

Article



# Assessing the Use of *Ziziphus spina-christi* as a Sustainable Solution for Biomonitoring of Urban Air Quality: A Case Study from Qatar

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Abstract: Globally, urbanization, industrialization, and transportation have worsened urban air quality in recent decades. Using sustainable, cost-effective methods to monitor and reduce air pollution is crucial. The best Nature-based Solution (NbS) for urban environmental cleanup is plants. Roadside plants are key carriers of air pollution and have various tolerances. Ziziphus spina-christi's air pollution tolerance was assessed using the Air Pollution Tolerance Index (APTI). The Bioconcentration Factor (BCF) examined the heavy metal accumulation capacity of Ziziphus spina-Christi's fruits and leaves. Two sampling sites were studied: a reference location remote from human activity and a densely populated metropolitan region. Ziziphus spina-christi is considered a tolerant species in Qatar, based on its calculated value of APTI in this study. Both total chlorophyll and ascorbic acid influence APTI levels and have a strong positive correlation with APTI. BCF values in leaves were higher than fruits indicating that the leaves of Ziziphus spina-christi have a greater potential for metal absorption than its fruits. Moreover, the leaves of Ziziphus spina-christi showed a potential for mercury accumulation (BCF > 1), thus it is a good candidate to be used for phytoremediation in areas of mercury contamination. The integration of both APTI and BCF methods is significant and beneficial in advising policymakers and urban planners regarding suitable tree species for sustainable urban development.

**Keywords:** Air Pollution Tolerance Index (APTI); Bioconcentration Factor (BCF); bioindicator; urban air quality; sustainable solution; *Ziziphus spina-christ* 

# 1. Introduction

The massive development of commercial, urban, and industrial activities and their combined emissions of air pollutants have made air quality a global environmental issue in the recent century [1]. Due to changes in physical developments like factories, buildings, and paved roads, green areas and open lands—which cool the city and improve air quality—have decreased [2]. Urbanization also boosted industrial and vehicular activity, worsening air quality [3]. Road traffic is a major source of urban air pollution [1,4]. Traffic-related emissions such as carbon monoxide (CO), nitrogen oxides (NOx), methane (CH<sub>4</sub>), non-methane gases, sulfur oxides (SOx), and particulate matter (PMs) can impact climate change [2]. Road traffic also releases heavy metals (HMs) like chromium (Cr), lead (Pb), cadmium (Cd), arsenic (As), zinc (Zn), copper (Cu), nickel (Ni), and mercury (Hg) from vehicle exhaust, tire wear, brake lining, and road surface. Air pollution in cities has several health impacts. Traffic-related air pollution's health consequences are a key transport problem. The WHO Regional Office for Europe expects ambient air pollution to cause 100,000 deaths a year in Europe in future decades, decreasing life expectancy by a year [5].



