

## GROUNDWATER DEGRADATION BY HUMAN ACTIVITIES

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### Summary

Groundwater shows generally settled and good water quality; however, its quality may deteriorate when contaminated with inorganic and organic chemicals by human activity. Under seepage from industrial liquid waste, drainage from livestock facilities, domestic drainage and mine drainage are considered causes of groundwater pollution. In industrial waste, they are metals such as chromium, cadmium, and nickel, which come from metal plating factory drainage, and volatile organic compounds (VOCs) such as trichloroethylene, and tetrachloroethylene used for degreasing and metal cleaning. In the discharge from livestock facilities can be detected microorganisms, organic matter, nitrogen compounds and antibiotics used for livestock. From domestic drainage are found organic matter and detergents, and a micro amount of pharmaceuticals. Pesticides for agricultural use are also often detected in groundwater

### 1. Introduction

Groundwater is widely used for various purposes such as domestic and industrial needs. Its origin is falling rain and snow reaching the surface of the earth and then permeating underground to form a water zone. Groundwater consequently contains a solution of

inorganic components found in the crust of the earth, and undesirable pathogenic microorganisms are generally removed through filtration during the infiltration process. Since ancient times, humans have utilized groundwater as drinking water, as domestic water for cooking and washing, and more recently, for agriculture, fisheries, and industry. In ancient ruins excavated in various parts of the world, large wells have been found in the center of ancient cities.

Since the industrial revolution, as mining and manufacturing developed rapidly, artificially synthesized chemical substances have been allowed to permeate the land. Such chemicals are carried underground where they degrade the condition of the groundwater. As scientific technologies and precision machine industries have developed, the problem of groundwater contamination by artificially synthesized organic compounds has become more widespread around the world.

Of the various substances dissolved from crust components during the process of rainwater infiltration underground, such substances as arsenic, nitrate ions and nitrite ions have a harmful influence on human health; however, those substances are never produced by ordinary human activities.

Major threats to human health occur when ions of cyanide, chromium and lead, which are particularly used in electro-plating plants, are allowed to contaminate groundwater. Recently, it was reported that groundwater had been contaminated by chlorinated organic chemicals (trichloroethylene and tetrachloroethylene) in Silicon Valley, California, USA. Great efforts of various kinds are required to prevent water contamination, particularly groundwater, which is essential for human life as the principal source of clean fresh water.

## **2. Causative materials contaminating groundwater**

Under seepage from industrial liquid waste, drainage from livestock facilities, daily life drainage and mine drainage are considered activities during which material from the surface permeates the groundwater and becomes a cause of pollution.

As mining developed around the world, a huge amount of groundwater was removed and put to use. A rapid increase in the population has also raised the need for water for daily life, and huge amounts of groundwater have been used for this purpose. If groundwater is extracted at a rate greater than the natural recharge rate, aquifers will become depleted and may become unusable. Furthermore, extraction may cause subsidence of the ground surface over the aquifer. In addition, developments in mining and manufacturing industries, and the modernization of agriculture have contaminated groundwater due to the presence of harmful chemical substances. Such substances as metals, cyanides, pesticides and chlorinated organic chemicals are known to be causative substances.

As a result of industrial liquid waste, there are metals such as chromium, cadmium and nickel, and cyanogen compounds which come from metal-plating factory drainage, and volatile organic compounds used for degreasing and metal cleaning. In the discharge from livestock facilities can be detected microorganisms, organic matter and nitrogen

compounds. From domestic drainage are found organic matter and detergents, and in mine drainage are often detected metals and inorganic materials. In addition, nitrate ions are found, which derive from nitrogen fertilizer and pesticides around the farm.

