industries	85	1	3
	Mediterranean and mountain areas	mediterranean or mountain	101	1	16
	Central, Western and other areas	oceanic	66	2	22
	Total number of sites		360	57	58

The largest number of potentially PAC-contaminated sites in France is found in Northern and Eastern parts of the country (Table 7). These regions contain most of the coal mining and carbochemistry sites in France, due to the joint occurrence of iron ore and coal. This explains the large number of coking sites in this area. Gas plants are more evenly distributed within the country, with a bias for large cities, such as Paris, Lyon and Marseille, and other populated areas. On the opposite, wood preservation sites are more found in rural or mountain areas, as these sites need lots of space.

During the data mining, a new group of sites with potential polar PAC contamination was identified, i.e. petroleum refining and storage sites that have underwent major thermal events, such as heavy fires, wartime bombing, and various industrial accidents. Such sites were not investigated within PACMAN but can often be identified from their BASOL records. This is left to be done.

9.2 Existing data on the occurrence of polar PAC at contaminated sites

The existing data on polar PACs at the identified sites are, as expected, scarce. At the beginning of PACMAN, data were available for one gasworks site, one coke production and four wood preservation sites in Sweden (Lundstedt et al. 2006a, 2007) as well as for two coke production sites in France (Benhabib et al. 2010, Biache et al. 2008, 2011) from previous research projects at UmU and CNRS, respectively. During the project time, additional data have been collected via consulting companies, authorities and analytical laboratories. In total, polar PAC data have been found for 14 additional sites in Sweden, while no additional data were found for French sites. These Swedish sites included 8 wood preservation sites, 3 gasworks sites, 1 dump site, 1 oil storage site and 1 general industrial site. Furthermore, polar PAC data were found for a number of samples (of urban soils, sediments and molluscs) collected within a national screening program (Brorström-Lundén et al. 2010), and for a PAC contaminated soil that underwent a biological treatment. Oxy-PAHs have been analysed in soil at 5 of the sites and in groundwater at 7 sites. The levels of individual oxy-PAHs varied between <0.1 - 7.7 mg/kg in soil, and between <0.1 – 7.0 µg/L in groundwater. In some cases these levels were similar to the measured PAH levels, while in some cases the oxy-PAH levels were about 100 times lower. However, it was difficult to identify any trends or correlations in this, which probably is because the data was very scattered. These oxy-PAH data have mainly been generated after 2008 and is most likely a result of the increased interest for these compounds influenced by PACMAN and previous project in this field (including the Polar PAC Network). In some of the older studies, a few N-PACs (e.g. carbazole) were included as indicators of creosote contamination.

To supplement the data found for Sweden and France, the scientific literature has also been screened for polar PAC data from the whole world (Table 8). However, even in this case the amount of available data was limited. Some data was available for a number of gasworks sites, wood preservation sites

and coke production sites in Germany (Bandowe and Wilcke 2010, Blotevogel et al. 2008, Blum et al. 2011, Meyer et al. 1999, Mundt and Hollender 2005, Neuwoehner et al 2009, Reineke et al. 2007, Schlanges et al 2008, Zamfirescu and Gratwohl 2001), two gasworks sites and an asphalt production site in Denmark (Johansen et al. 1997), a wood preservation site in Norway (Hartnik et al. 2007), and two gasworks sites, three wood preservation sites, a superfund site and a hazardous waste site in USA (Adams and Giam 1984, Lundstedt et al. 2006b, Park et al. 2008, Rostad 1984). Many of these studies have focused on groundwater contamination and in some of them relatively high levels of polar PACs, particularly N-PACs, have been measured in the water. In some cases, a clear enrichment of polar PACs (again with emphasize on N-PACs) compared to PAHs was seen in the groundwater plume with increased distance from the actual contamination source. Polar PACs have also been analyzed in urban soils and soils from industrial areas in Germany, Slovakia, Czech Republic, Uzbekistan, Switzerland and Thailand (Bandowe et al. 2010, 2011, 2014, Machala et al. 2001, Niederer 1998, Svabensky et al 2009, Wilcke et al 2014). In many cases, the relative levels of polar PACs (or at least of oxy-PAHs) were higher in these soils, as compared to heavily contaminated soils, although the absolute levels were lower. This might be due to a larger influence of atmospherically transformed PAHs.

Table 8. Peer-reviewed studies, before and outside PACMAN, in which polar PACs have been analyzed in samples from contaminated sites or related environments

Reference	Site, matrix and PACs analyzed
Adams and Giam 1984	Waste water from wood preservation site in USA. High levels of azaarenes (N-PACs) detected.
Bandowe et al. 2010	Urban and industrial soils from Uzbekistan. Lower absolute levels than at heavily contaminated sites, but higher proportions of polar PACs (oxy-PAHs).
Bandowe and Wilcke 2010	Gasworks soil and urban soil from Germany. Higher PAC levels at the gasworks site, but also higher proportions of oxy-PAHs than in the urban soil.
Bandowe et al. 2011	Urban soil from Slovakia. Lower absolute levels than at heavily contaminated sites, but higher proportions of polar PACs (oxy-PAHs).
Bandowe et al. 2014	Urban soils from Thailand. Lower absolute levels than at heavily contaminated sites, but higher proportions of polar PACs (oxy-PAHs and N-PACs)
Biache et al. 2008	Two coke prod. sites in France. High levels of both PAHs and oxy-PAHs in soil.
Benhabib et al. 2010	Coke prod. site in France. Several polar PACs detected in coal tar.
Biache et al. 2011	Coke prod. site in France. Several polar PACs detected in soil.
Blotevogel et al. 2008	Wood pres., coke prod., gasworks asphalt prod., and landfill sites in Germany. Heterocyclic compounds (incl. N-PACs) found in groundwater
Blum et al. 2011	Wood pres., gasworks and dump sites in Germany. High levels of heterocyclic compounds (incl. N-PACs) in groundwater
Eriksson et al 2000	Gasworks site in Sweden. High levels of both PAHs and oxy-PAH in soil.
Hartnik et al 2007	Wood pres. site in Norway. Several polar PACs identified in the most toxic fractions of groundwater samples
Johansen et al 1997	Two gasworks and one asphalt production sites in Denmark. Varying levels of heterocycles (incl. N-PACs) in the groundwater
Lundstedt et al 2003	Gasworks site in Sweden. High levels of both PAHs and oxy-PAHs in soil. Oxy-PAH-levels ~10% of total PACs
Lundstedt et al. 2006a	One gasworks, one coke prod., and four wood pres. sites in Sweden and one superfund site in USA (CRM 103-100). High levels of both PAHs and oxy-PAHs soils. Oxy-PAH levels between 10-40% of total PACs
Lundstedt et al. 2007	
Machala et al 2001	Sediment from an industrial area in Czech Republic. Oxy-PAHs and N-PACs up to 10 % of total PACs
Meyer et al 1999	Creosote contaminated soils from Germany. High levels of both PAHs and polar PACs (oxy-PAHs and N-PACs) in soil.
Mundt and Hollender 2005	Wood pres. site in Germany. High levels of heterocyclic compounds (incl. N-PACs) measured in groundwater
Neuwoehner et al 2009	Wood pres. site in Germany. High levels of quinoline derivatives measured in groundwater
Niederer 1998	Urban soils in Switzerland. Oxy-PAHs and nitro-PAHs detected in soils
Park et al 2008	Two gasworks sites and two wood preservation sites in USA. Several oxy-PAH detected in soils
Reineke et al 2007	Coke production site in Germany. N-PACs detected in groundwater.
Rostad et al. 1984	Hazardous waste site in USA. Several polar PACs detected in groundwater
Schlanges et al. 2008	One gasworks, one wood pres., and two coke prod. sites in Germany. High levels of polar PACs in groundwater
Svabensky et al. 2009	Industrial area in Czech Republic. Several N-PACs detected in soil
Wilcke at al 2014	Urban soil in Switzerland. Oxy-PAH levels about 20% of total PACs
Zamfirescu and Gratwohl 2001	Gasworks site in Germany. Several polar PACs were detected in the groundwater, and seem to be enriched there.

9.3 New data on the occurrence of polar PAC

To further supplement the previously existing data on polar PACs at contaminated sites, new data have been produced throughout the PACMAN project. In total, new polar PAC data have been generated for 15 Swedish sites, 7 French sites and 1 Belgian site. At some sites, several samples have been collected and analysed, while at other sites only one or a few samples have been investigated. At 22 of the 23 sites, soil samples have been collected while at one of the sites only groundwater has been sampled. At one of the sites, a more thorough investigation was performed, including samples of soil, groundwater, surface water and molluscs. In all samples, 16 PAHs, 11 oxy-PAHs and 4 N-PACs (Figure 3) have been analysed, but in some sample also a number of other PAHs and polar PACs have been analysed. The sampling and the accompanying analyses have in some cases been coordinated with the SNOWMAN project IBRACS who has performed availability studies on the soils.

9.3.1 Soil samples

In Table 9, examples of PAC levels (totals of PAHs, oxy-PAHs and N-PACs) found in soil samples from all the investigated sites are presented, together with the relative levels of oxy-PAHs and N-PACs (in relation to the total PAC-levels) calculated for each sample. Although, the absolute contamination levels often vary considerably within a site, the relation between the individual compounds and compound classes are usually more stable. In between sites, on the other hand, even the relation between the compounds may vary significantly, which is indicated by the relative levels shown in Table 9. However, this is even more obvious in Figure 4, where the PAC profiles for eight of the soils (four Swedish and four French) are shown. Clearly, different compounds dominate at different sites. For example, the gasworks sites seem to contain relatively much of the HMW PAHs, while the wood preservation sites have a clear dominance of pyrene and fluoranthene. The coke oven sites seem to be somewhere in between in this sense. When it comes to the polar PACs, the Swedish wood tar production sites seem to contain the largest fraction of these compounds, sometimes exceeding 30% of total PACs. However, the highest relative levels of the individual oxy-PAHs 9-fluorenone and 4H-cyclopenta[def]phenanthrene seem to be found in the coke oven soils and the wood preservation soils, respectively. These data, including the individual levels of each compound at each site, will be further evaluated with principal component analysis (PCA) and the result included in the coming article "*Occurrence of polar Polycyclic Aromatic Compounds at Contaminated Sites*" that is in preparation. Nevertheless, the data show that the polar PACs (in this case represented by oxy-PAHs and N-PACs) generally constitute a significant part of the total PAC load at these type of sites.

9.3.2 Groundwater samples

The contaminant profile found in the groundwater at a Swedish gasworks site is presented in Figure 5. It shows that the groundwater contamination was clearly dominated by LMW compounds, both when it comes to PAHs and oxy-PAHs, and also that it contained relatively much of the N-PACs. Unfortunately, no soil sample was available from this site, but when compared with the profiles found in the soils at the other gasworks sites (Figure 4), the groundwater seems to be enriched in the LMW compounds, which is not surprising considering their higher water solubilities. This is however further discussed in chapter 11 below. More groundwater data is also shown in section 9.4 below, dealing with the wood preservation site that was studied in more detail.

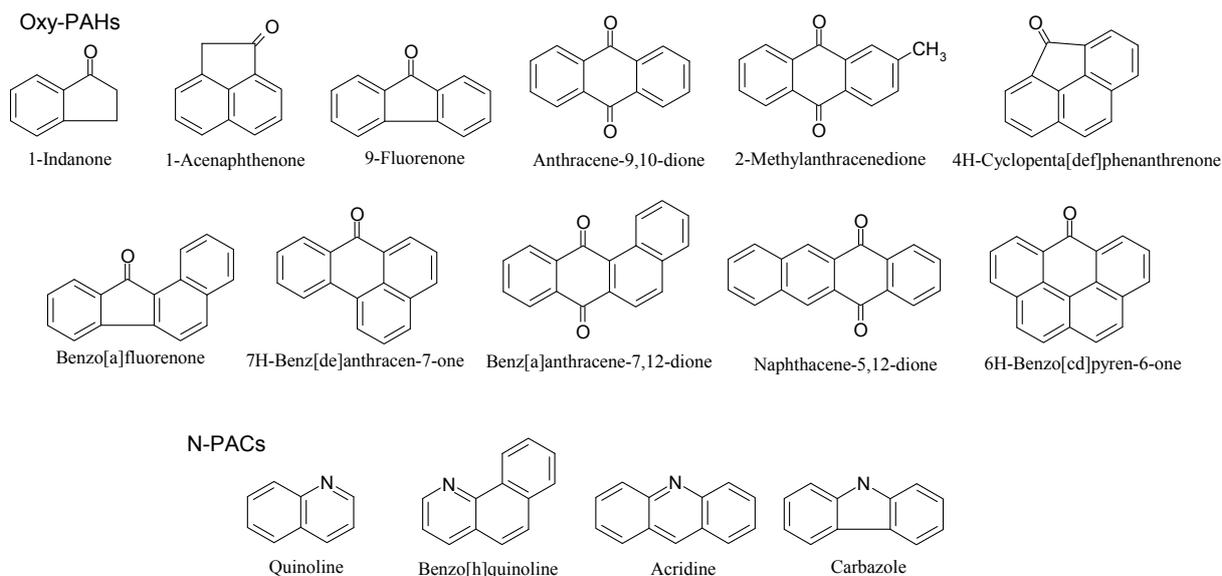


Figure 3. Molecular structures of the PACs analyzed in all samples within PACMAN

Table 8. Mass fraction ($\mu\text{g/g}$) of PAHs, oxy-PAHs and N-PACs found in soil at various PAC contaminated sites in Sweden and France, including gasworks, coke oven, wood preservation (wood pres.), wood tar production (wood tar), railway yard and mixed industrial sites. The relative levels of oxy-PAHs and N-PACs (fraction of total PACs) are also shown.

	Mass fraction Σ 16 PAHs ($\mu\text{g/g}$)	Mass fraction Σ 11 oxy-PAHs ($\mu\text{g/g}$)	Mass fraction Σ 4 N-PACs ($\mu\text{g/g}$)	Rel. level Oxy-PAH (%)	Rel. level N-PAC (%)
Swe gasworks 1	130	24	2.1	15	1.4
Swe gasworks 2	104	14	1.0	12	0.80
Swe gasworks 3	22	1.8	0.19	7.2	0.77
Swe coke oven	379	117	1.9	24	0.39
Swe wood pres. 1	2320	219	5.2	8.6	0.20
Swe wood pres. 2	1399	147	2.1	9.5	0.14
Swe wood pres. 3	1797	215	2.7	11	0.14
Swe wood tar 1	278	108	2.1	28	0.55
Swe wood tar 2	709	35	21	4.6	2.7
Swe wood tar 3	45	19	1.0	29	1.6
Swe wood tar 4	17	4.3	0.10	21	0.50
Swe railway yard	28	2.0	0.23	6.6	0.77
Swe industrial 1	40	2.9	0.35	6.7	0.81
Swe industrial 2	25	19	0.32	6.9	1.2
Fr gasworks	237	27	1.8	10	0.66
Fr coke oven 1	2651	371	22	12	0.71
Fr coke oven 2	1148	204	6.8	15	0.50
Fr coke oven 3	78	11	1.1	12	1.3
Fr coke oven 4	1158	103	8.8	8.1	0.69
Fr wood pres. 1	9905	2104	36	17	0.30
Fr wood pres. 2	83	11	1.6	12	1.7
Belgian gasworks	297	33	4.8	9.8	1.4

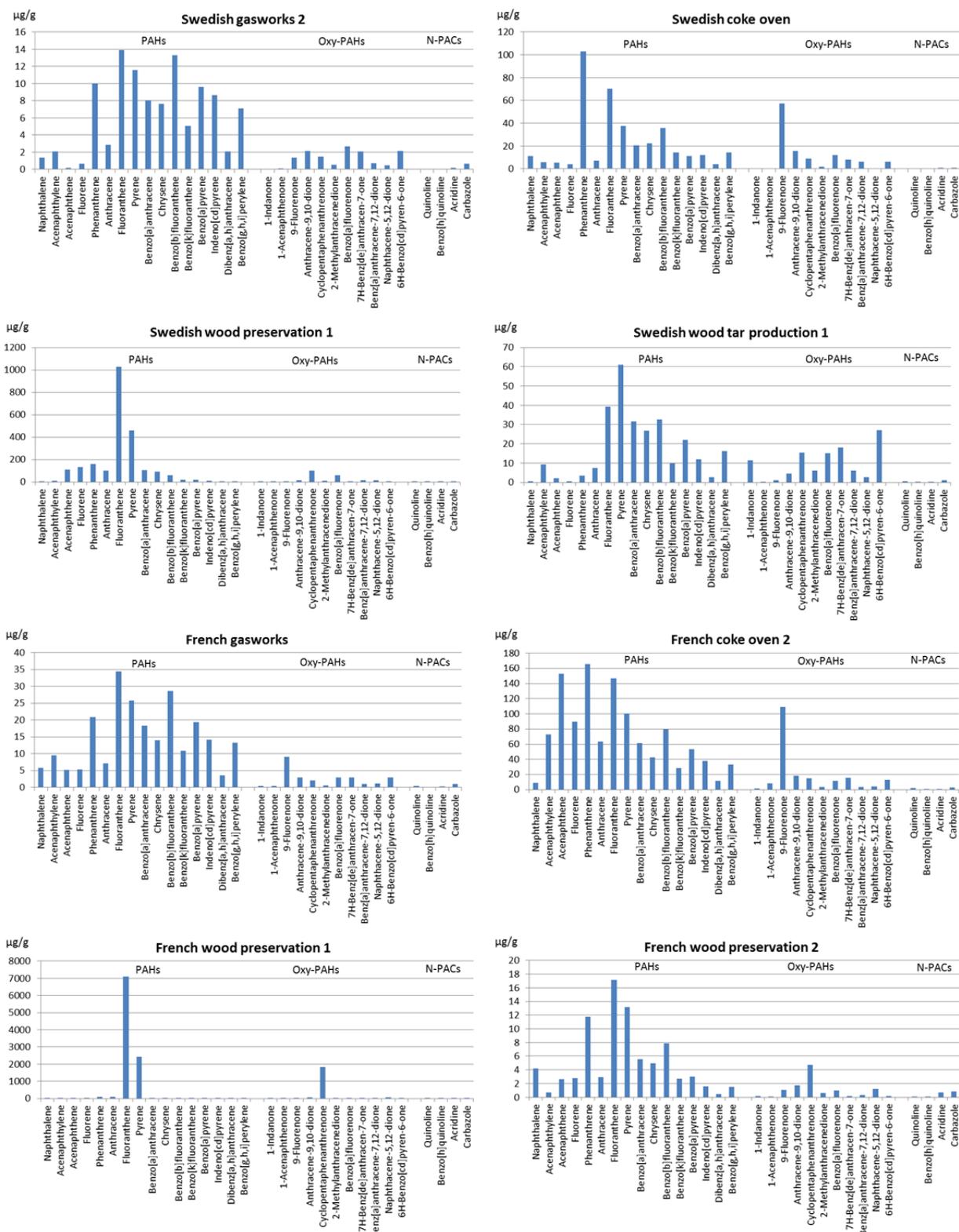


Figure 4. PAC-profiles in soil samples from eight of the PAC-contaminated sites listed in Table 8. PAHs to the left in each graph, oxy-PAHs in the middle and N-PACs to the right. The molecular weight of the PACs increase from left to right within each compound group in the graphs.

