
Time Plots, Trends and Seasonal Growth/ Decay of Cr Removal in Vertical Subsurface Flow Sewage Treatment Wetland

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ABSTRACT

The present research work aimed at analysing the time series and estimation of seasonal growth/ decay of heavy metals dynamics in the vertical subsurface flow constructed wetlands (VSSFCWs) planted with Typha, Phragmites, Vaccha, Arundo and Vetiver on gravel media. Monthly plant and wastewater samples were collected for 15 months from the VSSF CWs. Plant and water samples were pre-treated in the laboratory, digested using diacid and their heavy metal concentrations were determined using atomic absorption spectrophotometer after filtration. The Main results indicated that the maximum uptakes of metals by plant occurred in summer while the minimum plant uptake were recorded in winter, regardless of metal concentrations applied and the trends showed a slightly stable profile irrespectively to the level of concentration applied. For the adsorption processes of Cr in the media (gravel) of the constructed wetlands, it appeared that this process was not significantly changing as function of time, except for Cr 1.5 ppm.

Keywords: Growth; Decay; Seasonality

1. Introduction

In recent years, water availability has become an issue of global concern. The rising of good quality water demand and the generation of wastewater result from factors like high population growth coupled with urbanization and industrialization. Wetlands either constructed or natural offer a cheaper alternative technology for wastewater treatment. Constructed wetlands (CW) have recently emerged as efficient technology for secondary treatment of wastewater in developing countries because of its low cost, ease operation, maintenance and generally good performance^[1,2]. However, widespread demand for improved receiving water quality, and water reclamation and reuse, is currently the driving force for the implementation of CW all over the world^[3]. Constructed wetlands, in contrast to natural wetlands, are man-made systems or engineered wetlands that are designed, built and operated to emulate functions of natural wetlands for human desires and needs. Constructed wetlands have been defined as a “designed or man-made complex of saturated substrates, vegetation and water, used for human use and benefits”, predominantly for waste treatment purposes^[4]. Constructed wetlands are essentially characterized by their excellent efficiencies, minimal investment and operating cost, remarkable economic and social benefits in treating wastewater. In the past 30 years, researchers had set up a number of constructed wetlands in different conditions for different types of wastewater. Constructed wetlands appear today to be sustainable systems for wastewater treatment, and their main components are macrophytes and substrates^[5,6]. Many examples of the devastating consequences of the wastewater on formerly clean and useful rivers and lakes have aroused public and scientific awareness of the need not only to stop the practice of direct dumping but to try and reverse it by extracting the pollutants. The remarkable ability of aquatic plants to extract compounds and elements from water efficiently has become well recognized^[7]. These plants are used for removing nutrients (N and P), organic pollutants, inorganic pollutants and biological pollutants. The role of aquatic plant is to stabilize the surface of plant beds, improve hydraulic conductivity of the media, create aerobic condition, release organic matter and improve microbial growth^[3]. Emergent macrophytes are herbaceous (soft tissue and non-woody) vascular plants (higher plants) and have a structure consisting of aerial stems, leaves and an extensive root and rhizome system^[4]. They are rooted in

the soil and emerge or stand up right above the water surface. Depth penetration of the root system and exploitation of the substrate layer differs from species to species. Moreover, wetland plants show different biomass production rates (growth rates) and prefer specific environmental conditions (temperature, light demand, salinity tolerance and pH)^[4]. Many types of macrophytes (aquatic plants) are found in the nature and are commonly selected for wastewater treatment: free-floated plants, floated plants, submergent plants and emergent plants^[7]. The plant species most commonly used throughout the world are: common reed (*Phragmites karka*), Vaccha (*Acorus Calamus*) and cattails or Typha (*Typha Latifolia*), Arundo (*Arundo donax*), Vetiver (*Vetiveria Zizganoides*). Furthermore, rushes (*Juncus sp.*) and sedges (*Carex sp.*; *Cyperus sp.*) are also commonly used species. Emergent macrophytes are the primary plants used in constructed wetlands for wastewater treatment throughout the world^[4,5]. Substrates used in constructed wetlands include mineral soils (clay, silt, sand and gravel) and organic soils (compost and decomposed plant litter). The nature of the substrate material strongly affects the movement of water through the wetland (hydraulic conductivity). It provides a huge surface area for attached microorganisms additionally to plant biomass and xvd acts as filtration and adsorption medium for pollutants such as suspended solids^[4].

