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The Influence of Different Land Uses on Tungstate Sorption in Soils of the Same Geographic Area

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Abstract: The growing use of tungsten (W) in industrial applications has made it a critical element in modern production processes. This increasing demand is also contributing to the element's wider dispersion in the environment, including in soil. In addition to mining areas, it is necessary to evaluate the possible environmental effects of tungsten even in non-contaminated areas. The mobility and bioavailability of W in soil are essentially determined by the sorption processes that regulate its distribution between the liquid and solid phases of the soil. In this study, the effect of different land uses—natural, agricultural, and urban—on the sorption of W in soils of the same geographical area was addressed. The results showed that the maximum sorption can be found in natural soils, with a value of 528 mg/kg, while for agricultural and urban soils, the mean values are 486 and 392 mg/kg, respectively. Anthropic interventions seem to reduce this capacity in agricultural soils by about 8%, probably due to agronomic practices, and by even more, 26%, in urban soils, where the use of different materials can modify the original characteristics of the soils. These results show that variations in some of the main characteristics of soils, such as pH and organic matter content, also derived from different land uses, influence the sorptive properties of the soils.

Keywords: tungsten; land cover; soil pH; soil organic matter; Langmuir-type model

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1. Introduction

In recent years, there has been a growing interest in "critical elements", defined as those essential for new and emerging technologies but characterized by increasing demand and limited supply [1]. Among these elements, tungsten (W) stands out due to concerns over its limited reserves, which, at the current extraction rate of approximately 80,000 metric tons per year, are projected to be depleted within 50 years. This scenario necessitates the development of recovery processes from tungsten-containing waste materials, potentially leading to its increased release into the environment, including in soils beyond traditional mining areas, most of which are concentrated in China. China's share of global production exceeds 80% [2–4].

Tungsten is indispensable in numerous emerging industries, particularly in renewable energy, electronics, and other high-tech sectors, due to its unique properties, including the highest melting point among all metals and its exceptional resistance to weathering [5–7].

Tungsten concentrations in soils generally range from 0.5 to 80 mg/kg, with surface horizons typically exhibiting lower levels of 0.2 to 5 mg/kg. While natural sources remain the primary contributors to tungsten presence in soils, industrial effluents, military activities, air pollution, and improper waste management also significantly contribute to

tungsten contamination [2,3,8,9]. Although tungsten was historically considered biologically inert, recent research highlights its potential toxicological effects on humans and ecosystems [10–13].

Public concern about tungsten toxicity intensified after environmental tungsten exposure was linked to a leukemia cluster [14,15]. This association has raised awareness of tungsten's health risks, particularly regarding its increasing use in military applications [16]. As a replacement for lead in ammunition and a substitute for depleted uranium, tungsten is becoming more prominent in military technology [17]. In 2016, the U.S. EPA identified tungsten as a potential public health risk and added it to its National Priorities List [18].

Tungstate anion is the thermodynamically stable form of W in the environment [3,10,19]. In soil, the behavior of tungstate is strongly influenced by sorption processes which determine the distribution of the anion between the solid phase and soil solution.

Under specific environmental soil conditions, such as an alkaline soil pH, tungsten compounds can become mobile and leach into groundwater [20,21]. Additionally, tungsten can accumulate in the food chain, with its plant uptake influenced by soil characteristics [22–24]. Tungsten bioavailability in soils is primarily governed by sorption processes, which significantly influence its mobility and potential toxicity to living organisms [2].

In various countries, land use has undergone significant transformations, driven by economic and technological advancements [25,26]. Land use is an inherently geographical concept reflecting the interplay of natural and human activities. Assessing the impacts of land use transformations is an emerging scientific field requiring the integration of economic, environmental, and social dimensions [27–32]. New developments resulting from land use changes must prioritize safeguarding soil ecosystem services [33]. Among these services, sorption processes play a critical role in protecting the food chain and groundwater from contaminants [34]. Therefore, an investigation of the sorption of tungsten in soils with different land uses is of considerable interest in an environment continually shaped by human activities. In this paper, the word "sorption" includes all reactions involved in the passage of tungsten from the soil solution to the solid phase [35].

This study aims to evaluate how different land uses affect tungsten sorption in soils, focusing on natural (N), agricultural (A), and urban (U) soils, all uncontaminated and within the same geographical region in the Lake Maggiore area.

The Lake Maggiore area features a diverse landscape where natural and human influences coexist harmoniously. This region is characterized by a natural interplay of lakes and moraine hills, with vegetation shaped by the proximity of lake basins. These basins support Mediterranean plant growth, facilitated by the favorable soil composition near water bodies. Further inland, expansive wooded zones with Mediterranean vegetation remain intact.

The region is also marked by widespread urbanization, primarily consisting of small towns with populations generally under 10,000. These towns contain both natural soils and those influenced by urban development.

Local agriculture is predominantly small-scale, with limited large-scale arable land. These smaller agricultural properties produce high-quality niche products, catering to tourists and local residents who value fresh, premium goods. The area's economic affluence and emphasis on quality contribute to this preference for specialized agricultural produce.

2. Materials and Methods

2.1. Site Description and Soil Sampling

Soil samples were collected in the previously described Lake Maggiore area which is located between Italy and Switzerland, an area influenced by diverse human activities that have contributed to some modification in natural soils. However, unlike the lake

waters, which in the past suffered from industrial discharges of both organic and inorganic contaminants, resulting in significant challenges to water and sediment quality [36], the surrounding soils in this high-tourism area remain largely uncontaminated.

For this study, a total of 15 soil samples were collected, representing three different land uses: natural (N), agricultural (A), and urban (U). Samples were taken from a depth of 0–15 cm and reflect the region's uncontaminated soils, all exhibiting a very low and consistent natural tungsten concentration of approximately 0.10 mg/kg. The sampling points are reported in Figure 1.



Figure 1. Map of the study area.

2.2. Soil Characterization

Soil samples were air-dried and ground to be passed through a 2 mm sieve. Texture, pH, soil organic matter (SOM) content, and total iron (Fe) content were determined by standard Soil Science Society of America methods [37,38].