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**Copyright:** © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). Short-term and long-term air pollution exposure causes COPD, asthma, respiratory and cardiovascular illnesses, and mental and perinatal disorders in newborns and adults [6]. Qatar is one of the fastest-growing nations [7]. Qatar's Planning and Statistics Authority (PSA) anticipated 1,964,978 automobiles in 2022 and 3 million people in March 2023. Increased air emissions will damage air quality and harm the ecosystem and humans. Nature-based Solutions (NbS) are gaining popularity as effective techniques for reducing environmental pollution [3,8,9]. The European Commission defines NbS as "solutions that are inspired and supported by nature, which are cost-effective, simultaneously provide environmental, social, and economic benefits, and help build resilience" [10]. NbS is a cost-effective, sustainable, and effective way to monitor and mitigate urban air pollution [3,11]. Conventional solutions require continuous monitoring programs using fixed stations, which do not represent the area [12]. Urban vegetation is a cheap and easy way to monitor air quality across vast regions [13]. Air pollutants damage plants the most, especially leaves, which are the main receptors and environmental sinks. The Air Pollution Tolerance Index (APTI) measures plants' ability to tolerate air pollutants [12,14]. APTI helps classify plants as sensitive, intermediate, or resistant to air pollution [15,16]. Sensitive species with low APTI values are important early pollution indicators, while tolerant species with high APTI values are best for pollution mitigation. APTI uses four biochemical parameters-total chlorophyll, ascorbic acid, leaf extract pH, and relative water content—that are immediately impacted by air pollution and easy to quantify. Several studies evaluated the Air Pollution Tolerance Index of plant species along roadsides and in industrial, urban, and rural areas in India [14,15,17], China [18,19], Nepal [16], Saudi Arabia [20–22], Oman [23], and Iraq [24]. In addition, roadside plants may accumulate pollutants like HMs and be employed in phytoremediation. The bioconcentration factor (BCF) is one of the measures that can quantify a plant's phytoremediation capacity [25]. Numerous scholars have conducted investigations on the accumulation of heavy metals in roadside vegetation [26–30]. To our knowledge, there are no studies conducted in Qatar to assess the use of plants in biomonitoring and mitigation of air pollution. Thus, this study examines, for the first time in Qatar, the use of Sidr trees (Ziziphus spina-christi), which are evergreen trees native to Qatar and commonly found along roadsides, gardens, and residential areas, as a nature-based solution for biomonitoring air quality and phytoremediation of heavy metals. Here, we aim to investigate the tolerance of this tree species and its potential accumulation of HMs. The Air Pollution Tolerance Index and heavy metal accumulation potential of Sidr trees (Ziziphus spina-christi) along the roadside of a highly urbanized and active area in Qatar and at a control site were examined. While there is existing research on the assessment of using plants for biomonitoring air quality based on APTI, we added the use of BCF (for both leaves and fruits of the tree) to enhance the assessment. In this research, for the first time in arid climate, we incorporated the usage of both APTI and BCF to evaluate Ziziphus spina-christi trees as a sustainable option for biomonitoring of urban air quality and a potential phytoremediation solution of heavy metal pollution. Combining both APTI and BCF measures is useful in recommending suitable tree species for sustainable urban development, which is significant for policymakers and urban planners.

#### 2. Materials and Methodology

## 2.1. Study Area and Sampling Strategy

Two areas were selected for this study: The first is a rural area as a reference site located at the Northside of Qatar away from pollution sources (approximately 70 km from Doha). The second is a roadside area located near a high traffic density area, including universities, schools, and governmental institutions (Figure 1). In the summertime, temperatures can exceed 40 °C (104 °F) [31]. In August and September, relative humidity rises, making circumstances uncomfortable. The winter season has little erratic precipitation. Air pollution is often linked to traffic congestion, largely due to automobile emissions. This might increase PM2.5, PM10, NO2, CO, and VOCs [32]. Fully developed leaf and fruit samples were randomly collected in five independent replicates from *Ziziphus spina-christi*  trees at the height of 1.5 to 2 m during March (temperature 16–40 °C, with an average of P25 °C) [33]. The collected samples were immediately transferred to polythene bags and stored in a freezer set at -20 °C, then transferred to the laboratory for analysis.



**Figure 1.** Geographic position of study sites in Qatar. Maps show different land uses in the selected study sites.

### 2.2. Biochemical Parameters

## 2.2.1. Ascorbic Acid

The ascorbic acid was determined following the method used by the University of Canterbury (2021) [34]. In essence, 0.5 g of fresh leaves were crushed and added to 10 mL of distilled water for extraction. The extract was then transferred to a 15 mL centrifuge tube and centrifuged at 4500 RPM for 15 min. The clear extract was then titrated with 0.005 M Iodine solution to determine the ascorbic acid concentration.

## 2.2.2. Total Chlorophyll Content (TChl)

The total chlorophyll content was determined following the method described in the literature by Alhesnawi et al. (2018) and Alotaibi et al. (2020) [21,24]. The method entails using 0.20 g of leaves crushed and extracted with 10 mL of 80% acetone. The resulting solution is then incubated for 15 min and centrifuged for 3 min (2500 RPM), and the absorbance read at 645 nm and 663 nm. The total chlorophyll content was calculated using the below formula.

$$TChl\left(\frac{mg}{g}\right) = 20.2 \times A_{645} + 8.02 \times A_{663}$$
 (1)

where  $A_{645}$  and  $A_{663}$  are the absorbance at wavelengths of 645 nm and 663 nm.

## 2.2.3. pH of Leaf Extract

A sample of 0.5 g of leaves was ground, dissolved in 50 mL of distilled water, and filtered, and the pH was measured using a calibrated pH meter.

