



Cadmium in soils and groundwater: A review

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ABSTRACT

Cadmium (Cd) is a non-essential trace element that is widely distributed in the environment. Both geogenic and anthropogenic sources can elevate Cd concentrations in soils and groundwater, which are important for maintaining healthy supplies of food and safe drinking water. Elevated Cd doses are carcinogenic to humans. The WHO Guidelines for Drinking-Water Quality recommend a guideline value for Cd of 3 µg/L. Important anthropogenic Cd sources include mining, atmospheric deposition of combustion emissions, and the use of Cd-containing fertilizers. We document several cases of Cd pollution in soil and groundwater based on worldwide accounts. Besides anthropogenic Cd sources, Cd is also incorporated into sulfides, carbonates, and phosphorites resulting in elevated Cd concentrations in associated rock types. The crustal median Cd content is 0.2 mg/kg. In soils, Cd occurs at concentrations of 0.01 to 1 mg/kg with a worldwide mean of 0.36 mg/kg. Weathering can lead to Cd concentrations up to 5 µg/L in soil water and up to 1 µg/L in groundwater. In aqueous solutions, Cd generally occurs as the divalent Cd²⁺ and it is mobilized mainly in oxic, acidic conditions. Cadmium sorption is enhanced by the presence of high amounts of hydrous oxides, clay minerals, and organic matter, and its mobility is further influenced by pH, the redox state, and ionic strength of the solution. However, Cd can remain in solution as water-soluble complexes with anions, such as CdCl⁺ and Cd(SO₄)₂²⁻, and dissolved organic matter while sorption and precipitation decrease the aqueous concentration of most other heavy metals. As a consequence, Cd is one of the most mobile heavy metals in the environment. The elevated mobilization potential, e.g., through competition and ligand induced desorption, is the reason for faster Cd release from soil into groundwater than other heavy metals. The goal of this study was to present a broad overview of the origin and concentration of Cd in groundwater, and its reaction pathways in aquatic environments. To gain an overview of the hydrochemical behavior of Cd, cases of Cd pollution in soil and groundwater, studies investigating Cd release, and information about the legal framework were compiled.

1. Introduction

Cadmium (Cd) is one of the most toxic and mobile elements in the environment (e.g., Alloway and Jackson, 1991; Nies, 1999, 2003). It can replace calcium in minerals due to its similar ionic radius, identical charge and similar chemical behavior (e.g., Thornton, 1986). Therefore, Cd can enter the human body and accumulate to a high level in several organs (Hajeb et al., 2014; Pan et al., 2010). In contrast to other toxic elements such as mercury (Hg) and arsenic (As), Cd enters the human diet mainly through terrestrial pathways, e.g., through vegetables. In areas with both anthropogenic and geogenic elevated Cd concentrations in soil and groundwater, rice bioaccumulated Cd, leading to an elevated daily Cd uptake in China, Korea, and Jamaica (Liu et al., 2017; Sebastian and Prasad, 2014). However, Cd bioavailability is complex, for example, rice from the southern part of China contains more Cd than

rice from the northern part of China. Possible reasons are the more acidic soils, an overuse of nitrogen fertilizers, pollution through irrigation and atmospheric deposition, and the cultivation of rice with a higher affinity for Cd accumulation in southern China (Chen et al., 2018; Yang et al., 2016).

Chronic Cd poisoning, termed *itai-itai* disease first discovered in Japan in the early 20th century, causes renal tubular dysfunction, osteomalacia, and osteoporosis due to competition with Ca and other nutrients (Aoshima, 2016; Arain et al., 2015; Khan et al., 2017). Cadmium exposure is also associated to glucose metabolism disorders, breast and lung cancer, cerebral infarction and cardiac failure (Khan et al., 2017). According to WHO (2011), the tolerable monthly Cd intake is 25 µg/kg body weight due to its long biological half-life in humans of 10 to 35 years. Cadmium uptake occurs through ingestion and inhalation and prolonged exposure may lead to various types of cancer

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(Pan et al., 2010). Cadmium is therefore listed as a priority hazardous substance in the European Water Framework Directive, which required management plans to cease Cd releases to the environment (EC, 2000). In addition to the European Water Framework Directive, the European Groundwater Directive required the EU member states to set a threshold value for Cd in groundwater (EC, 2006). Each member state developed their own procedures to determine a threshold value and values ranged from 0.08 to 27 $\mu\text{g/L}$; eight EU member states do not have a threshold value for Cd due to missing risk assessments (EC, 2010). In drinking water, the guideline value for Cd is set to 3 $\mu\text{g/L}$ (WHO, 2011). The United States Environmental Protection Agency set the maximum contaminant level for Cd to 5 $\mu\text{g/L}$, which is the same in the European Union (UNEP, 2010) and China (Ministry of Health of China, 2006). The environmental quality standard for Cd in groundwater is 0.5 $\mu\text{g/L}$ in Denmark, and 10 $\mu\text{g/L}$ in Japan (UNEP, 2010) and China, respectively (Li et al., 2017).

Previous studies investigated the occurrence and behavior of Cd in soils and groundwater with respect to agricultural aspects (e.g., Bigalke et al., 2017; Grant, 2011; Holmgren et al., 1993), bioavailability (e.g., Carrillo-Gonzalez et al., 2006; Wang et al., 2010) and environmental remediation (e.g., Khan et al., 2017; Zwonitzer et al., 2003). However, most of these studies focused on specific subjects, such as local problems (e.g., Karak et al., 2015; Kozyatnyk et al., 2016), contamination issues (e.g., Akbar et al., 2006; Christensen et al., 1996; Kjeldsen et al., 2002) or interaction with a specific mineral, such as goethite (e.g., Buerge-Weirich et al., 2002; Chen et al., 2019; Wang and Xing, 2002). Most studies used modeling approaches and/or experimental settings with uncommonly high Cd concentrations for statements of hydrochemical behavior, particularly during sorption experiments (e.g., Ahmed et al., 2008; Krishnamurti and Naidu, 2003). Tabein et al. (2018) summarized the competitive release of Cd and other trace elements from naturally contaminated rocks during construction projects.

The focus of most previous studies was the examination of chemical reactions and transport behavior of Cd stemming from its complex interactions in aquatic systems, with only a few studies (e.g., Hem, 1972; Loganathan et al., 2012; Smolders and Mertens, 2013) on the general hydrochemical behavior of Cd. Thus, there exists a lack of general knowledge about Cd sources, its geochemical behavior, its role as a competitor with other heavy metals and the resulting Cd concentrations in groundwater. This is particularly evident compared to other well-investigated toxic elements such as As (e.g., Smedley and Kinniburgh, 2002), Hg (Barringer et al., 2013) or Mo (Smedley and Kinniburgh, 2017).

An overview of Cd sources, abundance and distribution in the environment is presented in the following paragraphs. Furthermore, the hydrogeochemical behavior of Cd is addressed with focus on complexation, sorption, and competitive behavior in the presence of other heavy metals.

2. Cadmium content in soil water and groundwater

Cadmium occurs usually up to 5 $\mu\text{g/L}$ in soil water (Smolders and Mertens, 2013) and up to 1 $\mu\text{g/L}$ in groundwater (Naseem et al., 2014). In groundwater in Pakistan, mean Cd concentrations of 10 $\mu\text{g/L}$ originated from Jurassic sulfide-bearing sedimentary rocks (Naseem et al., 2014). In Germany, background Cd concentrations in groundwater range from 0.11 $\mu\text{g/L}$ in loess aquifers below arable land to 2.7 $\mu\text{g/L}$ in sandy aquifers below forested lands (Duijnsveld et al., 2008). Aquifers in Germany were analyzed with respect to stratigraphy and petrography. A selection of relevant aquifer systems indicate a relation between rock type, groundwater milieu and Cd concentrations (Fig. 1). Cadmium 90th percentile as background levels ranged from less than 0.1 $\mu\text{g/L}$ in groundwater, e.g., in Paleozoic, Triassic and Jurassic aquifers, to above 1 $\mu\text{g/L}$ in Rotliegend, Cretaceous, and Cenozoic aquifers (BGR, 2014). Apart from calcium carbonate Cretaceous aquifers, limestone dominated aquifer systems had low Cd concentrations in

groundwater. Most of them belong to aquifer systems with alkaline conditions (Fig. 1).

A mean Cd background level of 0.2 $\mu\text{g/L}$ was calculated for Irish groundwater, which increased up to 0.5 $\mu\text{g/L}$ in groundwater originated from non-calcareous sediments (Tedd et al., 2017). Occasional Cd concentrations above 1 $\mu\text{g/L}$ were detected in groundwater in sandstone aquifers and in unconsolidated sand and gravel aquifer systems in the western part of the United States, while Cd concentrations were below 1 $\mu\text{g/L}$ in most samples, which were taken from 3124 wells in the United States (Ayotte et al., 2011). Groundwater from the glacial aquifer system in the United States shows Cd concentrations between 0.018 $\mu\text{g/L}$ and 1.0 $\mu\text{g/L}$; however, 84 % of groundwater samples (N = 847) were below the detection limit (Groschen et al., 2008). Neumayer and Matthes (1977) reported for groundwater in Northern Germany a natural variation of Cd concentrations from 2 $\mu\text{g/L}$ in Pleistocene glaciofluvial sediments to 20 $\mu\text{g/L}$ in Holocene sands covered by marsh sediments. Wessolek and Kocher (2002) reported for road traffic influenced soil water and groundwater in Northern Germany Cd concentrations of up to 27.8 $\mu\text{g/L}$ and 2.34 $\mu\text{g/L}$, respectively. In a survey of groundwater surrounding waste sites in the United States, Cd concentrations up to 6000 $\mu\text{g/L}$ were found (ATSDR, 2012). Leachates from municipal solid waste landfills in the European Union can reach Cd concentrations up to 2700 $\mu\text{g/L}$ (EU, 2007). Therefore, Cd concentrations above what would be considered natural background can be the result of both natural and anthropogenic processes.

