

Environmental Management

Cadmium Background Levels in Groundwater in an Area Dominated by Agriculture

Andreas Kubier,*† Kay Hamer,† and Thomas Pichler†

†Department of Geosciences, University of Bremen, Bremen, Germany

ABSTRACT

Cadmium is a highly toxic trace metal, which can be of geogenic or anthropogenic origin, for example, minerals, phosphate fertilizers, and combustion emissions. Due to its low sorption affinity compared to other heavy metals, Cd is easily mobilized, potentially resulting in elevated Cd concentrations in groundwater. This study assessed background levels of Cd in groundwater related to hydrogeology and hydrogeochemical processes through evaluation of a large hydrogeochemical data set composed of groundwater analyses from 6300 wells in Northwestern Germany. Calculated Cd background levels in groundwater were between 0.01 µg/L in hydrogeological units with mainly reducing conditions and 0.98 µg/L in less reducing groundwater recharge areas. The results showed that groundwater Cd concentrations above 0.5 µg/L (the German threshold value) are not necessarily elevated but could be the regional or ambient background level, depending on the hydrogeological unit. What would be considered as ambient background levels, however, indicated the influence by continuous intensive land use as well as the local geology, which is dominated by glacial deposits. Cadmium concentrations in groundwater were mainly controlled by hydrogeochemical and hydrogeological parameters and not by the amount of anthropogenic Cd input, in particular through the use of phosphate fertilizers. Instead, analyses of the solid phase revealed that Cd release from the aquifer matrix due to changes in hydrogeochemical parameters was more likely. Aquifer sediments in Northwestern Germany can be enriched in Cd originating from multiple sources, which in turn can cause elevated Cd concentrations in groundwater. *Integr Environ Assess Manag* 2020;16:103–113. © 2019 The Authors. *Integrated Environmental Assessment and Management* published by Wiley Periodicals, Inc. on behalf of Society of Environmental Toxicology & Chemistry (SETAC)

Keywords: Cadmium Geogenic Background levels Hydrogeochemistry Groundwater

INTRODUCTION

Cadmium is one of the most toxic and mobile elements in the environment (Alloway and Jackson 1991; Nies 1999, 2003). It bioaccumulates in several human organs (Pan et al. 2010; Hajeb et al. 2014) and is classified as carcinogenic (UNEP 2010). It is listed as a priority hazardous substance in the European Water Framework Directive (WFD; EC 2000), and due to its toxicity Germany implemented a threshold concentration of 0.5 µg/L (GrwV 2017). Therefore, it is important to identify and understand sources and pathways of Cd in the environment, particularly in groundwater because of its potential source for drinking water. Anthropogenic Cd sources include phosphate fertilizers, combustion emissions, sewage sludge, landfills, traffic, metal industry, mining, and environmental incidents (Merkel and Sperling 1998; Mirlean

and Roisenberg 2006; Sprynskyy et al. 2011; Bigalke et al. 2017). Atmospheric emission, wastewater reuse, and agricultural activities (UNEP 2010; Sprynskyy et al. 2011; ATSDR 2012) can serve as diffuse sources, causing a widespread distribution of Cd. Beyond this, Cd release into the environment can occur from geogenic sources, such as soils, sediments, and rocks (Birke et al. 2017). Processes controlling Cd concentrations in groundwater are mainly the dissolution of Cd-bearing minerals, such as sulfides, sorption, and desorption processes due to pH changes, advective transport, and formation of aqueous Cd complexes (Kjeldsen et al. 2002; Caetano et al. 2003; He et al. 2005). Compared to other trace metals, Cd has a low sorption affinity to mineral surfaces and thus is considered mobile (Lynch et al. 2014). There are 2 common possible explanations for elevated Cd concentrations in groundwater in areas dominated by farmland. The first could be the application of Cd-containing phosphate fertilizers, whereas the second could be the release of geogenic Cd, triggered by agricultural nitrate and phosphate fertilization (Kubier and Pichler 2019). A similar scenario was reported recently for U (e.g., Liesch et al. 2015; Riedel and Kübeck 2018).

* Address correspondence to a.kubier@uni-bremen.de

Published 1 August 2019 on wileyonlinelibrary.com/journal/ieam.

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

Cadmium can substitute for divalent cations, such as Ca, Fe, Zn, Pb, and Co, in several minerals due to their similar ionic radius, for example, in carbonate and phosphate rocks (Merkel and Sperling 1998; Smolders and Mertens 2013). Under oxic conditions, Cd can also accumulate in Fe oxides and hydrous oxides (Anderson and Christensen 1988; He et al. 2005). Cadmium can also replace Ca in apatite, which is the main constituent of phosphorites (Mar and Okazaki 2012). Consequently, Cd can be a common impurity in phosphate minerals and phosphoritic rocks, which are indispensable for fertilizer production. The average crustal Cd content is 0.1 to 0.2 mg/kg (UNEP 2010). Naturally, Cd occurs in concentrations of 0.1 to 1 mg/kg in soils of Europe and the United States (Smolders and Mertens 2013; Smith et al. 2014; Taylor et al. 2016). 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) and metamorphic rocks (0.11 to 1.0 mg/kg) (Hammons et al. 1978; Page et al. 1987; Mar and Okazaki 2012; Smolders and Mertens 2013). Cadmium contents in fertilizers result from the presence of Cd as a impurity in phosphate minerals and phosphoritic rocks. This pathway of Cd pollution into groundwater has been reported for the United States, Canada, Britain, Norway, Sweden, Finland, Denmark, Germany, Australia, and New Zealand (Grant 2011; Taylor et al. 2016; Bigalke et al. 2017). The Cd content, however, varies significantly between geologic occurrences, and there are no commercial means to entirely remove Cd during the phosphate fertilizer production (Mar and Okazaki 2012).

Information about the natural or so-called “background” concentration of potentially toxic elements, such as heavy metals, is necessary to evaluate contamination (Flem et al. 2018). Despite a multitude of studies concerning the background concentrations of many heavy metals (Lazareva and Pichler 2007; Pichler et al. 2011; Molinari et al. 2012), to date no such attempt has been made for Cd.

With this in mind, the goal of the present study was to differentiate between geogenic and anthropogenic (mainly fertilizer-derived) Cd and to evaluate how agricultural practices increased Cd concentrations in groundwater. For this purpose, it was necessary to evaluate trend tests of groundwater analyses with elevated Cd concentrations in order to identify changes and to calculate background levels for different regional areas with stable Cd concentrations to identify whether elevated Cd concentrations have a geogenic origin. The first part covered geospatial and statistical analyses of Cd in groundwater from 6300 wells in North-western Germany in relation to hydrogeology and land use. This region was deemed an appropriate model region because it provides a unique combination of different geological units, dominated by glacial influences, with some areas of solid rock and marine influences. Land use is primarily agricultural, interspersed with areas of woodland and moors (BKG 2018). Those factors were considered in the evaluation of elevated Cd concentrations in groundwater, and based on geospatial and statistical data it was possible

to better understand and estimate the role of geogenic Cd in groundwater.

CHARACTERIZATION OF GEOGENIC BACKGROUND

The natural baseline concentration of a substance in groundwater is defined as “the concentration of a given element, species or chemical substance present in solution, which is derived from natural geological, biological, or atmospheric sources” (Edmunds et al. 2003). However, it is difficult to define a baseline that refers to pre-anthropogenic element levels in shallow groundwater (Reimann and Garrett 2005). As a consequence, it should be favorable to use background values instead and to separate those into 1) natural background, the concentration uninfluenced by man, and 2) ambient background, the usual background concentration that consists of a natural pedogeochemical fraction and an anthropogenic fraction.

