Environmental Pollution 278 (2021) 116857

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Review

Targeting the right parameters in PAH remediation studies☆

Marie Davin [a], [b], *, Gilles Colinet [a], [1], Marie-Laure Fauconnier [b], [1]

[a] *Soil-Water-Plant Exchanges, University of Liège, Gembloux Agro-Bio Tech, 2 Passage des Déportés, 5030, Gembloux, Belgium*
[b] *Laboratory of Chemistry of Natural Molecules, University of Liège, Gembloux Agro-Bio Tech, 2 Passage des Déportés, 5030, Gembloux, Belgium*

ARTICLE INFO

Article history:
Received 26 April 2020
Received in revised form
17 February 2021
Accepted 28 February 2021
Available online 3 March 2021

Keywords:
Polycyclic aromatic hydrocarbons
Remediation
Soil
Aged
Bioavailability
Review

ABSTRACT

Contaminated land burdens the economy of many countries and must be dealt with.

Researchers have published thousands of documents studying and developing soil and sediment remediation treatments. Amongst the targeted pollutants are the polycyclic aromatic hydrocarbons (PAHs), described as a class of persistent organic compounds, potentially harmful to ecosystems and living organisms.

The present paper reviews and discusses three scientific trends that are leading current PAH-contaminated soil/sediment remediation studies and management.

First, the choice of compounds that are being studied and targeted in the scientific literature is discussed, and we suggest that the classical 16 US-EPA PAH compounds might no longer be sufficient to meet current environmental challenges.

Second, we discuss the choice of experimental material in remediation studies. Using bibliometric measures, we show the lack of PAH remediation trials based on co-contaminated or aged-contaminated material.

Finally, the systematic use of the recently validated bioavailability measurement protocol (ISO/TS 16751) in remediation trials is discussed, and we suggest it should be implemented as a tool to improve remediation processes and management strategies.

1. Introduction

Countries that are or have been heavily industrialized have their share of brownfield sites, which often present multiple types and levels of contamination. Brownfield sites are a legacy that will burden this generation, and probably many more to come, and need to be dealt with appropriately, because any unmanaged contamination is a potential threat towards the environment at large, and also because the majority of these sites cannot host any type of activity (agricultural, residential, or industrial) as long as they have not been remediated, which constitutes a huge economic loss. At a time when the world's population is growing fast, the sustainable use of natural resources is crucial to meet the United Nation "Sustainable Development Goals" (Umeh et al., 2017).

The objectives of a review are to highlight new progress, successes and sometimes failures. But most importantly a review should identify new directions or areas that lack data or knowledge. This is also the objective of this paper, which aims to question scientific approaches that have been leading contaminated soil remediation studies and management, and more specifically polycyclic aromatic hydrocarbon (PAH) remediation in soils/sediments. First, for the past few decades, worldwide scientific publications have focused on studying a rather short list of PAHs, namely the 16 PAHs from the American Environmental Protection Agency's (US-EPA) "Priority Pollutants" list published in 1978 (Keith, 2015), seemingly without ever questioning its content. Second, PAH remediation techniques have been developed for several decades, with the underlying goal of providing solutions to eliminate pollutants from contaminated environmental compartments. Yet, when performing a bibliometric analysis of all types of documents that have been published and studies that have been conducted, it is striking that only a small fraction of the publications on the matter have concentrated on realistic aged-contaminated soils, not to mention the lack of studies focusing on multiple contaminants. Finally, PAH remediation endpoints will be discussed. When it

---

☆ This paper has been recommended for acceptance by Yong Sik Ok.

* Corresponding author. Soil-Water-Plant Exchanges, University of Liège, Gembloux Agro-Bio Tech, 2 Passage des Déportés, 5030, Gembloux. Belgium.

E-mail addresses: mdavin@uliege.be (M. Davin), gilles.colinet@uliege.be (G. Colinet), marie-laure.fauconnier@uliege.be (M.-L. Fauconnier).

[1] These authors contributed equally to the paper.

https://doi.org/10.1016/j.envpol.2021.116857
0269-7491/

comes to environmental regulations and soil remediation guidelines, the driving assumption is that (aged-) contaminated soils must be remediated to the greatest possible extent. It has recently been pointed out in several reviews that there is a need to implement a risk-based approach using a bioavailability parameter to establish site management and decontamination strategies. But we suggest that this bioavailability parameter be taken further and used when developing remediation treatments, as it would bring valuable insight on the processes in place.

1.1. On the use of the 16 "Priority Pollutants" PAHs

The study of contamination as a (potential) threat to the environment and human population has given birth to thousands of scientific publications on the subject. Pollutants are traditionally separated into inorganic and organic pollutants. The list of inorganic pollutants is rather well-defined, as it comprises a series of trace metals and metalloids often referred to as "heavy metals" (Duffus, 2002). But the list of organic pollutants comprises dozens of groups (e.g. PAHs, PCBs, PCDDs, PCDFs, BTEX, …) and new pollutants are still being identified by scientists, as potentially harmful effects are highlighted by research everyday (e.g. pharmaceutical products) (Reichert et al., 2019). Besides, each group of organic pollutants often contains a large variety of compounds. For instance, PAHs are commonly defined as molecules made of two or more condensed aromatic rings placed in linear, angular or clustered arrangements (Dhar et al., 2019). When encountered in soil or sediment, they have two main origins: petrogenic (which usually implies that products of petroleum origin were spilled) and pyrogenic (meaning compounds are created during incomplete combustion) (Iqbal et al., 2008; Dhar et al., 2019). PAH contamination can arise due to natural causes (e.g. volcanic episodes or forest fires) but anthropogenic activities are mostly to blame (e.g. fuel combustion, waste incineration or accidental spillage) (Nzila, 2018). In the scientific literature, the PAH definition is commonly followed by the same list of 16 PAH compounds. It is however rarely mentioned that the list was established over 40 years ago, under time pressure, and needs to be re-assessed according to the knowledge that has been acquired over more recent decades and in response to today's environmental management challenges. The classical PAH watch list was established in 1976 by the US-EPA, when a general awakening took place with regard to the issue of organic water pollution. Among other classes of pollutants, the US-EPA selected 16 PAHs as "Priority Pollutants". These PAHs made it onto the list mainly because (i) they had previously been detected in several water contamination reports on North-American land (>5%) and (ii) they were commercially available so that a standard could be used to confirm their identity in analytical methods (Keith, 2015). The original list only contained specific isomers and apolar PAHs because at the time, the reference analytical instrument (gas chromatography coupled to mass spectrometry) was not reliable at detecting isomers, and commercial alkylated PAHs were difficult to find (Keith, 2015). Afterwards, this list served as a consistent basis for scientific research and the comparison of results (Andersson and Achten, 2015), and for other countries to establish environmental regulation guidelines (Keith, 2015). However, this list has not evolved with regards to the PAH compounds since it was first drawn up, despite the fact that health and environmental challenges have evolved, new knowledge has been acquired, and analytical methods have been developed.

There are more than 16 compounds to be concerned about, and it is interesting to note the slight disparity between the commonly cited 16 apolar PAHs in scientific research and the compounds present in legislation or international scientific committees' reports. Not all countries in the world are equipped with soil quality guidelines, but some do have other regulations that include hazardous substance watch lists. For example, in the European Union, there is still no Soil Protection Framework Directive, but there is a Water Framework Directive (WFD) (EC, 2020), a Food Regulation (EFSA, 2020), a Chemicals (REACH) Regulation and even a Persistent Organic Pollutants (POPs) Regulation (ECHA, 2020), which all take aim at the protection of human health and environment. On a broader scale, Canada is equipped with Soil Quality Guidelines (CCME, 2020) and the World Health Organization, though it does not provide soil quality guidelines, had experts work on an international programme on chemical safety and the establishment of environmental health criteria (WHO, 2020). When comparing the polycyclic aromatic compounds mentioned in these regulations or watch lists (all available in Supplementary Table 1) and the US-EPA list that most soil remediation studies lean on, a few discrepancies are evident. For instance (Table 1), the WHO mentions 17 compounds besides the usual 16, among which 15 are apolar compounds and several are isomers of compounds mentioned in the US-EPA list (e.g. benzo[j]fluoranthene and benzo[k]fluoranthene). Another example is the European food regulation list, which mentions 15 compounds, all of which are mentioned on the WHO list, but out of which only 8 compounds are common to the US-EPA list.

