Chapter 14
Bioremediation of Soil Contaminated with Arsenic

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Abstract Human-industrial activity causes a remarkable increase in the arsenic (As) environmental concentrations, with a potential impact in plant and animal health, and may cause severe losses in biodiversity. This metalloid is bioaccumulative through the food chain and highly associated with different types of cancers. To overcome the inherent drawbacks of physicochemical removal techniques, biological treatments arose as adequate and cost-effective remediation alternatives for As pollution. An interest arises from the endophytes, which live inside the host plant and have been studied for their plant growth-promoting properties, production of bioactive molecules, biocontrol processes, and As detoxification. The integration of bioremediation with multiple omic technologies provides, moreover, innovative

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approaches to handle As remediation. The aim of this review is to show the latest knowledge, advances, and applications in arsenic bioremoval. We will focus on the following items: (1) human and environmental health, (2) biological tools for remediation with an emphasis in plants-microbiome interactions and omic technologies, (3) advances in As speciation analysis, and (4) As biosensors.

Keywords Arsenic · Bioremediation. · Bioreactors · Analytical methods · Omics · Biosensor.

14.1 Introduction

Living soils house the largest deposit of genes from fungi, bacteria, protozoa, invertebrates, algae, etc. Therefore, the soil is considered the most dynamic, complex, and biodiverse habitat that exists providing many benefits for humans (Wall et al. 2015). However, they are subjected to important human disturbance being the main global change driver (Smith et al. 2016). Degraded soils cover 24% of the global land area (35 Mkm^2; Bai et al. 2008) and one third are polluted. The intense anthropogenic activities and the expansion of the industry have led to a large-scale increase in the release of toxic metals (As, Cr, Pb, Hg, Cd, U, etc.) into the environment (Horta et al. 2015). Toxic metals have affected the dynamics of the complex ecosystems present in the pedosphere, due to its toxicity, nonbiodegradable nature, and bioaccumulation capacity throughout the food chain (Gall et al. 2015). Arsenic (As) is a metalloid widely distributed occurring both in organic and inorganic forms and in natural and anthropogenic environments (soil and water). As are present in soils under different chemical forms or types of binding, which affect its bioavailability, mobility, and toxicity, due to its transfer to aquatic media and uptake by plants, with the subsequent introduction into the food chain (Zhao et al. 2010). The forms of As present in soils depend on the type and amounts of sorbing components of the soil, the pH, and the redox potential (Anawar et al. 2018). Thus, As(V) is the main As species in aerobic soils. It has a strong affinity for iron oxides/hydroxides in soil; therefore, the concentrations of arsenate in soil solutions are usually low (Zhao et al. 2010). However, in reducing environments such as flooded paddy soils, As(III) is the dominant As species. In fact, flooding of paddy soils leads to mobilization of arsenite into the soil solution and enhanced As bioavailability (Kumarathilaka et al. 2018). Regarding organic species of As (DMA, MMA, and TMAO), they also can be found in soils although their concentrations usually account for less than 5% of As total (Huang et al. 2011).

Since the beginning of the twentieth century, As was known as a causal factor of different types of cancers (O'Donovan 1924). However, it was not until the 1970s when scientific interest in the presence of As in the soil began as a potential source of this carcinogen (Fig. 14.1). Hot spots in the As distribution are South and North America, Asia, and Central Africa (Amini et al. 2008). Among the main anthropo-

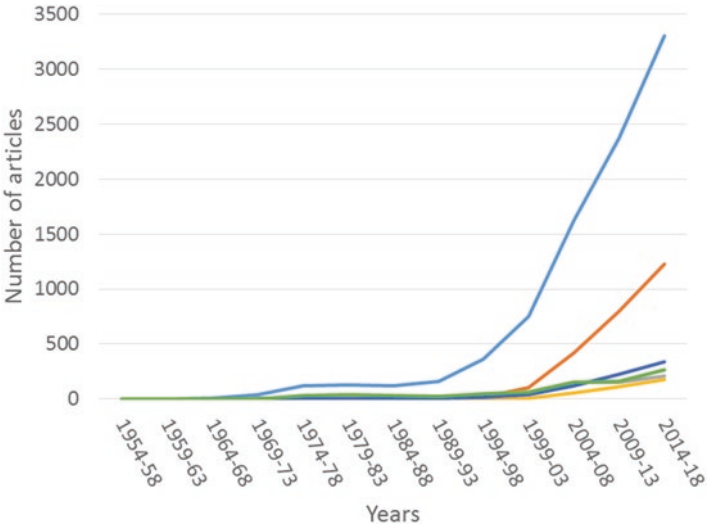

Fig. 14.1 Scientific production in terms of number of published papers whose subject was: As contaminated soils (*sensu lato*) (ligh blue), As and phytoremediation (orange), As and mycoremediation (gray), As and rizhosphere (yellow), As contaminated soils and prokaryotes (dark blue), As and microbiome from plant metaorganism (green)

genic sources of As in the environment, we can highlight the smelting of metals (specially copper), pharmaceutics and medical waste incineration, manufacturing, pesticides, cattle care, dyeing activity, fossil fuel utilization, wood burning, and semiconductor production, among others (Wang et al. 2017a; Gupta et al. 2019; Murcott 2012; Government of New South Wales 2017; Kant 2012; Shankar et al. 2014). The environmental impact of As is mainly displayed in two ways: (i) the in situ impact, as a contaminant in soil, air, and water – not only affecting biodiversity in animals and plants but also modifying or limiting microbial populations – and (ii) its presence in food chain, as a potent toxic and carcinogen, affecting human health. Both aspects are intimately related since As arrives at the food chain via plant uptake and vegetable accumulation that, at the same time, affects the feeding of farmed animals (Santra et al. 2013).

There are several physicochemical methods capable of removing As from contaminated water such as membranes, coagulation, anion exchange, disposable iron media, and softening adsorption (Bibi et al. 2017; Nidheesh and Singh 2017; Wang et al. 2018). However, the elimination or stabilization of As in contaminated soils is not feasible, in most cases, using this type of treatment. The use of indigenous organisms (mainly plants, fungi, and prokaryotes) to eliminate or stabilize the As of soils, through their metabolism, started in the 1990s (Fig. 14.1), and it has proved to be a successful eco-friendly option. Different terms have been used to describe the process to clean up contaminated environments based on the major microorganism responsible for recovery. As a general rule, when the biological agent is used, the term utilized is “bioremediation” (Kumar et al. 2011); but this term is also used when

sensu stricto microorganisms are employed (Sing 2014). The utilization of plants to remove the pollutants is known as "phytoremediation" (Wang et al. 2011), and the use of fungi is named "mycoremediation" (Barrech et al. 2018). The contribution of these techniques to the contaminated soils' recovery is shown in Fig. 14.1. The uptake and accumulation capacity of As in plants varies widely, from plants known as "excluders" that have limited capacity of As translocation from roots to leaves to "hyperaccumulator" species that are able to uptake and translocate large amount of As to different plant tissues. The presence of As in plants was first described by Hengl et al. (1930), but has not been considered as an approach to remove pollutants from the environment until the end of the twentieth century (Fig. 14.1). Phytoremediation can also be divided into diverse techniques (Ma et al. 2016) depending if the pollutant is converted into less toxic forms (phytodegradation) and volatile species (phytovolatilization), accumulated in the aerial part (phytoextraction), accumulated in the root (phytostabilization), or metabolized by the rhizosphere microorganisms (rhizodegradation; Tangahu et al. 2011). The different strategies (bio-, phyto-, and mycoremediation) are frequently addressed in isolation; however, an implementation in the recovery systems requires the assembly of all elements of the system. Interactions between plants and microorganisms show complex interactions playing a pivotal role in the removal of toxic metals (Basu et al. 2018).