2.3. Sorption Experiments

The sorption experiments were carried out by adding 25 mL of a solution containing sodium tungstate at increasing concentrations (from 0 to 900 mg/L) to 1 g of the soil sample in 60 mL polypropylene centrifuge tubes. To maintain a constant ionic strength of 0.01 M, NaCl was used as a background electrolyte. To select the equilibration time, increasing

contact times were tried using the highest tungstate concentration [39]. Data showed that the equilibrium time was around 18 h.

Thus, tungstate solutions were added to 1 g of soil under agitation at 25 °C for 18 h. After centrifugation (9500 rpm for 15 min), the W concentration in the supernatants was determined after filtration through a 0.2 μm paper Whatman filter. All the tests were performed in triplicate.

The amount of tungstate sorbed per unit mass of soil was calculated as the difference between the initial tungstate concentration and the equilibrium concentration in the solution, using the following expression:

$$q = \frac{V * (C_i - C_e)}{m} \quad (1)$$

where q is the quantity (mg/kg) of W sorbed per unit mass of soil, C_i is the initial W concentration (mg/L), C_e is the W concentration (mg/L) in solution at equilibrium, V is the added solution (mL) containing W, and m is the mass (g) of soil employed.

2.4. Tungsten Analysis

The W concentrations in all samples were measured by inductively coupled plasma–optical emission spectroscopy (ICPOES Varian AX Liberty, Varian, Milan, Italy). The original soil W concentration was analyzed according to the USEPA method 3050B using the specific digestion procedure with modifications reported by Bednar et al. 2007 [40]. All chemicals used in the experiments were of reagent-grade quality. All the analyses were performed in triplicate including certified reference materials and blanks to ensure the reliability and reproducibility of the results.

2.5. Quality Assurance and Quality Control

Quality assurance and quality control were accomplished by means of a certified reference soil material (NIST SRM 2710), with a standard solution being analyzed every 10 samples and at the end of the analytical series. The W limit of quantification (LOQ) was 0.05 mg/L. The recovery of spiked samples ranged from 93% to 101%, with an RSD of 1.86 of the mean.

2.6. Statistical Analysis

The reported results are the mean of the three replicates ± standard deviation (±SD). Statistical analysis was performed using STATISTICA v. 6.0 (Statsoft, Inc., Tulsa, OK, USA).

3. Results and Discussion

3.1. Soil Characteristics

The soil samples used in this study (Cambisol, according to FAO classification) were collected from the same geographic area but exhibited distinct characteristics, as summarized in Table 1. This region was specifically chosen for its locally driven land use planning, with minimal intervention from national authorities. Consequently, land use changes have occurred relatively uniformly, without the introduction of significant industrial activities that could add variability to soil properties.

The N soils of the area under study represent those that have developed without direct human influence, evolving solely through natural processes. These soils are characterized by a surface horizon rich in organic matter, including accumulations of decomposed plant residues. They typically exhibit a well-developed structure with relatively consistent pH values across the various sampling sites. The organic matter content is notably high, reflecting the natural cycle of organic inputs over time.

Table 1. Mean values of the soil characteristics of the 15 collected samples. Values are reported as mean ± standard deviation (SD).

Sample	pH	SOM (%)	Clay (%)	Silt (%)	Sand (%)	Fe (%)
1N	5.78 ± 0.03	8.6 ± 0.40	4.92 ± 0.73	15.70 ± 0.89	79.38 ± 1.12	4.4 ± 0.15
2N	5.82 ± 0.03	7.5 ± 0.39	4.19 ± 0.75	11.84 ± 0.81	83.97 ± 1.19	4.8 ± 0.11
3N	6.03 ± 0.02	6.5 ± 0.31	5.30 ± 0.83	6.25 ± 0.83	88.45 ± 1.23	5.3 ± 0.11
4N	5.51 ± 0.02	9.1 ± 0.40	6.50 ± 0.76	15.25 ± 0.71	78.25 ± 1.29	4.6 ± 0.13
5N	5.77 ± 0.03	8.8 ± 0.37	5.71 ± 0.81	14.98 ± 0.89	79.31 ± 1.34	5.2 ± 0.14
1A	7.20 ± 0.01	5.2 ± 0.29	4.74 ± 0.71	5.75 ± 0.62	89.51 ± 1.33	5.1 ± 0.11
2A	6.45 ± 0.02	5.9 ± 0.31	5.54 ± 0.85	9.10 ± 0.87	85.36 ± 1.29	4.6 ± 0.14
3A	6.36 ± 0.03	6.2 ± 0.24	3.93 ± 0.86	17.47 ± 0.73	78.60 ± 1.39	5.2 ± 0.15
4A	5.93 ± 0.03	6.4 ± 0.25	7.47 ± 0.95	9.53 ± 0.89	83.00 ± 1.27	4.8 ± 0.13
5A	5.60 ± 0.01	7.0 ± 0.35	9.15 ± 0.97	20.60 ± 0.89	70.25 ± 1.12	4.4 ± 0.14
1U	6.82 ± 0.02	5.6 ± 0.23	6.33 ± 0.87	18.39 ± 0.64	75.28 ± 1.19	5.9 ± 0.13
2U	6.44 ± 0.01	6.1 ± 0.33	7.21 ± 0.90	13.66 ± 0.77	79.13 ± 1.25	4.6 ± 0.12
3U	6.94 ± 0.03	5.0 ± 0.22	5.50 ± 0.72	18.21 ±0.81	76.29 ± 1.27	4.3 ± 0.14
4U	7.64 ± 0.02	4.3 ± 0.23	4.75 ± 0.74	11.70 ± 0.72	83.55 ± 1.36	3.8 ± 0.11
5U	7.30 ± 0.03	4.9 ± 0.26	3.97 ± 0.70	7.68 ± 0.85	88.35 ± 1.39	3.5 ± 0.13

Note: there is no statistically significant difference among the selected sampling points in the concentration of W, which showed a mean value of 0.12 ± 0.03 mg/kg.

