

A Review on Assessment of Hydrogeochemical Status of an Aquatic Environment

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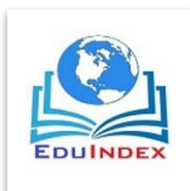
Abstract

Hydrogeochemical composition analysis is used to indicate the quality of aquatic environment. Hydrogeochemistry generally include the hydrological character of water such as temperature, pH, EC, TDS, turbidity, salinity, total hardness (TH), alkalinity (carbonate, bicarbonate), chloride, dissolved oxygen (DO), biological oxygen demand (BOD), Ca, Mg, Na, K, sulphate, nitrate, nitrite, phosphate and geochemical characteristics of sediment such as macro nutrients(N, P, K) level, CaCO₃, Ca, OC, sulphur, sediment texture, grain size distribution and heavy metal toxicity. Heavy metals are one of the serious pollutants in aquatic environment due to their toxicity. Increasing population and industrial revolution leads to increase the pollutant (including heavy metals and organic pollutant) levels in aquatic environment through various pathways. However, the low concentrations of heavy metals (Cd, Hg, Cr, Pb) exhibit extreme toxicity. This makes regular monitoring of aquatic environment to be necessary. This review provides an assessment of hydrogeochemical characteristics especially focus the source and effect of heavy metals in aquatic environment.

Key Words: Hydrogeochemistry, Sediment texture, Heavy metal.

INTRODUCTION

Water is vital to life. Water bodies provide habitat for numerous aquatic lives and help in conserving the biodiversity. Crop productivity, developmental activity and fish culture depends on water and soil fertility [1]. Now a day's most of the rivers and canals get pollution by adding hazardous chemicals, fertilizers, by industrialization, and urbanization. Among soil pollution heavy metal accumulation was one of the serious tasks, because heavy metals enter human and animal bodies through food chain and cause serious health hazards [2] [3].



Hydrogeochemistry is a tool to identify the quality of aquatic environment. It includes the hydrological character of water and the chemical constituents of sediment in aquatic environment. Hydrological character like temperature, pH, EC, TDS, turbidity, salinity, dissolved gases and nutrients influence the water quality directly or indirectly. These characteristics of water are very much influenced by the properties of bottom sediments. The bottom sediments act as a reservoir of nutrients. The sediment holds high bacterial load which helps in the decomposition and mineralization of organic deposits at the bottom [1]. Most of the contaminants can leave their finger prints in sediments [4].

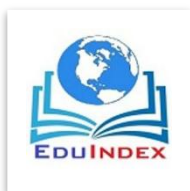
Trace elements occur in minute concentration in biological system. These elements are introduced into aquatic systems, rivers, lakes or ocean through atmospheric fallout, dumping wastes, accidental leaks, runoff of terrestrial systems (industrial and domestic effluents) and geological weathering [5]. Potassium and calcium are the essential components of aquatic ecosystem [1]. Some metals such as manganese, iron, copper and zinc are essential micronutrients, other such as mercury, cadmium and lead are not required even in small amounts by any organisms [5].

The accumulation of metals in sediments from both natural and anthropogenic sources occurs in the same way, thus making it difficult to identify and determine the origin of heavy metals present in the sediments [5]. Several analytical methods have been used for the determination of heavy metals in aquatic environment. These include; flame AAS, Atomic Fluorescence Spectrometry (AFS), Anodic Stripping Voltametry, ICP – AES, ICP – MS Graphite Furnace Atomic Absorption Spectrometry (GFAAS) [1]. The most common method for metal determination is AAS either as the flame or carbon furnace. It is a cheap and best technique for metal determination.

Assessment of present status of the particular aquatic environment have an increasing public awareness of the hazards exit from the contamination of the environment and need to protect it and also give an idea for future monitoring. Information gathered from the review would be useful to understand the hydrogeochemical status of an aquatic environment with reference to water and sediment characteristics.

Assessment of hydrogeochemical characteristics

The analysis of hydrogeochemical characteristics of an aquatic system have been performed using analytical techniques including titrimetric, gravimetric and instrumental techniques such as UV-VIS spectrometry, AAS etc., Various hydrological parameters were analysed using standard method as recommended by APHA (American Public Health



Association). Temperature readings were taken as soon as the sample were collected using graduated 110⁰ mercury thermometer or a digital thermometer of $\pm 0.01^{\circ}\text{C}$ accuracy. pH value were recorded using digital pH meter. EC were determined by using conductivity meter. Turbidity was determined by using Nephelometric turbidity meter.

