

Abstract

Uchalli Wetlands Complex (UWC) is of great ecological significance for Pakistan. It consists of Khabekki, Uchalli and Jahlar Lakes. Information concerning water quality, sediments and heavy metal concentrations in different compartments of these lakes is limited at present. Increasing amount of CO₂ in the biosphere become a global concern. Algae possess 100x more carbon sequestration potential than terrestrial plants. Carbon sequestration potential of UWC of algae need to be explored. The present research focuses on spatial and temporal determination of physico-chemical parameters and heavy metal (Cd, Pb, Ni, Cu, Zn, Cr, As and Mn) analysis in different matrices i.e., water, sediment, plants and fish of three selected lakes. The study also aimed to estimate the CO₂ sequestration potential of UWC algae spatially and temporally. Sampling was done for five major aquatic matrices i.e., water, sediment, plants, fish and algae during summer and winter seasons (2016-2017). Fifteen water and sediment samples (each) were taken during both the seasons from each lake. Standard methods were used to determine physical and chemical parameters of two major matrices (water and sediments). Inductively Coupled Plasma (ICP) (OES Optima 2100 DV manufactured by Perkin Elmer) was used to analyse heavy metal concentrations in water, sediments, plants and fish. Metal pollution index (MPI), bioconcentration factor (BCF), pollution load index (PLI), contamination factor (C_f), degree of contamination (C_d) and modified degree of contamination (mC_d) were calculated to explain the pollution level. Human health risk was assessed through target hazard quotient (THQ), hazard index (HI), target cancer risk (TR) and estimated daily intake (EDI) of heavy metals caused by consumption of contaminated fish. Samples of algae were collected from randomly selected sites of three lakes using quadrat method during summer and winter seasons. Composite samples of each lake were prepared to represent the overall scenario of each lake during each season. Algae in Uchalli and Jahlar Lakes were found in the form of mats/sheets, whereas algae in Khabekki Lake was unicellular or in colonial form making water greenish. Algae collected from Khabekki Lake (in the form of green water) was maintained and studied in the laboratory on daily basis to determine cell concentration, biomass productivity and specific growth rate. Samples of algae collected from the three lakes were dried to determine percentage of carbon, nitrogen, hydrogen and sulphur using an elemental analyser. Carbon values in algae were used to estimate the CO₂ sequestration of each lake. Analysis of variance (ANOVA) was

used to determine significance level; Pearson's correlation was used to find relationship and principal component analysis (PCA) was applied for source identification of studied parameters and heavy metals. In water, heavy metal concentrations in ascending order were as follows: Pb < As < Cd < Ni < Cr < Cu < Zn < Mn; Pb < Cd < Cu < Zn < Mn < Cr < Ni < As and Pb < Cd < Cr < Cu < Ni < As < Zn < Mn in Khabekki, Uchalli and Jahlar Lakes respectively. During the winter season this ascending order was: As < Pb < Cd < Ni < Cr < Cu < Zn < Mn, Pb < Cu < Zn < Cd < Mn < Cr < Ni < As and Pb < Cd < Cr < Cu < As < Ni < Zn < Mn in Khabekki, Uchalli and Jahlar Lake. Temporal data revealed that during the summer season, concentration levels of magnesium in Khabekki Lake; nickel and arsenic in Uchalli Lake; and nickel and magnesium in Jahlar Lake were higher than the Pakistan Environmental Quality Standards (PEQS) as well as the World Health Organization (WHO) standards. During the winter season, magnesium in Khabekki Lake; cadmium, nickel, arsenic in Uchalli Lake; and nickel and magnesium in Jahlar Lake were higher than their standard limits. Results of MPI revealed that the water in the studied lakes is not fit for human consumption. During the summer season, concentrations of heavy metal in the sediments in ascending order were as follows: Pb < Cd < Cu < Cr < Zn < Ni < Mn < As (Khabekki Lake); Cu < Pb < Ni < Cd < Cr < Zn < Mn < As in (Uchalli Lake) and Cu < Pb < Cd < Ni < Cr < Zn < Mn < As in Jahlar Lake. Whereas in the winter season, heavy metal concentrations in the ascending order were Cd < Cu < Pb < Cr < Ni < Zn < Mn < As; Cu < Pb < Ni < Cd < Cr < Zn < Mn < As and Cu < Cd < Pb < Cr < Ni < Zn < Mn < As in the Khabekki, Uchalli and Jahlar Lakes respectively. In sediments of UWC, heavy metal concentrations were below the European Union (EU) standards. C_d (1.023–5.309) showed low contamination, $m C_d$ values were below 1.5 indicating very low degree of contamination in Khabekki, Uchalli and Jahlar Lakes. In plants, heavy metal concentrations during the summer season followed the ascending order: Pb < Cd < Cu < Cr < Ni < Zn < As < Mn; Pb < Cd < Cu < Cr < Zn < Ni < Mn < As and Cd < Pb < Cu < Ni < Cr < Zn < As < Mn in Khabekki, Uchalli and Jahlar Lake respectively, whereas the ascending order in the Khabekki, Uchalli and Jahlar Lakes during the winter season was Pb < Cd < Cu < Cr < Zn < Ni < Mn < As; Cd < Pb < Cu < Ni < Cr < Zn < Mn < As and Pb < Cu < Cd < Cr < Ni < Zn < As < Mn respectively. In fish, the heavy metal concentrations showed ascending order as follows: As < Cu < Cr < Zn < Pb < Mn < Ni < Cd; and As < Cr < Zn < Pb < Cu < Cd < Mn < Ni during the summer and winter seasons, respectively. Temporal data revealed that during the summer