As-tolerant microbes have been already described more than a century ago (Green 1918; Green and Kestell 1920; Thom and Raper 1932). Current efforts have been focused in the identification of genes involved in As metabolism (Dowdle et al. 1996), the conversion to volatile species (Qin et al. 2006), and the genetic modification of microorganisms to improve their As tolerance (Kostal et al. 2004). Although the scientific studies are still scarce (Fig. 14.1), there is clear evidence that it may be possible to optimize bioremediation technologies. Emerging integrative approaches, such as (meta-)genomics, (meta-)transcriptomics, (meta-)bolomics, and (meta-)proteomics studies, are powerful tools to sequence partially or completely the As-metabolizing bacteria genome (Maizel et al. 2015) and to study the metagenome in As-contaminated soil (Luo et al. 2014) and the proteomic response to As stress (Belfiore et al. 2013). In summary, the eruption of omic and high-throughput technologies in bioremediation represents a pool of innovative methods that allows us to handle deep analysis and large amounts of data in each experiment (Fig. 14.2).

Chemical and geological analysis (Rinklebe et al. 2016) in combination with genomic and metagenomic techniques will provide insights into the specific roles of the complex biochemical pathways in the global As biogeochemical cycle. In addition, transcriptomic and proteomic techniques enable the scrutiny of the expression of those marker genes as indicators of enzymatic activity in response to the presence of As species, and metabolomic technologies inform about the As-derivative synthetized during the metabolic network established (Zhu et al. 2017; see Fig. 14.2). Other innovative technologies are underway in this subject, such as modeling of attenuation and environmental fate (Wallis et al. 2010), the use of nanoparticles in

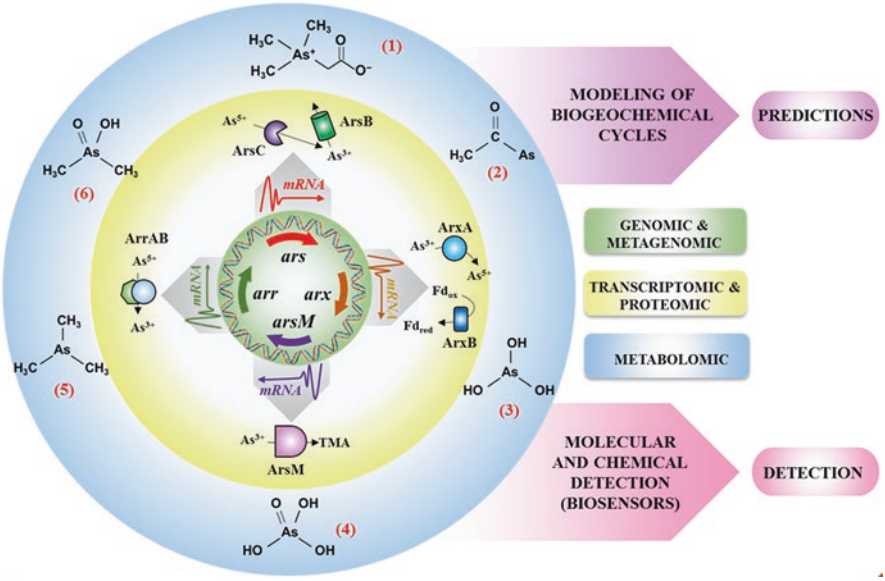

Fig. 14.2 General scheme of analytical technologies useful on arsenic bioremediation. Genomic techniques are represented in the green circle, and some examples of marker genes are presented: *ars* (arsenic resistance), *arr* (respiration of arsenate), *arx* (oxidation of arsenite) or *arsM* (methylation of arsenic species). Transcriptomic and proteomic are represented in the yellow circle: the clusters of genes are transcribed (zig-zag line) and the functions of the transcribed genes are cartooned. ArsC reduces arsenate (As^{5+}) to arsenite (As^{3+}) that is exported out of the cell by ArsB. ArxA oxidizes arsenite to arsenate with the collaboration of ArxB assisted by an oxidized ferredoxin (Fd_{ox}) that is then transformed into reduced ferredoxin (Fd_{red}). ArsM methylates arsenite to trimethylarsine (TMA) and the ArrAB proteins reduces arsenate into arsenite in a respiratory event. The blue circle represents some of the arsenic derivative metabolites produced as a consequence of the metabolism of arsenic compounds. Some examples are presented: arsenobetaine (1), acetylarsenic (2), arsenite (3), arsenate (4), trimethylarsine (5) and cacodylic acid (6). All the information obtained from the *omic* technologies can be used as support to develop molecular and chemical detection system (biosensor) and to perform predictions of environmental dynamics based on biochemical cycles modeling

controlling As mobilization (Gil-Díaz et al. 2014; Huang et al. 2018), process improvement through the use of organic amendments (Beesley et al. 2014; Onireti et al. 2017), bioaugmentation and biostimulation techniques (Chen et al. 2017a), or the use of dual-sensing bioreporters (Yoon et al. 2016).

There are many perspectives of analysis to approach the problem of the As contamination in soil environments. In the present chapter, we will focus on the following items: human and environmental health, biological tools for remediation, and advances in analytical and detection methods.

14.2 Human and Environmental Health

There is a major concern caused by environmental and health risks associated with the natural or anthropogenic widespread presence of As in soils and further migration to underground and surface waters worldwide. Therefore, the World Health Organization (WHO 2016) set up a safe limit of 10 μg/L for As concentration in drinking water. Dietary exposure to As, especially of inorganic As (iAs) forms, which are the most toxic forms, is a major concern in human health (EFSA 2014). Long-term exposures to As from drinking water and food can cause minor skin lesions, but it has also been associated with cardiovascular disease and diabetes. In addition, it is a known carcinogen able to cause skin, lung, bladder, liver, or kidney tumors, being lung cancer the most common cause of As-related mortality (WHO 2018). The greatest As threat to public health is related to groundwater contamination. As is naturally present at hazardous concentrations in the groundwater of many countries, including Argentina, Bangladesh, Chile, China, India, Mexico, and the United States. Drinking water, crops irrigated with contaminated water and/or growing in contaminated soil, and food prepared with contaminated water are the main sources of exposure. Figure 14.3 shows ranges and boundaries in total As concentrations detected in different water (Fig. 14.3a) and terrestrial (Fig. 14.3b)

