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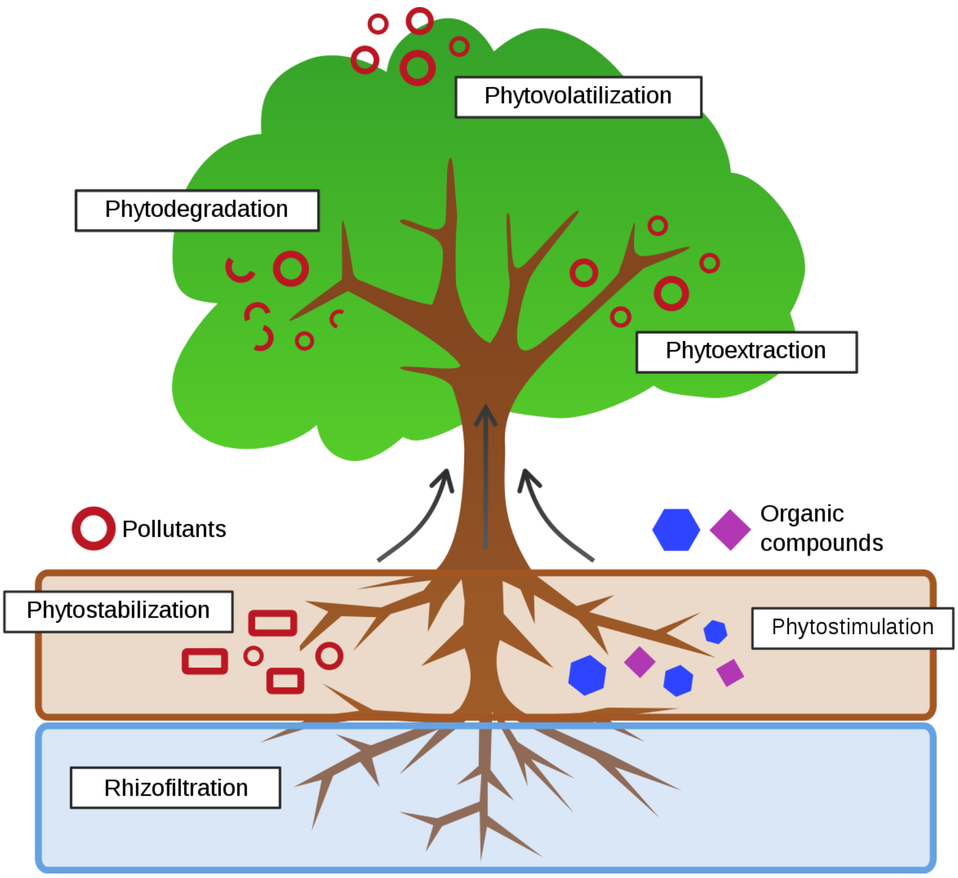

Gentle Remediation Options (GRO)

A Literature Review (Part 1/2)

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Department of Architecture and Civil Engineering
Division of Geology and Geotechnics
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Gothenburg, 2021

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SUMMARY

Soils are a non-renewable resource and comprise a key component of the world's stock of natural capital. Due to industrialisation, urbanisation and other patterns of unsustainable development, widespread land degradation in the form of contamination, soil sealing, compaction, etc. has impaired the capacity of soils to perform their essential functions and provide humans with vital ecosystem services. Brownfields are typically urban or peri-urban sites that have been affected by the former uses of the site, are or are perceived to be contaminated, and require intervention to bring them back to beneficial use. They also constitute an important and underutilised land and soil resource to provide ecosystem services in urban areas as an element of green infrastructure through the use of nature-based solutions such as gentle remediation options (GRO). Within the scope of the Ph.D. project " Enhancing ecosystem services by innovative remediation using gentle remediation options (ECO-GRO)", an in-depth but inexhaustive literature review has been carried out to build a theoretical understanding of GRO for the overall research project. This literature review report (part 1 of 2) will present a compilation of the main findings by beginning with A) core concepts of GRO including the background of their usage and development as well as key physiological mechanisms and processes; then B) mechanisms for the gentle remediation of organic (i.e. degradation and volatilisation) and inorganic contaminants (i.e. extraction and stabilisation) are reviewed, including the various strategies for implementation, practical aspects, key limitations, the possibilities to enhance effectiveness by combining with soil amendments and compilations of field studies demonstrating successful application. GRO mechanisms that are more specific in use like rhizofiltration and phytohydraulics are also briefly discussed as well as other remediation techniques included under the GRO umbrella such as bioremediation, mycoremediation and vermiremediation; C) the development in the field towards applying GRO to both manage risks and provide wider economic, social and environmental benefits, i.e. phytomanagement, is discussed at some length while considering its broader implications; and finally D) suitable plants for the various GRO mechanisms are discussed throughout the report but a specific section is set aside to discuss methods for selecting the most suitable plants as well as summarising the most applied plants.

Key words:

Gentle remediation options (GRO), phytomanagement, ecosystem services (ES), soil functions (SF), brownfields, contaminated sites, sustainable remediation, green infrastructure, nature-based solutions (NBS)

Contents

Preface

This literature review is the 1st part of two literature reviews which has been carried out at the Department of Architecture and Civil Engineering, Division of Geology and Geotechnics at Chalmers University of Technology in Gothenburg, Sweden. The work has been supervised by Professor Jenny Norrman and is performed as part of a Ph.D. research project entitled "Enhancing ecosystem services by innovative remediation using gentle remediation options (ECO-GRO)" which has been funded by the Swedish research council FORMAS (Grant number: 2018-01467)

Göteborg, Sweden

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Paul Drenning

List of notations

Abbreviations

BAF	Bio-accumulation factor
BCF	Bio-concentration factor
BCS	Bioavailable contaminant stripping
CBA	Cost –benefit analysis
DST	Decision support tool
ERA	Ecological (or ecosystem) risk assessment
ES	Ecosystem services
GRO	Gentle remediation options
MBC	Microbial biomass carbon
MCA	Multi-criteria analysis
MCDA	Multi-criteria decision analysis
MDS	Minimum dataset
NBS	Nature-based solutions
qPCR	Quantitative polymerase chain reaction
RBLM	Risk-based land management
SF	Soil functions
SDG	Sustainable Development Goals
SIR	Substrate-induced respiration
SQI	Soil quality indicators
SRC	Short-rotation coppice

1 Introduction

1.1 Background

Natural capital is defined by the Natural Capital Forum as the world's stock of natural assets including geology, soil, air, water and all living things (www.naturalcapitalforum.com). According to the European Commission, a major problem connected to our current resource consumption patterns is that our common pools of natural capital are treated as infinite, 'free' commodities whose value is not sufficiently accounted for in modern economic markets (EC, 2011a). This has inevitably led to detrimental resource depletion, pollution, and a wide range of associated threats to our long-term sustainability and resilience to environmental shocks, especially in urban areas (EC, 2011a; Olofsdotter et al., 2013). At present, resource consumption in urban areas accounts for almost 80% of global emissions of greenhouse gases. The legacy of industrialization over the past century has added the problem of widespread contamination in and around cities' soil and water systems. And cities in general are pushing at the limits of the established planetary boundaries (Olofsdotter et al., 2013; Rockström et al., 2009; Steffen et al., 2015). A series of agenda-setting reports by the European commission (e.g. *Vision for a Resource Efficient Europe, European Biodiversity Strategy to 2020*) have raised awareness of the widespread degradation of ecosystems by over-exploitation, land-use change, contamination, sealing, compaction, erosion, neglect, etc. which have led to rapid losses in biodiversity and diminished the total provided ecosystem services by approximately 60% worldwide in the past 50 years alone (EC, 2011a, 2011b, 2006; Ellen MacArthur Foundation, 2015). The concept of ecosystem services (ES) has become increasingly prevalent to denote nature's contribution to human welfare, and is commonly defined as 'the goods and services that humans derive from natural and human-modified systems on which societal welfare and economic development directly depend' (Millennium Ecosystem Assessment, 2005; TEEB, 2010). Soil as well can be considered a non-renewable resource as it takes many hundreds of years to form fertile topsoil, and land itself is a finite and shrinking resource (Breure et al., 2018). From an anthropocentric point-of-view, protecting and restoring these natural assets is imperative to human well-being for current and future generations. Urgent action is mandated by the European Commission and United Nations to curb the loss of biodiversity, resource degradation, and land-take by transitioning to a more sustainable development pattern that protects and preserves the value that these ecosystems represent.

Given the situation, soil and its functions have been raised to a position of critical importance for our common future through the (currently revisited) *Thematic Strategy on Soil Protection* (EC, 2006). Within the *Thematic Strategy*, seven essential soil functions (SF) have been established: (i) biomass production, including agriculture and forestry; (ii) storing, filtering and transforming nutrients, substances and water; (iii) biodiversity pool, such as habitats, species and genes: (iv) physical and cultural environment for humans and human activities; (v) source of raw materials; (vi) acting as a carbon pool; (vii) archive of geological and archaeological heritage (EC, 2006). The significance of SF and soil-based ecosystem services (ES) for realising the UN's Sustainable Development Goals (SDG) has also been addressed by directly linking them to many of the SDGs (e.g. S. Keesstra et al. 2018; S. D. Keesstra et al. 2016). Soil functions, Figure 1-1, are critical for the delivery of ecosystem services to humans, and thus it is critical to account for these and evaluate soil performance in urban development to maximize soil multi-functionality and SF and ES provisioning whenever possible (Bünemann et al., 2018; Lehmann and Stahr, 2010; Volchko et al., 2019, 2014b, 2013).

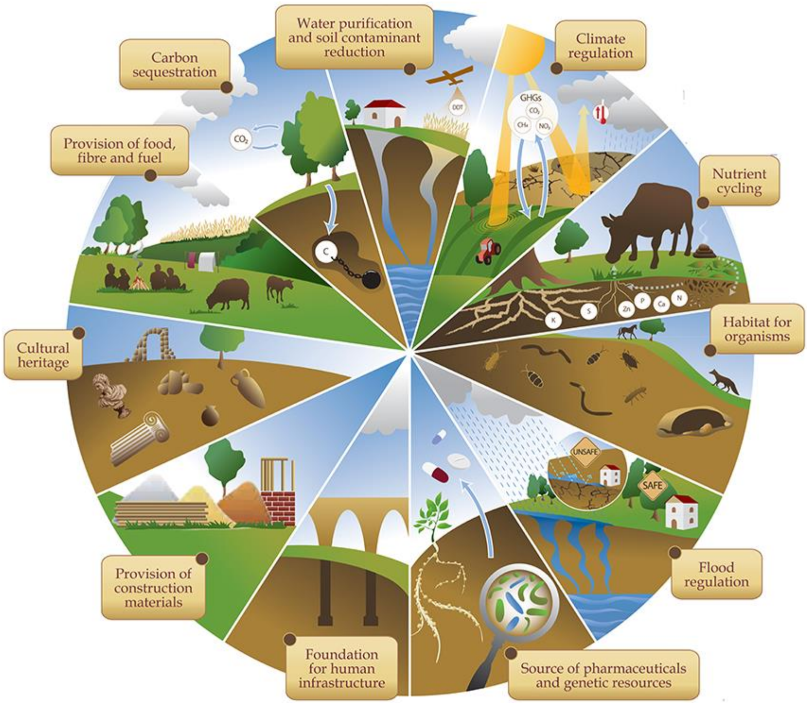

Figure 1-1. Schematic diagram of soil functions from the FAO, from (Baveye et al., 2016) *(CC-BY 4.0).*

Brownfields are underused areas with, in many cases, real or perceived soil and groundwater contamination which often is a barrier to redevelopment in terms of investment risks, ownership constraints, risk of future liability claims and public stigma (Ferber et al., 2006; Norrman et al., 2016a). In Europe, there are more than 2.5 million potentially contaminated sites caused by anthropogenic activity, i.e. brownfields, of which approximately 85 000 are in Sweden (Panagos et al., 2013). Soil contamination, along with other degradation processes, can negatively affect soil health (FAO et al., 2020; FAO and UNEP, 2021; Orgiazzi et al., 2016; Turbé et al., 2010), which is defined as '*the capacity of a given soil to perform its functions as a living system capable of sustaining biological productivity, promoting environmental quality and maintaining plant and animal health* (Doran and Zeiss, 2000). Instead of being viewed as a valuable resource to be cleaned and reused, contaminated soil is often viewed as a disposable waste, so conventional "quick and dirty" remediation techniques, usually based on removing or destroying the source of contamination, tend to entail irreversible damage to ecosystems (FAO et al., 2020; Gerhardt et al., 2017; Mench et al., 2010). Conventional remediation techniques are often resource intensive and entail multiple environmental externalities often resulting in a lifeless soil ecosystem unfit for 'soft' end uses like green spaces which require ecological functioning (Bardos et al., 2016; FAO et al., 2020; G. Lacalle et al., 2020; Volchko et al., 2014b). New practices are crucial for sustainable remediation and brownfield regeneration, because a significant amount of brownfield land area remains derelict or underutilized due to restoration being uneconomic or unsustainable using conventional methods (Bardos, 2014; Bardos et al., 2020b, 2018, 2016).This problem is of particular concern for large land areas or smaller, marginal sites where contamination inhibits immediate development, but economic return post-remediation does not justify the costs (Cundy et al., 2016).

Market and exploitation pressures and stakeholders' perception of uncertainties in time, costs, efficiency of alternative remediation options, and future liabilities have a crucial impact on the selection of treatment solutions at contaminated sites (SGI, 2012) and there is a hesitancy with regard to implementation of innovative treatment solutions in many remediation projects. The Swedish EPA (SEPA) is, despite large expenditures on tackling the contamination problem, concerned about the low level of innovation in remediation technologies and the slow progress of brownfield remediation; accordingly, they have set a goal to increase the usage of innovative *in-situ* remediation strategies (SEPA, 2013). Commonly today, contaminated masses are excavated and landfilled due to time constraints, low disposal fees and well-established effectiveness in removing the source of the contamination which is readily accepted by regulatory authorities (SGI, 2012). Perhaps most importantly, this conventional method is fast and allows for rapid redevelopment in urban areas with high land value. However, excavation entails numerous disadvantages, including the negative effects caused by transportation (use of fossil fuels, emissions and accident risks), use of virgin material for refilling at the sites, the production of waste for landfilling as well as significant economic and social costs (Bardos, 2014; Rosén et al., 2015). The choice of remediation strategy can be influenced by a more careful consideration of (I) site specific conditions of the soil (e.g. (Volchko et al., 2019, 2014a, 2014b)), (II) consideration of the site conditions in the early planning process (e.g. (Bardos et al., 2016; Menger et al., 2013; Norrman et al., 2016b)), and (III) consideration of redevelopment effects on the provision of ecosystem services at brownfields (e.g. (Ivarsson, 2015; Volchko et al., 2020)). There is an international consensus on promoting increased use of alternative, more sustainable remediation methods (Bardos et al., 2020a, 2016; Cundy et al., 2016; ISO, 2017; Maco et al., 2018; Menger et al., 2013; Rosén et al., 2015; SEPA, 2013; SGI, 2018).

A promising field of innovative remediation technologies which have received much attention in recent years are those involving plant- (phyto-), fungi- (myco-) and/or bacteria- (bio-) based methods with or without the use of soil amendments, i.e. gentle remediation options (GRO). Research has shown that GRO can provide both effective risk management and result in a net gain in ecological soil function (Cundy et al., 2016; Mench et al., 2010; Vangronsveld et al., 2009). Potentially, several contaminated sites with low or moderate risk can be treated within a budget for excavation and disposal of one high-risk site, increasing the overall remediation progress at national level in the long-term. As will be discussed in this report, GRO are low-cost, low impact *in situ* remediation technologies which could be stand-alone or a part of treatment trains, for example, combined with conventional excavation and disposal when excavations are unavoidable because of contamination hotspots or construction of foundations. Furthermore, when viewed in the broader context as nature-based solutions (NBS), these alternative techniques may gain wider acceptance as mainstream land management strategies and green infrastructure for broader situational applicability to contribute to sustainable development (Keesstra et al., 2018b; Song et al., 2019).

1.2 Aim and Scope

A literature review has been carried out as part of the Ph.D.-project "Enhancing ecosystem services by innovative remediation using gentle remediation options (ECO-GRO)". This report presents an in-depth but inexhaustive compilation of information that will be used to build a theoretical foundation for the overall research project. Concepts covered include the development and usage of GRO in scientific literature, key physiological mechanisms and processes that enable remediation, discussion of GRO for organic and inorganic contaminants, additional broader mechanisms included under the GRO umbrella and compilations of related field studies, which are referred to specifically in relevant sections. This report also aims to give a brief review of phytomanagement and important considerations for bio-based production and selecting the most suitable plants for different situations.

Gentle remediation options, including phytoremediation, bioremediation, etc., is a large, diverse field with a large, growing body of information that would need to be included in a literature review to cover all relevant concepts. Many reviews pertaining to GRO (particularly phytoremediation) have already been written (e.g. (Gerhardt et al., 2017; Mench et al., 2010; Vangronsveld et al., 2009)); thus, the goal with this report is not to summarise the existing field of research within the GRO umbrella but to extract best practices, opportunities, lessons learned, wider benefits as well as evidence-based empirical data related to expected time and effectiveness when using the various techniques, synthesize the state-of-the-art and present need-to-know concepts within the context of the Ph.D.-project. This report is the 1st part of two literature reviews concerning: 1) Gentle remediation options (GRO) and 2) Soil functions and ecosystem services. Soil functions and ecosystem services are the focus of the 2nd part of literature review and will not be discussed in-depth in this report.

Specific objectives with this literature review:

- Target literature review towards practical information necessary to carry out pilot studies, i.e. *what do we need to know to implement GRO?*
- Compile pertinent field studies to create a reference bank and body-of-evidence for GRO effectiveness in different situations.
- Identify influential sources or seminal works that lead the field to focus on for deriving the most valuable information.
- Gain the necessary background knowledge to have a sufficient understanding of the topics or themes addressed in the ECO-GRO Ph.D.-project and to identify areas of prior research to prevent duplication of effort (i.e. not re-inventing the wheel).
- Identify key themes and the intersectionality between related (yet disconnected) fields: gentle remediation options to soil functioning and ecosystem service provisioning. This will be accomplished within the ECO-GRO Ph.D.-project by combining the findings of both parts of literature review in the future thesis work.

1.3 Methodology

The overarching purpose of a literature review can be broadly described as a more or less systematic way of collecting and synthesizing previous research (Snyder, 2019). In addition to a number of seminal works and highly cited and relevant papers (referred to explicitly in relevant sections), a series of steps (according to the Chalmers Library Literature Review Guide[1]) were followed to create a 'semi-systematic' method to add a robustness to the review in searching for supplementary material, including:

1. **Problem formulation** – establishing the thematic areas and topics to be covered in the review, broadly including:
    - Techniques and strategies within GRO and how they can be utilised for risk management
    - Site-specific conditions and other factors important for GRO success
    - Connection to holistic land management and planning
    - Opportunities and synergies to enhance ecosystem services and improve overall soil quality and functioning by using GRO
2. **Formulating sensitive search terms** – including relevant research and exclude the greater bulk, to search for literature in the Scopus database that may be relevant to include in the review.
3. **Screen the selected literature** – by reading titles, abstracts, summaries, etc. to determine which are the most useful to include. Also, identify previously conducted reviews relevant

[1] Literature Review Guide at Chalmers University of Technology

to soil functions and ecosystem services and establish prominent, seminal works that have an outweighed influence in the field to rely more heavily upon.

4. **Analyse and interpret** – analysing the findings and conclusions of the most significant literature, extract the pertinent information, and synthesise according to pre-selected themes to clearly structure within the overall review.

Many searches in the Scopus database were carried out to isolate the most relevant scientific articles to include in this review, shown in Appendix I. To ensure that the searches were performed in a systematic, transparent way the PRISMA method was adoped[2].

Several reviews compiling field studies employing GRO have already been written. Most notably, Vangronsveld et al. (2009) compiled field studies employing phytoextraction and phytostabilisation processes and discussed them at length alongside a few degradation-based studies. Similarly, Gerhardt et al. (2017) compiled phytoremediation field studies by searching the Scopus database for "phytoremediation" and "field trial" or "field experiment" and "soil" between the years 2009-2016. A similar approach to Gerhardt et al. (2017) has been taken in this review to search the Scopus database for relevant GRO field applications. The search was broadened by making separate searches for phytoremediation, individual GRO mechanisms and additional terms of interest like "phytomanagement" then consolidated to remove duplicates. Searches were structured using an AND operator for each keyword then filtering to extract papers published between the years 2017-2020, see Table 1-1.

Table 1-1. Search terms used to find field applications of phytoremediation and other GRO techniques in the Scopus database.

Primary keywords	Secondary keywords	Tertiary keywords	Filter	Hits (relevant)
Phytoremediation	"field trial" or "field experiment" or "field study"	soil	Time period: 2017-2020	142 (68)
Phytoextraction				59 (31)
Phytostabilisation (or w/z)				25 (18)
Phytodegradation				1 (0)
Phytotransformation				0
Rhizodegradation				2 (1)
Rhizofiltration				1 (0)
Phytovolatilisation (or w/z)				2 (0)
In-situ immobilisation (or w/z)				6 (5)
Phytoexclusion				3 (2)
In-situ stabilisation (or w/z)				5 (4)
Phytomanagement				13 (11)
Gentle remediation options (GRO)				3 (3)
Monitored natural attenuation				0

Studies of particular interest or relevance to this project (depending on e.g. strategy used, climate zone, focus of the study, etc.) were highlighted for deeper reading and are also included

[2] http://www.prisma-statement.org/

in separate tables under either organic or inorganic remediation in the respective sections. Reference to other field studies with high relevance to this project, e.g. GREENLAND and PhytoSUDOE project field studies and CLU-IN Phytotechnology database[3], have also been included in the respective sections. For more technical information, the reader is referred to previously conducted reviews and research (Cundy et al., 2016; Gerhardt et al., 2017; Mench et al., 2010; Vangronsveld et al., 2009) and best practice guides for implementation (GREENLAND, 2014a; ITRC, 2009; Kennen and Kirkwood, 2015; Mench et al., 2019; Moreira et al., 2019; OVAM, 2019).

1.4 Terminology

Integrating key concepts of soil science like soil quality and soil quality indicators (including ecological soil health) into contaminated site investigation and management is a significant step in the right direction towards sustainable soil and land management where soil is *managed in accordance with the soil's capability and condition* (Volchko et al., 2019). By accounting for soil parameters beyond just contamination levels in decision-making the latent potential of the soil can be leveraged to turn sustainable ambitions to recover ecosystem functions through soil protection into action (Volchko et al., 2019). For, **the ultimate objective of any remediation process must be not only to remove the contaminants from the soils (or instead disrupt the source-pathway-receptor linkages) but also to restore soil quality** (Epelde et al., 2008a; FAO et al., 2020; Gómez-Sagasti et al., 2012).

Terms and definitions related to soils can vary significantly and be used interchangeably even within disciplines. To avoid confusion, it is necessary to establish a common language and terminology in the context of contaminated sites for the purposes of this review. Terms will be used according to the following definitions:

Bioavailability commonly refers to the readily available fraction of a contaminant that can freely cross cell membranes, i.e. be absorbed in an organism, yet there is no general consensus on how to measure bioavailability and how many endpoints should be tested (Kumpiene et al., 2017). **Bioaccessibility** is a similar and interrelated concept referring generally to potential bioavailability for animals and humans, i.e. labile fraction that can be released into solution to interact with an organisms, which is used in human health risk assessment by assessing *in-vitro* bioaccessibility to estimate uptake in the gastro-intestinal system (ISO, 2018; Kumpiene et al., 2017). As stated in ISO 17924, "In human health risk assessment, 'bioavailability' is specifically used in reference to absorption into systemic circulation, consistent with the toxicological use of the term. This encompasses bioaccessibility, which again is a combined measure of the processes determining the interaction between the metal associated with the soil and the liquid in the human digestion system" (ISO, 2018).

Brownfield has been defined as a site that has been affected by the former uses of the site or surrounding land, is derelict or underused, is mainly in fully or partly developed urban areas, requires intervention to bring it back into beneficial use, and may have real or perceived contamination problems (Ferber et al., 2006; ISO, 2017).

Brownfield regeneration/restoration is the management, rehabilitation and return to beneficial use of the brownfield land resource base in such a manner as to ensure the attainment and continued satisfaction of human needs for present and future generations in environmentally non-degrading, economically viable, institutionally robust and socially acceptable ways (Bardos et al., 2016).

Ecosystem services (ES) are commonly defined as the goods and services that humans derive from natural and human-modified systems on which societal welfare and economic

[3] https://clu-in.org/products/phyto/search/phyto_search.cfm

development directly depend (Millennium Ecosystem Assessment, 2005; TEEB, 2010). They are typically divided into 4 categories: i) provisioning (products obtained from ecosystems), ii) regulating (benefits obtained from regulation of ecosystem processes), iii) cultural (non-material benefits obtained from ecosystems), and iv) supporting (services necessary for the production of all other ecosystem services) (Millennium Ecosystem Assessment, 2005; TEEB, 2010).

Gentle remediation options (GRO) are risk management strategies or technologies that result in a net gain (or at least no gross reduction) in soil function as well as achieving effective risk management(Cundy et al., 2016).

Green infrastructure refers to a strategically planned network of natural and seminatural areas with other environmental features designed and managed to deliver a wide range of ecosystem services" (EC, 2013). A similar concept, **blue-green infrastructure** is defined as *interconnected networks of land and water that support species, maintain ecological processes, sustain air and water resources, and contribute to the health and quality of life for communities and people* (Olofsdotter et al., 2013).

Human health is often considered as a basic human right and is defined by the World Health Organization (WHO) as not simply being free from illness, but in a state of complete physical, mental and social well-being. Biodiversity can be considered as the foundation for human health as it underpins the functioning of the ecosystems on which we depend for our food and fresh water; aids in regulating climate, floods and disease; provides recreational benefits and offers aesthetic and spiritual enrichment. Biodiversity also contributes to local livelihoods, to both traditional and modern medicines and to economic development (Health and Biodiversity (cbd.int)).

Natural capital refers to the extension of the economic idea of manufactured capital to include environmental goods and services (Dominati et al., 2010). Natural capital consists of *stocks of natural assets (e.g. soils, forests, water bodies) that yield a flow of valuable ecosystem goods or services into the future* (COSTANZA and DALY, 1992; Dominati et al., 2010). Soils are considered here as natural capital and provide services such as recycling of wastes or flood mitigation (Dominati et al., 2010).

Nature-based solutions (NBS) are solutions that are inspired and supported by nature, which are cost-effective, simultaneously provide environmental, social and economic benefits and help build resilience. Such solutions bring more, and more diverse, nature and natural features and processes into cities, landscapes and seascapes, through locally adapted, resource-efficient and systemic interventions (EC, 2015; Science for Environment Policy, 2021). In a recently developed standard for NBS, IUCN defined NBS as *actions to protect, sustainably use, manage and restore natural of modified ecosystems, which address societal challenges, effectively and adaptively, providing human well-being and biodiversity benefits* (IUCN, 2020).

Phytomanagement is commonly defined as the long-term combination of profitable crop production with gentle remediation options (GRO) leading gradually to the reduction of pollutant linkages due to metal(loid) excess and restoration of ecosystem services (Cundy et al., 2016; GREENLAND, 2014a, 2014b; Brett H Robinson et al., 2009).

Phytotechnology has been used broadly to refer to a set of technologies using plants to remediate or contain contaminants in soil, groundwater, surface water or sediments (ITRC, 2009), but has been alternatively defined by the International Phytotechnology Society (phytosociety.org) as *the strategic use of plants to solve environmental problems by remediating the qualities and quantities of our soil, water and air resources and by restoring ecosystem services in managed landscapes.*

Soil biodiversity comprises the variation in soil life, from genes to communities, and the ecological complexes of which they are part, that is from soil microhabitats to landscapes (Turbé et al., 2010). This variation is generally described in terms of three interrelated attributes of biodiversity: composition, structure and function (Pulleman et al., 2012). Biodiversity is then considered as the quantity, variety and structure of all forms of life in soils, as well as related functions (Pulleman et al., 2012).

Soil fertility has its origins in agriculture primarily referring to the ability of the soil to supply essential plant nutrients and soil water in adequate amounts and proportions for plant growth and reproduction in the absence of toxic substances which may inhibit plant growth (Bünemann et al., 2018). Soil fertility is a difficult term for it can be referred to as both soil function and ecosystem service. Whenever possible, this term will be avoided in favour of more consistently used terms like primary productivity.

Soil functions is a loaded term which has been used alternatively to mean process, function, role, or service (Baveye et al., 2016; Bünemann et al., 2018). Confusing as the term may be, it has served as a conceptual foundation in soil management, most notably in EC 2006, so it is considered worthwhile to clarify and distinguish between soil *processes, functions and services* (Baveye et al., 2016). Accordingly, *soil functions* are here defined as *what the soil has the capability to do in its natural (undisturbed) state as a result of the (bundles of) soil processes (*e.g. soil formation, nutrient cycling, etc.*) arising out of the complex interaction between biotic and abiotic components in the soil environment* (Bünemann et al., 2018; Volchko et al., 2013). Soil functions thus can be viewed as *a subset of wider ecosystem functions* (Volchko et al., 2013)*, which underpin the delivery of ecosystem services* (Bünemann et al., 2018).

Note: this term is often used interchangeably with *ecosystem functions*.

Soil health accounts for soil's capacity beyond the direct utilitarian end use considerations as it has typically included soil's ecological attributes associated with soil biota, biodiversity, and the living and dynamic nature of soil (Bünemann et al., 2018; Doran and Zeiss, 2000; Garbisu et al., 2011; Karlen et al., 1997). The most frequently referred to definition defines soil health as *the capacity of soil to function as a vital living system, within ecosystem and land-use boundaries, to sustain plant and animal productivity, maintain or enhance water and air quality, and promote plant and animal health* (Doran and Zeiss, 2000). In a more agricultural context, Kibblewhite et al. (Kibblewhite et al., 2008) derive the definition of soil health as an essential feature of sustainable agriculture: *a healthy agricultural soil is one that is capable of supporting the production of food and fibre, to a level and with a quality sufficient to meet human requirements, together with continued delivery of other ecosystem services that are essential for maintenance of the quality of life for humans and the conservation of biodiversity.* A recently performed review (Bünemann et al., 2018) concluded that soil quality and soil health are essentially equivalent, so for this review the term soil quality will be favoured.

Soil quality has a generally agreed upon definition broadly meaning *the capacity of a soil to perform its functions necessary for its intended end use* (Garbisu et al., 2011; Karlen et al., 2003, 1997; USDA Natural Resource Conservation Service, 2015; Volchko et al., 2013). This inherently anthropocentric definition has been expanded in Bünemann et al. (Bünemann et al., 2018) to more broadly include ecological (i.e. biological) functioning *'within ecosystem and land-use boundaries to sustain biological productivity, maintain environmental quality, and promote plant and animal health*.' This expanded definition includes soil health (see above) and reflects more the complexity and site-specificity of soil functioning as well as indicates the multi-functionality of soils when functioning according to their capacity.

Sustainable remediation is the practice of demonstrating, in terms of environmental, economic and social indicators, that the benefit of undertaking remediation is greater than its impact and that the optimum remediation solution is selected through the use of a balanced decision-making process (Bardos, 2014), or simply the elimination and/or control of unacceptable risks in a safe and timely manner whilst optimising the environmental, social and economic value of the work (ISO, 2017).

1.5 Structure of the report and the limitations

The literature review report has been structured to present core concepts related to GRO with references made to external sources throughout. *Chapter 1* provides and introduction and background to the topic and its relevance to the broader Ph.D. project. *Chapter 2* first provides general background for GRO with reference to studies using the term (Appendix II) then presents the state-of-the-art and discusses core concepts related to GRO, including the main physiological mechanisms and processes (2.2); degradation and volatilisation mechanisms for gentle remediation of organic contaminants as well as a compilation table of field studies (2.3); extraction and stabilisation (including aided-stabilisation with amendments, also referring to Appendix III, and risk mitigation aspects of vegetation cover) mechanisms for gentle remediation of inorganic contaminants as well as compilation table of field studies (2.4); general discussion concerning the application of rhizofiltration (2.4) and phytohydraulics (2.5); and general discussion and description of the GRO mechanisms included within bioremediation (2.6), mycoremediation (2.7) and vermiremediation (2.8). *Chapter 3* broadens the discussion to the emerging concept of phytomanagement including bio-based production and provisioning of ecosystem services. *Chapter 4* provides a brief discussion with reference to additional sources concerning the primary consideration for the selection of suitable plants for various GRO purposes with reference to Appendix IV for a compilation of plants commonly used in GRO. *Chapter 5* provides a final discussion and concluding remarks, and *Chapter 6* provides additional sources for further reading to refer the reader for additional information not covered in this report.

The main limitation of this literature review is that it is not systematic and wholly inclusive of the field of scientific literature. Instead, a more targeted approach has been taken to focus on the narrower range of topics presented here and by relying primarily on select, highly cited or relevant sources. Many topics highly pertinent to GRO have not been included due to lack of time or with intent to discuss further in future reports, for which the reader is referred to other sources for further reading.

2 Gentle Remediation Options

As of February 8, 2021, 23 publications that make specific reference to "gentle remediation options" (in abstract, title or keywords) were found in the Scopus database. An additional 9 publications were found that used the shorter "gentle remediation" to describe the remedial techniques involving phytoremediation and/or soil amendments. The 29[4] relevant publications have been compiled into a table, shown in **Appendix II**, which was created to show how the term GRO has been used and developed over time. Reading the papers, one can see that using plants for remediation has developed from a predominantly decontamination-centric approach (largely using phytoextraction) from its conception into a more comprehensive (holistic) land management strategy based on a 'phytomanagement' approach. The more recent papers emphasise the wider benefits offered by the plants (and associated microbiome) to restore soil ecosystems and provide ecosystem services. For example, such keywords as 'phytomanagement', 'soil health', 'soil microbial properties', etc. are used frequently in later papers and support the development towards the newer paradigm. The specifics of using GRO within this paradigm is the primary focus of this review.

In terms of a general description, GRO was first mentioned in Onwubuya et al. (2009) but the coined term gentle remediation options (GRO) has its origins in the seminal paper by Cundy et al. (2013). GRO have since come to be defined as *risk management strategies or technologies that result in a net gain (or at least no gross reduction) in soil function as well as achieving effective risk management* (Cundy et al. 2016). GRO is the umbrella term covering many technologies based upon the use of plant (phyto-), fungi (myco-), and/or bacteria-based (bio-) methods with or without the use of chemical additives or soil amendments, see Figure 2-1. The use of earthworms (vermi-) for remediation has also seen increasing use lately is sometimes considered to be a GRO (e.g. (G. Lacalle et al., 2020)). These more innovative biological methods of soil remediation have arisen as alternatives to traditional physicochemical methods, which tend to be based on cost-intensive and environmentally destructive techniques, and to provide multi-functionality for: i) an effective removal of soil contaminants (in terms of decreasing total and/or bioavailable contaminant concentrations), ii) a reduction of soil ecotoxicity, iii) the legal and ethically required reduction of risks for both human health and the environment; and, concurrently, a recovery of iv) soil health and v) associated ecosystem services (Cundy et al., 2016; G. Lacalle et al., 2020; GREENLAND, 2014a).

[4] Three papers were excluded for not being written in English, accessible or of immediate relevance to the current review.

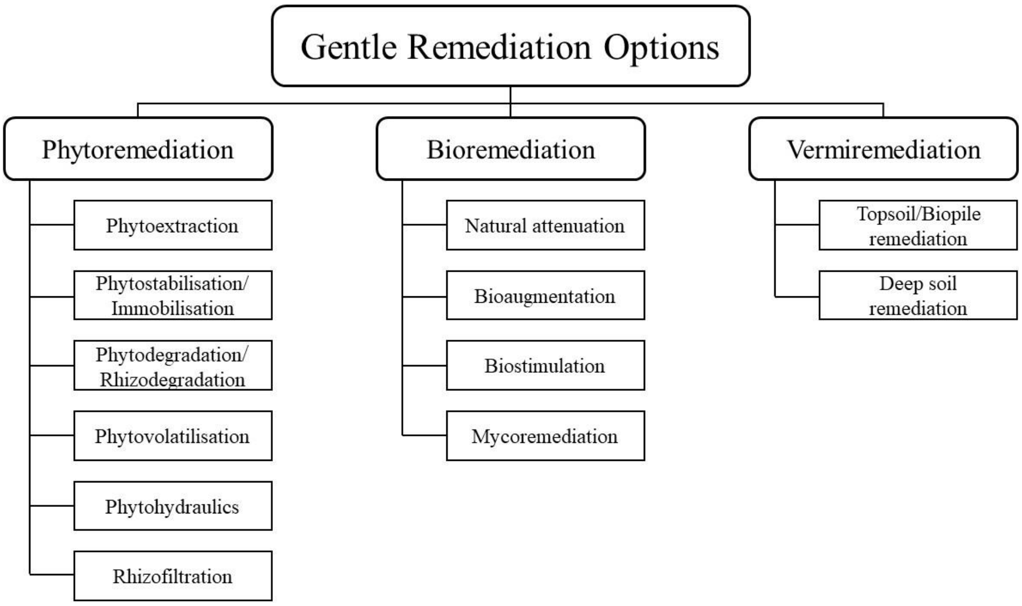

Figure 2-1. Gentle remediation options – categories and mechanisms, modified from (G. Lacalle et al., 2020).

