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CHAPTER 2

POLLUTANTS AND POLLUTANT TRANSPORT IN KARST AREAS

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Karst aquifers are an important source of water-supply in many regions. Indeed in some regions of countries participating in COST Action 65, karst groundwater is the only real water source. The available information suggests that in general the quality of karst water is fairly good. Therefore an important objective is the maintenance of this quality. In order to protect the karst water from pollution it is necessary to investigate the behaviour of contaminants and understand the natural factors that control this behaviour. The aim of working group 3 was to examine the main problems related to karst water contamination. This involved:

- identification of the most common contamination sources and describing them;
- determination of the main types of contaminants occurring in karst water;
- contrasting the behaviour of contaminants in karst and porous aquifers.

There is a considerable controversy about some concepts as contaminant, contamination, pollutant and pollution. Here the concepts given by Freeze & Cherry (1979) which were followed by Prohic (1989), were adopted. According to the aforementioned authors "all solutes introduced into the hydrologic environment as a result of man's activities are referred to as contaminants regardless of whether or not the concentrations reach levels that cause significant degradation of water quality. The term pollution is reserved for situations where contaminant concentrations attain levels that are considered to be objectionable."

Regarding the behaviour of contaminants in karst and porous aquifers, the following main differences should be noted:

- karst aquifers possess a very limited capacity of sorption and filtration which results in the rapid transport of contaminants;

- due to high flow velocities and consequent short residence time, the decay process is less effective and contaminants can reach wells and springs very quickly;
- oxidising conditions are common in karst groundwater and can lessen the concentration of some contaminants such as ammonia, Fe, Mn and some other heavy metals;
- karst regions are less sensitive to acid rain;
- in karst regions some types of contamination, such as in the case of accidents, can be more easily remedied, due to shorter residence time.

1. THE MAIN CHARACTERISTICS OF KARST WATER.

A full discussion on karst water characteristics will not be presented here. Only the main aspects relating to carbonate aquifers will be considered because the behavior of some contaminants, such as heavy metals, may be strongly influenced by the major components of karst waters. The reader interested in a deeper discussion of the factors influencing karst water composition should refer to Freeze and Cherry (1979), Bögli (1980), Appelo and Postma (1993), Dreybrodt (1988) and many others.

In general, the composition of karst water is quite simple. The most important processes affecting the solution of the rock are the dissolution of CO₂ in the unsaturated zone and dissolution of carbonate minerals (calcite and/or dolomite) in both the unsaturated and saturated zones. As a result, a large majority of karst waters have dominant bicarbonate, calcium and sometimes magnesium.

The main factor controlling karst water composition is the CO₂ pressure in soil. Harmon *et al.*, 1975, provide a relationship between that parameter and the temperature:

$$\log P_{\text{CO}_2} = -3.3 + 0.08 \cdot T(^{\circ}\text{C})$$

However, even under similar conditions of CO₂ pressure and temperature in soil, karst water composition can still change due to the conditions under which the dissolution processes are taking place. Traditionally, two end cases are considered; open-system and close-system dissolution. Dissolution takes place in an open-system when CO₂ is present in voids that are not entirely filled with water and when the consumption of this gas in the dissolution processes does not significantly affect CO₂ pressure, in such a way that this one can be considered constant.

Closed-system dissolution occurs when infiltrating water in equilibrium with CO₂ in soil, produces carbonate dissolution in the saturated zone, without contact with the gas phase.

Very often, karst water composition is the result of a mixture of the two processes. Carbonates are dissolved in open-system conditions during recharge in the unsaturated zone, but the water still retains some aggressiveness, reaching equilibrium with carbonate minerals in the saturated zone, under closed-system conditions.