3. Natural cadmium sources

3.1. Atmosphere

Significant sources of natural Cd emissions are weathering of rocks, airborne soil particles, e.g., from deserts, sea spray, forest fires, biogenic material, volcanoes, and hydrothermal vents (ATSDR, 2012; Richardson et al., 2001; UNEP, 2010). Soil particles are the predominant source of natural emissions to the atmosphere, followed by forest and bush fires, sea salt, volcanic emissions and meteoric dust. According to Pacyna and Pacyna (2001), the worldwide mean annual emission of natural Cd is about 1300 t. In contrast, the estimates of Richardson et al. (2001) are almost 41,000 t/a and thus, higher by a factor of 15. Contrary to previous studies, their calculations were based on improved data collection. Sources for anthropogenic Cd emissions are non-ferrous metal production, fossil fuel combustion, phosphate fertilizer manufacturing, iron, steel, and cement production, road dust, and municipal and sewage sludge incineration (ATSDR, 2012; Merkel and Sperling, 1998; Pacyna and Pacyna, 2001; UNEP, 2010). Anthropogenic Cd emissions have decreased by over 90 % in the last 50 years (ATSDR, 2012; Smolders and Mertens, 2013). The estimations of the natural and anthropogenic mean Cd emissions worldwide are given in Table 1.

Cadmium concentrations in the environment can be caused by wildfires and wildfire induced increases in Cd concentrations in soils and ashes have been reported (Campos et al., 2016; Demeyer et al., 2001). The examination of the long-term behavior showed decreasing Cd concentrations in the solid phase, because rainfall and a pH decrease with time-since-fire instigate desorption and mobility of Cd and other heavy metals (Bladon et al., 2014; Campos et al., 2016). Wildfires in California, for example, increased the mean Cd concentration in storm water by over two orders of magnitude (Burke et al., 2013). Cadmium concentrations in biomass ash can be up to 30 mg/kg, which provides an additional process to increase Cd concentrations in soil, because such ash is often used as a fertilizer. In the short term the bioavailable pool of Cd remains low due to an ash-induced pH increase and therefore stronger adsorption (Kepanek et al., 2005; Li et al., 2016; Perkiomaki and Fritze, 2005). With time, however, rainfall and a pH decrease will increase its bioavailability.

The total Cd deposition in Germany in 2014, for example, was

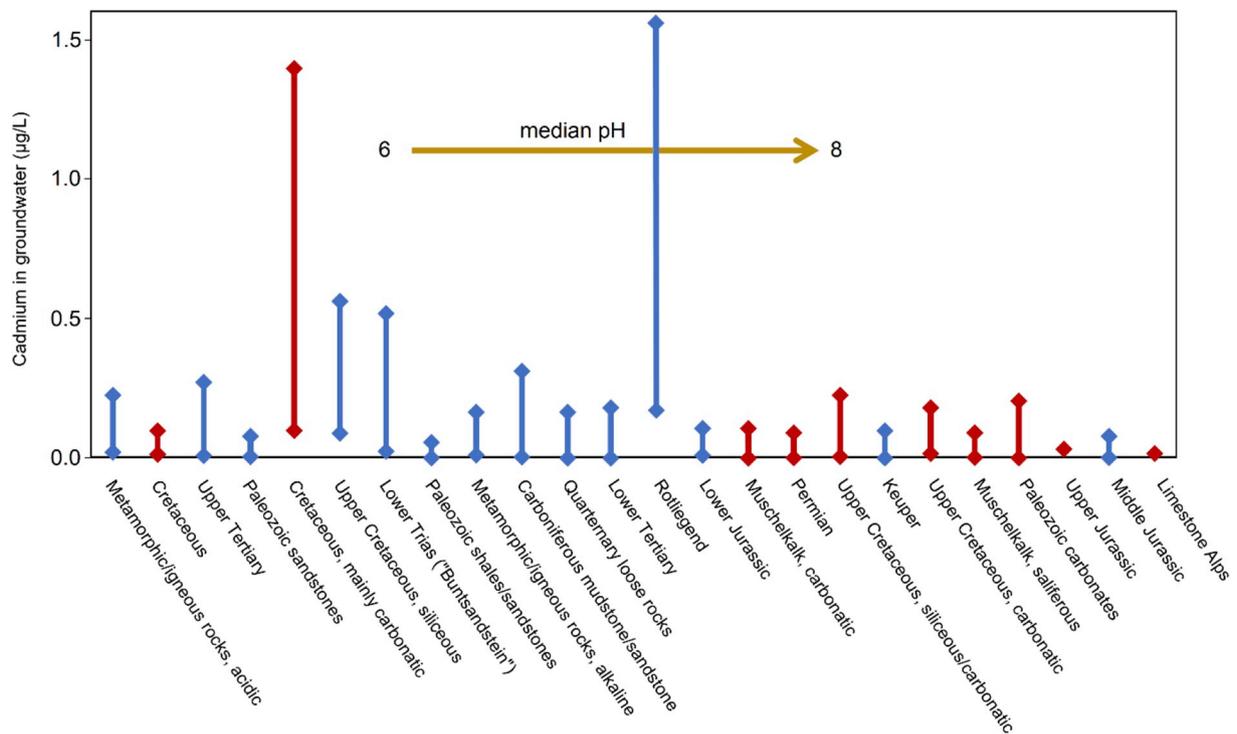


Fig. 1. Cadmium concentrations in groundwater related to stratigraphic and petrographic aquifer features (BGR, 2014). Bars represent 50th percentile (lower edge) and 90th percentile (upper edge) of Cd in groundwater. Red bars show limestone dominated aquifers, blue bars show miscellaneous aquifer material. Aquifer's order indicate median pH in groundwater from acidic (left) to alkaline (right). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 1
Worldwide mean Cd emissions to the atmosphere in the mid-90s.

Source	Cadmium (t/a)	Reference
Natural sources		a
Soil particles	24,000	
Forest and bush fires	13,000	
Sea salt	2000	
Volcanoes	1600	
Meteoric dust	$1,4 \times 10^{-4}$	
Anthropogenic sources		b
Non-ferrous metal production	2171	
Iron and steel production	64	
Stationary fossil fuel combustion	691	
Cement production	17	
Waste disposal (incineration)	40	
Sum	43,600	

^aRichardson et al. (2001); ^b Pacyna and Pacyna (2001).

12.8 t, of which 61 % originated from transboundary and natural emissions (Ilyin et al., 2016). In the southern agricultural part of Germany, deposition of Cd in 2014 were less than 0.25 g/(ha*a). In contrast, there were maximum concentrations of 1.4 g/(ha*a) in deposition in the atmosphere in the industrial western part of Germany (Ilyin et al., 2016).

3.2. Cadmium in rocks, sediments and soils

In general, Cd concentrations in sedimentary rocks (0.01 to 2.6 mg/kg) are higher than those in igneous rocks (0.07 to 0.25 mg/kg) or metamorphic rocks (0.11 to 1.0 mg/kg) (Hammons et al., 1978; Mar and Okazaki, 2012; Page et al., 1987; Smolders and Mertens, 2013). Average geogenic Cd concentrations in a variety of rock types are shown in Table 2.

The crustal median Cd content is 0.2 mg/kg (Gong et al., 1977). Cadmium can substitute for divalent cations, such as Ca, Fe, Zn, Pb, and

Table 2
Cadmium contents in rocks.

Rock type	Average Cd content (mg/kg)	Reference
Igneous		
Granitic rocks	0.12	a
Mafic rocks	0.11	b
Ultramafic rocks	0.02	b
Obsidian	0.25	a
Basalt	0.22	a
Metamorphic		
Gneisses	0.04	c
Schists	0.02	c
Sedimentary		
Bituminous shale (black shales)	0.8	a
Red shales	0.03	b
Bentonite	1.4	a
Marlstone	2.6	a
Red clay	0.56	c
Shale and claystone	1	a
Limestone	0.1	d
Sandstone	0.028	b
Carbonate stone	0.012	b
Organic sediment	0.5	d
Oceanic manganese oxides	8	d
Phosphorites	25	d

a: Thornton (1986); b: Gong et al. (1977); c: Page et al. (1987); d: Hammons et al. (1978).

Co in several minerals due to its similar ionic radius, e.g., in carbonate and phosphate rocks (e.g., Merkel and Sperling, 1998; Smolders and Mertens, 2013; Thornton, 1986; Wilkin, 2007). Pyrite, for example, can contain up to 52 mg/kg Cd (Abraitis et al., 2004). Table 3 lists the Cd content in several minerals, which could be considered important for the occurrence of Cd in the environment. Cadmium can substitute for Zn in sphalerite (ZnS) or smithsonite (ZnCO₃) (Merkel and Sperling, 1998; Tabein et al., 2018; Wen et al., 2015; Zhu et al., 2013). Sulfide

Table 3
Cadmium content of minerals (in mg/kg, except where noted; modified after Thornton, 1986).

