Artificial Floating Island with *Vetiver* for Treatment of Arsenic-Contaminated Water: A Real Scale Study in High-Andean Reservoir

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Abstract: Arsenic found in agriculture water reservoirs represents a threat to water security and safe agricultural products in developing countries. Small farms do not implement traditional water treatments due to the high cost; hence, a nature-based solution is an alternative to tackling this challenge. This paper investigated the potential of artificial floating island with *Vetiver* (AFIV) for the geogenic arsenic removal present in the reservoir of the Ilinizas páramo in Ecuador. We constructed two AFIV systems using PVC pipes in a reservoir batch type with a 3.6 m$^3$ treatment capacity. Arsenic and iron were analyzed in duplicated every 30 days at the affluent and effluent through 120 days. The average remediation of arsenic was recorded as 97% in water and 84% in sediment, while the average remediation of iron was 87% in sediment. The survival rate of macrophytes was 92%; they accumulated arsenic in its roots that acted as a barrier against the translocation. The research demonstrated that the use of AFIV has the potential to rehabilitate reservoirs contaminated with arsenic under adverse climatic conditions such as the páramo ecosystem.

Keywords: Arsenic uptake; artificial floating island; phytoremediation; *Vetiver*

1. Introduction

Water is one of the most important transport in which arsenic (As) enters into the human body, causing irreversible damage to health [1]; it is considered a class I chronic carcinogen, its toxicity can cause hypo and hyperpigmentation, keratosis, lung cancer, skin, and even urinary bladder, among others [2,3]. Several populations worldwide are vulnerable to this problem; a clear example of this is South America, where poisoning cases have been reported due to the presence of inorganic arsenic (As$_i$) in the water [4,5]. Specifically, Mexico, Nicaragua, Ecuador, Chile, Argentina, Peru, Brazil, and Uruguay have high As concentrations from natural geological origins (geogenic). Concerning Ecuador, Bundschuh et al. [6] found that about 500000 people are exposed in rural areas to the intake of As from water consumption. Also, Ecuador’s National Water Secretariat (SENAGUA) reported extreme As concentrations (up to 980 $\mu$g L$^{-1}$) in drinking-water and irrigation in multiple zones of Toacaso within the Ilinizas volcanic complex, in the Cotopaxi province [7].

Small farmers utilize As-contaminated water for the crops irrigations of Andean potatoes [8], ignoring the potential health hazard, especially when it is mobilized through the water-soil-crop-food chain. Potatoes are the world’s number one nongrain food commodity [9]. Despite this fact, In Ecuador, there is a lack of research about the As accumulation within this type of crop and its impact on the health of consumers in general.
The reservoirs are key freshwater resources, they play a crucial role in agricultural production and economic income [10], but unfortunately the As intake through the water-soil-crop-food chain represents an emerging threat to the health of populations [11,12] in the high Andean region of Ecuador. To provide the beneficial use of reservoirs over the long term is necessary to apply water treatment, management and policy for their sustainable exploitation according to the sustainable development goals (GDGs).

There are several traditional methods for removing As, like the use of adsorbents, chemicals and photochemicals process, photocatalytic, oxidation, coagulation-flocculation-precipitation, ion exchange, and membrane filtration [13]. These treatments are difficult to implement, however, particularly in developing countries. Conversely, the Nature-based solutions (NBS) use ecosystems and their services as a form of green infrastructure (GI) and a more flexible, in many cases, cost-effective solution [14]. The International Union for Conservation of Nature (IUCN) defines NBS as a new concept that encompasses all actions that rely on ecosystems and the services they provide to respond to various social challenges, such as climate change, food security or disaster risk [15]. In combination with GI, the NBS can provide ecosystem services such as regulation of micro-climates, flood prevention, water treatment, and food provision, which are beneficial for the urban environment [16]. Indeed, the artificial floating islands system is considered as an NBS; they work as a natural evolution of artificial wetlands or green filters, and they have been studied in several parts of the world for different applications, such as water quality improvement, habitat creation, purification of different types of wastewater [11,12,17,18].

