Assessment of inorganic pollutants removal from the Litani River contaminated stream in Lebanon by means of two wetland plants (*Sparganium erectum* and *Phragmites australis*)

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ABSTRACT

The contamination of surface water resources by inorganic pollutants originating from agricultural practices is a global challenge that has increased in recent years, undermining economic growth, as well as physical and environmental health of people. This study was conducted in June-July 2013 in South Bekaa Valley of Lebanon, on a set of 18 micro-lysimeters installed in the soil inside a 3.5 ha wetland, which was constructed along the Litani River to treat the polluted effluents. Plants of *Phragmites australis* and *Sparganium erectum* were grown in the micro-lysimeters, and supplied with irrigation at 100%, 150% and 175% of the soil field capacity. Water for irrigation was pumped from the Litani River.

Results showed that the control irrigated at 100% of field capacity was found to be more efficient in removing inorganic pollutants, namely nitrates (NO_3^-), sulfates (SO_4^{2-}) and phosphates (PO_4^{2-}), than treatments irrigated at 150% and 175% of field capacity. Moreover, the accumulation of the inorganic pollutants was found to be higher in the leaves of *P. australis* than *S. erectum*. This was associated with an absorption of sodium (Na^+) and potassium (K^+) in the leaves, leading to stabilizing the salinity and total dissolved solids in the soil water solution.

On the other hand, the efficiency of *P. australis* and *S. erectum* in removing copper (Cu^{2+}) from the polluted effluents was found to be stable throughout the sampling period. Plants uptake of copper increased in treatments irrigated at 150% and 175% of field capacity, compared to the control. This might be due to the high load of this toxic heavy metal in agricultural water effluents. Due to their high uptake efficiency, both aquatic plants provided unfavorable conditions for the interaction of copper with inorganic fertilizers, namely nitrate, phosphate and sulfate, and form insoluble precipitates, which then can be hardly removed from the soil.

We concluded that the process of treating the polluted effluents of the Litani River by phytoremediation can be considered efficient and cost-effective method. Additional efforts should be made to deliver a working technology, with a scant attention to the economic outlook of phytoremediation compared to other techniques.

Keywords: Inorganic pollutants, Wetland, Agricultural pollution, *Phragmites australis*, *Sparganium erectum*.

Introduction

The Litani River, Lebanon's largest and most vital waterway, faces severe pollution issues stemming from various sources. Widespread sewage disposal, unregulated industrial wastewater discharge, and illegal diversion practices have transformed the Litani into a significant threat to public health and environmental integrity (Khatib et al., 2018). Furthermore, agricultural activities along its banks exacerbate the problem, as contaminants from chemical fertilizers and pesticides used find their way into the river, further compromising its water quality and contributing to inorganic pollution (El Chamieh et al., 2023).

Conventional remediation methods, relying on high physical and chemical interventions, have been developed to address polluted soil and water sites. However, these methods are often economically burdensome and non-feasible in the long run. Consequently, there's a growing interest in alternative remediation technologies like phytoremediation, which offers efficiency, cost-effectiveness, and durability. Phytoremediation, leveraging the natural abilities of plants to remove, uptake, or stabilize contaminants, presents a sustainable solution to combat pollution in air, water, sediments, or soils (Ali et al., 2013).

The objectives of this study were to (i) assess the performance of two aquatic plants, *Sparganium erectum* and *Phragmites australis*, in removing inorganic pollutants from the contaminated waters of the Litani River, using a wetland simulated process, (ii) determine the effectiveness of the irrigation regime to treat the polluted effluents, and (iii) propose recommendations for adopting phytoremediation as a low-cost treatment technology.

Material and methods

The experiment was conducted at the Training and Extension Centre of the Litani River Authority in South Bekaa Valley in Lebanon during June-July 2013. The experimental set up consists of 18 iron-galvanized micro-lysimeters, each having an area of 2,374.6 cm^2 and a volume of 10,4483.5 cm^3, which were installed in the soil inside a 3.5 ha constructed wetland, and filled with soil from the surrounding fields. Plants of *Phragmites australis* and *Sparganium erectum* were grown in the micro-lysimeters, and supplied with irrigation at 100%, 150% and 175% of the soil field capacity (FC). Water for irrigation was pumped from the Litani River.