Mineral	Composition	Range
Sphalerite	(Zn,Cd)S	< 2 %
Greenockite	CdS	77.8 %
Chalcopyrite	CuFeS ₂	< 110
Marcasite	FeS ₂	< 50
Arsenopyrite	FeAsS	< 5
Galena	PbS	< 3000
Tetrahedrite	(Cu,Fe,Zn,Ag) ₁₂ SbAs ₄ S ₁₃	80 to 2000
Magnetite	Fe ₃ O ₄	< 0.31
Limonite	Hydrous iron oxides	< 1000
Mn-Oxides	Hydrous manganese oxides	< 1000
Anglesite	PbSO ₄	120 to > 1000
Calcite	CaCO ₃	< 1 to 23
Smithonite	ZnCO ₃	< 2.35 %
Otavite	CdCO ₃	65.18 %
Pyromorphite	Pb ₅ Cl(PO ₄) ₃	< 1 to 8
Scorodite	FeAsO ₄ 2H ₂ O	< 1 to 5.8
Apatite	Ca ₅ (F,Cl)(PO ₄) ₃	0.14 to 0.15
Bindheimite	Pb ₂ Sb ₂ O ₆ (O,OH)	100 to 1000
Silicates		0.03 to 5.8

minerals like pyrite (FeS₂) are essential constituents of reduced systems and thus, important sources and sinks for Cd (Bostick et al., 2000; Tabelin et al., 2018). Furthermore, Cd is known to be adsorbed by hydrous oxides such as Fe(III) hydrous oxide, which can be an important supply of Cd to the aqueous phase when redox conditions change from oxygenated to reducing (e.g., Descourvieres et al., 2010; Hinderstmann and Mansfeldt, 2014; Li et al., 2010). Cadmium can also replace Ca in apatite, which is the main constituent of phosphorites (Gnandi and Tobschall, 2002). Consequently, Cd can be a common impurity in phosphate minerals and phosphoritic rocks, which are important for fertilizer production. The Cd content, however, varies

significantly between geologic occurrences. Currently, there is no commercial means to entirely remove Cd during the production of phosphate fertilizers (Mar and Okazaki, 2012). Ranges of geogenic Cd contents in phosphates of the most important exporting countries are shown in Fig. 2. In Nauru, a Pacific island, the highest Cd contents were detected, reaching 240 mg/kg P₂O₅ (Mar and Okazaki, 2012). Raw phosphates from the USA and African countries also have wide ranges of Cd contents. Other exporting countries for raw phosphates are South Africa, Russia, Israel, Syria, Pakistan, Peru, and Brazil (Mar and Okazaki, 2012; Oosterhuis et al., 2000).

Like phosphorites, black shales can have an elevated Cd content due to high marine primary production and biogenic enrichment (Liu et al., 2017). Thus, weathering of black shales can be an essential geogenic source of Cd in the environment. Sulfide minerals in black shales are the primary source of Cd (Liu et al., 2017).

The concentration of Cd in a given soil is generally closely related to its abundance in the parent material, as well as input through atmospheric deposition, industrial or agricultural activities, minus output in the form of leaching, erosion, and harvested crops (Six and Smolders, 2014).

In uncontaminated soils worldwide, the average abundance of Cd is 0.36 mg/kg, although values can vary between continents, countries and soil types. For example, average concentrations are: 0.27 mg/kg in the USA (N = 3045), 0.01 mg/kg in Australia, 0.18 mg/kg in Brazil, 0.3 mg/kg in Japan, 0.2 mg/kg in Europe. In Europe, Cd concentrations are 0.3 to 1 mg/kg in Germany (N = 2947), 0.6 to 0.7 mg/kg in the UK (N = 5692), and 0.5 mg/kg in the Netherlands (N = 708) (Holmgren et al., 1993; Roberts, 2014; Smith et al., 2014; Taylor et al., 2016). Within the United States, Cd contents in uncontaminated soils exceeding 0.5 mg/kg are found in the Rocky Mountains, Great Plains and Mississippi delta, which are areas that also have elevated clay contents in the corresponding aquifer matrices (Holmgren et al., 1993; Smith et al., 2014). Within soil taxonomy, soils with organic matter (Histosols) and arid soils (Aridisols) have the highest median Cd

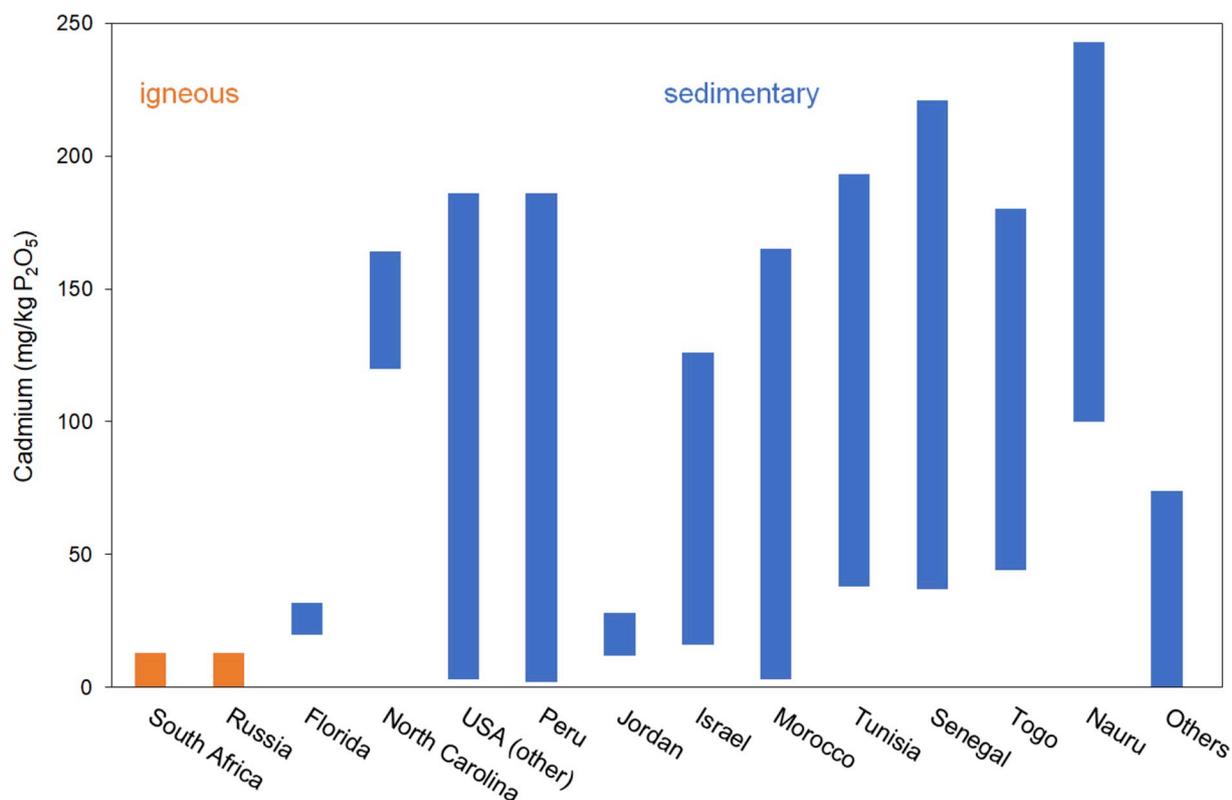


Fig. 2. Cadmium contents in raw phosphates by origin (Dittrich and Klose, 2008; Kharikov and Smetana, 2000; Mar and Okazaki, 2012; Oosterhuis et al., 2000; Roberts, 2014).

content with 0.62 mg/kg and 0.3 mg/kg, respectively, while the strongly weathered Spodosols (0.2 mg/kg), Alfisols (0.11 mg/kg), and Ultisols (0.05 mg/kg) have lower Cd contents (Holmgren et al., 1993). Cadmium contents in soils, however, generally decrease with depth (Hiller et al., 2001; Page et al., 1987). Background levels of geogenic Cd contents in German soils were calculated as the 90th percentile depending on land use and rock genesis. They confirm the observation of decreasing Cd contents with depth independent of rock genesis. The Cd levels range from 0.06 mg/kg in sandy subsoils to 1.8 mg/kg in soils at swamp locations, 1.88 mg/kg in soils above fluvial deposits at forest locations, and 2.0 mg/kg in sediments in the intertidal zone (LABO, 2017). Cadmium contents in soils in general depend on soil texture; elevated mean Cd contents can be found in soils with increasing contents of clay and peat (Holmgren et al., 1993; LABO, 2017).

Cadmium contents above 3 mg/kg are generally thought to indicate contaminated soil (Akbar et al., 2006). Concentration gradients in soils are common, where Cd increases with decreasing distance to industrial installations, roads and urban areas (Akbar et al., 2006; Page et al., 1987). This is comparable to Joimel et al. (2016), who reported that mean Cd contents in French soils showed an anthropization gradient of Cd concentrations with respect to land use, i.e., forest (0.13 mg/kg) < orchard and vineyard (0.18 mg/kg) < grassland (0.19 mg/kg) < farming (0.24 mg/kg) < garden (0.34 mg/kg) < urban, industrial, traffic, mining and military areas (1.30 mg/kg).

Locally Cd concentrations in soil above 3 mg/kg can be found without anthropogenic contamination. In forested areas, for example, the Cd content can reach up to 10 mg/kg due to the pedo-geochemical background (Baize and Sterckeman, 2001), while weathering of phosphorites from guano deposits produced Cd contents above 770 mg/kg in Jamaican soils (Garrett et al., 2008). In China, Korea, Finland, Sweden, and the United States, for example, black shales and associated soils show elevated Cd contents up to 42 mg/kg (Liu et al., 2017). Furthermore, oxidization of organic matter and sulfides in black shales causes acid rock drainage and thus, enhances Cd mobility (Liu et al., 2017).

In contrast to Eastern Europe, there is significantly more Cd in agricultural soils of Western Europe, which is caused by the different origin of P for fertilizers used in agriculture (Toth et al., 2016). As shown in Fig. 2, Russian magmatic Kola phosphate rock, which is the primary source of P fertilizers in Eastern Europe, has low Cd contents, while phosphate rock from Morocco, the main source of P for fertilizers in Western Europe, has elevated Cd contents (Toth et al., 2016). Birke et al. (2017) revealed another distribution pattern for Cd in agricultural soils in Europe. Besides a median Cd content of 0.18 mg/kg, Cd contents in agricultural soils differ between Northern Europe and Southern Europe, whose boundary coincides with the extension of the Quaternary glaciation. Soils in Northern Europe have median Cd contents of 0.13 mg/kg and thus, lower Cd contents compared to Southern Europe (median 0.22 mg/kg). Reasons for such a distribution pattern are differences in the amount of precipitation and drainage, lithology, weathering, grain size, and pH. However, anomalies can occur in Northern Europe due to soil mineralization, as well as in loess and clay dominated sediments and as anthropogenic overlaps (Birke et al., 2017).