Regarding risk management, GRO are primarily applied on contaminated soils to reduce contaminant transfer to local receptors by removing the bioavailable pool of inorganic contaminants (*phytoextraction*), removing or degrading organic contaminants (*phyto- and rhizodegradation*), filtering contaminants from surface water and waste water (*rhizofiltration*) or groundwater (*phytohydraulics*), and stabilising or immobilising contaminants in the soil matrix (*phytostabilisation, in-situ immobilization*) often in combination with vegetation cover using excluder plants (*phytoexclusion*) (Table 2-1). If well-designed, GRO can provide rapid risk management via pathway control through containment and stabilisation, coupled with a longer-term removal or immobilisation of the contaminant source, and managing the receptor's access to prevent exposure (GREENLAND, 2014a). In addition, substantial economic (e.g. biomass generation), socio-cultural (e.g. leisure and recreation), and environmental (e.g. ecosystem services and restoration of plant and microbial and animal communities) co-benefits are also possible through GRO application when intelligently applied (Cundy et al., 2016, 2013; GREENLAND, 2014a).

Table 2-1. List of definitions for GROs used to remediate soils contaminated by either trace elements or mixed contamination, adapted from (Bardos et al., 2020a; Cundy et al., 2016; GREENLAND, 2014a; OVAM, 2019).

GRO	Definition
Phytoextraction	Process in which plants and their associated microorganisms absorb contaminants and fix them in above-ground plant tissue that can then be removed from the site during harvesting.
Phytodegradation/ phytotransformation	The use of plants (and associated microorganisms like endophytic bacteria) to uptake, store and degrade contaminants.
Rhizodegradation	The use of plant enzymes and rhizospheric (in root zone) microorganisms to degrade organic contaminants.
Phytostabilisation	Reduction in the bioavailability and mobility of contaminants by immobilisation in root systems and/or living dead biomass in the rhizosphere soil.
Phytovolatilisation	The use of plants to remove contaminants from the growth matrix, transform them to less toxic forms and disperse them (or their degradation products) into the atmosphere.
In-situ immobilisation	Reduction in the bioavailability of contaminants by immobilisation or binding them to the soil matrix through the incorporation into the soil of organic or inorganic compounds to prevent excessive uptake and transfer into the food chain.
Phytoexclusion	The implementation of a stable vegetation cover using excluder plants which do not accumulate contaminants in the harvestable biomass, often combined with in-situ immobilisation.
Rhizofiltration	The removal of contaminants from aqueous sources (surface waters) by plant roots and associated microorganisms.
Phytohydraulics	Process in which plants and their microorganisms take up and evaporate water and thereby influence the groundwater level, the direction and velocity of the groundwater flow.
Bioremediation	Generic term applied to a range of remediation and risk management technologies which utilise soil microorganisms to degrade, stabilise or reduce the bioavailability of contaminants.
Mycoremediation	A form of bioremediation in which fungi-based methods are used to degrade, extract, stabilise or reduce the bioavailability or contaminants.
Vermiremediation	A remediation technique which utilises earthworms to remove or stabilise soil contaminants.

Similar concepts may also be suitable for groundwater (Cundy et al., 2013; GREENLAND, 2014a). Terminology can vary between users resulting in many different mechanisms; for example, the term 'phytotechnologies' has been used broadly to refer to *a set of technologies using plants to remediate or contain contaminants in soil, groundwater, surface water or sediments* (ITRC, 2009) and can include a wide variety of mechanisms (Figure 2-2). According to OVAM (2019), the term phytotechnologies has been used to emphasise that it also includes plant-based technologies that stabilise contaminants because phyto-'remediation' is often interpreted to indicate the sole aim of 'removing' the contaminants (i.e. the source), which may or may not be the case. The previous remediation-focused definition of phytotechnologies has since been expanded by the International Phytotechnology Society (phytosociety.org) to refer to *the strategic use of plants to solve environmental problems by remediating the qualities and quantities of our soil, water and air resources and by restoring ecosystem services in managed landscapes.* According to this definition, the use of plants to remediation environmental contaminants (i.e. phytoremediation) is just one of the many areas included within phytotechnologies, and can also encompass other functions such as restoring ecosystems and creating habitat, creating biofuels and other valued bio-products, greening of infrastructure for energy efficiency with green roofs, sequestering carbon to mitigate climate change, managing landfill and other waste streams with vegetative caps and treating wastewater and restoring water resources with engineered constructed wetlands.

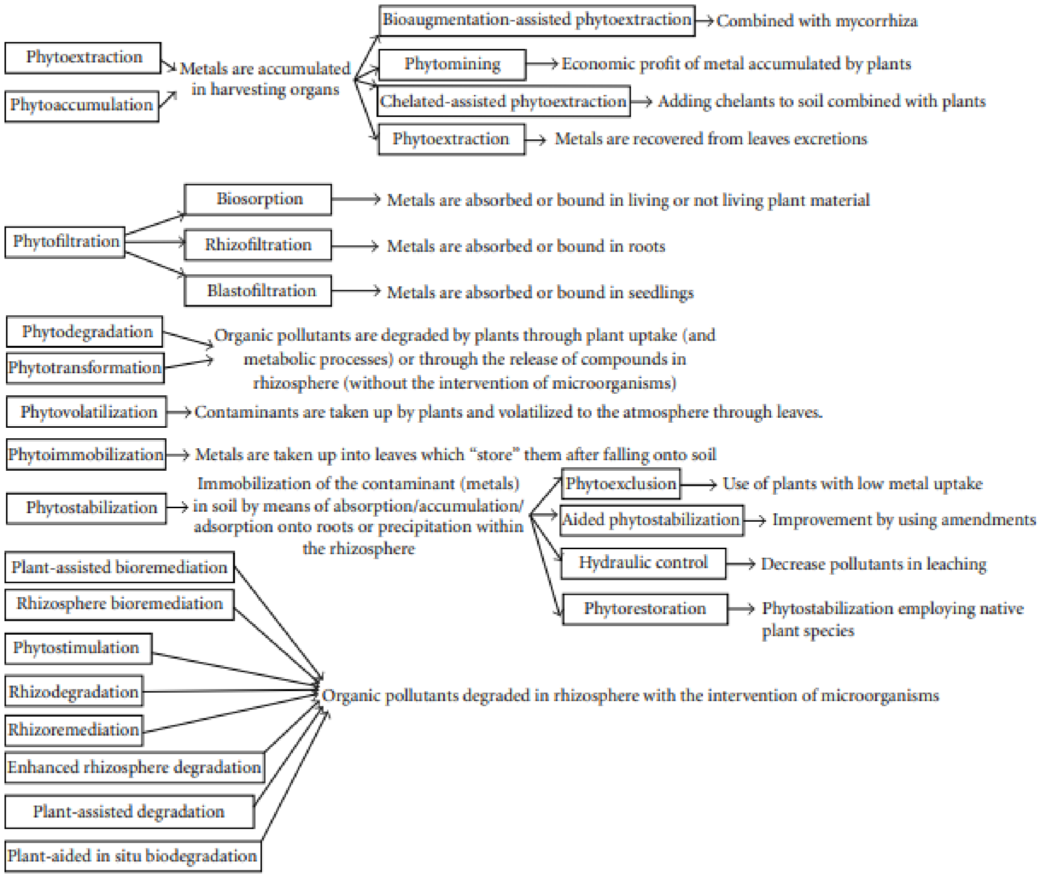

Figure 2-2. Classification of terminology frequently included under the term 'phytotechnologies' for soil remediation, from (Conesa et al., 2012)

GRO are well-suited to mitigate the risks posed by low to medium concentrations of both inorganic and organic contaminants though the timeframe for remediation can differ significantly between the contaminants and the mechanisms involved (Figure 2-3). The following sections will describe each of the mechanisms in detail.

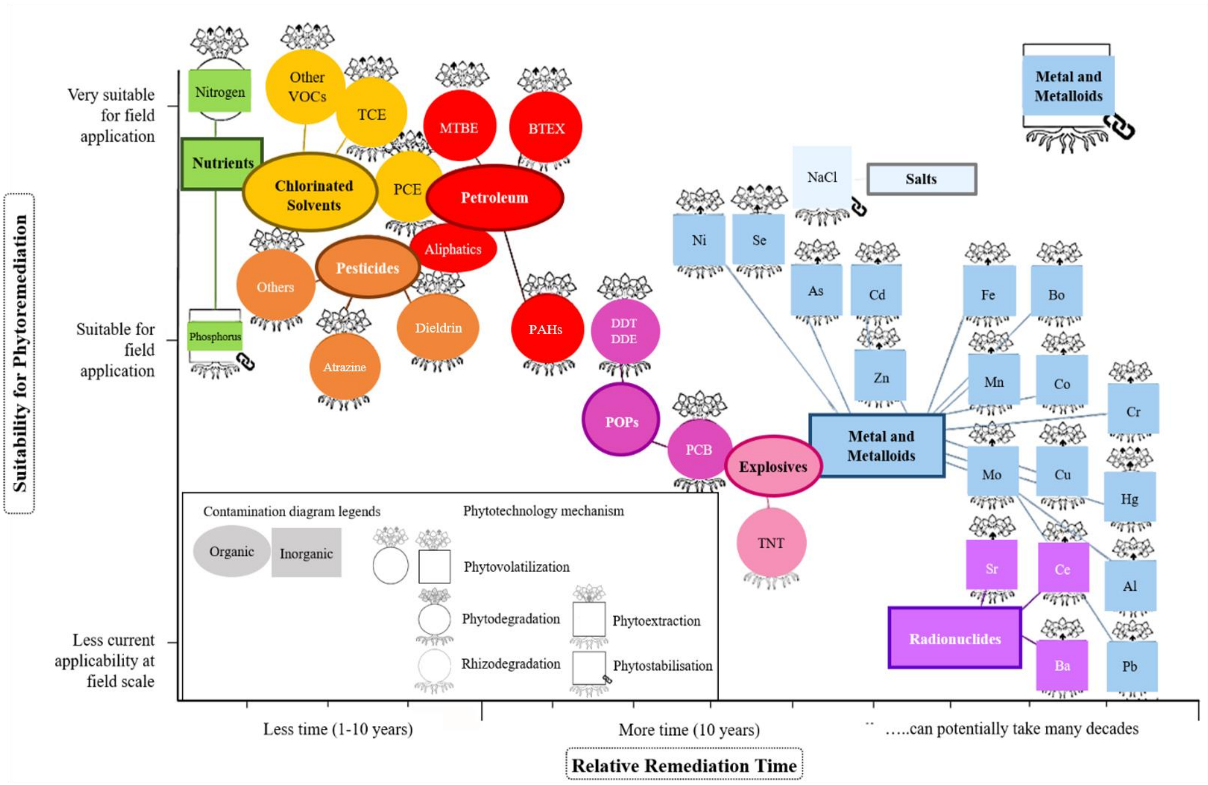

Figure 2-3. Relative remediation time for source removal and applicability of GRO (phytoremediation) mechanisms for groupings of contaminants. From (Chowdhury et al., 2020), *after* (OVAM, 2019) *and* (Kennen and Kirkwood, 2015).

2.1 Mechanisms and processes

This section focuses on the physiological action of plants that enable phytoremediation, which is a broad concept that is discussed here only in brief detail. The removal or stabilisation of contaminants in soil, sediment, or groundwater and surface water by phytoremediation can be done through various mechanisms and processes related to the processes that plants use to take up organic and inorganic compounds, with the help of plant-associated microorganisms (OVAM, 2019). The effectiveness of specific plants for remediation is dependent upon a variety of factors, including tolerance to contaminants, rooting depth/development and evapo-transpiration rates amongst others (McCutcheon and Schnoor, 2003), which is discussed more in section 4.

For general classification, McCutcheon and Schnoor (McCutcheon and Schnoor, 2003) identified many different processes that aid in phytoremediation, and use the following organising concepts to aggregate the plant physiological processes and distinguish between the various phytoremediation terminology (see (McCutcheon and Schnoor, 2003) for more thorough descriptions):

- Green Liver concept of plant metabolism – plant detoxification response to organic contaminants
- Separate processes that completely degrade or mineralise contaminants from the less desirable processes that only transform or partially degrade contaminants – including the critical role of microorganisms
- Distinguishing active plant uptake into biomass from sorption and other passive processes that sequester and stabilise contaminants in the soil or onto roots

Regarding the remediation processes generally, it is crucial to know whether the contaminant can be taken up by the plant (i.e. in a form that is accessible by the plant – **bio-/phytoavailable**) and/or is biodegradable (OVAM, 2019). Bioavailability can be influenced by a number of factors, including i) the form (speciation) of the contaminant and presence in different phases, ii) the charge of the soil and pH, iii) the presence and concentration of other soil elements, iv) physical environmental factors such as local climate, soil porosity and the addition or subtraction of organic matter and other amendments, v) the total concentration of the pollutant in the soil, and vi) the specific plant species (Kennen and Kirkwood, 2015). For organic contaminants, uptake is strongly dependent on the hydrophobicity of the molecules, as well as the plant species and environmental conditions. Hydrophobicity is expressed as the $\log K_{ow}$ (logarithm of the octanol-water partition coefficient), which is a unitless relative indicator of the tendency of an organic compound to adsorb to soil and living organisms (ChemSafetyPro, 2016; OVAM, 2019). $\log K_{ow}$ are generally inversely related to water solubility and directly proportional to molecular weight of a substance; meaning that substances with higher $\log K_{ow}$ values tend to adsorb more readily to organic matter in soils because of their low affinity for water and may even bio-concentrate in the lipids of living organisms (e.g. fish) once absorbed (ChemSafetyPro, 2016). In general, **a $\log K_{ow}$ of 0.5 – 3.5 means good uptake by plants**, while a substance with a higher value will mainly adsorb to plant roots with little to no translocation to the aboveground parts (OVAM, 2019). Highly water soluble compounds penetrate the xylem vessels of roots quickly, before they can be degraded by microorganisms in the rhizosphere, leading to degradation or possible volatilisation in-planta. $\log K_{ow}$ values are highly consequential to the success of phytoremediation of organic compounds, see Table 2-2 for a list of the approximate $\log K_{ow}$ values for commonly occurring organic contaminants.

Table 2-2. Log K_{OW} values of common organic contaminants, summarised from (Kennen and Kirkwood, 2015; McCutcheon and Schnoor, 2003; Weyens et al., 2009d).

Petroleum Products		**Persistent Organic Pollutants and Pesticides**	
PAHs	3.37 – 7.23	POPs	3.0 – 8.3
Benzene	2.13	PCBs	5.02 – 7.44
Toluene	2.69 – 2.73	DDT	6.36
Ethylbenzene	3.15	Chlordane	6.22
Xylenes	3.12 – 3.2	Lindane	3.55
MTBE	0.94	Atrazine	2.61 – 2.69
Aniline	0.9	Dioxins (TCDD)	6.8 – 7.4
Phenol	1.45		
Nitrobenzene	1.83 – 1.9	**Chlorinated Solvents**	
		PCE (Perchloroethylene)	3.4
Explosives		TCE (Trichloroethylene)	2.33 – 2.42
RDX	0.87 – 0.90	PCP (Pentachlorophenol)	5.04
HMX	0.17	Chlorobenzene	2.8
TNT	1.73	1,2,4- trichlorobenzene	4.25

Plant uptake of the contaminant is essential for many mechanisms, which mainly take place via the roots and thereafter is transported to the aboveground parts (or remains in the roots) for accumulation in the plant biomass or degradation in-planta (OVAM, 2019). Provided that the hydrophobicity of the organic compound is favourable for plant uptake, the so-called 'Green Liver' model provides a useful conceptual model for understanding how a plant might respond to the presence of xenobiotic or toxic compounds by metabolism or detoxification, see Figure 2-4. As photoautotrophic organisms, plants do not harbour the enzymes necessary to metabolise organic compounds for use as an energy source as might heterotrophic organisms like bacteria and fungi; therefore, plants themselves will not degrade organic substances, but rather transform them into water-soluble and less harmful forms to avoid potential toxicity to sensitive organelles (Burken, 2003; OVAM, 2019). It has been dubbed the Green Liver model because plant metabolism of organic compounds shares many processes with mammalian liver functions, but differs in the ultimate fate of the compound being sequestered instead of eliminated (Burken, 2003). The key steps include 1) the activation of compounds for metabolization via redox reactions (transformation), 2) detoxification or metabolization to soluble sugars by e.g. amino acids (conjugation), 3) removal of the compounds from the susceptible organelles (by sequestration in plant vacuoles and cell walls), and 4) storage in less photosynthetically active or metabolic organelles like old leaves, roots or woody material (compartmentalisation) (Burken, 2003; OVAM, 2019).

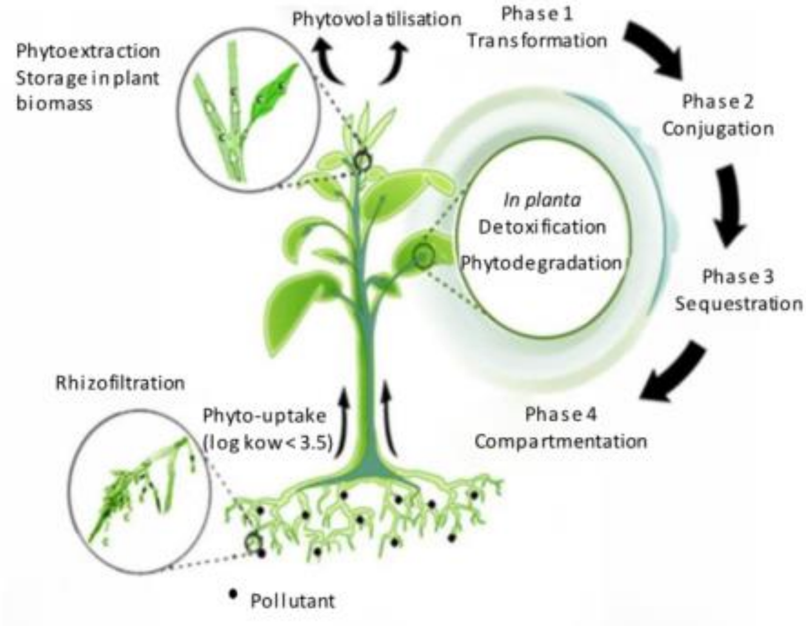

Figure 2-4. Green Liver model of plant response to xenobiotic compounds detailing plant uptake, transformation and degradation of contaminants in the plant, from (OVAM, 2019).

At the cellular level, similar to the Green Liver model, uptake and storage of organic and inorganic compounds is facilitated by a number of microbial-assisted processes, see Figure 2-5 and Figure 2-7. Considering inorganic compounds like metals, plant-associated chelators such as phytochelatins and siderophores can form metal complexes metal that enable them to be taken up by the plant, subsequently transported and translocated for eventual storage (OVAM, 2019). Metal-tolerant microorganisms can promote the extraction of metals through the secretion of acids and H^+, detoxify metals and improve the plant's biomass production as well as reducing stress by producing proteins like metallothioneins to reduce toxicity and oxidative stress (OVAM, 2019).

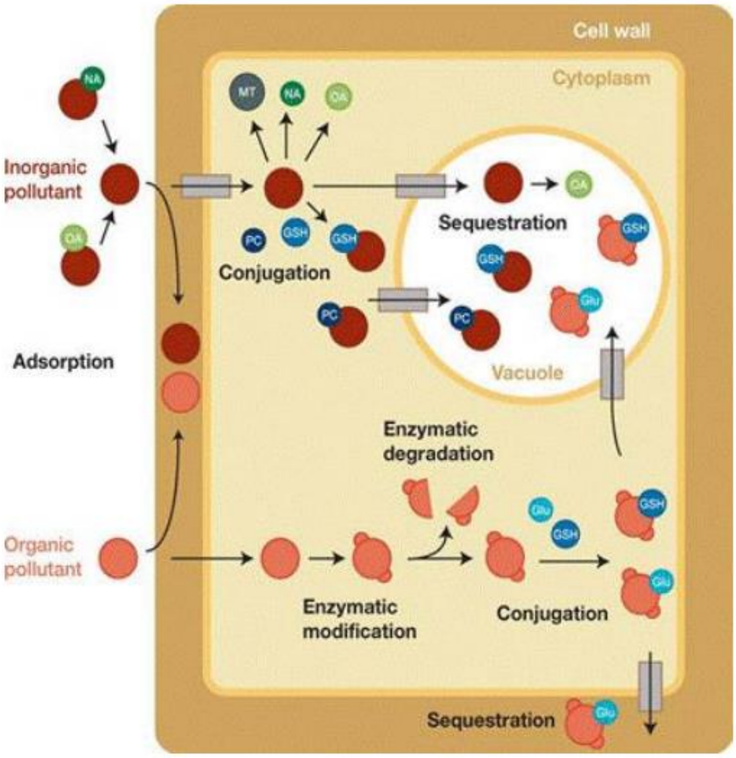

Figure 2-5. Mechanisms for the uptake and storage of organic and inorganic contaminants, from (OVAM, 2019). *PC = phytochelatins, OA = organic acids, GSH = glutathione, MT = metallothioneins, NA = nicotianamine, Glu = glutamic acid.*

In addition to transformation by the plant itself, plant-associated microorganisms (e.g. endophytic bacteria within the plant) play a key role in the degradation of organic compounds into CO_2 and water due to their wide variety of metabolic enzymes (OVAM, 2019). These microorganisms can also aid in sequestration of toxic metals in plants, as shown in Figure 2-6 and Figure 2-7.

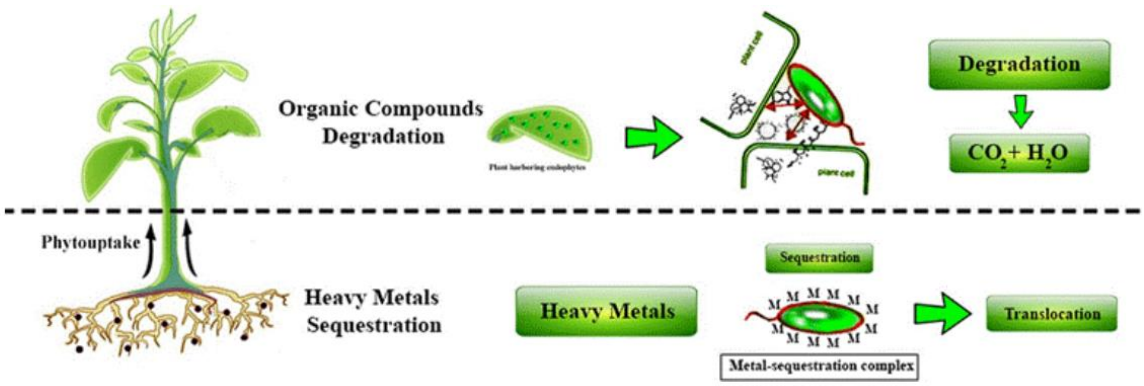

Figure 2-6. Endophytes in action against organic and inorganic contaminants, from (OVAM, 2019; Weyens et al., 2009d).

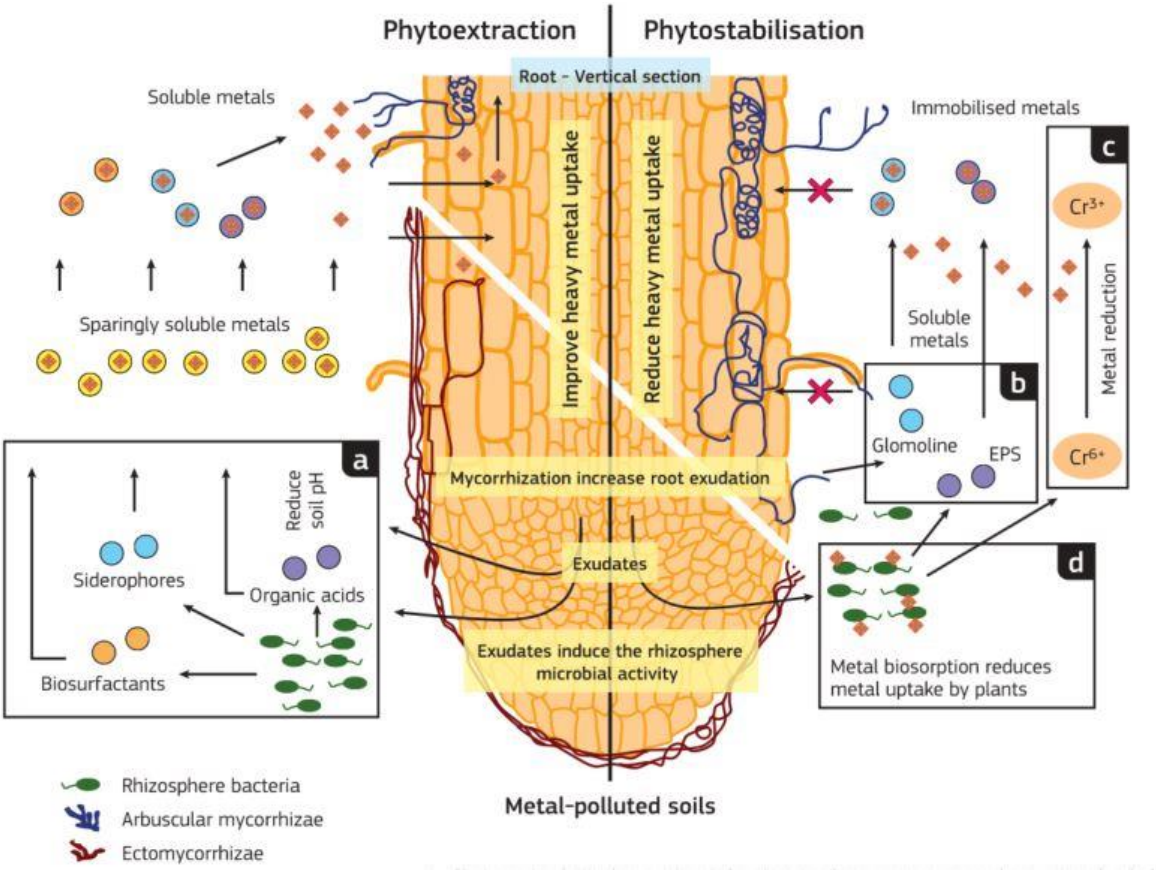

Figure 2-7. Plant-associated microbes accelerate the phytoremediation process in metal-contaminated soils by enhancing metal mobilisation/immobilisation. Plant-associated microbes contribute to mobilisation by a) producing metal-mobilising substances, such as siderophores, biosurfactants and organic acids. Plant-associated microbes contribute to immobilisation by b) producing metal-immobilising extracellular polymeric substances (EPS) or others (e.g. glomalin), c) metal reduction, and/or d) metal biosorption (i.e. direct absorption into microbial cells. From (Orgiazzi et al., 2016).

As stated by OVAM (2019), '*no matter which phytoremediation is applied, **the role of the associated microorganisms is undeniable.***' This statement is based on the growing body of evidence concerning the sheer abundance and diversity of microorganisms, both above and below ground, like bacteria (billions of cells and thousands of species per gram of soil) and fungi (0.5 mg per gram of soil and potentially up to 100 meters of fungal threads, hyphae) that enable a broad spectrum of interactions that can reinforce phytoremediation (OVAM, 2019; Weyens et al., 2009d, 2009c). Furthermore, plants and microorganisms are interdependent since **a soil without vegetation has a hundred to a thousand times fewer bacteria and fungi** than in the rhizosphere of a vegetated soil, which can also be further affected if contaminants are present (OVAM, 2019). Given that bacteria and fungi in the soil play vital roles in remediation as well as many ecosystem processes, it is crucial to study the impact of soil contamination on microbial communities and also to evaluate the effect of remediation in terms of restoring the physico-chemical soil structure and microbiological activity (OVAM, 2019). The full role of microorganisms in ecosystems and their application for remediation purposes is both important and complex, see e.g. (Jambon et al., 2018; OVAM, 2019; Thijs et al., 2017; Weyens et al., 2009d, 2009c; Wolfe and Hoehamer, 2003) for more detailed information.

2.2 Gentle remediation of organics

Breaking down organic contaminants into carbon dioxide, water, microbial biomass, bioenergy and/or less harmful by-products via endophytic and rhizospheric bacteria has seen definitive success in multiple studies and is one of the most promising areas for applying GRO as a quick, effective remediation strategy (Gerhardt et al., 2017; Kennen and Kirkwood, 2015; Mench et al., 2010; OVAM, 2019; Vangronsveld et al., 2009). The key to effective degradation is the presence of biologically active microorganisms, though, they may be impaired by contaminants (e.g. mixed contamination with toxic concentrations of metals) and poor soil quality (Mench et al., 2010; OVAM, 2019). In contrast to bioremediation, which typically focuses on stimulation or addition of bacteria without plants, the addition of plants into contaminated soil can enhance degradation. For example, a meta-analysis by Ma et al. (2010) examining PAH dissipation in soils concluded that plants have a promoting effect as the activity of PAH decomposers in soil is more likely to be enhanced by root activities than inhibited by other microorganisms due to e.g. competition and variations in species, habitats, etc. Generally speaking, plants are utilised for gentle remediation of organics in two primary ways (Kennen and Kirkwood, 2015):

1. **To speed up the natural attenuation process (degradation) –** plants themselves enable microbial activity by supplying sugars, oxygen, enzymes and a variety of root exudates (e.g. residual photosynthesis products like sugars as well as amino acids, flavonoids, proteins, fatty acids and phytohormones) into the root zone that are critical for a rich microbial life and can foster and induce the breakdown of organic compounds by certain bacteria for use as an energy source (Gerhardt et al., 2017; Jambon et al., 2018; Kennen and Kirkwood, 2015; Mench et al., 2010; OVAM, 2019; Robinson et al., 2006; Thijs et al., 2017). Roots growing and extending through the soil can also enable the faster spreading of microbes throughout the rhizosphere (aided also by the presence of earthworms) as they adsorb to the roots to more quickly colonise a larger volume of contaminated soil and reach more organic compounds (Mench et al., 2010; OVAM, 2019). As roots respire and use oxygen, they naturally remove water (acting as '**bio-pumps**') that then function as natural oxygen conduits to fuel bacterial communities necessary for the breakdown of many organic compounds (Kennen and Kirkwood, 2015; OVAM, 2019). The effectiveness of organic degradation can also be improved through *biostimulation* (improving the existing microbiome using additives) and/or *bioaugmentation* (introducing external microbes which may be better suited for degrading specific contaminants) to promote plant growth and tolerance and increase degradation rates using e.g. organic amendments like compost (Mench et al., 2010; OVAM, 2019; Vangronsveld et al., 2009), discussed further in section 2.3.2.

2. **To control, degrade and volatilise organic contaminants in groundwater (hydraulic control) –** lightweight, readily soluble organic compounds can dissolve easily in water and quickly leach into groundwater that can then spread the contaminant in a plume that can migrate off-site, which poses serious risks to both the environment and human health, (e.g. via drinking water) (Kennen and Kirkwood, 2015; OVAM, 2019). Planting stands of trees with high evapotranspiration rates in the path of the contaminated groundwater plume can allow a measure of hydraulic control; whereby, plants tap into the groundwater and pump up enough groundwater to induce a drawdown in the groundwater table thus influencing the dynamics and preventing spreading off-site while simultaneously degrading or volatilising contaminants (Kennen and Kirkwood, 2015; OVAM, 2019).

Gentle remediation of organics by degradation aims at the complete mineralisation of organic contaminants into carbon dioxide, nitrate, chlorine, ammonia and other elemental constituents of the initial molecule (Mench et al., 2010; OVAM, 2019). This remediation strategy has been proven viable for a wide variety of organic compounds, including 1) petroleum products –

polycyclic aromatic hydrocarbons (PAHs), aliphatic hydrocarbons, fuels and BTEX compounds; 2) persistent organic pollutants – polychlorinated biphenyls (PCBs), DDT and other pesticides; 3) explosives – nitro-aromatics such as trinitrotoluene (TNT); and 4) chlorinated solvents – linear halogenated hydrocarbons such as trichlorethylene (TCE) (Gerhardt et al., 2017; Kennen and Kirkwood, 2015; Mench et al., 2010; OVAM, 2019). Table 2-3 provides a short compilation of relevant field studies that demonstrate the effectiveness of GRO for remediation of organic compounds; see also the CLU-IN Phytotechnology database which lists 54 projects utilising rhizodegradation and 20 utilising phytovolatilisation. Brief detail will be provided in this section on the specific degradation mechanisms of phyto- and rhizodegradation as well as phytovolatilisation, see e.g. (Alkorta and Garbisu, 2001; Gerhardt et al., 2009; Gkorezis et al., 2016; Haritash and Kaushik, 2009; Jambon et al., 2018; Juwarkar et al., 2010; Kennen and Kirkwood, 2015; Megharaj et al., 2011; Mench et al., 2010; OVAM, 2019; Thijs et al., 2017; Vangronsveld et al., 2009; Wang et al., 2019) for more information.

Table 2-3. Compilation of field studies successfully demonstrating GRO for organic contaminants, ordered alphabetically by reference. Climate zones can vary within locations, see reference for more specific information. PD = phytodegradation; RD = rhizodegradation; PV = phytovolatilisation; EX = phytoextraction; ST = stabilisation; P-Hydro = phytohydraulics; IM = immobilisation; MR = mycoremediation.