Table I shows the influence of the type of dissolution on ground water composition. The first row corresponds to a pure closed-system. The next rows correspond to increasing quantities of calcite dissolved in an open-system, followed by dissolution in a closed-system until equilibrium is reached. The last row is an example of an entirely open-system. All concentrations are in mmol/kg. The calculations were made by using the geochemical model PHREEQE (Parkhurst *et al.*, 1980) with the initial conditions: temperature = 15 °C; pCO₂ = 10^{-2.1} bar.

Another important factor is the mineralogical composition of the karst reservoir. Taking into account that the most important carbonate minerals are calcite and dolomite, the following situations can occur: equilibrium of the karst water with calcite or dolomite, simultaneous equilibrium with both minerals, and sequential dissolution of calcite/dolomite or dolomite/calcite.

When water reaches equilibrium with dolomite it is very close to equilibrium with calcite. For that reason when dolomites are encountered first in groundwater paths, and water is allowed to equilibrate with it and the water next encounters calcite, no important changes in composition are to be expected. In this case, as well as in simultaneous equilibrium, both with calcite and dolomite, the dissolution processes are controlled mainly by the equilibrium with the second mineral.

Table I

Open system						Closed system					
Dissolved calcite	Satur. index	Total carbon	Ca	HCO ₃	pH	Dissolved calcite	Satur. index	Total carbon	Ca	HCO ₃	pH
0.000	$-\infty$	0.374	0.000	0.113	4.91	0.390	0	0.764	0.390	0.738	8.63
0.852	-0.9	2.063	0.852	1.699	7.06	0.274	0	2.337	1.125	2.228	7.74
0.924	-0.8	2.208	0.924	1.844	7.10	0.258	0	2.466	1.182	2.342	7.70
1.089	-0.6	2.526	1.089	2.171	7.17	0.220	0	2.756	1.308	2.596	7.62
1.284	-0.4	2.925	1.284	2.559	7.24	0.167	0	3.092	1.451	2.881	7.54
1.516	-0.2	3.387	1.516	3.019	7.30	0.096	0	3.483	1.612	3.204	7.46
1.648	-0.1	3.650	1.648	3.281	7.34	0.052	0	3.702	1.700	3.368	7.42
1.792	0.0	3.937	1.792	3.566	7.37	0.000	0	3.927	1.792	3.566	7.37

However, both scenarios are quite unusual. In fact, mainly due to kinetic reasons, groundwater is more frequently in equilibrium with calcite and undersaturated with respect to dolomite. So, sequential dissolution of calcite/dolomite is more common. In this case the increase in calcium and carbonate ions due to the dissolution of dolomite, cause supersaturation with respect to calcite (common ion effect). This leads to calcite precipitation which induces more dolomite dissolution. This process can proceed until the water reaches simultaneous equilibrium with both minerals. As a result of such reactions the following changes will be expected: slight increase in bicarbonate and pH, an increase in magnesium and a decrease in calcium. An example is presented in Table II. The first row shows groundwater composition in equilibrium with dolomite and a partial pressure of CO₂ = 10^{-2.1} bar. The second row shows the composition of a groundwater that was first in equilibrium with calcite with the same CO₂ pressure and which was then equilibrated with dolomite in closed-system. Both simulations were at the temperature of 15 ° C (concentrations in mmol/kg).

Table II

	Ca	Mg	HCO ₃	pH
Dolomite dissolution	1.160	1.160	4.610	7.48
Sequential dissolution calcite (open-system)/dolomite (closed-system)	0.961	0.980	3.848	7.62

Many other processes can modify karst water composition, the most important are: enrichment of CO₂ from sediments (e.g. lignites) or from organic matter oxidation, which leads to a renewed aggressiveness to carbonate minerals; sequential dissolution of calcite/gypsum or calcite/gypsum+dolomite (dedolomitization) and mixing with sea water in coastal aquifers.

2. POLLUTANT SOURCES

The pollution of karst aquifers can be seasonal, as in salt application for de-icing, or it can be accidental, as in spills on highways, etc. or chronic, as in landfills.

