Universität Bremen

Occurrence, reaction and transport behavior of cadmium in groundwater

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Summary

Cadmium (Cd) is a non-essential trace element that is widely distributed in the environment. Due to its low sorption affinity compared to other heavy metals, Cd is easily mobilized, potentially resulting in elevated Cd concentrations in groundwater. It remains in solution at near neutral pH (< 6.5). Due to its physicochemical similarity, Cd tends to substitute for elements such as calcium in chemical structures, leading to uptake and bioaccumulation by humans and animals. It is one of the most toxic elements in the environment.

There is a lack of information about the processes that control Cd concentration in groundwater and hence, there is a need for a detailed study of its behavior. Elevated Cd concentrations in groundwater can be resultant from a multitude of natural and anthropogenic sources. The release of Cd from phosphate fertilizers is presumably the primary anthropogenic source. Cadmium also enters groundwater via atmospheric deposition and point sources such as landfills and mining activities. The mobility of Cd in aquifers increases in the presence of oxygen and nitrate if it is associated with sulfide minerals, particularly pyrite. If associated with carbonate minerals, it can be released due to dissolution with decreasing pH.

The goal of the doctoral project was to provide a better understanding about the source, transport, and fate of Cd in groundwater through the evaluation of a large hydrogeochemical data set. According to the European Water Framework Directive, groundwater quality was evaluated in the European Union. The assessment of several groundwater bodies in Northern Germany resulted in a *poor chemical status* due to elevated Cd concentrations. A government research project was initiated to identify the sources, reactions, and the transport behavior of Cd based on data from 6,300 sampling locations. Northern Germany was considered an appropriate model because of its variety in lithology, land use, and publicly accessible data on groundwater quality. Therefore, data from the research project were particularly suitable to investigate Cd for the purposes of this doctoral project. In total, 4,594 groundwater analyses from the data set were exploitable for statistical analysis. The investigation contained time series analyses, calculation of background values for Cd in groundwater, and classification of water types to identify the main mechanisms that result in elevated Cd concentrations. Additionally, the findings were correlated with data concerning Cd contents in soil and atmospheric deposition provided from permanent soil monitoring sites.

The mean and median Cd concentrations of all samples (N = 4,595) 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 German Cd threshold of 0.5 µg/L (8 % of 4,594 analyses). Most samples (219 out of 363) exceeding 0.5 µg/L were located in the area of Pleistocene glacial deposits, the so-called *Geesten*, whose main land use is farmland (42 % of 363 sampling locations) and woodland (33 %). Samples with elevated Cd concentrations were mainly taken in the upper 15 m of groundwater. Cadmium concentrations in groundwater above 0.5 µg/L were found at locations that showed low groundwater protection due to shallow water tables and insufficient covering rocks of low permeability. The annual groundwater recharge rates at these locations were 150 to 250 mm. A time series analysis revealed 30 wells with increasing Cd concentrations were often associated with low pH, increased nitrate and further increased heavy metal concentrations, e.g., Mn, Ni, and Zn.

Above-threshold Cd concentrations were linked to specific groundwater compositions caused by woodlands in connection with acidification or farmland induced nitrate. The main parameters affecting Cd mobility were pH and redox potential, which were linked to Cd sorption to mineral surfaces and Cd release from carbonates and sulfides. Cadmium can remain in solution as water-soluble complexes with inorganic ligands, such as chloride and sulfate, as well as dissolved organic matter, while sorption and precipitation decrease the aqueous concentration of other heavy metals such as Pb and Cu.

Cadmium primarily occurred in shallow groundwater under oxic and autotrophic nitrate reducing conditions. In addition, hydrogeological factors enhanced groundwater recharge and limited Cd retention capacity by the aquifer matrix. Calculated Cd background levels in groundwater were between 0.01 µg/L in hydrogeological units of mainly reducing conditions and 0.98 µg/L in groundwater recharge areas. The mean background value of Cd in groundwater of marshlands and lowlands was 0.13 µg/L, which is approximately three times lower than the mean value of 0.36 µg/L observed in the Geesten.

There were no indications for significant anthropogenic Cd input. Apart from the general connection to farmland, there was no direct link to phosphate fertilizers as a

Cd source in the data set. It was suggested that elevated Cd concentrations in groundwater originated from the release of geogenic Cd from sediments through nitrate reduction coupled with pyrite oxidation. Atmospheric deposition as an important Cd source was unlikely because current rates of atmospheric Cd deposition are low. However, historic rates of atmospheric deposition were higher and caused Cd accumulation in plants and soils. Forest soils are an effective sink for atmospherically deposited Cd, but it is easily released under acidic conditions. Background levels of Cd in groundwater indicated influences by continuous intensive land use as well as the local geology, which is dominated by glacial deposits.

It can be assumed that Cd release is controlled by hydrochemical and hydrogeological parameters and that mobilization processes are more likely than a considerable amount of Cd input. Therefore, the origin of Cd in groundwater is presumably geogenic, and its release primarily induced by anthropogenic influences.

Kurzfassung

Cadmium (Cd) ist ein nicht-essentielles Spurenelement, das in der Umwelt weit verbreitet ist. Aufgrund seiner geringen Sorptionsaffinität im Vergleich zu anderen Schwermetallen wird Cd leicht mobilisiert, was potenziell zu erhöhten Cd-Konzentrationen im Grundwasser führen kann. Es bleibt bei annähernd neutralem pH-Wert (< 6,5) in Lösung. Wegen seiner physikochemischen Ähnlichkeit mit Elementen wie Calcium kann Cd diese in chemischen Strukturen ersetzen, was zur Aufnahme und Bioakkumulation in Mensch und Tier führt. Es ist eines der giftigsten Elemente in der Umwelt.

Informationen zu den Prozessen, die die Konzentration von Cd im Grundwasser steuern, fehlen, woraus sich die Notwendigkeit einer detaillierten Untersuchung zu seinem Verhalten ergibt. Erhöhte Cd-Konzentrationen im Grundwasser können sich durch eine Vielzahl natürlicher und anthropogener Quellen ergeben. Die Freisetzung von Cd aus Phosphatdüngern ist wahrscheinlich die hauptsächliche anthropogene Quelle. Cadmium kann auch durch die atmosphärische Deposition und Punktquellen wie Deponien und Bergbau in das Grundwasser gelangen. Die Mobilität von Cd im Grundwasserleiter steigt in Gegenwart von Sauerstoff oder Nitrat, wenn es in Verbindung mit Sulfidmineralen, besonders Pyrit, auftritt. In Karbonatmineralen vorliegend kann es bei deren Auflösung unter geringen pH-Werten freigesetzt werden.

Das Ziel dieses Promotionsvorhabens war es, durch die Auswertung eines großen hydrogeochemischen Datensatzes ein besseres Verständnis bezüglich Herkunft, Transport und Verbleib von Cd im Grundwasser zu liefern. Gemäß der Europäischen Wasserrahmenrichtlinie wurde die Grundwasserqualität in der Europäischen Union ausgewertet. Die Beurteilung einiger Grundwasserkörper in Norddeutschland führte aufgrund erhöhter Cd-Konzentrationen zu einem *schlechten chemischen Zustand*. Ein staatliches Forschungsprojekt wurde initiiert um, basierend auf einem Datensatz von 6.300 Messstellen, die Herkunft, Reaktionen und das Transportverhalten von Cd zu analysieren. Norddeutschland ist aufgrund seiner Vielfalt in Lithologie und Landnutzung sowie der öffentlich zugänglichen Daten zur Grundwasserqualität eine geeignete Modellregion. Deshalb waren die Daten des Forschungsprojektes besonders geeignet, um Cd als Gegenstand des Promotionsvorhabens zu untersuchen. Insgesamt waren 4.594 Grundwasseranalysen des Datensatzes für eine statistische Auswertung nutzbar. Die Untersuchung umfasste

Zeitreihenanalysen, die Berechnung von Hintergrundwerten für Cd im Grundwasser und die Einordnung in Wassertypen, um die wesentlichen Vorgänge zu identifizieren, die zu erhöhten Cd-Konzentrationen führen. Zusätzlich wurden die Ergebnisse mit Cd-Gehalten in Böden und atmosphärischer Deposition, die von Boden-Dauerbeobachtungsflächen stammen, verknüpft.

Der Mittelwert und der Median der Cd-Konzentrationen aller Proben (N = 4.595) lag bei 0,23 µg/L bzw. 0,08 µg/L. Zwei Drittel der Cd-Analysen lag unterhalb der Bestimmungsgrenze. Es gab 363 Grundwasseranalysen, bei denen der deutsche Schwellenwert für Cd von 0,5 µg/L überschritten wurde (8 % von 4.595). Die meisten dieser Proben (219 von 363) stammten aus dem Gebiet pleistozäner glazialer Ablagerungen, den so genannten *Geesten*, deren vorwiegende Landnutzung Ackerland (42 % der 363 Messstellen) und Wald (33 %) ist. Proben mit erhöhten Cd-Konzentrationen stammten überwiegend aus den oberen 15 m des Grundwassers. Cadmiumkonzentrationen im Grundwasser über 0,5 µg/L wurden an Standorten gefunden, die ein geringes Schutzpotenzial aufwiesen, was durch flache Grundwasserspiegel und unzureichende Überdeckung mit Gesteinen geringer Durchlässigkeit bedingt ist. Die jährliche Grundwasserneubildung an diesen Standorten lag bei 150 bis 250 mm. Die Zeitreihenanalyse ergab 30 Messstellen mit steigenden Cd-Konzentrationen, oft in Verbindung mit geringem pH-Wert sowie steigenden Konzentrationen von Nitrat und weiteren Schwermetallen, z.B. Mn, Ni und Zn.

Schwellwertüberschreitende Cd-Konzentrationen wurden mit charakteristischer Grundwasserbeschaffenheit in Verbindung gebracht, die an Waldstandorten durch Versauerung oder bei landwirtschaftlich genutzten Flächen durch eingetragenes Nitrat verursacht wurde. Die hauptsächlichen Parameter, die die Cd-Mobilität beeinflussen, waren pH-Wert und Redoxpotenzial, welche mit der Sorption von Cd an Mineraloberflächen und der Freisetzung aus Karbonaten und Sulfiden verbunden sind. Cadmium kann in wasserlöslichen Komplexen mit anorganischen Liganden wie Chlorid und Sulfat wie auch mit gelöster organischer Substanz in Lösung bleiben, während Sorption und Ausfällung die gelöste Konzentration anderer Schwermetalle wie Pb und Cu verringert.

Cadmium kam überwiegend im flachen Grundwasser unter oxischen und autotrophen nitratreduzierenden Verhältnissen vor. Zusätzlich verstärkten hydrogeologische Faktoren die Grundwasserneubildung und beschränkten die Rückhaltekapazität des Grundwasserleiters bezüglich Cd. Berechnete Hintergrundwerte für Cd im Grundwasser lagen zwischen 0,01 µg/L in hydrogeologischen Einheiten mit überwiegend reduzierenden Bedingungen und 0,98 µg/L in Grundwasserneubildungsgebieten. Der mittlere Hintergrundwert für Cd im Grundwasser der Marschen und Niederungen betrug 0,13 µg/L, was etwa dreimal weniger ist als der Mittelwert von 0.36 µg/L für die Geesten.

Es gab keine Anzeichen für einen signifikanten anthropogenen Cd-Eintrag. Abgesehen von der allgemeinen Verbindung zu Ackerland gab es im Datensatz keine direkte Verbindung zu Phosphatdüngern als Cd-Quelle. Es liegt nahe, dass erhöhte Cd-Konzentrationen im Grundwasser durch die an die Reduktion von Nitrat gekoppelte Oxidation von Pyrit als geogenes Cd aus dem Sediment freigesetzt wurden. Atmosphärische Deposition als wesentliche Cd-Quelle war unwahrscheinlich, da die derzeitige Rate der atmosphärischen Cd-Deposition gering ist. Allerdings waren frühere Raten der atmosphärischen Deposition höher und führten zur Cd-Anreicherung in Pflanzen und Böden. Waldböden sind eine effektive Senke für Cd aus atmosphärischem Niederschlag, jedoch kann es unter sauren Bedingungen wieder leicht gelöst werden. Hintergrundwerte für Cd im Grundwasser deuten auf den Einfluss einer stetigen, intensiven Landnutzung sowie die lokale Hydrogeologie, die von glazialen Ablagerungen geprägt ist, hin.

Es kann davon ausgegangen werden, dass die Freisetzung von Cd durch hydrochemische und hydrogeologische Parameter gesteuert wird und dass Mobilisierungsprozesse wahrscheinlicher sind als ein bedeutsamer Cd-Eintrag. Daher ist die geogene Herkunft des Cd im Grundwasser wahrscheinlich und dessen Freisetzung wird überwiegend durch anthropogene Einflüsse hervorgerufen.

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ATSDR	Agency for Toxic Substances and Disease Registry
BDF	Permanent soil monitoring sites
BGR	Federal Institute for Geosciences and Natural Resources of Germany
Cd	Cadmium
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DOS	Reduced organic sulfur
GrwV	Groundwater ordinance of Germany
LABO	Working Group of the Federal States on Soil Protection
LAWA	Working Group of the Federal States on Water Issues
LBEG	State Authority of Mining, Energy and Geology
LfU	State office of Environment of the Federal State of Brandenburg
MU	Ministry of the Environment, Energy, Construction and Climate Protection of the Federal State of Lower Saxony
N	Nitrogen (fertilizers)
NLWKN	Agency for Water Management, Coastal Defense and Nature Conservation of the Federal State of Lower Saxony
P	Phosphate (fertilizers)
PZC	Point of zero charge
SGD	Geological Surveys of the Federal States of Germany
SUBV	Senator for Environment, Construction and Transport of the Federal State of Bremen
UNEP	United Nations Environment Programme
WFD	European Water Framework Directive
WHO	World Health Organization

1. Introduction

1.1 Motivation and objectives

Groundwater composition is influenced by multiple inputs and hydrogeochemical processes (Figure 1.1). Main anthropogenic activities altering groundwater quality are agriculture, mining, combustion, and waste management (Rice and Herman, 2012). In addition to direct pollution of the subsurface (e.g., via wastewater and fertilizers application), atmospheric deposition of acids and trace elements such as cadmium (Cd) can cause widespread pollution of soils and groundwater. When entering the vadose zone and subsequent aquifer, microbial activity can alter water composition by depleting or increasing concentrations of nutrients, organic matter, and heavy metals (Figure 1.1). The hydrochemical evolution depends on water depth and age, which is controlled by aquifer properties and water-rock interactions such as sorption.

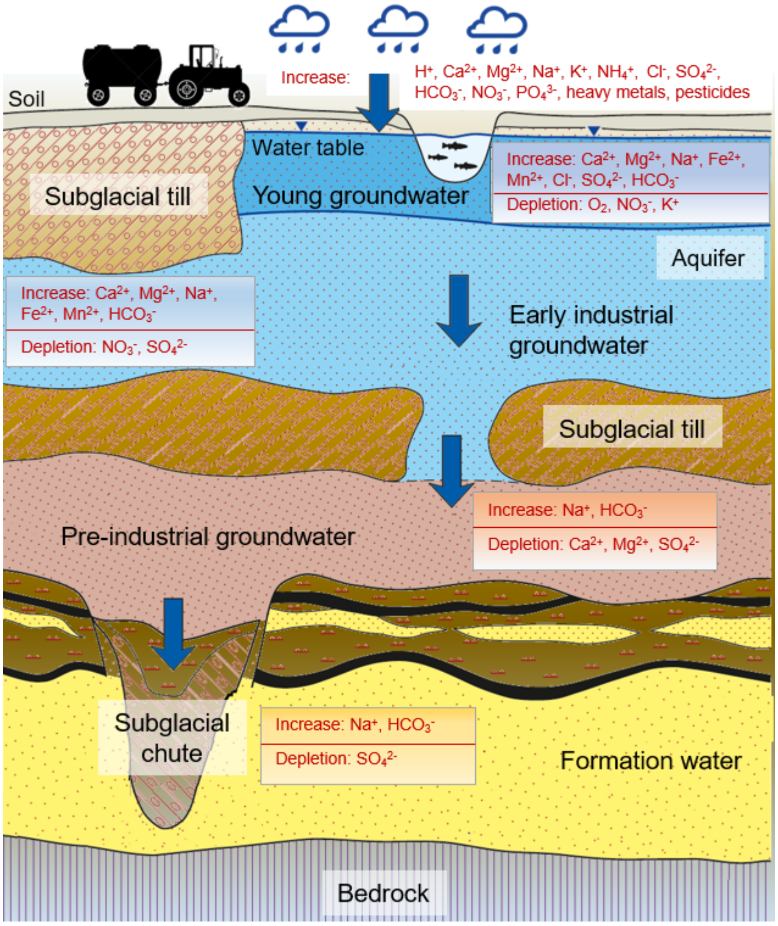

Figure 1.1: Chemical evolution of groundwater (adapted after Hotzan, 2011).

Cadmium is one of the most toxic and mobile elements in the environment (Alloway and Jackson, 1991; Nies, 1999, 2003). It can occur in the atmosphere, hydrosphere, pedosphere, and lithosphere and eventually in the biosphere. It is a well-known parameter regarding agriculture due to elevated Cd contents in phosphate fertilizers. As a consequence, Cd can accumulate in plants and water bodies and subsequently affects human health (Carrillo-Gonzalez et al., 2006). Many lab experiments and modeling work has been conducted to investigate the reaction and transport behavior of Cd. However, no large hydrogeochemical data sets have yet been used to further information on Cd behavior in groundwater.

The European Water Framework Directive (WFD) caused the member states of the European Union to investigate their individual groundwater resources in terms of quantity and quality (EC, 2000). Several groundwater bodies in Lower Saxony, Germany, were indicated as *poor chemical status*. In addition to nitrate and pesticides, 9 out of 123 groundwater bodies had a *poor* chemical status because of Cd concentrations exceeding the German threshold value of 0.5 µg/L (GrwV, 2017). Consequently, the administration of Lower Saxony initiated the research project "*Cadmium im Grundwasser Niedersachens*" dealing with a summarized investigation of a large-scale hydrochemical data set. The aim of this project was to determine whether elevated Cd concentrations were caused by geogenic or anthropogenic influences. The results of the research project were outlined in Kubier et al. (2018). A synopsis of this final report will be submitted as a peer-review paper in the German journal *Grundwasser* and is attached within the appendix. Data and analyses from the research project were particularly suitable to investigate Cd for the purposes of a doctoral project, which is described in the following chapters.

The aim of the doctoral project was to give a broad overview of Cd in soil and groundwater and to assess a large-scale hydrogeochemical data set in terms of redox state, geogenic background, and natural and anthropogenic influences on groundwater quality. Groundwater composition can be altered by point sources as well as diffuse influences. Both geogenic and anthropogenic factors can affect the natural groundwater composition (Figure 1.2). It is, therefore, necessary to determine the extent of Cd concentrations that are related to the *natural background*. In the case of above-threshold Cd concentrations in groundwater that are caused by the natural background, a *good* chemical status for the concerning groundwater body can be acknowledged (EC, 2006). It can be assumed that the sum of all these factors control Cd mobility and cause elevated Cd concentrations in groundwater.

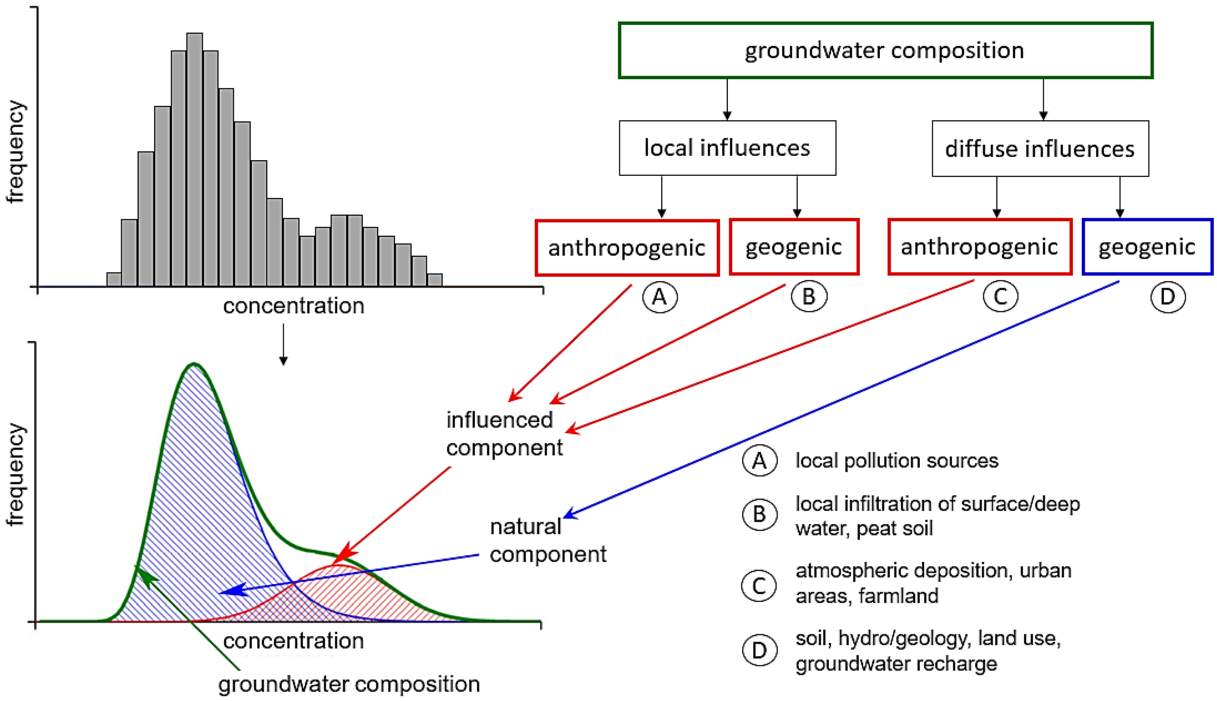

Figure 1.2: Classification and distribution of factors influencing groundwater quality.

The goals of this thesis were to:

- analyze Cd behavior in groundwater in time and space
- identify statistical relations between Cd and other hydrochemical parameters
- determine the natural background of Cd in groundwater, e.g., by calculating background levels
- identify influences from anthropogenic activities, hydrogeology, and hydrochemistry
- find an indication of water-rock interactions controlling Cd mobility, e.g., co-precipitation of Cd in sulfide minerals can occur in reducing groundwater milieu, while oxidation processes enhance Cd release

As a summary for possible cases of Cd release, three scenarios were developed (Figure 1.3). In scenario *I*, elevated Cd concentrations in groundwater are linked to rock types with increased Cd contents, e.g., sulfides. Cadmium is released in the context of weathering or naturally caused acidification. In scenario *II*, Cd originates from natural sources, but its release is caused by anthropogenic influences, e.g., atmospheric deposition or acidification linked to denitrification of nitrogen fertilizers. The most likely reason for elevated Cd in groundwater is expected in scenario *III*. In this case, Cd originates from P fertilizers and atmospheric deposition. Further entries are linked to industrial activities and traffic.

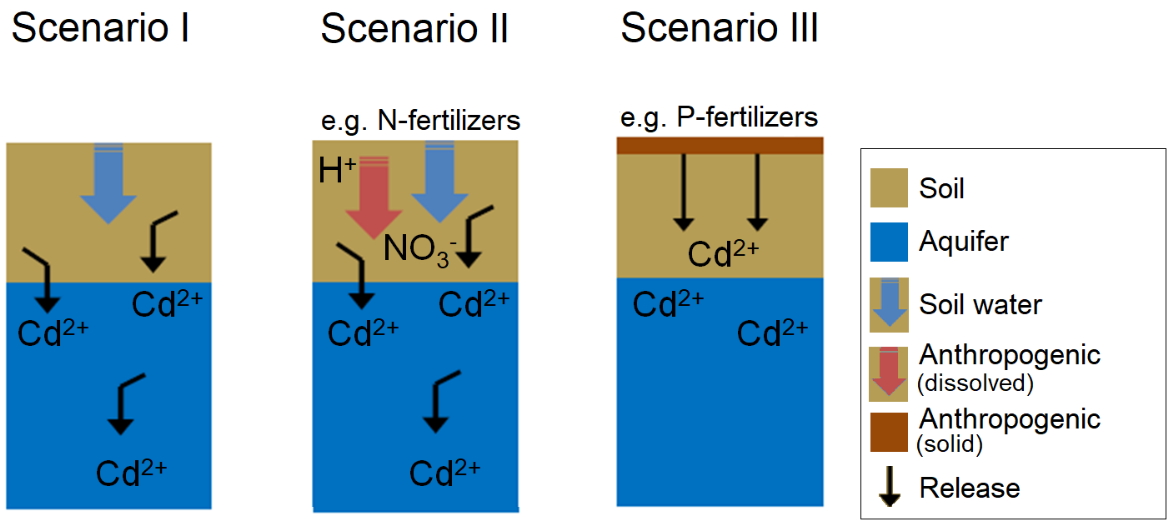

Figure 1.3: Scenarios abstracting Cd release.

1.2 Thesis structure

This thesis was written in the cumulative format and thus, consists of a collection of four research manuscripts, which have been submitted or will be submitted as joint-author articles to international peer-reviewed journals. The thesis is divided into six main chapters. This introductory chapter provides an outline of the motivation, objectives, and aims of the doctoral project as well as a short introduction to the necessity of investigating groundwater quality with an emphasis on Cd.

Chapter 2 deals with a general overview of the occurrence and behavior of Cd in soils and groundwater. Global studies regarding Cd pollution and investigations on Cd behavior in field and lab experiments are collected. The content of this chapter comprises the first five sections of a review paper that has been submitted to the journal *Applied Geochemistry*. This review paper is not included as a whole but split and used in the introductory (chapter 2) and concluding (chapter 6) sections as a frame for the research articles.

In chapter 3, the utilized data sets, data processing, and applied statistical methods, which are the basis of the two following chapters, are explained in detail.

Chapter 4 focuses on the assessment of a large hydrogeochemical data set to analyze the influence of pH, redox, and major elements as well as land use and hydrogeology on Cd concentrations in groundwater. This chapter was submitted to the journal *Science of the Total Environment*.

In chapter 5, the origin of elevated Cd concentrations in groundwater is investigated by calculating background levels and regarding possible geogenic and anthropogenic sources. This chapter was submitted to the journal *Integrated Environmental Assessment and Management*.

Finally, chapter 6 synthesizes the main conclusions of this thesis and also illustrates an outlook for future research opportunities in the researched field. Parts of this chapter belong to the concluding remarks of the review paper (manuscript 1).

In the appendix, manuscript 4 provides a summary of the main results from the research project "*Cadmium im Grundwasser Niedersachens*" (Kubier et al., 2018). As the final report of the research project, this manuscript is also written in German in order to target scientists and further stakeholders from Germany. The manuscript was attached within the appendix due to the use of another language. Manuscript 4 describes the legal framework of the project and the assessment of monitoring wells and permanent soil monitoring sites, the so-called *Boden-Dauerbeobachtungsflächen* (BDF), regarding Cd behavior in different environmental media. The manuscript is in preparation for submission to the journal *Grundwasser*.

1.3 Declaration of co-author contributions

This thesis includes three manuscripts, one review article and two research articles, which have been submitted to peer-review journals, and one manuscript that has been prepared for publication. The chapters are prepared under consideration of the journal requirements, to which they have been submitted or are intended for submission, but the style is adapted to the thesis style and headings, figures, tables, and formulae are numbered consecutively throughout the thesis. A complete list of references is given at the end of the thesis with the exception of the German-language manuscript, which is supplied as continuous text in the appendix. In the following, a detailed overview of the co-authors' contributions to each chapter is presented.

Chapters 2 and 6: *Cadmium in soils and groundwater: A review*

Authors: Andreas Kubier, Richard T. Wilkin and Thomas Pichler

Status: submitted to *Applied Geochemistry*, accepted with major revisions

With few exceptions, the initial text, graphics, and tables were prepared by AK. TP devised and planned the research project. RTW contributed parts of the third and fifth chapter. The co-authors contributed content and reviewed the manuscript before submission.

Chapter 4: *Cadmium in groundwater − A synopsis based on a large hydrogeochemical data set*

Authors: Andreas Kubier and Thomas Pichler

Status: submitted to *Science of the Total Environment*, accepted with revisions

The acquisition and assessment of data were performed by AK. AK wrote the first version of the manuscript, including, all graphics, and tables. TP helped with interpretation of the data and reviewed the manuscript before submission.

Chapter 5: *Cadmium background levels in groundwater in an area dominated by agriculture in Northwestern Germany*

Authors: Andreas Kubier, Kay Hamer and Thomas Pichler

Status: submitted to *Integrated Environmental Assessment and Management*, under review

The development of the overall idea was a flowing process, which greatly benefited from practical advice and regular discussions amongst the co-authors. AK was responsible for the acquisition and assessment of data and prepared the first version of text, graphics, and tables. KH and TP refined the text and content through contributions to the interpretation of the results and the discussion and reviewed the manuscript before submission.

