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Cadmium in groundwater — A synopsis based on a large hydrogeochemical data set

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HIGHLIGHTS

- Elevated cadmium concentrations occurred in oxic and nitrate reducing groundwater.
- Cadmium mobility was often linked to agricultural nitrate and pyrite oxidation.
- The ruling factors on cadmium mobility prevailed over the amount of Cd input.

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1. Introduction

Cadmium (Cd) is one of the most toxic and mobile elements in the environment (Alloway and Jackson, 1991; Nies, 1999; Nies, 2003). It

bioaccumulates in several organs (Hajeb et al., 2014; Pan et al., 2010) and is classified as carcinogenic (UNEP, 2010), which led to the establishment of a maximum contamination level (MCL) of 5 µg/L for Cd in drinking water in the United States and the European Union (UNEP, 2010). Considering its ecotoxicity, Cd was also listed as a priority hazardous substance in the European Water Framework Directive (WFD) (EC, 2000) and as a result, the German threshold value for Cd in groundwater was set to 0.5 µg/L (GrwV, 2017). Following implementation of the WFD criteria (EC, 2000), the assessment of groundwater bodies in Northern Germany, resulted in a classification of “poor chemical status” for 9 out of 123 groundwater bodies, due to elevated Cd concentrations.

Several reports identified agriculture and combustion emissions as the main anthropogenic Cd sources to the environment. Those pathways of Cd contamination to soil and groundwater were extensively investigated in the United States, Canada, Great Britain, Norway, Sweden, Finland, Denmark, Germany, Australia, and New Zealand (Bigalke et al., 2017; Grant, 2011; Taylor et al., 2016). Prominent anthropogenic Cd sources are phosphate fertilizers, sewage sludge, landfills, traffic, industrial and mining waste (Bigalke et al., 2017; Merkel and Sperling, 1998; Mirlean and Roisenberg, 2006; Sprynskyy et al., 2011). Depending on the origin of phosphate rocks, Cd in phosphate fertilizers can exceed 200 mg/kg P₂O₅ (Grant, 2011). The occurrence and behavior of Cd in groundwater has been studied 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; Pan et al., 2010; Wang et al., 2010) and environmental remediation (e.g., Khan et al., 2017; Zwonitzer et al., 2003). Most studies focused on specific subjects, such as local Cd pollution (e.g., Karak et al., 2015; Kozyatnyk et al., 2016), point source contamination (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). However, there is a lack of large-scale studies to investigate the geochemical behavior of Cd with respect to the influence of hydrogeochemical factors, such as changing redox conditions or changes in buffer capacity, which in turn greatly affect the retention capacity of the aquifer matrix.

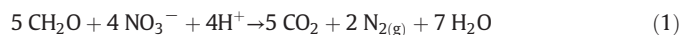
The goal of this study was to provide a better understanding about the source, transport and fate of Cd in groundwater through evaluation of a large hydrogeochemical data set. This was deemed a necessary step because natural processes cannot always be deduced from experimental studies alone. In large hydrogeochemical data sets, the general hydrogeochemical composition dominates over local anomalies, geogenic as well as anthropogenic. The evaluation was conducted by combining the general characterization of Cd chemistry and Cd interaction with changing groundwater redox state, with geospatial and statistical analyses of Cd concentrations in groundwater wells in Northern Germany in relation to hydrogeology and land use. That region was considered an appropriate model because of its variety in lithology, land use, and publicly accessible data on groundwater quality. Combining data analyses and water classification allowed identification of the main mechanisms that result in elevated Cd concentrations. All considered parameters were either directly related to Cd mobility or indirectly indicated Cd mobilizing processes. Therefore, the results can be used to predict hydrogeochemical conditions that lead to Cd release and mobility in aquifers; even without regular or extensive Cd analyses. In terms of risk assessment, Cd concentrations exceeding background levels or threshold values can be predicted by anticipating pertinent changes in groundwater chemistry.

2. Cadmium chemistry and groundwater redox state

Cadmium is not considered to be redox sensitive, e.g., it occurs in aqueous solution more or less only in its Cd²⁺ redox state (Smolders and Mertens, 2013), although changing redox conditions control Cd release and retention in aquifers. It is highly mobile in oxic and acidic waters. Cadmium can form soluble organic and inorganic complexes,

e.g., CdCl⁺, CdCl₂⁰, CdSO₄⁰, Cd(CO₃)₂²⁻, and CdOH⁺, which decrease Cd sorption under anoxic and more alkaline conditions (Carrillo-Gonzalez et al., 2006). To evaluate Cd mobility it is necessary to consider the different redox environments in an aquifer, specifically oxic, suboxic, nitrate reducing, Mn(IV) reducing, Fe(III) reducing, sulfate reducing, and methanogenic, which depend on the chemical composition of groundwater, microbially catalyzed reduction processes, and the behavior of the dominant redox couples (Borch et al., 2010). Hence, in addition to the sole use of redox potential and pH, microbially induced redox processes in groundwater can provide indicator parameters for conditions that affect Cd mobility (Jorgensen et al., 2009). Iron and manganese, and their minerals play an important role in environmental biogeochemistry regarding sorption, co-precipitation, and electron exchange, making them ideal proxies to monitor redox processes and the mobility of trace metals such as Cd (Borch et al., 2010). Table 1 shows an overview of the redox categories and the threshold concentrations of redox indicator parameters adopted from McMahon and Chapelle (2008) and Riedel and Kübeck (2018).

Cadmium can adsorb to or co-precipitate with a variety of minerals, such as sulfides, oxides, or carbonates when Eh decreases, pH increases or competitors such as Zn occur in solution (Carrillo-Gonzalez et al., 2006). Those parameters are influenced by natural processes like seasonal variations and anthropogenic activity, e.g., fertilization, landfill leachates and combustion emissions. Mollema et al. (2015) found that extensive groundwater abstraction induced pyrite oxidation, which in conjunction with fertilization enhanced Cd release from sulfides and clay minerals in the Netherlands. Generally, fertilization and denitrification caused by agricultural activities have frequently been reported to increase trace metal mobilization during the oxidation of reducing aquifers, e.g., in the USA (Böhlke, 2002; Hudak, 2018; Nolan and Weber, 2015), Germany (Banning et al., 2013; Cremer, 2002; Riedel and Kübeck, 2018; Wisotzky et al., 2018), Denmark (Larsen and Postma, 1997; Postma et al., 1991), the Netherlands (Zhang et al., 2009), Spain (Olias et al., 2008), Turkey (Keskin, 2010), and Japan (Hayakawa et al., 2013). Agricultural activities can be traced as plumes of nitrate and total dissolved ions in groundwater (Postma et al., 1991), particularly in the presence of oxygen. However, once oxygen is consumed, nitrate reduction commences, causing the demise of the plume. Rivett et al. (2008) gave an overview on the role of denitrification in microbial processes in aquifers, its origin, and mechanisms influencing denitrification, e.g., pH, O₂ concentration and pore space. Nitrate reduction is commonly subdivided into autotrophic and heterotrophic pathways when reported for anoxic groundwater environments (Jorgensen et al., 2009; Postma et al., 1991; Riedel and Kübeck, 2018). According to Postma et al. (1991) and Riedel and Kübeck (2018), heterotrophic nitrate reduction appears to be the most common nitrate removal pathway in groundwater (Eq. (1)):

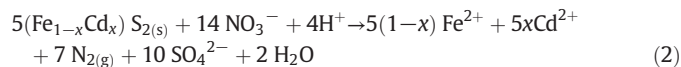


However, microbially mediated autotrophic nitrate reduction, including oxidation of sulfur minerals, such as pyrite, galena, and chalcopyrite, dominates in some aquifers. Sulfide minerals are essential constituents of reduced systems and are thus important sources and

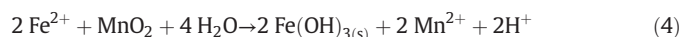
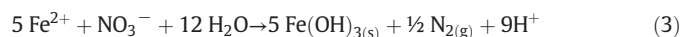
Table 1
Threshold concentrations of redox indicator parameters (McMahon and Chapelle, 2008; Riedel and Kübeck, 2018). All concentrations are given in mg/L.