PAHs are part of a larger group of polycyclic aromatic compounds (PACs) that are not always apolar and can contain heteroatoms such as oxygen, nitrogen, sulphur … (Bowman et al., 2019). PAHs themselves can be substituted with halogens, alkyl-, oxy-, hydroxyl-, amino- or nitro-functional groups, and then there is the

Table 1
Comparison of the polycyclic aromatic compounds on the US-EPA watch list (EPA, 2020) to the compounds present in the WHO (WHO, 2020) and the European Union Food Regulation (EFSA, 2020) watch lists. Compounds in bold are from the US-EPA watch list.

Compound	Watch list	
	WHO	European Union Food Regulation
1-methylphenanthrene	X	
5-methylchrysene	X	x
Acenaphthene	X	
Acenaphtylene	X	
Anthanthrene	X	
Anthracene	X	
Benzo[a]anthracene	X	x
Benzo[a]fluorene	X	
Benzo[a]pyrene	X	x
Benzo[b]fluoranthene	X	x
Benzo[b]fluorene	X	
Benzo[c]phenanthrene	X	
Benzo[e]pyrene	X	
Benzo[ghi]fluoranthene	X	
Benzo[ghi]perylene	X	x
Benzo[j]fluoranthene	X	x
Benzo[k]fluoranthene	X	x
Chrysene	X	x
Coronene	X	
Cyclopenta[c,d]pyrene	X	x
Dibenz[a,h]anthracene	X	x
Dibenzo(a,e)pyrene	X	x
Dibenzo(a,h)pyrene	X	x
Dibenzo(a,i)pyrene	X	x
Dibenzo(a,l)pyrene	X	x
Fluoranthene	X	
Fluorene	X	
Indeno[1,2,3-cd]pyrene	X	x
Naphthalene	X	
Perylene	X	
Phenanthrene	X	
Pyrene	X	
Triphenylene	X	

matter of NSO-heterocycles, which are aromatic rings containing nitrogen, sulphur or oxygen (Andersson and Achten, 2015). A comprehensive review on the matter of substituted and heteroatomic PACs' origin, properties and fate in the environment was published by Idowu et al. (2019), who insisted on the fact that such compounds are less studied than apolar PAHs. However, it is crucial that the scientific community and the legislators start taking these different types of PACs seriously. (i) Because many of these compounds are believed to be more genotoxic, mutagenic and carcinogenic than apolar PAHs (Bleeker et al., 1999; Park et al., 2008; Lundstedt et al., 2014; Andersson and Achten, 2015; Tian et al., 2017a). (ii) Because heteroatomic PACs are more polar, and therefore suspected to be more mobile in the environment (Bowman et al., 2019). (iii) Because depending on their origin, some of these compounds are present along with apolar PAHs (Idowu et al., 2019). Most PAHs of petrogenic origin are of low molecular weight (two or three rings) and they are mostly alkylated PAHs. However PAHs of pyrogenic origin are dominated by unsubstituted compounds of high molecular weight (four, five, six rings) (Bowman et al., 2019; Iqbal et al., 2008). But no matter their origin, PAHs can occur with PACs as co-contaminants (Tian et al., 2017b; Idowu et al., 2019). And (iv) because alkylated and heteroatomic PACs can appear through secondary processes acting on apolar PAHs, such as (photo)chemical degradation and biological degradation (Lundstedt et al., 2002; Hu et al., 2012; Chibwe et al., 2017; Tian et al., 2017a; Idowu et al., 2019).

The fact that substituted PAHs can be metabolites of the incomplete degradation of apolar PAHs should raise some questions regarding the way remediation strategies such as bioremediation are being led. Bioremediation relies on microbial biodegradation to mineralize PAHs, which takes place naturally in the environment. This is why metabolic pathways, especially the aerobic bacterial ones, have been intensively studied for decades (Ghosal et al., 2016). The 16 US-EPA PAHs are the usual targets of all these studies and, as several apolar PAH degradation pathways are now established, it is well known that mineralization processes can meet dead-ends (Idowu et al., 2019). When present in mixtures, phenomena of augmentation, cometabolism, or inhibition can influence both the extent and rate of individual PAH degradation, depending on the type of mixture but also on the degrading microbial consortia (Mahanty et al., 2011). These enhancing or inhibiting phenomena were highlighted by studies conducted in controlled conditions, implying a few PAHs (pure or in mixtures) and a few specific strains (in individual or mixed cultures) (Bouchez et al., 1995; Stringfellow and Aitken, 1995; Van Herwijnen et al., 2003; Mahanty et al., 2010; Ghosh and Mukherji, 2017). But these phenomena are not systematically encountered and are difficult to predict. PAHs encountered in a polluted environment are present in mixtures. But microbial communities are also much more diverse than can be accounted for in controlled culture studies, and it is thus likely that in the presence of mixed microbial species, degradative pathways complete each other and intermediate or dead-end metabolites can be substrates for other species (Mahanty et al., 2011; Vila et al., 2015). But when metabolites such as epoxides, quinones, ketones or hydroxylated-PAHs are left in the soil instead of undergoing complete mineralization, this should raise concern because such compounds may be more toxic than their parent PAH (Ghosal et al., 2016; Davie-Martin et al., 2017; Chibwe et al., 2017). Indeed, some studies have used bioassays to highlight the fact that although bioremediation treatments might lower the content of apolar PAHs, the general (geno)toxicity or mutagenicity of the treated soil could increase during the process (Hu et al., 2012; Chibwe et al., 2015). What is even more concerning is that the presence of toxic metabolites is not systematically monitored. Indeed, when soils are being remediated, the final remediation goals, whether in scientific studies or in realistic aged-contaminated soil remediation, are expressed as the lowering of the initial apolar PAH contents that must be achieved. But given that complete PAH degradation is difficult to achieve, and to predict, maybe it is time to consider adding the monitoring of transformation metabolites to the management of polluted soil, especially when remediation techniques are applied.

Fortunately, these topics have been at the centre of several research papers during the last few years. Besides showing that a soil's toxicity may increase during remediation, a few studies have focused on the isolation, purification, and identification of the metabolites responsible for this enhanced toxicity (e.g. Chibwe et al., 2017; Tian et al., 2017a) and very often, oxygen-containing metabolites have been highlighted. Also, analytical methods have been under development to detect nitro-PAHs, oxy-PAHs, hydroxy-PAHs, methyl-PAHs, halogenated-PAHs, or even N-heterocycles, sometimes along with apolar PAHs (Niederer, 1998; Cochran et al., 2012; García-Alonso et al., 2012; Tian et al., 2017a; Mueller et al., 2019; Bowman et al., 2019; Wickrama-Arachchige et al., 2020). Unlike for the determination of the 16 US-EPA PAHs, the analytical methods are diverse, and some have not yet achieved complete quantification. Attempts are being made to harmonize the methods (as was the case for some oxy-PAHs and N-heterocycles in the intercomparison study led by Lundstedt et al. (2014)), but the work is highly complicated by the fact that there is still a lack of consensus concerning the compounds that should be analysed, as well as a lack of reference materials. Of course, there are so many possible metabolites that it is impossible to monitor every by-product during remediation processes. But since analytical methods are being developed and awareness on the matter is increasing, it really is worth, from a risk-analysis point-of-view, starting to look for different types of polycyclic aromatic compounds, and including some of them in watch lists.

These few examples show a lag between regulations and research and highlight the fact that the scientific community should broaden the list of polycyclic aromatic compounds that are studied, not only in soil remediation studies but also in land management and environmental risk-assessment. First, this broadening would address environmental challenges faced by countries (and their regulations) with different hazardous pollutant watch lists, and second, it might highlight remediation or naturally occurring dead-ends and could bring new perspectives to land management strategies at large. Andersson and Achten (2015) initiated this process as they suggested, based on toxicity, occurrence, and ease of analysis, enlarging the classical list of 16 US-EPA PAHs by adding 24 compounds (alkylated and apolar PAHs) for environmental toxicity evaluation. They also suggested 23 NSO-heterocyclic compounds, 6 heterocyclic metabolites, 10 oxy-PAHs, and 10 nitro-PAHs that would be interesting to monitor in the future. But as mentioned previously, analytical methods are improving and progress is still being made to identify toxic metabolites, meaning reflection and research on this matter remain necessary.