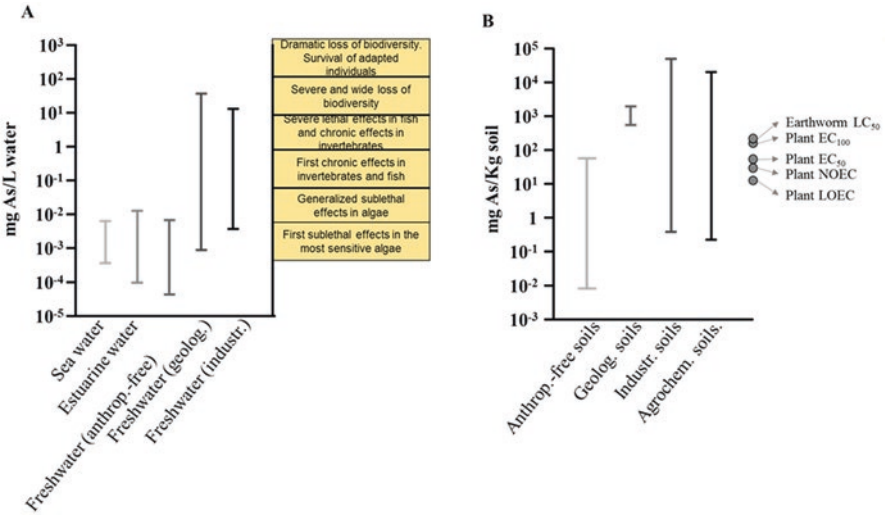

Fig. 14.3 Concentrations of arsenic in water (A) and soils (B), and its general biological effects. Data obtained from WHO (2001) report. Abbreviations: (i) 'anthrop.-free' means: anthropogenic input unlikely; (ii) 'geolog.' means: volcanic/geothermal origin; (iii) 'industry.' means: mining/chemical manufacture; (iv) 'agrochem.' means: treated with pesticides, sheep dips; (v) LC/EC mean: lethal/effective concentration; (vi) NOEC/LOEC mean: No observed/Lowest observed effect concentration; (vii) EC50/EC100 mean: concentration of a substance (toxic) at which 50%/100% of the population are affected; (viii) LC50 means: concentration of a substance causing dead in a 50% of the population

environments, indicating some reference values related to its general biological effect. As expected, the human-industrial activity causes a remarkable increase in the environmental concentrations of As, enhancing its potential impact in animal and plant health, even promoting severe losses in biodiversity (WHO 2018). Unfortunately, the majority of the data available from public surveys is still reported as total As, without information of the different As species present in the samples. Consequently, a risk assessment not considering the different species would lead to an overestimation of the health risk related to dietary As exposure. However, as reported by Yang et al. (2018) in a study performed in soils from China, the carcinogenic risk of As was found as relatively unacceptable in both industrial and agricultural regions.

Ingestion of As derivatives has been established as the main exposure pathway followed by dermal absorption. The general hazardous risk of noncarcinogenic As effects in human populations is in the following order: children, adult females, and adult males. However, adult females have the highest As-associated carcinogenic risk followed by adult males and children. For all the age classes except infants and toddlers, the main contributors to dietary exposure to iAs are foods belonging to "grain-based processed products" (in particular, wheat bread and rolls, rice, and rice-derived). Other food groups that contribute to iAs exposure are milk and dairy products (especially in infants and toddlers), vegetables, shellfish and seaweeds, and drinking water (Fig. 14.4). It is estimated that, in the United States and especially among the Native American communities, there are more than two million people who are exposed to concentrations higher than the maximum contaminant level allowed (>10 μg/L, according to the Environmental Protection Agency)

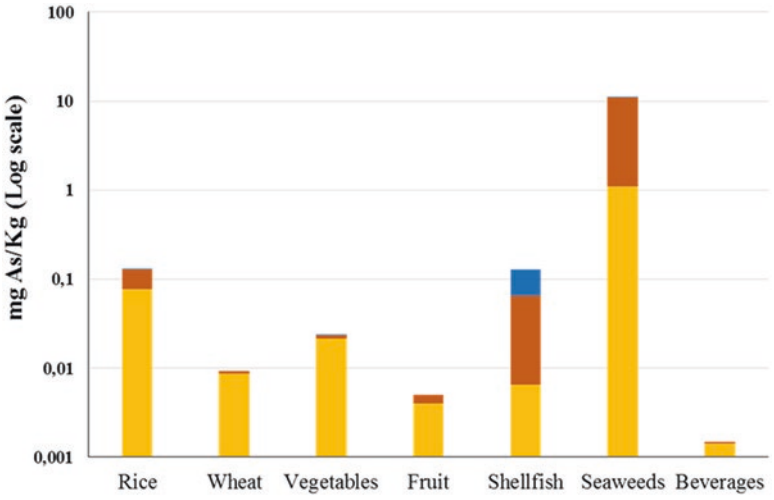

Fig. 14.4 Concentration and species distribution of As in food defined as major contributors of inorganic As (iAs), highly toxic (yellow), organic As (usually methylated) less toxic (brown) and non-toxic organic As (blue). Data obtained from Cubadda et al. (2017) and Lynch et al. (2014)

(Powers et al. 2019). Millions more are exposed to As below this concentration (Amini et al. 2008), which is of concern since the evidence suggests that there is no safe threshold (Schmidt 2014). The consumption of drinking water with moderate concentration of As, which is estimated to affect about 100 million people globally, may lead to a broad range of diseases from skin lesions to circulatory, respiratory, reproductive, and neurological complications, diabetes, hepatic, and renal dysfunction, and most of them may lead to the development of malignant tumors (Chen et al. 2009; reviewed in Abdul et al. 2015). Thus, it is possible to distinguish the effects of As on human health depending on the organ system affected. Different symptoms may appear in different parts of the integumentary system, where the skin is known to be particularly susceptible, showing the initial manifestations of As poisoning. With higher frequency in men than in women, and usually appearing 5–10 years after the exposure, the most common skin injuries are pigmentation, melanosis, and keratosis (Lindberg et al. 2008; Rahman et al. 2009). The brain appears to be a key target of As toxicity since its permeability through the blood-brain barrier. Both acute and chronic exposures to As may lead to central and peripheral neuropathies, but it typically affects peripheral nerves causing symptoms such as paresthesia, pain, and numbness in the limbs (Vahidnia et al. 2007; Mathew et al. 2010). The main mechanisms related to As-induced neurotoxicity are oxidative stress, disorganization of cytoskeletal structure, and neuronal apoptosis (via p38 and JNK kinases expression; Mundey et al. 2013; Namgung and Xia 2001).

Inhalation of As is not as common as its ingestion; however, some reports link mineral mining with a respiratory illness such as chronic cough, laryngitis, bronchitis, and rhinitis as a consequence of As exposure (Parvez et al. 2010). Moreover, long-term inhalation and ingestion of iAs could have deleterious effects on cardiovascular system functioning (Lewtas 2007) demonstrating a strong correlation between As exposure and atherosclerosis (via atherogenesis) and, although still debated, hypertension (Simeonova and Luster 2004). Since its metabolism/detoxification in the human body takes place in the liver, hepatic lesions may appear as a result of As acute and chronic exposure. Several injuries may occur depending on the doses of exposure. Hepatic diseases range from liver enlargement to more severe complications such as hepatic fibrosis, noncirrhotic portal fibrosis, cirrhosis, and liver cancer and sometimes lead to liver failure (Liu et al. 2002; Kapaj et al. 2006). Direct induction of apoptosis and oxidative stress are, again, among others, the main mechanisms involved in As-related hepatic toxicity and might also affect the renal system during the process of As elimination.