Redox category	O ₂	Mn	Fe	NO ₃ ⁻	SO ₄ ²⁻
1. Oxic	>0.5	<0.05	<0.1	-	-
2. Suboxic	<0.5	<0.05	<0.1	<2.2	-
3. Nitrate reducing (heterotrophic)	<0.5	<0.05	<0.1	>2.2	-
4. Nitrate reducing (autotrophic)	<0.5	-	>0.1	>2.2	>0.5
5. Mn(IV) reducing	<0.5	> 0.05	<0.1	<2.2	-
6. Fe(III) + sulfate reducing	<0.5	-	>0.1	<2.2	-
Methanogenesis	<0.5	-	>0.1	<2.2	<0.5

sinks for Cd (Bostick et al., 2000). According to Thornton (1986), the Cd concentration can be up to 20 g/kg in sphalerite (ZnS), 3 g/kg in galena (PbS), and 110 mg/kg in chalcopyrite (CuFeS₂), while pyrite (FeS₂) can contain up to 52 mg/kg Cd (Abraitis et al., 2004). In pyrites in North-western Germany, Houben et al. (2017) recently found Cd contents up to 1600 mg/kg. During dissolution of pyrite (Eq. (2)), trace metals, which were incorporated into the pyrite mineral structure during pyrite formation, such as Cd, Zn, As, Ni, and Cu (Böhlke, 2002), can be released:



In contrast to the heterotrophic reduction, an oxidation of iron and subsequent release of protons may occur in the presence of excessive nitrate (Riedel and Kübeck, 2018) or other oxidation agents (Larsen and Postma, 1997) (Eqs. (3) and (4)):



The presence of pyrite and organic matter in sediments are considered the main variables for redox front progression. Thus, pyrite oxidation was thought to be an important pathway to remove nitrate from groundwater in terms of protecting water quality in fertilizer-impacted aquifers (Postma et al., 1991). Redox conditions that lead to nitrate reduction coupled with pyrite oxidation have been linked to the release of sulfate, iron, and toxic trace elements (Böhlke, 2002). This is particularly relevant for Cd because it is released due to changing redox conditions, although Cd itself is not redox-sensitive.

3. Materials and methods

3.1. Study area and regional hydrogeology

The study area comprises the German federal states of Lower Saxony and Bremen in Northern Germany (Fig. 1) totaling an area of almost 48,000 km² (BKG, 2018). The northern part, which is the main part of the study area, consists of the Cenozoic North German Plain. The southern part consists of a Paleozoic and Mesozoic mountainous region, which belongs to the Central German Uplands (Elbracht et al., 2016). The consolidated rocks in the uplands rise to 1000 m above sea level.

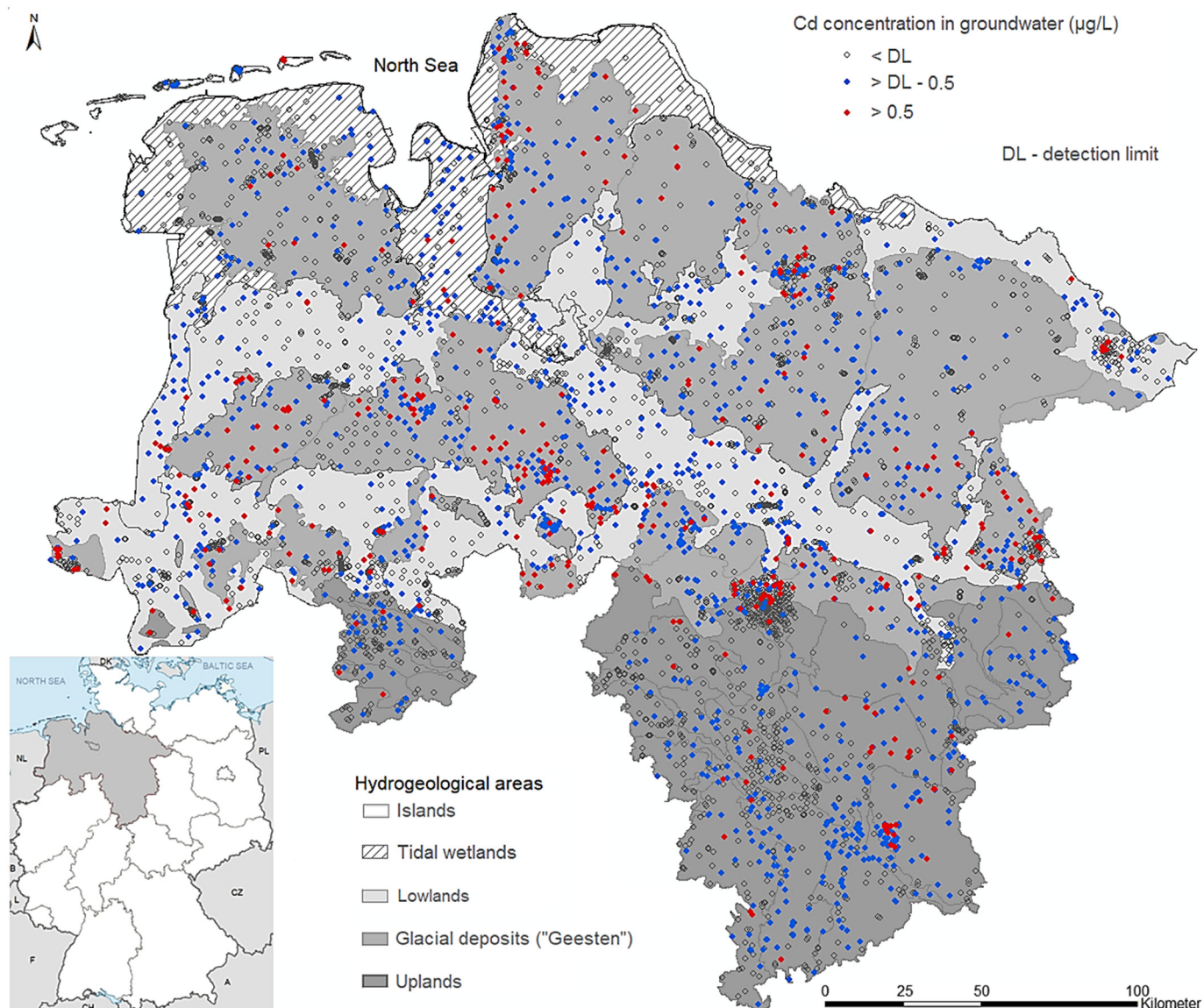


Fig. 1. Cadmium concentrations in shallow groundwater of the study area. The small figure gives the location of the study area in Germany.

The highest elevation, the Harz mountains, consist of Paleozoic rocks, while the aquifers of the fault-block mountains north of the Harz mountains consist of Mesozoic limestones and sandstones, partly covered by Pleistocene deposits (Wendland et al., 2008). In this study, the uplands were considered as one hydrogeological unit, while the North German Plain was divided into four different hydrogeological units: islands, tidal wetlands, lowlands, and Pleistocene glacial deposits, called "Geesten" (Fig. 1). Both, Holocene islands and tidal wetlands, are associated with the North Sea. Pleistocene lowlands developed along rivers and creeks. The Geesten mainly consist of sand and gravel and represent both, groundwater recharge areas and catchment areas for water supply (Elbracht et al., 2016). The landscape of the Northern German plain is nearly flat and covered mostly by Pleistocene sediments with increasing thickness to the north, particularly in deep sub-glacial channels of Elsterian age (Ehlers et al., 1984).