The island system is made up of a matrix or floating base to support the growth of macrophytes plants, which have proven to be efficient in the remediation of water containing nutrients, organic matter, and metals [19,20]. The floating base must combine a porous, permeable matrix resistant to environmental degradation with a substrate of polymer strands for microbial colonization [20]. System buoyancy can be provided by sealed polyvinyl or polypropylene tubes, polystyrene sheets, bamboo, cane, straw, barley, and inflatable vinyl pads [20–23]. Furthermore, it is necessary to use a macrophyte capable of supporting high As concentrations [24] to carry out the removal. In the last decades, research on the physiological characteristics of *Vetiver* (*Chrysopogon zizanioides*) has shown that it is an excellent candidate to be applied in a wide range of phytoremediation [25]. Through various mechanisms, *Vetiver* can adapt to wetland conditions, remove heavy metals by rhizofiltration [24] and translocate small amounts to the shoots [26]. A key point is the propagation by root divisions, rather than through rhizomes, stolons, or seed germination, which makes it a non-invasive plant [24] suitable for preventing propagation in vulnerable ecosystems such as the paramo. The use of AFIV is a promising strategy for As removal [27–29] that will allow and enhance the access to reliable water, increasing high-value products, and better nutritional status.

In this context, the aim of our work was to analyze the effectiveness of using *Vetiver* for treating water and sediments contaminated with As and iron (Fe) in the high—Andean reservoir. The objectives of the current study were (1) to evaluate the adaptation of *Vetiver* in the floating matrix in páramo setting, (2) to analyze the As decrease in the agricultural water reservoir (AWR) and (3) to identify the accumulation of As and Fe in *Vetiver* roots, shoots, and leaves.

2. Materials and Methods

2.1. Study Area and Materials

The AWR is located in the community of Chilla Grande (CCG) within the Illinizas paramo at 3190 m above sea level (mamsl) in the Cotopaxi province, Ecuador. According to its Land Management Plan [30], the prevailing soil types in the area include Entisol and Inceptisol. The land use is occupied mostly by 46% of native forests, an important agricultural area of 39%, 8% of paramos, other types of vegetation such as grasses or shrubs of 7%, and finally 1% without vegetation cover [31]. The climate of the region is characterized by a sub-humid condition, where the mean annual precipitation is 729 mm,
and the mean annual temperature is 11°C with a lack of thermal seasonality. The region depicts a steep relief dominated by volcanic rock, andesitic-to-dacitic edifice dated to Pleistocene and surrounded by pyroclastic deposits of Holocene [32].

The studied area plays a crucial role, since it is surrounded by páramo, a páramo in the provision of water for small farmers that subsist on agricultural activities, mainly from the growth of potato and maize [33,34]; unfortunately, high As concentrations are found in water that exceed 20000 µg L⁻¹. Taking into consideration that the World Health Organization (WHO) has established as a reference value of 10 µg L⁻¹; the contamination is extremely harmful because of its use in irrigation in crops without any treatment. Moreover, the presence of arsenate As (+5) is common in surface water [35] and it is mobilized to ecosystem through combination of natural processes [6], along with Fe [1].

2.2. Experimental Setup and Procedure

2.2.1. Floating Artificial Island Design and Construction

Two square floating matrices of 0.64 m² surface area (each one 0.8 m × 0.8 m) were constructed with PVC pipes of 50 mm of diameter; plus, discarded plastic PET bottles were used to obtain greater buoyancy. Above the frame, a plastic mesh with 25 holes (54 mm = diameter) was placed to attach the roots to coconut coir (Figure 1b). The crowns of the plants were located between the plastic mesh and the substrate; while its aerial part protrudes above the matrix and the roots extend below the floating structure towards the bottom of the water body (Figure 1c). Besides, a layer of pumice was placed on the matrix surface to provide stability.