Total hardness, calcium and magnesium were determined by EDTA method using eriochrome black-T (EBT) and murexide indicator respectively. Total alkalinity (TA), carbonate, bicarbonate were estimated by titrimetric method using phenolphthalein and mixed indicator. For chloride determination we use argentometric method. Dissolved oxygen was determined by Winkler's method. Nitrate, nitrite, phosphate concentration were determined by UV-VIS spectrophotometer. Sodium and potassium were determined by flame photometer.

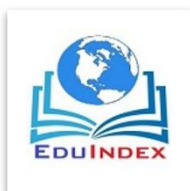
Organic Carbon (OC) was determined by wet oxidation method (Walkley-Black method) [6]. It was used to determine the readily oxidizable organic carbon content in the sediments [7]. Wet-chemical speciation method was generally used to analyze the Sulphur speciation in sediments. Total S contents were measured with an elemental analyzer. Textural studies of sand and clay were found out by using sodium hexametaphosphate. The silt content was measured by the pipette method. The nitric acid digestion method was the most efficient method for recovering metals from sediment [8]. Atomic absorption spectroscopy, either as flame or the carbon furnace method, is widely applied for trace metal analysis of sediments [7] [9].

Sampling

Water samples were collected in precleaned polypropylene bottles. These bottles were acidified with 1:1 dilute hydrochloric acid and rinsed with distilled water and also dried before collection of water samples. Samples were collected in separate polypropylene bottles for different hydrological parameters (physicochemical parameters, dissolved oxygen).

The surface sediment samples were collected using grab sampler. Sediment samples were dried and used for geochemical characteristics of sediment such as macro nutrients (N, P, K) level, CaCO_3 , Ca, OC, sulphur. Sediment core sample were collected using a PVC coring tube (7.5 diameter and 2.5m length) [7]. The sediment core samples were stored in deep freeze until analysis was performed. One gram of the sample, for metal analysis was dried in an air oven at 80°C and then made into fine powder using a mortar, sieved through a stainless steel mesh and stored in a plastic bag. Major elements were determined after preliminary treatment and decomposition of sediments.

Sources and Intensities of Hydrogeochemical characteristics



Temperature: It is an important factor, which regulates the biogeochemical activities in the aquatic environment. High temperature occurs in aquatic environment have been reduce the DO and has shown a positive impact on salinity.

pH: It is an important parameter for various biological and chemical process. If pH value is very high result will be difficulties in chlorination, incrustation and sedimentation [10]. The principal component regulating ion pH in natural waters is the carbonate, which comprises CO_2 , H_2CO_3 and HCO_3^- [2].

Electrical Conductivity (EC): Conductivity is a measurement used to determine mineralization of water. Electrical conductance is a good measure of dissolved solids. It explains total ionic substance in water sample. It can be controlled by electrodialysis, reverse osmosis and desalination [10]. Certain physiological effects on plants and animals are often affected by the number of available ions in the water [2].

Total Dissolved Solids (TDS): Dissolved salts are the main sources of TDS in aquatic environment. Maximum allowed limit for TDS in drinking water is 1500 mg/L (ICMP) [10].

Turbidity: High turbidity shows large amount of suspended solids. High turbidity was associated with disease causing bacteria and affects the life indirectly.

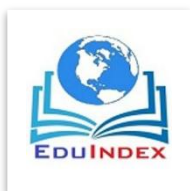
Salinity: Salinity plays an important role on the aquatic environment. High salinity reduces the pH in aquatic environment.

Total Hardness (TH): It's a main parameter of water mainly drinking and industrial purpose [10]. In water hardness caused by calcium and magnesium ions. Addition of detergents and sewage also increase hardness in water bodies.

Alkalinity: The degradation of plants, living organisms and organic wastes increase carbonate and bicarbonate, resulting in an increase alkalinity. Alkalinity is a measure of its capacity to neutralize acids, i.e. to absorb hydrogen ions, without significant pH change. This is due to the presence of hydroxide (OH^-), carbonate (CO_3^{2-}) and bicarbonate. Presence of carbonate and bicarbonate in water is an interchangeable process and depends upon the pH value of water [2].

Chloride: It's the main reason behind corrosion of steel and aluminium and comes in water mainly by inorganic fertilizers and irrigation drainage and rocks [10]. The greater value of chlorides in lake water is disposal of sewage and industrial waste.