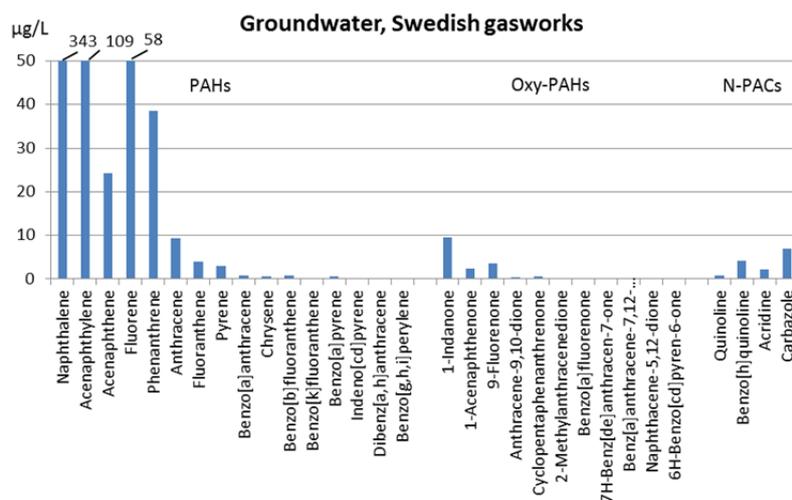


Figure 5. PAC-profile in a groundwater sample from a Swedish gasworks site, with PAHs to the left, oxy-PAHs in the middle and N-PACs to the right. The molecular weight of the PACs increase from left to right within each compound group in the graph.

9.4 Polar PACs at a Swedish wood preservation site – Holmsund, Umeå

One of the Swedish wood preservation sites, i.e. in Holmsund close to Umeå, Sweden, was selected for a more thorough investigation in order to understand the distribution of PACs at the whole site. Several samples of soil, groundwater, surface water and biota (molluscs) were thus collected from this site and its surroundings, and were analysed with regards to PAHs and polar PACs. The work was facilitated by a development project financed by the Swedish EPA (Naturvårdsverket) via the country administrative board of Västerbotten and the municipality of Umeå, and was carried out during risk assessment and remediation of the site.

9.4.1 Pre-study

In a pre-study performed by UmU before the start of PACMAN, the distribution of PAHs and oxy-PAHs in soil and groundwater at the site was screened. Ten samples of surface soil and nine samples of groundwater were then collected from the site and analysed. The results showed that the contaminants were distributed over the whole site, in both matrices, but also that the levels varied considerably from sample to sample. For example, the levels of PAHs (sum of 16 PAHs) and oxy-PAHs (sum of 12 oxy-PAHs) in soil varied between 1.7-14 000 µg/g and 0.19-1200 µg/g, respectively. Of these, the values on the high end are notably high as they correspond to a PAH- and oxy-PAH content of 1.4 and 0.12 %, respectively, which for PAHs exceeds the Swedish guideline values by more than 300 times. The ranges of concentrations for PAHs and oxy-PAHs found in both soil and groundwater are shown in Table 9, together with the relative amounts of oxy-PAHs (average and range) calculated for all samples. As seen, the average relative amounts (13 % for soil and 16 % for groundwater) indicate that the oxy-PAHs had been somewhat enriched in the groundwater compared to the soil. This would agree with the hypothesis that oxy-PAHs are more mobile as a result of their higher water solubilities. However, as also seen in Table 9, the relative amounts varied considerably, just like the absolute levels, which makes it difficult to draw any certain conclusion about this. Nevertheless, the study showed that more or less the whole site was severely contaminated with both PAHs and oxy-PAHs.

Table 9. Levels of PAHs, oxy-PAHs and found in soil and groundwater during the pre-study at the former wood preservation site in Holmsund, Sweden. The levels are given as intervals from the lowest to the highest values. The relative levels of oxy-PAHs (fraction of total PACs) are also given; with average values outside the parentheses and the interval within the parentheses, n= number of samples.

	In soil (n=10)	In groundwater (n=9)
Σ PAH ₁₆	1.7-14 000 µg/g	0.53-6400 µg/L
Σ Oxy-PAH ₁₂	0.19-1200 µg/g	0.082-140 µg/L
Fraction Oxy-PAH (%)	13 % (7.6-18 %)	16 % (1.3-51 %)

9.4.2 New samples of surface soil and groundwater

To supplement the results from the pre-study and investigate the situation further, additional samples were collected at the Holmsund site within PACMAN. Focus was directed towards ground- and surface water samples, depth profiles of soil and biota samples from the nearby bay, in order to elucidate the distribution behaviour of the polar PACs in relation to the PAHs. However, some samples of surface soil have also been analysed.

A summary of the results for the surface soil samples and the groundwater samples are presented in Table 10. Even this time the most contaminated soil sample contained very high PAC levels, i.e. up to 14 000 µg/g for PAHs, but the range was narrower compared to the former samples, which was because only hot-spot samples were selected in the new campaign. Even the levels in the groundwater samples were more homogenous this time, and were all assembled in the middle of the range from the former sampling campaign. However, this was more unexpected since these samples had been collected from several different spots, both on the site and outside the site. When it comes to the relative amounts of polar PACs, the fractions of oxy-PAHs were generally lower this time compared to the former sampling campaign. However, more notable is that the relative amounts of oxy-PAH₁₁ were lower in the groundwater than in the soil, which disagrees with the theory that oxy-PAHs have higher leachability. On the other hand, enhanced leachability of oxy-PAHs, in comparison to PAHs, has been observed clearly during previous column leaching experiments in the lab [Lundstedt et al. 2007], so there is probably another explanation to these results. One explanation would be that a large part of the PACs in the groundwater are adsorbed to small particles (colloids) and dissolved organic carbon (DOC), which will increase the water concentration of the less soluble compounds and thereby influence their observed partitioning between soil and water. Another explanation would be that there are selective interactions that may absorb some oxy-PAHs more than expected. A third explanation would be that dissolved oxy-PAHs are more susceptible to degradation than PAHs. The real explanation is probably a combination of these, although the compound specific data indicate that the latter two explanations might be more important at this particular site. Overall, there was thus an enrichment of LMW PACs, including all N-PACs, in the water phase compared to the soil (Figure 6a and b), showing that the more water soluble compounds were indeed more distributed in the water. This would then imply that all N-PACs studied are relatively water soluble (which they are), but also that they are more persistent in the water than the oxy-PAHs are.

For some of the groundwater samples the particle adsorbed contaminants were separated from the dissolved contaminants by filtration, after which the particles and solution were analysed separately. Figure 7 shows the results for one of those samples. LMW compounds are clearly more distributed in the dissolved phase than HMW compounds, both for PAHs and oxy-PAHs, but the difference between the compound classes are not dramatic. For the N-PACs, all four compounds can be considered as LMW compounds explaining why they are mainly distributed in the dissolved phase (supporting the discussion above). However, the result for the smallest and most water soluble N-PAC, Quinoline, deviated from this trend and were mainly distributed in the particle phase in all of these “divided” samples. It is so far unknown if this represents a real deviation or if it is an analytical artefact. This is however further discussed in section 9.4.5 below.

Table 10. Levels of PAHs, oxy-PAHs and N-PACs found in soil and groundwater at the former wood preservation site in Holmsund, Sweden for samples collected within PACMAN. The levels are given as intervals from the lowest to the highest values. The relative levels of oxy-PAHs and N-PACs (fractions of total PACs) are also given; with average values outside the parentheses and the intervals within the parentheses, n=number of samples.

	In soil (n=3)	In groundwater (n=8)
Σ PAH ₁₆	2100-14 000 µg/g	22-426 µg/L
Σ Oxy-PAH ₁₁	219-420 µg/g	0.82-17 µg/L
Σ N-PAC ₄	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-PAC (%)	0.39 % (0.05-0.93 %)	8.7 % (1.2-20 %)

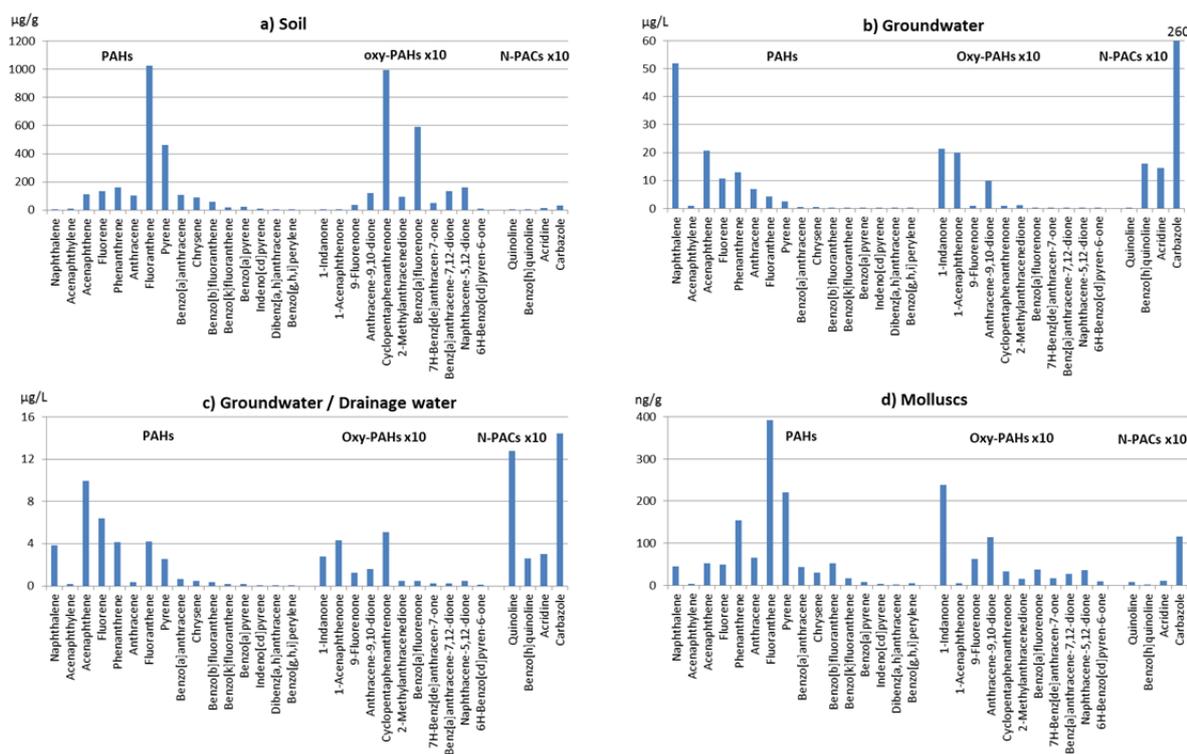


Figure 6. PAC-profiles in a) soil, b) groundwater, c) water from a drainage culvert, and d) molluscs from the nearby bay at the former wood preservation site in Holmsund, Sweden. PAHs to the left, oxy-PAHs in the middle and N-PACs to the right in each graph, with molecular weights increasing from left to right within each compound group. Note that the levels for all oxy-PAHs and N-PACs have been multiplied by 10 to facilitate the comparison.

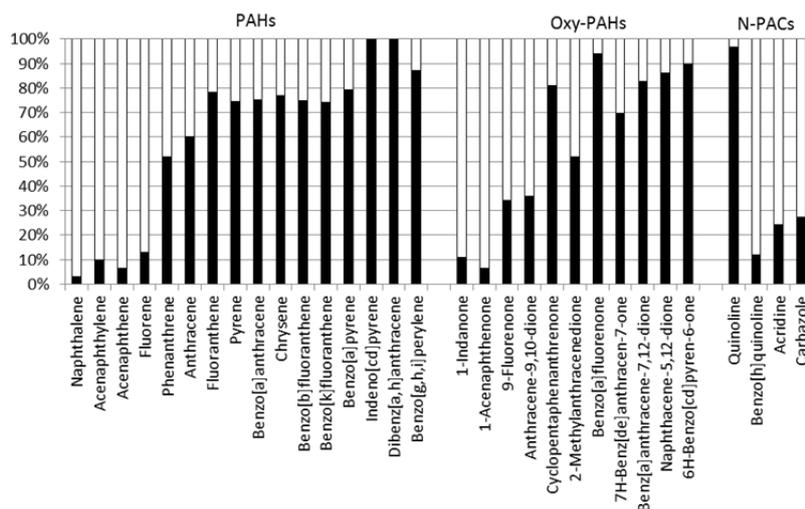


Figure 7. Distribution of selected PAHs, oxy-PAHs and N-PACs between dissolved (□) and particulate phase (■) in a groundwater sample from a former wood preservation site in Holmsund, Sweden. The molecular weight of the PACs increase from left to right within each compound group in the graph.

9.4.3 Depth profiles of soil

To further study the downward leakage of the contaminants in the ground, a number of depth profiles of soils were collected at the site. Two of these were analysed with respect to PAHs and polar PACs, one during the pre-study and one within PACMAN (Figure 8). The results show fluctuating PAC-levels, for both profiles, when moving downwards in the soil. The levels were highest in the surface soil, except for the oxy-PAHs in the pre-study profile that showed somewhat higher levels at 0.5-1 m, and were then alternately decreasing and increasing down through the profiles. However, in the profile collected during the pre-study (Figure 8a) the levels were within the same range at all depths, at least down to 2 m, i.e. between 190-420 µg/g for Σ 16 PAH and 26-84 µg/g for oxy-PAH₁₂, while in the newly collected profile (Figure 8b) the levels were drastically reduced below the first 0.5 m. The latter was probably because the PAC-levels in the surface soil of this profile were extremely high, i.e. 14 000 µg/g, 300 µg/g, and 140 µg/g for PAH₁₆, oxy-PAH₁₁ and N-PAC₄, respectively, and because this profile mainly consisted of clay with low permeability. The general fluctuation observed in both profiles was most likely a result of varying soil material at different depths and that the soil at the site had been disturbed several times by excavation and other activities after the first contamination took place.

When comparing the profiles for the different compound classes, no clear differences could be identified. The fluctuations for PAH and polar PACs were thus more or less correlated down through the profiles, and no enhanced leaching of any of the groups could therefore be verified. Even for individual compounds the differences were small. Only for the smallest, most water soluble PACs (containing two fused rings), a small enrichment (relative to other PACs) could be observed at deeper layers, and of these the polar PACs quinoline and 1-indanone seemed to be most enriched. So based on these results, it would be difficult to draw any certain conclusion about the differences in leaching behaviour and distribution between the compounds classes. The differences in distribution were small considering the compounds' intrinsic differences in water solubility. This can most likely, like for the soil-groundwater partitioning above, be explained by colloids, DOC and specific interactions that are reducing the differences in leachability between the compound classes, and by degradation processes that are more active on the polar PACs (particularly the oxy-PAHs) than on PAHs.

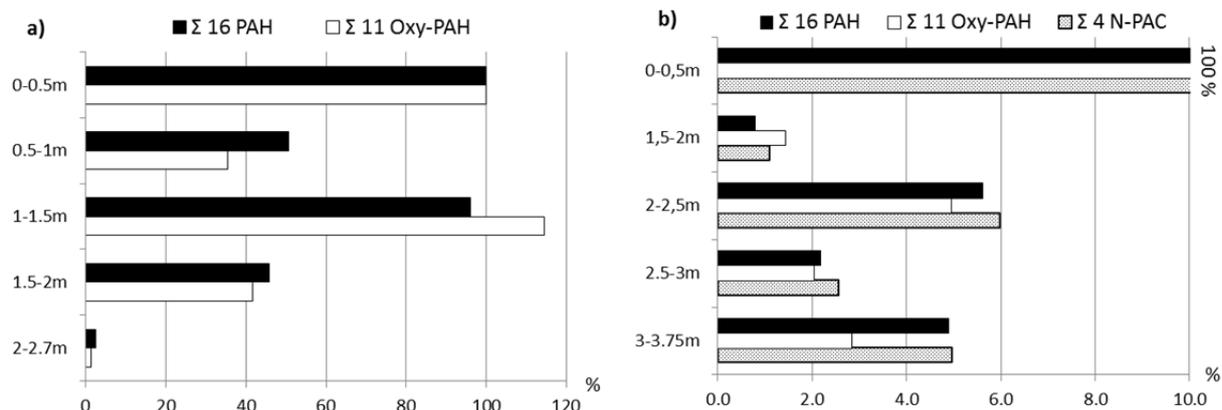


Figure 8. Relative levels of PAHs, oxy-PAHs and N-PACs (fractions of the levels in the surface soil) in depth profiles of soil from a former wood preservation site in Holmsund, Sweden.