Previous studies mainly focussed on the efficiency of the whole system regardless of the contribution of the components such as plant uptake, sedimentation, filtration or adsorption on the matrix (sand, soil, gravel) which are important to understand the mechanism and designing efficient CW^[6,8,9]. In the cases contributions of component of the constructed wetland were investigated, these were confined to the contribution of different macrophytes for the elimination of metal pollution^[10,11] ignoring the contribution of the substrates (sand, soil, gravel). The removal of heavy metals on soil materials^[12] and constructed wetlands with gravel^[13,14,8,9] has been tested in defined conditions^[14] found that gravel had 43 % pollutant removal efficiency^[13] obtained maximum removal efficiencies for Cr (98%) and Cd (96%) in constructed wetland vegetated on gravel beds^[9] showed different removal efficiencies for iron (Fe: 44%), Copper (Cu: 91%), zinc (Zn: 85%), aluminium (Al: 96%) and lead (Pb: 88%) in constructed wetland planted with Typha on a sandy substrate^[8] also obtained different removal efficiencies for chromium (Cr: 51%), nickel (Ni: 47%), iron (Fe: 45%) and mercury (Hg: 43%) in constructed wetlands vegetated on gravel lining beds. All these removal efficiencies values were due to the contribution of plants, substrates and microbes present in the system. In contrast,^[15] showed that the removal efficiency of Pb on gravel was very high (95-99%). Some plant species have developed tolerances to certain metals and can accumulate significantly higher amounts of them, such as *Typha Latifolia* for Pb, Zn and Cu or *Cyperus malaccensis* for Cu^[16]. Vegetation in constructed wetlands serves many other important purposes. These include soil stabilization/flow moderation, oxygen transport, metal-rhizome adsorption, carbon source, and metal uptake into plant tissue. Aquatic plants can assist in the 'baffling' of water flow to assist in even infiltration of water into substrate and to prevent preferential flow pathways. This is important in order to maintain desired oxygen concentrations and to maximize substrate particle contact with contaminants^[17]. If the removal processes of metals in VSSFCWs were previously studied, the variation of the removal efficiency profile need to be studied and understood for the range of pollutants, the wetland nomenclatures and the plants. This paper investigated the time series and estimation of seasonal growth/ decay of Cr dynamics in the vertical subsurface flow constructed wetlands (VSSFCWs) planted with Typha, Phragmites, Vaccha, Arundo and Vetiver Typha.

2. Materials and Methods

2.1 Description of the experimental plot and operating conditions

The experimental setup consisted of subsurface flow constructed wetlands (VSSF CW) in form of 50 litres plastic container at Indian Agricultural Research Institute, in New Delhi, India. Each wetland microcosms had a cylindrical shape, a diameter of 35 cm and a height equal to 50 cm. The wetland microcosms were filled with gravel (size ranging from 1 to 3 mm for fine gravel and from 5 mm to 25 mm for coarse gravel and a total weight of 60.1 kg per wetland) to a depth of 35 cm and planted with Typha, Phragmites, Vaccha, Arundo and Vetiver. These plant species had similar age and height at a spacing of 2-5 cm. The experiment was replicated thrice. To find the relative contribution of vegetation, the unvegetated wetland microcosm (containing only gravel) was also used for each treatment (this time without

replication). These microcosms were irrigated with Cr solutions of two different strengths each. The solution concentrations of Cr 1.5 and 3.0 ppm. Solutions containing Cr were prepared using available standard solution of Cr (Atomic Absorption STD solution, 250 ml packed size, made by CDR®). As a whole, there were 04 wetland microcosms for each metal concentration level (02 in total) and per plant (05 species in total), and yield a total of 40 wetland microcosms for the whole experiment.

2.2 Metal solutions preparation and irrigation of wetland microcosms

Irrigation phase was scheduled at the beginning of each month and 20 l of synthetic wastewater containing Cr (1.5 ppm, 3.0 ppm) were applied to irrigate the sets of VSSF CWs available on the field. The water volume demand to supply each set of CWs (on the basis of 20l/wetland microcosm) using of synthetic wastewater.

The depth of water was generally at 5 cm above the gravel bed after each irrigation. Samples of influent wastewater were collected (during irrigation phase) in 125 mL bottles previously washed and acidified, and 2-3 drops of nitric acid were mixed to the samples to avoid metal complexation^[18]. The hydraulic retention time (HRT) was 22 days. After this period, plant samples collection (in order to assess the concentration of heavy metals uptake after 22 days), emptying of wetland microcosms, and collection of effluent wastewater. Then, the monthly irrigation of the system was immediately planned. This experiment was conducted in the Vertical Subsurface Flow Constructed Wetlands experimental plot during 15 months.