Location	Contaminants	GRO	Plant Species	Enhancement/ Amendment	Results	Duration	Comment	Reference
Italy	PCB, heavy metals (V, Cr, Sn, Pb)	PD/RD, EX/ST	Hybrid poplar (*Populus generosa x nigra*) cv. Monviso	Drip irrigation, mulching	A significant decrease in PCB congeners (up to 90%) and heavy metal reduction observed where poplar trees were present - lighter congeners were detected in leaves but most contaminants were absorbed into roots	420 days	Microbial analyses shown an improvement in soil quality - microbial activity generally increased in poplar rhizosphere in some cases up to 1m from the trunk and 40cm depth	(Ancona et al., 2017)
Belgium	BTEX, Ni, Zn	PD/RD, P-Hydro	Hybrid poplar (*Populus trichocarpa* x *deltoides*) cv. Hoogvorst, Hazendans	None	After 3 seasons hydraulic control was observed by tree stands 'cutting off' plume migration - after 4 seasons the plume decreased significantly and disappeared completely during periods of highest activity (after summer) - the BTEX compounds were effectively degraded by a endophytic and rhizospheric bacteria associated with poplar	6 years	Roots did not reach the groundwater table in first 13 months of planting - once the BTEX plume was remediated, the toluene-degrading rhizobacteria and endophytic bacteria decreased below detection limit indicating that their population resulted from selective enrichment by the presence of the contaminants	(Barac et al., 2009)
USA	Toluene – CH3	PD/RD/ EX/PV, P-Hydro	Hybrid poplar (*Populus deltoides* x *nigra* OP-367)	Planted in nutrient-amended boreholes	Peak toluene mass removal from 313-743 ug/day - Streptomyces enriched poplar roots indicating it as an important poplar endophyte at toluene-impacted sites aiding in biodegradation	1 year	Demonstrated the viability of phytoremediation for complicated hydrogeology at fractured bedrock site	(BenIsrael et al., 2020)

USA	VOCs – CCl_4	PD/RD, P-Hydro, RF	Mixed tree stand of predominantly Niobe willow (*Salix x 'Niobe'*), Eastern Cottonwood (*Populus deltoides*)	Treatment chain: hotspot removal by air stripping - phytoremediation along groundwater plume - and polishing with constructed wetland	'Integrated' phytomanagement system decreased CCl4 spread to nearby creek by 99% - removes 300-600g of CCl_4 annually largely by uptake into plants (especially Cottonwood, accounting for 69% in later years) and subsequent breakdown with limited volatilisation - tree stand captured an estimated 59,400-131,400 L/day - an estimated 35% of removal occurred in the wetland	10+ years	A range of wider social and environmental benefits were also realised over the large (ca. 59 ha) area, including carbon sequestration of ca. 77 tons CO_2/ha-yr, re-establishing native prairie vegetation and educational and recreational benefits - significant installation, monitoring, maintenance and other costs (exceeding $1.5 million)	(Cundy et al., 2020)
Canada	PCB	EX/ST, IM	Zucchini/pumpkin (*Cucurbita pepo* ssp. *Pepo)*	Granulated activated carbon (GAC), biochar (Burt's and BlueLeaf)	PCB uptake in zucchini reduced by 74, 72 and 64% with GAC, Burt's and BlueLeaf biochar respectively	36 days earthworm toxicity lab test with amendments; 50 days field test with plants	Mechanically mixing carbon amendments with PCB soils improved effectiveness of treatment and further reduced uptake in plant shoot and roots and earthworms (BSAF) - biochar increased plant biomass more than control and GC	(Denyes et al., 2013)
Canada	ΣDDT	EX, ST	Zucchini/pumpkin (*Cucurbita pepo* ssp. *Pepo)*	Granulated activated carbon (GAC), biochar (Burt's and BlueLeaf)	Biochar significantly reduced DDT accumulation in earthworms (49%) and showed no detrimental effects to invertebrate health - GAC caused toxic effects to earthworms and did not significantly reduce DDT accumulation - carbon amendments reduced DDT and DDE metabolites in porewater as measured by POM	50 days earthworm toxicity lab test with amendments; 60 days field test with plants	None of the carbon amendments reduced plant uptake of DDT - zucchini BAF reached threshold at 10 µg/g - POM accurately predicted worm but not plant bioavailability (overpredicted plant uptake)	(Denyes et al., 2016)
Israel	Diesel	PD/RD	Vetiver (*Vetiveria zizanoides* L.)	Chemical fertilisers	Reduction up to 79% in total concentrations when planted with vetiver - other growing plants recovered biomass production to non-polluted levels after 8-9 months of planting	15 months	Economic evaluation based on cost-benefit analysis (CBA) showed net-present values (NPV) of phytoremediation to better than traditional techniques, primarily from ecosystem services perspective	(Dudai et al., 2018)

USA	DDE	EX	Zucchini/pumpkin (*Cucurbita pepo* ssp. *Pepo* cv. Raven)	PGP endophytic bacteria strains - *Sphingomonas taxi UH1, Methylobacterium radiotolerans UH1, Enterobacter aerogenes UH1*	Inoculated plants had higher biomass production (no effect on BAF) - resulted in higher accumulated amounts of DDE in plants - BAF of roots and stems ranged from 19 - 25	100 days	DDE-degrading bacteria were isolated during the experiment - conclusion that inoculation of *C. pepo* plants with a consortium of endophytic bacteria can increased the phytoremediation potential by up to 46%	(Eevers et al., 2018)
USA	BTEX and gasoline range organics (GRO)	PD/RD, P-Hydro	Hybrid poplar (*Populus deltoides x nigra*, DN-34)	Chemical fertilisers	BTEX and GRO decreased by 81, 90, 67, 78 and 82%, respectively, in soil - and 34, 84, 12, 19 and 59%, respectively, in groundwater - Concentrations of oxygen, methane and CO_2 in soil gas demonstrated that tree roots dewatered soils and allowed penetration of oxygen deep into the soil profile boosting rhizodegradation	11 years	Although required clean-up time can limit phytoremediation, it has proven to be a cost-effective strategy for site improvement if imminent pathways for human exposure and risk are not an issue - 2840 trees/ha	(El-Gendy et al., 2009)
USA	Total petroleum hydrocarbons (TPH)	P-Hydro	Poplar (*Populus* spp.), willow (*Salix* spp.)	'Treewell' borehole planting to reach deeper aquifers; drip irrigation and fertiliser	High groundwater uptake and plume control was achieved with models suggesting between 23-59 L/day per tree and roots extending down to 5m depth	4 years	Reductions in TPH concentrations were not specifically mentioned in this study	(Ferro et al., 2013)
USA	MTBE	PD/RD/ PV, P-Hydro	Hybrid poplar (*Populus deltoides x nigra* DN-34, Imperial Carolina)	None	Excellent plant growth (mean height of ca. 3m) and high water uptake rates already after 8 months - water absorbing roots were present down to 3m - water modelling showed that uptake by trees was greater than water flow into the aquifer indicating that groundwater dynamics by inciting a drawdown - lab studies showed MTBE removal by poplars up to 67%	3 seasons	A 3-part study including i) laboratory bioreactor study examining the fate and transport of MTBE in hybrid poplar trees (evapotranspiration), ii) mathematical modelling investigated unsaturated/saturated groundwater flow, iii) field study in Houston, TX with MTBE-contaminated groundwater controlled with hybrid poplar trees - *showed that phytohydraulic containment of MTBE by deep-rooted (phreatophytic) trees can be achieved*	(Hong et al., 2001)

Germany	TNT	PD/RD, MR	Spruce (*Picea abies*), poplar (*Populus tremula*), elder (*Sambucus nigra*)	Site was first prepared with soil grader - straw with white-rot fungi (*Trametes versicolor, Pleurotos ostreatus*) was blended into soil - trees infected with mycorrhizal fungi (*Pisolithus tinctorius, Paxillus involutus*)	Spruce shown to take up nitro-aromatics on all sites - bioassays collectively indicate clear toxicity and impaired soil functioning that responds slowly to disturbance (grading) - grading stimulated microbial activity in the aerobic zone enhancing degradation - bioaugmented fungi species boosted initial recovery from disturbance and subsequent degradation - plants enhanced microbial activity and prevented erosion, dust and leaching	1 year	The grading procedure effectively reduced the contamination (almost 90% within the first six months regardless of the initial levels). The phytoremediation measure as a whole reduced hazards of transport of nitro-aromatics by dust or leachate, initiated a secondary succession of the soil ecosystem that could transform the remaining TNT and metabolites over a longer period of time, and thus proved to be an effective decontamination measure applicable for a large area (120 ha).	(Koehler et al., 2002)
USA	Total petroleum hydrocarbons (TPH)	PD/RD	Red fescue (*Festuca rubra),* ryegrass (*Lolium multiflorum*)	Chemical fertilisers	All treatment groups decreased TPH concentrations (by 80-95%) to be within guideline values - lower TPH concentrations correlated with high amounts of woody vegetation (trees and shrubs) - more woody and native vegetation established at unfertilised plots	15 years	Long-term study evaluating remediation and revegetation success at 15 years with no active management - native and non-native vegetation had extensively colonised the site, with more abundant vegetation on diesel contaminated soils than the poorer quality crude oil contaminated soils - long-term study suggests that initial treatment with native tree species in combination with grasses could be an effective strategy for TPH contaminated sites to promote ecological recovery	(Leewis et al., 2013)
Italy	Total petroleum hydrocarbons (TPH) and heavy metals (Cd, Pb, Zn)	PD/RD, EX	Lombardy poplar (*Populus nigra* var. Italica), princess/empress tree (*Paulownia tomentosa*), Scotch broom (*Cytisus scoparius*)	Chemical fertilisers	Reduction in average total content of TPH and heavy metals by 30-50% and 20-40% respectively to reach guideline values - increase in dehydrogenase and soil enzymes related to C and P cycles	3 years	Phytotoxicity test with *Raphanus sativus* showed improved growth after 3-year treatment indicating reduction in soil toxicity	(Macci et al., 2013)

Italy	Total petroleum hydrocarbons (TPH), PCB and heavy metals (Cd, Cr, Cu, Ni, Pb, Zn)	PD/RD, EX	Silver poplar (*Populus alba*), princess/empress tree (*Paulownia tomentosa*), Scotch broom (*Cytisus scoparius*)	Horse manure	Reduction in average total content of heavy metals, TPH and PCB by 35%, 40% and 70% respectively to reach guideline values - planted areas with amendment showed higher microbial metabolism activity indicating improved soil quality and functionality	2 years	Poplar contributed most to organic removal - princess tree showed high metal removal - Scotch broom was least effective for removal but most effective for soil metabolic stimulation	(Macci et al., 2016)
Canada	ΣDDT	EX/ST	Zucchini/pumpkin (*Cucurbita pepo* ssp. *Pepo* cv. Howden)	None	Per square meter, *C. pepo* has the highest DDT shoot extraction (1.38 mg) at the moderately contaminated site - *P. virgatum* could potentially extract more DDT (2.1 mg) than *C. pepo* (0.7 mg) at the high DDT contaminated site	83 days	*C. pepo* BAF was highest in moderately DDT contaminated soils (5 mg/kg) and decreased at higher concentrations (>10 mg/kg) - grass species were potentially better phytoextractors (in total amounts) at high DDT concentrations	(Paul et al., 2015)
Belgium	TCE	PD/RD/ PV, P-Hydro	Hybrid poplar (*Populus deltoides x* (*P. trichocarpa x P. deltoides*)) cv. Grimminge	TCE-degrading endophyte *Pseudomonas putida* W619-TCE	Evapotranspiration of TCE through hybrid poplar leaves decreased by up to 90% in inoculated species - the phytoremediation set-up enabled control of the groundwater plume	3 months	Since *P. putida* W619-TCE was engineered via horizonal gene transfer, its deliberate release is **not** restricted under European genetically modified organisms (GMO) regulations	(Weyens et al., 2009b)

2.2.1 Degradation

Phytodegradation refers to the process of plant uptake of contaminants and consequent degradation *in the plant* by metabolic processes (Figure 2-4) or enzymes secreted by the plant or microorganisms (e.g. dehalogenases, nitro-reductases, oxophytodienoate reductases, polyphenol oxidases, peroxidases, laccases, dehydrogenases, hydrolases) (Gerhardt et al., 2017, 2009; OVAM, 2019; Wolfe and Hoehamer, 2003). The secreted enzymes work both inside and outside of the plant and can still be active even after the plant has died (OVAM, 2019). Within the plant, contaminants are broken down into smaller molecules (or less toxic degradation products) and CO_2, which can then be released by the plant into the atmosphere. Phytodegradation is dependent on the bioavailability of the contaminants, which, as previously mentioned, the hydrophobicity of the organic compounds is a major determining factor (i.e. $\log K_{ow}$ between 0.5 – 3.5). Organic compounds amendable to plant uptake include various chlorinated solvents, herbicides, pesticides, insecticides, explosives and low molecular weight petroleum products (OVAM, 2019). However, effective degradation is not guaranteed upon uptake as compounds can prove to be phytotoxic, resistant to complete breakdown or preferentially volatilised (e.g. TCE and BTEX compounds) and released by evapotranspiration via the leaves (OVAM, 2019; Vangronsveld et al., 2009). Effectiveness of *in-planta* degradation is highly dependent on the microorganisms to break down contaminants and prevent volatilisation (discussed in the following section). Similar to phytodegradation, **rhizodegradation** entails similar degradation processes but refers specifically to degradation occurring in the rhizosphere through microbial activity (OVAM, 2019). Many organic compounds are too hydrophobic to be taken up by plants (e.g. PAHs, PCBs) but can be degraded outside the plant, which occurs to some extent even if a compound is absorbed into the plant (OVAM, 2019).

Plant-associated microorganisms also play an important role to make the contaminants more bioavailable and to mobilise contaminants for either uptake or degradation; for example, some microorganisms produce **(bio)surfactants** that are capable of releasing oils from the soil complex to render them more available for plant uptake (OVAM, 2019). Mobilisation caused by microorganisms (as opposed to being chemically induced by e.g. chelating agents) is advantageous from a risk assessment perspective since the microorganisms act on a highly local, micro-scale in the immediate vicinity of the roots allowing rapid uptake or degradation and avoiding leaching of contaminants to spread into groundwater (Mench et al., 2010; OVAM, 2019). This process is summarised by OVAM (OVAM, 2019) in the following way: "an active plant (e.g. in the summer months) stimulates microbial life in the environment of the roots, which increases the production of mobilizing agents, but at the same time the absorption capacity of an active plant is also greater. When adding mobilising soil additives, a large part of the contamination is released at the same time, while the plant is unable to absorb all of this at the same time."

Isolating microorganisms (species and functional groups) that are vital for degradation of specific organic compounds is a difficult task, with much ongoing research, and most often the degradation genes are encoded on plasmids (i.e. small circular pieces of DNA in a bacterium) that can be exchanged freely between bacteria – *genetic fluidity* (OVAM, 2019). In terms of degradation effectiveness, OVAM (OVAM, 2019) recommends a feasibility analysis for natural degradation (without amendments) by assessing the abundance of degrading microorganisms (by e.g. quantitative PCR or DNA fingerprinting); maintaining that fewer than **10^5 microorganisms per gram of soil** (or mL of groundwater) will result in too slow of a degradation for practical purposes. Furthermore, some bacterial species are more effective than others for degradation of organic contaminants but are competing for limited resources. Degradation occurring even without some of these species indicates that there is functional redundancy in microorganisms to efficiently remove a contaminant (OVAM, 2019). Transgenic organisms have also been tested for enhanced degradation and improved plant tolerance and show promise for eventual field application, provided that they are not considered Genetically Modified Organisms (GMO) which is prohibited in the EU (Aken et al., 2010; Gerhardt et al., 2009; Jambon et al., 2018; OVAM, 2019; Thijs et al., 2017). Regarding which species are considered active in degradation, certain bacterial and fungal communities have been identified as being particularly important for remediation of organic compounds, including (see e.g. (Aken et al., 2010; FAO et al., 2020; Haritash and Kaushik, 2009; Jambon et al., 2018; OVAM, 2019; Thijs et al., 2017, 2016) for more information):

- **Chlorinated contaminants** – *Halomonas* spp., *Pseudomonas* spp. (e.g. *P. putida* for TCE)
- **Oils, PAHs and other petroleum products** – *Pseudomonas* spp. (e.g. *P. aeruginosa, P. alcaligenes, P. mendocina, P. fluoresens*), *Acinetobacter* spp., *Burkholderia* spp., *Mycobacterium* spp., *Haemophilus* spp., *Rhodococcus* spp., *Paenibacillus* spp., *Methylobacterium* spp., *Arthrobacter* spp.
- **PCBs –** *Burkholderia* spp. (e.g. *B. xenovorans*), *Pseudomonas* spp., *Comamonas* spp., *Rhodococcus* spp., *Bacillus* spp.
- **Explosives –** *Pseudomonas* spp., *Enterobacteriaceae* spp.
- **Dioxins –** *Pseudonocardia* spp. (e.g. *P. dioxanivorans* CB1190)

Fungi can also be highly useful for gentle remediation of organic contaminants. Jambon et al. (2018) provide an extensive review of insights and applications of plant-bacteria-fungi interactions to enhance the effectiveness of gentle remediation of organic contaminants. Regarding more direct remediation, the term '**mycoremediation**' has sometimes been used to refer to the use of fungi for remediation purposes (Stamets, 2005), and is discussed more in Section **2.7**.

Plants also directly influence the bacterial and fungal community structure (i.e. taxonomic and metabolic diversity) as well as their abundance and activity (e.g. soil microbial biomass, respiration and nitrogen mineralisation) in the rhizosphere (Burges et al., 2018; Epelde et al., 2008a; Gómez-Sagasti et al., 2012; Mench et al., 2010; Touceda-González et al., 2017a, 2017b). Certain plant species have been identified as being more effective for remediating specific organic contaminants due to their ability to 'selectively recruit', a function of their specific root exudates, bacterial and fungal communities to the rhizosphere that are both tolerant to the contamination (e.g. metallophyte and other tolerant plants on highly contaminated soils (Barrutia et al., 2011; Epelde et al., 2012, 2010a)) as well as able to break down the contaminants present in the soil (Jambon et al., 2018; Mench et al., 2010; Thijs et al., 2017). A few examples of plant species capable of remediating specific types of contaminants are listed below (see (Gawronski et al., 2011; Kennen and Kirkwood, 2015; OVAM, 2019) for more detailed compilations):

- **Poplar** (*Populus* spp.) trees (and hybrids or transgenic variants (Doty et al., 2007)) have been shown to be highly effective at remediating a wide variety of organic contaminants, including i) taking up and degrading VOCs like TCE and CCl_4 (without generating more toxic by-products) *in-planta* with limited volatilisation (Cundy et al., 2020; Wang et al., 2004a; Weyens et al., 2009b) – estimated effectiveness (removal rate) per tree of 0.88 g/yr for TCE (Doucette et al., 2013) and 0.053 ± 0.037 g/yr for PCE (Andrew James et al., 2009); ii) degrading BTEX compounds in the rhizosphere (Barac et al., 2009); iii) degrading explosives (nitro-aromatics) like TNT (Gawronski et al., 2011; Koehler et al., 2002); and iv) promoting degradation of PCB congeners while improving soil microbial community (Ancona et al., 2017).

- **Willow** (*Salix* spp.) trees have been demonstrated to be useful for stimulating the aerobic degradation of organic compounds like BTEX and other light-weight petroleum products due to their 'ventilation system' developed for growing in frequently oxygen deficient soils to transport oxygen to the root zone. Also, willow trees transpire large amounts of water, which is especially advantageous in saturated soils to aerate previously flooded soils (Trapp et al., 2014).

- **Grass species** in the Poaceae family (e.g. *Lolium perenne, Poa pratensis, Festuca rubra, Festuca ovina, Festuca arundinacea*) have been effectively demonstrated to degrade petroleum compounds by increasing the abundance of phenol- and alkane-degrading bacteria and increasing the microbial biomass; for example, at a discontinued, oil shale dump site (Juhanson et al., 2007; Mench et al., 2010) and at an aged petroleum contaminated soil that could be further enhanced with endophytic fungi (Soleimani et al., 2010). The grass family is considered one of the most important for phytoremediation of organic contaminants such as PAHs and other petroleum hydrocarbons as well as heavy metals (Gawronski et al., 2011).

  Grass species (Bermuda grass, bent grass and lawn grass) and leguminous white clover (*Trifolium repens* L.) have also been tested for degradation of dibenzofuran (generally considered as a dioxin or dioxin-like compound), which showed that white clover was both highly tolerant to the contamination as well as capable of selectively increasing microbes in the rhizosphere that can degrade these compounds (Wang and Oyaizu, 2009).

- **Leguminous plants**, in the Fabaceae family, are also highly useful for GRO application as they can both improve soil fertility (fostering N-fixing bacteria) and stimulate the growth of soil microbes that are capable of degrading organic compounds like PAHs and PCBs (Gawronski et al., 2011; Kennen and Kirkwood, 2015; Kidd et al., 2015). Plant species in this family can exude high amounts of flavonoids (chemicals with 6 rings highly similar to PAHs) that can stimulate the development of specific rhizobial microorganism communities, which, when overpopulated, would face food source shortages and start to degrade PAHs and PCBs by using them as carbon sources for energy to fuel their living processes (Gawronski et al., 2011).

- ***Miscanthus x giganteus*** (giant perennial silvergrass or simply miscanthus) has proven to be highly useful for the biostimulation of PAH degradation (e.g. pyrene, phenanthrene) due to its specific compositions of root exudates boosting degrading microbes as well as its high tolerance to contamination (Nsanganwimana et al., 2014; Técher et al., 2011).

- **Mulberry** trees release phenolic root exudates that can enhance the degradation of PCBs by boosting the activity of PCB-degrading bacteria like *Burkholderia xenovorans* LB400 (Aken et al., 2010; Fletcher and Hegde, 1995; Hegde and Fletcher, 1996)

- **Wildflower** species (main of the Asteraceae family, e.g. *Senecio glaucus*) growing in sand polluted with petroleum were found to foster the growth of oil-degrading bacteria (*Arthrobacter*) around their roots which degraded the petroleum compounds and prevented toxic effects (Radwan et al., 1995; Trapp et al., 2014)

The effectiveness of phyto- and rhizodegradation is highly variable and dependent on factors such as the type of organic compounds present, bioavailable and total concentrations, soil type, weathering of contaminants and plant species and tolerance amongst others (Mench et al., 2010; OVAM, 2019). For example, compounds like PAHs and PCBs that are highly hydrophobic are difficult to remediate since they are poorly soluble and sorb strongly to the soil matrix, especially if weathered, and may require the addition of bio-surfactants or amendments like compost to degrade in-situ (Aken et al., 2010; Haritash and Kaushik, 2009; Kennen and

Kirkwood, 2015; Mench et al., 2010; OVAM, 2019). In fact, for some such recalcitrant contaminants like DDT and PCBs, **phytoextraction** by certain plant species with unique root exudates (e.g. zucchini and pumpkin) to mobilise and uptake the contaminants has been shown to be a more effective mechanism than degradation (Denyes et al., 2016, 2013; Wang et al., 2004b; White et al., 2006, 2003; Whitfield Åslund et al., 2010, 2008). **Phytostabilisation,** with or without the use of soil amendments, is also a valid strategy for such recalcitrant organic compounds (OVAM, 2019).

Effectiveness is also time-dependent and may be low in the first vegetation season, compared to unplanted control, but improves with successive crops (Mench et al., 2010). Challenges remain, yet there are numerous examples of successful remediation via phyto- and rhizodegradation at both the greenhouse and field scale (Gerhardt et al., 2017; Mench et al., 2010; OVAM, 2019; Vangronsveld et al., 2009). As shown in Table 2-3, the time taken for degradation can vary considerably, and reports of organic contaminant removal rates by established, mature phytoremediation systems are rare in the published scientific literature (Cundy et al., 2020; Limmer et al., 2018). A few studies have estimated the removal rates (through a combination of extraction, degradation and volatilisation) of trees for various petroleum products and chlorinated solvents; for example, by measuring sap concentrations and transpiration rates, which are strongly influenced by contaminant and tree characteristics, as well as groundwater contaminant concentrations (Cundy et al., 2020; Limmer et al., 2018). Estimates range from 0.053 ± 0.037 g/yr/tree for PCE by poplar (Andrew James et al., 2009); 0.041 and 0.88 g/yr/tree for TCE by eucalyptus and hybrid poplar (Doucette et al., 2013); 3.1 g/yr/tree for TCE by silver birch (Lewis et al., 2015); 1.3, 0.025 and 0.10 kg/yr/tree (50th percentile) for benzene, toluene and chlorobenzene respectively by hybrid poplar and Russian olive (Limmer et al., 2018); and 0.2-0.4 g/yr/tree for CCl_4 by Niobe willow and Eastern Cottonwood (Cundy et al., 2020). Similarly, Gobelius et al. (2017) analysed the capacity of native tree species growing at an airport in Sweden to take up Σ_{26}PFAS into their biomass and estimated that mixed tree stands of silver birch (*Betula pendula*) and Norwegian spruce (*Picea abies*) with an understory of ground elder (*Aegopodium podagraria*) could potentially remove up to 1.4 g/yr-ha (Gobelius et al., 2017).

Various attempts have been made to mathematically model biodegradation rates, and can be based on such factors as using the natural half-life of organic compounds to predict biodegradation rates (primarily useful in wastewater treatment plants) (Mitsch and Jorgensen, 2004). However, the biodegradation rate in water or soil is difficult to estimate because the number of microorganisms can vary considerably between soil and water systems (Mitsch and Jorgensen, 2004). For a more general idea of an organic contaminants degradation potential, Mitsch and Jorgensen (2004) provide a (very) rough first estimation that can be made on the basis of molecular structure and biodegradability according to the following rules and evaluation on a point-scale:

- Polymer compounds are generally less biodegradable than monomer compounds: 1 point for a molecular weight >500 and ≤ 1000; 2 points for >1000.
- Aliphatic compounds are more biodegradable than aromatic compounds: 1 point for each aromatic ring.
- Substitutions, especially with halogens and nitro groups, will decrease the biodegradability: 0.5 points for each substitution, 1 whole point if it is a halogen or a nitro group.
- Introduction of a double or triple bond generally means an increase in the biodegradability (double bonds in aromatic rings not included): -1 point for each double or triple bond.

- Oxygen and nitrogen bridges [–O– and –N– (or ═)] in a molecule will decrease the biodegradability: 1 point for each oxygen or nitrogen bridge.
- Branches (secondary or tertiary compounds) are generally less biodegradable than the corresponding primary compounds: 0.5 points for each branch.

For each compound, the number of points can be totalled and then classified according to the following point system:

≤1.5 points: the compound is readily biodegraded (e.g. more than 90% will be biodegraded in a biological treatment plant)

2.0 – 3.0 points: the compound is biodegradable (e.g. 10-90% will be removed in a biological treatment plant)

3.5 – 4.5. points: the compound is slowly biodegradable (e.g. <10% removed in a biological treatment plant)

5.0 – 5.5. points: the compound is very slowly biodegradable (e.g. hardly removed in biological treatment plant and 90% biodegradation in soil or water will take 6+ months)

≥6.0 points: the compound is refractory (half-life time in soil or water is counted in years)

For a more precise estimate, the TIMBRE project (Trapp et al., 2014) proposes mass balances and mathematical modelling to predict the enhanced degradation due to the presence of plant species. This premise is based on the fact that simply by aerating soils by removing water from soil, through the actions of roots functioning as 'bio-pumps', plants can increase the electron acceptors needed for the degradation of many contaminants, including many petroleum products such as gasoline and other fuels (Trapp et al., 2014). Thus, an enhanced biodegradation model was developed based on the surplus flux of oxygen into the root zone of plants (e.g. 2.1-4.3 µmol O_2 per tree/hr for *Salix viminalis* in saturated soils). The unit flux of oxygen, J (kg/day-m²), can be calculated with Fick's 1st Law of diffusion (Equation 1), which provides a measure of the oxygen that is transported into the rhizosphere to degrade organic compounds. The effective diffusion in either liquid or gas, D_{eff}, is calculated from the diffusion coefficient of oxygen in water or soil (Equation 2).

$$J = A * D_{eff} * \Delta C \quad (1)$$

$$D_{eff} = D_x * P_w * T \quad (2)$$

In Equation 1: A is the unit area (m²), ΔC is the concentration gradient between soil surface and 1 m depth ($C(O_2) = 0$) – for gas phase diffusion, the gradient ΔC is 20.95 vol. %O2/m³ air or 300 g/m³ and for diffusion in water, ΔC is the saturation concentration (10.0 mg/L at 15 ºC). In Equation 2: D_x is the diffusion coefficient of oxygen in water or air (m²/day), P_w is the volume fraction of water- or air-filled pores (e.g. 50%) and T is a labyrinth or tortuosity factor (0.12). See TIMBRE (Trapp et al., 2014) for more details and application to estimate degradation rates of octane in water-saturated and aerated conditions with and without willow trees.

Regardless of method, OVAM (2019) recommends extensive feasibility testing to determine degradation effectiveness and the need for optimisation and enhancement. In most cases, lab or greenhouse experiments are recommended to determine the effectiveness of degradation.

For further information, many reviews have been carried out for the bio- and phytoremediation of specific groups of contaminants, including PAHs (Bamforth and Singleton, 2005; Haritash and Kaushik, 2009; Huang et al., 2004; Kathi and Khan, 2011), PCBs (Aken et al., 2010; Vergani et al., 2017), pesticides (Gavrilescu, 2005), DDT (Purnomo et al., 2011) and chlorinated compounds (Nzengung and Jeffers, 2001).

2.2.2 Volatilisation

Phytovolatilisation refers to the process by which volatile contaminants are excreted from the leaves of plants by evapotranspiration (OVAM, 2019). As detailed in the green liver model, plants can take up certain hydrophilic organic compounds (i.e. $logK_{ow}$ between 0.5 – 3.5) and metabolise them into different, less toxic forms for sequestration; however, some plants preferentially release volatile contaminants (e.g. TCE and BTEX compounds) by transpiration via the leaves. The Henry's law constant (H_i), a dimensionless value providing a measure of a compound's tendency to move into air relative to water, is a useful indication for whether a contaminant is likely to be volatilised by plants (Kennen and Kirkwood, 2015). Generally speaking, H_i values can be divided into three ranges: 1) $H_i < 10^{-3}$ indicates a contaminant that moves predominantly in an aqueous state via porewater; 2) $H_i > 10^{-1}$ indicates a contaminant that is predominantly gaseous in soil pore gas; 3) H_i in between these values ($10^{-3} < H_i < 10^{-1}$) indicates that a contaminant is mobile in both air and water and plants can likely volatilise it (Kennen and Kirkwood, 2015). For example, lightweight petroleum products like BTEX and VOCs like TCE have H_i values that fall within this range of potential volatilisation (Kennen and Kirkwood, 2015; McCutcheon and Schnoor, 2003; Schnoor, 1997).

The phytovolatilisation mechanism can indeed remove certain contaminants from soil, but it can also simply shift the problem to another environmental compartment (i.e. air) and contaminants may eventually be redeposited to the soil downstream of the site by precipitation (Gerhardt et al., 2017; OVAM, 2019; Vangronsveld et al., 2009). Even if a contaminant has been converted to less toxic form, its release means it is still in the environment though it may be diluted in the atmosphere to such low levels that it poses insubstantial risks (Gerhardt et al., 2017) or is degraded by photolysis (i.e. UV and hydroxyl radicals in the atmosphere). In general, volatilisation should be avoided or limited to the greatest extent possible and monitored (OVAM, 2019). Therefore, phytovolatilisation can only be applied if the volatile contamination is rapidly degraded once it enters the atmosphere or the release occurs under controlled conditions (OVAM, 2019). Preferably, microorganisms can be used to enhance the degradation processes so that degradation occurs within the plant or rhizosphere (OVAM, 2019; Vangronsveld et al., 2009). For instance, specific, customised endophytic bacteria have been successfully inoculated into plants to greatly reduce or eliminate altogether the volatilisation of TCE and BTEX compounds by enhancing degradation thereby decreasing phytotoxicity and evapotranspiration (OVAM, 2019; Vangronsveld et al., 2009; Weyens et al., 2009a, 2009b). Ongoing research has had success in isolating the bacteria that possess these degradative genes, equipping them with additional desirable characteristics and re-inoculating into suitable host plants to further enhance their beneficial effects for use in other situations (OVAM, 2019; Vangronsveld et al., 2009; Weyens et al., 2009a, 2009b). For example, TCE evapotranspiration was reduced by up to 90% in field conditions when hybrid poplar (*Populus deltoides x* (*P. trichoarpa x P. deltoides*) cv. Grimminge) was inoculated with the TCE-degrading endophyte *Pseudomonas putida* W619-TCE (Weyens et al., 2009b).

2.3 Gentle remediation of inorganics and persistent organics

Historically, much of the interest in phytoremediation has been focused on the use of plants to extract metals from soil (e.g. (Salt et al., 1998, 1995)). Extraction is the primary mechanism for removing the inorganic contaminants (e.g. metals, salts), and **phytoextraction** is arguably the most well-known and thoroughly tested GRO. However, due to several failures to perform as expected (Cundy et al., 2016; Kennen and Kirkwood, 2015), the exceedingly long timeframe required (Robinson et al., 2015) and other significant obstacles, phytoextraction has seen limited full-scale application (Dickinson et al., 2009). A distinct advantage with phytoextraction is that it can work without further disturbing the site, which is believed to be of great importance for its public acceptance (Vangronsveld et al., 2009). **Phytostabilisation** is an alternative strategy for managing inorganics that instead entails leaving the contaminants in place and aiming to limit mobility and toxicity to ecological receptors by reducing bioavailability and solubility (Cundy et al., 2016; Gerhardt et al., 2017; Mench et al., 2010; OVAM, 2019; Vangronsveld et al., 2009).

Gentle remediation of inorganics can aim to mitigate risks by either 1) gradually removing the source of the contamination by harvesting plants that have accumulated the contaminants, or 2) managing the exposure pathways by reducing the spreading of contaminants in porewater, groundwater or the atmosphere (Mench et al., 2010; OVAM, 2019; Robinson et al., 2006; Vangronsveld et al., 2009). These two strategies are predominantly applied to manage metal(loid)s, including As, Cd, Cu, Cr, Hg, Ni, Pb, Zn, etc., as well as salts, excess nutrients, radionuclides and even certain organic contaminants like DDT and PCBs (Gerhardt et al., 2017; Kennen and Kirkwood, 2015; Mench et al., 2010; OVAM, 2019; Vangronsveld et al., 2009). Table 2-4 provides a short compilation of relevant field studies that demonstrate the effectiveness of GRO for remediation of inorganic compounds; see also the CLU-IN Phytotechnology database which lists 53 projects utilising phytoextraction and 29 utilising phytostabilisation. Brief detail will be provided in this section on the specific mechanisms of phytoextraction and phytostabilisation, see e.g. (Ali et al., 2013; Ashraf et al., 2019; Burges et al., 2018; Dickinson et al., 2009; Gerhardt et al., 2017; Kennen and Kirkwood, 2015; Kidd et al., 2015; Mench et al., 2010; OVAM, 2019; Robinson et al., 2006; Brett H. Robinson et al., 2009; Vangronsveld et al., 2009; Wang et al., 2019) for more information.

Table 2-4. Compilation of field studies (and a few pot experiments for BCS) successfully demonstrating GRO for inorganic contaminants, grouped according to GRO type. EX = phytoextraction; BCS = bioavailable contaminant stripping; ST = phytostabilisation; IM = immobilisation; PE = phytoexclusion; PM = phytomanagement.

Experiment (Location)	Contaminants	GRO	Plant Species	Enhancement	Results	Duration	Comment	Reference
Austria (pot exp. - "rhizobox")	As	EX (BCS)	Chinese brake fern (*Pteris vittata)*	None	Reduced most labile pool of As - Decrease by 19,3% in As flux (resupply of As from solid phase to solution)	3 months	As not significantly decreased in the rhizosphere soil solution after one cropping, apparently due to large buffer capacity of soil and ion competition with DOC - As mainly acquired from less available As pools	(Fitz et al., 2003)
Italy (field and pot exp.)	As, Co, Cu, Pb, Zn	EX (BCS), ST	White willow *(Salix alba*), poplar (*Populus alba, P. nigra, P. tremula)*	Shallow ploughing, minimal tillage, mixing with imported soil and chemical fertiliser	Heavily contaminated pyrite waste site - BCS was not feasible due to low translocation from roots to shoots and impaired above-ground productivity	2 years	The most significant finding was of coarse and fine roots proliferation in surface layers that provided a significant sink for trace elements - conclude that phytostabilisation and effective immobilisation of metals and As could be achieved at the site by soil amelioration combined with woody species establishment.	(Vamerali et al., 2009)
Italy (pot exp.)	Hg	EX (BCS)	Indian mustard *(Brassica juncea*), annual meadow grass (*Poa annua),* sunflower *(Helianthus annus)*	Increased bioavailability using mobilising agent $(NH_4)_2S_2O_3$ - to estimate long-term bioavailability	Reduction in max bioavailable Hg by 95.7%	2 growing cycles	Only *B. juncea* successfully transported significant concentrations of Hg into above-ground biomass, otherwise it was sequestered in the roots - labile pool of Hg depleted after one growing cycle	(Pedron et al., 2013; Petruzzelli et al., 2012)
Switzerland	Zn	EX (BCS)	Tobacco (*Nicotiana tabacum)* and sunflower (*Helianthus annus)* - efficient cultivars	Somaclonal variants with enhanced metal uptake and tolerance - crop rotations of tobacco, energy	Lowered labile pool of Zn by 45-70% over 5 years; at larger site reduced labile Zn by up to 58% in individual samples and 15-30% on average after one harvest - increased the amount of land	5 years and 1 year	Mass balance confirmed Zn uptake from labile and non-labile Zn pools and no leaching into deeper soil layers - time span also estimated using first order decay function (non-linear) assuming more	(Herzig et al., 2014)

				maize and sunflower with fertilisation	that met the Swiss benchmark values		complex soil chemistry including sorption and retention processes - planting positively affected soil pH leading to metal immobilisation	
Belgium	Cd, Zn	EX (BCS)	Alpine pennygrass (*Noccaea caereulescens)*	Nitrogen fertilisation (w/ and w/out), varying planting density (50 and 100 plants/m²)	Reduction in labile Cd and Zn by 25% and 9% from 'Ganges' and 'NMET' respectively (w/fertilizer and high density)	6 months	Tested metallicious ('Ganges') and non-metallicious ('NMET') varieties - increased biomass production w/fertilizer but metal uptake varied - lower individual biomass at higher density but higher overall biomass production and uptake	(Jacobs et al., 2018)
Switzerland	Cd, Cu, Zn	EX	Indian mustard (*Brassica juncea)*, sunflower (*Helianthus annus*), tobacco (*Nicotonia tabacum*), basket willow (*Salix viminalis)*, alpine pennygrass (*Noccaea caerulescens*), yellowtuft (*Alyssum murale)*, maize (*Zea mays)*	Chemical fertiliser	Total extraction and translocation into biomass was found to be low except for willows in 3rd year (average g/ha - 44 Cd, 187 Cu, 3851 Zn) and *T. caerulescens* (average g/ha - 179 Cd, 50 Cu, 5052 Zn) - roots for all plants except *T. caerulescens* reached to 0.75m (at varying but generally decreasing cumulative density)	3 years	Studied plant metal uptake and root development (length, size) to determine phytoextraction efficiency (by ratio between cumulative root density and above ground biomass - to concentrate metals in shoots) - *T. caerulescens* judged to be most efficient extractor in shallow soils - maize and willows had greatest root density and area at depth - shows the importance of matching a plant's root system to the extent of contamination at varying depths in the field	(Keller et al., 2003b)
Belgium	Cd, Cr, Cu, Ni, Pb, Zn	EX	Basket willow (*Salix viminalis)*	None	Extraction of metals per hectare-yr: 5034g Zn, 83g Cd, 145g Cu, 83g Pb, 12g Ni, 6g Cr - higher amounts in the leaves versus stems - could be improved with a clone more suited to extraction	1 year	High biomass production ranging from 13.2-17.8 ton/ha-yr - combination of energy cropping and phytoremediation with *Salix* spp. allows for economic revalorisation of contaminated sites during remediation - most effective for Cd and Zn	(Meers et al., 2005)

Belgium	Cd, Zn	EX	Maize *(Zea mays)*, rapeseed (*Brassica napus*), tobacco *(Nicotiana tabacum*), willow (*Salix* spp.), poplar (*Populus* spp.)	EDTA	Willow and tobacco were most promising for extracting Cd - based on linear extraction it would take at least 58 years to reduce Cd from 5mg/kg to 2 mg/kg at the site	2 years	Willow clones Lodes, Zwarte Driebast and Tora judged best for Cd removal - Poplar clones Grimminge and Koster performed best	(Vangronsveld et al., 2009)
Switzerland	Cd, Zn	EX	Maize *(Zea mays* L.), tobacco (*Nicotiana tabacum* L.), sunflower (*Helianthus annus* L.) - crop rotation	Elemental sulphur, ammonium sulphate, NTA	Addition of elemental sulphur decreased soil pH and increased Cd and Zn accumulation in plants - results show that phytoextraction for soil cleansing would take centuries due to low extraction rates	6 years	The land could be used to generate profitable crops, including the production of safe (low Cd) stock fodder fortified with Zn, green manure for micronutrient-deficient soils or bioenergy	(Fässler et al., 2010)
China	As, Cd, Pb	EX	Chinese brake fern *(Pteris Vittata)*, sedum *(Sedum alfredii)*	Chemical fertiliser	Significant decrease in available concentrations - 55,3% As, 85,8% Cd, 30,4% Pb	2 years	Intercropping with cash crops (sugar cane and mulberry tree) to generate income, evaluated via cost-benefit analysis - crops met national contaminant standards	(Wan et al., 2016)
Belgium	Cd, Pb, Zn	EX	Tobacco (*Nicotiana tabacum* L. - somoclonal variant), sunflower (*Helianthus annus* L. - mutant), poplar (*Populus* spp. - experimental clones), willow (*Salix* spp. - SRC)	Rototilled soil, chemical fertiliser, herbicide	Tobacco clones and sunflower mutants showed efficient extraction of Cd and Zn, respectively - highest simultaneous extraction of Cd and Zn with willow clone Zwarte Driebast in SRC - remediation period to reach legal threshold values for pseudo-total Cd content estimated to be at least 60 years (shorter time period for bioavailable CaCl2-extractable Cd - as in BCS)	2-4 years	Highest biomass production observed for an experimental poplar clone with 9.9-ton dw/ha-yr - combining phytoextraction potential and economic and environmental aspects, the SRC option is proposed as the most suitable crop for implementing metal phytoextraction	(Thijs et al., 2018)