The A soils have been intentionally managed and modified to support agricultural activities. Modifications include plowing, which reduces soil compaction and enhances porosity, potentially altering the soil's original structure. Fertilizer application is presumed to contribute to changes in soil properties. While the organic matter content remains relatively high, it shows variability and a slight decline compared to that of N soils. pH values are more variable across sampling sites and tend to be more alkaline, reflecting the influence of agricultural practices.

The U soils are significantly affected by human activities and urban infrastructure. These soils often comprise a mixture of natural and anthropogenic materials, with their original characteristics substantially altered by urbanization processes. Their organic matter content is generally lower than in N soils and varies widely between sampling points. Similarly, pH values are more variable and tend to shift toward alkalinity, highlighting the transformative effects of urban development on soil properties

The soils of the study area exhibit significant variability in pH, ranging from acidic values with a minimum of 5.51 (4N) to a maximum of 7.64 (5U). Overall, the pH values are predominantly below 7.0. However, when the soils are grouped by land use, a greater consistency in pH is observed. Natural soils display mild acidity, with pH values ranging from 5.61 (4N) to 6.03 (3N). Agricultural soils exhibit higher pH values ranging from 5.6 (5A) to 7.2 (1A). The most alkaline values are found in urban soils, with two samples (4U and 5U) showing pH levels exceeding neutrality.

The organic matter content in the study area's soils is relatively high compared to in typical Italian soils, ranging from 4.3% (4U) to 9.1% (4N). On average, natural soils have the highest organic matter content at 6.5%, followed by agricultural soils at 5.5%. Urban soils exhibit the lowest organic matter content, likely due to the inclusion of anthropogenic materials, such as residual construction debris, in samples like 4U and 5U, which also show pH levels above neutrality.

Overall, the distribution of pH and organic matter appears closely related to land use, as illustrated in Figure 2.

These findings align with previous studies conducted in distinct geographical areas with varied sources and land uses. Both pH and organic matter, which profoundly influence numerous soil processes, including sorption, are notably affected by human activities [41–43].

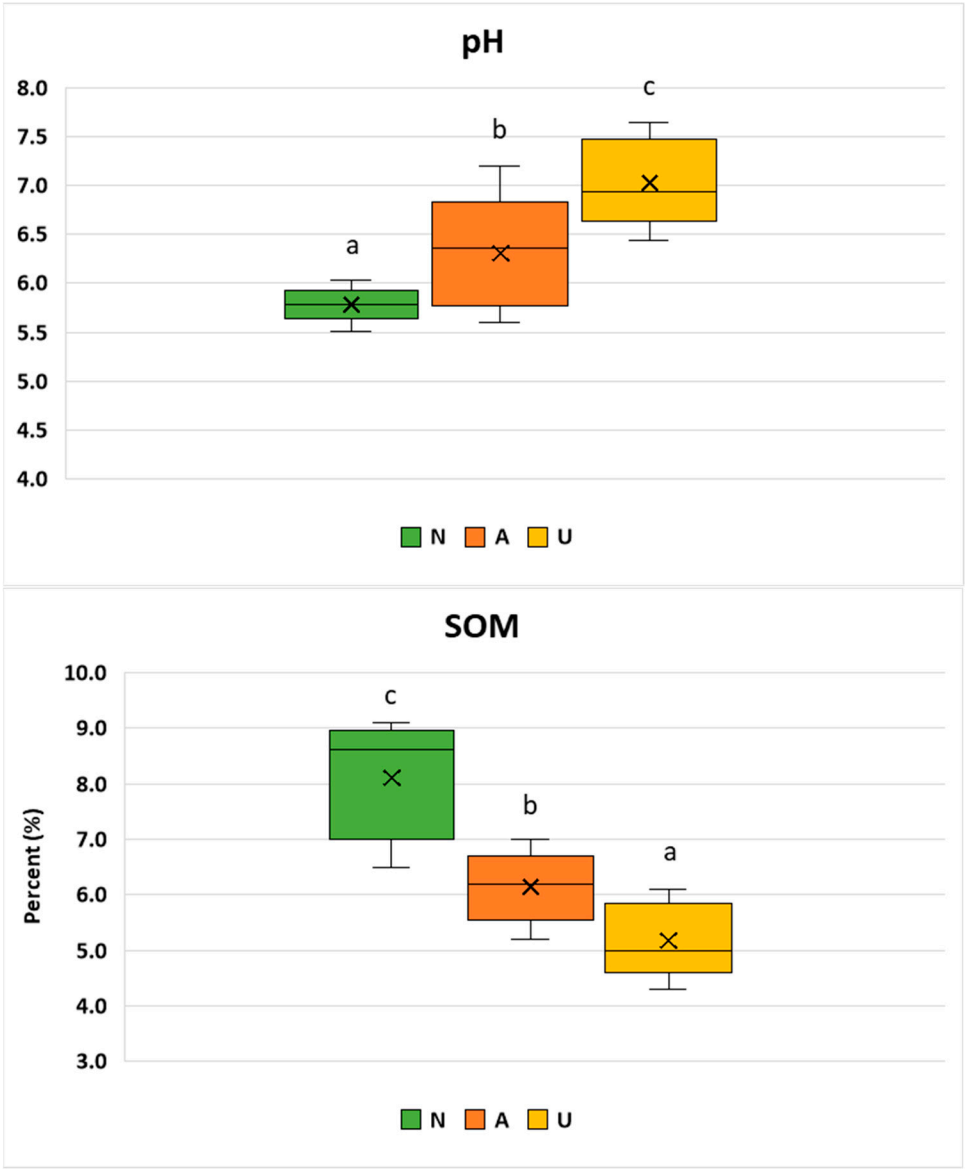


Figure 2. Boxplots representing the distribution of pH values and organic matter content in the soils from different land uses, with central lines marking the median values. Values followed by different lowercase letters are significantly different at $p < 0.05$.

A soil texture analysis revealed a predominance of the sandy fraction, with values ranging from approximately 70% (5A) to 89% (1N), and an average of around 81%. Unlike pH and organic matter, the soil texture and total Fe content appear to be minimally influenced by land use. Figure 3 illustrates that no statistically significant differences are observed among the texture and Fe content values. The inclusion of Fe content in the analysis is due to the role of Fe oxides and hydroxides, which possess high specific surface areas and are considered critical in tungsten sorption processes [2].