### 3. Metals and inorganic compounds

#### 3.1 Chromium

Chromium is used for surface metal coating in electro-plating plants. It is first processed by chemical precipitation or adsorption methods using ion exchange resin and charcoal, and then it is drained. During the washing process, if water leakage or illegal liquid waste dumping occurs, chromium-contaminated water may infiltrate the ground, and cause groundwater contamination. Furthermore, since the metal-coating process usually requires cyanide, such as in potassium cyanide, this can cause groundwater contamination in the same manner as chromium. Both chromium (VI) and chromium (III) are known as stable chemical forms. Of the two substances, chronic exposure to chromium (VI) has the potential to cause pulmonary cancer in humans, but its exposure route is mainly by inhalation through the respiratory tract. Such symptoms as vomiting, diarrhea and stomach pains are known to be attributable to chromium (VI) poisoning, and nephropathy is sometimes reported. Another example of a situation that can lead to groundwater contamination is inadequate treatment of waste from puddling plants. If this is allowed to infiltrate groundwater, the metals it contains can present a serious threat to human health. The most dangerous are lead, cadmium, mercury and selenium. Chronic exposure to lead inhibits the generation of hemoglobin in blood, which causes anemia. It may also become a cause of nephropathy due to induction of the abnormal metabolism of sodium in the kidneys. Chronic exposure to cadmium also causes nephropathy with such symptoms as proteinuria and glycosuria. Inorganic mercury is easily accumulated in the kidney, causing damage to epidermal cells of the proximal tubules.

#### 3.2 Arsenic

Country/Region	Concentration range ( $\mu\text{g L}^{-1}$ )	Area ( $\text{km}^2$ )	Population exposed
Bangladesh	<0.5-2500	150,000	Ca. $3 \times 10^7$
West Bengal	<10-3200	23,000	$6 \times 10^6$
Taiwan	10-1820	4000	$10^5$
Inner Mongolia	<1-2400	4300	?
Xinjiang	40-750	38,000	500
Hungary	<2-176	110,000	29,000
Argentina	<1-5300	$10^6$	$2 \times 10^6$
Northern Chile	100-1000	125,000	500,000
South-west USA	<1-2600	5000	$3 \times 10^5$
Mexico	8-620	32,000	$4 \times 10^4$

Table 1: Naturally-occurring As problems in world groundwater (UN2001)

Arsenic is used widely such as for semiconductor material, pigments, and pesticides, and it is also widely distributed in natural geology. Recently, it was reported that in Asian regions such as the Bengal district of India, China and Bangladesh, arsenic, as a natural component of the Earth's crust, is dissolved in groundwater, causing serious effects on the health of local people, particularly where there is no other water supply. Long-term uptake of arsenic in water causes dermatocarcinoma.

The results, which the United Nations investigated in 2001, are shown in Table -1. It is being detected in the concentration range of  $\mu\text{g L}^{-1} \sim \text{mg L}^{-1}$  levels from groundwater in many countries.

The main cause is from geology and it causes arsenopyrites ( $\text{FeAsS}$ ), and arsenic seems to dissolve in the groundwater. However, one cause of the arsenic pollution of groundwater is that deeper groundwater is used which contains arsenic from drought. The cause of the drought is suspected as being a result of climatic change by global warming.

### **3.2.1. Chemical form and environment dynamic phase of the arsenic.**

Arsenic is a metalloid element which can be either a metal or nonmetal, and many organic arsenic compounds which show different chemical property to inorganic are known to have multiple redox states, and in a charcoal element to form a stable covalent bond. Although arsenic generally exists stably under oxidative conditions near neutrality in the condition of pentavalent valence, it easily reduces under reductive conditions and with biological action, and it is alkylated, and changes to a chemical compound of three valences which show high reactivity and toxicity. Arsine and these alkyl derivatives are volatile at ordinary temperature and show high toxicity. Arsenic acids, methanearsonic acid salt, cacodylic acid, are used as pesticides such as in wood preservative, herbicide, and insecticide. Sprayed arsenic compound moves through the environment, influenced by the redox state, pH, biological activity and others. It returns to the ground in rainwater as atmospheric arsine, which is oxidized to pentavalene in air, and it may permeate underground.