Shallow groundwater has a mean age of some decades, depending on the aquifer thickness. As a consequence, groundwater composition in European countries like Germany is often influenced anthropogenically. Farmland, for example, covers half of the German landscape (BKG 2018), and farming was conducted intensively for more than a century. Hence, the term “natural background” should not be applied to farmland but only to areas not influenced by man.

The chemical composition of groundwater is influenced by a variety of factors related to both natural causes and anthropogenic activities. Natural factors can be rainfall, chemical and biological processes in the unsaturated zone, the components of the aquifer material, the water flow, and the resulting redox environment in the aquifer (Biddau et al. 2017). Agricultural or industrial activities can have an effect on the composition of shallow groundwater (Kellner et al. 2015; Liesch et al. 2015; Biddau et al. 2017); however, it seems that the predominant process would be chemical interaction between the aqueous and the solid phase in the aquifer (Wendland et al. 2008). The occurring types of chemical reactions depend on local geological conditions and include mineral dissolution and precipitation, redox reactions, cation exchange, sorption, and mixing (Edmunds et al. 2003). Therefore, the major geogenic factors that influence Cd concentrations in groundwater are the petrographic properties of the aquifer matrix in the vadose and groundwater-saturated zones together with regional hydrological and hydrodynamic conditions (Wendland et al. 2008), for example, variations between wet and dry seasons (Mehrabi et al. 2015; Lu et al. 2018).

According to the German groundwater regulation, the background level is the natural concentration of a parameter at a given location, that is, without any influence by human activity (GrwV 2017). Different approaches were developed to determine background concentrations in groundwater. There were direct approaches using historical data or groundwater dating using isotopes (Edmunds et al. 2003; Biddau et al. 2017). Indirect methods using indicator

parameters were also used to identify pollution (Edmunds et al. 2003). A common method in soil science is the calculation of enrichment factors (Reimann and Garrett 2005) comparable to trace metal pollution indices in water (Mehrabi et al. 2015; Lu et al. 2018). In general, graphic evaluation is a simple way to compare different samples and to draw conclusions about their origin, for example, pie diagrams and dendrograms (Guler et al. 2002). The classification of water types is a consequent development of using indicator parameters and diagrams. They can explain elevated contents of potential pollutants and possible sources of components in groundwater. Several approaches to groundwater classification and source separation exist (e.g., Khadra and Stuyfzand 2014; Liesch et al. 2015; Hepburn et al. 2018).

In addition, statistical tools can help to derive concentrations or relations that indicate the origin and behavior of substances in the environment. Bivariate statistics, such as correlation analysis, were performed in some studies to reveal the same behavior and thus the origin of trace metals in groundwater (Liesch et al. 2015; Lu et al. 2018). More advanced techniques include multivariate statistics, such as cluster analysis (Flem et al. 2018), factor analysis (Huang et al. 2013), and multicriteria evaluation (Banning et al. 2009; Khadra and Stuyfzand 2014). According to Hinsby et al. (2008), potential outliers can be identified by, for example, using ionic balance or indicator parameters such as nitrate. This approach allows the elimination of compromised data from further statistical analyses, such as misbalanced analyses or analyses with nitrate exceeding a threshold value. Another possibility is the identification of outliers that are 1.5 times above the interquartile range, which is the difference between the value corresponding to the 75th percentile and the 25th percentile as applied for box and whisker plots. Another approach defines outliers as the mean ± 2 times the standard deviation in order to avoid calculations assuming a normal distribution, which is uncommon in geochemical data sets (Reimann et al. 2005; Ducci and Sellerino 2012). Cumulative probability plots can be used as a component separation to identify multiple populations within the data set and to remove single outliers without certain data set preparations (Reimann et al. 2005; Wagner et al. 2011; Preziosi et al. 2014). The background level is usually derived as the 90th percentile of the normal population in a data set with respect to the ubiquitous human impact on groundwater (Hinsby et al. 2008; Godbersen et al. 2012). Both box plots and probability plots are the preferred methods of deriving representative values because they show unbiased statistical data and disregard analytical and sampling errors (Edmunds et al. 2003).

MATERIALS AND METHODS

Study area and regional hydrogeology

The present study area comprises the German federal states of Lower Saxony and Bremen in Northwestern Germany (Figure 1) totaling almost 48 000 km² (BKG 2018).

The study area consists of the Cenozoic North German Plain as the main part to the north and the mountainous region to the south, which belongs to the Central German Uplands (Elbracht et al. 2016). In the present study, the uplands were considered as 1 hydrogeological unit, whereas the North German Plain consists of 4 different hydrogeological units: islands, tidal wetlands, lowlands, and Pleistocene glacial deposits, called “Geesten.” As mostly unconfined upper aquifers, they represent groundwater recharge areas as well as catchment areas for water supply (Elbracht et al. 2016). The highest elevation, the Harz Mountains, consists of Paleozoic rocks, whereas the aquifers of the fault-block mountains north of the Harz Mountains consist of Mesozoic limestones and sandstones (Wendland et al. 2008), partly covered by Pleistocene deposits (Figure 1). The 5 hydrogeological areas divide into 80 subareas, which are hydrogeological units that feature a homogeneous structure with respect to natural areas and topographical borders (Elbracht et al. 2016).

Due to the different hydrogeological settings, the groundwater chemistry is heterogeneous within the study area. The following groundwater types were found: 1) groundwater from the islands was primarily of the bicarbonate-predominated alkaline-earth type, 2) groundwater from tidal wetlands is mainly Fe and sulfate reducing and belongs to alkaline waters with decreasing bicarbonate contents, 3) groundwater in the lowlands and the Geesten was predominantly of the alkaline-earth type with decreasing bicarbonate contents, and 4) groundwater in the uplands appeared to be oxidic, bicarbonate dominated, and was of the bicarbonatic-sulfatic alkaline-earth type.

The main land use in the present study area is farmland (46%), followed by woodland (22%), grassland (21%), and urban areas (7%) (BKG 2018). Most groundwater Cd concentrations that exceeded 0.5 $\mu\text{g/L}$ were found in the western part of the Geesten (Figure 1), which is characterized by intensive livestock farming and agriculture (LSKN 2011; Wriedt et al. 2019). That observation seems to be closely related to the input of nitrate into groundwater, either by fertilizers or by effluent or manure application (Kubier and Pichler 2019).

Data

The data set was compiled from the federal database maintained by the Niedersächsischer Landesbetrieb für Wasserwirtschaft, Küsten- und Naturschutz (NLWK), the Landesamt für Bergbau, Energie und Geologie (LBEG), the Senator für Umwelt, Bau und Verkehr (SUBV) of Bremen, and the administration of Hannover representing the water management and geological surveys of Lower Saxony and Bremen. The data set included more than 24 000 samples from 6300 observation wells and production wells. The data was collected by the various state and federal agencies as part of a continuous groundwater monitoring program and included samples taken between 1976 and December 2015. Sampling and analysis followed established procedures (DVWK 1992).