2.1. Urban waste water

In practically all the pilot areas there are urban areas of varying density that can be a source of contamination. The most important problems arise from those settlements that do not have treatment plants and sewage systems and where wastes are disposed of at the surface, in water courses, karst depressions and swallow holes.

Pollution originating from this type of source is mainly composed of metabolites of organic compounds, phosphates, boron, ammonia, nitrite, nitrate, bacteria and viruses, and detergents. Heavy metals can also be found, especially when industrial sewage is mixed with urban sewage.

An important source, which is very commonly disregarded is urban runoff. Urban runoff contains several contaminants such as hydrocarbons and oils originating from vehicle emissions and leaks, fertilisers, pesticides, pet faeces, etc. Rain water runoff from some roofs can produce considerable amounts of copper and zinc due to the acidic character of rain.

2.2 Industrial waste water

In some countries, industrial pollution is not of great concern because waste water is treated. It is very hard to describe industrial waste water because it can be different from one type of industry to another. A great number of industries, like distilleries, food plants and slaughterhouses, produce organic contaminants. In some regions an important seasonal source of pollution comes from olive oil processing plants. Leather plants, which are common in many karstic areas, produce sewage with high amounts of COD, Cr, etc., as well as solid wastes.

2.3. Other specific wastes

Leakage from gasoline tanks and sewage, containing mineral oils and hydrocarbons can come from filling stations located in karstic areas. In some areas filling stations have to take special measures in order to avoid groundwater contamination. Isolated septic tanks can also be a source of pollution as in Ireland. Sewage from hunting lodges and skiing resorts may pose problems in countries such as Austria and Switzerland.

2.4. Landfills

This pollution source can be dangerous in countries where excavations, such as abandoned quarries or closed depressions are used. Unlike other terrains, carbonate rocks have a generally high vertical permeability, for this reason leachate originating from waste disposal sites can reach the saturated zone very quickly. Furthermore, as many karstic regions are thinly populated they may often be selected as location for landfills. The general lack of understanding of karst vulnerability increases the risk of pollution from these sources.

Leachates originating from waste disposal sites and landfills can have very high alkalinity and COD, organic nitrogen and ammonia. Inorganic compounds (e.g. Cl and Na) can exceed one gram per litre. The strong reducing conditions, present beneath landfills, can favour the transport of some metals, especially Fe and Mn. Those conditions are also responsible for the presence of gases like nitrogen, methane and H₂S. The presence of sulphide can inhibit high heavy metal concentrations due to the very low solubility product of some sulphides.

2.5. Highways

Pollution originating from this source can be the result of; salt application for highway de-icing, hydrocarbons, oils and heavy metals from highway washing, accidental spills, etc. Analysis of water draining a section of the highway near Postojna (SLO) shows an extremely high chloride content (up to 19.3 g/l of Cl) due to the salt application. Up to 1.1 ml/l of Pb and 0.034 mg/l of Cd has been founded in the same area.

2.6. Agricultural activities

The impact of groundwater from agricultural activities is due to the usage of fertilisers and pesticides and the storage or disposal of livestock or fowl wastes on land.

Most fertilisers used are chemically manufactured, however, animal and human wastes are also used as organic fertilisers. The most common result of agricultural activities is the increase of nitrate in groundwater. Other components of fertilisers like phosphate and potassium are much less mobile.

Contamination coming from livestock and fowl wastes consists mainly of nitrogenated compounds, organic matter and micro-organisms.

Another consequence of agricultural activities may be a general increase in dissolved salts due to recycling of water by irrigation.

3. TYPES OF POLLUTANTS. FACTORS CONTROLLING THEIR BEHAVIOUR

This classification of pollutants was made in terms of their origin and typical behaviour.

3.1. Micro-organisms

Karst aquifers are, in general very sensitive to pollution by micro-organisms due to the fact that important parameters which control the microbe population, like decay and filtration, are mostly absent. Due to the rapid circulation in karst channels and other large voids, recharge water can reach outlets very quickly and so residence time can be short. This prevents the efficient decay of microbes. It has been observed that an increase in microbial content after heavy rains was due to the mobilisation of microbes present in the upper unsaturated zone.

