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# Phytoremediation of polluted soils and waters by native Qatari plants: Future perspectives<sup>☆</sup>

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## ABSTRACT

Because pollution is predicted to worsen and sources of quality water for agriculture and other human activities are limited, many countries have been motivated to seek novel water sources. Qatar relies on groundwater and water desalination to meet its water needs, and additional water resources will be needed to avoid unexpected crises in the future. Industrial wastewater (IWW) is an alternative water source, and much research activities should be focused on developing innovative and contemporary approaches to removing pollutants from IWW. Phytoremediation methods, shown to be efficient methods of removing and degrading contaminants of various kinds from polluted waters and soils, require knowledge of the native plants and associated microorganisms. In Qatar, many native plants (monocot and dicot, indigenous or introduced) have been shown to be greatly effective in remediating polluted areas. This article is a guide for Qatari scientists aiming to identify promising native plants and associated microbes for IWW phytoremediation. In it, we review the basic components of bioremediation and summarize the principle phytoremediation approaches and preferred recycling options. The multiple mechanisms and methods of phytoremediation for cleansing polluted soils and waters are also discussed as are details of the metabolic reactions degrading the organic components of oil and gas. Finally, heavy metal accumulation is addressed. Wastewater from industrial and domestic activities is currently being used to create green areas around Doha, Qatar, and such areas could be at risk of contamination. Many native Qatari plants and soil-dwelling microbes are efficient at removing organic and inorganic contaminants from polluted soils and waters, and some are promising candidates for achieving a clean environment free of contaminants.

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## 1. Introduction

Ecological restoration and maintenance of a healthy environment with sustainable, successful approaches to deal with environmental risks are based on five principles: (1) Information, (2) Problems, (3) Plans, (4) Solutions, and (5) Monitoring (Yasseen and Al-Thani, 2013). Multiple research centers have been actively tackling the environmental issues resulting from the detection of oil and gas in Qatari land and water, which coincided with an expansion in industrial activities and growth of urban areas. These centers have published studies focused on biological, chemical, and environmental aspects of wild and marine life, which included vegetation and flora of Qatar, and the ecology of plants, marine

biology, and the nutritional, agricultural, medicinal, and aesthetic values of plants. Also, these studies covered the eco-physiological aspects, and conservation and restoration of vegetation (Batanouny, 1981; Rizk, 1986; Rizk and Al-Nowaihi, 1989; Rizk and El-Ghazaly, 1995; Rizk et al., 1999; Abulfatih et al., 2001; Al-Easa et al., 2003; Abdel-Bari et al., 2007; Abdel-Bari, 2012). The data, information and conclusions contained in these studies have been considered as the cornerstone needed for the future research to preserve the precarious environment as a result of the expansion of oil and gas exploration, extraction and production in the Arabian Gulf region.

Water security is considered to have a major role in the food security of countries, especially those lacking natural water resources and under various threats (e.g., environmental, and political). Thus, to help solve the problems of water scarcity within the Arabian Gulf region, this article discusses the potential roles for native Qatari plants and microorganisms in the remediation of wastewater produced during various anthropogenic and industrial

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activities. In fact, oil and gas companies are disposing of industrial wastewater (IWW) by pumping it deep into the ground, removing it for the time being from the possibility of causing direct pollution of the environment. Such activities might cause serious pollution to ground water in the long run. On the other hand, Qatar often experiences severe arid conditions, lacks fresh water of rivers, lakes, streams, etc., and is surrounded by the saline water of the Arabian Gulf. The State of Qatar relies on groundwater resources (wells) to support its agriculture sector. Indeed, the seawater desalination processes to support agriculture and provide drinking water are expensive. Therefore, scientists, universities, research centers, and decision-makers are committed to utilizing all possible capabilities, including the superior financial status of the country, to establish long-term programs to maintain the lifestyle of the people and to take every possible measure to immunize the country from unforeseen threats. For example, the Government of Qatar has started a program, as a precautionary measure, of storing water in strategic reservoirs that could be used during crises and emergencies. As part of the principles to restore and maintain the environment, serious plans and solutions have been suggested to solve the problems facing the ecosystem in this region. Recently, joint projects between energy companies and research centers have been carried out to investigate the abilities of native plants and the associated microbes to improve the quality of IWW produced during the production and processing of oil and gas. However, the outcomes of these projects have not yet been published (Yasseen, 2014). Many native plants have been recognized as having mechanisms to deal with harsh environments such as salinity and water stress (Yasseen and Al-Thani, 2013; Yasseen, 2016). In recent years, important biological relationships between microorganisms and native plants have emerged, confirming that many of the bacteria species inhabiting these environments play significant roles in enabling these plants to resist those environmental conditions and perhaps pollution (Al-Thani and Yasseen, 2018a). A huge number of plants and microorganisms have been recognized for their ability to remove and/or degrade contaminants of various kinds from polluted waters and soils. In Qatar, many native plants, including those of wetlands (monocot and dicot, indigenous or introduced) along with the microbial species associated with or adjacent to them, have been shown to have great efficacy at remediating IWW and polluted areas (Al-Sulaiti et al., 2013; Yasseen, 2014). Moreover, other biological approaches have emerged in the last two decades to tackle various problems and challenges that arising at many sectors of health, the economy, and agriculture, the use of microorganisms proved particularly useful (Glick, 2014; Hanin et al., 2016; Al-Thani and Yasseen, 2018b). For example, some microorganisms have been suggested to increase the resistance of plants against abiotic stresses through solute production [such as soluble sugars, trehalose, and other compatible solutes (e.g., proline and glycinebetaine)] (Al-Thani and Yasseen, 2018a, 2018b; Yasseen et al., 2018).

Therefore, this article was designed as a guide for Qatari scientists aiming to identify promising native plants and associated microbes for the phytoremediation of IWW, bearing in mind that little has been addressed and published about this problem in this country. Thus, the review discusses the different sources of water in the State of Qatar and the impacts of IWW on various sectors of health and economy, which include chemical factors (organic and inorganic), and biotic factors (like parasites and microbes). The main part of this article is about the perspectives of the roles of native plants, including wetland plants, and the different metabolic pathways and mechanisms operating in these plants to remove, degrade and metabolize pollutants in waters and soils in this region. Finally, a summarized diagram of phytoremediation approaches and recycling options has been given.

## 2. Wastewater use in Qatar

The Arabian Gulf region in general, and Qatar in particular, have highly saline soils and little rainfall ( $\leq 152$  mm per year) (Yasseen and Al-Thani, 2013); with limited sources of good quality water. The early reports of Economic & Social Commission for Western Asia, ESCWA (1996) have shown that groundwater is the main source of water in Qatar, followed by non-conventional resources (e.g., desalination of seawater, at least two major desalination plants are operating in this country), and the treatment of wastewater (from industrial and anthropogenic activities) (Abulfatih et al., 2002). In fact, this country relies on these sources to meet its needs for agriculture sector and domestic uses. However, the groundwater discharged from wells is of variable quality and salinity, thus driving the search for alternative water resources. The priority of local authorities is to minimize the deterioration of groundwater by reducing the pumping of water from wells and to adopt other wastewater recycling options. Wastewater requires a significant number of treatments to meet the required standards for irrigation, rangeland restoration, livestock consumption, and drinking water. Two main sources of wastewater have been suggested in Qatar.

The first is treated wastewater produced from domestic and industrial activities. This water has been used to create green areas around Doha and to boost the production of forage (Abulfatih, 2002). Examples of wastewater ponds (Electronic Supplementary Materials, Figs. 1A and B and 2A and B) in Qatar are described in the Ecology of Wastewater Ponds in Qatar (Abulfatih et al., 2002).

A second alternative water source is IWW produced during oil and gas extraction. The term industrial wastewater has been used to describe liquid wastes that result from industrial processes. There are two types of industrial wastewater: (a) the wastewater that originates from geological formation and accompanies the extracted oil and gas; and (b) wastewater that is produced during oil and gas extraction and processing. These waters are considered to result from human actions. Some unpublished reports have revealed that all such industrial waters are pumped deep into the earth and might mix with groundwater, which could pose a threat to water quality in wells, which might then be used in agricultural activities. Worldwide, the volume of the wastewater produced during these processes was estimated to be more than 200 million bbl daily [bbl: Unit of volume for crude oil and petroleum products, it equals to 42 US gallons or 159 L] (Khatib and Verbeek, 2003). Some solutions and measures have been suggested to manage and deal with this huge volume of water. These include avoiding the production of water onto the surface, injecting the produced water deep into the lower layers of the Earth, treating the water in such a way that it meets international standards, reusing the water in oil and gas operations, and various agricultural and general public uses (Arthur et al., 2005; Yasseen, 2014). However, these solutions involve significant risks, and their implementation demands honest, contemporary, and innovative approaches. In Qatar, the amount of IWW might rapidly increase as gas and oil production increases.

## 3. Impacts and health issues

The impacts of IWW on humans and wildlife involve chemical (inorganic and organic) and biotic (parasites and microorganisms) factors.