Appendix: *Cadmium im Grundwasser Nordwestdeutschlands − Herkunft, Mobilisierung und Bewertung nach Wasserrahmenrichtlinie*

Authors: Andreas Kubier, Dörte Budziak, Dieter de Vries, Jörg Elbracht, Kay Hamer and Thomas Pichler

Status: to be submitted to *Grundwasser*

This manuscript is a summary of the research project, which was funded by the federal state of Lower Saxony. The research project was developed and promoted by the institutions the co-authors are representing. Project progress greatly benefited from practical advice and regular discussions with all co-authors. AK wrote the first version of all text, graphics, and tables. The co-authors had valuable contributions to the interpretation of the results and the discussion and reviewed the manuscript.

2. Cadmium in soils and groundwater

Andreas Kubier[a], Richard T. Wilkin[b] and Thomas Pichler[a]*

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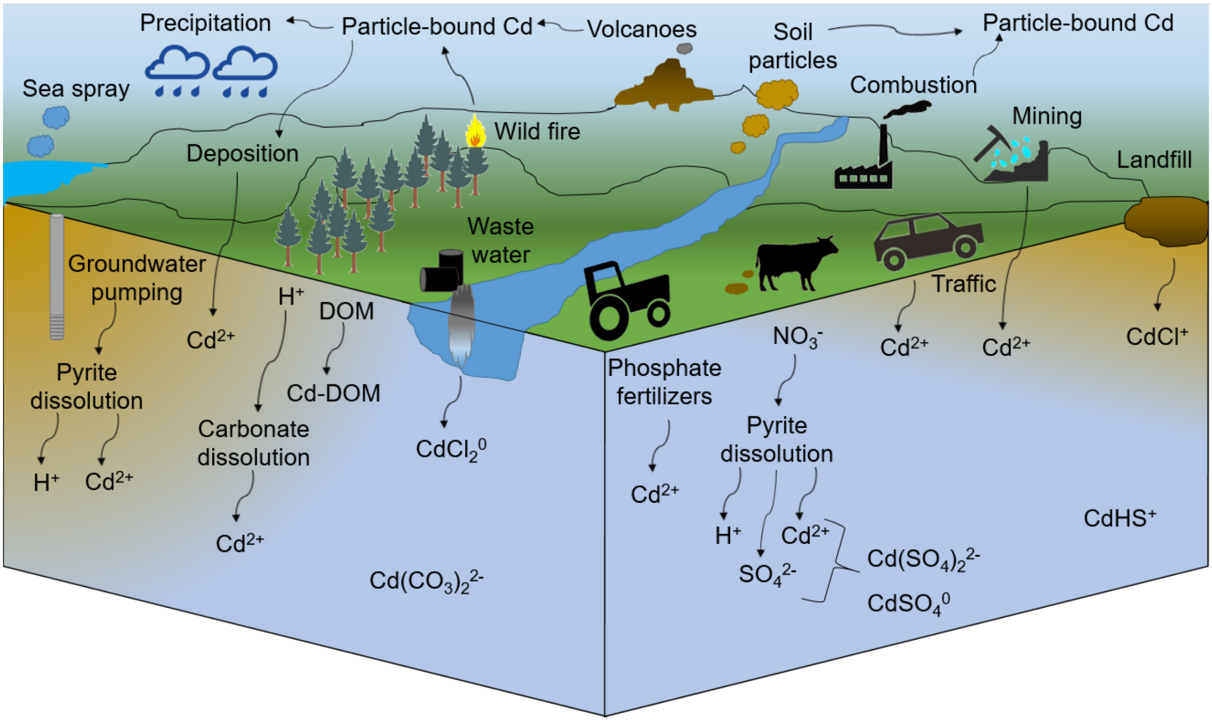
This chapter belongs to a manuscript that has been submitted to the journal *Applied Geochemistry* and has been *accepted with major revisions.*

Abstract

Cadmium (Cd) is a non-essential trace element that is widely distributed in the environment. Both geogenic and anthropogenic sources can elevate Cd concentrations in soils and groundwater, which are important for maintaining healthy supplies of food and safe drinking water. Elevated Cd doses are carcinogenic to humans. The WHO Guidelines for Drinking-Water Quality recommend a guideline value for Cd of 3 µg/L. Important anthropogenic Cd sources include mining, atmospheric deposition of combustion emissions, and the use of Cd-containing fertilizers. We document several cases of Cd pollution in soil and groundwater based on worldwide accounts. Besides anthropogenic Cd sources, Cd is also incorporated into sulfides, carbonates, and phosphorites resulting in elevated Cd concentrations in associated rock types. The crustal median Cd content is 0.2 mg/kg. In soils, Cd occurs at concentrations of 0.01 to 1 mg/kg with a worldwide mean of 0.36 mg/kg. Weathering can lead to Cd concentrations up to 5 µg/L in soil water and up to 1 µg/L in groundwater. In aqueous solutions, Cd generally occurs as the divalent Cd^{2+} and it is mobilized mainly in oxic, acidic conditions. Cadmium sorption is enhanced by the presence of high amounts of hydrous oxides, clay minerals, and organic matter, and its mobility is further influenced by pH, the redox state, and ionic strength of the solution. However, Cd can remain in solution as water-soluble complexes with anions, such as $CdCl^{+}$ and $Cd(SO_4)_2^{2-}$, and dissolved organic matter while sorption and precipitation decrease the aqueous concentration of other heavy metals such as Zn and Cu. As a consequence, Cd is one of the most mobile heavy metals in the

environment. The elevated mobilization potential, e.g., through competition and ligand induced desorption, is the reason for faster Cd release from soil into groundwater than other heavy metals. The goal of this study was to present a broad overview of the origin and concentration of Cd in groundwater, and its reaction pathways in aquatic environments. To gain an overview of the hydrochemical behavior of Cd, cases of Cd pollution in soil and groundwater, studies investigating Cd release, and information about the legal framework were compiled.

Graphic Abstract



2.1 Introduction

Cadmium (Cd) is one of the most toxic and mobile elements in the environment (e.g., Alloway and Jackson, 1991; Nies, 1999, 2003). It can replace calcium in minerals due to its similar ionic radius, identical charge and similar chemical behavior (e.g., Thornton, 1986). Therefore, Cd can enter the human body and accumulate to a high level in several organs (Hajeb et al., 2014; Pan et al., 2010). In contrast to other toxic elements such as mercury (Hg) and arsenic (As), Cd enters the human diet mainly through terrestrial pathways, e.g., through vegetables. In areas with both anthropogenic and geogenic elevated Cd concentrations in soil and groundwater, rice bioaccumulated Cd, leading to an elevated daily Cd uptake in China, Korea, and Jamaica (Liu et al., 2017; Sebastian and Prasad, 2014). However, Cd bioavailability is complex, for example, rice from the southern part of China contains more Cd than rice from the northern part of China. Possible reasons are the more acidic soils, an overuse of nitrogen fertilizers, pollution through irrigation and atmospheric deposition, and the cultivation of rice with a higher affinity for Cd accumulation in southern China (Chen et al., 2018; Yang et al., 2016).

Chronic Cd poisoning, termed *itai-itai* disease first discovered in Japan in the early 20th century, causes renal tubular dysfunction, osteomalacia, and osteoporosis due to competition with Ca and other nutrients (Aoshima, 2016; Arain et al., 2015; Khan et al., 2017). Cadmium exposure is also associated to glucose metabolism disorders, breast and lung cancer, cerebral infarction and cardiac failure (Khan et al., 2017). According to WHO (2011), the tolerable monthly Cd intake is 25 µg/kg body weight due to its long biological half-life in humans of 10 to 35 years. Cadmium uptake occurs through ingestion and inhalation and prolonged exposure may lead to various types of cancer (Pan et al., 2010). Cadmium is therefore listed as a priority hazardous substance in the European Water Framework Directive, which required management plans to cease Cd releases to the environment (EC, 2000). In addition to the European Water Framework Directive, the European Groundwater Directive required the EU member states to set a threshold value for Cd in groundwater (EC, 2006). Each member state developed their own procedures to determine a threshold value and values ranged from 0.08 to 27 µg/L; eight EU member states do not have a threshold value for Cd due to missing risk assessments (EC, 2010). In drinking water, the guideline value for Cd is set to 3 µg/L (WHO, 2011). The United States Environmental Protection Agency set the maximum contamination level for Cd to 5 µg/L, which is the same in the European Union (UNEP, 2010) and China (Ministry of Health of China, 2006). The environmental quality standard for Cd in groundwater is 0.5 µg/L in Denmark, and 10 µg/L in Japan (UNEP, 2010) and China, respectively (Li et al., 2017).

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

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

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

2.2 Cadmium content in soil water and groundwater

Cadmium occurs usually up to 5 µg/L in soil water (Smolders and Mertens, 2013) and up to 1 µg/L in groundwater (Naseem et al., 2014). In groundwater in Pakistan, mean Cd concentrations of 10 µg/L originated from Jurassic sulfide-bearing sedimentary rocks (Naseem et al., 2014). In Germany, background Cd concentrations in groundwater range from 0.11 µg/L in loess aquifers below arable land to 2.7 µg/L in sandy aquifers below forested lands (Duijnisveld et al., 2008). Aquifers in Germany were analyzed with respect to stratigraphy and petrography. A selection of relevant aquifer systems indicate a relation between rock type, groundwater milieu and Cd concentrations (Figure 2.1). Cadmium 90th percentile as background levels ranged from less than 0.1 µg/L in groundwater, e.g., in Paleozoic, Triassic and Jurassic aquifers, to above 1 µg/L in Rotliegend, Cretaceous, and Cenozoic aquifers (BGR and SGD, 2014). Apart from carbonatic Cretaceous aquifers, limestone dominated aquifer systems had low Cd concentrations in groundwater. Most of them belong to aquifer systems with alkaline conditions (Figure 2.1).

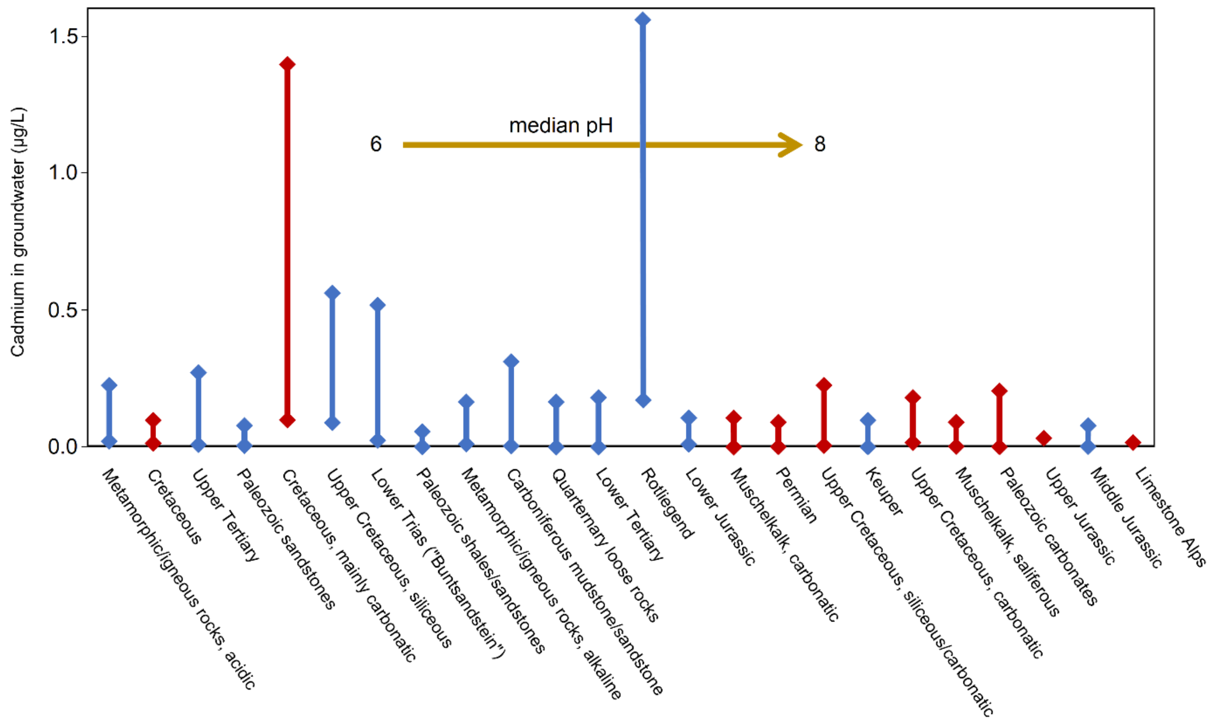


Figure 2.1: Cadmium concentrations in groundwater related to stratigraphic and petrographic aquifer features (BGR and SGD, 2014). Bars represent 50th percentile (lower edge) and 90th percentile (upper edge) of Cd in groundwater. Red bars show limestone dominated aquifers, blue bars show miscellaneous aquifer material. Aquifer's order indicate median pH in groundwater from acidic (left) to alkaline (right).

A mean Cd background level of 0.2 µg/L was calculated for Irish groundwater, which increased up to 0.5 µg/L in groundwater originated from non-calcareous sediments (Tedd et al., 2017). Occasional Cd concentrations above 1 µg/L were detected in groundwater in sandstone aquifers and in unconsolidated sand and gravel aquifer systems in the western part of the United States, while Cd concentrations were below 1 µg/L in most samples, which were taken from 3,124 wells in the United States (Ayotte et al., 2011). Groundwater from the glacial aquifer system in the United States shows Cd concentrations between 0.018 µg/L and 1.0 µg/L; however, 84 % of groundwater samples (N = 847) were below the detection limit (Groschen et al., 2008).

Neumayer and Matthess (1977) reported for groundwater in Northern Germany a natural variation of Cd concentrations from 2 µg/L in Pleistocene glaciofluvial sediments to 20 µg/L in Holocene sands covered by marsh sediments. Wessolek and Kocher (2002) reported for road traffic influenced soil water and groundwater in Northern Germany Cd concentrations of up to 27.8 µg/L and 2.34 µg/l, respectively. In a survey of groundwater surrounding waste sites in the United States, Cd concentrations up to 6,000 µg/L were found (ATSDR, 2012). Leachates from municipal solid waste landfills in the European Union can reach Cd concentrations up to 2,700 µg/L (EU, 2007). Therefore, Cd concentrations above what would be considered natural background can be the result of both natural and anthropogenic processes.

2.3 Natural cadmium sources

2.3.1 Atmosphere

Significant sources of natural Cd emissions are weathering of rocks, airborne soil particles, e.g., from deserts, sea spray, forest fires, biogenic material, volcanoes, and hydrothermal vents (ATSDR, 2012; Richardson et al., 2001; UNEP, 2010). Soil particles are the predominant source of natural emissions to the atmosphere, followed by forest and bush fires, sea salt, volcanic emissions and meteoric dust. According to Pacyna and Pacyna (2001), the worldwide mean annual emission of natural Cd is about 1,300 t. In contrast, the estimates of Richardson et al. (2001) are almost 41,000 t/a and thus, higher by a factor of 15. Contrary to previous studies, their calculations were based on improved data collection. Sources for anthropogenic Cd emissions are non-ferrous metal production, fossil fuel combustion, phosphate fertilizer manufacturing, iron, steel, and cement production, road dust, and municipal and sewage sludge incineration (ATSDR, 2012; Merkel and Sperling, 1998; Pacyna and Pacyna, 2001; UNEP, 2010). Anthropogenic Cd emissions have decreased by over 90 % in the last 50 years (ATSDR, 2012; Smolders and Mertens, 2013). The estimations of the natural and anthropogenic mean Cd emissions worldwide are given in Table 2.1.

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

Table 2.1: Worldwide mean Cd emissions to the atmosphere in the mid-90s.

Source	Cadmium (t/a)	Reference
Natural sources		a
Soil particles	24,000	
Forest and bush fires	13,000	
Sea salt	2,000	
Volcanoes	1,600	
Meteoric dust	$1{,}4 \times 10^{-4}$	
Anthropogenic sources		b
Non-ferrous metal production	2,171	
Iron and steel production	64	
Stationary fossil fuel combustion	691	
Cement production	17	
Waste disposal (incineration)	40	
Sum	43,600	

a: Richardson et al. (2001); b: Pacyna and Pacyna (2001)

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

2.3.2 Cadmium in rocks, sediments and soils

In general, Cd concentrations in sedimentary rocks (0.01 to 2.6 mg/kg) are higher than those in igneous rocks (0.07 to 0.25 mg/kg) or metamorphic rocks (0.11 to 1.0 mg/kg) (Hammons et al., 1978; Mar and Okazaki, 2012; Page et al., 1987; Smolders and Mertens, 2013). Average geogenic Cd concentrations in a variety of rock types are shown in Table 2.2.

Table 2.2: Cadmium contents in rocks.

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

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

The crustal median Cd content is 0.2 mg/kg (Gong et al., 1977). Cadmium can substitute for divalent cations, such as Ca, Fe, Zn, Pb, and Co in several minerals due to its similar ionic radius, e.g., in carbonate and phosphate rocks (e.g., Merkel and Sperling, 1998; Smolders and Mertens, 2013; Thornton, 1986; Wilkin, 2007). Pyrite, for example, can contain up to 52 mg/kg Cd (Abraitis et al., 2004). Table 2.3 lists the Cd content in several minerals, which could be considered important for the occurrence of Cd in the environment. Cadmium can substitute for Zn in sphalerite (ZnS) or smithsonite ($ZnCO_3$) (Merkel and Sperling, 1998; Tabelin et al., 2018; Wen et al., 2015; Zhu et al., 2013). Sulfide minerals like pyrite (FeS_2) are essential constituents of reduced systems and thus, important sources and sinks for Cd (Bostick et al., 2000; Tabelin et al., 2018).

Table 2.3: Cadmium content of minerals (in mg/kg, except where noted; modified after Thornton, 1986).

Mineral	Composition	Range
Sphalerite	(Zn,Cd)S	< 2 %
Greenockite	CdS	77.8 %
Chalcopyrite	$CuFeS_2$	< 110
Marcasite	FeS_2	< 50
Arsenopyrite	FeAsS	< 5
Galena	PbS	< 3,000
Tetrahedrite	$(Cu,Fe,Zn,Ag)_{12}SbAs_4S_{13}$	80−2,000
Magnetite	Fe_3O_4	< 0.31
Limonite	Hydrous iron oxides	< 1,000
Mn-Oxides	Hydrous manganese oxides	< 1,000
Anglesite	$PbSO_4$	120 − >1,000
Calcite	$CaCO_3$	< 1-23
Smithonite	$ZnCO_3$	< 2.35 %
Otavite	$CdCO_3$	65.18 %
Pyromorphite	$Pb_5Cl(PO_4)_3$	< 1−8
Scorodite	$FeAsO_4\ 2H_2O$	< 1−5.8
Apatite	$Ca_5(F,Cl)(PO_4)_3$	0.14−0.15
Bindheimite	$Pb_2Sb_2O_6(O,OH)$	100−1,000
Silicates		0.03−5.8

Furthermore, Cd is known to be adsorbed by hydrous oxides such as Fe(III) hydrous oxide, which can be an important supply of Cd to the aqueous phase when redox conditions change from oxygenated to reducing (e.g., Descourvieres et al., 2010; Hindersmann and Mansfeldt, 2014; Li et al., 2010). Cadmium can also replace Ca in apatite, which is the main constituent of phosphorites (Gnandi and Tobschall, 2002). Consequently, Cd can be a common impurity in phosphate minerals and phosphoritic rocks, which are important for fertilizer production. The Cd content, however, varies significantly between geologic occurrences. Currently, there is no commercial means to entirely remove Cd during the production of phosphate fertilizers (Mar and Okazaki, 2012). Ranges of geogenic Cd contents in phosphates of the most important exporting countries are shown in Figure 2.2. In Nauru, a Pacific island, the highest Cd contents were detected, reaching 240 mg/kg P_2O_5 (Mar and Okazaki, 2012). Raw phosphates from the USA and African countries also have wide ranges of Cd contents. Other exporting countries for raw phosphates are South Africa, Russia, Israel, Syria, Pakistan, Peru, and Brazil (Mar and Okazaki, 2012; Oosterhuis et al., 2000).

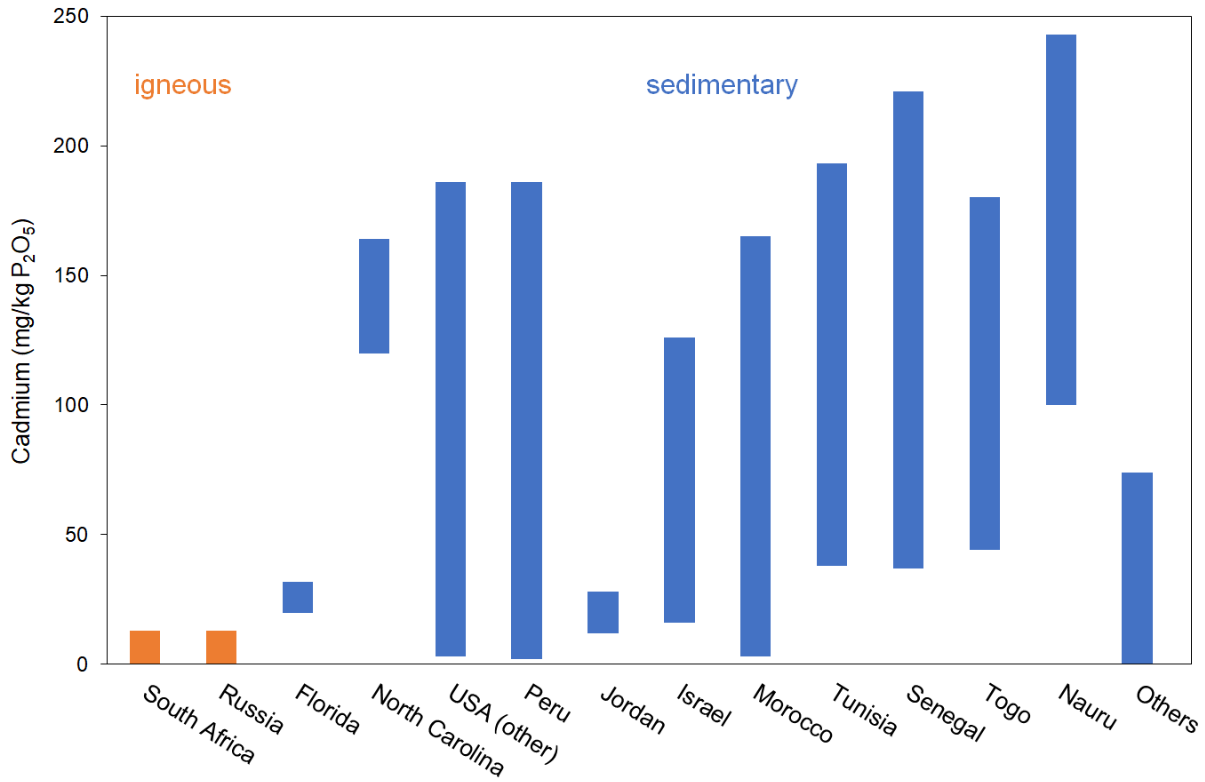


Figure 2.2: Cadmium contents in raw phosphates by origin (Dittrich and Klose, 2008; Kharikov and Smetana, 2000; Mar and Okazaki, 2012; Oosterhuis et al., 2000; Roberts, 2014).

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

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

In uncontaminated soils worldwide, the average abundance of Cd is 0.36 mg/kg, although values can vary between continents, countries and soil types. For example, average concentrations are: 0.27 mg/kg in the USA (N = 3,045), 0.01 mg/kg in Australia, 0.18 mg/kg in Brazil, 0.3 mg/kg in Japan, 0.2 mg/kg in Europe. In Europe, Cd concentrations are 0.3 to 1 mg/kg in Germany (N = 2,947), 0.6 to 0.7 mg/kg in the UK (N = 5,692), and 0.5 mg/kg in the Netherlands (N = 708) (Holmgren et al., 1993; Roberts, 2014; Smith et al., 2014; Taylor et al., 2016). Within the United States, Cd contents in uncontaminated soils exceeding 0.5 mg/kg are found in the Rocky Mountains, Great Plains and Mississippi delta, which are areas that also have elevated clay contents in the corresponding aquifer matrices (Holmgren et al., 1993; Smith et al., 2014). Within soil taxonomy, soils with organic matter (Histosols) and arid soils (Aridisols) have the highest median Cd content with 0.62 mg/kg and 0.3 mg/kg, respectively, while the strongly weathered Spodosols (0.2 mg/kg), Alfisols (0.11 mg/kg), and Ultisols (0.05 mg/kg) have lower Cd contents (Holmgren et al., 1993). Cadmium contents in soils, however, generally decrease with depth (Hiller et al., 2001; Page et al., 1987). Background levels of geogenic Cd contents in German soils were calculated as the 90th percentile depending on land use and rock genesis. They confirm the observation of decreasing Cd contents with depth independent of rock genesis. The Cd levels range from 0.06 mg/kg in sandy subsoils to 1.8 mg/kg in soils at swamp locations, 1.88 mg/kg in soils above fluviatile deposits at forest locations, and 2.0 mg/kg in sediments in the intertidal zone (LABO, 2017). Cadmium contents in soils in general depend on soil texture; elevated mean Cd contents can be found in soils with increasing contents of clay and peat (Holmgren et al., 1993; LABO, 2017).

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

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

In contrast to Eastern Europe, there is significantly more Cd in agricultural soils of Western Europe, which is caused by the different origin of P for fertilizers used in agriculture (Toth et al., 2016). As shown in Figure 2.2, Russian magmatic Kola phosphate rock, which is the primary source of P fertilizers in Eastern Europe, has low Cd contents, while phosphate rock from Morocco, the main source of P for fertilizers in Western Europe, has elevated Cd contents (Toth et al., 2016). Birke et al. (2017) revealed another distribution pattern for Cd in agricultural soils in Europe. Besides a median Cd content of 0.18 mg/kg, Cd contents in agricultural soils differ between Northern Europe and Southern Europe, whose boundary coincides with the extension of the Quaternary glaciation. Soils in Northern Europe have median Cd contents of 0.13 mg/kg and thus, lower Cd contents compared to Southern Europe (median 0.22 mg/kg). Reasons for such a distribution pattern are differences in the amount of precipitation and drainage, lithology, weathering, grain size, and pH. However, anomalies can occur in Northern Europe due to soil mineralization, as well as in loess and clay dominated sediments and as anthropogenic overlaps (Birke et al., 2017).

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

2.4 Anthropogenic cadmium sources

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

The worldwide main Cd use, and thus primary source of Cd directed to landfills with municipal solid waste, is nickel-cadmium batteries (Khan et al., 2017; UNEP, 2010). Municipal solid wastes in Europe have Cd contents of 0.3 to 12 mg/kg, mean Cd concentrations in the leachates were estimated as 0.5 to 3.4 µg/L (EU, 2007). Additional Cd containing products are pigments, coatings and platings, stabilizers for polyvinyl chloride (PVC), and alloys (ATSDR, 2012). Table 2.4 lists the major anthropogenic (industrial) sources for elevated Cd in soils.

Table 2.4: Cadmium contents in soils affected by industrial activities (Kabir et al., 2012).

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

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

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

Phosphate fertilizers contain an average of 77 mg Cd /kg P_2O_5 in the Eastern Mediterranean countries (Azzi et al., 2017), 36 mg Cd/kg P_2O_5 in Europe (Six and

Smolders, 2014) and 60 mg Cd /kg P_2O_5 in Germany (Schütze et al., 2003). In Europe, the average usage of phosphate is 43 kg/(ha*a) (Grant, 2011). In addition, the Cd input via deposition was calculated over different time scales and regions. Table 2.5 gives an overview of several studies about Cd inputs and outputs in soil. Depending on land use and distance to urban areas, either atmospheric deposition or application of P fertilizers are the main input of Cd.

Table 2.5: Mean annual inputs and outputs of soil Cd in g/ha.