1.2. On the use of realistic aged-contaminated soil in research

During the past three decades, the development of PAH remediation techniques in soils/sediments has become more diverse. Research tends to evolve quickly and to spread in many directions, and it is useful, once in a while, to establish the state-of-the-art of a topic. To make the work sustainable, it is often necessary to narrow the topic to a few specific items. For example in the matter of PAH soil/sediment remediation, reviews describing recent advances in remediation techniques have focused on certain categories of treatment, such as the electroremediation of PAHs (Pazos et al., 2010), the extraction agents used for PAH soil washing (Von Lau et al., 2014), the surfactant-enhanced remediation of PAHs (Lamichhane et al., 2017), and the microbe-enhanced phytoremediation of PAHs (Sarma et al., 2019). This section of the paper focuses on the fact that the long-term objective of research on remediation treatments is to develop techniques to treat PAH-contaminated soils/sediments of all ages and types. Indeed, the ultimate goal is to identify solutions to the management and remediation of contaminated land. Published techniques can be more or less efficient, cost-effective, or environmentally friendly, but they all are being led under the same banner, since they all start by exposing the need for PAH remediation due to their potential or confirmed toxicity. However, when examined as a whole, they sometimes seem to be slightly out of focus.

Several databases were explored to highlight published documents that actually studied aged-contaminated soils/sediments and tested techniques on realistic matrices, with all their complexity. The point was not to dissect every single study and its outcome, but to question whether the scientific community is taking the testing of remediation treatments as far as it can, or should. Therefore, bibliometric tools were used. All details are available in the supplementary material. Please note that for the sake of clarity, single terms representing groups of search terms are used (e.g., “aged” states for “aged or ancient or former or historical”), and a few representative treatments are discussed that aim to cover as much of the diversity of remediation publications as possible.

The first three searches narrowed down the number of published documents (1) on PAHs in general, (2) on PAHs in soils or sediments, and (3) on the remediation of PAHs in soils or in sediments (Table 2a). Out of 2901–87248 documents related to PAHs (1), depending on the database, 1156 to 28789 documents focus on PAHs in soils or in sediments (2), which represents an average 31 ± 4% of the total number of PAH documents (1). Also, 260 to 6267 documents focus on PAH remediation in soils or in sediments (3), representing respectively 7 ± 1% and 22 ± 1% of the total number of PAH documents (1) and of the PAH in soil/sediment documents (2) (Table 2b).

Two other searches were conducted to highlight the documents that focused (4) on soils or sediments presenting with multiple types of contamination, and (5) on aged soils or sediments with multiple contaminants, both regarding PAH remediation (3) (Table 2a). The highest percentage of relevant studies was 0.23% and 0% respectively (Table 2b) and clearly shows the lack of attention that has been given to the matter of multiple contaminants in the area of PAH soil/sediment remediation to date, even though most contaminated areas present with multiple types of contamination (Deary et al., 2018). This does not necessarily mean that studies are not being conducted on soils/sediments presenting with multiple contaminants, but more probably that research in general has not yet moved on to trying to remediate several types of contaminants at a time. An interesting example of a phytoremediation trial assisted by the addition of a complexing agent on soil co-contaminated with cadmium and fluorene was published by Wang et al. (2018). The soil was spiked with the pollutants prior to the trial, but the study shows interest in multiple contaminant clean-up strategies.

Publications concerning PAH remediation in soils/sediments (3) were narrowed down to several categories of treatment (heating, electrokinetic or electrochemical, washing, solubilisation, chemical oxidation, bioremediation and phytoremediation), then narrowed again to highlight the aged character of the pollution (Table 3a). The proportions of documents focusing on aged experimental material within each category of treatment, as well as in remediation documents in general (3), was then calculated (Table 3b). The average proportions are displayed in Fig. 1. Values range from 7 ± 1% for electrokinetic and electrochemical treatments to 33 ± 11% for heating treatments. Concerning documents on PAH remediation in general, the average proportion was 12 ± 0.4%. This, combined with the very low number of documents related to multiple contaminants, shows that the scientific community is not yet working on realistic soils/sediments on a regular basis.

When developing a remediation process, scientists try to understand the mechanisms that rule it, which is why very often preliminary studies tend to focus on one, then a few representative PAHs at a time, and to work in simplified controlled conditions. So, it is common to start working in aqueous media, for example to study biodegradation mechanisms, and then move on to freshly spiked soil. But whilst working with simplified models brings very valuable information and is always the best way to screen the potential of an innovative technique, it is unfortunately not representative of the reality of the aged-contaminated soils that are to be dealt with. Indeed, most contaminated land displays multiple contaminants, of either organic or inorganic nature, which have been in place for decades and have partitioned, sometimes very deeply, into the soil compartment. There were enough published studies on this matter to acknowledge that these ageing processes greatly complicate the remediation process, especially when the long-term objectives are to remove the pollution to the greatest possible extent, and to bring pollutant contents down.

The question is, why is there, apparently, still such little work being carried out on realistic soils/sediments? Is it because scientists tend to lose sight of their final objective, i.e., the remediation of realistic contaminated land? Is it because there is still a lack of knowledge that should be acquired by working in controlled experimental conditions before actually moving on to realistic conditions? Or worse, is it because the results of experiments on realistic soils/sediments are so negative or inconclusive that they are not being shared for common knowledge? Technical difficulties in leading reproductive and representative experiments on realistic soil samples are probably the main issue. Indeed, pollution is rarely to never present in a homogeneous way in the environment. Research should be as reproducible as possible and thus requires work on homogenous material, meaning manipulations such as sieving and mixing are often necessary. This *de facto* will render the experimental material less representative than the state it was originally in. Also, two experimental materials, no matter how similar in physico-chemical properties (particle distribution, moisture, compaction, oxygenation, but also types and levels of contaminants), will never be exactly the same, making conclusions on one specific realistic material difficult to generalize. A simple example is the variety of source materials through which PAHs can be transported and released into the soil compartment. Whether PAHs are brought in through non-aqueous phase liquids (NAPLs, such as gasoline) or solids (such as coke) will influence the release and sorption of PAHs in soil/sediment (Yu et al., 2018), even if those different source materials might lead to similar levels of PAH contamination. Finally, and as mentioned previously, the source and origin of PAHs (e.g., pyrogenic or pyrolytic) will determine the types of co-contaminants (e.g., other PACs, but also heavy metals, other organic pollutants such as PCBs, BTEX …). In an ideal research scenario, complete knowledge of the experimental material levels and types of contaminants would be necessary to gather as much information on the remediation processes and interactions at stake. But the variety of contaminants present in realistic soils/sediments renders exhaustive characterization extremely difficult (if not impossible) and expensive. A good start would be to narrow down this characterization to a few main groups of contaminants and to examine the effects co-contaminants and remediation techniques have on each other.

Table 2

a. Number of documents published in English on PAHs (1), on PAHs in soils or sediments (2), on the remediation of PAHs in soils or sediments (3), on the remediation of PAHs in soils or sediments presenting with multiple contaminants (4), and on the remediation of PAHs in aged soils or sediments presenting with multiple contaminants (5) in a series of databases until the end of year 2019. b. Proportions of the numbers of documents published in English on several topics compared to a larger pool of documents. The numbers displayed in the calculated proportions line represent the number of a search question presented in part a of the table.