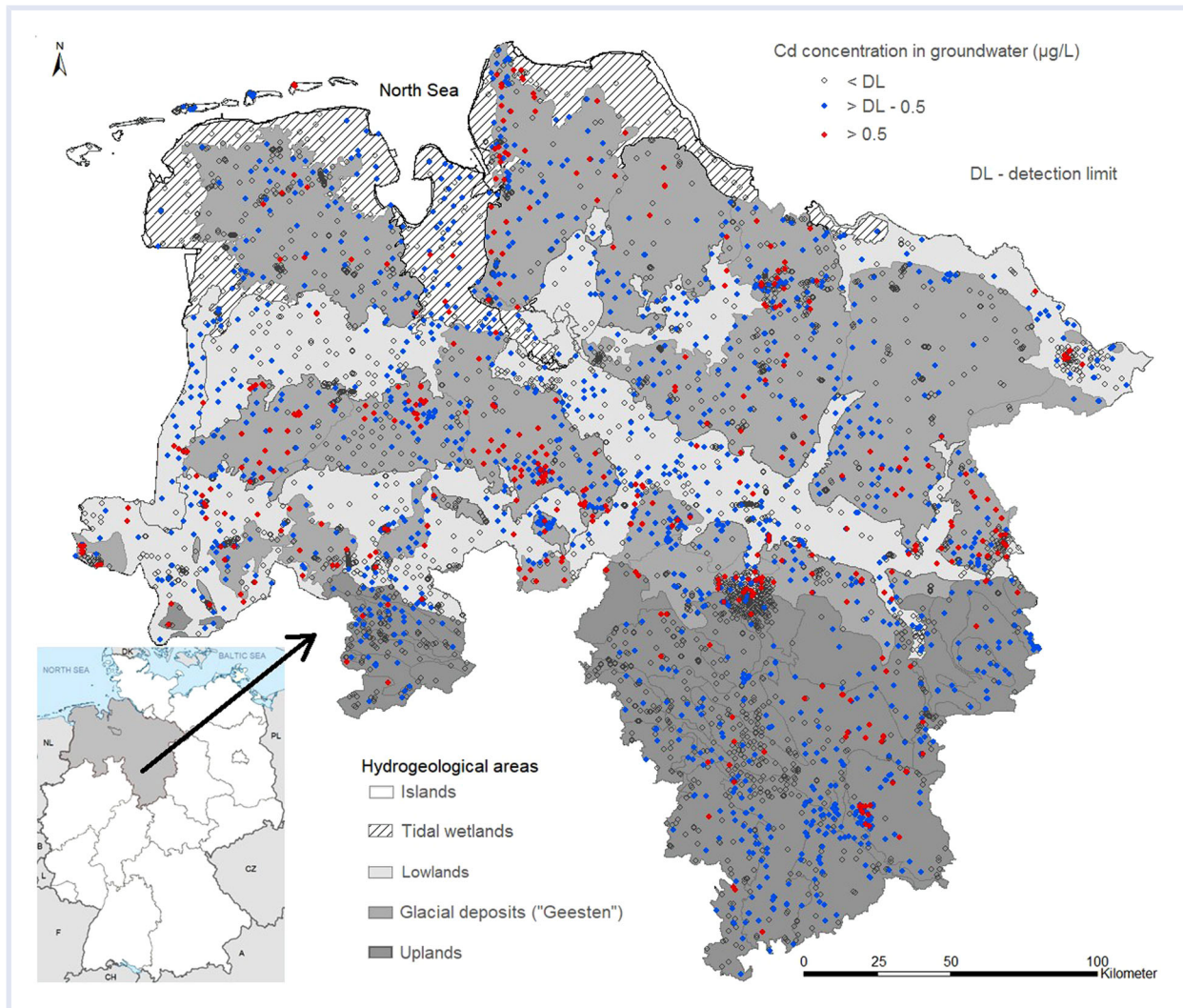


Figure 1. Cadmium concentrations in shallow groundwater of the study.

The data set included in situ parameters, such as pH and redox potential, and the following main components and trace elements: Na, K, Ca, Mg, SO_4 , Cl, HCO_3 , NO_3 , Fe, Mn, Cd, Co, Cr, Cu, Ni, Pb, PO_4 , U, and Zn. Analyses with a Cd detection limit above $1.0 \mu\text{g/L}$ were discarded in order to avoid values of half the detection limit that met the German threshold value of $0.5 \mu\text{g/L}$ for Cd in groundwater (GrwV 2017). Similar to Wagner et al. (2011), the most recent data were chosen for each sampling location to avoid a potential bias toward the more frequently sampled locations. Furthermore, the evaluation of recent data ensured lower Cd detection limits, down to $0.002 \mu\text{g/L}$, which was considered advantageous, rather than a conversion to median values. Consequently, 5512 groundwater analyses were exploitable for statistical analysis.

Statistical analysis

The sampling points were classified according to hydrogeological units and land use using ArcGIS (ESRI 2018) to reveal possible effects of geogenic release or fertilizers on

Cd concentrations in groundwater. Data from the land use mapping project CORINE Land Cover from 2012 (BKG 2018) were used. Lateral transport of Cd with groundwater and influence from adjacent areas were disregarded. The number of classes were reduced to practical size, for example, 5 hydrogeological units instead of 10 and 4 land use classes instead of 32. Results were given as boxplots using SPSS statistics 24 (IBM 2016) and empirical cumulative distribution functions. Wells with at least 4 Cd analyses that included 1 Cd value in excess of the German threshold value of $0.5 \mu\text{g/L}$ were examined with the Mann-Kendall trend test.

For the calculation of background levels, all recent Cd analyses from wells with more than 1 value were used. The probability plot was used to determine the geogenic background of Cd in groundwater. The background levels were calculated for all hydrogeological subareas according to Wagner et al. (2011), but contrary to their approach, analyses from wells with a screen depth below 50 m were also considered to avoid a fixed exclusion criterion. Additionally,

wells with analyses before 2005 were used to ensure a high data density. In contrast to Wagner et al. (2011), analyses from wells that failed the Mann-Kendall trend test were not used to calculate background values because those wells underwent changes in groundwater quality, and thus they were not suitable. Using the probability plot, it was possible to determine and exclude outliers at the top and bottom of each data set in order to achieve a lognormal distribution. In case of more than 10 available analyses, the 90th percentile of the normal population was set as natural background for Cd. In case of $N < 10$, subareas that had similar hydro-geochemical or stratigraphic-genetic characters were aggregated to determine a common Cd background level.

RESULTS AND DISCUSSION

Cadmium in groundwater in relation to hydrogeological units and land use

The conduction of empirical cumulative distribution functions was preferred over simple statistical analyses such as correlation to compare the behavior of Cd in groundwater between groups of similar size. As discussed in Riedel and Kübeck (2018), the observation of linear relationships in a large data set would cause misleading results.

Two thirds of the Cd concentrations in groundwater were below the detection limit. There were 363 analyses that exceeded the German Cd threshold of 0.5 $\mu\text{g/L}$ (7% of 5512 analyses), which were mainly encountered in the Geesten area (Figure 2) (219 of 363 analyses), indicating a relation between hydrogeological unit and Cd concentration.

Groundwater within islands, tidal wetlands, and lowlands showed lower median Cd concentrations, between 0.03 $\mu\text{g/L}$ and 0.05 $\mu\text{g/L}$, compared to groundwater in the Highlands and Geesten area (Figure 2). The 90th percentile of Cd concentrations in the Geesten was 0.58 $\mu\text{g/L}$, thus exceeding the 90th percentile of the other hydrogeological areas and the German Cd threshold of 0.5 $\mu\text{g/L}$ (GrwV 2017). The Geesten is a recharge area, so groundwater is mainly influenced by surface input and interactions during seepage. In addition, there is a limited retention of pollutants due to the low sorption capacity of the glacial deposits that form the Geesten (Elbracht et al. 2016). Nitrate input due to agriculture in conjunction with a low nitrate reduction potential of glacial deposits (Cremer 2015) would lead to the dissolution of pyrite, a sulfide known to contain Cd (Abraitis et al. 2004; Houben et al. 2017) and thus provide a mechanism for the release of geogenic Cd to groundwater. Once in solution, the formation of complexes with inorganic and organic ligands would prevent adsorption by hydrous ferric oxides, keeping Cd in solution in the vadose zone (Hammons et al. 1978; Carrillo-Gonzalez et al. 2006; Najafi and Jalali 2015).