![Figure 1. Artificial float island schema: (a) top view; (b) side view; and (c) actual Artificial float island with Vetiver (AFIV).](image-url)
well as a VLDPE (very low-density polyethylene). For the source of water, a natural stream was used, by coupling a 10” pipe to a channel. For the water evacuation, a 2” pipe was installed, regulated by a valve. Finally, the reservoir was filled to half capacity to water depth of 0.5m, and AFIV was installed (Figure 2b).

Figure 2. Irrigation reservoir configuration with AFIV: (a) system site configuration and (b) actual reservoir with AFIV.

2.2.2. Adaptation of Chrysopogon zizanioides in the Páramo and Installation in the Floating System

For a better establishment of the grasses, there was an adaptation stage [36] of 120 days, which time, *Vetiver* was not exposed to any As polluted soil and water. In the first phase (60 days), 200 *Vetiver* cuttings of 20 cm long were transplanted in soil type of the order Mollisoles, with abundant organic matter; clayey textures, slightly acidic pH, and good natural fertility [31], typical of the páramo conditions (Figure 3a). In the second phase (60 days), 100 plants were selected, as well as the healthiest and greater number of roots, in order to be placed in the four artificial floating islands (25 plants in each one) and maintained in an AWR As-free (Figure 3b).

Figure 3. *Vetiver* plant adaptation: (a) soil and (b) water.

At the end of this period, only 2 artificial floating islands with *Vetiver* (AFIV) were installed for the experimentation; while the remaining were used to replace plants that did not adapt from the treatment systems. The experimentation in the contaminated AWR was conducted during 120 days.
2.3. Sample Analysis

2.3.1. Sample Collection

The samplings of water and sediments were performed in duplicated every 30 days at the affluent and effluent, respectively, all through 120 days. The samples were collected in accordance to the Ecuadorian Technical Standard for methods of water quality sampling [37]. Water quality was tested at the upper water layer (5 cm below the water surface) due to the short water depth of AWR. The sampling protocol for sediments was based on accepted environmental practice of [38].

At the affluent, 1 kg of sediment sample was taken at a depth of 20 cm, collected from three different points, and then homogenized [39]. Concerning the sediment effluent, these were collected from AWR, from the bottom, every 30 days.

2.3.2. Water and Sediments Samples Analysis

For As analysis, water samples were collected from each site and stored into a pre-acid-washed 500 mL polytetrafluoroethylene (PTFE) bottle. Guaranteed reagent hydrochloric acid (HCl) was added to adjust the pH value of samples to <2 for storage. Another 500 mL sample was collected in a pre-washed polyethylene bottle for measuring other parameters. The global position system (GPS) coordinates of sampling sites were recorded using a Garmin (KS, US) GPSMAP 60s. All water samples were stored in a cooler with icepacks before being sent back to the laboratory, and kept in 4 °C before analysis.

The water and sediment samples were immediately sent to the Public Metropolitan Drinking Water and Sanitation Company, (EPMAPS) where As was determined by method of 1632A (USEPA) using an atomic absorption spectrophotometer (HG-AAS).

Subsequently, sediment samples were analyzed at EPMAPS using the EPA method 7062 (U.S. EPA 1994a) for the digestion of soils, in order to assess As content, by means of an atomic absorption spectrometry. In addition, water quality parameters like pH and water temperature (WT) were tested; the temperature was performed by submerging a mercury-filled Celsius thermometer. Regarding the pH value, it was tested by using a YSI-Pro Plus multi-parameter water quality meter.

2.3.3. Hydrometeorological Data

The meteorological conditions data were recollected on-site and the Sigchos (M363) meteorological station that belongs to the National Institute of meteorology and hydrology of Ecuador (INAMHI). Temperature and water level measurements were performed at the same time that water samples were tested. To estimate the precipitation and calculate the AWR volume, a manual water level gauge was installed, where the water level variation was transformed to precipitation depth and compared with the observed precipitation, located at the meteorological station.