Different studies have reported varying results regarding the influence of land use on soil texture in distinct geographic areas [44,45]. Our findings suggest that soil texture in the studied region is primarily shaped by pedogenic processes that have acted over time, rather than by recent anthropogenic interventions. Similarly, the total Fe content, which plays a critical role in tungstate sorption [46], appears to be governed predominantly by long-term weathering and pedogenesis. No significant influence of land use on Fe content was observed.

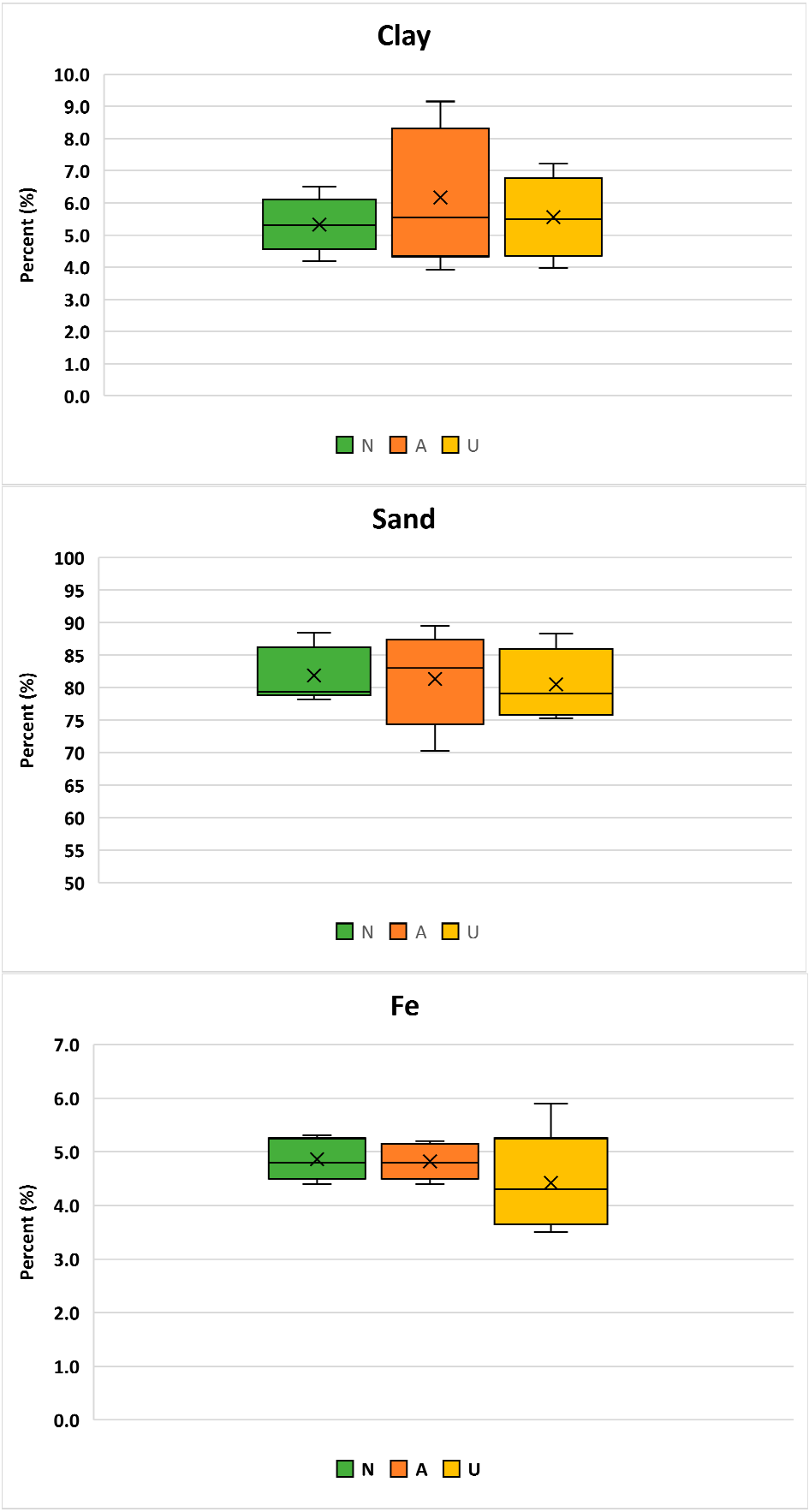


Figure 3. Boxplots representing the distribution of clay, sand, and Fe content (%) in the soils from different land uses, with central lines marking the median values.

3.2. W Sorption

The sorption of tungstate in the 15 soil samples was evaluated at their native pH levels by constructing sorption isotherms that plot the quantity of tungstate sorbed (q_e) against its equilibrium concentration in solution (C_e). Under the experimental conditions employed, tungstate sorption exhibits a curvilinear pattern (Figure 4). Such non-linear sorption behavior is commonly observed in soil sorption studies and is typically associated with the presence of multiple sorption mechanisms [47,48].

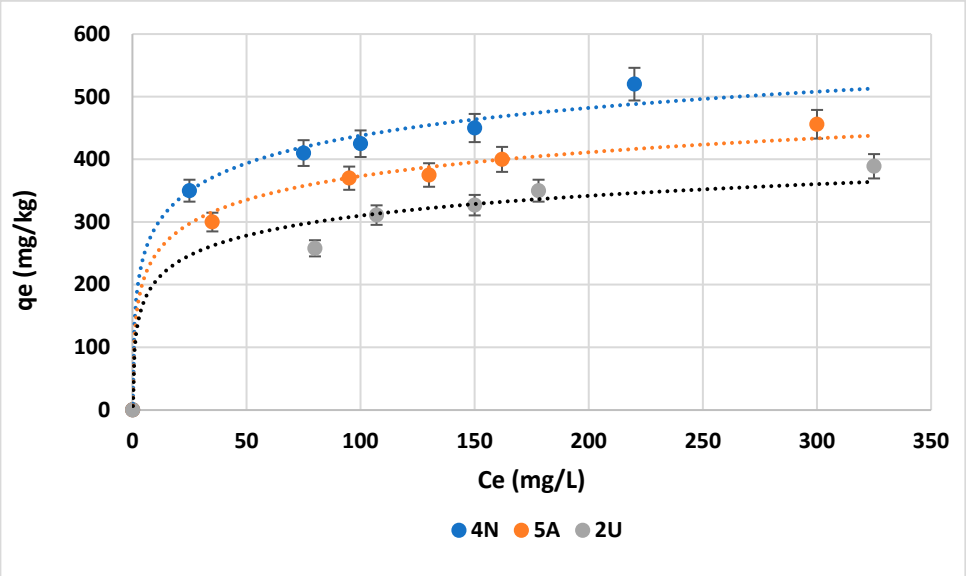


Figure 4. Sorption isotherms for the different soil uses. Data refer to the soil samples with the highest qmax values for each land use: N, A, and U.