Finally, As can also affect the reproductive system causing infertility problems. In males, gonad dysfunction appears through a reduced synthesis of testosterone and cell apoptosis/necrosis (Davila-Esqueda et al. 2012; Shen et al. 2013). In females, As exposure through drinking water during pregnancy causes complications from premature delivery to fetal loss (Chakraborti et al. 2003). As a teratogen, As can also affect fetus development, producing growth retardation or fetal death, but in most cases, birth defects are accumulated leading to an increase of infant mortality (Wu et al. 2011).

14.3 Biological Tools for Remediation

14.3.1 Microorganisms in As-Contaminated Soil

The heavy metal and metalloid toxicity is a consequence of their affinity for different cellular components by forming metal-biomolecule complexes that might cause diverse adverse effects. At high concentrations, heavy metals and metalloids can inhibit essential metabolic functions and cause cell death (Hobman and Crossman 2014; Silver and Hobman 2007). To survive in environments contaminated with heavy metals, microorganisms have developed resistance or tolerance to high levels of these metals (Ahmed 2012), and many specific genes have been detected for resistance to toxic ions of heavy metals. It is possible to ascribe the microorganism resistance mechanisms to two classes: (i) the first depends on cellular metabolic activity, processes of oxidation, reduction, methylation, secretion, or intracellular accumulation, and (ii) the second mechanism does not depend on this metabolic activity; it is a passive process of uptake mediated by cell wall components, exopolysaccharides, proteins, or siderophores (Rajendran et al. 2003).

Genes responsible for As resistance have been described in many isolated microorganisms (Zhu et al. 2014) and also in environmental metagenomic samples (Zhu et al. 2017). Arsenate (AsV) and arsenite (AsIII) enter into the cell most probably through phosphate (Pi) transporters and aquaglyceroporins, respectively. The more widely spread genes in bacteria are organized in the *ars* cluster (Fig. 14.2), mainly arranged as *arsRCDAB* (Stolz et al. 2006; Ben Fekih et al. 2018). The *arsR* gene encodes a transcriptional repressor that controls the whole cluster (Busenlehner et al. 2003) and responds to the arsenite as inducer (Wu and Rosen 1993); *arsC* gene encodes the arsenate reductase responsible for the reduction of arsenate to arsenite (Mukhopadhyay et al. 2002); *arsAB* genes encode the energy-dependent arsenite translocator (Rosen 1999; 2002); and gene *arsD* encodes a metallochaperone that increases affinity of the transporter ArsAB for the arsenite (Lin et al. 2007). In addition to the *ars* genes of As resistance, some bacteria are able to use arsenate as an electron acceptor or arsenite as an electron donor. The *arr* genes are responsible for the anaerobic respiratory reduction of arsenate to arsenite (Silver and Phung 2005), and the arsenotrophic oxidation of arsenite is a transformation that can occur in oxic or anoxic conditions catalyzed by arsenite oxidases encoded by either the *aio* cluster (aerobic environments) or the *arx* cluster (anaerobic environments) (van Lis et al. 2013; Zargar et al. 2010). There are other genes with strong relevance in As resistance but less represented in microorganisms. Some bacteria, for example, are able to methylate As oxyanions with the participation of enzymes coded by *arsM* or *arsH* (Bentley and Chasteen 2002; Yuan et al. 2008; Ye et al. 2007). The presence of these genes can be detected by genetic analysis after isolation and cultivation of bacteria or by screening through metagenomic technologies that can analyze total DNA present in a given amount of soil. However, the As-resistant genes are widespread in nature, and their presence is not a conclusive probe to determine a record of As contamination in a given environment. Nevertheless, most of As-resistant

genes are organized in clusters tightly controlled by regulators that ensure their expression only when As compounds are present in the medium (Andres and Bertin 2016). Thus, the environmental transcriptomic analysis can be used as a powerful tool to monitor bacterial activity in As-contaminated environments (Sun et al. 2004; Evans 2015). Besides the identification of the expression of genes related to the As resistance, environmental metabolomic is a comprehensive method able to detect metabolites released by microorganisms into the environment (VerBerkmoes et al. 2009). Thus, metabolomic analysis is a powerful tool to detect marker analytes in soils or water that unequivocally can be correlated with bacterial As metabolism such as methylated compounds [mono-(MMA), di-(DMA), tri-methylarsenic acid, trimethylarsine oxide (TMAO)] or volatile compounds like trimethylarsine (TMA) (Bentley and Chasteen 2002; Qin et al. 2006). Moreover, the recent understanding of the role of some As-derivative metabolites synthetized by bacteria such as arsenobetaine (Hoffmann et al. 2018), arsenosugars (Xue et al. 2018), or many other organoarsenic compounds (Chen and Rosen 2016) might also increase the number of molecules that can be used as markers of enzymatic transformation of As species in environmental samples.

From the above, integrating all the multiple omic technologies become crucial to elucidate the dynamic and complex interactions between microbial communities and the As biogeochemical cycle in the environment (Zhu et al. 2017). Interestingly, modeling approaches linking all omic data analyses will also predict the dynamics of As species in soil and waters providing capable tools to improve remediation technologies (Dunivin et al. 2018).

14.3.2 Plant Growth-Promoting Microorganisms (PGPMOs) to Improve Phytoremediation Approaches

Recent studies have shown that plant microbiomes (archaea, bacteria, protists, fungi, and viruses) and their symbiotic interactions play important roles in plant growth and response to abiotic and biotic stresses, helping to adapt the plant to the niche occupied (Mueller and Sachs 2015; Sim et al. 2019). In particular, plant growth-promoting microorganisms (PGPMOs) are a variety of microbes such as bacteria, cyanobacteria, and fungi including arbuscular mycorrhizal fungi (Mishra et al. 2017), representing 80% of the plants. PGPMOs are actively involved in plants growth and yield buffering the biotic and abiotic stress through diverse mechanisms, such as pathogen protection, phytohormone production, and nutrient acquisition (Vacheron et al. 2013, Ma et al. 2016, Martínez-Hidalgo and Hirsch 2017). Pathogen defense can be carried out directly through the production of antibiotics or enzymes that affect the growth of the pathogen such as β-glucanase chitinases (Martínez-Hidalgo et al. 2014, Martínez-Hidalgo et al. 2017) or indirectly by inducing the defensive systems of plants (Martínez-Hidalgo et al. 2015). PGPMOs are important producers of phytohormones such as auxin, gibberellin, and cytokinin that directly