France	Cu	EX	Crop rotation - tobacco (*Nicotonia tabacum*) and sunflower (*Helianthus annus*)	Compost (5% w/w) and dolomitic limestone (0.2% w/w)	Significant increase in biomass and soil respiration - increase in activity for all soil enzymes - shift in bacterial communities - increase in genetic abundance	Since 2008	Phytomanagement led to increases in soil microbial biomass (ATP content), respiration and enzyme activities, but effects varied amongst the different sites - overall results suggest that phytomanagement influences soil biological activity (positively) in the long term - most pronounced changes were at sites where organic amendments were used in combination with plants	(Kumpiene et al., 2014; Touceda-González et al., 2017b)
Germany	As, Cd, Pb	EX	Willow (*Salix* sp. - clone *Tora)*	Short-rotation coppice, no amendments	Significant increase in microbial biomass - increase in activity some soil enzymes - no significant changes in bacterial communities - increase in abundance for one gene	Since 2005		
Sweden	Cr, Zn	EX	Willow (*Salix* sp. - clone *Tora)*	Short-rotation coppice, no amendments	No significant improvement in soil biological activity (lower biomass) - increase in activity for some soil enzymes, decrease in others - showed a pronounced shift in bacterial communities - increase in abundance for a few genes	Since 1997		
Belgium	Cd, Zn, Pb	EX	Willow (*Salix* sp. - clone *Tora)*	Short-rotation coppice, no amendments	Significant increase in microbial biomass - increase in activity some soil enzymes - no significant changes in bacterial communities - no increase in genetic abundance	Since 2005		
Austria	As, Cd, Pb, Zn	ST, IM/PE	Maize and barely cultivars and grass mixture	Gravel sludge, siderite-bearing materials, loamy powder, or red mud in different combinations	Strong shifts in bacterial communities - increase in abundance for few genes	Since 2003		
Poland	Cd, Zn, Pb	ST, IM/PE	Revegetation with grass mixture	By-product limestone and municipal	Strong shifts in bacterial communities - increase in abundance for most genes	Since 1997		

				biosolids at high/low rates				
France	Cu	ST, IM/PE	Revegetation with *Cytisus striatus, Populus nigra, Rumex acetosella, Agrostis capillaris, Agrostis gigantea*, and other grasses	Zerovalent iron grit (2%) and compost (5%)	Significant increase in biomass and soil respiration - increase in activity for all soil enzymes - shift in bacterial communities - increase in genetic abundance	Since 2006		
Switzerland	Cd, Pb, Zn	EX	Tobacco (*Nicotiana tabacum)*		Slight increase in TE concentrations in pore water	>3 years	Lettuce plants growing on untreated soils had, in general, lower shoot DW yields than those grown in the control soil (garden soil) and at 4/10 sites shoot DW yield was higher in phytomanaged sites than untreated soils - phytoextraction had a slightly better effect on shoot biomass than phytostabilisation - in general GRO had no significant effect on soluble TE concentrations - Multivariate analysis showed a gradient of soil amelioration from untreated to GRO-managed soils, having a positive impact on shoot yield due to decreased phytotoxicity, with the strongest ameliorating effect at brownfield/mine sites versus agricultural soils - the best results were achieved by compost amendment followed by phytoextraction, with nutrient and organic matter addition improving soil quality and favouring plant growth	(Quintela-Sabarís et al., 2017) – 10 field trials as part of the EU Greenland project (overlap with Touceda-Gonzales et al. 2017 and Kumpiene et al. 2014)
Germany	As, Cd, Pb	EX	Willow (*Salix* sp. - clone *Tora)*					
Sweden	Cd, Cr, Zn	EX	Willow (*Salix* sp. - clone *Tora)*		Slight increase in TE concentrations in pore water			
France	Cd, Zn	EX	Basket willow (*Salix viminalis* L.)					
Belgium	Cd, Zn, Pb	EX	Willow (*Salix* sp. - clone *Tora)*					
France	Cu	EX	Crop rotation - tobacco (*Nicotonia tabacum*) and sunflower (*Helianthus annus*)	Compost (5% w/w) and dolomitic limestone (0.2% w/w)				
Spain	Cu	EX	Tobacco (*Nicotiana tabacum)*	Compost				
Austria	As, Cd, Zn, Pb	ST, IM/PE	Maize (*Zea mays*) and barley (*Hordeum vulgare*)	Soil amendment				
France	Cd, Cu, Pb, Zn	ST, IM/PE	Tufted hairgrass (*Deschampsia cespitosa* L.) and willow (*Salix spp.* - clones Inger, Tordis)	Basic slag (Optiscor)				

Poland	Cd, Zn, Pb	ST, IM/PE	Revegetation with grass mixture	By-product limestone and municipal biosolids at high/low rates	Decrease in concentrations with high addition of biosolids			
France	Cu	ST, IM/PE	Revegetation with *Cytisus striatus*, *Populus nigra*, *Rumex acetosella*, *Agrostis capillaris*, *Agrostis gigantea*, and other grasses	Zerovalent iron grit (2%) and compost (5%)				
Spain	Cu	ST, IM/PE	Goat willow (*Salix caprea* L. - cv. Mauerbach), native species of *Salix viminalis* L. and *Populus nigra* L.	Compost	Compost strongly reduced Cu uptake in shoots			
Field	As, Cd, Cu, Ni, Pb, Zn	EX, ST	Birch (*Betula* spp.), alder *(Alnus* spp.), willow *(Salix* spp.), poplar *(Populus* spp.), larch *(Larix* spp.)	None	Significant decreases in bioavailable metal concentrations in hotspots at each site - higher Cd, Zn uptake in plants than reflected in EDTA-extractable concentrations - potential Cd, Zn hotspot reduction within 25-50-year plant life cycle	3 years	EDTA was found to be a cheaper, easier and reliable indicator of bioavailability and risk - short-rotation coppice provides effective risk management and remediation for hotspots of residual metals and As-contaminated land as well as a potentially profitable economic return	(French et al., 2006)
Spain	Cd, Zn	EX, ST	Silver poplar (*Populus alba)*	None	Decrease of available metal concentrations - MBC and enzyme activity significantly increased with presence of trees in all areas	2 years	Addition of organic matter through root exudates and litter improved soil pH in acid soils - litter deposition did not increase metal concentration - demonstrable improvement in soil quality	(Ciadamidaro et al., 2014)

France	Cu	EX, ST	Sunflower (*Helianthus annus*) - tobacco (*Nicotonia tabacum)* crop rotation, grass mixture *(Agrostis* spp.)	Compost, dolomitic limestone	Decreased Cu extractability with treatments - compost increased Cu solubility but no observed Cu-induced phytotoxicity - Cu uptake and translocation by plants was not observed indicating no risk to food chain - compost led to notable shifts in soil microbial populations	7-9 years	Phytomanagement enhanced natural revegetation through improvement of soil physico-chemical properties and underlying soil functions, particularly with compost-based amendments	(Burges et al., 2021, 2020; Mench et al., 2018)
Sweden	Cu, Pb	ST	Commercial grass/herb seed mix	Alkaline fly ashes and peat	Cu and Pb leaching were reduced on average by 98% and 97% respectively	400 days	Microbial biomass and respiration were significantly increased in treated soils (qCO2, an indicator of microbial stress, was lower) and all measured enzyme activities were also significantly increased	(Kumpiene et al., 2009)
Romania	Cd, Pb, Zn	ST	Miscanthus or silvergrass (*Miscanthus sinensis x giganteus)*	Red mud	Red mud reduced mobile fractions to 12.6, 2.5 and 0.2% of total values for Cd, Zn and Pb respectively thereby increasing easily mobilizable and immobile fractions	5 years	*M. sinensis x giganteus* grew successfully with low metal accumulation (can be considered an excluder) though produced more biomass on less contaminated plots	(Pavel et al., 2014)
France (field and pot exp.)	Cu, Pb, Zn	ST	Giant miscanthus or elephant grass *(Miscanthus* x *giganteus)*	20,000 plants/ha	Bioaccessible fractions (as a percentage of pseudo-total conc.) in gastric phase - Cd (65-77%), Pb (80%), Zn (36-52%) and intestinal phase - Cd (18-35%), Pb (5-30%), Zn (36-52%) - miscanthus varied in efficiency for reducing the bioaccessibility of each metal	Short-term greenhouse (93 days), long-term field (3 years)	Compared to uncultivated soils, phytostabilisation using miscanthus provided evidence for substantial, complex effects on oral bioaccessibility of Cd, Pb and Zn - fractionation showed that Cd and Zn were much more mobile (labile) than Pb with slight changes in metal distribution over time which may be attributable to miscanthus-induced changes soil parameters (i.e. pH, organic matter) - biomass was well-suited for use as bioenergy	(Pelfrêne et al., 2015)

England	As, B, Cd, Cr, Cu, Pb, Hg, Ni, Zn	ST	Reed canarygrass (*Phlaris arundinacea)*, giant silvergrass (*Miscanthus* x *giganteus*), willow (*Salix* sp.), switchgrass (*Panicum virgatum*)	Green waste compost (500 ton/ha)	Reed canarygrass had the highest biomass yield, lowest cost for establishment, time to maturity, and lowest contaminant levels (4-7 odt/ha)	3-5 years	Estimated energy yield from reed canarygrass of 97 GJ/ha at contamination levels acceptable for domestic pellets	(Lord, 2015)
USA (Field and pot exp.)	As, Pb, Zn	ST	Native grasses (buffalo grass, arizona fescue, quailbush, mountain mahogany, mesquite, catclaw acacia)	Compost	Canopy cover developed ranging from 21-61% in compost-amended soils, no plants grew on unamended tailings - bacterial counts increased 1.5-4x - low accumulation in plant tissue below animal toxicity limits	41 months	60-day greenhouse pot studies translated successfully to the field trial though individual plant success was lower in the field - self-propagation by seeds was observed in some plants as well as creation of 'fertility islands' from seeds spreading to composted and unseeded plots - deemed more cost-effective than the commonly applied soil cap and plant strategy	(Gil-Loaiza et al., 2016)

Sweden	Cu, Pb, Zn	ST	Willow (*Salix* spp. - clones Klara and Inger)	Minimal maintenance	Chemical toxic pressures were found to be in the same range or lower than initial values, no leachate inhibitory effects were found in Microtox tests and nematode analysis indicated improved ecological conditions - no risk to grazing animals was found	3 years	Used a Triad ecological risk assessment approach - This study shows that cultivation of brownfields using phytostabilising willow clones can reduce the ecological risks, improve the soil quality of the site and provide revenue if the biomass is sold for e.g. bioenergy production – using bioenergy crops for phytostabilisation on brownfields can contribute to preserve and improve eco-system services, create economic regeneration of these areas and at the same time be a sustainable risk management option.	(Enell et al., 2016)
Spain	Cu	ST	Willow (*Salix spp.*), poplar *(Populus nigra* L.), common bent (*Agrostis capillaris* L. - cv. Highland	Composted municipal solid wastes	Decreased in Cu bioavailability and improved soil quality (e.g. pH) leading to establishment of healthy vegetation cover - stimulation of soil enzyme activities largely by compost but also due to plant root activity	3 years	Induced shifts in the microbial community structure over time - *S. viminalis* and *A. capillaris* showed best plant growth and biomass production - beneficial effects of phytostabilisation were maintained at least 3 years after treatment	(Touceda-González et al., 2017a)

Spain	Cd, Pb, Zn	ST	Red fescue (Festuca rubra)	Cow slurry, sheep manure, paper mill sludge mixed with poultry manure	Paper mill sludge mixed with poultry manure treatment resulted in the highest (long-term) reduction of Cd, Pb and Zn bioavailability - least effects shown for reduction in Pb bioavailability - differences in effectiveness between less (better) and more contaminated sites	5 years	Paper mill sludge showed greatest (long-term) stimulation of soil microbial activity and diversity - varying effect on some parameters (positive in relation to N and S cycles) and large differences between the less (higher) and more contaminated sites - using an aggregated soil quality index, cow slurry and sheep manure treated soils showed a lower soil quality while paper sludge showed either no change or slightly positive at the less contaminated site - sheep manure showed a significant improvement in soil quality at the more contaminated site and paper sludge was also positive most due to increase dehydrogenase activity	(Garaiyurrebaso et al., 2017) ((Galende et al., 2014) for short-term effects, which showed contrasting results)
Spain	As (202), Cd (4.4), Cu (119), Pb (471), Zn (381)	ST	Silver poplar *(Populus alba*), European nettle tree (*Celtis australis*), narrow-leafed ash (*Fraxinus angustifolia*), evergreen oak (*Quercus ilex*), olive tree (*Olea europaea*), carob (*Ceratonia siliqua*), stone pine (*Pinus pinea)*	Biosolid compost and sugar beet lime	Amendments significantly improved soil quality and effects remained even 14 years later - substantial decreases in metal availability in the rhizosphere of *Ceratonia, Fraxinus* and *Populus* due to increased soil pH - amendments reduced BAF in grass species - *Populus* had highest BAF and translocation for Cd and Zn - BAF for all species was low for As, Cu and Pb	since 2002	*Pinus* had the highest BAF in roots for Cd and *Celtis* had highest for Cu and Zn - a three-stage phytoremediation approach is proposed: amendment addition to improve soil quality and reduce metal availability/mobility - tree planting to stabilise soil - long-term monitoring of metal availability in soils and concentrations in organisms	(Madejón et al., 2018)

France	Cd, Mn, Zn	ST	Tested 38 different types of trees	Endomycorrhizal fungi - *Rhizophagus irregularis*	Lowest BAF, high tolerance: *Alnus subcordata* (Caucasian alder), *Platanus orientalis* (old world sycamore), *Ulnus pumila* (siberian elm), *Ostrya carpinfolia* (european hop-hornbeam), *Acer* spp. (maple) - Highest BAF, high resistance: *Salix aquatica grandis* (willow), *Populus oxford* (poplar), *Betula papyrifera* (paper birch, canoe birch), *Quercus rysophylla* (loquat leaf oak) -	2 years	Endomycorrhizal fungus had no significant impact on growth of tree species	(Ciadamidaro et al., 2019)
France	Cd, Cu, Pb, Zn, PAH	ST	Poplar (*Populus* spp. - tested 14 genotypes, alder *(Alnus glutinosa)*	Poplar SRC - 1000 stems/ha - arbuscular mycorrhizal fungi - plant-growth promoting bacteria	Decreased metal availability over time - improvement in soil quality - large variation in other genotypes: Vesten most productive and accumulated least metals, Trichobel genotype accumulated most metals - isolated bacteria exhibited plant-growth promoting traits and resistance to toxicity and possible degrading genes - poplar biomass production significantly enhanced by mycorrhizal inoculation	10 years	Higher metal content of bark tissues concentrated in branches led to conclusion that only stem wood be harvested, instead of the whole tree, which will enable a reduction in the risks encountered with TE-enriched biomass in valorisation process - *multiple studies were performed at the same site (*BIOFILTREE, PHYTO-POP) *and present complementary results*	(Chalot et al., 2020; Ciadamidaro et al., 2017; Foulon et al., 2016; Kidd et al., 2021)

Belgium	Cd, Pb, Zn	ST, IM/PE	Red fescue (*Festuca rubra*), common bentgrass *(Agrostis capillaris)*	Cyclonic ashes ('beringite'), compost	Water-extractable metal fraction of the treated soil was up to 70x lower compared to non-treated soil	5-12 years	Old smelting site even 12 years after treatment showed healthy soil and regeneration by vegetation - both physico-chemical and biological evaluations performed throughout time span (5, 7, 10 and 12 years after planting) indicate strong immobilisation of metals and reduced availability for biota - noted higher diversity and recolonisation of treated area by perennial species due to mycorrhizal fungi	(Vangronsveld et al., 2009, 1996)
Austria	Cd, Pb, Zn	ST, IM/PE	Native grass mixture	gravel sludge, red mud (slurrying or injecting)	Significant decreases in NH4-NO3 extractable metal concentrations - 50% Cd, up to 90% Pb, over 90% Zn - reduction of elements in seepage water by 40%, 45% and 50% respectively	10 years	Uptake into grasses significantly reduced and met threshold for fodder crops - microbial biomass increased - human bioaccessibility decreased for Pb	(Friesl-Hanl et al., 2017; Friesl et al., 2006)
France	As, Pb	ST, IM/PE	Basket willow (*Salix viminalis*)	Biochar, compost, iron grit	Decreased pseudo-total concentrations (dilution effect) and bioavailable concentrations with amendments - metal(loids) were mainly accumulated in roots with low translocation	69 days	Biochar and compost application improved soil fertility and plant growth - iron grit had negative effects on plant growth - use of amendments shown to be valid strategy to restore a highly contaminated mining technosol	(Lebrun et al., 2020, 2019)
Spain	As, Cu	ST, IM/PE	Rye (*Secale cerale* L.)	Iron sulphate, lime, paper mill sludge, biochar, compost	All treatments resulted in reduction of soluble and extractable Cu (55-94%) - As was not significantly mobilised	2 years	Treatments with organic amendments improved soil quality and enhanced rye growth - combination of Fe-sulphate and biochar showed most promising results to improve soil fertility, decrease plant As and Cu uptake and enhance soil C-sequestration	(Fresno et al., 2020)

Spain	Non-detect - primarily poor soil quality	PM	Rapeseed (*Brassica napus* - cv. Expower)	Bio-stabilised material (BSM) from commingled municipal solid wastes	BSM-amended soils became more productive and had greater functionality than non-amended soils - increase in basal respiration and microbial activities related to C and N cycling - biomass and functional groups were not significantly altered	260 days	Phytomanagement is shown to promote circular economy and is a valid strategy for restoring degraded, peri-urban vacant soils - restored parameters linked to improved ecosystem services of removal, retention and delivery of nutrients for plants and decomposition of wastes and organic matter	(Míguez et al., 2020)

2.3.1 Extraction

Phytoextraction is a GRO strategy to remove the source of contamination that utilises the capacity of plants to function as 'bio-pumps' take up contaminants from soil and groundwater into their biomass, which can then be removed from the site by harvesting the plant (Mench et al., 2010; B. H. Robinson et al., 2003; Vangronsveld et al., 2009). In general, the phytoextraction process consists of a) cultivating appropriate plant/crop species on the contaminated site; b) removal of harvestable, contaminant-enriched plant biomass; and c) post-harvest treatment of the enriched biomass by composting, incineration, landfilling, etc. to reduce the volume and/or weight of the biomass for either disposal as hazardous waste (if so classified) or for use as a valuable bio-resource (e.g. as bioenergy feedstock) (Burges et al., 2018; Mench et al., 2010; OVAM, 2019; B. H. Robinson et al., 2003; Robinson et al., 2006; Vangronsveld et al., 2009).

According to Vangronsveld et al. (2009), there are three basic strategies of trace element, i.e. metal(loid), phytoextraction common in practice: (1) continuous or natural phytoextraction using hyperaccumulators (e.g. *Thlaspi caerulescens*); (2) continuous or natural phytoextraction of trace elements using fast-growing, high biomass producing plants (e.g., *Salix* or *Populus* spp.); (3) enhanced or chemically-assisted phytoextraction by using soil amendments (e.g., chelators or acidifying amendments) to increase trace element mobility in the soil for greater uptake in plants. The maximum trace element uptake in all these approaches depends on two main variables: **trace element concentration in harvestable plant parts**, which can be estimated using the bio-accumulation (or bio-concentration) factor (BAF/BCF), and **harvestable biomass yield** as high biomass production results in greater amounts of contaminants being removed (Burges et al., 2018; Keller, 2005; Keller et al., 2003a; Robinson et al., 2015, 2006; Vangronsveld et al., 2009). A meta-analysis has shown that while phytoextraction can still play an important role in removing moderate amounts of metals, it appears to be less effective beyond critical metal concentrations due toxic effects in the plants (Audet and Charest, 2007). Several other important facts should also be considered when phytoextraction potential is calculated, including the plant-available (**bio-/phytoavailable**) fraction of the trace element in the soil, root density and spatial distribution, the number of consecutive crops per annum as well as the trace element decrease during the process of extraction as an indicator of effectiveness (Burges et al., 2018; Keller, 2005; Keller et al., 2003a; Robinson et al., 2015, 2006; Vangronsveld et al., 2009). Brief detail and examples of these main strategies follows:

1) Trace element phytoextraction using hyperaccumulators – this strategy was one of the earliest phytoextraction applications and relies on the inherent capacity of certain plant species that can accumulate inordinately high concentrations of certain metals (1-10% of mass) in their plant tissue without experiencing toxic or growth inhibiting effects (Salt et al., 1998, 1995; Vangronsveld et al., 2009). At least 500 such species have been identified covering many different plant families, Brassicaceae in particular is well-represented, but not all of these are suitable for commercial use at field-scale due to their accumulating of only specific metals, producing small amounts of biomass, growing slowly and/or being potentially invasive (Burges et al., 2018; Pollard et al., 2014; Sarma, 2011; Tang et al., 2012; Vangronsveld et al., 2009). Nickel is by far the most commonly accumulated metal among the hyperaccumulator plants (>450 taxa) that generally occur on serpentine (ultramafic) soils, but hyperaccumulating species for As, Cd, Mn, Se and Zn have also been reported (Ali et al., 2013; Kennen and Kirkwood, 2015; Pollard et al., 2014; Sarma, 2011). Some examples of frequently tested species (see e.g. (Ali et al., 2013; Burges et al., 2018; GREENLAND, 2014b; Kennen and Kirkwood, 2015; Pollard et al., 2014; Sarma, 2011) for expanded lists and more detail) include:

- *Noccaea* (or *Thlaspi*) *caerulescens* (alpine pennygrass) and other *Thlaspi* spp. for Cd and Zn (Epelde et al., 2010a, 2008a; Tang et al., 2012; Vangronsveld et al., 2009)
- *Alyssum* spp. for Ni (Ali et al., 2013; Sarma, 2011; Tang et al., 2012)
- *Pteris vittata* (brake fern) and other *Pteris* spp. for As (Fitz et al., 2003; Tang et al., 2012; Vangronsveld et al., 2009)

In terms of application, the wide tolerance of hyperaccumulators to metal toxicity is clearly advantageous, especially for highly contaminated soils like mining spoils, and their unique microbiome is being extensively studied by researchers, though is yet to be fully understood (Epelde et al., 2010b; OVAM, 2019; Thijs et al., 2017). It has also been proposed that valuable metals could be recovered from the ash of enriched biomass in a process dubbed '**phytomining**', though it has only been proven to be economically viable for Ni or Au recovery (Ali et al., 2013; Chaney et al., 2007; Kidd et al., 2015; Tang et al., 2012; Wang et al., 2019).

2) Trace element phytoextraction using high biomass-producing plants – many phytoextraction applications have shifted focus from hyperaccumulating species to instead utilise plants that accumulate lower concentrations of metals in their tissue but compensate by producing large amounts of harvestable biomass. Extraction efficiency may be lower on a per mass basis but the corresponding increase in biomass can result in greater overall effectiveness and surpass that of the hyperaccumulator species (Gerhardt et al., 2017; OVAM, 2019; Vangronsveld et al., 2009). Significant improvements in efficiencies is also possible, when selected and/or improved cultivars of high yielding and metal extracting plants are used, together with appropriate fertilization and multi-cropping techniques (Herzig et al., 2014; Kidd et al., 2015; Vangronsveld et al., 2009). Some examples of high biomass, metal accumulating plant species that are commonly applied (see e.g. (Andersson-Sköld et al., 2013; Burges et al., 2018; Gawronski et al., 2011; GREENLAND, 2014a, 2014b; Kennen and Kirkwood, 2015; Kidd et al., 2015; Mench et al., 2010; OVAM, 2019; Vangronsveld et al., 2009) for expanded lists and more detail) include:

- **Tree species** like *Salix* spp. (willow) and *Populus* spp. (poplar) for Cd, Zn, Cu and other metals (Chalot et al., 2020; Greger and Landberg, 1999; Kacálková et al., 2015; Meers et al., 2005; Mench et al., 2010; Quintela-Sabarís et al., 2017; Ruttens et al., 2011; Touceda-González et al., 2017b; van Slycken et al., 2013; Witters et al., 2009). Metal accumulation can differ significantly between species and clones of the same species which must be taken into account when selecting a certain plant for extraction or stabilisation (Greger and Landberg, 1999; Meers et al., 2007; Mleczek et al., 2010; van Slycken et al., 2013; Vangronsveld et al., 2009). A meta-analysis has shown differential accumulation of various metals in the different plant parts of willow species, i.e. roots (Pb), twigs/stems (Cd, Pb, Zn) or leaves (Cd) (Tőzsér et al., 2017). It has even been recommended that due to higher metal accumulation in twigs/stems of poplars only stem wood should be harvested, instead of the whole tree (Chalot et al., 2020).
- **Annual crops** that be grown in combination (crop rotation), *Helianthus annus* (sunflower) and *Nicotiana tabacum* (tobacco) in particular, for Cd, Zn, Pb, Cu and other metals (Burges et al., 2020; Fässler et al., 2010; Herzig et al., 2014; Kidd et al., 2015; Mench et al., 2010, 2018; Quintela-Sabarís et al., 2017; Thijs et al., 2018; Touceda-González et al., 2017b; Vangronsveld et al., 2009). Other annual crops can also accumulate significant concentrations of metals, e.g. *Brassica juncea* (indian mustard), *B. napus* (rapeseed) and other *Brassica* spp., *Zea mays* (maize), and *Triticum aestivum* (wheat) (Fässler et al., 2010; Gomes, 2012; Meers et al., 2010; Mench et al., 2010; Van Ginneken et al., 2007).

- **Perennial, herbaceous legumes** (e.g. *Medicago sativa* (alfalfa/lucerne), *Glycine max* (soybean), *Lupinus albus, L.* spp. (lupin)) and **grasses** (e.g. *Lolium perenne* (English ryegrass), *Lolium multiflorum* (Italian ryegrass), *Festuca rubra* (red fescue), *F. arundinacea* (tall fescue) and *F. ovina* (sheep's fescue)) that can be grown in combination with other crops (intercropping/row cropping) have also been shown to accumulate metals and are especially valued due to their high tolerance to contaminants (Edrisi and Abhilash, 2016; Gawronski et al., 2011; Gomes, 2012; GREENLAND, 2014a; Kidd et al., 2015; Mench et al., 2010; Tang et al., 2012; Tripathi et al., 2016a, 2016b). These and other so-called 'green manure' plants like borage (*Borago officinalis*) and white mustard (*Sinapsis alba*) can be highly useful for both restoring soil quality as well as reducing bioavailability and ecotoxicity of metal(loid)s (Foucault et al., 2013).

  Note: Depending on site conditions, the specific species or cultivar and soil amendments, these plant species can either accumulate or stabilise metals.

- Large biomass producing **bioenergy grasses** like *Miscanthus x giganteus* (giant perennial silvergrass or simply miscanthus), *Phalaris arundinacea* (reed canarygrass) and have also been shown to accumulate various metals and produce useful biomass on contaminated sites (Kidd et al., 2015; Lord, 2015; Mehmood et al., 2017; Nsanganwimana et al., 2014; Pandey et al., 2016; Tripathi et al., 2016a).

  Note: Depending on site conditions, the specific species or cultivar and soil amendments, these plant species can either accumulate or stabilise metals.

Deliberate selection of plant species to produce valuable biomass and generate wider environmental and economic benefits is purported to be the foundation of a successful phytoextraction (or stabilisation) project for commercial application (Andersson-Sköld et al., 2013; Bardos et al., 2011; Conesa et al., 2012; Cundy et al., 2016; Enell et al., 2016; Evangelou et al., 2012; Gomes, 2012). Aspects of biomass production in GRO are discussed more in Section 3.

3) Enhanced phytoextraction using chemicals or other amendments – this approach aims to overcome one of the main limitations of phytoextraction: natural uptake restricted by metal bioavailability (Dickinson et al., 2009; Robinson et al., 2006; Vangronsveld et al., 2009). Chelating agents such as ethylene-diamine tetra-acetic acid (EDTA) can be used to 'induce hyperaccumulation' by desorbing the metals from soil and forming complexes that can be more easily taken up in plant roots (Robinson et al., 2006; Vangronsveld et al., 2009). This strategy is noted as being especially useful for Pb which is less bioavailable for plants and mainly present in precipitates (Epelde et al., 2008b; Vangronsveld et al., 2009). However, in most cases, the use of chelating agents, EDTA in particular, is not advised due to the substantial risks of the more mobile pool of metal-complexes not being entirely taken up by plants and leaching through the soil profile into groundwater (Dickinson et al., 2009; Epelde et al., 2008b; OVAM, 2019; Robinson et al., 2006; Vangronsveld et al., 2009). Furthermore, EDTA is not readily degraded under natural conditions, thus persistent in the environment, and has been shown to be toxic to both plants and soil biota (Dickinson et al., 2009; Epelde et al., 2008b; OVAM, 2019; Robinson et al., 2006; Vangronsveld et al., 2009). Alternatively, more easily biodegradable, less toxic chelating agents like ethylene diamine disuccinate (EDDS) could be used instead for e.g. Pb extraction (Epelde et al., 2008b). Metals could also be rendered more bioavailable by slightly acidifying the soil by use of chemical fertilisers, organic acids or other amendments in a more controlled manner (Vangronsveld et al., 2009). Plants themselves excrete H^+ ions through their roots, which, combined with other roots exudates like organic acids, can acidify the rhizosphere by up to 2 pH units to increase the local solubility of metals and render them more bioavailable (Mench et al., 2010; OVAM, 2019; Robinson et al., 2006;

Vangronsveld et al., 2009). Plant-microbial interactions can also be exploited to enhance the mobilisation, uptake and storage of metals; for example, by harnessing arbuscular mycorrhizal fungi or stimulating microbes that produce biosurfactants, siderophores and organic acids can reduce toxicity and increase bioavailability for uptake (Figure 2-5) (Dickinson et al., 2009; OVAM, 2019; Robinson et al., 2006; Weyens et al., 2009c, 2009d).

Successful phytoextraction would reduce the total (or bioavailable) concentrations of contaminants in soil to below the level at which they pose risks to human health, soil ecosystem, groundwater and other ecological receptors (alone or in combination with other technologies) and comply with environmental regulations (Dickinson et al., 2009; B. Robinson et al., 2003; Robinson et al., 2006; Vangronsveld et al., 2009). From an economic viewpoint, this should be achieved at a lower cost than other remediation alternatives, or the cost of inaction (Dickinson et al., 2009; B. Robinson et al., 2003; Robinson et al., 2006; Vangronsveld et al., 2009). Additional environmental risks must also be considered in evaluating the viability of phytoextraction, including the risks of 'secondary poisoning' or the transfer of metals into the food chain by e.g. invertebrates feeding on plants or birds feeding on willow leaves (Dickinson et al., 2009). Substantial higher trophic-level accumulation of metals has seldom been found but in specific cases, and the risks to grazing animals can be minimised by selecting non-accumulating plant variants (Dickinson et al., 2009; Enell et al., 2016). Furthermore, phytoextracted contaminants need to be harvested and processed and its eventual fate depends on whether it is classified as a waste or a resource according to metal concentrations in the biomass and regulatory frameworks (Andersson-Sköld et al., 2013; Gerhardt et al., 2017). For example, there is a risk that metals accumulated in leaves could simply be recycled into the surface layers as they fall at the end of every season, so they must also be harvested for full removal effect (Dickinson et al., 2009; Gerhardt et al., 2017; Vangronsveld et al., 2009). Harvested biomass will also have to be processed and can be handled in a variety of ways dependent upon whether it is classified, according to regulatory authorities, as a useful resource for bioenergy, eco-catalysis, etc. or as a waste that must be disposed of via incineration or at a landfill, see e.g. (Bert et al., 2017; Evangelou et al., 2012; Gomes, 2012; Vigil et al., 2015; Witters et al., 2012b, 2012a).

The time expectations surrounding phytoextraction have typically been compared to that of traditional remediation options to be commercially viable; meaning that it should be completed within a '**reasonable timeframe**' (e.g. <10 or <25 years) (Gerhardt et al., 2017; B. Robinson et al., 2003; Robinson et al., 2006; Van Nevel et al., 2007; Vangronsveld et al., 2009). Estimating the time required for phytoextraction, which can potentially take up to a few decades, is thus a critical aspect of determining the feasibility of phytoextraction. A preliminary estimate can be calculated by determining the approximate mass of metal removed by each crop harvest (Equation 3), and corresponding bioaccumulation factor (Equation 4), then calculating the approximate time required to reduce the initial soil concentration in the soil to a target end value (Equation 5) (Robinson et al., 2015, 2006):

$$X = BP \tag{3}$$

$$BAF = \frac{P}{M} \tag{4}$$

$$t = \frac{M_i - M_f}{P(M)B(M)} \tag{5}$$

Where, X = metal extracted per hectare (g/ha), B = crop biomass production (ton/ha), P = metal concentration in the plant (g/ton), BAF = bioaccumulation factor, and M = metal concentration in soil (g/ha), Mi = initial conc., Mf = final conc. For a general example, Robinson et al. (Robinson et al., 2015) calculated the minimum required BAF of plants in order to reduce the metal concentrations in soils by a certain percentage (% cleansing) within a 25-year period (Table 2-5). The authors note that the minimum required BAF will increase with increasing heterogeneity in metal and root distribution in the soil due to decreased efficiency.

Table 2-5. Estimated minimum bioaccumulation factors (BAF) required of plants to reduce metal concentrations in a soil by a certain percentage of the initial amount (% cleansing) in a 25-year period given a certain biomass production, adapted from (Robinson et al., 2015).

% Cleansing	Biomass Production		
	5 ton/ha	10 ton/ha	20 ton/ha
10	2.3	1.1	0.6
20	4.8	2.4	1.2
30	7.7	3.8	1.9
40	11.0	5.5	2.7
50	14.8	7.4	3.7
60	19.5	9.7	4.9
70	25.4	12.7	6.4
90	47.6	23.8	11.9

Since this model assumes a linear decay extraction rate, Equation 5 provides the shortest possible time for phytoextraction time because it does not incorporate spatial or temporal heterogeneity (see (Brett H. Robinson et al., 2009; Robinson et al., 2015) for calculating a site heterogeneity factor for changing plant-available metals around the root), but can give a useful indication of which scenarios are not suitable for phytoextraction (Robinson et al., 2006). Also, considering that the available pool of contaminants is steadily shrinking over time, the efficiency of phytoextraction is highest in the beginning then gradually decreases (Herzig et al., 2014; Vangronsveld et al., 2009). Therefore, a first-order decay (non-linear) function, which assumes a more complex soil chemistry with sorption and retention processes, more accurately reflects the realistic (decreasing) efficiency of phytoextraction per the extraction rate as it is calculated from this decreasing pool (Herzig et al., 2014). For comparison, Herzig et al. (Herzig et al., 2014) estimated a remediation time span, for reducing bioavailable Zn concentrations of 6 mg/kg using tobacco and sunflower clones, of 1-5 years based on linear decay but between 3-12 years using the first order decay function.

Due to inherent inefficiencies necessitating a long remediation time-frame, phytoextraction with the narrow focus of exclusively taking up metals as a stand-alone technology may indeed rarely be suitable for strictly remediation purposes (Dickinson et al., 2009; Robinson et al., 2015, 2006; Van Nevel et al., 2007). However, alternative extraction strategies like **soil polishing** (reducing marginally elevated concentrations to threshold levels) and **bioavailable contaminant stripping** (reducing the soluble, plant-available fraction of metals thereby reducing environmental risk) are viable niche-solutions which could be more widely applicable at various scales (Dickinson et al., 2009; Gerhardt et al., 2017; Herzig et al., 2014; Mench et al., 2010; Brett H. Robinson et al., 2009; Robinson et al., 2015, 2006; Van Nevel et al., 2007; Vangronsveld et al., 2009). Bioavailable contaminant stripping targets the labile (i.e. soluble and exchangeable) contaminant pool instead of the total metal content for remediation, which can shorten remediation times from decades to just a few years (Gerhardt et al., 2017; Herzig et al., 2014; Vangronsveld et al., 2009). This risk-based approach is based on the premise that the main risks from contaminants to humans and ecological receptors is dependent on the soluble and exchangeable fraction of contaminants and not on the total content of metals in the soil, much of which may be inaccessible to humans and other living organisms (Herzig et al., 2014; Vangronsveld et al., 2009). For example, Herzig et al. (2014) showed that using non-GMO mutant clones of tobacco and sunflower the labile (0.1 M $NaNO_3$-extractable) concentrations of zinc (6 mg/kg) could be lowered by 45-70% within 5 years, with up to 58% in individual samples (15-30% on average) being reduced after the first harvest. There have been numerous studies successfully adopting the bioavailable contaminant stripping approach to reduce labile contaminant pools (labelled BCS in Table 2-4), including using *Noccaea caerulescens* to strip bioavailable Cd and Zn (Jacobs et al., 2018); using *Pteris vittata* to strip bioavailable As (Fitz et al., 2003); using *Brassica juncea, Poa annua,* and *Helianthus annus* to strip bioavailable Hg (Pedron et al., 2013; Petruzzelli et al., 2012); and a less successful study that attempted to use *Salix* sp. and *Populus* spp. to strip bioavailable As, Co, Cu, Pb and Zn at a heavily contaminated pyrite waste site (Vamerali et al., 2009).

