



THE GROUNDWATER CONTAMINATED WITH CADMIUM: A SYSTEMATIC REVIEW

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Article info	Abstract
<p>Received: 2022-08-12 Accepted: 2022-09-26 Published: 2022-12-31</p> <p>DOI -Crossref: 10.32649/ajas.2022.176912</p> <p>Cite as: Jebril, N. M., R. Boden, and C. Braungardt. (2022). The groundwater contaminated with cadmium: a systematic review. <i>Anbar Journal of Agricultural Sciences</i>, 20(2): 483-494.</p> <p>©Authors, 2022, College of Agriculture, University of Anbar. This is an open-access article under the CC BY 4.0 license (http://creativecommons.org/licenses/by/4.0/).</p>	<p>Cadmium (Cd) groundwater contamination is a widespread problem that causes severe environmental and health concerns. Excessive concentrations of Cd, which contaminate water, have been detected in several countries, have consequently attracted attention, and raised significant concern. The differences in Cd contamination relate not just to the source strength but also to the pathways whereby the Cd transfer to and transport within aquifers depends on its chemistry and geochemistry. Cadmium is a non-essential element for life, and it is toxic to Homo Sapiens. The United States Environmental Protection Agency (US EPA) and the International Agency for Research on Cancer (IARC) classified some elements, including Cd, As, Hg, and Pb, as human carcinogens based on animal, molecular, and epidemiological models. The current information on cadmium contaminated groundwater was summarised in this review in response to this concern.</p>



Review Article

Keywords: Cadmium, Groundwater, Contamination, Heavy metals.

المياه الجوفية الملوثة بالكاديوم: مراجعة منهجية

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الخلاصة

يعد تلوث المياه الجوفية بالكاديوم (Cd) مشكلة واسعة الانتشار تسبب مخاوف بيئية وصحية شديدة. تم اكتشاف تركيزات مفرطة من الكاديوم التي تلوث المياه في العديد من البلدان وبالتالي جذبت الانتباه وأثارت قلقًا كبيرًا. لا تتعلق الاختلافات في تلوث الكاديوم بقوة المصدر فحسب بل تتعلق أيضًا بالمسارات التي يعتمد من خلالها انتقال الكاديوم إلى طبقات المياه الجوفية ونقلها داخلها على الكيمياء والجيوكيمياء. الكاديوم عنصر غير أساسي للحياة، وهو سام للإنسان. صنفت وكالة حماية البيئة الأمريكية (US EPA) والوكالة الدولية لأبحاث السرطان (IARC) بعض العناصر، بما في ذلك Cd و As و Hg و Pb، كمواد مسرطنة بشرية بناءً على النماذج الحيوانية والجزئية والوبائية. تم تلخيص المعلومات الحالية حول المياه الجوفية الملوثة بالكاديوم في هذه المراجعة استجابة لهذا المشكلة.

كلمات مفتاحية: كاديوم، مياه جوفية، التلوث، المعادن الثقيلة.

Introduction

Human and industrial activities have led to a marked increase in the level of cadmium in the environment across the globe. The estimated global average level of Cd in uncontaminated soil is 0.36 mg/kg, in soil water is 5 µg/L and in unpolluted groundwater less than 1 µg/L (30). Cadmium groundwater contamination is a widespread problem that causes severe environmental and health concerns. An average Cd level of 0.2 µg/L was determined in Irish groundwater (49). (38) reported that health risks are associated with cadmium in groundwater. Therefore, cadmium is listed as a priority hazardous substance in the European Water Framework Directive (15).

Groundwater: Most of the water on the Earth's surface is saline (96.5%) and is present in oceans, glaciers, and ice caps, the remainder being freshwater (3.5%). Saline waters are unusable by humans, while the usable water comes from freshwater resources such as groundwater, lakes, and rivers. Groundwater represents 99% of the Earth's freshwater US Geological Survey (55) and is a significant source of drinking water for humans, who require at least 2 litres of water per day. Groundwater is considered an essential stage in the hydrologic cycle, formed where surface water leaks into the subsurface, into vast reservoirs of water in aquifers and subterranean rivers. In its

natural state, the quality of groundwater is high, being almost free from pathogens and water were drawn from uncontaminated aquifers does not usually require complex treatment. However, pollution present in the soil or the catchment of an aquifer, in general, can be transferred into the groundwater (52). The importance of groundwater to human endeavour can be illustrated with some examples: In England and Wales, one-third of the domestic water supplies (2,400 million L per year) comes from groundwater (28) and in the Middle East, groundwater is a significant source of domestic supplies owing to having just two rivers, Tigris (Turkey and Iraq) and Euphrates (Turkey, Syria, and Iraq). The geochemistry of groundwater varies depending on the local mineralogy present above and throughout the aquifer, the contact time of groundwater with the rock holding the water, and the local biogeochemical processes. Usually, groundwater is high in calcium, magnesium, bicarbonates, calcium chlorides, and magnesium sulphates, contributing to its alkalinity, making it 'hard' (7). This hardness is, for example, due to the biological process of the organic matter, which is present in the soil zone, producing carbon dioxide, which leads to the formation of carbonic acid and bicarbonate ion:

$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$, which gives a pH of groundwater between 6.0 and 8.5 (58).