Dissolved Oxygen (DO): High dissolved oxygen in water bodies indicates good aquatic life. Depletion of dissolve oxygen in water is due to high temperature and increase microbial activity.



Biochemical Oxygen Demand (BOD): The higher value of BOD during winter was due to input of organic wastes and enhanced bacterial activity.

Calcium (Ca): It's a most important element present in water. It comes mainly by limestone rocks but very high concentration of it affected the absorption of other essential minerals in the body [10]. Calcium increases during summer due to calcium being absorbed by living organisms in winter.

Magnesium (Mg): It comes in water mainly by minerals, some time it gives undesirable tastes to water samples [10].

Sodium (Na): Sodium is a natural constituent of raw water, highly reactive metal that is never found in nature in the uncombined state [2]. But its concentration is increased in aquatic environment by pollutional sources such as rock salt, precipitation runoff, detergents, addition of sewage, salt water intrusion. High concentration of it causes high in blood pressure (hypertension) and heart disease [10].

Potassium (K): It's mainly found in water by dissolved fertilizers. It is responsible for kidney problem coronary artery disease, adrenal problem and diabetes [10].

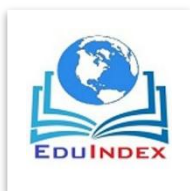
Sulphate (SO_4^{2-}): It comes in water body by dissolution of gypsum and industrial discharge (dissolved Ca/Mg/Fe sulphates) [10]. High level of sulphate, change the taste of water and also cause intestinal irritation for human.

Nitrate (NO_3^-) and Nitrite (NO_2^-): It comes in water mainly by fertilizers (inorganic), sewage discharge (organic). If it is high in water cause blue baby syndrome and ability of blood to transport oxygen is reduced [10].

Phosphate (PO_4^{3-}): Same sources as of nitrate [20]. The main impact associated with phosphate pollution is eutrophication [2].

Macro nutrients (N, P, K) and Calcium (Ca) in sediment: The essential components of aquatic ecosystems are organic and inorganic form of potassium and calcium which influence organic productivity.

Calcium carbonate (CaCO_3): Calcium carbonate are mainly used in construction industry (limestone, marbles), ingredient in cement, oil industry, sugar industry etc. The main source of calcium carbonate in aquatic environment is sedimentary rocks, corals. Excessive consumption of it can be hazardous and cause poor digestion and milk-alkali syndrome.



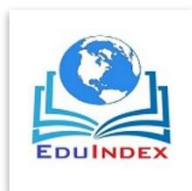
Organic Carbon (OC): Organic contents of the sediments are reflected in the determination of organic carbon. The OC content indicates the incorporation of organic material from the land. The high concentrations of OC were associated with oxygen depletion of bottom sediment and excessive bloom of microbes in the sediment. Lower concentrations are unfavorable for the growth of benthic organisms that are important food for many species [10]. In most unpolluted aquatic environment OC content of the sediment is < 5% .The optimum range of OC in pond sediment is 1 – 3% [7].

Sulphur: Sediment is an important repository and sink for sulphur (S). Acid is the main reason to increase S content in sediment. The anaerobic zones in the aquatic ecosystems are strongly affected by the chemical form of S [11].

Sediment texture and Grain size: Sediment core samples were subjected to grain size analysis and also found sediment texture. Grain size can be found out through sieving. Decrease in the content of metals as sediment particle size increases. The fractions less than 173 μm and 204 μm contain considerable percentages of large grains which are usually low in trace metals. The fraction less than 63 μm is most nearly equivalent to the material carried in suspension [9].

Heavy Metals: Once the metals are released to the environment, they are transferred to the sediments through adsorption onto suspended matter and subsequent sedimentation [4].

Metal	Permissible limit in portable water
Fe	1.0 mg/l
Cr	0.1 mg/l
Cu	2 mg/l
Ni	0.2 mg/l
Cd	0.01 mg/l
Pb	0.05 mg/l
Ar	10 ppb
Zn	5 mg/l
Al	0.2 mg/l



Mercury (Hg): Mercury is generally considered to be one of the most toxic metals found in the environment. It is a global pollutant with complex and unusual physical and chemical properties. The usage of mercury is widespread in industrial process and in various products, (e.g. batteries, lamps, thermometers, amalgam). The major natural source of Hg is the degassing of the earth's crust, emissions from volcanoes and evaporation from natural bodies of water. Once mercury enters the food chain, progressively larger accumulation of mercury compounds takes place in humans and animals. Toxicity of mercury results mental disturbance and impairment of speech, hearing, vision and movement [1]. Mercury also brings about genetic defects [13].