Number of documents	Question number	1	2	3	4	5
	Searching terms	PAHs				
			soils or sediments			
				remediation		
					multiple contaminations	
						aged
Database						
AGRICOLA		17613	5735	1404	0	0
Agricu. & Environ. Science Collection		87248	28789	6267	2	0
Agricu. Science Collection		20514	6891	1661	0	0
Agriculture Science Database		2901	1156	260	0	0
ASP		47249	6150	1407	2	0
CAB ABST		29566	10886	2629	4	0
Environment Complete		24177	8650	1992	4	0
Environmental Science Collection		68228	22674	4738	2	0
Environmental Science Database		9781	3574	795	0	0
Environmental Science Index		66508	22466	4692	2	0
GreenFILE		11936	4648	917	1	0
Medline		20474	4963	884	2	0
Scopus		70111	13368	3283	6	0
TOXLINE		15765	4044	732	0	0

Proportion of documents	Calculated proportions	2/1	3/1	3/2	4/3	5/3
	Searching terms	PAHs				
		soils or sediments				
			remediation			
					multiple contaminations	
						aged
Database						
AGRICOLA		33%	8%	24%	0.00%	0.00%
Agricu. & Environ. Science Collection		33%	7%	22%	0.03%	0.00%
Agricu. Science Collection		34%	8%	24%	0.00%	0.00%
Agriculture Science Database		40%	9%	22%	0.00%	0.00%
ASP		13%	3%	23%	0.14%	0.00%
CAB ABST		37%	9%	24%	0.15%	0.00%
Environment Complete		36%	8%	23%	0.20%	0.00%
Environmental Science Collection		33%	7%	21%	0.04%	0.00%
Environmental Science Database		37%	8%	22%	0.00%	0.00%
Environmental Science Index		34%	7%	21%	0.04%	0.00%
GreenFILE		39%	8%	20%	0.11%	0.00%
Medline		24%	4%	18%	0.23%	0.00%
Scopus		19%	5%	25%	0.18%	0.00%
TOXLINE		26%	5%	18%	0.00%	0.00%
Mean		**31%**	**7%**	**22%**	**0.08%**	**0.00%**
Sd		8%	2%	2%	0.08%	0.00%
CI (5%)		4%	1%	1%	0.04%	0.00%

Another good way of transitioning towards the study of more realistic soils/sediments could be through the more systematic use of m-cosms (i.e., microcosms and mesocosms). For example Leroy et al. (2015) used tanks as mesocosms, placed outdoors (thus in realistic conditions) to study the effect of several plant species on the dissipation of PAHs in artificially contaminated soil. A different approach, involving microcosms, was used by our team when studying the effect of commercial saponins on PAH bioremediation in an aged-contaminated soil. In this case, a realistic soil was treated and placed in controlled incubation conditions (Davin et al., 2018). Such intermediate experimental set-ups, even though they might be expensive to run, allow links to be created between highly controlled laboratory studies and complex, but realistic, field studies (Albarano et al., 2020). They also allow for scientific reproducibility by keeping some variables under control, and could be systematically introduced in the development and the up-scaling of remediation techniques.

As challenging as working on more realistic material might be, it should not be postponed because it is too complex. It is crucial that, once research has provided encouraging results in controlled conditions, the potential new treatment is brought to the next level: the testing on realistic soils/sediments, and preferably a variety of them. And if the next level is inconclusive or somewhat disappointing, it is still important to publish these outcomes so that other researchers can try and improve the treatment, and not waste time repeating the same experiment, which will likely be considered a failure too. After all, that's what science is based on: sharing knowledge. But in order to do so, changes are needed within the

Table 3

a. Number of documents published in English on the remediation of PAHs in soils or sediments (3), on the remediation of PAHs in aged soils or sediments (6), and on specific treatments of PAHs in soils or sediments. Search numbers 7, 9, 11, 13, 17, and 19 are for specific treatments in soils or sediments in general, and search numbers 8, 10, 12, 14, 16, 18, and 20 are for specific treatments in aged soils or sediments. b. Proportions of the numbers of documents published in English on several topics compared to a larger pool of documents. The numbers displayed in the calculated proportions line represent the number of a search question presented in part a of the table.

Number of documents	Question number	3	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
	Searching terms	PAHs															
		soils or sediments															
		remediation												/			
				heating		electrokinetic or electro-chemical		washing		solubilisation		chemical oxidation		bioremediation		phytore-mediation	
			aged		aged		aged		aged		aged		aged		aged		aged
Database																	
AGRICOLA		1404	158	8	1	27	2	1	0	1	0	45	8	674	75	278	31
Agricu. & Environ. Science Collection		6267	808	48	14	159	12	24	5	12	2	197	33	3640	471	1109	139
Agricu. Science Collection		1661	191	12	2	37	2	3	1	3	0	55	11	833	98	320	38
Agriculture Science Database		260	33	4	1	10	0	2	1	2	0	10	3	159	23	42	7
ASP		1407	172	19	3	58	5	48	6	55	4	34	9	779	98	244	28
CAB ABST		2629	319	18	4	71	5	75	9	61	8	49	9	1383	175	460	49
Environment Complete		1992	241	20	7	72	6	61	9	56	7	49	12	1056	128	280	34
Environmental Science Collection		4738	641	39	13	132	10	22	5	11	2	151	25	2884	390	816	107
Environmental Science Database		795	97	7	3	19	2	4	1	4	1	22	6	455	55	167	22
Environmental Science Index		4692	634	39	13	130	10	22	5	11	2	151	25	2856	386	813	106
GreenFILE		917	116	11	3	45	4	35	7	34	6	21	4	449	61	154	16
Medline		884	108	5	2	27	1	26	1	20	1	20	4	442	57	153	19
Scopus		3283	372	40	10	115	9	119	11	133	12	191	28	2194	234	484	52
TOXLINE		732	99	1	1	27	1	1	0	3	0	28	2	319	47	137	16

Proportion of documents	Calculated proportions	6/3	7/3	8/7	9/3	10/9	11/3	12/11	13/3	14/13	15/3	16/15	17/3	18/17	19/3	20/19
	Searching terms	PAHs														
		soils or sediments														
		remediation														
			heating		electrokinetic or electro-chemical		washing		solubilisation		chemical oxidation		bioremediation		phytore-mediation	
		aged		aged		aged		aged		aged		aged		aged		aged
Database																
AGRICOLA		11%	0%	13%	0%	7%	0%	0%	0%	0%	1%	18%	12%	11%	5%	11%
Agricu. & Environ. Science Collection		13%	0%	29%	1%	8%	0%	21%	0%	17%	1%	17%	13%	13%	4%	13%
Agricu. Science Collection		11%	0%	17%	1%	5%	0%	33%	0%	0%	1%	20%	12%	12%	5%	12%
Agriculture Science Database		13%	0%	25%	1%	0%	0%	50%	0%	0%	1%	30%	14%	14%	4%	17%
ASP		12%	0%	16%	1%	9%	1%	13%	1%	7%	1%	26%	13%	13%	4%	11%
CAB ABST		12%	0%	22%	1%	7%	1%	12%	1%	13%	0%	18%	13%	13%	4%	11%

Environment Complete															
Environmental Science Collection	12% 14%	0%	35% 33%	1%	8%	0% 1%	25% 13%	0% 1%	18% 13%	1%	24% 17%	12% 13%	12% 14%	3% 4%	12% 13%
Environmental Science Database	12%	0%	43%	1%	11%	0%	25%	0%	25%	1%	27%	13%	12%	5%	13%
Environmental Science Index	14%	0%	33%	1%	8%	0%	23%	0%	18%	1%	17%	13%	14%	4%	13%
GreenFILE	13%	0%	27%	1%	9%	1%	20%	1%	18%	0%	19%	10%	14%	3%	10%
Medline	12%	0%	40%	1%	4%	1%	4%	0%	5%	0%	20%	9%	13%	3%	12%
Scopus	11%	0%	25%	1%	8%	1%	9%	1%	9%	1%	15%	16%	11%	4%	11%
TOXLINE	14%	0%	100%	1%	4%	0%	0%	0%	0%	1%	7%	8%	15%	3%	12%
Mean	**12%**	**0%**	**33%**	**1%**	**7%**	**0%**	**18%**	**0%**	**10%**	**1%**	**20%**	**12%**	**13%**	**4%**	**12%**
Sd	1%	0%	21%	0%	3%	0%	13%	0%	8%	0%	6%	2%	1%	1%	1%
CI (5%)	0.4%	0.0%	11%	0.1%	1%	0.2%	7%	0%	4%	0.1%	3%	1%	1%	0.3%	1%

scientific community. On the one hand, researchers should publish all kinds of results, as long as they are scientifically robust, and on the other hand, journal editors and reviewers should provide researchers with the opportunity to share disappointing or unexpected outcomes, and even encourage them to do so.

1.3. On the use of the bioaccessibility parameter in remediation studies

Three decades ago, the scientific community started to focus on the concept of PAH bioavailability. Researchers were gathering encouraging results and increasing knowledge regarding PAH metabolism (mainly under aerobic conditions) in the laboratory, but failed to predict outcomes in field conditions (Sanseverino et al., 1993). They were facing poor PAH mineralization rates and yields even under favourable conditions. Research and publications focused on several aspects of bioavailability: (i) defining it, (ii) identifying the factors that influence it, (iii) measuring it, and (iv) increasing it for degrading microorganisms (in the context of remediation).