According to Epelde et al. (2008), '*When assessing the success of a phytoextraction process, up till now, emphasis has mostly been placed on metal removal, it is important to highlight that* ***the ultimate objective of a phytoextraction process must be to restore soil health*.**' In the definition proposed by Doran and Zeiss (Doran and Zeiss, 2000), soil health is defined as *the continued capacity of soil to function as a vital living system, within ecosystem and land-use boundaries, to sustain biological productivity, promote the quality of air and water environments and maintain plant, animal and human health.* Hence, it has been argued that indicators of soil health are needed to properly assess the efficiency of a phytoextraction process (Epelde et al., 2008a; G. Lacalle et al., 2020; Gómez-Sagasti et al., 2012). For example, Epelde et al. (2010a, 2008a) showed that the presence of alpine pennygrass (*N. caerulescens*) has been shown to increase soil microbial properties and vegetation has been shown to positively affect soil conditions (i.e. due to presence of organic compounds and root exudates and providing surfaces for microbial colonization) leading to higher values of microbial activity in the rhizosphere versus non-rhizosphere soil. Furthermore, the time required for remediation might be unacceptably long (estimated up to 36 years) but the beneficial effects on soil health can happen in the first season which further reinforces the idea that recovery of soil health is an important goal to consider in a phytoextraction (and general remediation) project.

2.3.2 Stabilisation

According to Mench et al. (2010), there is no universal method for **phytostabilisation**. The term itself encompasses a broad strategy that typically entails the use of plants to immobilise or inactivate contaminants in and around the root system that can also be 'aided' through the use of various soil amendments (GREENLAND, 2014a; Mench et al., 2010; OVAM, 2019; Vangronsveld et al., 2009). This GRO was introduced as an alternative strategy to phytoextraction due to the latter's inherent limitations and inefficiencies (i.e. full removal can take decades); where, instead of source removal, the plants are used to reduce the mobility and bioavailability of contaminants in the environment thus mitigating adverse effects (Epelde et al., 2009a; Gerhardt et al., 2017; Mench et al., 2010; OVAM, 2019; Vangronsveld et al., 2009). Phytostabilisation is predominantly applied to immobilise metals in soil but it can also be useful for capturing recalcitrant organic compounds like PAHs that can then be degraded over time via **rhizodegradation** (OVAM, 2019). More specifically, phytostabilisation uses plants and their associated microbes for long-term containment of contaminants such as metals in solid matrices through adsorption, absorption and accumulation in the roots, precipitation in the root zone or by physical stabilisation of the soil that either prevents or minimises their mobility in the food chain, downward percolation to groundwater and re-entrainment of contaminated particulates for direct inhalation or ingestion by humans (Cundy et al., 2016; Epelde et al., 2009b; Gerhardt et al., 2017; Mench et al., 2010; OVAM, 2019; Vangronsveld et al., 2009). In theory, plant–microbe consortia will facilitate metal sorption and precipitation in the rhizosphere and/or accumulation of metals into root tissues, resulting in decreased labile (i.e.

easily mobilised) pools, as well as assisting the plant in overcoming phytotoxicity (Mench et al., 2010; OVAM, 2019; Vangronsveld et al., 2009). Decreases in labile pools might only be depleted initially before equilibrium is restored; however, an important conclusion from longer phytostabilisation trials is that it has not been shown to increase the lability of metals during the planting trials or afterwards (e.g. (French et al., 2006; Herzig et al., 2014; Vangronsveld et al., 1996)). One of the main features of phytostabilisation is improving the quality of the soil to enable the revegetation of contaminated, derelict brownfield sites, which, with its associated natural attenuation mechanisms, is recognised to be the most realistic remedial action to reduce the risks of exposure to receptors at many of these sites (Dickinson et al., 2009). Phytostabilisation is a true remediation technology but still requires considerable further attention, as a metal-stabilising effect is certainly not always clear cut, and will always require extensive long-term monitoring (Dickinson et al., 2009; Mench et al., 2010; Vangronsveld et al., 2009).

Plant species for phytostabilisation must be tolerant to metals and poor conditions, have an extensive root system, produce large amounts of biomass, translocate very low or negligible amounts of metals from root-to-shoot and ideally are native species or at least non-invasive (Alkorta et al., 2010; Burges et al., 2018; Gómez-Sagasti et al., 2012). Metal uptake can vary considerably between species in the same genus or even clonal variants of the same species, so careful consideration is required to select suitable species as some characteristics (e.g. stress tolerance) may still be desirable (Burges et al., 2018; Dickinson et al., 2009; Mench et al., 2010; OVAM, 2019; Vangronsveld et al., 2009) Some examples of low or non-accumulating plant species that are commonly applied (see e.g. (Andersson-Sköld et al., 2013; Burges et al., 2018; Gawronski et al., 2011; GREENLAND, 2014a, 2014b; Kennen and Kirkwood, 2015; Kidd et al., 2015; Mench et al., 2010; OVAM, 2019; Vangronsveld et al., 2009) for expanded lists and more detail) include:

- **Tree species** that are non- or low-accumulating can be used in phytostabilisation, and reforesting on brownfields is an effective risk management strategy entailing a wide range of co-benefits (Dickinson, 2000; Dickinson et al., 2000; French et al., 2006). As previously noted, willow (*Salix* spp.) and poplar (*Populus* spp.) are frequently used for extraction but there are individual species or cultivars that exclude metals (e.g. *Salix* spp. cv. Klara and Inger) that are well-suited for short-rotation coppicing to produce clean, useful woody biomass (Andersson-Sköld et al., 2014, 2013; Enell et al., 2016; French et al., 2006; Gawronski et al., 2011; GREENLAND, 2014b; Kidd et al., 2015; Mleczek et al., 2010; van Slycken et al., 2013). However, other characteristics in relation to biomass conversion, yield and survivability (e.g. biomass yield, calorific value, bulk density, moisture content, ash and extractive content, pest resistance, metal tolerance, need for fertilisation, etc.) may be just as valuable in selecting for clones (Andersson-Sköld et al., 2014; Ciadamidaro et al., 2019; GREENLAND, 2014b; Kidd et al., 2015). Many other types of trees that meet many of the above-mentioned criteria have also been employed for phytostabilisation (see (Ciadamidaro et al., 2019) for a comprehensive screening of accumulating vs. non-accumulating tree species for use in phytomanagement of marginal lands), including *Alnus glutinosa, A. incana, A. subrcordata* (alder – highly useful as a pioneer species that improves soil fertility by nitrogen fixation), *Betula pendula* (silver birch – also a pioneer species with high tolerance and native to Sweden), *Picea abies* (Norwegian spruce), *Pinus sylvestris* (Scots pine), *Acer* spp. (maple), *Platanus orientalis* (Old world sycamore), *Ostya carpinifolia* (European hop-hornbeam), *Sorbus* spp. (ash, whitebeam and rowan) (Ciadamidaro et al., 2019; Dickinson, 2000; French et al., 2006; GREENLAND, 2014b; Hermle et al., 2006; Kidd et al., 2015; Mench et al., 2010; OVAM, 2019). The symbiosis that many tree species have with mycorrhizal fungi also greatly enhances plant growth and tolerance at contaminated sites (Ciadamidaro et al., 2019, 2017; Kidd et al., 2015). Leguminous, nitrogen-fixing trees and shrubs and in the plant family Fabaceae (e.g. *Acacia* spp. and *Robinia pseudoaccacia,* black locust or pseudo-acacia) are also highly tolerant and applicable for phytostabilisation (and aiding degradation) as well as improving soil quality (Gawronski et al., 2011; Kidd et al., 2015).

- **Perennial, herbaceous legumes** (e.g. *Medicago sativa* (alfalfa/lucerne), *Trifolium* spp. (clover), *Lupinus albus*, *L.* spp. (lupin)) and **grasses** (e.g. *Lolium perenne* (English ryegrass) and *Lolium multiflorum* (Italian ryegrass), *Poa pratensis* (meadowgrass), *Festuca rubra* and *F. ovina* (ryegrass), *Agrostis* spp. (bentgrass)) that can be grown in combination with other crops (intercropping/row cropping) have also been successfully used for stabilisation of metals and are especially valued due to their high tolerance to contaminants (Burges et al., 2018, 2016; Garaiyurrebaso et al., 2017; Gomes, 2012; GREENLAND, 2014b; Kidd et al., 2015; Mench et al., 2010; Quintela-Sabarís et al., 2017; Touceda-González et al., 2017b, 2017a; Tripathi et al., 2016a; Vangronsveld et al., 1996). These and other so-called 'green manure' plants like borage (*Borago officinalis*) and white mustard (*Sinapsis alba*) can be highly useful for both restoring soil quality as well as reducing bioavailability and ecotoxicity of metal(loid)s (Foucault et al., 2013). In extremely contaminated sites (e.g. smelter wastelands, mine spoils), grass species have been proven effective to establish a vegetation cover (typically in combination with amendments) in an otherwise barren, toxic landscape, including *Poa pratensis, Agrostis capillaris, Festuca arundinacea, Festuca rubra* and *Festuca ovina* (Epelde et al., 2009b; GREENLAND, 2014b; Vangronsveld et al., 1996).

  Note: As previously noted, these plant species can either accumulate or stabilise metals but most often are used for stabilisation purposes due to consistently low uptake.

- Large biomass producing **bioenergy grasses** like *Miscanthus* spp. (perennial silvergrass or simply miscanthus), *Panicum virgatum* (switchgrass), *Arundo donax* (giant reed) and *Phalaris arundinacea* (reed canarygrass) have also been successfully tested for stabilisation of various metals and production of useful biomass on contaminated sites (Kidd et al., 2015; Lord, 2015; Mehmood et al., 2017; Nsanganwimana et al., 2014; Pandey et al., 2016; Pavel et al., 2014; Pelfrêne et al., 2015; Tripathi et al., 2016a). These bioenergy crops are highly attractive due to their wide climatic adaptability, low production costs, suitability to marginal land (e.g. tolerance to contamination), relatively low water requirements, low nutrient and agrochemical needs and potential for wide environmental benefits like carbon sequestration through their deep and well-developed root systems (Andersson-Sköld et al., 2013; GREENLAND, 2014b; Zegada-Lizarazu and Monti, 2011). Their low metal(loid) uptake and translocation from roots to shoots, combined with a potential use in bioenergy, make these species attractive candidates for phytostabilisation (Andersson-Sköld et al., 2013; GREENLAND, 2014b).

  Note: As previously noted, these plant species can either accumulate or stabilise metals but most often are used for stabilisation purposes due to consistently low uptake.

- In phytostabilisation, many plants have been demonstrated to exclude metals (i.e. **phytoexclusion**) by avoiding metal uptake altogether, immobilising metals in the roots or restriction of metal uptake to the shoots to avoid sensitive organelles. **Annual crops** that exclude specific metals for uptake, particularly Cd, are highly prized particularly for use on agricultural soils where contaminant transfer into the food chain is a risk (Dickinson et al., 2009; GREENLAND, 2014b; Kidd et al., 2015; Tang et al., 2012). Many such staple crops like cereals and vegetables have been shown to have the ability to either exclude toxic metals like Cd from uptake or translocate only miniscule amounts to their harvestable, edible biomass, including certain species/cultivars of wheat (*Triticum* spp.), barley (*Hordeum vulgare*), rice (*Oryza sativa*), potato (*Solanum tuberosum*), soybean (*Glycine max*) and maize (*Zea mays*). The use of metal-excluding cultivars of annual crops can be an effective option for mitigating the risk of contaminant transfer into the food chain on agricultural land (Andersson-Sköld et al., 2013; Dickinson et al., 2009; GREENLAND, 2014b; Kidd et al., 2015; Tang et al., 2012). By adopting such strategies, it is possible to safely cultivate food crops in contaminated soils by either i) selectively cultivating phytoexcluder crop varieties or clones, ii) co-cropping contaminant accumulating species with non-accumulating or excluding food crop varieties to further reduce plant uptake in food crops, or iii) pre-cultivating contaminant accumulating species to strip the bioavailable fraction and reduce contaminant uptake in subsequent crops (GREENLAND, 2014b; Greger and Landberg, 2015; Kidd et al., 2015; Tang et al., 2012).

A successful phytostabilisation will establish either a long-term succession of plant communities or a sustainable cropping rotation that promotes soil development processes, enhances nutrient cycles, stabilises microbial communities and maintains sustainable soil ecosystem functions with either no or acceptable residual pollutant linkages, e.g. human and animal exposure (Cundy et al., 2016; GREENLAND, 2014a; Mench et al., 2010). Constraints are imposed by current environmental legislation being based on total and not bioavailable concentrations, the need for a site to be permanently vegetated to ensure effectiveness which can limit future land use options and is therefore suitable for sites of lower economic value, and the need for long-term monitoring and maintenance (Mench et al., 2010; Robinson et al., 2006; Vangronsveld et al., 2009). **The time required to implement phytostabilisation is dependent on the establishment of the plant species;** for example, it will take 2-4 years with fast-growing perennial tree species like willow and poplar (Robinson et al., 2006). In general, the quickest remedial effects can be expected from soil amendments that provide a relatively 'instant' effects (e.g. biochar reducing bioavailability of PCB and DDT, thus reducing uptake by earthworms, within 50 days (Denyes et al., 2016, 2013)). Rhizomatous grasses too (e.g. *Miscanthus*, switchgrass) can establish within a few weeks (e.g. 6-8 weeks) and have been recommended to quickly provide soil cover and limit the dispersion of soil particles by physical processes whilst shrubs and trees become established (Mench et al., 2010; OVAM, 2019).

Phytostabilisation in combination with (or without) soil amendments has been successfully used for risk management and soil restoration in a variety of applications (see e.g. (Gerhardt et al., 2017; GREENLAND, 2014a, 2014b; Kidd et al., 2015; Kumpiene et al., 2019, 2014; Mench et al., 2010; Quintela-Sabarís et al., 2017; Touceda-González et al., 2017b; Vangronsveld et al., 2009) for compilations); such as:

- **Hydraulic control of groundwater** (Pivetz, 2001; Robinson et al., 2007, 2006);
- **Mining spoils or tailings** (Epelde et al., 2014, 2009b; Gajić et al., 2018; Garau et al., 2021; Gil-Loaiza et al., 2016; Kumpiene et al., 2012; Madejón et al., 2018; Mendez and Maier, 2008; Rock et al., 2012; Touceda-González et al., 2017a; US EPA, 2007)
- **Old smelting sites** (Gray et al., 2006; Pavel et al., 2014; US EPA, 2007; Vangronsveld et al., 2009, 1996);
- **Agricultural soils** (Friesl-Hanl et al., 2017; Friesl et al., 2006; GREENLAND, 2014a, 2014b; Kim et al., 2018);
- **Former wood preservation sites** (Burges et al., 2021, 2020; Hattab et al., 2014);
- **Vegetated caps for landfills** (Pivetz, 2001; Rock et al., 2012; US EPA, 2007);

- **Other types of derelict post-industrial sites** (Dickinson, 2000; French et al., 2006; GREENLAND, 2014a, 2014b; Kumpiene et al., 2009; Míguez et al., 2020; US EPA, 2007).

A key aspect of (aided) phytostabilisation is that it can both reduce the toxicity of contaminants as well as improve ecosystem functioning by restoring soil health and increasing microbial activity, biomass and diversity in the long-term (Burges et al., 2018; Epelde et al., 2009b; Kumpiene et al., 2009; Touceda-González et al., 2017a, 2017b). Indeed, the demonstration of the recovery soil functionality and soil health at contaminated sites might be a key factor to increase the acceptance of phytostabilisation as a remediation option (Epelde et al., 2009b; Kumpiene et al., 2009; Vangronsveld et al., 2009). For which, the sensitivity, rapid response, and integrative character of biological indicators of soil health (e.g. respiration, microbial biomass, soil enzymes) are valuable tools for evaluating the short- and long-term assessment of the effectiveness of phytostabilisation processes (Burges et al., 2018; Epelde et al., 2014, 2009b; Gómez-Sagasti et al., 2012). Following an extensive review of in-situ immobilisation (including aided phytostabilisation), Kumpiene et al. (2019) conclude that most of the field studies implementing these techniques show a certain degree of improvement in the soil and/or vegetation status following soil amendment. As soil toxicity decreases, plants and microorganisms will colonize the treated soil, which will induce dissolution/precipitation reactions and drive the geochemical soil conditions away from equilibrium, but the net effects of such processes on trace elements circulation can only be evaluated by monitoring the sites over extended time periods (Kumpiene et al., 2019).

2.3.3 Soil amendments

The use of soil amendments such as liming agents, phosphates, apatites, various metal oxyhydroxides, industrial waste products and organic amendments has been widely shown to be an effective way to reduce both the bioavailability of metals in soil and uptake by plants (referred to as ***in-situ* (chemical) immobilisation** if amendments are used independently without plants) (Dickinson et al., 2009; GREENLAND, 2014b; Kidd et al., 2015; Kumpiene et al., 2019, 2008; Mench et al., 2010; Vangronsveld et al., 2009). In the case of **aided phytostabilisation**, single or combined amendments are first incorporated into the soil to decrease the labile contaminant pool and phytotoxicity by inducing various sorption and/or precipitation processes prior to establishment of contaminant tolerant or excluder plants (Epelde et al., 2009b; Mench et al., 2010; Vangronsveld et al., 2009). Broadly speaking, in the case of inorganics in particular, whether to mobilise or immobilise contaminants by manipulating their bioavailability in soil is a key factor to consider when deciding upon a GRO strategy based on extraction or stabilisation, respectively (Bolan et al., 2014), and various soil amendments can be used to achieve different aims (Figure 2-8).

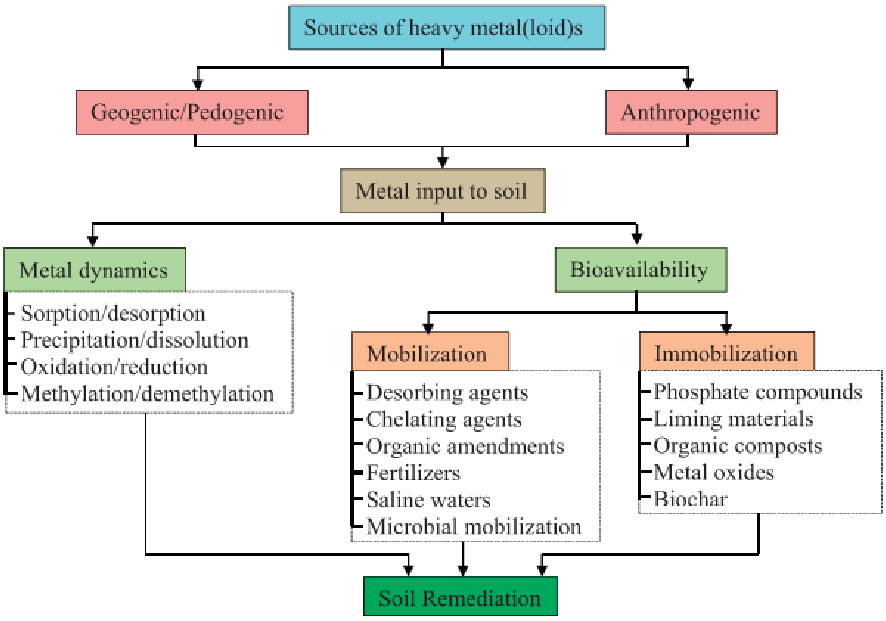

Figure 2-8. Soil amendments for remediation of metal(loid)s, from (Bolan et al., 2014).

The utilisation of organic and inorganic amendments could also enable the recycling of wastes, residues and diverse by-products to promote a circular economy (Chowdhury et al., 2020; G. Lacalle et al., 2020; Gómez-Sagasti et al., 2018; Míguez et al., 2020). Organic amendments in particular (e.g. compost, biochar, domestic wastes, sewage sludge or biosolids, animal manures and slurries) are especially useful for improving soil quality to enable the establishment of vegetation in poor soils by e.g. improving soil physical properties like bulk density and pore structure, improving water infiltration and holding capacity, improving soil fertility by adding essential micro- and macronutrients, balancing soil pH, re-establishing microbial communities and increasing soil organic matter (Burges et al., 2018; Epelde et al., 2009b; GREENLAND, 2014b; Kidd et al., 2015; Vangronsveld et al., 2009). For example, Zanuzzi et al. (2009) demonstrated that combining organic matter amendments with calcium-carbonate rich materials can stimulate soil formation at acidic mine tailing deposits by building soil organic matter and accelerating the establishment of a functional ecosystem. However, organic amendments must be used with caution due to their potential effects on metal(loid) bioavailability which depend on the nature of the organic matter (e.g. dissolved organic matter from non-stabilised organic amendments or 'green waste compost' may increase metal mobility), possible addition of contaminants if the source material is contaminated (e.g. sewage sludge or municipal biosolids), possible immobilisation of essential nutrients (e.g. due to the high sorption capacity of biochar), or if plant roots do not extend past the fertile amended soil into the underlying contaminated soil (Burges et al., 2018; Kidd et al., 2015; Vangronsveld et al., 2009). According to Vangronsveld et al. (2009), a thorough evaluation of the overall effects of ameliorants on the developing ecosystem and the sustainability (durability) of trace element immobilisation in contaminated soils is crucial for the acceptance of immobilisation/stabilisation strategies, for which evaluation should combine physico-chemical and biological methods. Soil amendments commonly used for *in-situ* immobilisation and aided phytostabilisation of trace elements can be broadly broken down into inorganic and organic amendments (GREENLAND, 2014b) (see (Bolan et al., 2014; Gómez-Sagasti et al., 2018; Kumpiene et al., 2019, 2008; US EPA, 2007; Vangronsveld et al., 2009; Wang et al., 2019) for thorough reviews of their mechanisms and applications and **Appendix III** for a compilation of the relevant properties for the main categories of organic amendments):

1. **Inorganic –** rock phosphate (a major source of P fertilisers), Thomas basic slag (a by-product of the iron industries), wood ashes, cyclonic ashes, zerovalent iron grit, Linz-Donawitz slag, siderite, gravel sludge, red mud, drinking water residues
2. **Organic –** animal manures and slurries, biosolids (sewage sludge), composted biosolids, green waste composts, biochar

2.3.4 Vegetation cover

One of the main features of GRO strategies including plants is improving the quality of the soil to enable the revegetation of contaminated, derelict brownfield sites (Dickinson et al., 2009). A **vegetation cover**, including resultant root growth and exudates, stimulated soil biota and provision of litter through leaf fall, may also produce beneficial changes in soil parameters that improve soil aggregation and binding of contaminants (Dickinson et al., 2009). From a risk assessment perspective, GRO are useful as 'primary prevention strategies' in various applications to reduce or eliminate human exposure to contaminants (Henry et al., 2013). This can be accomplished by GRO managing exposure to both humans and environmental risk objects (i.e. soil ecosystem, groundwater and surface water) by controlling the source of the contamination, managing the exposure pathways and protecting the receptors (Cundy et al., 2016; GREENLAND, 2014a). Establishing a vegetation cover can be a suitable primary prevention strategy at sites where phytoextraction is not possible due to constraints imposed by phytotoxicity, timescale and/or if it poses risks to grazing livestock or if there is not alternative treatment easily available (Mench et al., 2010). Also, in many cases, contaminated topsoil is left barren or with sparse vegetation thus prone to spreading contaminants off-site by wind erosion as dust emission, water erosion via stormwater runoff into local surface water or by leaching into groundwater (Burges et al., 2018; Cundy et al., 2016; Gerhardt et al., 2017; Mench et al., 2010; OVAM, 2019; Vangronsveld et al., 2009). Barren or sparsely vegetated brownfields can pose significant human health risks due to inhalation of dust-borne contaminants, which can be the most significant risk to human health at some sites (Dickinson et al., 2009; Gil-Loaiza et al., 2018; Mendez and Maier, 2008). In terms of risk management, vegetation cover can provide 1) **erosion control** by physically stabilising the soil with fibrous root networks, increasing soil porosity and extensive canopy cover to reduce runoff and prevent horizontal and lateral migration (GREENLAND, 2014a; ITRC, 2009; Kennen and Kirkwood, 2015; Mench et al., 2010; OVAM, 2019; Vangronsveld et al., 2009).; 2) **hydraulic control** by both influencing the flow of groundwater and reducing the flux of contaminants (i.e. spreading or leaching) to groundwater via plants acting as 'bio-pumps', especially those with high rates of evapotranspiration (Barac et al., 2009; Ferro et al., 2013; GREENLAND, 2014a; ITRC, 2009; Kennen and Kirkwood, 2015; Mench et al., 2010; OVAM, 2019; Pivetz, 2001; B. H. Robinson et al., 2003; Vangronsveld et al., 2009)); 3) **dust control** by greatly reducing the emission of fine particulates mobilised by wind, including PM1, PM2.5 and PM4 (i.e. particulate matter of 1, 2.5 and 4 μm diameter respectively) which represent the greatest health risks and potential for long-distance transport, and total dust flux from metal(loid) contaminated sites by at least 60% or that comparable to undisturbed grasslands (Cundy et al., 2016; Gil-Loaiza et al., 2018; GREENLAND, 2014a; Henry et al., 2013; Mendez and Maier, 2008). Especially in urban areas, vegetation can further improve air quality by capturing airborne contaminants (e.g. PCBs) as they adhere to the waxy cuticle of plant leaves and bark (Henry et al., 2013). 4) Vegetation can also function as a natural barrier between humans and the contaminated soil to '**manage receptor access**' and mitigate exposure by soil ingestion or dermal contact (Bert et al., 2012; Cundy et al., 2016; GREENLAND, 2014a; Kidd et al., 2015). The positive effects can also be compounded through the use of effective agronomic techniques (Kidd et al., 2015).

2.4 Rhizofiltration

Rhizofiltration does not fit neatly into the previous categorisation as it can be applied for a wide variety of contaminants, both organic and inorganic, but in highly specific conditions. This GRO mechanism can protect water resources through removal of contaminants from aqueous sources (i.e. surface water, wastewater or extracted groundwater) by accumulation into or adsorption onto plant roots as well as degradation by associated microorganisms (GREENLAND, 2014a; Kennen and Kirkwood, 2015; McCutcheon and Schnoor, 2003; OVAM, 2019; Pivetz, 2001). Most often, the term rhizofiltration is used to describe application of vegetation to filter contaminants from surface water as e.g. constructed wetlands, wastewater irrigation or stormwater filters (Kennen and Kirkwood, 2015; McCutcheon and Schnoor, 2003; OVAM, 2019; Pivetz, 2001). Stormwater filters can also be referred to as bioswales, vegetated swales, vegetated filter strips, rain gardens and detention basins, all of which are solutions tailored to the particular contaminant(s), stormwater flow volume and velocity, climate and space available for the installation (Kennen and Kirkwood, 2015). The terminology may differ, but rhizofiltration is essentially the key mechanism underlying much of 'Low Impact Development' (LID) and 'Sustainable Urban Drainage Systems' (SUDS), which have become key features or 'Best Management Practices' (BMP) for sustainable urban stormwater management and green infrastructure (Cundy et al., 2016; Kennen and Kirkwood, 2015; Menger et al., 2013). GRO may be particularly valuable in combination with urban flood management strategies by intercepting and delaying stormwater runoff, surface and groundwater flow management, reducing contaminant transfer to water bodies, soil erosion prevention, and by increasing permeable surface area for greater infiltration (Cundy et al., 2016; Kennen and Kirkwood, 2015; Menger et al., 2013).

The time required for risk mitigation by rhizofiltration is dependent upon vegetation establishment, though it varies in application, and has been demonstrated to reduce contaminant concentrations in water outflow within 1-2 years as part of an 'integrated phytomanagement system' (ANL, 2008; Cundy et al., 2020). It has also been used in Sweden as willow short-rotation coppice to provide ongoing treatment for various wastewaters such as nutrients from urban wastewater, landfill leachate, log-yard runoff and to stabilise sewage sludge and wood-ash (Dimitriou and Aronsson, 2005). Many applications show that rhizofiltration systems can also provide effective, continuous wastewater treatment (Kennen and Kirkwood, 2015; Marchand et al., 2010; Pivetz, 2001).

Either aquatic (e.g. macrophytes) or terrestrial plants can be used for rhizofiltration; for example, *Phragmites australis* (common reed) and *Typha* spp. (reed, cattail) are basic species for use in constructed wetlands that are highly tolerant to a range of contaminants including high salinity (Gawronski et al., 2011; McCutcheon and Schnoor, 2003; Pivetz, 2001). More extensive lists of viable plants are available in (Kennen and Kirkwood, 2015; OVAM, 2019), and the Sustainable Technologies Evaluation Program has an extensive guide for the design of vegetation for managing stormwater including lists of suitable plants (Plant lists - LID SWM Planning and Design Guide (sustainabletechnologies.ca)). Only 3 projects utilising rhizofiltration are listed in the CLU-IN Phytotechnology database.

2.5 Phytohydraulics and hydraulic control

In contrast to rhizofiltration, **phytohydraulics** is a term that has more recently come into use (only 1 result for "phytohydraulic" on Scopus database (Hong et al., 2001) and 38 projects utilising "hydraulic control" were listed in the CLU-IN phytotechnology project database) to describe the management of contaminants present in groundwater (OVAM, 2019). It is based on the capacity of plants to root into groundwater aquifers and transpire sufficient amounts of water to influence the flow of groundwater and flux of contaminants into groundwater bodies (i.e. **hydraulic control**) (OVAM, 2019). Typical application would entail planting trees as a barrier to contain a contaminated groundwater plume and limit the spread of contamination, or functioning as a groundwater 'bio-pump' treatment system (OVAM, 2019). The specific term 'phytohydraulics' may not be common jargon, however there are numerous examples of trees being used for hydraulic control of contaminated groundwater plumes (e.g. (Barac et al., 2009; El-Gendy et al., 2009; Ferro et al., 2013; Hong et al., 2001; Pivetz, 2001)). The most suitable plant species for phytohydraulics are **phreatophytes**, which are deep-rooting to reach groundwater (up to 10 meters), transpire large amounts of water, prefer wet soils and can tolerate water saturated conditions (Kennen and Kirkwood, 2015; OVAM, 2019). The most prominent examples are tree species like willow (*Salix* spp.) poplar (*Populus* spp.), but also include other deep-rooted trees such as alder (*Alnus* spp.), ash (*Fraxinus* spp.) and oak (*Quercus* spp.) and tap-rooted, herbaceous species like alfalfa (*Medicago sativa*) or many grass species accustomed to surviving drought or water-scarce conditions as in deserts or prairies (Kennen and Kirkwood, 2015; McCutcheon and Schnoor, 2003; OVAM, 2019).

Inherent limitations in using plants can limit the degree of hydraulic control gained; including the depth of rooting that may not reach deeper groundwater tables or is influenced by seasonal fluctuations, winter dormancy of the plants reducing transpiration, contaminants present in soil possibly inhibiting root growth and impenetrable layers of e.g. clay or bedrock preventing roots from reaching the groundwater (Kennen and Kirkwood, 2015; OVAM, 2019). To account for the main limitation, rooting depth, the phytohydraulics system can be combined with engineered solutions to improve its effectiveness, for example, by planting trees deeper in drilled boreholes or trenches to allow roots to penetrate to greater depths (Figure 2-9).

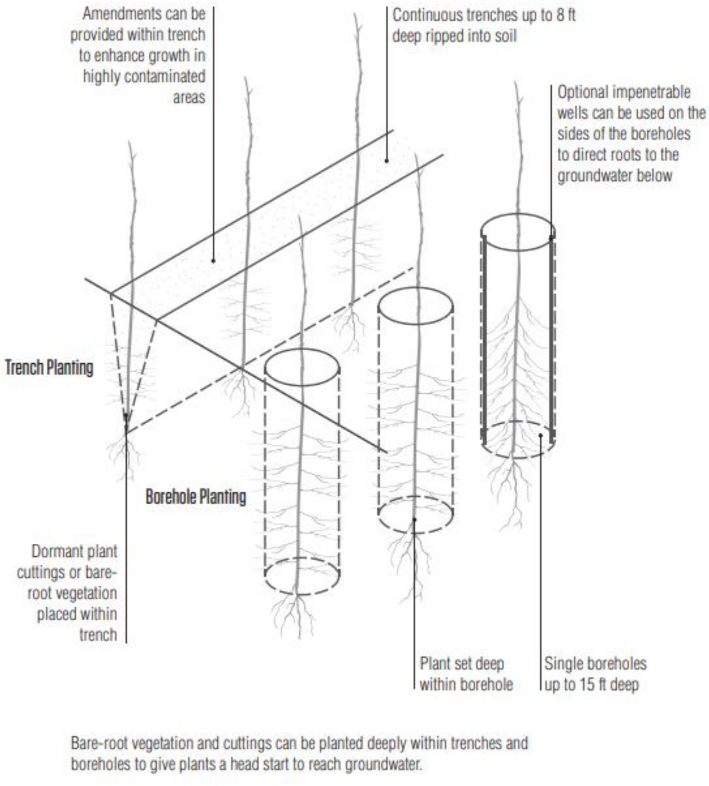

Figure 2-9. Deep-root planting techniques, from (Kennen and Kirkwood, 2015).

This type of technique allowing for deeper rooting is standard practice for many commercial phytotechnology applications (Kennen and Kirkwood, 2015; OVAM, 2019). For example, a commercial product that has seen much success is the so-called TreeWell® system[5]. Shown below in Figure 2-10, the TreeWell system is an engineered phytoremediation system that facilitates hydraulic connection between plant roots and the target groundwater through deeper rooting (potentially up to 15 meters) by planting in a drilled borehole lined with an impenetrable barrier to encourage roots to grow downwards. Groundwater is drawn into the system at greater rates thereby enabling plume capture and hydraulic control. Soil amendments or microbial inoculants can also be added into the borehole to improve growing conditions, reduce phytotoxicity and potentially improve contaminant degradation or capture into highly absorbent amendments like biochar. These systems are estimated to cost between $2500-6000 (CAD) per unit, with 50-70 units per acre at most sites, capable of pumping 1-1.5 million gallons (4-6 million litres) per year which is sufficient to replace many existing, inefficient pump and treat systems.

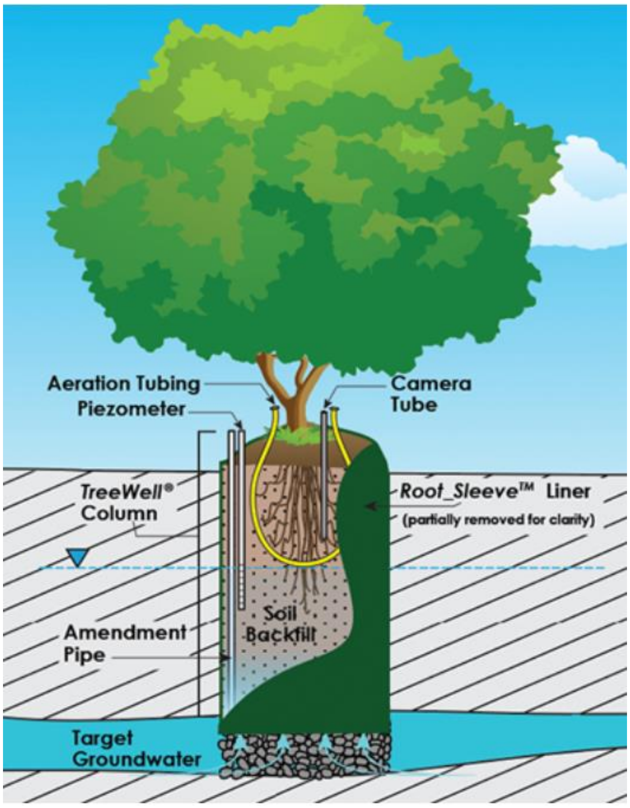

Figure 2-10. TreeWell phytoremediation system design, from TreeWell (geosyntec.com).

The groundwater velocity also impacts the effectiveness groundwater plume containment. OVAM (2019) provides a rule of thumb for designing phytohydraulic systems: "the distance that the contaminant must cover under the planting must be at least twice the distance covered by the most mobile component of the contamination of the most mobile degradation parameters per year." Meaning that to account for fast-flowing groundwater (and winter dormancy), the planting system should consist of multiple rows and be wide to enough to capture the groundwater plume in the direction of flow and be capable of taking up and transpiring groundwater proportional to the flow rate (OVAM, 2019). In other words, for guaranteed effective hydraulic control via groundwater uptake, a tree stand must take up 3x the Darcy flux through the capture zone (Ferro et al., 2013). Trees with high evapotranspiration rates are therefore advantageous for such applications, examples of which are shown below in Figure

[5] TreeWell® Technology | Applied Natural Sciences, Inc. (treemediation.com)
TreeWell (geosyntec.com)

2-11, as well as evergreen conifers that will not be as affected during winter months and a tree stand of mixed species is encouraged.