The sorption isotherms for the different soil uses are reported in Figure 4. The data refer to the soil with the highest qmax for each land use.

Regardless of land use, the isotherms display similar "L-type" patterns [49], indicative of a strong affinity between tungstate and the soil surface at low concentrations, followed by a plateau as saturation is approached. The isotherms were analyzed using both the Langmuir and Freundlich models, with the Langmuir equation providing a better fit based on higher correlation coefficients. Thus, the very frequently used "Langmuir-type equation" [39] was used to describe the sorption isotherms:

$$qe = \frac{K * qmax * C_e}{1 + K * C_e} \quad (2)$$

where C_e denotes the concentration (mg/L) of tungstate in solution, q_e denotes the concentration (mg/kg) of tungstate sorbed into the soil, qmax (mg/kg) denotes the maximum sorption of the soil, and K (L/mg) is the Langmuir coefficient related to the bonding energy of tungstate.

Under the pH conditions of the studied soils, the dominant tungsten species was the fully dissociated tungstate ion, as polytungstate formation is expected primarily under more acidic conditions, where up to 50% of total tungsten may exist in polymerized forms [50,51]. The sorption data indicated a saturation trend, suggesting that the available surface sites for tungstate sorption became fully occupied under the experimental conditions. The soils' sorption capacities followed this order: natural (N) > agricultural (A) > urban (U).

Despite the Langmuir model's assumption of uniform sorption energies across surface sites, it remains widely used in soil science for describing sorption processes, particularly as saturation is approached. The L-type isotherms observed in this study were well described by

the Langmuir model across the concentration range. Previous studies have similarly applied the Langmuir model to describe tungsten sorption on various soils and soil components [52–54].

The heterogeneity of the soil surfaces investigated, characterized by sorption sites with differing binding energies, supports the observed high affinity for tungstate, even at low solution concentrations. At lower tungstate concentrations, sorption is likely dominated by the formation of inner-sphere surface complexes, indicative of specific sorption mechanisms. As tungstate concentrations increase, the predominant mechanism likely shifts to exchange reactions, resulting in the formation of outer-sphere surface complexes [55]. In soils with a high organic matter content, advanced techniques such as X-ray photoelectron spectroscopy (XPS) have revealed the formation of inner-sphere tungsten complexes. Additionally, attenuated total reflectance–Fourier-transform infrared spectroscopy (ATR-FTIR) has demonstrated an increase in weakly adsorbed polytungstates, which exhibit greater mobility compared to tungsten monomers under similar conditions [56]. The type of surface complex formed is influenced by surface coverage, a behavior observed in other anions such as arsenate [57].

Similar behaviors have been documented for anions structurally analogous to tungstate, including molybdate [58], phosphate [59], and arsenate [60]. The Langmuir parameters derived for soils with different land uses are presented in Table 2. These findings underline the broader applicability of the observed mechanisms to anion sorption processes in soils.

Table 2. Langmuir parameters for the investigated soils. In each column, values followed by different lowercase letters are significantly different at $p < 0.05$.

Sample	qmax (mg/kg)	K (L/g)	R^2
1N	527 d	0.020 a	0.973
2N	525 d	0.022 a	0.985
3N	515 d	0.026 a	0.974
4N	545 d	0.024 a	0.984
5N	528 d	0.031 a	0.950
1A	475 c	0.029 a	0.964
2A	482 c	0.028 a	0.970
3A	479 c	0.028 a	0.980
4A	490 cd	0.027 a	0.994
5A	503 c	0.026 a	0.993
1U	410 b	0.029 a	0.965
2U	419 b	0.029 a	0.930
3U	400 b	0.030 a	0.988
4U	360 a	0.031 a	0.954
5U	372 a	0.028 a	0.971

An analysis of these data, alongside the soil characteristics reported in Table 1, revealed that pH is the most critical parameter influencing tungsten sorption in the studied soils. Specifically, the sorption of WO_4^{2-} was higher in the acidic soils and lower in the alkaline soil, regardless of the land use. These findings align with previous research on tungsten sorption across various materials, including oxides [19,21,61,62], clays, peat [53], and soils [52]. Such research consistently highlights soil pH as a key determinant of tungstate sorption capacity. Soil pH governs both the solubility of tungstate ions and the reactive properties of the sorbing surfaces [52,63]. Variations in soil pH can significantly alter the sorption efficiency of WO_4^{2-}, as demonstrated in studies involving Italian soils [39,64]. The results from this study further emphasize the critical role of soil pH in regulating tungstate sorption processes, underscoring its influence on the availability and behavior of tungstate ions in soil.

The relationship between the soils' pH and the sorption maxima of all the sampled soils is reported in Figure 5.