Settling on concepts and definitions alone has been at the centre of many publications and reviews (Ehlers and Luthy, 2003; Semple et al., 2003, 2004, 2007; Reichenberg and Mayer, 2006; Ortega-Calvo et al., 2015). Concepts as crucial as “chemical activity”, “bioavailability”, “bioaccessibility”, “non-extractable residues” (NERs) and the processes that govern them were defined, and will not be repeated here. Please note that the term “bioavailability” is used as a generic term.

The factors and the sorption/desorption mechanisms influencing organic compounds’ bioavailability (including PAHs) have been, and still are being, thoroughly investigated and reviewed. They include (i) soil/sediment properties such as solid and dissolved organic matter (SOM and DOM) content, particle size, chemical structure, composition, polarity, mineral composition and organo-mineral associations; (ii) environmental factors (pH, temperature, moisture …); (iii) characteristics of the contamination such as the source material (atmospheric emission, solid, semi-solid, NAPLs), the presence of co-contaminants, and the initial amounts of pollutants, and (iv) microbial capacities such as the type and variety of degrading species, their morphological, behavioural, and physiological adaptations, and chemotactic capabilities (Ortega-Calvo et al., 2013; Duan et al., 2015; Ren et al., 2018; Yu et al., 2018).

Several methods to measure bioavailability have been developed and also reviewed (Semple et al., 2007; Cui et al., 2013; Riding et al., 2013; Cachada et al., 2014). Recently, the ISO/TS 16751 norm (2018, revised in 2020) settled some debates on bioavailability measurement by defining a protocol using either a strong sorbent (Tenax®) or complexing agents (cyclodextrins) to determine the “bioavailable fraction” of non-polar organic compounds (such as PAHs), also named “environmental availability”. The norm uses biomimetic surrogates, which are meant to imitate a potential maximal uptake from the aqueous solution by organisms. This environmental availability is defined in norm ISO 17402 (2008) as “the fraction of a contaminant actually or potentially available to organisms”, which is the definition of bioaccessibility by Semple et al. (2004). It is different from the environmental bioavailability, which includes uptake by the organisms and is dependent on the biological group or even the species. Indeed, aqueous diffusion (which requires a biomimetic method to measure environmental availability) is not the only mechanism through which organisms might be exposed to pollutants. Higher organisms, like mammals and invertebrates, can access pollutants through the ingestion of soil material, then residual fractions might be released in the gut due to chemical conditions (Umeh et al., 2017). Thus, it is essential

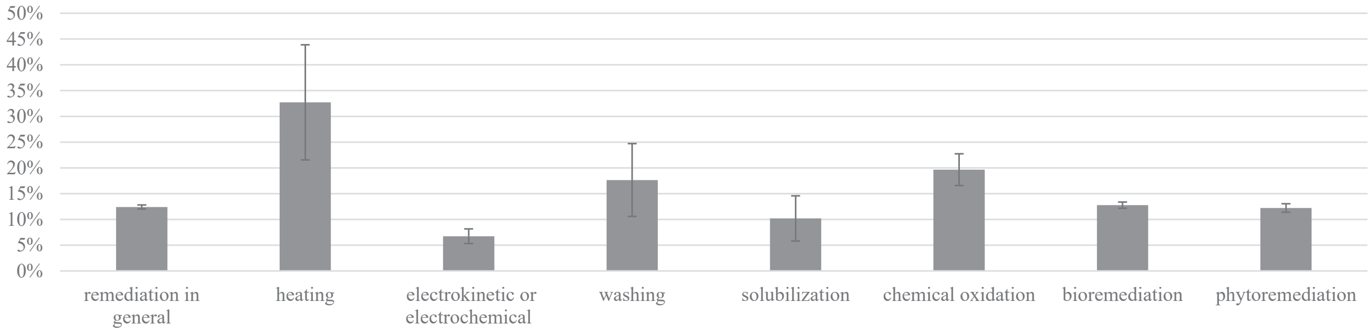

Fig. 1. Proportions of documents on aged soils/sediments in several clusters of documents on PAH remediation treatments. Values are means ± confidence intervals ($\alpha = 0.05$). See Supplementary Table 3 for detailed numbers and calculations.

to keep in mind that the ISO/TS 16751 norm is a tool that allows the estimation of the environmental availability in general, but does not represent bioavailability to all types of organisms. In relation to soil/sediment remediation, bioavailability is now assimilated to the availability to microorganisms such as bacteria and fungi, and it is based on the assumption that the rapidly desorbable fraction (i.e. the bioavailable fraction) of a contaminant represents the endpoint of bioremediation (Hu et al., 2014). This precision is important because as was demonstrated by Hu et al. (2014), a pollutant's removal through bioremediation can sometimes be higher than could have been predicted through bioavailability measurements. Thus, it is important to keep in mind that bioavailability is a tool that should be used as a complement to other decision-making tools.

Nevertheless, now that the norm exists, the scientific community should start implementing it in soil/sediment remediation studies.

When countries are equipped with a legislation regulating environmental pollution and setting remediation goals, endpoints are established on the assumption that when environmental harm has been done, it has to be repaired to the greatest possible extent. Even for some countries where legislation is based on risk-assessment (e.g. Canada, New Zealand, Australia, USA, UK, the Netherlands, and Belgium), the total extractable content is at the basis of management strategies. For example, in Belgium (Walloon region), the management strategy of a brownfield site is based on a risk-analysis. Coefficients based on exposure scenarios, toxicological data, soil physico-chemical properties, etc. are applied to the content to which the targets (e.g., humans) are considered to be exposed, leading to a value that is then considered acceptable or not. The content to which coefficients are applied is assumed to be a pollutant's total extractable concentration. But this assumption has been thought to overestimate risks for some time now. As discussed previously, the interactions between a pollutant and the matrix it is in are complex and tend to become stronger with time. This means that the complete removal of a pollutant can become technologically infeasible or very expensive as time goes by. It also means that risks could be overestimated if the risk-analysis estimates that the total extractable pollutant content is bioavailable to organisms (which is potentially true in the case of ingestion, but not in the case of dermal contact, for example). So complete removal of a pollutant could actually be unnecessary in some cases.

Several authors have discussed this issue, and suggested that several pieces of information should be used in the decision-making process: the pollutants' total concentrations (based on classical exhaustive extraction methods) of course, but also their bioavailability. Norm ISO/TS 16751 is very useful to determine the environmental availability, but it should be complemented with biological assays, or chemical surrogates suitable for different biological groups, such as mammals (Alexander, 2000; Latawiec et al., 2011; Duan et al., 2015). And although progress still needs to be made in developing such methods, it is encouraging to know that some work has already been accomplished on PAH bioavailability in food using *in vitro* digestion, and that it could be implemented on soils/sediments as well (Hamidi et al., 2016).

On the other hand, implementing bioavailability measurement in soil/sediment remediation studies would bring considerable insight to the processes taking place during trials. The bioavailability concept was originally studied to explain the lack of proper biodegradation during bioremediation. Recently, the assessment of bioavailability has largely been discussed as a tool for risk-analysis in contaminated land management, as explained previously. But it should also be used as a tool to follow the evolution of that risk throughout the actual remediation process, and not only as a way to plan the extent of clean-up that should be achieved. This would mean using bioavailability assessment for all types of remediation techniques, on all types of soils/sediments being remediated. Throughout remediation research, many trials and methods have based their strategy on increasing bioavailability. State-of-the-art reviews on techniques enhancing bioavailability exist (Ortega-Calvo et al., 2013) or have been included in remediation reviews which evaluated progress in PAH remediation treatments (Gan et al., 2009; Kuppusamy et al., 2017; Lamichhane et al., 2017; Sarma et al., 2019). But none of these reviews, to the best of our knowledge, have reported the systematic assessment of bioavailability throughout remediation trials. As indicated throughout this section, bioavailability is at the centre of risk-analysis because it is what makes a pollutant a danger to its environment or not. So, the determination, but also the evolution of a pollutant's bioavailability should be taken into account in remediation studies. From a remediation point-of-view, it would bring considerable insight to the processes at work and help understand the dynamics of the treatment, and from a risk-analysis point-of-view, it would provide continuous data to feed the risk-analysis assessments, and could be used in combination with the total concentration contents to follow the evolution of land clean-up and of risk, and to determine where to stop. Evidently, since bioavailability applies by essence to historical pollution to evaluate its danger, such work has to be associated with aged material, as this realistically presents pollutants with lowered bioavailability. Recently, studies have started to assess the bioavailability of PAHs in soils/sediments after undergoing remediation. Posada-Baquero et al. (2019, 2020) recently applied the ISO/TS 16751 norm to determine the environmental availability of PAHs in aged-contaminated soils before and after remediation treatments, and our team measured PAH bioaccessibility throughout a bioremediation trial (Davin et al., 2019) and a rhizoremediation trial (Davin et al., 2020) before the norm came out.