2.3 Determination of metal contents in water and plant samples

To assess the effective metal content in pore water of wetlands, the influent samples were analysed in the laboratory. Briefly, 50 ml influent solution prior mixed with 15 ml of diacid was taken in 100 mL conical flask and digested on hot plate. After filtration (Whatman N°42 filter paper and diluted to 50 mL), the total contents of Cr were determined by Atomic Absorption Spectrophotometer (AAS) (model LABINDIA AA 8000) and expressed as mg/l.

Additionally, individual plant samples (root and shoot) were collected from the constructed wetland microcosms and first dried in air, then in oven at 60 °C for 2 days. Thereafter, 0.5 g of each dried ground sample was digested in diacid, filtered through a Whatman N°42 filter paper and diluted to 25 ml. Afterward, the plant samples were analysed for their content in Cr using Atomic Absorption Spectrophotometer (AAS) (model LABINDIA AA 8000). Concentrations obtained were reported as ppm or mg/l and multiplied by 50 to convert in mg/kg of dried weight (DW) of plant.

Time series analysis depicts the randomness, trend and periodicity in data and act as a pre-requisite of several simple forecasting methods. To accomplish this, regression equations were developed using the data acquired from the experiment as independent and dependent variables. Further, time series plots, trends and autocorrelation functions were presented to understand the pattern in the data and identify the high and low data values during the period of the experiment. Equally, autocorrelation functions were plotted to assess the seasonality in the data series. The nomenclatures used to depict the experimental time period in the time series plot is shown in Table 1. In this section, the plant uptake represents heavy metal contents in the whole plant.

| No. | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|-------|------------------|------------------|------------------|---------------|---------------|--------------|--------------|------------------|------------------|
| Month | December 2013 | January 2014 | February 2014 | March 2014 | April 2014 | May 2014 | June 2014 | November 2014 | December 2014 |
| No. | 10 | 11 | 12 | 13 | 14 | 15 | | | |
| Month | January 2015 | February 2015 | March 2015 | April 2015 | May 2015 | June 2015 | | | |

Table 1. Annotations used in time plots

3. Results and Discussion

3.1 Time series analysis for plant uptake of Chromium (Cr)

Time series response of Cr uptake by different plant species under three influent concentration levels of i.e. 1.5 ppm, 3.0 ppm are discussed below:

3.1.1 Influent concentration of Cr 1.5 ppm

The Cr uptake with influent concentration of 1.5 ppm for different plant species at different time periods are presented in Figure 1. The peak values of Cr uptake in the overall plant species ranged from 0.8 to 1.0 mg/kg (dw) and occurred in June 2014 and June 2015 (summer), while the lowest (0.2 mg/kgdw) in April, June 2014 (summer), November 2014 (rabi) and June 2015 (summer).

The plant uptake of Cr slightly increased with time but had very low slopes (0.00003 to 0.002) and intercept (0.4 to 0.6 mg/kg) for Typha, Phragmites, Vaccha Arundo and Vetiver (**Figure 1**).

The Cr removal in vegetated systems ranged from 0.41 to 0.56 mg/kg while it was approximately 0.58 mg/kg in unvegetated wetlands. The unvegetated wetland showed a slightly better performance for Cr removal compare to the vegetated systems. The amount of Cr removed was the highest (0.54 and 0.57 mg/kg) in Phragmites and Vaccha followed by 0.50 mg/kg in Vetiver and the minimum (0.42 mg/kg) in Typha and Arundo.