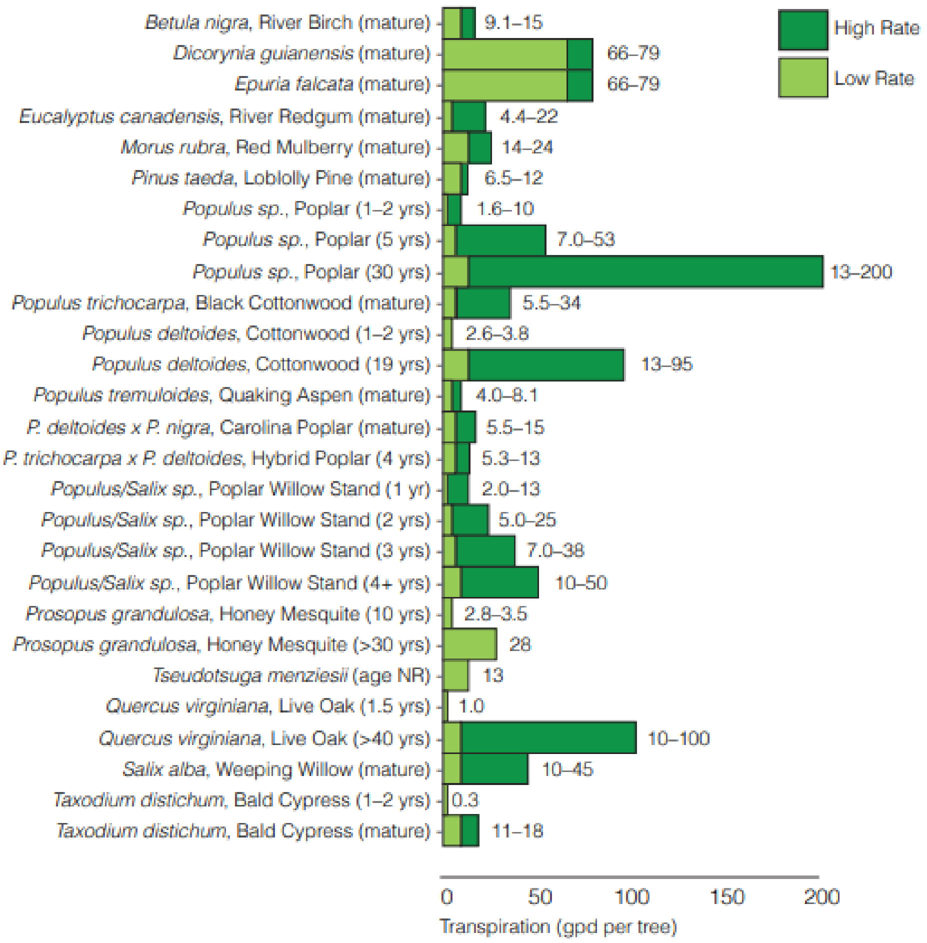

Figure 2-11. Example plant species with high evapotranspiration rates, from (Kennen and Kirkwood, 2015).

2.6 Bioremediation

Bioremediation is a broad umbrella term, which has 56,768 hits on the Scopus database as of February 29, 2021, that refers to the use of bacteria and/or fungi (discussed under mycoremediation) to remediate contaminated sites, primarily regarding organic contaminants such as mineral oils, petroleum hydrocarbons, PAHs, PCBs, pesticides, chlorinated solvents, etc. Natural decontamination processes or bioremediation could also be regarded as an essential 'regulating ecosystem service' performed by microorganisms, earthworms and other soil organisms functioning in healthy soils (FAO et al., 2020; Orgiazzi et al., 2016; Turbé et al., 2010). The naturally occurring processes of dissolution, volatilisation, sorption and biodegradation at sites polluted with light non-aqueous phase liquids (LNAPL) and petroleum hydrocarbons have been well-demonstrated and are even considered to be viable remediation techniques, referred to as monitored natural attenuation (MNA) or natural source zone depletion (NSZD) (Garg et al., 2017; US EPA, 2006; Wilson, 2011).

In general, there are three main approaches for the bioremediation of contaminated sites (FAO et al., 2020; Fingerman and Nagabhushanam, 2019; G. Lacalle et al., 2020; Haritash and Kaushik, 2009; Kuppusamy et al., 2016; Megharaj et al., 2011; Megharaj and Naidu, 2017; US EPA, 2006):

1. **(Monitored) natural attenuation –** natural decontamination processes are carried out by the native microbial populations present at the site, which is left undisturbed and monitored over time.
2. **Bioaugmentation** – selected microbial strains that possess greater capacity to degrade the target contaminants at a faster rate are inoculated into the soil or groundwater. Well-designed bioaugmentation selects for previously isolated (from the same soil or similarly contaminated soils) and cultivated microbial strains that have been proven effective to degrade certain contaminants. Microbes are then inoculated specifically or in combination with other strains ("microbial cocktail") as a consortium that could combine different metabolic activities and potentially enhance degradation.
3. **Biostimulation** – existing microbes present at site are stimulated by modifying the environment (e.g. moisture, pH, nutrients, oxygen) with various amendments to enhance biodegradation of target contaminants. Common applications include the addition of nutrients or slow-release fertilisers like organic amendments to stimulate the microbes and surfactants to increase the bioavailability of contaminants and improve degradation. Figure 2-12 shows a conceptual diagram of in-situ biostimulation via enhanced aerobic biodegradation.

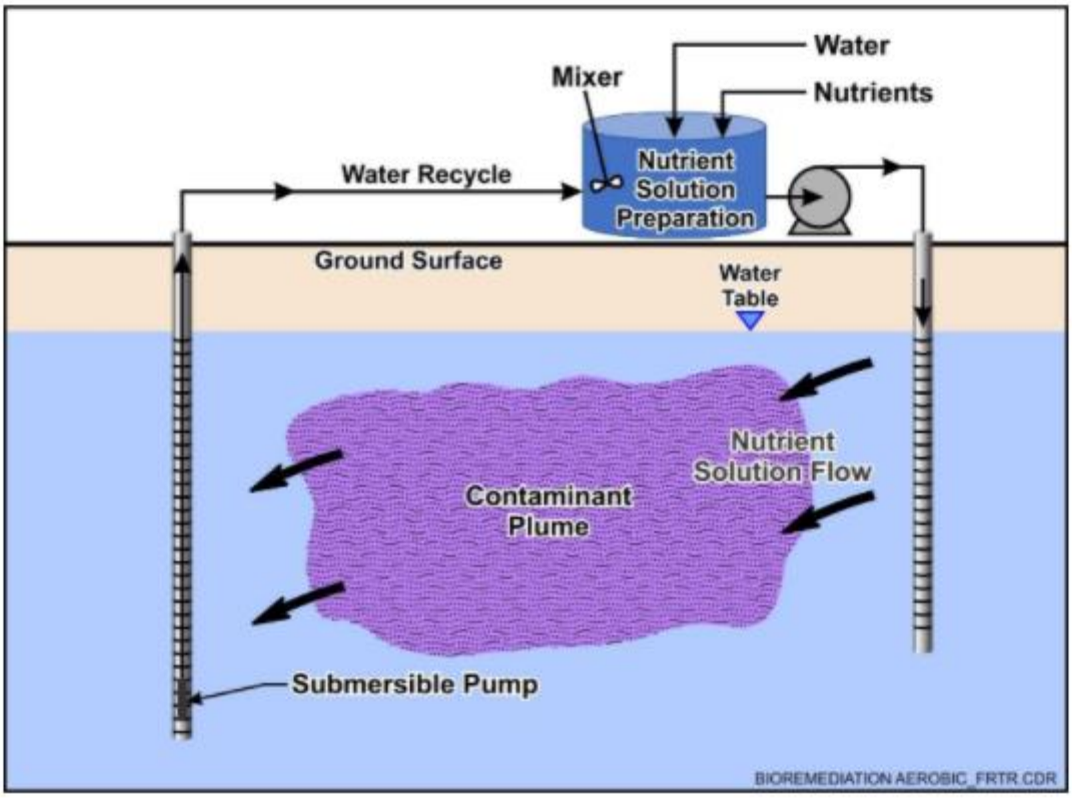

Figure 2-12. Conceptual diagram of enhanced aerobic biodegradation in groundwater, from Federal Remediation Technologies Roundtable (frtr.gov).

The major factors impacting the effectiveness of contaminant degradation are: i) the environment – physico-chemical characteristics of the soil, temperature, pH, moisture content, nutrient availability, toxicity; ii) the microbial communities – development or stimulation of degrading microbial populations in the soil, horizontal gene transfer, microbial diversity, production of toxic metabolites, metabolic activity; and iii) the contaminants - their chemical nature, bioavailability, readiness for degradation, toxicity; iv) growth substrates –

bioavailability and concentrations of contaminants and substrates, limiting factors like nutrients and preferential degradation of other food substrates than the contaminants; v) aerobic or anaerobic processes – electron acceptor/donor availability and reduction/oxidation potential. Bioaugmentation and biostimulation can be applied either in-situ (e.g. bioventing) or ex-situ (e.g. land farming, bioreactor, composting) though in-situ is more attractive and cost-effective since it is less disruptive to soils. Bioremediation techniques have been used in a variety of applications and have often achieved significant contaminant reduction, see e.g. (Cristaldi et al., 2017; Fingerman and Nagabhushanam, 2019; G. Lacalle et al., 2020; Haritash and Kaushik, 2009; Kuppusamy et al., 2016; Megharaj et al., 2011; Megharaj and Naidu, 2017; US EPA, 2006) for more thorough reviews and information.

2.7 Mycoremediation

In terms of using fungi directly for remediation (i.e. not necessarily in combination with plants), the term **mycoremediation** has sometimes been used (Stamets, 2005), though it is not yet widespread, with only 259 hits on the Scopus database as of February 29, 2021. It is more commonly included within the much broader umbrella term of bioremediation, of which 5,339 hits on Scopus for "bioremediation" including "fungi" or "mushroom". Fungi have proven to be useful for effectively remediating a wide variety of contaminants by biodegradation, biosorption and bioconversion; including heavy metals, persistent organic pollutants, textile dyes, chlorinated solvents, PAHs and other petroleum products, pharmaceuticals, pesticides, herbicides and insecticides (see e.g. (Akhtar and Mannan, 2020; Deshmukh et al., 2016; Kulshreshtha et al., 2014) for reviews).

Regarding organic contaminants, certain saprotrophic fungi have the property of PAH degradation, including *Phanerochaetec hrysosporium*, *Bjerkandera adusta*, and *Pleurotus ostreatus* (oyster mushroom) as some common PAH-degrading fungi (Haritash and Kaushik, 2009). Highly active mycorrhiza (*Pisolithus tinctorius*, *Paxillus involutus)* and white-rot fungi (*Trametes versicolor*, *Pleurotus ostreatus*) have also been used enhance remediation of a TNT contaminated site (Koehler et al., 2002). Spent mushroom waste from oyster mushroom (*Pleurotus ostreatus*) and other brown- and white-rot fungi have also been demonstrated to degrade DDT compounds (Purnomo et al., 2011, 2010). Oyster mushroom has also been shown to effectively degrade PCBs in field test with up to 50% degradation in 12 weeks of treatment (Stella et al., 2017). Table 2-6 presents a brief compilation of fungal species that can be useful for degradation of certain organic contaminants (Stamets, 2005).

Table 2-6. Species of fungi capable of remediating organic contaminants, adapted from (Stamets, 2005).

	Anthracenes	Benzopyrenes	Chlorine	Dimethyl methyl phosphonate (VX, Soman, Sarin)	Dioxin	Persistent Organophosphates	PAHs	PCBs	Pentachlorophenols (PENTAs)	TNT	Brown (B) or White (W) Rot
Antrodia radiculosa									X		B
Armillaria ostoyae				X							W
***Bjerkandera adjusta* (smoky polypore/bracket)**		X					X				W
Gloephyllum trabeum					X						B
***Grifola frondosa* (hen-of-the-woods)**								X			W
Irpex lacteus							X				W
***Lentinula edodes* (shiitake)**							X	X	X		W
***Meruliporia incrassata* ("house-eating fungus")**									X		B
***Mycena alcalina* (stump fairy helmet)**			X								?
Naematoloma frowardii (=Hypholoma)							X			X	W
Phanerochaete chrysosporium		X					X		X	X	W
***Pleurotus eryngii* (king trumpet/oyster mushroom)**					X						W
***Pleurotus ostreatus* (oyster mushroom)**		X		X	X		X	X		X	W
***Pleurotus pulmonarius* (Indian/Italian/lung oyster)**					X					X	W
***Psilocybe* spp.**				X		X					W
Serpula lacrymans							X				B
***Trametes hirsuta* (hairy bracket)**									X		W
***Trametes versicolor* (turkey tail)**	X			X	X	X			X	X	W

Some species of fungi also have the capacity for biosorption, functioning essentially as phytoextraction, to accumulate metals in their biomass that can then be removed by harvesting the fruiting mushroom bodies (Akhtar and Mannan, 2020; Deshmukh et al., 2016; Kulshreshtha et al., 2014). Varieties of fungi, such as *Pleurotus* spp., *Aspergillus* spp., and *Trichoderma* spp., have been proven to be effective for the removal of lead, cadmium, nickel, chromium, mercury, arsenic, copper, boron, iron and zinc (Akhtar and Mannan, 2020; Deshmukh et al., 2016; Kulshreshtha et al., 2014).

2.8 Vermiremediation

As of February 29, 2021, the term "**vermiremediation"** results in 65 hits on the Scopus database (482 hits for "bioremediation" AND "earthworm") and has been used more frequently in recent years (about half of the papers are published since 2019) since its first use in 2002. As a remediation technique, vermiremediation refers to the use of earthworms for the removal of contaminants from soil, see Figure 2-13. Soil fauna ('ecosystem engineers') can function as dispersal agents for both microorganisms that degrade organic contaminants and the contaminants themselves through the soil profile (FAO et al., 2020). Soil invertebrates such as earthworms have also been shown to improve decontamination of organic (e.g. pesticides) and inorganic contaminants (metals) by plants and microorganisms (FAO et al., 2020; G. Lacalle et al., 2020; Orgiazzi et al., 2016; Rodriguez-Campos et al., 2014; Turbé et al., 2010). In general, as earthworms burrow through soil they mix and alter the physico-chemical and biological properties of the soil by i) increasing availability of nutrients like C and N; ii) ingesting and mixing the soil with organic material; iii) affecting soil structure, pore space and aeration through burrowing; and iv) changing the soil bacterial and fungal communities by modifying the structure and size of soil aggregates. All of which can result in increased soil enzyme production and microbial activity and greater interaction with contaminants by increasing bioavailability thus resulting in enhanced biodegradation. The 'vermicasts' left behind as earthworms excrete soils are carbon- and microbe-rich and, besides improving soil quality, can also bind contaminants to stabilise them in the soil matrix (G. Lacalle et al., 2020; Rodriguez-Campos et al., 2014; Sinha et al., 2008; Zeb et al., 2020).

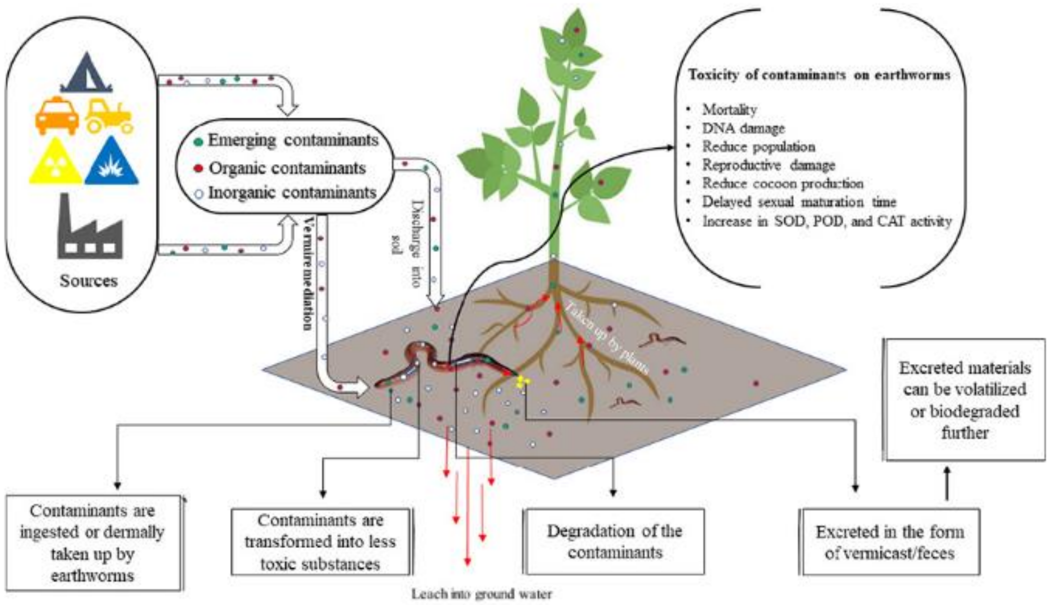

Figure 2-13. Processes involved in vermiremediation, from (Zeb et al., 2020).

Removal can occur for both inorganic and organic contaminants, but earthworms are more commonly studied for their potential to remove organic contaminants, such as herbicides, DDT, PCBs, PAHs and other petroleum hydrocarbons, particularly for large areas like agricultural fields with historic pesticide contamination (G. Lacalle et al., 2020; Rodriguez-Campos et al., 2014; Sinha et al., 2008; Zeb et al., 2020). For example, vermiremediation as a standalone GRO or in combination with other GRO has been shown to be effective for remediating mixed chromium (VI) and lindane contamination as well as improving soil quality (Aparicio et al., 2021; Lacalle et al., 2020). Sinha et al. (2008) provide another illustrative example where earthworms (adding up to 200 worms/kg soil) were used to effectively reduce PAH concentrations by up to 50-100% in as soon as 11 weeks. The authors further elaborate on the substantial improvement to soil quality which can transform "wasteland into wonderland." See e.g. (Rodriguez-Campos et al., 2014; Zeb et al., 2020) for more thorough reviews and studies demonstrating vermiremediation for a variety of contaminants.

There are three different types of earthworms classified according to their behaviour and location in the soil matrix (G. Lacalle et al., 2020; Rodriguez-Campos et al., 2014):

1. **Epigeic –** live at or near the soil surface where they feed on leaf litter, decaying roots and dung. These type of earthworms (e.g. *Eisenia fetida, E. andrei, Lumbricus rubellus*) are therefore useful to remediate surface topsoil layers and can even be inoculated into biopiles or windrows for bioremediation where deep burrowing may not be necessary. *E. festida* is also a valuable bioindicator species and is used in ecotoxicity bioassays (e.g. ISO 11268-1 & -2).
2. **Endogeic –** live in deeper mineral soil below the soil surface where they horizontally burrow through and feed on soils. These species (e.g. *Aporrectodea caliginosa, Allolobophora chlorotica*), can, therefore, be useful to remediate deeper surface layers.
3. **Anecic –** live in permanent, deep vertical burrows to feed on both surface litter and soil. These species (e.g. *Lumbricus terrestris, Aporrectodea longa*) are well-suited for the remediation of a broader soil profile both shallow and deep where burrowing is required.

The ecology of earthworms is a key consideration for evaluating their use to remediate soils. Earthworms have been shown to tolerate moderate to high concentrations of contaminants through efficient detoxification mechanisms. However, to guarantee their survival, it may be necessary to ameliorate the soil with soil amendments to reduce the toxicity posed by contaminants, which may inhibit them, and improve soil quality to aid improve the soil environment. In addition, the potential ecotoxicological risk posed by contaminants bioaccumulating in earthworms and transferring into the food chain must be taken into consideration. Besides their use for remediation purposes, earthworms are also valuable ecosystem engineers (i.e. due to modifying soil structure and pore space for water infiltration, etc.) and play a crucial role in ecosystem functioning (G. Lacalle et al., 2020; Rodriguez-Campos et al., 2014; Sinha et al., 2008; Zeb et al., 2020).

3 Phytomanagement

A promising new direction in the application of GRO is the development of **phytomanagement**; commonly defined as "*the long-term combination of profitable crop production with gentle remediation options (GRO) leading gradually to the reduction of pollutant linkages due to metal(loid) excess and restoration of ecosystem services*" (Cundy et al., 2016; GREENLAND, 2014a, 2014b; Brett H Robinson et al., 2009). Phytomanagement has even been enshrined in the new Soil Decree in the Wallonia region as "*a project to grow plant species on a site with characteristics such as that it is, as it stands, not usable for food or residential use, or showing signs of abandonment or alteration of the soil*" (Champoeva, 2019; Evlard, 2019). This definition and new legislative framework allows for greater possibilities of growing useful biomass on a contaminated site and contribute to the overall aims of the Soil Decree to "*preserve and improve quality, prevent soil depletion and soil pollution, identify potential sources of pollution, organise pollution investigations and determine how to clean up polluted soils*" (Champoeva, 2019; Evlard, 2019).

An initial search in the Scopus database carried out on February 4, 2020 for "phytomanagement" showed 171 hits with 15 deemed relevant after screening titles and abstracts and limiting to studies including "ecosystem services" or "soil quality" or "soil health" or "soil fertility". Searching again on March 18, 2021, showed many additional studies, 39 in 2020 alone, implying that this term is growing in usage. The remainder of this section will discuss the key concepts in phytomanagement.

Regarding the general applicability of standard phytoremediation practices at metal-contaminated sites, Burges et al. (2018) conclude in their review:

> "In the last two decades, extensive work has been conducted on the search for phytotechnologies for the remediation and management of metal contaminated sites (i.e., phytoextraction, phytostabilisation). As an outcome of this review, we conclude that there are still serious limitations for these phytotechnologies to become efficient and cost-effective on a field and commercial scale. Although, in the early days of phytoremediation, there was a perception that these phytotechnologies could return contaminated sites to productive use, their limitations have caused a shift of paradigm toward the search for the many values (e.g., economic, environmental and societal benefits) that can be obtained from the large-scale application of phytomanagement. This shift in practice from phytoremediation to phytomanagement carries with it an improved cost-benefit ratio, opening the door for reclaiming previously neglected contaminated sites of low development value."

In its broadest sense, phytomanagement encompasses a range of land management strategies to generate a sustainable and profitable site use by e.g. biomass production that maximises the wider benefits offered by GRO, see Figure 3-1, including such ecosystem services as nutrient cycling, carbon storage, water regulation and purification, erosion control, fertility maintenance, etc. (Burges et al., 2018; Cundy et al., 2016; G. Lacalle et al., 2020; Gerhardt et al., 2017; GREENLAND, 2014b, 2014a). This can either be a short-term, temporary solution (e.g. as a 'holding strategy' until a different site use is decided) or as long-term land management for a 'soft' end use as for green land uses and recreational greenspaces (Bardos et al., 2020a, 2016; Cundy et al., 2016). A requirement for successful phytomanagement, therefore, is that is should either cost less than other remediation alternatives or be a profitable operation (Conesa et al., 2012; Brett H. Robinson et al., 2009). According to Conesa et al. (2012), the critical success factor for these systems is that the remediation and economic goals are given equal weightings. Furthermore, phytomanagement should entail the best site-specific, cost-effective management option for managing risks at a site, and can be wholly based on GRO but it does not proscribe the use of other remediation technologies to achieve the best outcome, e.g. as part of a treatment chain (Brett H. Robinson et al., 2009). For example, stabilisation and immobilisation mechanisms to decrease mobility and bioavailability of contaminants with (i.e. 'aided') or without amendments is promising both as a stopgap remediation strategy to reduce risks and for enabling synergies to garner wider benefits at a contaminated site (Brett H. Robinson et al., 2009). In long-term operations at trace element contaminated sites, source removal by phytoextraction is relatively unimportant and secondary to the overall goal of producing valuable biomass while mitigating health and environmental risks through other mechanisms, and a 'reasonable timeframe' of <25 years can be useful to distinguish between practical phytoextraction and long-term phytomanagement (GREENLAND, 2014b; Brett H. Robinson et al., 2009). For example, a thorough review by Nsanganwimana et al. (2014b) shows the feasibility for phytomanagement using *Miscanthus* spp. to restore ecosystem services; which, owing to the perennial growth and its ability to stabilize trace elements and degrade some organic pollutants, could potentially limit pollutant transfer into different environmental compartments by reducing i) contaminant leaching from the root zone and groundwater contamination, ii) contaminant run-off (water erosion) and surface water contamination, iii) dust emission into the atmosphere due to wind erosion and seasonal soil tillage, and iv) pollutant transfer into plant above-ground parts and thus transfer into food chains. Cundy et al. (2020) also provide an illustrative example of an 'integrated phytomanagement strategy' that effectively combines the use of spray irrigation with a mixed tree stand for phytoremediation and constructed wetland to remove CCl_4 from groundwater thus mitigating risks while also providing a range of environmental and social benefits including carbon sequestration (ca. 77 tons/ha-yr), education and recreational benefits.

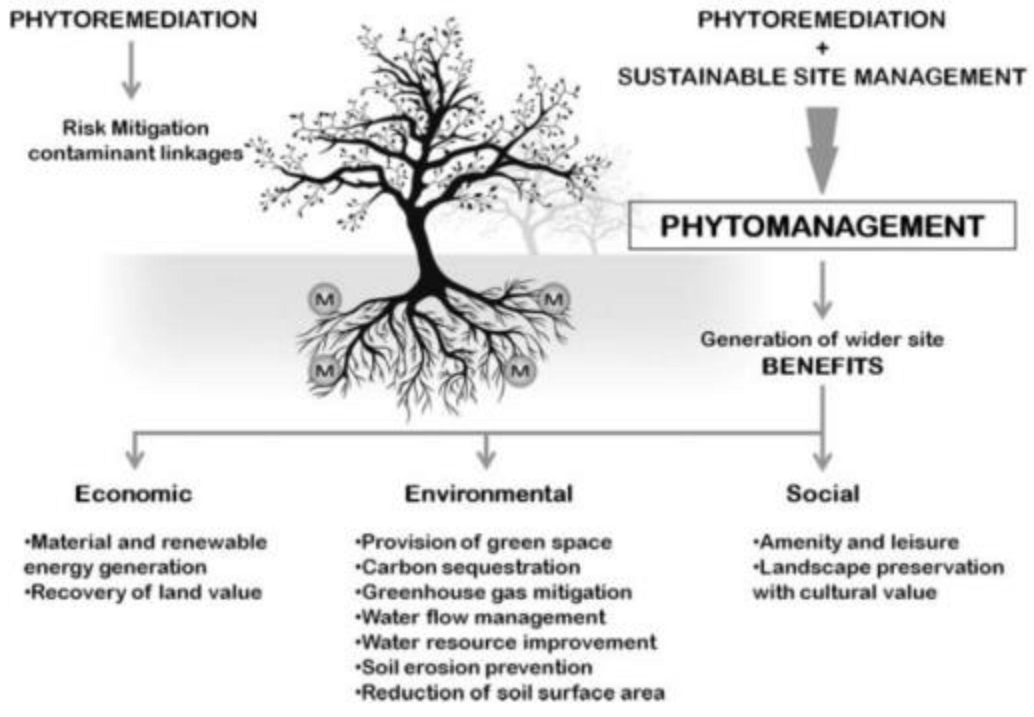

Figure 3-1. Schematic representation of the phytomanagement approach, from (Burges et al., 2018).

In terms of phytomanagement purposed for bio-based production for bioenergy, useful guides were created in the Rejuvenate project (Andersson-Sköld et al., 2014, 2013; Bardos et al., 2011), which developed a methodology for designing and implementing profitable biomass production on marginal land while effectively managing risks by stabilising the contaminants using plants. These and other 'crop-based' systems for risk-based land management (RBLM) have successfully demonstrated the benefits of vegetation-, energy crop-, or generally nature-based solutions for both managing risks and providing wider value at contaminated sites including the provisioning of ecosystem services (Andersson-Sköld et al., 2014, 2013; Bardos et al., 2020a, 2011; Cundy et al., 2016; Enell et al., 2016; Gomes, 2012; GREENLAND, 2014a). Stabilisation, rather than uptake of contaminants, is well-suited to this type of strategy where the future usage and economic return of the produced biomass can be dependent upon contaminant concentrations in the various plant tissue (Andersson-Sköld et al., 2014, 2013; Enell et al., 2016; Evangelou et al., 2012). Also, large land areas, preferably even >5 ha, are more advantageous than small, fragmented or high-value urban sites for economically feasible bio-energy crop production (Andersson-Sköld et al., 2014; Evangelou et al., 2012). Many studies have evaluated the significant possibilities of producing biomass on contaminated or marginal land to i) emphasise the economic and environmental benefits of producing crops for bioenergy (and for other uses like wood, biochar, biofortified products, etc.) and phytoremediation on contaminated land (e.g. (Evangelou et al., 2012; G. Lacalle et al., 2020; Gomes, 2012; Licht and Isebrands, 2005; Schröder et al., 2018)), ii) safely grow food crops in contaminated agricultural soils (e.g. (GREENLAND, 2014b; Greger and Landberg, 2015; Haller and Jonsson, 2020; Kidd et al., 2015; Tang et al., 2012)), and iii) leverage the value proposition for soft reuse of brownfields and contribute to a circular economy in soil and land management (e.g. (Bardos et al., 2016; Breure et al., 2018; Menger et al., 2013; Preuß and Ferber, 2005)). To better illustrate these possibilities, Schröder et al. (2018) developed a useful framework for how to mobilise marginal lands for biomass production, see Figure 3-2.

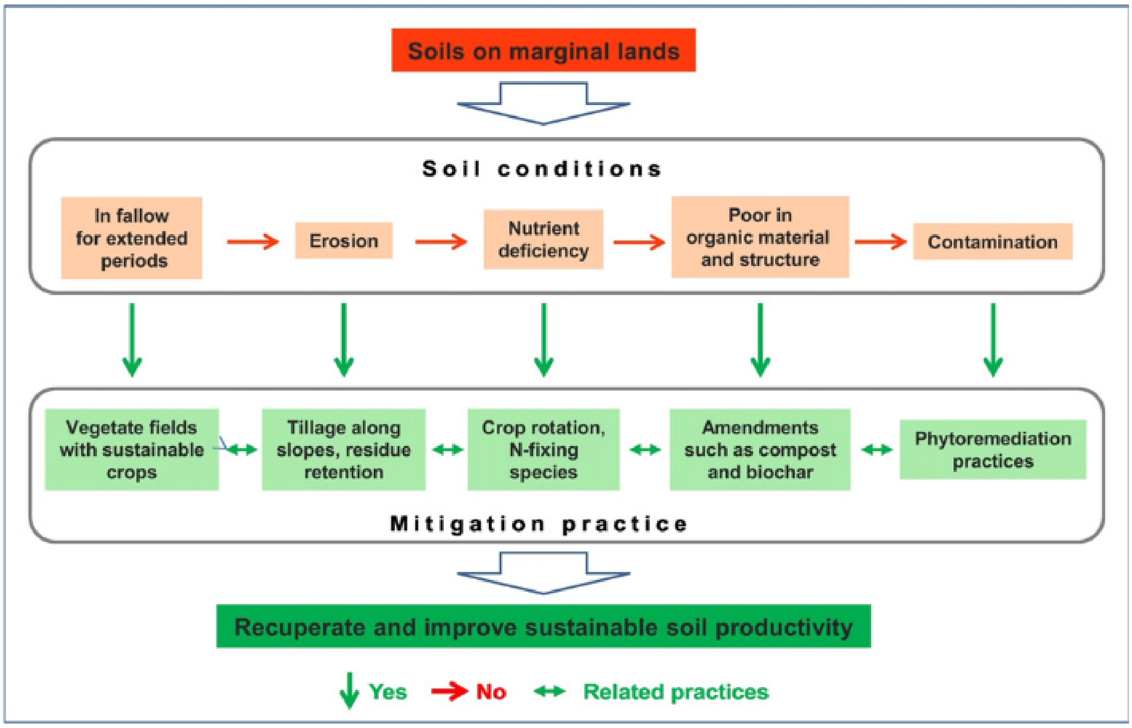

Figure 3-2. Decision tree for improving and optimising the productivity of soils on marginal lands, from (Schröder et al., 2018).

Best practices and guidance for phytomanagement can be found in the now finished Greenland project (GREENLAND (Gentle remediation of trace element contaminated land) (europa.eu)) and their "Best Practice Guidance for Practical Application of Gentle Remediation Options (GRO)" (GREENLAND, 2014a, 2014b), and associated papers pertaining to e.g. development of a decision-support tool (Cundy et al., 2015), broader discussion of GRO, its wider benefits and involvement of stakeholders in planning (Cundy et al., 2016, 2013), and more in-depth studies concerning viable analyses for measuring the performance of GRO (Kumpiene et al., 2014), agronomic techniques for improving their effectiveness (Kidd et al., 2015), and various studies analysing the results of field trials (Hattab et al., 2014; Mench et al., 2014; Quintela-sabarís et al., 2017; Touceda-González et al., 2017b).

More recently, the PhytoSUDOE project (finished as of 2020) – "Demonstration of the improvement in soil biodiversity, functionality and ecosystem services through phytomanagement in contaminated and degraded soils within the Interreg Sudoe area" (Phytosudoe) – and its continuation (as of 2021) Phy2SUDOE (phy2sudoe (phytosudoe.eu)) aim to further develop upon viable phytomanagement strategies to incorporate GRO for managing the risks associated with the presence of contaminants in degraded sites. Simultaneously, other benefits from vegetation are highlighted, including i) generation of useful bio-products from harvested biomass (e.g. wood, resin, essential oils, bioenergy, ecocatalysts), and ii) enhancing the supply of ecosystem services (e.g. C-sequestration, erosion control, creation of habitats) and improving soil functionality and biodiversity. Specific strategies tested in field trials include standard phytoremediation strategies enhanced with soil amendments and/or bacterial inoculates and mycorrhizal fungi. Different plant species and cropping patterns will also be tested, including:

- **Tree plantations** – Short rotation coppice (SRC) plantations: woody plants, such as poplars and willows, with known phytoextraction (cadmium, zinc), phytostabilisation (copper, lead) and rhizodegradation capacities will be cultivated. In general, species with rapid growth and tolerance to contaminants will be used.
- **Agricultural crops –** High-biomass annual or perennial herbaceous species (e.g. rapeseed, sunflower, tobacco, grasses, etc.) will be cultivated in rotation, intercropping or monoculture.
- **Intercropping –** To improve phytoremediation efficiency in some plots, woody plantations will be intercropped with agricultural crops (agroforestry systems) or intercropping will be established using woody plants and leguminous species or plants which form associations with nitrogen fixing microorganisms (e.g. *Salix*/*Populus* with alfalfa or *Alnus* spp.).

Such best practices can be viewed as 'windows of opportunity' for the successful application of phytomanagement. See (Garbisu et al., 2019; Mench et al., 2019; Moreira et al., 2019) for best practices and technical guidance delivered with the PhytoSUDOE project. Many papers have been published within the project, including studies pertaining to e.g. the use of plant growth promoting bacterial strains or degradative bacterial strains to improve phytoremediation effectiveness (Balseiro-Romero et al., 2017a, 2017b; Benidire et al., 2021), the value of organic amendments for use in phytomanagement (Gómez-Sagasti et al., 2018), the value of preserving and promoting biodiversity (e.g. metallophytes) present at contaminated sites (Garbisu et al., 2020), and evaluations of phytomanagement field and pilot studies for their remediation effectiveness and effects on microbial properties to restore soil health (Burges et al., 2021, 2020; Lacalle et al., 2018; Mench et al., 2018; Touceda-González et al., 2017b; Xue et al., 2020, 2018).

4 Plant selection

As has been stressed throughout this review, selecting the most suitable plants for each situation is crucial for GRO success. Many authors have compiled extensive lists of plant species that have been successfully demonstrated for the remediation of inorganic or organic contaminants, seeAppendix IV and (Gawronski et al., 2011; GREENLAND, 2014b; ITRC, 2009; Kennen and Kirkwood, 2015; Kidd et al., 2015; Mench et al., 2010; OVAM, 2019; Vangronsveld et al., 2009). In general, some of the important criteria in selecting plants (largely relevant for **phytoextraction**) include the following (Ali et al., 2013):

- High growth rate
- Production of more above-ground biomass
- Widely distributed and highly branched root system
- More accumulation of the target heavy metals from soil
- Translocation of the accumulated heavy metals from roots to shoots
- Tolerance of the toxic effects of the target heavy metals
- Good adaptation to prevailing environmental and climatic conditions
- Resistance to pathogens and pests
- Easy cultivation and harvest
- Repulsion to herbivores to avoid food chain contamination

Many of the above-listed criteria are still relevant for **phytostabilisation**, but the most important factors are related heavy metal tolerance; size, growth rate and rooting depth; low heavy metal accumulation in above-ground plant parts; and climatic adaptation and pest resistance (Ciadamidaro et al., 2019). Also, the capacity for accumulation of metals can vary significantly between clones of the same plant species (e.g. willow species) which can impact the selection of specific cultivars for use in extraction or stabilisation (Enell et al., 2016; Greger and Landberg, 1999; Keller, 2005; Meers et al., 2007; van Slycken et al., 2013). Concerning **phyto/rhizodegradation,** large root absorption area, big root tip mass, high enzyme activity, and increase of bioavailability from root exudates are critical factors to the successful implementation of GRO for soil organic contaminants (OVAM, 2019; Vangronsveld et al., 2009). Equally important is the fact that soil properties and the specific microbial community in the rhizosphere is heavily influenced by the plants themselves which could have a significant impact on remediation success (Epelde et al., 2010b; Gerhardt et al., 2017; OVAM, 2019; Thijs et al., 2017; Vangronsveld et al., 2009). Many of these key properties of plants and microorganisms can be improved through the use of **genetic modification**, selective breeding, using high performance clones, etc. to e.g. enhance resistance to toxicity, improve effectiveness of contaminant degradation or accumulation, enhance microbial activity, or enhance biomass production (Wang et al., 2019).