### 3.1. Chemical contents

Case studies of two major ponds in Qatar reported data on the chemical composition of water and sediments (Abulfatih et al.,

2002). For example, the trace elements in wastewater and sediment samples followed the order: Mn > Cu > Cr > Pb > Ni, and Cd and Hg were close to or below the limits of detection. These elements were at the same level of control soil samples, and significantly less than the recognized upper acceptable limits for agriculture and drinking quality water (Sweileh, 2002). This study concluded that such water could be used in agriculture if other water quality requirements are met. In another investigation on the same ponds, the levels of contamination by PCBs (polychlorinated biphenyls) and TOM (total organic matter) were slight (Al-Naimi, 2002). However, with time and the continuous pumping of wastewater, organic contaminants could build up to reach dangerous levels. Industrial wastewater, on the other hand, is produced in substantial amounts annually during gas and oil extraction and processing. Such water is mainly contaminated with organic components such as petroleum hydrocarbons and heavy metals (Sale et al., 2011). In addition to the oil, industrial wastewater contains organic components such as greases, phenols, sulfides, ammonia, and suspended solids. The organic petroleum hydrocarbons are of two main types: (1) aliphatic and (2) aromatic. The aliphatic types include alkanes (like methane, ethane, propane), alkenes, alkynes, and cycloalkanes, and these compounds contain chains of carbon atoms strung together. The aromatics include mono-aromatics [such as benzene, toluene, ethylbenzene, and xylene (collectively known as BTEX)], and polycyclic aromatic hydrocarbons (PAHs; e.g., naphthalene, phenanthrene, anthracene, benzo- $\alpha$ -pyrene), which typically contain multiple benzene rings bonded together (Frick et al., 1999; Yasseen, 2014). Also, many heavy metals are found in wastewater, some of which are essential for plant growth, including Fe, Mn, Zn, Cu, Mo, and Ni. Other detected heavy metals have not been recognized as essential elements for plant growth, such as Cd, Al, V, Cr, Pb, Hg, As, Co, and Se (Taiz and Zeiger, 2010). Crude oil is rich in heavy metals such as Cd, Cr, Cu, Ni, Pb, V, Zn, etc. (Osuji and Onojake, 2004; Wake, 2005), while other heavy metals are associated with crude gas (Hg and As). Sulfur and halogen compounds (containing chlorine, Cl, and fluorine, F) and nitrogen compounds (amines, ammonia, and nitrogen oxides) are also detected (Al-Shalchi, 2005). During the last decade, some reports have concluded that organic and inorganic contaminants were accumulated with expansion in the industrial activities in the soils, waters, and air might damage the environment in the Arabian Gulf region (El Raey, 2006; Naser, 2013; Freije, 2015).

### 3.2. Microorganisms and parasites

Microbiological studies of wastewater and the moist soils around the major ponds at the outskirts of Doha City revealed the presence of coliform bacteria (*Escherichia coli*; *E. coli*) in the untreated ponds than in the treated ones (Al-Thani, 2002). These bacteria are also present in moist soils near sites where wastewater is constantly discharged. Moreover, the untreated ponds contain prominent other bacterial species that are not present at the same levels in the treated ponds. These bacteria include *Aeromonas hydrophilia*, *Pseudomonas aeruginosa*, *Klebsiella pneumoniae*, and *Chromobacterium violaceum*. Also, some other bacteria were found in the wet soils adjacent to the untreated ponds; these include *Streptomyces* sp., *Bacillus* sp., and *Macroccoccus* sp. The implications of the presence of these bacteria regarding bioremediation and phytoremediation will be discussed in the sections below (sections 4.1, 4.3, and 5.0). This study confirmed that coliform bacteria did not reach the groundwater. However, further follow up is needed to monitor the possible future impact on people and wildlife, as the treated wastewater is used to irrigate green areas and gardens, as well as the fields of some range plants (Al-Sharafi et al., 2001). Moreover, some animals (birds, fishes, frogs, and cattle) were

spotted drinking from these ponds, and the untreated ponds should be entirely avoided to protect people and wildlife from the hazardous effects of pathogens and chemical contaminants (Abulfatih et al., 2002). Parasites are an additional concern. Kardousha (2002) found that the untreated ponds and the tankers carrying such wastewater were highly polluted with *Ascaris lumbricoides* eggs, while the treated ponds were free of these eggs. However, fecal debris of some visitor cattle and livestock such as camels, sheep, and goats, and other inhabitant animals at the treated ponds contained eggs of *Trichostrongylus* sp., *Fasciola hepatica*, and *Capillaria* sp., as well as other nematodes.

Algal flora, on the other hand, can be used to evaluate the pollution status of any water body (e.g., ponds, lakes, and rivers) receiving sewage and industrial wastewater. This is because the presence of some algae can be considered as a sign of freshwater pollution (Brook, 1965; Stein, 1973; Palmer, 1980; Yasseen et al., 2001). Investigating the algal flora in some treated and untreated ponds in Qatar, Abulfatih (2002) found that cyanobacteria (blue-green algae), *Anabaena*, *Anacystis*, *Lyngbya*, *Oscillatoria*, and *Spirulina*, were dominant in these ponds, suggesting ongoing eutrophication. Moreover, some green algae were also encountered (*Chlorella*, *Oedogonium*, *Scenedesmus*, *Spirogyra*, and *Zygnema*), and diatoms were abundant. Algal scum and the extremely offensive odor from these ponds, especially the untreated ponds, is considered as a sign of high activity of anaerobic microorganisms. Other living organisms, such as ciliates and nematodes, are also found in these ponds. This study had concluded that the algal floras were different between treated and untreated ponds. For example, in the untreated ponds, the main cyanobacteria were *Oscillatoria* and *Spirulina*, and one genus of Chlorophyta; *Chlorella*. The treated ponds, on the other hand, were rich in other cyanobacteria such as *Anabaena*, *Anacystis* and one genus of Chlorophyta; *Spirogyra*. However, both ponds contained other species of algae, which were similar to each other. These studies did not detect large differences in pollution when comparing the types of ponds. However, efforts are needed to clean the wastewater so that it can be used in agriculture and municipal gardens and parks. On the other hand, studies performed elsewhere, for example in Yemen, have found that sewage water and pollution with microorganisms and parasites have reached drinking water wells, thereby creating a serious health hazard (Nasher et al., 1997). However, some differences were detected when comparing the sewage pools and well pools that had been used for irrigation of crop fields (Yasseen et al., 2001).

### 4. Phytoremediation mechanisms operating in native plants

Even though the land of Qatar is considered arid to semi-arid, with a limited number of plant species adapted to moist soils, some native plants can live as aquatic plants. Many of these native plants have proven efficient at absorbing and metabolizing pollutants, including heavy elements and organic compounds. A comprehensive survey in the literature has been done to determine the native plants, including aquatic plants, that can grow in moist soils, as well as to investigate their ability to survive in contaminated soils and waters (Abdel-Bari, 2012; Al-Sulaiti et al., 2013; Yasseen, 2014). Tables 1 and 2 list native Qatari plants, their habitats and distribution, and their possible ability to remediate heavy metals and organic components produced during various industrial activities. Many of these plants have been used worldwide as efficient remediators for various types of pollutants; however, other plants have been largely ignored or not been tested yet.

There are seven main methods and mechanisms adopted by plants, microorganisms, and algae to cope with various types of pollutants. These include (1) Rhizosphere biodegradation, (2) Phyto-stabilization, (3) Phyto-accumulation (Phyto-extraction), (4)