season, Cd (0.0942) value was higher whereas all other heavy metals were in higher concentration during the winter season. During summer and winter seasons BCF values indicated potential accumulation of heavy metals such as Cd (29.4375, 9.4814), Pb (16.66, 4.375), Ni (4.9875, 6.206), Cu (0.222, 0.8453), Zn (0.0169, 0.18), Cr (0.4712, 0.5514) and Mn (0.0408, 0.5072). Different indices used to assess risks to human revealed that fish in Khabekki Lake were safe for human consumption. Samples of algae collected from Khabekki Lake showed maximum cell concentration ($1 \times 10^8/\text{ml}$) and biomass productivity ($4.6 \times 10^6/\text{mg L}^{-1} \text{d}^{-1}$) during the the month of September, while the highest average specific growth rate (0.1013d^{-1}) was observed during the month of December. Algae collected from Uchalli Lake showed highest sequestration of CO_2 ($75.69\text{gm}^{-2}\text{month}^{-1}$) and Khabekki Lake showed lowest ($3.56 \text{gm}^{-2}\text{month}^{-1}$) sequestration of CO_2 . Pearson's correlation applied on data sets of water, sediment, plants, fish and algae showed significant correlation ($P < 0.05$) and ($P < 0.01$) between various physical and chemical parameters and heavy metal concentrations. ANOVA presented significant differences between mean values of different physico-chemical parameters and heavy metals concentrations with respect to seasons, lakes and season*lakes. In the case of algae, significant differences were noted only with respect to lakes. Results of PCA results showed that TDS, EC, salinity, Ni, Na, K, Cr and Cu had anthropogenic source of origin, while Mn, temperature, Pb, nitrate, chloride, Ca, DO and Zn had natural sources. Hardness, alkalinity, sulphate, Mg, pH and As could be due to both natural and anthropogenic sources. Sediment data PCA analysis indicated natural sources of origin for Ca, Na, Zn, Pb, Cr and Cu, whereas anthropogenic sources were responsible for phosphate, Mg, sulphate, nitrate and nitrogen. Both natural and anthropogenic sources were responsible for As, chlorides, K and EC. Plants heavy metals PCA analysis showed that anthropogenic activities might have caused nickel, lead, chromium, zinc, copper pollution; cadmium, arsenic pollution was from natural sources and magnesium was from both natural and anthropogenic sources. In fish Zn, As, Pb, Cr, Mn and Cd were transferred from water; Cu could be due to both these sources. This study concluded that quality of water was not fit for direct human consumption and this observation raises the need for water treatment before use. Heavy metal contaminations in sediments were not upto dangerous levels. Fish showed potential for Cd, Pb and Ni accumulation that can cause severe health risk to humans. Algal cells have high potential to fix CO_2 and to reduce CO_2 concentrations in the environment.