Open Horizon Scientific Review

Vol. 03 No.02 2025

Groundwater Quality Assessment and Hydrochemical Processes in Urbanizing Regions

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ABSTRACT

Groundwater is a vital source of drinking and irrigation water for rapidly growing cities, yet urbanization alters recharge, flow and chemical composition of aquifers. This article reviews approaches for assessing groundwater quality and interpreting hydrochemical processes in urbanizing regions. Sampling strategies, analytical quality control and graphical classification of hydrochemical facies are described, followed by the natural controls of rock weathering, evaporation, ion exchange and redox reactions. Anthropogenic sources including leaking sewers, landfills, industrial sites, road salt and stormwater are examined, with emphasis on nitrate, salinity and trace element contamination. Water quality indices, drinking water guidelines, multivariate statistics, geochemical modeling and environmental tracers are discussed as complementary tools for interpretation. Health risk assessment and management measures such as wellhead protection, sewer rehabilitation and managed recharge are outlined, and priorities for monitoring and research are identified for safeguarding urban groundwater.

Key words: *groundwater quality, hydrochemistry, urbanization, nitrate contamination, water quality index*

Introduction:

More than half of the world's population now lives in urban areas, and the proportion continues to rise, especially in Asia and Africa. Cities depend on water for domestic, industrial and commercial use, and where surface supplies are limited or unreliable, groundwater provides an accessible and often cheaper alternative. Because groundwater is naturally protected by overlying soil and is stored in large volumes, it has traditionally been regarded as safe, but this assumption is increasingly questioned (Foster and Chilton, 2003).

Urban growth modifies the water cycle and introduces numerous contaminants to the subsurface. At the same time, the chemical composition of groundwater is controlled by natural processes such as mineral dissolution, ion exchange and redox reactions, which must be understood in order to distinguish natural water quality from pollution. Hydrochemical investigation combines field and laboratory data with graphical, statistical and modeling approaches to reveal these processes and to evaluate suitability for use.

The aim of this article is to provide a coherent overview of groundwater quality assessment and hydrochemical

processes in urbanizing regions. The discussion is organised around nine thematic outlines covering urban impacts, sampling and analysis, hydrochemical facies, natural controls, pollution sources, key contaminants, quality indices, statistical and modeling tools, and health risk and management, followed by an overall summary.

1. Urbanization and Groundwater Systems

Groundwater supplies a large share of the drinking water, irrigation and industrial water used worldwide, and in many rapidly growing cities it is the principal or only source available. Urbanization changes the quantity and quality of groundwater simultaneously. Impervious surfaces such as roads and roofs reduce direct infiltration of rainfall, while leaking water mains, sewers, septic systems, storm drains and artificial recharge can in contrast increase recharge to the aquifer, in some cities exceeding natural recharge (Lerner, 2002).

These modified flow paths carry a distinctive mix of solutes. Urban recharge may contain nutrients from sewage, salts from de-icing and wastewater, hydrocarbons and metals from traffic and industry, and a variety of organic chemicals from household and commercial use. At the same time, intensive pumping lowers water tables, creates cones of depression, induces flow from polluted shallow layers or surface water bodies, and can draw in saline water in coastal settings.

The degradation of aquifers is a global concern because remediation is slow and expensive, and contaminants may persist for decades after the source is removed. Studies of aquifer degradation have highlighted that population growth, land-use change and weak regulation combine to put groundwater under growing stress, and that the problem is greatest in developing regions with limited monitoring (Foster and Chilton, 2003). Understanding hydrochemical processes is the basis for assessing and protecting these resources.

2. Sampling Design and Analytical Protocols

A reliable assessment starts with a sampling programme that captures the spatial and temporal variability of the aquifer. Wells are usually chosen to represent different land-use zones, depths, hydrogeological units and distances along flow paths, and sampling is repeated across seasons, typically before and after the monsoon or recharge period. Metadata on well construction, screen depth, pumping history and surrounding land use are indispensable for interpretation.