## 2.2.4. Relative Water Content (RWC)

The relative water content was determined following the method described by Alhesnawi et al. (2018) and Alotaibi et al. (2020) and calculated using the below formula [21,24].

$$RWC = \frac{FW - DW}{TW - DW} \times 100 \tag{2}$$

where *FW* denotes fresh weight, *DW* denotes the dry weight, and *TW* denotes the turgid weight.

### 2.3. Air Pollution Tolerance Index (APTI)

The Air Pollution Tolerance Index was determined using the measured ascorbic acid, total chlorophyll concentration, pH, and relative water content. The *APTI* was calculated using the formula developed by Singh and Rao in 1983 [15].

$$APTI = \frac{A(TChl + pH) + RWC}{10}$$
(3)

where *A* is the ascorbic acid of leaf in mg/g (dry weight), *TChl* is the total chlorophyll of leaf in mg/g (dry weight), pH is the leaf-extract pH, and *RWC* is the relative water content of leaf tissue in percentage.

Based on *APTI* values, plants are categorized as sensitive, intermediate, moderately tolerant, and tolerant (Table 1).

Table 1. Plants categories	based on APTI values adag	pted from (Singh et al	i. (1991)) [ <mark>35</mark> ]
			· · · · · ·

APTI	Response
$\leq 14$	Sensitive
15–19	Intermediate
20–24	Moderately tolerant
>24	Tolerant

#### 2.4. Chemical Analysis of Metals

Dried and homogenized soil sample of approximately  $0.25 \pm 0.05$  g was weighed and mixed with 9 mL of concentrated nitric acid and 3 mL hydrofluoric acid (Puriss, Honeywell, Muskegon, MI, USA) in a 50 mL PTFE tube before digestion using a microwave digestion system (MARS-6, C.E.M. Corporation, Matthews, NC, USA) according to US EPA (2007) [36]. For leaf and fruit samples, they were washed three times with Milli-Q ultra-pure water (IQ 7010, Merck, MA, USA) to remove the particulate matter (PM) deposited on the surface before being freeze-dried (SP VirTis AdVantage Pro, ATS, Sewickley, PA, USA) until a constant weight was reached. Then, approximately  $0.5 \pm 0.05$  g of dried, ground, and homogenized sample powder was weighed in a 50 mL PTFE digestion tube, to which 5 mL of concentrated HNO<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> were added [37]. The digestion was carried out using a microwave digestion system (MARS 6, C.E.M., NC, USA). The digested samples were then preserved with 3 mL of nitric acid and diluted up to 50 mL with reagent-grade water before being analyzed with ICP-OES (Optima 7300DV-Perkin Elmer, Waltham, MA, USA) and direct mercury analyzer (DMA-80 evo, Milestone Srl, Sorisole, Italy).

## 2.5. Quality Assurance and Control

The establishment of analytical quality assurance was achieved with the examination of reagent blanks and certified reference materials (CRM). Two certified reference materials (CRMs) were employed in this study. The first CRM utilized was NIST-2709a, which is specifically designed for San Joaquin soil. It had a certified value of  $0.90 \pm 0.20$ . Two reference materials were used in this study: (i) NIST 1566a, obtained from the National Institute of Standards and Technology, which is a standard reference material for oyster tissue and (ii) NIST 1573a, also obtained from the National Institute of Standards and Technology, which is a standard reference material for tomato leaves. The approved value of this substance is ( $0.034 \pm 0.00$ ). In order to ensure adequate quality, 10% of the total samples tested have been allocated as quality control (QC) samples. The analysis of all samples was conducted in triplicate, with an average weight of 0.25  $\pm$  0.05 g. The recovery percentage obtained ranged from 89% to 102%.

#### 2.6. Bioconcentration Factor (BCF)

The Bioconcentration Factor (*BCF*) of HMs in plant tissue (i.e., leaves and fruit) can be defined as the capability of plant tissues for element accumulation from the soil [38]. It can be measured by dividing the measured concentration of metals in the plant tissue by the metal concentration in the substrate [39].

$$BCF = \frac{\text{Concentration of Metal}_{(\text{plant tissue})}}{\text{Concentration of Metal}_{(\text{soil})}}$$
(4)

*BCF* is used as an index to determine the ability of plants to accumulate HMs. Based on *BCF*, the plant can only absorb the metal without accumulation if  $BCF \le 1$ , while it can accumulate the metal if BCF > 1 [29,40]. Higher *BCF* values indicates that the plant has higher potential of phytoaccumulation [28].

