

Mini Review on Heavy Metals in Groundwater; Pollution and Removal

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Abstract

Studies on heavy metal pollution in groundwater resources have been carried out due to human need for drinking water through wells. There are several heavy metals in groundwater as Arsenic, lead, Cadmium, chrome, mercury etc. Investigating the heavy metal pollution of groundwater resources as a source of actual results based on the results of chemical analyzes in different time periods (wet periods and droughts) and its implementation in the GIS system and analysis in the qualitative study phase, is a common method in this research.

Theoretical motive for such studies is the GIS map as a model for changing the physicochemical parameters and its practical motive for policy making for water harvesting, drinking water treatment and contamination, and attempts to prevent it from growing in different regions. Part of this research is to study the researches of Iran and the world with the approach of studying groundwater with different methods for information interpolation, use of various indicators of water quality. The results of this research will be in the form of summarizing the methods and views of the active researchers in this field, the ability to create the idea (idea) and the method of work for future research in the same field.

Key words: Heavy Metals, Groundwater, Pollution

Introduction

Water resources cover the essential part of the earth surface, even though clean water reserve may be very little in terms of amount within the globe. Groundwater is the major source of fresh water for drinking, irrigation, industrial and other economic sectors (Uddin et al., 2017:). Fresh water availability decreases day by day in the world due to contamination, specifically in developing countries. A number of researchers and scientists reported that the groundwater quality status in Bangladesh is in critical stage. Day by day groundwater and surface water reserves are being depleted due to numerous natural and anthropogenic causes. Water pollution is the major concerning issue for many developing countries. Trace metal contamination of groundwater is one of the major and prior challenge on lives owing to their toxicity, Persistence, and extensive bioaccumulation. Trace metal contamination of groundwater represents an important environmental problem and needs more attention. More than one trace element has high concentration level that exceed the allowable limits of any health guiding principles. Typically, that may create various health and safety complications for human health. Not only anthropogenic influence but also other natural factors are responsible for converting physico-chemical characteristics of water. (Uddin, Md Galal, et al. 2018)

Usual Water sources are as below:

Groundwater, surface water (rivers and lakes) and water which is evaporated from dams are named blue water. Rain is the main source of blue and green water. Green water is saved in soil as humidity. Grey water is a kind of water which is polluted during goods production. These kinds of waters are coming to natural water systems. In this part we just explain about surface and groundwater.

a) surface water

It is the main water source for human and water of the biggest cities are provided from surface water. Surface water is supplied from rain water and ground water too. When rain comes to ground, part of it penetrates into soil, and a part is evaporated. If just rain was the source of surface water, after a while rivers become dry. So melting of snow and spring penetrations can make rivers survive during all year. Surface water can save different mineral and organic material of ground as solution or suspension. Also surface waters are exposed to different pollutions as domestic, industrial and irrigation wastewater. (Shariatpanahi, 2012)

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b) Groundwater

Penetration of surface water into soil and between rocks can make groundwater. Half of ground water sources are located below 800 meter from ground surface. (Shariatpanahi, 2012)

The variability of recharge is a key to understanding the susceptibility of aquifers to contamination from surface-derived sources. Recharge may be categorized as diffuse or focused. Diffuse recharge refers to that which occurs over large areas as water from precipitation infiltrates and percolates through the unsaturated zone to the water table. Focused recharge refers to water moving downward to an aquifer from a surface-water body, such as a lake, stream, or canal. Arid regions commonly are characterized by deep water tables, losing streams, and focused recharge. (Nolan et al. 2007)

c) effective factor on water quality

Following tables indicate effective factors on groundwater and surface water.

Table 1. summary of effective factors on surface water quality (Shariatpanahi, 2012)

Effective factor	Main changes in surface water quality
Precipitation	Soluble gases in air Soluble gases from industries Particle matters from factory stacks Material from ground as leaves and grasses
Domestic usage	Organic material as oil and grease Excrement of human bodies Bacteria, viruses, paper, tissues, detergents...
Industrial usage	Degradable organic matter by living beings which need oxygen. Solid minerals. Chemical residues as acids and Alkaline. Metal ions
Agriculture usage	Increase in ions and salts concentration. Fertilizer residues. Pesticides and herbicides residues.

Table 2- summary of effective factors on groundwater quality (Shariatpanahi, 2012)

Effective factor	Main changes in surface water quality
Precipitation	Gases as H ₂ , SH ₂ , N ₂ , CO ₂ , O ₂ Minera and soluble materials as bicarbonates, calcium sulfate. Soluble salts as iron, manganese, fluoride
Domestic usage	Detergents Nitrates, sulfates, salts Organic soluble materials
Industrial usage	Soluble salts from surface water penetration
Agriculture usage	Salts from agriculture activities

Table 3- effective general condition on water quality (Shariatpanahi, 2012)

Effective factor	Result
Weather conditions	Snowmelt flooding the muddy light and contain many bacteria. Flooding and drought, rich in minerals and is hard to simulate groundwater. Snowmelt flooding caused by heavy rains and floods that fewer bacteria may be muddy effect next lines.
Geographical conditions	Flood areas with a flood lands slope and is covered with various plants.
Ground condition	Clayey soils. Color is organic soils or swamps. Mud, fertilizers, herbicides and insecticides farm land into the water. Mud and microbes may be transferred between rocks into groundwater. Minerals depend on the formation of Earth.

season of the year	Autumn floods shall carry dead plants that create color, taste, organic and biological extracts is. Water soluble salts in the dry season increases. Only seasonal crop water plant and grow plants may be retrieved.
Management	Agricultural soils and other soils are bare deposits. Woodland and swamps organic materials in their production.
Periodic changes	The amount of oxygen produced by plankton Lg-hay day and night is different. Wastewater flows vsries in 24 hours.

Groundwater is the most vital natural resource, which forms the core of the ecological system. It has become the major source of water supply for drinking, domestic, household, agricultural, industrial, recreational, and environmental activities etc. This has led to an increase in the demand of water supply which is met mostly from the exploitation of groundwater resources. Nowadays groundwater is a very important concern for mankind since it is directly linked with human safety. Determination of physical, chemical and bacteriological quality of groundwater is important for assessing various usages. Variation in groundwater quality in an area is a function of physical and chemical parameters that are greatly influenced by natural processes such as geological formations and anthropogenic activities. (Selvakumar et al., 2017)

Assessment of the vulnerability of groundwater has become a useful tool for decision support in monitoring the pollution. The use of GIS in models makes it possible to assess the vulnerability of groundwater by superimposing different spatially referenced hydrogeological parameters that affect groundwater contamination. (Aboubacar Modibo SIDIBE et al. 2018)

Environmental pollution by heavy metals has attracted much attention worldwide because they rapidly accumulate in the natural environment. Heavy metals in aquatic environments enter the ocean by direct emissions or by surface runoff and can come from natural sources, such as geologic weathering and atmospheric inputs, or from human activities, such as industrial and agricultural sewage discharge. Furthermore, some heavy metals such as mercury, cadmium, chromium, lead (Campbell and Gailer), and metalloid arsenic can transform into persistent metallic compounds with high toxicity. They are a major source of water pollution and have long been considered critical contaminants in aquatic ecosystems because of their toxicity, persistence, nondegradability and bioaccumulation characteristics. Bioaccumulation of these compounds in organisms' results in magnified toxicity along the food chain, thereby threatening both aquatic ecosystems and human health. Heavy metals can accumulate in the adipose tissue and livers of humans and animals, which adversely effects the nervous, circulatory, and immune systems. Moreover, some heavy metals, such as Cadmium and Chromium can be carcinogenic when stored in the body for long periods of time. Due to their damaging effects on the ecological environment and in human health, it is necessary to include heavy metal contamination in aquatic. (Zhang, Yinan, et al. 2018)

According to (Kobielska et al, 2018) one of the sources of heavy metals in water is Geological sources: Heavy metals (that is metals with density over 5 g cm⁻³ such as arsenic, cadmium, chromium, copper, lead, mercury, nickel and zinc) polluting our water is a rapidly growing global concern. These elements can be found within the environment – be it in water reservoirs, the atmosphere or soil – in excess, due to various anthropogenic actions. It is also important to note the natural sources of heavy metal pollution. These include all types of rocks (igneous, sedimentary and metamorphic), which, through their interactions with the surrounding environment (i.e., weathering, erosion, soil formation and the rock cycle in general), transport and redistribute heavy metals. Heavy metals most commonly found in rock-forming minerals include those which most easily leach due to mineral weathering such as nickel, cobalt, manganese, zinc, copper, and vanadium, in addition to metals that have intermediate stability such as scandium, yttrium and others.