2.3.4. Estimation of heavy metals in Vetiver plants and its phytoextraction ability

At the end of the experiment, the Vetiver samples of each unit were harvested from the matrix and transported to the laboratory for analysis. Root, shoot and leaves samples were sent to the University of Americas (UDLA) laboratory. The specimen of 0.5 g of previously dried sample and 10 mL of 67% metal-free HNO₃ was added. Initially, it was digested according to the digester Plant Material protocol CEM, and after that, the content of As and Fe was analyzed through ICP—OES (Inductive Plasma Coupling—Optical Emission Spectrometry). The phytoextraction ability of the plants was evaluated by calculating the translocation factor (TF) according to the method of (Wu et al. 2011), that is expressed as mg kg⁻¹.

\[
TF = \frac{(\text{Metal})_{\text{tissues}}}{(\text{Metal})_{\text{root}}} 
\]
Regarding the removal efficiency of the treatment of As and Fe for each unit was calculated using
the following equation:

$$\text{Removal Efficiency} \% = \frac{(C_i - C_e)}{C_i} \cdot 100$$ (2)

where $C_i$ is the concentration of the waste material in the influent and $C_e$ is the concentration of the
waste material in the effluent.

3. Results

3.1. Plant Adaptation in the Floating System

The macrophyte used in the experiment is a tropical grass; capable of surviving extreme environmental
conditions [28,40] such as the Illinizas páramo, where short-term microclimatic measurements indicate
that air temperatures barely reach 12 °C during the day, and night frosts may occur at any time of the
year [41]. *Vetiver* is a non-invasive non-aggressive, and non-competitive with native grasses [42], thus being
a suitable plant for rhizofiltration in a fragile ecosystem, previous adaptation process.

Regarding the first phase of adaptation in soil, *Vetiver* cuttings became purple (Figure 3a) due to
the environmental conditions of a cold climate. The color of change is negatively correlated with the
cold temperature, but thanks to its capacity of adaptability, *Vetiver* was able to recover in a satisfactory
way [43,44], and its survival reached 85%, considering the 200 plants installed. In the second phase,
already being set in a hydroponic environment, in the absence of As, the plants gradually turned green
once more due to the use of coconut fiber that can yield or absorb heat quickly; facilitating constant root
development, both in hot and cold seasons [21]. Along with the pumice, the plants on the floating matrix
reached a survival rate of 92%. At the end of the adaptation process, the plant roots reached 30 cm in the
matrix floating, and they were set up in the AWR with extreme As concentrations (Figure 4a). The two
AFIV (25 plants on each) were monitored for 120 days, with a survival rate of 95.88% (with only one
plant replacement each island), despite the high concentrations of contaminants [45].

![Figure 4](image-url)

**Figure 4.** Root system length at (a) the beginning and (b) elapsed 120 days of the treatment. (c) observed
natural high As concentration.

Although As is a non-essential element for plants and toxic for many crops, it was demonstrated in
the experiment that As exposure did not induce toxicity in *Vetiver* [28]. This metalloid did not interfere
with the physiological and biological activity, even if there was a slow growth of the roots; in the end,
it reached 1 m long (Figure 4b) in about six months promoting phytoremediation processes.

3.2. Water Quality Assessment

The evaluation of AFIV has proved to be efficient in the removal of As in water and As-Fe in
sediments. In the four replicates (each 30 days), during the 120 days of experimentation, the average
remediation of As was recorded as 97% in water (Figure 5a) and 84% in sediment (Figure 5b), while the average remediation of Fe in sediment was 87% (Figure 5c). This result complies well with the reports that *Vetiver* can be used as a candidate in the restoration of As water [17,27–29,46]. In addition, it was found to be effective for extreme concentrations [28].

**Figure 5.** As removal in: (a) water; (b) sediments and (c) Fe removal in sediments.

The treatment of AWR in the CCG shows that *Vetiver* is the most suitable plant in terms of As removal. The efficiency of this macrophyte compared with other species As phyto remediation capacities in different water bodies of water [47] (Figure 6), shown best results for *Vetiver*.