Elevated Cd contents in soils and sediments are generally linked to the abundance of clay minerals, carbonates, organic matter, and hydrous oxides, as well as certain physicochemical conditions, such as elevated pH, and/or anoxic conditions (e.g., Appel and Ma, 2002; Buerge-Weirich et al., 2002; He et al., 2005). While Cd is often bound to the less stable exchangeable, carbonate and hydrous oxide fraction other heavy metals, such as Pb and Cu, are stronger bound to the organic and sulfidic fraction (Eggleton and Thomas, 2004; Zwonitzer et al., 2003). This is a likely explanation for the peculiar hydrochemical behavior and easy mobilization of Cd, when compared to other heavy metals.

4. Anthropogenic cadmium sources

Anthropogenic Cd inputs into soil and groundwater are combustion emissions, sewage sludge, landfills, traffic, metal industry, mining and incidents (Bigalke et al., 2017; Merkel and Sperling, 1998; Mirlean and Roisenberg, 2006; Sprynskyy et al., 2011). Similar to uranium (U), a common reason for elevated Cd concentrations in soil and groundwater is the use of phosphate fertilizers, which contain Cd as an impurity. This pathway of Cd addition to groundwater was investigated in the United States, Canada, Britain, Norway, Sweden, Finland, Denmark, Germany, Australia, and New Zealand (Bigalke et al., 2017; Grant, 2011; Taylor et al., 2016). The studies suggest that P fertilizer application changes soil chemistry. Additionally, Cd can potentially get transferred to the food chain and act toxic to biota. Sources for Cd can be of local or diffuse character. Local sources such as mines (e.g., Merkel and Sperling, 1998), industrial sites (e.g., Cloquet et al., 2006) or abandoned mine deposits (e.g., Monna et al., 2000) lead to elevated concentrations, however, mostly on a small spatial scale. Atmospheric emission, wastewater reuse or agricultural activities can serve as diffuse sources causing a widespread distribution of Cd in the environment (ATSDR, 2012; Knappe et al., 2008; Schuetze et al., 2003; Sprynskyy et al., 2011; UNEP, 2010).

The worldwide main Cd use, and thus primary source of Cd directed to landfills with municipal solid waste, are nickel-cadmium batteries (Khan et al., 2017; UNEP, 2010). Municipal solid wastes in Europe have Cd contents of 0.3 to 12 mg/kg, mean Cd concentrations in the leachates were estimated as 0.5 to 3.4 µg/L (EU, 2007). Additional Cd containing products are pigments, coatings and platings, stabilizers for polyvinyl chloride (PVC), and alloys (ATSDR, 2012). Table 4 lists the major anthropogenic (industrial) sources for elevated Cd in soils.

The contribution range of contamination sources to the amount of Cd present in soils that is available for leachate into groundwater, is 10 to 25 % from livestock manure, 15 to 50 % from atmospheric deposition, 30 to 55 % from mineral fertilizers and 2 to 5 % from sludges and composts (Belon et al., 2012; Nicholson et al., 2003). In addition to anthropogenic activities, the natural variability in rocks and minerals can be a reason for elevated Cd in associated soils (Baize and Sterckeman, 2001; Birke et al., 2017). Since Cd is easily mobilized, soil should not necessarily be considered a permanent sink, but rather a significant temporary storage for Cd (Christensen, 1984b), which can easily affect groundwater concentrations on different timescales, e.g., annual (wet vs. dry season) or decadal (dry vs. wet years).

Besides U, Cd has the highest phosphate fertilizer to background soil ratio and thus, a high potential risk of accumulation in soils, uptake by plants or increased loss in terms of leaching (Taylor et al., 2016). However, a Swiss survey did not confirm the enrichment of Cd on arable land due to P fertilizers, as it was observed for U originated from P fertilizers. There are possible reasons for missing Cd enrichment in soil, namely the removal of Cd via harvest, interferences like Cd input as atmospheric deposition, and application of manure and sewage sludge to grassland as reference areas, which were contaminated with Cd. However, there is a significant enrichment of both Cd and U in topsoil (Bigalke et al., 2017).

Phosphate fertilizers contain an average of 77 mg Cd per kg P₂O₅ in

Table 4
Cadmium contents in soils affected by industrial activities (Kabir et al., 2012).

Source	Cadmium content	
	Mean (mg/kg)	Max (mg/kg)
Mining and metal industry	37.6	289
Fertilizers, chemicals, petroleum production	0.51	2.13
Textiles	42.0	83.6
Leathers	0.63	1.26
Nonmetallic mineral products	25.8	72.0

Table 5
Mean annual inputs and outputs of soil Cd in g/ha.

Inputs			Outputs		Remarks (Location, period)	Reference
Atmospheric Deposition	Phosphate fertilizers	Others (e.g., manure)	Leaching	Crop offtake		
1.7	5.6	0.64	0.68	0.28	Germany, farming, the 1990s	Schuetze et al. (2003)
5	–	–	0.68	–	Germany, forest & urban, the 1990s	Schuetze et al. (2003)
2.5 to 4.5	–	–	–	–	German uplands, forest, the 1990s	Beisecker et al. (2012)
2.06	–	–	3.35	–	German uplands, forest, the 2000s	Beisecker et al. (2012)
0.96	0.28	0.43	0.87	0.8	Lower Saxony (Germany), farming, 1990s/2000s	Kamermann et al. (2015)
4	0.9	6.3	1.6	–	China, the 2000s	Luo et al. (2009)
1.9	1.6	–	–	–	European countries, 2000	Grant (2011)
9.8	1.0	1.4	–	–	Belgium, the 1990s	UNEP (2010)
0.25	0.98	0.56	–	–	Farquhar et al., 1997	Six and Smolders (2014)
0.35	0.79	0.15	2.56	0.2	European countries 2010	Six and Smolders (2014)
> 0.5	–	–	–	–	Western, Eastern and Southern Europe, 2003	UNEP (2010)
1.4	–	–	–	–	West Germany, industry, 2014	Ilyin et al. (2016)
0.25	–	–	–	–	South Germany, farming, 2014	Ilyin et al. (2016)
0.19	< 0.071	0.148	–	–	Farquhar et al., 1997	UNEP (2010)
0.3	–	–	–	–	Northern Europe, 2003	UNEP (2010)
0.32	–	–	–	–	Near the European coast, 2005	OSPAR (2008)
> 0.32	–	–	–	–	Greater North Sea, 2005	OSPAR (2008)
< 0.1	–	–	–	–	Wider Atlantic, 2005	OSPAR (2008)
> 0.1	–	–	–	–	Central Atlantic & Southern coast of Greenland, 2005	OSPAR (2008)
< 0.05	–	–	–	–	Arctic Ocean, 2005	OSPAR (2008)

the Eastern Mediterranean countries (Azzi et al., 2017), 36 mg Cd per kg P₂O₅ in Europe (Six and Smolders, 2014) and 60 mg Cd per kg P₂O₅ in Germany (Schuetze et al., 2003). In Europe, the average usage of phosphate is 43 kg/(ha*a) (Grant, 2011). In addition, the Cd input via deposition was calculated over different time scales and regions. Table 5 gives an overview of several studies about Cd inputs and outputs in soil. Depending on land use and distance to urban areas, either atmospheric deposition or application of P fertilizers are the main input of Cd.

According to Six and Smolders (2014) the average total Cd input to European soils decreased to 1.3 g/(ha*a) due to low-emission process technologies, such as off-gas and waste water treatment. At the same time, the average Cd leachate output into groundwater was 2.6 g/(ha*a) causing a negative mass balance, which was caused by accumulation of previously elevated Cd input in soils, followed by its release to groundwater (Six and Smolders, 2014). In contrast to continental deposition rates of more than 0.3 g/(ha*a), Cd deposition decreases with distance from anthropogenic sources to below 0.05 g/(ha*a) in the Arctic Ocean (OSPAR, 2008) (Table 5).

Cadmium pollution in soil and groundwater is observed worldwide. Main groups are *mining, industry, waste management, agriculture, and urban areas*. An overview of documented cases of Cd contamination in soil and groundwater is given in Table 6. Example cases were selected as locations with maximum Cd levels depending on the type of pollution. Soil Cd pollution from Zn smelters, for example, can be caused by leaching of solid waste (Voglar and Lestan, 2010) or by atmospheric deposition (Bi et al., 2006), causing soil Cd concentrations of up to 344 mg/kg and 74 mg/kg, respectively. Similarly, groundwater contamination can also occur simultaneously from different sources and along different pathways at a single location, which can inhibit to identification of a significant Cd source, pathway or geogenic Cd anomaly. Consequently, other investigations, e.g., isotopic Cd fractionation (e.g., Cloquet et al., 2006; Zhu et al., 2013), are recommended.

5. Hydrochemical behavior

5.1. Basics

In aqueous solution Cd generally occurs as the divalent Cd²⁺ cation

(Smolders and Mertens, 2013). Solution pH influences Cd mobility due to metal hydrolysis, ion-pair formation, solubility of organic matter, surface charge of oxy-hydroxides, organic matter and clay edges. With increasing pH, metal retention to mineral surfaces increases via adsorption and precipitation (Appel and Ma, 2002; Buerge-Weirich et al., 2002; He et al., 2005).