▪ Sources of groundwater pollution

Water shortage is becoming in many arid and semi-arid countries the main constraint for economic welfare and sustainable regional development. High spatial and temporal imbalances between water demand and availability characterize these water deficient regions, where water scarcity is further increased by its quality deterioration, caused by point sources and nonpoint pollution sources. (Zereg et al, 2018)

The migration of pollution via subsurface water is a very complicated physical problem that has attracted focus of some researchers within the field of hydrology. The migration of these pollutants is taking place within geological formation having very complex properties. It is worth noting that the flow of groundwater is mostly influence by the structure of the geological formation. (Alkahtani et al, 2017)

According to (Galitskaya et al, 2017) The modeling of ground- and surface water contamination showed that the area of sewage influence on groundwater is limited and that there is no hazard of river water contamination in the long-term perspective 1.

The modeling results permitted assessing the hazard of contaminated soils as the secondary long-acting source of groundwater contamination.

In the key site “Marino” among heavy metals the total highest concentrations were registered for Mn, Pb, Cu and Zn (up to 7727, 4480, 2982, and 1157 mg/kg, respectively). In general, the geochemical associations that show the technogenic contamination may be represented as follows (the index on the right of the chemical element symbol designates the maximal value the ratio of actual component content to its baseline concentration in Marino district):

in the fill ground - $Pb_{112} Cu_{60} Cd_{11} Ni_{6,4} Hg_{5,7} Zn_{4,8} Mn_{1,8}$ and in the alluvial deposits -

$Hg_{77} Pb_{29} Cu_{9,3} Cd_{3,5} Zn_3 Mo_{2,6} Sb_{2,6} Ni_{2,3} Mn_{2,1}$. High contrast anomalies were observed for Hg, Pb, Cu, Ni, Cd, Zn, which is associated with the specific use of the study area. The highest concentrations of elements were found in the fill ground and the bulk of the territory shows the trend to decreasing the element concentration with the depth. Based on Eigen values and varimax rotation four factors explained 69.6 % of total variance in fill dump soils.

Factor 1 as the main factor (33.2 %) has loadings on Pb, Cd, Cu, Co. This association is considered to represent ground contamination by the industrial sewage sludge. Three factors explained 67.4 % of total variance in alluvial deposits. Factor 1 as the main factor (43.5 %) has loadings on As, Sb, Co. This element association is believed to be related to the wastewater of textile and leather industry, discharged to the disposal fields in the early 20th century.

Groundwater in above-Jurassic aquifer present pH in the range of 7.12-7.35; and a dry residue value between 308 and 862.0 mg/l. The Russian standards for the main components are exceeded mainly for oil products, NH_4^+ , Fe, Mn and Cd.

Polluting elements Pb, Cu, Zn and Ni (the concentration of which in grounds exceeds MPC significantly) appear to be present in the groundwater in amounts lower than MPC, which is explained by the high adsorption capacity of ground.

(Naghypour et al., 2018) describe the concentrations of arsenic, cadmium, copper, nickel, lead and zinc in the surface soils and groundwater's of Kiwi gardens and its relation to chemical fertilizers in Amlash city, Guilan Province, in Iran.

(Schmoll et al., 2006) talked about sources of pollution as below:

- **Storage Tanks:** May contain gasoline, oil, chemicals, or other types of liquids and they can either be above or below ground. There are estimated to be over 10 million storage tanks buried in the United States and over time the tanks can corrode, crack, and develop leaks. If the contaminants leak out and get into the groundwater, serious contamination can occur.
- **Septic Systems:** On-site wastewater disposal systems used by homes, offices or other purpose arrangements that are not connected to a city sewer system. Septic systems are designed to slowly drain away human waste underground at a slow, harmless rate. An improperly designed, located, constructed, or maintained septic system can leak bacteria, viruses, household chemicals, and other contaminants into the groundwater causing serious problems.
- **Uncontrolled Hazardous Waste:** In many developed countries around the world, more precisely in the United State of America today, there are thought to be over 20,000 known abandoned and uncontrolled hazardous waste sites and the numbers grow every year. Hazardous waste sites can lead to groundwater contamination if there are barrels or other containers laying around that are full of hazardous materials. If there is a leak, these contaminants can eventually make their way down through the soil and into the groundwater.
- **Landfills:** Landfills are the places where our garbage is taken to be buried. Landfills are supposed to have a protective bottom layer to prevent contaminants from getting into the water. However, if there is no such layer or it is cracked, contaminants from the landfill (car battery acid, paint, household cleaners, etc.) can make their way down into the groundwater.
- **Chemicals and Road Salts:** The widespread use of chemicals and road salts is another source of potential groundwater contamination. Chemicals include products used on lawns and farm fields to kill weeds and insects and to fertilize plants, and other products used in homes and businesses. When it rains, these chemicals can seep into the ground and eventually into the water. Road salts are used in the wintertime to melt ice on roads to keep cars from sliding around. When the ice melts, the salt gets washed off the roads and eventually ends up in the water.

(RoyChowdhury et al. 2017) talked about some heavy metals in their research.

Arsenic (As) is a metalloid found in almost all types of environmental matrices. Arsenic ranks No. 1 in the Agency for Toxic Substances and Disease Registry's (ATSDR) Priority

List of Hazardous Substances, and is a known human carcinogen. Soluble inorganic arsenic is acutely toxic. Arsenic can be found in four valence states: elemental arsenic (As 0), arsenate (As V), arsenite (As III), and arsine gas (AsH₃-III). Arsenate is predominant in aerobic environments, whereas arsenite dominates under reducing conditions. Elemental arsenic and arsine can be found under extreme reducing conditions.

Inorganic arsenic intake over a long period can lead to arsenicosis. Arsenic poisoning can impact the nervous system, gastrointestinal system, and renal system, and can create skin lesions, diabetes, cardiovascular diseases, and cancer. Organic arsenic compounds are commonly found in seafood, but they are less harmful, as the human body can rapidly eliminate them. Prolonged human exposure to As-contaminated groundwater has occurred in countries such as Bangladesh, India, Thailand, and Vietnam. A 2010 WHO report estimated

9100 deaths and 125,000 disability-adjusted life years in Bangladesh due to the consumption of As-contaminated drinking water in 2001. In countries like the United States, inorganic arsenic was used as a wood preservative in the form of copper chromate arsenic (CCA), which became a predominant source of As contamination of soil. As of 2003, CCA is banned from any form of residential use in the United States. Inorganic arsenical pesticides were used in apple orchards, vegetable fields, cotton fields, and in cattle dipping vat sites to control ticks in livestock. Organic arsenic compounds were also used as pesticides, mainly for cotton crops. These historical uses of arsenic compounds resulted in widespread contamination of soil and water matrices, and posed a threat to human health. In 2001, the United States Environmental Protection Agency (USEPA) reduced the standard for As in drinking water in the United States from 50 to 10 mg/L.