Finally, let us keep in mind that if, as suggested previously, intermediate PAH metabolites or other PACs were to be added to the list of compounds of interest in the matter of environmental remediation, their bioavailability would also have to be monitored throughout remediation processes. Indeed, it was previously mentioned that as some of these compounds are more polar, they are also probably more mobile and bioavailable. This needs to be verified, as it is crucial that remediation techniques actually diminish the general toxicity and threat pollutants pose towards the environment. Here again, some researchers (Hu et al., 2014) have started to examine this issue when they investigated possible links between the biodegradable and the desorbable fractions of compounds such as oxy-PAHs, but also apolar PAH degradation metabolites. They obtained mixed results depending on the type of compound and concluded that although bioremediation could generate genotoxic metabolites, these compounds were not necessarily desorbable from the soil, and thus bioavailable. This finding is yet another argument supporting the need to implement and expand the assessment of bioavailability in remediation trials.

2. Conclusions

This paper has reviewed and questioned a few scientific parameters that have been leading soil and sediment PAH remediation studies and management for the past few decades.

The first parameter is the list of PAH compounds that are being studied and targeted in the scientific literature. We have shown that the classical 16 US-EPA compounds might no longer be sufficient to meet current environmental challenges and quality guidelines throughout the world. We suggest that it might be relevant to expand the variety of studied and remediated PAHs, but also PACs, in soils/sediments to meet remediation challenges and prevent toxic dead-ends.

The second parameter is the choice of experimental material in remediation studies. We have shown with bibliometric measures that neither co-contaminated nor aged-contaminated material have been systematically used in PAH remediation trials to date, even though such material is the most representative of realistic remediation challenges when it comes to land management. We thus suggest that researchers start using aged-contaminated and co-contaminated material more systematically in their trials. We also strongly advise that all types of results, even inconclusive ones, be shared with the scientific community.

The final parameter concerns the use of bioavailability measurement. A norm was just published that allows the evaluation of environmental availability (ISO/TS 16751). It was mainly developed as a tool to improve risk-analysis based management of contaminated land, but we suggest such measurement should be systematically included in remediation trials, on realistic soil material, to improve our understanding of remediation processes as well as management tools.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2021.116857.

References

Albarano, L., Costantini, M., Zupo, V., Lofrano, G., Guida, M., Libralato, G., 2020. Marine sediment toxicity: a focus on micro- and mesocosms towards remediation. Sci. Total Environ. 708, 134837. https://doi.org/10.1016/j.scitotenv.2019.134837.

Alexander, M., 2000. Aging, bioavailability, and overestimation of risk from environmental pollutants. Environ. Sci. Technol. 34 (20), 4259–4265. https://doi.org/10.1021/es001069+.

Andersson, J., Achten, C., 2015. Time to say goodbye to the 16 EPA PAHs? Toward an up-to-fate use of PACs for environmental purposes. Polycycl. Aromat. Comp. 35, 330–354. https://doi.org/10.1080/10406638.2014.991042.

Bleeker, E.A.J., Van Der Geest, H.G., Klamer, H.J.C., De Voogt, P., Wind, E., Kraak, M.H.S., 1999. Toxic and genotoxic effects of azaarenes : isomers and metabolites. Polycycl. Aromat. Comp. 13 (3), 191–203. https://doi.org/10.1080/10406639908020563.

Bouchez, M., Blanchet, D., Vandecasteele, J.P., 1995. Degradation of polycyclic aromatic hydrocarbons by pure strains and by defines strain associations: inhibition phenomena and cometabolism. Appl. Microbiol. Biotechnol. 43, 156–164. https://doi.org/10.1007/BF00170638.

Bowman, D.T., Jobst, K.J., Helm, P.A., Kleywegt, S., Diamond, M.L., 2019. Characterization of polycyclic aromatic compounds in commercial pavement sealcoat products for enhanced source apportionment. Environ. Sci. Technol. 53 (6), 3157–3165. https://doi.org/10.1021/acs.est.8b06779.

Cachada, A., Pereira, R., da Silva, E.F., Duarte, A.C., 2014. The prediction of PAHs bioavailability in soils using chemical methods: state of the art and future challenges. Sci. Total Environ. 472, 463–480. https://doi.org/10.1016/j.scitotenv.2013.11.038.

CCME, 2020. Canadian council of ministers of the environment. Canadian Environmental Quality Guidelines. http://ceqg-rcqe.ccme.ca/fr/index.html#void. (Accessed 20 March 2020).

Chibwe, L., Geier, M.C., Nakamura, J., Tanguay, R.L., Aitken, M.D., Massey Simonich, S.L.M., 2015. Aerobic bioremediation of PAH contaminated soil results in increased genotoxicity and developmental toxicity. Environ. Sci. Technol. 49, 13889–13898. https://doi.org/10.1021/acs.est.5b00499.

Chibwe, L., Davie-Martin, C.L., Aitken, M.D., Hoh, E., Massey Simonich, S.L., 2017. Identification of polar transformation products and high molecular weight polycyclic aromatic hydrocarbons (PAHs) in contaminated soil following bioremediation. Sci. Total Environ. 599–600, 1099–1107. https://doi.org/10.1016/j.scitotenv.2017.04.190.

Cochran, R.E., Dongari, N., Jeong, H., Beránek, J., Haddadi, S., Shipp, J., Kubátová, A., 2012. Determination of polycyclic aromatic hydrocarbons and their oxy-, nitro-, and hydroxy-oxidation products. Anal. Chim. Acta 740, 93–103. https://doi.org/10.1016/j.aca.2012.05.050.

Cui, X., Mayer, P., Gan, J., 2013. Methods to assess bioavailability of hydrophobic organic contaminants: principles, operations, and limitations. Environ. Pollut. 172, 223–234. https://doi.org/10.1016/j.envpol.2012.09.013.

Davie-Martin, C.L., Stratton, K.G., Teeguarden, J.G., Waters, K.M., Simonich, S.L.M., 2017. Implications of bioremediation of polycyclic aromatic hydrocarbon-contaminated soils for human health and cancer risk. Environ. Sci. Technol. 51 (17), 9458–9468. https://doi.org/10.1021/acs.est.7b02956.

Davin, M., Starren, A., Deleu, M., Lognay, G., Colinet, G., Fauconnier, M.-L., 2018. Could saponins be used to enhance bioremediation of polycyclic aromatic hydrocarbons in aged-contaminated soils? Chemosphere 194, 414–421. https://doi.org/10.1016/j.chemosphere.2017.11.174.

Davin, M., Starren, A., Marit, E., Lefébure, K., Fauconnier, M.-L., Colinet, G., 2019. Investigating the effect of Medicago sativa L. and Trifolium pratense L. root exudates on PAHs bioremediation in an aged-contaminated soil. Water Air Soil Pollut. 230–296. https://doi.org/10.1007/s11270-019-4341-4.

Davin, M., Renard, E., Lefébure, K., Fauconnier, M.L., Colinet, G., 2020. Temporal evolution of PAHs bioaccessibility in an aged-contaminated soil during the growth of two Fabaceae. Int. J. Environ. Res. Publ. Health 17, 4016. https://doi.org/10.3390/ijerph17114016.

Deary, M.E., Ekumankama, C.C., Cummings, S.P., 2018. Effect of lead, cadmium, and mercury co-contaminants on biodegradation in PAH-polluted soils. Land Degrad. Dev. 29 (6), 1583–1594. https://doi.org/10.1002/ldr.2958.

Dhar, K., Subashchandrabose, S.R., Venkateswarlu, K., Krishnan, K., Megharaj, M., 2019. Anaerobic microbial degradation of polycyclic aromatic hydrocarbons: a comprehensive review. In: de Voogt, P. (Ed.), Reviews of Environmental Contamination and Toxicology. Springer Nature, Switzerland. https://doi.org/10.1007/398_2019_29.

