Groundwater Pollution: Human and Natural Sources and Risks

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ABSTRACT

Urban and rural centers are usually concentrated in areas with adequate quantities of water sources. Underground water constitutes the major water source for most of these areas. The quality of underground water ranges from good quality fresh water (potable), to medium (domestic, industrial) or inappropriate quality for any use. The water quality depends on various anthropogenic and natural factors that cause pollution and contamination. Anthropogenic factors that affect groundwater quality can be classified into direct (e.g., over-pumping, unlimited use of fertilizers, mining activities, waste dumps, or even cemeteries, among others), and indirect ones (e.g., extended urban development, local climatic conditions, water basins and river network interruption). Natural degradation of groundwater quality occurs due to seawater intrusion, geothermal brine infiltration in geothermal fields, rock-water leaching interactions and radioactive decay of isotopes such as uranium and thorium, in order to produce radon which is found in rocks and soils. Another classification of groundwater pollution sources also includes point and non-point sources. Groundwater pollution occurs with the presence of several contaminants such as heavy metals, pathogenic microorganisms, pesticides, nitrate, pharmaceuticals and others, which can also cause a negative impact on human health and ecosystem preservation. The Argolic Plain (Greece) is a characteristic example of groundwater quality degradation due to both anthropogenic and natural factors. Aidipso and Methana regions (Greece) are examples of natural groundwater quality degradation due to rock-water leaching and the presence of geothermal
INTRODUCTION

Groundwater resources represent one of the most important treasures of our planet; fresh water that is located below the ground surface and stored in underground saturated geological formations. As water is the main and necessary element of life, aquifers significantly affect the ecological balance of the planet and are directly related to the status of the ecosystems and the human health. Groundwater pollution is today one of the greatest threats to the environment and specifically to the human progress. Rapid population increase, climate change and multiple human activities put in danger the availability of fresh water resources and degrade the quality of groundwater. Many sources of groundwater pollution can be distinguished, either anthropogenic (due to human activities) such as urban runoff, industrial effluents, wastewater discharges or natural such as seawater intrusion, rock erosion and radon contamination by radioactive decay of uranium and thorium series.

The diversity of the pollution sources yields a respective variety of contaminants that contaminate groundwater bodies. Especially, synthetic organic compounds and micro-contaminants represent an emerging concern for the health status of the ecosystems and the human society, given that groundwater is a major potable water source. This chapter summarizes the different pollution sources of groundwater and discusses the related environmental and human health risks arising from the presence of the various contaminants in the aquifers.

GROUNDWATER RESOURCES AND ITS BENEFITS

The water volume on earth is practically stable and it is estimated at the height of $1600 \times 10^6 \text{ km}^3$ (Gleick, 2014). Part of this quantity is trapped in Earth’s mantle and is known as juvenile water or magmatic water. The water covering Earth’s surface is estimated at the height of $1,370 \times 10^9 \text{ km}^3$ and comprises a water body of 2,700 m thickness, covering a surface of $510 \times 10^6 \text{ km}^2$ (Oki and Kanae, 2006). Seawater represents 97.2% of global water volume and is not subjected to human uses such as irrigation, watering or industrial uses (Giordano, 2009; Gleick, 2014). Additionally, a 2.1% of ice and snow, as well as 0.001% of steam, is also not exploited. This results in 0.6% of the global water quantity that can be used and consumed by humans and which is estimated at the height of $8.2 \times 10^6 \text{ km}^3$. Out of
this amount, 12% represents runoff water and lake water resources and the rest (approximately $7.2 \times 10^6$ km³) the underground water resources (Leap, 2007; de Vries, 2007). However, almost half of these underground water resources occur at depths below 800 m which makes it difficult to reach, while 0.6% of the underground water represents humidity and other loses. Finally, it is estimated that the available fresh water resources for humans are approximately $0.1 \times 10^6$ km³ and $3.0 \times 10^6$ km³ of surface and groundwater resources, respectively (Oki and Kanae, 2006). These estimations indicate the necessity of preserving fresh water resources availability for all life forms on the planet, due to the significant role of the water itself for the living organisms.

Fresh water resources are important not only for humans but for every form of life on Earth. Water resources consumption comprises of underground water (95–96%), surface water such as lakes, rivers etc. (3.5%) and soil moisture (1.5%) (Giordano, 2009). As water scarcity problems occur in many parts of the world, groundwater exploitation appears as the easiest way to cover the increasing water demands (Oki and Kanae, 2006; Giordano, 2009). An estimation of the mean water resources consumption in industrialized countries is approximately 315 liters per day for domestic use, personal hygiene, gardening, potable water and cooking uses. Potable water and cooking use represents approximately 8 liters per day which is the most important for survival (Giordano, 2009). Millions of people have died over the last decades due to lack of access to clean potable water. Adding up the use of water resources for urban and rural purposes, and industrial production, it can be estimated that the equivalent available quantity of water resources to each person is approximately 7.5 m³ per day.

GROUNDWATER POLLUTION

Over-consumption of fresh water resources reduces the available quantities for future generations since water is a consumable resource and the major constitute of the life cycle. Water resources contamination has direct effects in all living organisms which depend on the hydrologic cycle.