Lead (Pb) is the second most hazardous metal according to the ATSDR's Priority List of Hazardous Substances, and is a "probable human carcinogen." Both natural and anthropogenic sources play major roles in Pb exposure in the environment. Some of the major sources of Pb contamination in the environment include mining and smelting, welding of metals with Pb paint, batteries, leaded gasoline, paper and pulp, and explosives. Lead-based paints are one of the major sources of Pb contamination in residential units. Although the USEPA banned the use of Pb-based paints in the United States in 1978, still more than 21 million homes currently exist throughout the country with Pb-based paints. Due to the natural and anthropogenic activities like weathering, flaking, scrapping, chipping, and waste disposal, Pb from the exterior paints leaches out and tracks its way to the interior of the house as Pb-rich dust. Children younger than 6 years are more susceptible to chronic exposure of Pb due to their hand-to-mouth activities. Over 50% of ingested Pb is absorbed via the gastrointestinal tract and penetrates the immature blood-brain barrier of children, causing severe damage in their developing neurological systems.

An incident of extensive Pb poisoning in residents of Flint, MI, indicates that Pb in water distribution pipes could also be a major health hazard. In the summer of 2014, the city of Flint began using water from the Flint River as a cost-saving measure, switching from Lake Huron, which had been their water source for the past 50 years. The Huron Lake water had low chloride and low chloride-to-sulfate mass ratio, and orthophosphate was added as corrosion inhibitor. However, the Flint River water had high chloride and high chlorideto- sulfate mass ratio, and no orthophosphate was added. The water distribution system includes a large proportion of lead pipes, which corroded due to the change in water chemistry, leaching out Pb. Very high Pb levels were detected in the water, and the percentage of children with elevated blood lead levels increased two- to threefold. Since water distribution systems in many cities have not been updated, this incident has raised widespread concern about Pb poisoning from public water systems in the United States

Mercury (Hg) ranked No. 3 in ATSDR's Priority List of Hazardous Substances. Mercury causes severe risk to human health, particularly to the children in their early developing stages.

Mercury can be found in the environment in different forms, such as elemental (or metallic), inorganic (such as HgCl₂), and organic (such as methyl- and ethyl-mercury). Mercury toxicity impacts the nervous system, digestive system, immune system, renal system, and ocular system, but the most prevalent impact is caused during early organ development periods in children.

A major source of environmental release of Hg is caused by coal-fired power plants. Other sources include waste incineration, oil pipelines, and manometers from pressure measuring stations, residential heating systems, and mining. After its release into the environment, elemental mercury is naturally transformed into methyl mercury, which bioaccumulates in fish and shellfish. Inhalation of elemental mercury and consumption of mercury-contaminated fish and shellfish are the major sources of human exposure to mercury pollution.

Major sources of Cd exposure are Ni/Cd batteries, Zn and Pb refineries, pigments and stabilizers for polyvinyl chloride, alloys, electronic products, fertilizers, pesticides, and disposal of industrial wastes. Cadmium coatings are used in marine vessels, and other vehicles, for corrosion prevention. Cadmium toxicity impacts the kidneys leading to kidney dysfunction. It also impacts skeletal and respiratory systems and affects several enzymes.

Cadmium is very persistent in the environment and bioaccumulates in mollusks, crustaceans, and vegetables over time. Once it enters the human body it is very difficult to remove.

Chromium (Cr) is known to be a human carcinogen. It is a naturally occurring element found in rocks, soils, and volcanic dust. Chromium is also found in plant and animal bodies as a trace metal, which means that small quantities of chromium are necessary for growth of living organisms but that excessive amounts can be extremely toxic to them. Anthropogenic activities that are responsible for elevated chromium levels in the environment are electroporating processes, disposal of industrial wastes, wood preservatives, textile dyeing, and leather tanning.

Chromium can be found in three different forms, namely, trivalent (Cr III), hexavalent (Cr VI), and metallic (Cr 0). Metallic Cr is used for steel production. Chromium toxicity impacts the immune system, renal system, and respiratory system and can cause cancer.

According to (Basahi et al. 2018) Enhancement (Al, Cr, Cu, Mn, Mo, Pb and V) and depletion (B, Ba, Fe, Sr) of trace metals are noticed in the ground water after FF (flash flood), which is due to dilution, dissolution/desorption, flushing of weathered layer, saline sources and surface input. Before and after FF, 57-63%(Pb), 55-56%(V), 43- 16%(B), 27-0%(Ba), 15-5%(Sr), 6-3%(Fe), 0-16%(Al), 0-9%(Cr) and 1-2% (Mn) of groundwater samples, respectively, exceeded the drinking water standards. Coastal wells have elevated B, Sr and Mn concentration due to saline water intrusion. Integrated pollution evaluation indices

(Heavy metal pollution index (HPI), Contamination index (Cd) and Heavy metal evaluation index (HEI)) reveal that number of samples in the unsuitable classes are increased after FF event (HPI: 13% to 55%; Cd: 11% to 38%; HEI: 5% to 19%) and groundwater quality is degraded due to the trace metals enhancement after FF especially in the downstream wells. Wells in the upstream is flushed by FF recharge and groundwater flow accumulated the metals in the downstream and coastal region. This study demonstrates that metal accumulation and mobility are regulated by the groundwater flow in the study region. Pearson correlation analysis and Principle component analysis also justify that water chemistry is influenced by the saline sources, flushing of weathered layer, natural processes and anthropogenic inputs. Continuous groundwater monitoring is an important task to protect and manage valuable groundwater resources in the arid region.

- *Groundwater pollution with heavy metals*

According to (Schmoll et al, 2006) More than 50% of the world's population relies on groundwater for drinking water as well as irrigation purposes. However, groundwater is vulnerable to pollutants. Contamination of groundwater may occur when anthropogenic products such as gasoline, oil, road salts and chemicals enter a groundwater system, causing the groundwater to be unsuitable and harmful for human use. Material existing above groundwater can enter underlying soil and eventually reach the aquifer. This can be seen in cases where pesticides and fertilizers, as well as road salt, toxic materials from mine sites, and used motor oil migrate or seep through the subsurface and eventually to the aquifer over a period of time. To add, contamination of groundwater can also be a result of untreated waste from septic tanks, toxic chemicals coming from underground storage units, and leaky landfills. Consuming these contaminated waters may lead to serious health issues. To expand, contamination generated from septic tanks is associated with diseases such as hepatitis and dysentery; and toxins leached from wells into aquifer are associated with poisoning. Additionally, contaminated groundwater becomes a danger to wildlife species, and polluted water may lead to long-term health issues such as cancer.

Following table shows minimal, maximal and average concentration of chemical elements (mg/kg) at the key sites. (Galitskaya et al. 2017)

Table 4: minimal, maximal and average concentration of chemical elements

element	Min			Max			Mean		
	1	2	3	1	2	3	1	2	3
Pb	43.2	7.8	42.9	4480	1169.2	106	326	134.3	65.3
Cd	0.2	0.1	0.3	10.9	4.3	0.7	1.5	1	0.5
Cu	23.4	14.7	8.8	2981.7	463.2	42.9	252.4	102.2	220
Zn	56.9	17.8	58.1	1157.2	626.7	161	281.7	117.3	81.6
Ni	14.4	8	18.9	746.2	227.1	54.6	96	60.3	30.8
Co	0.1	0.1	5.7	10.7	3	22.9	1.8	1.4	10.2
Mo	0.01	0.01	0.6	6.6	7.9	2.2	1.4	0.7	1.4
Cr	2.7	2.4	10.8	207.8	94.3	80.4	60.2	31.6	33.2
As	0.1	0.1	5.1	3.3	1.6	14.7	0.6	0.2	8.25

According to Naghipour et al. 2018 Heavy metal concentration in well water samples before and after fertilization in Kiwi Gardens, Amlash City in 2017 ($\mu\text{g/l}$) are shown in following table.