Regarding diversity, Mench et al. (2010) provide a valuable discussion and state that polyclonal plantations are recommended at least for trees to reduce the risk of major damage by pests and diseases over a long time period. Monocultures are more susceptible to such threats and may offer little ecological value as opposed to polyclonal and more biodiverse plantings which can improve ecological functioning and provide habitat (Mench et al., 2010). For example, increasing the number of willow genotypes in short-rotation coppice can enhance species diversity in the associated arthropod community, which may promote ecosystem functions within plantations (Müller et al., 2018). Furthermore, agronomic techniques like intercropping, co-cropping, agroforestry, etc. can be used to promote a more diverse cropping system to improve plant productivity and yield as well as improve overall ecosystem functionality (Kidd et al., 2015; Mench et al., 2010), see Kidd et al. (2015) for an extensive review of agronomic techniques to improve the effectiveness of GRO.

Other important considerations may be crucial factors in selecting plants such as i) rooting depth to reach deeper contamination or the groundwater table (Figure 4-1); ii) plant tolerance to contaminants to ensure plant survivability and resistance to any potential phytotoxic effects (see e.g. (McCutcheon and Schnoor, 2003; Trapp et al., 2014)); iii) biomass yield to maximise extraction or achieve profitable biomass production (Figure 4-2); and iv) evapotranspiration rates to achieve effective hydraulic control by selecting plants with a greater pumping capacity (Figure 2-11). Rooting depth in particular is a critical aspect of selecting the right plant which could make or break the success of GRO. Plants must be able to reach the contaminants in order to have an effect and root structure and depth vary widely between species and site-specific context, see e.g. (Keller et al., 2003b; McCutcheon and Schnoor, 2003).

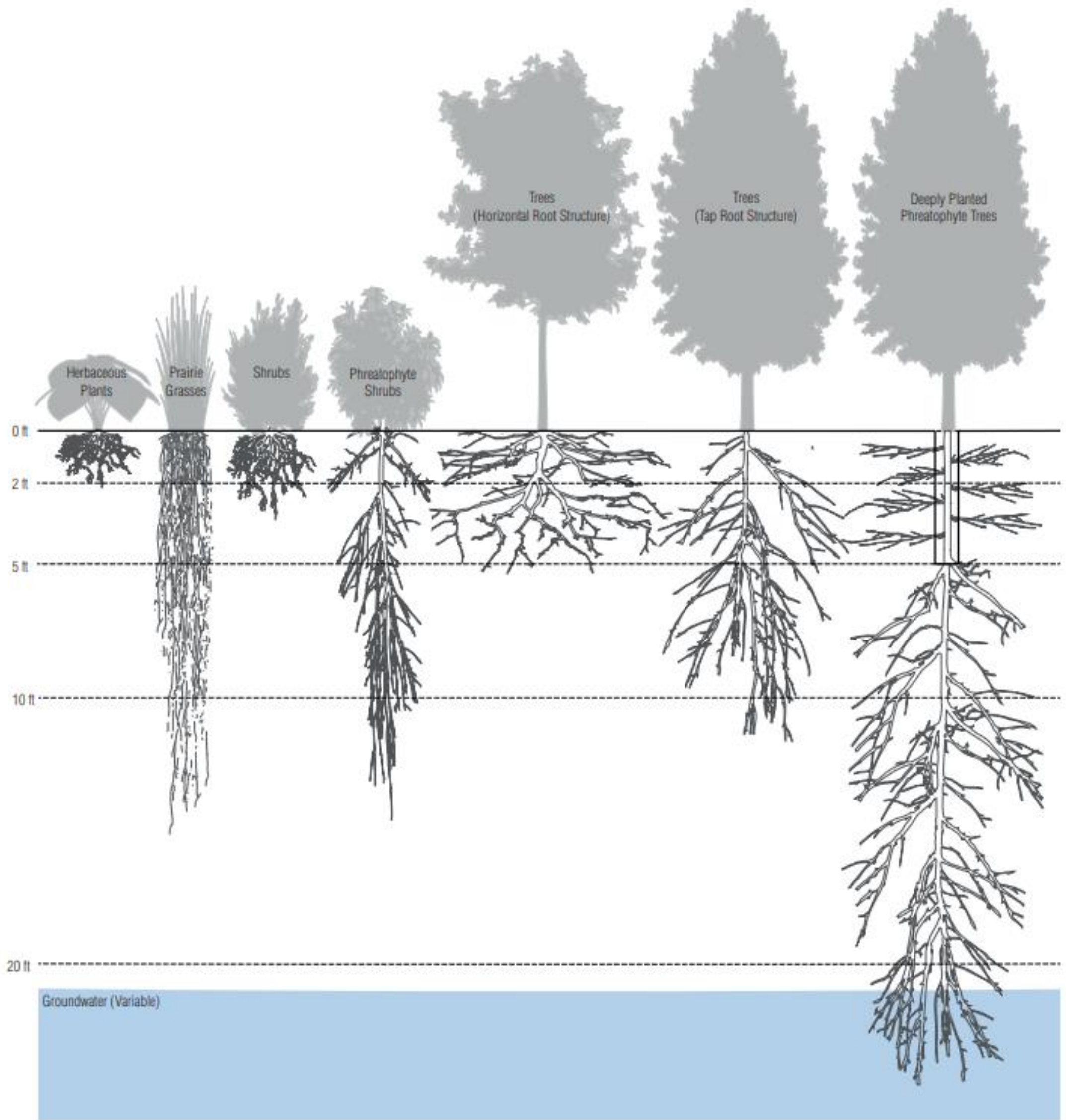

Figure 4-1. Typical plant root depths, from (Kennen and Kirkwood, 2015).

Latin	Common	Vegetation Type	USDA Hardiness Zone	Native to
Bambuseae	Bamboo	Herbaceous	varies	Asia
Brassica juncea	Indian Mustard	Herbaceous	9–11	Russia to Central Asia
Brassica napus	Rapeseed	Herbaceous	7+	Mediterranean
Cannabis sativa	Hemp	Herbaceous	4+	Asia
Chrysopogon zizanioides	Vetiver Grass	Herbaceous	9–11	India
Helianthus annuus	Sunflower	Herbaceous	Grown as annual	North and South America
Linum usitatissimum	Flax	Herbaceous	4+	Asia
Miscanthus giganteus	Giant Chinese Silver Grass	Herbaceous	5–9	China, Japan
Panicum virgatum	Switchgrass	Herbaceous	2–9	North America
Populus spp.	Poplar	Tree	varies	varies
Salix spp.	Willow	Tree/Shrub	varies	varies
Sorghum bicolor	Sorghum	Herbaceous	8+	Africa
Zea mays	Corn	Herbaceous	Grown as annual	North and South America

Figure 4-2. Example list of high biomass species commonly used in GRO application, from (Kennen and Kirkwood, 2015).

Methodologies for selecting can be checklist-based procedures as in the ITRC (ITRC, 2009) plant species screen process (Figure 4-3) or the Rejuvenate decision-support tool (Andersson-Sköld et al., 2014, 2013). Other methodologies consider an iterative approach based on broad testing of potentially viable plant species in greenhouses or small-scale pilot tests before implementing at full field scale, e.g. "phased phytoremediation strategy" (Licht and Isebrands, 2005) or "phyto-recurrent selection" (Zalesny et al., 2016; Zalesny and Bauer, 2007).

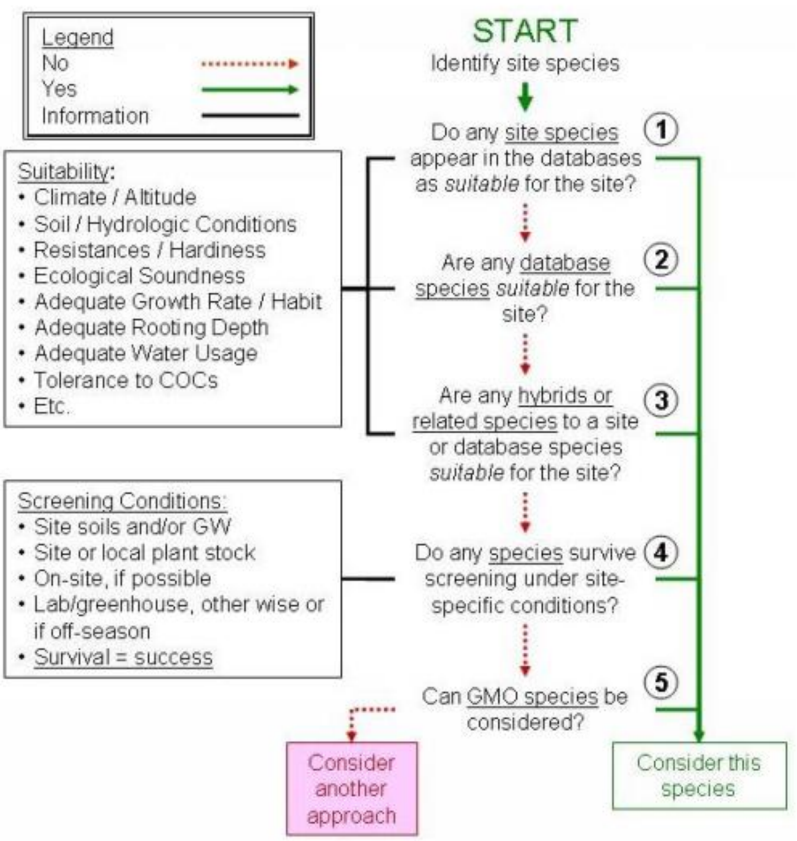

Figure 4-3. Plant species screening process, from (ITRC, 2009).

Some plant species are used more often than others due to their reliable effects in many situations and contexts. According to OVAM (2019), the plants most used and studied for GRO in the Flanders region of Belgium are:

- Poplar (*Populus* spp.)
- Willow (*Salix* spp.)
- Maple (*Acer* spp.)
- Grasses (*Festuca* spp., *Agrostis* spp., *Molina caerula*)
- Leguminous plants (*Medicago sativa, Lotus* spp., *Trifolium* spp.)
- Agricultural and horticultural crops (*Zea mays*, *Brassica juncea*, *Helianthus annus*, *Triticum* spp., *Cucurbita* spp.)
- Metal hyperaccumulators (*Noccaea caerulescens*)
- Aquatic plants (*Phragmites* spp., *Typha* spp.)

There are many more viable plant alternatives than those presented in this short list and it is encouraged to use plants that are native to the specific region which may have properties that are better suited to the contaminants present and site-specific conditions (OVAM, 2019). It is also encouraged to explore country-specific plant databases that may hold naturally occurring species useful for GRO. In summary, the following plant characteristics are optimal for the different GRO mechanisms (OVAM, 2019):

Plant selection

- **Phytodegradation** – plant has the ability to absorb the contaminant and degradation products are non-toxic.
- **Rhizodegradation –** plant excretes many enzymes and should not absorb the contaminant, suitable root growth (depth and extent) and possibility to associate with a diverse and efficient microbiome.
- **Phytovolatilisation –** possibility to absorb and volatilise the contaminant.
- **Phytoextraction** – plant tolerates, translocates and accumulates high concentrations of metals in the harvestable aboveground parts (stem and leaves) and has high growth rate and biomass production.
- **Phytostabilisation and rhizofiltration** – plants can remove metals, no translocation of metals from the roots to the shoot and fast-growing root system.
- **Phytohydraulics** – possibility of keeping the contaminant on site by influencing the groundwater depth, flow and direction.

5 Discussion and concluding remarks

GRO are sustainable, nature-based solutions that can be used to effectively manage risks posed by inorganic and organic contaminants in a wide variety of applications. Regarding their effectiveness, Wang et al. (2019) carried out a comprehensive review of ongoing and completed field trials and provided a summary that captures some of the key factors influencing the performance of GRO. As shown in Figure 5-1, there are many factors that affect the effectiveness of GRO, some of which have been covered in this report. In brief, an initial feasibility assessment concerning the type of contaminant, concentrations, **bioavailability**, soil properties and other important factors are essential to determine the viability of GRO. To improve the chances for success, the GRO strategy can be enhanced through well-informed plant selection, well-designed planting systems, **agronomic practices** like intercropping and crop rotations, the use of **soil amendments** including compost and biochar and biostimulation or bioaugmentation to improve the microbial community.

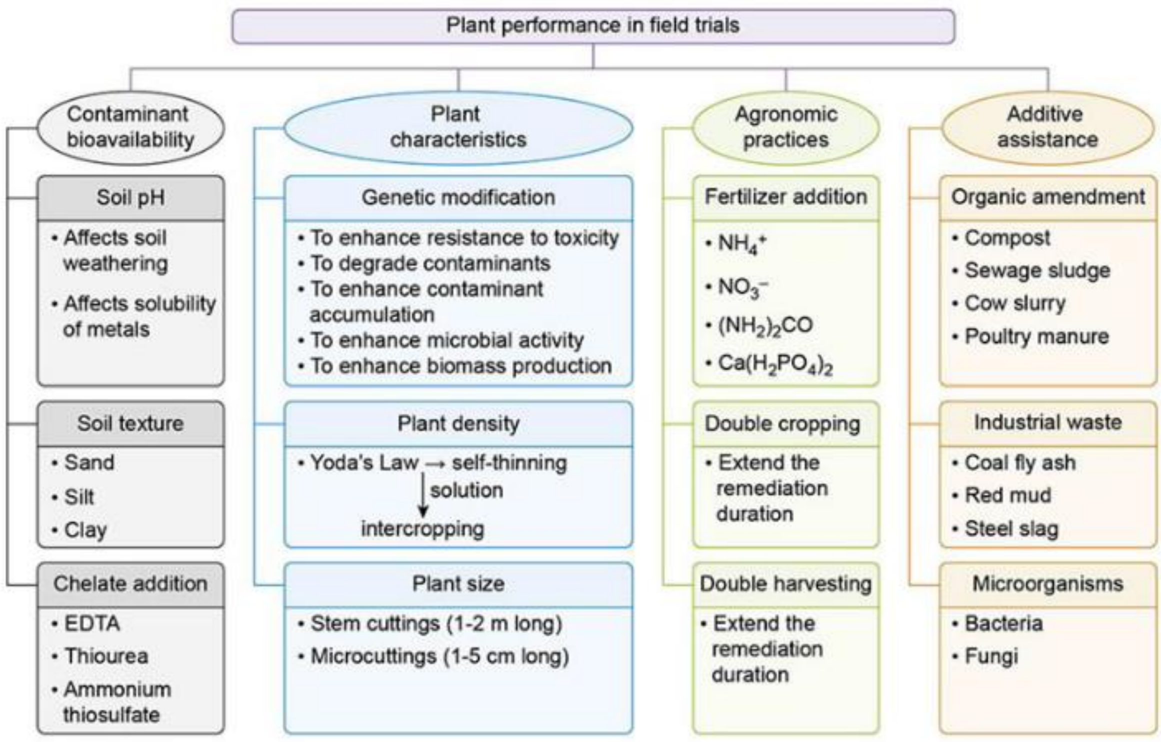

Figure 5-1. Factors determining the performance of plant-based remediation technologies in field trials, from (Wang et al., 2019).

Another important consideration when applying GRO is their multi-functionality as part of a holistic **phytomanagement** strategy. That is, their capacity for remediation forms a core, but not total, part of the wider benefits offered by GRO. Their potential to improve soil quality and ameliorate the soil ecosystem to improve the provisioning of ecosystem services is a key aspect that should be taken into account during options appraisal as well as when evaluating their success. For, as previously mentioned, **the ultimate objective of any remediation process must be not only to remove the contaminants from the soils (or disrupt source-pathway-receptor linkages) but also to restore soil quality** (Epelde et al., 2008a; Gómez-Sagasti et al., 2012).

However, despite their many benefits, GRO are still referred to as an emerging technology and have yet to be fully accepted as a viable remediation alternative since their remains a hesitancy towards their application from consultants, contractors and regulators. This is evidenced by the availability (or lack thereof) of demonstration projects, particularly in Sweden, that provide a convincing body-of-evidence. Many obstacles still exist that inhibit their widespread adoption and application at scale, including, but not limited to, a status quo bias and preference for conventional methods like dig-and-dump by practitioners (Montpetit and Lachapelle, 2017); 'nonknowledge' by practitioners regarding their functionality, methods and dealing with uncertainties, limitations or inefficiencies in GRO application (Bleicher, 2016); ecological risks from secondary poisoning due to wildlife grazing on metal-enriched plants or the improper handling of harvested biomass that may have higher concentrations of risk elements (Wang et al., 2019). In general, the main challenges and limitations to the application of GRO include the following (see e.g. (Cundy et al., 2016; Gerhardt et al., 2017) for more discussion):

- Uncertainties relating to the required timeframes for GRO and their effectiveness (both short- and long-term) as risk management methods
- Lack of awareness about GRO as viable remediation alternatives and perceived lack of applicability for some types of sites and contaminants
- Insufficient knowledge and experience in applying GRO
- Need for long-term monitoring
- Lack of convincing pilot projects and field studies, particularly long-term studies
- Limited availability of consultants and contractors offering GRO commercially

Poorly conceived GRO application in the 1990s (e.g. unsuitable application, lack of supporting science, unrealistic expectations, etc.) led to mixed performances in the field which resulted in a crash in stakeholder confidence that is still recovering (Cundy et al., 2016; Kennen and Kirkwood, 2015). Legal frameworks which predicate removal or destruction of the source of contamination to reach generic soil concentration targets based on total amounts (i.e. not bioavailable concentrations) also pose significant barriers (Cundy et al., 2016). Many, if not all, of these challenges can be overcome through **a deliberate and well-considered GRO design**. Importantly, GRO are not automatically sustainable as the delivery of wider economic, environmental and societal benefits depend on many site-specific factors – such as the need for irrigation, fertilisation, etc.; the presence of local conversion chains for the produced biomass to use as a resource instead of disposing as a waste; and design considerations like planting monocultures versus creating diverse site ecosystems, invasive versus native species, etc (Cundy et al., 2016). Taking a holistic approach to consider GRO within a broader land management strategy, as in **phytomanagement**, creates possibilities through regenerating marginal land, producing biomass for bioenergy and provisioning urban green spaces to also generate health and social benefits. Due consideration of the advantages and potential disadvantages of GRO by adequately valuating their **overall value**, in terms of both direct financial returns as well as wider tangible and intangible forms of value, will be critical to leverage GRO as a viable site management alternative to enable soft re-use more broadly at brownfield sites (Bardos et al., 2016; Cundy et al., 2016).

6 Further reading

It is impossible to cover the full breadth of GRO including its mechanisms, application and broader implications. This section is to refer the reader to other sources for nuanced details.

Reports and Books

GREENLAND, 2014– Best Practice Guidance for Practical Application of Gentle Remediation Options (GRO) and Appendices – available at: GREENLAND (Gentle remediation of trace element contaminated land) (europa.eu)

ITRC, 2009 – *Phytotechnology Technical and Regulatory Guidance and Decision Trees, Revised.* Available at: Phytotechnology Technical and Regulatory Guidance and Decision Trees, Revised (itrcweb.org)

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Kate Kennen and Niall Kirkwood, 2015 – *Phyto: Principles and resources for site remediation and landscape design*, Routledge. Available at: Phyto: Principles and Resources for Site Remediation and Landscape Design (routledge.com)

OVAM, 2019 – *Phytoremediation: Code of Good Practice.* Available at: Phytoremediation (ovam.be)

PhytoSUDOE – *Demonstration of the improvement in soil biodiversity, functionality and ecosystem services through phytomanagement in contaminated and degraded soils within the Interreg Sudoe area.* Phytomanagement best practices and guidance material. Available at: Home - phytosudoe

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Appendices

8 Appendix I

As of February 3, 2020, a blanket search for "phytoremediation" resulted in 13, 879 hits. The highest cited paper by (Salt et al. 1998) has been cited 1770 times since its publication. Filtering through these results and using sensitive search terms to find those that are most relevant to this literature review is a challenge. Also, previously conducted reviews and seminal works (primary sources) have been extracted and referred to specifically for reference throughout this review. Additionally, certain papers have been recommended by professionals in the field so extra weight will be placed upon them. The table below shows the process of finding relevant literature in the Scopus database in this phase of the literature review:

Search Terms – Phytoremediation/GRO

Feb. 3, 2020

"Phytoremediation" AND "_____"

Search Terms	***Hits***	***Year of Origin***	***Highest Citation Score***	***Relevance***
AND "meta-analysis"	18	2007	Audet and Charest 2007 (94)	8
AND "systematic review"	8	2017	Wang et al. 2017 (90)	2
LIMIT to *reviews*	986	1996	Haritash and Kaushik 2009 (1468)	
LIMIT to *reviews* + *heavy metal*	218	1997	Ali et al. 2013 (1133)	
LIMIT to *phytoextraction*	933			
LIMIT to *degradation*	421			
AND "removal rates"	300			
AND "soil quality" OR "soil health" OR "soil fertility"	381	1995	Garbisu et al. and Epelde et al. papers	
LIMIT to keyword - *soil quality*	157	2001		10
AND "risk management"	33	2000	Kuppusamy et al. 2017 (146)	7
Feb. 4, 2020				
AND "ecosystem services"	71	2008	Dickinson et al. 2009 (169)	22

"phytotechnology"	133	2000	Rezania et al. 2016 (141)	
+ "pollution" or "contamination"	61	2003	-	6
+ "remediation"	38	2002	-	6
"phytomanagement"*	171	2005	Robinson et al. 2009 (147)	15
LIMIT to *reviews*	10			5
+ "soil quality" or "soil health" or "soil fertility"	17			8
Feb. 7, 2020				
AND "plant selection" (screening)	48	1997	Labeau et al. 2008 (218)	-
AND "bioaugmentation"	177		Kuiper et al. 2004	-

*Usage of the term "phytomanagement" varies per paper, e.g. 'phytomanagement' can mean: 1) Greenland/Robinson et al. definition of maximizing co-benefits or 2) Phytoremediation to 'manage' a site using vegetation

Search Terms – Pre-conditions

Feb. 4, 2020

"Phytoremediation" AND "_____"

Search Terms	***Hits***	***Year of Origin***	***Highest Citation Score***	***Relevance***
AND "site-specific"	58	1998	Mulligan et al. 2001 (956)	7
AND "site characterization"	12			1
AND "site suitability"	0			
AND "site conditions"	24			1
AND "pre-conditions"	0			
AND "conditions"	2615		Haritash et al. 2009 (1468)	
AND "brownfield"	40	1999	Mench. Et al. 2010 (217)	16

AND "uncertainty"	41	1998	Mench et al. 2010 (217)	9
AND "regulation"	483			
And "monitoring"	799			
Feb 13, 2020				
AND "technosol"	33	2013	Sylvain et al. 2016 (41)	-
Feb. 14, 2020				
AND "indicators"	340	1994	He et al. 2005 (693) – Garbisu et al., Epelde et al.	-
September 3, 2020				
AND bioaccessibility	21	2006	Mench et al. 2006 (88)	6 (8)
AND bioavailability	941	1995 - Salt et al.	Haritash et al. 2009 (1584)	

Search Terms – Soil functions

Feb. 4, 2020

"Phytoremediation" AND "_____"

Search Terms	***Hits***	***Year of Origin***	***Highest Citation Score***	***Relevance***
And "ecosystem services"	71	2008	Dickinson et al. 2009 (169)	22
AND "soil functions"	14	2006	Gomez-Sagasti et al. 2012 (88)	8

"Brownfields" OR "contaminated sites" (or "contaminated land" or "marginal land" or "polluted soil" or "contaminated land" or "polluted land) AND "_____"

Search Terms	***Hits***	***Year of Origin***	***Highest Citation Score***	***Relevance***
AND "soil functions"	35	2002	Van Straalen 2002 (69)	10

AND "soil quality"	230	1994	Luo et al. 2012 (306)	-
AND "soil health"	31	2000	Dickinson et al. 2009 (169)	8
AND "ecosystem services"	73	2003	Dickinson et al. 2009 (169)	
AND "ecosystem services analysis"	0			
AND "ecosystem services mapping"	1	2018	Cortinovis and Geneletti 2018 (9)	1
AND "ecosystem services assessment"	0			
AND "green infrastructure"	20	2011	Mathey et al. 2015 (31)	-
AND "nature-based solutions"	7	2016	Song et al. 2019 (22)	3
Feb. 6, 2020				
AND "ecological risk assessment"	149		Linkov et al. 2009 (143)	-
LIMIT to "ecosystem services"	3	2012	Thomsen et al. 2012 (39)	3
March 24, 2020				
AND "decision support"	203		Li et al. 2007 (153)	-

August 21, 2020

"Brownfields" OR "contaminated sites" (or "contaminated land" or "marginal land" or "polluted soil" or "contaminated land" or "polluted land) AND "____"

Search Terms	***Hits***	***Year of Origin***	***Highest Citation Score***	***Relevance***
AND "minimum data set"	2	2014	Volchko et al. 2014 (30)	2
AND "soil quality indicators"	14	1999	Schindelbeck et al. 2008 (62)	6

AND "soil functions	56		Hinojosa et al. 2004 (175) (Gomez-Sagasti et al. 2012 (88))	
AND "soil health"	78		Dickinson et al. 2009 (178)	
Oct 10, 2020				
And "ecosystem service mapping"	5	2014	Gret-Regamy et al. 2014 (40)	2
AND "ecosystem services"	196			
Oct 20, 2020				
And "ecosystem service assesment"	0			
And "ecosystem service valuation"	0			
And "ecosystem service analysis"	1		Wells et al. 2018 (6) - marginal agricultural lands	

Search terms – Ecosystem services

Feb 12, 2020

Search Terms	*Hits*	*Year of Origin*	*Highest Citation Score (of relevance)*	*Relevance*
"ecosystem services mapping"	128			
AND "ecological risk assessment"	87	Sergeant, A. 2000 (6)	E.g. Faber 2013	14
"soil ecosystem services"	167		Dominati et al. 2010 (362)	
March 5 - *soil ES*				
And "endpoints"	109	Cairns Jr. 1994 (21)	Keeler et al. 2012 (201) + Faber et al.	-

AND "indicators"	2643		Lavalle et al. 2006 (664)	-
AND "typology"	230			
And "demand"	2200			-
And "future needs"	34			-
And "design"	2250			-
And "optimize"	389			-
And "semi-quantitative"	27	Everard et al. 2009 (3)	Schipanski et al. 2014 (157)	2
And "remediation"	266		Becerril et al. Garbisu et al., Mench et al., Cundy et al., Epelde et al.	
April 20 , 2020				
"soil ecosystem health"	33	Lau et al. 1997 (11)	Thomsen et al. 2012 (41) Park et al. 2011 (38) - nematodes Chae et al. (13) - beta-glucosidase	3

9 Appendix II

Compilation of GRO papers and field studies

- **Type*:*** *'general'* refers to a review or a general discussion of GRO and their wider application, *'method'* refers to integration within a decision-support framework *(i.e. Greenland project)*, *'analysis'* refers to an in-depth study of a specific factor of GRO, '*experiment'* refers to a controlled trial by e.g. pot experiments, and *'field'* refers to a field trial experiment and discussion of application and results.
- **Application**: refers to the context within the authors are discussing the use of GRO

Type	Title	Application and Key findings	Reference (citations)
Experiment	*Immobilization of heavy metals by polynuclear aluminium and montmorillonite compounds*	Modified montmorillonite compounds and polynuclear Al13 were investigated as potential binding agents to reduce heavy metal solubility in soil solutions. In summary, the four binding agents were found to immobilize nickel, copper, zinc, and cadmium, whereas the effect on the solubility of lead was rather small. Therefore, the aluminium based binding agents may be used for the gentle remediation of soils polluted by nickel, copper, zinc, or cadmium.	Lothenbach et al. 1997 (146)
Analysis	*Regional mass flux balancing for controlling gentle soil remediation operations*	The objective of the study was to test the suitability of PROTERRA for planning and monitoring gentle soil remediations. For this purpose, the authors applied the PROTERRA method to the contaminated agricultural land in and around Dornach, Switzerland, to assess copper flux balances. The calculations showed that atmospheric deposition and the application of pesticides and manure are important pathways for the inputs of copper.	Von Steiger et al. 1998 (4)
Experiment	*Laboratory and field scale evaluation of geochemical controls on groundwater transport of nitroaromatic ammunition residues*	Examined the relative importance of natural organic matter and complex formation with clays for NAC sorption at aquifer material and evaluated the potential of decreasing or enhancing the mobility of NACs in contaminated aquifers by stimulated cation exchange. Results indicate that NAC sorption to the bulk aquifer matrix was dominated by complex formation at clays, and electrolyte injection affected the saturation of the aquifer matrix which has implications for the gentle remediation of sites contaminated with nitroaromatic explosives.	Weissmahr et al. 1999 (64)
Experiment	*Phytoextraction of Cd and Zn from agricultural soils by Salix ssp. and intercropping of Salix caprea and Arabidopsis halleri*	Assessed the viability of extracting metals from contaminated soils using high-biomass, metal-accumulating *Salix* spp. and intercropping with *A. halleri*, and potential as a low-cost, gentle remediation strategy. Results from outdoor pot experiment showed that there was uptake of Cd (BAF 27) and Zn (BAF 3) with potential total removal of up to 20% of Cd and 5% Zn after after three vegetation periods.	Wieshammer et al. 2007 (98)

Method	*Developing decision support tools for the selection of "gentle" remediation approaches*	Presented the results from the European Union ERANET SNOWMAN project SUMATECS (Sustainable Management of Trace Element Contaminated Sites), and critically reviewed available decision support tools in terms of their fitness for purpose for the application of gentle remediation technologies. Stakeholder feedback indicates a lack of knowledge amongst stakeholders of currently available decision support tools. They propose that decision support which focuses on gentle remediation is more strongly incorporated into existing, well-established (national) decision support tools / decision-frameworks, to promote more widespread use and uptake.	Onwubuya et al. 2009 (56)
Experiment	*Phytoaccumulation of cadmium from soil by Populus*	Assessed the viability of extracting metals from contaminated soils using high-biomass, metal accumulating *Populus* spp., and potential as a low cost, gentle remediation strategy. In a pot experiment, total removal of Cd (BAF 27) of up to 20% after one vegetation period was shown for poplar species.	Chen and Jiang 2010 (0)
Field	*Gentle remediation at the former "Pertusola Sud" zinc smelter: Evaluation of native species for phytoremediation purposes*	The master plan for a soil clean-up of the former zinc smelter "Pertusola Sud" (Crotone, Italy) considered gentle remediation options for a specific area where both by-products and industrial wastes had been disposed in the past. Native species growing spontaneously in the metal-contaminated area were tested for metal uptake capability, some of which were considered hyper-accumulators.	Marchiol et al. 2013 (37)
General	*Developing principles of sustainability and stakeholder engagement for "gentle" remediation approaches: The European context*	Established a formative definition and capability for risk management: Gentle Remediation Options (GRO) are risk management strategies or techniques for contaminated sites that result in no gross reduction in soil functionality (or a net gain) as well as risk management. Intelligently applied GROs can provide: (a) rapid risk management via pathway control, through containment and stabilisation, coupled with a longer term removal or immobilisation/isolation of the contaminant source term; and (b) a range of additional economic (e.g. biomass generation), social (e.g. leisure and recreation) and environmental (e.g. CO2 sequestration) benefits. The importance of effective stakeholder engagement is discussed at length.	Cundy et al. 2013 (98)
General	*Arsenic phytoextraction by Pteris vittata L. and frond conversion by solvolysis: An integrated gentle remediation option for restoring ecosystem services in line with the biorefinery and the bioeconomy*	Long-term study showed decrease in bioavailable As concentrations over time using a hyperaccumulating fern species, *Pteris vittata* L. Varying temperature solvolysis could also be used to provide valuable bioproducts for use in biorefinieries.	Mench et al. 2014 (1)
Analysis	*Selecting chemical and ecotoxicological test batteries for risk assessment of trace element-contaminated soils (phyto)managed by gentle remediation options (GRO)*	As part of the GREENLAND project, a minimum test battery was established to assess effectiveness of GRO at test sites by critically reviewing and testing various chemical and ecotoxicological assays. Based on the results, a minimum risk assessment battery to compare/biomonitor the sites phytomanaged by GROs might consist of the NH4- NO3 extraction and the bean Plantox test including the stress enzyme activities.	Kumpiene et al. 2014 (32)
	Developing Effective Decision Support for the Application of "Gentle" Remediation Options: The GREENLAND Project	As part of the GREENLAND project, a simple and transparent decision support framework was created for promoting the appropriate use of gentle remediation options and encouraging participation of stakeholders, supplemented by a set of specific design aids for use when GRO appear to be a viable option. The framework is presented as a three phased model or Decision Support Tool (DST), in the form of a Microsoft Excel-based workbook, designed to inform decision-making and options appraisal during the selection of remedial approaches for contaminated sites.	Cundy et al. 2015 (16)

General	*Agronomic Practices for Improving Gentle Remediation of Trace Element-Contaminated Soils*	This paper supports the move from greenhouse to field conditions which requires incorporating agronomical knowledge into the remediation process and the ecological restoration of ecosystem services. As a review, it summarizes agronomic practices against their demonstrated or potential positive effect on GRO performance, including plant selection, soil management practices, crop rotation, short rotation coppice, intercropping/row cropping, planting methods and plant densities, harvest and fertilization management, pest and weed control and irrigation management. Potentially negative effects of GRO, e.g., the introduction of potentially invasive species, are also discussed. Lessons learnt from long-term European field case sites are given for aiding the choice of appropriate management practices and plant species.	Kidd et al. 2015 (99)
Field/ Experiment	*Plant responses to a phytomanaged urban technosol contaminated by trace elements and polycyclic aromatic hydrocarbons*	Medicago sativa was cultivated at a former harbor facility near Bordeaux (France) to phytomanage a soil contaminated by trace elements (TE) and polycyclic aromatic hydrocarbons (PAH). In parallel, a biotest with Phaseolus vulgaris was carried out on potted soils from 18 sub-sites to assess their phytotoxicity. The study determined the changes in plant responses in technosol (i.e. human-made soil) resulting from phytomanagement that showed positive responses to restoration.	Marchand et al. 2016 (7)
Experiment	*Effect of Medicago sativa L. and compost on organic and inorganic pollutant removal from a mixed contaminated soil and risk assessment using ecotoxicological tests*	A 5-month greenhouse trial was performed to test the efficiency of Medicago sativa L., singly and combined with a compost addition (30% w/w), to treat soils contaminated by petroleum hydrocarbons (PHC), Co and Pb collected at an auto scrap yard. After 5 months, total soil Pb significantly decreased in the compost-amended soil planted with M. sativa, but not total soil Co. Compost incorporation into the soil promoted PHC degradation, M. sativa growth and survival, and shoot Pb concentrations [3.8 mg kg^{-1} dry weight (DW)]. Residual risk assessment after the phytoremediation trial showed a positive effect of compost amendment on plant growth and earthworm development.	Marchand et al. 2016 (9)
General	*Brownfields to green fields: Realising wider benefits from practical contaminant phytomanagement strategies*	A comprehensive discussion on the wider benefits gained for GRO and their application as a land management strategy to both manage risks along contaminant linkages, and can generate a range of wider economic, environmental and societal benefits in contaminated land management (and in brownfields management more widely). This paper discusses challenges to the practical adoption of GROs in contaminated land management, and outlines the decision support tools and best practice guidance developed in the European Commission FP7-funded GREENLAND project aimed at overcoming these challenges.	Cundy et al. 2016 (54)
Field	*Microbial community structure and activity in trace element-contaminated soils phytomanaged by Gentle Remediation Options (GRO)*	Studied the effects of three GRO (aided-phytostabilisation, in situ stabilisation and phytoexclusion, and aided-phytoextraction) on the soil microbial biomass and respiration, the activities of hydrolase enzymes involved in the biogeochemical cycles of C,N,P, and S, and bacterial community structure of trace element contaminated soils (TECS) from six field trials across Europe. Overall, the results demonstrate that phytomanagement of trace-element contaminated sites influences soil biological activity in the long term.	Touceda-Gonzalez et al. 2017 (16)

