CLEAN Soil Air Water
www.clean-journal.com

Factors Affecting Spatial and Temporal Variability of Metals in Drainage Water from Arable Fields

Martina Baborowski, Holger Rupp, Katrin Wendt-Potthoff, Nadine Tauchnitz, and Ralph Meissner*

Respecting fertilizer application, the metal content in drainage water is studied under conventional agricultural management from 2013 to 2014 in two adjacent fields located in the North German Plain. Findings are compared with data of nutrients, main ions, and dissolved organic carbon, as well as element contents in fertilizers and geogenic background values of soils. Comparatively low metal concentrations are found in drainage water. These results are in line with metal contents of applied mineral fertilizers, of cattle slurry, and random analysis of the two soils considered. Relating to effective ordinances, the applied fertilizers occasionally pose a risk for the groundwater or downstream water bodies. Concentrations of some metals (Al, Co, Cr, Pb, and V) are rather affected by soil erosion than by fertilizers. Besides fertilizers and soil erosion, mainly pedo-hydrological conditions, which differ between the two fields, influence element profiles in tile drainage by the extent of anoxia and subsequent denitrification and sulfate reduction. Against the background of climate change, further investigations with respect to possible changes in soil water budget are necessary.

1. Introduction

Subsurface drainage systems are important for agricultural production, especially in lowland areas. They are installed to regulate the soil water regime to prevent waterlogging of agricultural sites. On the one hand, they improve topsoil conditions by amelioration. On the other hand, drainage systems may affect water quality downstream, because they are working as drainage elements of loaded soil water.[1] Drainage systems may systematically collect nutrients and contaminants derived from spatially disperse sources and aggregate them at cumulative concentrations downstream.[1–3] The downstream directed transport of contaminants from agricultural fields may influence groundwater quality. On a catchment scale, tile drainage may aggravate diffuse pollution of adjacent surface water bodies by shortening the residence time of water in the soil.[4] As reported for the federal state Mecklenburg-Western Pomerania (North-Eastern Germany), ≈47 % of nitrogen and 12 % of phosphorus emissions to the Baltic Sea originate from tile drainage.[4–6] For the Hupsel brook catchment (Eastern part of the Netherlands) it was shown that tile drains contributed 90–92 % to the annual nitrate and metal loads.[7]

Emissions via drains might be more influenced by pedo-hydrological conditions than by management practices. It is known that soil properties determine the occurrence of microbial communities in soils.[8,9] This might substantially control decomposition and absorption processes in soils and thus the mobility of nutrients and metals. In this context soil texture, moisture, organic matter content, pH, and geogenic background (e.g., occurrence of pyrite) were reported as the most important factors.[10–14]

In order to reduce or to avoid pollution transfer from tile drainage systems into the groundwater and surface water, knowledge of sources, amount, transport, and the fate of drainage water contamination is necessary. Such information can support the optimization of best management practices in agriculture.[15] Many studies focused on nitrate losses,[1,16–18] phosphate losses,[18–22] and organic carbon losses[23–25] of tile drained agroecosystems, and also on denitrifying microbial processes.[26] Although the application and composition of inorganics[27–30] and organic fertilizers[31–34] are being discussed

M. Baborowski
Helmholtz Centre for Environmental Research—UFZ
Department River Ecology
Magdeburg 39114, Germany
E-mail: martina.baborowski@ufz.de
H. Rupp, R. Meissner
Helmholtz Centre for Environmental Research—UFZ
Department Soil System Science
Falkenberg 55, Altmärkische Wische 39615, Germany
K. Wendt-Potthoff
Helmholtz Centre for Environmental Research—UFZ
Department Lake Research
Magdeburg 39114, Germany
N. Tauchnitz
State Institute for Agriculture and Horticulture Saxony-Anhalt
Centre for Agronomy and Crop production
Bernburg 06406, Germany

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/clen.202000364

© 2021 The Authors. CLEAN – Soil, Air, Water published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution-NonCommercial License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited and is not used for commercial purposes.

DOI: 10.1002/clen.202000364

Figure 1. Experimental site and its position in the catchment area of the River Elbe. (Sampling points marked with red dots, main collector marked with blue lines; Aerial image: Google Earth V 9.132.0.3. Gagel, Germany. 52°50'57''N 11°35'24''E. Eye alt 3388 m. GeoBasis-DE/BKG(@2009). http://www.earth.google.com/web).

with respect to their metal content in recent studies, less information on metal pollution in tile drainage water is available.