Two factors were studied:

- P: Plant species: *Phragmites australis* and *Sparganium erectum*;
- I: Irrigation level: Control irrigated at 100% of field capacity (FC) and two treatments irrigated at 150% and 175% of FC.

In total six treatments and three replicates, each representing a combination of plant species × irrigation level (P × I) distributed in a completely randomized design (CRD). Statistical analyses were made by paired t-test using STATISTICA, Software version 10 (Hill and Lewicki, 2007; Statsoft Inc., 2011). The Student's t-test was used to detect the significance of pollutant's concentration in leaves between plant species and irrigation treatments.

Leaf samples were collected from the lysimeters-grown plants weekly over two months (June-July 2013). Samples were placed into labeled plastic bags and stored in a refrigerator at 0°C to maintain the stability of ions into the leaf sap. Leaf samples were then dried out in a forced air oven at 80°C for 48 hours. Dry leaves were stored at room temperature (18–22°C) in closed glass jars, and kept in the dark until laboratory analyses were performed.

Physicochemical parameters, namely electrical conductivity (EC) and total dissolved solids (TDS) were measured using a tracer pocket tester (JENWAY 470 Conductivity/TDS meter), which offers a wide measuring range. To prepare the solution for EC and TDS measurements, 0.2 g of air dried leaf samples was treated with 50 ml of acetic acid (CH_3COOH, 2%) in a 100 ml flask, followed by shaker agitation for 30 minutes at 200 rounds per minute. Subsequently, the solution was filtered using Whatman qualitative filter paper N1, to remove all substrate residues from the solution (Brown et al., 2000; US-EPA, 2001).

The concentrations of nitrate (NO_3^-) and sulfates (SO_4^{2-}) were determined on the same leaf solutions using LaMotte SMART2 Colorimeter, which gives direct readings for complete on-site laboratory analysis. Moreover, phosphates (PO_4^{2-}) were determined spectrophotometrically using Thermo Helios Aquamate 2000E UV-Vis Spectrophotometer (190 nm-1100 nm). On the other hand, the concentrations of ions sodium (Na^+) and potassium (K^+) were determined using a digital microprocessor flame photometer (AE-FP8201-A) using the Standard Operating Procedure (SOP) for operation, cleaning and calibration used in inorganic chemical analysis.

For measuring copper (Cu^{2+}) concentration in leaves, the following procedure was followed: 0.5 mg of leaf dried tissue was weighed using a precise electronic balance and transferred into 50 ml Erlenmeyer flask. Then, 10 ml of nitric acid (HNO_3) 99%, and 4 ml of hydrogen peroxide (H_2O_2) 100%, were added to the flask containing the dried leaf tissue. After allowing the mixture to stand for 16 hours to ensure decomposition of the organic matter, membranes, and proteins, the mixture was transferred into an acid condenser and placed on a hotplate set initially at 20°C for 30 minutes and then increased to 50°C for 2 to 3 hours. Once cooled, the solution was filtered using a 0.4 micrometer filter mesh connected to a syringe to remove any organic intrusion, resulting in a clear substrate. The filtered substrate was transferred into a 25 ml volumetric flask and adjusted with deionized water. Finally, the concentration of copper heavy metal was determined using an atomic absorption spectrophotometer (240FS AA fast sequential atomic absorption spectrometer).

The reduction efficiency (RE, in %) of the concentration of pollutants was assessed according to the International Water Association (Sperling, 2007), which proposes an equation for this intent (Singh, 2013). The efficiency of the plants in terms of the removal percentage of pollutants (NO_3^-, PO_4^{2-}, SO_4^{2-}, Na^+, K^+, and Cu^{2+}) was computed using the following formula:

$$RE\ (\%) = 100\ \frac{(Ci - Ce)}{Ci} \quad (1)$$

Where, C_i and C_e are initial and final concentrations, respectively (in mg/L).

Results

The leaves samples of the control treatment have higher nitrate concentrations for both plant species, with slightly higher levels observed in *Phragmites australis* compared to *Sparganium erectum*.

The control exhibited the highest phosphate concentrations for both plant species. On the other hand, higher concentrations were notably observed in the leaves of *Sparganium erectum* compared to *Phragmites australis,* suggesting species-specific differences in phosphate uptake and accumulation (US-EPA, 2000).