Although the mean Cd concentration for all land use classes was similar, between 0.05 $\mu\text{g/L}$ and 0.1 $\mu\text{g/L}$ (Figure 3), an elevated 90th percentile of Cd was observed in the case of farmland (0.57 $\mu\text{g/L}$) and woodland (0.45 $\mu\text{g/L}$). Most groundwater samples showing Cd concentrations above 0.5 $\mu\text{g/L}$ belonged to wells that occurred in association with farmland (42% of 363 sampling locations) and woodland (33%), indicating an influence from seepage. The

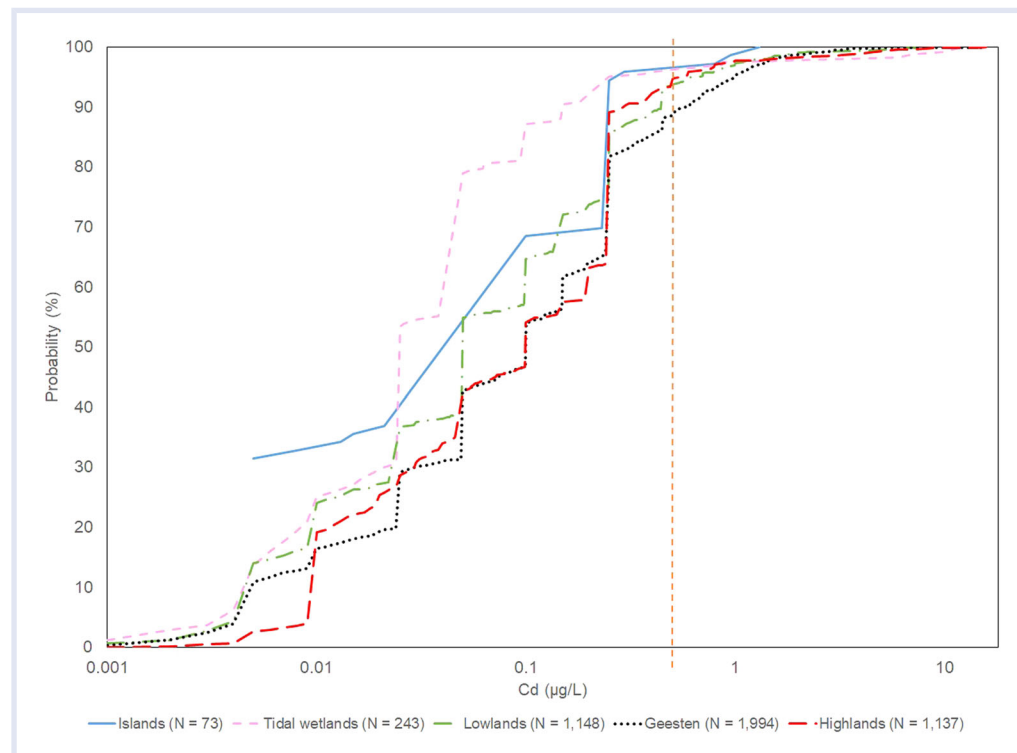


Figure 2. Empirical cumulative distribution functions for Cd concentrations, classified by hydrogeological areas. The dashed vertical line represents the German Cd groundwater threshold value of 0.5 $\mu\text{g/L}$.

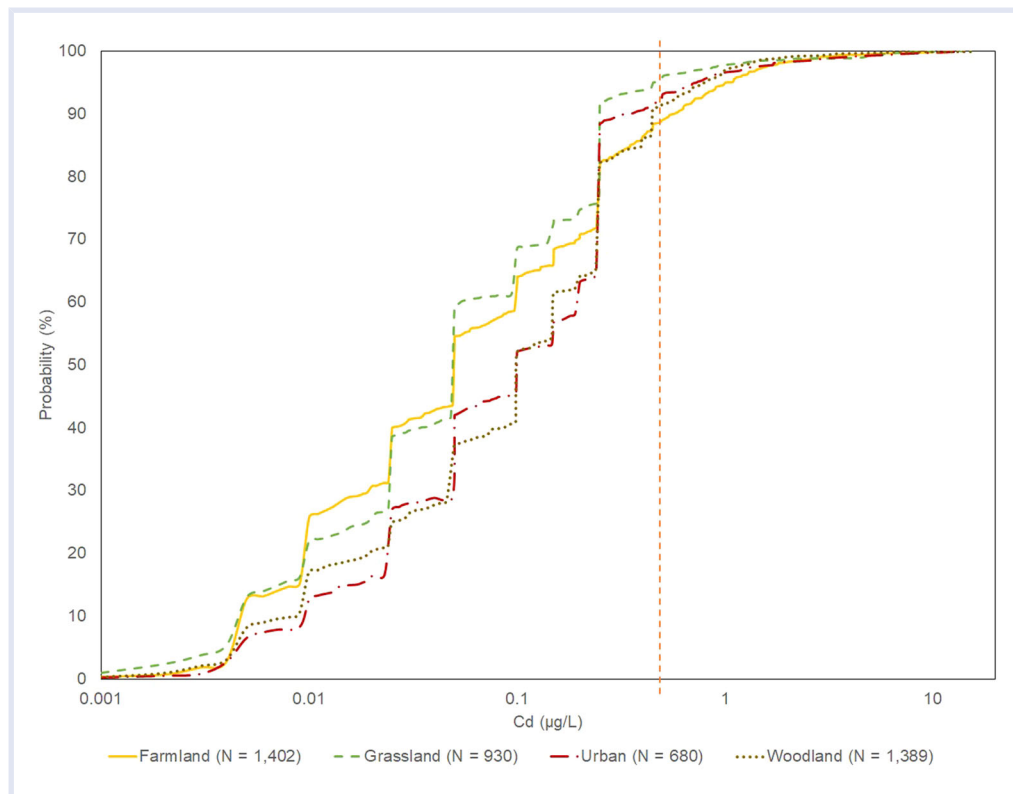


Figure 3. Empirical cumulative distribution functions for Cd concentrations, classified by land use. The dashed vertical line represents the German Cd groundwater threshold value of 0.5 µg/L.

relation to water depth supported that assumption because most elevated Cd concentrations were detected in the upper 15 m below the water table where water chemistry evolves fast and is influenced by human impact (Edmunds et al. 2003).

Assessment of elevated Cd concentrations in groundwater

The trend test revealed 157 wells (3% of 5512 wells) with an unstable temporal development of Cd concentrations, and those were discarded for the calculation of background levels. Of those 157 wells, 30 wells showed an increase of Cd concentrations with time and were mainly screened in the upper 15 m below the water table. Those wells were located in the Geesten, and the most recent Cd concentrations were between 0.28 µg/L and 4.8 µg/L. They often had a low pH and elevated nitrate and heavy metal concentrations, for example, Mn, Ni, and Zn. Those observations were in agreement with the chemical behavior of Cd, that is, under oxygenated conditions solubility increases as pH decreases (Merkel and Sperling 1998). The Cd²⁺ ion itself is not redox sensitive. However, it is indirectly tied to redox conditions due to the incorporation into redox-sensitive minerals, such as pyrite. Consequently, it can be assumed that Cd release was linked to hydrogeochemical processes that were caused by agricultural activities, for example, through nitrate reduction coupled with pyrite oxidation (Böhlke 2002).