Cadmium preferentially remains in solution at a pH of less than 6.5 and under oxygenated conditions (Bruemmer et al., 1994; Merkel and Sperling, 1998). The Cd²⁺ ion itself is not redox-sensitive, but it is indirectly tied to redox conditions due to the formation of redox-sensitive aqueous complexes, such as CdHS⁺, which occurs in anoxic and sulfidic conditions, and stable precipitates, such as sphalerite (ZnS), galena (PbS), and chalcopyrite (CuFeS₂), which can contain Cd as a trace element (Ditoro et al., 1990; Tabelin et al., 2018). As indicated in Fig. 3, the solubility-limiting phases of Cd are CdS, CdCO₃, and Cd(OH)₂. Depending on the Cd concentration, the stability fields of the Cd species can expand or contract (Ahmed et al., 2008; Brookins, 1986; Merkel and Sperling, 1998).

5.2. Solubility and complexation

The environmentally mobile Cd fraction consists of water-soluble Cd, unspecific adsorbed Cd, and organo-metallic complexes (Bruemmer et al., 1994; Kabata-Pendias, 2011; Loganathan et al., 2012). The adsorbed phase consists of Cd bound at mineral surfaces or bound weakly as insoluble organo-metallic complexes. This fraction is likely responsible for transient fluctuations of Cd concentrations in natural waters. The stable Cd fraction is associated with the soil matrix or bound as surface complexes in oxy-hydroxides, organic matter, silicates, sulfides, or other stable minerals (Ahmed et al., 2008; Bruemmer et al., 1994). Furthermore, Cd is the only heavy metal with affinity for the easily solubilized fraction in typical sequential solid-phase extraction protocols (e.g., Al Hussein et al., 2013; Carlson and Morrison, 1992). This fraction includes water-soluble, exchangeable and acid-soluble components, and thus, the bioavailable Cd content. Usually, this Cd is introduced artificially via deposition; whereas, Cd originated from geogenic materials is typically present in the residual insoluble fraction (Chavez et al., 2016; Liu et al., 2017).

Cadmium forms water-soluble complexes with anions, such as

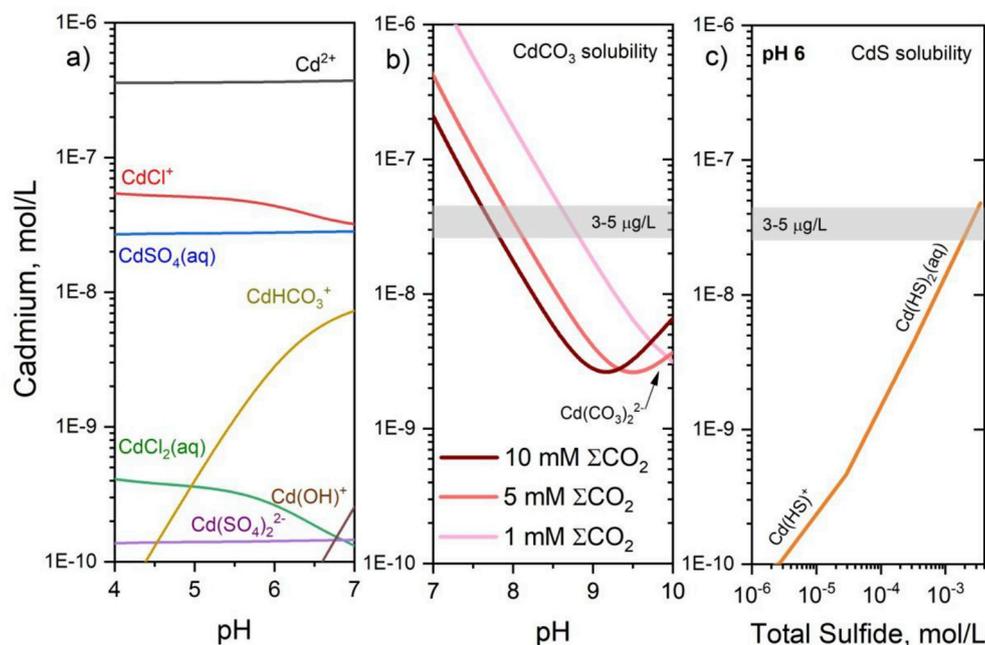


Fig. 4. Concentration versus pH diagrams showing a) Cd speciation from pH 4 to 7 for the composition Cd ($10^{-6.4}$ M), Cl (10^{-3} M), ΣCO_2 (10^{-3} M), and SO_4 (10^{-3} M). b) Otavite solubility as a function of pH and ΣCO_2 from 10^{-3} to 10^{-2} M. c) Concentration versus dissolved sulfide diagram showing the solubility of CdS at pH 6. Reference concentrations for drinking water standards are shown (3 to 5 $\mu\text{g/L}$).

Table 7
Complex forming constants of Cd (Parkhurst and Appelo, 1999).

Reaction	log K
$\text{Cd}^{2+} + \text{H}_2\text{O} = \text{CdOH}^+ + \text{H}^+$	-10.08
$\text{Cd}^{2+} + 2 \text{H}_2\text{O} = \text{Cd}(\text{OH})_2 + 2 \text{H}^+$	-20.35
$\text{Cd}^{2+} + 3 \text{H}_2\text{O} = \text{Cd}(\text{OH})_3 + 3 \text{H}^+$	-33.3
$\text{Cd}^{2+} + 4 \text{H}_2\text{O} = \text{Cd}(\text{OH})_4 + 4 \text{H}^+$	-47.35
$\text{Cd}^{2+} + \text{Cl}^- = \text{CdCl}^+$	1.98
$\text{Cd}^{2+} + 2 \text{Cl}^- = \text{CdCl}_2^0$	2.6
$\text{Cd}^{2+} + 3 \text{Cl}^- = \text{CdCl}_3^-$	2.4
$\text{Cd}^{2+} + \text{CO}_3^{2-} = \text{CdCO}_3^0$	2.9
$\text{Cd}^{2+} + 2\text{CO}_3^{2-} = \text{Cd}(\text{CO}_3)_2^{2-}$	6.4
$\text{Cd}^{2+} + \text{HCO}_3^- = \text{CdHCO}_3^+$	1.5
$\text{Cd}^{2+} + \text{SO}_4^{2-} = \text{CdSO}_4^0$	2.46
$\text{Cd}^{2+} + 2\text{SO}_4^{2-} = \text{Cd}(\text{SO}_4)_2^{2-}$	3.5
$\text{Cd}^{2+} + \text{F}^- = \text{CdF}^+$	1.1
$\text{Cd}^{2+} + 2\text{F}^- = \text{CdF}_2^0$	1.5
$2\text{Cd}^{2+} + \text{H}_2\text{O} = \text{Cd}_2\text{OH}^{3+} + \text{H}^+$	-9.39
$\text{Cd}^{2+} + \text{H}_2\text{O} + \text{Cl}^- = \text{CdOHCl}^0 + \text{H}^+$	-7.404
$\text{Cd}^{2+} + \text{NO}_3^- = \text{CdNO}_3^+$	0.4
$\text{Cd}^{2+} + \text{HS}^- = \text{CdHS}^+$	10.17
$\text{Cd}^{2+} + 2\text{HS}^- = \text{Cd}(\text{HS})_2^0$	16.53
$\text{Cd}^{2+} + 3\text{HS}^- = \text{Cd}(\text{HS})_3^-$	18.71
$\text{Cd}^{2+} + 4\text{HS}^- = \text{Cd}(\text{HS})_4^{2-}$	20.9

equilibrium constants for complex formation (Gardiner, 1974). The equilibrium constants for Cd, listed in Table 7, were taken from PHREEQC (Parkhurst and Appelo, 1999). The most stable Cd complexes are with chloride, carbonate, sulfate, and bisulfide anions as ligands (Fig. 4a). Previous studies dealing with Cd complex formation often used data from modeling or laboratory experiments conducted with high metal concentrations. Hence, such results may underestimate the mobility of heavy metals under natural conditions, especially with respect to the complexity of organic matter (Christensen et al., 1996).

Cadmium present in sulfide minerals or bound to organic material is generally released when redox conditions change from reducing to oxidizing; this change generally causes metal sulfides to dissolve and organic matter to mineralize (Martinez et al., 2002; Simpson et al., 2000; Tabelin et al., 2018). There is also a change in the amount of Cd binding forms as groundwater conditions shift from reducing to oxidizing (Zoumis et al., 2001). During oxidation of pyrite or acid volatile sulfides (AVS), like amorphous FeS, mackinawite (FeS) or greigite

(Fe_3S_4), Cd and other heavy metals are released. However, Cd is comparatively more mobile than, for example, Ni, Pb and Cu due to different mineral solubilities and sorption behavior, a stronger co-precipitation of Pb and Cu with iron sulfides, and the formation of stable Cd complexes (Caetano et al., 2003).

In floodplain soils, significant changes in the concentrations of Cd and other heavy metals affected by the concentrations of dissolved Fe, Mn, and S were observed. Fluctuations in the concentrations of these redox-sensitive elements can be caused by temporal dynamics of pH, redox potential, and DOC as daily cycles and longer-term seasonal influences (Husson, 2013; Shaheen et al., 2014).

Due to the influence of landfill leachate and forested land on the composition of seepage water, Cd remains in the soluble phase as labile complexes and also as organic complexes. In contrast, Cu, Cr, and Pb predominantly occur in association with colloids or as less mobile complexes. Complex formation of Cd and further heavy metals is controlled by ionic strength effects, the presence of ligands, and the presence of competing cations like Ca or other metals (Baun and Christensen, 2004; Beisecker et al., 2012; Christensen, 1985; Kjeldsen et al., 2002).

