

# GROUNDWATER CONTAMINATION, PROTECTION AND REMEDIATION

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## Summary

The awakening of environmental conscience that the world population has experienced during the last thirty years, and the appearance of dramatic episodes of contamination around the world during the last century, have provoked in many countries the need to promote laws, regulations or actions to minimize or prevent the negatives effects of human activities in all parts of the hydrological cycle.

This article describes the commoner types of contaminants, their principal classifications and the main contamination processes that have been documented in groundwater, and presents an approximation to the state of art in prevention and control methodologies, as well as actual trends in pollution remediation in subterranean waters.

### 1. The Concept of Groundwater Quality.

In the past, aquifer water level was the main quantitative factor that determined the level of groundwater exploitation. The growth of studies about aquifer behavior, the threat or the reality of contamination episodes in most groundwater masses, and concern that groundwater resource shows a very long renewal time, have led, in recent decades, to the concept of groundwater quality assuming the same importance as quantity, and the need to preserve them both in an integrated management system.

Quality aspects usually decide whether groundwater is suitable for a definite use or, if it is necessary to treat the water or dilute with other water from other sources. In the case of a natural aquifer, without anthropogenic influence, the natural composition of the groundwater depends basically on the following factors:

- The geological characteristics of the aquifer,
- The speed of circulation across the aquifer,
- The initial composition of infiltration water,
- Mixing with other waters, and
- The movement rules of the transported substances in aqueous media, as well as the hydrodynamic factors.

In most cases, this natural quality has been permanently changed by anthropic actions like over-abstraction, industrial spills, modifications in the recharge water quality, with no or only very long term possibility of remediation. In such cases, the term *initial concentration*, to define the actual quality state of the aquifers, could be more appropriate than the natural one.

However, the concept of groundwater quality (and therefore, the deterioration degree) is also connected with its use. Table 1 summarizes the main requirements in quality and quantity of the main groups of users.

Consumer	Characteristics related with the quality of the water	Characteristics related with the quantity of water.
Industrial activities	Industry needs water with characteristics that do not raise costs	Ability to obtain enough water (generally during the whole year)

	or render impossible the industrial processes.	from a modest depth, in order not to raise extraction costs.
Agricultural activities	Agriculture needs water with low concentrations of chlorides, sulphates and heavy metals. Nitrates are generally accepted in the range that will be positive for the growth of plants.	The same requirement as for industry, but mainly during periods of irrigation
Urban water supply	Water quality is usually regulated by law. The need is for water with low mineralization. Water companies often have to take legal action against activities that diminish the quality of the water, or raise the price of the treatment	The need is for sufficient water to meet the demand, with long term guarantees
Tourist uses	Requires the same quality as urban water supply	Large quantities of water, but often centred around relatively small time periods.
Bottled or mineral water	In some countries, quality is regulated by law. Normally, such water must have low mineralization, or it may have to be treated with very energy-consuming processes.	Sufficient water to meet the demand.
Water for environmental uses	The need is for quality that permits ecosystem maintenance, with minimum possible modifications.	The quantity must be sufficient not to disturb the natural equilibrium of ecosystems, and, in some cases, to permit restoration of the original extent of the habitat.

Table 1. Quality and quantity groundwater objectives in relation to use

## 2. Contamination of Subterranean Waters.

A contaminant, or polluting agent, is a chemical compound that, because of its abnormal concentration in groundwater, produces an alteration of the previous composition, degrading it for a particular use.

Table 2 shows the compositional rank of the majority of the subterranean waters not polluted by human activity. Pollution of groundwater differs from that of surface waters in the difficulty of detection, the higher persistence, and difficulty of remediation.

The low velocity of groundwater in most aquifers often ensures that, when contamination is discovered, its origin is not clearly defined or no longer exists, and the contaminant is widespread throughout the aquifer, affecting large volumes of water.

<b>Major ions</b>	Cl-	10-250 ppm
	SO <sub>4</sub>	2-150 ppm
	HCO <sub>3</sub> <sup>-</sup>	50-350 ppm
	Na	10-150 ppm

	Ca <sub>2</sub>	10-250 ppm
	Mg <sub>2</sub>	1-100 ppm
<b>Minor ions</b>	NO <sub>3</sub> , CO <sub>3</sub> , NO <sub>2</sub> , F, K, F, NH <sub>4</sub> , Mr, Mn	0.01-10 ppm
	Br, PO <sub>4</sub> , Bo,Al	<0.1 ppm.

Table 2. Composition range of inorganic ions in the majority of natural groundwaters

### 3. Contamination Classification Systems.

Investigation of pollution processes and development of mitigation technology has resulted in different classifications, with diverse objectives. The classification may be qualitative or quantitative, and generally describes a single aspect of the whole phenomena. The most significant groups are:

- Classifications concerned with the polluting compounds, their concentration level or their physico-chemical characteristics. Examples of this group are the DNALP and LNALP carbon-compounds classification or the establishment of contamination levels of more compounds, (e.g. nitrates), according to their concentration in groundwater.
- Classifications concerned with physico-chemical processes. In this case, the contamination evolution is described like a series of chemical reactions that occur under more or less defined eH, pH,  $\log f_{O_2}$  (fugacity of Oxygen) or temperature conditions.
- Classifications concerned with the different parts of the aquifer. The contamination is described as a sum of behaviors or/and reactions produced in the unsaturated zone, or in the saturated zone of aquifer.
- Classifications related with the geometry of the source. In this case, it is usual to talk about punctual, diffuse or lineal contamination.
- Classifications related to the type of flow.