### **3.3 Cyanide**

Cyanide dissolved in water causes a change in pH of the solution and is also diffused as volatile hydrogen cyanide. When it reaches the groundwater, it is gradually volatilized, and eventually decomposes. When cyanide is taken orally, under acid pH conditions in the stomach, hydrogen cyanide is liberated. Some of this is then taken into the lungs, where it inhibits the effect of cytochrome oxidase in the electron transport system to terminate cellular respiration.

### **3.4 Nitrate and nitrite**

Nitrate nitrogen ( $\text{NO}_3\text{-N}$ ) is detected frequently in the groundwater at high density as well as as a volatile organochlorine compound. In humans, nitrate nitrogen is reduced to nitrite nitrogen, and causes methemoglobinemia (cyanosis, suffocation symptoms).

As a supply source in groundwater, it infiltrates rainfall, agriculture materials (organic and inorganic fertilizers, plant residue), livestock drainage, domestic drainage and industrial liquid waste.

- Rainfall: Although nitrogen oxides exist in the atmosphere, and therefore, nitrate nitrogen is contained in rainfall, its load is limited, because the concentration decreases with the increase in the amount of rainfall.
- Agriculture: The nitrogen fertilizers used for farmland permeate underground, and become a problem.

The nitrogen fertilizers used in paddy fields have limited use, and the effect on the groundwater is limited from absorption to the crop.  $1\text{t ha}^{-1}$  per year may be used in a plowed field crop for eclipse leaf vegetables, and a considerable part may permeate underground. For example, the groundwater of farmland, which uses  $500\text{kg h}^{-1}$  of nitrogen fertilizer in one year, has 13 times higher nitric acid than groundwater without fertilizer.

- Waste water treatment: When domestic drainage and industrial liquid waste infiltrate soil, high nitrate nitrogen is often found in the groundwater. In particular, nitrate nitrogen concentration rises with the soil infiltration of septic waste discharge.

In general, the discharge contains organic nitrogen (Org-N), ammonia nitrogen ( $\text{NH}_4\text{-N}$ ), nitrite nitrogen ( $\text{NO}_2\text{-N}$ ), and nitrate nitrogen, and these are oxidized in the soil to nitrate nitrogen. The result of dealing with the discharge of septic waste in a soil infiltration disposing facility is shown in Table 2. Nitrate nitrogen is increased remarkably in the groundwater, while  $\text{NH}_4\text{-N}$  and org-N are decreased by soil infiltration.

	Effluent ( $\text{mg L}^{-1}$ )	Seepage water ( $\text{mg L}^{-1}$ )	Removal rate (%)
BOD	53.1	0.6	99
$\text{NH}_4\text{-N}$	125	8.6	93
$\text{NO}_2\text{-N}$	0.2	0.89	-
$\text{NO}_3\text{-N}$	0.22	87	-
Org-N	6.84	0.83	94
Total nitrogen	132	95.8	27
Total phosphorous	9.75	0.03	100

Table 2: Water qualities of effluent and soil infiltration water

Partly to minimize the exposure to metals which cause damage to human health, the WHO maintains guidelines for the allowable concentrations of contaminants in drinking water. These guidelines include both organic and inorganic compounds, some of which are naturally present in the Earth's crust. These guidelines are used when national drinking water standards are established.

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### **Biographical Sketch**

**Yoshiteru Tsuchiya** is a Lecturer in the Faculty of Engineering of Kogakuin University, where he has been in his present post since 2000. He obtained a Bachelor Degree in Meiji Pharmaceutical College in 1964. He worked for Department of Environmental Health in Tokyo Metropolitan Research Laboratory of Public Health until 2000. In the meantime, he obtained a Ph.D in Pharmaceutical Sciences from Tokyo University. From 2002 to 2003, he worked for the Yokohama National University Cooperative Research and Development Center as Visiting Professor. He has written and edited books on risk assessment and management of waters. He has been the author or co-author of approximately 70 research articles. He is member of Japan Society on Water Environment, Pharmaceutical Society of Japan, Japan Society for Environmental Chemistry, Japan Society of Endocrine Disrupters Research, and International Water Association.(IWA)