Inputs			*Outputs*		Remarks (Location, period)	Reference
Atmospheric Deposition	Phosphate fertilizers	Others (e.g., manure)	Leaching	Crop offtake		
1.7	5.6	0.64	0.68	0.28	Germany, farming, the 1990s	Schütze et al. (2003)
5	-	-	0.68	-	Germany, forest & urban, the 1990s	Schütze et al. (2003)
2.5−4.5	-	-	-	-	German uplands, forest, the 1990s	Beisecker et al. (2012)
2.06	-	-	3.35	-	German uplands, forest, the 2000s	Beisecker et al. (2012)
0.96	0.28	0.43	0.87	0.8	Lower Saxony (Germany), farming, 1990s/2000s	Kamermann et al. (2015)
4	0.9	6.3	1.6	-	China, the 2000s	Luo et al. (2009)
1.9	1.6	-	-	-	European countries, 2000	Grant (2011)
9.8	1.0	1.4	-	-	Belgium, the 1990s	UNEP (2010)
0.25	0.98	0.56	-	-	France 2000	Six and Smolders (2014)
0.35	0.79	0.15	2.56	0.2	European countries 2010	Six and Smolders (2014)
> 0.5	-	-	-	-	Western, Eastern and Southern Europe, 2003	UNEP (2010)
1.4	-	-	-	-	West Germany, industry, 2014	Ilyin et al. (2016)
0.25	-	-	-	-	South Germany, farming, 2014	Ilyin et al. (2016)
0.19	< 0.071	0.148	-	-	Finland, 2004	UNEP (2010)
0.3	-	-	-	-	Northern Europe, 2003	UNEP (2010)
0.32	-	-	-	-	Near the European coast, 2005	OSPAR (2008)
> 0.32	-	-	-	-	Greater North Sea, 2005	OSPAR (2008)
< 0.1	-	-	-	-	Wider Atlantic, 2005	OSPAR (2008)
> 0.1	-	-	-	-	Central Atlantic & Southern coast of Greenland, 2005	OSPAR (2008)
< 0.05	-	-	-	-	Arctic Ocean, 2005	OSPAR (2008)

According to Six and Smolders (2014) the average total Cd input to European soils decreased to 1.3 g/(ha*a) due to low-emission process technologies, such as off-gas and waste water treatment. At the same time, the average Cd leachate output into groundwater was 2.6 g/(ha*a) causing a negative mass balance, which was caused by accumulation of previously elevated Cd input in soils, followed by its release to groundwater (Six and Smolders, 2014). In contrast to continental deposition rates of more than 0.3 g/(ha*a), Cd deposition decreases with distance from anthropogenic sources to below 0.05 g/(ha*a) in the Arctic Ocean (OSPAR, 2008) (Table 2.5).

Cadmium pollution in soil and groundwater is observed worldwide. Main groups are *mining*, *industry*, *waste management*, *agriculture*, and *urban areas*. An overview of documented cases of Cd contamination in soil and groundwater is given in Table 2.6. Example cases were selected as locations with maximum Cd levels depending on the type of pollution. Soil Cd pollution from Zn smelters, for example, can be caused by leaching of solid waste (Voglar and Lestan, 2010) or by atmospheric deposition (Bi et al., 2006), causing soil Cd concentrations of up to 344 mg/kg and 74 mg/kg, respectively. Similarly, groundwater contamination can also occur simultaneously from different sources and along different pathways at a single location, which can inhibit to identification of a significant Cd source, pathway or geogenic Cd anomaly. Consequently, other investigations, e.g., isotopic Cd fractionation (e.g., Cloquet et al., 2006; Zhu et al., 2013), are recommended.

Table 2.6: Types of Cd pollution in soil and groundwater

Source	Type of pollution	Example case	Maximum Cd level	Reference
Mining				
Pb-Zn mining/ refinery	1. Atmospheric deposition and waste water	Jinding, China	Soil: 531 mg/kg	Wen et al. (2015)
	2. Waste water	Coeur d'Alene basin, Idaho, USA	Groundwater: 77 µg/L	Paulson (1997)
Fe-Ni-Co mining	Waste material	Several sites in Albania	Soil: 14 mg/kg	Shallari et al. (1998)
Cu mining	Waste water	Canchaque, Peru	Soil: 499 mg/kg	Bech et al. (1997)
Au-Cu mining	Waste water	Bolnisi, Georgia	Soil: 121.5 mg/kg	Avkopashvili et al. (2017)
Au-Ag-Pb-Zn mining	Waste water	Chloride, Arizona USA	Groundwater: 19 µg/L	Rosner (1998)
Phosphorite mining	Mining waste, transport	Kpogamé, Hahotoé, Togo	Soil: 43 mg/kg	Gnandi and Tobschall (2002)
Pb mining and refinery	Atmospheric deposition	Příbram, Czech Republic	Soil: 48 mg/kg	Rieuwerts and Farago (1996)

Table 2.6 (continued)

Source	Type of pollution	Example case	Maximum Cd level	Reference
As refinery	Waste material	Reppel, Belgium	Soil: 79 mg/kg	Cappuyns et al. (2002)
Zn smelter	1. Waste material	Celje, Slovenia	Soil: 344 mg/kg	Voglar and Lestan (2010)
	2. Atmospheric deposition	Hezhang County, China	Soil: 74 mg/kg	Bi et al. (2006)
Industry				
Metal industry	Atmospheric deposition	Unnao, India	Groundwater: 74 μg/L	Dwivedi and Vankar (2014)
Cement factory	Atmospheric deposition	Qadissiya, Jordan	Soil: 13 mg/kg	Al-Khashman and Shawabkeh (2006)
Ceramic industry	1. Sewage sludge	Castellon, Spain	Soil: 72 mg/kg	Jordan et al. (2009)
	2. Atmospheric deposition	Yixing, China	Soil: 5.9 mg/kg	Lin et al. (2015)
Textile industry	Waste water	Haridwar, India	Soil: 83.6 mg/kg Groundwater: 40 μg/L	Deepali and Gangwar (2010)
Pigment manufacture	Atmospheric deposition	Staffordshire, UK	Soil: 16 mg/kg	Vangronsveld et al. (2009)
Various (e.g., textile, electro-plating)	Waste water	Coimbatore, India	Soil: 12.8 mg/kg	Malarkodi et al. (2007)
Waste management				
Landfill	Leachate	Taoyuan, Taiwan Alexandria, Egypt	Soil:378 mg/kg Groundwater: 51 μg/L	Chen and Liu (2006) Abd El-Salam and Abu-Zuid (2015)
Brownfield	Waste water	Xiangjiang River, China	Groundwater: 474 μg/L	Li et al. (2017)
Electronical waste recycling	Waste water	Krishna Vihar, India	Soil: 47.7 mg/kg Groundwater: 280 μg/L	Panwar and Ahmed (2018)
Household wastes	Waste water	Ikare, Nigeria	Groundwater: 580 μg/L	Ololade et al. (2009)
Sewage and waste disposal	Waste water	Sekondi-Takoradi Metropolis, Ghana	Groundwater: 90 μg/L	Affum et al. (2015)
Disposal facilities	Leachate	Great lakes region, USA	Soil: 32 mg/kg	Beyer and Stafford (1993)
Agriculture				
P fertilizer production	Atmospheric deposition	Rio Grande, Brazil	Soil: 9.3 mg/kg Groundwater: 3 μg/L	Mirlean and Roisenberg (2006)
P fertilizer application	Infiltration	Cauvery River basin, India	Groundwater: 60 μg/L	Vetrimurugan et al. (2017)
Sewage sludge application	Irrigation	Several sites in Spain	Soil: 90 mg/kg	Moral et al. (2005)

Table 2.6 (continued)

Source	Type of pollution	Example case	Maximum Cd level	Reference
Urban areas				
Road traffic	Infiltration	Celle, Germany	Groundwater: 2.34 µg/L	Wessolek and Kocher (2002)
Sewerage	Leakage	Rastatt, Germany	Groundwater: 5 µg/L	Eiswirth and Hotzl (1997)

2.5 Hydrochemical behavior

2.5.1 Basics

In aqueous solution Cd generally occurs as the divalent Cd^{2+} cation (Smolders and Mertens, 2013). Solution pH influences Cd mobility due to metal hydrolysis, ion-pair formation, solubility of organic matter, surface charge of oxy-hydroxides, organic matter and clay edges. With increasing pH, metal retention to mineral surfaces increases via adsorption and precipitation (Appel and Ma, 2002; Buerge-Weirich et al., 2002; He et al., 2005).

Cadmium preferentially remains in solution at a pH of less than 6.5 and under oxygenated conditions (Brümmer et al., 1994; Merkel and Sperling, 1998). The Cd^{2+} ion itself is not redox-sensitive, but it is indirectly tied to redox conditions due to the formation of redox-sensitive aqueous complexes, such as $CdHS^{+}$, which occurs in anoxic and sulfidic conditions, and stable precipitates, such as sphalerite (ZnS), galena (PbS), and chalcopyrite ($CuFeS_s$), which can contain Cd as a trace element (Ditoro et al., 1990; Tabelin et al., 2018). As indicated in Figure 2.3, the solubility-limiting phases of Cd are CdS, $CdCO_3$, and $Cd(OH)_2$. Depending on the Cd concentration, the stability fields of the Cd species can expand or contract (Ahmed et al., 2008; Brookins, 1986; Merkel and Sperling, 1998).

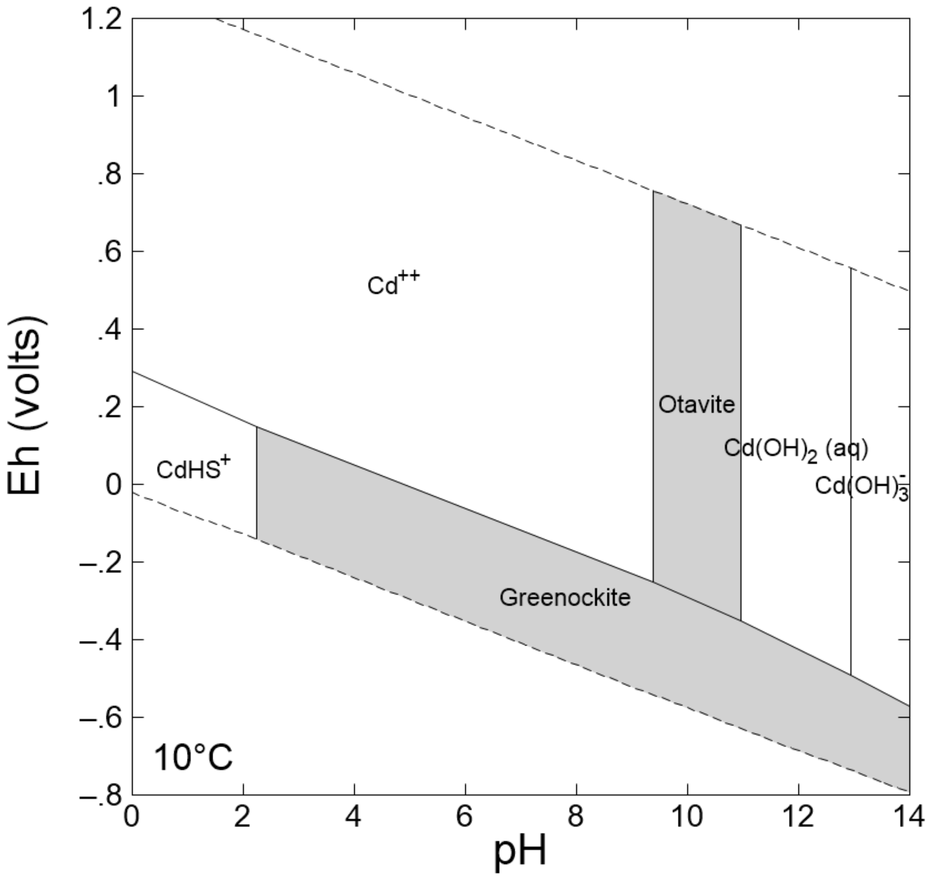


Figure 2.3: Eh vs. pH diagram for Cd. The concentrations of dissolved species are $[Cd^{2+}] = 10^{-8}$, $[HCO_3^-] = 10^{-3}$, $[SO_4^{2-}] = 10^{-3}$.

2.5.2 Solubility and complexation

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

Cadmium forms water-soluble complexes with anions, such as $CdCl^{+}$ or $CdSO_4^{0}$, but also complexes with dissolved organic matter (DOM) (Bolan et al., 2003; Carrillo-Gonzalez et al., 2006; Gardiner, 1974; Loganathan et al., 2012). As a result, Cd can remain in solution while sorption decreases the aqueous concentration of other heavy metals. Furthermore, inorganic and organic complexation can lead to dissolution of Cd from oxy-hydroxides, phosphates, or sulfides (Beisecker et al., 2012; Carrillo-Gonzalez et al., 2006; Eggleton and Thomas, 2004; Hammons et al., 1978; Najafi and Jalali, 2015).

Depending on groundwater composition, 55 % to 90 % of the total soluble Cd is present as divalent Cd^{2+} ions, while the remaining Cd is present as organic and inorganic complexes like: $CdCl^{+}$, $CdCl_2^{0}$, $CdCl_3^{-}$, $Cd(SO_4)_2^{2-}$, $CdSO_4^{0}$, $CdHCO_3^{-}$, $CdCO_3^{0}$, $Cd(CO_3)_2^{2-}$, $CdOH^{+}$, $Cd(OH)_2^{0}$, $Cd(OH)_3^{-}$, Cd_2OH^{3+}, $CdNO_3^{+}$ (Baun and Christensen, 2004; Krishnamurti and Naidu, 2003; Merkel and Sperling, 1998; Sauve et al., 2000; Wilkin, 2007) (Figure 2.4a). The predominance of Cd complexation with inorganic carbon increases with pH and precipitation of $CdCO_3$ (otavite) is favorable at pH > 8 (Figure 2.4b). For typical groundwater inorganic carbon concentrations, a minimum solubility for otavite occurs around pH 9−10; above this pH solubility increases due to the stability of the $Cd(CO_3)_2^{2-}$ complex. Under anoxic and sulfidic conditions, Cd complexes occur as $Cd(HS)_2^{0}$, $Cd(HS)_3^{-}$, $Cd(HS)_4^{2-}$ and $CdHS^{+}$ (Astruc, 1986). The solubility of CdS (greenockite) is generally low, but equilibrium Cd concentrations increase with increasing dissolved sulfide (Figure 2.4c). Complex formation is generally important in the case of low Cd concentrations and depends on ligand concentrations and the equilibrium constants for complex formation (Gardiner, 1974). The equilibrium constants for Cd, listed in Table 2.7, were taken from PHREEQC (Parkhurst and Appelo, 1999). The most stable Cd complexes are with chloride, carbonate, sulfate, and bisulfide anions as ligands (Figure 2.4a).

Previous studies dealing with Cd complex formation often used data from modeling or laboratory experiments conducted with high metal concentrations. Hence, such results may underestimate the mobility of heavy metals under natural conditions, especially with respect to the complexity of organic matter (Christensen et al., 1996).

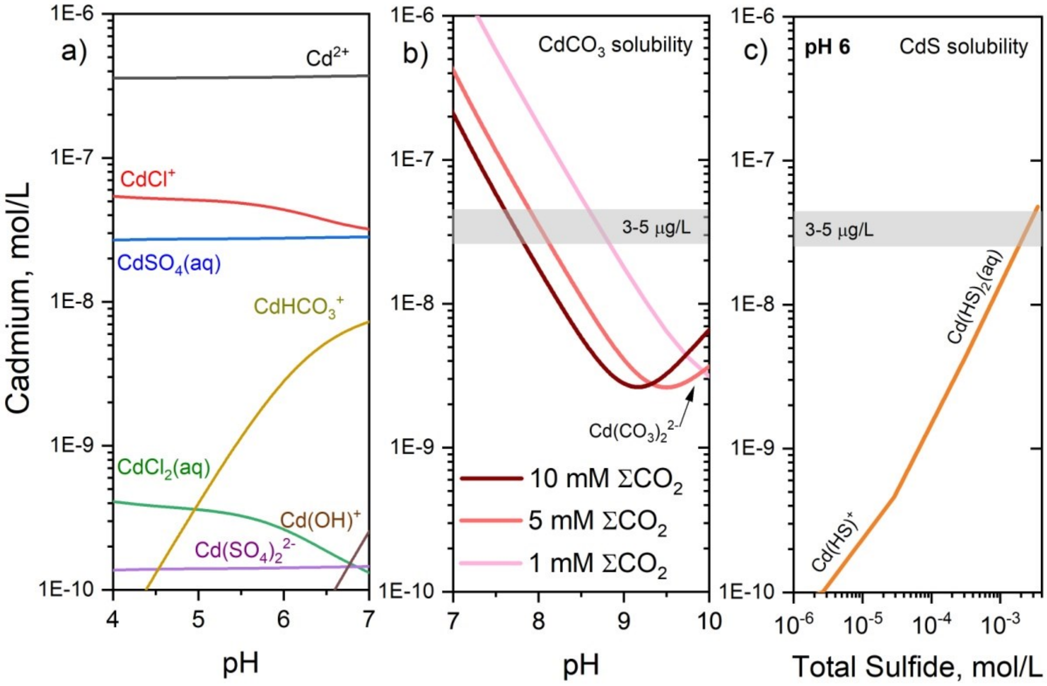


Figure 2.4: Concentration versus pH diagrams showing a) Cd speciation from pH 4 to 7 for the composition Cd ($10^{-6.4}$ M), Cl (10^{-3} M), ΣCO_2 (10^{-3} M), and SO_4 (10^{-3} M). b) Otavite solubility as a function of pH and ΣCO_2 from 10^{-3} to 10^{-2} M. C) Concentration versus dissolved sulfide diagram showing the solubility of CdS at pH 6. Reference concentrations for drinking water standards are shown (3 to 5 µg/L).

Cadmium present in sulfide minerals or bound to organic material is generally released when redox conditions change from reducing to oxidizing; this change generally causes metal sulfides to dissolve and organic matter to mineralize (Martinez et al., 2002; Simpson et al., 2000; Tabelin et al., 2018). There is also a change in the amount of Cd binding forms as groundwater conditions shift from reducing to oxidizing (Zoumis et al., 2001). During oxidation of pyrite or acid volatile sulfides (AVS), like amorphous FeS, mackinawite (FeS) or greigite (Fe_3S_4), Cd and other heavy metals are released. However, Cd is comparatively more mobile than, for example, Ni, Pb and Cu due to different mineral solubilities and sorption behavior, a stronger co-precipitation of Pb and Cu with iron sulfides, and the formation of stable Cd complexes (Caetano et al., 2003).

Table 2.7: Complex forming constants of Cd (Parkhurst and Appelo, 1999).

Reaction	log K
$Cd^{2+} + H_2O = CdOH^+ + H^+$	-10.08
$Cd^{2+} + 2\ H_2O = Cd(OH)_2 + 2\ H^+$	-20.35
$Cd^{2+} + 3\ H_2O = Cd(OH)_3^- + 3\ H^+$	-33.3
$Cd^{2+} + 4\ H_2O = Cd(OH)_4^{2-} + 4\ H^+$	-47.35
$Cd^{2+} + Cl^- = CdCl^+$	1.98
$Cd^{2+} + 2\ Cl^- = CdCl_2^0$	2.6
$Cd^{2+} + 3\ Cl^- = CdCl_3^-$	2.4
$Cd^{2+} + CO3^{2-} = CdCO_3^0$	2.9
$Cd^{2+} + 2CO_3^{2-} = Cd(CO_3)_2^{2-}$	6.4
$Cd^{2+} + HCO3^- = CdHCO_3^+$	1.5
$Cd^{2+} + SO4^{2-} = CdSO_4^0$	2.46
$Cd^{2+} + 2SO_4^{2-} = Cd(SO_4)_2^{2-}$	3.5
$Cd^{2+} + F^- = CdF^+$	1.1
$Cd^{2+} + 2F^- = CdF_2^0$	1.5
$2Cd^{2+} + H_2O = Cd_2OH^{3+} + H^+$	-9.39
$Cd^{2+} + H_2O + Cl^- = CdOHCl^0 + H^+$	-7.404
$Cd^{2+} + NO_3^- = CdNO_3^+$	0.4
$Cd^{2+} + HS^- = CdHS^+$	10.17
$Cd^{2+} + 2HS^- = Cd(HS)_2^0$	16.53
$Cd^{2+} + 3HS^- = Cd(HS)_3^-$	18.71
$Cd^{2+} + 4HS^- = Cd(HS)_4^{2-}$	20.9

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

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

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

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

2.5.3 Sorption

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

Cadmium as a positively charged ion is adsorbed onto negatively charged mineral surfaces until the point of zero charge (PZC) is exceeded (He et al., 2005). Hence, groundwater pH is the driving factor controlling the availability of binding sites with the aquifer matrix. In Table 2.8, the PZC of several important minerals are listed. Sorption of Cd at pH values below the PZC is an indication of fixation via inner-sphere surface complexation or adsorption to permanent negative binding sites, e.g., at vermiculite, smectite, or organic matter surfaces (Appel and Ma, 2002). In contrast to other metals such as Pb and Cu, Cd sorption on kaolinite was inhibited at pH below 7 indicating a lower affinity for specific inner-sphere surface complexation at hydroxyl groups, ≡SOH, compared to preferred ion exchange at non-specific permanent negatively charged sites, $\equiv X^-$, resulting in higher mobility of Cd (Srivastava et al., 2005). The amount and type of surface complexation is also influenced by ionic strength. At pH 6, for example, almost 70 % of Cd is adsorbed onto kaolinite in a 0.001 M solution as $\equiv X_2^- \cdot Cd^{2+}$ on the one hand, while Cd sorption mainly occurs as inner-sphere complex $\equiv SOCd^+$ decreased to 30 % in a 0.1 M solution on the other hand (Gu and Evans, 2008).

Table 2.8: Point of zero charge of several sorbents (Langmuir, 1997; Stumm and Morgan, 1996).

Mineral	Name	pH_{PZC}
SiO_2	quartz	2.0
α-Fe_2O_3	hematite	4.2−6.9
γ-Fe_2O_3	maghemite	6.7
Fe_3O_4	magnetite	6.5
α-FeOOH	goethite	7.8
5 $Fe_2O_3 \cdot$ 9 H_2O [$Fe(OH)_3$, amorphous]	ferrihydrite	8.5
β-MnO_2	pyrolusite	7.2
δ-MnO_2	birnessite	2.8
kaolinite	kaolinite	4.6
Na feldspar	Na feldspar	6.8

Usually, Cd fixation follows the two-site-sorption model. In the first step, Cd is adsorbed at highly energetic binding sites. The second step involves a slow, time dependent diffusion of Cd into the mineral matrix (Carrillo-Gonzalez et al., 2006; He et al., 2005; Loganathan et al., 2012; Strobel et al., 2005). After Smolders and Mertens (2013), a general sorption equation with surface functional groups is:

$$S\text{-}OH + Cd^{2+} \leftrightarrow S\text{-}OCd^{+} + H^{+} \qquad \text{(equation 2.1)}$$

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

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

$$Cd^{2+} + CaCO_{3(s)} = CdCO_{3(s)} + Ca^{2+} \qquad \text{(equation 2.2)}$$

In this case, Cd can substitute for Ca by forming new crystals at the mineral surface. Initially, fast adsorption of Cd occurs at the calcite surface, followed by slower diffusion of Cd into the crystal lattice. After that, formation of a calcium-cadmium carbonate solid solution occurs. These processes are controlled by pH and competition with Mg^{2+} within the hydrated surface layer (Davis et al., 1987). If there is bicarbonate in the liquid phase, Cd can form complexes or precipitate as otavite (Figure 2.4c) and thus, decrease the pH value in poorly buffered systems (Ahmed et al., 2008):

$Cd^{2+} + HCO_3^- \leftrightarrow CdCO_3^0 + H^+$ (equation 2.3)

At silicate surfaces, Cd sorption occurs as outer-sphere surface complexation with permanent negative loadings or as inner-sphere complexation with variable loadings. At Fe-, Mn- and Al-oxide surfaces, Cd fixation occurs by ion exchange with surface OH groups (Loganathan et al., 2012). Due to inner-sphere complexation, substantial uptake of Cd occurs at surfaces of goethite (α-FeOOH), lepidocrocite (γ-FeOOH), and pyrite (FeS_2) (Parkman et al., 1999; Randall et al., 1999) as

$\equiv FeOH + Cd^{2+} \leftrightarrow FeOCd^+ + H^+$ (equation 2.4)

or as

$\equiv FeOH + Cd^{2+} \leftrightarrow FeOHCd^{2+}$ (equation 2.5)

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

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

$Ca_{10}(PO_4)_6(OH)_2 + xCd^{2+} \rightarrow (Cd_x,Ca_{10-x})(PO_4)_6(OH)_2 + xCa^{2+}$ (equation 2.6)

Further Cd sorption or substitution occurs in P fertilizer compounds, such as fluorapatite ($Ca_{10}(PO_4)_6F_2$), tricalcium phosphate ($Ca_3(PO_4)_2$), gypsum ($CaSO_4$), and cadmium lead phosphate hydroxide (($CdPb_9(PO_4)_6(OH)_2$) (Azzi et al., 2017).

However, depending on the phosphate concentration in solution, there is influence on the mobile Cd fraction. Cadmium mobility increases at low P concentrations due to pH decreases and elevated ionic strength (Grant, 2011). However, Cd can precipitate, e.g., as $Cd_3(PO_4)_2$ at high P and Cd concentrations (Grant, 2011; Xiong, 1995). In the case of low Cd concentrations, phosphate induced surface complex formation can occur due to reduced PZC or co-adsorption of Cd and phosphate as an ion pair (Grant, 2011; Wang and Xing, 2002). Phosphate can block meso- and micro-pores, e.g., on the goethite surface, which inhibits Cd diffusion into the mineral structure and thus, decreases sorptive uptake (Wang and Xing, 2002). In the case of ferrihydrite, phosphate enhances Cd sorption by the formation of stable ternary complexes at the surface (Tiberg and Gustafsson, 2016):

$2\ FeOH^{½-} + 2\ H^+ + Cd^{2+} + PO_4^{3-} \leftrightarrow (FeO)_2HCdPO_3H^0 + H_2O$ (equation 2.7)

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

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

2.5.4 Competition

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

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

The diffusion rate of Cd into goethite is lower than that of Zn and Ni (Brümmer et al., 1986). Cadmium sorption to Fe and Mn oxides is retarded in presence of other cations, and it decreases due to competition in the order: $Ca^{2+} > K^{+} > Na^{+}$ (Christensen, 1984b; Wang et al., 2010). In the pH range 3 to 8, release of unspecific adsorbed Cd occurs, which increases with increasing salinity. An increase of ionic strength generally leads to a release of heavy metals in the order: Cd > Zn > Cu > Pb (Herms and Brümmer, 1984; Kuntze et al., 1984). The presence of appropriate anions also influences sorption behavior. While Cl^{-} and NO_3^{-} restrain Cd sorption due to the formation of soluble inorganic complexes, CO_3^{2-}, $H_2PO_4^{-}$ and HSO_4^{-} enhance Cd sorption due to surface precipitation (Wang et al., 2010).

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

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

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

3. Data sets, methods and processing

The origin and extent of the provided hydrochemical analyses from the Geological and Hydrological Surveys of Lower Saxony and Bremen are explained in the following chapters. In total, 6,276 groundwater analyses were provided and different statistical analyses were applied to different data sets dependent on the objective. A general evaluation of the data showed a heterogeneous distribution in the study area (Figure 3.1). Besides a sufficient representation of all hydrogeological areas in the data set, some border areas revealed underrepresentation, while urban areas showed higher density in sampling locations.

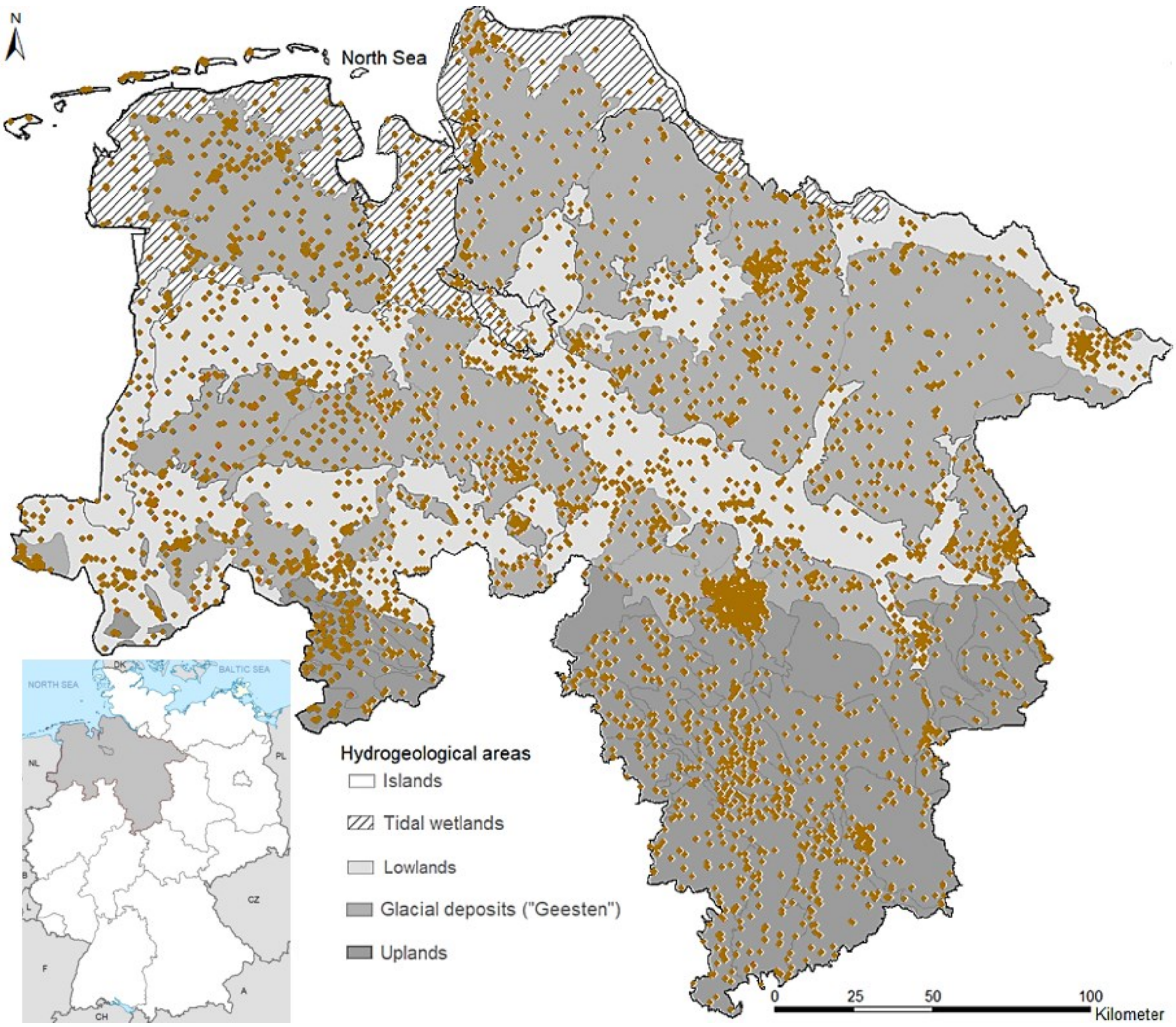


Figure 3.1: Sampling locations in the study area (N = 6,267). The small figure gives the location of the study area in Germany.