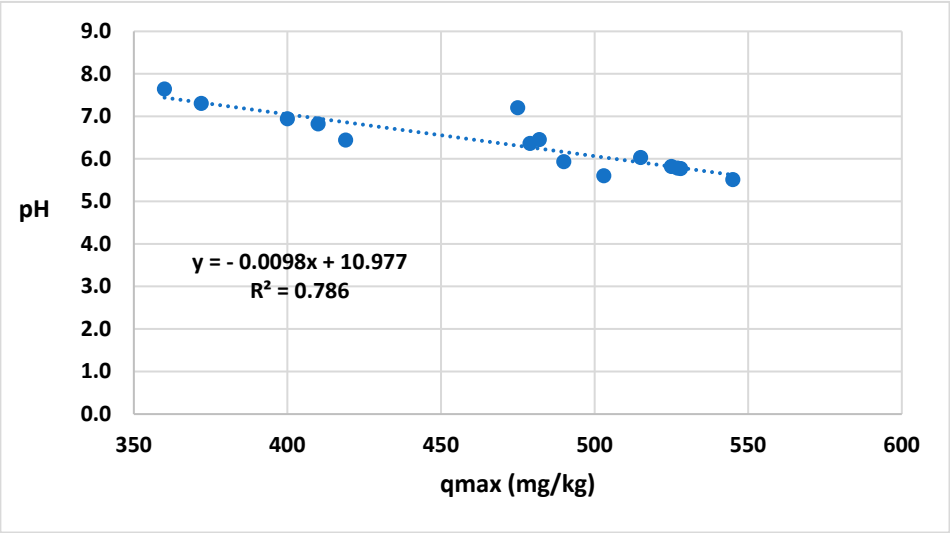


Figure 5. Relationship between the soils' pH and the sorption maxima of all the sampled soils.

The higher sorption capacity of soils at lower pH levels can be attributed to the increased presence of positively charged sorbent surface sites. Additionally, the carboxylic groups of humic materials exhibit a positive charge density due to protonation under acidic conditions [58]. This enhances electrostatic attraction between the positively charged soil surfaces and the negatively charged tungstate ions as soil pH decreases. Conversely, at higher pH levels, the soil surface becomes negatively charged, reducing its interactions with tungstate and resulting in a significant decrease in tungstate sorption.

The influence of pH on tungstate sorption is particularly pronounced within soils belonging to the same land use category. As soil pH increases, sorptive properties diminish, a trend that is especially evident in natural and agricultural soils.

Considering all the soils sampled, the maximum sorption observed was also correlated with the organic matter content (Figure 6).

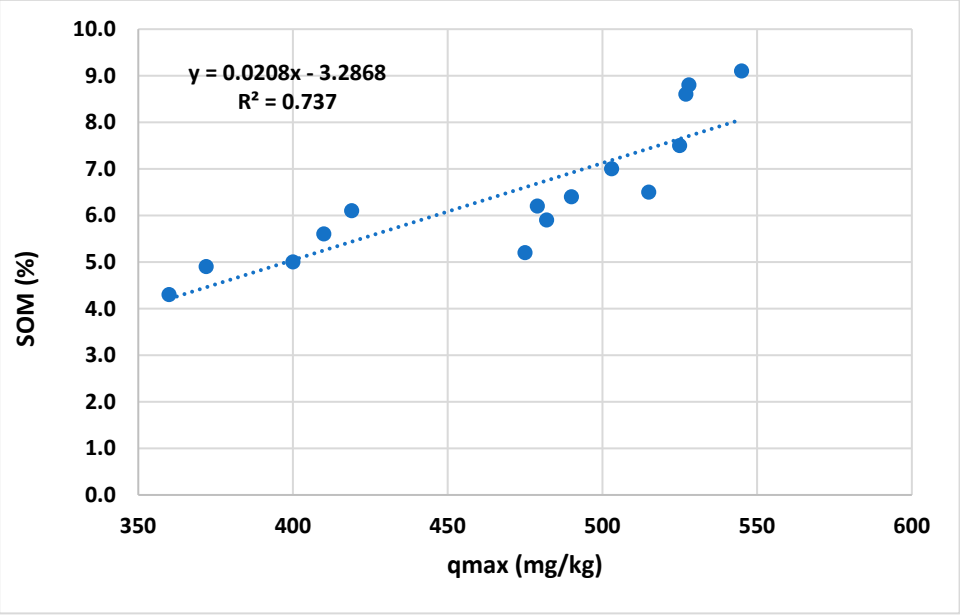


Figure 6. Relationship between the SOM content and sorption maxima of all the sampled soils.

This observation is in accordance with earlier studies on tungsten sorption in Italian soils [64] and organic substrates, where stable complexes between tungstate and humic substances were identified [53]. Similar behavior has been observed for other elements like arsenic and antimony, where humic materials with high binding capacities significantly affect sorption on variable-charge soil minerals [65,66].

The trend of higher sorption associated with greater soil organic matter (SOM) content is particularly apparent within each land use category. Natural soils (N) exhibit the highest tungstate sorption capacities, corresponding to their elevated organic matter content, followed by agricultural (A) and urban (U) soils in decreasing order. Previous research has demonstrated that land use changes can significantly alter soil carbon content [67,68], which in turn affects sorption properties.

A difference in land use can induce multiple changes in sorption properties by modifying physicochemical characteristics, even in soils with the same geological origin. Land use has been reported to influence soil pH [69,70] and drive changes in the composition of organic matter [71], with consequent changes in its interactions with mineral soil phases and the microbial cycle [72,73].

Other soil parameters, such as clay, sand, and Fe content, show weaker correlation within individual land use categories. The absence of a correlation between total Fe content and qmax may be due to the relatively uniform Fe content across all 15 soil samples, making it difficult to isolate its specific contribution to the sorption process.

The relationship between the clay, sand, and total Fe content and sorption maxima for all the sampled soils is reported in Figure 7.