Assessment of background levels

On the basis of the 80 hydrogeological subareas in combination with 5355 Cd analyses, background levels for Cd in groundwater were determined to be between 0.01 µg/L and 0.98 µg/L. Low Cd background levels were observed in hydrogeological units with mainly reducing conditions. Elevated background levels that exceeded the German threshold value of 0.5 µg/L for Cd were calculated for 9 of 80 subareas, which exclusively belonged to the Geesten and the Highlands (Figure 4). Background levels for Cd in groundwater in the Harz Mountains are at best ambiguous due to the influence of mining activities in the past (Monna et al. 2000).

In general, Cd background levels in the Geesten were higher than in the other hydrogeological units. For 7 minor subareas, no Cd background level could be calculated due to missing analyses. There were 24 Cd concentrations above 0.5 µg/L (7% out of 363 analyses) that were in the range of the background levels, indicating a geogenic origin of Cd in groundwater. Consequently, 93% of the groundwater analyses exceeded both the German Cd threshold and those background levels, indicating geogenic anomalies or anthropogenic influences.

Despite the ubiquitous human influence through the centuries-old cultivation of the landscape, impacting the natural background of compounds in groundwater (Wagner et al. 2011), the applied method of using probability plots was a reliable tool to assess groundwater composition and

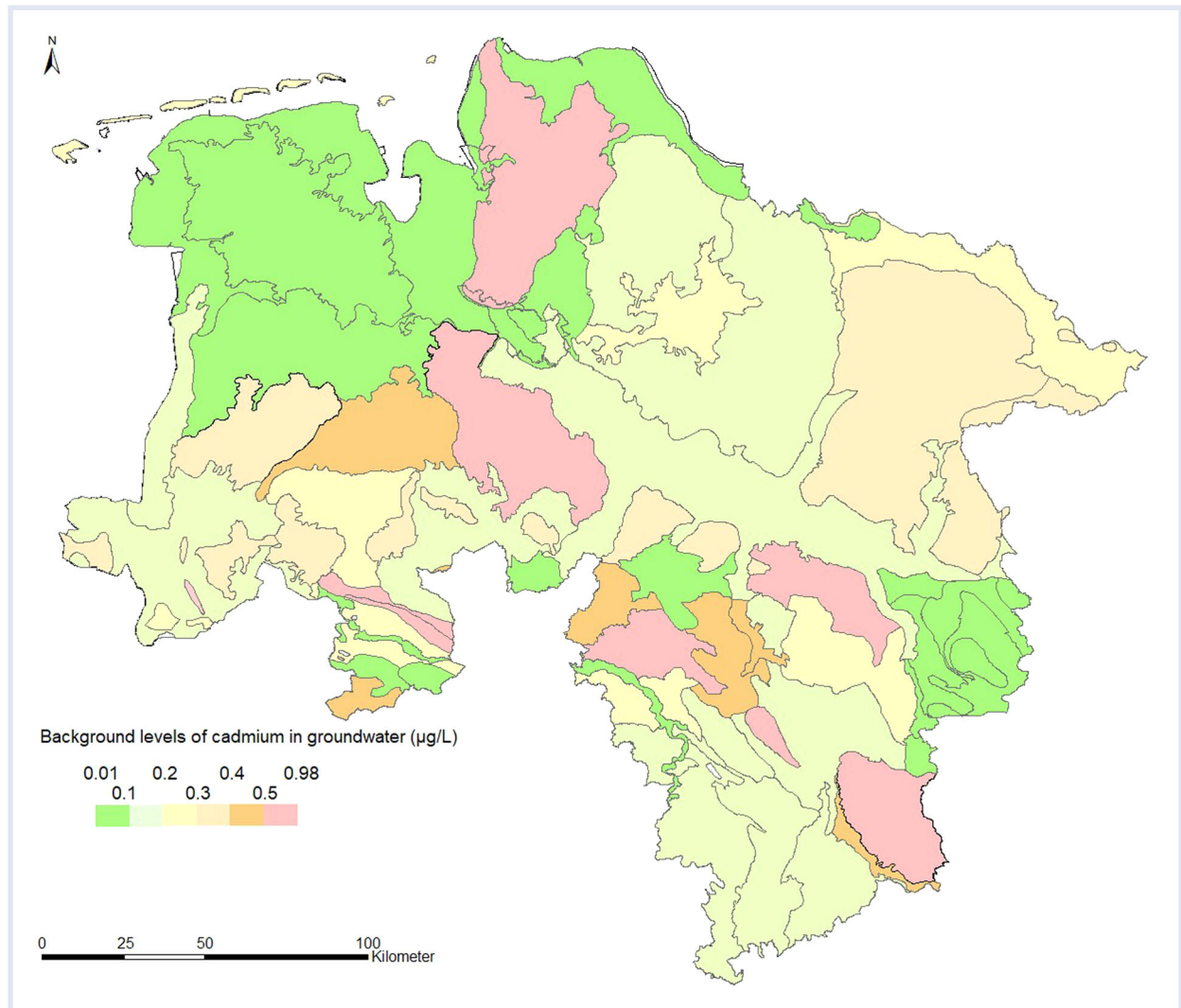


Figure 4. Background levels of Cd in groundwater, classified by hydrogeological subareas.

to derive background levels. The background levels for Cd were mainly elevated in the sandy aquifers of the Geesten area where agricultural activities in combination with little minor groundwater cover protection seemingly have an impact on the “natural background” of Cd.

Alternatively, the occurrence of elevated Cd background levels in the Geesten area (Figure 4) could have been caused by Cd release from glacial deposits and the low sorption capacity of the Geesten sediments, when compared to finer-grained and organic-rich sediments present in the lowlands and wetlands. The Quaternary sedimentary cover in the northern part of Central Europe is known to be enriched in Cd relative to the remainder of Central Europe. Birke et al. (2017) concluded that apart from its glacial history, the Cd budget in this region must have been influenced by mineralization, bonding to organic matter in organic-rich soils, Cd emissions from Zn smelters, and an agricultural overprint. Contrary to Cd, other heavy metals have a higher sorption capacity to mineral surfaces (Lynch et al. 2014), which can be an explanation of missing

elevated concentrations, for example, of Zn, Pb, and Ni, in groundwaters where Cd concentrations were increased. Antoniadis and Tsadilas (2007) observed poor Cd sorption affected by competition with Ni and Zn, which can be a reason for elevated Cd concentrations in the data set, whereas elevated Ni and Zn concentrations in groundwater were missing.

It was difficult to compare the results from our study to findings from other regions due to the use of different analytical methodologies. Furthermore, different threshold values in different countries lead to dissimilar assessments of elevated Cd concentrations in groundwater. For example, the German threshold value for Cd of $0.5 \mu\text{g/L}$ (GrwV 2017) is 20 times lower than the Chinese threshold value of $10 \mu\text{g/L}$ (Li et al. 2017). Hence, it is difficult to compare reports in which the risk assessment is based on different threshold values. For example, findings of Cd concentrations above the German threshold value might be disregarded in countries like Japan because, there, target values for unpolluted groundwater are much higher. The occurrence of elevated

Cd concentrations also strongly depends on the frame of investigation. Typically, the focus of large-scale measurement campaigns is the general groundwater composition, and thus the results are based mainly on groundwater monitoring wells that feature long screens and a low spatial and temporal resolution. Additionally, such large-scale campaigns often use sampling and analytical methods with lower sensitivities that are not suitable to detect trace concentrations of heavy metals like Cd.