Consequently, geostatistical methods were not suitable without substantial manipulation of data and thus, loss of information. Instead, statistical methods were applied that can deliver robust results based on raw data. In some cases, adoptions were necessary regarding the percentage of analyses below the detection limit. Cadmium in the groundwater of the study area usually occurred in concentrations below 0.2 µg/L, while Cd detection limits in the data set range from 0.002 µg/L to 1,000 µg/L. Therefore, for some assessments, high detection limits were deleted or detection limits were replaced by half of the detection limit.

Using ArcGIS, further information from CORINE land cover, hydrogeological, and geological maps were added to the groundwater analyses. Stratigraphic information was also added with respect to the screen depth of the sampling locations. Microsoft office tools such as MS Access and MS Excel were used to identify multilevel wells and to delete duplicates in the data set. Additionally, screen length, depth below the water table, and depth below the surface were calculated for each sampling location.

Different parts of the data set were used for certain issues (Figure 3.2). In the case of groundwater classification, for example, all recent plausible analyses were considered. The plausibility was proofed by the ionic balance (equation 3.1), which was calculated as:

$$\text{Ionic balance} = (\sum\text{cations [meq/L]} - \sum\text{anions [meq/L]}) \,/\, (0.5 \times (\sum\text{cations [meq/L]} + \sum\text{anions [meq/L]})) \times 100 \qquad (3.1)$$

The considered cations were K^+, Na^+, NH_4^+, H^+, Ca^{2+}, Mg^{2+}, Fe^{2+}, Mn^{2+} and Al^{3+}; the considered anions were Cl^-, HCO_3^-, NO_3^-, SO_4^{2-} and PO_4^{3+}. In accordance with Domenico and Schwartz (1998), analyses with an ionic balance (IB) ≤ 10 % were disregarded.

Statistical evaluation was performed based on all available analyses with IB ≤ 10 %. In contrast, trend tests considered all available Cd analyses (Figure 3.2). To calculate background levels for Cd, all recent Cd values from groundwater sampling sites were used disregarding the IB of the particular analysis. Trend analysis and statistic evaluation were the basis for the calculation of background levels, which were also regarded for the classification of water types (Figure 3.2). Further information on the statistical evaluation is in the following chapters.

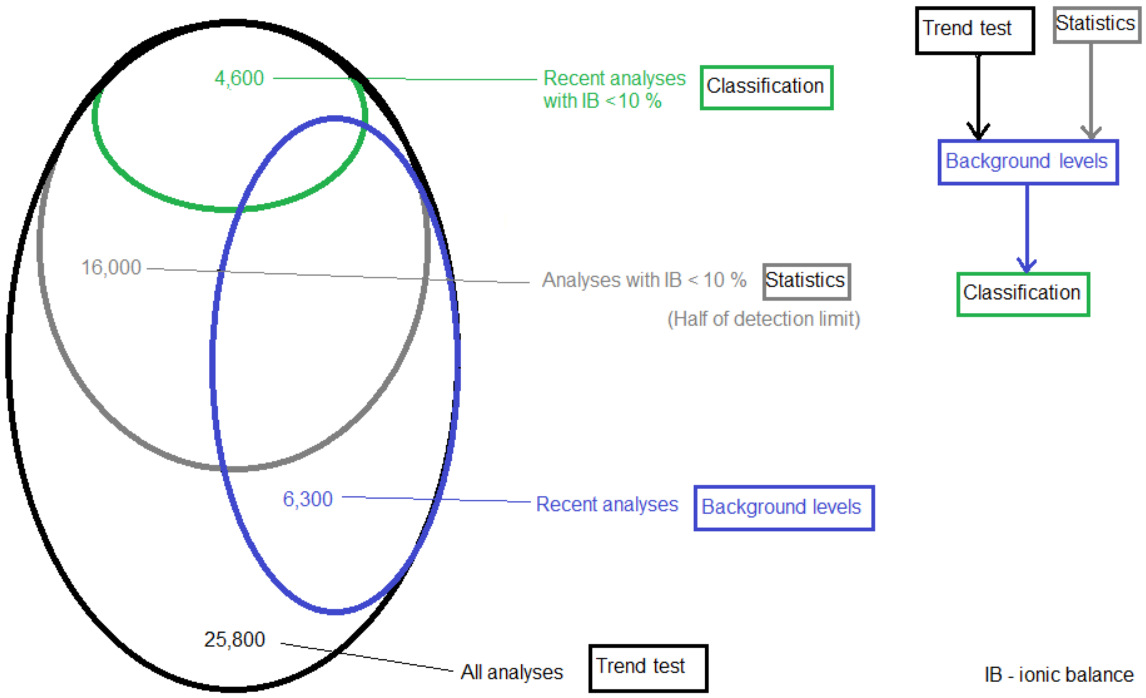


Figure 3.2: Illustration of the components of the Cd data set and their applications.

4. Cadmium in groundwater − A synopsis based on a large hydrogeochemical data set

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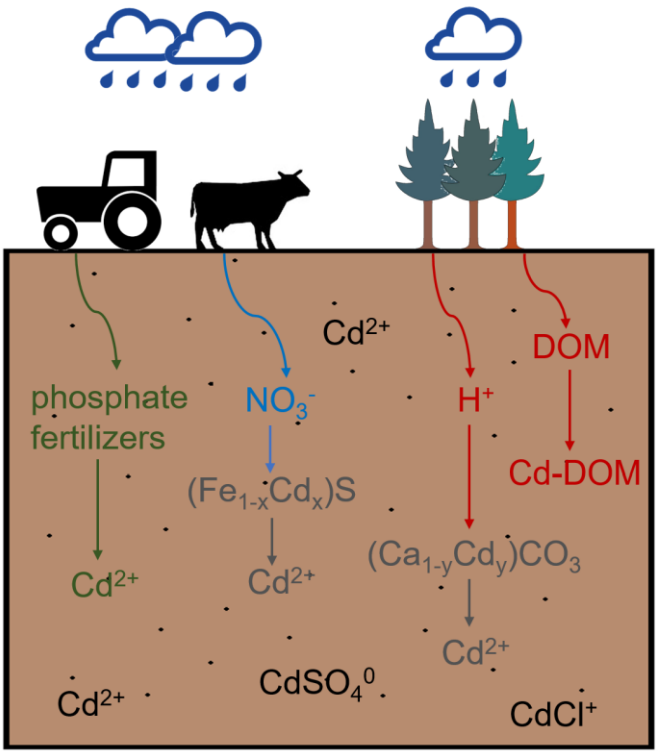
Abstract

Elevated cadmium (Cd) concentrations in groundwater have widespread implications for water supply and agriculture. The aqueous chemistry of Cd is considered not complex; however, aside from intense industrial pollution, multi-faceted hydrogeochemical interactions control Cd mobility. Therefore, the behavior of Cd in groundwater was investigated through statistical analyses of a large hydrogeochemical data set, which contained analyses from 6,300 sampling locations in Northern Germany. Cadmium concentrations of above 0.5 µg/L were linked to groundwater conditions caused (1) by woodlands in connection with acidification or (2) elevated nitrate concentrations beneath farmland due to fertilization. Comparably, both geogenic and anthropogenic Cd input were less important. The main hydrogeochemical parameters affecting Cd mobility were pH and redox potential, which are linked to Cd sorption to mineral surfaces and Cd release from carbonates and sulfides, such as pyrite. Thus, Cd concentrations were primarily elevated when groundwater conditions were oxic and autotrophic nitrate reducing. In addition, enhanced groundwater recharge and limited Cd retention capacity by the aquifer matrix were responsible for elevated Cd concentrations in groundwater, potentially breaching legal regulations.

Graphic Abstract



4.1 Introduction

Cadmium (Cd) is one of the most toxic and mobile elements in the environment (Alloway and Jackson, 1991; Nies, 1999, 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 P_2O_5 (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, increasing Cd concentrations exceeding background levels or threshold values can be predicted considering potential changes in groundwater chemistry.

4.2 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 Cd^{2+} 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., $CdCl^{+}$, $CdCl_2^{0}$, $CdSO_4^{0}$, $Cd(CO_3)_2^{2-}$, 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, 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 and thus, Cd (Borch et al., 2010). Table 4.1 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., 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.

Table 4.1: 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

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, O_2 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 (equation 4.1):

$$5\ CH_2O + 4\ NO_3^- + 4\ H^+ \rightarrow 5\ CO_2 + 2\ N_{2(g)} + 7\ H_2O \tag{4.1}$$

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 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 ($CuFeS_2$), while pyrite (FeS_2) can contain up to 52 mg/kg Cd (Abraitis et al., 2004). In pyrites in Northwestern Germany, Houben et al. (2017) recently found Cd contents up to 1,600 mg/kg. During dissolution of pyrite (equation 4.2), 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:

$$5(Fe_{1-x}Cd_x)\,S_{2(s)} + 14\,NO_3^- + 4\,H^+ \rightarrow 5(1-x)\,Fe^{2+} + 5x\,Cd^{2+} + 7\,N_{2(g)} + 10\,SO_4^{2-} + 2\,H_2O \qquad (4.2)$$

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) (equation 4.3 and 4.4):

$$5\,Fe^{2+} + NO_3^- + 12\,H_2O \rightarrow 5\,Fe(OH)_{3(s)} + \tfrac{1}{2}\,N_{2(g)} + 9\,H^+ \qquad (4.3)$$

$$2\,Fe^{2+} + MnO_2 + 4\,H_2O \rightarrow 2\,Fe(OH)_{3(s)} + 2\,Mn^{2+} + 2\,H^+ \qquad (4.4)$$

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.

4.3 Materials and methods

4.3.1 Study area and regional hydrogeology

The study area comprises the German federal states of Lower Saxony and Bremen in Northern Germany (Figure 4.1) totaling an area of almost 48,000 km^2 (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 up to 1,000 m above sea level. 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 (Wendland et al., 2008), partly covered by Pleistocene deposits. 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* (Figure 4.1). 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 is nearly flat and covered mostly Pleistocene sediments with increasing thickness to the north, particularly in deep sub-glacial channels of Elsterian age (Ehlers et al., 1984).

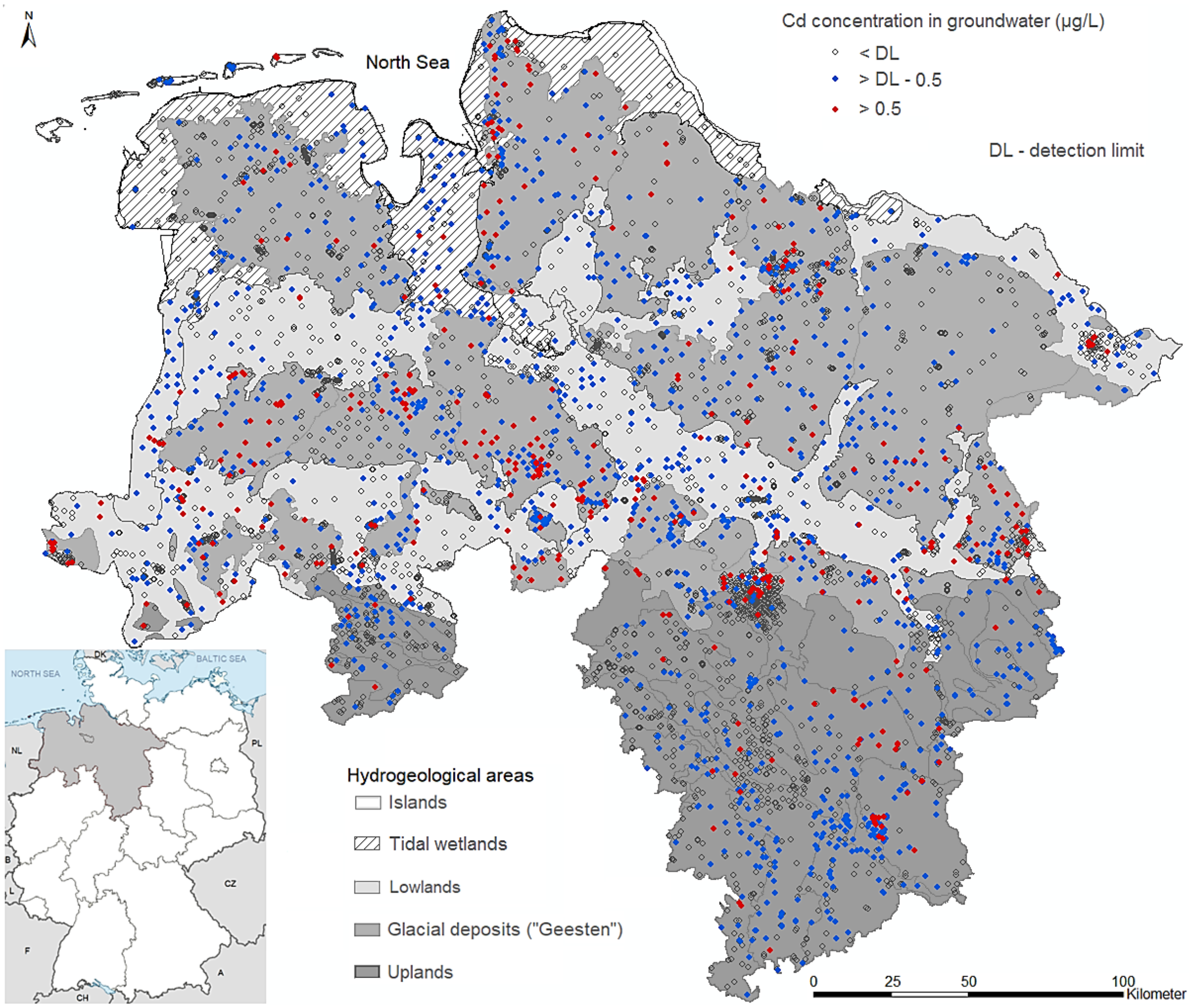


Figure 4.1: Cadmium concentrations in shallow groundwater of the study area. The small figure gives the location of the study area in Germany.

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 oxic, 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 the hydrogeological units was not considered.

4.3.2 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 more than 24,000 samples from 6,300 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 was sampled once, while 2,200 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 times series to median values.

The data set included in situ parameters, such as pH, redox potential (Eh), oxygen, and electric conductivity (EC), and the following main components and trace elements: Na, K, Ca, Mg, SO_4, Cl, HCO_3, NO_3, NH_4, Fe, Mn, Ag, Al, As, B, Ba, Bi, Br, Cd, Co, Cr, Cu, dissolved organic carbon (DOC), F, Hg, Li, Mo, Ni, NO_2, Pb, PO_4, Sb, Se, SiO_2, Sn, Sr, Tl, 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, 4,594 groundwater analyses from the data set were exploitable for statistical analysis.

4.3.3 Statistical analysis

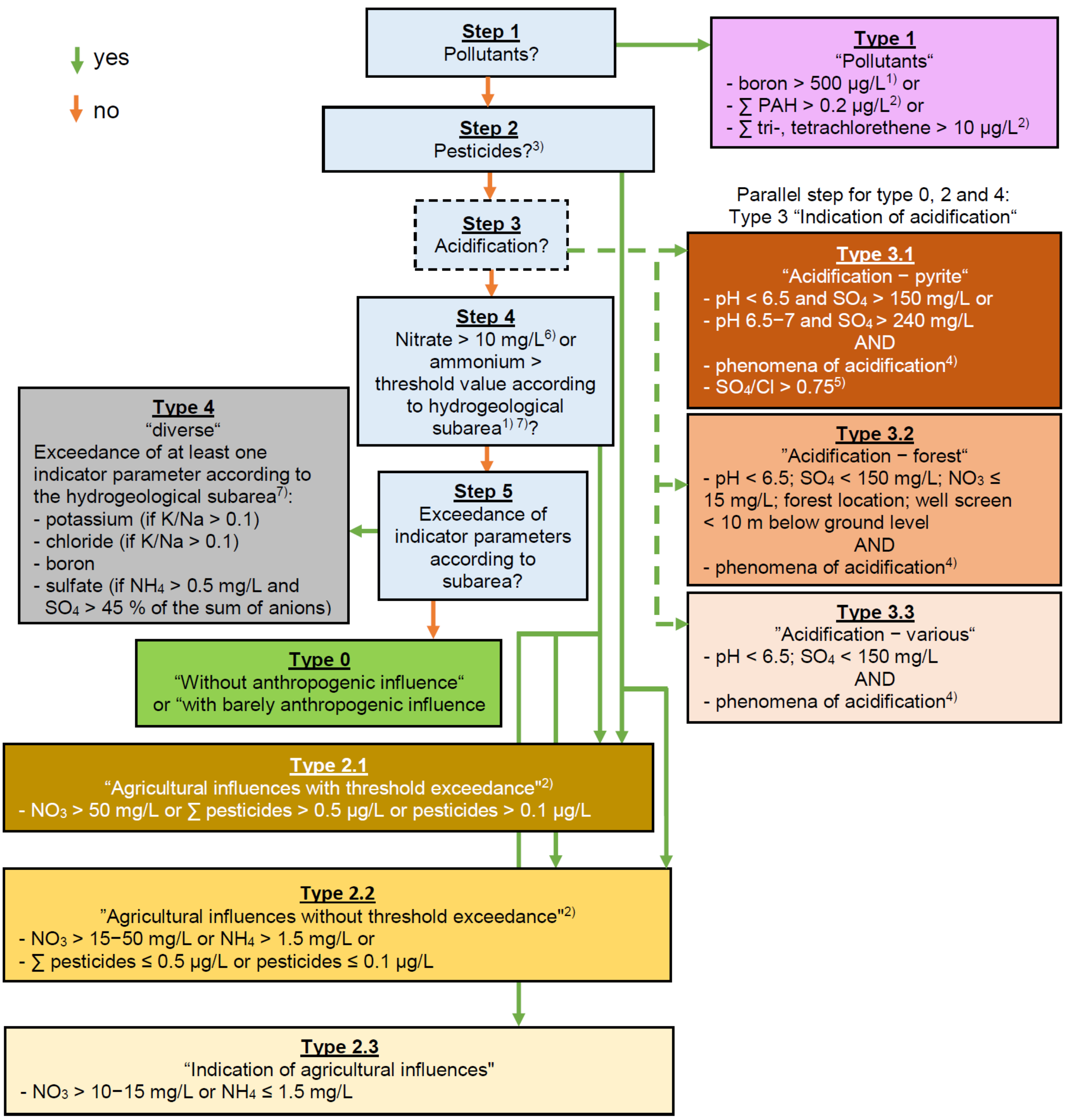
In contrast to other studies examining large data sets, multivariate statistical methods, such as principal component analysis (PCA), were not applied in order to avoid misleading results due to missing postulations for the data set, e.g., multivariate normal distribution. Instead, Spearman rank correlation (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., *oxic*, *suboxic, manganese-*, *nitrate-*, *iron- and sulfate reducing* (Table 4.1) (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 4.1 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 4.1.

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 Figure 4.6). 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 categorized groundwater samples 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 (Figure 4.2). Some adaption was necessary to account for the relatively larger presence of moors in the study are (compared to the rest of central Europe) and their influence on hydrogeochemistry, as well as the marine influences from the North Sea (footnotes in Figure 4.2). The following parameters were utilized: (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 every 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 data groups.



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.

Figure 4.2: Flowchart of the assessment scheme for the classification of influence types in groundwater (adapted after LfU, 2015).

4.4 Results and discussion

4.4.1 Occurrence of Cd in groundwater

The mean and median Cd concentrations of all samples (N = 4,594) 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 4,594 analyses). Most samples (219 out of 363) exceeding 0.5 µg/L were located in the Geesten area (Figure 4.1) where the main land use is farmland (42 % of 363 sampling locations) and woodland (33 %). The samples were mainly taken from depths less than 15 m and Cd concentrations above 0.5 µg/L were generally found at sampling locations of less than 10 m. Those locations showed a higher vulnerability due to shallow depths and were missing a low permeability confining layer (LBEG, 1982, 2004). The annual groundwater recharge rates at these 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 4.2). On the other hand, the 90th percentile of Cd was elevated in those samples collected in the farmland and woodland units (Table 4.2). The Kruskal-Wallis test revealed a significant difference among the land use units ($X^2(8) = 141.212$, $p = 0.0001$).

Table 4.2: 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	1,389	0.10	0.45
Farmland	1,402	0.05	0.57
Grassland	930	0.05	0.25
Urban area	680	0.10	0.35

Spearman's rank correlation coefficients (two-tailed significance at the 0.01 level) for Cd and the parameters are listed in Table 4.3. 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.

Table 4.3: 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		

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 4.3), 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 influences on the occurrence of Cd in groundwater. The negative correlation of Cd with parameters indicating alkaline (HCO_3) or reducing conditions (Fe, NH_4) 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 (HCO_3, SiO_2) (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 (Figure 4.3). 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 more immobile at a pH above 6, due to sorption by minerals such as Fe(III) hydrous oxide and precipitation as $CdCO_3$ and $Cd(OH)_2$ (Carrillo-Gonzalez et al., 2006), 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 NH_4 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 (Figure 4.4). 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).

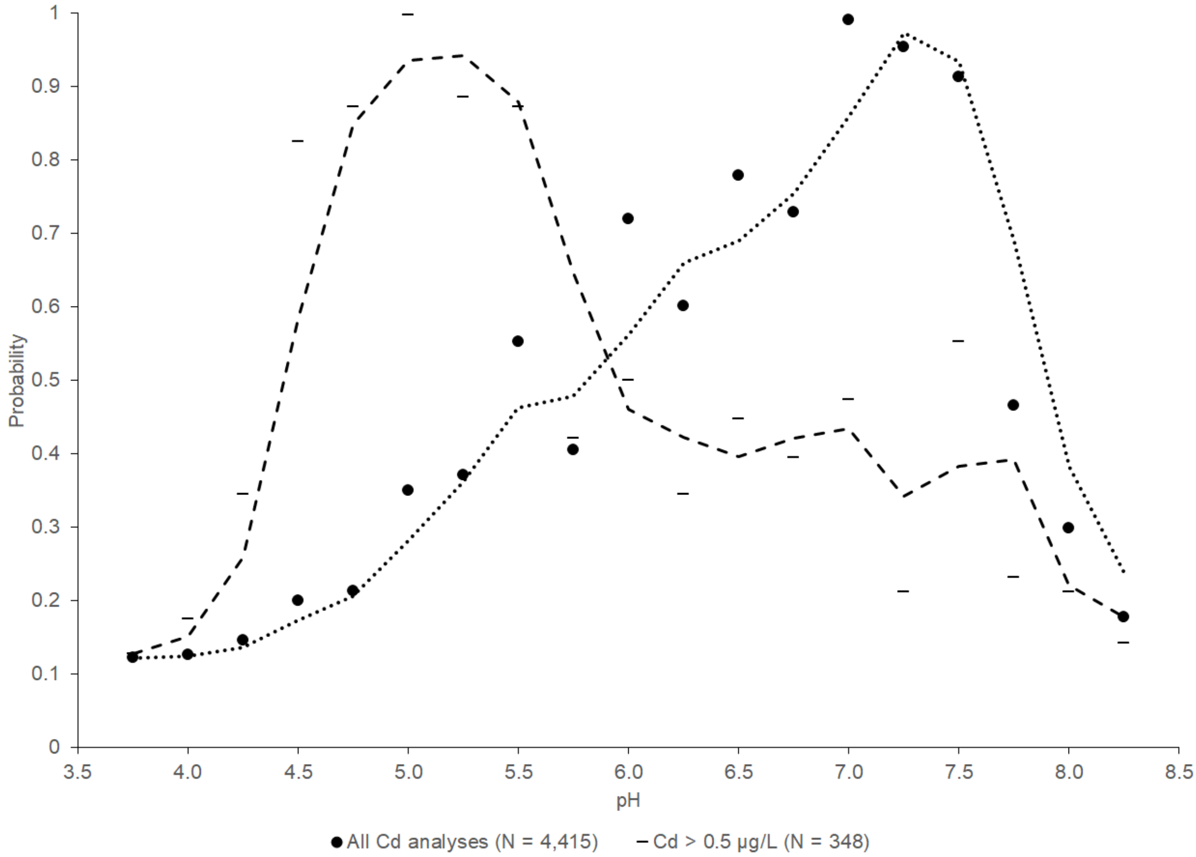


Figure 4.3: Probability of Cd concentrations above the detection limit in the complete data set (closed circles) and Cd above 0.5 µg/L (dashes), which is the German threshold value, as a function of pH. The dotted and dashed lines illustrate the basic trends (moving average).

In contrast to the elevated Cd concentrations, the highest frequency of all analyses was at an Eh between 50 mV and 250 mV (Figure 4.4). The general character of groundwater in Northern Germany was anoxic and therefore impeded Cd solubility for the main part of the study area.

The electric conductivity (EC) can be used as a proxy for mineral weathering (Riedel and Kübeck, 2018) but also as an indicator for saltwater 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 both 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.

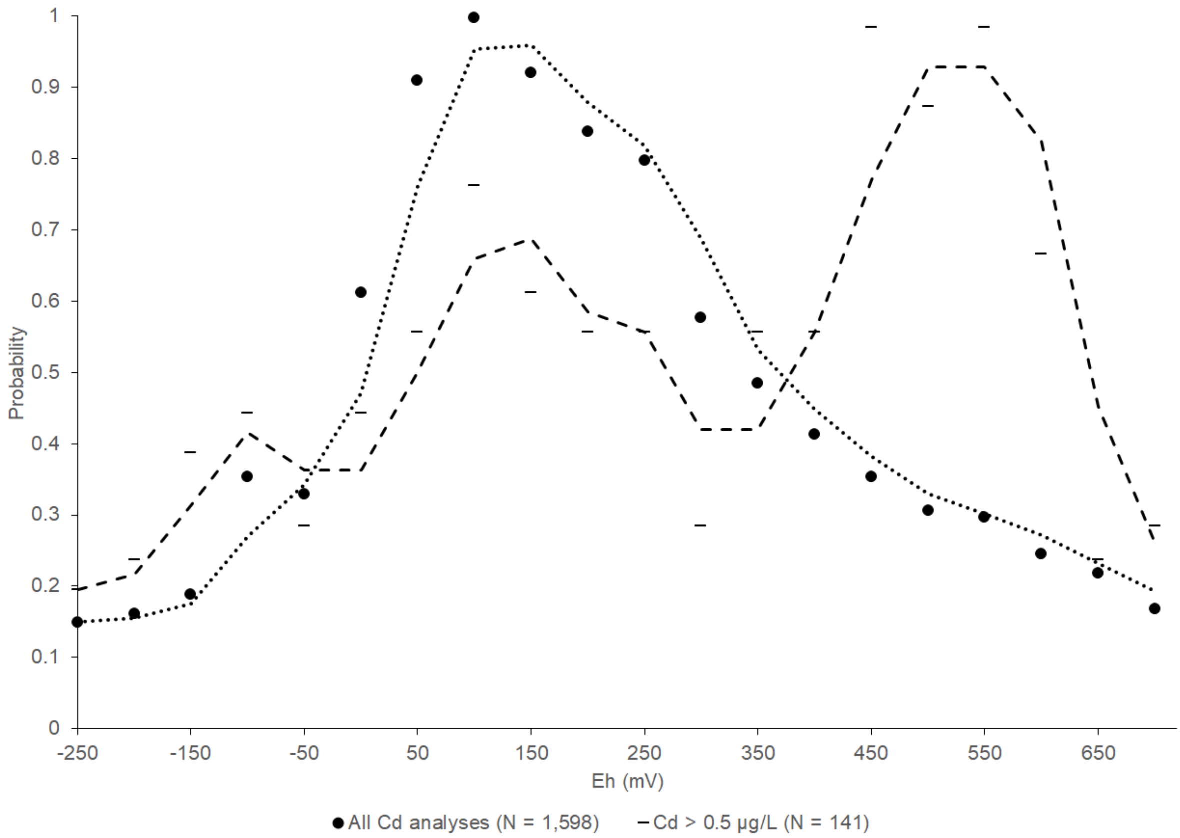


Figure 4.4: Probability of Cd concentrations above the detection limit in the complete data set (closed circles) and Cd > 0.5 µg/L (dashes), which is the German threshold value, as a function of Eh. The dotted and dashed lines illustrate the basic trends (moving average).