Most developed areas lack of fresh water resources due to over-abstraction, over-consumption and limited actions in order to preserve these resources. Large cities of the developed world are characterized by urban, agricultural and industrial development which requires respectively high quantities of water. The over-consumption of the regional water resources leads to qualitative degradation of these resources (Giordano, 2009). The quality of underground water in developed areas ranges from good quality fresh water (potable), to medium quality (domestic, industrial) and to inappropriate quality for any use. Degradation of the water quality is the result of various pollutant sources both anthropogenic and natural.
Anthropogenic factors consist of direct activities such as over-abstraction, wastewater treatment plant effluent discharge, unlimited use of fertilizers, mining activities, waste dumps and cemeteries, among others and indirect such as extended urban development, microclimate, water basins and river network interruption. Natural degradation of good quality water occurs due to seawater infiltration and intrusion which has similar negative results as over-abstraction, geothermal brine infiltration which occurs in geothermal fields, rock-water leaching interactions, and radioactive decay of uranium and thorium series that yields to radon contamination which could result in increased concentrations of elements that degrade underground water quality.

**Pollution Sources: Classification**

Pollution can be generally generated by groundwater contamination and water quality degradation. Contamination is the result of domestic and public wastes, industrial waste (organic, inorganic, trace elements etc.), mining activities (chemical, trace elements, infiltration etc.), among others. Degradation is the result of the development, use and reuse of water sources such as infiltration, over-pumping, seawater mixing, surface water contamination and rock-water interaction.

Water resources pollution and the respective groundwater quality degradation are caused by various human activities which result in the change of water physicochemical characteristics. Most pollutant sources include the disposal of contaminants generated by water use. Contamination of surface water sources is easier to locate. In contrast, underground water contamination sources are difficult to identify, and it sustains for decades.

Groundwater pollution sources can be classified based on different parameters:

(a) **Origin**: Natural or anthropogenic (human activities)

(b) **Geometry of the source**: Point (e.g., landfills, waste dumps, septic tanks, underground tanks), linear (roads) and diffused (e.g., nitropollution, acid rain, uranium decay).

(c) **Transmission rate**: Continuous transmission and recurrent (periodic or not).

**Anthropogenic and Natural Pollution Sources**

The most common pollution sources are the anthropogenic ones. This category generally includes:

- The disposal of wastewater and solid waste,
- The disposal of industrial wastewater,
• The use of fertilizers, pesticides and insecticides,
• The by-products and waste from of mining activities,
• The disposal of nuclear energy waste.

Anthropogenic sources can be caused by different activities such as:

• Over-pumping,
• Unlimited use of fertilizers,
• Mining activities,
• Waste dumps,
• Extended urban development,
• Change of climatic conditions (microclimate),
• Water basins,
• Misuse of chemicals,
• Disposal of organic and inorganic elements,
• Heaps and sewage storage (infiltration),
• River network interruption,
• Mineral processing of radioactive minerals,
• Cemeteries.

Pollutants such as trace elements are concentrated in the discharge material/water from various anthropogenic activities such as mining, urban and agricultural sewage, fertilizers, fuels etc. and can be toxic and lethal to humans. For instance, the following elements have been detected in groundwater sources: Al, Sb, As, Ba, Be, B, Cr, Co, Cu, Au, Fe, Li, Mn, Hg, Mo, Ni, Se, Ag, Sr, Ta, Sn, Ti, U, Va and Zn.

Furthermore, pollution by increased concentrations of nutrients (ions or organic components of nitrogen and phosphorus) has been linked with the use of fertilizers, livestock and agricultural activities and sewages leak. Other contaminants that have been detected in groundwater and are related to human activities are hydrocarbons, halogens, biphenyls and biological contamination (bacteria, viruses, parasites). Infiltration of disposals, mining activities, and sewages leak results in pollution by other inorganic compounds that can be toxic and are associated with the salinity of water resources due to high concentrations of Ca, Mg, Na, Cl and F.

Groundwater can also be polluted through natural causes, i.e., the results of cycles or of natural phenomena. This category includes the following sources:

• Easy to dissolve rocks (gypsum, mineral salt etc.),
• Intense evaporation, especially in shallow aquifers which causes elevation of groundwater and salt deposition,
• Degradation of water sources in areas located in geothermal/volcanic fields,
• Rock oxidation,
• Seawater intrusion,
• Decay of radioisotopes from uranium-rich bedrock,
• Chemical reactions of elements in the air or in the water (both natural and/or anthropogenic).

**Point and non-point Pollution Sources**

Possible water pollutant sources are numerous and can also be classified into point sources and diffuse pollution sources (Fig. 1). As Fig. 1 shows, pollution of surface waters is directly related with underground water pollution, thus, pollution of surface water usually results in respective groundwater pollution. Groundwater pollution sources are summarized in Table 1.