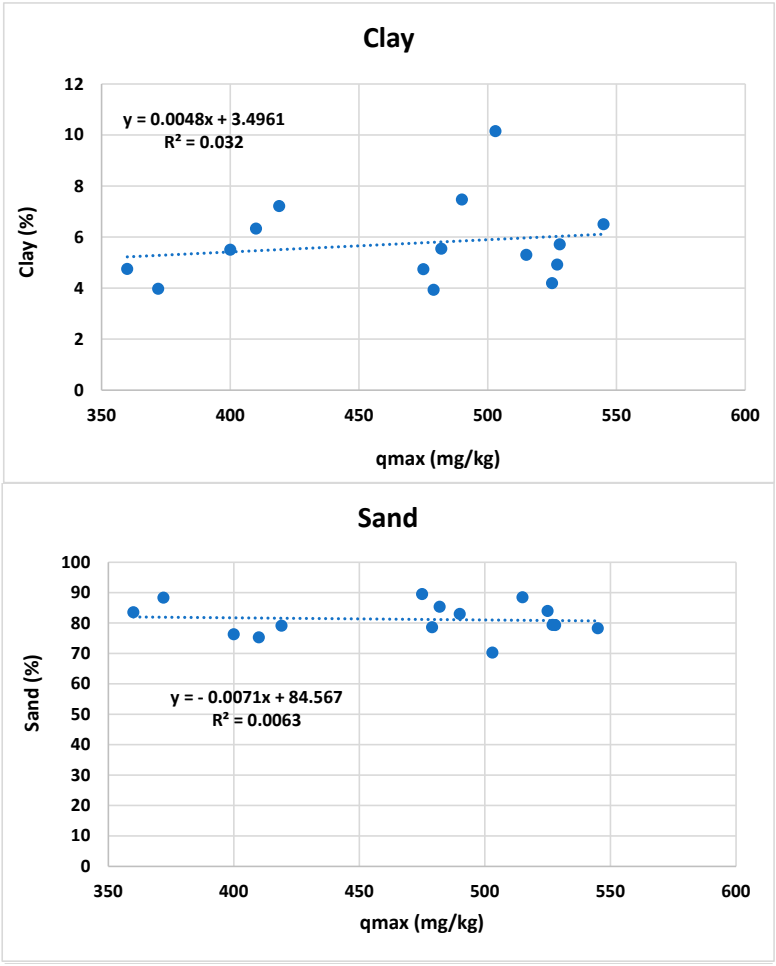


Figure 7. *Cont.*

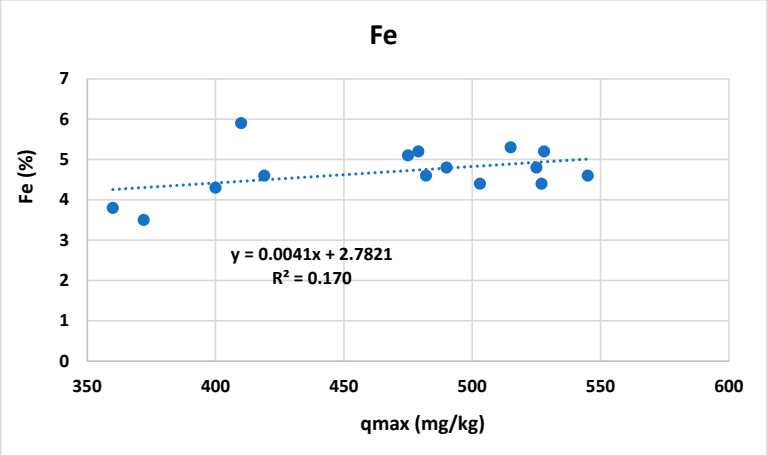


Figure 7. Relationship between the soils' clay, sand, and total Fe content and the sorption maxima of all the sampled soils.

These results highlight the significant impact of land use changes on soil characteristics. Human activities in urban and agricultural areas have been recognized as major contributors to soil degradation [74]. Likewise, the significant effect of land use type on the Langmuir maximum sorption capacity has been reported for phosphate, an anion structurally similar to tungstate. These differences in sorption maxima were attributed to soil characteristics, including pH, organic matter content, and Fe compounds [75,76].

A comparable trend in sorption capacity across different land use types has also been described for fluoroquinolone antibiotics. A reduction in maximum sorption was observed when transitioning from natural (forest) soils to agricultural soils, primarily due to a decrease in humic matter—an essential parameter for the sorption of organic compounds [71].

3.3. Distribution Coefficient Kd

The sorption behavior of tungstate can also be described using the distribution coefficient, Kd, which is defined as the ratio of the concentration of WO_4^{2-} sorbed onto the soil to its concentration in the equilibrium solution.

The trend in Kd versus the equilibrium concentration for soils with the highest qmax values across different land uses is shown in Figure 8. The graphs reveal noticeable variations in sorption capacity among the soils, particularly at low concentrations of WO_4^{2-}. These findings suggest that WO_4^{2-} is preferentially retained onto sites with a high affinity for tungstate ions during the initial stages of sorption. Natural (N) and agricultural (A) soils exhibit a greater number of these high-affinity sites, which form inner-sphere complexes due to their specific properties. Once these sites are saturated, sorption shifts to lower-affinity sites where outer-sphere complexes dominate, resulting in reduced differences in Kd values among the three soil types.

The trend in Kd highlights a saturation effect since the sorption reaches a limit after a certain amount of added tungstate, and additional increases in concentration do not result in increased sorption.

The characteristics of the sorption reactions can also be described by the variation in Gibbs free sorption energy [77,78] according to the equation

$$\Delta G = -RTlnKe$$

where R = gas constant (0.008314 kJ mol^{-1} K^{-1}); and T = temperature in Kelvin (K).

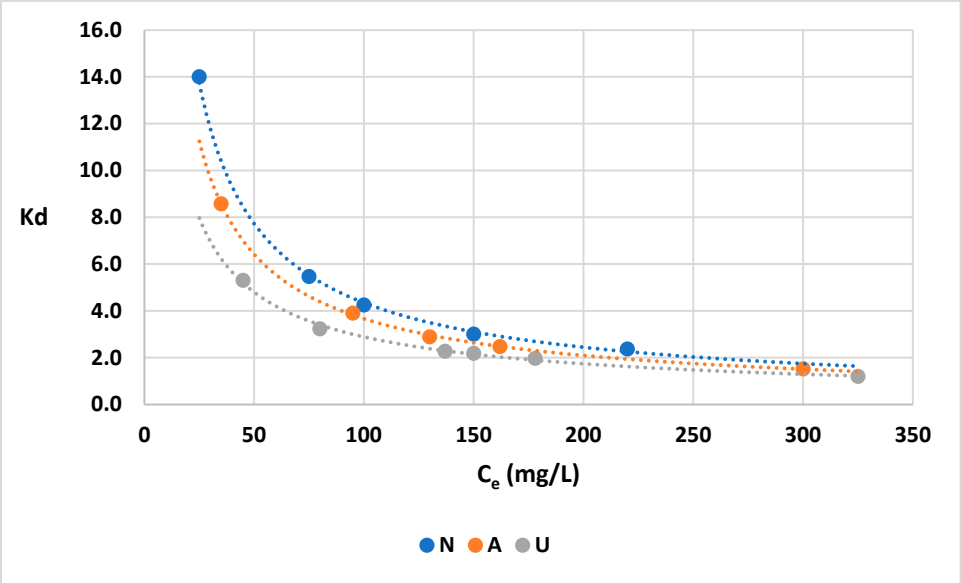


Figure 8. Kd trends of N, A, and U soils versus equilibrium concentrations (C_e).