affect the growth of plants (Olanrewaju et al. 2017). The production of siderophores by the PGPMOs occurs under Fe-limiting conditions improving the uptake of Fe in the form of ferric ions (Fe^{3+}) and the increase in bioavailability of other essential nitrates through mineralization of organic matter that improves the nutrition and growth (Martínez-Hidalgo et al. 2014; Johnstone and Nolan 2015; Etesami 2018). Different studies conducted using various bacteria have shown that PGPMOs improve both plant growth and tolerance to As. The As stabilization and elimination mechanisms in these helper microorganisms seem similar to those described in non-symbiotic fungi and bacteria (Molina et al., in press). The number of publications on the successful application of endophytic microorganism inoculants to plants for bioremediation is extensive and increasing (Fig. 14.1). A plethora of bacteria such as *Kocuria* sp. and *Bacillus* sp. (Mallick et al. 2018), *Variovorax* sp. and *Phyllobacterium* sp. (Mesa et al. 2017), *Agrobacterium radiobacter* (Wang et al. 2011), *Rhizoglomus intraradices* and *Glomus etunicatum* (Wang et al. 2011; Wu et al. 2015; Spagnoletti and Lavado 2015), *Enterobacter* sp. (Nie et al. 2002), or *Bacillus thuringiensis* (Babu et al. 2013) have shown to be PGPMOs and offer resistance to As. In addition, fungi associated with plants such as *Trichoderma* (Tripathi et al. 2017) or *Piriformospora indica* (Mohd et al. 2017) and arbuscular mycorrhizal (AM) fungi (Chen et al. 2017b) have shown to be good candidates as PGPM reducing the As stress to the host plants. Despite this fact, the problems associated with heavy metal and metalloid contamination, particularly with As, are numerous, and its investigation should not be neglected. Recently, the posttranscriptional regulation of gene expression using RNA-induced silencing complexes (RISCs) mediated by siRNAs (noncoding RNA molecules involved gene expression regulation) has been considered as a potential tool to improve the plant-PGPMO interaction and bioremediation in heavy metal-contaminated soils. Other tools recently discovered are the riboswitches (RNA elements) that regulate mRNA expression and the ribozymes (catalytic RNAs) able to initiate or inhibit gene expression. These new tools are becoming powerful for bioremediation studies providing clear mechanisms of gene regulations (Du Toit 2015; Furukawa et al. 2015; Topp and Gallivan 2010).

14.3.3 Metaorganisms

Plants must be considered as a complex plurigenomic organism (metaorganism) formed by the plant itself, its microbiome, and the set of interspecific interactions that are established (Thijs et al. 2016). The microbiome is complex and is part of the rhizosphere, endosphere, or phyllosphere. The potential microbiome-host interactions can be favorable or competitive (Novotná and Suárez 2018). Previous studies have shown how certain bacteria favor the formation of mycorrhizae (Duponnois and Garbaye 1991; Vivas et al. 2003), while others inhibit the growth of fungal pathogens (Berg et al. 2005; Fikri et al. 2018). However, microbiome interactions are not static and change with their host at different life cycle stages or in response to changing environmental conditions. Microbiome interactions can evolve between

trophic states of pathogenesis, symbiosis, mutualism, and parasitism (Newton et al. 2010). Despite lack of data, it is reasonable to think that an equilibrium will be established between favoring and competitive interactions within the complex host-microbiome in response to abiotic factors, such as environmental stress.

To further the knowledge about microbe-host interactions in response to abiotic stress, our study research group studied the relationships between bacterial and fungal endophytes isolated from *Jasione montana* L., collected from soils highly contaminated with As (García-Salgado et al. 2012; Gutiérrez-Ginés et al. 2015). Prokaryotes and fungi were identified by the molecular markers 16S rDNA and ITS rDNA, respectively. Five fungal (*Curvularia* sp. MC-L1, *Fusarium* sp. MC-A, *Fusarium* sp. MC-D, *Fusarium* sp. MC-J, and fungus MC-H) and eight bacteria (*Kocuria* sp. MC-K2, *Arthrobacter* sp. MC-D3a, *Kocuria* sp. MC-D3b, *Pantoea* sp. MC-J, *Kocuria rosae* MC-D2, *Pantoea conspicua* MC-K1, *Arthrobacter* sp. MC-D3a, and *Rhodococcus rhodochrous* MC-D1) were finally used, and a mixture of all endobacteria was also prepared. All fungal endophytes were tolerant to arsenate (Table 14.1) although the As minimum lethal concentrations (AsV-MLC) were lower than those for bacteria (> 300 mM). *Arthrobacter* sp. MC-D3a did not survive at arsenate concentrations higher than 7 mM (Table 14.1). The dual cultures of the selected fungi with single or a mixture of endophytes bacteria caused fungal phenotypic changes, such as growth inhibition percentages depending on the culture medium used (LB, Luria-Bertani agar, frequently used to bacteria and PDA, Potato Dextrose Agar, more suitable for fungi) (Table 14.1). Some endobacteria can decrease fungal development with values even above the 50% of the inhibition, whereas the mixture appears to increase (e.g., *Curvularia* sp. MC-L1 vs endobacteria mixture) or reduce (e.g., *Fusarium* sp. MC-D vs bacteria mixture) the growth inhibition percentage if we compare with the effect of the single bacteria (Table 14.1). This ability of endophytic bacteria to modulate the growth of potentially pathogenic fungi has been previously described (Fikri et al. 2018). Other physiological and phenotypic changes like the suppression in the formation of sporangia (Fig. 14.5e) or the production of excreted compounds of unknown nature have been observed (Fig. 14.6). Previous reports have also shown how *Enterobacter cloacae* prevented the germination of a pathogenic fungus (van Dijk and Nelson 2000) and how *Acinetobacter* sp. reduced the endophytic fungus colony diameter and spore germination rate (Wang et al. 2013). Moreover, we observed how fungus MC-H (Fig. 14.5f) produced chlamydospores (thick-walled resting spores) in the border with *P. conspicua*, as a mechanism of defense against bacteria (Li et al. 2012). When metaorganisms are subject to abiotic stresses, interactions are established and modulated and may change in response to the environmental stress (Fig. 14.6). Our results showed, during dual culture experiments, different responses of growth inhibition under As conditions (Fig. 14.7). Fungus MC-H, growing with *R. rhodochrous* MC-D1 or *Kocuria* sp. MC-K2 under As conditions, showed how it increased growth (30% and 60%, respectively) but controlled the reproductive machinery, inhibiting the sporangia development. These patterns were opposite under favorable

Table 14.1 Percentage of growth inhibition of endophytes fungi therefore to growth with several endobacteria or endobacteria mixture isolated from *J. montana*. In parentheses the AsV minimum lethal concentration. n.a.= not available