Fig. 1:

Major point sources include municipal and industrial wastewater treatment plant effluents, which can be located in urban, industrial or agricultural regions (Pal *et al*., 2010; Lapwoth *et al*., 2012). It is not unusual that wastewater treatment plants, combined sewage-stormwater overflows treatment plants or improper treatment of hospital effluents do not provide a final effluent of appropriate quality. Specific organic micropollutants might end up in this way in surface and groundwaters (Stefanakis *et al*., 2014). Other point sources of groundwater pollution are industrial activities
such as food processing, mining activities, manufacturing plants, livestock farms and landfill sites. Moreover, other human activities which could result in groundwater pollution are disposal of contaminants to percolation ponds, seepage pits, trenches, dry streambeds, disposal wells and injection wells.

Table 1: Potential pollution sources of groundwater.

<table>
<thead>
<tr>
<th>Category</th>
<th>Source of contamination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Residential</td>
<td>Air pollution</td>
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<tr>
<td></td>
<td>Septic tanks</td>
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<tr>
<td></td>
<td>Household wastewater</td>
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<td></td>
<td>Sewer network</td>
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<td></td>
<td>Household waste</td>
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<td></td>
<td>Fuel oil</td>
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<td></td>
<td>Furniture stripping/refinishing</td>
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<td>Paints</td>
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<tr>
<td>Municipal</td>
<td>Municipal sludge spreading in land</td>
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<td></td>
<td>Air pollution</td>
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<td></td>
<td>Streets and parking lots</td>
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<td></td>
<td>Municipal incinerators</td>
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<td>Municipal landfills</td>
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<td></td>
<td>Sewer lines</td>
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<td></td>
<td>Road maintenance depots</td>
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<tr>
<td></td>
<td>Wastewater treatment plants effluents</td>
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<tr>
<td>Commercial</td>
<td>Airports</td>
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<td></td>
<td>Metal plating</td>
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<td></td>
<td>Construction areas</td>
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<td></td>
<td>Medical institutions</td>
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<td></td>
<td>Car washes</td>
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<td></td>
<td>Research laboratories</td>
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<td></td>
<td>Cemeteries</td>
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<td>Railroad tracks</td>
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<td></td>
<td>Dry cleaners</td>
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<td>Laundromats</td>
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<td>Gas stations</td>
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<td>Scrap/junkyards</td>
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<td></td>
<td>Golf courses</td>
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<td></td>
<td>Recycling facilities</td>
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<td>Industrial</td>
<td>Chemical industry/storage</td>
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<td>Metal fabricators</td>
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<td></td>
<td>Electronics manufacture</td>
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<td>Petroleum production</td>
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<td>Mining and mine drainage</td>
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<td>Pipelines</td>
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<td></td>
<td>Metalworking shops</td>
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<td></td>
<td>Storage tanks</td>
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<td></td>
<td>Toxic/hazardous spills</td>
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<td></td>
<td>Wells</td>
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<tr>
<td>Agriculture</td>
<td>Animal feedlots</td>
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<td>Fertilizer storage/use</td>
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<td>Irrigation sites</td>
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<td>Manure spreading areas</td>
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<td>Sludge reuse</td>
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<td></td>
<td>Chemical spills</td>
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<td></td>
<td>Livestock waste</td>
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<td></td>
<td>Pesticides</td>
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<td>Tanks</td>
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<td></td>
<td>Wells</td>
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</table>

Domestic wastewater from residences, institutions or other facilities such as confectioneries, restaurants, laundries etc. is a major pollution point source. It mainly consists of water containing organic and inorganic compounds, as well as bacteria and viruses. Its unpleasant odor is mainly attributed to the organic matter which is subjected to aerobic or anaerobic bacterial decomposition. The color of the wastewater also indicates its age and origin. Organic matter in domestic wastewater can be faeces, urine,
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paper, soaps, detergents, food residuals, fats and oils, while inorganic materials include ammonia, ammonium salts, clay, phosphorus etc (Stefanakis et al., 2014). The production of domestic wastewater differs from region to region and from country to country; a typical production rate varies between 150–500 L per person. Wastewater disposal creates pollution problems to the environment such as eutrophication, groundwater pollution and limitation of the natural self-purification capacity of water. In small and remote settlements, septic tanks are the most common method for wastewater disposal. Collection and transfer of wastewater to a centralized treatment facility aims to increase the level of wastewater treatment which allows the safe disposal to a water body, the reuse of the final treated effluent or its applications to the soil.

The major pollutants in domestic wastewater are the suspended solids, organic compounds, nutrients (nitrogen and phosphorus) and pathogenic microorganisms. Moreover, the use of household chemicals such as synthetic detergents, solvents, oils, medicines, batteries, gasoline etc. can also results in groundwater contamination. Storage of these compounds in basements and garages could also introduce these substances to groundwater during flooding incidents. When these compounds are thrown in the household trash, they will end up in community landfills which usually are not capable of handling hazardous materials.