Therefore, this study aims to fill this gap, by assessing unpublished data of metal concentrations in tile drainage waters.

Thereby, it was investigated if metal patterns from mineral and organic fertilizers can be detected in the resulting drainage waters from agricultural fields.

We hypothesized that the metal composition of drainage water in fields with comparable climatic conditions and different crop management is mainly determined by the pedo-hydrological characteristics of the sites. We tested this hypothesis using a data set of samples collected in the field, over a period of 2 years (2013–2014). The data reflect results of measurements under real ambient conditions and conventional agricultural management practices of a local agricultural cooperative.

The findings were discussed against the background of existing nutrient analyses, main ions of salts, and organic matter from sub-studies,[18,35] performed in the same study area between December 2011 and October 2015. Additional information from State Institute for Agriculture and Horticulture Saxony-Anhalt were provided for the data evaluation and are also integrated in the study.

2. Experimental Section

2.1. Study Site

The study site is located in the northern part of the federal state Saxony-Anhalt (Germany), in the catchment area of River Elbe (**Figure 1**). It consists of two adjacent agricultural fields of comparable size (field I: 52.836975 N, 11.582780 E; field II: 52.840085 N, 11.596513 E). With regard to the slope, field I is relatively leveled. In contrast, field II has a slope of 0.4 % (terrain falls from northwest to southeast).

In the two fields, a systematic sub-soil-drainage system with PVC-suction drains (inner diameter of 63 to 110 mm) was installed at a depth of about 0.8 m in the 1970s. The lateral drains were placed at an interval of about 10 m, discharging the water to the main collector. The drained area of field I was 24 ha, that of field II was 26 ha. Since 1989 the fields were conventionally managed by the Agricultural Cooperative "Altmärkische Höhe," e.G., Lückstedt using similar fertilization and crop management practices.

The sites belonged to the temperate zone of Central Europe within the transition zone from maritime to continental climate with an average precipitation of 524.5 mm (1968–2007) and an average temperature of 9.2 °C (1994–2007). Climate data referred to the lysimeter facility of the UFZ at Falkenberg (coordinates 52.859780 N, 11.812595 E), which was located 15 km east of the study area.

Dominant soil types of both fields were Luvisols or Stagnic Gleysol Luvisols and Stagnic Gleysols on boulder sand overlaying boulder clay, as well as, Gleysols on loamy sand, overlaying sand, and loam.[36] In field I, boulder clay was lying in alternating strata with sand layers, which can be characterized as a partially confined aquifer. Here, flow regime and drain-rate depended on both groundwater table fluctuations and percolating seepage water.[35,37] In field II, the groundwater level varied between 1.3 and 2.4 m below ground level, and confined groundwater was not present.

Using non-monolithically filled lysimeters with a soil stratification similar to field II[35] managed in the Falkenberg

© 2021 The Authors. CLEAN – Soil, Air, Water published by Wiley-VCH GmbH

Table 1. Soil properties of the investigated fields.

Year	Parameter		Depth, Field I			Depth, Field II		
			0–30 cm	30–60 cm	60–90 cm	0–30 cm	30–60 cm	60–90 cm
2012	Sand [%]		75.7	76.6	75.5	66.3	65.3	66.1
2012	Silt [%]		15.5	11.3	13.4	18.2	20.1	18.5
2012	Clay [%]		5.3	5.9	8.7	11.6	14.9	15.0
2012–2014	C_{tot} [%]	Mean	0.7	0.3	0.2	1.0	0.5	0.5
		Min	0.7	0.2	0.1	0.8	0.4	0.3
		Max	0.8	0.3	0.3	1.2	0.7	0.7
		n	5	5	5	5	5	5
2012–2014	TOC [%]*)	Mean	0.7	0.2	0.1	1.0	0.5	0.2
		Min	0.6	0.2	0.1	0.8	0.3	0.1
		Max	0.8	0.3	0.2	1.1	0.6	0.4
		n	5	5	5	5	5	5
2012–2014	N_{tot} [%]	Mean	0.07	0.03	0.02	0.10	0.05	0.02
		Min	0.06	0.02	0.01	0.08	0.03	0.02
		Max	0.08	0.03	0.03	0.12	0.07	0.03
		n	5	5	5	5	5	5
2012–2014	pH	Mean	5.6	6.2	6.2	6.3	6.8	7.3
		Min	5.1	6.1	6.1	5.8	6.4	7.0
		Max	6.1	6.5	6.5	6.8	7.2	7.6
		n	5	5	5	5	5	5
2012–2014	CEC [$cmol_c\ kg^{-1}$]**)	Mean	6.6	6.2	6.4	9.5	9.8	10.0
		Min	6.2	4.3	5.6	7.5	7.8	9.0
		Max	7,5	10.7	7.0	12.1	11.4	11.2
		n	5	5	5	5	5	5