**Table 1**  
Native Qatari dicots that have the potential for use in the phytoremediation of moist lands.

| Plant species                 | Habitat and distribution               | Status*    | Phytoremediation                             |   | References   |
|-------------------------------|--|------------|--|---|--|
|                               |  |            | Inorganic                                    | Organic   |  |
| <i>Abutilon</i> spp.          | Sandy clayed soils                     | Int.       | Cd   | –   | Varun et al. (2015); Hammami et al. (2016)   |
| <i>Acacia</i> spp.            | Rodats, wadis & depressions            | Ind.       | As, Cu, Fe, Ni, Pb, U                        | –   | Masvodza et al. (2013); Fathi et al. (2014)  |
| <i>Amaranthus</i> spp.        | Wasteland & garden soils               | Int.       | As, Cd, Cr, Cs, Cu, Hg, Ni, Pb, Zn           | Petroleum hydrocarbons                                | Mellem (2008); Abubakar et al. (2014); Ziarati and Alaedini (2014); Mohsenzadeh and Rad (2015)                   |
| <i>Beta vulgaris</i>          | Agricultural fields                    | Int.       | Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn               | Petroleum hydrocarbons                                | Ciura et al. (2005); Oleszczuk and Baran, 2007; Laleian (2011) (website)**; Song et al. (2012)                   |
| <i>Chenopodium album</i>      | Agricultural fields                    | Int.       | Cs, Pb                                       | Hydrocarbons & organic components                     | Leicach et al. (2003); Moogouei et al., 2011; Nazli Alipour et al. (2014)  |
| <i>Citrullus colocynthis</i>  | Depressions with sandy stony soils     | Ind.       | Cd, Cr, Co, Cu, Fe, Ni, Pb, Zn               | –   | Badr et al. (2012); Ibrahim et al. (2013)  |
| <i>Cressa cretica</i>         | Moist saline soils                     | Ind.       | Heavy metals & toxic ions                    | Biodiesel   | Liang et al. (2017)  |
| <i>Datura innoxia</i>         | Cultivated fields                      | Int.       | Cd, Cr, Cu, Ni, Pb, Ni                       | –   | Wao et al., 2014   |
| <i>Erodium</i> spp.           | Moist sandy soils, shallow depressions | Ind.       | Pb, Zn                                       | –   | Mahdavian et al. (2017)  |
| <i>Euphorbia</i> spp.         | Many types of habitats                 | Int., Ind. | Cd, Cr, Cu, Pb, Zn                           | –   | Jimenez et al. (2011); Husnain et al. (2013)   |
| <i>Frankenia pulverulenta</i> | Moist saline soils                     | Ind.       | Zn & other heavy metals                      | Petroleum hydrocarbons                                | Galfati et al. (2011); Jaafari et al. (2014)   |
| <i>Geranium molle</i>         | Sandy soils                            | Ind.       | Zn & other heavy metals                      | –   | Sajad et al. (2016)  |
| <i>Lactuca</i> spp.           | Waste lands, roadsides                 | Int.       | Zn   | –   | Wazny et al. (2018)  |
| <i>Launaea</i> spp.           | Disturbed areas, roadsides             | Ind.       | –  | Oil pollution   | Malallah et al., 1998  |
| Plant species                 | Habitat and distribution               | Status*    | Phytoremediation                             |   | References   |
|                               |  |            | Inorganic                                    | Organic   |  |
| <i>Lepidium sativum</i>       | Moist ground & disturbed areas         | Int.       | Cd, Hg                                       | –   | Vakili and Aboutorab (2013); Smolinska and Rowe (2015)   |
| <i>Lycium shawii</i>          | Most habitats, not Sabkhas             | Ind.       | Cd, Cu, Ni, Pb, Zn                           | –   | Ibrahim et al. (2013)  |
| <i>Medicago</i> spp.          | Garden soils & roadsides               | Ind., Int. | Cd, Cu, Hg, Zn                               | Petroleum hydrocarbons & organic compounds            | Ciura et al. (2005); Garcia de la Torre et al. (2013); Montiel-Rozas et al. (2016)                               |
| <i>Melilotus albus</i>        | Garden soils,                          | Int.       | Heavy metals                                 | Organic compounds                                     | Halecki and Klatka, 2018   |
| <i>Nerium oleander</i>        | Moist garden soils                     | Int.       | Cr, Fe, Ni, Pb, Zn                           | –   | Trigueros et al. (2012); Elloumi et al. (2017); Khandare et al. (2017)   |
| <i>Oxalis corniculata</i>     | Moist garden soils                     | Int.       | Hg   | Polycyclic aromatic hydrocarbons                      | Peng et al. (2013); Liu et al. (2018)  |
| <i>Phyla nodiflora</i>        | Moist soils                            | Int.       | Cu, Pb, Zn                                   | –   | Yoon et al. (2006)   |
| <i>Plantago</i> spp.          | Moist depressions                      | Ind.       | Zn   | –   | Sajad et al. (2016)  |
| <i>Pluchea</i> spp.           | Moist & disturbed residential areas    | Int.       | Cr, Cu, Fe, Al, Pb, Zn                       | –   | Samanpanish et al., 2006; Majid et al., 2012   |
| <i>Portulaca oleracea</i>     | Moist areas, roadsides & fields        | Int.       | As, Cd, Cr, Fe, Zn                           | Bisphenol derivatives                                 | Tiwari et al. (2008); Okuhata et al. (2013); Tandon et al. (2014); Hammami et al. (2016)                         |
| <i>Prosopis</i> spp.          | Depressions                            | Ind.       | Cd, Cu, Ni, Zn                               | –   | Gardea-Torresdey et al. (2005); Furini et al. (2015); Bekele et al. (2018)                                       |
| <i>Ricinus communis</i>       | Irrigation canals & fields             | Cul.       | As, Cd, Pb, Mn, Ni, Cu (Leaves), & V (Roots) | Hexachlorocyclohexane (HCH), DDT, heptachlor & aldrin | Vwioko and Fashemi (2005); Vwioko et al. (2006); Niu et al. (2007); Baudhdh et al. (2015); Rissato et al. (2015) |
| Plant species                 | Habitat and distribution               | Status*    | Phytoremediation                             |   | References   |
|                               |  |            | Inorganic                                    | Organic   |  |
| <i>Scrophularia</i> spp.,     | Rain pools, shallow depressions        | Ind.       | Pb, Zn                                       | –   | Cao et al. (2008), 4th European Bioremediation Conference, 2008  |
| <i>Sida</i> spp.              | Agricultural fields                    | Int.       | Cd, Cr, Cu, Ni, Pb, Zn                       | Petroleum hydrocarbons                                | Stephen, and Ijah (2011); Ogunkunle et al. (2014); Antonkiewicz et al., 2017                                     |



|                                  |                                 |            |                            |  |   |
|----------------------------------|---------------------------------|------------|----------------------------|--|---|
| <i>Solanum</i> spp.              | Moist grounds                   | Int.       | Cd, Cu, Ni, Pb, Zn         | Polycyclic aromatic hydrocarbon                        | Yu et al. (2015); Kundan et al. (2017); Zia-ur-Rehman et al., 2017      |
| <i>Sonchus</i> spp.              | Moist areas, Fields & roadsides | Int.       | Cu, Fe, Pb, Zn             | —  | Surat et al., 2008; Fang et al. (2016)                                  |
| <i>Tamarix aphylla</i>           | Moist habitats                  | Int., Nat. | Cd, Cu, Fe, Mn, Ni, Pb, Zn | Polycyclic aromatic hydrocarbons                       | Al-Taisan (2009); Betancur et al., 2012                                 |
| <i>Teucrium polium</i>           | Saline & shallow depressions    | Ind.       | Co, Ni                     | —  | Yaman, 2014   |
| <i>Trianthema portulacastrum</i> | Moist gardens & field soils     | Int.       | Cd, Hg                     | —  | Kavitha and Jegadeesan (2014)   |
| <i>Vigna</i> spp.                | Roadsides                       | Int.       | Al, Pb                     | Petroleum hydrocarbons, dyes & other organic compounds | Masakorala et al. (2013); Jayanthi et al., 2014; Raj and Rebecca (2014) |

- No reports.

\*Status: Ind: Indigenous; Int: Introduced; Cul.: Cultivated, Nat: Naturalized.

\*\*Laleian (2011): [https://nature.berkeley.edu/classes/es196/projects/2011final/LaleianA\\_2011.pdf](https://nature.berkeley.edu/classes/es196/projects/2011final/LaleianA_2011.pdf).

Rhizo-filtration, (5) Phyto-volatilization, (6) Phyto-degradation (Phyto-transformation), and (7) Hydraulic control. The details of these mechanisms have been well documented and discussed (Pivetz, 2001; Van Epps, 2006; Erakhrumen, 2007; Yasseen, 2014). Qatari native plants and microorganisms adopt the bioremediation and phytoremediation activities in the polluted soils and water using most of these methods as shown in the following sections.

#### 4.1. Bioremediation

Microorganisms (bacteria, fungi, algae, and protozoa) play significant roles in soil biology as bio-remediators and through phytoremediation methods. In the latter approach, it is difficult to separate the microbial roles from those of the plants (Kremer, 2013; Yasseen and Al-Thani, 2013). Bioremediation methods have been suggested among the alternatives to phytoremediation techniques, which include natural attenuation and engineering techniques.

However, bioremediation could be a cost-effective clean-up technique to achieve complete or partial degradation of organic contaminants in the soil and water in the absence of plants. Two types of bioremediation (*ex situ* and *in situ*) have been adopted for successful degradation of organic pollutants into non-toxic or less toxic components (Yasseen, 2014). *In situ* bioremediation uses engineering techniques, while the *ex situ* bioremediation process is achieved by mixing the contaminated soil with water (and possibly other components) after extracting them from their location. Some details of these methods have been discussed by some authors (Frick et al., 1999; Yasseen, 2014). After the degradation is completed, water is removed from the solid phase, and the evaluation of biodegradation is monitored continuously to ensure that the process is completed successfully. Three basic components are needed for the bioremediation processes to succeed: (a) the presence of microorganisms, (b) the presence of biodegradable contaminants, and (c) the medium of bioremediation process or bioreactor (Frick et al., 1999). Microbial organisms efficient in bioremediation have been reported by many authors (Ndimele, 2010; Yasseen, 2014). However, little data have been published regarding the promising bacteria and fungi for bioremediation and phytoremediation in Qatar. Unpublished data have revealed some microbial species that might play important roles in remediating soils polluted with IWW. For example, the following species of bacteria were found in soil contaminated with IWW from the oil and gas industry: *Staphylococcus* spp., *Lactococcus lactis*, *Micrococcus luteus*, *Kocuria kristinae*, *Bacillus megaterium*, *Pseudomonas* spp., *Stenotrophomonas maltophilia*, *Sphingomonas paucimobilis*, *Burkholderia* spp., and *Enterobacter cloacae*. Yeast species found in those soils included: *Candida* spp., *Trichosporon mucoides*, *Cryptococcus* spp., *Pichia angusta*, and *Kloeckera* spp.

Therefore, any future research plans should concentrate on these species and possibly other microbes and fungi that might be found around the rhizosphere of native plants adapted to moist soils and/or aquatic life.

#### 4.2. Heavy metals

Many native plants among the flora of Qatar have been recognized as efficient phytoremediators, and Table 3 provides a list of the elements best remediated by these plants. As, Cd, Co, Cr, Cs, Cu, Fe, Hg, Mn, Ni, Pb, and Zn have been identified as the metals most remediated by these native plants.

As far as the essentiality for the plant nutrition is concerned, these elements can be classified as essential (Fe, Cu, Mn, Ni, and Zn), possibly essential (Co, B, Se, and V), and toxic and/or non-essential (Ag, Al, As, Cd, Cr, Cs, Hg, Pb, Sb, and U).