3.2. Hydrocarbons

Very little is known about the behaviour hydrocarbons in karst aquifers. Their presence in karst water has been reported in some countries (HR, G). The source of the hydrocarbons can be; the drainage from roads, urban runoff, as well as during the transport, storage, handling and use of these substances.

As many karst aquifers have a thick unsaturated zone it is possible that volatilisation can be an important process. It is possible that sorption and fissure infillings may retard the contamination plume.

3.3. Pesticides

Like many other organic compounds, pesticides in the soil are controlled by degradation, volatilisation and sorption. Degradation is a biochemical process that leads to the breakdown of complex molecules into simpler forms in such a way that the final product can be oxidised to CO₂. The speed of this process is highly dependent on the type of pesticide, microbiological population in

the soil and environmental factors (soil moisture, percentage of clay, temperature, etc.) Adsorption and absorption of pesticides and other organic compounds, in soils, are mainly controlled by the presence of organic matter. The retardation factor can be estimated by the expression:

$$R = 1 + \frac{\rho_b}{\varepsilon} K_{oc} \cdot f_{oc}$$

where: R = retardation factor

ρ_b is the bulk density of the soil

ε is the porosity

K_{oc} is the partition coefficient organic carbon-water

f_{oc} is the fraction of organic matter in the soil

On the other hand K_{oc} can be estimated either by the octanol-water partition coefficient, K_{ow} , or by the solubility, these relationships being obtained by linear regression. For example Hassett *et al.* (1983) suggest the expression

$$\begin{aligned} \log K_{oc} &= 0.088 + 0.909 \cdot \log K_{ow} \\ \log K_{oc} &= 3.95 - 0.62 \cdot \log S \end{aligned}$$

where S is the solubility in mg/l. Similar expressions can be found in Karichhoff *et al.* (1979), Karichhoff (1981) and Schwarzenbach and Westall (1981). For example the retardation factor for the parathion in a soil with 0.1% of organic matter and a porosity of 0.3 can be about 30. Other compounds can have even stronger sorption. This low mobility implies large residence time in soils therefore favouring decay by the previously mentioned processes. Up to now pesticides have hardly been noticeable in karst waters. This seems to indicate that these processes are efficient enough in normal situations. However, accidental spills on bare karst, uncontrolled dumping of pesticides packing and the infiltration of surface waters can be harmful.

3.4. Heavy metals

Metal ions in groundwater are influenced by several processes such as complexation reactions, redox processes, sorption, dissolution/precipitation and coprecipitation. Redox processes can also control the toxicity of some metals, e.g. Cr and metalloids, e.g. As. In the presence of strong binding ligands, transport of metal ions can be faster than would be expected in the absence of such ligands (Davis *et al.*, 1993). One of those ligands, the carbonate ion, is present in karst water. For example, by using analytical data provided by the Spanish team (Spring P2) the following results were obtained:

Metal	Free ion	Carbonate and bicarbonate complexes	other (OH-, etc.) complexes
Cu	0.7%	27.0%	70.3%
Pb	0.7%	98.3%	0.0%
Zn	28.7%	67.9%	3.4%

which show that heavy metals are transported as complex rather than free ions.

Both metallic cations and anions are sorbed on calcite. Their sorption depends on pH and CO₂ pressure (Zachara *et al.*, 1993). According to these authors, cations exchange with surface calcium and anions with surface carbonate.

The CEC (cation exchange capacity) is strongly dependent on the surface area, i.e. on the granularity. The French team (Gheysans *et al.*, 1986; Fallot *et al.*, 1983) found a maximum of 0.1 meq/100 g for cross grained limestones.

Zachara *et al.* (1993) by comparing experimental results with computer modelling, obtained a constant for ion exchange $\log K_{Zn/Ca} = 2.45$, for low concentrations in Zn, and 2.2 for higher concentrations (1 ppb). These values mean a strong preference for Zn.