Carboxyl and phenolic functional groups are abundant in natural organic matter; however, less abundant functional groups like thiols and amines form stable complexes with Cd in DOM and soil organic matter (Karlsson et al., 2007). Furthermore, there is a component of Cd binding groups in organic matter that cause reduction of free Cd^{2+} (Karlsson et al., 2007). Reduced organic sulfur (DOS), which consists of thiols, is often part of the hydrophilic fraction of DOC. This fraction is more mobile than the hydrophobic fraction in the context of weak sorptive retention. In contrast to Cd, most heavy metals form complexes with the less mobile hydrophobic fraction (Kaiser and Guggenberger, 2005). Furthermore, Cd has a different selectivity than other heavy metals, because it mainly forms complexes with the neutral hydrophilic DOM fraction, while other heavy metals are bound to acidic hydrophobic and acidic hydrophilic DOM fractions (Kozyatnyk et al., 2016). At forest locations, the amount of DOS fractions and thus, of Cd in seepage water showed seasonal variations. Hydrophobic DOM is related to plant-derived material and is the most important constituent of DOS during growing seasons in summer and autumn, while the share of hydrophilic DOM related to microbial activity is more substantial in winter and spring (Kaiser and Guggenberger, 2005).

Apart from the general behavior of heavy metals that includes

bonding to high molecular weight DOM, Cd belongs to a group of metals that interact more with low molecular weight DOM (Kozyatnyk et al., 2016). Furthermore, Cd tends to be replaced by other heavy metals, because its interaction with DOM is the weakest of the heavy metals and in the case of complexation with DOM, Cd bonds at weak sorption sites, which are abundant in the small DOM size fractions (Kozyatnyk et al., 2016).

5.3. Sorption

The most important parameters that control Cd solubility and mobility in aquatic environments are pH, concentration of dissolved organic and inorganic carbon (DOC, DIC), and the presence of clay and oxy-hydroxides, such as Fe, Mn, and Al (Anderson and Christensen, 1988; Appel and Ma, 2002; Gardiner, 1974; Krishnamurti and Naidu, 2003; Lin et al., 2016; Onyatta and Huang, 2006). Cadmium concentrations in groundwater are often controlled by sorption and co-precipitation rather than by chemical equilibrium (Carrillo-Gonzalez et al., 2006). As Anderson and Christensen (1988) reported, there is a correlation between the distribution coefficient K_d of Cd and the following parameters in the order: pH > cation exchange capacity > oxy-hydroxides > clay > organic matter. Furthermore, Cd sorption decreases with increasing ionic strength due to competition with other cations, decreasing activity of Cd^{2+} , formation of ion pairs/complexes with lower sorption affinity, lower pH and changes in the electrostatic potential (Loganathan et al., 2012). Depending on temperature, Cd sorption occurs as endothermic or exothermic reactions (He et al., 2005; Karak et al., 2015).

Cadmium as a positively charged ion is adsorbed onto negatively charged mineral surfaces until the point of zero charge (PZC) is exceeded (He et al., 2005). Hence, groundwater pH is the driving factor controlling the availability of binding sites with the aquifer matrix. In Table 8, the PZC of several important minerals are listed. Sorption of Cd at pH values below the PZC is an indication of fixation via inner-sphere surface complexation or adsorption to permanent negative binding sites, e.g., at vermiculite, smectite, or organic matter surfaces (Appel and Ma, 2002). In contrast to other metals such as Pb and Cu, Cd sorption on kaolinite was inhibited at pH below 7 indicating a lower affinity for specific inner-sphere surface complexation at hydroxyl groups, $\equiv\text{SOH}$, compared to preferred ion exchange at non-specific permanent negatively charged sites, $\equiv\text{X}^-$, resulting in higher mobility of Cd (Srivastava et al., 2005). The amount and type of surface complexation is also influenced by ionic strength. At pH 6, for example, almost 70 % of Cd is adsorbed onto kaolinite in a 0.001 M solution as $\equiv\text{X}_2^- \cdot \text{Cd}^{2+}$ on the one hand, while Cd sorption mainly occurs as inner-sphere complex $\equiv\text{SOCd}^+$ decreased to 30 % in a 0.1 M solution on the other hand (Gu and Evans, 2008).

Usually, Cd fixation follows the two-site-sorption model. In the first step, Cd is adsorbed at highly energetic binding sites. The second step involves a slow, time dependent diffusion of Cd into the mineral matrix

Table 8

Point of zero charge of several sorbents (Langmuir, 1997; Stumm and Morgan, 1996).

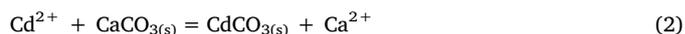
Mineral	Name	pH _{PZC}
SiO ₂	quartz	2.0
α -Fe ₂ O ₃	hematite	4.2 to 6.9
γ -Fe ₂ O ₃	maghemite	6.7
Fe ₃ O ₄	magnetite	6.5
α -FeOOH	goethite	7.8
5 Fe ₂ O ₃ · 9 H ₂ O [Fe(OH) ₃ , amorphous]	ferrihydrate	8.5
β -MnO ₂	pyrolusite	7.2
δ -MnO ₂	birnessite	2.8
kaolinite	kaolinite	4.6
Na feldspar	Na feldspar	6.8

(Carrillo-Gonzalez et al., 2006; He et al., 2005; Loganathan et al., 2012; Strobel et al., 2005). After Smolders and Mertens (2013), a general sorption equation with surface functional groups is:

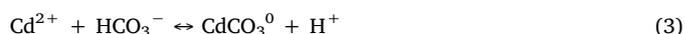


Co-precipitation is a possible mechanism of Cd fixation at high Cd concentrations in solution, whereas chemisorption is expected at low Cd concentrations (Ahmed et al., 2008).

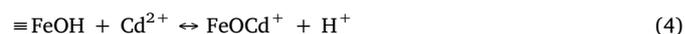
Cadmium in solution can precipitate together with calcite in a solid solution:



In this case, Cd can substitute for Ca by forming new crystals at the mineral surface. Initially, fast adsorption of Cd occurs at the calcite surface, followed by slower diffusion of Cd into the crystal lattice. After that, formation of a calcium-cadmium carbonate solid solution occurs. These processes are controlled by pH and competition with Mg^{2+} within the hydrated surface layer (Davis et al., 1987). If there is bicarbonate in the liquid phase, Cd can form complexes or precipitate as otavite (Fig. 4c) and thus, decrease the pH value in poorly buffered systems (Ahmed et al., 2008):



At silicate surfaces, Cd sorption occurs as outer-sphere surface complexation with permanent negative loadings or as inner-sphere complexation with variable loadings. At Fe-, Mn- and Al-oxide surfaces, Cd fixation occurs by ion exchange with surface OH groups (Loganathan et al., 2012). Due to inner-sphere complexation, substantial uptake of Cd occurs at surfaces of goethite (α -FeOOH), lepidocrocite (γ -FeOOH), and pyrite (FeS₂) (Parkman et al., 1999; Randall et al., 1999) as

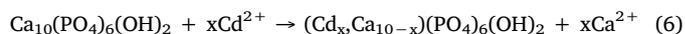


or as



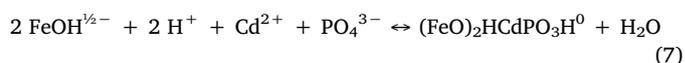
In contrast, adsorption capacity at the mackinawite (FeS) surface is lower due to surface precipitation (Parkman et al., 1999).

At phosphate mineral surfaces, Cd is bound via surface complexation or co-precipitation as a substitute for Ca^{2+} , e.g., in hydroxy-apatite (Bolan et al., 2003):



Further Cd sorption or substitution occurs in P fertilizer compounds, such as fluorapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$), tricalcium phosphate ($\text{Ca}_3(\text{PO}_4)_2$), gypsum (CaSO_4), and cadmium lead phosphate hydroxide ($(\text{CdPb}_9(\text{PO}_4)_6(\text{OH})_2)$) (Azzi et al., 2017).

However, depending on the phosphate concentration in solution, there is influence on the mobile Cd fraction. Cadmium mobility increases at low P concentrations due to pH decreases and elevated ionic strength (Grant, 2011). However, Cd can precipitate, e.g., as $\text{Cd}_3(\text{PO}_4)_2$ at high P and Cd concentrations (Grant, 2011; Xiong, 1995). In the case of low Cd concentrations, phosphate induced surface complex formation can occur due to reduced PZC or co-adsorption of Cd and phosphate as an ion pair (Grant, 2011; Wang and Xing, 2002). Phosphate can block meso- and micro-pores, e.g., on the goethite surface, which inhibits Cd diffusion into the mineral structure and thus, decreases sorptive uptake (Wang and Xing, 2002). In the case of ferrihydrite, phosphate enhances Cd sorption by the formation of stable ternary complexes at the surface (Tiberg and Gustafsson, 2016):



Sorption onto organic matter occurs with negative carboxyl or phenol groups but also via the formation of chelate complexes

(Loganathan et al., 2012). In the case of DOC, Cd sorption is pH dependent and occurs at $\text{pH} > 4$; whereas, sorption onto clay is pH-independent (Hammons et al., 1978). Depending on pH, type of organic matter and soil type, Cd sorption increases because of complexation with the negative binding sites of humic acids, which can sorb at positively charged soil surfaces. Cadmium sorption may decrease due to formation of soluble Cd-organic complexes (Bolan et al., 2003; Loganathan et al., 2012). Cadmium sorption onto organic matter decreases with increasing soil depth due to aging and subsequent degradation of organic matter (Mahara et al., 2007).

As Loganathan et al. (2012) reported, some experiments showed complete reversibility of Cd sorption onto soils and minerals, e.g., kaolinite and calcite, while others noted incomplete desorption due to Cd diffusion into the solid phase matrix, chemisorption on high-energy sites, and surface precipitation. Cadmium desorption increases with decreasing pH and concentration of organic ligands in solution, e.g., citrate, which enhances desorption due to complexation (Christensen, 1984a; Loganathan et al., 2012; Wasylenki et al., 2014). Cadmium desorption may also occur as pseudohysteresis, which means retarded desorption because higher activation energy is necessary for desorption than sorption. Apart from that, incomplete desorption processes to reach true equilibrium can occur due to slow reaction kinetics (Loganathan et al., 2012), because there is an initial rapid release of Cd from Al and Fe oxides that is followed by a slow release caused by strong binding of Cd, e.g., as ion exchange in the mineral structure of apatite (Strobel et al., 2005). Cadmium added by deposition, e.g., from sludge, fertilizers or lime is weakly bound, and therefore, it is mobilized during desorption. In contrast, natural Cd is dissolved slowly due to cation exchange (Strobel et al., 2005). In terms of sedimentary lithologies, Cd is mainly bound to finer-grained material such as silt and clay (Descourvieres et al., 2010).