Cadmium sources

Overall, 50% of the groundwater samples with Cd concentrations above 0.5 µg/L had nitrate concentrations above 50 mg/L, which is the threshold value for groundwater (EC 2006; GrwV 2017). Those groundwater samples were collected mainly from wells in the Geesten hydrogeological unit. There, it can be assumed that the relatively high annual groundwater recharge of 200 mm to 400 mm (Elbracht et al. 2016) caused fast seepage of nitrate surplus from agriculture (Wriedt et al. 2019). Denitrification caused changes in the redox composition and subsequent acidification of groundwater, for example, by pyrite oxidation (Böhlke 2002). Consequently, Cd was released during sulfide dissolution or it was desorbed due to decreasing pH. Apart from the general connection to farmland, there was no direct link to phosphate fertilizers as a Cd source in the data set because elevated Cd groundwater concentrations were also present in nonagricultural areas. Furthermore, elevated concentrations of other trace metals, such as, Zn, U, and Pb, which can also occur as impurities in phosphate fertilizers (Carrillo-Gonzalez et al. 2006; Grant 2011), were not observed. Beyond this, elevated Cd concentrations in groundwater are at best an ambiguous proxy for the application of phosphate fertilizers because phosphate can either decrease or enhance Cd mobility (Seaman et al. 2001; Carrillo-Gonzalez et al. 2006; Grant 2011). Atmospheric deposition as a common Cd source was also unlikely because today there is low Cd input via atmospheric deposition. However, higher rates of atmospheric deposition in the past caused Cd accumulation in plants and soils, which are currently being released. In European soils, for example, Cd input via atmospheric deposition decreased from 3.0 g·ha⁻¹·y⁻¹ in 2002 to currently 0.35 g·ha⁻¹·y⁻¹. Presently, Cd output from soils via leaching is 2.56 g·ha⁻¹·y⁻¹ (Six and Smolders 2014).

Large parts of the Geesten are covered by forests (woodlands). Huang et al. (2011) stated that forest soils are an effective sink for atmospherically deposited pollutants, whose release is controlled by pH and dissolved organic carbon (DOC). Our results are in agreement with the Huang et al. (2011) study, given that the release of Cd from forest soils is mainly controlled by a decrease in pH. This relation is also accompanied by the elevated 90th percentile of Cd in groundwater within the woodlands of 0.45 µg/L in our study. Godbersen et al. (2012) found elevated Cd background concentrations of 0.8 µg/L in groundwater in sandy soils under forested land in Northern Germany.

Groundwater from the islands and tidal wetlands hydrogeological units had reducing conditions, and thus limited elevated Cd concentrations were observed. Both units are without considerable agriculture. In addition, these hydrogeological units had low background levels for Cd.

According to Banning et al. (2009), it is necessary to select a set of parameters that can be used to identify geogenic sources of trace elements. Hence, potential Cd sources and the corresponding amount of soluble Cd need to be linked to groundwater Cd concentrations at the study scale. Background values for sandy subsoils in Northern Germany are between 0.07 mg/kg and 0.4 mg/kg (LABO 2017). These concentrations are by no means elevated and fit well into the range generally accepted for Cd concentrations in sedimentary rocks (0.01 to 2.6 mg/kg) (Hammons et al. 1978; Smolders and Mertens 2013). Nevertheless, elevated concentration of a trace element in the aquifer matrix is not required to cause a considerable increase of that element in the corresponding groundwater (e.g., Price and Pichler 2006; Wallis et al. 2011).

Recently, however, pyrites were identified as Cd-bearing minerals in reducing aquifers in the Emsland region in northwestern Lower Saxony (Houben et al. 2017). Cadmium content for pyrites reached up to 300 mg/kg in the median, 1600 mg/kg in the maximum, and depending on the pyrite content in the aquifer matrix, up to 2.6 mg/kg in the bulk sediment (Houben et al. 2017). That study was spatially limited to a relatively small area, although it is conceivable that similar values could be encountered locally in glacial deposits, which are common in our study area (Birke et al. 2017; Houben et al. 2017). Thus glacial deposits in the study area could be a significant source of geogenic Cd, which is already evident by the relatively higher Cd concentrations in groundwater in the Geesten hydrogeological unit.

Our study suggests that elevated Cd concentrations in groundwater are related to 1) the occurrence of farmland or woodland, 2) insufficient groundwater cover protection of sandy aquifers, and 3) release of geogenic Cd from sediments through nitrate reduction coupled with pyrite oxidation. Besides, an input of anthropogenic Cd from historical industrial and agricultural processes cannot be excluded (Birke et al. 2017).

SUMMARY AND CONCLUSIONS

A large chemical data set for groundwater in Northwestern Germany was utilized to characterize the “geogenic” Cd background in shallow groundwater, using statistical methods, such as the trend test, in conjunction with consideration of the general chemical behavior of Cd in aqueous media.

The major findings and conclusions are as follows:

- There were 7% of 5512 groundwater analyses that exceeded the German threshold value for Cd of 0.5 µg/L.
- Cadmium background levels in groundwater ranging between 0.01 µg/L and 0.98 µg/L do not represent

pre-anthropogenic levels and thus cannot exclude influences by human activity.

- There was no direct evidence that the application of phosphate fertilizers had considerable impact on Cd concentrations in groundwater. However, it is favorable to use fertilizers low in Cd impurities in order to minimize further Cd input.
- Although recent Cd input via atmospheric deposition has been decreasing, Cd accumulation in soil could have occurred in the past and thus could be a source for today's Cd concentration in groundwater.
- Elevated background levels of Cd in groundwater were related to the Geesten, which are glacial deposits that are groundwater recharge areas.
- Relatively elevated Cd concentrations in groundwater were found more frequently in agricultural areas. Due to the association with nitrate, Cd release is considered anthropogenically induced.
- The presence of Cd in groundwater was linked to hydrogeochemical conditions that facilitate Cd release from the aquifer matrix, such as low pH and changing redox conditions, from reducing to oxidizing. Nevertheless, Cd concentration in groundwater did not correspond to its concentration in the aquifer matrix.

Based on our observations, we also conclude that in order to advance the study of what are considered natural or ambient background concentrations and to make results comparable across political boundaries, it will be necessary to agree on consistent methodologies to be followed.

Acknowledgment—This study was partly funded by Niedersächsischer Landesbetriebs für Wasserwirtschaft, Küsten- und Naturschutz (NLWKN) with funds from the State of Lower Saxony Division of Groundwater, Forschungsprojekt 62170-11-02/CD A31. We are thankful for the continued discussion of this topic with Dörte Budziak, Jörg Elbracht and Dieter de Vries. Comments by the associate editor and 2 anonymous reviewers helped to improve readability and focus of this review.

Disclaimer—The authors declare no conflicts of interest.

Data Availability Statement—Data used in this study are not available publicly nor by request from authors. The mentioned administrative authorities provided data and calculation tools for this study as part of a research project. Further accessibility of particular analyses (e.g., coordinates, concentrations) was prohibited.