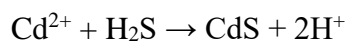
Additionally, the occurrences of minor ions such as: borate, nitrate, potassium, strontium, fluoride, iron, and trace ions such as: aluminium, cadmium, arsenic, barium, chromium, copper, lead, manganese, lithium, phosphate, selenium, silver, uranium and zinc dissolved in groundwater at concentrations below 0.1 mg/L, contribute to the minerals content of groundwater. Elevated metal contents in groundwater are generally linked to the abundance of clay minerals, organic matter, carbonates, and hydrous oxides, as well as physicochemical conditions, such as pH, and/or anoxic conditions. For example, differences in arsenic concentration in groundwater were previously documented because of constant redox conditions (19). It was found that the metal mobility increased with the decrease of groundwater pH (due to seasonal change in pH or pollution), while the hardness and salinity cause the immobilisation metals (36). For instance, high pH in the soil immobilises Cd, thus forming CdCO_3 and $\text{Cd}(\text{OH})_2$ precipitate (32).

Groundwater contamination: Pollution is defined as the condition in which substances that are not normally found or where they occur are above the natural background levels that lead to pollution, causing damage to living resources and risks to human health (11). Population increase, urbanisation, industrialisation, and agricultural activities have led to the deterioration of the quality and the chemistry of groundwater in many areas of the world. While undoubtedly important, assessment and monitoring of aquifer parameters can be expensive, and therefore numerical methods are increasingly applied to groundwater quantity, movement, and quality (5). For example, different models can be used to predict element concentrations in water systems. Recently, (33) have estimated the risk to groundwater by modelling the fate of contaminants and their transport. (41) used the tableau-input coupled kinetic equilibrium transport–unit world model (TICKET–UWM) for evaluating of copper in surface water. A study performed

by (42) to assess the environmental impact on groundwater, using Piper's diagram and Gibbs plot, showed that the interaction between rock, water, and the anthropogenic activity were the most critical processes that controlled groundwater chemistry. Notably, due to human activities, approximately two-thirds of groundwater bodies in England and one-third of those in Wales are at risk due to pollution from nitrate and other pollutants, such as phosphate, oil, pesticides, solvents, and cadmium (59). High concentrations of nitrate, fluoride, and arsenic have increased groundwater risk in India and Bangladesh (1). Globally, most groundwater is contaminated with some elements, which can affect human health and the overall health of the ecosystem. For example, groundwater contamination in 59 out of 64 regions in Bangladesh has been reported with 300 µg/L of arsenic (10) exceeded the maximum recommended concentration for as in drinking water (10 µg/L, World Health Organisation- International Agency for Research on Cancer (60).

Contamination and human health: Arsenic is commonly used in the manufacturing of herbicides, insecticides, fungicides, and insecticides, which increases its level in the environment. US EPA (54) reported that wood treatment with arsenic was estimated to release 48.9 million metric tons in 2015. In addition to the agricultural arsenic applications, arsenic has also been used in veterinary medicine to eradicate tapeworms in sheep and livestock and the medical field in the treatment of syphilis, trypanosomiasis, amoebic and dysentery. Furthermore, the Food and Drug Administration (FDA) recently stated that arsenic trioxide might be used in the treatment of acute leukemia in localised cells. These applications have increased the concentrations of arsenic to 5 mg/kg in soil, 10 µg/L in surface and groundwater, and between 1–2 µg/L in seawater (24). Lead is commonly used in many applications such as industrial, agricultural, and domestic products and processes. Lead-acid batteries were estimated to account for 83% of the 152,000 metric tons of lead used in various industries in the United States in 2004. The assessment of metals in the UK recorded that the annual mean concentrations of lead emission in rural locations reached 7.58 ng/mL in 2003 and more contamination of lead (102.88 ng/mL) was recorded in an industrial location, Brookside Bilston Lane (29). Mercury is used in the manufacture of fungicides, batteries, thermostats, and dental amalgams. In Iraq, the use of treated wheat with methyl mercury as a fungicide in 1955 caused poisoning to livestock and humans a dire consequence, which is referred to as the Iraq poison grain disaster (2). Because of this, the agricultural demand for mercury began to decline after this disaster suddenly. However, the total mercury consumption by industrial sectors such as artisanal gold mining, vinyl chloride monomer production, batteries, lamps was increased from 3000 metric tonnes in 2005 to 6027 metric tonnes in 2015 in which East and Southeast Asia were the highest consumers of mercury with 2882 metric tonnes (United Nations Environment Programme [UNEP] (53). In water, the dominant form of mercury is methylmercury (MeHg). This strong neurotoxin bioaccumulates easily in the food chain and poses a major risk to human health, primarily through fish consumption (35).