9.4.4 PAC levels in the molluscs

To investigate the transport of PACs from the site to the nearby bay (300 m from the actual site in the direction of the groundwater flow) and their accumulation in water living biota, molluscs were collected from three habitats within the bay as well as from a reference habitat 1.3 km further away along the coast line. The molluscs were analysed with respect to the same PACs as the other samples, and the results showed that the molluscs in the whole bay contained elevated levels of both PAHs and polar PACs. The levels were particularly high in the molluscs collected in the inner parts of the bay, which is closest to the site and also the place for the outlet of a culvert that drains the ground between the site and the bay (and possibly also parts of the actual site). The PAC concentrations in the molluscs from this habitat were more than 100 times higher for PAHs, 20 times higher for oxy-PAHs and about 10 times higher for N-PACs as compared to the reference habitat.

The PAC profile in the molluscs were like a mix of the profiles found in the soil and the groundwater (Figure 6d), with a PAH pattern similar to that in the soil and an oxy-PAH pattern more like that in the groundwater. This can be explained by that the molluscs mainly are exposed to the PACs present in the groundwater, but that the more lipophilic PAHs are more efficiently accumulated. Overall, the relative amount of oxy-PAHs in the molluscs constituted 5 % of the total PAC content, which is higher than in the latest collected groundwater but lower than in the soil (Table 10). For the N-PACs, constituting 1.2 % of the total PAC load in the molluscs, the situation was the opposite. Their relative amount was thus higher than in the soil, but lower than in the groundwater. It looks like only carbazole of the N-PACs was taken up and accumulated to a large extent (Figure 6d). For comparison, the results for a sample of water collected from the drainage water culvert have been included in Figure 6c. It shows a pattern similar to that in the groundwater (Figure 6b), but with a slightly higher proportion of medium sized PACs such as fluoranthene, pyrene and cyclopenta[def]phenanthrene and much higher proportion of quinoline.

It should be noted that the molluscs were collected much later than the soil and groundwater samples in this comparison. In fact, the molluscs were collected after the main contaminated area had been remediated, which is further described below.

9.4.5 Remediation of the site and purification of drainage water

Due to the high levels of PACs occurring at the site and the associated risk for human exposure and leakage to the nearby bay, the whole area was extensively remediated during 2012. The remediation, led by the municipality of Umeå, was carried out through excavation and landfilling of the contaminated material. During these activities, large volumes of drainage water emerged from the soil, which due to its contamination had to be purified before it could be discharged into the bay. A temporary water treatment plant was therefore installed at the site, in which the water was purified through several particle removal steps (filtration) followed by a carbon adsorbent in the end. For PACMAN, water samples were collected before and after the treatment plant in order to investigate how well it removed the different PACs.

According to these samples the treatment plant removed all PACs to a high degree and to levels well below the levels in the groundwater just outside the site. The levels of most PACs were thus reduced by more than 99 % as a result of the treatment, and only one compound, quinoline, was removed to a lower degree than 95 %, although close to 90 % (further discussed below). Overall, PAHs, oxy-PAHs and N-PACs were removed to a similar degree. In all groups, the LMW compounds were removed somewhat less efficiently but the difference was not large, and in between the groups the difference between similar compounds was even smaller. The results are summarized in Figure 9 in which the weak relative enrichment of LMW PACs after the treatment can be discerned. From this figure it is however obvious that most of the remaining PACs after the treatment are found in the dissolved phase (white part of the bars) as opposed to the sample of the untreated water in which most PACs were found adsorbed to small particles and DOC (black part of the bars). The exception is, again, quinoline which was found to 80 % in the particle phase after the treatment. This was unexpected, considering its high water solubility, and it can therefore be suspected that this result is biased in some way, especially since the concentration of this compound after the treatment also was unexpectedly high. However, since high particle associated quinoline levels have been measured in other water samples from this site (Figure 7) the result cannot be rejected without further investigation, but this has not been possible within the frames of this project.

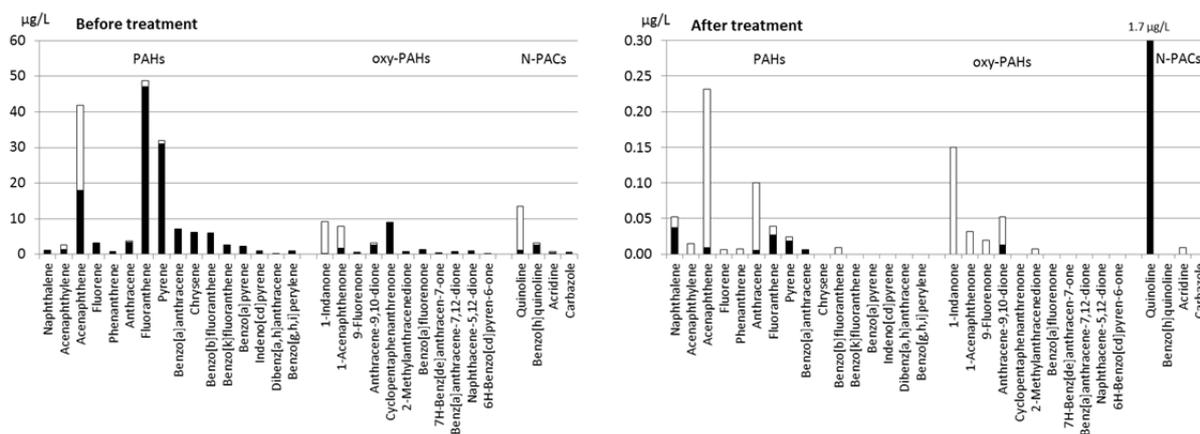


Figure 9. PAC profiles for the drainage water at the former wood preservation site in Holmsund, Sweden, before and after passage through the water treatment plant, showing both the dissolved (□) and the particle bound (■) fractions of the PACs.

9.5 Project status and deliverables

All deliverables for this WP have been fulfilled (Table 11). The inventories of PAC-contaminated sites in Sweden and France have been completed, just as the compilation of existing data on the occurrence of polar PACs at such sites. New polar PAC data have been produced for several sites (more than the three stated in the project plan), although a detailed investigation of both soil and groundwater has only been carried out at one site (the Swedish wood preservation site in Holmsund). Two peer-reviewed articles directly connected to this WP have been published so far, and two manuscripts are in preparation (see below).

- Lundstedt S., Bandowe B.A.M., Wilcke W., Boll E., Christensen J.H., Vila J., Grifoll M., Faure P., Biache C., Lorgeoux C., Larsson M., Frech Irgum K., Ivarsson P., Ricci M. (2014) *First intercomparison study on the analysis of oxygenated polycyclic aromatic hydrocarbons (oxy-PAHs) and nitrogen heterocyclic polycyclic aromatic compounds (N-PACs) in contaminated soil*. Trends in Analytical Chemistry 57: 83-92.
- Arp HP.H., Lundstedt S., Josefsson S., Cornelissen G., Enell A., Allard A-S., Berggren Kleja D. (2014) *Native Oxy-PAHs, N-PACs and PAHs in historically contaminated soils from Sweden, Belgium and France: Their soil-porewater partitioning behavior, bioaccumulation in Enchytraeus crypticus and bioavailability*. Environmental Science & Technology 48:11187-11195.
- Lundstedt et al., *Occurrence of polar Polycyclic Aromatic Compounds at Contaminated Sites (manuscript in preparation)*
- Lundstedt et al. *Occurrence and distribution of polar PACs at a former wood preservation site (manuscript in preparation)*

Table 11. Deliverables for WP3 within PACMAN

	Deliverables	Fulfilment and comments
DL3.1	Inventory of the existing PAC-contaminated sites in Sweden and France, and a survey of the existing knowledge regarding the occurrence and distribution of polar PACs at such sites.	Fulfilled
DL3.2	New data on the occurrence and distribution of polar PACs at three contaminated sites in Sweden and France	New data from more than three sites, but a thorough investigation at one site only.

10 Assessment of remediation methods for PAC-contaminated soils – WP4

10.1 Report on existing technologies for PAC remediation

BRGM has compiled a review report (22 pages), including more than 100 references, on the existing technologies for remediation of PAC contaminated sites. The focus of this bibliography was to identify technologies that are used and those that potentially can be used to treat PAC-contaminated soil. Six important remediation techniques were identified:

- a) Solvent washing of soil
- b) Biological degradation; *in situ* and *ex situ*
- c) Phytoremediation
- d) Chemical oxidation
- e) Thermal treatment
- f) Microwave treatment.

A summary of the report is given below, but for more detailed information, including the references, we refer to the full report [Colombano and Mouvet 2012].

a) The principle of soil washing techniques is to treat the contaminated soil with solvents in order to desorb and extract the contaminants from the soil. The extraction efficiency is influenced by the solvent polarity, the soil to solvent ratio, the contact time, various soil characteristics and the physico-chemical properties of the contaminants. Several studies have been performed on this topic, and overall they show that PAHs can be efficiently extracted (up to 95%) with many types of solvents, e.g. ethanol, 2-propanol, acetone, 1-pentanol and ternary mixtures of solvents and water, provided that it is performed in several steps (at least three). Several attempts have also been made to enhance the efficiency even more. Water based extraction solvents may also be used. For example, by adding ionic and non-ionic surfactants some studies revealed extraction efficiencies for phenanthrene between 33.9 and 84%. However, one disadvantage of using surfactants is that surfactant-PAH complexes may in some cases resorb to the soil particles resulting in an even lower extractability/degradability of the PAH. Another option is to use water solutions of cyclodextrins, such as methyl- β -cyclodextrin, which are nontoxic, cyclic oligosaccharides with the ability to form complexes with organic contaminants. These have also been shown to increase the desorption of PAHs from soil. Other ways to wash PAHs from soil is to use vegetable oil or supercritical fluid extraction (SFE). By using water modified supercritical carbon dioxide, extraction efficiencies above 90% have been obtained for the whole range of PAHs. For subcritical water, extraction efficiencies around 80% have been obtained. However, under oxidative conditions the total removal rate for this technique may reach 99%.

b) Biological methods based on *in-situ natural attenuation* are limited by the fact that a great proportion of the PAHs is sorbed to soil and thus not bioavailable. As a consequence the PAH content in the water phase is too low to maintain the bioremediation process. This can be circumvented through biostimulation (adding nutrients, electron acceptors etc. to the soil), bioaugmentation (adding microorganisms to the soil) and enhanced solubilisation of the PAHs using surfactants (mainly non-ionic) and cyclodextrins. Oxygen releasing compounds (ORCs) such as sodium carbonate peroxyhydrate ($\text{Na}_2\text{CO}_3 \cdot 1.5 \text{H}_2\text{O}_2$), magnesium peroxide (MgO_2) and calcium peroxide (CaO_2) may also be added to increase the degradation rates. Significant improvements of the degradation rates have been observed when using these amendments.

PAH contaminated soils have also been treated successfully using *ex-situ* compost and slurry techniques. For example, a complete removal of PAHs within 12 weeks was achieved by a land

farming bioremediation process which was based on liming, fertilizing and tilling. In another study, composting of PAH contaminated soils resulted in removal efficiencies ranging between 35 and 80% after 42 and 100 days of treatment, respectively.

c) Plants and *phytoremediation* have been successfully used to remove low molecular weight (LMW) PAHs from soil, with removal efficiencies between 40 and 99% over a 3-18 months treatment period. Larger PAHs, on the other hand, seem to be unaffected by this treatment.

d) Compared to biological treatment techniques, those based on chemical oxidation are faster resulting in shorter treatments times. The most commonly used chemical oxidants are hydrogen peroxide (H_2O_2) and *persulfate*, but also *ozone* and *potassium permanganate* ($KMnO_4$) have been used. H_2O_2 may be used alone or in combination with ferrous ions (Fe^{2+}) under acidic conditions, which is then referred to as Fenton's reagent. The resulting reaction produces highly reactive hydroxyl (OH)-radicals that will oxidize organic compounds like PAHs. Removal rates between 8-100% have been observed for PAHs by using this reagent, usually with higher efficiencies for LMW-PAHs. However, the reaction rates also vary from compound to compound which probably is due to differences in reactivity connected to the molecular structure. The removal rate is also influenced by various experimental conditions (e.g. pH, reaction time, treatment steps, UV radiation, H_2O_2 concentration, addition of Fe^{2+} , ratio of H_2O_2 amount to soil mass), as well as by the properties of the soil (e.g. organic carbon content, degree of aging). Several modifications of Fenton's reagent have also been used. For example, with the addition of salt stabilizers, such as potassium dihydrogen phosphate or peroxides, to reduce the dissociation rate of H_2O_2 , and chelating agents to improve the reaction efficiency at neutral pH. Furthermore, surfactants, vegetable oil and various organic solvents have been used in combination with Fenton's reagent to increase the dissolution (and thereby the availability) of the PAHs from the soil material. By using ethanol/Fenton, for instance, treatment removal rates up to 99.5% have been obtained. The Fe^{2+} -ions have sometimes also been replaced by the iron containing mineral Goethite, which then also have led to a lower need for acidification of the system.

Similarly to the activation of H_2O_2 by Fe^{2+} , persulfate can be activated to produce sulfate radicals by the addition of Fe^{2+} or other transition metals, or alternatively by various thermal or chemical treatments. The Fe^{2+} addition may be combined with an organic chelating agent to increase the Fe^{2+} stability. For $KMnO_4$, removal rates up 71% have been obtained, but in some studies the rates have been much lower (below 14%). Ozone has also been successfully used to oxidize PAHs, with removal rates between 50 and 100%. Injection of gaseous ozone has proved to be more efficient than aqueous ozone, which is due to a better diffusivity of the former. Furthermore, repeated ozone-treatments are generally more efficient than one single treatment.

Chemical oxidation methods may be used alone or as a pretreatment prior to biological methods. The idea of combining the technologies is that the chemical methods may produce transformation products that are readily available for the microorganisms. However, there is a disagreement whether this will actually improve the degradation results. Sometimes lower removal rates have been obtained by combining chemical and biological methods compared to using the biological methods alone. This may be due to microbial inhibition caused by the chemicals used or the transformation products formed.

e) *Thermal processes* to treat PAH contaminated soils may be very efficient with removal rates exceeding 90% using incineration at temperatures between 870 and 1200°C. However, even thermal desorption processes at temperatures between 300 and 350°C have shown very high removal efficiencies, in some studies as high as 87.0-99.9%.

f) Successful tests have also been made with microwave treatment of PAH contaminated soil. In fact, in one study no PAHs were found in the soil after the treatment.

It should be noted that most of the studies mentioned above have been performed on unsubstituted PAHs while very few have included polar PACs. There is however a concern that the polar PACs may

be degraded to a different degree and also that some types of polar PACs, e.g. oxy-PAHs and hydroxyl-PAHs, may be formed during the course of the treatment. Both these phenomenon have been observed in previous studies. Another important observation from previous studies is that the presence of polar PACs may influence the biodegradation of PAHs and vice versa. Inhibition of the degrading microorganisms may thus be caused by toxic effects of these other compounds, while stimulation may be due to cometabolic effects.

10.2 Degradation experiments performed on PAC-contaminated soils

In order to increase the knowledge of the fate of polar PACs in degradation processes applied on PAC-contaminated soils, experiments have been performed on three different soils at the CNRS (Georessources and LIEC) laboratories in Nancy, France. The soils investigated originate from three French industrial sites, i.e. a gasworks site (Rennes), a coke oven site (Neuves-Maisons) and a wood preservation site (confidential site). The degradation technologies that have been applied on the soils are pure H₂O₂-oxidation, a Fenton-like oxidation involving H₂O₂ and magnetite (Fe₃O₄) as catalyst, a KMnO₄-oxidation, and a microbiological slurry treatment. These technologies are relevant to study in this aspect since they are all efficient enough to be used for PAH-remediation, but may at the same time give rise to polar PAC formation during the course of the treatment.

10.2.1 Chemical treatments

The three chemical oxidation technologies were applied on the soils directly as well as after a one week preheating period (100 °C) under inert atmosphere (N₂), aiming at increasing the availability of the contaminants. The results show that the preheating had most effect on the gasworks and coke oven soils and less effect on the wood preservation soil, at least in terms of increasing the availability and the subsequent oxidation of the total extractable organic matter (EOM, Table 12). However, when it comes to the PAC removal, the pretreatment only showed effect on the coke oven soil, which is because this soil had the lowest contaminant availability in the beginning.

Table 12. Increase in degradation efficiency of dichloromethane extractable organic matter (EOM) in the soils, for each oxidation technology, as a result of soil preheating.

	Coke oven soil	Gasworks soil	Wood pres. soil
H ₂ O ₂ -oxidation	25 %	15 %	3 %
Fenton like oxidation	23 %	35 %	0 %
KMnO ₄ -oxidation	20 %	14 %	0 %

Despite the relatively large effect of the preheating on the coke oven soil, the lowest PAC reduction was still seen in this soil. When H₂O₂ or Fenton was used as oxidants, only around 30 % of the PACs were removed in this soil during a one week treatment (Figure 10a). Again, the low contaminant availability in this soil would be the explanation. Surprisingly, the removal efficiency was greater in the gasworks soil than in the wood treatment soil for all treatments (Figure 10a). Considering the effect of the preheating on the EOM (Table 12), the availability was expected to be higher in the wood preservation soil, but still the PACs were more efficiently removed in the gasworks soil. A plausible explanation to this is that the oxidant dose was a limiting factor in the treatment of the wood preservation soils, since the doses used were identical for all three soils even if the contaminant levels in the wood preservation soil were ten times higher. Even in the KMnO₄-treatment, the PAC removal was higher in the gasworks soil (93 %) than in the wood preservation soil (62 %). Overall, the KMnO₄-treatment was most efficient in reducing the PAC-levels in all soils, including the coke oven soil. This indicates that KMnO₄-treatment is less dependent on the availability of the contaminants.