ORCID

Andreas Kubier  <http://orcid.org/0000-0002-2504-7185>

REFERENCES

- Abratis PK, Pattrick RAD, Vaughan DJ. 2004. Variations in the compositional, textural and electrical properties of natural pyrite: A review. *Int J Miner Process* 74:41–59.
- Alloway BJ, Jackson AP. 1991. The behavior of heavy-metals in sewage sludge-amended soils. *Sci Total Environ* 100:151–176.
- Anderson PR, Christensen TH. 1988. Distribution coefficients of Cd, Co, Ni, and Zn in soils. *J Soil Sci* 39(1):15–22.
- Antoniadis V, Tsadilas CD. 2007. Sorption of cadmium, nickel, and zinc in mono- and multimetal systems. *Appl Geochem* 22(11):2375–2380.
- [ATSDR] Agency for Toxic Substances and Disease Registry. 2012. A toxicological profile for cadmium. Atlanta (GA). 430 p.
- Banning A, Coldewey WG, Gobel P. 2009. A procedure to identify natural arsenic sources, applied in an affected area in north Rhine-Westphalia, Germany. *Environ Geol* 57(4):775–787.
- Biddau R, Cidu R, Lorrai M, Mulas MG. 2017. Assessing background values of chloride, sulfate and fluoride in groundwater: A geochemical-statistical approach at a regional scale. *J Geochem Explor* 181: 243–255.
- Bigalke M, Ulrich A, Rehmus A, Keller A. 2017. Accumulation of cadmium and uranium in arable soils in Switzerland. *Environ Pollut* 221:85–93.
- Birke M, Reimann C, Rauch U, Ladenberger A, Demetriades A, Jahne-Klingberg F, Oorts K, Gosar M, Dinelli E, Halamic J et al. 2017. GEMAS: Cadmium distribution and its sources in agricultural and grazing land soil of Europe—Original data versus clr-transformed data. *J Geochem Explor* 173:13–30.
- [BKG] Bundesamt für Kartographie und Geodäsie [Federal Agency for Cartography and Geodesy]. 2018. Corine land cover (clc10)—Land cover model Germany, reference year 2012. Leipzig (DE). 16 p.
- Böhlke JK. 2002. Groundwater recharge and agricultural contamination. *Hydrogeol J* 10(1):153–179.
- Caetano M, Madureira MJ, Vale C. 2003. Metal remobilisation during re-suspension of anoxic contaminated sediment: Short-term laboratory study. *Water Air Soil Pollut* 143(1–4):23–40.
- Carrillo-Gonzalez R, Simunek J, Sauve S, Adriano D. 2006. Mechanisms and pathways of trace element mobility in soils. *Adv Agron* 91:111–178.
- Cremer N. 2015. Nitrat im Grundwasser – Konzentrationsniveau, Abbauprozesse und Abbaupotenzial im Tätigkeitsbereich des Ertverbandes [Nitrate in groundwater - concentration levels, degradation processes and degradation potential in the area of operations of the Ertverband]. Bergheim (DE): Ertverband. 311 p.
- Ducci D, Sellerino M. 2012. Natural background levels for some ions in groundwater of the Campania region (southern Italy). *Environ Earth Sci* 67(3):683–693.
- [DVKW]. Deutscher Verband für Wasserwirtschaft und Kulturbau. 1992. Entnahme und Untersuchungsumfang von Grundwasserproben [Extraction and scope of investigations of groundwater samples]. Hamburg (DE): Parey. 36 p.
- [EC] European Commission. 2000. Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for community action in the field of water policy. *OJ L327*. 22.12.2000. 72 p.
- [EC] European Commission. 2006. Directive 2006/118/CE of the European Parliament and of the Council of 12 December 2006 on the protection of groundwater against pollution and deterioration. *OJ L372*. 27.12.2006. 13 p.
- Edmunds WM, Shand P, Hart P, Ward RS. 2003. The natural (baseline) quality of groundwater: A UK pilot study. *Sci Total Environ* 310(1–3):25–35.
- Elbracht J, Meyer R, Reutter E. 2016. Hydrogeological areas and subareas in lower Saxony. Hannover (DE): Landesamt für Bergbau, Energie und Geologie [State Authority of Mining, Energy and Geology]. 118 p.
- [ESRI] Environmental Systems Research Institute. 2018. ArcGIS desktop 10. Redlands (CA).
- Flem B, Reimann C, Fabian K, Birke M, Filzmoser P, Banks D. 2018. Graphical statistics to explore the natural and anthropogenic processes influencing the inorganic quality of drinking water, ground water and surface water. *Appl Geochem* 88:133–148.
- Godbersen L, Duijnsveld WHM, Utermann J, Gabler HE, Kuhnt G, Bottcher J. 2012. Application of groundwater thresholds for trace elements on percolation water: A case study on percolation water from northern German lowlands. *J Environ Qual* 41(4):1253–1262.
- Grant CA. 2011. Influence of phosphate fertilizer on cadmium in agricultural soils and crops. *Pedologist* 3(54):143–155.
- [GrwV] Groundwater Ordinance. 2017. Grundwasserverordnung vom 9. November 2010 (bgbl. I s. 1513), die zuletzt durch artikel 1 der verordnung