Field measurements of temperature, pH, electrical conductivity, dissolved oxygen and redox potential

should be taken at the time of sampling after the well has been purged until readings stabilise, since these parameters change rapidly once water is exposed to the atmosphere. Samples for cations and trace elements are filtered and acidified, whereas samples for anions are stored cool, and bottles must be rinsed and preserved according to standard methods to avoid contamination and loss.

In the laboratory, major cations are measured by atomic absorption, inductively coupled plasma techniques or ion chromatography, and anions by ion chromatography or titration. Quality control includes blanks, duplicates, standard reference materials and checks of ionic balance, in which the difference between total cation and anion charge should normally be within about five percent. Samples that fail the balance should be examined for analytical errors or missing constituents. Isotopic and microbiological analyses can complement chemical data.

3. Hydrochemical Facies and Water Types

The relative proportions of major ions reflect the geological, biogeochemical and anthropogenic influences on water, and graphical methods help to classify them. The trilinear diagram introduced by Piper plots the percentages of major cations and anions on two triangles and projects them onto a central diamond, allowing water samples to be grouped into hydrochemical facies such as calcium-bicarbonate, sodium-chloride or mixed types (Piper, 1944).

Typical sequences are observed along flow paths. Recharge areas commonly show young, low-mineralised calcium-magnesium-bicarbonate water, which evolves toward sodium-bicarbonate and eventually sodium-chloride or sulphate-dominated water in discharge areas as water-rock interaction proceeds and residence time increases. In urban areas, this natural evolution is overprinted by anthropogenic inputs that shift samples toward chloride, nitrate and sulphate, producing mixed or anomalous facies in shallow wells.

Other graphical tools include the Durov diagram, Stiff diagrams for spatial display, Schoeller plots to compare multiple samples, and ionic ratio plots. Comparisons of graphical and statistical classification methods have shown that each has advantages, and that combining approaches provides a more robust interpretation of water types (Guler et al., 2002). Facies mapping across the urban area helps to identify zones of contamination and mixing of different waters.

4. Natural Controls: Weathering, Evaporation, and Ion Exchange

Even in urban aquifers, natural processes control much of the baseline

chemistry. A widely used diagram plots total dissolved solids against the ratio of sodium to sodium plus calcium, and identifies three end-member mechanisms: atmospheric precipitation, rock weathering and evaporation-crystallisation (Gibbs, 1970). Most groundwater samples fall in the rock dominance field, indicating that interaction between water and aquifer minerals is the main control, though anthropogenic inputs can shift points toward the evaporation field.

Weathering of carbonate and silicate minerals releases calcium, magnesium, sodium, potassium and bicarbonate, with carbonate dissolution being particularly rapid and silicate weathering slower. Ratios of ions, such as calcium plus magnesium against bicarbonate plus sulphate, help to distinguish carbonate from silicate sources and to identify evaporite dissolution. Cation exchange on clays can soften water by exchanging calcium and magnesium for sodium, and chloro-alkaline indices indicate the direction of exchange.

Redox processes also play a part. Oxygen is consumed by oxidation of organic matter, followed by reduction of nitrate, manganese oxides, iron oxides and sulphate in sequence, according to the energy yield of each reaction. These processes control the mobility of iron, manganese, arsenic and nitrogen species, and explain why groundwater chemistry can change sharply over short distances. The geochemical principles governing these reactions are described in detail in standard texts (Appelo and Postma, 2005).

5. Anthropogenic Contamination Sources in Urban Areas

Urban groundwater is exposed to many point and diffuse contamination sources. Leaking sewers and septic systems introduce nitrogen, chloride, boron, pharmaceuticals and pathogens. Landfills and dumpsites generate leachate rich in ammonium, chloride, dissolved organic carbon and metals. Industrial sites contribute solvents, hydrocarbons, heavy metals and other process chemicals, and gas stations and storage tanks are common sources of petroleum products. Cemeteries, drainage canals and wastewater irrigation add further inputs.