#### 2.7. Statistical Analysis

A One-way (ANOVA) test was performed to evaluate the mean variation between the sample groups. Pearson correlation (2-tailed) analysis at the 0.05 level was performed to reveal the relationships between five parameters (pH, Ascorbic Acid, TChl, RWC, and APTI). Principal Component Analysis (PCA) was performed based on five parameters (pH, Ascorbic Acid, TChl, RWC, and APTI) of the *Ziziphus spina-Christi*. The extracted factors with initial eigenvalues < 1 and the varimax method were used for rotation with Kaiser normalization. The statistical data analysis was carried out with IBM-SPSS-25 and Minitab-17 software.

## 3. Results and Discussions

The APTI determination relies on various biochemical parameters: total chlorophyll, ascorbic acid, leaf pH, and relative water content [41,42]. Each contributes to the overall tree species categorization. The descriptive statistics of all biochemical parameters and APTI for all 12 sites (roadside areas and rural areas) are shown in Table 2. A One-way (ANOVA) test was performed to evaluate the mean variation between the sample groups. Significant variations (p < 0.05) were observed in all variables at 95% CI along roadsides in Qatar.

**Table 2.** Summarized descriptive analysis for ascorbic acid, mg/g (dry weight), total chlorophyll, mg/g (dry weight), pH, relative water content (%), and APTI.

		Site		
		Rural Area (Reference Site)	Roadside Area	
According A and may (a (dry quaight)	$Mean \pm Std$	$38.93\pm0.90$	$42.94 \pm 4.73$	
Ascorbic Acia, mg/g (ary weight)	Range	37.70-40.23	34.98–54.70	
	$Mean \pm Std$	$5.94\pm0.06$	$3.32\pm1.00$	
lotal Chlorophyll, mg/g (dry weight)	Range	5.89-6.02	1.94-4.87	
	$Mean \pm Std$	$6.15\pm0.01$	$6.17\pm0.08$	
рп	Range	6.15–6.16	6.05–6.36	
D lating Matrix Constant 0/	$Mean \pm Std$	$92.18 \pm 1.91$	$78.82 \pm 4.41$	
Relative Water Content, %	Range	89.09–94.13	71.83–90.24	
	$Mean \pm Std$	$56.29 \pm 1.13$	$48.88 \pm 7.80$	
APII	Range	54.68-57.81	39.55-63.01	

## 3.1. Ascorbic Acid

Ascorbic acid is a reductant and an antioxidant found in all plant growing parts [43,44]. It plays a significant role in photosynthetic carbon fixation; its role is correlated with its concentration [45]. Plants that retain high ascorbic acid levels even under contaminated habitats are thought to be air pollution resistant [46,47]. Numerous studies have demonstrated a positive correlation between raised levels of ascorbic acid and the ability of plant species to tolerate increased air pollution [17,48,49]. Furthermore, another research has hypothesized that the presence of traffic-induced stress leads to an observable elevation in the levels of ascorbic acid in plants [50]. Ascorbic acid helps uphold the plant cell stability in harsh conditions by scavenging cytotoxic free radicals [51,52]. In addition, it is a strong reducing agent in plants that triggers many defenses mechanisms [53]. In this study, all data from roadside samples displayed high ascorbic acid values that may indicate the species' tolerance to air pollution within the sample zone and reference area. The ascorbic acid average value at roadside areas was higher (42.94 mg/g) than in rural areas (38.93 mg/g). The results obtained in our study is consistent with the data shown in Table 3 and Figure 2 of the Kingdom of Saudi Arabia (KSA) study [21]. However, the calculated ascorbic acid values are high compared to other values found in the literature (e.g., [54]) (Table 3, Figure 2), which may indicate variation in both the environment and the sampling areas' climates.



**Figure 2.** Comparison plot of biochemical parameters and APTI of *Ziziphus spina-christi* from the literature. *Y*-axis on the left side of the graph represents the range of ascorbic acid (A) (mg/g), total chlorophyll (T-Chl) (mg/g), pH, relative water content (RWC) (%), and Air Pollution Tolerance Index (APTI). NA means Not Available.

Table 3. Comparison of APTI and biochemical parameters of Ziziphus spina-christi from the literature.