Due to the different hydrogeological settings, groundwater chemistry is heterogeneous within the study area. Groundwater in the islands is predominantly of the bicarbonate predominated alkaline-earth type, while groundwater in the tidal wetlands is mainly iron- and sulfate reducing and belongs to alkaline waters with dominant sulfate and chloride contents. Groundwater in the lowlands and the Geesten is mainly of the alkaline-earth type with predominant sulfate and chloride contents. Groundwater in the uplands is oxidic, bicarbonate predominated and of the bicarbonatic-sulfatic alkaline-earth type.

The main land use in the study area is farmland (46%), followed by woodland (22%, where 7% are deciduous woods, 13% are coniferous woods, and 2% are mixed woodlands), grassland (21%), and urban areas (7%). (BKG, 2018). Further specification of land use according to the hydrogeological units was not considered.

3.2. Data

The data set was compiled from the federal states database maintained by the *Niedersächsischer Landesbetrieb für Wasserwirtschaft, Küsten- und Naturschutz* (NLWKN), the *Landesamt für Bergbau, Energie und Geologie* (LBEG), the *Senator für Umwelt, Bau und Verkehr* (SUBV) of Bremen and the administration of the city of Hannover representing the water management agencies and geological surveys of Lower Saxony and Bremen. The data set included >24,000 samples from 6300 sampling locations, including observation wells, production wells, and springs. The data was collected by the various state and federal agencies as part of a continuous groundwater quality monitoring program and included samples taken between 1976 and December 2015. Half of the sampling locations were sampled once, while 2200 sampling locations were sampled at least four times.

Similar to Wagner et al. (2011) who described the evaluation of background values for several trace elements in shallow groundwater units in Germany, the most recent data were chosen for each sampling location to avoid a potential bias towards the more frequently sampled locations. Furthermore, the evaluation of recent data ensures lower Cd detection limits, down to 0.002 µg/L, which was considered advantageous rather than conversion of time series to median values.

The data set included in situ parameters, such as pH, redox potential (Eh(SHE)), oxygen, and electric conductivity (EC), and the following main components and trace elements: Na, K, Ca, Mg, SO₄, Cl, HCO₃, NO₃, NH₄, Fe, Mn, Ag, Al, As, B, Ba, Bi, Br, Cd, Co, Cr, Cu, dissolved organic carbon (DOC), F, Hg, Li, Mo, Ni, NO₂, Pb, PO₄, Sb, Se, SiO₂, Sn, Sr, Ti, U, V, and Zn. The following indicator parameters for anthropogenic influences were also considered: the sum of polycyclic aromatic hydrocarbons (PAH), tri- and tetrachlorethene, and selected pesticides (atrazine, bentazone, desethylatrazine, 2,6-dichlorbenzamide).

Values below the detection limit were replaced by half of the detection limit assuming a normal distribution of values below the detection limit. Analyses with incorrect ion balance (exceeding 10%) and a Cd detection limit ≥1 µg/L were discarded in order to avoid values of half the detection limit that meet the German threshold value of 0.5 µg/L for Cd

in groundwater (GrwV, 2017). Consequently, 4594 groundwater analyses from the data set were exploitable for statistical analysis.

3.3. Statistical analysis

In contrast to other studies examining large data sets, multivariate statistical methods, such as principal component analysis (PCA), were not applied in order to avoid misleading results due to missing postulations for the data set, e.g., multivariate normal distribution. Instead, Spearman rank correlation (Spearman, 1904) was used to consider 34 chemical and physicochemical parameters. The probability of Cd concentrations exceeding the threshold of 0.5 µg/L (GrwV, 2017) was compared across a range of reported values for pH, redox potential (Eh), and electric conductivity (EC) using probability density functions. The range of values was divided into equally sized, smaller ranges, followed by the calculation of the Cd probability for each subrange. Statistical calculations were done with the computer code SPSS.

The individual samples were categorized according to hydrogeological units and land use units using ArcGIS (ESRI, 2018) to reveal possible effects on Cd concentrations in groundwater. The influence of redox processes on the occurrence of Cd in groundwater was investigated through the definition of redox classes in compliance with the redox framework, which is based on threshold concentrations of indicator parameters for certain redox conditions, e.g., *oxidic, suboxidic, manganese-, nitrate-, iron- and sulfate reducing* (Table 1) (McMahon and Chapelle, 2008; Riedel and Kübeck, 2018). Due to the possibility that groundwaters with different redox states could have mixed during sampling, some samples did not fit the scheme in Table 1 leading to the definition of an additional "mixed" type. Furthermore, it has to be taken into account that Eh values were measured in the field (DIN 38404-C6:1984-05, 1984), which display mixed potentials and must not necessarily correspond to the redox classes in Table 1.

A straightforward classification of samples was applied to determine general characteristics of the groundwater composition. With respect to the abundance of the major elements in the Piper diagram, analyses could be assigned to seven water types, A to G, according to Furtak and Langguth (1967). The usual illustration of Piper diagrams disregard nitrate as a main anion. In our study, strongly elevated nitrate concentrations of up to 400 mg/L (Wriedt et al., 2019) necessitated the addition of nitrate to the amount of chloride and sulfate (Piper diagram in Fig. 6). In order to combine the classification and the range of Cd concentrations in groundwater, boxplots were generated and grouped into the seven water types using SPSS.

It was necessary to apply another water type classification in order to get information about groundwater origin, anthropogenic overprint, and conditions for Cd release/solubility. For this purpose, a scheme was tailored to available data, as well as geological and hydrogeochemical features of the study area. The so called "influence types" of groundwater composition divided the groundwater in the study area into five types and further subtypes depending on the occurrence of indicator parameters. Based on the assessment scheme according to LfU (2015), our procedure considered pollutants, acidification, agricultural, and diverse influences (Fig. 2). Some adaptation was necessary to account for the relatively larger presence of moors in the study area (compared to the rest of central Europe) and their influence on hydrogeochemistry, as well as the marine influences from the North Sea (footnotes in Fig. 2). The following parameters were utilized: pollutants (step 1), pesticides (step 2), parameters indicating acidification (step 3), nitrogen compounds (step 4), and parameters indicating diverse influences (step 5). In case of a negative decision at any step, a groundwater sample was treated as "without anthropogenic influence" or "with barely anthropogenic influence" (type 0).

The nonparametric Kruskal-Wallis test was used to test for significant differences among the data groups.