Road de-icing salt and the use of salt in water softening and industrial processes lead to increased chloride and sodium, and long-term monitoring has demonstrated progressive salinisation of freshwater in urbanising regions (Kaushal et al., 2005). Stormwater infiltration can transport metals, polycyclic aromatic hydrocarbons and nutrients to the subsurface, and construction and building materials can release sulphate and alkalinity through dissolution of concrete and mortar.

The conceptual figure below illustrates how concentrations of conservative and reactive constituents may increase with the proportion of urban land cover in the recharge area, while bicarbonate, controlled mainly by natural processes, changes little. The figure is illustrative, since real relationships depend on local hydrogeology, but it demonstrates why chloride, nitrate, sulphate and total dissolved solids are widely used as indicators of anthropogenic influence.

6. Nitrate, Salinity, and Trace Element Pollution

Nitrate is the most widespread groundwater contaminant in many regions. Sources in urban areas include sewage leakage, septic effluent and fertiliser used on lawns and peri-urban farmland, while non-agricultural sources are often underestimated (Wakida and Lerner, 2005). Nitrate is highly mobile in oxygenated groundwater and persists, while denitrification in reducing conditions can lower concentrations. Elevated nitrate poses health risks, including methaemoglobinaemia in infants. Isotopes of nitrogen and oxygen in nitrate, along with ratios such as chloride to bromide, help to distinguish between manure, sewage and fertiliser sources (Bohlke, 2002).

Salinity increases through evaporation, dissolution of evaporites, saltwater intrusion in coastal aquifers, wastewater inputs and return flow from irrigation. High salinity limits the use of water for drinking and irrigation and may mobilise other contaminants by competitive desorption. Fluoride, often of geogenic origin from fluoride-bearing minerals, becomes concentrated in alkaline, sodium-rich waters, and its occurrence may be aggravated by overpumping and evaporation.

Trace elements such as arsenic, lead, chromium, nickel, cadmium and manganese may derive from natural sources or from industrial and urban activities. Arsenic is mobilised under reducing conditions through dissolution of iron oxides or under alkaline oxidising conditions through desorption, and affects groundwater in many regions of the world (Smedley and Kinniburgh, 2002). Distinguishing geogenic from anthropogenic sources requires understanding of redox conditions, mineralogy and spatial patterns, since management responses differ greatly.

7. Water Quality Indices and Drinking Water Standards

Compliance with drinking water standards is the first step in evaluating quality. International guidelines specify health-based limits for parameters such as nitrate, arsenic, fluoride, lead and microbial indicators, and many countries adopt or adapt these as national standards (WHO, 2017). Comparing measured concentrations with guideline

values quickly identifies parameters of concern and the proportion of wells that are unsuitable for drinking.

Water quality indices condense many parameters into a single score to communicate overall quality. In the common weighted arithmetic approach, each parameter is given a weight according to its importance for health and a sub-index is calculated relative to the standard, and the sum gives a final value that is classified from excellent to unsuitable. Such indices are simple and useful for mapping, but they involve subjectivity in the choice of parameters and weights, and should be used alongside parameter-specific information.

For irrigation, suitability is assessed using indicators such as sodium adsorption ratio, percent sodium, residual sodium carbonate and salinity hazard, which describe the risk to soil structure and crops. Geographic information systems allow the interpolation of results and the production of maps that reveal spatial patterns and hotspots, which can guide the location of new wells, treatment and monitoring.

8. Multivariate Statistics and Geochemical Modeling

Hydrochemical datasets contain many variables and samples, and multivariate statistics help to extract the underlying processes. Correlation analysis shows relationships among parameters, principal component analysis reduces dimensionality and identifies groups of variables with common sources, and hierarchical cluster analysis groups samples with similar chemistry into water types. Evaluations of graphical and multivariate methods concluded that combining them provides a more reliable classification than either approach alone (Guler et al., 2002).