Industrial wastewater refers to wastewater from various industries, excluding the wastewater from the staff facilities, and is another point source of groundwater pollution. This type of wastewater is a result of the water used in the industrial processes, which contains various compounds in low or high concentrations, both biological (e.g., wastewater of the food industry, paper industry and textile treatment) and non-biological (wastewater of the chemical industry containing pollutants such as acids, bases, chlorine, metals, cyanide, salts, hydrocarbons, phosphates) (Stefanakis et al., 2014). Compared to municipal wastewater, industrial wastewater contains some toxic substances and presents difficulties to be effectively treated. High demands for cooling water, processing water and cleaning water in the manufacturing and processing industry may result in groundwater pollution when this used water is discharged and re-entered to the hydrological cycle. Spillage, leakage and/or improper handling or storage of hazardous materials is another source of pollution. Furthermore, there are differences between the wastewater characteristics of the various industries. Part of the industrial wastewater is characterized as dangerous/hazardous wastewater (e.g., hospital wastewater) and there are specific conditions and environmental limitations for its disposal to the environment.

Hospital wastewater represents a major environmental threat and creates serious issues for the natural environment and human health. It is reported that hospital wastewater is 5 to 15 times more toxic than typical
urban outflows (Panouillères et al., 2007). The main problems with hospital wastewater are the large daily volumes produced (which is more than five times higher than the typical household production; Labert et al., 1999), the content of various microbiological and chemical substances (Kümmerer, 2001) and the fact that this wastewater is often discharged to the sewer network system without any previous treatment (Emmanuel et al., 2005). Potential pollutants and contaminants in hospital wastewater that may result in groundwater bodies are pathogenic microorganisms (including antibiotic resistant bacteria), heavy metals, radioisotopes, organohalogens, pharmaceuticals and drug residues (Emmanuel et al., 2009).

Landfills are also considered as an important pollution point source of groundwater. Municipal waste includes food residues, paper, glass, plastic materials, vegetable materials, fabrics, wood, tires etc. and sometime small amounts of hazardous waste (such as colors, mineral oils, detergents). If recycle programs are applied, content of glass, paper and metals are low. These wastes also contain water at a percentage of 25–60%. Leachates from landfills are rich in nitrogen, chloride, mercury, iron etc. Contamination of aquifers in landfill sites has been detected in many cases around the world over the last decades. Usually, parameters that result in groundwater contamination are bad design or construction of the landfill, inappropriate selection of the installation site or false characterization of the hydrogeologic regime and soil permeability, among others. Landfill projects usually include groundwater monitoring programs (frequent samplings and analyses, groundwater elevations measurements), while in cases when there are nearby water bodies, monitoring of surface water is also required (Keister and Repetto, 2007). Contamination of groundwater with pharmaceutical compounds in landfill sites has been reported in the USA (Buszka et al., 2009), in Croatia (Ahel et al., 1998) and in Denmark (Holm et al., 1995). However, today respective issues in landfill sites have been minimized but not eliminated.

Mining waste are produced during the mining of mineral resources in mines and coal mines, and are a mixture of water and powdered mineral and possibly of heavy metals as by-products (Stamatis et al., 2001; Garba et al., 2014). During the excavations, protective soil is removed and, thus, the possible pollutants reach the aquifer. Usually, mining activities are extended below the groundwater surface and drainage is necessary. This water is rich in metals and is known as acidic mine water (Giri and Singh, 2015). The excavated area is often used as waste deposit area after the end of mining exploitation, which also results in possible pollution of groundwater. Heavy metal pollution in groundwater due to mining activities poses a threat to human health, especially when groundwater resources are used as drinking water supplies, given that many metals have been identified as potential carcinogenic substances under chronic exposure (Azcue, 1999; Giri and Singh, 2015).
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Non-point sources are difficult to be identified and they can cover large, extended geographical areas (Lapworth et al., 2014). This type of sources includes natural, chemical, infiltration and anthropogenic sources, such as stormwater and urban runoff, highway runoff, and agricultural land (use of fertilizers).

The use of fertilizers, pesticides, herbicides and animal waste in agriculture is a major non-point source of groundwater contamination (Velthof et al., 2009; Savci, 2012; Cruz et al., 2013; Stefanakis et al., 2014). The water which is returned from irrigated areas is filtered to the groundwater along with dissolved substances. In this way, elements existing in the fertilizers reach the groundwater, especially in cases of permeable soil formations. Contamination may also occur due to spillage of pesticides and/or fertilizers during handling, the use of chemical substances upstream and/or in the vicinity of a well, runoff from the loading and washing of pesticide sprayers and other application equipment, among others. Drainage wells are often used by farmers in order to improve the drainage of agricultural land and increase its productivity. However, this allows for the direct contamination of groundwater through the washing down of pollutants as agricultural runoff. Storage of the chemicals used in agriculture near to wells also contributes to groundwater contamination. Common pollutants are nitrate, which have a great mobility and can easily move from the unsaturated zone to the aquifer. In the unsaturated zone the dissolved substances move vertically towards the underground level and in the saturated zone the hydraulic slope causes the horizontal movement of the groundwater and the pollutants. The excessive use of fertilizers results in the increase of nitrate and the respective degradation of the aquifers. Large amounts of water used for irrigation (approx. 10%) return and supply the underlying aquifer (irrigation return flow). This water contains salts and minerals, which are added with the dilution during the irrigation process or with minerals of the fertilizers. Common ions in the irrigation return flow are Ca$^{+2}$, Mg$^{+2}$, Na$^+$, NO$_3^-$, Cl$^-$, SO$_4^{-2}$ and HCO$_3^-$.