Country	Site	Ascorbic Acid (mg/g)	Total Chlorophyll (mg/g)	рН	Relative Water Content (%)	APTI	Reference
KSA	Reference/rural	35.30	1.08	5.52	89.10	32.20	[21]
KSA	Roadside site	78.60	0.69	5.55	72.00	56.20	[21]
Egypt	Roadside	30.11	0.32	6.40	90.40	29.26	[54]

Country	Site	Ascorbic Acid (mg/g)	Total Chlorophyll (mg/g)	рН	Relative Water Content (%)	APTI	Reference
Oman	Roadside	5.52	2.35	7.07	75.39	12.74	[23]
Iraq	Reference/rural	5.87	1.50	6.90	76.86	12.62	[24]
Iraq	Roadside	6.16	1.27	6.30	70.33	11.68	[24]
Qatar	Reference/rural	38.93	5.94	6.15	92.18	56.29	This study
Qatar	Roadside	42.94	3.32	6.17	78.82	48.88	This study

Table 3. Cont.

# 3.2. Total Chlorophyll

Chlorophyll is a guide of productivity of the tree species [55]. This parameter shows the plant photosynthetic ability and thus its biomass growth. Reports indicate that chlorophyll content depends on the species kind, pollution levels, and other biotic and abiotic conditions; certain pollutants increase the chlorophyll content while others may reduce it [56]. The chlorophyll molecule can be degraded due to high quantity of pollutants in the atmosphere [17]. In this study, the total chlorophyll values ranged from 5.89 to 6.02 mg/gin rural areas and 1.94 to 4.87 mg/g in roadside areas, showing a reduction in chlorophyll at the roadside. Data from our results indicate the average highest chlorophyll content was observed in the reference site (as expected), 5.94 mg/g. These high values indicate low pollution within the area or may indicate that the plant has become tolerant to pollution [57,58]. Shyam et al. (2006) reported that elevated chlorophyll might also result from a reduced accumulation of dust particles on the surface of the leaves [59]. Samples collected from the roadside sampling area showed a significant reduction in the chlorophyll content of up to 69%. These results agree with previous data by Achakzai et al. (2017), who reported the decrease in total chlorophyll content with increased pollution [48]. Rahmawati et al. (2014) suggested that the air pollutant may affect the chemistry of the chlorophyll molecule [60], in which hydrogen atoms replace magnesium within the chemical matrix, reducing the efficiency of the chloroplast, photosynthesis, and the conductance of stomata and increasing leaf fall [61-63]. Others such as Bakiyaraj et al. (2014) reported that lower chlorophyll content was associated with a higher level of pollution [64]. Our data imply a high polluted site with low chlorophyll levels.

## 3.3. pH

Within plants, pH plays a significant role by regulating the function of the plant's enzymes that are responsible for many of the chemical reactions that take place within plants. The activity of enzymes is affected by pH, and each enzyme has an optimal pH range at which it functions most efficiently, some requiring higher pH than others do [48]. Moreover, pH can also play more roles in metabolic reactions and disease resistance [65,66]. Acidic pollutants such as SO<sub>2</sub> and NO<sub>x</sub> decrease the pH nature of the leaf and thus adversely affect the plant. Tolerance of the plant then governs the rate of pH drop. An increase in the pH increases the plant's resistance to air pollutants attained by the chemical conversion of hexose sugar to ascorbic acid in the foliar tissue of plants [67]. Our results indicate that the pH in roadside areas was slightly higher than in rural areas. Our pH data are in agreement with similar studies conducted in the region [21] (Table 3, Figure 2).

#### 3.4. Relative Water Content

The relative water content plays a vital role in the ability of plants to endure pollution as water regulates many physiological processes under high stress from contaminants [47]. The RWC gauges the water's balance (uptake and release) [68,69]. This parameter governs the permeability of the outer non-aqueous surface layer of the protoplasm within the tree species [70] and thus accounts to some extent for the tolerance against pollutants [48]. As the air around the plant gets polluted, the plant's cell permeability increases [71]. This, in turn, results in an increased loss of water and nutrients, triggering a domino effect leading to the immature senescence of leaves [72]. High water levels within a plant species can also counteract high acidity with its cells sap and control drought conditions [17]. Elevated values of RWC indicate drought resistance species, while reduced levels may be the result of pollutants affecting the rate of transpiration within the plant [73,74]. Moreover, Rai (2016) proposed a direct link between physiological functions and RWC in stressed conditions [75]. In this study, the RWC% mean value in rural areas was considerably higher than in roadside areas (92.18% vs. 78.82%). This is in agreement with previous studies from similar regions as both Alotaibi et al. (2020) and Alhesnawi et al. (2018) reported higher RWC% at rural areas in comparison to roadside areas (Table 3, Figure 2) [21,24].