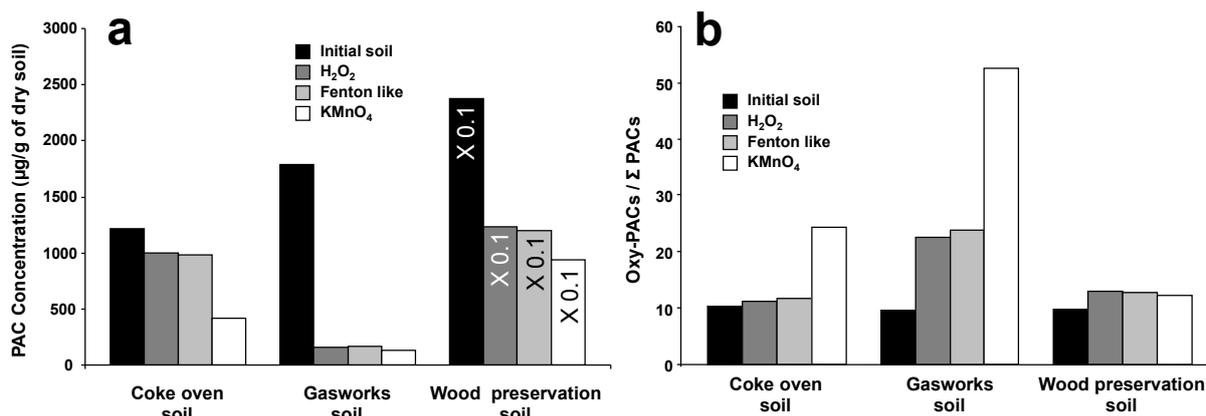


Figure 10. (a) Total concentrations of PACs (including PAHs, oxy-PAHs and N-PACs) and (b) ratio of oxy-PAHs to sum of PACs, in the initial soil and after the remedial treatments (hydrogen peroxide, Fenton like oxidation and potassium permanganate) of the coke oven, the gasworks and the wood preservation soils.

In general, the polar oxy-PAHs were removed more slowly than the PAHs in all chemical treatments, indicating that the oxy-PAHs were more persistent or (which is more likely) that there was a simultaneous formation of these compounds during the oxidation (Figure 10b). The effect was most obvious when considering the PAC contribution to the EOM. In Figure 11, the mass fraction of PAHs and polar PACs in the gasworks and coke oven soils are shown together with their contribution to the EOM during the course of the KMnO₄-treatment. It is clear that the polar PACs are more slowly removed and also that their contribution to the EOM actually increases during the treatment. The same effect could be seen in the other treatments, but was in these cases less pronounced.

In support of the theory of formation, the levels of some individual polar PACs (oxy-PAHs) were actually found to increase in the soils during the KMnO₄-treatments. For example, as shown in Figure 12, the levels of 9-fluorenone and anthracene-9,10-dione were found to increase during the initial hours of the KMnO₄-treatment of the gasworks soil. The levels were then decreasing, ending up on approximately the initial levels after one week of treatment. This also emphasizes the risk involved in terminating a remedial treatment too early.

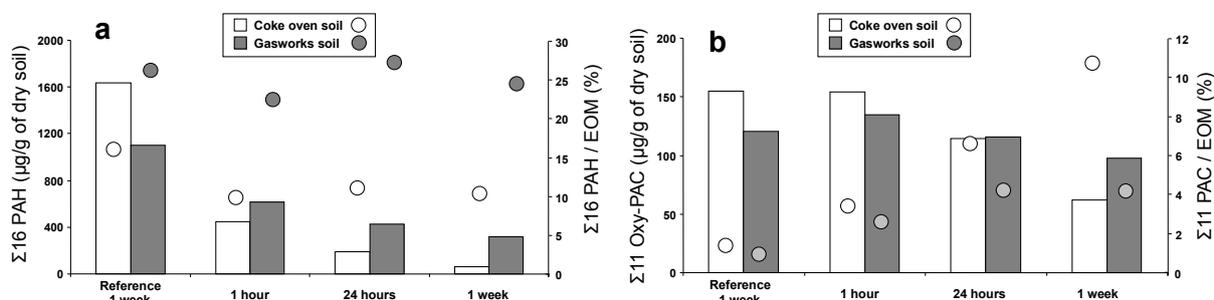


Figure 11. Change in a) the levels of PAHs and the ratio PAH/EOM, and b) the level of polar PACs and the ratio polar PAC/EOM, during KMnO₄-treatment of the gasworks (white) and coke oven (grey) soils. The bars are representing the levels and the circles are representing the ratios.

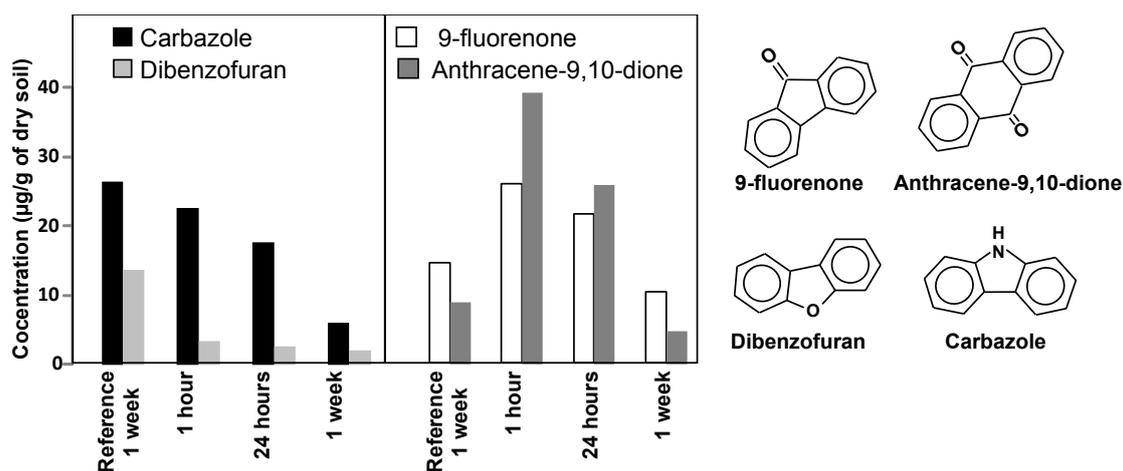


Figure 12. Evolution of the levels of dibenzofuran, carbazole, 9-fluorenone and anthracene-9,10-dione during KMnO₄-treatment of the gasworks soil.

10.2.2 Microbiological treatment

The microbiological treatment was performed on all three soils using bioslurry systems and bacterial inoculum from authentic PAC-contaminated soils. The biotreatments initiated an intense CO₂-production in the wood preservation soil and the gasworks soil, indicating high degradation activities in these soils (Figure 13). In the coke oven soil, however, the CO₂-production was much lower, indicating a lower degradation activity. The PAC analyses confirm these conclusions. The PAH levels were thus most extensively reduced in the wood treatment soil, and least reduced in the coke oven soil (Figure 14).

When it comes to the polar PACs, these followed the same trends as the PAHs in the coke oven soils and the gasworks soil, with moderate removal rates. However, in the wood preservation soil the removal rates of the polar PACs were significantly lower than of the PAHs. This indicates a simultaneous formation of polar PACs as a result of the extensive transformation of PAHs in this soil.

The results were further supported by microbial analyses, showing that the PAC removal was correlated with an increased diversity of bacterial and fungal species and also an increased proportion of species capable of degrading PACs. The bacterial and fungal communities were thus dominated by members of the Verrucomicobra phylum and Basidimycota, respectively.

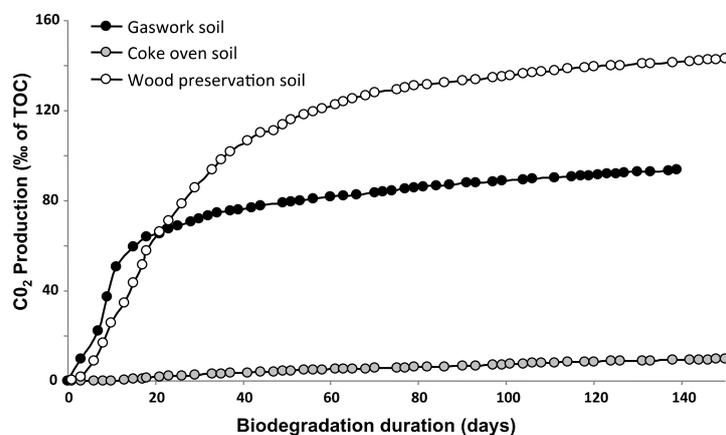


Figure 13. Accumulated amounts of CO₂ (as % of TOC) generated during microbial treatment of the coke oven soil, the gasworks soil, and the wood preservation soil.

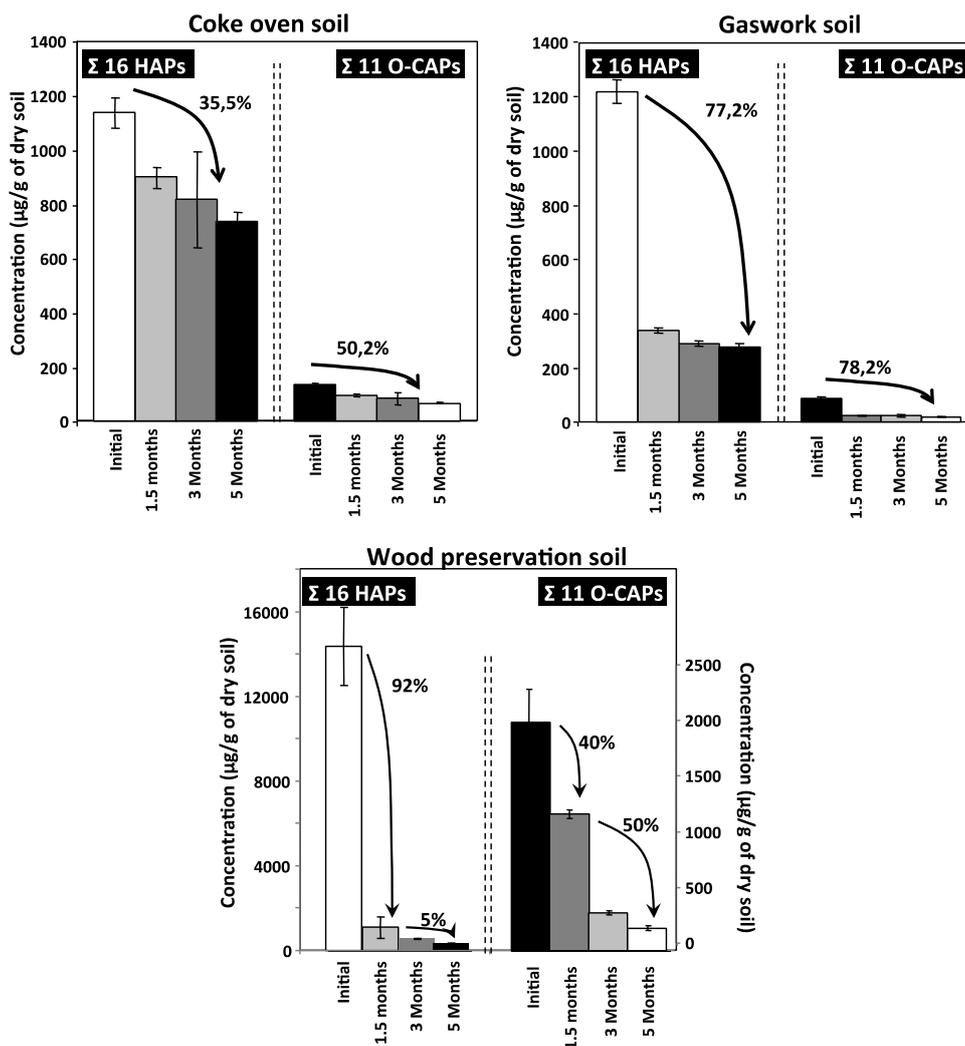


Figure 14. Reduction in levels of PAHs and polar PACs, after 1.5, 3 and 5 months of microbial treatments of the coke oven soil, the gasworks soil, and the wood preservation soil.

10.3 Project status and deliverables

Both deliverables proposed for this project have been fulfilled (Table 13). The report on existing remediation technologies have been completed, and data on the formation of polar PACs during four (instead of three) remediation process have been generated. Nine peer-reviewed articles directly connected to this WP have been published so far and one additional manuscript has been submitted for publication (see below).

- Usman M., Faure P., Rubya C., Hannaet K. (2012) *Remediation of PAH-contaminated soils by magnetite catalyzed Fenton-like oxidation*. Applied.Catalysis.B: Environmental 117-118: 10-17.
- Usman M., Faure P., Rubya C., Hannaet K. (2012) *Application of magnetite-activated persulfate oxidation for the degradation of PAHs in contaminated soils*. Chemosphere 87:234-240.
- Biache C., Faure P., Mansuy-Huault L., Cébron A., Beguiristain T., Leyval C. (2013) *Biodegradation of the organic matter in a coking plant soil and its main constituents*. Organic geochemistry 56: 10-18.
- Biache C., Mansuy-Huault L., Faure P. (2013). *Impact of oxidation and biodegradation on the most commonly used polycyclic aromatic hydrocarbon (PAH) diagnostic ratios: Implications for the source identifications*. Journal of Hazardous Materials., 267, 31-39.

- Cébron A., Faure P., Lorgeoux C., Ouvrard S., Leyval C. (2013) *Experimental increase in availability of a PAH complex organic contamination from an aged contaminated soil: Consequences on biodegradation*. Environmental pollution 177:98-105
- Biache C., Kouadio O., Lorgeoux C., Faure P. (2014) *Impact of clay mineral on air oxidation of PAH-contaminated soils*. Environmental Science and Pollution Research 21: 11017-11026
- Biache C., Kouadio O., Hanna K., Lorgeoux C., Faure P. (2014) *Role of goethite during air oxidation of PAH contaminated soils*. Chemosphere, 117, 823-829.
- Hanser O., Biache C., Boulangé M., Parant S., Lorgeoux C., Billet D., Michels R., Faure P. (2015) *Evolution of dissolved organic matter during abiotic oxidation of coal tar - comparison with contaminated soils under natural attenuation*. Environmental Science and Pollution Research 22: 1431-1443.
- Biache C., Lorgeoux C., Anadriatsihoarana S., Colombano S., Faure P. (2015) *Effect of pre-heating on the chemical oxidation efficiency: implications for the PAH availability measurement in contaminated soils*. Journal of Hazardous Materials 286: 55-63.
- Usman M., Chaudhary A., Biache C., Faure P., Hanna K. (2015) *Thermal pretreatment as a novel way to increase availability of PAHs for their successive chemical oxidation in contaminated soils* (submitted manuscript)

Table 13. Deliverables for WP4 within PACMAN

	Deliverables	Fulfilment and comments
DL4.1	Report on the existing technologies for remediation of PAC-contaminated sites, and to what extent these may generate polar PACs.	Completed
DL4.2	New experimental data on the formation of polar PACs during three typical remediation processes for PAC-contaminated soils.	Completed

11 Leaching behavior of polar PACs – WP5

11.1 Leaching tests in the laboratory

Column leaching tests have been performed in triplicate on three soils according to the plan in the project proposal. These soils originate from a Swedish wood preservation site, a Swedish gasworks sites and a French coke oven site. In addition, single column leaching test have been performed on seven other soils in collaboration with the SNOWMAN project IBRACS. Two of these soils originate from the same Swedish gasworks site as above, one from another French coke oven site and four from a Swedish wood tar production site. All these soils have also been investigated with a passive sampler based method, using polyoxymethylene membranes (POM), which measures the truly dissolved concentration in a water suspension of the soil. Like the column leaching tests, the POM studies have been performed in collaboration with the IBRACS project.

The column test applied was an Equilibrium Recirculation column test for hydrophobic organic compounds (ER-H, Gamst et al. 2007) that aims to simulate leaching at chemical equilibrium. In this, the soil (approx. 250 g) is packed in between two layers of quartz sand in a glass column, after which a leachate consisting of water with 0.001 M calcium chloride and 0.015 M sodium azide (biocide) is recirculated through it for seven days. The total liquid-solid ratio in the experiment was around 5, and the flow rate around 20 mL/h. The PAC concentrations in the leachate were determined after the leaching period. For the POM method, the soil (10 g) was shaken with water (35 mL) containing 0.001 M calcium chloride and 0.015 M sodium azide, and a POM strip (~0.1 g, 76 μm thick) for 28 days, after which the PAC amounts in the POM strips were analysed (Arp. et al 2014).

The results show that the leaching in the columns (which probably also holds for leaching in the field) was highly influenced by DOC and colloid facilitated transport, meaning that a large fraction of the leached PACs actually was adsorbed to DOC and small particles and was not freely dissolved in the leachate. This phenomenon reduces the difference in leachability between PAHs and polar PACs, compared to what can be predicted from their water solubilities and octanol-water partitioning coefficients (K_{OW}), since the less soluble PAHs will be more strongly associated with DOC and colloids than the more soluble polar PACs. It will also, of the same reason, reduce the difference in leachability between HMW PACs and LMW PACs. This can be seen in Table 14, where the averages of the determined $\log K_{TOC}$ (total organic carbon normalized soil-water partitioning coefficients) are listed. Although the ER-H-derived K_{TOC} are lower for LMW PACs than for HMW PACs, and lower for oxy-PAHs and N-PACs than for similar PAHs (e.g. anthracene-9,10-dione and acridine vs. anthracene), the difference is not that large. In fact, for HMW compounds there is no difference at all between PAHs and oxy-PAHs.