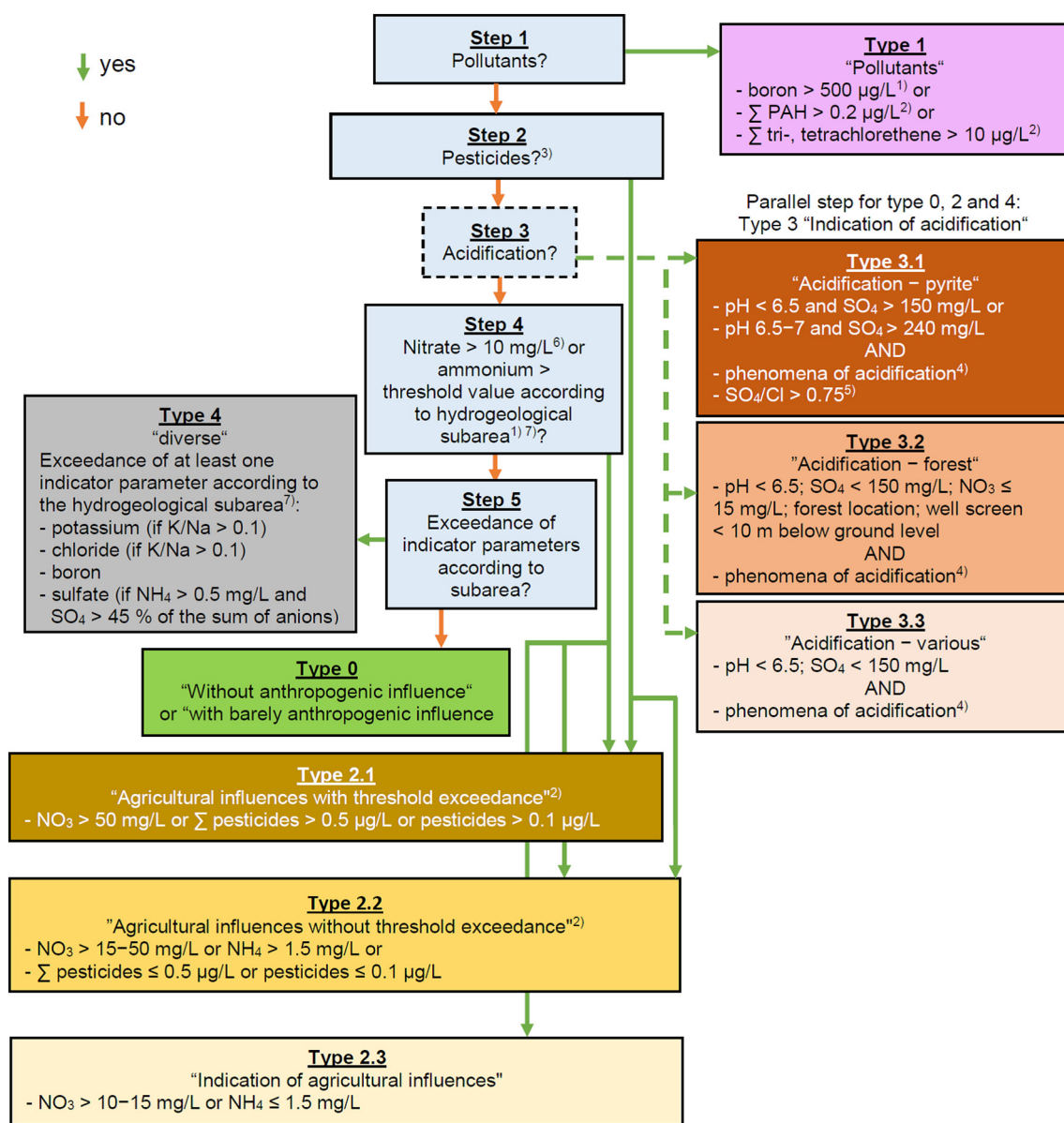


Fig. 2. Flowchart of the assessment scheme for the classification of influence types in groundwater (adapted after LfU, 2015). 1) In the hydrogeological areas of the North Sea islands, tidelands and tidal wetlands, and, in case of ammonium linked to moors, geogenic induced elevated contents are also accepted. 2) Insignificance threshold value for groundwater (LAWA, 2016). 3) Exemplary chosen pesticides: atrazine, bentazone, desethylatrazine, and 2,6-dichlorbenzamide. 4) Criteria for the assessment of acidification after Merten (2003). 5) Empirical value for the identification of pyrite oxidation via denitrification (Cremer, 2015). 6) Exclusion criterion after Hinsby et al. (2008). 7) Threshold values correspond to 90th percentile of the "hydrogeochemical units" (BGR and SGD, 2014) that are representative for the hydrogeological subareas in Lower Saxony and Bremen.

4. Results and discussion

4.1. Occurrence of Cd in groundwater

The mean and median Cd concentrations of all samples ($N = 4594$) were 0.23 µg/L and 0.08 µg/L, respectively. Two thirds of the Cd analyses were below the detection limit. There were 363 analyses exceeding the Cd threshold of 0.5 µg/L (8% of 4594 analyses). Most samples (219 out of 363) exceeding 0.5 µg/L were located in the Geesten area (Fig. 1) where the main land use is farmland (42% of 363 sampling locations) and woodland (33%). The samples were mainly taken from depths <15 m and Cd concentrations above 0.5 µg/L were generally found at sampling locations of <10 m. Those locations showed a higher vulnerability due to shallow depths and were missing a low permeability confining layer (LBEG, 1982; LBEG, 2004). The annual groundwater recharge rates at those locations were 150 to 250 mm (LBEG, 2008).

There was no considerable difference between the median Cd concentrations in each of the land use units (Table 2). On the other hand, the 90th percentile of Cd was elevated in those samples collected in the farmland and woodland units (Table 2). The Kruskal-Wallis test revealed a significant difference among the land use units ($X^2(8) = 141.212$, $p = 0.0001$).

Table 2
Cadmium concentrations of the sampling locations dependent on the main land use units.

Land use	N	Cd median (µg/L)	Cd 90th percentile (µg/L)
Woodland	1389	0.10	0.45
Farmland	1402	0.05	0.57
Grassland	930	0.05	0.25
Urban area	680	0.10	0.35

Table 3
Spearman's rank correlation coefficients for Cd.

Parameter	Correlation coefficient	Parameter	Correlation coefficient
Sb	0.66	Cr	0.36
Pb	0.62	Se	0.33
Cu	0.59	O ₂	0.26
Co	0.52	SiO ₂	-0.41
Tl	0.52	PO ₄	-0.38
Ni	0.51	HCO ₃	-0.23
Zn	0.49	Fe	-0.22
Hg	0.44	NH ₄	-0.22
U	0.39	pH	-0.2
NO ₃	0.37		

Spearman's rank correlation coefficients (two-tailed significance at the 0.01 level) for Cd and the parameters are listed in Table 3. The strongest correlation was observed between Cd and antimony (Sb), followed by lead (Pb), a range of other trace metals, and nitrate. Negative correlations were found between Cd and parameters indicating reducing or alkaline conditions. Correlation with pH was also negative.

Despite the large number of analyses, correlations in the data set were found suggesting a general behavior of Cd and other parameters. The significant correlation with other trace metals, such as Sb, Pb, Cu, and Ni, suggests a similar mobilization behavior of these elements controlled by either changes in pH, changes in redox conditions or anthropogenic input. Considerable amounts of these trace metals are often included in pyrite (Abraitis et al., 2004; Lazareva and Pichler, 2007). Although Larsen and Postma (1997) observed a similar behavior between Ni and Mn during pyrite oxidation, there was not such a correlation between Mn and Cd as it was observed between Ni and Cd in the data set (Table 3), which can be a result of the higher redox-sensitivity of Mn. Missing elevated sulfate concentrations, which are coupled to pyrite dissolution, can be masked by the ubiquitous occurrence of sulfate in groundwater in the study area. This is caused by anthropogenic input, such as atmospheric deposition of combustion emissions and fertilization as well as the water-rock equilibrium of sulfate minerals. Furthermore, the positive correlation with nitrate is an indicator of agricultural influence on the occurrence of Cd in groundwater. The negative correlation of Cd with parameters indicating alkaline (HCO₃) or reducing conditions (Fe, NH₄) can be explained by the preferential conditions of Cd solubility. Phosphate is strongly adsorbed by sediments that are rich in clay and metal oxides in oxic, acidic water (Domagalski and Johnson, 2012) resulting in a negative correlation with Cd, which is much less adsorbed and thus remains preferentially in solution. The correlation analysis indicates that Cd mobility is not connected to conditions of weathering of silicate bearing minerals (HCO₃, SiO₂) (Prasanna et al., 2010).