#### 3.5. APTI

The reaction of most plants to the stress bought on by different contaminants, whether this emanates from the water, soil, or air, depends on the species. The APTI is a significant tool that is used as a measure of the sensitivity of plants, which helps in the selection of pollution tolerant plants for mitigation purposes [17,47]. Plants with elevated APTI are a good choice and show tolerance to air pollution. In our study, the APTI range of roadside and rural areas was between 39.55–63.01 and 54.68–57.81, respectively. Based on our calculated values of APTI and the APTI categories by Singh et al. (1991) (Table 1), Ziziphus spina-christi is tolerant to air pollution in our study area [35]. The tolerance of Ziziphus spina-christi to air pollution was also found to be high (i.e., tolerant species) in Saudi Arabia [21] and Oman [23]. The same species (i.e., Ziziphus spina-christi) was reported to have intermediate tolerance to air pollution in Egypt [54] and Iraq [24]. Our data indicate that *Ziziphus spina-christi* is tolerant to air pollution within sampled sites in Qatar and is a good candidate for air pollution mitigation and can be used where air pollution is of particular concern such as in industrial areas, urban areas, and heavy traffic roadsides, which would result in lower air pollution loads. As stated earlier, depending on the climatic nature of the site, other studies may contradict our findings (e.g., [24,54]) with regards to the species. Nevertheless, there are no data concerning this species and subject in Qatar yet. Thus, it would be appropriate to conduct more studies on this species, including other native plant species compatible with Qatar climate, and investigate their utilization to mitigate air pollution and its effects.

The Air Pollution Tolerance Index combines the data of four biochemical parameters, ascorbic acid, total chlorophyll content, pH, and relative water content, to give a better understanding with regard to the response of plants to pollution [76,77]. A Pearson correlation analysis was performed between all biochemical parameters and APTI. APTI showed a strong positive correlation (p < 0.01) with both total chlorophyll (coefficients 0.83) and ascorbic acid (coefficient 0.76). In contrast, a weak correlation was observed between RWC, pH, and APTI (Table 4 and Figure 3). Alotaibi et al. (2020) reported a strong positive correlation of APTI with ascorbic acid, while it had weak correlation with the rest of the parameters [21]. A strong positive correlation between APTI and ascorbic acid was also reported by [24].

	pН	Ascorbic Acid	Total Chlorophyll	RWC	APTI
pН	1				
Ascorbic Acid	0.05	1			
Total Chlorophyll	0.063	0.27 *	1		
RWC	-0.21	-0.33 *	0.30 *	1	
APTI	0.08	0.76 **	0.83 **	0.04	1

**Table 4.** Pearson correlations (2-tailed) between variables at 95% CI. (\* Correlation is significant at the 0.05 level (2-tailed), \*\* Correlation is significant at the 0.01 level (2-tailed)).



**Figure 3.** Correlation of biochemical parameters with APTI values. (**A**) Total chlorophyll (mg/g) vs. APTI. (**B**) pH vs. APTI. (**C**) Ascorbic acid (mg/g) vs. APTI. (**D**) Relative water content (%) vs. APTI.

The Principal Component Analysis (PCA) method was used to identify significant factors influencing APTI levels. Table 5 represents the correlation matrix between variables (total chlorophyll, ascorbic acid, pH, relative water content, and APTI). Eigenvalues of the principal components greater than or equal to one are classified as statistically significant. The percentage variance of components 1 and 2 was calculated using the PCA method. PC1 (total chlorophyll, ascorbic acid, and APTI) represented 45%, while PC2 (pH and RWC) indicated 27% with an approximate total cumulative of 73% (Figure 4). The results indicate that the cluster of two components (total chlorophyll and ascorbic acid with APTI) represented 45%. In contrast, PC2 (pH and RWC) indicated 27%, pointing to the former two as main parameters when determining the ATPI. The Pearson's correlation also shows this as both total chlorophyll and ascorbic acid showed a strong positive correlation with APTI (Table 4, Figure 3). As shown in Figure 4, ascorbic acid and total chlorophyll are substantially correlated with APTI among the four biochemical parameters.