On the other hand, a larger difference was seen among the K_{TOC} values obtained from the POM experiments (Table 14). In this case a clear difference was seen between coefficients for HMW and LMW compounds as well as between PAHs and structurally similar polar PACs. This is due to the differences in water solubilities among the compounds and the fact that the POM only measures the truly dissolved fraction of the compounds. The same conclusions can be drawn from Figure 15 where the determined $\log K_{TOC}$ values (for both ER-H and POM) have been plotted against the $\log K_{OW}$ for each compound. It is clear that there is a good correlation between the POM derived K_{TOC} and K_{OW} (Figure 15b), while the ER-H derived values (Figure 15a) seem to be biased with an increasing deviation with increasing hydrophobicity of the compounds. This can be explained in the same way as above, i.e. that DOC and colloids act as carriers for the PACs in the leachates, and for HMW PAHs in particular, which leads to elevated water concentrations and thereby lower K_{TOC} .

The column based method seem thus to give a measure of both the freely dissolved PACs and the PACs adsorbed to colloids and DOCs, while the POM method only measures the freely dissolved concentration. As a consequence, the POM method would be the preferred method for estimating

bioavailability and toxicity, while the column method probably would give a better estimate of leaching and mobility in the field, since that usually is driven by a combination of colloid and DOC facilitated transport and transport of freely dissolved contaminants. The two methodologies could therefore very much complement each other during risk assessment of contaminated sites.

An additional observation that was seen in the POM data (Figure 15b) is that the determined K_{TOC} for oxy-PAHs and N-PACs were slightly higher than those for PAHs of similar hydrophobicity (K_{OW}), which means that the polar PACs were dissolved a little bit less than what would be predicted from their K_{OW} . This can be explained either by the existence of specific interactions (other than the general hydrophobic interactions) between the polar PACs and the soil particles as discussed in section 9.4.2, or alternatively by a systematic bias in the K_{OW} data used. The latter is possible since most of the K_{OW} values used, which were collected from the EPI Suite database (US EPA 2012), have been predicted through a molecular increment based approach, and have not been experimentally determined.

Table 14. Averages of Total organic carbon normalized soil-water partitioning coefficients ($\log K_{TOC}$) for various PACs in 10 different contaminated soils (from 5 sites) determined through a column leaching test (ER-H) and a passive sampler based method (POM). Three soils were tested in triplicate and seven soils in single tests.

$\log K_{TOC}$	Average $\log K_{TOC}$ ER-H determined (n = 16)	Average $\log K_{TOC}$ POM determined (n = 16)
Naphthalene	4,3±0,7	4,3±0,1
Acenaphthylene	4,8±0,9	5,6±0,4
Acenaphthene	3,9±0,8	3,8±1,0
Fluorene	4,2±0,9	4,4±0,8
Phenanthrene	4,6±0,9	5,3±0,4
Anthracene	4,9±0,9	5,6±0,3
Fluoranthene	5,1±1,1	6,0±0,2
Pyrene	5,1±1,1	6,1±0,3
Benzo[a]anthracene	5,1±1,1	7,0±0,3
Chrysene	5,0±1,1	6,8±0,3
Benzo[b]fluoranthene	5,1±1,1	7,4±0,3
Benzo[k]fluoranthene	4,9±1,0	7,4±0,3
Benzo(a)pyrene	5,1±1,0	7,6±0,3
Indeno[cd]pyrene	5,0±1,0	8,0±0,1
Dibenz[a,h]anthracene	4,8±1,0	7,9±0,2
Benzo[g,h,i]perylene	5,0±1,0	8,0±0,1
1-Indanone	3,4±0,7	2,4±0,6
1-Acenaphthenone	4,0±0,8	3,6±0,4
9-Fluorenone	4,1±0,7	4,4±0,5
Anthracene-9,10-dione	4,5±0,9	4,7±0,4
4H-Cyclopenta[def]phenanthrenone	4,8±1,0	5,5±0,3
2-Methylantracenedione	4,7±0,9	5,4±0,4
Benzo[a]fluorenone	5,0±1,1	6,7±0,3
7H-Benz[de]anthracen-7-one	5,0±1,0	6,3±0,3
Benz[a]anthracene-7,12-dione	5,0±1,0	6,8±0,2
Naphthacene-5,12-dione	5,0±1,0	6,6±0,2
6H-Benzo[cd]pyren-6-one	5,1±1,0	7,1±0,3
Quinoline	4,0±0,7	3,4±0,5
Benzo[h]quinoline	4,5±0,9	4,5±0,4
Acridine	4,4±0,8	4,8±0,3
Carbazole	4,4±0,8	4,8±0,5

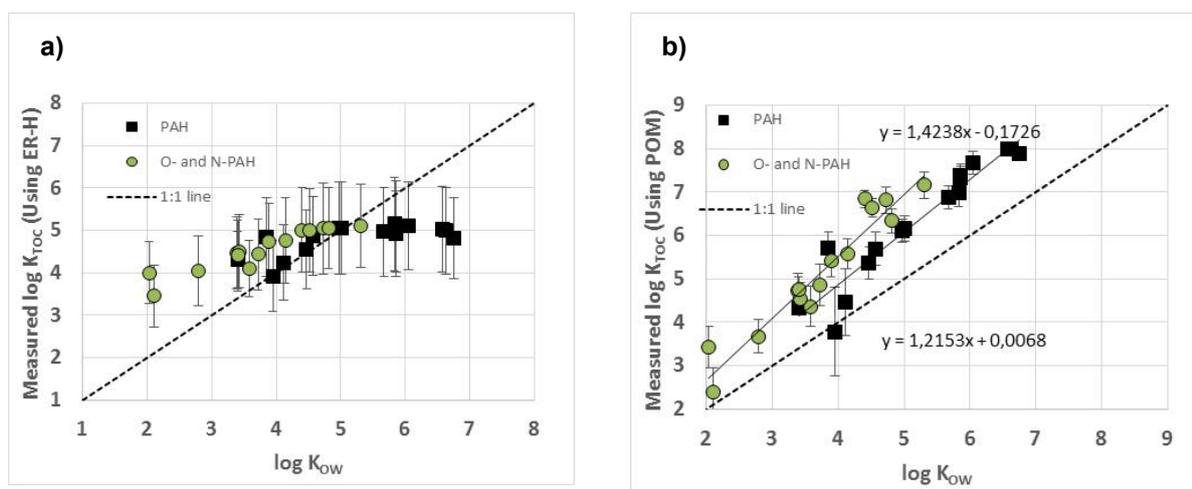


Figure 15. Measured $\log K_{TOC}$ values for selected PAHs and polar PACs (same as in Table 14) obtained by a) the ER-H-test and b) the POM method, and plotted against the $\log K_{OW}$ -values (collected from the EPI Suite database) for each compound. Error bars represents standard deviation determined from either the 16 ER-H- or 16 POM-experiments. Figures reproduced from Arp et al 2014 and Enell et al. 2015.

11.2 Leaching studies in the field using lysimeters

In order to evaluate the consequences of in situ chemical oxidation (ISCO) on the formation and leaching of PACs, a coking plant soil have been treated in several lysimeter columns (1 m² of area and 2m deep) at the experimental station of GISFI (Homecourt, France). Two columns have thus been treated with Fenton's reagent (hydrogen peroxide and iron sulphate), one column with persulfate activated with hydrogen peroxide and one reference column with water only. The treatments were applied in June 2010, and cores were sampled from each column immediately after the treatments and two years later. Samples for PAC analyses were collected from four depths in each core plug, i.e. 0-7 cm, 7-12 cm, 20-30 cm and 71-90 cm. The results are summarized in Figure 16 and 17.

The results show that the treatments had limited capacity to oxidize the PACs in the soil (Figure 16). The levels decreased at some depths but increased at other depths, and overall, the degradation was low. This is most likely due to the limited contaminant availability in the soil used. The soil originated from the same coke oven site as the soil in the previously described oxidation studies in the laboratory (Section 10.2, WP4), in which it was shown that the treatments were limited by low contaminant availability in this soil.

The lysimeter treatments also had limited effect on the polar PAC proportion in the soil. An increase in the relative levels of polar PACs (in relation to PAHs) could be seen in the beginning of the treatment at the surface of the persulfate column, and after two years in the deepest layers of one of the Fenton columns (Figure 17). However, besides that the differences were small, both between treatments and between different column depths. Only a weak decrease in the relative polar PAC levels could be observed, at most depths in all columns, after the two years treatment period. These results indicate that the polar PACs were somewhat more efficiently removed than the PAHs during the treatment period, while no indication of formation or increased leaching of polar PACs could be observed.

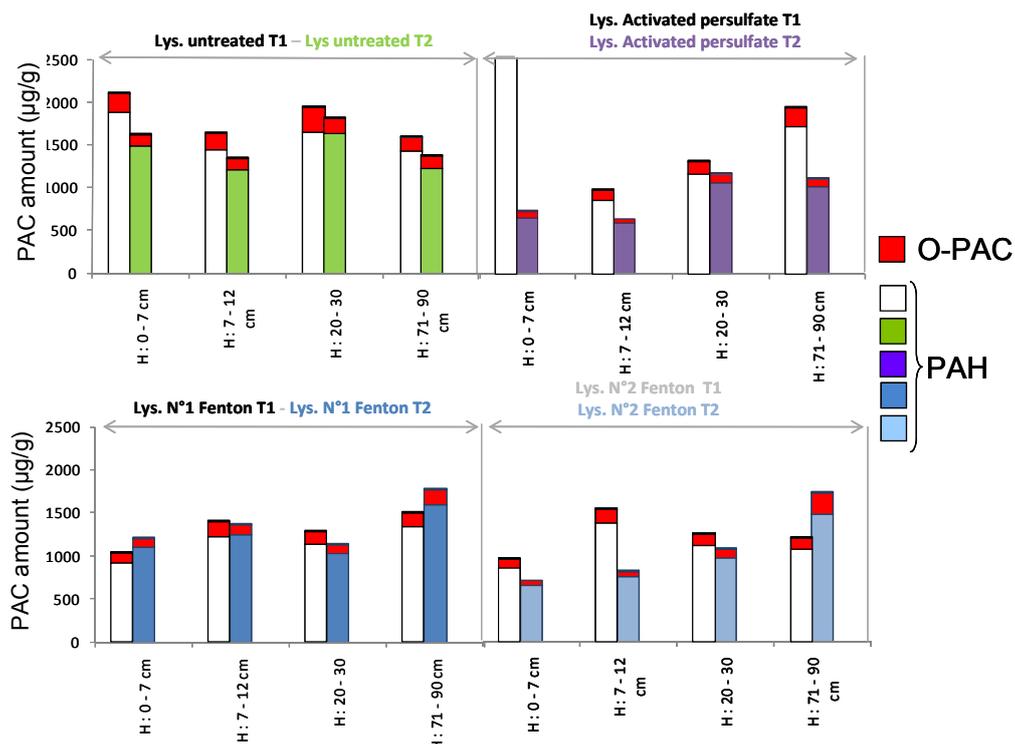


Figure 16. PAC levels at different depths in the lysimeter columns, showing the untreated (top left), the persulfate treated (top right) and the two Fenton treated (bottom) lysimeters. The white bars to the left show the levels immediately after the application of the oxidants and the coloured bars to the right show the levels two years later.

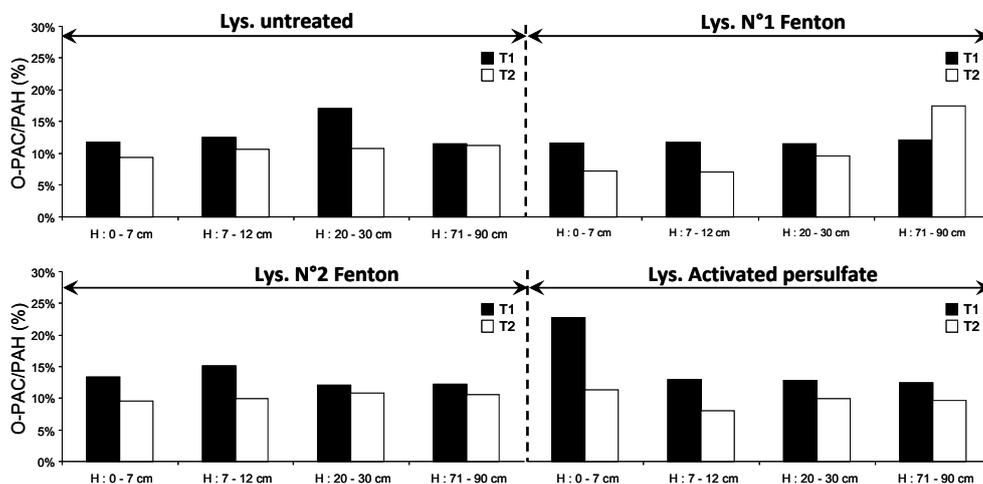


Figure 17. Polar-PAC/PAH ratios at different depths in the lysimeter columns. The black bars show the ratios immediately after the application of the oxidants (T1) and the white bars show the ratios two years later (T2).

In order to further investigate the leaching behaviour of the PACs in the lysimeters, percolation water was collected from the bottom of two of the columns, i.e. the persulfate treated and the reference lysimeters, and was analysed for PACs. However, the results show that the polar PAC proportions in the water were, like in the soil, quite similar for the two columns, with no indication of enhanced leaching as a result of the treatment (Figure 18).

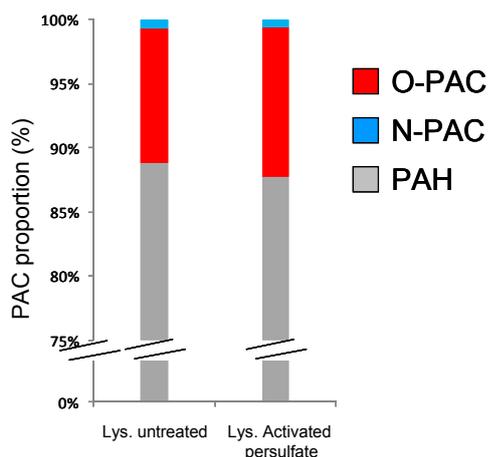


Figure 18. Relative proportions of PAHs, oxy-PAHs and N-PACs in percolation water from the untreated and persulfate treated lysimeter columns

As a next step in the lysimeter studies, some high water infiltration experiments were planned. However, due to the limited effect of the first treatments applied, which was linked to the low contaminant availability in the soil used, these experiments were replaced by controlled lab leaching experiments. These were applied on two contrasted soils, i.e. a gasworks and a coke oven soil, and involved the treatments already used in WP4, i.e. Fenton like oxidation, KMnO_4 -oxidation and biodegradation. The results show a clear increase of polar PACs (oxy-PAHs in particular) in relation to PAHs in the water after all treatments. The increase was highest after the KMnO_4 -treatment, which also gave rise to increased oxy-PAH levels in the soil (Figure 19).

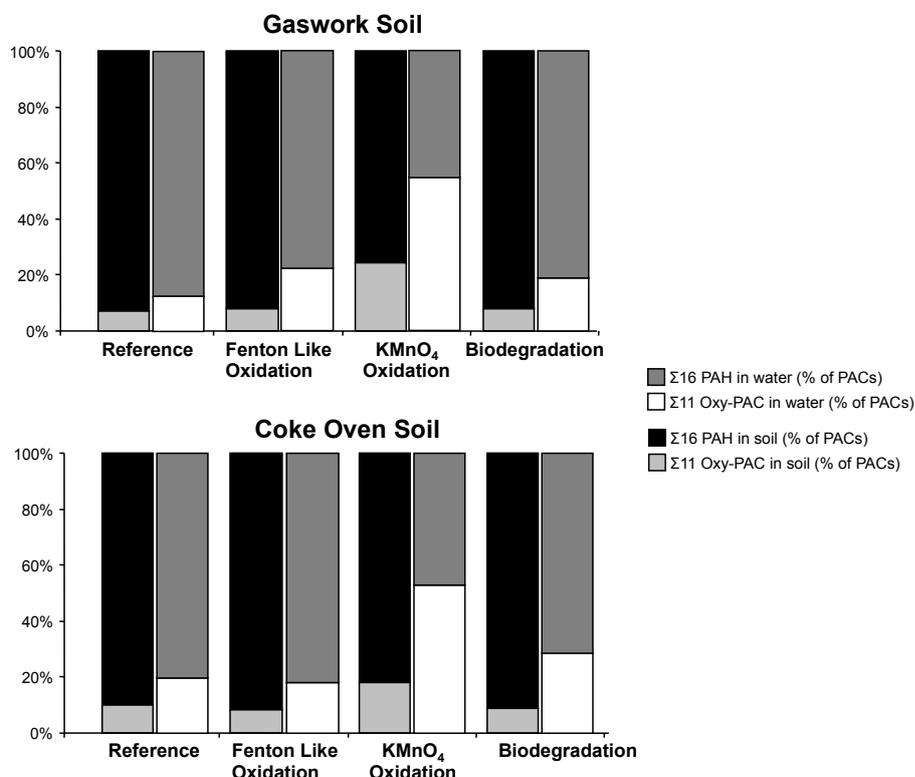


Figure 19. Proportions of $\Sigma 16$ PAH and $\Sigma 11$ Oxy-PAHs in soil and water after various remedial treatments (reference - no treatment, Fenton like oxidation, KMnO_4 -oxidation and biodegradation) of a gasworks and a coke oven soils.