4.4.2 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, 2,875 (72 %) could be assigned to one of the seven redox categories (Figure 4.5). Iron(III) and sulfate reducing conditions were most common (N = 1,661), 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 1,144 (28 %) of the samples, thus they were grouped as *mixed* groundwaters (Figure 4.5). 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 a new equilibrium during/after mixing, as mentioned in Riedel and Kübeck (2018).

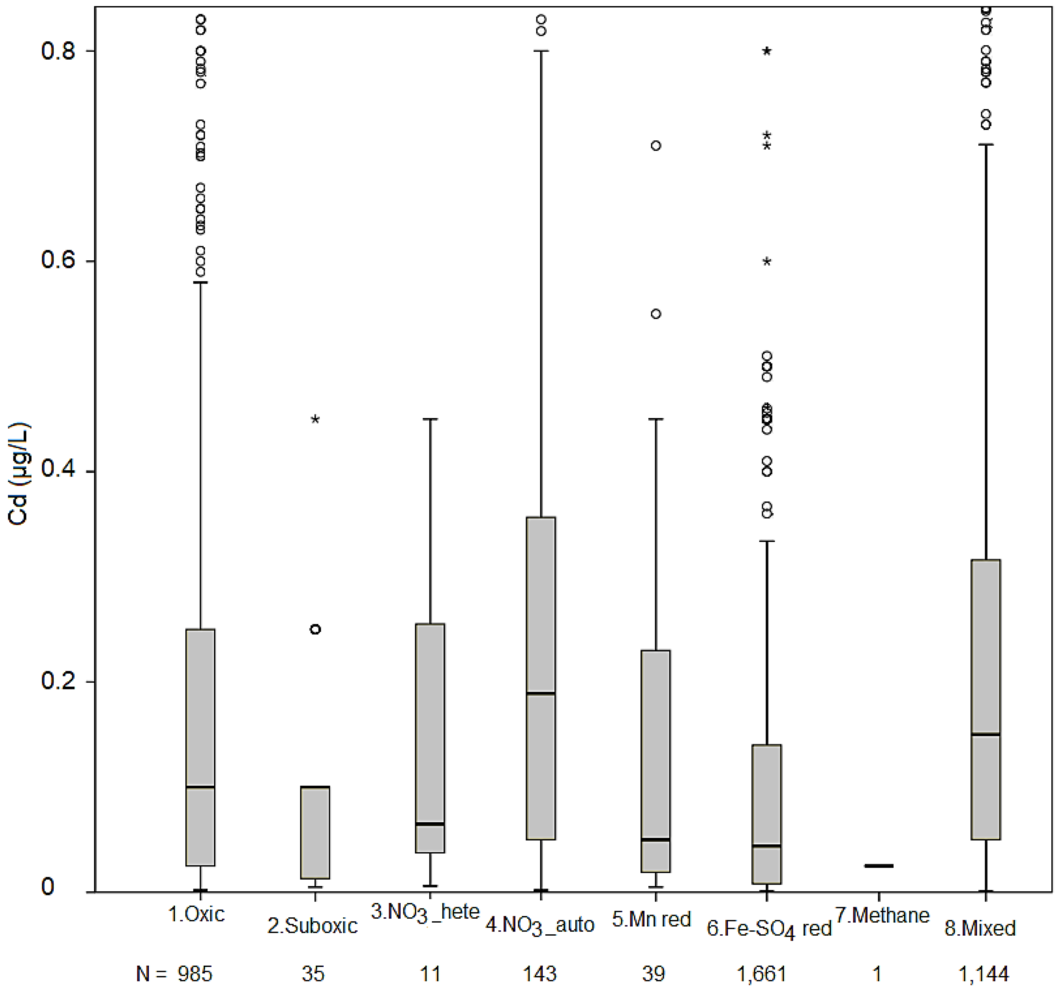


Figure 4.5: Occurrence of Cd in groundwaters that are characterized by different redox conditions as defined in Table 4.1. Boxes show the 25th, 50th (median) and 75th percentile concentrations, whiskers show 1.5 times the interquartile range, circles show outliers, stars show extreme values.

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 (Figure 4.6). 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 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 (equation 4.2 and 4.3) (Böhlke, 2002). In contrast, a greater capacity for sorption and ion exchange primarily alters the composition of cationic main components.

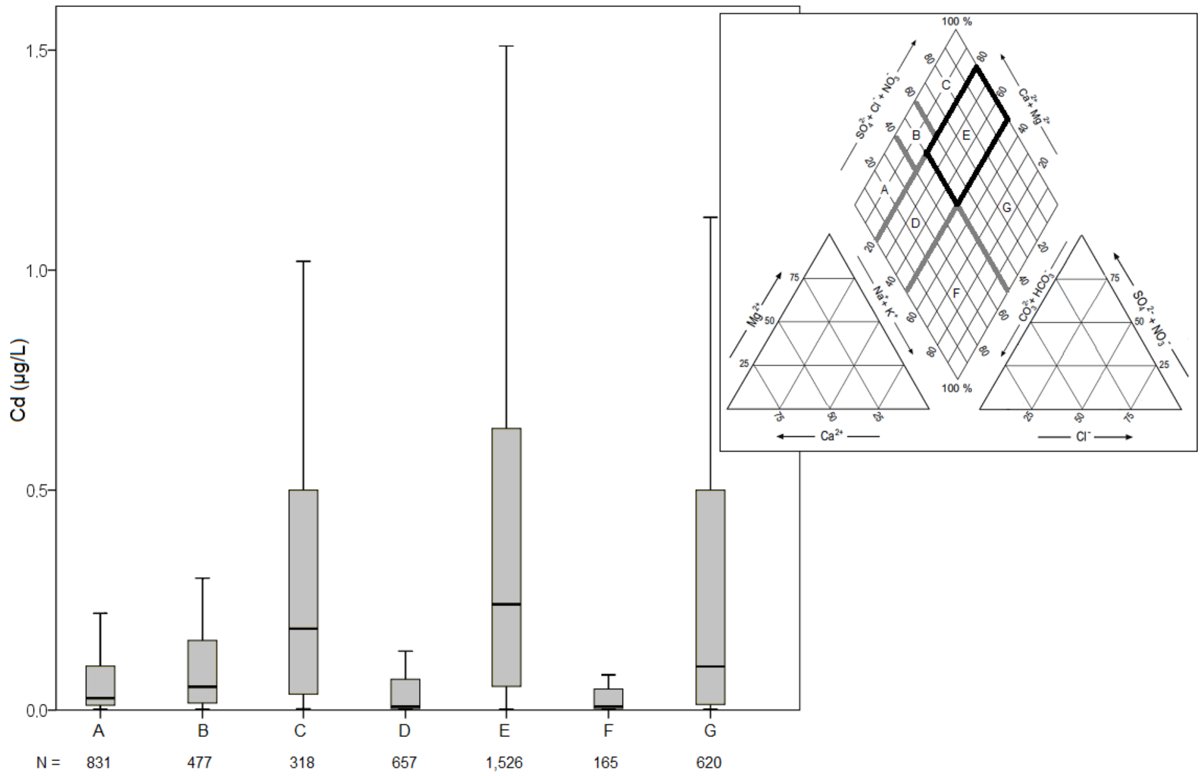


Figure 4.6: Occurrence of Cd in groundwater types according to Furtak and Langguth (1967) based on the abundance of the major elements in the Piper diagram (small figure). Outliers were excluded. Water type E (bold frame) had highest Cd mean value and range.

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 (equation 4.3). Figure 4.5 demonstrates the close relation 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 (Figure 4.5), 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 electron donors due to agriculture, such as nitrate and 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 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 heavy metals are removed due to adsorption. As suggested by Larsen and Postma (1997), due to pyrite oxidation and subsequent precipitation of $Fe(OH)_3$ (equation 4.3 and 4.4), 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 (equation 4.2), 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 (Figure 4.4).

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 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 4.3). Nevertheless, autotrophic nitrate reduction could be responsible for, or correspond to, Cd mobility (equation 4.2) 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 the 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 (equation 4.3), 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 (Figure 4.2) showed a considerable relationship between Cd concentrations and anthropogenic influences, in particular agricultural influences and indications of acidification (Figure 4.7). Half of the groundwater analyses were attributed to type *0*, which implied water *without* or *with barely anthropogenic influence*. With respect to land use, groundwater underlying grassland and woodland had the highest amount of water analyses without anthropogenic influences (50 %), while almost half of farmland related groundwater showed agricultural influences (type *2*). In most cases, agricultural influences were given as elevated nitrate concentrations. Within the subtypes of agricultural influences (type *2*), median Cd concentrations increased with increasing nitrate concentrations (Figure 4.7). 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 indications of acidification, was at the level of the German groundwater threshold value of 0.5 µg/L (Figure 4.7) 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 anthropogenic influences* (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*).

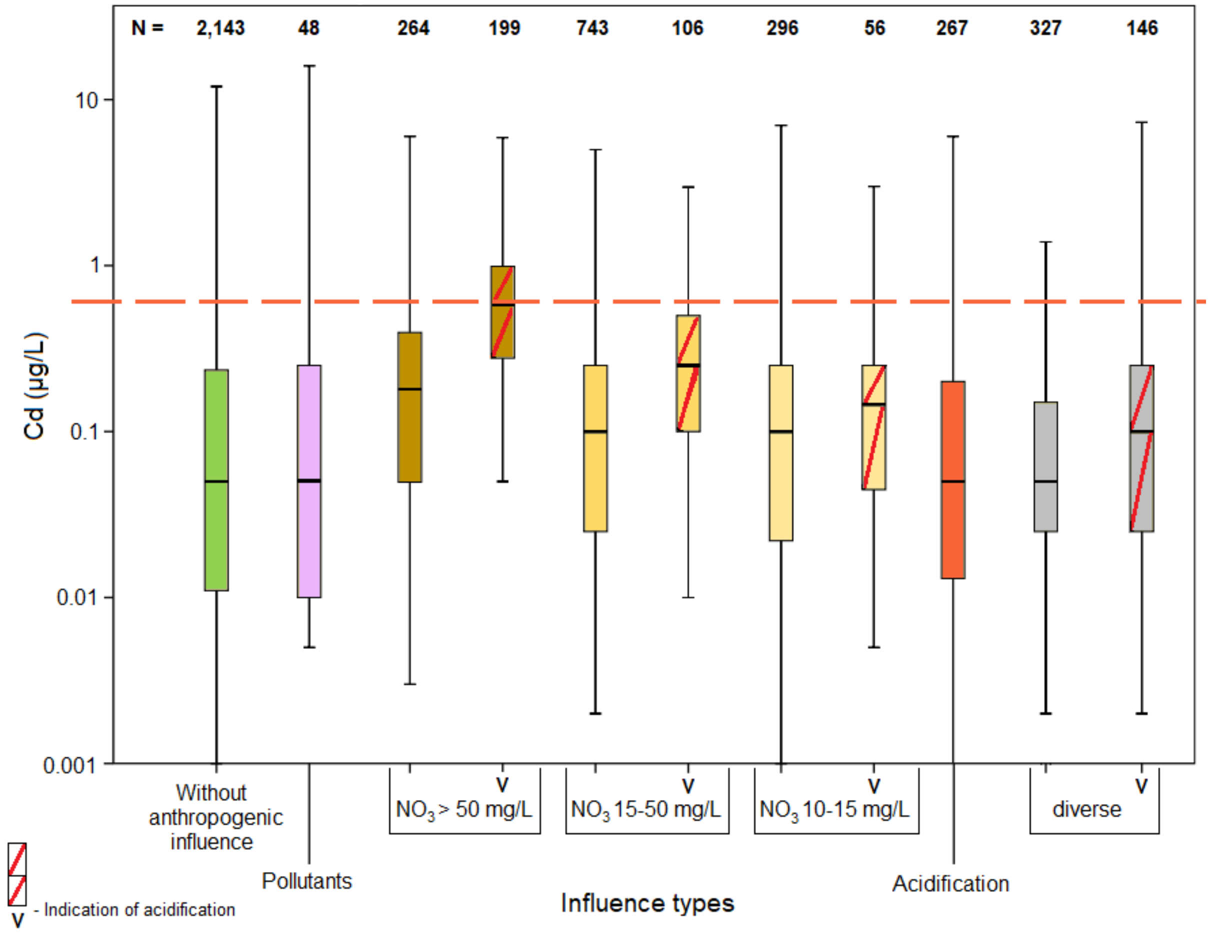


Figure 4.7: Boxplots of Cd concentrations classified by influence types. The color scheme of the boxplots is according to Figure 4.2. The dashed line illustrates the German groundwater threshold value of 0.5 µg/L. Outliers were excluded. The Kruskal-Wallis test revealed a significant difference among the influence types ($X^2(10)$ = 517.885, p = 0.0001).

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 4.2, Figure

4.7), Cd can enter the subsurface either 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 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 (Sprynskyy et al., 2011). In addition to the positive correlation with selected trace metals, e.g., Co, Cu, and Ni (Table 4.3), 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 Cd input. This is in concord with the observation in Figure 4.3, 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 (Figure 4.5 and Figure 4.6).

4.5 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 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 $CaCO_3$ 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 interest

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

Acknowledgements

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5. Cadmium background levels in groundwater in an area dominated by agriculture in Northwestern Germany

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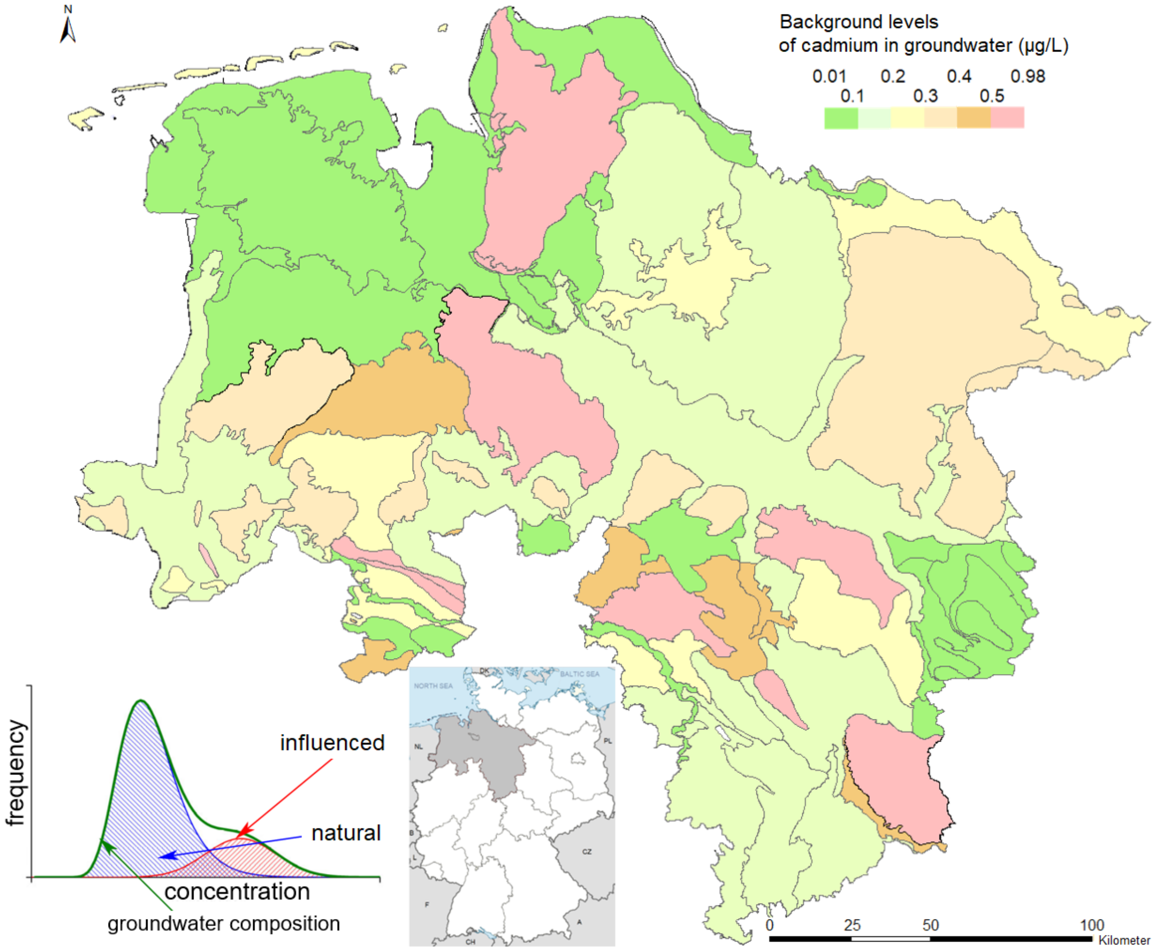
Abstract

Cadmium (Cd) is a highly toxic trace metal, which can be of geogenic or anthropogenic origin, e.g., 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 comprised of groundwater analyses from 6,300 sampling locations in Northwestern Germany. Calculated Cd background levels in groundwater were between 0.01 µg/L in hydrogeological units of mainly reducing conditions and 0.98 µg/L in groundwater recharge areas. The results showed that Cd concentrations above 0.5 µg/L in groundwater could be a regional background level, depending on the hydrogeological unit. What would be considered as current background levels, however, indicated 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 the amount of anthropogenic Cd input, in particular through the use of phosphate fertilizers. Instead, aquifer matrix analysis revealed that changes in hydrogeochemical parameters affecting Cd release from the solid phase were 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.

Graphic Abstract



5.1 Introduction

Cadmium (Cd) 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 (Hajeb et al., 2014; Pan et al., 2010) and is classified as carcinogenic (UNEP, 2010). It is listed as a priority hazardous substance in the European Water Framework Directive (WFD; EC, 2000). 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 (Bigalke et al., 2017; Merkel and Sperling, 1998; Mirlean and Roisenberg, 2006; Sprynskyy et al., 2011). Atmospheric emission, wastewater reuse, and agricultural activities (ATSDR, 2012; Sprynskyy et al., 2011; UNEP, 2010) 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 like sulfides, sorption and desorption processes due to pH changes, advective transport, and formation of aqueous Cd complexes (Caetano et al., 2003; He et al., 2005; Kjeldsen et al., 2002). Compared to other trace metals, Cd has a low sorption affinity to mineral surfaces and thus, an increased mobility potential (Lynch et al., 2014). There are two 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, while the second could be the release of geogenic Cd, triggered by agricultural nitrate and phosphate fertilization. A similar scenario was reported recently for uranium (e.g., Liesch et al., 2015; Riedel and Kübeck, 2018).

Cadmium can substitute for divalent cations, such as Ca, Fe, Zn, Pb, and Co in several minerals due to their similar ionic radius, e.g., 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 (Smith et al., 2014; Smolders and Mertens, 2013; 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; Mar and Okazaki, 2012; Page et al., 1987; Smolders and Mertens, 2013). Cadmium contents in fertilizers result from the presence of Cd as a common 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 (Bigalke et al., 2017; Grant, 2011; Taylor et al., 2016). 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; Molinari et al., 2012; Pichler et al., 2011), to date no such attempt has been made for Cd.

With this in mind, the goal of this 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 wells in Northwestern 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). These 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 for its concentration in groundwater.

5.2 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).

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) where it is conducted intensively for more than a century. Hence, it should be avoided to use the term "*natural background levels*", as they are mentioned in many studies dealing with background concentrations.

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 (Biddau et al., 2017; Kellner et al., 2015; Liesch et al., 2015), 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 type 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 influencing 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), e.g., variations between wet and dry seasons (Lu et al., 2018; Mehrabi et al., 2015).

According to the German groundwater regulation, the background level is the natural concentration of a parameter at a given location, i.e., 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 (Biddau et al., 2017; Edmunds et al., 2003). Indirect methods were also used based on the chemical groundwater composition, e.g., the use of indicator parameters 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 (Lu et al., 2018; Mehrabi et al., 2015). In general, graphic evaluation is a simple way to compare different samples and to draw conclusions about their origin, e.g., pie diagrams and dendrograms (Güler 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 of groundwater classification and source separation exist (e.g., Hepburn et al., 2018; Khadra and Stuyfzand, 2014; Liesch et al., 2015). Further approaches to classify water types and their disadvantages have already been discussed (Stuyfzand, 1993).

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 multi-criteria evaluation (Banning et al., 2009; Khadra and Stuyfzand, 2014). According to Hinsby et al. (2008), preselection methods can be applied to identify outliers, e.g., by 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 (Ducci and Sellerino, 2012; Reimann et al., 2005). 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 (Preziosi et al., 2014; Reimann et al., 2005; Wagner et al., 2011). 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 (Godbersen et al., 2012; Hinsby et al., 2008). Both, box plots and probability plots, are the preferred methods of deriving representative values since they show unbiased statistical data disregarding analytical and sampling errors (Edmunds et al., 2003).

5.3 Materials and methods

5.3.1 Study area and regional hydrogeology

The study area comprises the German federal states of Lower Saxony and Bremen in Northwestern Germany (Figure 5.1) totaling almost 48,000 km^2 (BKG, 2018). The area consists of five hydrogeological units. Both, islands and tidal wetlands are associated with the North Sea. Lowlands developed along rivers and creeks. Pleistocene glacial deposits, the so-called *Geesten*, mainly consist of sandy and gravel sediments. As mostly unconfined upper aquifers, they represent groundwater recharge areas as well as catchment areas for water supply (Elbracht et al., 2016). These four hydrogeological units belong to the North German Plain, which changes over to the Central German Uplands in the southern part of the study area rising up to 1,000 m above sea level and a moderate relief. The highest elevation, the Harz mountains, consists of Paleozoic rocks, while 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 5.1). The five hydrogeological areas divide into 80 subareas, which are hydrogeological units featuring 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. Groundwater from the islands predominantly occurs as bicarbonate predominated alkaline-earth type, while groundwater from tidal wetlands is mainly iron- and sulfate reducing and belongs to alkaline waters with decreasing bicarbonate contents. Groundwater in the lowlands and the Geesten is predominantly of alkaline-earth type with decreasing bicarbonate contents. Groundwater in the uplands appears to be oxic and is labeled as bicarbonate dominated and bicarbonatic-sulfatic alkaline-earth.

The main land use in the study area is farmland (46 %), followed by woodland (22 %), grassland (21 %), and urban areas (7 %) (BKG, 2018). Most groundwater Cd concentrations exceeding 0.5 µg/L were found in the western part of the Geesten (Figure 5.1), which are characterized by intensive livestock farming and agriculture (LSKN, 2011; Wriedt et al., 2019).

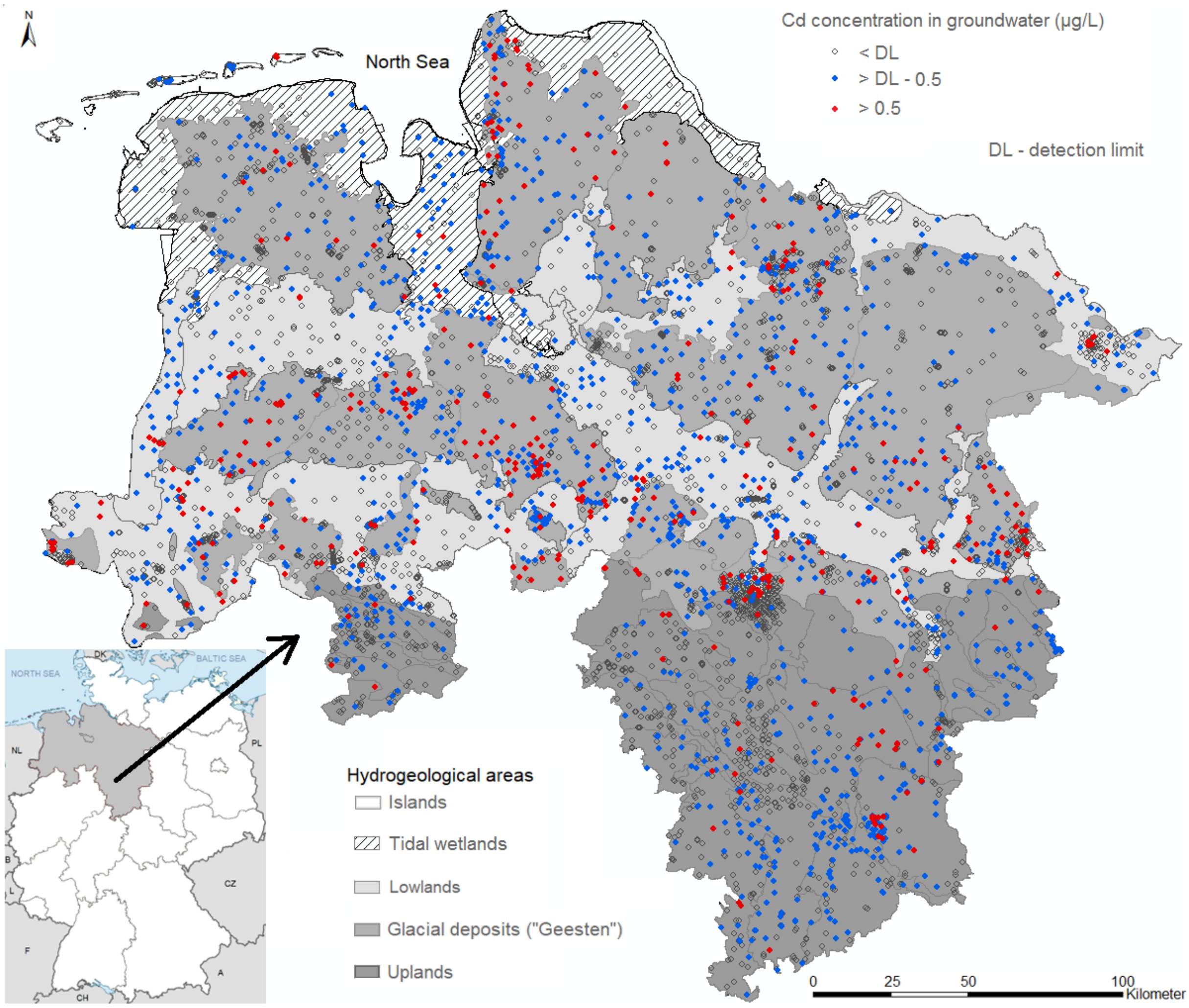


Figure 5.1: Cadmium concentrations in shallow groundwater of the study.

5.3.2 Data

The data set was compiled from the federal 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 Hannover representing the water management and geological surveys of Lower Saxony and Bremen. The data set included more than 24,000 samples from 6,300 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 monitoring program and consists of samples taken between 1976 and December 2015. Sampling and analysis followed established procedures (DVWK, 1992).

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 µg/L were discarded in order to avoid values of half the detection limit that met the German threshold value of 0.5 µg/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 towards the more frequently sampled locations. Furthermore, the evaluation of recent data ensures lower Cd detection limits, down to 0.002 µg/L, which were considered advantageous rather than a conversion to median values. Consequently, 5,512 groundwater analyses were exploitable for statistical analysis.

5.3.3 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, e.g., five hydrogeological units instead of ten and four land use classes instead of 32. Results are given as boxplots using SPSS statistics 24 (IBM, 2016) and empirical cumulative distribution functions. Wells with at least four Cd analyses including one Cd value exceeding the German threshold value of 0.5 µg/L were examined with the Mann-Kendall trend test.

For the calculation of background levels, all recent Cd analyses from wells with more than one 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 also used to ensure a high data density. In contrast to Wagner et al. (2011), analyses from wells failing stable trends at the Mann-Kendall test were not used in our study to calculate background values because those wells represented processes changing the groundwater quality and thus, they were not suitable to represent a nearly natural background. Using the probability plot, it was possible to determine and exclude outliers at the top and bottom of each data set in order to approach lognormal distribution. In case of more than ten 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 hydrogeochemical or stratigraphic-genetic characters were aggregated to determine a common Cd background level.

5.4 Results and discussion

5.4.1 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 exceeding the Cd threshold of 0.5 µg/L (7 % of 5,512 analyses), which were mainly encountered in the Geesten area (Figure 5.2) (219 out 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 µg/L and 0.05 µg/L, compared to groundwater in the Highlands and Geesten area (Figure 5.2). The 90th percentile of Cd concentrations in the Geesten was 0.58 µg/L and thus, exceeding the 90th percentile of the other hydrogeological areas and the Cd threshold of 0.5 µg/L (GrwV, 2017). Due to the character of the Geesten as recharge areas, 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 forming 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 up to 1,600 mg/kg Cd (Houben et al., 2017) and thus provide a mechanism for the release of geogenic Cd to groundwater.

Furthermore, the formation of complexes with inorganic and organic ligands would prevent adsorption by hydrous ferric oxides keeping Cd in solution in the vadose zone (Carrillo-Gonzalez et al., 2006; Hammons et al., 1978; Najafi and Jalali, 2015).