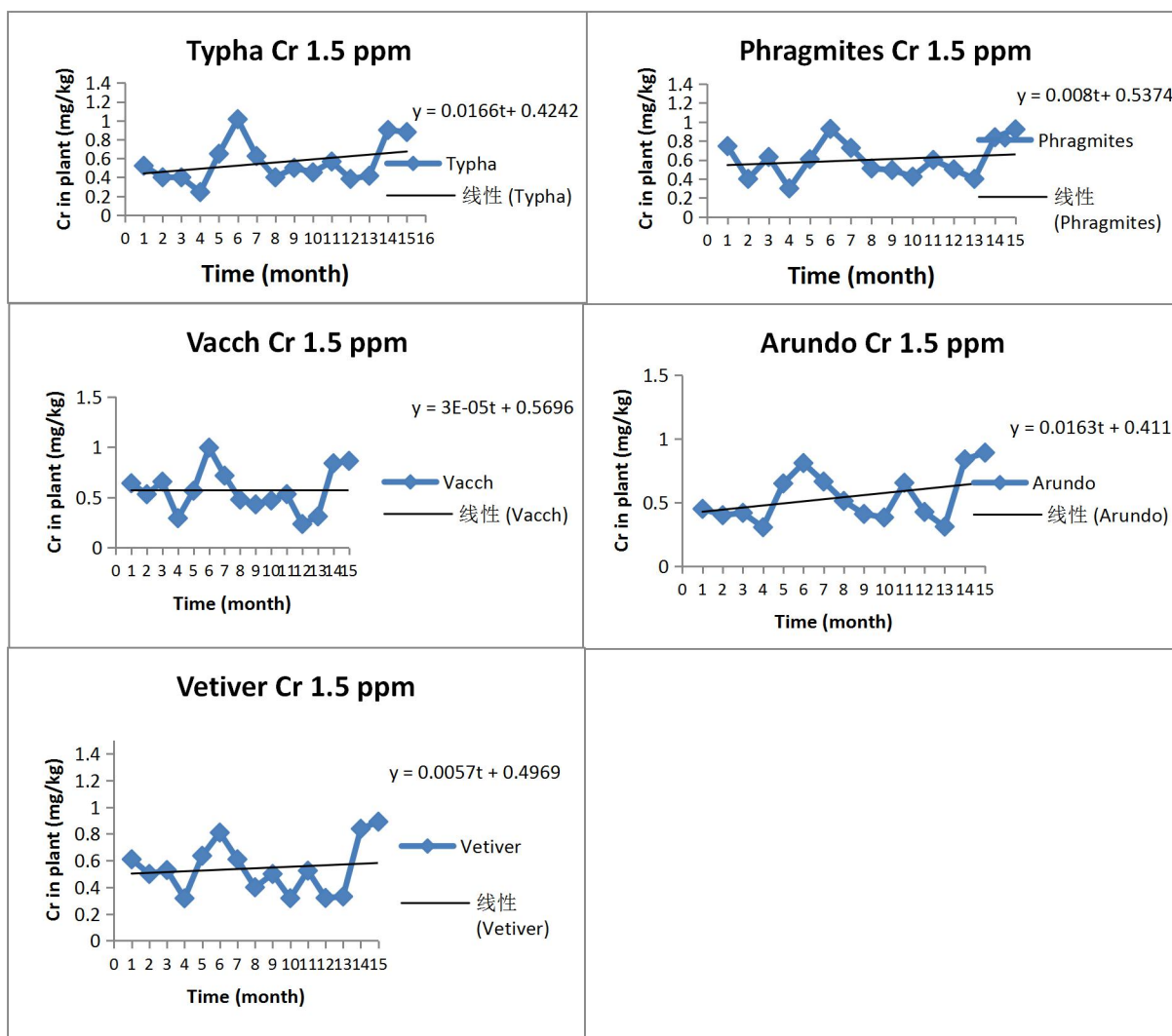


Figure 1; Time Plots and trends of Cr 1.5 ppm uptake in plants.

3.1.2 Influent concentration of Cr 3.0 ppm

The Cr uptake at influent concentration of 3.0 ppm for different plant species at different time periods is presented in **Figure 2**. The Cr removal values were found to be the highest in March 2015(rabi) and lowest (0.2-0.8 mg/kg dw in different plant species) in May 2015 (summer). The amount of Cr removed also differed amongst the plant species, being the highest (3.0mg/kg dw) whereas the other species could remove only 1.7 to 2.1mg Cr/kg dw. The amount of Cr removed was found in the following order: Typha (1.42 mg/kg)>Vetiver (1.36 mg/kg)>Phragmites (1.31

mg/kg)>Vaccha (1.26 mg/kg)>Arundo (1.00 mg/kg).

The uptake of Cr by Typha, Phragmites, Vaccha, Arundo, and Vetiver when plotted against time showed a slightly downward trend with negative slope (-0.0057 to -0.001) and positive intercept (1.0 to 1.4) values. Overall, the vegetated system performed better than the unvegetated system.