- vom 4. Mai 2017 (bgbl. I s. 1044) geändert worden ist. Bundesrepublik Deutschland [Groundwater Ordinance of 9 November 2010 (Federal Gazette I p 1513), which was last amended by Article 1 of the Ordinance of 4 May 2017 (Federal Law Gazette I p 1044). Federal Republic of Germany]. Bonn (DE). 3 p.
- Guler C, Thyne GD, McCray JE, Turner AK. 2002. Evaluation of graphical and multivariate statistical methods for classification of water chemistry data. *Hydrogeol J* 10(4):455–474.
- Hajeb P, Sloth JJ, Shakibazadeh S, Mahyudin NA, Afsah-Hejri L. 2014. Toxic elements in food: Occurrence, binding, and reduction approaches. *Compr Rev Food Sci Food Saf* 13(4):457–472.
- Hammons AS, Huff EJ, Braunstein HM, Drury JS, Shriner CR, Lewis EB, Whitfield BL, Towill LE. 1978. Reviews of the environmental effects of pollutants: IV. Cadmium. Cincinnati (OH): United States Environmental Protection Agency, Oak Ridge National Laboratory. 253 p.
- He ZL, Xu HP, Zhu YM, Yang XE, Chen GC. 2005. Adsorption-desorption characteristics of cadmium in variable charge soils. *J Environ Sci Health* 40(4):805–822.
- Hepburn E, Northway A, Bekele D, Liu GJ, Currell M. 2018. A method for separation of heavy metal sources in urban groundwater using multiple lines of evidence. *Environ Pollut* 241:787–799.
- Hinsby K, de Melo MTC, Dahl M. 2008. European case studies supporting the derivation of natural background levels and groundwater threshold values for the protection of dependent ecosystems and human health. *Sci Total Environ* 401(1–3):1–20.
- Houben GJ, Sitnikova MA, Post VEA. 2017. Terrestrial sedimentary pyrites as a potential source of trace metal release to groundwater - A case study from the Emsland, Germany. *Appl Geochem* 76:99–111.
- Huang GX, Sun JC, Zhang Y, Chen ZY, Liu F. 2013. Impact of anthropogenic and natural processes on the evolution of groundwater chemistry in a rapidly urbanized coastal area, south China. *Sci Total Environ* 463: 209–221.
- Huang JH, Ilgen G, Matzner E. 2011. Fluxes and budgets of Cd, Zn, Cu, Cr and Ni in a remote forested catchment in Germany. *Biogeochemistry* 103(1–3):59–70.
- [IBM] International Business Machines Corporation. 2016. SPSS statistics base 24. Armonk (NY). 202 p.
- Kellner E, Hubbard JA, Ikem A. 2015. A comparison of forest and agricultural shallow groundwater chemical status a century after land use change. *Sci Total Environ* 529:82–90.
- Khadra WM, Stuyfzand PJ. 2014. Separating baseline conditions from anthropogenic impacts: Example of the damour coastal aquifer (Lebanon). *Hydro Sci J* 59(10):1872–1893.
- Kjeldsen P, Barlaz MA, Rooker AP, Baun A, Ledin A, Christensen TH. 2002. Present and long-term composition of msw landfill leachate: A review. *Crit Rev Environ Sci Technol* 32(4):297–336.
- Kubier A, Pichler T. 2019. Cadmium in groundwater – A synopsis based on a large hydrogeochemical data set. *Sci Total Environ* 689:831–842.
- [LABO] Bund/Länder-Arbeitsgemeinschaft Bodenschutz. 2017. Background values for inorganic and organic parameters in soil. Working Group of the Federal States on Soil Protection. 59 p.
- Lazareva O, Pichler T. 2007. Naturally occurring arsenic in the Miocene hawthorn group, southwestern Florida: Potential implication for phosphate mining. *Appl Geochem* 22(5):953–973.
- Li F, Qiu ZZ, Zhang JD, Liu WC, Liu CY, Zeng GM. 2017. Investigation, pollution mapping and simulative leakage health risk assessment for heavy metals and metalloids in groundwater from a typical brownfield, middle china. *Int J Env Res Pub He* 14(7):768.
- Liesch T, Hinrichsen S, Goldscheider N. 2015. Uranium in groundwater - Fertilizers versus geogenic sources. *Sci Total Environ* 536:981–995.
- [LSKN] Landesbetrieb für Statistik und Kommunikationstechnologie Niedersachsen [Lower Saxony State Office for Statistics and Communications Technology]. 2011. Statistische Monatshefte Niedersachsen Nr. 9 [Monthly Statistical Bulletin Lower Saxony No. 9]. Hannover (DE). p 502–571.
- Lu YT, Zang XH, Yao H, Zhang SC, Sun SB, Liu F. 2018. Assessment of trace metal contamination in groundwater in a highly urbanizing area of Shenfu New District, northeast China. *Front Earth Sci-Prc* 12(3):569–582.
- Lynch SFL, Batty LC, Byrne P. 2014. Environmental risk of metal mining contaminated river bank sediment at redox-transitional zones. *Minerals-Basel* 4(1):52–73.
- Mar SS, Okazaki M. 2012. Investigation of Cd contents in several phosphate rocks used for the production of fertilizer. *Microchem J* 104:17–21.
- Mehrabi B, Mehrabani S, Rafiei B, Yaghoubi B. 2015. Assessment of metal contamination in groundwater and soils in the Ahangan mining district, west of Iran. *Environ Monit Assess* 187(12):727.
- Merkel BJ, Sperling B. 1998. Hydrogeochemische Stoffsysteme Teil ii [Hydrogeochemical systems part II]. Bonn (DE): Wirtschafts- und Verl.-Ges. Gas und Wasser. 375 p.
- Mirlean N, Roisenberg A. 2006. The effect of emissions of fertilizer production on the environment contamination by cadmium and arsenic in southern Brazil. *Environ Pollut* 143(2):335–340.
- Molinari A, Guadagnini L, Marcaccio M, Guadagnini A. 2012. Natural background levels and threshold values of chemical species in three large-scale groundwater bodies in northern Italy. *Sci Total Environ* 425:9–19.
- Monna F, Hamer K, Leveque J, Sauer M. 2000. Pb isotopes as a reliable marker of early mining and smelting in the northern Harz province (Lower Saxony, Germany). *J Geochem Explor* 68(3):201–210.
- Najafi S, Jalali M. 2015. Effects of organic acids on cadmium and copper sorption and desorption by two calcareous soils. *Environ Monit Assess* 187(9):1–10.
- Nies DH. 1999. Microbial heavy-metal resistance. *Appl Microbiol Biotechnol* 51(6):730–750.
- Nies DH. 2003. Efflux-mediated heavy metal resistance in prokaryotes. *FEMS Microbiol Rev* 27(2–3):313–339.
- Page AL, Chang AC, El-Amamy M. 1987. Cadmium levels in soils and crops in the United States. In: Hutchinson TC, Meema KM, editors. Lead, mercury, cadmium and arsenic in the environment. Chichester (UK): Wiley. p 119–146.
- Pan JL, Plant JA, Voulvoulis N, Oates CJ, Ihlenfeld C. 2010. Cadmium levels in Europe: Implications for human health. *Environ Geochem Health* 32(1):1–12.
- Pichler T, Price R, Lazareva O, Dippold A. 2011. Determination of arsenic concentration and distribution in the Floridan aquifer system. *J Geochem Explor* 111(3):84–96.
- Preziosi E, Parrone D, Del Bon A, Ghergo S. 2014. Natural background level assessment in groundwaters: Probability plot versus pre-selection method. *J Geochem Explor* 143:43–53.
- Price RE, Pichler T. 2006. Abundance and mineralogical association of arsenic in the Suwannee limestone (Florida): Implications for arsenic release during water-rock interaction. *Chem Geol* 228(1–3):44–56.
- Reimann C, Filzmoser P, Garrett RG. 2005. Background and threshold: Critical comparison of methods of determination. *Sci Total Environ* 346(1–3):1–16.
- Reimann C, Garrett RG. 2005. Geochemical background - Concept and reality. *Sci Total Environ* 350(1–3):12–27.
- Riedel T, Kübeck C. 2018. Uranium in groundwater - A synopsis based on a large hydrogeochemical data set. *Water Res* 129:29–38.
- Seaman JC, Arey JS, Bertsch PM. 2001. Immobilization of nickel and other metals in contaminated sediments by hydroxyapatite addition. *J Environ Qual* 30(2):460–469.
- Six L, Smolders E. 2014. Future trends in soil cadmium concentration under current cadmium fluxes to European agricultural soils. *Sci Total Environ* 485:319–328.
- Smith DB, Cannon WF, Woodruff LG, Solano F, Ellefsen KJ. 2014. Geochemical and mineralogical maps for soils of the conterminous United States. Reston (VA): US Geological Survey. 386 p.
- Smolders E, Mertens J. 2013. Cadmium. In: Alloway JB, editor. Heavy metals in soils – Trace metals and metalloids in soils and their bioavailability. 3rd ed. Dordrecht (NL): Springer. p 283–299.
- Sprynskyy M, Kowalkowski T, Tutu H, Cozmuta LM, Cukrowska EM, Buszewski B. 2011. The adsorption properties of agricultural and forest soils towards heavy metal ions (Ni, Cu, Zn, and Cd). *Soil Sediment Contam* 20(1):12–29.
- Taylor M, Kim N, Smidt G, Busby C, McNally S, Robinson B, Kratz S, Schnug E. 2016. Trace element contaminants and radioactivity from phosphate fertiliser. In: Schnug E, De Kok LJ, editors. Phosphorus in agriculture: 100% zero. Dordrecht (NL): Springer. p 231–266.
- [UNEP] United Nations Environment Programme. 2010. Final review of scientific information on cadmium. 118 p.

- Wagner B, Walter T, Himmelsbach T, Clos P, Beer A, Budziak D, Dreher T, Fritsche HG, Hubschmann M, Marczinek S et al. 2011. A web map service for background groundwater chemistry in Germany. *Grundwasser* 16(3): 155–162.
- Wallis I, Prommer H, Pichler T, Post V, Norton SB, Annable MD, Simmons CT. 2011. Process-based reactive transport model to quantify arsenic mobility during aquifer storage and recovery of potable water. *Environ Sci Technol* 45(16):6924–6931.
- Wendland F, Blum A, Coetsiers M, Gorova R, Griffioen J, Grima J, Hinsby K, Kunkel R, Marandi A, Melo T et al. 2008. European aquifer typology: A practical framework for an overview of major groundwater composition at European scale. *Environ Geol* 55(1):77–85.
- Wriedt G, de Vries D, Eden T, Federolf C. 2019. Regionalisierte Darstellung der Nitratbelastung im Grundwasser Niedersachsens [Mapping groundwater nitrate concentrations in Lower Saxony]. *Grundwasser* 24(1):27–41.