Some anions and cations show a high reversible exchange reaction (e.g. NO₃) whereas others, like Phosphate, Li, K are adsorbed or precipitated on the surface irreversibly (Gheysans *et al.*, 1986).

According to these results it can be foreseen that, even in absence of soil, some attenuation is possible for specific compounds. The capacity for exchange in limestones depends on granularity, percentage of clay minerals, iron hydroxides and organic matter.

3.5. Nitrogenated compounds

The behaviour of nitrogen compounds in soils is well known. These compounds mainly come from the application of fertilisers and the breakdown of organic matter. In short, the most reduced member of the group is the ammonia and the most oxidised is the nitrate. In oxidising conditions nitrate is always the dominant species. As the majority of karst waters occur in such conditions nitrate usually will be the dominant species. In general, nitrate is absent only in cases of deep flow under confined conditions, e.g. the Chalk aquifer (UK), and presence of organic matter, or other reductant. Observations confirm these assumptions and very few cases of the presence of ammonia in deep karst waters have been described.

3.6. Inorganic compounds

The increase in the concentration of some ions like Ca, Mg, sulphate and chloride can sometimes inhibit the normal use of karst water. This increase can be due to natural causes or to pollution. Examples of natural causes are the dissolution of gypsum and other evaporites and sea water intrusion.

The main sources of pollution responsible for the increase of inorganic ions are salt application on roads, leachates from landfills, injection of urban waste water and agriculture. In some regions, solid precipitation and relatively high concentrations of some compounds in rain can be supplementary source of pollution. For instance, concentrations of Boron up to 5 ppm in rain water were detected in Castellón (Spain).

As a result of fertiliser application, some inorganic components can increase by direct or indirect causes. The mobile components of fertilisers, like sulphate and chloride can pass directly to groundwater without significant absorption. Other components can be partially absorbed or undergo geochemical alteration which prevents their passage to groundwater (phosphate and potassium). As a result of the ammonia and potassium exchange the concentration of calcium, magnesium and sodium can be increased in groundwater.

3.7. Radioactive isotopes

The nuclear accident at Chernobyl has shown the extent to which the groundwater in karst aquifers is affected by such a disaster. Even when such accidents happen far from a karstic area,

mainly ^{131}I , ^{137}Cs and ^{134}Cs are likely to occur in springs. Open karst systems are more sensitive to the introduction of radioisotopes than karst systems with topsoil. Topsoil and organic material in the karst system can sorb radioisotopes. Karst springs must not be used for water supply after nuclear accidents. Therefore the location of nuclear power plants, reprocessing plants and radioactive waste disposal sites in karstic areas poses a serious threat to karstic aquifers. In the event of nuclear contamination, tritium is the first radioisotope that appears in springs. High velocity karst systems have low self purification for nearly all radioisotopes, so therefore they will appear in springs. However, the short residence time means that radionuclides leave the system in a short time and a decrease in radionuclide concentration is to be expected in springs if the recharge area is not exposed to further contamination.

4. SALINIZATION PROCESSES

In some countries salinization processes can be an important source of contamination of karst aquifers. Sea water intrusion is the main process causing salinization in the aquifers. From a hydrodynamic point of view, karst aquifers have the highest transmissivity values and high sensitivity to a rapid sea water intrusion. Depending on the hydrodynamic conditions (degree of karstification, exploitation, etc.) the diffusion zone can have different thickness. Normally changes of position occur very rapidly, affecting a large part of the aquifer. Most of the Mediterranean coastal karst aquifers are seriously affected (e.g. Puglia, Italy) or soon will be (e.g. Campo de Dalias, Spain).