There are two main metal phytoremediation mechanisms used

**Table 2**

Native Qatari monocots that have the potential for use in the phytoremediation in moist lands.

| Plant species                 | Habitat and distribution    | Status*         | Phytoremediation                           |  | References   |
|-------------------------------|-----------------------------|-----------------|--|--|--|
|                               |                             |                 | Inorganic                                  | Organic  |  |
| <i>Aeluropus</i> spp.         | Saline sand soils           | Ind.            | Heavy metals                               | Petroleum hydrocarbons                                 | Yasseen (2014); Alavi et al. (2016); Rafiee et al. (2017)                                      |
| <i>Arundo donax</i>           | Moist and wet areas         | Int.            | As, Cd, Cu, Ni, Pb                         | –  | Alshaal et al., 2015; website**  |
| <i>Chloris gayana</i>         | Moist fields                | Int.            | Ag, As, Cd, Cu, Pb, Sb, Zn                 | –  | Keeling and Werren, 2005; Yasseen (2014)   |
| <i>Cynodon dactylon</i>       | Moist grounds               | Ind.            | As, Cd, Co, Cr, Cs, Cu, Ni, Pb, Se, Zn     | Organic components                                     | Oh et al. (2014); Mustapha et al. (2018)   |
| <i>Cyperus</i> spp.           | Moist sandy soils           | Ind., some Int. | Cd, Cr, Pb                                 | Petroleum hydrocarbons                                 | Efe and Okpali (2012); Subhashini and Swamy (2014)   |
| <i>Desmostachya bipinnata</i> | Moist grounds               | Int.            | Cd, Zn                                     | –  | Rashid et al., 2008; Liang et al. (2017)   |
| <i>Digitaria sanguinalis</i>  | Moist grounds               | Int.            | Heavy metals                               | Petroleum hydrocarbons                                 | White Jr et al. (2003); Xu et al. (2016)   |
| <i>Echinochloa</i> spp.       | Moist grounds               | Int.            | Cd, Cr, Pb                                 | Petroleum hydrocarbons                                 | Subhashini and Swamy (2014)  |
| <i>Halodule uninervis</i>     | Marine, shallow depths      | Ind.            | Cu, Fe, Ni, Pb                             | Petroleum hydrocarbons                                 | Durako et al. (1993); Bu-Olayan and Thomas (2010)  |
| <i>Halophila</i> spp.         | Marine, shallow depths      | Ind.            | Cu, Cd, Pb, Zn                             | –  | Ralph and Burchett, 1998   |
| <i>Juncus rigidus</i>         | Swamp brackish waters       | Ind.            | Heavy metals                               | Industrial wastewater & organic components             | Zahrán et al. (1979), 1993; Smialek et al. (2006); Syranidou et al. (2017)                     |
| <i>Leptochloa fusca</i>       | Wet-moist grounds           | Int.            | Pb, U                                      | Organic components                                     | Ahsan et al. (2017); Hussain et al. (2018);  |
| Plant species                 | Habitat and distribution    | Status*         | Phytoremediation                           |  | References   |
|                               |                             |                 | Inorganic                                  | Organic  |  |
| <i>Panicum coloratum</i>      | Moist wasteland             | Int.            | Heavy metals                               | Polycyclic aromatic hydrocarbons                       | Qiu et al. (1997); Balcom and Crowley (2009); Mahjoub (2014)                                   |
| <i>Phalaris</i> spp.          | Sandy clayed soils          | Ind.            | Cu, Ni, Zn                                 | –  | Korzeniowska et al. (2011); Korzeniowska and Stanisławska-Głubiak, 2018                        |
| <i>Phragmites australis</i>   | Wetland                     | Int., Nat.      | Cd, Cu, Fe, Ni, Pb, Zn                     | Oil and gas components, industrial wastewater & sewage | Nie et al. (2011); Kleche et al. (2013); Oliveira et al. (2014); Bello et al. (2018)           |
| <i>Sporobolus</i> spp.        | Saline sandy soils          | Ind.            | Heavy metals & toxic ions                  | Petroleum hydrocarbons                                 | Yasseen (2014); Mishra and Sangwan (2016)  |
| <i>Typha domingensis</i>      | wetland                     | Int.            | Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Zn | Organic components                                     | Chandra and Yadav (2010); Yasseen (2014); Bonanno and Cirellib (2017); Anning and Akoto (2018) |
| <i>Urochloa trichopus</i>     | Moist ground                | Int.            | Cd, Pb, Zn                                 | Organic compounds                                      | De Souza et al., 2017; Brandão et al., 2018  |
| <i>Zannichellia palustris</i> | Freshwater and sewage ponds | Int.            | B, & other heavy metals                    | –  | Website**  |

- No report.

\*Status: Ind: Indigenous; Int: Introduced; Cul.: Cultivated, Nat: Naturalized.

\*\*<http://www.arundo-donax.com/blog/arundo-for-phytoremediation/>.\*\*[https://www.researchgate.net/publication/303337938\\_Boron\\_removal\\_of\\_contaminated\\_water\\_by\\_two\\_aquatic\\_plants\\_Zannichellia\\_palustris\\_L\\_and\\_Ruppia\\_maritima\\_L](https://www.researchgate.net/publication/303337938_Boron_removal_of_contaminated_water_by_two_aquatic_plants_Zannichellia_palustris_L_and_Ruppia_maritima_L).

**Table 3**  
Native plants in Qatar that could be potentially used in the phytoremediation of heavy metals.

| Metal <sup>a</sup>  | Plant species  |
|---------------------|--|
| Ag                  | <b>Monocot:</b> <i>Chloris gayana</i>  |
| Al                  | <b>Dicot:</b> <i>Pluchea</i> spp., <i>Vigna</i> spp.<br><b>Monocot:</b> <i>Typha domingensis</i>   |
| As                  | <b>Dicot:</b> <i>Acacia</i> spp., <i>Amaranthus</i> spp., <i>Portulaca oleracea</i> , <i>Ricinus communis</i><br><b>Monocot:</b> <i>Arundo donax</i> , <i>Chloris gayana</i> , <i>Cynodon dactylon</i> , <i>Typha domingensis</i>  |
| B                   | <b>Monocot:</b> <i>Zannichellia palustris</i>  |
| Cd                  | <b>Dicot:</b> <i>Abutilon</i> spp., <i>Amaranthus</i> spp., <i>Beta vulgaris</i> , <i>Citrullus colocynthis</i> , <i>Datura innoxia</i> , <i>Euphorbia</i> spp., <i>Lepidium sativum</i> , <i>Lycium shawii</i> , <i>Medicago</i> spp., <i>Portulaca oleracea</i> , <i>Prosopis</i> spp., <i>Ricinus communis</i> , <i>Sida</i> spp., <i>Solanum</i> spp., <i>Tamarix aphylla</i> , <i>Trianthema portulacastrum</i><br><b>Monocot:</b> <i>Arundo donax</i> , <i>Chloris gayana</i> , <i>Cynodon dactylon</i> , <i>Cyperus</i> spp., <i>Desmostachya bipinnata</i> , <i>Echinochloa</i> spp., <i>Halophila</i> spp., <i>Phragmites australis</i> , <i>Typha domingensis</i> , <i>Urochloa trichopus</i>  |
| Co                  | <b>Dicot:</b> <i>Citrullus colocynthis</i> , <i>Teucrium polium</i><br><b>Monocot:</b> <i>Cynodon dactylon</i>   |
| Cr                  | <b>Dicot:</b> <i>Amaranthus</i> spp., <i>Beta vulgaris</i> , <i>Citrullus colocynthis</i> , <i>Datura innoxia</i> , <i>Euphorbia</i> spp., <i>Nerium oleander</i> , <i>Pluchea</i> spp., <i>Portulaca oleracea</i> , <i>Sida</i> spp.<br><b>Monocot:</b> <i>Cyperus</i> spp., <i>Cynodon dactylon</i> , <i>Echinochloa</i> spp., <i>Typha domingensis</i>  |
| Cs                  | <b>Dicot:</b> <i>Amaranthus</i> spp., <i>Chenopodium album</i><br><b>Monocot:</b> <i>Cynodon dactylon</i>  |
| Cu                  | <b>Dicot:</b> <i>Acacia</i> spp., <i>Amaranthus</i> spp., <i>Beta vulgaris</i> , <i>Citrullus colocynthis</i> , <i>Datura innoxia</i> , <i>Euphorbia</i> spp., <i>Lycium shawii</i> , <i>Medicago</i> spp., <i>Phyla nodiflora</i> , <i>Pluchea</i> spp., <i>Prosopis</i> spp., <i>Ricinus communis</i> , <i>Sida</i> spp., <i>Solanum</i> spp., <i>Sonchus</i> spp., <i>Tamarix aphylla</i><br><b>Monocot:</b> <i>Arundo donax</i> , <i>Chloris gayana</i> , <i>Cynodon dactylon</i> , <i>Halodule uninervis</i> , <i>Halophila</i> spp., <i>Phalaris</i> spp., <i>Phragmites australis</i> , <i>Typha domingensis</i>  |
| Fe                  | <b>Dicot:</b> <i>Acacia</i> spp., <i>Beta vulgaris</i> , <i>Citrullus colocynthis</i> , <i>Nerium oleander</i> , <i>Pluchea</i> spp., <i>Portulaca oleracea</i> , <i>Sonchus</i> spp., <i>Tamarix aphylla</i><br><b>Monocot:</b> <i>Halodule uninervis</i> , <i>Phragmites australis</i> , <i>Typha domingensis</i>  |
| Hg                  | <b>Dicot:</b> <i>Amaranthus</i> spp., <i>Lepidium sativum</i> , <i>Medicago</i> spp., <i>Oxalis corniculata</i> , <i>Trianthema portulacastrum</i><br><b>Monocot:</b> <i>Typha domingensis</i>   |
| Mn                  | <b>Dicot:</b> <i>Beta vulgaris</i> , <i>Ricinus communis</i> , <i>Tamarix aphylla</i><br><b>Monocot:</b> <i>Typha domingensis</i>  |
| Ni                  | <b>Dicot:</b> <i>Acacia</i> spp., <i>Amaranthus</i> spp., <i>Beta vulgaris</i> , <i>Citrullus colocynthis</i> , <i>Datura innoxia</i> , <i>Lycium shawii</i> , <i>Nerium oleander</i> , <i>Prosopis</i> spp., <i>Ricinus communis</i> , <i>Sida</i> spp., <i>Solanum</i> spp., <i>Tamarix aphylla</i> , <i>Teucrium polium</i><br><b>Monocot:</b> <i>Arundo donax</i> , <i>Cynodon dactylon</i> , <i>Halodule uninervis</i> , <i>Phalaris</i> spp., <i>Phragmites australis</i> , <i>Typha domingensis</i>   |
| Metals <sup>a</sup> | Plant species  |
| Pb                  | <b>Dicot:</b> <i>Acacia</i> spp., <i>Amaranthus</i> spp., <i>Beta vulgaris</i> , <i>Chenopodium album</i> , <i>Citrullus colocynthis</i> , <i>Datura innoxia</i> , <i>Erodium</i> spp., <i>Euphorbia</i> spp., <i>Lycium shawii</i> , <i>Nerium oleander</i> , <i>Phyla nodiflora</i> , <i>Pluchea</i> spp., <i>Ricinus communis</i> , <i>Scrophularia</i> spp., <i>Sida</i> spp., <i>Solanum</i> spp., <i>Sonchus</i> spp., <i>Tamarix aphylla</i> , <i>Vigna</i> spp.<br><b>Monocot:</b> <i>Arundo donax</i> , <i>Chloris gayana</i> , <i>Cynodon dactylon</i> , <i>Cyperus</i> spp., <i>Echinochloa</i> spp., <i>Halodule uninervis</i> , <i>Halophila</i> spp., <i>Leptochloa fusca</i> , <i>Phragmites australis</i> , <i>Typha domingensis</i> , <i>Urochloa trichopus</i> |
| Sb                  | <b>Monocot:</b> <i>Chloris gayana</i>  |
| Se                  | <b>Monocot:</b> <i>Cynodon dactylon</i>  |
| U                   | <b>Dicot:</b> <i>Acacia</i> spp.<br><b>Monocot:</b> <i>Leptochloa fusca</i>  |
| V                   | <b>Dicot:</b> <i>Ricinus communis</i>  |
| Zn                  | <b>Dicot:</b> <i>Amaranthus</i> spp., <i>Beta vulgaris</i> , <i>Citrullus colocynthis</i> , <i>Erodium</i> spp., <i>Euphorbia</i> spp., <i>Frankenia pulverulenta</i> , <i>Geranium mole</i> , <i>Halophila</i> spp., <i>Lactuca</i> spp., <i>Lycium shawii</i> , <i>Medicago</i> spp., <i>Nerium oleander</i> , <i>Phyla nodiflora</i> , <i>Plantago</i> spp., <i>Pluchea</i> spp., <i>Portulaca oleracea</i> , <i>Prosopis</i> spp., <i>Scrophularia</i> spp., <i>Sida</i> spp., <i>Solanum</i> spp., <i>Sonchus</i> spp., <i>Tamarix aphylla</i><br><b>Monocot:</b> <i>Chloris gayana</i> , <i>Cynodon dactylon</i> , <i>Desmostachya bipinnata</i> , <i>Phalaris</i> spp., <i>Phragmites australis</i> , <i>Typha domingensis</i> , <i>Urochloa trichopus</i>                |