The pH is known to be a major factor influencing Cd mobility (Anderson and Christensen, 1988). While Cd is immobile in oxide and carbonate minerals under alkaline and neutral conditions, it can become mobile in acidic waters, due to dissolution of its host mineral. Thus far, there has been no large-scale study that investigated the behavior of Cd in groundwater with respect to pH. The groundwaters in the study area provided a range of pH values between 3.5 and 8.5, which is caused by the abundance of different natural areas and land use units influencing the groundwater composition. The occurrence of Cd above 0.5 µg/L was mostly found at a narrow range of pH values between 4.5 and 5.5. Thus, a pH-controlled Cd solubility was not likely for a major part of the studied groundwaters because the highest frequency of observations above the detection limit was observed at a pH around 7 (Fig. 3). Groundwater samples with Cd concentrations exceeding the threshold value of 0.5 µg/L, however, occurred in a pH range where Cd sorption is inhibited (Spark et al., 1995). This was particularly in the Geesten areas, which are characterized by fast water infiltration and hence lower bicarbonate concentrations resulting in a limited buffer capacity. Land use in the Geesten also affected Cd mobility. Forest soils, for

example, that mainly occurred in the Geesten showed elevated concentrations in organic matter. However, there was no correlation between Cd and DOC in the data set, although Cd-organic complexes are considered very stable (Krishnamurti and Naidu, 2003). One explanation of this lack of correlation could be dissolved organic matter can reduce Cd sorption at lower pH due to competition of organic matter and protons with Cd for sorption sites (Sprynskyy et al., 2011), hence, adding Cd and removing organic matter from groundwater. On the other hand, Cd becomes less mobile at a pH above 6, due to sorption by minerals such as Fe(III) hydrous oxide and precipitation as CdCO₃ and Cd(OH)₂ (Carrillo-Gonzalez et al., 2006 #35), but this occurred mainly in the tidal wetlands, lowlands, and uplands hydrogeological units. In contrast, woodland and farmland induced acidification can lower the pH of groundwater, e.g., due to nitrification of NH₄ derived from fertilizers (Mollema et al., 2015), and thus keep Cd in solution.

Although Cd itself is not redox-sensitive, the redox potential (Eh) can control Cd mobility. When groundwater systems change from anoxic to oxic, Cd can get released from sulfide minerals (e.g., Carrillo-Gonzalez et al., 2006; Jones and Pichler, 2007; Price and Pichler, 2006). Therefore, groundwaters with different Cd concentrations were analyzed with respect to Eh, which occurred between -280 mV and 740 mV in our study area. Elevated Cd concentrations were found at an Eh range between 450 mV to 600 mV, while the highest probability of Cd detection for the complete data set was at an Eh between 50 mV and 250 mV (Fig. 4). The elevated Cd concentrations primarily occurred in groundwater in the Geesten area and there can be explained by the presence of acidic and oxic groundwater. A similar case of acidifying redox reactions causing mobilization of heavy metals was reported by Mollema et al. (2015).

The electric conductivity (EC) can be used as a proxy for mineral weathering (Riedel and Kübeck, 2018) but also as an indicator for salt-water intrusion and anthropogenic influences, such as drainage from landfills, wastewater discharge, agricultural and atmospheric sources (Böhlke, 2002; Gemitzi, 2012; Postma et al., 1991; Zhang et al., 2009). Other than pH and Eh, the EC did not correlate with Cd and therefore, the sum of reactions resulting in the EC did not provide an indication about the origin of Cd. The highest frequency of all Cd analyses above the detection limit and Cd concentrations above 0.5 µg/L occurred in an EC range between 300 µS/cm and 600 µS/cm.

4.2. Biogeochemical aspects of Cd mobility in groundwater

Cadmium concentrations are strongly coupled to the redox conditions in groundwater in our study area. Of the samples, 2875 (72%) could be assigned to one of the seven redox categories (Fig. 5). Iron (III) and sulfate reducing conditions were most common (N = 1661), followed by oxic groundwaters (N = 985). The highest median Cd concentration of 0.19 µg/L was observed under autotrophic nitrate reducing conditions. Furthermore, most Cd concentrations above 0.5 µg/L were found in oxic groundwaters. Low Cd concentrations were found in suboxic, methanogenic, manganese-, iron- and sulfate reducing conditions, which facilitate precipitation of sulfides such as pyrite and thus, Cd immobilization by coprecipitation (Carrillo-Gonzalez et al., 2006). It was not possible to assign any redox category to 1144 (28%) of the samples, thus they were grouped as "mixed" groundwaters (Fig. 5). This group had the widest range of concentrations, which could be caused by collecting water from different redox zones, due to long screen lengths in the respective wells. Those samples most likely did not have the time to establish equilibrium during/after mixing, as mentioned in Riedel and Kübeck (2018).

With respect to different water types according to Furtak and Langguth (1967), it was observed that the mean Cd concentration decreased with bicarbonate content and increased with sulfate and nitrate content (Fig. 6). Highest Cd concentrations with respect to median and range of the boxplots occurred in groundwater water type E, characterized as a chloride/sulfate/nitrate dominated alkaline-earth water with

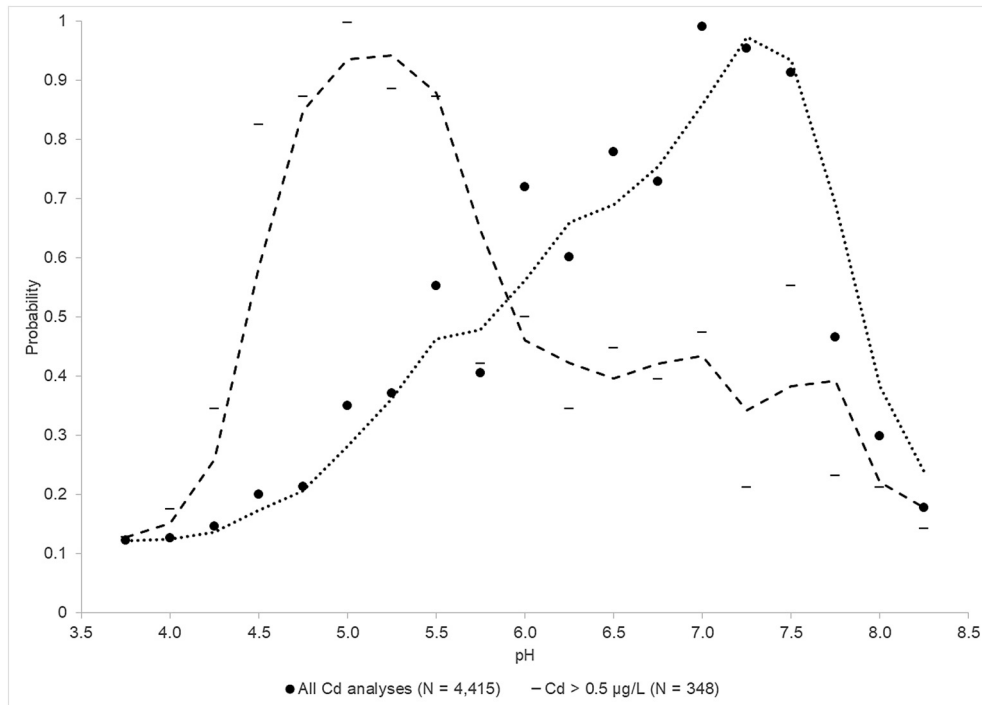


Fig. 3. Probability of Cd concentrations above the detection limit in the complete data set (closed circles) and Cd above 0.5 µg/L (dashes), which is the German threshold value, as a function of pH. The dotted and dashed lines illustrate the basic trends (moving average).

higher alkali content. In addition, water types C and G, which also indicate dominating chloride/sulfate/nitrate contents, showed similar elevated Cd concentrations. Consequently, for the classification of Cd concentrations the proportion of cations was of minor influence compared to the anions. In addition to acidification, which causes a reduced buffer capacity and lower bicarbonate concentration, redox processes such as denitrification influence the composition of anionic main components (Eqs. (2) and (3)) (Böhlke, 2002). In contrast, a greater capacity

for sorption and ion exchange primarily alters the composition of cationic main components.