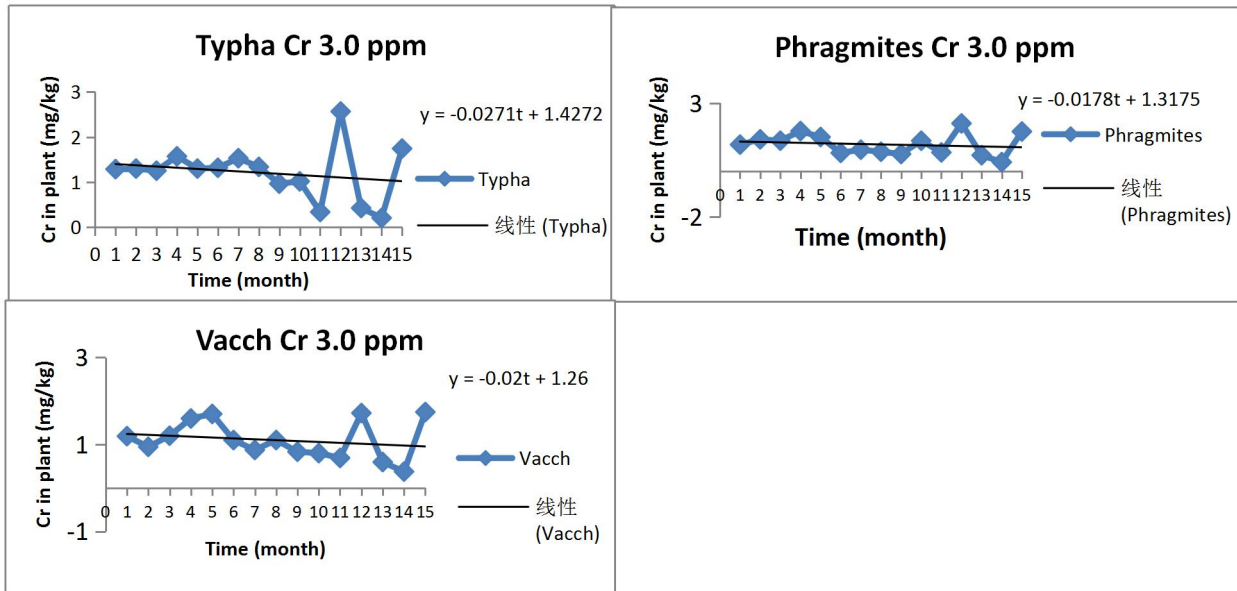


Figure 2; Time Plots and trends of Cr 3.0 ppm uptake in plants.

3.2 Time series analysis of Cr adsorbed in unvegetated wetlands

This section of the study presents the results of time series analysis of Cr concentrations adsorbed in unvegetated tanks for different concentration levels. In unvegetated tanks, the time series analysis was also performed for different influent concentration level of Cr (1.5 and 3.0 ppm). At Cr 1.5 ppm level, the maximum adsorbed values (0.77 to 1.2 mg/kg) were found in December 2013, April 2014, and January 2015, while the lowest values (0.35 to 0.55 mg/kg) observed in March 2014, May 2014, June 2014, and from May to June 2015 (Figure 3). At 3.0 ppm Cr, the peak concentrations adsorbed in unvegetated tank ranged from 0.745 to 0.9 mg/kg and were observed in December 2013, April and June 2014, January and April 2015, while the lowest concentrations of Cr 3.0 ppm adsorbed (0.45 to 0.52 mg/kg) were found in February 2014 and June 2015.

The adsorption of Cr in unvegetated wetlands showed a slightly upward trend irrespective of the influent concentration (Figure 2).