<sup>a</sup> Other elements might also be involved in phytoremediation (such as Ba, F, Li, Mo, Sn, Ti, and W). Tables 1 and 2 include all the required references.

by plants in Qatar: (1) Phyto-extraction or phyto-accumulation, in which plants absorb elements from the contaminated soil and accumulate them in various plant organs. This mechanism is often referred to as phytomining; where the plant tissues are considered mines, and harvesting of elements from plant tissues is deemed mining; (2) Phyto-stabilization, in which metals are immobilized (e.g., by adsorption and precipitation). To achieve this, plant roots release substances into the soil; these include organic matter, phosphates, and alkalizing agents. Unless properly disposed of, metals accumulated in plant tissues might negatively impact the environment and human life (e.g., via the food chain).

Multiple data (Abdel-Bari et al., 2007; Usman et al., 2019) about the response of some native plants and cultivated crops in Qatar to soil contaminated with industrial wastewater from oil and gas fields have produced four important findings: (1) the levels of heavy metals and essential elements in the soil were at normally acceptable levels (Chapman and Pratt, 1961); (2) the concentration of these elements and metals in plant tissues were within the normal range; (3) the reduction in the growth of many crops and native plants cannot be attributed to the accumulation of heavy metals and/or the elements normally found in saline environments; and (4) some elements such as Cu, Zn and Cr were

accumulated in plant tissues, which requires further investigation using modern technology (Peng et al., 2016). Moreover, the use of crops (e.g., leafy vegetables) for phytoremediation has been reported in many studies. However, this approach is widely considered disadvantageous (Epstein, 1983; Lasat, 2000; Yasseen, 2014; Yasseen, 2016), as these crops might accumulate and introduce some of these elements into the food web either directly or indirectly (via animal meats) (Van Epps, 2006).

#### 4.3. Organic components

Many studies have described approaches to detoxify these compounds. Such methods have been referred to as the Green Liver Model because it is reminiscent of the detoxification processes that take place in the human liver (Campos et al., 2008). Multiple methods and mechanisms have been identified for the degradation of organic compounds, including petroleum hydrocarbons in the plant tissues: (1) Rhizosphere biodegradation, where microorganisms degrade organic compounds after exudates are released by the plant roots to the rhizosphere to enhance the process of degradation. (2) Phyto-volatilization, where the degradation ends with volatilized metabolites that are released into the air through the

stomata of leaves during transpiration. (3) Phyto-degradation (Phyto-transformation), which is a typical Green Liver Model. Many plants are able to metabolize organic pollutants by three main methods: (a) plants absorb the whole compounds and destroy them inside the plant tissues, (b) plants secrete some substances outside the root system to destroy these compounds; and after the degradation has occurred externally, the digested units are absorbed for further degradation, and (c) the degradation of organic compounds takes place outside the plant body through the activity of some microorganisms; their action depends upon the ability of plants to secrete substances that facilitate the degradation. In all cases, the small units of organic molecules are incorporated into metabolic pathways and become useful metabolites (Yasseen, 2014). In general, many plants that are well adapted to aquatic life and moist lands can remediate petroleum hydrocarbons and other organic compounds produced during industrial processes (Table 4). Some plants, however, might tolerate the presence of organic compounds at the rhizosphere, with their plasma membranes acting as barriers to prevent these compounds from entering the plant tissues. Such mechanisms have been found in some plants and been shown to help resist high salt stress (Yasseen and Al-Thani, 2013).

Details of the chemical components can be found in the references listed in Tables 1 and 2; these tables include all the required references.

Looking at the most available heavy metals found in crude oil and gas (As, Cd, Cr, Cu, Hg, Ni, Pb, V, and Zn), the following Qatari native plants are the most important candidates for successful phytoremediation of contaminated waters and soils: *Amaranthus* spp., *Ricinus communis*, *Typha domingensis*, *Nerium oleander* and *Phragmites australis*, bearing in mind that monitoring is implemented, as a main final step of the principles for successful ecological restoration and maintaining a healthy environment. Below, we describe some Qatari native plants that might fulfill both the Phytomining and Green Liver Model criteria, noting their principle advantages and disadvantages.

**Dicot Plants:** Mainly used to remediate moist soils.

*Ricinus communis* (castor oil plant) is considered a cultivated species in irrigated fields and canals and is efficient in phytoremediation of heavy metals and organic components. Interesting results were obtained by Vwioko and Fashemi (2005) who studied the growth response of this plant to different concentrations of spent lubricating oil (SLO). Although high concentrations (5%) of SLO reduced plant height, stem girth, leaf area, fresh and dry weights, and root length, low concentrations (1%) improved these growth parameters. These data indicate that *R. communis* might metabolize organic components to produce some intermediate metabolites that boost growth (Kvesitadze et al., 2009; Yasseen, 2014). Another study using this plant reported that under a high concentration of SLO, *R. communis* accumulated Mn, Ni, and Pb in the leaves, while V was most accumulated in the roots. Some of

these heavy metals are toxic when exceeding a certain level in the growth medium (Vwioko et al., 2006). In hydroponic systems, the ability to accumulate metals differed with species, and *R. communis* proved efficient at removing Cd and Pb from the growth medium (Niu et al., 2007). Rissato et al. (2015) found that *R. communis* is efficient at degrading and removing persistent organic pollutants (POPs); such as hexachlorocyclohexane (HCH), DDT, heptachlor, aldrin, and others. Baudh et al. (2015) identified the *Ricinus* plant as a non-edible emerging phytoremediator, which is a robust and industrially important oil yielding multipurpose shrub. In recent studies (Yasseen et al., 2018; Al-Thani and Yasseen, 2018a, 2018b), it has been suggested that the associated and adjacent microorganisms might have crucial roles in bioremediation and phytoremediation processes.