Table 5- heavy metal concentration in well water samples before and after fertilization in Kiwi gardens, Amlash city in 2017 ($\mu\text{g/L}$)

Number of samples	As		Cd		Cu		Ni		Pb		Zn	
	before	after	before	after	before	after	before	after	before	after	before	after
1	ND	ND	0.172	0.193	0.459	0.653	2.510	8.670	0.362	0.759	7.170	7.480
2	ND	ND	0.129	0.159	0.699	1.320	2.200	9.400	ND	0.257	5.201	6.050
3	ND	ND	0.160	0.169	ND	1.810	3.630	4.310	0.192	0.408	2.480	6.190
4	ND	ND	0.180	0.194	ND	1.390	2.520	4.970	ND	0.430	1.760	5.320
5	ND	ND	0.153	0.361	ND	1.950	2.410	4.570	0.282	0.379	3.970	9.520
6	ND	ND	0.135	0.223	ND	0.048	3.790	5.830	0.227	0.313	2.150	3.070
7	ND	ND	0.133	0.183	ND	0.486	2.880	4.070	0.282	0.422	3.160	3.200
8	ND	ND	0.138	0.144	ND	0.173	5.180	5.300	0.310	0.361	2.080	2.800
9	ND	ND	0.113	0.235	ND	0.043	7.510	8.610	0.220	0.226	1.310	2.150
10	ND	ND	0.163	0.169	ND	0.109	5.230	6.220	0.180	0.320	0.999	2.430
11	ND	ND	0.194	0.243	ND	0.474	3.550	4.610	0.249	1.02	0.880	2.530
12	ND	ND	0.153	0.324	ND	ND	5.990	7.010	ND	0.357	1.470	3.870
13	ND	ND	0.111	0.226	ND	ND	3.790	5.500	0.226	0.280	1.890	4.560
14	ND	ND	0.960	0.171	ND	1.290	2.620	4.090	0.156	0.225	1.05	1.78
15	ND	ND	0.102	0.229	ND	0.534	1.080	4.100	0.241	0.393	1.270	2.850
16	ND	ND	0.119	0.206	ND	ND	1.720	3.030	0.240	0.270	1.930	2.220
17	ND	ND	0.076	0.275	ND	ND	2.850	4.170	0.112	0.755	1.310	2.570
18	ND	ND	0.164	0.165	ND	ND	4.430	5.620	0.281	0.287	4.260	6.410
19	ND	ND	0.143	0.156	ND	0.104	2.970	5.180	0.244	0.259	1.930	7.74
20	ND	ND	0.202	0.296	ND	0.374	1.280	3.440	0.251	0.982	3.540	10.300
average	ND	ND	0.185	0.216	0.579	0.717	3.407	5.435	0.238	0.435	2.490	4.652
Min	ND	ND	0.076	0.144	0.459	0.043	1.080	3.030	0.112	0.225	0.880	1.780
Max	ND	ND	0.960	0.361	0.699	1.950	7.510	9.400	0.362	1.020	7.170	10.300
S.D	ND	ND	0.185	0.059	0.169	0.658	1.615	1.767	0.058	0.242	1.624	2.586
Iranian Irrigation Standards	1		10		200		200		5000		2000	

Table 6- heavy metal concentrations in soil samples before and after fertilization in Kiwi Gardens, Amlash City in 2017 (mg/kg)

Number of samples	As		Cd		Cu		Ni		Pb		Zn	
	Before	after	Before	after	Before	after	Before	after	Before	after	Before	after
1	ND	0.680	0.020	0.120	28.580	35.970	8.910	15.710	15.830	18.110	39.890	83.870
2	0.007	ND	ND	ND	17.680	19.730	8.860	10.22	14.960	17.840	32.380	52.540
3	ND	ND	ND	0.050	14.900	37.030	9.890	13.580	12.390	14.100	38.0100	40.600
4	ND	ND	ND	ND	24.660	35.740	6.390	13.880	14.140	15.440	29.300	41.900
5	0.300	ND	ND	0.004	19.050	23.490	9.330	20.850	13.710	15.130	35.920	36.550
6	ND	ND	ND	0.002	23.250	23.400	11.900	11.950	13.110	14.970	32.660	43.600
7	0.090	ND	ND	0.310	8.070	42.25	16.450	18.020	14.43	24.520	42.270	60.050
8	0.130	ND	ND	ND	24.580	26.380	12.250	13.090	14.870	15.990	37.530	54.450
9	ND	ND	ND	0.04	20.850	24.410	10.09	13.400	13.720	18.090	47.400	57.840
10	ND	ND	ND	0.001	16.440	24.200	10.600	17.100	14.770	18.940	49.600	69.120

11	ND	ND	ND	ND	17.420	25.710	10.03	14.770	12.080	15.720	24.220	75.460
12	0.140	ND	ND	ND	20.930	23.110	10.290	21.280	13.610	15.900	38.150	47.710
13	ND	ND	ND	ND	21.890	24.850	14.200	16.360	15.610	17.100	37.820	42.630
14	0.780	ND	ND	ND	3.420	14.670	8.270	9.100	15.240	16.800	28.290	30.570
15	0.600	ND	0.130	0.19	14.180	16.410	9.850	12.220	14.320	15.450	31.300	35.630
16	0.500	ND	ND	ND	18.090	20.050	8.900	11.910	11.570	12.010	83.530	87.850
17	ND	ND	ND	ND	22.490	22.990	11.870	16.780	15.800	16.070	43.800	45.020
18	0.72	ND	ND	ND	20.180	21.160	9.500	13.240	13.520	14.350	46.040	60.490
19	1.260	0.090	0.050	0.090	14.03	21.900	7.110	14.430	9.200	14.290	45.510	46.500
20	1.16	0.050	ND	0.050	17.030	17.510	8.330	10.180	13.38	13.700	31.290	31.350
Average	0.517	0.273	0.066	0.085	18.386	25.048	10.151	14.555	13.091	16.266	39.745	52.186
Min	0.007	0.050	0.020	0.001	3.420	14.670	6.390	9.100	11.570	12.010	24.220	30.570
Max	1.260	0.680	0.130	0.310	28.580	42.250	16.450	24.280	15.830	24.520	83.530	87.850
S.D	0.431	0.352	0.056	0.098	5.790	7.280	2.328	3.668	3.475	2.588	12.409	16.545
The Dutch MPA for soils	1-10		<1		1-10		1-10		>10		>10	

Table 7- heavy metals concentrations in five highly used fertilizers of Kiwi Gardens, Amlash City in 2017 (mg/kg)