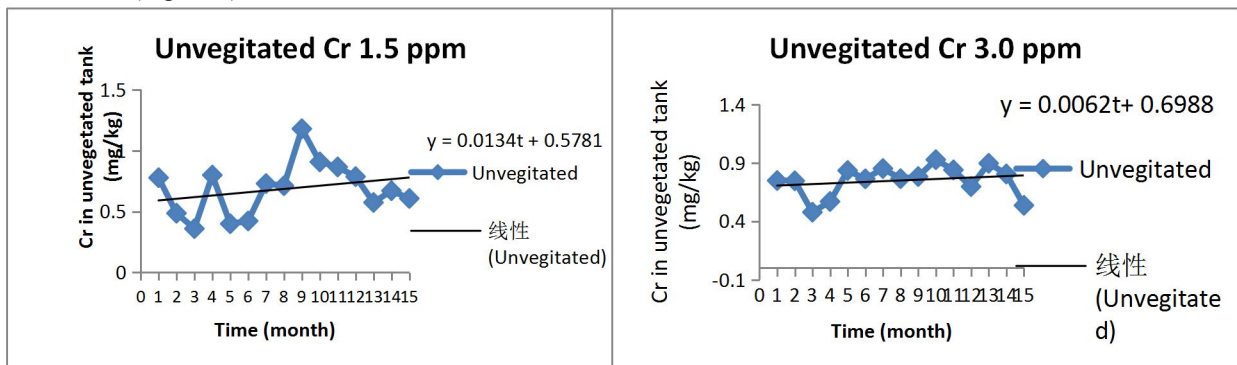


Figure 3; Time plots and trends for Cr adsorbed in unvegetated wetlands.

The time series data showed variable heavy metals uptake by different macrophytes and adsorption on gravel in constructed wetlands irrespective of plant species and concentration of heavy metals in the influent. These variations could be due to the change in seasons (rainfall, temperature, etc.) which influences the plant growth and indirectly the internal factors affecting the adsorption of heavy metals on substrates in constructed wetlands.

At 1.5 and 3.0 ppm Cr concentration was found to be the highest in summer and the lowest in winter (Rabi) at low (1.5 ppm) Cr concentration level. However, plant uptake was higher in Rabi (winter) than in the summer at 3.0 ppm Cr level. Substantial water losses due to high evapotranspiration were considered a major component in the water balance and pollutant removal in constructed wetlands, particularly where treated wastewater are destined for reuse^[19,20]. Metal concentrations in plant tissues were more in summer because of the higher evapotranspiration and loss of water led to increase the elemental concentration in the outflow water and other compartments of constructed wetland^[21]. Similarly, lower evapotranspiration values and dilution of metal concentration due to precipitation in rainy season resulted in reduced heavy metal uptake by plants in winter^[22]. Moreover, increase in transpiration rate increases hydraulic retention time and consequently the nutrient uptake^[22].

Vegetated wetlands were able to remove higher amount of Cr compared to unvegetated one. It was because of additional and cumulative effect amount of metal removed by plants over time^[21]. Cr removal showed a slightly upward trend at low concentration (Cr 1.5 ppm planted or not planted) but a slightly downward trend for medium concentration (3.0ppm Cr). Among different macrophytes tested for removal of Ni, Phragmites performed better at 0.5 and 1.0 ppm Ni level but Typha was found better at 5.0 Ni concentration. In case of Cr, wetlands planted with Vaccha resulted in higher Cr removal at low Cr influent concentration but Typha performed better at medium and high Cr concentration. ^[21] also found Typha and Phragmites appropriate for treating wastewater containing Cr.

However, the plant uptake is one of the processes contributing towards metal removal and does not define the overall performance of a given CW because of many other diverse and complex physicochemical and biological processes occurring in CW^[6].

4. Conclusion

The study indicated that the VSSF CWs planted with Typha, Phragmites, Arundo, Vetiver and Vaccha were efficient for the treatment of wastewater containing different amounts of Cr (1.5 and 3.0 ppm). The removal of heavy metals was higher in planted wetlands compared to unplanted indicating the importance of macrophytes in the removal processes in constructed wetlands. The metal removal had a seasonal variation within the 15 months of study period having higher removal in summer and compared to winter in general. The time series analysis data indicated that heavy metals plant uptake by different macrophyte species viz: Typha, Phragmites, Vaccha, Vetiver and Arundo in constructed wetlands was high in summer and low in winter. The performance of vegetated wetlands in removal of heavy metals from the aqueous media was found better compare to unplanted wetlands. For removal of Cr, plant uptake (> 60%) was the major process compared to adsorption (< 20 %) irrespective of t of macrophyte species and metal concentration in the influent. During the investigation period (15 months), the trend of plant uptake of Cr was slightly increased at low concentration (Cr 1.5 ppm) but slightly decreased at medium concentration (3.0 ppm). The appreciation of the temporal variation of the performance of constructed wetlands vegetated or not is very useful in the design and selection of macrophyte species for the treatment of various type of wastewater containing heavy metals and other types of pollutants.

Author Contributions

This work was carried out in collaboration between all authors. Altogether, authors designed the study, wrote the protocol, the first draft of the manuscript, and managed the analyses of the study. Besides, authors collected data, performed the statistical analysis, managed the literature searches, read and approved the final manuscript.

Conflict of Interest

No conflict of interest was conveyed by the authors.

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