Additionally, the use of manure and biosolids, i.e., treated municipal sludge, and their application to agricultural land is a common strategy to enhance the nutrient levels in the soil (Lapworth et al., 2012), but it may also result in residual concentrations of several pollutants in groundwater through soil application and surface runoff (Infascelli et al., 2009; Clarke and Smith, 2011; Cruz et al., 2013; Lockhart et al., 2013; Stefanakis et al., 2014).

Natural groundwater contamination also falls within the category of non-point sources. The presence of various elements and impurities in groundwater may not be originated from anthropogenic sources. Seawater intrusion is an issue with global dimensions since it contributes to the degradation of coastal freshwater aquifers (Werner et al., 2013). Over-pumping of groundwater and respective decline in the groundwater level,
change in land-use and climate change effect are the main reasons for the incursion of seawater to the coastal groundwater bodies. Seawater intrusion results in a decrease of available freshwater storage volume and the contamination of the production wells in the area, while less than 1% of seawater is enough to change the water quality to inappropriate for drinking purposes (WHO, 2011). Moreover, seawater intrusion is also connected with the presence of specific contaminants and elements in groundwater bodies around the world, e.g., mercury (Grassi and Netti, 2000; Protano et al., 2000), increased salinity (Moujabber et al., 2006) and ions/cations such as Na⁺, Mg²⁺, Ca²⁺, K⁺, Cl⁻ among others (Barlow and Reichard, 2010; Werner, 2010; Park et al., 2012; Singaraja et al., 2014).

The type and concentration of the natural elements in groundwater also depends on the nature of the geological materials that surround the groundwater body. Sedimentary rocks and soils usually indicate the presence of various compounds such as magnesium, calcium and chlorides or even chromium in groundwater (Megremi et al., 2013; Russioniello et al., 2013; Umar et al., 2013). Other dissolved constituents such as boron, arsenic and selenium have also been detected in groundwater bodies at relatively high concentrations. All of these elements can be found naturally in soils and rocks and can get dissolved in groundwater. Local conditions regulate the levels of these constituents in groundwater.

Radon contamination may accumulate in the groundwater by non-point sources such as large extent of plutonic rocks being in contact with aquifer or lake or even by point sources such as faults and fractures. High uranium content bearing minerals (e.g., zircons) may exist in igneous or metamorphic rocks or in soils. Decay of uranium series results in increase of radium and uranium series (²²²Rn), while faults and fractures in an uranium rich bedrock facilitate migration of high uranium concentration in the water (Richon et al., 2010). However, it is worthy to note that due to its very short half-life (3.8 days for ²²²Rn; Tanner 1964), the radon concentration in water decreases as the distance from the contamination source increases. For the same reason, surface water and unsaturated soil show less ²²²Rn concentration than the saturated soil and groundwater where radon is continuously produced by the surrounded rocks or due to the lack of diffusional loss to the atmosphere. Variations of radon groundwater concentration are linked to the degree of weathering in the rocks and soils, and to the rise and fall of the local water table (e.g., Lambourn, UK; Mullinger et al., 2008).

Artificial recharge of groundwater is often used to maintain or increase the water level in order to minimize the effects of over-abstraction. Usually, treated wastewater (industrial or municipal) or urban and stormwater runoff is used for this purpose, which could potentially re-contaminate groundwater with residual pollutant concentrations (Díaz-Cruz and Barceló, 2008; Lapworth et al., 2012). Excess drinking water might also be
used for artificial recharge, but the risk in this case is the potential introduction of disinfection/chlorination by-products such as trihalomethanes (THMs) and haloacetic acids to the groundwater table. Recharge with surface waters could also represent a pollution source (Díaz-Cruz and Barceló, 2008). It is reported that the use of lake water for groundwater recharge through ponds and wells in Germany resulted in the introduction of pharmaceuticals (e.g., carbamazepine, primidone, bezafibrate, diclofenac and propyphenazone) to the local aquifer (Heberer and Adam, 2004; Grünheid et al., 2005; Heberer et al., 2011).

GROUNDWATER CONTAMINANTS

The quality of groundwater is very important for the environment and life preservation. Human use of natural resources results in qualitative degradation of groundwater. Pollution refers to any degradation of the natural water quality. According to the Directive 2000/60/EU (European Commission, 2000) for water policy, pollution is the consequence of human activities, direct or indirect introduction to the air, water or soil of substances or heat which can harm and damage human health or the quality of the aqueous ecosystems or terrestrial ecosystems. Contamination refers to the pollution that represents a threat for human health. Contamination mainly includes microbiological pollution and is related to the presence of pathogenic microorganisms, as a result of human activities.