		Fungus MC-H	*Curvularia* sp. MC-L1 (220 mM)	*Fusarium* sp. MC-A (220 mM)	*Fusarium* sp. MC-D (220 mM)	*Fusarium* sp. MC-J (70 mM)
LB	*Kocuria* sp. MC-K2 (450 mM)	60	53.8	0	33	n.a.
	P. conspicua MC-K1 (450 mM)	67	42.3	17	76	n.a.
	K. rosae MC-D2 (450 mM)	62	42.3	0	19	n.a.
	R. rhodochorus MC-D1 (450 mM)	60	53.8	0	0	n.a.
	Anthrobacter sp. MC-D3a (7 mM)	52	40	23	0	n.a.
	Kocuria sp. MC-D3b (300 mM)	0	40	0	0	n.a.
	Pantoea sp. MC-J (300 mM)	60	54	5	14	n.a.
	Endobacteria Mixture	69	73	13	33	0
PDA	*Kocuria* sp. MC-K2 (450 mM)	0	0	0	0	0
	P. conspicua MC-K1 (450 mM)	58	48	4	0	0
	K. rosae MC-D2 (450 mM)	0	0	0	0	0
	R. rhodochorus MC-D1 (450 mM)	0	0	0	0	0
	Anthrobacter spo. MC-D3a (7 mM)	0	0	12	0	0
	Kocuria sp. MC-D3b (300 mM)	0	24	0	0	0
	Pantoea sp. MC-J (200 mM)	24	40	0	25	15
	Endobacteria Mixture	61	52	35	27	80

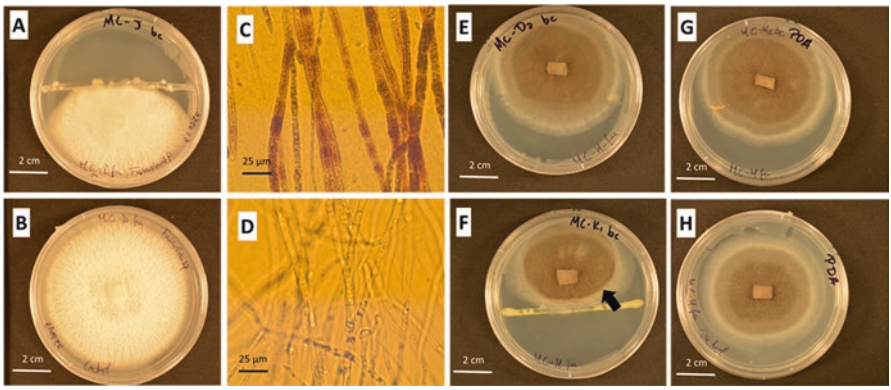

Fig. 14.5 Dual culture test in PDA at room temperature after 18 days. Inhibition of *Fusarium* sp. MC-D by *Pantoea* sp. MC-J (**A**). *Fusarium* sp. Control (**B**). *Fusarium* sp. MC-D hyphae invaded by *Pantoea* sp. on the border, Stained with 3, 30-diaminobenzidine tetrachloride (White et al. 2014) (**C**). Detail of *Fusarium* sp MC-D control (**D**). Fungus MC-H vs K. *rosae* MC-D2 with suppression in the production of sporophytes (**E**). MC-H vs P. *conspicua* with growth inhibition and chlamydospores production (arrow) on the border (**F**). MC-H vs *Kocuria* sp. without phenotypic changes apparent (**F**). MC-H axenic culture (**H**)

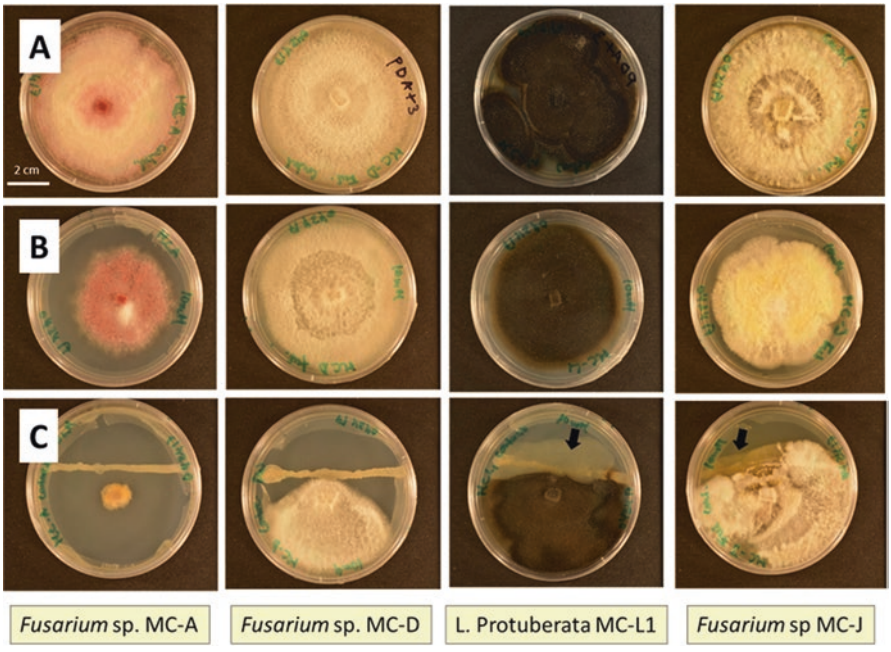

Fig. 14.6 Fungus growing on PDA control, at room temperature, after 18 days (**A**), on 10 mM arsenate PDA (**B**) and dual culture test between single endophyte fungus and mixture endophyte bacteria (**C**). Arrows show unknown exolites production

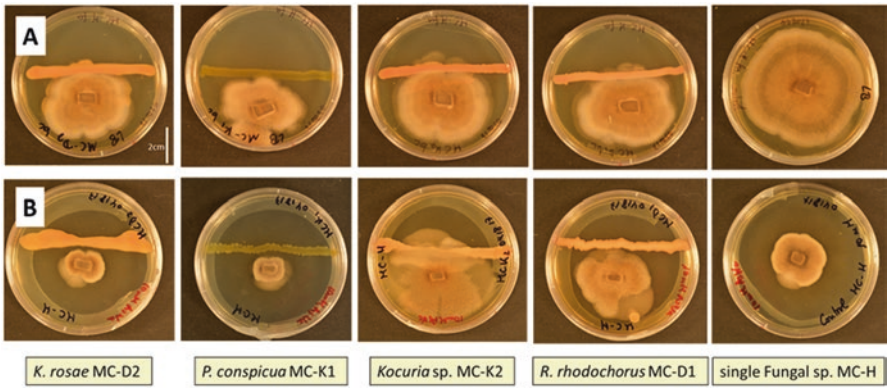

Fig. 14.7 Dual culture test between fungus MC-H and several endophytic bacteria isolated from J. *montana* on PDA (**A**) and on 10 mM arsenate PDA (**B**)

conditions, where *R. rhodochrous* MC-D1 or *Kocuria* sp. MC-K2 inhibited the growth of the fungus MC-H. These results suggest that under stress conditions, positive interactions in detriment of the competitive ones are favored (Liancourt et al. 2017).