Notably, leaf samples exhibited higher sulfate concentrations in the control treatment, compared to treatments irrigated at 150% and 175% of field capacity, thus indicating a potential reduction in sulfur uptake with increased water availability in the root zone of aquatic plants (Li et al., 2024).

The findings indicate that both specie exhibited an increase in sodium concentration in their leaves until late June, followed by a decline, which was observed in all treatments. In parallel, *Phragmites australis* consistently showed higher [Na^+] concentrations compared to *Sparganium erectum*. Additionally, the highest concentrations of sodium were observed in the control treatment, while treatment irrigated at 175% of field capacity showed the lowest concentrations.

Both *Phragmites australis* and *Sparganium erectum* exhibited a steady increase in potassium concentration in their leaves over time, with *Phragmites australis* generally showing higher concentrations compared to *Sparganium erectum*. Additionally, the highest concentrations of potassium were observed in the control treatment, while plants irrigated at 150% and 175% of field capacity showed lower concentrations.

Salinity, in terms of electrical conductivity (EC), initially increased with time in the leaves, until reaching a point at which salt accumulation seemed to be stabilized, suggesting a balance between salt uptake and plant adaptation mechanisms to salinity. Interestingly, higher irrigation application levels (150% and 175%) led to lower salinity concentrations in the leaves of both *Phragmites australis* and *Sparganium erectum*.

The concentration of total dissolved solids (TDS) in the leaves of *Phragmites australis* and *Sparganium erectum* increased with time, with however greater TDS accumulation in the leaves of the latter than the former. In addition, treatment irrigated at 175% of field capacity exhibited the highest TDS concentrations, followed by treatment irrigated at 150% of field capacity, while the control treatment showed the lowest TDS values.

Both *P. australis* and *S. erectum* exhibited increased copper concentration in their leaves over time, with the former showing higher concentrations compared to the latter. Additionally, higher concentrations of copper (Cu^{2+}) were observed in samples irrigated at 175% of field capacity, while samples of the control showed the lowest concentrations.

Table 1 presents the percentages of ion removal efficiency by means of the two aquatic plants, across the different irrigation treatments. The efficiency of pollutant removal has been shown to be influenced by the irrigation regime, with the control irrigated at 100% of field capacity being more effective in reducing nitrate, phosphate, and sulfate levels than irrigated treatments at 150% and 175% of field capacity. The uptake of copper (Cu^{2+}) was more consistent across different irrigation levels, so that both plants have a stable capacity for heavy metal absorption.

The data also indicates that while nitrate and sulfate removal efficiencies increased initially, they eventually decreased across all treatments, leading to negative removal efficiency values. In contrast, potassium removal efficiency was highest under increased irrigation, with both *Phragmites australis* and *Sparganium erectum* showing substantial removal at 175% field capacity.

Table 1. Removal efficiency by means of two plants, *Phragmites australis* and *Sparganium erectum.*

Removal Efficiency (According to Eq. 1)	*Phragmites australis*			*Sparganium erectum*		
	C	T-150	T-175	C	T-150	T-175
Copper	81.37615	88.29268	82.22222	87.55319	86.86792	87.04478
Phosphate	58.33333	40	47.82609	70.2381	57.14286	62.5
Sulfate	-42.8571	-42.8571	-25	-41.4141	-28.5714	0
Nitrate	16.66667	-42.8571	-25	-41.4141	-28.5714	0
Sodium	18.96552	22.22222	-46.7742	20.75472	8.235294	-11.2903
Potassium	43.21429	50.38462	59.375	54.09836	55.17241	62.2

Conclusions

The results indicated that both plant species successfully reduced the concentrations of nitrates (NO_3^-), phosphates (PO_4^{2-}), and sulfates (SO_4^{2-}). However, *Phragmites australis* showed a greater capacity for removing these pollutants from water compared to *Sparganium erectum*. Additionally, the study found that both aquatic plants were effective in stabilizing salinity levels and total dissolved solids (TDS) in the soil water solution.

We concluded that phytoremediation provides a viable and cost-effective solution for improving water quality in polluted water bodies like the Litani River (LRBMS 2012 and 2014). Future efforts should focus on optimizing the phytoremediation process, considering economic factors, and scaling up the technology for broader application (Karam et al., 2023).

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