*) TOC, total organic carbon; **) CEC, cation exchange capacity.

lysimeter facility, experiments with conservative tracers under comparable soil conditions showed that the transport of solutes with the leachate to a depth of 100 cm below ground level takes about 1.5 to 2 years.[38] Hence, the precipitation of the previous 1.5 to 2 years had to be considered for interpretation of recent solute fluxes.

Soil physical properties including bulk density, porosity, water contents at different soil suctions (pF stages) and saturated hydraulic conductivity are given in Bednorz et al.[35] and **Table 1**.

Regarding solubility of carbonic acid, calcium carbonate and the oxides of aluminum and iron in soil solution, a carbonic acid/carbonate buffer range (pH 6.2 to 8.6) was characteristic.[39]

Regarding nitrate reduction processes in North-German groundwaters including the study site, pyrite was important as a reductive agent. It was widespread as lignite scree in the subsurface, pyritized fossils, crystallized mineral oil components, or as deposition in reducing horizons of Gleysols.[40]

The fields were managed following usual conventional practices (**Table 2**).

Both fields were mineral fertilized by the Lückstedt agricultural cooperative by means of a fertilizer spreader from Amazone (Amazonen-Werke, Hasbergen, Germany). The mentioned mineral fertilizer application rates (Table 2) were applied as granulate according to the phenological development stage of the cultivated crops in up to three partial applications. Nitrogen was fertilized in the form of calcium ammonium nitrate (CAN, 26 % N, 10 % Ca), granulated urea (48 % N), and ammonium sulfate nitrate (ASN, 26 % N, 13 % S). For phosphorus fertilization, nitrogen phosphate (12 % N and 25 % P) was applied. Potassium was supplied in the form of grained potash (40 % K_2O, 6 % MgO, 3 % Na, 4 % S). The commercial mineral fertilizers used were not mixed.

2.2. Sampling

Drainage water was obtained from the collection drain (manhole) at the outlet of each drain division (auto-sampler ISCO 3700, Teledyne Isco, Lincoln, USA). Daily samples were taken (600 mL, one pumping cycle per day) and stored in polypropylene bottles within the auto-sampler. Each sample was divided into two subsamples, one for analysis of main ions, nutrients, and dissolved organic carbon (DOC), the other for metal analysis. Due to seasonally varying sample volumes not all parameters could be analyzed at all times.

For fertilizer characterization, 20 subsamples (50 g each) were randomly taken from the mineral fertilizer heaps at the farmyard, stirred and merged to mixed fertilizer samples of 1000 g. Slurry samples (2 L) were taken from the storage tank after homogenization and analyzed by the State Institute for Agriculture and Horticulture Saxony-Anhalt.

At the end of the study period in 2014, about 30 topsoil samples were taken for analyzing metal pollution in soils. They were

© 2021 The Authors. CLEAN – Soil, Air, Water published by Wiley-VCH GmbH

Table 2. Agricultural management of field I and field II with overview of fertilization.

Year	Field	Crop	Mineral fertilization				Organic fertilization		
			N [kg ha^{-1}]	P [kg ha^{-1}]	K [kg ha^{-1}]	S [kg ha^{-1}]	Slurry [m^3 ha^{-1}]	N [kg ha^{-1}]	Nitrification inhibitor*) [L ha^{-1}]
2011	I	Corn	93.4	—	—	—	—	—	—
2011	II	Winter rye	188.5	—	85.3	63.3	—	—	—
2012	I	Corn	117.8	—	—	—	—	—	—
2012	II	Winter wheat	202.2	—	—	—	—	—	—
2013	I	Winter wheat/catch crop	226.8	—	—	—	—	—	—
2013	II	Corn/catch crop	72.0	21.3	—	15.0	30.0	53.2	—
2014	I	Corn	70.0	—	—	—	30.0	81.0	3.0
2014	II	Corn	70.0	—	—	15.0	30.0	81.0	3.0

*) PIADIN®.

obtained by groove drill punctures from randomly selected sampling points of each field and were used to compile mixed samples (about 1000 g soil material of each field) for further analysis (fraction <2 mm).