5.4. Competition

Depending on the chloride concentration, formation of soluble Cd chloride complexes occurs producing species with different charges (e.g., CdCl^+ , CdCl_2^0 , CdCl_3^- , CdCl_4^{2-}), which reduce Cd sorption substantially (Herms and Brummer, 1984), more so in comparison to Cu and Pb (Caetano et al., 2003). In the presence of other ligands such as sulfate and phosphate, Cd sorption increases because of the influence of cation exchange capacity and the withdrawal of competing cations such as Ca via complexation. In the presence of other heavy metals, e.g., Fe, Cd is adsorbed only to permanent negative binding sites (Loganathan et al., 2012). As opposed to Pb and Cu, Cd sorption to perthitic feldspar and muscovite is weak via outer-sphere surface complexation; whereas, Cd is bound strongly to biotite via ion exchange or inner-sphere surface complexation (Farquhar et al., 1997). In contrast to Cd, which is often bound to the easily solubilized fraction of soils and sediments, other heavy metals like Pb and Cu are often bound firmly to the organic, sulfidic, and residual fraction and thus, have a lower mobilization potential (Eggleton and Thomas, 2004; Zwonitzer et al., 2003). Some reports conclude that the fractionation depends on parent rock composition and redoxpotential (Liu et al., 2017; Zoumis et al., 2001).

The general order of affinity for heavy metal interaction with organic matter is as follows: $\text{Cu}^{2+} > \text{Cd}^{2+} > \text{Fe}^{2+} > \text{Pb}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Mn}^{2+} > \text{Zn}^{2+}$ (Bolan et al., 2003). The adsorption of Cd at pH values above eight decreases in the presence of organic ligands due to competition between the formation of organo-metallic complexes and surface adsorption, e.g., at the surface sites of goethite (Buerge-Weirich et al., 2002).

The diffusion rate of Cd into goethite is lower than that of Zn and Ni (Bruemmer et al., 1986). Cadmium sorption to Fe and Mn oxides is retarded in presence of other cations, and it decreases due to competition in the order: $\text{Ca}^{2+} > \text{K}^+ > \text{Na}^+$ (Christensen, 1984b; Wang et al., 2010). In the pH range 3 to 8, release of unspecific adsorbed Cd occurs, which increases with increasing salinity. An increase of ionic

strength generally leads to a release of heavy metals in the order: $\text{Cd} > \text{Zn} > \text{Cu} > \text{Pb}$ (Herms and Brummer, 1984; Kuntze et al., 1984). The presence of appropriate anions also influences sorption behavior. While Cl^- and NO_3^- restrain Cd sorption due to the formation of soluble inorganic complexes, CO_3^{2-} , H_2PO_4^- and HSO_4^- enhance Cd sorption due to surface precipitation (Wang et al., 2010).

The level of mobility of heavy metals in solution in terms of varying pH and ionic strength is in the order: $\text{Cd}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Cu}^{2+} > \text{Pb}^{2+}$ (Eaton et al., 2012; Herms and Brummer, 1984; Hiller et al., 2001; Spark et al., 1995). Although Cd and Zn share similar geochemical behavior (Thornton, 1986), the limiting pH of Cd mobility is 6.5 and is thus higher than that of Zn (between 5.5 and 6.0) and other heavy metals (Ni 5.5; Co 5.5; Cu 4.5; Cr 4.0 to 4.5; Pb < 4) (Beisecker et al., 2012; Knappe et al., 2008).

Zinc is the most efficient competitor of Cd for sorption sites. The sorption affinity of heavy metals regarding soils and minerals such as kaolinite generally follows, with few exceptions and depending on the adsorbent and other factors, the Irving-Williams order: $\text{Hg}^{2+} > \text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} \approx \text{Co}^{2+} > \text{Cd}^{2+}$ (Christensen, 1987; Gu and Evans, 2008; Loganathan et al., 2012; Ozverdi and Erdem, 2006). The enhanced sorption behavior of Pb and other competing heavy metals is caused by their smaller hydrated radius, their greater affinity for most functional groups of organic substances and their higher electronegativity (Appel and Ma, 2002). However, sorption at the calcite surface followed the selectivity sequence: $\text{Cd}^{2+} > \text{Zn}^{2+} \geq \text{Mn}^{2+} > \text{Co}^{2+} > \text{Ni}^{2+} \gg \text{Ba}^{2+} = \text{Sr}^{2+}$ (Zachara et al., 1991).

In addition to Cd input, phosphate fertilizers application also decreases Cd sorption because of the competition of other components like NH_4 or Zn, which can replace Cd from binding sites (Grant, 2011).

6. Case studies of elevated Cd concentrations in soil and groundwater

6.1. Ancient Cd contamination in Japan (*itai-itai disease*)

One of the most common diseases induced by Cd exposure is the *itai-itai* (meaning “ouch-ouch”) disease as in Toyama Prefecture, Japan, in the first half of the 20th century. The Jinzu River basin was the first known area with Cd pollution (Aoshima, 2016; ATSDR, 2012; Roberts, 2014; UNEP, 2010). The Jinzu River supplies 20 km² of fields for paddy rice culture through several irrigation canals. Cadmium and other heavy metals originated in slag from a mine 30 km upstream. The expansion of mining activity in the Kamioka lead and zinc mine and smelting during the First and Second World War led to insufficient consideration for handling waste material and large amounts of Cd deposited for approximately 60 years (Aoshima, 2016).

Related to irrigation of the surrounding rice paddies, the soil and thus, the rice were contaminated with Cd until around 1960. The stream water was also used in households and as a drinking water supply. As a consequence, the *itai-itai* disease, caused by chronic Cd poisoning in combination with a low-calcium diet, became endemic among the inhabitants of the Jinzu River basin (Aoshima, 2016; ATSDR, 2012). Typical symptoms of Cd poisoning are osteoporosis and renal tubular dysfunction. In 1968, the Japanese government officially recognized the disease as being caused by Cd exposure. In an extensive survey, Cd and Zn levels in the soils were determined to be four times higher than in non-polluted samples. However, in rice samples, Cd contents were elevated 2.5 times higher than in rice from non-polluted areas. The mean Cd levels in the liver, pancreas, and thyroid of patients with the *itai-itai* disease were five times higher than reference cases. As a result, 15 km² of the upper soil layer in the contaminated area had to be replaced (Aoshima, 2016).

6.2. Elevated Cd contents in ecuadorian cacao

Cacao is the most important crop in Ecuador, with a cultivated area of nearly 500,000 ha (Chavez et al., 2016). However, Cd concentrations in Ecuadorian cacao beans are the highest when compared to other cultivation areas. They exceed the critical value of 0.6 mg Cd/kg established by European Union and thus, affect worldwide chocolate production (Chavez et al., 2015). Possible reasons for Cd accumulation in soil and plants are anthropogenic influences like contamination of irrigation water by mining activities and phosphate fertilizers, but also natural sources such as volcanic ash and continental dust (Chavez et al., 2015). Nevertheless, distribution of Cd in the soil fractions affects the bioavailability of Cd, which is an indicator of the Cd source in the water and therefore in the cacao beans (Chavez et al., 2016). Apart from pH, the plant-available Cd content of the soil is the most critical parameter controlling uptake with total Cd contents up to 2.5 mg/kg (Chavez et al., 2015). As opposed to elevated Cd in soils caused primarily by weathering of parental material (e.g., Liu et al., 2017), the primary Cd pool in Ecuadorian soils are the water soluble, exchangeable, and acid-soluble fractions indicating an anthropogenic Cd source. Furthermore, acid-soluble Cd contents bound to organic matter in the soil correlates with Cd values in the cacao beans. Therefore, the dynamics of both soil pH and organic matter have to take into account for remediation of contaminated soil (Chavez et al., 2016).

6.3. Anthropogenic influences on Cd release in northwestern Germany

Groundwater in Northwestern Germany can have Cd concentrations exceeding the German threshold value of 0.5 µg/L. The assessment of a large-scale hydrogeochemical data set made it possible to investigate different aspects of Cd mobility with respect to hydrogeology, land use, and groundwater chemistry (Kubier et al., 2019; Kubier and Pichler, 2019). The main part of the area consists of sandy and gravelly Pleistocene glacial deposits and represents both, groundwater recharge areas and catchment areas for water supply. Due to the different hydrogeological settings, groundwater chemistry was heterogeneous. Reducing groundwater occurred in tidal wetlands and lowlands, while groundwater in Pleistocene glacial deposits aquifers was predominantly oxic with decreasing bicarbonate content. Most groundwater Cd

concentrations above 0.5 µg/L were found in the western part of the area characteristic of intensive livestock farming and agriculture (Wriedt et al., 2019). Excessive nitrate input from fertilization can cause denitrification processes in groundwater. During autotrophic nitrate reduction, Cd, which is incorporated into the pyrite mineral structure during pyrite formation, can be released.

The study revealed that Cd concentrations in groundwater were mainly controlled by hydrogeochemical parameters. The amount of anthropogenic Cd input, in particular through the use of phosphate fertilizers, was of secondary importance. Instead, aquifer sediments can be enriched in Cd. Cadmium release was suggested to occur in terms of acidification and oxidation (Kubier and Pichler, 2019). In the Emsland region in the northwestern part of the area, pyrites in reducing aquifers were analyzed recently. Cadmium contents amounted to 300 mg/kg in median, 1600 mg/kg in maximum in the pyrites and, depending on pyrite content in the aquifer, 2.6 mg/kg in sediment (Houben et al., 2017). It is probable that these values are typical for glacial deposits, which are representative of larger parts of Northern Germany (Houben et al., 2017).