Table 2 presents the main pollutants and contaminants in groundwater, their sources and their main effects on human health and the ecosystems. The most common pollutants in water are:

- Heavy metals (Hg, Pd, Cd, Cr, Cu etc.),
- Toxic compounds (As, Se, CN\textsuperscript{-} etc.),
- Inorganic compounds (NO\textsubscript{3}\textsuperscript{-}, NO\textsubscript{2}\textsuperscript{-}, PO\textsubscript{4}\textsuperscript{3-} etc.),
- Synthetic organic compounds (phenols, chlorinated hydrocarbons, detergents, pesticides, paint colors, petroleum products etc.),
- Radioactive substances (radon caused by uranium and thorium series decay),
- Pathogenic microorganisms (bacteria and viruses) which can cause diseases, e.g., dysentery, diarrhea.

Groundwater contaminants can be classified based on their physicochemical characteristics, e.g., their preference for association with the aqueous phase or with other particles. This parameter is very important since it regulates the contaminant transport behavior and toxicology. It is also connected with the appropriate treatment process that will be applied for the remediation of a contaminated area.
Table 2: Groundwater pollutants and contaminants, their sources and main effects on human health and the ecosystems.

<table>
<thead>
<tr>
<th>Pollution source</th>
<th>Pollutant</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical industry, factories, Mining</td>
<td>Cu, Pb, Zn, Cd, HgCo, Cr, Ag, As, CN</td>
<td>Accumulation in the food chain, cancer, nervous system diseases, bone marrow and red blood cells attack, skin diseases</td>
</tr>
<tr>
<td>Chemical industry</td>
<td>Phenols, PAHs, PCBs, Ammonia, detergents, papers fibers</td>
<td>Limit the oxygen amount Eutrophication Toxic products (ammonia, phenols) Limit the biodiversity Cancer, carcinogenicity</td>
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<tr>
<td>Food industry</td>
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<td>Eutrophication</td>
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<td>Pharmaceutical industry</td>
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<tr>
<td>Paper industry</td>
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<tr>
<td>Municipal wastewater, pharmaceutical industry</td>
<td>Antibiotics and other pharmaceuticals</td>
<td>Immune system disorders (under investigation)</td>
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<tr>
<td>Municipal wastewater, landfills</td>
<td>Microbial contamination</td>
<td>Immune system disorders, nervous system diseases (under investigation)</td>
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<tr>
<td>Chemical industry, combustion of municipal solid waste</td>
<td>Dioxins</td>
<td>Cancer</td>
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<td>Automobile paints, carbody, military bases</td>
<td>Solvents</td>
<td>Carcinogenicity</td>
</tr>
<tr>
<td>Landfills</td>
<td>Heavy metals, Gases, organic compounds, inorganic compounds</td>
<td>Pollution of aquifers</td>
</tr>
<tr>
<td>Agricultural activities</td>
<td>Agrochemicals: fertilizers, herbicides, pesticides, nitrates</td>
<td>Increase of nitrate ions, Cancer, nervous system diseases</td>
</tr>
<tr>
<td>Livestock</td>
<td>Nitrogen, phosphorus, bacteria, fungi</td>
<td>Carcinogens, Pollution and contamination of surface and groundwater</td>
</tr>
<tr>
<td>Slaughterhouses</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acid rain</td>
<td>Sulfide and nitrogen oxides</td>
<td>Destruction of crops, forests etc.</td>
</tr>
<tr>
<td>Nuclear power plants</td>
<td>Radiation to the water</td>
<td>Genetic alterations, accumulation in the food chain</td>
</tr>
<tr>
<td>Refineries</td>
<td>Hydrocarbons, petroleum, benzene, asphalt</td>
<td>Destruction of fauna and flora, hinder water oxygenation, carcinogenicity</td>
</tr>
<tr>
<td>Leakage of hydrocarbons</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mining activities</td>
<td>Suspended solids, mineral compounds, toxic wastewater</td>
<td>Air pollution and pollution of groundwater</td>
</tr>
<tr>
<td>Power plants Industries</td>
<td>Warm water</td>
<td>Death of fishes, Decrease of oxygen, Increase of metabolism rate of organisms</td>
</tr>
<tr>
<td>Industries</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aquifer over-abstraction, Seawater intrusion</td>
<td>Salts, minerals</td>
<td>Destruction of coastal aquifer, decline in groundwater levels</td>
</tr>
</tbody>
</table>
The main physicochemical parameters of groundwater pollutants are:

- **Solubility:** The maximum amount that can be dissolved in a certain volume of the solvent, under specific conditions. The solubility of a contaminant in the groundwater affects its fate, transport and toxicity in the groundwater body. Solubility depends on pH value, chemical composition of the contaminant, the electrical charge, the electron availability and the temperature, among others.

- **Volatility:** The ability of the molecules to escape from the surface of the fluid and to be transferred to the gas phase.

- **Adsorptivity:** The adsorption ability of a substance by the soil particles.

- **Decomposition rate:** The time needed for the decomposition of a substance into other compounds; this rate may include the half-life time of radioactive isotopes.

- **Partition coefficient:** Expresses the distribution of a pollutant between two means, e.g., solid-liquid, gas-liquid.