11.3 Project status and deliverables

All deliverables for this WP have been fulfilled, even if a part of the field studies (high water infiltration experiments) were replaced by controlled lab leaching experiments (Table 15). Two peer-reviewed articles directly connected to this WP have been published so far, and two manuscripts are in preparation.

- Arp HP.H., Lundstedt S., Josefsson S., Cornelissen G., Enell A., Allard A-S., Berggren Kleja D. (2014) *Native Oxy-PAHs, N-PACs and PAHs in historically contaminated soils from Sweden, Belgium and France: Their soil-porewater partitioning behavior, bioaccumulation in Enchytraeus crypticus and bioavailability. Environmental Science & Technology 48:11187-11195.*
- Josefsson S., Arp HP.H., Berggren Kleja D., Enell A., Lundstedt S. (2015) *Determination of polyoxymethylene (POM) – water partitioning coefficients for oxy-PAHs and PAHs. Chemosphere 119:1268-1274.*
- Enell A., Lundstedt S., Arp HP.H., Josefsson S., Cornelissen G., Berggren Kleja D., *Comparison of a column leaching test and a passive sampler test for assessment of mobility and partitioning of native oxy-PAHs, N-PACs and PAHs in historically contaminated soils (manuscript in preparation)*
- Boulangé M. et al., *Consequences of chemical and biological remediation treatments on Polar PAC leachability (manuscript in preparation).*

Table 15. Deliverables for WP5 within PACMAN

	Deliverables	Fulfilment and comments
DL5.1	New data on the mobility of polar PACs in soil, including soil-water partitioning coefficients that can be directly used in risk assessment models.	Completed
DL5.2	Report on the leaching of polar PACs and parent PAHs under natural field conditions in lysimeters with various remediation treatments.	Completed
DL5.3	Report on the leaching of polar PACs and parent PAHs under additional irrigation and induced water infiltration in lysimeters with various remediation treatments.	Completed as laboratory experiments.

12 Toxicity and risk assessment of polar PACs – WP6

12.1 Review on the toxicity of polar PACs

The review on the toxicity of polar PACs has been delayed but is under preparation. The work is carried out as a collaboration between Staffan Lundstedt, and three partners within the Polar PAC Network, i.e. Dr. Paul White at Health Canada, Ottawa, Canada, Dr. Benjamin Bandowe at Bern University, Bern, Switzerland and Dr. Kristian Dreij at Karolinska Institutet, Stockholm, Sweden. The data collected so far show that polar PACs may cause a variety of toxic effects in humans and other organisms, and some of those effects are summarized in Table 16. Among the effects observed, some have been measured for individual compounds, but in general it seems to be more common with data for mixtures of polar PACs obtained through fractionation of authentic sample extracts. In many of those studies the fractions containing the polar PACs have been found to be among the most toxic ones. However, some data have also been found for individual polar PACs, and to exemplify this, a summary of the information collected for oxy-PAHs is given below.

Table 16. Some toxic effects observed for polar PACs, as individual compounds or in mixtures, and references to relevant studies.

Toxic Effects	References
Acute toxic effects on aquatic and terrestrial organisms	Brack et al. 2003, Lampi et al 2006, Xie et al. 2006
Effect on growth and reproduction	Mallakin et al. 1999, Paumen et al. 2009, Kobeticova et al 2008, 2011
Cytotoxicity to human cells	Zhu et al. 1995, Shang et al. 2014
Endocrine disruption	Kurihara et al. 2005, Fertuck et al. 2001
Oxidative stress	Shimada et al. 2004, Kumagai et al. 2002
Genotoxicity, mutagenicity and carcinogenicity	Durant et al. 1996, Brack et al. 2003, Arlt et al. 2008, Sen and Field 2013

12.1.1 Oxy-PAHs

Oxy-PAHs have been observed to cause a variety of adverse effects, in a wide range of organisms [Lundstedt et al 2007]. For example, acute toxic effects, such as lethality and cytotoxicity, have been observed in bacteria, invertebrates, plants, fish, and mammalian cells [Brack et al. 2003, Lampi et al. 2006, Mallakin et al. 1999, McConkey et al. 1997, Shang et al. 2014]. In addition, genotoxic and mutagenic effects have been observed in bacterial, fish and mammalian cells system [Dasgupta et al. 2014, Hu et al 2007, Lynes 2006, Sen and Field 2013] endocrine effects in yeast and mammalian cells [Hashimoto et al 2007, Kurihari et al 2005, Machala et al. 2001], and developmental effects in fish embryos [Knecht et al. 2013]. Common for these effects are that most of them seem to be initiated by oxidative stress in the cells. It is well known that PAH quinones can induce redox cycling that may lead to the generation of reactive oxygen species (ROS) and subsequently oxidative stress [Bolton et al 2000], but it seems like also the PAH ketones may induce similar ROS formation in cells [Knecht et al. 2013, Westman et al. 2014]. The ROS may react with cellular macromolecules, such as lipids, proteins and DNA, and thereby cause functional or genetic damage to the cell, which may lead to cytotoxic and mutagenic effects for instance [Kumagai et al 2002, Shang et al. 2014]. The effects are generally reduced in the presence of antioxidants, such as N-acetyl cysteine (NAC) [Reed et al 2003, Shang et al. 2014], which further supports the theory that oxidative stress is involved. Many of the effects observed are also believed to be mediated through activation of the aryl hydrocarbon (Ah) receptor with subsequent induction of cytochrome P450 monooxygenases (CYP) and other downstream targets

[Nebert et al. 2004]. The oxy-PAHs are probably weaker receptor activators compared to unsubstituted PAHs, but they are still active [Larsson et al. 2014, Misaki et al. 2007].

Oxy-PAHs have also been shown to cause developmental effects in zebra fish with yolk sac edema and body axis curvature as the most prominent effects, which are similar to the effects caused by the dioxin TCDD [Knecht et al. 2013]. Even these effects were shown to be mediated through the Ah receptor pathway, and most likely with involvement of oxidative stress. Furthermore, oxy-PAHs present in river sediments and coastal waters have been shown to exert estrogenic activity in yeast and mammalian cells, which potentially can lead to endocrine disruption during development [Hashimoto et al. 2007, Kurihara et al. 2005, Machala et al. 2001]

The potencies of oxy-PAHs vary from compound to compounds as well as with the toxicological end point studied. However, the structure of the compounds seems to play an important role. For example, ortho-quinones (e.g. 9,10-phenanthrene quinone) are generally more toxic than para-quinones (e.g. 1,4-phenanthrene quinone) [Hatae et al. 2013, Motoyama et al. 2009], which probably is connected to the finding that ortho-quinones generally are more potent inducers of oxidative stress [Reed et al. 2003, Shang et al. 2014]. This has been detected in different test systems as higher levels of hydrogen peroxide production and intracellular calcium, depletion of glutathione and reaction with cellular thiols leading to damaged cellular macromolecules [Kubatova et al. 2006, Kumagai et al. 2002, Motoyama et al. 2009, Shang et al. 2014, Taguchi et al. 2007]. In many cases, the oxy-PAHs are more toxic than their corresponding PAHs (parent PAHs). For example, there are several studies showing that photolytic oxygenation of PAHs may result in transformation products (including oxy-PAHs) that are more toxic to aquatic and terrestrial plants [Mallakin et al. 1999, McConkey et al. 1997], marine bacteria [Brack et al. 2003] and aquatic invertebrates [Lampi et al. 2006, Xie et al. 2006] than the parent PAHs. There are also studies showing that oxy-PAHs may have higher estrogenic activity than their corresponding PAHs [Kurihara et al. 2005, Machala et al. 2001]. However, when it comes to mutagenic activity, oxy-PAHs are generally less potent than the unsubstituted PAHs [Durant et al. 1996, Lynes 2006], although there are some studies showing the reverse [Brack et al. 2003, Sakai et al. 1985]. It should also be noted that oxy-PAHs do not always require exogenous mammalian metabolic activation to manifest their mutagenicity in bacterial systems but appear to react with DNA and other macromolecules directly. Unsubstituted PAHs, on the contrary, always require such metabolic activation to induce a mutagenic response [Pickering 1999].

12.2 Project synthesis

From the toxicity review summarized above it is obvious that several polar PACs are considerably toxic and may constitute a hazard to exposed humans and organisms. The question is to what extent humans and organisms are exposed, and whether polar PACs have to be considered, assessed and managed separated from the PAHs at PAC contaminated sites. This is what PACMAN has been all about, i.e.:

- to elucidate to what extent polar PACs add extra risk to PAC contaminated sites
- to provide suggestions how this potential risk can be managed and reduced

12.2.1 Occurrence and distribution of polar PACs

The data collected and produced within PACMAN confirms that polar PACs, like other PACs, are highly relevant contaminants in the environment in general, and at certain contaminated sites in particular. The inventories performed within the project show that Sweden and France most likely house more than 1000 PAC contaminated sites each, and that this number probably would be a lot higher if all potentially PAC contaminated sites were included. Hence, severe PAC contamination is, as expected, a frequently occurring environmental problem in both Sweden and France, and there is

no indications that these two countries are unique in this sense, not in Europe nor compared to countries in the rest of the world.

Furthermore, the data on PAC levels generated within PACMAN show like previously existing data that polar PACs constitute a significant fraction of the total PAC-load at many contaminated sites. Although the polar PAC levels often are correlated with the PAH levels, which would indicate that the compounds classes can be assessed together, there are exceptions to this. Sometimes the relative proportions of polar PACs may be higher, which would result in a larger risk contribution from these compounds. This seems to be particularly common in somewhat less contaminated environments, e.g. urban areas, and may be due to secondary formation of polar PACs (e.g. oxy-PAHs) as the PACs are transported away from the primary source of emission or a hot spot. This can also be observed at the outskirts of a contaminated area where the total levels are lower.

Furthermore, groundwater can potentially be enriched in polar PACs as compared to the proportions found in the soil at a site. This have been observed in some previous studies, especially for N-PACs, and also to some extent in the studies performed within PACMAN. Higher proportions of the more water soluble LMW PACs were thus observed in the groundwater at PAC contaminated sites, and also a clear enrichment of N-PACs overall. However, no clear enrichment of oxy-PAHs compared to PAHs was observed, despite the oxy-PAHs' higher water solubilities. This could be due to DOC and colloid facilitated transport of the more hydrophobic PAHs, selective interactions between soil and the oxy-PAHs reducing their leachability, and a more efficient degradation of oxy-PAHs in the water. The importance of these processes are probably varying from soil to soils and from situation to situation, considering that enhanced leachability of oxy-PAHs, compare to PAHs, has been observed during previous leaching experiment in the lab [Lundstedt et al. 2007].

On the other hand, during the leaching experiments performed within PACMAN, only small differences were observed between the compound classes like between LMW and HMW PACs in general. This indicates that the leaching processes were strongly influenced by DOC and colloids that enhanced the "dissolution" and mobility of the more hydrophobic compounds. This DOC and colloid facilitated transport is probably an important factor in the field as well, although the difference observed between the N-PACs and the oxy-PAHs in field suggest that other processes also contribute. A more pronounced degradation of oxy-PAHs, compared to N-PACs, in the groundwater would at least partly explain this difference. In the leaching test the degradation was reduced with biocides which can explain the more similar results obtained for N-PACs and oxy-PAHs in these experiments.

Likewise, the POM experiments performed in the lab, in the presence of a biocide, showed that both oxy-PAHs and N-PACs potentially can be more available for uptake in organisms in accordance with their higher water solubilities, while the comparison between filtered and non-filtered groundwater showed a less clear picture. The N-PACs were indeed, like LMW PACs in general, largely distributed in the dissolved phase, but when comparing PAHs and oxy-PAHs of similar structures the difference was not large. This would agree with the hypothesis that dissolved oxy-PAHs are more easily degraded than both PAHs and N-PACs.

Water living organisms, such as mollusc, should be most extensively exposed to the dissolved fraction of the contaminants, which for PACs generally would mean LMW compounds. For the molluscs collected near the Swedish wood preservation sites, the observed oxy-PAH and N-PAC profiles agreed fairly well with this theory. These profiles were thus quite similar to those in the dissolved fraction of the groundwater, containing mainly LMW oxy-PAHs and carbazole as the dominant N-PAC. However, the PAH profile in the molluscs was more similar to that in the soil with MMW PACs as the dominant compounds. The reason to this is probably that the observed profile in the molluscs is a combination of what they take up and what they accumulate. LMW 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 MMW PACs. For the oxy-PAHs and N-PACs, other processes might be involved as well, such as enhanced metabolism and excretion of specific compounds.

12.2.2 Formation of polar PACs during remediation

When it comes to the risk that polar PACs (oxy-PAHs) may be formed as PAC contaminated sites or material are remediated, this is only of concern when a method based on PAC degradation or transformation is involved, e.g. biodegradation, chemical oxidation and thermal treatment. When extraction or separation based technologies are used, e.g. solvent washing and thermal desorption, such formation should not be an issue. On the other hand, one should be aware of that the extraction and separation efficiencies may differ between compounds and compound classes, and also that extraction and separation technologies are not solving the problem permanently, but are only moving it somewhere else. For the degradation based technologies studied within PACMAN, i.e. H₂O₂-oxidation, a Fenton like oxidation, KMnO₄-oxidation and a bioslurry treatment, polar PAC formation was mainly observed when the PAH depletion was intense. This means that the PAC production was most pronounced during the early hours of the KMnO₄-oxidation of soils from a gasworks and a wood treatment site, and was mainly observed as a generally slower depletion of oxy-PAHs as compared to PAHs, and also in some cases as an actual increase of some individual oxy-PAHs. The reasons behind this relatively intense PAH depletion combined with oxy-PAH formation in these specific treatments were that KMnO₄ is a relatively strong and efficient oxidant and that the PACs were more available in these soils than in the third soil studied, which came from a coke oven site. In fact, availability was a key factor in all these experiments, which limited the degradation rates on the one hand but also the formation and accumulation of oxy-PAHs on the other hand.

Hence formation and accumulation of oxy-PAHs seems mainly to be a problem during harsh oxidation conditions when the degradation rate is strongly enhanced. 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 PAC will be degraded if the process degrades PAHs, even though the oxy-PAH depletion may be a bit delayed.

12.2.3 Cost benefit analysis

It is difficult to say exactly how much more risk that will be identified and captured by considering polar PACs in addition to the PAHs at PAC contaminated sites. The polar PACs will indeed add extra risk to the sites, but a large part of it will probably be captured and taken care of even if the risk assessment and remediation is based on PAH data only. However there are some circumstances where risks caused by polar PACs may be overlooked if they are not specifically considered:

- 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.

The PACMAN project has not come up with any alarming results, in terms of polar PAC levels that are evolving extremely different from the PAH levels, for any of these situations, but indications of potential problems have been observed for all of them. A certain enrichment of N-PACs has thus been observed in surface- and groundwater as well as in deeper soil layers in the investigations performed within PACMAN, and even if no such enrichment was seen for oxy-PAHs in this project it has been observed in previous studies. However, generally it seems like the oxy-PAHs are more subjected to degradation processes in the groundwater than N-PACs and PAHs. In previous studies, it has also been observed that soils highly influenced by exhaust gases and soils in which the PACs have been subjected to atmospheric transformation processes to a large extent contain larger proportions of oxy-PAHs than heavily contaminated soils. This can at least partly be explained by an atmospheric

transformation of PAHs into oxy-PAHs, while being airborne, and can be relevant also for the PAC profiles found at the outskirts of a contaminated area to which the contaminants mainly have come via dusting and evaporation/condensation processes. Furthermore, the results produced within PACMAN show, like some previous studies, that there is a clear risk for oxy-PAH formation and accumulation if remediation techniques based on PAC degradation are used. This risk is probably maximized if a powerful oxidation technique is used that will accelerate the PAH depletion greatly, but the risks exists for other degradation techniques as well, e.g. biodegradation. Although the oxy-PAHs most often will be degraded as well if the process is run long enough, it is important to verify that this actually happens and to make sure when the process can be safely terminated.

Based on these facts it would be suggested to first of all include a number polar PACs among the analysed compounds during risk assessment and remediation of PAC contaminated sites. This is of particular importance for surface- and groundwater samples, samples from environments that may have been contaminated by such waters (e.g. sediments, biota etc.), samples of deeper soil layers, samples from the outskirts of a contaminated site, and not least samples from remediation process that involve PAC degradation. In some situations, it may then be necessary to make a more extensive treatment of contaminated waters, to dig deeper and wider in the soil at some sites, and to run degradation processes a bit longer, to make sure that also the polar PACs are properly taken care of.

How much extra this will cost will of course vary from site to site, but generally the first step that includes a more extensive analysis, would probably only lead to a moderate increase of the cost. As a rough estimate the price for each sample in which also polar PACs are analysed will be doubled. However, polar PACs do not have to be analysed in all samples, but only in those mentioned above. On the other hand, in some cases, extra samples may have to be collected (of water for instance) but most often these samples are collected anyway during the delimitation of the contaminated area. If then the polar PACs turn out to be a separate problem in one of the aforementioned situations, the subsequent remediation might be somewhat more costly, depending on the extra measures that need to be taken. For example, if extra water treatment is needed - that will add an extra cost; if a more extensive excavation is needed - that will add another cost; and finally if treatment processes have to be run for a longer time - this is adds another additional cost. However as a general judgement, measures already taken for PAHs will most often be enough to also capture the polar PACs, but it is important to make sure that this is the case in each individual situation.

The resources available within PACMAN were too limited to perform a full cost-benefit analysis (CBA) of the option to include polar PACs in the risk assessment and remediation of PAC contaminated sites, It was therefore here limited to the discussion above. However, in appendix 1, an example of a simplified CBA in which the potential impacts of taking polar PACs into account in the remediation decision process is also given. This simplified CBA was based on some case study sites, but since the supporting data from these sites were sparse it was mainly performed with generic data. Critical factors that were identified were:

- Whether polar PACs are still resident in the soil, and if the can be transferred to groundwater, which affects the risks for health impacts. If their mobility is large, their potential impacts may also be extended beyond the site boundaries.
- Whether contaminated groundwater must be remediated or not, i.e. if polar PACs have reached it. The cost of water remediation exceeds by far the cost of soil remediation.