2.3. Physical and Chemical Measurements

2.3.1. Hydrological Measurements

Area-specific drainage discharge of the fields was measured in a Venturi-channel, placed in two manholes. Here, the water level was continuously registered by an ultrasonic detector. Hourly averages were recorded by a data logger.

A soil hydrological measuring station was set up on field I and field II, respectively, on which the volumetric soil water content in 0.35, 0.50, and 0.85 m below ground level was measured continuously using ThetaML3 probes (Delta-T Devices, Cambridge, UK). Hourly average values were recorded in a data logger.

2.3.2. Measurements in Drainage Water

The pH-value was measured by a pH electrode (WTW, Weilheim, Germany).

Solute concentrations were analyzed in samples filtered through 0.45 µm Millipore syringe filters.

The main ions sodium (Na^+), potassium (K^+), calcium (Ca^{2+}), manganese (Mg^{2+}), chloride (Cl^-), and sulfate (SO_4^{2-}), were analyzed by ion-exchange chromatography (IC, Thermo Fisher Scientific, Idstein, Germany).

Nitrite (NO_2-N), nitrate (NO_3-N), ammonium (NH_4-N), and total phosphorus (P_{tot}) were analyzed according to German Industrial Standards (DIN 38405–38406) using photometry (Libra S11, Biochrom, Holliston, USA).

DOC and total nitrogen (N_{tot}) were determined using a C-analyzer (Dimatec, Essen, Germany), in accordance with German Industrial Standards (DEV, H3).

The metals aluminum (Al), arsenic (As), boron (B), barium (Ba), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), lead (Pb), antimony (Sb), uranium (U), vanadium (V), and zinc (Zn) were analyzed using mass spectrometry with inductively coupled plasma (ICP-MS, Agilent Technologies, 7500c series, Waldbronn, Germany). For this purpose, water samples were taken in acid-cleaned (HNO_3, 10 %) polyethylene bottles and acidified with HNO_3 (10 mL L^{-1}, 65 %, supra-pure). The unfiltered sample was analyzed after digestion in a microwave with HNO_3/H_2O_2 (5 mL HNO_3 65 %; 2 mL H_2O_2 per 50 mL sample).[41]

2.3.3. Measurements in Mineral Fertilizers and Soils

In comparison to the metals, measured in drainage water, the elements Al, As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, U, V, and Zn were analyzed in mineral fertilizer and soil samples using energy dispersive X-ray fluorescence analysis (EDXRF, XLAB 2000, Spectro Instruments, Kleve, Germany).[42,43] Slurry samples were analyzed at the State Institute for Agriculture and Horticulture Saxony-Anhalt. Here, soil and fertilizer samples were analyzed using ICP-MS (Varian 820 MS, Agilent Technologies/Varian, Waldbronn, Germany) for As, Cd, Cr, Hg, Mo, Ni, and Pb, as well as optical emission spectrometry with inductively coupled plasma (ICP-OES, Varian Vista Pro, Agilent Technologies/Varian, Waldbronn, Germany) for Cu, Fe, Mn, Al, and Zn.

2.4. Statistical Analysis

Multivariate statistics were performed using STATISTICA 13.0. To discover the dimensionality of the drain water data set and to identify meaningful underlying variables, factor analysis (FA) was performed (rotation method: Varimax raw, extraction method: Principal components). For sake of clarity, loadings >0.6 were considered as statistically significant. Parameters for which more than 25 % of the values were below the analytical detection limit were not used for modeling.

The software package OriginPro was used to calculate Box-Whisker plots and to describe the cross-correlation function of two signals $x(t)$ and $y(t)$ with different time shifts between the two signals. This tool for signal analyses was applied to

© 2021 The Authors. CLEAN – Soil, Air, Water published by Wiley-VCH GmbH

Table 3. Median, maximum, and minimum values of main ions, nutrients, and organic carbon in drain water of the investigated fields in 2013 and 2014 (all data in mg L^{-1}; pH-value without dimension). Different letters indicate significant differences ($p < 0.05$, Kruskal–Wallis-Test) between fields (H1-vertical) and years (H2-horizontal).