Field	*Non-destructive soil amendment application techniques on heavy metal-contaminated grassland: Success and long-term immobilising efficiency*	The study aimed to find a practical solution for large-scale contaminations in hilly regions that prevents erosion. Field application of amendments without destroying the vegetation cover (grassland) involved two approaches: (a) slurrying (Slu) the amendments into cut gaps in the vegetation cover and (b) injecting (Inj) the amendments through the vegetation cover. They investigated the immobilising and long-term efficiency of treatments [gravel sludge (2.5%) + red mud (0.5%) (GS + RM)]. Risk assessment was based on soil, plant and water samples taken over a period of 10 years. Ammonium-nitrate-extractable Cd was reduced up to 50%, Pb up to 90%, and Zn over 90% and immobilisation also increased microbial biomass and decreased human bioaccessibility for Pb.	Friesl-Hanl et al. 2017 (6)
General	*Opinion: Taking phytoremediation from proven technology to accepted practice*	An overview of phytoremediation of soil is provided, with the focus on field applications, to provide a frame of reference for the subsequent discussion on better utilization of phytoremediation. The authors consider reasons why phytoremediation is underutilized, despite clear evidence that, under many conditions, it can be applied quite successfully in the field. They also offer suggestions on how to gain greater acceptance for phytoremediation by industry and government. A new paradigm of phytomanagement, with a specific focus on using phytoremediation as a "gentle remediation option" (GRO) within a broader, long-term management strategy, is also discussed.	Gerhardt et al. 2017 (66)
Field	*Assessing phytotoxicity of trace element-contaminated soils phytomanaged with gentle remediation options at ten European field trials*	Assess 10 field trials that were part of the GREENLAND network to assess the performance of GRO at metal-contaminated sites to reduce phytotoxicity. GRO implementation had a limited effect on TE concentrations in the soil pore water, although use of multivariate Co-inertia Analysis revealed a clear amelioration effect in phytomanaged soils.	Quintela-Sabaris et al. 2017 (22)
Field	*A Comparative Study on Poaceae and Leguminosae Forage Crops for Aided Phytostabilization in Trace-Element-Contaminated Soil*	The objectives of this study were to compare the effect of the type of forage crops at the "family" level (Poaceae and Leguminosae) on aided phytostabilization using physical (water stable aggregation), chemical (Mehlich-3 extraction), and biological assessments (dehydrogenase activity). Chemical assessment showed that the reduction in bioavailability of trace elements was partly observed in legume crops. The translocation of trace elements from root to shoot was low in all plants, indicating that the cultivation of the plants used in this study is safe with regards to the spread of trace elements into the environment. The results suggest that forage crop cultivation in contaminated agricultural soil could ameliorate soil quality after chemical stabilization.	Kim et al. 2018 (3)
Experiment	*Brassica napus has a key role in the recovery of the health of soils contaminated with metals and diesel by rhizoremediation*	In order to implement a phytomanagement strategy on calcareous alkaline peri-urban soils simultaneously contaminated with several metals and diesel, we evaluated the effectiveness of Brassica napus L., a profitable crop species, assisted with organic amendment and zero-valent iron nanoparticles (nZVI). A two-month phytotron experiment was carried out using two soils, i.e. amended and unamended with organic matter. The authors concluded that rhizoremediation with B. napus combined with an organic amendment is promising for the phytomanagement of calcareous soils with mixed (metals and diesel) contamination	Lacalle et al. 2018 (17)

Experiment	*Effectiveness and ecotoxicity of zero-valent iron nanoparticles during rhizoremediation of soil contaminated with Zn, Cu, Cd and diesel*	The application of metallic nanoparticles, such as zero-valent iron nanoparticles (nZVI), for soil remediation is highly promising, but their effectiveness and potential ecotoxicity must be further investigated. In this study, data is presented on soil chemical (pseudo-total and CaCl2-extractable metal concentrations; petroleum hydrocarbon concentrations) and biological properties (microbial properties and phytotoxicity) after the application of nZVI to soil simultaneously contaminated with Zn, Cu, Cd and diesel, in the absence and presence of other remediation treatments such as the application of an organic amendment and the growth of Brassica napus plants. Overall, the application of nZVI had no effect on contaminant removal, nor on soil microbial parameters, however it did cause an indirect toxic effect on plant root elongation due to the interaction of nZVI with soil organic matter.	Lacalle et al. 2018 (4)
Experiment	*Effectiveness of biochar obtained from corncob for immobilization of lead in contaminated soil*	Tested the effectiveness of biochar (from pyrolysis of corncob) to immobilise lead in soils in a laboratory experiment. Laboratory tests indicated that unmodified biochar obtained a maximum retention of 61.46% of lead, while the modified biochar (10% H2O2 treatment) obtained only 44.53% retention. In the pot experiments, the modified biochar indicated high germination and growth of seeds (up to 89.8%).	Rodriguez et al. 2019 (1)
Analysis	*Investigation and Assessment for an effective approach to the reclamation of Polycyclic Aromatic Hydrocarbon (PAHs) contaminated site: SIN Bagnoli, Italy*	Native plant species were screened for their remediation potential for the removal of Polycyclic Aromatic Hydrocarbons (PAHs) contaminated soil of Bagnoli brownfield site (Southern Italy). Functional metagenomics showed changes in dioxygenases, laccase, protocatechuate, and benzoate-degrading enzyme genes. Indolacetic acid production, siderophores release, exopolysaccharides production and ammonia production are the key for the selection of the rhizosphere bacterial population. Data demonstrated that the natural plant-bacteria partnership is the best strategy for the remediation of a PAHs-contaminated soil.	Guarino et al. 2019 (2)
Experiment	*Biochar and compost as gentle remediation options for the recovery of trace elements-contaminated soils*	To verify the effectiveness of biochar and compost for stabilisation of metals and benefit to microbial communities, biochar, compost and their combinationwere added to two sub-alkaline soils contaminated with Sb, As, and trace metals such as Ni and Cr. Most of the treatments (especially 3% biochar) reduced labile TE pools (water-soluble and exchangeable) and increased their residual (non-extractable) fractions. The amendments addition had both stimulating and inhibiting effects on the activity of soil microbial communities. Overall, the results from this study showed that the amendments investigated (particularly 3% biochar) can be effectively used for GRO of sub-alkaline soils, being able to reduce labile TE and to increase the metabolic potential and actual biochemical activities of the respective soil microbial communities.	Abou Jaoude et al. 2020 (2)
General	*Integrated and Sustainable Management of Post-industrial Coasts*	Review current approaches to managing contamination in post-industrial coastlines, discuss emerging integrated management strategies (building on low input approaches to sustainable brownfields regeneration) and present an approach and framework for assessing and comparing different scenarios for coastal brownfield regeneration to soft re-use and other end-points. This framework can be applied to explore the opportunities for synergy and realization of wider environmental, economic and societal benefits between coastal protection, dredged material re-use and the management of brownfield land. As such, the approach we propose supports planning and options appraisal to realize maximum benefit and value from integrated coastal management strategies.	Bardos et al. 2020 (2)

General	*Greening the browns: A bio-based land use framework for analysing the potential of urban brownfields in an urban circular economy*	This paper (1) provides a tentative selection of Urban Greenspaces (UGSs) relevant for brownfields, and a compilation of ecosystem services provided by the selected UGSs, and (2) presents a framework covering the 14 selected bio-based land uses on brownfields, including GRO interventions over time. This framework provides three practical tools: the conceptualization of linkages between GROs and prospective UGS uses, a scatter diagram for the realization of 14 UGS opportunities on brownfields, and a decision matrix to analyze the requirements for UGS realization on brownfields.	Chowdhury et al. 2020 (1)
Experiment	*Gentle remediation options for soil with mixed chromium (VI) and lindane pollution: biostimulation, bioaugmentation, phytoremediation and vermiremediation*	This study assessed the individual and combined effectiveness of GROs in recovering the health of a soil artificially polluted with hexavalent chromium [Cr(VI)] and lindane. A greenhouse experiment was performed using organically-amended vs. non-amended mixed polluted soils. Soil health recovery was determined based on Cr(VI) and lindane concentrations, microbial properties and toxicity bioassays with plants and worms. Cr(VI) pollution caused high toxicity, but some GROs were able to partly recover soil health: (i) the organic amendment decreased Cr(VI) concentrations, alleviating toxicity; (ii) the actinobacteria consortium was effective at removing both Cr(VI) and lindane; (iii) B. napus and E. fetida had a positive effect on the removal of pollutants and improved microbial properties. The combination of the organic amendment, B. napus, E. fetida and the actinobacteria consortium was the most effective strategy.	Lacalle et al. 2020 (3)
General	*Enhancing ecosystem services at urban brownfield sites - What value does contaminated soil have in the built environment?*	Gentle remediation options (GRO) are scalable nature-based techniques which provide significant opportunities for multi-functionality: managing risks posed by contaminants and at the same time enhance ecosystem services (ES) by improving the soil ecosystem in a low-impact, cost-effective manner. GRO align with an increasing interest in taking a holistic view on soil and land management to protect and improve the soil ecosystem for direct human benefit in the form of ES as well as for its indirect, intrinsic value as a haven for biodiversity. This short review aims to present a synthesis of ideas to raise awareness for urban planners about GRO techniques as nature-based solutions which can promote green infrastructure in the urban environment.	Drenning et al. 2020 (0)

10 Appendix III

Relevant properties of main categories of organic amendments as reported in literature, as reported in Schröder et al. (2018). Green and orange colour indicates positive and negative effects respectively; yellow colour indicates presence of both positive and negative effects; grey colour indicates a lack of knowledge. Numbers next to category headings indicate referred sources, see (Schröder et al., 2018) for details.

Properties	COMPOST[1]	ANIMAL MANURE[2]	DIGESTATE (anaerobic digestion)[3]	BIOCHAR[4]
Increase in content of organic matter	increases soil organic matter, humic substances	increases soil organic matter, depends on animal diet	depends on feedstock - humic acids (mainly solid fraction)	affects the stability of existing organic matter
Modification of C:N ratio			low C/N ratio due to digestion	increase
Improvement of water holding capacity	Increases		improves	increases due to surface structure
Supply of nutrients (N, P, etc.) nutrient balance	enhances nutrient supply	leaching of N and P – content differs with animal species	depends on feedstock - mineral N, P (mainly liquid fraction), possible leaching	reduces leaching of nutrients / slow release fertilizer - provides P and K
Modify pH	lowers pH		high pH	increase in soil pH of acidic soils
Modification of cation exchange capacity	Increases			increase in soils with low CEC
Improvement of texture and aggregation state	amelioration of structure and porosity	reduces density	reduces density, increase in aggregate stability	increase in porosity, stability of aggregates
Sequestration of pollutants/contaminants	through humic substances		not reported	can sequester pollutants, but also increase mobility
Addition of pollutants/contaminants	might contain persistent pollutants	micronutrients supplied to animals	might contain persistent pollutants, metals	can contain pollutants, in this case it is not usable
Decrease in salinity	Improvement		can increase salinity with repeated applications	can sequester salts and modify CEC
Soil conservation (e.g. minimise erosion)	remediates degraded soils		still to be investigated	still to be investigated
Increase in microbial biomass	increase	Increase	considerable increase	increase
Increase in microbial diversity	increase or decrease	Increase	significant changes	significant differences
Stimulation of specific microorganisms	no indication	antibiotic resistance	dominance of slowly growing microorganisms	arbuscular and ectomycorrhiza
Increase in enzymatic activities	increase in soil microbial activity	Increase	nitrogen mineralization, other enzymes	reports on increase in enzymatic activities
Increase in diversity of fauna	Limited observations, differing effects		limited observation, increase	Limited observations, differing effects
Effects on plants growth	positive	very positive	positive	mostly positive
Increase of yield	Positive	Positive	fertilizer capacity	reports on increase of crop yield
Increase of product quality	not significant			not assessed
Improve in defense against pathogens	Positive effects			Limited observations, positive effects
Origin, raw materials	biomass from different sources		biomass from different sources	biomass from different sources
Production requirements	requires large amounts of energy, long time			depends on biomass feedstock - importance of temperature
Standardisation of product	Quality assessment differs in the countries	not possible	not possible	just starting
Cost (including transport)	moderate		depends on feedstock	depends on feedstock - high
Positive carbon emission	emissions during composting	emissions of CH_4 and N_2O, NH_3	during digestion GHG emissions, NH_3 emission	could stimulate CO_2 emissions by microbes
Negative carbon emission	carbon sequestration in humic substances		decrease of emissions from manure	removal during growth of biomass, C - sequestration
Legislation, norms on applicability	Differences among countries		can be amendment or fertilizer	limited
Social acceptability	well established	well established	Low	not yet tested
Additional benefits (e.g. energy production)	scalable to farm		production of biogas	reduction of N_2O emissions
Ecosystem services of relevance				

11 Appendix IV

Plant species table – compilation of plants relevant for GRO application and potential wider benefits, grouped according to plant type.

Plant Type	Latin name (common name)	Family	Tolerance	Distribution	Remediation potential - inorganics	Remediation potential - organics	Associated microbes	Additional benefits	Reference
Biomass (annual)	*Glycine Max L.* (soybean)	Fabaceae	Prefers well-drained, loamy soil; wide range of soil conditions	Worldwide	Extraction of Cd, Cr, Ni, As, Fe, Zn	Degradation of PAH, POPs, and atrazine	Fosters nitrifying bacteria	Land reclamation; bioenergy, bioethanol, biochar	(Edrisi and Abhilash, 2016; Tang et al., 2012; Tripathi et al., 2016a)
Biomass (annual)	*Nicotiana tabacum, silvestris,* spp. (tobacco)	Solanaceae	Sensitive to temperature, air, ground humidity and soil type; best for warmer climates	North America, Europe	Extraction of Cd, Cr, Pb, Zn and other trace elements			Successful *in-vitro* cultivars of tobacco targeting specific metals; useful biomass	(Gawronski et al., 2011; Herzig et al., 2014; Kidd et al., 2015)
Biomass (annual)	*Cucurbita pepo* spp. (zucchini, pumpkin, squash)	Cucurbita	Requires good quality soil for high yield; high water demand; susceptible to pests			Uptake of DDT, PCBs and other POPS		Forage for pollinators, high biomass production	(Denyes et al., 2016, 2013; Paul et al., 2015; White, 2001; White et al., 2006, 2003; Whitfield Åslund et al., 2010, 2008)
Fibre (annual)	*Cannabis sativa L.* (hemp)	Cannabaceae	Prefers loamy soils; tolerant of high metal concentrations	Worldwide	Extraction of Cd, Cr, Cu, Ni, Pb, and Zn; Stabilisation	Degradation of PAHs and pesticides (currently tested for PFAS uptake)		Biofuel production, bioenergy or in other bio-products as fibre; large biomass quantity and fast growing; natural control of pests/weeds	(Gawronski et al., 2011; Pandey et al., 2016; Tang et al., 2012; Zegada-Lizarazu and Monti, 2011)

Fibre (annual)	*Hibiscus cannabinus* (kenaf)	Malvaceae	Tolerant of high metal concentrations (metallophyte?)	Worldwide	Extraction of As, Fe, Cd and Pb; Stabilisation	Degradation of lubricant oils		Biofuel production, bioenergy or in other bio-products as fibre; large biomass quantity; natural control of pests/weeds	(Kidd et al., 2015; Pandey et al., 2016; Tang et al., 2012; Zegada-Lizarazu and Monti, 2011)
Fibre (annual)	*Linum usitatissimum L.; Camelina sativa* (flax and camelina)	Linaceae	Suitable to a wide range of soil types	Worldwide	Extraction of Cd, Ni and other metals	Degradation of PAHs and atrazine	Enhanced interaction with soil mycorrhiza	Biofuel production, bioenergy or in other bio-products as fibre; large biomass quantity; well-suited for rotation with deep-rooted crops	(Andersson-Sköld et al., 2013; Pandey et al., 2016; Tripathi et al., 2016b; Zegada-Lizarazu and Monti, 2011)
Grain (annual)	*Beta vulgaris* (sugar beet)	Betaceae	Medium to high grade agricultural soil; temperate climate with mean summer temp. Around 21C; uniform soil moisture	Europe, North America	Stabilisation, Cd-exclusion cultivars; tolerant to high salinity			Biofuel production (bioethanol); useful for co-cropping systems to maximise benefits (e.g. rotation with winter wheat)	(Andersson-Sköld et al., 2013; Gawronski et al., 2011; GREENLAND, 2014b)
Grain or grass (annual)	*Zea mays* (maize or corn)	Poaceae	Long, warm growing seasons; medium to high grade agricultural soil	Worldwide	Stabilisation, Cd-exclusion cultivars		Fosters AMF	Biofuel production (bioethanol); useful for co-cropping systems to maximise benefits (e.g. use as biomass feedstock)	(Andersson-Sköld et al., 2013; Gawronski et al., 2011; GREENLAND, 2014b; Kidd et al., 2015; Tang et al., 2012; Vangronsveld et al., 2009; Witters et al., 2012b)
Grain or grass (annual)	*Hordeum vulgare* (barley)	Poaceae	Medium to high grade agricultural soil	Worldwide	Stabilisation, Cd-exclusion cultivars; tolerance to high salinity		Fosters AMF	Biofuel production (bioethanol); useful for co-cropping systems to maximise benefits	(Andersson-Sköld et al., 2013; Gawronski et al., 2011; GREENLAND,

									2014b; Kidd et al., 2015; Tang et al., 2012)
Grain or grass (annual)	*Sorghum bicolor L.* (great millet, biomass sorghum)	Poaceae	Higher abiotic conditions, grows in diverse climates and suitable for dryland conditions	North America, Australia, Sweden			Fosters AMF	Biofuel production (bioethanol) or in other bio-products; large biomass quantity; well-suited for rotation with deep-rooted crops; can be used as biomass feedstock	(Kidd et al., 2015; Mehmood et al., 2017; Pandey et al., 2016; Zegada-Lizarazu and Monti, 2011)
Grain or grass (annual)	*Triticum aestivum* (winter wheat)	Poaceae	Medium to high grade agricultural soil	Worldwide	Stabilisation, Cd-exclusion	Degradation of PAHs	Fosters AMF	Biofuel production (bioethanol) or in other bio-products; large biomass quantity; well-suited for rotation with deep-rooted crops; can be used as biomass feedstock	(Andersson-Sköld et al., 2013; Gawronski et al., 2011; GREENLAND, 2014b; Kidd et al., 2015; Tang et al., 2012)
Grass groundcover (annual)	*Sinapis alba* (white mustard)	Brassicaceae	Wide tolerance	Worldwide	Extraction of various metals; Stabilisation			Green manure cover crop; culinary uses for seeds	(Foucault et al., 2013; Gawronski et al., 2011)
Grass groundcover (perennial)	*Festuca rubra, F. arundinacea, F. ovina* (spp) (fescue)	Poaceae	Wide tolerance - tolerant to pollution; Well-drained soils in cool, temperate climates, shade tolerant; neutral and acidic soils	Northern hemisphere	Metal excluder, Stabilisation	Degradation of PAHs and hydrocarbons; degradation (and low uptake) of DDT	Fosters nitrifying bacteria and AMF; supports *Pseudomonas* sp.	Soil stabilisation, erosion prevention, Co-cropping, wild animal forage, improves soil health - supports general increase in microbial activity and numbers in rhizosphere; suitable for acidic mine tailings	(Epelde et al., 2009b; Gajić et al., 2018; Gawronski et al., 2011; Lunney et al., 2004; Mench et al., 2010; Vangronsveld et al., 2009; Wang et al., 2017)

Grass groundcover (perennial rhizomatous grass - PRG)	*Miscanthus x giganteus, sacchariflorus and sinensis* (giant perennial silvergrass, miscanthus or elephant grass)	Poaceae	Low to medium grade agricultural soil; prefers well-drained soils but wide range of tolerance	Europe, USA, Japan, China	Extraction of As, Sn, Cd, Cr, Cu, Ni, Pb, Zn, and Al; Stabilisation; highly tolerant to pollution	Degradation of PAHs, hydrocarbons (increases degrading microbes) and pesticides	Fosters AMF	Biofuel and bioenergy; carbon sequestration, soil restoration, large biomass quantity; (*M. giganteus*) non-invasive genetic mutant; resistant to pests and disease; increases carbon input and microorganism diversity and activity; prevents erosion and runoff - dense, fibrous root system; habitat provisioning	(Andersson-Sköld et al., 2013; Gawronski et al., 2011; Kidd et al., 2015; Mehmood et al., 2017; Nsanganwimana et al., 2014; Pandey et al., 2016; Pavel et al., 2014; Tripathi et al., 2016b)
Grass groundcover (perennial rhizomatous grass - PRG)	*Phlaris arundinacea* (reed canarygrass)	Poaceae	Temperate regions; suitable to wet soils, colder climates, and flood plains	Northern Europe, USA, Canada, Russia	Extraction of As, Sn, Cd, Cr, Cu, Ni, Pb, Zn, and Al; highly tolerant to pollution	Degradation of PAHs and pesticides	Fosters AMF	Biofuel and bioenergy; carbon sequestration, soil restoration, large biomass quantity; drought tolerant - suitable for warm regions	Pandey et al. 2016; Lord et al. 2015; Mehmood et al. 2017; Andersson-Sköld et al. 2013; Gawronski et al. 2011
Grass groundcover (perennial rhizomatous grass - PRG)	*Panicum virgatum* (switchgrass)	Poaceae	Temperate regions; drought-resistant, tolerant to adverse conditions; best in warmer climates	North America, Europe	Stabilisation	Uptake of DDT; degradation of atrazine and PAHs	Fosters AMF	Biofuel and bioenergy; carbon sequestration, soil restoration, large biomass quantity; drought tolerant - suitable for warm regions	Greenland appendices 2014; Paul et al. 2015; Lewandowski et al. 2003
Grass groundcover (perennial)	*Lolium perenne, L. multiflorum,* spp (perennial ryegrass)	Poaceae	Wide tolerance - highly tolerant to pollution (*potentially invasive*)	Europe, Asia, northern Africa	Stabilisation; uptake of salts	Degradation of PAHs and hydrocarbons; degradation (and low uptake) of DDT	Fosters AMF	Soil stabilisation, erosion prevention, Co-cropping, wild animal forage, improves soil health - supports general increase in microbial activity and numbers in rhizosphere; suitable for acidic mine tailings	(Epelde et al., 2009b; Gajić et al., 2018; Gawronski et al., 2011; Kelsey and White, 2005; Kirk et al., 2005; Lunney et al., 2004; Wang et al., 2017)

Grass groundcover (perennial)	*Poa annua, P. pratensis* (annual meadow grass, bluegrass or meadow-grass)	Poaceae	Wide tolerance - highly tolerant to pollution (*potentially invasive*)	North America, Worldwide	Extraction of Hg	Degradation of PAHs and hydrocarbons	Fosters AMF	Pioneering species	(Gajić et al., 2018; Pedron et al., 2013)
Grass groundcover (perennial)	*Deschampsia cespitosa* (tufted hairgrass)	Poaceae	Wide tolerance - highly tolerant to pollution	Worldwide	Stabilisation, highly tolerant to pollution	Degradation of PAHs and hydrocarbons	Fosters AMF	Ornamental plant	(Gawronski et al., 2011)
Grass groundcover (perennial)	*Vetiveria zizanioides* (vetiver)	Poaceae	Wide tolerance - highly tolerant to pollution	India, Worldwide	Stabilisation	Degradation of PAHs and hydrocarbons; degradation of DDT	Fosters AMF	Multiple uses in various bioproducts; many sterile genotypes preventing invasiveness	(Dudai et al., 2018; Gawronski et al., 2011)
Grass groundcover (perennial)	*Agrostis capillaris* (common bent)	Poaceae	Wide tolerance - highly tolerant to pollution and acidity	Eurasia	Stabilisation; Excluder phenotypes; Extraction possible	Degradation of PAHs and hydrocarbons	Fosters AMF	Soil stabilisation, erosion prevention; suitable for acidic mine tailings	(GREENLAND, 2014b; Kidd et al., 2015; Touceda-González et al., 2017a; Vangronsveld et al., 1996)
Grass groundcover (perennial)	*Eriphorum angustifolium* (common cottongrass)	Cyperaceae	Wide tolerance; tolerant to pollution and acidity	North America, North Asia and Northern Europe	Stabilisation			Suitable for acidic mine tailings; resistant to cold and frost	(Gawronski et al., 2011)
Grass groundcover (perennial)	*Thynopyrum ponticum/ intermidium* (wheatgrass)	Poaceae	Wet, alkaline soil; temperate conditions	Eurasia	Reduce soil salinity; Stabilisation, Cd-excluding cultivars			Biofuel production; large biomass quantity	(Kidd et al., 2015; Mehmood et al., 2017)

Herbaceous fern (perennial)	*Pteris vittata* (Chinese brake fern)	Pteridacea	Tolerant to pollution (*potentially invasive*)	Worldwide - Asia, Europe, Africa, Australia	As hyperaccumulator				(Fitz et al., 2003; Tang et al., 2012)
Herbaceous groundcover (perennial)	*Noccaea caerulescens* (alpine pennygrass) - formerly *Thlaspi caerulescens*	Brassicaceae	Highly adaptable to diverse soil conditions, tolerant to high metal conc.	Scandinavia, Europe	Hyperaccumulator of Cd, Ni, Zn; extracts Pb			Improves microbial activity (e.g. soil enzyme activity) Useful for co-cropping systems to maximise benefits, soil restoration	(Epelde et al., 2010b, 2010a, 2008a; Jacobs et al., 2018; Tang et al., 2012)
Herbaceous groundcover (perennial)	*Arabidopsis halleri* (rockcress)	Brassicaceae		Europe, North America, Asia	Hyperaccumulator of Cd and Zn				(GREENLAND, 2014b)
Herbaceous groundcover (perennial)	*Trifolium repens, T. pretens* (white and red clover)	Fabaceae	Wide tolerance - highly tolerant to pollution (*potentially invasive*)	Worldwide	Stabilisation	Degradation of PAHs and PCBs (incl. furans and dioxins)	Fosters nitrifying bacteria	Improves soil fertility, taproot improves soil structure, ornamental, important forage for pollinators	(Barrutia et al., 2011; Gajić et al., 2018; Hechmi et al., 2014; Wang and Oyaizu, 2009)
Herbaceous groundcover (perennial)	*Lupinus albus, luteus, angustifolius* spp. (lupin)	Fabaceae	Wide tolerance; can survive on very poor soil - tolerant to heavy metals (*potentially invasive)*	Worldwide	Extraction of Mn, Pb, Cr, Hg; Stabilisation	Stimulate degradation of PAHs and PCBs	Fosters nitrifying bacteria	Green manure cover crop improves soil functionality - leguminous rhizomes stimulate microbial community; drought tolerance; wild animal forage; ornamental plant	(Balseiro-Romero et al., 2016; Garau et al., 2021; Gawronski et al., 2011; White et al., 2005)
Herbaceous groundcover (perennial)	*Medicago sativa* (alfalfa/ lucerne)	Fabaceae	Wide tolerance; can survive on very poor soil - tolerant to heavy metals	Worldwide	Stabilisation	Stimulate degradation of PAHs and PCBs (increases degrading	Fosters nitrifying bacteria; fosters AMF	Green manure cover crop improves soil functionality - leguminous rhizomes stimulate microbial	(Gawronski et al., 2011; Hechmi et al., 2014; Kirk et al., 2005; Lunney et al., 2004; Marchand et al.,

						microbes); Uptake and degradation of DDT		community; drought tolerance; forage crop	2018; Mitton et al., 2014; Wu et al., 2008)
Herbaceous groundcover (perennial)	*Vicia sativa, Vicia.* spp. (common vetch)	Fabaceae	Wide tolerance - cold and heat tolerant	Worldwide	Stabilisation	Stimulate degradation of PAHs and PCBs (increases degrading microbes)	Fosters nitrifying bacteria	Green manure cover crop improves soil functionality - leguminous rhizomes stimulate microbial community; beneficial to pollinators; food for insects; forage crop	(García-González et al., 2018; White et al., 2005)
Herbaceous groundcover (perennial)	*Armeria maritima* (thrift or sea thrift)	Plumbaginaceae	Highly tolerant to Pb and other metals	Worldwide	Stabilisation of Pb			Ornamental plant; pioneer plant establishes on contaminated sites	(Gawronski et al., 2011)
Herbaceous groundcover (perennial)	*Alyssum murale*, spp. (yellowtuft)	Brassicaceae			Hyperaccumulator of Ni				(Ali et al., 2013; Keller et al., 2003b)
Herbaceous groundcover (perennial)	*Sedum alfredii* (sedum)	Crassulaceae	Wide tolerance; drought tolerant	Northern hemisphere	Cd hyperaccumulator			*Sedum* spp. are used in green roofs	(Rosenkranz et al., 2017; Wan et al., 2016)
Oil crop (annual)	*Ricinus communis L.* (castor bean)	Euphorbiaceae	Sandy and clayey loamy soil; tolerant of high metal concentrations	Worldwide, south Europe	Stabilisation or uptake of Cd	Degradation and uptake of DDT and organochlorine pesticides (POPs)		Soil restoration; biodiesel, multi-purpose oil, solubiliser for toiletry and cosmetics	(Edrisi and Abhilash, 2016; Huang et al., 2011; Pandey et al., 2016; Rissato et al., 2015; Tripathi et al., 2016a)

Oil crop (annual)	*Brassica juncea L. Coss., B. carinata* (Indian Mustard, Ethiopian Mustard)	Brassicaceae	Sandy to heavy clay soils, shallow soil, calcareous inceptisols	Worldwide	Extraction of Cd, Zn, Pb, Ni, Hg (high)			Biofuel production (biodiesel) and bioenergy; carbon sequestration, land reclamation - use as green manure	(Edrisi and Abhilash, 2016; Gawronski et al., 2011; Pedron et al., 2013; Zegada-Lizarazu and Monti, 2011)
Oil crop (annual)	*Brassica napus* (rapeseed)	Brassicaceae	Requires good quality soil for high yield	Worldwide	Extraction of As, Sn, Cd, Cr, Cu, Ni, Pb, Zn, and Al (high)	Degradation of PAHs and PCBs		Biofuel production (biodiesel) and bioenergy; Soil restoration, large biomass quantity	(Gawronski et al., 2011; Witters et al., 2012b; Zegada-Lizarazu and Monti, 2011)
Oil crop (annual)	*Helianthus annus L.* (sunflower)	Asteraceae	Clay, most sandy soils, inceptisols	Worldwide	Extraction of Cd, Cr, Pb, Ni, As, Fe, Zn, Hg	Degradation of PAHs and atrazine; degradation and uptake of DDT/DDE and POPs		Biofuel production (bioethanol), charcoal; land reclamation, drought resistant; efficient use of soil resources; large biomass quantity; natural control of pests/weeds	(Edrisi and Abhilash, 2016; Gawronski et al., 2011; Herzig et al., 2014; Nikolić and Stevović, 2015; Tripathi et al., 2016a; Zegada-Lizarazu and Monti, 2011)
Woody biomass (Shrub/tree)	*Robinia pseudoacacia* (black lotus)	Fabaceae	Wide tolerance; can survive on very poor soil - tolerant to heavy metals (*potentially invasive*)	Worldwide	Stabilisation; Bioindicator of pollution (Cd, Pb, Zn) - uptake of various metals	Stimulate degradation of PAHs and PCBs	Fosters nitrifying bacteria	Green manure cover crop improves soil functionality - leguminous rhizomes stimulate microbial community; drought tolerance; ornamental plant	(Dadea et al., 2017; Gawronski et al., 2011; Stolarski et al., 2017)
Woody biomass (Shrub/tree)	*Caragana arborescens* (siberian peashrub)	Fabaceae	Wide tolerance; can survive on very poor soil - tolerant to heavy metals (*potentially invasive*)	Worldwide	Stabilisation	Stimulate degradation of PAHs and PCBs	Fosters nitrifying bacteria	Green manure cover crop improves soil functionality - leguminous rhizomes stimulate microbial community; drought	(Gawronski et al., 2011)

								tolerance; ornamental plant	
Woody biomass (Shrub/tree)	*Amorpha fruticosa* (desert false indigo)	Fabaceae	Wide tolerance; can survive on very poor soil - tolerant to heavy metals (*potentially invasive*)	Worldwide	Stabilisation	Stimulate degradation of PAHs and PCBs	Fosters nitrifying bacteria	Green manure cover crop improves soil functionality - leguminous rhizomes stimulate microbial community; drought tolerance; ornamental plant	(Gawronski et al., 2011; Xue et al., 2018)
Woody biomass (Shrub/tree)	*Rosa rugosa* (rugosa rosa, Japanese rose)	Rosaceae	Tolerant to pollution (*potentially invasive*)	Asia	Bioindicator of pollution (Cd, Pb, Zn) - uptake of various metals			Commonly used for erosion prevention or planted along highway medians; can be used as a natural barrier against preventing access	(Gawronski et al., 2011)
Woody biomass (Shrub/tree)	*Cotoneaster franchetti* (cotoneaster)	Rosaceae	Tolerant to pollution (*potentially invasive*)	Asia, Europe, North America	Effectively absorbs airborne pollutants both inorganic and organic			Ornamental plant; 'super plant' for urban air purification	RHS Gardening; (Blanuša et al., 2020)
Woody biomass (Shrub/tree)	*Paulownia tomentosa* (princess/ empress tree)	Paulowniaceae	Tolerant to pollution (*potentially invasive*)	Asia, Europe, North America	Extraction of metals			Ornamental plant, fast-growing, useful biomass	(GREENLAND, 2014b; Macci et al., 2016, 2013)
Woody biomass (Shrub/tree)	*Morus alba, M. rubra* (mulberry)	Moraceae	Tolerant to pollution (*potentially invasive*)	Asia, worldwide		Exudates phenolic compounds stimulating breakdown of POPs and PAHs		Useful biomass	(Aken et al., 2010; Fletcher and Hegde, 1995; Wan et al., 2017, 2016)

Woody biomass	*Liquidambar styraciflua L.* (American sweet gum or Satin walnut or Alligator wood)	Altingiaceae	Loamy, sandy, clay; well-drained soil	Worldwide	Extraction of various metals; Stabilisation	Degradation of POPs		Bioenergy, paper and pulp; soil restoration	(Edrisi and Abhilash, 2016; Tripathi et al., 2016a)
Woody biomass	*Eucalyptus grandis (W. Hill), E. camalduensis (Dehnh), E. globulus (Labill)* (Eucalyptus, Flood gum or Rose gum)	Myrtaceae	Temperate, tropical and subtropical regions; poor soils	Worldwide	Excess phosphate/nutrient removal; Extraction of As; Stabilisation			Biomass, biogas, plywood, biochar; essential oils, various bio-products; fast growing, high biomass quantity	(Edrisi and Abhilash, 2016; Pandey et al., 2016; Tripathi et al., 2016a; Zalesny et al., 2016)
Woody biomass	*Pinus taeda L., Pinus sylvestris L.* (loblolly pine, Scots pine)	Pinaceae	Predominantly ultisols; sandy soils; tolerant of acid soils	Worldwide	Excess phosphate removal; Extraction of various metals	Degradation of POPs		Biomass, biogas, plywood, biochar; fast growing, high biomass quantity	(Edrisi and Abhilash, 2016; Madejón et al., 2018; Placek et al., 2016; Tripathi et al., 2016a; Zalesny et al., 2016)
Woody biomass	*Betula pendula,* spp. (silver birch)	Betulaceae	Most soils in cold, temperate regions; can establish on a wide range of soils conditions including derelict land	Europe - *native to Sweden*	Stabilisation; Extraction of Cd, Zn, Mn; Bioindicator of pollution (Cd, Pb, Zn) - uptake of various metals	Degradation of PAHs; filters airborne pollutants; uptake of PFAS		Pioneering species; habitat provisioning; useful biomass; urban air purification	(Ciadamidaro et al., 2019; Dadea et al., 2017; Dickinson, 2000; Gobelius et al., 2017; GREENLAND, 2014b; Hermle et al., 2006)
Woody biomass	*Alnus* spp. (alder)	Betulaceae	Most soils in cold, temperate regions; can establish on a wide range of soils conditions		Stabilisation		Fosters nitrifying bacteria, ectomyco	Pioneering species; improves soil functionality - valuable for intercropping	(Ciadamidaro et al., 2019; Dickinson, 2000; GREENLAND, 2014b; Kidd et al.,

			including derelict land			rrhiza and AMF		2015; Zalesny et al., 2016)
Woody biomass (SRC)	*Populus alba, deltoides* spp. – (poplar) - (hybrid aspen - *P. tremula x P. tremuloids*)	Salicaceae	Loamy soils; inceptisols; well-drained soils with adequate moisture; can establish on derelict land	Worldwide	Extraction of various metals; Stabilisation	Degradation of PAHs; TNT, TCE, VOCs and POPs	Fosters AMF	Biomass, biogas, plywood, biochar; fast growing, high biomass quantity; carbon sequestration - extensive testing of clones and hybrids - deep rooting and phreatophytic	(Andersson-Sköld et al., 2013; Chalot et al., 2020; Ciadamidaro et al., 2019; Edrisi and Abhilash, 2016; Gawronski et al., 2011; GREENLAND, 2014b; Licht and Isebrands, 2005; Mehmood et al., 2017; Pandey et al., 2016; Ruttens et al., 2011; Tripathi et al., 2016a; Zalesny et al., 2016)
Woody biomass (SRC)	*Salix viminalis, alba*, spp. (willow species)	Salicaceae	Most soils in cold, temperate regions; can establish on a wide range of soils conditions including derelict land	Europe, North America, Australia - *native to Sweden*	Extraction of Cd, Cr, Mn, Fe, Ni, Cu, Zn, Pb, Rb, Sr, Ti, Co; Stabilisation	Degradation of chlorinated solvents and POPs; low uptake of DDT; organic pollutants can accumulate on leaves in urban areas e.g. PAHs, PCBs, dioxins	Fosters AMF	Biomass, biogas, plywood, biochar; fast growing, high biomass quantity; carbon sequestration, increases faunal biodiversity - extensive testing of clones and hybrids (properties vary with clone e.g. Klara, Inger, Tora) - deep rooting and phreatophytic	(Andersson-Sköld et al., 2013; Delplanque et al., 2013; Edrisi and Abhilash, 2016; Enell et al., 2016; Gawronski et al., 2011; GREENLAND, 2014b; Kidd et al., 2015; Licht and Isebrands, 2005; Mehmood et al., 2017; Mitton et al., 2012; Pandey et al., 2016; Ruttens et al., 2011; Tripathi et al., 2016a; van Slycken et al., 2013; Witters et al., 2009; Zalesny et al., 2016)