Component	Initial Eigenvalues			Mariahlan	Rotated Component Matrix	
Component -	Total	% of Variance	Cumulative %	variables	PC1	PC2
1	2.279	45.589	45.589	APTI	0.994	-0.102
2	1.399	27.979	73.568	TChl	0.871	0.288
3	0.950	18.997	92.565	Ascorbic Acid	0.700	-0.537
4	0.371	7.417	99.983	RWC	0.139	0.900
5	0.001	0.017	100.000	pН	0.061	-0.477

Table 5. Eigenvalues and total variance of the Principal Component Analysis.



**Figure 4.** Two-dimensional component analysis for APTI, total chlorophyll, ascorbic acid, pH, and RWC.

## 3.6. BCF

Bioconcentration factor is a vital measure to investigate a plant's potential in the remediation of heavy metals [25]. The accumulation of Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn, and Hg by the *Ziziphus spina-christi* was assessed using BCF in the leaves and fruits as depicted in Figure 5. Generally, BCF values were higher in leaves than fruits implying that leaves of *Ziziphus spina-christi* have a greater potential for metal absorption than its fruits. The results showed that both the leaves and fruits of the studies plant species had BCF values < 1 for all the investigated elements except Hg where BCF > 1 in both leaves and fruits of *Ziziphus spina-christi*. The metal concentrations were obtained in the order of Hg > Zn > Cu > Ni > Pb > Mn > Cr > Cd > Co > Ba > Fe > Al in the leaves and Hg > Zn > Pb > Cu > Ni > Cd > Fe > Mn > Cr > Co > Ba > Al in the fruits. The highest BCF obtained was Hg 4.301 and 2.32 in leaves and fruits, respectively. These findings suggest that the leaves and fruits of *Ziziphus spina-christi* can accumulate Hg; however, they can absorb but not accumulate Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn. Our findings suggest that the native *Ziziphus spina-christi* has the ability to accumulate Hg and therefore is a good

candidate to be used for phytoremediation in areas of mercury contamination. El-Amier and Alghanem (2018) estimated the BCF of four metals (Zn, Cu, Cd, and Pb) in leaves of *Ziziphus spina-christi* from an urban area in Egypt [28]. The results obtained in their study align with our findings for the elements Zn, Cu, and Pb, since both studies observed BCF < 1. However, their study found a BCF of more than 1 for Cd, suggesting that the leaves of *Ziziphus spina-christi* have the ability to accumulate this particular element. Based on the values of BCF higher than 1 of Fe, Pb, and Cd in the leaves of *Ziziphus spina-christi* in an industrial area in Iran, Abbaszadeh-Dahaji et al. (2019) concluded that for phytoextraction of heavy metals in both urban and industrial areas, *Ziziphus spina-christi* can be considered as a suitable species [78]. Furthermore, Rafati et al. (2019) conducted a study to determine the BCF of four heavy metals (iron, manganese, lead, and cadmium) in the leaves of *Ziziphus spina-christi* in an industrial region of Iran. The findings of their research indicated that the BCF for cadmium exceeded 1, suggesting that this particular plant species has the potential to be utilized for phytoremediation purposes in regions affected by cadmium contamination [30].



Figure 5. BCF of twelve elements in leaves and fruits of Ziziphus spina-christi.

## 4. Conclusions

In this study, Ziziphus spina-christi showed a different response to air pollution that alerts biochemical parameters of the tree. Our study revealed that the rural site was the least disturbed by anthropogenic activities based on high levels of both total chlorophyll and relative water content and low levels of ascorbic acid. APTI is a significant tool for future planning and can help efficiently in the selection of plants for biomonitoring of air quality in urban areas. Plants with higher APTI values are considered tolerant species. They can be used as a sink to different air pollutants, while those with lower APTI values are considered sensitive and valuable as bioindicators of air pollution. Based on the calculated APTI in our study, Ziziphus spina-christi is considered a tolerant species and therefore is recommended to be incorporated into the green belt design in Qatar to enhance the air pollution mitigation in the state. Additionally, based on our results, Ziziphus spina-christi leaves showed that they accumulate mercury and thus have great potential to be used for phytoremediation of mercury contamination. Further studies are suggested to investigate other plant species in Qatar (especially native plants) around different pollution sites (i.e., urban, industrial, and roadside) to help identify effective species for reducing pollutants or as bioindicators air pollution.

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