**Figure 6.** Comparison of *Chrysopogon zizanioides* and macrophytes plants used for phytoremediation (adapted from [47]).

As commonly present in water is pH-dependent of the arsenic (H$_3$AsO$_4$) and arsenous (H$_3$AsO$_3$) acid systems respectively. These anions have acidic characteristics, and the stability and dominance of a specific species depend on the pH of the solution. An important parameter is pH, when it indicates an average value 4.78 (Figure 7) due to the fact that As($+5$) is negatively charged, which explains its higher efficiency in the removal systems, compared to the As($+3$) that, at those pH values, has no charge at
The dependence of metal uptake on pH is related to both the surface functional groups on the surface charge of ferric oxyhydroxides changes from a positive to a negative value as pH increases. Due to nitrification may be neutralized by bicarbonate ions. Macrophytes in releasing oxygen promote the nitrification process. Produced protons due to nitrification may be neutralized by HCO$_3^-$ ions, resulting in a pH increase [49]. The overall mean surface charge of ferric oxyhydroxides changes from a positive to a negative value as pH increases. Hence, to promote adsorption and removal of oxyanions of, for example, As, Fe co-precipitation must occur under acidic conditions [50]. A low rate of nitrification can therefore improve the efficiency of a constructed wetland in terms of oxyanions.

**Table 1.** Estimation of heavy metal contents in shoot, root, and leaves of *Vetiver* in As and Fe contaminated water before and after the installation of the AFIV system.

| Period                        | As Concentration (mg kg$^{-1}$) | Fe Concentration (mg kg$^{-1}$) |
|------------------------------|---------------------------------|---------------------------------|
|                              | Root                            | Shoots                          | Leaves                          |
| Before the installation of   | ND                              | ND                              | 3721.30                         | NA                             | NA                             |
| AFIV system                  |                                 |                                 |                                 |                                |                                |
| After treatment period       | 494.50                          | 71.92                           | 30.05                           | 1037.49                        | 362.77                         |
| Translocation factor (TF)    | 0.15                            | NA                              | 0.31                            | NA                             | NA                             |
| Plant metal content mg        | 298.23                          | 2388.67                         |

ND: not detected. NA: not analyzed.

Besides, heavy Metals may become associated with Fe oxides [53,54] as a result of the adsorption or co-precipitation phenomena. The process is presumed not to be important in the long-term removal and retention of metals because of the Fe and manganese oxides, being redox sensitive, may redissolve following changes in oxygen concentration. Treated waters in wetlands may be rich in Fe, which will precipitate as oxides, oxyhydroxides, or hydroxides in the oxidizing environment at the wetland surface. For example: a natural wetland in North Wales, England was reported to effectively retain heavy metals, like As in association with Fe oxides [55]. In addition, As was reported to be retained on Fe plaques at the surface of plant roots [56].
The acidic pH of the water may have helped for the high As and Fe, accumulation in the roots. Most phytoremediation studies have mainly focused on the evaluation of remediation effectiveness, while laying little emphasis on efficiency stability against numerous factors in the natural environment [57]. For instance, the low temperature in the study zone could have influenced relatively higher As removal, due to stronger sorptive forces in cold temperatures [58]. Moreover, a key point is the recognition of the seasonality in As mobility, but there have been few investigations of As cycling in cold regions [59], and even less in páramo ecosystems.

3.3. Translocation of As into the tissues of the Vetiver

The concentrations of As and Fe in Vetiver shoots, roots, and leaves are shown in Table 1, distributed in greater quantity in Vetiver roots than in shoots and leaves [60–62] with less translocation to the aerial parts. The maximum concentration of accumulated As in the roots (494.50 mg kg\(^{-1}\)) was almost 7 times higher than in the shoots (71.92 mg kg\(^{-1}\)) and nearly 16 times higher than in the leaves (30.05 mg kg\(^{-1}\)). With regard to Fe, the maximum accumulation was retained by the roots (3377.09 mg kg\(^{-1}\)), nearly 3 times higher than the sprouts (1037.49 mg kg\(^{-1}\)), and around 9 times higher than the leaves (362.77 mg kg\(^{-1}\)), which resulted in less translocation to the aerial parts [46].