Besides influences from agriculture, elevated Cd concentrations were also related to woodland indicating Cd release from forest soils that are an effective sink for atmospherically deposited pollutants. Low pH and high concentrations of dissolved organic carbon enhance Cd transport into groundwater (Kubier et al., 2019).

7. Summary and conclusions

Cadmium is a heavy metal with specific hydrochemical characteristics causing its potential mobility in groundwater. It remains in solution at near neutral pH (< 6.5) in contrast to the typical fixation of other heavy metals. Cadmium sorption is weak in competitive situations. Cadmium tends to form stable dissolved complexes with both inorganic and organic ligands, which inhibit sorption and precipitation. In particular, its behavior with DOM can cause Cd mobility and provides a unique hydrogeochemical position for Cd relative to other heavy metals such as Zn, Ni, and Cu. Cadmium can replace Ca in the context of mineral formation and co-precipitation, and this is relevant regarding absorption into the human body.

Cadmium accumulation in soils can occur, where Cd mobility is

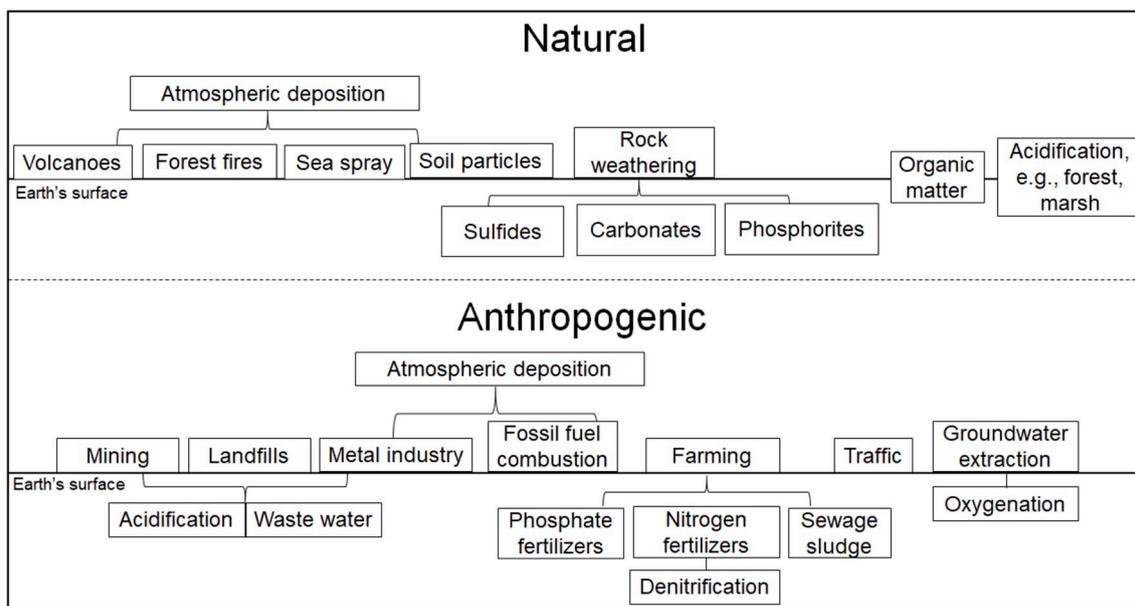


Fig. 5. Cadmium sources and influences on Cd release into groundwater.

inhibited, e.g., Cd can precipitate under anoxic conditions; Cd sorption is accompanied by enrichment of organic matter or clay. Anthropogenic sources of Cd in soils are direct input of waste material from mining and industry as well as agricultural application, e.g., as sewage sludge and phosphate fertilizers. Transport of Cd from soil into groundwater depends on hydrogeochemical factors regulating Cd mobility. Besides direct input of waste water, e.g., as runoff and leakage, or atmospheric deposition, Cd leaching from waste material, landfills, and fertilization only can happen where Cd release is promoted by replacement, formation of soluble complexes, acidification, or oxidation. Mining wastes usually go together with oxidation reactions and subsequently strongly decreased pH. Excessive N fertilization also decreases soil pH, which is associated with increased ionic strength and enhanced Cd mobility. Summarizing data on the number of soil and groundwater systems with Cd problems cannot be provided, because there exist only case studies dealing with specific contamination issues (Table 6). Further information on the amount of impacted areas and Cd fluxes from selected sites into groundwater are not available. Besides, the range and partially absence of national threshold values for Cd in soil and groundwater makes it difficult to identify impacted areas on an international scale.

An overview of the most relevant Cd sources and influences on Cd release into soil and groundwater is given in Fig. 5. Atmospheric Cd deposition can be caused by anthropogenic and natural sources. Many reports dealing with Cd deposition consider higher estimations of Cd input from anthropogenic sources. More recent studies, however, calculated a natural amount of Cd deposition exceeding the anthropogenic amount, especially with respect to increasing off-gas cleanings. Consequently, atmospheric deposition of natural sources accounts 93 % of Cd emissions, especially from soil particles and wild fires (Table 1). Natural Cd release from weathering occurs in sulfidic and carbonatic systems due to Cd accumulation in sulfides, e.g., pyrite, and exchange of Ca in carbonates. The resulting Cd concentrations in groundwater depend on groundwater milieu. Cadmium release from calcareous systems and subsequent transport in groundwater is only possible in acidic waters (Fig. 1). Acidification can be related to natural influences, e.g., forest and marsh, but also caused by anthropogenic input, e.g., acid mine drainage. Anthropogenic Cd input from phosphate fertilizers into soil, for example, can exceed atmospheric deposition (Table 5). Drivers for Cd mobility are soil texture, content of organic matter, land use, and hydrochemical milieu. Soils with increasing amount of fine-grained material, organic matter, swamp and forest as land use as well as moderate pH and redox can contain elevated Cd contents. Cadmium leachate is controlled by quantity and quality of seepage; organic and inorganic ligands promote mobility of Cd bound in soluble complexes. In soils that are sandy and poor in organic matter feature low sorption capacity, Cd transport into groundwater, and a subsequent reduction of previously accumulated Cd can occur.

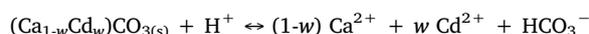
Cadmium pollution of soil and groundwater is a worldwide problem that affects resources for food and drinking water mainly in Asia and Africa. Further efforts to clean waste water, inhibit leachate of contaminated material, e.g., in landfills and mines, and reduce use of Cd contaminated phosphate fertilizers are necessary to decrease anthropogenic Cd output. As Fig. 2 indicates, the amount of Cd input into soil as an impurity in phosphate fertilizers depends on the origin. Thus, changes in fertilizer management do not consequently result in decreasing crop yields.

Depending on time scale, geographic position and land use, there are different scenarios for the quantity of Cd input into groundwater and the amounts of various sources, mainly deposition and P fertilizers. Apart from that, anthropogenic Cd input occurred in some areas in the past, which led to delayed Cd leaching into groundwater from soil and aquifer solids. There are other anthropogenic influences, e.g., fertilization and acidification, altering the hydrogeochemistry and thus enhancing the release of natural occurring Cd. The outline of these processes can be abstracted as the following scenarios of Cd release.

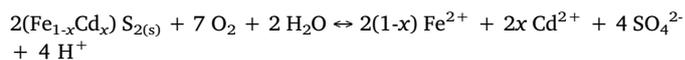
- (1) "Natural origin and release of Cd." Elevated Cd concentrations in groundwater are linked to rock types with increased Cd contents, e.g., sulfides. Cadmium is released in the context of weathering or naturally caused acidification.
- (2) "Anthropogenically induced release of naturally occurring Cd." In this case, Cd originates from natural sources, but its release is caused by anthropogenic influences, e.g., atmospheric deposition or acidification linked to denitrification of nitrogen fertilizers.
- (3) "Anthropogenic Cd input." According to the most likely reason for elevated Cd in groundwater, Cd originated from P fertilizers and atmospheric deposition. Further entries are linked to industrial activities and traffic.

In case of (1) and (2), Cd originates mainly from sorption or co-/precipitation in association with sulfide, carbonate and phosphate minerals. That is why Cd release occurs during the dissolution of these minerals according to the following three model processes (a) to (c).

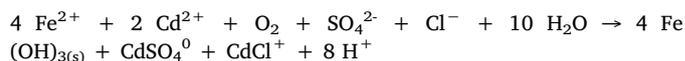
(a) Calcite dissolution (under acidic conditions) (equation (8)):



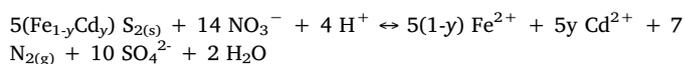
(b) Oxidation of sulfide minerals, e.g., pyrite (under oxic conditions) (equation (9)):



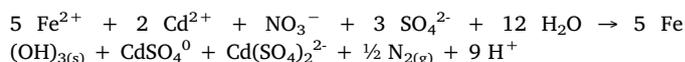
Possible subsequent reaction (equation (10)):



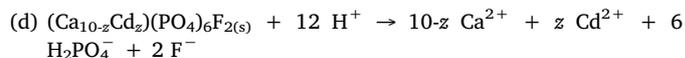
(c) Chemolithotrophic denitrification (under anoxic conditions) (equation (11)):



Possible subsequent reaction (equation (12)):



In case of (3), Cd originates from direct entry or dissolution of phosphate fertilizers. As a result, Cd is released, e.g., from fluorapatite, using soil acids, shown in reaction (d) (equation (13)):



Declaration of interest

The authors certify that there is no actual or potential conflict of interest in relation to this article.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <https://doi.org/10.1016/j.apgeochem.2019.104388>.

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