Cadmium chemistry and geochemistry: Cadmium is a post-transition metal of the d-block, with an atomic number of 48 and a relative atomic mass of 122.411 g/mol. Under surface environmental conditions (temperature, pressure, redox), its chemistry is dominated by the Cd (II) oxidation state, and Cd (I) is sometimes also observed (16). Redox potential (Eh) does not affect the solubility of Cd directly, as Cd (II) is the stable oxidation state, Cd mobility is indirectly related to the redox conditions when forms redox-sensitive aqueous complexes. The impact of Eh changes on Cd reduction or oxidation in natural environments has not been observed (19). Depending on the composition of the groundwater, free Cd²⁺ comprises 55 % to 90 % of the total soluble Cd, while the remaining forms of Cd are inorganic complexes (23). In the Earth's crust, Cd occurs in association with zinc minerals, mostly in sphalerite (ZnS) in the form of greenockite (CdS), owing to their similar electron configuration (13). Production figures for Cd vary between years in the range of 20,000 to 28,000 metric tons. For example, the US GS (56) estimated 23,520 metric tons of Cd were produced in 2017 by China (the top producer), South Korea, Japan, Canada, Mexico, Kazakhstan, Russia, Peru, Netherlands, and Poland. The British Geological Survey reported that more than 26,500 metric tons of Cd were produced in 2016 by the countries listed above and in addition: Bulgaria, Germany, Norway, Turkey, USA, Argentina, Brazil, and India (8). Secondary Cd minerals include cadmoselite (CdSe), cadmium metacinnabar (Hg, Cd) S), monteponite (CdO), and otavite (CdCO₃), which are rare and not used commercially (13). These natural forms of Cd in the Earth's crust have an average of 890 nmol/kg (48). In anaerobic environments, anaerobic, sulfate-reducing microorganisms (SRM) contribute in the biogeochemical cycling of Cd, forming CdS:



These microorganisms use sulfate as their terminal electron acceptor, producing hydrogen sulfide (39). In addition to SRM, *Geobacillus* species may also immobilise Cd to carbonate precipitation (CdCO₃) at pH ≥ 7 (27). CdS and CdSe are also chemically produced from mined greenockite and used as CdS and Cd₂SSe for the production of pigments for use in inks, paints, and plastics. Such pigments are becoming a human health concern in common household products, as high levels of cadmium have been found in paints on enamel drinking glasses, ceramics, and children's toys (50). Cd has wide-ranging applications in the production of nickel-cadmium batteries, plating metals, and as a neutron absorber in nuclear reactors (45). Rechargeable, nickel-cadmium batteries contribute to 85% of the total cadmium consumption globally; however, the use of Cd has risen with the increase of the expenditure on coatings, pigments, stabilisers, alloys and electronic compounds (Agency for Toxic Substances and Disease Registry) [ATSDR], (22). Like all metals, Cd cannot be degraded biologically after being released into the environment. Cadmium-containing mining waste, products, and compounds have to be recycled or treated before safe storage or disposal into the environment. The majority of waste Cd is found in coal ash, cement production waste, and sewage sludge (45). Anthropogenic sources contribute 85% – 90% of the total yearly emission of Cd to the air (19,700 tonnes/year in 2000), while natural sources were estimated at 150-2,600 tonnes/year in 2000 (61). The forms of Cd

in the atmosphere predominantly consist of Cd, CdO, CdS, and CdCl. The typical atmospheric residence time of Cd is about 1 – 10 days, which is sufficient for it to be transported up to a thousand kilometers before the deposit occurs. The continuous volcanic emissions, smelting, fossil fuel combustion, and refuse incineration leads to levels of Cd in the air, which exceed the Cd inhaled daily (5 ng/mL), resulting in concern about annual production levels and their consequent impact on human health. The average Cd concentrations which are discharged from the effluents of metal plating industries were 0.13 – 0.17 μM , whereas the highest concentration (8.8 μM) was discharged from lead-acid mine drainage (20). United States Environmental Protection Agency (20) estimated that 0.15 metric tons of Cd was released into surface water in 2009. The concentration of Cd in the flow of rainwater in urban areas ranges from 0.8 μM to 1.2 μM (14). Due to the pollution from the Orinoco and the Amazon rivers, Cd concentration in the Gulf of Mexico is higher, exceeding 4.4 μM (26). Excessive concentrations of Cd, which contaminate water, have been detected in several countries, have consequently attracted attention, and raised significant concern. Cd concentrations in various freshwater types, many of which exceed environmental quality standards (e.g., 4.4 μM in Irish groundwater in the UK, (49), are listed in Table 1.