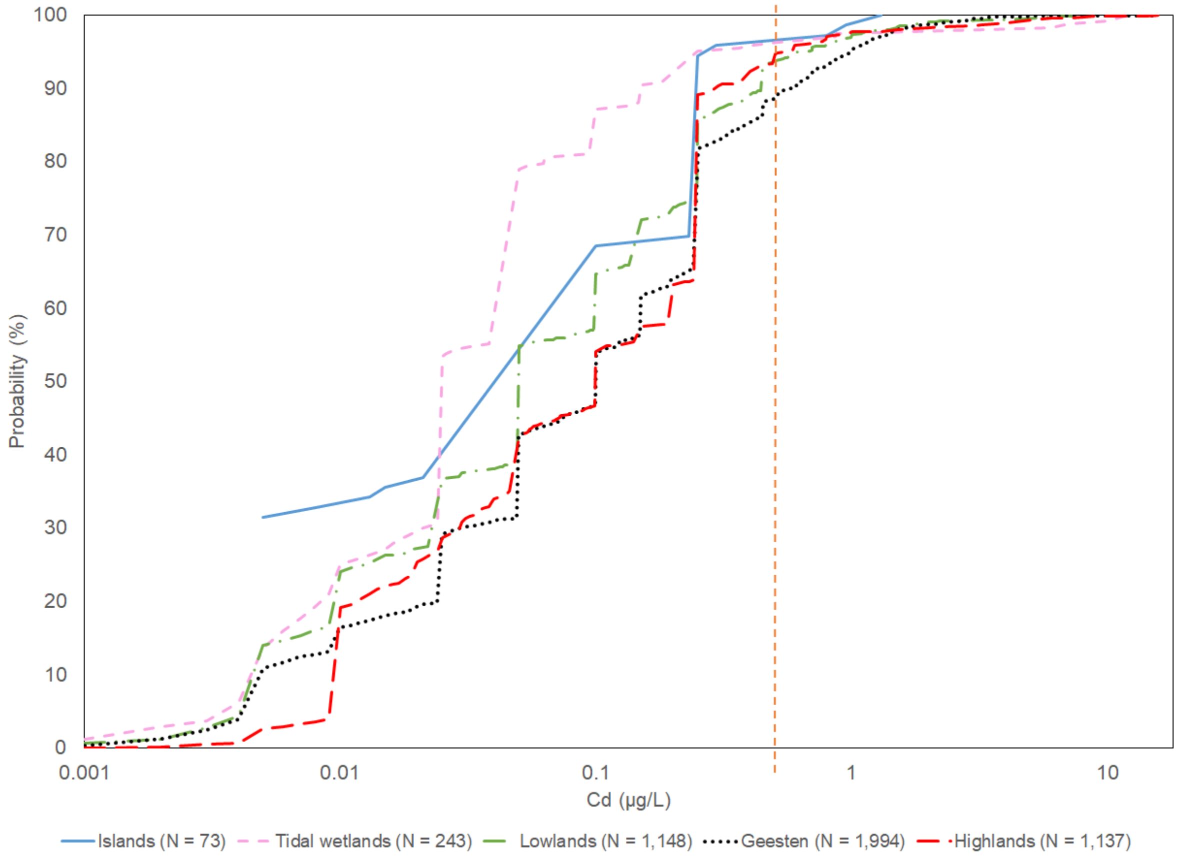


Figure 5.2: Empirical cumulative distribution functions for Cd concentrations, classified by hydrogeological areas. The dashed vertical line represents the German Cd groundwater threshold value of 0.5 µg/L.

While the mean Cd concentration for all land use classes was similar, between 0.05 µg/L and 0.1 µg/L (Figure 5.3), an elevated 90th percentile of Cd was observed in case of farmland (0.57 µg/L) and woodland 0.45 µg/L). Most groundwater samples showing Cd concentrations above 0.5 µg/L belonged to wells that occurred in association with farmland (42 % of 363 sampling locations) and woodland (33 %) indicating an influence from seepage. The relation to water depth supported that assumption because most elevated Cd concentrations were detected in the upper 15 m below water table where water chemistry evolves fast and is influenced by human impact (Edmunds et al., 2003).

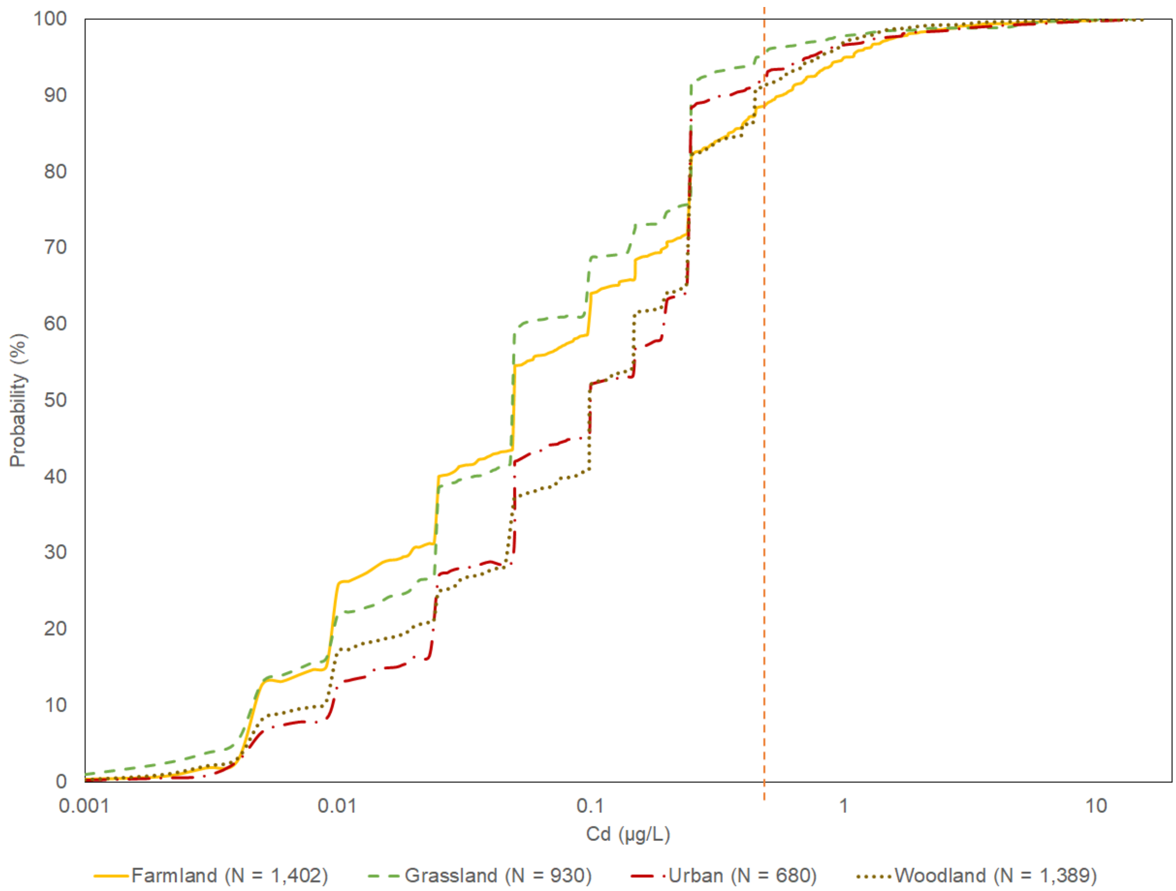


Figure 5.3: Empirical cumulative distribution functions for Cd concentrations, classified by land use. The dashed vertical line represents the German Cd groundwater threshold value of 0.5 µg/L.

5.4.2 Assessment of elevated cadmium concentrations in groundwater

The trend test revealed 157 wells (3 % of 5,512 wells) with an unstable temporal development of Cd concentration and those were discarded for the calculation of background levels. Of those 157 wells, 30 wells had increasing Cd concentrations mainly occurring in the upper 15 m below the water table. Similar to the occurrence of elevated Cd concentrations, those wells were also located in the Geesten areas. The most recent Cd concentrations were between 0.28 µg/L and 4.8 µg/L. The 30 wells with increasing Cd concentrations were often associated with low pH, increased nitrate and further increased heavy metal concentrations, e.g., Mn, Ni, and Zn. These observations are in agreement with the chemical behavior of Cd, which is preferentially in solution at a pH of less than 6.5 and under oxygenated conditions (Merkel and Sperling, 1998). The Cd^{2+} ion itself is not redox-sensitive, but it is indirectly tied to redox conditions due to the incorporation into redox-sensitive stable precipitates (see above).

Consequently, it can be assumed that Cd release was linked to hydrogeochemical processes that were caused by agricultural activities, e.g., through nitrate reduction coupled with pyrite oxidation (Böhlke, 2002).

5.4.3 Assessment of background levels

The data set comprised 5,355 Cd analyses for calculating background levels. On the basis of the 80 hydrogeological subareas, background levels for Cd in groundwater were between 0.01 µg/L and 0.98 µg/L. Low Cd background levels were observed in hydrogeological units of mainly reducing conditions. Elevated background levels that exceeded the German threshold value of 0.5 µg/L for Cd were calculated for 9 out of 80 subareas, which belonged to the Geesten and the Highlands (Figure 5.4). 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 seven 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, Cd threshold and background levels indicating geogenic anomalies or anthropogenic influences.

Despite the ubiquitous human impact through the centuries-old cultivation of the landscape and thus, the overprint of 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 to derive background levels. The background levels for Cd were mainly elevated in the Geesten areas indicating that the combination of agricultural activities, livestock farming, the presence of sandy aquifers and thus, a minor groundwater cover protection had influence on the *natural background* of Cd.

Alternatively, the occurrence of elevated Cd background levels in the Geesten area (Figure 5.4) can be caused by Cd release from glacial deposits or the low sorption capacity of the sediment compared to finer-grained and organic material in the lowlands and wetlands. The Quaternary sedimentary cover in the northern part of

Central Europe is known to be enriched in Cd (Birke et al., 2017). 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 (Birke et al., 2017). 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, e.g., 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, while elevated Ni and Zn concentrations in groundwater were missing.

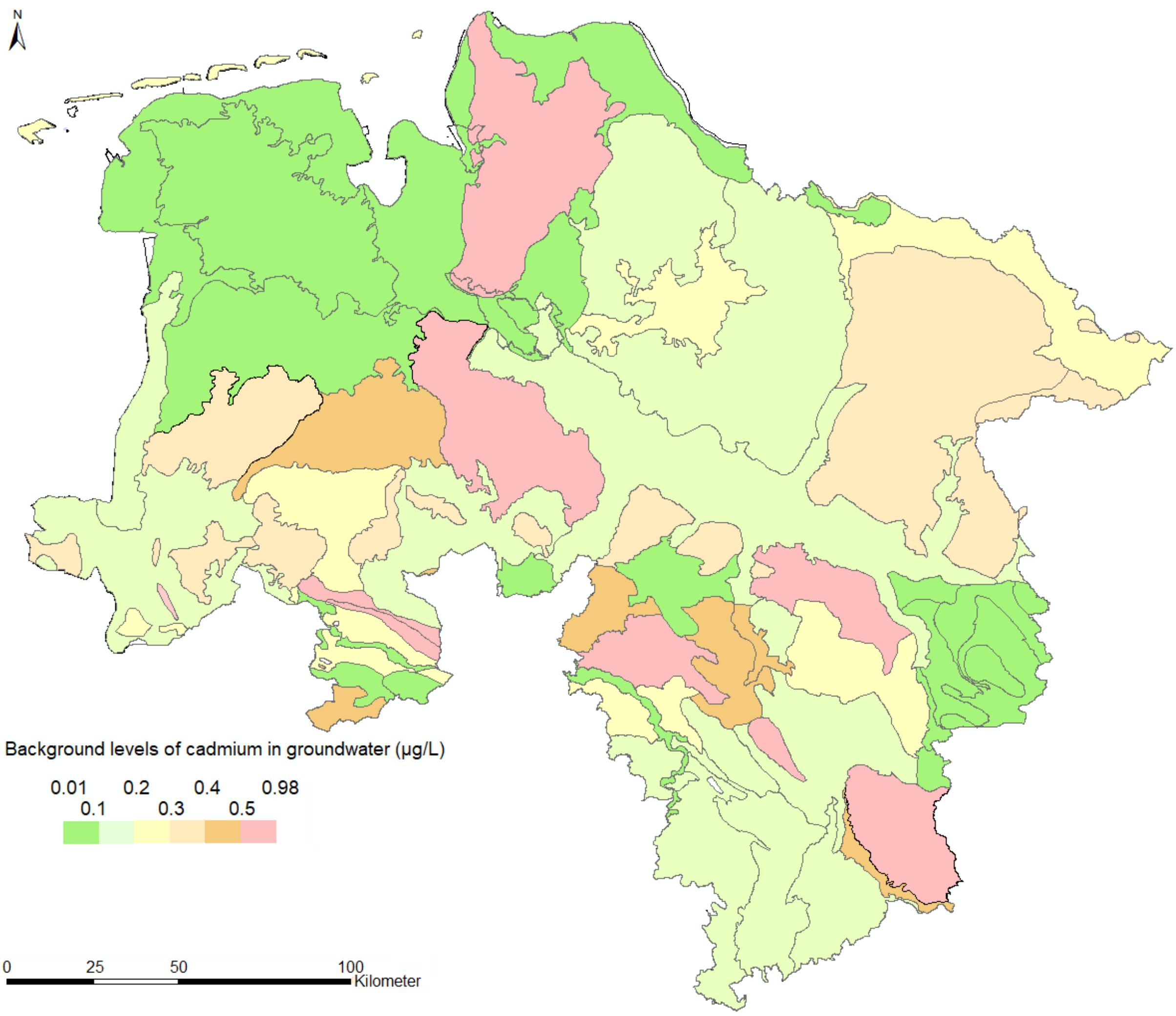


Figure 5.4: Background levels of Cd in groundwater, classified by hydrogeological subareas.

It is difficult to compare the results from our study to findings from other regions because there are no standardized procedures to characterize background levels and to assess what are elevated trace metal concentrations in groundwater. 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 µg/L (GrwV, 2017) is twenty times lower than the Chinese (Li et al., 2017). Hence, it is difficult to compare reports where the risk assessment is based on varying threshold value. Findings that, for example, exceed the threshold value of Cd in Germany 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 mainly based on groundwater monitoring wells featuring 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.

5.4.4 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 mainly collected 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, e.g., 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 non-agricultural 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 Cd mobility or enhance Cd mobility (Carrillo-Gonzalez et al., 2006; Grant, 2011; Seaman et al., 2001). Atmospheric deposition as 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, but presently being released. In European soils, for example, Cd input via atmospheric deposition decreased from 3.0 g/(ha*a) in 2002 to currently 0.35/(ha*a). Presently, Cd output from soils via leaching is 2.56 g/(ha*a) (Six and Smolders, 2014).

In the Geesten large parts are additionally covered by forests (woodlands). Since the release of Cd from forest soils is mainly controlled by a decrease in pH our results are in agreement with the study of Huang et al. (2011), who stated that forest soils are an effective sink for atmospherically deposited pollutants, whose release is controlled by pH and dissolved organic carbon (DOC). This 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, 1,600 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 industrial and agricultural processes cannot be excluded (Birke et al., 2017).

5.5 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 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 % out of 5,512 groundwater analyses exceeding 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 which 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.

Declaration of interest

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

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Data Accessibility Statement

The mentioned administrative authorities provided data and calculation tools for this study as part of a research project. A further accessibility of particular analyses (e.g., coordinates, concentrations) was prohibited.

6. Conclusions and outlook

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

Cadmium accumulation in soils can occur, where Cd mobility is inhibited, e.g., Cd can precipitate under anoxic conditions; Cd sorption is accompanied by enrichment of organic matter or clay. Anthropogenic sources of Cd in soils are direct input of waste material from mining and industry as well as agricultural application, e.g., as sewage sludge and phosphate fertilizers. Transport of Cd from soil into groundwater depends on hydrogeochemical factors regulating Cd mobility. Besides direct input of waste water, e.g., as runoff and leakage, or atmospheric deposition, Cd leaching from waste material, landfills, and fertilization only can happen where Cd release is promoted by replacement, formation of soluble complexes, acidification, or oxidation. Mining wastes usually go together with oxidation reactions and subsequently strongly decreased pH. Excessive N fertilization also decreases soil pH, which is associated with increased ionic strength and enhanced Cd mobility. Summarizing data on the number of soil and groundwater systems with Cd problems cannot be provided, because there exist only case studies dealing with specific contamination issues (Table 2.6). Further information on the amount of impacted areas and Cd fluxes from selected sites into groundwater are not available. Besides, the range and partially absence of national threshold values for Cd in soil and groundwater makes it difficult to identify impacted areas on an international scale.

An overview of the most relevant Cd sources and influences on Cd release into soil and groundwater is given in Figure 6.1. Atmospheric Cd deposition can be caused by anthropogenic and natural sources. Many reports dealing with Cd deposition consider higher estimations of Cd input from anthropogenic sources. More recent studies, however, calculated a natural amount of Cd deposition exceeding the anthropogenic amount, especially with respect to increasing off-gas cleanings. Consequently, atmospheric deposition of natural sources accounts 93 % of Cd emissions, especially from soil particles and wild fires (Table 2.1). Natural Cd release from weathering occurs in sulfidic and carbonatic systems due to Cd accumulation in sulfides, e.g., pyrite, and exchange of Ca in carbonates. The resulting Cd concentrations in groundwater depend on groundwater milieu. Cadmium release from calcareous systems and subsequent transport in groundwater is only possible in acidic waters (Figure 2.1). Acidification can be related to natural influences, e.g., forest and marsh, but also caused by anthropogenic input, e.g., acid mine drainage. Anthropogenic Cd input from phosphate fertilizers into soil, for example, can exceed atmospheric deposition (Table 2.5). Drivers for Cd mobility are soil texture, content of organic matter, land use, and hydrochemical milieu. Soils with increasing amount of fine-grained material, organic matter, swamp and forest as land use as well as moderate pH and redox can contain elevated Cd contents. Cadmium leachate is controlled by quantity and quality of seepage; organic and inorganic ligands promote mobility of Cd bound in soluble complexes. In soils that are sandy and poor in organic matter feature low sorption capacity, Cd transport into groundwater, and a subsequent reduction of previously accumulated Cd can occur.

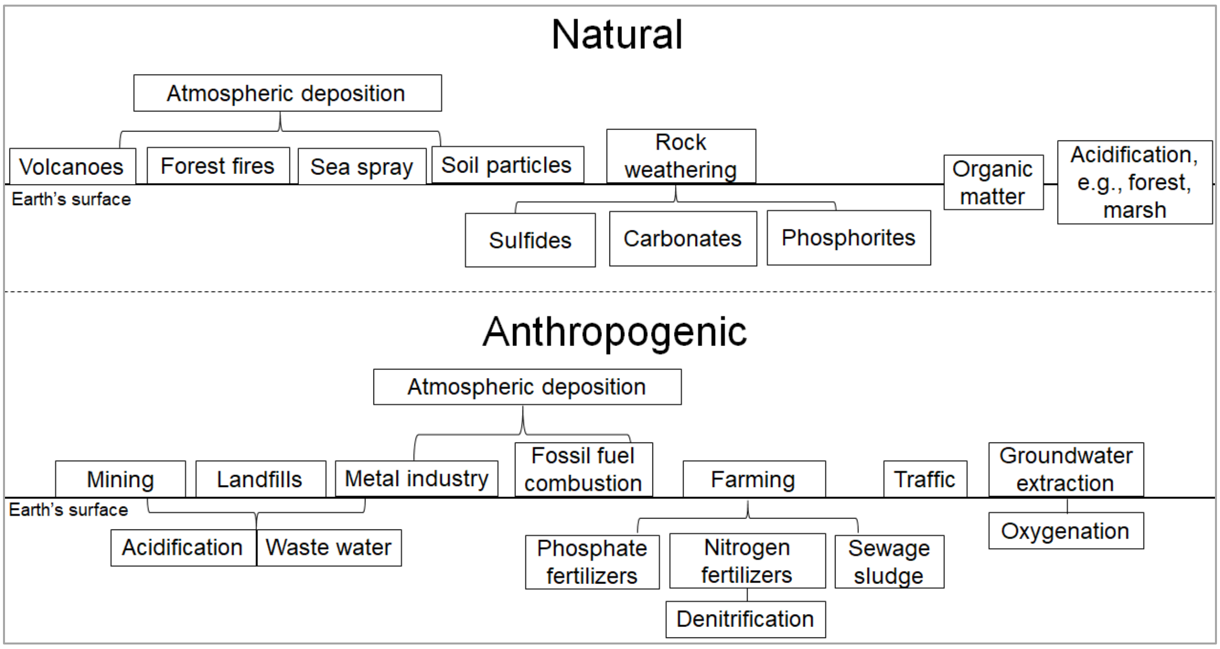

Figure 6.1: Cadmium sources and influences on Cd release into groundwater.

Cadmium pollution of soil and groundwater is a worldwide problem that affects resources for food and drinking water mainly in Asia and Africa. Further efforts to clean waste water, inhibit leachate of contaminated material, e.g., in landfills and mines, and reduce use of Cd contaminated phosphate fertilizers are necessary to decrease anthropogenic Cd output. As Figure 2.2 indicates, the amount of Cd input into soil as an impurity in phosphate fertilizers depends on the origin. Thus, changes in fertilizer management do not consequently result in decreasing crop yields.

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

(1) “*Natural origin and release of Cd*”

Elevated Cd concentrations in groundwater are linked to rock types with increased Cd contents, e.g., sulfides. Cadmium is released in the context of weathering or naturally caused acidification.

(2) “*Anthropogenically induced release of naturally occurring Cd*"

In this case, Cd originates from natural sources, but its release is caused by anthropogenic influences, e.g., atmospheric deposition or acidification linked to denitrification of nitrogen fertilizers.

(3) “*Anthropogenic Cd input*"

According to the most likely reason for elevated Cd in groundwater, Cd originated from P fertilizers and atmospheric deposition. Further entries are linked to industrial activities and traffic.

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

a) Calcite dissolution (under acidic conditions) (equation 6.1):

$$(Ca_{1\text{-}w}Cd_w)CO_{3(s)} + H^+ \leftrightarrow (1\text{-}w)\ Ca^{2+} + w\ Cd^{2+} + HCO_3^- \tag{6.1}$$

b) Oxidation of sulfide minerals, e.g., pyrite (under oxic conditions) (equation 6.2):

$$2(Fe_{1\text{-}x}Cd_x)\ S_{2(s)} + 7\ O_2 + 2\ H_2O \leftrightarrow 2(1\text{-}x)\ Fe^{2+} + 2x\ Cd^{2+} + 4\ SO_4^{2-} + 4\ H^+ \tag{6.2}$$

Possible subsequent reaction (equation 6.3):

$$4\ Fe^{2+} + 2\ Cd^{2+} + O_2 + SO_4^{2-} + Cl^- + 10\ H_2O \rightarrow 4\ Fe(OH)_{3(s)} + CdSO_4^0 + CdCl^+ + 8\ H^+ \tag{6.3}$$

c) Chemolithotrophic denitrification (under anoxic conditions) (equation 6.4):

$$5(Fe_{1\text{-}y}Cd_y)\ S_{2(s)} + 14\ NO_3^- + 4\ H^+ \leftrightarrow 5(1\text{-}y)\ Fe^{2+} + 5y\ Cd^{2+} + 7\ N_{2(g)} + 10\ SO_4^{2-} + 2\ H_2O \tag{6.4}$$

Possible subsequent reaction (equation 6.5):

$$5\ Fe^{2+} + 2\ Cd^{2+} + NO_3^- + 3\ SO_4^{2-} + 12\ H_2O \rightarrow 5\ Fe(OH)_{3(s)} + CdSO_4^0 + Cd(SO_4)_2^{2-} + \tfrac{1}{2}\ N_{2(g)} + 9\ H^+ \tag{6.5}$$

In case of (3), Cd originates from direct entry or dissolution of phosphate fertilizers. As a result, Cd is released, e.g., from fluorapatite, using soil acids, shown in reaction d) (equation 6.6):

d) $$(Ca_{10\text{-}z}Cd_z)(PO_4)_6F_{2(s)} + 12\ H^+ \rightarrow 10\text{-}z\ Ca^{2+} + z\ Cd^{2+} + 6\ H_2PO^-_4 + 2\ F^- \tag{6.6}$$

A couple of future perspectives arise from the results presented in the thesis. It can be assumed that the issue of anthropogenic Cd pollution in groundwater, e.g., caused by combustion emissions and waste water, is local or regional, rather than global. In Northern Germany, the assessment revealed no pollution of Cd but nitrate. The release of Cd and increasing Cd concentrations in groundwater are presumably at least anthropogenically induced. Hydrochemical parameters such as redox conditions and pH are more important than Cd sources themselves. The amount of naturally released Cd, however, was underestimated in the past, as the evaluation of Richardson et al. (2001) showed. To get further information on the potential Cd pool at local and regional scale, future research should investigate the Cd fate in areas of Cd pollution or areas that are affected by intensive exploitation such as farming. Besides the common anthropogenic pollution, the replacement of other elements in minerals can occur naturally and causes geogenic Cd pollution, e.g., in Switzerland (Bigalke et al., 2017).

On the one hand, soil and aquifer matrix as possible Cd sources can be analyzed regarding their Cd contents. Sequential extractions indicate the origin and mobilization potential of contaminants in groundwater depending on different extracting agents applied to the samples (Desaules, 2012). To investigate the contents of Cd and additional trace metals, such as Co, Cr, Cu, Ni, Pb, V, and Zn, and the binding character, the modified BCR three-step sequential extraction procedure (Rauret et al., 1999), for example, can be applied to distinguish between the acid extractable, reducible, and oxidizable fractions and subsequently to estimate the amount of mobilizable contaminants. On the other hand, isotopic analysis can also be a possibility to indicate Cd sources. Several studies investigated isotopic compositions of Cd, Pb, and Cd/Pb ratios in sediments and soils to distinguish between pollution sources (e.g., Imseng et al., 2018; Monna et al., 2000; Xing et al., 2019). Cadmium isotopic fractionation can occur during different processes such as natural weathering, atmospheric deposition, adsorption, and plant uptake resulting in characteristic isotope compositions. In addition, further investigation on the Cd input from fertilizers and atmospheric deposition, e.g., at permanent soil monitoring sites, is also recommended to monitor the anthropogenic Cd input.

Data sets from other areas, e.g., with similar land use and hydrogeology but more suitable sampling locations with short screens, can be collected, assessed, and compared with the results from the doctoral project to get further information on Cd behavior. As mentioned above, different threshold values in different countries have to be taken into account. Another potential approach is to proceed with the existing sampling locations within the data set and to study the changes in Cd concentrations in date and frequency of sampling to identify seasonal variations and their influences on the redox front progression. In the case of sampling locations featuring continuously elevated Cd concentrations, direct push technology can be applied to investigate the spatial distribution of influences within the catchment area of a sampling location.

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Appendix: Cadmium im Grundwasser Nordwestdeutschlands − Herkunft, Mobilisierung und Bewertung nach Wasserrahmenrichtlinie

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Der Anhang entspricht einem Manuskript, das in Vorbereitung zur Einreichung bei der Zeitschrift *Grundwasser* ist.

Zusammenfassung

In Niedersachsen und Bremen offenbarte das flächendeckende Grundwassermonitoring Cadmiumkonzentrationen, die zu einer Einstufung von 9 von insgesamt 123 Grundwasserkörpern in den schlechten chemischen Zustand nach Wasserrahmenrichtlinie (WRRL) führten. Cadmium kann geogen vorkommen oder als Bestandteil von Düngern und Emissionen, die über die Atmosphäre wieder als Deposition in den Untergrund gelangen, auftreten. In der vorliegenden Studie wurden an Grundwasseranalysen Zeitreihen ausgewertet, Hintergrundwerte für Cadmium in verschiedenen Raumeinheiten abgeleitet und hydrochemische Zusammenhänge untersucht. Zusätzlich wurden Düngerdaten und Bodenanalysen des Monitorings an repräsentativen Boden-Dauerbeobachtungsmessstellen betrachtet. Ein Eintrag von Cd durch Phosphat-Dünger kann nicht ausgeschlossen werden, er beträgt im Mittel 0,74 g/(ha*a). Der Cadmiumanteil, der aktuell über die atmosphärische Deposition und den Boden in das Grundwasser gelangt sein kann, hat einen vergleichbar geringen Anteil, 0,2 g/(ha*a). Die Datenauswertung zeigte einen deutlichen Zusammenhang zwischen Cadmium im Grundwasser und landwirtschaftlicher Nutzung, insbesondere durch erhöhte Nitratkonzentrationen und Versauerung. Hydrogeologische Rahmenbedingungen und anthropogen bedingte Einflüsse auf die Steuergrößen pH-Wert und Redoxpotenzial, die zur

verbesserten Mobilisierung des Cadmiums im Grundwasser führen, spielen dabei eine größere Rolle als ein potentieller Eintrag durch Dünger oder atmosphärische Deposition.