Parameter	Field	2013				H1	H2	2014				H1	H2
		Median	Min	Max	*n*			Median	Min	Max	*n*		
pH	I	8.4	8.3	8.4	13	a	a	8.2	7.7	8.4	17	a	b
	II	8.3	8.3	8.5	3	a	a	8.0	7.7	8.1	15	b	b
Na^+	I	20.0	11.1	26.7	205	a	a	19.2	11.4	24.1	162	a	b
	II	22.5	10.8	25.2	154	b	a	22.7	10.0	32.1	255	b	a
K^+	I	1.7	0.3	35.7	205	a	a	1.7	0.8	10.8	162	a	a
	II	1.8	0.6	4.5	154	a	a	1.3	0.2	4.2	255	b	b
Ca^{2+}	I	139	77.0	180	205	a	a	130	85.2	177	162	a	b
	II	150	62.3	194	154	b	a	158	88.1	273	255	b	a
Mg^{2+}	I	12.0	7.6	18.0	205	a	a	11.4	6.1	14.1	162	a	b
	II	18.5	10.1	31.8	154	b	a	19.8	9.3	24.0	255	b	b
Cl^-	I	59.8	24.1	107	205	a	a	56.0	24.2	74.6	162	a	b
	II	35.5	16.5	52.1	154	b	a	38.9	15.2	55.2	255	b	b
SO_4^{2-}	I	140	68.8	212	205	a	a	135	59.3	161	162	a	b
	II	99.0	55.1	139	154	b	a	115	8.0	160	255	b	b
NO_3-N	I	1.8	0.1	38.2	205	a	a	2.3	0.4	28.8	162	a	b
	II	26.2	8.2	33.3	154	b	a	21.7	13.3	44.4	255	b	b
NO_2-N	I	0.006	<LOQ	0.374	205	a	a	0.005	0.001	0.308	162	a	a
	II	0.020	0.002	0.686	154	b	a	0.074	0.001	1.508	255	b	b
NH_4-N	I	<LOQ	<LOQ	0.189	205	a	a	<LOQ	<LOQ	0.083	162	a	a
	II	0.015	<LOQ	0.214	154	a	a	<LOQ	<LOQ	0.126	255	a	a
N_{tot}	I	2.4	0.2	37.9	205	a	a	2.7	0.4	31.9	162	a	b
	II	27.8	8.7	35.0	154	b	a	23.5	15.6	52.5	255	b	b
P_{tot}	I	0.017	<LOQ	0.079	29	a	a	0.015	<LOQ	0.069	17	a	a
	II	0.020	0.004	0.132	5	a	a	0.011	0.002	0.050	15	a	a
DOC	I	5.0	2.3	14.9	109	a	a	4.9	0.2	13.7	162	a	a
	II	5.2	0.5	11.3	80	a	a	4.8	0.1	16.3	255	a	a

LOQ, limit of quantification.

identify the response to precipitation events in discharge. The method thus indicated leachate fluxes from the soil surface to the drainage pipes. A significance level $P < 0.05$ was considered for evaluation. To indicate significant differences in drainage water quality between the fields and years, the Kruskal–Wallis H-test was performed, using the same software package. It is a rank-based non-parametric test that can be used to determine statistically significant differences between two or more groups of an independent variable on a dependent variable. A probability value <0.05 was considered as statistically significant.

3. Results and Discussion

3.1. Main Ions, pH, Nutrients, and Dissolved Organic Carbon in Drainage Water

Significant differences existed between the fields for Na^+, Ca^{2+}, Cl^-, Mg^{2+}, NO_3-N, NO_2-N, SO_4^{2-}, N_{tot} in both study years and pH and K^+ in 2014 (**Table 3**). Main ions were dominated by Ca^{2+} and SO_4^{2-}. Significant higher median concentrations of Cl^- and SO_4^{2-} occurred in field I, higher median concentrations of Ca^{2+}, Mg^{2+}, NO_3-N, NO_2-N, and N_{tot}, in field II.

Higher NO_3-N concentrations in drain water of field II compared to field I were explained by differences in crop rotation and fertilization[18] (see also Section 2.1). In this study, soil tillage caused a higher N-mineralization and subsequently a sudden increase of NO_3-N in drain water. Soil heterogeneity strongly affected the water flow regime, resulting in diminished importance of agricultural management.[35] The highest nutrient concentrations (NO_3-N, Ca^{2+}) occurred in winter due to missing plant uptake and higher water flow. Concentrations noticeably decreased in the vegetated period. Neglecting the atmospheric N fixation by soil bacteria, higher concentrations of NO_2-N coincided with high concentrations of NH_4-N after the application of mineral fertilizers.[18]

Spreading of slurry can lead to an increase in soil pH-values[44] which may explain high pH values in 2013 and 2014 (Table 3).

DOC concentrations and pH values showed the least variation between the fields and years (Table 3). DOC values were low and comparable for both fields (Table 3), as expected for the mainly sandy soils of the study site.