From a hydrochemical point of view sea water intrusion is responsible for the increase in content of some species (chloride, sulphate, sodium, etc.) and the modification of the equilibrium conditions. This modification can lead to reactions between the mixing water and the solid matrix (precipitation/dissolution of carbonates, ionic exchanges, etc.). The most important consequence of sea water intrusion is the degradation of water quality, preventing its normal use. In some cases (e.g. Crevillente aquifer, Spain) due to excessive drawdown, over-exploitation can modify the natural flow regime, enabling the upward movement of salt water derived from evaporitic deposits, and which have a relative low flow velocity. This phenomenon is especially important in those karst aquifers where the abstraction is much higher than the recharge and where the depletion is therefore very fast. In the Crevillente aquifer the watertable has dropped 14 meters/year. In agricultural areas with a thin soil directly overlying karst formations, irrigation with saline waters using a flooding system, (as is used in the southern parts of Italy, Portugal and Spain) favours high evaporation and increases the groundwater salt content as a result of infiltration of the irrigation water.

5. PHYSICAL, CHEMICAL AND BIOLOGICAL CHANGES

There are two types of changes: short period (seasonal) and long term trends. Few data are available for the long term trends. This is because either there are no long term records or because analytical methods are recent (e.g. pesticides). In the few cases where there are adequate records the majority of the chemical parameters do not show any discernible trend, except nitrate, which shows an increase. On the other hand, short term variations of some inorganic and micro-biological parameters show an increase after heavy rain as a result of the flushing out of contaminants from the surface and the epikarst. However, some compounds show a decrease due to dilution.

6. HYDROGEOLOGICAL FACTORS WHICH CAN INFLUENCE THE INPUT AND TRANSPORT OF POLLUTANTS

The behaviour of each pollutant indicates that the vulnerability of a karst system and the severity of contaminations depend on several factors:

6.1. Reservoir structure

When the karst drainage is well developed with a few karst channels draining large areas, the rate of movement is rapid, dispersion is negligible and the pollution can reach outlets quickly. On the other hand, when the groundwater flow is more diffuse, dispersion and other processes can be more important due to longer residence time and the more intimate contact with the rock, which favours water/rock interaction processes.

6.2. Overlying formations.

The presence of a detrital cover or overburden formation is the most important natural protection for karst aquifers. As already pointed out, many pollutants can be controlled by physical processes such as filtration and bio-geochemical processes including redox reactions, sorption, etc. The overburden can be effective protection against some groups of pollutants (pesticides and other organic contaminants, micro-organisms, heavy metals, ammonia, etc.).

6.3. Thickness and degree of karstification of unsaturated zone

Although the self-purification capacity of the karst unsaturated zone is less than the capacity of soils and porous formations, some attenuation is possible, depending on the unsaturated zone thickness and degree of karstification. Favourable conditions occur when the unsaturated zone is thick and poorly karstified. This allows a slower vertical movement and a more intimate contact with the rock, favouring self-cleaning processes (e.g. decay and sorption).

6.4. Means of access of pollutants.

As a consequence of the heterogeneity of the karst aquifers the spread of pollution is very dependent on the type of access to the system. If the pollutant gains direct access to an underground stream, for example through a swallow-hole or parts of the karst surface permitting an easy connection with groundwater, the pollution can travel very rapidly and the attenuation and dispersion are minimal. For that reason, the practice common in some regions, of disposing of wastes in sinkholes and other karst structures can be very dangerous and must be avoided.

6.5. Modifications in flow conditions

Attention should be paid to modifications in flow conditions. For instance, excessive drawdown can induce polluted water. Of course, the reverse is also possible, i. e. in certain conditions clean water can be induced and provide some dilution of pollution. Modifications in the conditions of natural recharge, like deforestation and reduction in permeability, and artificial recharge can also produce water quality changes.

6.6. Entry of surface water.

A very common feature of karst regions is the total or partial sinking of surface streams, coming from unkarstified regions. As the water quality of these surface streams is frequently poor, they can cause serious pollution. In this way, some compounds that could be attenuated in normal conditions, gain entry to the saturated zone.

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