A-1 Projekt

Mit der Verabschiedung der EU-Wasserrahmenrichtlinie (WRRL) haben sich die Mitgliedsstaaten verpflichtet, Umweltziele für ihre Gewässer zu erreichen (RL 2000/60/EG). Voraussetzung dafür sind ein flächendeckendes repräsentatives Monitoring und die regelmäßige Bewertung der Ergebnisse. Bei Verfehlen der Umweltziele, im Grundwasser spricht man vom guten mengenmäßigen und chemischen Zustand, gilt es, geeignete Maßnahmen durchzuführen, die dann später die Umweltziele erreichen lassen. Als Kriterien für den guten qualitativen Zustand der Grundwasserkörper (GWK) gelten Konzentrationen im Grundwasser für Stoffe, die in der Grundwasser-Tochterrichtlinie (RL 2006/118/EG) genannt sind. In Deutschland wurden diese europäischen Vorgaben in der Grundwasserverordnung konkretisiert und dort u. a. Schwellenwerte festgeschrieben (GrwV, 2017; Anlage 2). Zusammen mit den Schwellenwerten beschreibt die Grundwasserverordnung auch die Methoden, mit deren Hilfe die weitestgehend unbeeinflusste Hintergrundkonzentration von Parametern in Grundwasserkörpern sowie Trends bestimmt und beurteilt werden. Der Schwellenwert für Cadmium (Cd) liegt bei 0,5 µg/L (GrwV, 2017). Dieser wurde zusammen mit abgeleiteten Hintergrundwerten für die Bewertung der GWK in Niedersachsen und Bremen herangezogen. Bei 9 von 123 GWK wurde keine plausible Begründung für erhöhte Cd-Konzentrationen oberhalb des Schwellenwertes oder alternativ zu den bestimmten Hintergrundwerte gefunden, so dass der chemische Zustand bei der Beurteilung nach WRRL in diesen Gebieten als schlecht eingestuft worden ist (MU, 2015a, 2018). Mögliche Quellen des Cd und die bei der Mobilisierung beteiligten Prozesse waren Gegenstand des Forschungsprojektes „Cadmium im Grundwasser Niedersachsens“ (Kubier et al., 2018), welches als Maßnahme nach WRRL initiiert wurde (MU, 2015b).

Die grundsätzliche Frage war, ob das Cd geogen vorhanden ist oder ob anthropogene Einflüsse zum Eintrag, bzw. zur Mobilisierung des Cd im Grundwasser geführt haben. Quellen und Faktoren, die die Cd-Konzentration im Grundwasser beeinflussen können, lassen sich in oberirdische und unterirdische sowie in natürliche und anthropogene Faktoren einteilen (Abbildung A-1). Im Falle natürlicher Ursachen kann eine Hintergrundkonzentration für Cd im Grundwasser abgeleitet werden, die, falls sie oberhalb des Schwellenwertes von 0,5 µg/L liegt, anstatt des Schwellenwertes für das betroffene Gebiet als Bewertungskriterium für den chemischen Zustand von Grundwasserkörpern oder Teilen derselben herangezogen wird (GrwV, 2017). Als anthropogene Ursachen sind der Eintrag von Cd aus der Atmosphäre oder als Nebenbestandteil von Phosphat-Düngern genauso denkbar wie die Mobilisierung von im Sediment vorhandenem Cd durch Einträge, die wiederum diese Cd-Anteile mobilisieren.

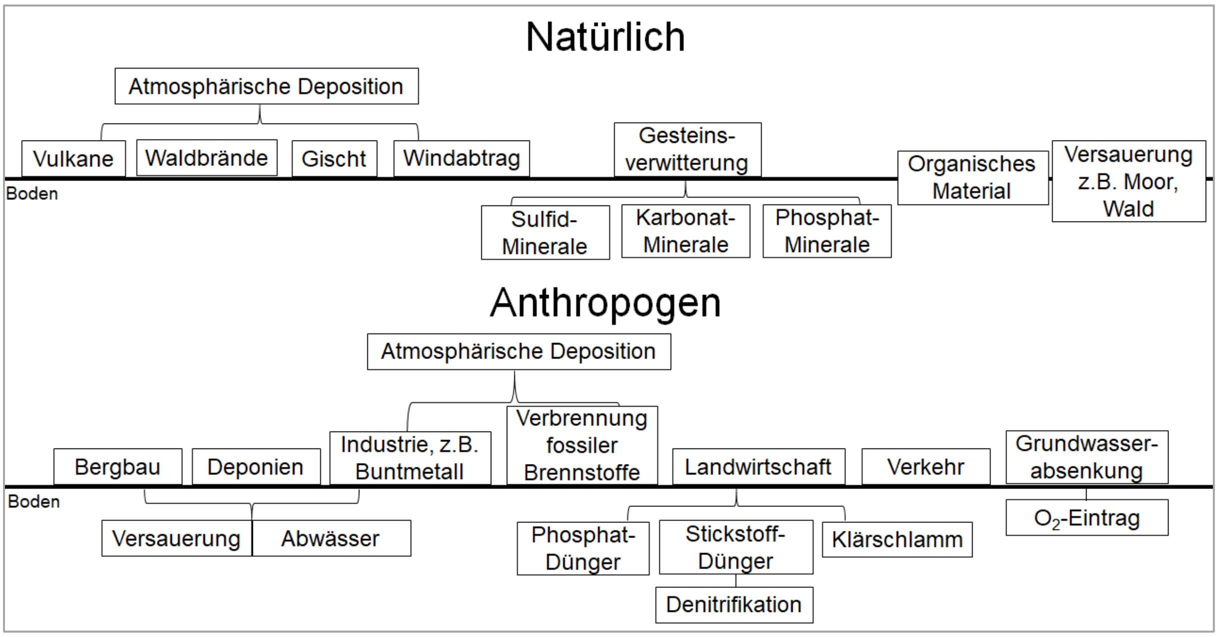


Abbildung A-1: Schema der natürlichen und anthropogenen Cd-Einträge bzw. Einflüsse auf die Freisetzung von Cd ins Grundwasser.

Figure A-1: Natural and anthropogenic Cd sources and influences on Cd release into groundwater.

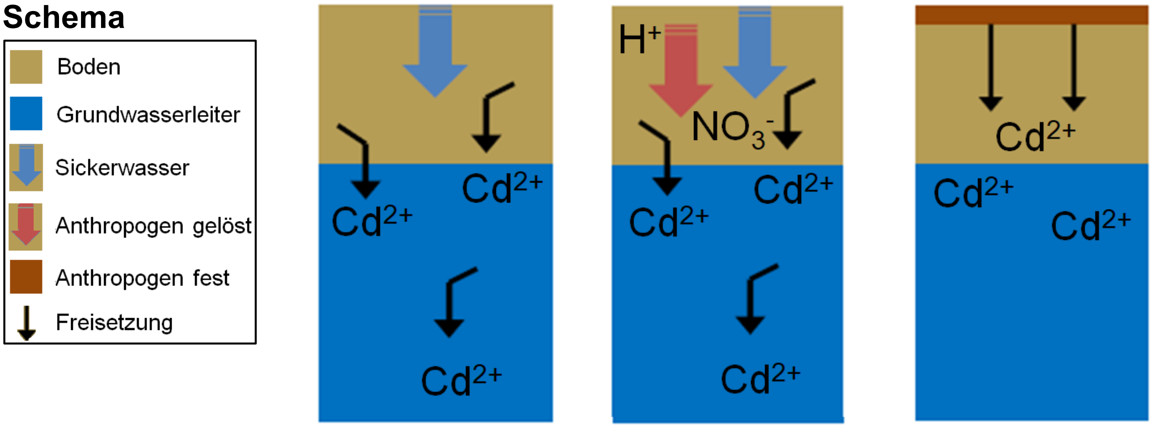
Zur Klärung der Frage, ob eines dieser drei Szenarien (Tabelle A-1) zutrifft und die erhöhten Cd-Konzentrationen im Grundwasser erklären kann, wurden zusätzlich zu Grundwasseranalysen der Landesmessnetze Niedersachsens und Bremens sowie den Analysen von atmosphärischer Deposition, Sickerwasser und Boden an den Boden-Dauerbeobachtungsflächen (BDF) in Niedersachsen (z. B. Höper und Meesenburg, 2012) Daten zur Beschaffenheit der eingesetzten Düngemittel aus der Literatur herangezogen. Damit sollten Gebiete identifiziert werden, die bereits erhöhte Cd-Konzentrationen im Grundwasser aufweisen, sowie Gefährdungsgebiete mit potenziell erhöhten Cd-Werten im Grundwasser. Für diese Gebiete ließen sich bei Kenntnis der beteiligten Prozesse, die die Mobilität von Cd beeinflussen, dann Maßnahmenfelder benennen, die zukünftig zur Reduzierung der Cd-Konzentrationen oder der Gefahr einer Mobilisierung führen können.

Tabelle A-1: Szenarien der Cd-Freisetzung bzw. -Eintragung.

Table A-1: Scenarios of cd release and contamination.

Szenario	I: Geogener Ursprung, natürliche Mobilisierung	II: Geogener Ursprung, anthropogen induzierte Mobilisierung	III: Anthropogener Eintrag
Cd-Herkunft	Minerale (Sulfide, Karbonate, Hydr-/ Oxide, Tone), organisches Material	Minerale (Sulfide, Karbonate, Hydr-/ Oxide, Tone), organisches Material	Phosphat-Dünger, atmosphärische Deposition, Punktquellen (z.B. Abwasser, Deponie)
Cd-Freisetzung	Lösung aus Mineralen, Desorption von Hydr-/ Oxiden, Tonen oder organischem Material	Lösung aus Mineralen, Desorption von Hydr-/ Oxiden, Tonen oder organischem Material	Lösung im Boden, Verlagerung mit Sickerwasser
Ursache der Freisetzung	Versauerung (Wald, Moor), saisonal schwankender Grundwasserstand	Eintrag von Säuren, Nitrat, Salz, „Liganden“; Grundwasserabsenkung	Versickerung ins Grundwasser

Schema



A-2 Untersuchungsgebiet

Der Großteil Niedersachsens und Bremens ist geologisch durch das Pleistozän geprägt und somit dem Nord- und mitteldeutschen Lockergesteinsgebiet zugeordnet. An der Küste sind fluviatile Gezeitenablagerungen zu finden, weiter nach Süden finden sich Schmelzwasserablagerungen, Flussablagerungen oder Moore. Südlich der Linie Nordhorn-Hannover-Wolfsburg schließt sich das Mitteldeutsche Bruchschollenland an, wobei auch dort verbreitet quartäre Ablagerungen an der Geländeoberfläche auftreten. Schließlich ist im Südosten der Harz als Teil des Mitteldeutschen Grundgebirges anzutreffen (Elbracht et al., 2016). Die Gliederung des Quartärs in Niedersachsen zeigt, dass sich während der Kaltzeiten teils bedeutende Ablagerungen gebildet haben. Diese Sedimente haben je nach Lage und Stoßrichtung der Gletscher eine unterschiedliche Herkunft und damit Zusammensetzung. Neben Einflüssen auf die Gesteinschemie wurden durch die glazialen Prozesse auch die Topografie und die Hydrogeologie des Untersuchungsgebietes geprägt.

Die maßgeblichen Bezugsflächen für die Beurteilung der Grundwasserqualität nach WRRL sind die Grundwasserkörper (GWK) (MU, 2015a, 2018). Niedersachsen und Bremen sind demnach in 123 GWK unterteilt. Diese orientieren sich an den Teileinzugsgebieten der Oberflächengewässer. Da sie nach hydraulischen Kriterien zugeschnitten sind und somit weder geologische noch hydrochemische Eigenheiten im Grundwasserleiter abbilden können, wurde für die weitere Betrachtung im Rahmen der vorliegenden Studie die hydrogeologische Gliederung in Großräume, Räume und Teilräume verwendet (Elbracht et al., 2016). Die Teilräume der Geesten und Niederungen dominieren das Untersuchungsgebiet (Abbildung A-2). Die Geesten unterscheiden sich dabei im Vergleich zu den Niederungen insbesondere durch ihr Relief, die Herkunft des Materials und geologische Entstehung, sowie auch hydrogeologisch durch höhere Flurabstände, eine hohe Grundwasserneubildung und ein geringes Schutzpotenzial (Ad-hoc-Arbeitsgruppe Hydrogeologie, 2016; Elbracht et al., 2016). Im Untersuchungsgebiet ist die Landnutzung überwiegend durch die Landwirtschaft geprägt. Die Hälfte der Fläche wird als Ackerland genutzt, ein Fünftel als Grünland und ein weiteres Fünftel als Wald.

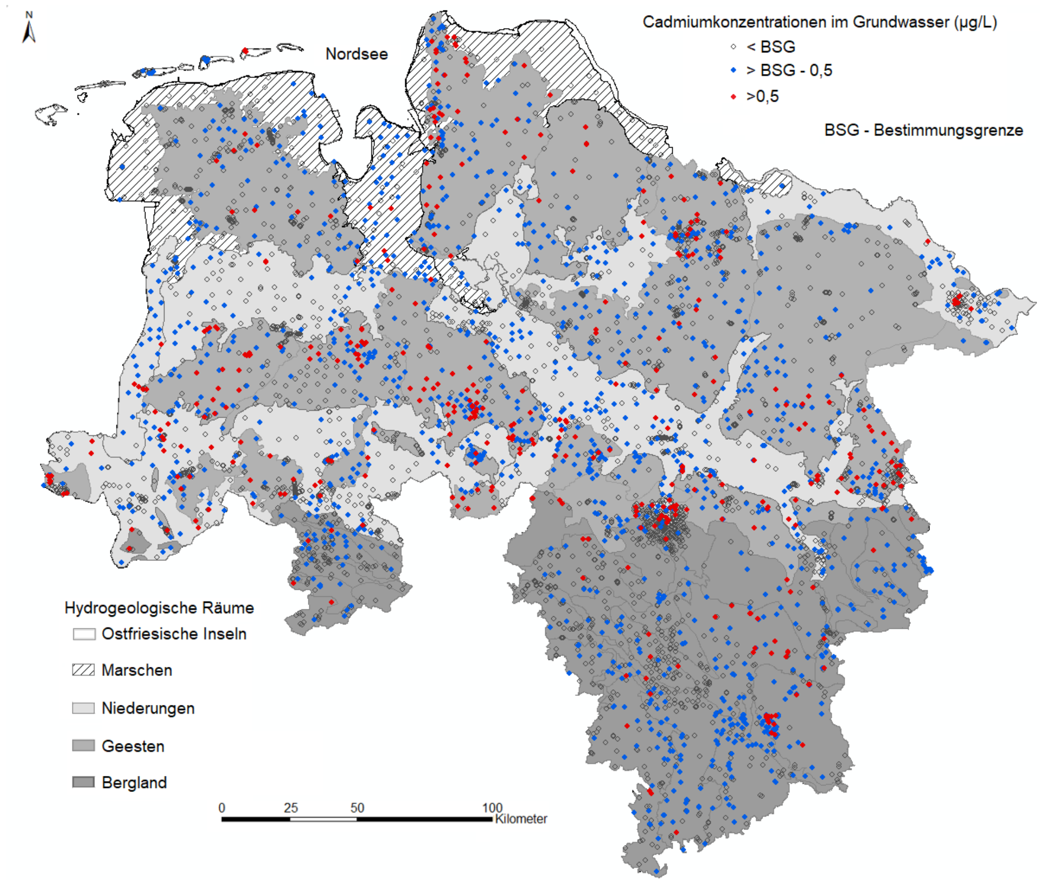


Abbildung A-2: Cadmiumkonzentrationen im Grundwasser Niedersachsens und Bremen.

Figure A-2: Cadmium concentrations in groundwater of Lower Saxony and Bremen.

A-3 Methodik

A-3.1 Datensatz

Grundwasseranalysen aus Niedersachsen wurden bereitgestellt durch das Landesamt für Bergbau, Energie und Geologie (LBEG), den Niedersächsischen Landesbetrieb für Wasserwirtschaft, Küsten- und Naturschutz (NLWKN, 2014) und die Landeshauptstadt Hannover sowie aus Bremen durch den Senator für Umwelt, Bau und Verkehr (SUBV). Die Probenahme und Analyse wurden nach etablierten Standards (DVWK, 1992) durchgeführt. Der Datensatz umfasste ca. 26.000 Analysen von 6.300 Grundwasser-Messstellen. Zur Qualitätssicherung wurde für jede Grundwasseranalyse die Ionenbilanz berechnet (DVWK, 1999). Zusätzlich zu den hydrochemischen Daten, bestehend aus Vor-Ort-Parametern, Hauptparametern und Spurenstoffen, wurden auch die Stammdaten (Koordinaten, Filtertiefe usw.) und der Wasserstand der Grundwasser-Messstellen abgefragt. Der Datensatz wurde in ArcGIS (ESRI, 2018) eingeladen und grafisch projiziert. Über das Verschneiden mit Layern der topografischen, geologischen und hydrogeologischen Karten wurde der Datensatz um folgende Attribute ergänzt: Landnutzung (LBM-DE2012), geologische Einheit (LBEG, 2000), hydrogeologische Einheit (LBEG, 2004), Schutzpotenzial, Grundwasseroberfläche und -neubildung (LBEG, 2008, 2015).

Neben den Grundwasseranalysen wurden auch Daten zu Bodengehalten von 81 Boden-Dauerbeobachtungsflächen (BDF) ausgewertet. Die Analysen von landwirtschaftlich genutzten BDF (BDF-L) stammten von LBEG sowie NLWKN und Daten von Forst-BDF (BDF-F) wurden von der Nordwestdeutschen Forstlichen Versuchsanstalt (NW-FVA) Göttingen geliefert. An 22 so genannten Intensiv-BDF (BDF-I) werden zudem regelmäßig das Sickerwasser und teilweise auch die atmosphärische Deposition beprobt und analysiert (Höper und Meesenburg, 2012).

A-3.2 Auswertung

Der Datensatz wurde zunächst hinsichtlich der zeitlichen und räumlichen Entwicklung der Cd-Konzentrationen ausgewertet. Mit dem Tendenz-Test nach Mann-Kendall wurde dazu der Trend an den Messstellen analysiert (vgl. GrwV, 2017, Anlage 6). Dabei wurde geprüft, ob die zeitliche Entwicklung der Cd-Konzentrationen einen signifikanten Verlauf aufwies. An Grundwasser-Messstellen mit mindestens vier Cd-Analysen mit wenigstens einer Analyse Cd > 0,5 µg/L wurden diese als Zeitreihen angesehen und deren Trendverlauf untersucht. Aus der weiteren Auswertung wurden solche Messstellen entfernt, die nur vereinzelte oder nicht plausible erhöhte Cd-Konzentrationen aufwiesen. Für die weitere Einschätzung der gemessenen Cd-Konzentrationen war eine Trennung des natürlichen vom anthropogen beeinflussten Daten-Anteil wichtig, was die Anwendung des statistischen Verfahrens des Wahrscheinlichkeitsnetzes entsprechend Wagner et al. (2011) ermöglichte, wobei Hintergrundwerte für Cd im Grundwasser abgeleitet werden konnten. Als Grundlage wurde die jeweils zuletzt gemessene Analyse jeder Messstelle berücksichtigt. Es sind bei Messstellen mit Zeitreihen nur die mit dem Ergebnis „gleichbleibend" des Trendtests verwendet worden. Zudem wurden nur Analysen berücksichtigt, bei denen die Bestimmungsgrenze < 1 µg/L Cd betrug. Der Hintergrundwert für Cd im Grundwasser ergab sich nach Entfernen der Anomalien oberhalb und unterhalb der Normalpopulation als 90. Perzentil (GrwV, 2017) für die Hydrogeologischen Teilräume.

Anhand der Daten der BDF wurden die jährlichen Cd-Frachten in der atmosphärischen Deposition berechnet (Keuffel-Türk et al., 2012). Zusätzlich wurden die Cd-Gehalte in den Bodenanalysen der BDF, als Königswasseraufschluss sowie als EDTA-Extrakt, ausgewertet und daraus jeweils der Anteil des mobilisierbaren Cd im Boden und im Humus berechnet. An den BDF mit Schwermetallanalysen in der wässrigen Phase (BDF-I) wurden die Zeitreihen für Cd in Deposition, Sickerwasser und, wenn vorhanden, von Grundwasser-Messstellen ausgewertet. Informationen zur Beprobungstiefe, -häufigkeit und der Analytik sind Höper und Meesenburg (2012) zu entnehmen.

A-4 Ergebnisse und Diskussion

A-4.1 Verteilung der Cadmiumkonzentrationen

Niedersachsen und Bremen werden flächendeckend mit Grundwasser-Messstellen abgedeckt (Abbildung A-2). Der im Projekt genutzte Datensatz beider Bundesländer umfasste 6.275 Grundwasser-Messstellen mit insgesamt 25.782 Analysen. Die Hälfte der Messstellen wurde nur einmal beprobt. Demgegenüber standen vereinzelte Messstellen mit bis zu 44 Cd-Werten. Bei 2.223 Messstellen lagen ≥ 4 Analysen vor, so dass hier ein Trendtest vorgenommen werden konnte. Die Analysen stammten aus einem Zeitraum von 1976 bis 2016. Cadmiumkonzentrationen > 0,5 µg/L traten meist im flachen Grundwasser auf. Die meisten untersuchten Wässer stammten aus Tiefen bis zu 20 m (Niederungen) bzw. 60 m (Geest) unter Geländeoberkante. Es gab 737 Messstellen bzw. dort 2.147 Analysen mit Cd-Konzentrationen, die den Geringfügigkeitsschwellenwert von 0,5 µg Cd/L (Keppner, 2011) überschritten. Die Verteilung der Filtertiefen unter GOK aller Messstellen bzw. der Messstellen mit Cd > 0,5 µg/L zeigt, dass im Vergleich zum gesamten Datensatz die Spannweite der Filtertiefen bei Messstellen mit erhöhten Cd-Konzentrationen kleiner ist und dass Cd > 0,5 µg/L im Durchschnitt im flacheren, oberflächennahen Grundwasser auftrat (Abbildung A-3).

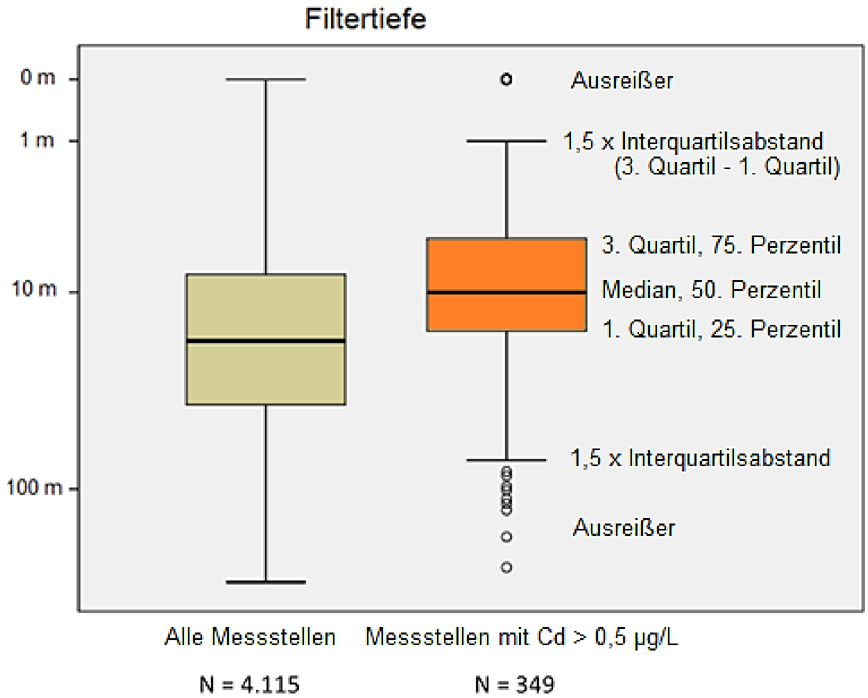


Abbildung A-3: Boxplots der Filtertiefe aller Messstellen (links) und der Messstellen mit Cd > 0,5 µg/L (rechts). Die Tiefenangabe ist logarithmisch dargestellt.

Figure A-3: Boxplots of screen depth from all sampling locations (left) and sampling locations with Cd > 0.5 µg/L (right). Depth is displayed logarithmically.

Von den insgesamt 2.223 Zeitreihen-Messstellen lagen an 210 Messstellen plausible Zeitreihen mit Konzentrationen > 0,5 µg/L vor. Davon hatten 30 Zeitreihen einen steigenden Verlauf und 53 gleichbleibend hohe Cd-Konzentrationen. Auffällig war, dass Messstellen mit N ≥ 4 und Cd > 0,5 µg/L überwiegend in den Teilräumen der Geest lagen. Viele Messstellen, besonders mit steigendem Verlauf der Zeitreihe, befanden sich in der Syker Geest (Abbildung A-4). Ein exemplarischer Verlauf von Zeitreihen mit erhöhten Cd-Konzentrationen (Abbildung A-5) zeigt, wie sich die Konzentrationen von Cd und Nitrat an der Messstellengruppe Hüven in der Sögeler Geest von 1987 bis 2014 entwickelten. Während im Bereich des tiefen Filters weder Cd noch Nitrat zu beobachten waren, war im flachen Grundwasser im Schnitt eine stetige und gleichförmige Zunahme bei beiden Parameter zu erkennen. Cadmiumkonzentrationen stiegen bis auf 4,8 µg/L. Daraus lässt sich schließen, dass Cd im oberflächennahen Grundwasser – direkt oder indirekt – durch anthropogene Aktivitäten beeinflusst wird.

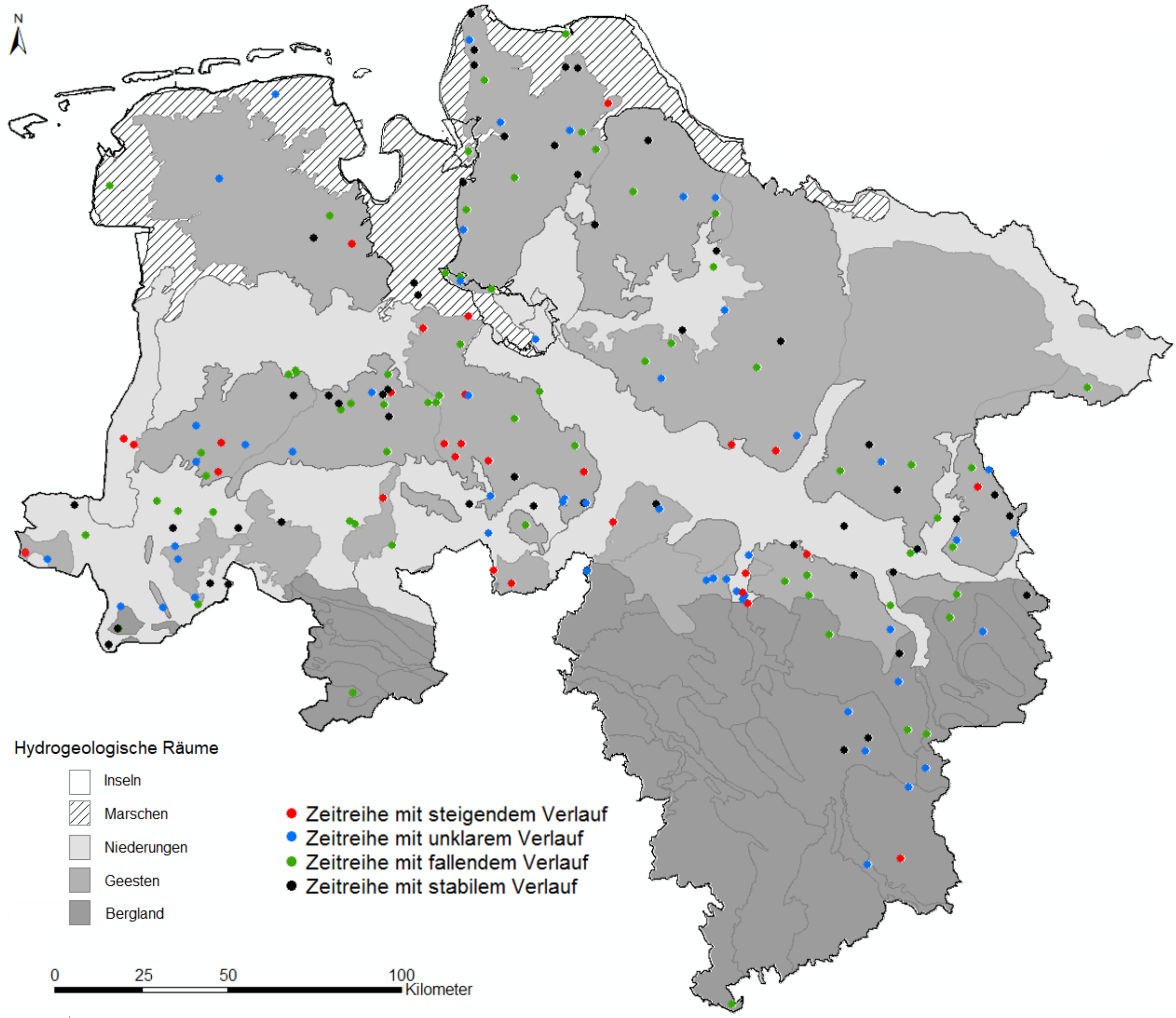


Abbildung A-4: Messstellen mit Cd-Zeitreihen in den Teilräumen.