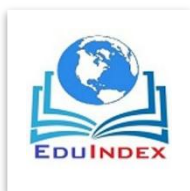
Chromium (Cr): The mining and mineral processing activities probably accountant for Cr concentration. They contended that the enrichment of Cr at high levels in particulate matter might be due to domestic and industrial waste inputs [14]. The waste water as results of tanning process is an important source adding Cr pollutant to the environment which causes many health hazards to all sort of life. Several health problems are related to chromium consumption such as chronic ulceration and perforation of the nasal septum and allergic skin reactions [13].

Copper (Cu): Copper is an essential substance to human life. Commonly, copper is either formed within sedimentary, within ocean basins in sedimentary rocks [2]. Copper is an essential element in mammalian nutrition as a component of metallo-enzymes in which it acts as an electron donor or acceptor. But in high doses it can cause number of adverse health effects anaemia, liver and kidney damage, stomach and intestinal irritation, problem in the synthesis of haemoglobin and acute of chronic damage to the nervous system [1].

Nickel (Ni): Nickel is a carcinogenic metal and any overexposure to it can cause a decreased body weight, heart, and liver damage and skin irritation [13].

Cadmium (Cd): It is the most harmful of all the heavy metal pollutants. It is a by-product of the mining and smelting of lead and zinc. It is contributed to the waters and sediments through anthropogenic sources like paints, pigments, glass enamel, deterioration of the galvanized pipes, insecticides, fungicides sludge and commercial fertilizers containing Cd are used in agriculture[1] [2]. Cadmium and some of its compounds are considered carcinogenic and may cause damage to all types of body cells. The main target organs for Cd are the kidneys and liver.

Lead (Pb): Lead is number two (after arsenic) on the top 20 list of the most poisoning heavy metals. It is naturally present in the environment. The high level of Pb in sediments could be attributed to the industrial and agricultural discharge. Higher levels of Pb often occur in water



bodies near high ways and large cities due to high gasoline combustion [1]. Its target organs are the bones, brain, blood, kidneys, reproductive and cardiovascular systems, and thyroid gland [9].

Zinc (Zn): It is the essential minerals for humans, plants, animals and micro organism. They accumulate considerable amount of zinc in their system without any damaging effects [2]. Little is known about its toxic effects toward human beings [13]. High levels of Zn may cause pancreatitis, anemia, muscle pain, acute renal failure and death [1]. Excessive intake of Zn may lead to vomiting, abdominal pains, nausea, lethargy and dehydration [3].

Guideline levels of metals in sediment described in the literature [9]

	Zn (mg/kg)	Mn (mg/kg)	Cu (mg/kg)	Cd (mg/kg)	Pb (mg/kg)	Fe (mg/kg)	Cr (mg/kg)
ATSDR	1.00	1.00		0.02	0.90		0.20
EPA	9.80	9.30	2.80	0.583	3.70	1.88	3.63
NOAA	3.80	4.00	2.50	0.10-0.30	1.70	0.18	1.30

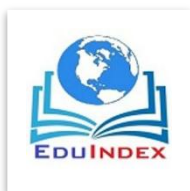
Different water quality index calculations

Sodium Adsorption Ratio: Assess the suitability of water for irrigation purposes. SAR parameter evaluates the sodium hazard in relation to calcium and magnesium concentrations. It can be calculated as: $SAR = \frac{m_{Na^+}}{\sqrt{m_{Ca^{2+}} + m_{Mg^{2+}}}}$ m- concentration of ion (in mmol/L)

Sodium percent: Sodium percent values used for classifying irrigation water quality. %Na is calculated by the following formula:

$\%Na^+ = \frac{Na^+}{Ca^{2+} + Mg^{2+} + K^+ + Na^+} \times 100$ Where all the concentrations are expressed in meq/L

SAR	% of Na	Status of water
< 10	<20	Excellent
10-18	20-40	Good
18-26	40-80	Doubtful



>26	>80	Unsuitable
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Residual Sodium Carbonate: RSC was used to quantify the effects of carbonate and bicarbonate. The RSC has the following equation:

$$RSC = (CO_3^{2-} + HCO_3^-) - (Ca^{2+} + Mg^{2+})$$

Where all the concentrations are expressed in meq/L

Metal Index: $MI = \sum_{i=1}^N \left[\frac{C_i}{(MAC)_i} \right]$

MAC - maximum allowable concentration; C - concentration of each element

The higher the concentration of a metal compared to its respective MAC value, the worse the quality of the water. MI value > 1 is a threshold of warning.

