GEOCHEMICAL CONTROL ON ECOSYSTEM IN PERSPECTIVE OF ECOLOGICAL AND HEALTH RELATED ISSUES IN DIR KOHISTAN, PAKISTAN

Shafi Ullah, Ph. D. Scholar, NCE in Geology, UoP

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Abstract

This study in detail evaluated the environmental quality of surface water (SW) and groundwater (GW), soil, sediments, and various plant species in Dir-Kohistan, Pakistan. The analysis included physicochemical parameters, major and traces metals, ecological risk assessment, and human health risk assessment. An integrated assessment of these environmental matrices was conducted to determine contamination status, pollution sources, ecological impacts, and potential health risks to human. The physicochemical characteristics of water samples were found within the permissible limits of WHO, US EPA, and Pak-EPA standards. However, nitrate concentrations surpassed the US EPA guideline in 3.51% of groundwater samples, while total hardness exceeded the recommended limit of WHO and US EPA (300 mg/L) in 34.09% of surface water and 66.67% of groundwater samples. The concentrations of Na, K, Ca, Mg, Mn, Cu, Cr, Ni, Zn, and Co) remained within acceptable limits, whereas elevated Fe concentrations were detected in 81.82% of surface water and 56.14% of groundwater samples. Lead (Pb) contamination exceeded the Pak-EPA permissible limit (≤50 µg/L) in 63.64% of surface water and 38.60% of groundwater samples. Cadmium (Cd) concentrations exceeded the US EPA guideline (5 µg/L) in 38.64% of surface water and 1.75% of groundwater samples, while comparison with the WHO guideline (3 µg/L) indicated contamination in 68.18% of surface water and 12.28% of groundwater samples. The groundwater was generally found safe for drinking purposes, whereas surface water posed potential health risks due to elevated Pb and Cd concentrations. In human health risk assessment the average daily dose (ADD) followed the order Zn > Cu > Pb > Cd > Co > Cr > Ni > Fe > Mn in surface water and Zn > Cu > Pb > Co > Cd > Cr > Ni > Fe > Mn in groundwater. Hazard quotient (HQ) values identified Pb and Cd as the principal contributors to human health risk through surface water consumption. The mean hazard index (HI) values remained below the safety threshold; however, maximum HI values exceeding

threshold value (1) indicated that prolonged consumption of contaminated surface and groundwater may cause adverse non-carcinogenic health effects.

Soil analyses revealed acceptable physicochemical properties (pH, EC, salinity, and TDS). The soil samples were mostly found contaminated with elevated concentrations of Ni, Zn, Cd, Ag, Co, Cr, and Pb relative to international soil quality guidelines. Ecological risk assessment identified strong contamination by Cd and Ag, moderate to strong contamination by Fe, Mn, Cu, and Pb, moderate contamination by Co and no contamination by Ca, Ni, Zn and Cr. Pollution Load Index (PLI) indicated moderate pollution, whereas the geo-accumulation index (Igeo) classified Ca, Mg, Fe, Mn, Cu, Ni, Zn, Co, Cr, and Pb as "unpolluted to moderately polluted," Cd as "strongly polluted," and Ag as "very strongly polluted." Enrichment factor (EF) analysis revealed extremely severe enrichment for Ag and moderately severe enrichment for Cd, confirming anthropogenic inputs, while the remaining elements predominantly originated from geogenic sources. Hierarchical cluster analysis (HCA) demonstrated strong associations among Cu-Cd, Ni-Ag, and Co-Cr, with K behaving as an outlier. Comparison between agricultural and control soils further indicated higher concentration of Na, K, Ca, Cu, Cd, Co, and Pb in agricultural soils, suggesting contributions from agricultural practices, whereas Mg, Fe, Mn, Ni, Zn, Ag, and Cr were found higher in control soil which primarily controlled by natural geological processes.

Sediment analyses specified that physicochemical parameters remained within environmentally acceptable ranges. Major elements followed the order Na > K > Ca > Mg > Fe > Mn, while trace metals were distributed as Pb > Cu > Zn > Co > Ag > Ni > Cr > Cd. Mean concentrations of Cu and Ni exceeded Interim Sediment Quality Guideline (ISQG)-low values but remained below ISQG-high thresholds, indicating limited biological effects. However, 47.06% of sediment samples exceeded ISQG-high values for Ni, and average Cd concentrations also surpassed ISQG-high values, indicating possible adverse biological effects. Elevated concentrations of Co, Ag, and Pb further suggested ecological concern. Ecological indices revealed very high contamination factors for Cd and Ag, considerable contamination by Fe, Mn, Cu, and Pb, moderate contamination by Mg and Co, and low contamination for Ca, Ni, Zn, and Cr. Pollution Load Index indicated moderate pollution, while Igeo classified Cd and Ag as strongly to very strongly polluted. Enrichment factor analysis confirmed anthropogenic enrichment of Ag and Cd and geogenic origins for the remaining elements. Cluster analysis showed strong associations among Ca-Mg, Fe-Mn, Zn-Pb, Co-Cr, and Ni-Ag, with K, Ni, and Ag exhibiting distinct clustering behavior.

The concentrations of eight heavy metals (Cu, Zn, Pb, Ni, Mn, Cd, Cr, and Co) were determined in eighteen commonly consumed plant species, including cereals, vegetables, fruits, and leafy plants. Copper and Zn concentrations remained within WHO permissible limits; however, Pb, Ni, Mn, Cd, Cr, and Co exceeded recommended limits in several species. Comparison with phytotoxicity thresholds identified Co accumulation in apple, common mallow, peach, pumpkin, turnip, pear, persimmon, tomato, potato, walnut, common bean, lettuce, toothed dock, pea, and maize. Estimated Daily Intake (EDI) values indicated dietary exposure to Pb, Ni, and Cd through consumption of several plant species, whereas Target Hazard Quotient (THQ) and Total Target Hazard Quotient (TTHQ) remained below unity, suggesting no significant non-carcinogenic health risks associated with current dietary intake.