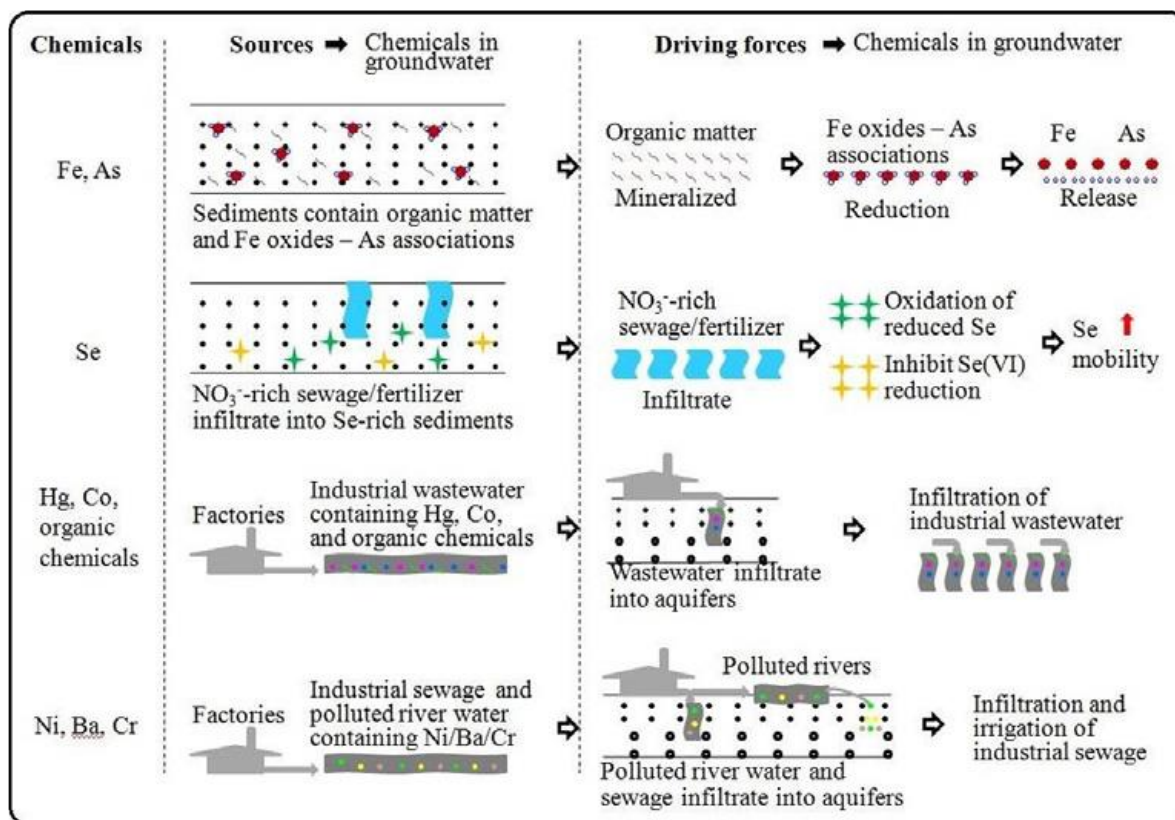
parameters	As	Cd	Cu	Ni	Pb	Zn
Urine	0.668	0.027	0.642	12.100	1.220	8.770
Triple superphosphate	9.060	0.013	5.260	9.130	1.650	7.030
Potassium sulfate	0.160	0.078	0.601	13.940	0.420	1570.950
Zinc sulfate	0.118	3.530	0.524	66.050	2.554	28592.300
Complete	1.137	0.047	4.086	13.203	0.420	610.700
Average	2.228	0.739	2.222	22.884	1.252	1017.950
SD	3.841	1.560	2.275	24.199	0.899	1227.319
Min	0.668	0.013	0.524	9.130	0.420	7.030
Max	9.060	3.530	5.260	66.050	2.554	28592.300
Canadian MAC	75	20	-	180	500	1850

According to Huang et al. 2018 Undrinkable groundwater related to heavy metal (loid)s was mainly due to Fe and As.

Groundwater Fe/As was mainly driven by reduction reaction in Fe/As rich sediments.

Groundwater Se was mainly driven by the infiltration of NO₃ – into sediments.

• Groundwater Ni/Ba/Cr/Hg/Co and organic chemicals mainly from industrialization



The method in Hepburn et al. 2018 identified two major sources of heavy metals in groundwater: 1. Point sources from local or up-gradient groundwater contaminated by industrial activities and/or legacy landfills; and 2. Contaminated fill, where leaching of Cu, Mn, Pb and Zn was observed. Across the precinct, metals were most commonly sourced from a combination of these sources; however, eight locations indicated at least one metal sourced solely from fill leaching, and 23 locations indicated at least one metal sourced solely from impacted groundwater. Concentrations of heavy metals in groundwater ranged from 0.0001 to 0.003 mg/L (Cd), 0.001e0.1mg/L (Cr), 0.001e0.2 mg/L (Cu), 0.001e0.5 mg/L (Ni), 0.001e0.01 mg/L (Pb), and 0.005 e1.2mg/L (Zn). Our method can determine the likely contribution of different metal sources to groundwater, helping inform more detailed contamination assessments and precinct-wide management and remediation strategies.

According to Kobielska et al. 2018 anthropogenic sources for common heavy metals are shown in following table.

Table 8- anthropogenic sources for common heavy metals pollutants along with their provisional guideline limits according to WHO and their toxicity

Heavy metals	Anthropogenic sources	Provisional maximum tolerable daily intake (PMTDI) (g ⁻¹)	toxicity
As	Animal feed additive, algacides, herbicides, insecticides, fungicides, pesticides, rodenticides, sheep dip, tanning and textile, pigments, veterinary medicine, ceramics, special glasses, metallurgy, electronic components, non-ferrous smelters, electrical generation (coal and geothermal), light filters, fireworks	0.01	Phytotoxic, arsenicosis, keratosis, possible vascular complications, carcinogenic
Cd	Neutron absorbers, nickel cadmium batteries, anti-corrosive metal coating, alloys, plastic stabilizers, coal combustion, pigments	0.003	Phytotoxic, bio-accumulate, itai-itai disease, carcinogenic
Cr	Data storage, plating, ferro-alloy manufacturing, textiles and leather tanning, wood treatment, passivation of corrosion of cooling circuits, pigments	0.05	Cr3+ not detrimental to mammals, Cr6+ very toxic, carcinogenic

Cu	Water pipes, chemicals and pharmaceutical equipment, kitchenware, roofing alloys, pigments	2	Relatively not detrimental, narrow tolerance for plants
Pb	Alloys, cermics, plastics, glassware, lead-acid batteries, cable sheathing, sheets, solder, pipes and tubing, pigments	0.01	Pb poisoning through gasoline, plumbing and paints
Hg	Amalgamation, electrical and measuring apparatus, catalysts, dental fillings, Hg vapor lamps, solders, X-ray tubes,	0.006	Biomagnification in aquatic environments, Minamata disease
Ni	An alloy in the steel industry, computer components, catalysts, ceramic and glass molds, rods, pigments	0.07	Contact dermatitis, asthma, chronic respiratory infections carcinogenic
Zn	Zn alloys, PVC stabilizers, gold precipitation from cyanide solution, in chemicals and medicines, and medicines, anti-corrosion coating, cans, barriers, rubber industry, welding and soldering fluxes, paints	0.3-1 mg/kg of body weight per day	Relatively not detrimental to mammals

Also Kobielska et al. 2018 have written that Anthropogenic sources in ground water are as: Groundwater reservoirs which are the main source of drinking water and of great importance to humankind, are contaminated mainly by organic and inorganic pollutants of anthropogenic origin. This pollution may lead to the poisoning of both aquatic and land animals, and ultimately poses a risk to human health. Monitoring and controlling potential sources of pollution is therefore vital. This includes sources such as runoff from agricultural and industrial sites, urban areas, mining and hazardous disposal sites, landfills, dredged sediments, sewage systems, railways and motorways. Groundwater contamination can also result in redistribution of heavy metals throughout the environment, be it via uptake by plants or sorption/complexation (to particulate organic matter). A general overview showing the transportation of heavy metals within groundwater systems is illustrated in. Many human activities that contribute to heavy metal pollution can be tied, in broad terms, to the processes of production, consumption and disposal of products, across areas ranging from industry to agriculture and transportation. The elements released by such activities can come both from diffuse, as well as point sources and are introduced into the environment as either gasses or particulates in aqueous or solid forms. Agricultural sources of pollution include substances used for crop management such as fertilizers.