© 2021 The Authors. CLEAN – Soil, Air, Water published by Wiley-VCH GmbH

Table 4. Median, maximum and minimum values of element concentrations (in µg L^{-1}) in drain water of the investigated fields in 2013 and 2014. Different letters indicate significant differences ($p < 0.05$, Kruskal–Wallis test) between fields (H1-vertical) and years (H2-horizontal); values higher than existing limits are given in bold.

		2013						2014							
Element	Field	Median	Min	Max	*n*	H1	H2	Median	Min	Max	*n*	H1	H2	Trigger value[45] path soil–groundwater	Insignificance threshold[46] groundwater
Al	I	<LOQ	<LOD	6650	205	a	a	<LOQ	<LOD	376	162	a	b	—	—
	II	<LOQ	<LOD	16 400	154	b	a	<LOQ	<LOD	1590	255	a	b		
As	I	<LOQ	<LOD	**20.4**	205	a	a	<LOQ	<LOD	2.4	162	a	b	10	3.2
	II	<LOQ	<LOQ	**11.4**	154	b	a	LOQ	<LOD	2.1	255	b	a		
B	I	12.0	<LOD	69.0	205	a	a	6.0	<LOD	82.0	162	a	b	—	180
	II	30.6	6.0	73.0	154	b	a	32.0	10.0	60.0	255	b	b		
Ba	I	82.0	50.0	**1580**	205	a	a	82.0	51.0	136	162	a	a	—	175
	II	83.0	55.0	**614**	154	a	a	80.0	55.0	182	255	a	a		
Cd	I	<LOQ	<LOD	**3.4**	205	a	a	<LOD	<LOD	**13.9**	162	a	b	5	0.3
	II	<LOD	<LOD	**1.2**	154	b	a	<LOD	<LOD	**1.5**	255	b	b		
Co	I	<LOQ	<LOQ	**9.1**	205	a	a	<LOQ	<LOD	0.5	162	a	b	50	2.0
	II	<LOQ	<LOQ	**13.3**	154	a	a	<LOQ	<LOD	1.2	255	b	a		
Cr	I	<LOQ	<LOQ	**19.1**	205	a	a	0.8	<LOD	**14.3**	162	a	b	50	3.4
	II	<LOQ	<LOQ	**59.8**	154	a	a	0.7	<LOD	4.7	255	b	b		
Cu	I	2.4	0.5	**18.6**	205	a	a	2.9	0.9	**18.0**	162	a	b	50	5.4
	II	3.1	1.6	**30.9**	154	b	a	3.8	2.1	**37.4**	255	b	b		
Fe	I	612	53	275 000	205	a	a	776	32.0	12 600	162	a	a	—	—
	II	41.0	<LOQ	47 900	154	b	a	44.0	<LOD	2550	255	b	a		
Mn	I	66.0	<LOD	18 900	205	a	a	87.0	<LOD	582	162	a	a	—	—
	II	<LOQ	<LOD	2680	154	b	a	<LOD	<LOD	83.0	255	b	b		
Mo	I	<LOQ	<LOQ	3.3	205	a	a	0.5	<LOD	11.9	162	a	b	50	35
	II	<LOQ	<LOQ	2.3	154	b	a	LOQ	<LOD	0.9	255	b	a		
Ni	I	2.0	<LOQ	**18.6**	205	a	a	2.0	0.7	**32.5**	162	a	b	50	7
	II	2.0	0.5	**32.4**	154	a	a	2.4	1.4	6.4	255	b	b		
Pb	I	<LOQ	<LOD	**35.5**	205	a	a	0.6	<LOD	5.7	162	a	b	25	1.2
	II	<LOQ	<LOD	**83.0**	154	a	a	<LOQ	<LOD	**17.4**	255	b	a		
Sb	I	<LOQ	<LOQ	**7.2**	205	a	a	<LOQ	<LOD	2.0	162	a	a	10	5
	II	<LOQ	<LOQ	2.1	154	a	a	<LOQ	<LOD	**7.3**	255	a	a		
U	I	<LOQ	<LOD	5.7	205	a	a	<LOQ	<LOD	2.2	162	a	b	—	—
	II	1.4	0.9	5.8	154	b	a	1.5	0.9	3.3	255	b	a		
V	I	0.4	<LOQ	**40.2**	205	a	a	LOQ	<LOQ	2.4	162	a	a	—	4
	II	0.5	LOQ	**82.6**	154	b	a	0.7	0.3	**7.2**	255	b	b		
Zn	I	7.0	<LOD	**79.0**	205	a	a	22.0	<LOD	**317**	162	a	b	500	60
	II	13.0	<LOD	**131**	154	b	a	13.0	<LOD	**168**	255	b	a		

LOQ, limit of quantification; LOD, limit of detection.