Duan, L., Naidu, R., Thavamani, P., Mealim, J., Megharaj, M., 2015. Managing long-term polycyclic aromatic hydrocarbon contaminated soils : a risk-based approach. Environ. Sci. Pollut. Res. 22, 8927–8941. https://doi.org/10.1007/s11356-013-2270-0.

Duffus, J.H., 2002. "Heavy metals" - a meaningless term? (IUPAC technical report). Pure Appl. Chem. 74 (5), 793–807. https://doi.org/10.1351/pac200274050793.

EC, 2020. European commission, environment, water, water Framework directive. https://ec.europa.eu/environment/water/water-framework/priority_substances.htm. (Accessed 19 March 2020).

ECHA, 2020. European chemicals agency. https://echa.europa.eu/legislation. (Accessed 17 March 2020).

EFSA, 2020. European Food Safety Authority. EC 1881/2006. COMMISSION REGULATION (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs. http://www.efsa.europa.eu/en/topics/topic/chemical-contaminants. (Accessed 19 March 2020).

Ehlers, L.J., Luthy, R.G., 2003. Contaminant bioavailability in improving risk assessment and remediation rests on better understanding bioavailability. Environ. Sci. Technol. 37, 295–302. https://doi.org/10.1021/es032524f.

EPA, 2020. United States environmental protection agency. https://www.epa.gov/eg/toxic-and-priority-pollutants-under-clean-water-act. (Accessed 17 March 2020).

Gan, S., Lau, E.V., Ng, H.K., 2009. Remediation of soils contaminated with polycyclic aromatic hydrocarbons (PAHs). J. Hazard Mater. 172 (2–3), 532–549. https://doi.org/10.1016/j.jhazmat.2009.07.118.

García-Alonso, S., Barrado-Olmedo, A.I., Pérez-Pastor, R.M., 2012. An analytical method to determine selected nitro-PAHs in soil samples by HPLC with fluorescence detection. Polycycl. Aromat. Comp. 32 (5), 669–682. https://doi.org/10.1080/10406638.2012.725196.

Ghosal, D., Ghosh, S., Dutta, T.K., Ahn, Y., 2016. Current state of knowledge in microbial degradation of polycyclic aromatic hydrocarbons (PAHs): a review. Front. Microbiol. 7, 1369. https://doi.org/10.3389/fmicb.2016.01369.

Ghosh, I., Mukherji, S., 2017. Substrate interaction effects during pyrene biodegradation by Pseudomonas aeruginosa RS1. J. Environ. Chem. Eng. 5 (2), 1791–1800. https://doi.org/10.1016/j.jece.2017.03.016.

Hamidi, E.N., Hajeb, P., Selamat, J., Razis, A.F.A., 2016. Polycyclic aromatic hydrocarbons (PAHs) and their bioaccessibility in meat: a tool for assessing human cancer risk. Asian Pac. J. Cancer Prev. APJCP 17 (1), 15–23. https://doi.org/10.7314/APJCP.2016.17.1.15.

Hu, J., Nakamura, J., Richardson, S.D., Aitken, M.D., 2012. Evaluating the effects of bioremediation on genotoxicity of polycyclic aromatic hydrocarbon-contaminated soil using genetically engineered, higher eukaryotic cell lines. Environ. Sci. Technol. 46, 4607–4613. https://doi.org/10.1021/es300020e.

Hu, J., Adrion, A.C., Nakamura, J., Shea, D., Aitken, M.D., 2014. Bioavailability of (geno)toxic contaminants in polycyclic aromatic hydrocarbon-contaminated soil before and after biological treatment. Environ. Eng. Sci. 31 (4), 176–182. https://doi.org/10.1089/ees.2013.0409.

Idowu, O., Semple, K.T., Ramadass, K., O'Connor, W., Hansbro, P., Thavamani, P., 2019. Beyond the obvious: environmental health implications of polar polycyclic aromatic hydrocarbons. Environ. Int. 123, 543–557. https://doi.org/10.1016/j.envint.2018.12.051.

Iqbal, J., Overton, E.B., Gisclair, D., 2008. Polycyclic aromatic hydrocarbons in Louisiana rivers and coastal environments: source fingerprinting and forensic analysis. Environ. Forensics 9 (1), 63–74. https://doi.org/10.1080/15275920801888301.

ISO/TS 16751, 2020. Soil Quality - Environmental Availability of Non-polar Organic Compounds - Determination of the Potential Bioavailable Fraction and the Non-bioavailable Fraction Using a Strong Adsorbent or Complexing Agent.

ISO 17402, 2008. Soil Quality - Requirements and Guidance for the Selection and Application of Methods for the Assessment of Bioavailability of Contaminants in Soil and Soil Materials.

Keith, L.H., 2015. The source of U.S. EPA's sixteen PAH priority pollutants. Polycycl. Aromat. Comp. 35, 147–160. https://doi.org/10.1080/10406638.2014.892886.

Kuppusamy, S., Thavamani, P., Venkateswarlu, K., Lee, Y.B., Naidu, R., Megharaj, M., 2017. Remediation approaches for polycyclic aromatic hydrocarbons (PAHs) contaminated soils : technological constraints, emerging trends and future directions. Chemosphere 168, 944–968. https://doi.org/10.1016/j.chemosphere.2016.10.115.

Lamichhane, S., Krishna, K.C.B., Sarukkalige, R., 2017. Surfactant-enhanced remediation of polycyclic aromatic hydrocarbons: a review. J. Environ. Manag. 199, 46–61. https://doi.org/10.1016/j.jenvman.2017.05.037.

Latawiec, A.E., Swindell, A.L., Simmons, P., Reid, B.J., 2011. Bringing bioavailability into contaminated land decision making: the way forward? Crit. Rev. Environ. Sci. Technol. 41 (1), 52–77. https://doi.org/10.1080/00102200802641780.

Leroy, M.C., Legras, M., Marcotte, S., Moncond'huy, V., Machour, N., Le Derf, F., Portet-Koltalo, F., 2015. Assessment of PAH dissipation processes in large-scale outdoor mesocosms simulating vegetated road-side swales. Sci. Total Environ. 520, 146–153. https://doi.org/10.1016/j.scitotenv.2015.03.020.

Lundstedt, S., Haglund, P., Öberg, L., 2002. Degradation and formation of polycyclic aromatic compounds during bioslurry treatment of an aged gasworks soil. Environ. Toxicol. Chem. 22 (7), 1413–1420.

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. TrAC Trends Anal. Chem. (Reference Ed.) 57, 83–92. https://doi.org/10.1016/j.trac.2014.01.007.

Mahanty, B., Pakshirajan, K., Dasu, V.V., 2010. Batch biodegradation of PAHs in mixture by Mycobacterium frederiksbergense: analysis of main and interaction effects. Clean Technol. Environ. Policy 12 (4), 441–447. https://doi.org/10.1007/s10098-009-0229-0.

Mahanty, B., Pakshirajan, K., Dasu, V.V., 2011. Understanding the complexity and strategic evolution in PAH remediation research. Crit. Rev. Environ. Sci. Technol. 41 (19), 1697–1746. https://doi.org/10.1080/10643389.2010.481586.

Mueller, A., Ulrich, N., Hollmann, J., Zapata Sanchez, C.E., Rolle-Kampczyk, U.E., von Bergen, M., 2019. Characterization of a multianalyte GC-MS/MS procedure for detecting and quantifying polycyclic aromatic hydrocarbons (PAHs) and PAH derivatives from air particulate matter for an improved risk assessment. Environ. Pollut. 255, 112967. https://doi.org/10.1016/j.envpol.2019.112967.

Niederer, M., 1998. Determination of polycyclic aromatic hydrocarbons and substitutes (nitro-, oxy-PAHs) in urban soil and airborne particulate by GC-MS and NCI-MS/MS. Environ. Sci. Pollut. Res. 5 (4), 209–216. https://doi.org/10.1007/BF02986403.

Nzila, A., 2018. Biodegradation of high-molecular-weight polycyclic aromatic hydrocarbons under anaerobic conditions: overview of studies, proposed pathways and future perspectives. Environ. Pollut. 239, 788–802. https://doi.org/10.1016/j.envpol.2018.04.074.