Geochemical modeling complements statistics by providing a mechanistic basis. Speciation calculations determine the saturation indices of minerals and show whether water is in equilibrium with, or undersaturated or supersaturated with respect to, minerals such as calcite, dolomite, gypsum and fluorite. Inverse modeling identifies the mass transfer of minerals and gases that can explain the change in chemistry between two points along a flow path, and reactive transport models simulate the coupled flow and reaction.

Environmental tracers further constrain processes. Stable isotopes of oxygen and hydrogen reveal recharge sources and evaporation, tritium and radiocarbon indicate residence time and the proportion of young water, and strontium and sulphur isotopes help to track mineral and pollution sources. The integration of chemistry, isotopes and

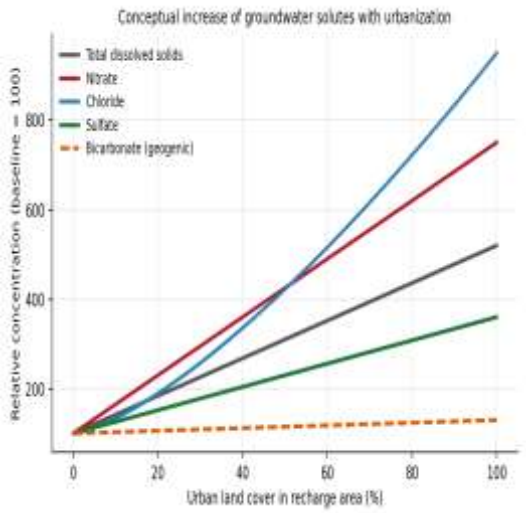
numerical modeling gives the most dependable picture of the origin and fate of contaminants in complex urban aquifers.

9. Health Risk, Management, and Future Directions

Human health risk assessment translates concentrations into potential effects on exposed people. For non-carcinogenic contaminants, a hazard quotient compares the estimated daily intake with a reference dose, and for carcinogens such as arsenic, a lifetime cancer risk is calculated from exposure and slope factors. Infants and children are usually the most sensitive group, and assessments should consider dermal as well as oral exposure. Uncertainty in exposure assumptions and in toxicity values should be stated explicitly.

Management measures include protecting recharge areas and wellheads, controlling leakage from sewers and storage tanks, proper siting of waste disposal, regulating industrial discharges, reducing road salt use, managing aquifer pumping, and promoting managed aquifer recharge with treated stormwater or wastewater. Where contamination exists, remediation options include pump and treat, permeable reactive barriers, in situ oxidation or biodegradation and, for drinking water, point-of-use or community treatment. Climate change and over-abstraction add pressure on aquifers worldwide (Taylor et al., 2013).

Future research should prioritise long-term, high-frequency monitoring supported by low-cost sensors, integration of remote sensing and geospatial data, assessment of emerging contaminants such as pharmaceuticals, microplastics and per- and polyfluoroalkyl substances, and the use of machine learning for prediction of vulnerability and contamination. Effective governance, public participation and investment in sanitation and water infrastructure remain the foundation for sustaining safe groundwater in expanding cities.



Summary

Urbanization transforms groundwater systems by changing recharge patterns and introducing contaminants from sewage, waste, industry, road salt and stormwater. The chemistry of urban groundwater

therefore reflects both natural processes, including weathering, evaporation, ion exchange and redox reactions, and anthropogenic inputs that raise chloride, nitrate, sulphate and total dissolved solids. Careful sampling, quality-controlled analysis and graphical classification of hydrochemical facies provide the foundation for interpretation.

Nitrate, salinity and trace elements such as arsenic and fluoride are the main concerns for human health. Water quality indices, comparison with drinking water guidelines, multivariate statistics, geochemical modeling and isotopic tracers together allow identification of sources and processes, while health risk assessment informs priorities. Protecting recharge zones, repairing sewers and storage systems, regulating industrial and waste disposal, and managing abstraction are necessary to maintain safe groundwater, supported by long-term monitoring and integrated urban water governance.

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