- **Toxicity:** Causes adverse conditions to the ecosystems, once exposed to the pollutant. It is expressed by the lethal dose (LD₅₀), which is the dose (mg/kg of body weight) for which 50% of the organisms exposed for a specific time period survive. Toxic pollutants can be heavy metals, organic substances, toxic gases etc.

Groundwater contaminants can also be of organic and inorganic nature. Organic contaminants can further be classified to volatile, semi-volatile and non-volatile, according to their chemical composition. Based on its water solubility, a pollutant can be dissolved or in a non-aqueous phase. Toxic wastewater from industries, mines etc. contain substances that can cause significant damages or even death to humans and animals. Generally, hazardous wastewater includes the following four categories of pollutants:

- **Inorganic wastewater** suspended or diluted contains heavy metals (lead, mercury), arsenic, cadmium and cyanide.

- **Organic water soluble wastewater** (Aqueous Phase Liquids–APLs): Wastewater of the pharmaceutical industry, the agricultural pesticide industry, solvents, dyes.

- **Organic non-water soluble wastewater** (Non-aqueous Phase Liquids–NAPLs): This category includes lubricants, oil paints, oily solvents, petroleum products. Non-mixable compounds with a density smaller than water density (LNAPLs) such as benzene, petroleum etc. float on water, accumulate on the surface of the aquifer and only diffuse horizontally. Hydrocarbons possess the ability of remaining for a long time on the surface of groundwater, resulting in an unpleasant odor. The heavier DNAPLs (chlorinated hydrocarbons) move vertically in
the unsaturated and saturated zone and deposit on the impermeable substrate, thus polluting the aquifer in depth.

- Viscous liquids, sludge and solids: This category includes refinery wastewater and wastewater from the cleaning tank of oil tankers.

A specific category of high interest is the group of the so-called emerging contaminants (Molnaa, 2007; Stefanakis et al., 2014). These contaminants are relatively newly discovered, in principle unregulated and can be found in surface and groundwater. This group includes pharmaceutical substances, personal care products, hormones, endocrine disruptor compounds, steroids, surfactants, flame retardants, industrial additives, nanomaterials etc. Groundwater contamination with these micro-pollutants nowadays represents a major concern compared to other freshwater resources (Lapworth et al., 2012). Most of these contaminants have only recently emerged (i.e., over the last 15–20 years) as contaminants with potential environmental and public health risks (Lapworth et al., 2012). Emerging contaminants are not only newly created chemical compounds; this group includes compounds which are recently introduced into the environment (such as industrial additives), compounds that are present in the environment for many years, but their significance and related risks were realized only over the last years (such as pharmaceuticals) and already known compounds whose potential impact on the environment and humans was only recently realized (such as hormones). Gradual development of analytical techniques and detecting instrumentation allowed for the detection of these compounds in natural waters even at trace concentrations (Fatta et al., 2007; Richardson and Ternes, 2011). The main issue with these contaminant groups is that they are not effectively removed in conventional water/wastewater treatment plants, while their fate in the environment still remains largely unknown (Fent et al., 2006; Wiesner et al., 2009; Lapworth et al., 2012).

The Directive on Environmental Quality Standards 2008/105/EC (also known as the Priority Substances Directive; European Commission, 2008) set the quality standards for 33 priority substances and 8 other pollutants that are persistent, bioaccumulative and toxic. The review of this list in 2012 resulted in the proposal to include for the first time 15 new compounds to this priority list (European Commission, 2012), while for the first time three pharmaceutical compounds (the endocrine disruptors 17 alpha-ethinylestradiol (EE2), 17 beta-estradiol (E2) and diclofenac) were included among the regulated substances in the EU countries. More stringent standards will be adopted for newly-identified compounds in the EU by 2018. The level of risk related with emerging contaminants is fluctuating from growing risk (for recognized substances) to future/unidentified risk (for new chemicals-drugs), which means that monitoring programs should be more frequently implemented in the near future for the evaluation of the related risks and hazards.
Current status of knowledge indicates a widespread contamination of groundwater resources by various emerging contaminants that are detected at potentially environmentally significant concentrations (Lapworth et al., 2012). The most common compounds detected include a range of pharmaceuticals and personal care products and industrial and lifestyle compounds such as caffeine, ibuprofen, carbamazepine, sulfamethoxazole and bisphenol A (Loos et al., 2010). Endocrine disruptors are globally detected in groundwater resources at environmentally significant concentrations ($10^3$–$10^4$ ng/L). Characterization of these contaminants in wastewater and surface water bodies is ongoing and at a greater extent than in groundwater (Pal et al., 2010; Lapworth et al., 2012). Thus, additional research is needed in this field, especially to identify the impacts of long-term exposure to these compounds. The pollutants are introduced to the organism through the digestive tract, respiration system or skin and they accumulated in the fat (e.g., PCBs), the bones (e.g., Pb, F), the kidneys (e.g., Cd) and the blood plasma. Thus, they can significantly affect human health.