*Nerium oleander* L. is an important plant species of the family Apocynaceae (Rizk and Al-Nowaihi, 1989). *N. oleander* L. is poisonous to humans and livestock (Rizk and El-Ghazaly, 1995), but is also considered as a medicinal plant (it has been used to treat cancer, uterine stimulant, emmenagogue, abortifacient, and malaria). *N. oleander* L. could be a good candidate for phytoremediation, it was efficient in fluoride removal, as well as in removing other chemical components (e.g., phosphogypsum) and proved a good mediator for many heavy metals (Pb, Cr, Zn, Fe, and Ni) (Trigueros et al., 2012; Elloumi et al., 2017; Khandare et al., 2017). Nevertheless, the phytoremediation processes using this plant species has not yet been seriously tested in Qatar.

Four species of *Amaranthus* spp. have been recognized among the flora of Qatar. These are *Amaranthus caudatus*, *A. Graecizans*, *A. Hybridus*, *A. viridis*. The *Amaranthus* plant is an annual herb normally found in gardens, wastelands, and weed fields. Some species are common in date palm plantations, while others are found at roadsides in Doha after rains. These species were introduced with agriculture, and some are grown as a vegetable crop and considered nutritious, while others are collected as fodder and eaten as wild spinach. Studies around the world have shown that this plant is efficient in phytoremediation. For example, Mellem (2008) evaluated the potential of the phytoremediation of *A. dubius* for Cr, Hg, As, Pb, Cu, and Ni. The outcomes of this study indicated that all these metals were found in the root system, however, the ability to transport these metals to the aerial parts was variable depending on the type of element and the concentration. One important finding can be reported here that *A. dubius* is high tolerant plant to As with high ability to extract it (as hyperaccumulator) from contaminated soils, and hence can be exploited for commercialization processes. Other studies were carried out on other species of the genus *Amaranthus* in Nigeria and Iran, which have shown that it is efficient in the phyto-extraction of many heavy metals (including Pb, Cd, Cu, Ni, and Zn) (Abubakar et al., 2014; Ziarati and Alaedini, 2014), and that *Amaranthus* and its associated microorganisms (bacteria and fungi) can metabolize petroleum hydrocarbons (Mohsenzadeh and Rad, 2015). This study concluded that

**Table 4**

Native plants in Qatar that could be potentially used in the phytoremediation of petroleum hydrocarbons and other organic components.

| Component                     | Plant species   |
|-------------------------------|---|
| Petroleum hydrocarbons        | <b>Dicot:</b> <i>Amaranthus</i> spp., <i>Beta vulgaris</i> , <i>Chenopodium album</i> , <i>Frankenia pulverulenta</i> , <i>Launaea</i> spp., <i>Medicago</i> spp., <i>Oxalis corniculata</i> , <i>Sida</i> spp., <i>Solanum</i> spp., <i>Tamarix aphylla</i> , <i>Vigna</i> spp.<br><b>Monocot:</b> <i>Aeluropus</i> spp., <i>Cyperus</i> spp., <i>Digitaria sanguinalis</i> , <i>Echinochloa</i> spp., <i>Halodule uninervis</i> , <i>Juncus rigidus</i> , <i>Panicum coloratum</i> , <i>Phragmites australis</i> , <i>Sporobolus spicatus</i> |
| Industrial organic compounds  | <b>Dicot:</b> <i>Chenopodium album</i> , <i>Medicago</i> spp., <i>Melilotus albus</i> , <i>Vigna</i> spp.<br><b>Monocot:</b> <i>Cynodon dactylon</i> , <i>Juncus rigidus</i> , <i>Leptochloa fusca</i> , <i>Phragmites australis</i> , <i>Typha domingensis</i> , <i>Urochloa trichopus</i>   |
| Other organics & hydrocarbons | <b>Dicot:</b> <i>Cressa cretica</i> , <i>Launaea</i> spp., <i>Portulaca oleracea</i> , <i>Ricinus communis</i><br><b>Monocot:</b> <i>Phragmites australis</i> , <i>Typha domingensis</i>  |
| Pesticides                    | <b>Dicot:</b> <i>Ricinus communis</i>   |



phytoremediation using *A. retroflexus* and the associated fungi is more effective than either the plant or fungi separately, and that the plant roots could enhance the process of bioremediation of these fungi, possibly by secreting natural exudates to supply nutrients to the microorganisms within the rhizosphere.

Three species of the *Medicago* genus have been recognized among the flora of Qatar. These are *Medicago laciniata* (indigenous), *M. polymorpha* (indigenous), and *M. sativa* (cultivated). A large number of articles have shown that these species are efficient phytoremediation plants. For example, *M. sativa* was effective at removing Cd, Mn, Cu, Ni, Pb, and Zn from contaminated soil (Ciura et al., 2005). Adopting some modern biotechnological methods to select cultivars of *Medicago* species, Hg-tolerant cultivars were selected that might serve as source material for genetic improvement, as model cultivars to study Hg tolerance in legumes, and to develop soil phytoremediation approaches (García de la Torre et al., 2013). Another study (Marchand et al., 2014) has addressed the underground storage tanks used for the draining of waste cars, which contain many hazardous materials, including hydrocarbons, that pose a significant threat to the environment, including wildlife and human health. *M. sativa* growing in such locations showed a significant reduction in its dry biomass compared to locations not contaminated with such compounds. Other studies have addressed *M. polymorpha*, which has been tested for the remediation of heavy metals (Cd, Cu, and Zn) (Montiel-Rozas et al., 2016). This plant released low molecular weight organic acids, such as oxalic and malic acids, which proved active in alleviating the negative impact of contaminated soil with heavy metals. Other studies were conducted on *M. sativa*, for example, Marchand et al. (2016) showed that soil amendments (by compost addition) could improve the efficiency of this plant to remediate soils contaminated with petroleum hydrocarbons (PHC) and heavy metals, especially Pb. The roles of the microorganisms associated with and adjacent to plants (wild and cultivated) are crucial in the processes of phytoremediation. Yasseen (2014), in his review, discussed the roles played by native plants and legumes, such as *Medicago* spp. (as these plants can fix nitrogen, thereby boosting the rate of phytoremediation). In fact, root nodule symbiosis enables nitrogen-fixing bacteria to convert atmospheric nitrogen into ammonia, which then enters the metabolic pathways that end in amino acids and proteins. It has been proven that such a symbiotic association between *Medicago* plants and rhizobia is successful in remediating PHCs and heavy metal contaminated soils (Yan, 2012). Jadia and Fulekar (2008) conducted a study using alfalfa (*M. sativa*) to remediate soil contaminated with heavy metals (Cd, Ni, and Pb), and by providing vermicompost to the growth medium as a natural fertilizer, the remediation potential and biomass production were increased, and the uptake of many essential elements (Mg, Fe, Zn, Mn, and Cu) was increased substantially. Recently, Aroua et al. (2019) conducted a study on *M. sativa* and identified two bacteria species (*Achromobacter spanium* and *Serratia plymuthica*, isolated from the nodules) capable of photo-stabilizing pesticide-contaminated soils.

**Monocot Plants:** Monocot plants are mainly used to remediate wetlands zones.

*Phragmites australis* (common reed) is the only representative of the genus *Phragmites* among the flora of Qatar (Abdel-Bari, 2012). *P. australis* was introduced as fodder grass and became naturalized at ponds in Qatar; it is commonly found in depressions with brackish water (Electronic Supplementary Materials, Fig. 3), at sewage disposal sites, and areas of the high-water table. *P. australis* has proven efficient in the phytoremediation of soils and waters polluted with various industrial contaminants. Nie et al. (2011) studied the interactions between *P. australis* and its associated microorganisms during phytoremediation of petroleum

compounds, they found that these interactions are useful in determining the efficiency of this process. Moreover, the outcomes of this study enhance our understanding of the effects of petroleum pollution on plant-microbe interactions in the phytoremediation of petroleum-polluted soil. Kleche et al. (2013) and others have studied the ability of this plant to accumulate and transfer heavy metals (Cd, Zn, Cu, Pb, Fe, Mn, and Ni) from water polluted with discharges from industrial sources (Oliveira et al., 2014; Bello et al., 2018). They found that this plant is highly tolerant to high levels of heavy metals, has great ability to accumulate Fe and Zn and perhaps other heavy metals in the root system, and proved as a purifying power for these elements. Moreover, other recent works have confirmed the potential of *P. australis* to contribute to the phytoremediation processes in Qatar (unpublished data), and that petroleum hydrocarbons might boost the growth of this plant; *P. australis* has the ability to metabolize these compounds and resist high concentrations of heavy metals around its roots and rhizomes, as well as within the plant tissues. Therefore, for future plans to remediate waters and soils in Qatar, *P. australis* is a unique good candidate with the great potential to clean polluted water. As a fodder grass, it would be important to monitor its heavy metals content during phytoremediation (Yasseen, 2014). *P. australis* used in phytoremediation could also be used in paper, furniture, and construction industrial activities (Brix et al., 2014), and then recycling these products to avoid introducing toxic metals into the food chain.