12.3 Project status and deliverables

All deliverables for this WP have been more or less fulfilled (Table 16). The review on the toxicity of polar PACs has been delayed, but is in progress and data collected in the process are included in this report and the overall synthesis of the project. The publication most directly connected to this WP is

the toxicity review, which is in preparation. However, several other publications with connections to this WP have been published during the project (see below)

- Niziolek-Kierecka M., Dreij K., Lundstedt S., Stenius U. (2012) *γH2AX, pChk1 and Wip1 as potential markers of persistent DNA damage derived from Dibenzo[a,h]pyrene and PAH-containing extracts from contaminated soils*. *Chemical Research in Toxicology* 25: 862-872.
- Arp HP.H., Lundstedt S., Josefsson S., Cornelissen G., Enell A., Allard A-S., Berggren Kleja D. (2014) *Native Oxy-PAHs, N-PACs and PAHs in historically contaminated soils from Sweden, Belgium and France: Their soil-porewater partitioning behavior, bioaccumulation in *Enchytraeus crypticus* and bioavailability*. *Environmental Science & Technology* 48:11187-11195.
- Lemieux C.L., Long A.S., Lambert I.B., Lundstedt S., Tysklind M., White P.A. (2015) *In Vitro mammalian mutagenicity of complex polycyclic aromatic hydrocarbon mixtures in contaminated soils*. *Environmental Science & Technology* 49: 1787-1796.
- Lemieux C.L., Long A.S., Lambert I.B., Lundstedt S., Tysklind M., White P.A. (2015) *Cancer risk assessment of polycyclic aromatic hydrocarbon contaminated soils determined using bioassay-derived levels of benzo[a]pyrene equivalents*. *Environmental Science & Technology* 49: 1797-1805.
- Wincent E., Jönsson M.E., Bottai M., Lundstedt S., Dreij K. (2015) *Aryl hydrocarbon receptor activation and development toxicity in zebrafish in response to soil extracts containing unsubstituted and oxygenated PAHs*. *Environmental Science & Technology* 49: 3869-3877.
- Lundstedt S., Dreij K., Bandowe B.A.M., White P.A. *Toxic effects of polar Polycyclic Aromatic Compounds*. (manuscript in preparation).

Table 16. Deliverables for WP6 within PACMAN

	Deliverables	Fulfilment and comments
DL6.1	A review paper describing the toxic effects of polar PACs in humans and the environment.	Initiated but delayed.
DL6.2	A synthesis of the project focusing on knowledge gaps that have been filled as well as those that remains to be filled in order to perform proper risk assessments of PAC-contaminated sites, and to assess the usefulness and risk of different remediation methods.	Fulfilled
DL6.3	A cost-benefit analysis of including polar PACs in the process of risk assessment and remediation of PAC-contaminated sites.	Fulfilled

13 Conclusions

The overall objectives of PACMAN was to increase the knowledge pertaining to polar PACs in order to elucidate to what extent these compounds add extra risk to contaminated sites, and to provide suggestions how this risk can be managed and reduced.

The project show that polar PACs are highly relevant environmental contaminants that are particularly abundant at certain industrial sites, e.g. sites of former gasworks, coke oven plants, wood treatment facilities and wood tar factories . At many of these sites the polar PACs constitutes a significant fraction of the total PAC load, and their levels are not always correlated with the PAH levels. Larger proportions of polar PACs may, for example, be found in surface and groundwater at PAC contaminated sites, in deeper layers of the soil at the sites, and at the outskirts of the contaminated areas. Furthermore, 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 or even accumulate in the process due to a simultaneous formation of oxy-PAHs via oxidation of PAHs. 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 analysed compounds as PAC-contaminated sites are risk assessed and remediated. 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 analysing 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

The risk assessment and possible remediation of the contaminated site have then to be adapted to the results obtained for the polar PACs, in addition to the results for the PAHs, which in the worst case might lead to a more extensive excavation of the site, a more extensive water treatment program, and a prolongation of the treatment times when remediation processes based on PAC degradation are used. However, based on the results generated within PACMAN, this will seldom be necessary.

The polar PACs to monitor could be those that were analyzed 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 sizes, in order to embrace the whole range of the polar PACs' physico-chemical properties. Likewise, it would also be suggested to include one or two HMW N-PACs among the selected compounds. A suggested selection would be:

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)

Due to limited resources, no nitro-PAHs and oxy-PAHs were studied within PACMAN. However, according to previous investigations these compounds are most likely less relevant for PAC contaminated sites.

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Appendix 1 - Cost benefit analysis

A1.1 Introduction

The following section is an attempt to a cost-benefit analysis (CBA) of the option to include polar PACs in the process of risk assessment and remediation of PAC contaminated sites. The analysis will focus on the extra costs that may arise as a result of more expensive analyses, more extensive excavations etc., as well as the benefits gained in terms of additional risk that possibly may be identified and described; all as a result of the inclusion of polar PACs in the assessment process. However, due to the limited resources in this project, the CBA is performed on a rather general level, with the aim to identify key factors that may influence the scenario.

A1.1.1 Decision support tools

It is difficult to compare remediation scenarios. For polar PACs we typically face a complex issue, with conflicting factors affecting the decision. Decision support tools are commonly used for contaminated sites, to guide decision makers towards an optimal site management scenario.

There are many decision support tools to manage "hardly comparable" scenarios (CLARINET, 2002). The main analytical tools for decision support are: environmental risk assessment, life cycle analysis, cost-benefit analysis, multi-criteria analysis, multi-attribute analysis (CLARINET, 2002).

Environmental risk assessment is the process of reviewing risks for ecosystems, animals, people and other receptors (groundwater, buildings). Health risk assessment is a decision support tool commonly used in the context of potentially contaminated sites management in many countries (CLARINET, 2002).

Life cycle analysis (LCA) determines the environmental impacts caused by a service or a product, throughout its life. In the case of a product, it evaluates the impact on the environment associated with primary materials and the energy needed to manufacture the product, waste, emissions generated and potential environmental impacts. In the polar PACs context, the analysis of the life cycle can be applied to remediation scenarios. This method should help defining the remediation technique which has minimal impact on the environment (nuisances, required products, waste, etc.).

Cost-benefit analysis (CBA) is an economic tool aimed at determining whether the benefits of an investment, policy or choice outweigh the costs or not. Decision making in many countries is now often seen as a balance between costs and benefits. When applied to mega-sites, remediation work must show a net profit over costs. Costs are considered also from an environmental perspective and an economic and social point of view. Some factors, such as social or environmental impacts, are a priori not be quantified monetarily and sustainably. Economists, however, can monetise them by associating each of their values with a confidence interval.

Cost-effectiveness analysis (CEA) is a simplified version of the CBA and is the analysis of cost effectiveness. The benefits are not estimated monetarily, but as individual scores. An overall rating is assigned to profits then divided by the cost to measure effectiveness (Beranger et al., 2006).

Multi-criteria analysis (MCA) is often used in decision making. Where the decision maker is faced with several possible scenarios, he defines a set of criteria to evaluate them. For polluted sites management, the evaluation criteria are complex and often conflicting (technical, environmental, economic, social, and legal). No scenario will be evident for all parties, because no scenario will offer the best performance for all criteria. The very purpose of MCA is then to define the scenario that best satisfies a set of potentially conflicting criteria. MCA considers all the criteria to be considered in

choosing a scenario, assigns each a weight according to its relative importance, and a note for each scenario compared to all criteria, and finally aggregates the result (NATO / CCMS Pilot Study, 2000). There are three major families of MCA tools: complete aggregation, partial aggregation, local aggregation. They all take into account costs, health and environmental risks, societal values associated with the benefits of rehabilitation, technical feasibility, etc. They differ in how are compared different scenarios to be classified.

In our study, we will consider cost-benefit analysis (CBA).

A1.1.2 General approach

A generic guidance has been developed for the transparent and consistent assessment of the costs and benefits for remediation of land contamination (Postle, et al., 1999). This guidance supports a primary model procedure entitled Evaluation and Selection of Remedial Measures (DETR, 2000), and it provides a framework by which the costs and benefits of two or more options for the remediation of a contaminated site can be assessed. In this framework the level of assessment builds in sophistications moving from Step I to Step IV, with assessment carried out for previous steps feeding into the work required by subsequent steps reducing duplication of efforts. Generally, as the complexity of site conditions and potential remediation techniques increase, so will the need for more detailed assessment requirements. The steps provide a logical and clear pathway toward identifying the preferred remedial option and they allow site specific issues to be taken into account (Figure A1-1)

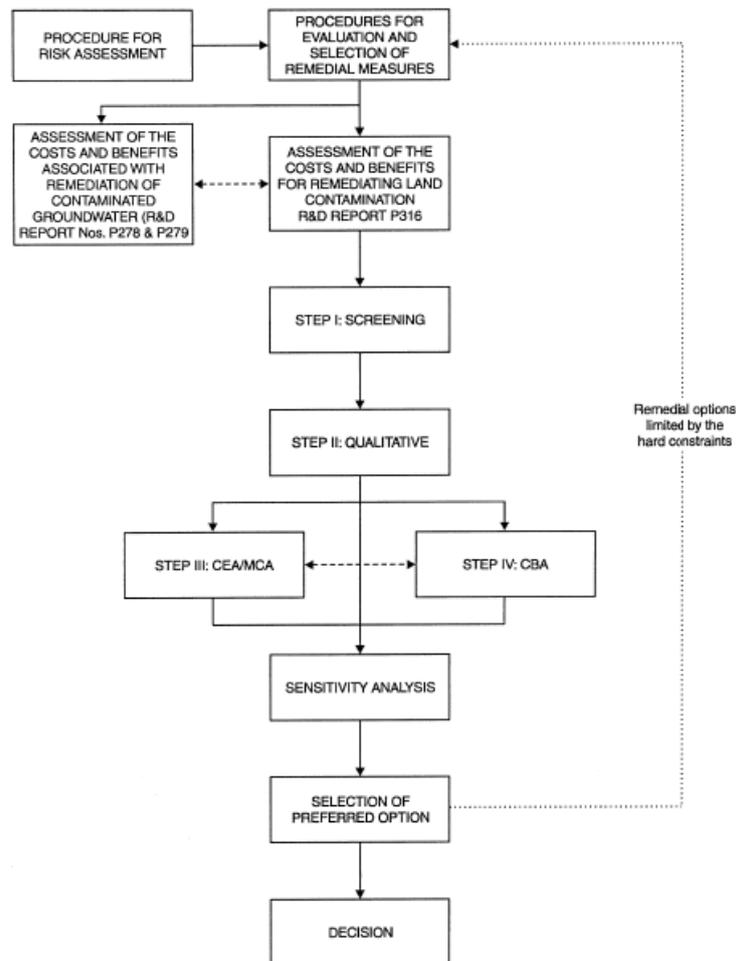


Figure A1-1. Inter-relationship between other relevant guidance and the steps in the assessment of costs and benefits for remediating land contamination (Postle, et al., 1999)

Steps I and II involve the identification of impacts, with Step II including a simple CEA. Steps III and IV examine the significance of impacts in more details through the use of scoring and weighting and monetary valuation. Step V involves undertaking sensitivity analysis which then leads to selection of the preferred option, or may result in a review of the hard constraints set when following through the Evaluation and Selection of Remedial Measures Model Procedure.

A1.2 Application to Polar PACs contaminated soils

By applying this framework the most cost effective option could be recommended for the remediation of PAC contaminated sites including polar PACs. The most cost effective option is that which meets a single objective at the lowest costs or which provides the greatest level of net benefit per unit of expenditure (UK Environmental Agency, 1999). Site specific factors can easily be built into the assessment. Outputs from the risk assessment for polar PACs at PAH contaminated sites provided from the project can be used.

Within WP6 the first step of the framework (Step I), an initial screening step was performed, to examine the characteristics of the contamination problem of PACs including polar PACs. The objective of this Step I was to determine which of the main appraisal methods is the most appropriate for a site. The screening methodology is composed of an analysis of the data availability for selected sites followed by the main assessment. The outcome of this step will not be an indication as to which remediation option is preferred, but as to the detail what is likely to be required to allow the preferred option to be clearly determined. Step I considers site details in terms of land use, the types of remedial options that can be used and the amount of time available for remediation. Data requirements for this step are modest with only very general data being required including the proposed end use of the site, the number of potential remedial options (this is broken down in approaches and techniques, where approaches cover a risk management type approach and techniques look at the technical detail), scale issue- time constraints, costs, etc. and the degree to which a remedial option can meet the remedial objectives. The results of WP3, WP4 and WP5 from the risk assessment of PAC contaminated sites gained during the project were used to compile necessary site specific data and data on remediation techniques, respectively.

A1.3 Application of the screening methodology

A1.3.1 Main relevant data from WP4 and WP 5

Data collected from WP4 suggest that in general, polar PACs were removed more slowly than PAHs in all chemical treatments, indicating either that polar PACs were more persistent or (which is more likely) that there was a simultaneous formation of these compounds during the oxidation. For biological techniques, polar PACs were found to follow a similar trend as PAHs in coke oven soils and in gasworks soil, with a lower removal rate of polar PAC in the coke oven soil. However, for these compounds the removal rate was even lower in the wood preservation soil.

Data collected from WP5 (oxidation in lysimeters) show that polar PACs were somewhat more efficiently removed than the PAHs during the treatment period, while no indication of formation or increased leaching of polar PACs could be observed. However, a weak decrease in the relative polar PAC levels could be observed at most depths in all columns after the two years treatment period. These results indicate that the polar PACs were somewhat more efficiently removed than the PAHs during the treatment period, while no indication of formation or increased leaching of polar PACs could be observed.

A1.3.2 Selection of the sites and background details

The screening methodology was applied to two sites in France which were selected as case studies since they were addressed in all WPs of the project: an ancient gas works site (case study 1) and a coke oven site (case study 2). At both sites, the concentrations of PAHs and polar PACs were determined (WP3), different treatment techniques were tested with soil collected from those sites (WP4) and leaching experiments were performed after treatment (WP5).

Data for the two sites (gas works and coking plant) are not sufficient to properly unwind the CBA method in full.

Therefore, both sites were treated as fictitious cases based on the following data:

- Treatment of PACs taking in consideration only the 16 regulated PAHs (following the current regulatory practice),
- Treatment of PACs taking in consideration (N, S, O) polar PACs existing in the initial pollution and newly formed (during cleanup).

Note that these two cases can be met only if i / PACs have accepted toxicological values and ii / PACs are taken into account by the regulations of the countries (reference levels).

Also, the two following schematic situations were taken into account:

- Case 1: Pollution does not reach the roof of the aquifer (pollution confined in the unsaturated zone)
- Case 2: Soil pollution affecting groundwater.

A1.3.3 Prescreening

The main techniques for the treatment of PAHs, and thus for polar PACs, are summarised in Table A1-1 below (UK Environment Agency, 2004).

Potentially applicable remediation techniques are:

1. Containment
2. Biological remediation in situ and ex situ
3. Solvent flushing or soil washing
4. Phytoremediation
5. Chemical oxidation
6. Thermal treatment (incineration and thermal desorption).

Phytoremediation and solvent flushing/soil washing are not commonly used until now.

Currently, in France, the management of PAH polluted sites is, for financial reasons, often carried out using thermal treatment (incineration, desorption), chemical oxidation, containment, restrictions of use, and for lower concentrations, biological treatment (ADEME, 2009; Basias, 2010; Basol, 2010).

Thereby, treatment of soils polluted by high concentrations of PAHs is essentially based on thermal processes: incineration for tar phases ; thermal desorption for total hydrocarbon concentrations greater than 40000 - 50000 mg/kg, and for lower concentrations, chemical oxidation or biodegradation (only lower concentrations for the latter) (UK Environment Agency, 2004; ADEME, 2009 ; Colombano et al., 2010).

Table A1-1: Remediation Option Applicability Matrix: Organic Substances (UK Environment Agency, 2004)

REMEDIATION OPTION APPLICABILITY MATRIX: ORGANIC SUBSTANCES								
Remediation option	Applicable media	Applicable substances						
		VOCS	Halogenated hydrocarbons	Non-halogenated hydrocarbons	PAHs	PCBs	Dioxins and furans	Pesticides and herbicides
CIVIL ENGINEERING METHODS								
Containment – cover systems	S	✓	✓	✓	✓	✓	✓	✓
Containment – hydraulic barriers	W	✓	✓	✓	✓	✓	✓	✓
Containment – In-ground barriers	S, W	✓	✓	✓	✓	✓	✓	✓
Excavation and disposal	S	✓	✓	✓	✓	✓	✓	✓
BIOLOGICAL METHODS								
Natural attenuation	W	✓	✓	✓	✓	x	x	✓
Biopiles	S	✓	x	✓	✓	x	x	✓
Bioventing	S	✓	✓	✓	✓	x	x	x
Biosparging	S, W	✓	✓	✓	✓	x	x	✓
Landfarming	S	✓	x	✓	✓	x	x	✓
Slurry phase biotreatment	S	✓	✓	✓	✓	x	?	✓
Windrow turning	S	✓	x	✓	✓	x	x	✓
CHEMICAL METHODS								
Chemical oxidation	S, W	✓	✓	✓	✓	x	x	✓
Chemical dehalogenation	S	✓	✓	x	x	✓	✓	x
Soil flushing	S	✓	✓	✓	✓	x	x	x
Solvent extraction	S	✓	✓	✓	✓	✓	✓	✓
Surface amendments	S	x	x	x	x	x	x	x
PHYSICAL METHODS								
Dual phase SVE	S, W	✓	✓	✓	x	x	x	x
Air sparging	W	✓	✓	✓	x	x	x	x
Soil vapour extraction (SVE)	S	✓	✓	✓	x	x	x	x
Permeable reactive barriers (PRBs)	W	✓	✓	✓	✓	✓	✓	✓
Soil washing	S	x	✓	✓	✓	✓	x	✓
STABILISATION AND SOLIDIFICATION METHODS								
Hydraulic binders (e.g., cement)	S	x	x	?	✓	✓	✓	?
Vitrification	S	✓	✓	✓	✓	✓	✓	✓
THERMAL METHODS								
Incineration	S	✓	✓	✓	✓	✓	✓	✓
Thermal desorption	S	✓	✓	✓	✓	✓	x	✓

Thereby, treatment of soils polluted by high concentrations of PAHs is essentially based on thermal processes: incineration for tar phases ; thermal desorption for total hydrocarbon concentrations greater than 40000 - 50000 mg/kg, and for lower concentrations, chemical oxidation or biodegradation (only lower concentrations for the latter) (UK Environment Agency, 2004; ADEME, 2009 ; Colombano et al., 2010).