3.2. Metal Concentrations in Drainage Water

Metal concentrations strongly fluctuated with time and fields (**Table 4**). Noteworthy are significantly higher median concentrations of Fe and Mn in field I compared to field II, and significantly higher concentrations of B, Cu, U, and V in field II compared to field I in 2013 and 2014. In both fields median concentrations of Cr were significantly higher in 2014 compared to 2013, while median Zn concentrations behaved conversely in the two years.

Still, metal concentrations in drainage waters were comparatively low. Within the 17 elements investigated, concentrations of As, B, Co, Mo, Sb, and U in about 25 % of the samples, and concentrations of Al, Cd, Mn, and Pb in about 50 %, were below or near the analytical detection limit.

All median element concentrations (Table 4) were below the trigger values of Federal Soil Protection and Contaminated Site Ordinance (BBodSchV)[45] for the path soil–groundwater. Only maximum concentrations of As, Cr, and Pb exceeded the trigger values in a few samples in both fields. The element-

© 2021 The Authors. CLEAN – Soil, Air, Water published by Wiley-VCH GmbH

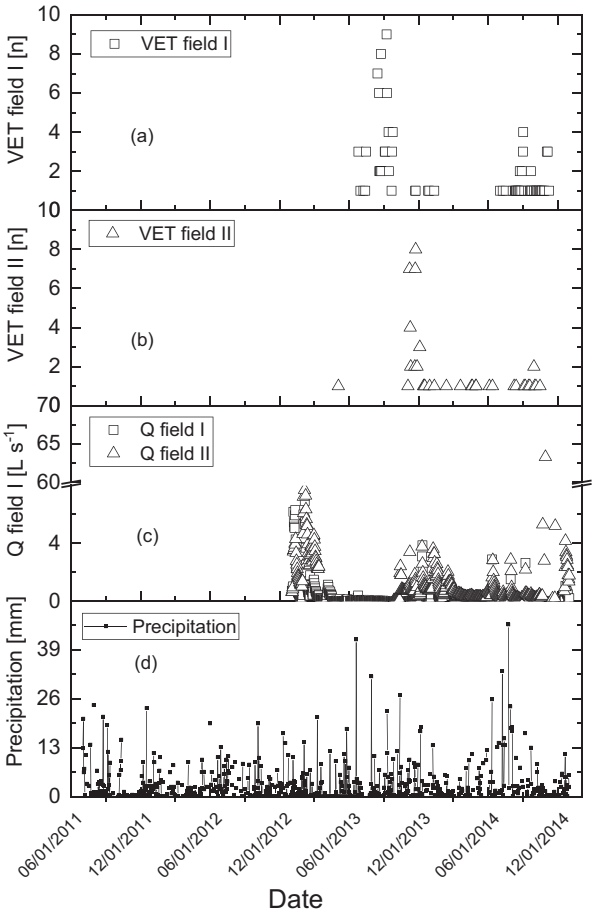

Figure 2. Number of elements per day with values exceeding threshold (VET) for a) field I, b) field II, and discharge (Q) for c) fields I and II; d) shows precipitation measured at the lysimeter facility Falkenberg.

specific minor threshold of concern for groundwater[46] which is considerably lower compared to trigger values for the path soil–groundwater[45] was also not exceeded by median element concentrations (Table 4). Only a few single values (on average 2.6 % of the total numbers) of Ba, Cd, Cu, Ni, V, and Zn exceeded minor thresholds of concern. If threshold values were exceeded, this usually applied to several elements at the same time.