In this study, we observed the close connection between Cd mobilization and hydrogeochemical conditions where elevated Cd concentrations were dependent on low pH and high redox potential. As a consequence, elevated Cd concentrations in groundwater can be used as indicator of oxidation of reduced aquifers, when oxygen or nitrate are introduced (Eq. (3)). Fig. 5 demonstrates the close relationship

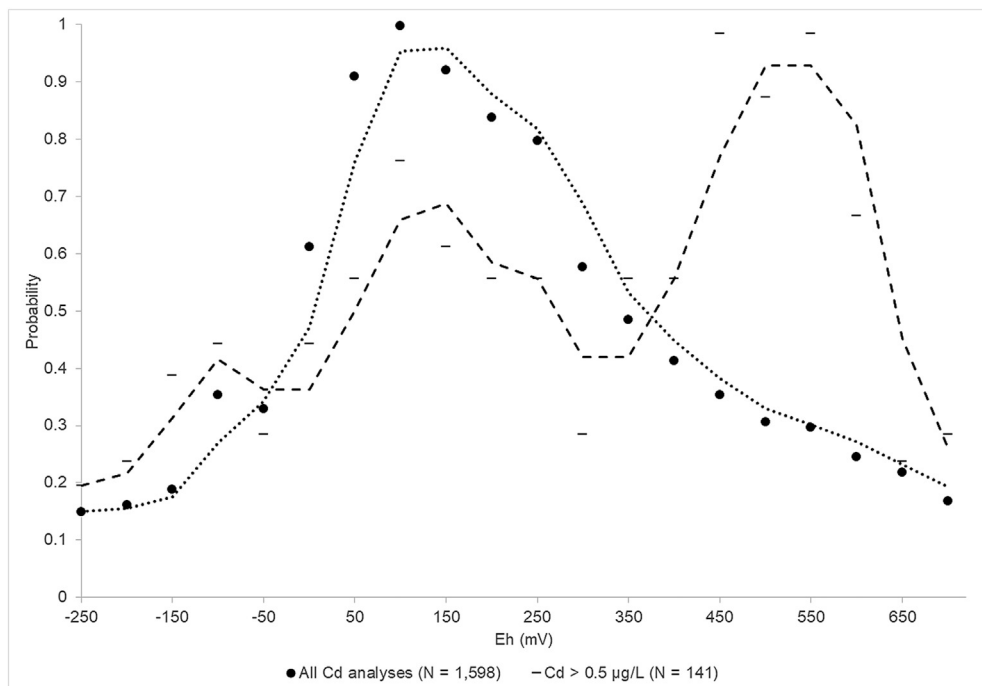


Fig. 4. Probability of Cd concentrations above the detection limit in the complete data set (closed circles) and Cd > 0.5 µg/L (dashes), which is the German threshold value, as a function of Eh. The dotted and dashed lines illustrate the basic trends (moving average).

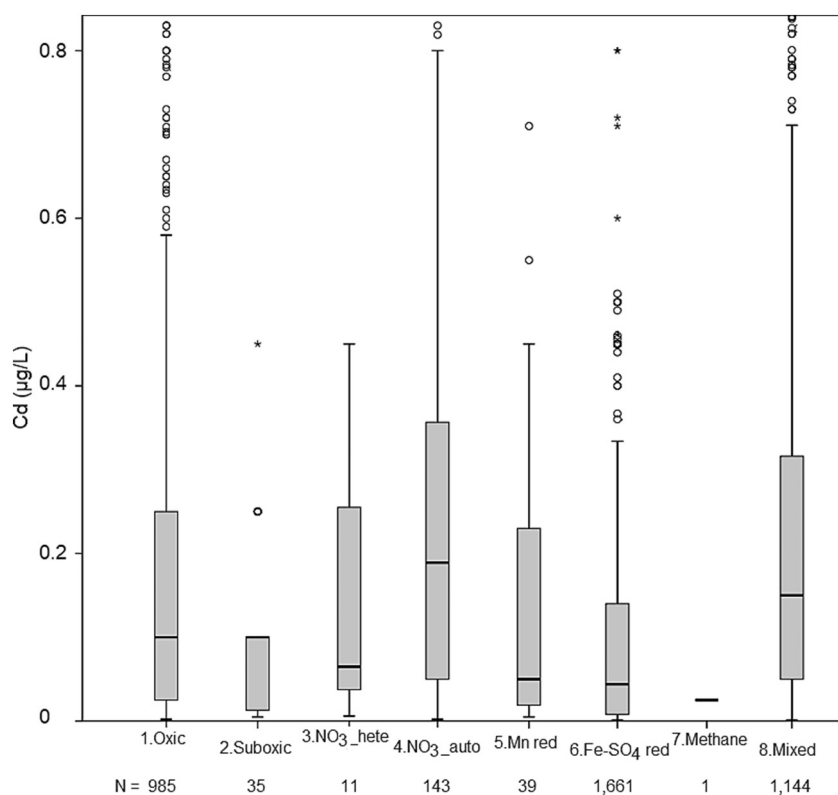


Fig. 5. Occurrence of Cd in groundwaters that are characterized by different redox conditions as defined in Table 1. Boxes show the 25th, 50th (median) and 75th percentile concentrations, whiskers show 1.5 times the interquartile range, circles show outliers, stars show extreme values.

between the in-situ parameters pH and Eh and the biogeochemical zonation, because both, oxic and nitrate reducing groundwater, have the highest median Cd concentrations and interquartile ranges. Nevertheless, a considerable amount of analyses (28%) belonged to mixed groundwaters. This would indicate chemical data for groundwaters collected from unfitting wells, e.g., wells with long screens that most likely draw from different aquifers thus, distorting the redox conditions for areas with elevated Cd concentrations.

Groundwater in the uplands with fast infiltration into karstic aquifers was mainly oxic, while the percentage of groundwaters with nitrate reducing conditions was highest in the lowlands. Both redox categories were linked to elevated Cd concentrations in groundwater (Fig. 5), particularly in the Geesten area, which is characteristic for a region with intensive agriculture and a low groundwater protection potential by the covering sediments (Elbracht et al., 2016; LSKN, 2011). The groundwater in the Geesten in their character as recharge areas shows excessive nitrate concentrations (Wriedt et al., 2019), which can oxidize pyrite that occurs in Pleistocene sediments (Houben et al., 2017). The connection of the resulting Cd mobilization and acidifying redox reactions in the data set was also revealed in the Netherlands (Mollema et al., 2015).

In contrast to the Cenozoic unconsolidated rock area in the North, the percentage of woodland and extensive agriculture in the uplands in the South was higher indicating a lower input of agricultural oxidants, such as nitrate, and reducing agents, such as C_{org} . This suggests that elevated Cd concentrations are not necessarily linked to oxic conditions in groundwater. Therefore, the exclusive evaluation of redox categories may be misleading when investigating mechanisms that cause Cd mobility.

The lack of other systematically elevated trace metals also linked to pyrite oxidation in groundwater, such as Ni, Co, and Cu, in the presence of elevated Cd can be explained by adsorption. One of the most important factors controlling the mobility of heavy metals in groundwater is pH (Anderson and Christensen, 1988). The affinity of sorption by oxyhydroxides occurring in soils and aquifers in terms of varying pH is: $Pb > Cu > Ni > Zn > Co > Cd$ (Herms and Brümmer, 1984; Spark et al.,

1995). As a consequence, Cd can remain in solution in groundwaters of pH above 6 while the other heavy metals are removed due to adsorption. As suggested by Larsen and Postma (1997), due to pyrite oxidation and subsequent precipitation of $Fe(OH)_3$ (Eqs. (3) and (4)), a removal of trace elements, either by adsorption or co-precipitation, is possible. Apart from the ubiquitous occurrence of anthropogenically introduced sulfate in the groundwater, e.g., as fertilizers and atmospheric deposition (Böhlke, 2002; Postma et al., 1991), the absence of elevated sulfate concentrations as characteristic for pyrite oxidation (Descourvieres et al., 2010) can also be caused by other reactions. Divergence from the reaction stoichiometry (Eq. (2)), as observed in Denmark and the Netherlands, could indicate sulfide oxidation by chemolithotrophic denitrifiers and subsequent elemental sulfur production (Zhang et al., 2009). This would present another explanation for the lack of elevated trace metals in groundwater, because sulfate reduction can be coupled with re-precipitation of trace metals (Böhlke, 2002).