Nevertheless, the adequate treatment must be chosen depending on PAHs concentrations in soils and on the targeted efficiency.

CBA simulations will thus be performed taking into account the following treatment processes: confinement, chemical oxidation, biological and thermal treatments.

A1.3.4 Costs

Costs are presented in Table A1-2 for the main remediation technologies. They are valid for France but are similar to those in other European countries.

Table A1-2: Costs of the main remediation techniques (Adapted from Colombano et al., 2010)

Technologies		Units	Costs (lower range)	Costs (low average)	Costs (high average)	Costs (higher range)
In situ remediation technologies (with on site or off site treatment of the recovered product)						
Physical methods (pollution evacuation)	Venting	€/t (soils)	15	18	25	50
	Slurping	€/m ³ (pumped/treated water)	25	27	35	65
	Sparging	€/m ³ (in situ treated water)	15	20	32	55
	Pump and treat (depth<20m)	€/m ³ (pumped/treated water)	4	13	20	60
	Pumping well (depth between 5 to 15m)	€/well	2000	3000	4000	6000
	Skimming - without any other treatment (depth<15m)	€/m ³ (pumped/treated water)	5	15	28	60
Physical methods (pollution trapping)	Cover systems - Non waterproof Landfill Cap (without revegetation) (depth< 0,6m)	€/m ² cover	5	8	13	20
	Cover systems - Waterproof Landfill Cap (depth<1m)	€/m ² cover	30	40	50	60
	Vertical Barriers - Slurry trenches, slurry walls, underground barriers (depth <15 m)	€/m ² vertical barriers	75	140	175	400
	Containment (in situ) (depth<15 m)	€/t (soils)	15	20	30	150
	Hydraulic containment techniques without wastewater treatment (depth<15m)	€/m ³ (pumped/treated water)	2	10	15	40
	Physico-chemical stabilization	€/t (soils)	50	70	105	160
Chemical methods	In situ soil flushing	€/t (soils)	20	45	65	120
	Chemical oxydation/reduction - groundwater	€/m ³ (in situ treated water)	30	40	60	115
	Chemical oxydation - soils	€/t (soils)	40	45	65	95
Thermal methods	Chemical reduction - soils	€/t (soils)	30	60	85	120
	In situ thermal desorption	€/t (soils)	70	105	140	155
Biological methods	Enhanced natural biodegradation	€/m ³ (in situ treated water)	25	28	40	60
	Bioventing	€/t (soils)	15	18	30	50
	Biosparging	€/m ³ (in situ treated water)	15	20	32	55
	Monitored natural biodegradation	€/m ³ (in situ treated water)	12	20	25	65
	Phytoremediation - phytoextraction (without intake of soil)	€/m ² (in situ treated soils)	18	25	34	40
	Phytoremediation - phytostabilisation (without intake of soil)	€/m ² (in situ treated soils)	2	4	7	12
Others	Permeable reactive barrier	€/m ² (area of the barrier)	150	410	480	3 000
On site or off site remediation technologies (without transport costs for the off site treat)						
Physical methods (pollution evacuation)	Excavation (classical methods)	€/m ³ (excavated soils)	5	7	13	50
	Separation (on site or off site)	€/t (soils after excavation)	8	16	25	80
	Soil washing (on site or off site)	€/t (soils after excavation)	35	45	55	100
	Soil washing and chemical extraction (off site)	€/t (soils after excavation)	75	145	180	220
Physical methods (pollution trapping)	Containment (on site)	€/t (soils after excavation)	15	25	38	130
	Inert Landfill	€/t (soils after excavation)	5	10	15	20
	Non-hazardous Landfill	€/t (soils after excavation)	40	55	75	80
	Hazardous Landfill	€/t (soils after excavation)	80	105	135	150
	Physico-chemical stabilization (off site before landfill)	€/t (soils after excavation)	70	105	140	190
	Physico-chemical stabilization (on site)	€/t (soils after excavation)	25	45	75	120
Chemical methods	Chemical extraction and solvent extraction (off site)	€/t (soils after excavation)	80	240	285	1300
	Chemical oxydation and reduction (on site)	€/t (soils after excavation)	40	50	70	120
Thermal methods	Incineration (off site)	€/t (soils after excavation)	190	250	305	1050
	Cement (off site)	€/t (soils after excavation)	40	45	55	75
	Thermal desorption (on site or off site)	€/t (soils after excavation)	60	70	80	110
	Vitrification (off site)	€/t (soils after excavation)	250	340	415	800
	Pyrolysis and thermolysis (off site)	€/t (soils after excavation)	75	115	135	150
Biological methods	Bioreactor (on site or off site)	€/t (soils after excavation)	50	70	80	120
	Biopile (on site)	€/t (soils after excavation)	30	36	50	70
	Biopile (off site)	€/t (soils after excavation)	50	52	55	80
	Composting (on site or off site)	€/t (soils after excavation)	15	21	28	40
	Landfarming (on site or off site)	€/t (soils after excavation)	12	13	18	35

A1.3.5 Discussion of the impact of the inclusion of PACs in the CBA

The inclusion of PACs in the soil treatments has the following consequences:

- due to the greater solubility of the PACs, a larger polluted area (incompatibility between the proposed uses and pollution),
- due to the greater solubility of the PACs, the need to treat groundwater in some cases,
- due to the production of PACs during the remediation process, the need to use larger amounts of oxidants,
- due to the slower degradation of PACs during the biological treatment, the need to deal with longer remediation time.

Taking into account the PACs will therefore have a financial impact (larger soil volumes to be treated, more frequent treatment of groundwater, greater processing times, larger amounts of additives).

These impacts are difficult to quantify with available data. However, we will try to illustrate the financial impact of the PACs included in the two remediation case studies:

- Case 1: Pollution does not reach the roof of the aquifer (pollution confined in the unsaturated zone)
- Case 2: Soil pollution affecting groundwater.

The characteristics of the two case studies are presented in the tables A1-3 and A1-4 below.

Table A1-3: Characteristics of Case Study # 1

Case study 1: Pollution confined in the unsaturated zone	Units	Quantities
Area	m ²	1 500.00
Depth	m	3.00
Volume	m ³	4 500.00
Tonnage	t	8 100.00

Table A1-4: Characteristics of Case Study # 2

Case study 2: Pollution in the saturated and unsaturated zones	Units	Quantities
Area	m ²	1 500.00
Depth	m	3.00
Volume	m ³	4 500.00
Tonnage	t	8 100.00
Aquifer thickness (top of water table – substratum depth)	m	7.00
Volume of polluted water in the aquifer (assuming panache 5 times larger than the source)	m ³	15 750.00
Treatment duration	an	2.00
Renewal of the volume of water in the treated area	-	4.00

Estimates of abatement costs were made from the data summarized in Tables A1-5 and A1-6 and the following assumptions: use of larger quantities of reagents, higher volumes to take into account and more important treatment durations.

Table A1-5: Estimated potential financial impacts of remediation taking into account PACs and PAHs (case study 1)

Treatment	€t*	t	Total €
Case 1 - hypothesis 1 - initial treatment			
Highly concentrated pollution: incineration	277.50	8 100	2 247 750
Concentrated pollution: thermal desorption	75.00	8 100	607 500
Moderately concentrated pollution: chemical treatment in situ	55.00	8 100	445 500
Low concentration pollution: biopile on site	43.00	8 100	348 300
Case 1 - Hypothesis 2 - no change in volume to be treated; changes in unit costs of treatment			
Highly concentrated pollution: incineration	277.50	8 100	2 247 750
Concentrated pollution: thermal desorption	75.00	8 100	607 500
Moderately concentrated pollution: chemical treatment in situ (x1,15)**	63.25	8 100	512 325
Low concentration pollution: biopile on site (x1,2)***	51.60	8 100	417 960
Case 1 - Hypothesis 3 - changing the volume to be treated (* 1.30); changes in unit costs			
Highly concentrated pollution: incineration	277.50	10 530	2 922 075
Concentrated pollution: thermal desorption	75.00	10 530	789 750
Moderately concentrated pollution: chemical treatment in situ (x1,15)**	63.25	10 530	666 022.50
Low concentration pollution: biopile on site (x1,2)***	51.60	10 530	543 348

*: Excluding transport and excavation; **: Higher consumption reagents; *** Longer processing time

Table A1-6: Estimated potential financial impacts of remediation taking into account PACs and PAHs (case study 2)

Treatment	€t* or €m ³ *	t or m ³	Total €
Case 2 - hypothesis 1 - initial treatment (unsaturated zone)			
Concentrated pollution: thermal desorption	75.00	8 100	607 500
Pump and treat	16.5	0	0
Chemical oxidation - groundwater	50.00	0	0
Case 2 - hypothesis 2 - treatment of saturated and unsaturated zones			
Concentrated pollution: thermal desorption	75.00	8 100	607 500
Pump and treat	16.5	63 000	1 039 500
Chemical oxidation - groundwater	50.00	15 750	787 500
Case 2 - hypothesis 3 - treatment of saturated and unsaturated zones - no change in the volume to be treated; changes in unit costs of treatment			
Concentrated pollution: thermal desorption	75.00	8 100	607 500
Pump and treat	16.5	63 000	1 039 500
Chemical oxydation - groundwater (*1,15)	57.50	15 750	905 625
Case 2 - hypothesis 4 - treatment of saturated and unsaturated zones; changing the volume to be treated (* 1.30); changes in unit costs of treatment			
Concentrated pollution: thermal desorption	75.00	10 530	789 750
Pump and treat	16.5	81 900	1 351 350
Chemical oxidation - groundwater (*1,15)**	57.50	20 475	1 177 312.50

*: Excluding transport and excavation; **: Higher consumption reagents

The calculation assumptions taken into account are: average unit costs for remediation works in France, soil and water to be treated volume increases (30%), increased reagent needs for chemical treatments (15%), increased treatment time for the biological treatment (20%). These work assumptions are based on the results of PACMAN. They need to be refined by further studies. The results of these preliminary calculations are shown in the graphs below. These financial estimates do not include excavation costs, transport and analysis costs (especially PACs analysis extra costs)

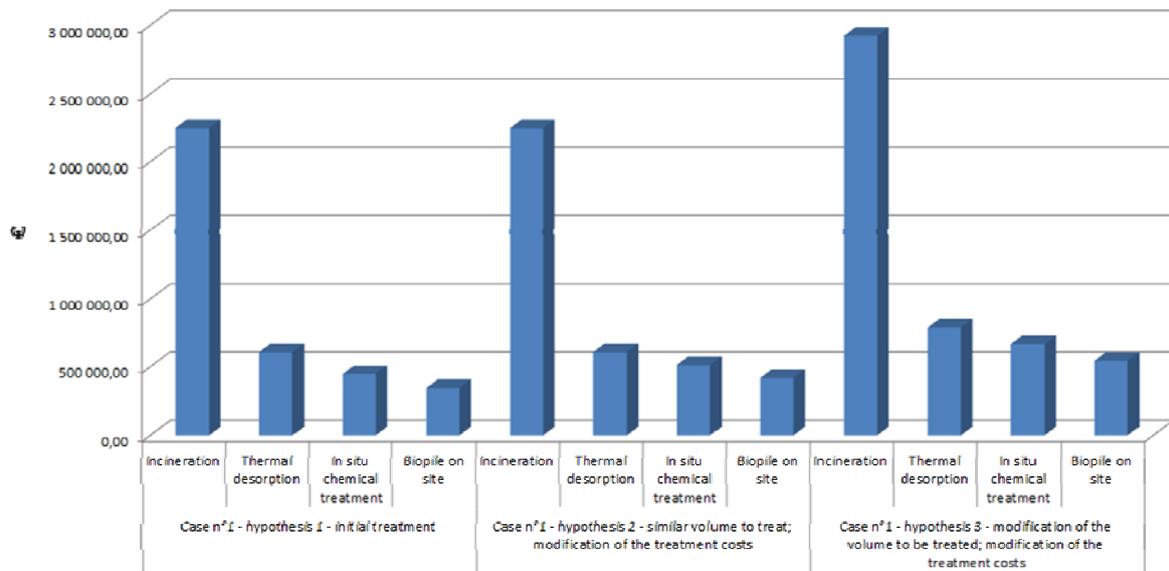


Figure A1-2: Illustration of the potential financial impact on remediation when taking into account PACs and PAHs (case study 1)

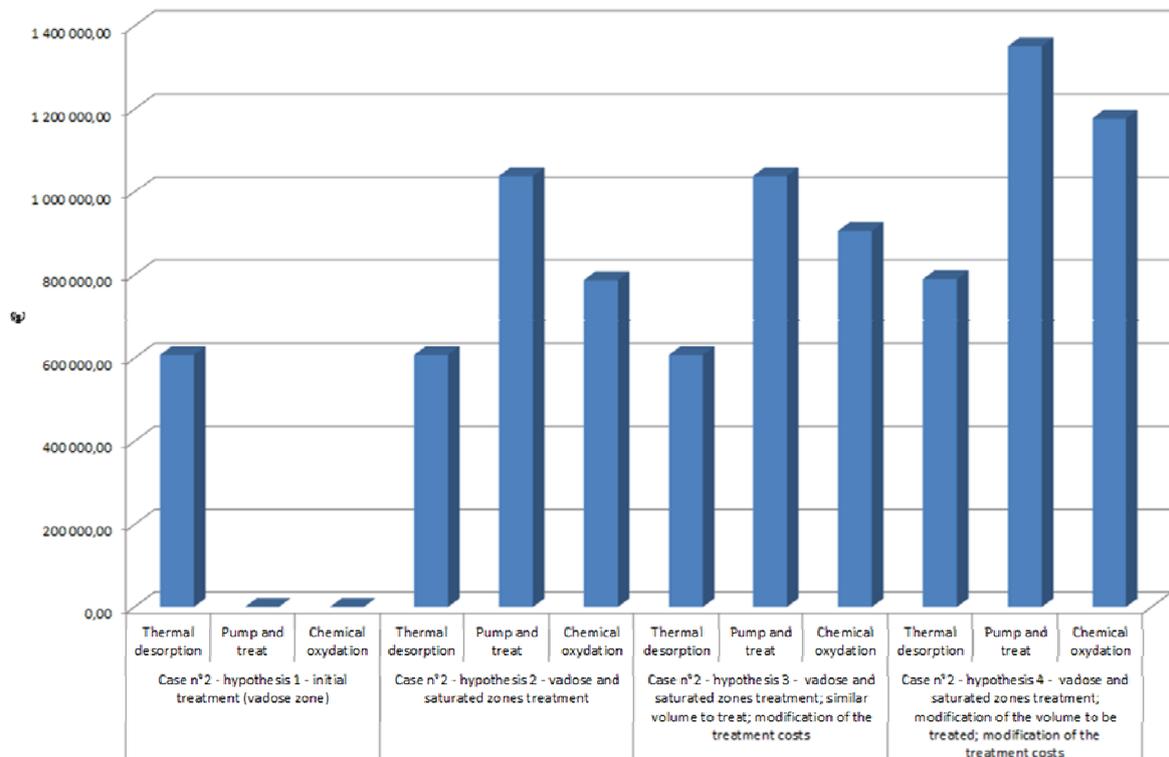


Figure A1-3: Illustration of the potential financial impact on remediation when taking into account PACs and PAHs (case study 2)

For thermal desorption, incineration and pump and treat, financial impacts will probably be related only to soil volume increases or water to be treated. Note that some assumptions should be further validated, especially the hypothesis that PACs might adsorb less on active carbon.

By combining the different assumptions, we find that the financial impact can be significant for some remediation techniques, namely ISCO and biological treatment: + 56% for biological treatment of soils and + 49% for chemical treatment of soil and groundwater.

A1.4 Conclusions

The first step of framework to assess the costs and benefits of two or more options for the remediation of two PAC contaminated sites in France considering also polar PACs was performed for the first time. Within this screening step, the matrices revealed were used to give an indication of which step will be the most appropriate exit point from the assessment for the two case studies. For future case studies similar to either of both sites, more sophisticated levels are recommended as a combined Cost-Effectiveness Analysis (CEA) and Multi-Criteria Analysis (MCA) and/or a Cost-benefit Analysis (CBA) (Step IV). However, it should be mentioned that the recommendation resulting of this approach would not be definitive. To make the final decision to whether a more detailed step is required, the subsequent qualitative appraisal (Step II of the framework) should be performed, using various indicators to allow a reliable final decision.

It was probably too ambitious to perform a CBA analysis on sites where remediation was completed many years earlier. It would make more sense to do it on a current project, for which operational data and actual costs may be used.

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