Ortega-Calvo, J.J., Tejeda-Agredano, M.C., Jimenez-Sanchez, C., Congiu, E., Sungthong, R., Niqui-Arroyo, J.L., Cantos, M., 2013. Is it possible to increase bioavailability but not environmental risk of PAHs in bioremediation? J. Hazard Mater. 261, 733–745. https://doi.org/10.1016/j.jhazmat.2013.03.042.

Ortega-Calvo, J.J., Harmsen, J., Parsons, J.R., Semple, K.T., Aitken, M.D., Ajao, C., Eadsforth, C., Galay-Burgos, M., Naidu, R., Oliver, R., Peijnenburg, W.J.G.M., Rombke, J., Streck, G., Versonnen, B., 2015. From bioavailability science to regulation of organic chemicals. Environ. Sci. Technol. 49 (17), 10255–10264. https://doi.org/10.1021/acs.est.5b02412.

Park, J., Ball, L.M., Richardson, S.D., Zhu, H.O., Aitken, M.D., 2008. Oxidate mutagenicity of polar fractions from polycyclic aromatic hydrocarbon – contaminated soils. Environ. Toxicol. Chem. 27 (11), 2207–2215.

Pazos, M., Rosales, E., Alcántara, T., Gómez, J., Sanromán, M.A., 2010. Decontamination of soils containing PAHs by electroremediation: a review. J. Hazard Mater. 177, 1–11. https://doi.org/10.1016/j.jhazmat.2009.11.055.

Posada-Baquero, R., Martín, M.L., Ortega-Calvo, J.J., 2019. Implementing standardized desorption extraction into bioavailability-oriented bioremediation of PAH-polluted soils. Sci. Total Environ. 696 https://doi.org/10.1016/j.scitotenv.2019.134011, 134011.

Posada-Baquero, R., Jiménez-Volkerink, S.N., García, J.L., Vila, J., Cantos, M., Grifoll, M., Ortega-Calvo, J.J., 2020. Rhizosphere-enhanced biosurfactant action on slowly desorbing PAHs in contaminated soil. Sci. Total Environ. 720, 137608. https://doi.org/10.1016/j.scitotenv.2020.137608.

Reichenberg, F., Mayer, P., 2006. Two complementary sides of bioavailability: accesibility and chemical activity of organic contaminants in sediments and soils. Environ. Toxicol. Chem. 25 (5), 1239–1245. https://doi.org/10.1897/05-458R.1.

Reichert, G., Hilgert, S., Fuchs, S., Azevedo, J.C.R., 2019. Emerging contaminants and antibiotic resistance in the different environmental matrices of Latin America. Environ. Pollut. 255, 113140. https://doi.org/10.1016/j.envpol.2019.113140.

Ren, X., Zeng, G., Tang, L., Wang, J., Wan, J., Liu, Y., Yu, J., Yi, H., Ye, S., Deng, R., 2018. Sorption, transport and biodegradation – an insight into bioavailability of persistent organic pollutants in soil. Sci. Total Environ. 610–611, 1154–1163. https://doi.org/10.1016/j.scitotenv.2017.08.089.

Riding, M.J., Doick, K.J., Martin, F.L., Jones, K.C., Semple, K.T., 2013. Chemical measures of bioavailability/bioaccessibility of PAHs in soil: fundamentals to application. J. Hazard Mater. 261, 687–700. https://doi.org/10.1016/j.jhazmat.2013.03.033.

Sanseverino, J., Werner, C., Fleming, J., Applegate, B., King, J.M.H., Sayler, G.S., 1993. Molecular diagnostics of polycyclic aromatic hydrocarbon biodegradation in manufactured gas plant soils. Biodegradation 4, 303–321.

Sarma, H., Nava, A.R., Prasad, M.N.V., 2019. Mechanistic understanding and future prospect of microbe-enhanced phytoremediation of polycyclic aromatic hydrocarbons in soil. Environ. Technol. Innov. 13, 318–330. https://doi.org/10.1016/j.eti.2018.12.004.

Semple, K.T., Morriss, A.W.J., Paton, G.I., 2003. Bioavailability of hydrophobic organic contaminants in soils: fundamental concepts and techniques for analysis. Eur. J. Soil Sci. 54, 809–818. https://doi.org/10.1046/j.1365-2389.2003.00564.x.

Semple, K.T., Doick, K.J., Jones, K.C., Burauel, P., Craven, A., Harms, H., 2004. Peer reviewed: defining bioavailability and bioaccessibility of contaminated soil and sediment is complicated. Environ. Sci. Technol. 38 (12), 228A–231A. https://doi.org/10.1021/es040548w.

Semple, K.T., Doick, K.J., Wick, L.Y., Harms, H., 2007. Microbial interactions with organic contaminants in soil: definitions, processes and measurement. Environ. Pollut. 150 (1), 166–176. https://doi.org/10.1016/j.envpol.2007.07.023.

Stringfellow, W.T., Aitken, M.D., 1995. Competitive metabolism of naphthalene, methylnaphthalenes, and fluorene by phenanthrene-degrading pseudomonas. Appl. Environ. Microbiol. 61 (1), 357–362. https://doi.org/10.1128/aem.61.1.357-362.1995.

Tian, Z., Gold, A., Nakamura, J., Zhang, Z., Vila, J., Singleton, D.R., Collins, L., Aitken, M.D., 2017a. Non-target analysis reveals a bacterial metabolite of pyrene implicated in the genotoxicity of contaminated soil after bioremediation. Environ. Sci. Technol. 51 (12), 7091–7100. https://doi.org/10.1021/acs.est.7b01172.

Tian, Z., Vila, J., Wang, H., Bodnar, W., Aitken, M.D., 2017b. Diversity and abundance of high-molecular-weight azaarenes in PAH-contaminated environmental samples. Environ. Sci. Technol. 51 (24), 14047–14054. https://doi.org/10.1021/acs.est.7b03319.

Umeh, A.C., Duan, L., Naidu, R., Semple, K.T., 2017. Residual hydrophobic organic contaminants in soil: are they a barrier to risk-based approaches for managing contaminated land? Environ. Int. 98, 18–34. https://doi.org/10.1016/j.envint.2016.09.025.

van Herwijnen, R., van de Sande, B.F., van der Wielen, F.W.M., Springael, D., Govers, H.A.J., Parsons, J.R., 2003. Influence of phenanthrene and fluoranthene on the degradation of fluorene and glucose by Sphingomonas sp. strain LB126 in chemostat cultures. FEMS Microbiol. Ecol. 46 (1), 105–111. https://doi.org/10.1016/S0168-6496(03)00202-2.

Vila, J., Tauler, M., Grifoll, M., 2015. Direct bacterial PAH degradation in marine and terrestrial habitats. Curr. Opin. Biotechnol. 33, 95–102. https://doi.org/10.1016/j.copbio.2015.01.006.

Von Lau, E., Gan, S., Ng, H.K., Poh, P.E., 2014. Extraction agents for the removal of polycyclic aromatic hydrocarbons (PAHs) from soil in soil washing technologies. Environ. Pollut. 184, 640–649. https://doi.org/10.1016/j.envpol.2013.09.010.

Wang, G., Jiang, Y., Hu, S., Guo, Y., 2018. Aspartic acid-β-cyclodextrin-assisted phytoremediation of soil co-contaminated with cadmium and fluorene using alfalfa (Medicago sativa L.). Environ. Eng. Sci. 35 (4), 279–288. https://doi.org/10.1089/ees.2016.0460.

WHO, 2020. World health organization, international program on chemical safety. Environmental Health Criteria. http://www.inchem.org/documents/ehc/ehc/ehc202.html. (Accessed 20 March 2020).

Wickrama-Arachchige, A.U.K., Hirabayashi, T., Imai, Y., Guruge, K.S., Dharmaratne, T.S., Ohura, T., 2020. Accumulation of halogenated polycyclic aromatic hydrocarbons by different tuna species, determined by high-resolution gas chromatography Orbitrap mass spectrometry. Environ. Pollut. 256, 113487. https://doi.org/10.1016/j.envpol.2019.113487.

Yu, L., Duan, L., Naidu, R., Semple, K.T., 2018. Abiotic factors controlling bioavailability and bioaccessibility of polycyclic aromatic hydrocarbons in soil: putting together a bigger picture. Sci. Total Environ. 613–614, 1140–1153. https://doi.org/10.1016/j.scitotenv.2017.09.025.