Pollution Index: $PI = \sqrt{\frac{\left[\frac{C_i}{S_i}\right]_{max}^2 + \left[\frac{C_i}{S_i}\right]_{min}^2}{2}}$

C_i: concentration of metal in river water, S_i: national water quality criterion

PI	Status
< 1	No effect
1-2	Slightly affected
2-3	Moderately affected
3-5	Strongly affected
> 5	Seriously affected

Different Sediment Quality Index calculations and Evaluation

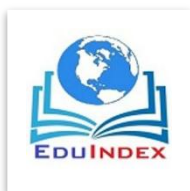
Sediment Enrichment Factor: $SEF = \frac{C_i - C_0}{C_0}$

C_i - Total concentration of each metal I measured in the sediment,

C₀ - The heavy metal background level established for the ecosystem studied.

SEF < 1 crustal origin; SEF > 1 anthropogenic origin

Contamination factor and Degree of contamination: A contamination factor (C_fⁱ) and the degree of contamination (C_d) to describe the contamination of given toxic substance given by:



$$C_f^i = \frac{C_{0-1}^i}{C_n^i} \text{ and } C_d = \sum_{i=1}^7 C_f^i$$

C_{0-1}^i = mean content of the substance; C_n^i = reference value for the substance

C_f^i	C_d	Evaluation
$C_f^i < 1$	$C_d < 7$	Low degree of contamination
$1 < C_f^i < 3$	$7 < C_d < 14$	Moderate degree of contamination
$3 < C_f^i < 6$	$14 < C_d < 28$	Considerable degree of contamination
$C_f^i > 6$	$C_d > 28$	Very high degree of contamination

A new Pollution Index: $PIN = \sum_{i=1}^n \frac{W_i^2 C_i}{B_{1i}}$

W_i - The class of contaminant i considering the degree of contamination (from 1 to n=5),

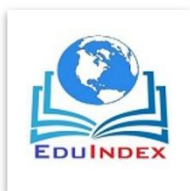
C_i - The concentration of contaminant in baseline value-clean sediments.

PIN	Evaluation
0-7	Clean
7-95.1	Trace contaminated
95.1-518.1	Lightly contaminated
518.1-2548.6	Contaminated
2548.6-∞	Highly contaminated

Index of geo accumulation: $NI_{geo} = \ln \frac{C_n}{1.5XB_n}$

B_n - The concentration of the metal n in unpolluted sediments; C_n - Concentration of the metal.

NI_{geo}	Evaluation
$NI_{geo} < 1$	Unpolluted



$1 < NI_{geo} < 2$	very lightly polluted
$2 < NI_{geo} < 3$	lightly polluted
$3 < NI_{geo} < 4$	moderately polluted
$4 < NI_{geo} < 5$	highly polluted
$NI_{geo} > 5$	very highly polluted

Mean Sediment Quality Guideline quotient:

$$SQG - Q = \frac{\sum_{i=1}^n PEL - Qi}{n} \quad PEL - \text{The probable effect level}$$

$$PEL - Q = \frac{\text{contaminant}}{PEL} \quad PEL - Q - \text{The probable effect level quotient}$$

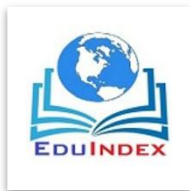
SQG - Q	Evaluation
$SQG - Q \leq 0.1$	Unimpacted; lowest potential for observing adverse biological effects
$0.1 < SQG - Q < 1$	Moderate impact potential for observing adverse biological effect
$SQG - Q \geq 1$	Highly impacted potential for observing adverse biological effects.

CONCLUSION

Thus this makes periodical monitoring of aquatic environment to be imperative and necessary to confirm their suitability. This review provides to assess the hydrogeochemical characteristics of an aquatic environment and also stated that do not release untreated industrial, municipal waste water into surrounding water bodies.

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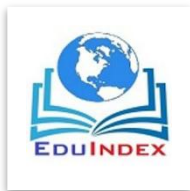
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