Phosphatic fertilizers for example contain cadmium and zinc in proportions dependent upon the type of rock they are derived from: higher Cd content for sedimentary derivatives and lower for igneous rock derivatives. Pesticides no longer contain heavy metals, however past usage of metal-rich products led to accumulation of arsenic, lead and mercury within soil and groundwater.

Sewage effluents have been commonly used for soil enrichment during the past 100 years due to their high nutrient content.

Despite their advantages, sewage effluents can also contain boron, cadmium, copper, lead, nickel and zinc which may cause toxicity in plants.

Industrial activities are also major contributors to heavy metal pollution in the environment. This is of particular concern for areas of the world that have yet to introduce modern legislation regarding this matter. The main industrial sources of pollution include mining, coal combustion, wastewater and the disposal of product waste. Mining produces large quantities of waste rock, still containing trace heavy metals (As, Cu, Cd, Pb, Hg), which are deposited within mine tailings and exposed to weathering and oxidizing conditions leading to acid drainage. This in turn mobilizes the heavy metals, which then permeate into the surrounding rock, soils and in some cases drinking water sources. Another industrial source of pollution, fossil fuel combustion, contributes mainly toward atmospheric heavy metal (As, Cd, Mo, Zn and Pb from gasoline additives) pollution. Solid waste from industrial processes is another major contributor to pollution due to the common lack of oversight over disposal sites allowing the waste to come in contact with soil or groundwater.

In Chen et al. 2016, for each of six heavy metals (i.e. Fe, Zn, Mn, Pb, Cd and Cu) in groundwater, we use >330 data points together with mixed-effect models to indicate that (i) human activity modes significantly influence the Cu and Mn but not Zn, Fe, Pb and Cd levels, and (ii) annual mean temperature (AMT) only significantly influences Cu and Pb levels, while annual precipitation (AP) only significantly affects Fe, Cu and Mn levels. Given these differences, we suggest that the impacts of human activity modes and climate on heavy metal “spread” in groundwater are biased.

According to Su et al. 2018 a total of 13 tailing samples, 145 surface soil samples, and 29 water samples were collected, and the concentrations of major heavy metals, including Cr, Mn, Co, Ni, Cu, Zn, As, Cd, Pb, and Se, were determined. The results show that the tailings contained high levels of heavy metals, with Cu, Zn, As, Cd, and Pb occurring in the ranges of $739\text{--}4.15 \times 10^3$, $1.81 \times 10^3\text{--}5.00 \times 10^3$, $118\text{--}1.26 \times 10^3$, $8.14\text{--}57.7$, and $1.23 \times 10^3\text{--}6.99 \times 10^3$ mg/kg, respectively.

Heavy metals also occurred at high concentrations in the mine drainages (15.4–17.9 mg/L for Cu, 21.1–29.3 mg/L for Zn, 0.553–0.770 mg/L for Cd, and 1.17–2.57 mg/L for Pb), particularly those with pH below 3. The mean contents of Cu, Zn, As, Cd, and Pb in the surface soils of local farmlands were up to 7 times higher than the corresponding background values, and results of multivariate statistical analysis clearly indicate that Cu, Zn, Cd, and Pb were largely contributed by the mining activities.

In particular, mine tailings, which contain a range of heavy metals at rather high levels, are dumped in the mining district without any protective measures taken. The fine grains of mine tailings and the leachate generated from the tailings could easily cause pollution of nearby soils and surface water during rainfalls. Although the scale and the productivity of small-scale mining activities are limited, they could cause alarming heavy metal pollution to the surrounding area, which deserves significant attention.

The results from the application of the model in Sidibe et al. 2018 area show that a large majority of the aquifer is at high risk of nitrate contamination if good agricultural practices are not applied. This is due to the huge amounts of fertilizer used on most cultivated crops grown throughout the study area. Heavy-metal pollution is very dangerous for both humans and groundwater sources. Further studies need to be carried out in the mining areas and especially in the gold-panning area.

- *Removal methods of heavy metals from groundwater*

According to Hepburn et al. 2018 A method for heavy metal source separation in groundwater within anthropogenically modified sediments has been developed.

The method utilises three steps: 1) statistical categorisation of the data; 2) analysis of soil leaching values (SLVs); and 3) examination of vertical profiles of metal composition and lithology with depth.

Major sources of heavy metals to groundwater were identified as artificially imported fill, and plume-impacted groundwater, both of which have the potential to impact surface water ecosystems at groundwater discharge points. However, groundwater across most of the precinct is predominantly drained by a sewer, thus lowering the risk to nearby waters.

The review in Kobielska et al. 2018 looks at metal–organic frameworks (MOFs) which have been recently developed and studied for potential applications in heavy metal removal from water. They provide an overview of the current capabilities and important properties of MOFs used for this purpose.

According to Kobielska et al. 2018 It is apparent that this steadily growing research area has quite a variety of adsorbents already available, with many reported MOFs having desirable features for adsorptive removal of heavy metals—many of which can be post-synthetically modified to further target specific contaminants, have wide-ranging adsorption mechanisms and capacities ranging anywhere from hundreds to a few mg g⁻¹, requiring anywhere between 10 min and a week of contact with the solution. In addition, the MOF adsorbents can function within either a wide range of pH values, or only within a (sometimes very) narrow window, be it of acidic, neutral or basic pH. Besides their high potential in selective adsorption and separation of heavy metal ions from water it is worth noting that a major challenge faced by majority of the MOFs is their poor water stability.

Detailed information about the water and chemical stability of MOFs has already been thoroughly reviewed elsewhere.

What this overview shows, is that there is not clearly one single “best” MOF property that makes the material an effective adsorbent.

Overall, there are still opportunities for more detailed studies, in particular toward understanding the adsorption mechanism of heavy metals in different MOFs. Engineered forms of MOFs should also be tested and methods of employing MOFs and MOF composites as adsorbents should be considered such as their use in filters which are either permanent (for frameworks which can be reused) or one-time use (where the MOF filters are perishable and need to be exchanged). Finally, more standardized testing of MOF materials against various water contaminants in addition to a better understanding of desirable properties for MOF-based adsorbents will help to propel this application forward in the future for this promising class of porous materials.

In Schmol et al. 2006 some remediation techniques are as bellow:

A systematic approach for the assessment and remediation of contaminated sites is necessary in order to facilitate the remediation process and avoid undue delays. The most important aspects of the approach include site characterization, risk assessment, and selection of an effective remedial action. Innovative integration of various tasks can often lead to a faster, cost-effective remedial program. Site characterization is often the first step in a contaminated site remediation strategy. It consists of the collection and assessment of data

representing contaminant type and distribution at a site under investigation. The results of a site characterization form the basis for decisions concerning the requirements of remedial action. Additionally, the results serve as a guide for design, implementation, and monitoring of the remedial system.

Each site is unique; therefore, site characterization must be tailored to meet site-specific requirements. An inadequate site characterization may lead to the collection of unnecessary or misleading data, technical misjudgment affecting the cost and duration of possible remedial action, or extensive contamination problems resulting from inadequate or inappropriate remedial action. Site characterization is often an expensive and lengthy process; therefore, it is advantageous to follow an effective characterization strategy to optimize efficiency and cost.