Table 1 Total concentrations of Cd in different freshwater bodies reported in the literature. The standard guideline concentration for Cd in drinking water is 3 $\mu\text{g/L}$ (61), equivalent to 0.027 μM .

Freshwater	Average (range) of concentration of Cd (μM)	pH	Reference
Aquifer impacted by landfill, Gazipur, Delhi, India	0.13 (0.10-0.17)	6.3-6.9	(34)
Aquifer impacted by mining, Dhanbad, India	22 (20-24)	**	(40)
Aquifer impacted by mining, Phoenix, Nevada, USA	3.8 (3.2-4.4)	6.5-7.9	(15)
Aquifer impacted by mining, Techatticup, Nevada, USA	4.7 (4.1-5.3)	**	(47)
Rural aquifer, Qatar	7.6 (6.8-8.4)	7.8-7.9	(30)
Pigeon spring, Snake Gulch, Kanab Creek, USA	124.5 (120-128)	6.7-8.0	(6)
Aquifer impacted by mining, Antiquary, Bolivian Altiplano	36.4 (31-42)	7.8-9.4	(43)
Aquifer impacted by mining, Sorval Guarda, Portugal	622 (603-642)	**	(4)
Aquifer impacted by industries, Birmingham, UK	61 (5.8-6.4)	**	(46)
*Aquifer impacted by Landfill, Vejen, Denmark	60 (55-63)	**	(12)

Aquifer impacted by mining, North-western Arizona, USA	1.4 (1.1-1.6)	**	(44)
Rural aquifer, Dhemaji, Assam, India	0.5 (0.08-1.0)	**	(9)
Aquifer impacted by a river, Washington state	45 (42-48)	**	(51)
Aquifer impacted by River Ubeji River, Delta State, Nigeria	1.2 (0.75-1.5)	**	(21)
Aquifer impacted by River Basin, Seini, Romania	0.21 (0.12-0.31)	7.8-8.5	(18)
Aquifer impacted by mining, Yorkshire, UK	472 (423-432)	**	(3)
Glacial aquifer, Alaska, USA	1.2 (0.45-25)	**	(25)

* No control of reference site established except for aquifer impacted by Landfill, Vejen, Denmark was 6.3-6.6 μM .

** No pH established.

High concentrations in rivers and aquifers are possible due to the activities of mining industries and leaching from soil contamination, as reported by (57). Aquifers impacted by past or present mining activities have been reported to contain the highest Cd concentrations by sources collected in Table 1 (e.g., Portugal, 622 μM (37) and the UK, 427 μM) (3), but also show more modest contamination ($< 5 \mu\text{M}$, e.g., USA) (17 and 47). High concentrations of Cd were also recorded in areas within proximity to industrial activities, such as brass manufacture, metal-working, automotive engineering, jewellery making, armaments, and brewing in Birmingham, UK (61 μM) (46). Landfill appears to contribute to contamination of the aquifer with Cd in Vision, Denmark (59 μM Cd) (12), but less so in Gazipur, India (0.14 μM) (34). The groundwater in rural areas, is usually less contaminated with Cd, for example, in India (0.08 to 1.0 μM Cd) (9). These differences in Cd contamination relate not just to the source strength but also to the pathways whereby the Cd transfer to and transport within aquifers depends on its mobility, for which pH is an important parameter. The pH range varied from 6.6 to 8.5. Cd speciation and mobility is strongly affected by pH, with the highest movement in the pH range of 4.5 to 5.5, and likely precipitation occurring at a pH > 7.5 (36).

Conclusion: cadmium treatment is needed for water and more effective methods. Water treatment through physical, chemical, and biological techniques is an important aspect of water cleansing, and many studies have been undertaken to identify and develop treatment technologies. Cadmium is listed as a priority hazardous substance in the European Water Framework Directive and the health risks are associated with cadmium in groundwater. The cadmium mobility increased with the decrease of groundwater pH, while the hardness and salinity cause the cadmium immobilisation. Depending on the composition of the groundwater, free Cd^{2+} comprises 55 % to 90 % of the total soluble

Cd, while the remaining forms of Cd are inorganic complexes. Cadmium is a non-essential element for life, and it is toxic to *Homo Sapiens*. The United States Environmental Protection Agency (US EPA) and the International Agency for Research on Cancer (IARC) classified some elements, including Cd, As, Hg, and Pb, as human carcinogens. Furthermore, chronic exposure to low levels of Cd is associated with several diseases.

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