*Typha domingensis* (southern cattail) is the only member of the *Typha* genus among the flora of Qatar. *T. domingensis* was introduced as a wetland plant and has been used widely as a fodder plant. In fact, this plant provides delicious and nutritious fruits and has edible leaves, seeds, flowers, stem, and roots. *T. domingensis* is considered the most widely distributed plant around the world, and in the Middle East, it is common in the marshes of southern Iraq (<http://www.plantsoftheworldonline.org/taxon/urn:lsid:ipni.org:names:836837-1>). Its phytoremediation potential has been tested, and proved efficient in accumulating many heavy metals, including Al, As, Cd, Cr, Cu, Fe, Hg, Mn, Ni, Pb, and Zn. Moreover, its activity has been tested in remediating organic components (Frick et al., 1999; Chandra and Yadav, 2010; Bonanno and Cirellib, 2017; Anning and Akoto, 2018; Hoang et al., 2018). The data of these works indicate that *Typha* spp. are the best for phytoremediation of metal-contaminated habitats, and have been described as useful for clean-up programs addressing environments contaminated with toxic heavy metals and petroleum hydrocarbons (Ndimele, 2010; Gomes et al., 2014; Yasseen, 2014; Chandanshive et al., 2017; Hoang et al., 2018). Therefore, future research should test the potential of this plant for remediating water contaminated with petroleum hydrocarbons.

Among the flora of Qatar, the genus *Juncus* is represented by *Juncus rigidus* (an indigenous, range plant; its local names Rasha or Tanda). This plant is found throughout Qatar; at coastlines, swamps of brackish water, in saline depressions (Electronic Supplementary Materials, Fig. 4), and across all wetland areas (Batanouny, 1981). The nutritive value of *J. rigidus* plant was reported by Al-Easa et al. (2003) as carbohydrates and fiber are the main constituents, followed by proteins, while few lipids were found in the plant tissues. Regarding the amino acids, leucine was dominant among the essential amino acids detected in *J. rigidus*; however, glutamic acid, aspartic acid, and proline were the main non-essential amino acids found in the tissues of this plant. The main heavy metal found at high concentrations in its tissues was Si, followed by Mn and Mg. *J. rigidus* is found in hot and arid regions of the world and has agro-industrial potentials, as its culms can be used in papermaking, and its nutrition values make this plant of great importance among the native plants in Qatar (Zahrán et al., 1993). Moreover, its high salt

resistance and potential in desalinating sea water make it a useful plant in removing pollutants from moist soil contaminated with heavy metals and organic components (Smialek et al., 2006; Syranidou et al., 2017). Therefore, this plant could be a good candidate for any phytoremediation program in Qatar.

Among the flora of Qatar, two species of the genus *Sporobolus* have been recognized as indigenous range plants. Both of these species (*S. ioclados* and *S. spicatus*) have a local name of Sukham. *S. ioclados* has been found at the wetland zones of both untreated and treated ponds at the outskirts of Doha City (Electronic Supplementary Materials, Fig. 5), and was tested for phytoremediation of soil contaminated with petroleum hydrocarbons (unpublished data). This plant was less affected by IWW of petroleum hydrocarbons relative to other crops (e.g., barley) and Rhodes grass (*Chloris gayana*). Thus, *S. ioclados* might be useful in phytoremediation efforts to clean soil polluted with IWW.

There are also some interesting unpublished data available from the Research Centers at Qatar University. The IWW produced during oil and gas extraction and processing in Qatar and used for agricultural purposes have introduced low levels of total petroleum hydrocarbons (TPHs) and polycyclic aromatic hydrocarbons (PAHs) to the soil, but this is assumed not to have had a major negative impact on plant growth and development. However, these data revealed that seed germination and the subsequent growth of the studied plants were substantially reduced. Moreover, improved IWW (by using sand filters to remove some of the suspended material from the crude IWW) had the same negative impact as the crude IWW. This finding suggests that the adverse effect of IWW on plant growth could be attributed to other organic components, such as MEG (mono-ethylene glycol) and KHIs (kinetic hydrate inhibitors), or possibly other components that are added during these processes (extraction and processing). Further research should be done to identify the responsible organic components and to test some native plants that have been proven efficient in phytoremediation, such as *Phragmites australis* (common reed), *Sporobolus ioclados*, *Typha domingensis*, and *Juncus rigidus*. Other native plants should also be tested, such as *Ricinus communis*, *Nerium oleander*, and *Amaranthus* spp., which are not edible for humans and cattle.

## 5. Biochemical pathways

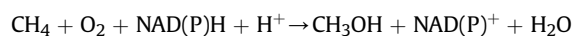
Considering the possible pathways for the degradation of organic components of IWW of oil and gas, we propose that many of these pathways are operating in the native plants of Qatar which is the best explanation of the Green Liver Model:

### 5.1. Alkane degradation

Alkanes (saturated hydrocarbons,  $C_nH_{2n+2}$ ) are a major fraction of crude oil, and the enzymes that catalyze their degradation have been identified in all domains of life, including plants and microorganisms (bacteria, fungi, yeasts). Some recent studies have provided evidence that plant-microbe interactions play crucial roles in the remediation of petroleum hydrocarbons (Gkorezis et al., 2016). However, the limits of such interactions are unclear. The degradation of alkanes in the soil-plant system depends on the soil conditions, plant species, microbes, and the type of alkane compound in this system. As nonpolar molecules, alkanes are soluble in organic solvents and slightly soluble in polar solvents (e.g., water). Therefore, their movement across the plasma membranes of plants and microorganisms depends upon their molecular weight and solubility in the lipid bilayer of the plasma membranes. Low molecular weight alkanes can easily access living cells without intervening carriers or channels. However, those of a high molecular

weight access cells either by adherence or by a surfactant-mediated process (Surfactants: compounds that interfere with two immiscible fluids, or fluids and solid to increase the contact surface areas) (Singh et al., 2012). Degradation of alkanes might take place aerobically or anaerobically, and many microbes have been reported to carry out the degradation of aliphatic compounds. These microorganisms include *Arthrobacter* sp. (Gram-positive bacteria), *Acinetobacter* sp. (Gram-negative bacteria), *Candida* sp. (Yeast), *Pseudomonas* sp. (Gram-negative bacteria), *Rhodococcus* sp. (Gram-positive bacteria), *Streptomyces* sp. (Gram-positive bacteria), *Bacillus* sp. (Gram-positive bacteria), and *Aspergillus japonicus* (Fungi, Ascomycota), among others.

The degradation of alkanes involves at least three groups of enzymes: methane monooxygenase (MMOs), alkane hydroxylase, and cytochrome P450 monooxygenase (Singh et al., 2012), which catalyze the conversion of alkanes to primary alcohols. For example, MMO is capable of catalyzing an oxidizing C–H bond in alkanes (methane as an example), in which NAD(P)H is utilized to split the O–O bond of  $O_2$ , in which one atom of oxygen is reduced to water and the second is incorporated into the substrate (methane) to yield methanol.



Early reports (Durmishidze, 1977) have discussed the pathways of detoxification of certain air-polluting organic compounds, including alkane components in plants, and the biochemical foundations of these reactions (Ndimele, 2010; Yasseen, 2014). Alkane hydroxylase is another enzyme found in some aerobic bacteria that can catalyze the degradation of alkanes to primary alcohols. The third enzyme is cytochrome P450 monooxygenase (CYP450), which has been identified in many living organisms, including bacteria and plants (Rojo, 2009). The subsequent alkane metabolism in plant cells involves alcohol dehydrogenase reactions, producing fatty acids and other metabolites that actively contribute to the plant metabolism. The general pathway can be shown:

n-alkane → Primary alcohols → Fatty acids → Acetyl – Co A → Other metabolites.

Thus, converting petroleum hydrocarbon components into useful metabolites can be considered as a crucial event in the metabolic pathways, through which dangerous toxic compounds are converted to useful metabolites by microorganisms. A specific example is the degradation of ethane (example of an alkane) to acetyl Co-A: the latter can be converted to many key metabolites of the Krebs cycle and used in the biosynthesis of fatty acids (Yasseen, 2014), as shown in Fig. 1.

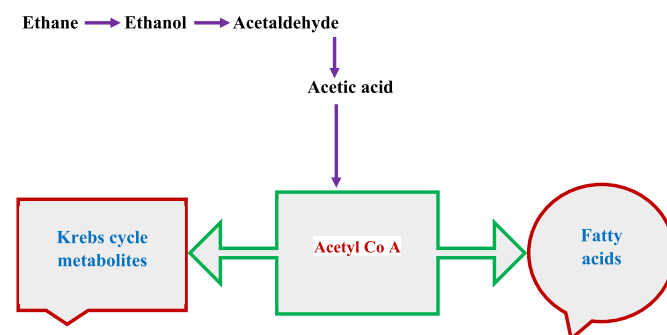


Fig. 1. The degradation of ethane to acetyl Co-A and other important metabolites.

## 5.2. Degradation of aromatic compounds

Aromatics are cyclic unsaturated hydrocarbons with alternating double bonds. The simplest aromatic hydrocarbon is benzene, which can be degraded in plant tissues, which leads to the formation of some phenolic compounds (e.g., catechol and muconic acid), and further reactions might generate important key metabolites of the Krebs cycle (TCA cycle) (Fig. 2) (Kvesitadze et al., 2009). Moreover, a good example of incomplete degradation of some organic compounds (e.g., pesticides) was reported by Sandermann (1987), who demonstrated that the transformation of organochlorine pesticides and the hydroxylation of 2,4-D is followed by conjugation with glucose and malonyl residues and subsequent deposition in vacuoles (Fig. 3).