The equilibrium constant Ke can be derived as the intercept of linear plots of Kd values against the initial concentration C_i [79]. Table 3 presents the derived equation and the corresponding Gibbs free energy (ΔG) values, along with the R^2 values for each case. The values of Δ*G* provide insight into the spontaneity of the sorption process, where negative values indicate that sorption is thermodynamically favorable.

Table 3. Free energy of sorption (ΔG) for soils from different land uses. The data refer to soils from different land uses which showed the highest qmax values. Kd denotes the distribution coefficient, and C_i denotes the initial concentration.

Soil	Equation: Kd vs. C_i	R^2	lnKd	ΔG
N	Kd = −0.0508 C_i + 12.477	0.68	2.53	−6.26
A	Kd = −0.0224 C_i + 7.4399	0.66	2.01	−4.07
U	Kd = −0.0073 C_i + 3.5409	0.89	1.26	−3.13

These results underscore the impact of soil properties on the sorption of WO_4^{2-}. N soil displayed the most negative ΔG values, suggesting a stronger sorption capacity, likely attributable to specific characteristics of this soil type, such as its lower pH and organic matter content. The relative strength of interaction forces between tungstate ions and soil surfaces is reflected in the free energy changes, with the sorption capacities ranked as follows: N soil > A soil > U soil.

To further assess the suitability of the studied soils for tungstate sorption, the separation factor (R_L) was calculated using the Langmuir equation. The separation factor is a dimensionless constant denoted by the equation

$$R_L = \frac{1}{1 + K * C_i} \quad (3)$$

where K is the constant of the Langmuir equation, and C_i is the initial WO_4^{2-} concentration [80,81].

The R_L value determines whether the sorption is favorable or unfavorable. In the former case, R_L is less than 1, while it is greater than 1 in the case of unfavorable sorption. When sorption is irreversible, the constant R_L becomes equal to zero.

Considering the isotherms at the highest W concentration added [82,83], the separation factor R_L indicates some differences in sorption across soil types. The average R_L values

range from 0.025 for N soils to 0.039 for A soils, with an intermediate value of 0.036 for U soils.

The lowest R_L value being observed in N soils suggests a strong affinity for tungstate, indicating that these soils could act as effective sinks by immobilizing tungstate and reducing its mobility in the environment. In contrast, A soils exhibit less efficient tungstate sorption, which could lead to greater mobility and an increased risk of leaching into groundwater.

This reduced sorption capacity in A soils can be attributed to the presence of competing anions, particularly phosphates commonly used as fertilizers. It has been indicated that phosphate effectively reduces tungstate sorption in soils [84], while molybdate has been described to compete with tungstate in sorption onto gibbsite and ferrihydrite [85].

Phosphate ions often exhibit a higher affinity for soil sorption sites than tungstate [46,85,86], potentially outcompeting tungstate and increasing the R_L value. Recently, it has been reported that in the presence of co-occurring arsenate, the sorption of tungstate decreased in different soils from about 8% to about 38% [38].

Similarly, the slightly elevated R_L values in U soils may result from several additional competing anions, including arsenic [87].

Regardless of land use, the low R_L values observed for all investigated soils highlight a general favorability for tungstate sorption in the studied area.

Sustainable land use planning requires balancing agricultural and urban development with the preservation of natural resources, as they are interconnected. Poor soil management has led to issues like erosion and nutrient loss, threatening long-term sustainability. Effective environmental management requires predicting the mobility and bioavailability of substances or elements based on interactions with soil properties. This enables long-term monitoring, the identification of environmental trends, and an assessment of land resource potential from local to regional levels. Sorption processes are among the most important in soils for conducting thorough environmental impact assessments.

By preventing irreversible damage and promoting the protection of natural resources, such assessments contribute to the sustainable management of soils and their ecosystem services.

4. Conclusions

In many countries, land use has undergone substantial transformations driven by economic and technological advancements. These anthropogenic influences have significantly altered the properties governing chemical, physical, and biological processes in soil, as well as its capacity to deliver essential ecosystem services. Among these services, sorption processes are particularly critical, as they regulate the bioavailability of substances and their potential migration into groundwater.

This study highlights variations in the sorption capacity of soils within the same geographical region, driven by differences in land use. Specifically, with regard to tungsten (W), natural soils demonstrated the highest sorption capacity. Human activities were found to reduce this capacity, with agricultural soils showing an average decrease of approximately 8% in maximum sorption capacity and urban soils exhibiting a more pronounced decline of about 26%.

To comprehensively evaluate the impact of land use on sorption processes, it is crucial to compare soils from the same geographic region to minimize variability. However, to extend these findings to a broader context, future studies should include a more diverse range of soils from different areas and under varying conditions. Despite these limitations, the results of this study underscore the fundamental role of soils in sustainable development and highlight the urgent need for policymakers and regulatory agencies to prioritize soil quality in land management strategies.

Differences in soil sorption characteristics within a landscape significantly affect food production and water quality, while also playing a critical role in mitigating climate change and preserving biodiversity. Therefore, land use planning should aim to achieve an optimal balance between environmental sustainability, economic viability, and societal needs tailored to specific regions.

The findings from this study contribute to a deeper understanding of the environmental fate of tungsten, a relatively understudied element in soil science. Given its growing use in a variety of industrial and consumer products, tungsten may increasingly enter soils from diverse sources. Investigating its behavior and potential impacts is thus essential for the development of effective environmental management strategies.

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