Figure A-4: Sampling locations with Cd time series in the subareas.

Bis auf wenige kleine Teilräume konnten flächendeckend Hintergrundwerte für Cd abgeleitet werden. Viele Teilräume haben sehr geringe Hintergrundwerte, vor allem in den Niederungen betragen sie oft Cd < 0,2 µg/L. Die Hintergrundwerte in den Marschen und Niederungen lagen im Mittel bei 0,13 µg/L. Im Gegensatz dazu wiesen die Grundwässer der Geesten meist erhöhte Werte auf, bei einem Mittelwert für Cd von 0,36 µg/L. Die Syker Geest und die Bederkesa Geest hatten Hintergrundwerte > 0,5 µg Cd/L. Das Grundwasser in den Geesten wies generell höhere Hintergrundwerte für Cd als andere Hydrogeologische Teilräume auf, da dort die Grundwasserneubildung stattfindet. Das Grundwasser ist geprägt vom Kontakt mit der Bodenzone und hat meist geringe pH-Werte sowie ein oxisches Milieu, beides Randbedingungen, die zu höherer Cd-Mobilität und dadurch höheren Cd-Konzentrationen führen (Carrillo-Gonzalez et al., 2006). Zudem ist der Ausgangspunkt des Grundwassers das oft landwirtschaftlich überprägte Sickerwasser, welches z. B. Nitrat eintragen und damit ebenfalls das hydrochemische Milieu verändern kann. Nach Kunkel et al. (2004) ist in Deutschland natürliches, von Menschen unbeeinflusstes oberflächennahes Grundwasser nicht mehr vorhanden, da Rodung, Ackerbau, Melioration etc. die hydrochemischen Verhältnisse seit Jahrhunderten beeinflusst haben. Je nach Landnutzung gelangen Einträge in das Grundwasser, so dass die hydrochemischen Verhältnisse zur Wandlung von vormals geogenes in ein durch eine Jahrhunderte wirkende Kulturlandschaft ubiquitär überprägtes Grundwasser schließen lassen. Demnach sind auch die hier abgeleiteten Hintergrundwerte kein Indikator für rein geogen bedingtes Cd. Ein weiterer Grund für die erhöhten Hintergrundwerte in den Geesten kann die mögliche Herkunft des Cd aus den eiszeitlich abgelagerten Gesteinen (Saale- und Weichsel-Kaltzeit) sein, welche dort als Grundwasserleiter dienen. Beim Kontakt, z. B. mit Nitrat, können Sulfidminerale gelöst werden und Cd in das Grundwasser gelangen (Böhlke, 2002). Einige Geesten haben ungewöhnlich geringe Hintergrundwerte mit Cd < 0,1 µg/L, was im Bereich der Hintergrundwerte der Marschen und vieler Niederungen liegt und zeigt, dass diese Geesten als Moorgeesten bzw. Übergang zum Bergland einen anderen hydrogeologischen und hydrochemischen Charakter haben.

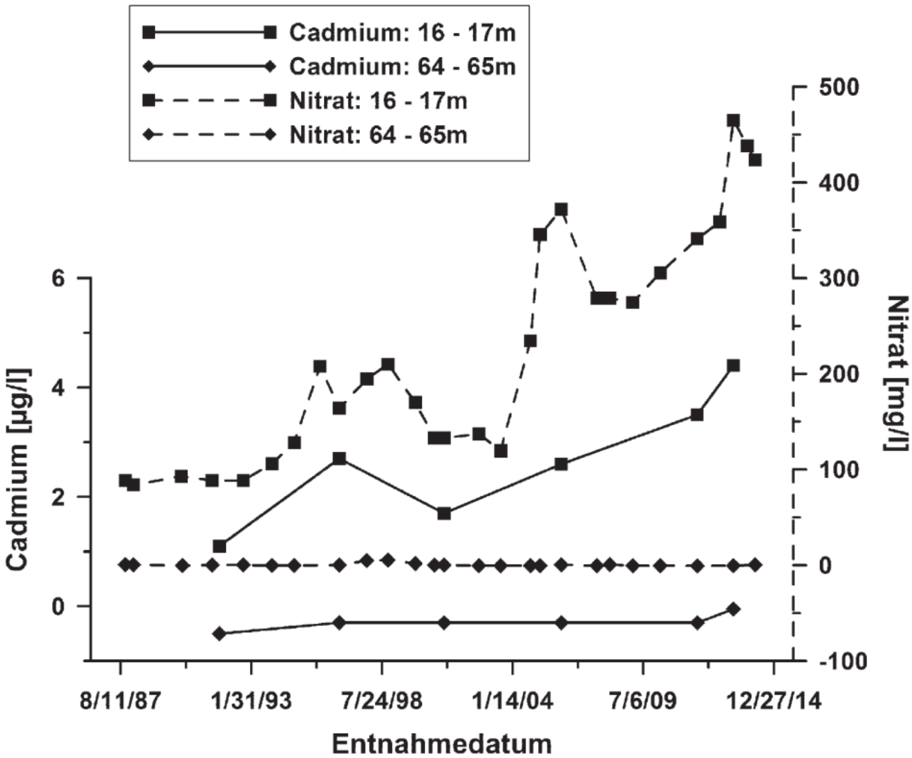


Abbildung A-5: Zeitreihen für Cd und Nitrat an der Messstellengruppe Hüven I (Filtertiefe 16 m – 17 m) und Hüven II (Filtertiefe 64 m – 65 m). Der Flurabstand beträgt ca. 7,7 m (Budziak et al., 2017).

Figure A-5: Time series of Cd and nitrate at the well collective Hüven I (screen depth 16 m − 17 m) and Hüven II (screen depth 64 m − 65 m). Depth to water table is approx. 7.7 m (Budziak et al., 2017).

Beim Einsatz der Methode nach Wagner et al. (2011) ist die Dokumentation wichtig, die darstellen muss, inwieweit sich der ursprüngliche Datensatz beim Ausschluss von Ausreißern geändert hat, bevor dann Hintergrundwerte abgeleitet werden. Die Ableitung auf Hydrogeologischen Teilräumen basierender Hintergrundwerte hat gezeigt, dass es möglich und sinnvoll ist, diese kleinräumigen Einheiten als Bezugsflächen für die Ableitung von Kennzahlen zur Grundwasserbeschaffenheit zu verwenden. Dadurch können geologische Heterogenitäten besser berücksichtigt und geogen bedingte erhöhte Cd-Konzentrationen als Hintergrundwerte räumlich besser erklärt werden. Dies hat auch den Vorteil, mögliche Maßnahmen im wasserwirtschaftlichen Handeln auf besser zugeschnittene Kulissen begrenzen zu können.

Von den 6.275 beprobten Grundwasser-Messstellen wurden an 737 Cd Konzentrationen > 0,5 µg/L gemessen. Eine Betrachtung der 364 Messstellen, die Cd > 0,5 µg/L als zuletzt gemessenen plausiblen Wert aufwiesen, zeigte, dass solche Grundwässer überwiegend durch hohe Nitratkonzentrationen und Versauerung geprägt waren. Damit entsprachen 14 % der Messstellen dem Szenario *I „geogener Ursprung*“. Drei Viertel waren dem Szenario *II* oder *III* zuzuordnen. Daher kann davon ausgegangen werden, dass die erhöhten Cd-Konzentrationen häufig mit anthropogenen Aktivitäten in Verbindung stehen. Auf Grundlage dieser Punktinformationen, die um weitere Eigenschaften der betroffenen Standorte ergänzt wurden, konnten Kriterien und damit auch Gebiete für ein Cd-Verlagerungsrisiko abgeleitet werden. Neben der landwirtschaftlichen Beeinflussung und Versauerung sind Bereiche betroffen und damit als gefährdet einzustufen, die in den Teilräumen der Geesten liegen. Als typische Landnutzung wurden Acker und Wald ausgemacht. Weitere Rahmenbedingungen sind flache Filtertiefen bis zu 15 m unter GOK im Bereich von Grundwässern mit einem Flurabstand bis 10 m. Die Gebiete mit Cd-Verlagerungsrisiko, die sich daraus ergeben, sind zum Großteil deckungsgleich mit der Maßnahmenkulisse Nitratreduktion (Abbildung A-6) des Landes Niedersachsen.

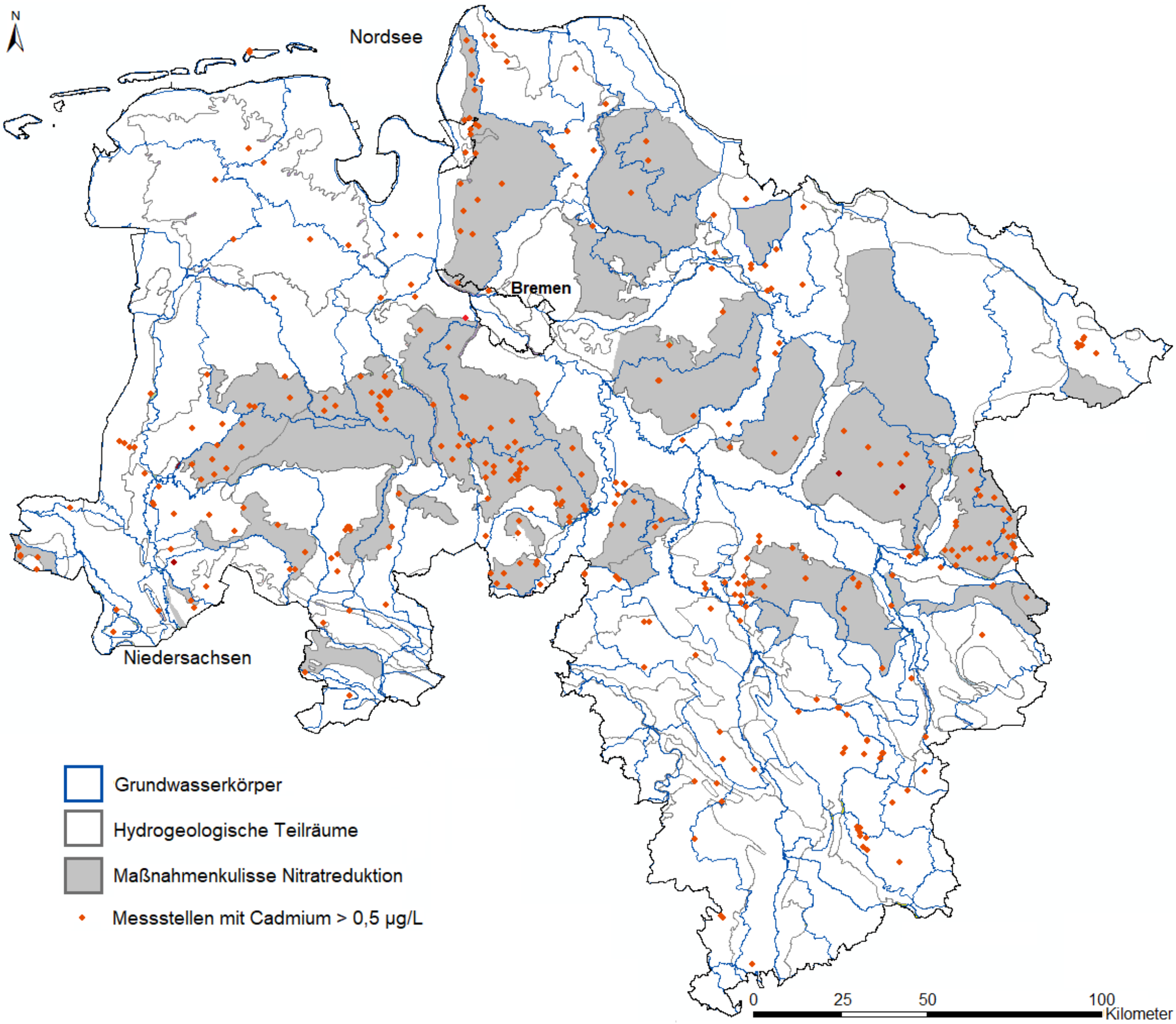


Abbildung A-6: Grundwasser-Messstellen mit Cd > 0,5 µg/L und Gebiete mit der Maßnahmenkulisse zur Nitratreduktion (MU, 2015b, verändert).

Figure A-6: Sampling locations with Cd > 0.5 µg/L and areas of the action programme to reduce nitrate (MU, 2015b, modified).

A-4.2 Cadmiumeinträge und -freisetzung

Die Cd-Konzentration des Grundwassers hängt u. a. von der Geologie und Hydrogeologie ab, da die Menge der Grundwasserneubildung, der Flurabstand, das Schutzpotenzial des Grundwasserleiters, dessen Sorptionskapazität und schließlich auch der Anteil des im Grundwasserleiter gebundenen geogenen Cd relevante Größen sind. Schwerpunkte erhöhter Cd-Konzentrationen im Grundwasser von Niedersachsen und Bremen sind die Geesten (Abbildung A-2). Diese Bereiche haben ein geringes Schutzpotenzial der Grundwasserüberdeckung und eine bedeutende Grundwasserneubildung. Messstellen mit erhöhten Cd-Konzentrationen liegen überwiegend in Bereichen mit einer Grundwasserneubildung von 150 mm/a bis 250 mm/a. Demgegenüber hat der Großteil der

Messstellen ohne auffällige Cd-Konzentrationen meist eine Neubildung < 200 mm/a und dann häufig im Bereich ≤ 50 mm/a. Solche Randbedingungen sind notwendige Voraussetzungen für den direkten Eintrag von Cd oder für den Eintrag von Stoffen zur Veränderung des pH-Wertes und/oder Redoxmilieus (Sauerstoff oder Nitrat).

Für 16 BDF ließen sich Cd-Frachten aus der atmosphärischen Deposition berechnen. Die meisten Zeitreihen zeigten über den Zeitraum 1982 bis 2014 eine stetige Verringerung der Cd Konzentrationen zwischen 1,0 g/(ha*a) und maximal 20 g/(ha*a) auf aktuelle Werte zwischen 0,1 g/(ha*a) und maximal 1,1 g/(ha*a). Diese Werte liegen im Bereich bundesweiter Abschätzungen von Ilyin et al. (2016), die Depositionswerte für Nordwestdeutschland zwischen 0,3 g Cd/ha und 0,6 g Cd/ha jährlich angeben. Auch Six und Smolders (2014) haben einen mittleren Cd-Eintrag durch Deposition von 0,25 g/(ha*a) bestimmt. In Tabelle A-2 sind die berechneten und der Literatur entnommenen Cd-Frachten für Böden in Nordwestdeutschland zusammengefasst. Neben der Verringerung der Cd-Einträge aus der Atmosphäre lassen sich auch kleiner werdende Einträge aus Phosphat-Düngern beobachten.

Tabelle A-2: Cadmium-Frachten in Böden Nordwestdeutschlands.

Table A-2: Cadmium inputs and outputs to soils of Northwestern Germany.

	Cadmium-Fracht in g/(ha*a) (Min – **Median** – Max)		
	1980er – 1990er	2000er	2010er
Einträge			
Atmosphärische Deposition[a b]	1 – **1** – 20	0,4 – 1,2	0,1 – **0,2** – 1,1
P-Dünger[b c]	0,28 – **2,5** – 5,6	0,0 – **1,4** – **3,7**	**0,74**
Klärschlamm[b]	n.v.		**0,05**
Gülle[b]	n.v.	n.v.	**0,01**
Kalkung[b]	n.v.	n.v.	**0,07**
Austräge			
Ernte[b c]	**0,3**	0,1 – 1,2	**0,2**
Versickerung[b c]	n.v.	0,15 – 0,9	**2,56**

[a] diese Studie; [b] Kamermann et al. (2015); [c] Six und Smolders (2014)

Je nach Standort ergeben sich verschiedene Sickerwasserraten, so dass zwischen 20 % und 45 % der Cd-Frachten aus der Deposition grundwasserwirksam sind. Somit erreichen aktuell zwischen 0,01 g Cd /(ha*a) und 0,4 g Cd /(ha*a) potenziell das Grundwasser; Prozesse wie Ausfällung und Sorption sind dabei nicht berücksichtigt. Die Cd-Konzentrationen im Sickerwasser waren meist gering oder zeigten eine Verringerung mit der Zeit. Die jeweils zuletzt gemessenen Werte für Cd liegen bei den BDF F zwischen 0,12 µg/L und 1,1 µg/L. Die Werte liegen unterhalb des 90. Perzentils der Cd-Konzentrationen im oberflächennahen Grundwasser unter Wald von 1,8 µg/L im Fuhrberger Feld (Engel, 2002). Ebenso sind sie im Rahmen des Hintergrundwertes im Sickerwasser unter Forst im Norddeutschen Tiefland als 90. Perzentil von 2,7 µg/L (Duijnisveld et al., 2008). Bei den BDF-L sind die zuletzt gemessenen Cd-Konzentrationen des Sickerwassers < 0,35 µg/L, was ebenfalls im Bereich der Hintergrundkonzentrationen für Ackerstandorte von 2,4 µg/L nach Engel (2002) bzw. 0,76 µg/L nach Duijnisveld et al. (2008) liegt. Generell gelangen an Waldstandorten größere Frachten aus der Atmosphäre in den Untergrund als auf Freiland, da die Bäume durch die Blattoberfläche mehr Stoffe aufnehmen (*Auskämmeffekt*) (Keuffel-Türk et al., 2012).

Die mittleren Cd-Gehalte im Boden lagen, je nach Aufschlussart, zwischen 0,002 mg/kg und 1,8 mg/kg an den BDF-F und zwischen 0,001 mg/kg und 1,66 mg/kg an den BDF-L (die drei BDF Nordenham, Schladen und Gorleben an belasteten Standorten wiesen Cd-Gehalte bis zu 14,3 mg/kg auf). Die mittleren Cd-Gehalte des Bodens zeigten einen Zusammenhang mit der Landnutzung, da die Cd-Gehalte in der Reihenfolge Grünland > Acker > Forst abnahmen, was auch deutschlandweit von Huschek et al. (2004) festgestellt wurde. Der Zusammenhang ergibt sich aus dem Zusammenspiel verschiedener Faktoren, welche die Mobilität des Cd beeinflussen. Der mittlere pH-Wert der Böden nahm in der Reihenfolge Acker > Grünland > Forst ab. Die Substratart und damit die Korngröße der Böden zeigten, dass Standorte mit Grünland primär Ton, Moor und Lehm aufwiesen, während bei Acker und Forst eher Sand und Schluff mit deutlich geringerer Sorptionskapazität (Duijnisveld et al., 2008) auftraten. Bereits Schilli et al. (2011) untersuchten diese Zusammenhänge und stellten fest, dass weitere Faktoren dafür sorgen, dass die Cd-Gehalte im Boden, im Gegensatz zu den anderen untersuchten Schwermetallen, nicht primär durch das Ausgangsgestein der Bodenbildung erklärt werden konnten. Neben der Substratart und der höheren pH-Wert Sensibilität von Cd beeinflussen der Auskämmeffekt und der organische Horizont an Forststandorten, Sonderfälle wie der Bereich des durch Bergbau beeinflussten Harzes sowie Einträge durch atmosphärische Deposition und Mineraldünger den Cd-Gehalt des Bodens, während die Gehalte von Cr, Ni, Cu, Zn und Pb kaum durch äußere Einflüsse beeinflusst sind (Schilli et al., 2011).

Mit der Tiefe verringerten sich die Cd-Gehalte des Bodens. Die Bindungsformen von Cd waren, wie auch Krishnamurti und Naidu (2003) beschrieben, pH-abhängig. So stieg der Anteil des mobilisierbaren Cd (als EDTA-Extrakt) in den Bodenproben bei pH-Werten unter 4,5 deutlich an. Mit zunehmendem Zersetzungsgrad des Humus wurden neben geringer werdenden pH-Werten auch höhere Cd-Gehalte in den Humuslagen gemessen. Erhöhte Cd-Gehalte im Boden sind das Resultat der auf ihn wirkenden Faktoren. Im Umkehrschluss sind Standorte mit geringem pH-Wert, sandigem Substrat und gesteigerten Einträgen durch atmosphärische Deposition (Auskämmeffekt) oder Landwirtschaft (Phosphat-Dünger) besonders geeignet, eingetragenes bzw. mobilisiertes Cd mit dem Sickerwasser abzugeben, so dass im Grundwasser erhöhte Cd-Konzentrationen zu erwarten sind (Mollema et al., 2015).

Niedersachsen ist eine der Regionen Deutschlands, die landwirtschaftlich am intensivsten genutzt wird und in der es zu einem gesteigerten Einsatz an Stickstoff- und Phosphat-Düngern kommt (Wendland et al., 1993). Stickstoffüberschüsse und Versickerung führen zu erhöhten Nitratgehalten, die schließlich das Grundwasser erreichen (Köhler et al., 2006; Wendland et al., 1993). Aus diesem Grund hat das Land Niedersachsen in der Maßnahmenkulisse „*Nitratreduktion*“ (MU, 2015b) Gebiete festgelegt (Abbildung A-6), um einer weiteren Verschlechterung der Grundwasserqualität entgegenzuwirken und Maßnahmen zur Verbesserung der Situation herbeizuführen. Aus der Karte wird ersichtlich, dass die Messstellen mit Cd > 0,5 µg/L zum Großteil in diesen Gebieten liegen.

Durch die fortschreitende Oxidation über die Nitratverlagerung in tiefere Schichten kommt es zur Redoxkonversion, was das hydrochemische Verhalten redoxsensitiver Stoffe verändert. Dazu zählt indirekt auch Cd, welches in Sulfiden gebunden sein kann, so dass beim wiederholten Vorrücken der Nitratabbaufront das Cd zunächst mobilisiert wird und dadurch lokale Anreicherungen an der Redoxgrenze entstehen können. Bei der Pyritoxidation werden adsorbierte Schwermetalle wie Cd freigesetzt (Böhlke, 2002; Cremer, 2002), so dass dessen Konzentration im Grundwasser an die autotrophe Denitrifikation gekoppelt ist (Gleichung A-1).

$$5(Fe_{1-x}Cd_x)S_{2(s)} + 15\ NO_3^- + 5\ H_20 \rightarrow 5(1-x)\ FeOOH + 5x\ Cd^{2+} + 7{,}5\ N_{2(g)} + 10\ SO_4^{2-} + 5\ H^+ \quad \text{(A-1)}$$

Pyrit ist neben organischem Material ein wichtiger Elektronendonator für den Nitratabbau (Denitrifikation) im anoxischen Grundwasser (Hinsby et al., 2008; Jorgensen et al., 2009). Bergmann et al. (2013) erläuterten, wie hoch der Anteil an Pyrit und organischer Substanz im Grundwasserleiter ist und in welchem Umfang beide das Nitratabbauvermögen am jeweiligen Standort darstellen. Die Denitrifikation puffert dabei Nitrateinträge in das Grundwasser, bis es zum Nitratdurchbruch kommt. Indikatoren wie erhöhte Sulfatkonzentrationen konnten nur teilweise festgestellt werden, da Sulfat anthropogen und durch Lösungsprozesse eingetragen wird (Böhlke, 2002). Andere Begleitstoffe in Pyrit, z. B. Zn und Co, sind erst bei geringeren pH-Werten mobilisierbar und adsorbieren eher als Cd (Herms und Brümmer, 1984). Im Emsland untersuchte Pyrite in reduzierten Grundwasserleitern wiesen Cd-Gehalte im Mittel von 300 mg/kg, im Maximum von 1.600 mg/kg und, je nach Pyritgehalt im Grundwasserleiter, bis 2,6 mg/kg im Sediment auf (Houben et al., 2017). Von ähnlichen Werten kann auch in anderen Regionen in Norddeutschland ausgegangen werden. Durch eine unterschiedliche Zusammensetzung der Sulfidminerale im Grundwasserleiter zeigt sich die an die

Denitrifikation gekoppelte Pyritoxidation in erhöhten Konzentrationen von Ni, Co, Zn und As in der Niederrheinischen Bucht (Cremer, 2002), sowie in erhöhten Urankonzentrationen in Baden-Württemberg (Riedel und Kübeck, 2018) und Mecklenburg-Vorpommern (van Berk und Fu, 2017). Die Kombination aus Nitrateintrag, geogenem Cd und Pyritoxidation führt in Niedersachsen dagegen zu erhöhten Cd-Konzentrationen im Grundwasser.

A-5 Schlussfolgerungen

Die möglichen anthropogenen flächendeckend auftretenden Cd-Einträge im Untersuchungsgebiet (siehe Abbildung A-1) umfassen P-Dünger, Klärschlamm und Deposition von Industrieemissionen. Es liegen keine ausreichenden Kenntnisse zu Art und Menge der ausgebrachten P-Dünger vor. Dadurch können Grundwasseranalysen mit erhöhten Cd-Konzentrationen, die anthropogenen beeinflusst, nicht eindeutig dem Szenario *II* oder dem Szenario *III* zugeordnet werden. Informationen zu Phosphatsalden, die auf Landkreisebene basieren, sind LWK Niedersachsen (2016) und Wiesler et al. (2015) zu entnehmen.

Es wurden aktuell keine Hinweise auf direkten Cd-Eintrag festgestellt; in der Vergangenheit erhöhte Cd-Frachten aus der atmosphärischen Deposition haben sich mit der Zeit deutlich verringert. Stattdessen ergab die Datenauswertung der Grundwasseranalysen zusammen mit der Auswertung der Analysen von Boden-Dauerbeobachtungsflächen, dass die Cd-Konzentration im Grundwasser durch verschiedene Faktoren gesteuert wird. Der pH-Wert und das Redoxpotenzial haben wesentlichen Einfluss auf die Cd-Mobilität (Carrillo-Gonzalez et al., 2006). Diese wird über anthropogene Einträge in Form von Nitrat oder Säuren erhöht. Die Cd-Festlegung und Cd-Freisetzung in Böden wird durch Landnutzung, Substratart und die Grundwasserbeschaffenheit reguliert. Da die Geesten, insbesondere im Westen Niedersachsens, Regionen mit intensiver Landwirtschaft sind, lassen sich die erhöhten Cd-Konzentrationen mit dem dort auftretenden landwirtschaftlich geprägten, versauerten Grundwasser in Verbindung bringen (Wriedt et al., 2019). Insgesamt können Kriterien abgeleitet werden, welche zu erhöhten Cd-Konzentrationen beitragen (Tabelle A-3). Darunter fallen landwirtschaftliche genutzte Gebiete, organisch geprägte Gebiete wie Wald, Moore und Marschen sowie allgemein Bereiche der Grundwasserneubildung.

Tabelle A-3: Beispiele für Kriterien erhöhter Cd-Konzentrationen im Grundwasser.

Table A-3: Examples of criteria for elevated Cd concentrations in groundwater.

Kriterium	Merkmale	Für Cd relevante Prozesse
Nutzung Landwirtschaft	Geringer pH, hohe Konzentrationen an Nitrat, Sauerstoff und weiteren Schwermetallen	Freisetzung durch Pyrit-Oxidation; durch Säureeintrag Mobilisierung z. B. aus Eisenoxiden; ggf. direkter Eintrag aus Düngung (P-Dünger)
Nutzung Wald	Geringer pH, hohe Konzentrationen an DOC und weiteren Schwermetallen	Mobilisierung durch Säureeintrag, ggf. direkter Eintrag aus Deposition (Auskämmeffekt)
Standort Moor/Marsch	Reduzierendes Milieu: Fehlen von NO_3, O_2, teils SO_4, dafür Fe, teils DOC, HCO_3 oder CH_4 erhöht	Mobilisierung durch Säureeintrag, Freisetzung aus Sulfiden und organischem Material, Transport als stabile an-/organische Komplexe
Grundwasser-Neubildung	Saisonale Schwankungen von pH, Cd, Ni, Zn, SO_4/Cl, O_2	Wechselnde De-/Sorption durch Schwankungen im Grenz-pH-Bereich und Redoxmilieu, auch bei Ni und Zn

Beispiele für Maßnahmen, die aus den Ergebnissen des Forschungsprojektes abgeleitet werden können, sind:

1. Neubewertung des chemischen Zustands der Grundwasserkörper.
2. Anpassung der Rahmenbedingungen der Cd-Mobilität bei der Bewirtschaftung betroffener Flächen, z.B. durch Kalken.
3. Beratung bei der Anwendung von P-Düngern zur Minimierung anthropogener Cd-Einträge.

Danksagung

Das Forschungsprojekt wurde aus Zuwendungen des Landes Niedersachsen zum Maßnahmenprogramm im Bereich Grundwasser zur Umsetzung der EU-Wasserrahmenrichtlinie finanziert. Wir danken dem Niedersächsischen Landesbetrieb für Wasserwirtschaft, Küsten- und Naturschutz (NLWKN), dem Landesamt für Bergbau, Energie und Geologie (LBEG), dem Senator für Umwelt, Bau und Verkehr (SUBV) Bremen, der Stadt Hannover und der Nordwestdeutschen Forstlichen Versuchsanstalt (NW-FVA) für die Bereitstellung der chemischen Daten.

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