Cadmium can also be derived from pH-dependent desorption or release of sorbed or co-precipitated Cd during dissolution, e.g., of $Fe(III)$ oxyhydroxides, which was generated during periods of higher pH (Descourvieres et al., 2010). Compared to other trace metals, Cd has the lowest sorption affinity, because it forms stable aqueous complexes and thus, Cd has an elevated mobility (Fest et al., 2005; Lynch et al., 2014). In addition, other studies observed an increase of Cd concentrations when Eh decreased, which was attributed to the reductive dissolution of Mn and Fe oxides and thus, Cd release (Hindersmann and Mansfeldt, 2014; Li et al., 2010). A similar behavior can be assumed for the Cd concentrations in the data set where Cd concentrations were above 0.5 µg/L at Eh values below 200 mV (Fig. 4).

4.3. The role of nitrate and phosphate fertilizers for the amount of Cd in groundwater

Northern Germany is a region with abundant agriculture, a wide distribution of sandy soils and thus, elevated nitrate concentrations are

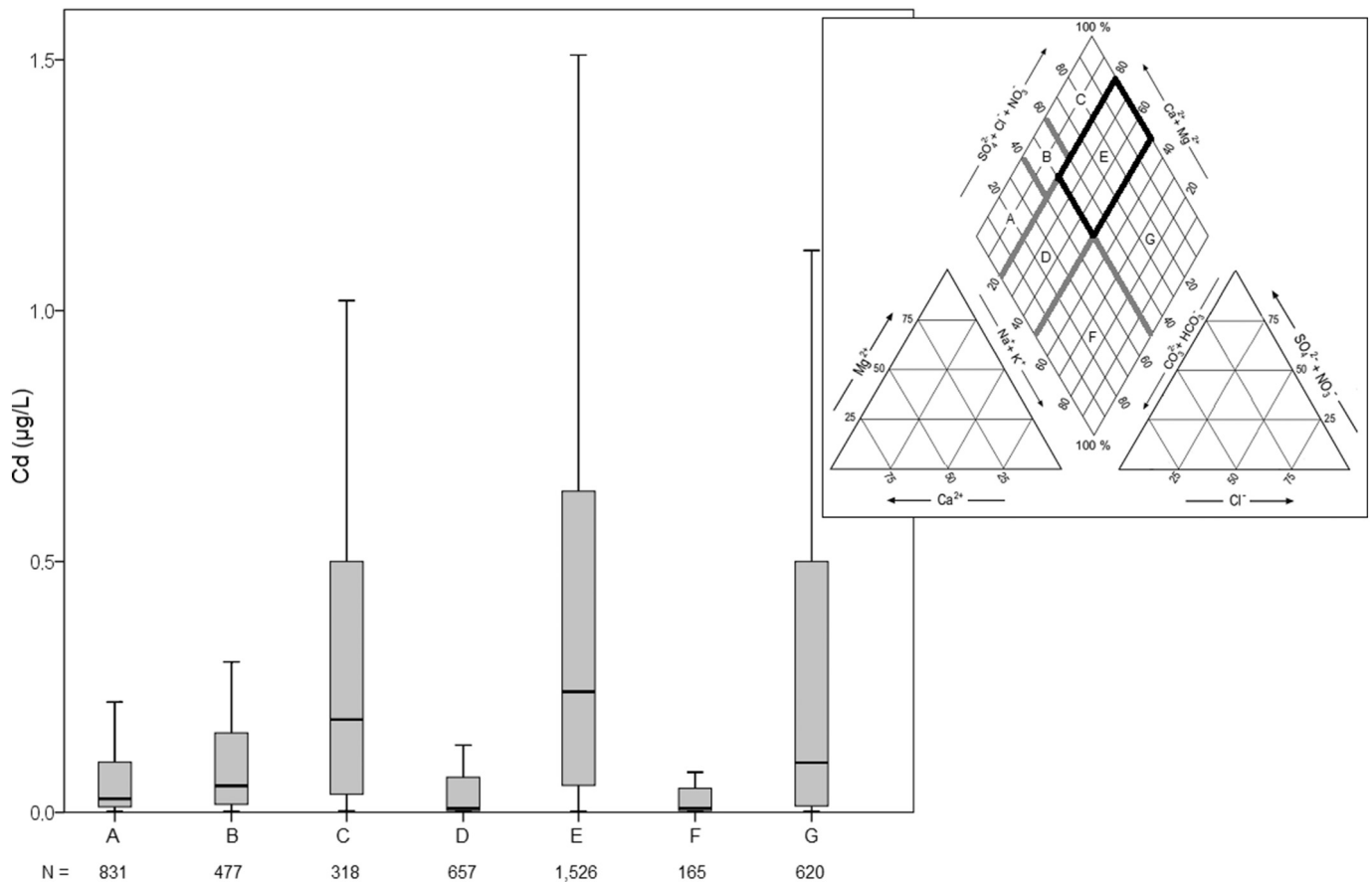


Fig. 6. Occurrence of Cd in groundwater types according to Furtak and Langguth (1967) based on the abundance of the major elements in the Piper diagram (small figure). Outliers were excluded. Water type E (bold frame) had highest Cd mean value and range.

commonly found in groundwater, particularly in the Geesten area (Köhler et al., 2006; Wriedt et al., 2019). Although often found together, elevated nitrate and elevated Cd concentrations did not correlate well in the data set ($r = 0.37$, Table 3). Nevertheless, autotrophic nitrate reduction could be responsible for, or correspond to, Cd mobility (Eq. (2)) as was recently observed for uranium release (Nolan and Weber, 2015; Riedel and Kübeck, 2018). Both Cd and uranium can occur as impurities in carbonate and phosphate rocks (Liesch et al., 2015; Thornton, 1986) and thus, the presence of Cd in groundwater can be attributed to both, weathering of Cd containing minerals (geogenic background) and anthropogenic input (mineral fertilizers). However, anthropogenic interference may promote natural processes that will eventually lead to elevated Cd concentrations in groundwater. Oxidation and acidification, e.g., through groundwater pumping, acidic atmospheric deposition and excessive nitrate input from fertilization (Eq. (3)), can easily mobilize Cd and elevate Cd concentrations in groundwater. Han et al. (2018) found that Cd was released from paddy fields following application of nitrogen fertilizers in the Hunan Province, Southern China and conducted that its release was facilitated by changing redox conditions caused by recurring drying-wetting. Seasonal variations in groundwater levels in Northern Germany could have a similar effect. Groundwater recharge occurs mainly during the winter months and as a result, the depth to water table varied up to 5 m at several sampling locations.

The application of the assessment scheme to determine influence types in groundwater (Fig. 2) showed a considerable relationship between Cd concentrations and anthropogenic impact, in particular agricultural impact and indication of acidification (Fig. 7). Half of the groundwater analyses were attributed to type 0, which implied water without or with barely anthropogenic impact. With respect to land use,

groundwater underlying grassland and woodland had the highest amount of water analyses without any anthropogenic impact (50%), while almost half of farmland related groundwater showed an agricultural impact (type 2). In most cases, the agricultural impact was indicated as elevated nitrate concentrations. Within the subtypes of agricultural influences (type 2), median Cd concentrations increased with increasing nitrate concentrations (Fig. 7). Additionally, in combination with indications of acidification, median Cd concentrations were raised within the influence types. The median Cd concentration of those 199 analyses that matched with nitrate concentrations above the threshold value of 50 mg/L (type 2.1), as well as indication of acidification, was at the level of the German groundwater threshold value of 0.5 µg/L (Fig. 7), indicating a coupled influence of pH and nitrate surplus on the Cd concentrations. The lowest median Cd concentrations of 0.05 µg/L were observed for analyses without any anthropogenic impact (type 0), analyses with diverse influences (type 4), groundwater matching elevated concentrations of pollutants (type 1), and analyses with acidification only (type 3). In total, 78% of the Cd analyses exceeding 0.5 µg/L were related to groundwater that was affected by pollutants (type 1), agricultural (type 2) or diverse influences (type 4).