**EXAMPLES OF GROUNDWATER POLLUTION**

The Argolis Plain in Peloponnesse, Greece is a characteristic example of the degradation of underground water quality in Europe due to anthropogenic and natural factors. Two more examples are the regions of Aidipso and Methana in Greece where quality degradation of underground water occurs naturally due to rock-water leaching and the presence of geothermal fields. The Argolis Plain hosts the wide hydrologic basin of Inachus river. Inachus River is a 5th class river of a 569 branches with a total of 474 km in length. Argolis Plain comprises of limestone, flysch and schist, Neogene sediments and alluvial deposits. Alluvial deposits are the main underground water reservoir for the local communities. About 69% of the total rainfall precipitation accounts for the evapotranspiration rate, 5% for surface runoff and 30% for infiltrating the underground water reservoirs. The area is characterized by agricultural activities and local development of urban areas. All reservoirs contain fresh water. Chemical analyses of samples from all water reservoirs indicated increased nitrate pollution in alluvial deposits and in the contact of alluvial deposits with the limestone and conglomerate. The increased nitrate pollution is the result of agricultural activities in the area. Hydrogeological study of the water reservoir indicated that the alluvial deposits are replenished by fresh water from the conglomerate and limestone. These result in a decreased content of other pollutants such as chloride (Cl), phosphate (PO$_4^{3-}$) etc.

However, most of the alluvial deposit water-tables have a degraded water quality. Lack of an integrated strategy for a proper and sound irrigation program and for the local urban areas, as well as insufficient management of fertilizer use in the agricultural areas, has led to the gradual degradation
of the freshwater resources in the Argolis Plain. More specific, over-abstraction to even deeper parts of the water-tables resulted in seawater intrusion followed by increased Cl in the groundwater resources, while the over-use of fertilizers enriched the water-tables with elements such as \( \text{PO}_4^{3-} \) and nitrate \( (\text{NO}_3^-) \). The levels of nitrate in the groundwater are so high and do not allow for its use as potable water since it can cause low oxygen levels in blood and the sudden death of infants (blue baby syndrome).

Additional degradation occurs due to the natural phenomenon of the seawater intrusion (seawater is moving towards the mainland) which is the result of natural and geological conditions. As a result of water quality degradation in the Argolis Plain, the communities have searched for alternative fresh water sources such as the springs of Anavalos and Kefalari located southwest of the alluvial basin of the Argolis Plain, hosted in limestone. It is characteristics that archaeological evidence and historical references in the area indicate that the level of the groundwater table level has been significantly declined (down to several hundred meters), and the overall water quality has been degraded so that sometimes it cannot be used even for irrigation.

Natural degradation of underground water quality can also be found in regions that are close to geothermal fields or volcanic areas. Aidipsos and Methana are characteristic examples of this case in Greece. The underground water in these regions is subjected to rock-water leaching and the presence of geothermal fields. Water sources in volcanic/geothermal areas are able to leach elements from rocks during the underground water circulation. Geothermal fields and volcanic areas are characterized by rock formations rich in elements that are considered as risk elements for potable water such as As, Cd, Zn, Cu, Pb etc. These elements are leached from the rock-water interactions and enrich the underground water in relatively high concentrations. Additionally, thermal waters are present in geothermal areas and volcanic fields that are mixed with shallow reservoirs of fresh water resulting in degradation of the water quality. Geothermal fields and volcanic areas that are close to the shore are also subjected to seawater infiltration/mixing that results in further degradation. As a result, in areas subjected to such natural degradation processes of fresh water there is a high need for alternative water sources, e.g., springs in rock formations such as limestone, treatment of existing water sources or seawater desalination to produce fresh water for domestic and industrial uses.

Additionally, several fractures and faults in granitic rocks such as in Maine (U.S.A.) show high radon activity like in the Lucerne pluton (~380 Ma) and the Silurian Gouldsboro pluton (~419 Ma). The high radon activity is related to the presence of iron oxides and a preferential enrichment of uranium (Worthington et al., 2015). A correlation has been identified in many instances where radon anomalies occur within
Quaternary faults such as in Italy (Tansi et al., 2005), in Germany (Kemski et al., 1992), and in France, in the Pyrenees (Baubron et al., 2002).

CONCLUSIONS

Groundwater resources are vital for human life and health, societal development and the preservation of the natural ecosystems. Today, quality degradation of groundwater bodies represents a major worldwide issue. Various and multiple sources have been identified which include a series of both natural and anthropogenic factors. Human activities such as over-abstraction, insufficient wastewater treatment and disposal, industrial activities and use of fertilizers in agriculture represent the main sources of groundwater contaminants. Seawater intrusion is a problem detected in many coastal regions around the world, which results in the salinity and other contaminants increase in coastal groundwater bodies and make them inappropriate for use as drinking water. Radioactivity of uranium series increases radon contamination with significant radon concentration in saturated soils or in groundwater. Groundwater pollution includes a large variety of contaminants, such as organic and inorganic pollutants and synthetic chemical pollutants. The presence of specific groundwater contaminants such as heavy metals, nitrate and emerging contaminants possess significant risks for human health and their regulation is an ongoing issue.

REFERENCES


Groundwater Pollution: Human and Natural Sources and Risks