A plant bacterial endophyte can also penetrate the hyphal wall of the fungus and settle inside the hyphae (Fig. 14.5a, b, c, and d) suggesting a fungal growth control by symbiotic bacteria (Fig. 14.5 a and b). Endobacteria have been isolated from AM cytoplasm (Bianciotto and Bonfante 2002; Bonfante and Anca 2009; Naumann et al. 2010) that are able to modify gene expression and physiology of the fungus (Salvioli et al. 2010). These bacteria can enhance the growth of AM fungi (Adams et al. 2009: Bonfante and Anca 2009) and be transmitted horizontally (Moebius et al. 2014) and vertically (Sharma et al. 2008; Bonfante and Anca 2009). In the association of AM fungi-bacteria, and Ghignone (2016) demonstrated that fungal infection with the endobacterium increased the fungal sporulation events, raised the fungal bioenergetic capacity, and elicited mechanisms to detoxify reactive oxygen species. Moreover, Chen et al. (2016) established a relationship between diversity of endobacteria and virulence of the fungus. In relation to pathogenic fungi, some endobacteria are responsible for fungal pathogenicity (Partida-Martinez and Hertweck 2005), while others modulate their antagonistic effects (Minerdi et al. 2008). These results indicate that bacteria living in the cytoplasm of fungi still represent an unexplored area of biology.

Despite the lack of studies on microbiomes, interactions (pathogenesis, mutualisms, or parasitism) depend on the specificity of the response, the type of stresses, and the scale of the interactions. Therefore, the idea of a metaorganism (host-microbiome interactions), linked with the omics strategies, will provide a successful tool for heavy metal decontamination process.

14.3.4 Enzymes and Bioreactors

To overcome the inherent drawbacks of physicochemical techniques, biological treatments arose as adequate and cost-effective remediation alternatives for As pollution. Bioremediation systems exploit microbial metabolic machinery ability, as whole cells or their isolated enzymes, to catalyze precipitation-dissolution processes, sequestration reactions, or biotransformations of As and As compounds (Plewniak et al. 2018). Unlike physicochemical technologies, biological technologies are much more effective at very low concentration ranges, even at the picomolar level (Sevcenco et al. 2015).

Many prokaryotic species are known to be able to include As within their metabolism. In addition, many bacterial genes involved in As metabolic pathways and resistance have been identified (Fig. 14.2). However, despite many microbial species and genes encoding As-related enzymes, only some of them have been described in pilot or industrial scale bioremediation processes developed in bioreactors.

The use of single enzymes immobilized on solid supports increases their stability and permits their repeated use in consecutive cycles of treatment, improving the economic viability of the whole process since the cost of enzymes at industrial scale is usually large. Arsenate reductase from *Pseudomonas alcaligenes* cross-linked immobilized on alginate beads has been used for the remediation of water containing arsenate at trace levels (< 1 ppm), yielding a biosorption capacity of 96.2 μg/g (Banerjee et al. 2017). Large enzymes such as ferritin, from the hyperthermophilic archeon *Pyrococcus furiosus*, showed a remarkable capacity to bind arsenate by interacting with the iron oxyhydroxide encapsulated inside ferritin nanocages (Sevcenco et al. 2015). This biosorption process is attractive for scaling up due to the developed heterologous overexpression of the gene that encodes ferritin from *P. furiosus* in *Escherichia coli*. This protein showed high thermostability and the ability to reuse the biosorbent.

Besides immobilized isolated enzymes, whole-cell biomass can be used as effective biosorbent for As sequestration from water. Biosorption presents, as a benefit, high elimination performance, low cost and minimum use of chemical and biological sludge. This technology can be applied either as living or as dead cells without clear evidence of which of the two alternatives is more effective since the results are sometimes contradictory and the biosorption mechanisms are complex and not clearly defined (AsadiHaris et al. 2018; Hlihor et al. 2017; de Bashan and Bashan 2010). However, the use of dead cells has a series of advantages, such as that the biomass can be reused, the system can be operated under extreme pH conditions (favorable for sorption but not compatible with living cells), and it is not necessary to use any growth media (AsadiHaris et al. 2018).

The ex situ bioremediation of As-polluted water, sludge, and soil can be carried out in bioreactors using a wide range of microorganisms harnessing their metabolism to perform a variety of transformations. For example, sulfate-reducing bacteria (SRB) are known to use sulfate as the terminal electron acceptor for their metabolism and, thus, produce insoluble metal or metalloid sulfides. For As, the removal

efficiency by the action of SRB depends not only on the specific microbial strain, but also on the presence of different carbon sources and other metals within the medium. A SRB consortium isolated from an antimony mine slurry achieved up to 96% As (III) and As (V) removal when Fe (II) was present and ethanol as carbon source was added in the anaerobic pilot bioreactor (Liu et al. 2018). Higher As removal efficiency, up to 99.8%, can be reached in a continuous attached growth reactor in the absence of oxygen with simultaneous nitrate depletion using a bacterial consortium obtained from a sewage treatment plant (Shakya and Ghosh 2018). In summary, the use of controlled bioreactors is an efficient approach to remove As contamination reducing time consumption although is more expensive than biosorption techniques.

14.4 Advances in Analytical Methods

14.4.1 Sample Treatment Methods for Speciation Analysis

The making of adequate decisions for the recovery of systems contaminated with arsenic involves the use of appropriate techniques and protocols that allow us to make a precise approximation of the concentration and As species present. The As speciation analysis in soils requires the application of single and sequential extraction methods. Single extraction methods are generally preferred due to their simplicity and efficiency for mobility studies of toxic elements, which is related to the environmentally accessible metal fraction when soil conditions change, and their potential bioavailability, related to the easily accessible metal fraction to plants and soil microorganisms. For this purpose, weak neutral salt solutions ($CaCl_2$ or $NaNO_3$) are used for the leaching of heavy metals present in exchangeable fractions in soils (Alvarenga et al. 2013), whereas ethylenediaminetetraacetic acid (EDTA) and acetic acid solutions are used to estimate the possible bioavailability of heavy metals from environmental samples to living organisms (García-Salgado and Quijano 2016). Ultrasonic and microwave energy have been applied to reduce the extraction time and the sample-extractant consumption (Arain et al. 2008; De la Calle et al. 2013; García-Salgado and Quijano 2016; Li et al. 2014; Relić et al. 2013; Wang et al. 2015). García-Casillas et al. (2014) obtained quantitative recoveries for BCR (Community Bureau of Reference) 486 and 700, reducing extraction times from hours to a few minutes.

For As extraction, the use of EDTA can be insufficient to remove both cationic and anionic metal species in contaminated soils. It has been proposed the combination of this solvent with organic reducing agents, such as oxalic, ascorbic, citric, or malic acids, or their salts, which can also be used by their own (Nguyen Van et al. 2017; Wei et al. 2018), or with dithionite (Wang et al. 2017b). Martínez-Sánchez et al. (2011) have proposed dithionite-citrate buffered with sodium bicarbonate as the most effective solvent for As extraction from soils affected by old mining

activities. Fleming et al. (2013) used ammonium acetate to study the extractability and bioavailability of As in historically contaminated orchard soil. The hydroxylamine hydrochloride, which is a solvent commonly used in one of the steps of the sequential extraction methods, can also be used for single As extraction in soils (Palumbo-Roe et al. 2015). Another solvent applied for As extraction is 1 M ammonium nitrate, according to the German DIN 19730:1997, which describes a method for the extraction of readily available trace elements from soils by shaking (Antoniadis et al. 2017). Finally, phosphoric acid and phosphate mixtures have been also used for As extraction from soils, to evaluate the As exchangeable fraction (García-Salgado et al. 2012; Sadee et al. 2016), as well as ammonium sulfate for weakly retained As (Moreno-Jiménez et al. 2010).