Our work showed that Vetiver roots act as a barrier that prevents the translocation of As into the aerial parts, avoiding plant toxicity. Due to the union of metals and organic ligands present in the medium, which have a greater affinity for metals [63].

3.4. Use of AFIV in AWI of High Andean Ecosystems

The CCG crops are located between 3000-3600 mamsl, which is the ideal height for optimal growth of the Andean potato [64], but a bigger concern is the As presence, that is probably being accumulated in the potatoes. In Ecuador, there are no studies to corroborate this information; but as a reference, we analyzed the West Bengal-India, where As is present in irrigation water for potatoes. Samal et al. [65] reported a considerable amount of As average accumulation in the potato of 291 ± 176 µg kg\(^{-1}\), much higher than in the leafy vegetables.

Through AFIV is possible to remove high As concentrations in AWR, and later use it for irrigation, mainly in the dry season, which corresponds to June to November, according to data from the meteorological station M363. Potatoes crop consumes from 600 to 700 mm of water, distributed during the vegetative cycle (181 to 211 days for the Andean potatoes) [66,67], in consequence the precipitation is not long enough in most of the year. Based on hydrometeorological data and crop water requirements, the experimental AWR can supply water for irrigating potato crops with an extension around 20 to 500 m\(^2\), depending on the water deficit that varies between 0.2–2.6 mm day\(^{-1}\). Regarding of raw water for filling AWRs is not a restriction, because surface water is sufficient and it could be used after 30 days of treatment, with to 96% As removal for the first cycle of potatoes crops irrigation [67]. Finally, to manage time constraints for the period of crop, the community has a set of reservoirs that can be rotated, as a way to achieve a uniform coverage. In case of setting up the AFIV in AWRs with greater capacities, the pilot-scale study suggested that 10% of AWR should be covered with AFIV [18]. However, to determine parameters of design for different volumes, further studies are needed to the full-scale of AFIV.

4. Conclusions

This research investigated the Arsenic (As) removal performance of artificial floating island with Vetiver (AFIV) in the irrigation water treatment for potato crops in the Ilinizas páramo in Ecuador.

The two islands of 0.64 m\(^2\) were constructed with low-cost material and set up in a reservoir batch type with a 3.6 m\(^3\) treatment capacity. The removal rate was 97% for As in water, 84% for As in sediment, 87% for Fe in sediment, and the pH reached 6.37.

The success of phytoremediation with AFIV depended on a variety of environmental factors, including the presence of a high concentration of As, together to Fe, temperature, weathering, and pH.
These factors acted directly to the enhancement of bioavailability of contaminants and the ability of plants to take up and accumulate contaminants in root and shoots.

Despite the environmental conditions of the study area, the results of this research shown that Vetiver is an excellent candidate for the restoration of As in water. The growth of Vetiver on the matrix floating reached a survival rate of 92%, and they established with well-developed root and shoots. The Vetiver roots acted as a barrier against As translocation, with a maximum concentration of accumulated As in the roots (494.50 mg kg$^{-1}$), that was almost 7 times higher than in the shoots (71.92 mg kg$^{-1}$) and nearly 16 times higher than in the leaves (30.05 mg kg$^{-1}$). Concerning Fe, the maximum accumulation was retained by the roots (3377.09 mg kg$^{-1}$), nearly 3 times higher than the sprouts (1037.49 mg kg$^{-1}$), and around 9 times higher than the leaves (362.77 mg kg$^{-1}$).

From the obtained results, the constructed AWR and AFIV system support access to appropriate quantity and quality of water. This study has demonstrated that AFIV can be used to irrigate small farmland in the dry season, but for its scaling, it is necessary to conduct more investigation at different scales.

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