This example suggests incomplete degradation of organic compounds; however, plants might have the ability to limit the resulting intermediate components to the vacuoles, thereby avoiding their negative impact on plant metabolism. Rissato et al. (2015) have studied the ability of castor oil plant (*Ricinus communis* L.) to remediate soils contaminated with pesticides. This plant has been used in phytoremediation processes for both heavy metals and organic compounds of various types. As a medicinal plant, Rizk and El-Ghazaly (1995) have reported many uses for *R. communis* L., including abortifacient, uterine stimulant, diuretic, carminative,

inflammation, pains, ascites, fever, and many other diseases of the respiratory and digestive systems. It is interesting to report that, despite the reported medical uses, all parts of *R. communis* L. are poisonous to humans and animals. Further studies are needed to determine the metabolites responsible for this toxicity. Also, more studies should be carried out to determine the physiological and biochemical pathways involved in the degradation of organic components during phytoremediation by native Qatari plants, especially those cultivated for medicinal, economic, industrial, and fodder purposes. It would also be wise to study the heavy metal contents of these plants to determine safe recycling options and to ensure that toxic heavy metals are kept out of the food chain.

We propose that efforts to remediate heavy metals should focus on those plants that are efficient at accumulating these elements and are not edible for humans and domestic animals (such as cattle and livestock). Other edible native plants should be tested for their ability to remediate petroleum hydrocarbons and heavy metals providing that monitoring processes are carried out efficiently to keep humans, livestock and others away from risky contaminants. As reported earlier in this review, the current levels of heavy metals in the Qatari soils and native plants are at acceptable normal range. However, the future is fraught of real risks from the continued expansion in industrial activities and by continuing pumping IWW deep into the soil, threatening the ecosystem and safety of humans and wildlife. In all cases, the extraction of heavy metals from plant tissues and their involvement in various industrial activities are the preferred recycling option. Fig. 4 summarizes the principal phytoremediation approaches.

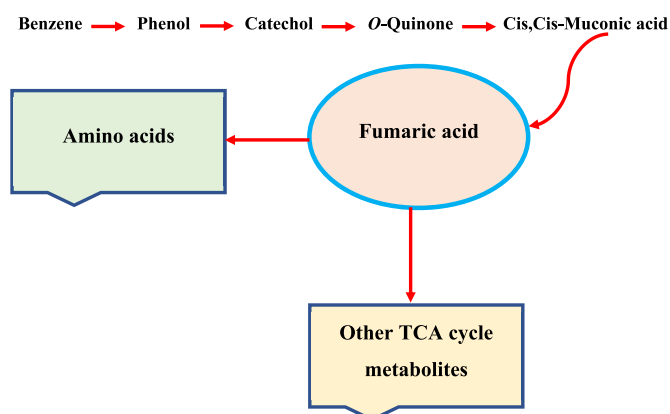


Fig. 2. The degradation of benzene in plant tissues to produce amino acids and other TCA metabolites.

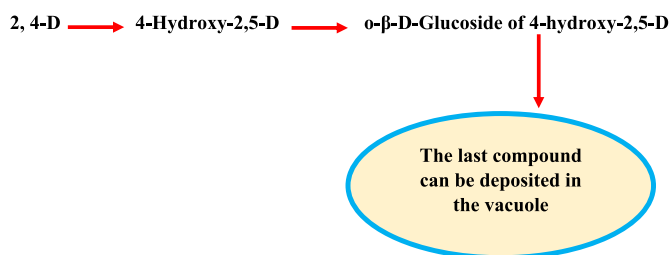
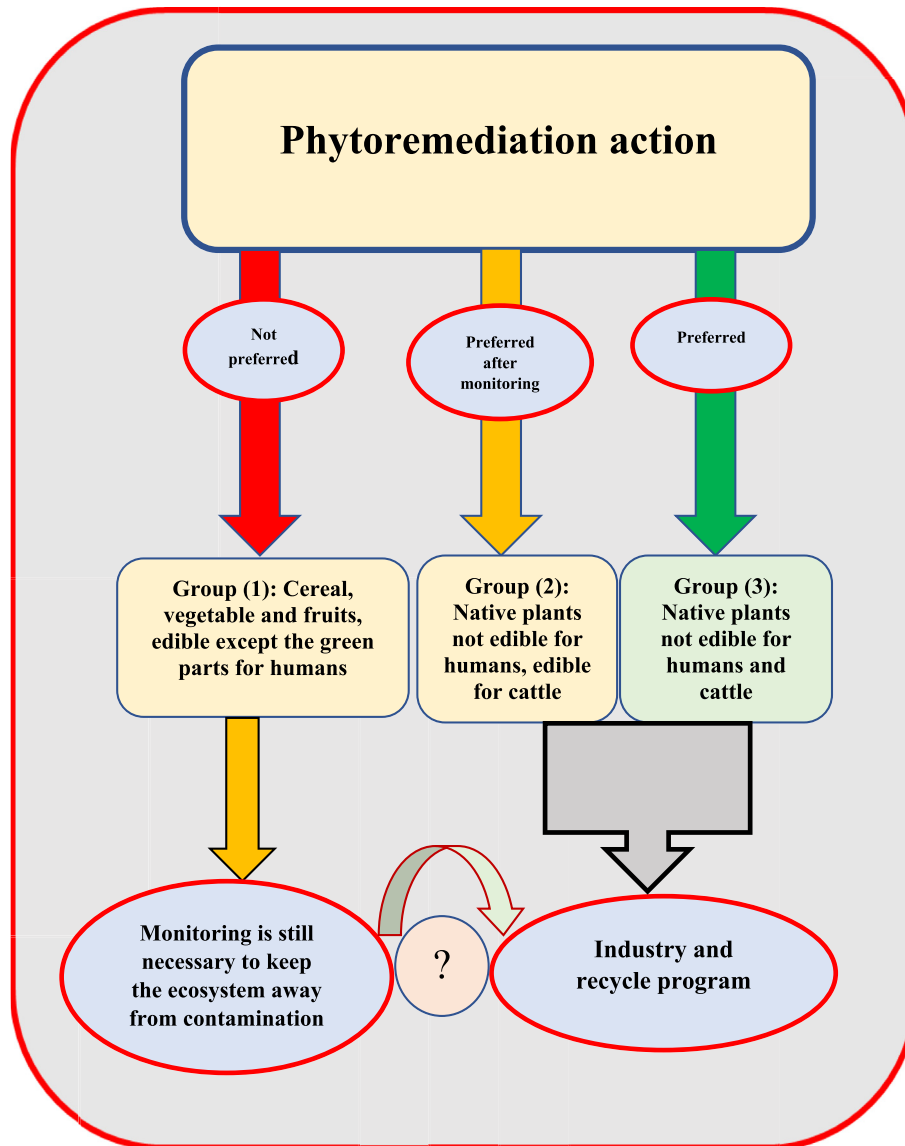


Fig. 3. Degradation of pesticides in plant tissues and deposit of the resulted metabolites in vacuoles.

## 6. Concluding remarks and future perspectives

As one of the leading gas and oil producers, Qatar is concerned about the consequences of organic and inorganic pollutants and their accumulation in soil and water. Injection of industrial wastewater deep into the ground, pumping it onto the land surface to natural ponds, or using such water in agricultural purposes would put the ecosystem at risk. Innovative and contemporary solutions are needed to address such threats. Creative scientists can use native plants and microorganisms to convert pollutants and impurities into products useful for biochemical activities. There are many prominent examples of this in nature. For example, photosynthesis reduces the risk of CO<sub>2</sub> accumulation by converting it into food and producing O<sub>2</sub>. Therefore, serious work should be done to test the ability of these native plants (and their associated microorganisms) to remediate inorganic and organic components. In fact, seeking for standards from plants and microbes which have the potential for use in bioremediation and phytoremediation have been encountered with many difficulties, which can be summarized as (1) various pollutants affecting the ecosystem (organic and inorganic); IWW is of various characteristics and chemical composition, (2) plants have different methods and techniques of phytoremediation, (3) plants react differently to pollution in water, soil and air, (4) different environmental conditions of the experiments, (5) different techniques used in the experiments of phytoremediation, (6) various microorganisms associated with plants interact differently which might affect the efficiency of plants to remove, degrade, and metabolize pollutants, (7) other variables might affect the process; need to be explored. However, we propose that the following candidate species should be prioritized in future research; *Aeluropus* spp., *Amaranthus* spp., *Beta vulgaris*, *Chenopodium album*, *Cyperus* spp., *Digitaria sanguinalis*, *Echinochloa* spp., *Frankenia pulverulenta*, *Halodule uninervis*, *Juncus rigidus*, *Launaea* spp., *Medicago* spp., *Oxalis corniculata*, *Panicum coloratum*, *Phragmites australis*, *Ricinus communis*, *Nerium oleander*, *Sida* spp., *Solanum* spp., *Sporobolus* spp., *Tamarix aphylla*, *Typha domingensis*, and



**Fig. 4.** Possible phytoremediation approaches to protecting the ecosystem from pollution. Some examples of plant groups: Group (1): *Hordeum* spp., *Triticum* spp., *Zea mays*, etc.; Group (2): *Medicago* spp., *Phragmites australis*, *Typha domingensis*, *Juncus rigidus*, *Sporobolus* spp., *Chloris gayana* etc.; Group (3): *Ricinus communis*, *Nerium oleander*, etc.

*Vigna* spp. Also, much work still needs to be done to identify the microorganisms that are associated with these native plants.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envpol.2019.113694>.

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