An effective site characterization includes the collection of data pertaining to site geology, including site stratigraphy and important geologic formations; site hydrogeology, including major water-bearing formations and their hydraulic properties; and site contamination, including type, concentration, and distribution. Additionally, surface conditions both at and around the site must be taken into consideration. Because little information regarding a particular site is often known at the beginning of an investigation, it is often advantageous to follow a phased approach for the site characterization. A phased approach may also minimize financial impact by improving the planning of the investigation and ensuring the collection of relevant data. Phase I consists of the definition of investigation purpose and the performance of a preliminary site assessment. A preliminary assessment provides the geographical location, background information, regional hydrogeologic information, and potential sources of contamination pertaining to the site. The preliminary site assessment consists of two tasks, a literature review and a site visit. Based on the results of the Phase I activities, the purpose and scope of the Phase II exploratory site investigation need to be developed. If contamination was detected at the site during the course of the preliminary investigation, the exploratory site investigation must be used to confirm such findings as well as obtain further data necessary for the design of a detailed site investigation program. A detailed work plan should be prepared for the site investigations describing the scope of related field and laboratory testing.

The work plan should provide details about sampling and testing procedures, sampling locations, and frequency, a quality assurance/quality control (QA/QC) plan, a health and safety (S and H) plan, a work schedule, and a cost assessment. Phase III includes a detailed site investigation in order to define the site geology and hydrogeology as well as the contamination profile. The data obtained from the detailed investigation must be adequate to properly assess the risk posed at the site as well as to allow for effective designs of possible remedial systems.

As with the exploratory investigations, a detailed work plan including field and laboratory testing programs as well as QA/QC and S and H plans should be outlined. Depending on the size, accessibility, and proposed future purpose of the site, this investigation may last anywhere from a few weeks to a few years. Because of the time and the effort required, this phase of the investigation is very costly. If data collected after the first three phases is determined to be inadequate, Phase IV should be developed and implemented to gain additional information.

Additional phases of site characterization must be performed until all pertinent data has been collected.

Depending on the logistics of the project, site characterization may require regulatory compliance and/or approval at different stages of the investigation. Thus, it is important to review the applicable regulations during the preliminary site assessment (Phase I). Meetings with regulatory officials may also be beneficial to insure that investigation procedures and results conform to regulatory standards. This proactive approach may prevent delays in obtaining the required regulatory permits and/or approvals. Innovative site characterization techniques are increasingly being used to collect relevant data in an efficient and cost-effective manner. Recent advances in cone penetrometer and sensor technology have enabled contaminated sites to be rapidly characterized using vehicle-mounted direct push probes. Probes are available for directly measuring contaminant concentrations in situ, in addition to measuring standard stratigraphic data, to provide flexible, real-time analysis. The probes can also be reconfigured to expedite the collection of soil, groundwater, and soil gas samples for subsequent laboratory analysis. Noninvasive, geophysical techniques such as ground-penetrating radar, cross-well radar, electrical resistance tomography, vertical induction profiling, and high resolution seismic reflection produce computer-generated images of subsurface geological conditions and are qualitative at best. Other approaches such as chemical tracers are used to identify and quantify contaminated zones, based on their affinity for a particular contaminant and the measured change in tracer concentration between wells employing a combination of conservative and partitioning tracers.

Risk assessment

Once site contamination has been confirmed through the course of a thorough site characterization, a risk assessment is performed. A risk assessment is a systematic evaluation used to determine the potential risk posed by the detected contamination to human health and the environment under present and possible future conditions. If the risk assessment reveals that an unacceptable risk exists due to the contamination, a remedial strategy is developed to assess the problem. If corrective action is deemed necessary, the risk assessment will

assist in the development of remedial strategies and goals necessary to reduce the potential risks posed at the site. The USEPA and the American Society for Testing and Materials (ASTM) have developed comprehensive risk assessment procedures. The USEPA procedure was originally developed by the United States Academy of Sciences in 1983. It was adopted with modifications by the USEPA for use in Superfund feasibility studies and RCRA corrective measure studies. This procedure provides a general, comprehensive approach for performing risk assessments at contaminated sites. It consists of four steps:

- Hazard identification.
- Exposure assessment.
- Toxicity assessment.
- Risk characterization.

Remediation Action

When the results of a risk assessment reveal that a site does not pose risks to human health or the environment, no remedial action is required. In some cases, however, monitoring of a site may be required to validate the results of the risk assessment. Corrective action is required when risks posed by the site are deemed unacceptable. When action is required, remedial strategy must be developed to insure that the intended remedial method complies with all technological, economic, and regulatory considerations. The costs and benefits of various remedial alternatives are often weighed by comparing the flexibility, compatibility, speed, and cost of each method. A remedial method must be flexible in its application to ensure that it is adaptable to site-specific soil and groundwater characteristics. The selected method must be able to address site contamination while offering compatibility with the geology and hydrogeology of the site. Generally, remediation methods are divided into two categories: in situ remediation methods and ex situ remediation methods. In situ methods treat contaminated groundwater in-place, eliminating the need to extract groundwater. In situ methods are advantageous because they often provide economic treatment, little site disruption, and increased safety due to lessened risk of accidental contamination exposure to both on-site workers and the general public within the vicinity of the remedial project. Successful implementation of in situ methods, however, requires a thorough understanding of subsurface conditions. Ex situ methods are used to treat extracted groundwater. Surface treatment may be performed either on-site or off-site, depending on site-specific conditions. Ex situ treatment methods are attractive because consideration does not need to be given to subsurface conditions. Ex situ treatment also offers easier control and monitoring during remedial activity implementation.

Some techniques for groundwater remediation

Groundwater remediation techniques span biological, chemical, and physical treatment technologies.

Most ground water treatment techniques utilize a combination of technologies.

Some of the biological treatment techniques include bio-augmentation, bioventing, biosparging, bioslurping, and phyto-remediation. Some chemical treatment techniques include ozone and oxygen gas injection, chemical precipitation, membrane separation, ion exchange, carbon absorption, aqueous chemical oxidation, and surfactant enhanced recovery. Some chemical techniques may be implemented using nano-materials. Physical treatment techniques include, but are not limited to, pump and treat, air sparging, and dual phase extraction. Biological treatment technologies. Within this category, we have the following well-known techniques:

- Bio-augmentation: If a treatability study shows no degradation (or an extended lab period before significant degradation is achieved) in contamination contained in the groundwater, then inoculation with strains known to be capable of degrading the contaminants may be helpful. This process increases the reactive enzyme concentration within the bioremediation system and subsequently may increase contaminant degradation rates over the non-augmented rates, at least initially after inoculation.
 - Bioventing is an in situ remediation technology that uses microorganisms to biodegrade organic constituents in the groundwater system. Bioventing enhances the activity of indigenous bacteria and archaea and stimulates the natural in situ biodegradation of hydrocarbons by inducing air or oxygen flow into the unsaturated zone and, if necessary, by adding nutrients. During bioventing, oxygen may be supplied through direct air injection into residual contamination in soil. Bioventing primarily assists in the degradation of adsorbed fuel residuals, but also assists in the degradation of volatile organic compounds (VOCs) as vapors move slowly through biologically active soil.
 - Biosparging is an in situ remediation technology that uses indigenous microorganisms to biodegrade organic constituents in the saturated zone. In biosparging, air (or oxygen) and nutrients (if needed) are injected into the saturated zone to increase the biological activity of the indigenous microorganisms. Biosparging can be used to reduce concentrations of petroleum constituents that are dissolved in groundwater, adsorbed to soil below the water table, and within the capillary fringe.
- Bioslurping combines elements of bioventing and vacuum-enhanced pumping of freeproduct that is lighter than water (light non-aqueous phase liquid or LNAPL) to recover free-product from the groundwater and soil, and to bio-remediate soils. The bioslurper system uses a "slurp" tube that extends into the free-product layer. Much like a straw in a glass draws liquid, the pump draws liquid (including free-product) and soil gas up the tube in the same process stream. Pumping lifts LNAPLs, such as oil, off the top of the water table and from the capillary fringe meaning an area just above the saturated zone, where water is held in place by

capillary forces. The LNAPL is brought to the surface, where it is separated from water and air. The biological processes in the term “bioslurping” refer to aerobic biological degradation of the hydrocarbons when air is introduced into the unsaturated zone.