There was no indication in the data set that the application of phosphate fertilizers has an impact on Cd concentrations in Northern Germany, although phosphate fertilizers are a known source of Cd. This relationship may be obscured, because with fertilization, an independent secondary Cd contamination can occur due to the release of geogenic Cd from the aquifer matrix. Fertilization increases ionic strength, decreases pH and phosphate competes for adsorption sites all of which enhance Cd mobility (Grant, 2011). Due to the significant linkage to farmland (Table 2, Fig. 7), Cd can enter the subsurface either

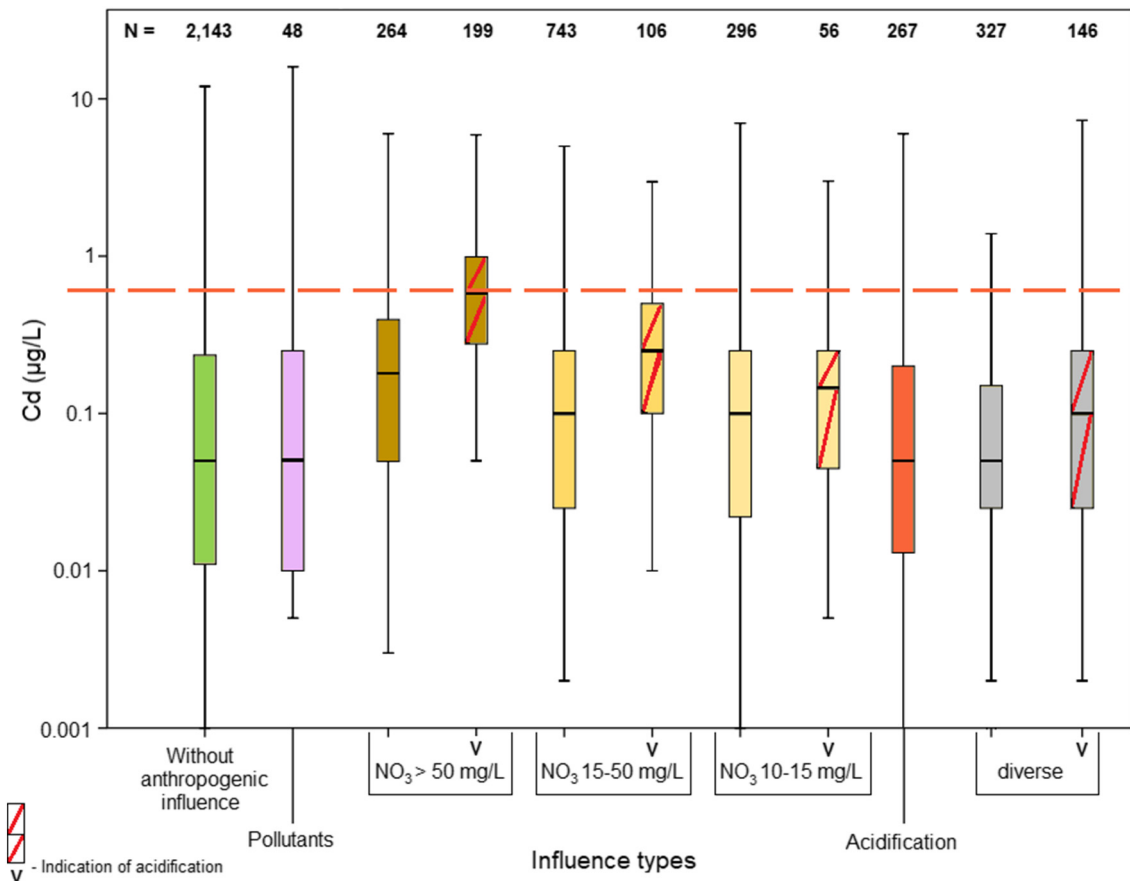


Fig. 7. Boxplots of Cd concentrations classified by influence types. The color scheme of the boxplots is according to Fig. 2. The dashed line illustrates the German groundwater threshold value of 0.5 µg/L. Outliers were excluded. The Kruskal-Wallis test revealed a significant difference among the influence types ($X^2(10) = 517.885, p = 0.0001$).

as a trace element in phosphate fertilizers or it is mobilized in the course of denitrification either from pyrite or with decreasing pH inhibiting Cd sorption at mineral surfaces. However, the determination of the Cd mobility is of greater importance than the quantification of its origin. Several studies revealed a significant potential Cd pool in the environment whose release depends on topographic, hydrostratigraphic and agronomical conditions (e.g., Houben et al., 2017; Richardson et al., 2001). The most important parameters controlling Cd concentrations in groundwater are pH, the concentration of DOC, and the amount of clay minerals and oxyhydroxides in the aquifer (Anderson and Christensen, 1988; Krishnamurti and Naidu, 2003; Lin et al., 2016). Our study, which based on a large-scale data set, supported these relationships, which previously were investigated at model and laboratory scales.

Apart from agricultural areas, elevated Cd concentrations are also present in groundwater beneath woodlands. On the one hand, lateral transport of polluted groundwater from farmland could have happened (Zhang et al., 2009), while on the other hand, forest locations are rich in organic matter, low in pH and thus, formation of soluble metal-organic complexes should get in the way of Cd sorption (Sprynsky et al., 2011). In addition to the positive correlation with selected trace metals, e.g., Co, Cu, and Ni (Table 3), it can be assumed that Cd release is controlled by acidification and oxidation and that mobilization processes like pH-dependent desorption (Kjoller et al., 2004) are more likely than a considerable amount of anthropogenic Cd input. This is in concord with the observation in Fig. 3, where the highest probability of elevated Cd concentrations was seen at a pH between 4 and 5.5. The association of Cd to both acidic and nitrate oxidizing groundwaters was further elucidated through the connection to nitrate containing water types (Fig. 5 and Fig. 6).

5. Conclusions

Despite abundant research of single mechanisms controlling Cd mobility in aqueous solutions, e.g., sorption behavior of Fe oxyhydroxides, release from contamination sites, and bioavailability of Cd originated from fertilizers, there has been no study of Cd behavior in groundwater on the basis of a large-scale data set. Groundwater in Northern Germany can have Cd concentrations exceeding the German threshold value of 0.5 µg/L making it possible to investigate different aspects of Cd mobility with respect to hydrogeology, land use, and groundwater chemistry. Due to the lack of point source contamination, such as mining or industrial emissions, no single mechanism was considered responsible for elevated Cd concentrations in groundwater in Northern Germany. However, several conditions were identified that seemingly facilitated the mobility of Cd:

1. Land use with considerable anthropogenic or natural influences on groundwater composition, such as farmland or woodland.
2. Hydrogeological factors, such as sandy aquifers, distance to water table and a considerable amount of groundwater recharge promoting rapid infiltration of electron acceptors into the subsurface.
3. Abundance of Cd containing minerals in the aquifer matrix, such as sulfides, phosphorites, and carbonates.
4. Hydrochemical conditions that cause Cd release such as low pH, oxic or autotrophic nitrate reducing conditions.
5. A groundwater of the chloride/sulfate/nitrate dominated alkaline-earth water type, preferably with a higher alkali content and minor bicarbonate content.
6. Strongly elevated nitrate concentrations in addition with indications of acidification.

7. The occurrence of ligands such as organic matter and chloride that form Cd complexes, thus increasing its solubility and mobility.

To reduce Cd release in agricultural areas, a decrease of nitrate-based fertilization could be an option. Other approaches, such as liming with CaCO₃ have to be carefully evaluated, because their application may cause the release of co-occurring metals. Uranium mobility, for example, increases with increasing pH.

Our study showed that several approaches can be used or have to be combined to investigate the fate of Cd in groundwater, which is linked to groundwater redox state, groundwater composition, and the interference of anthropogenic activities. Nevertheless, tracing the origin of Cd appears as a challenging task that needs to consider additional issues of anthropogenic input and geogenic sources.

Declaration of Competing Interest

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

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