In practice, to describe all the aspects associated with a contamination event, it is necessary to use a combination of terms that belongs to more than one classification group.

### 4. Principal Groundwater Contaminant Types and Processes.

There are a very large number of elements and compounds that are able to cause contamination in aqueous media. In subterranean waters, the principal pollution agents are chemical (inorganic or organic compounds, of natural or synthetic origin) and, to a smaller degree, biological.

#### 4.1. Inorganic Pollution Agents

The inorganic contaminants are compounds that, in general, show a high persistence inside the aquifers. In many cases, their main effect is basically an increment of groundwater salinity, but under certain conditions, some inorganic compounds, like the heavy metals group, become a very toxic contaminant.

In groundwater, the majority of these compounds have a similar velocity of circulation to the subterranean water when they reach the saturated zone. The main representative of this group are the major ions—Cl, SO<sub>4</sub>, NO<sub>3</sub>, HCO<sub>3</sub>, K, Mn, Mg—and heavy metals such as like Pb, Zn, Cd, Hg or Cr.

The mobility in water of these compounds is controlled by their capacity for dissolution, which is very high in some ions like chloride, sulfate and the rest of major ions, but very low in the heavy metals.

In the heavy metals group, the basic factors that control the degree of dissolution of these pollutants in groundwater are variations in REDOX and pH; these affect their equation of equilibrium. In general, with pH = 7 and in oxidizing conditions, the metals are usually fixed in the sediment, staying outside of the dissolution and therefore, not polluting the water. Reduction changes in the solution, at constant pH (in the absence of sulfur), increases the capacity of dissolution of most of these elements in water. The presence of sulfur, on the other hand, causes reactions with the metals, forming sulfides.

The solubility of most metals increases significantly if the element forms a complex with organic molecules.

Isomorphic substitutions, where atoms of the metal occupies vacant positions or substitute ions in the crystalline structure of aquifer minerals, leads to diminishing concentrations of these contaminants in groundwater. Because of these processes, in aquifers with a certain clayey fraction, it is possible for Fe or Mg to substitute for Si or Al, in the structure of the silicates.

#### 4.2. Natural Degradation of Groundwater Quality.

The processes of natural degradation of groundwater quality have historically received smaller attention than anthropogenic ones. However, current studies indicate that these processes, caused normally by dissolution of natural mineral compounds in groundwater, could have an important effect on human and animal health. Table 3 shows the tolerable concentration of these compounds in water, and the aquifer context where this type of pollution usually occurs.

Chemicals Characteristic or compound	Type of aquifer	Tolerable concentration for human consumption (ppm)
Salinity	Coastal, deep, or large time of water circulation aquifers. Evaporite aquifers.	1500
Chlorides	Coastal, deep, or large time of water circulation aquifers. Evaporite aquifers.	350
Sulphates	Evaporite aquifers	400
Iron	Deltaic aquifers, aquifers with reduced conditions	0.2
Manganese	Deltaic aquifers, aquifers with reduced conditions.	0.05
Fluor	Volcanic-igneous aquifers	1.5
Arsenic or other	Aquifer that crosses mineralized	0.05

heavy metals	masses, aquifers in metamorphic rocks. (Black Shales)	
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Table 3. Principal natural inorganic contaminants, with their tolerable concentrations, for drinking use.

Salinity increment by chloride or sulfate is the most usual natural degradation of this type. In most cases, it is the exploitation of deeper aquifers with high salinity, with badly designed wells, that connect different aquifers levels, which provoke degradation of quality in overlying aquifers.

Natural degradation causing high fluorine concentrations, has been described in active volcanic zones or fractured aquifers with fluorite-vein deposits. They tend to be associated with high incidence of fluorosis in the local population.

Contamination is also caused by incorporation of heavy metals in groundwater related to the presence of geochemical anomalies—veins or beds with metal sulfides. The danger of this type of compound is in their high toxicity, even in very low concentrations.

An especially significant element is arsenic, which is usually present as stable iron and arsenic sulfide, but under suitable conditions this complex is readily oxidized to more soluble sulfates or arsenate.

Because of the geological origin of these contaminations, treatment processes and remediation of this type of pollution are very expensive and do not provide a permanent solution.

In many countries, therefore, it is usual to mix such water with water from other sources, in order to dilute the concentration before distribution. The alternative, if possible, is simply to stop using the arsenic-contaminated groundwater.

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### **Biographical Sketch**

**Fidel Ribera Urenda** was born in Barcelona, Spain, in 1966. He graduated in Applied Geology in 1990 in Barcelona University and obtained his Doctor's degree in Geology in 1998, at the Autonomous Barcelona University. He also has a post-graduate degree in Groundwater Hydrology from Polytechnical University of Catalonia (1996) and Master of Geology and Environmental Engineering from Polytechnical University of Madrid (1994). Since 1990, he has worked in different applied geology areas like mineral exploration or geochemistry of hydrothermal ore deposits, and in recent years he has worked in groundwater projects, as a technical coordinator of the FCIHS (Fundación Centro Internacional de Hidrología Subterránea) in Barcelona. H