Regarding sequential extraction methods, they are used for the partitioning of heavy metals into different soil fractions: the water soluble and exchangeable, bound to carbonates, to Fe/Mn oxides, to organic matter, and the residual fraction (Tessier et al. 1979). This procedure was simplified by the BCR and later modified by Rauret et al. (1999). The main shortcomings from these conventional methods are high extraction time and reagent consumption, lack of selectivity, and poor reproducibility. Improvements on them are focused on (a) acceleration of batch leaching by sonication or microwave treatment (Rusnák et al. 2010), (b) reduction of sample handling by the application of continuous flow techniques (Savonina et al. 2012), (c) reduction of matrix effect by matrix separation or matrix matched calibration, and (d) application of internal standardization (Heltai et al. 2015).

Alternative sequential extraction methods have been developed for As fractionation in soils, because of the anionic nature of As ions unlike the heavy metals (Javed et al. 2013; Kreidie et al. 2011; Larios et al. 2012; Shiowatana et al. 2001, Tan et al. 2018; Wenzel et al. 2001). For example, several of these schemes have been proposed to replace the acetic acid solution by alkaline medium, for releasing As from the exchangeable fraction (Javed et al. 2013; Larios et al. 2012; Shiowatana et al. 2001; Tan et al. 2018). Also, alkaline solutions are used for dissolving the As associated with Fe/Al oxides/hydroxides (Larios et al. 2012; Shiwatana et al. 2001; Wang et al. 2017c), reporting higher percentages than those obtained with hydroxylamine solution. Several of these procedures increase the number of fractions (to 8 or 10), in order to differentiate between the As bound to amorphous or crystalline Fe, Al, and Mn oxyhydroxides, and therefore reduce the As bound to the residual fraction. In this way, authors reported the use of oxalate, citrate, or ascorbic acid solutions (Javed et al. 2013; Kreidie et al. 2011; Larios et al. 2012; Wenzel et al. 2001).

Conventional and As-specific sequential extraction methods have been applied to highly polluted soils (Kalyvas et al. 2018; Kim et al. 2014; Larios et al. 2013; Moreno-Jiménez et al. 2010; Wang et al. 2017c). The authors reported As contents lower than 10% in bioavailable fractions (soluble + exchangeable), while As was predominantly bound to amorphous and crystalline Fe oxyhydroxides (up to about 50%). Nevertheless, the absence of commercially available reference materials certified in As concentrations bound to the different soil fractions makes the validation of this kind of methods difficult, so recovery studies must be performed (Larios et al. 2013).

Apart from chemical methods, other extraction procedures such as diffusive gradients in thin-film technique (DGT) have proved to be effective for the determination of the bioavailability of trace elements in flooded soils (Zhang et al. 2018). Also, the effect of nanomaterials on As volatilization and extraction from this kind of soils has been studied (Huang et al. 2018).

14.4.2 Biosensors in as Analytical Methods

A biosensor is a device that presents a combination of biotechnology and microelectronics (Gronow 1984). It comprises (i) a biological component such as an enzyme, an antibody, a DNA, or a whole cell; (ii) a transducer, e.g., electrochemical, optical, or thermal; and (iii) a signal amplifier. Biosensors can be designed to detect a multitude of molecules, e.g., xenobiotics, pesticides, heavy metals, and many other pollutants (Saleem 2013). Various types of biosensors of As species (more commonly, arsenite) have been developed, and they can be grouped into whole-cell-based biosensors and cell-free-based biosensors (Kaur et al. 2015; Pothier et al. 2018).

The design of whole-cell As biosensors is mainly based on the ArsR transcriptional regulator that control the expression of the *Pars* promoter controlling the *ars* cluster. This protein is able to recognize arsenite or arsenate (Busenlehner et al. 2003; Wu and Rosen 1993) allowing the expression of a gene fusion of the *Pars* promoter and some reporter genes encoding β-galactosidase (*lacZ*) (Date et al. 2010; Cortés-Salazar et al. 2013; Huang et al. 2015), luciferase (Bakhrat et al. 2011; Sharma et al. 2013; Hou et al. 2014), green fluorescent protein (Chen et al. 2012; Truffer et al. 2014; Li et al. 2015; Ravikumar et al. 2017; Aye et al. 2018), or carotenoids (Fujimoto et al. 2006; Yoshida et al. 2008). However, some As biosensors are based on proteins encoded by the *ars* cluster like the ArsA-ArsD protein pair able to recognize As(III) (Liu et al. 2012).

The cell-free biosensors of As are primarily based on the ability of different biomolecules (DNA, proteins, aptamers, or nanomaterials) to interact with some As species. DNA can interact with As by electrostatic forces through the grooves of the double helix or by intercalation between the stacked base pairs of native DNA (Arora et al. 2007). Although these biosensors are able to detect the very low amount of As, their specificity is low (Liu and Wei 2008; Solanki et al. 2009). Some proteins have also shown their ability to sense As through a mechanism based on the affinity of some As oxyanions to bind and oxidize the sulfur groups of the proteins (Sarkar et al. 2010; Sanllorente-Méndez et al. 2012; Irvine et al. 2017). Aptamers are oligonucleotide or peptides modified to bind specifically a selected number of analytes. Some As aptamers are ultrasensitive to arsenite in aqueous detection, and they base their detection on gold nanoparticle aggregation (Wu et al. 2012; Wu et al. 2013; Pan et al. 2018). Nanomaterial-modified electrode interfaces for electrochemical sensing of As are based on unique chemical, physical, and electronic properties of the nanoparticles, enhancing the sensitivity, selectivity, field portability, and multi-

plexed detection capability of these kind of biosensors (Song et al. 2016; Vaishanav et al. 2017; An and Jang 2017; Kempahanumakkagari et al. 2017).

A high number of As biosensors have been developed in the last few years to detect As species in diverse environments. However, some limitations such as stability, sensibility, or specificity are still pending for solutions. New technologies such as synthetic biology or surface plasmon resonance are called to bypass some of the limitations of the current As biosensors (Fig. 14.7) (Kaur et al. 2015).

14.5 Conclusion

As speciation analysis requires the application of extraction procedures. In soils or sediments, this is carried out through sequential extraction methods, which permit discrimination between different As solid-phase associations. These analytical approaches allow us to inquire into soil composition and determine which remediation technique is more appropriate. Today, it is known that the interactions of plants with their microbiome and particularly with the PGPMOs will improve the effectiveness of plant-metaorganism. Therefore, through the resources that nature offers, plant endophytes and PGPMOs from As-tolerant plants can be used to improve bioremediation approaches. Microbiome interactions depend on the specificity of the response, the type of stress, and the scale of the interactions. Recent tools discovered, such as riboswitches and posttranscriptional regulation of gene expression, have been considered as potential tools to improve plant-PGPMO interactions. Other technologies such as biosensors, synthetic biology, or surface plasmon resonance have been developed to detect efficiently As species in diverse environments. Chemical and geological analysis and the idea of metaorganisms (host-microbiome interactions) linked with *omics* strategies will provide successful eco-friendly tools to remove As from contaminated environments.

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