- In the phyto-remediation process certain plants and trees are planted, whose roots absorb contaminants from groundwater over time, and are harvested and destroyed. This process can be carried out in areas where the roots can tap the groundwater. Few examples of plants that are used in this process are Chinese Ladder fern *Pteris vittata*, also known as the brake fern, is a highly efficient accumulator of arsenic. Genetically altered cottonwood trees are good absorbers of mercury and transgenic Indian mustard plants soak up selenium well.

Chemical treatment technologies

- Chemical precipitation is commonly used in wastewater treatment to remove hardness and heavy metals. In general, the process involves addition of agent to an aqueous waste stream in a stirred reaction vessel, either batchwise or with steady flow. Most metals can be converted to insoluble compounds by chemical reactions between the agent and the dissolved metal ions. The insoluble compounds (precipitates) are removed by settling and/or filtering.
- Ion exchange for groundwater remediation is virtually always carried out by passing the water downward under pressure through a fixed bed of granular medium (either cation exchange media and anion exchange media) or spherical beads. Cations are displaced by certain cations from the solutions and ions are displaced by certain anions from the solution. Ion exchange media most often used for remediation are zeolites (both natural and synthetic) and synthetic resins.
- Carbon absorption: The most common activated carbon used for remediation is derived from bituminous coal. Activated carbon absorbs volatile organic compounds from groundwater by chemically binding them to the carbon atoms.
- Chemical oxidation: In this process, called In Situ Chemical Oxidation or ISCO, chemical oxidants are delivered in the subsurface to destroy (converted to water and carbon dioxide or to nontoxic substances) the organic molecules. The oxidants are introduced as either liquids or gasses. Oxidants include air or oxygen, ozone, and certain liquid chemicals such as hydrogen peroxide, permanganate and persulfate. Ozone and oxygen gas can be generated on site from air and electricity and directly injected into soil and groundwater contamination. The process has the potential to oxidize and/or enhance naturally occurring aerobic degradation. Chemical oxidation has proven to be an effective technique for dense non-aqueous phase liquid or DNAPL when it is present.
- Surfactant enhanced recovery increases the mobility and solubility of the contaminants absorbed to the saturated soil matrix or present as dense non-aqueous phase liquid.

Surfactant-enhanced recovery injects surfactants (surface-active agents that are primary ingredient in soap and detergent) into contaminated groundwater. A typical system uses an extraction pump to remove groundwater downstream from the injection point. The extracted groundwater is treated above-ground to separate the injected surfactants from the contaminants and groundwater. Once the surfactants have separated from the groundwater they are reused. The surfactants used are non-toxic, food-grade, and biodegradable.

Surfactant enhanced recovery is used most often when the groundwater is contaminated by dense non-aqueous phase liquids (DNAPLs). These dense compounds, such as trichloroethylene (TCE), sink in groundwater because they have a higher density than water.

They then act as a continuous source for contaminant plumes that can stretch for miles within an aquifer. These compounds may biodegrade very slowly. They are commonly found in the vicinity of the original spill or leak where capillary forces have trapped them.

Physical treatment technologies

- Pump and treat is one of the most widely used groundwater remediation technologies. In this process groundwater is pumped to the surface and is coupled with either biological or chemical treatments to remove the impurities.
- Dual-phase vacuum extraction

Dual-phase vacuum extraction (DPVE), also known as multi-phase extraction, is a technology that uses a high-vacuum system to remove both contaminated groundwater and soil vapor. In DPVE systems a high-vacuum extraction well is installed with its screened section in the zone of contaminated soils and groundwater. Fluid/vapor extraction systems depress the water table and water flows faster to the extraction well. DPVE removes contaminants from above and below the water table. As the water table around the well is lowered by pumping, unsaturated soil is exposed. This area, called the capillary fringe, is often highly contaminated, as it holds undissolved chemicals, chemicals that are lighter than water, and vapors that have escaped from the dissolved groundwater below. Contaminants in the newly exposed zone can be removed by vapor extraction. Once above ground, the extracted vapors and liquid-phase organic and groundwater are separated and treated.

Use of dual-phase vacuum extraction with these technologies can shorten the cleanup time at a site, because the capillary fringe is often the most contaminated area.

- Monitoring-wells are often drilled for the purpose of collecting groundwater samples for analysis. These wells, which are usually six inches or fewer in diameter, can also be used to remove hydrocarbons from the contaminant plume within a groundwater aquifer by using a belt style oil skimmer. Belt oil skimmers, which are simple in design, are commonly used to remove oil and other floating hydrocarbon contaminants from industrial water systems.

A monitoring-well oil skimmer remedies various oils, ranging from light fuel oils such as petrol, light diesel or kerosene to heavy products such as No. 6 oil, creosote, and coal tar. It consists of a continuously moving belt that runs on a pulley system driven by an electric motor. The belt material has a strong affinity for hydrocarbon liquids and for shedding water. The belt, which can have a vertical drop of 100+ feet, is lowered into the monitoring well past the LNAPL/water interface. As the belt moves through this interface it picks up liquid hydrocarbon contaminant, which is removed and collected at ground level as the belt passes through a wiper mechanism. To the extent that DNAPL hydrocarbons settle at the bottom of a monitoring well, and the lower pulley of the belt skimmer reaches them, these contaminants can also be removed by a monitoring-well oil skimmer.

Typically, belt skimmers remove very little water with the contaminant, so simple weir type separators can be used to collect any remaining hydrocarbon liquid, which often makes the water suitable for its return to the aquifer. Because the small electric motor uses little electricity, it can be powered from solar panels or a wind turbine, making the system self-sufficient and eliminating the cost of running electricity to a remote location.

According to Schmoll et al. 2006 the main purpose of heavy metal remediation is to minimize the risk of these toxic compounds to human and ecological health. The selection of an appropriate remediation method depends on the characteristics of the site, extent of the heavy metal contamination, and regulatory limits for the heavy metal(s) of concern in that regulatory domain. The remediation methods can be broadly divided into three major categories: (1) physical methods, (2) chemical methods, and (3) biological methods.

Conclusion

Groundwater is one of the most important sources of fresh water in the world. In this paper, heavy metal contamination and its purification methods are concentrated.

Most ground water treatment techniques utilize a combination of technologies.

Some of the biological treatment techniques include bio-augmentation, bioventing, biosparging, bioslurping, and phyto-remediation. Some chemical treatment techniques include ozone and oxygen gas injection, chemical precipitation, membrane separation, ion exchange, carbon absorption, aqueous chemical oxidation, and surfactant enhanced recovery. Some chemical techniques may be implemented using nano-materials.

Chen et al. 2016 revealed the real presence of bias for the effects of human activity modes and climate on groundwater heavy metal “spread”. Although human activity modes and climate only significantly affect a part of heavy metals in groundwater, it does not mean that we no longer need to keep a cautious eye on those heavy metals that were not significantly influenced.

Furthermore, finding the linkage between groundwater quality and human activities as well as climate change is vital to the sustainable use of groundwater. Thus, the present work is also helpful in groundwater health risk assessment, pollution prevention and resources management.

According to Sun et al. 2018 to prevent further deterioration of the local environment, the government should significantly step up the efforts on supervision and management of small-scale mines, including the abandoned ones, and implement effective measures, such as developing tailing ponds and applying geomembrane cover, to prevent continuous releases of heavy metals from the dumped mining tailings.

According to Sidibe et al. 2018 the establishment of a quality control network is essential to protect groundwater sources for consumption. In addition, groundwater vulnerability mapping should not replace detailed hydrogeological studies for specific aquifers, but rather should be the first step towards protecting groundwater resources.

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