To evaluate the frequency and timing of exceedances, the numbers of elements per day with values exceeding the threshold (VET), precipitation, and discharge are shown in **Figure 2**. A cross-correlation between discharge (quarterly sums of 2013 and 2014) and precipitation (quarterly sums of 2011, 2012, 2013, and 2014) resulted in a correlation coefficient r_s of 0.81 and r_s of 0.36 for field I and field II and a time lag of 18 months, respectively. Hence, high discharge rates at the field I from January 2013 until June 2013 were likely caused by precipitation events in 2011 (July–December). Comparable relations between precipitation in the third quarter 2012 and discharge in first quarter 2014 became apparent at field I. The linkage between precipitation and discharge was less pronounced at field II due to lateral fluxes above the continuous surface of highly impermeable sub-soil horizons. Comparing VET of the fields, the peaks show a similar pattern, but the peaks appear delayed at field II. The time delay between field I and field II may be explained by the topography of the terrain. Due to a slight downward slope in the eastern direction, a general groundwater flow from west to east is expected throughout the study area. Accordingly, we assume a flow directed from field I via field II toward an open ditch. It can be assumed that lateral fluxes on the way from field I to field II will be drained with a time lag and consequently appear later at the sampler operating in field II. Unfortunately, the available data do not allow quantification of these fluxes yet. The delayed appearance of peaks with comparable patterns occurs despite the differences in crop management and fertilization in both fields. It indicates the importance of the different pedo-hydrological conditions on metal concentrations in the drainage water.

To discover the dimensionality of the data set, the factor analysis was performed for both fields (**Table 5**, **Figure 3**). The elements Al, As, B, Cd, Mn, Mo, and U were excluded from FA because their concentrations were too often below the analytical detection limit. In both fields, three factors were responsible for the data structure. They explained 65.8 % (field I) and 60.9 % (field II) of the total variance of the dataset. The structure was similar for both fields. The first factor explained 31.1 % (field I) and 32.9 % (field II) of the variance. Here, only factor loadings of metals were statistically significant. The second factor was dominated by SO_4^{2-}, Cl^-, NO_3-N, and N_{tot} (20.9 % of the variance, field I) and by Ca^{2+}, SO_4^{2-}, Cl^-, NO_3-N, and N_{tot} (17.7 % of the variance, field II). In the third factor only loadings of main ions were statistically significant (Ca^{2+} and Mg^{2+} for field I; Na^+ and Mg^{2+} for field II). Their proportion of the variance was 13.8 % for field I and 10.4 % for field II. Comparison of factor loadings 1 versus 2 (Figure 3) showed a spatial separation of metals from main ions and nutrients in the coordinate system. Zinc took an intermediate position, especially for field II.

One parameter from each factor was selected exemplarily to display the variation of concentrations over time. Iron (factor 1) was selected as an indicator for iron clogging and erosion influences, NO_3-N (factor 2) as nitrogen species and Mg^{2+} (factor 3) as an ingredient of mineral fertilizers. Hydrographs of the respective element concentrations and precipitation between 2013 and 2014 are displayed in **Figure 4**, the variability of concentrations in **Figure 5**. Peak values for Fe were significantly higher in field I compared to field II. Concentrations of NO_3-N and Mg^{2+} were slightly increased in field II compared to field I. No direct relation between precipitation and concentration peaks can be derived. Taking into account the results of leaching experiments,[38] it would be helpful to take the residence time of fertilizer-borne metals in the soil into consideration. However, no data for the years before 2013 were available.

Nevertheless, the FA-based separation of nitrogen components and main ions from metals in both fields points out that element concentrations in drainage waters were mainly caused by other sources than fertilization. Beside fertilizers, soil organic matter, and soil minerals may play a role.

For example, the intermediate position of Zn in field I in contrast to field II may be associated with anoxia in field I, leading to precipitation of Zn sulfides during sulfate reduction or release of both sulfate and Zn during sulfide-mediated denitrification.

© 2021 The Authors. CLEAN – Soil, Air, Water published by Wiley-VCH GmbH

Table 5. Results of the factor analysis (FA) of field I and field II; parameters with loadings >0.6 are given in bold.

Field I			
Parameter	Factor 1	Factor 2	Factor 3
Ba	**0.92**	0.14	0.07
Cu	**0.78**	−0.09	−0.21
Cr	**0.90**	0.11	−0.14
Fe	**0.92**	0.12	0.09
Ni	**0.76**	−0.12	−0.14
Zn	0.25	0.05	−0.50
V	**0.94**	0.06	0.07
K^+	0.04	0.18	0.39
Na^+	0.16	0.17	**0.61**
Ca^{2+}	−0.08	−0.20	**0.78**
Mg^{2+}	0.00	−0.11	**0.82**
SO_4^{2-}	−0.03	**0.83**	0.13
Cl^-	0.04	**0.95**	0.11
NO_3-N	−0.11	**−0.93**	0.19
NO_2-N	−0.13	−0.21	0.10
N_{tot}	−0.11	**−0.93**	0.18
Explained variance			
65.8 %	31.1 %	20.9 %	13.8 %

Field II			
Parameter	Factor 1	Factor 2	Factor 3
Ba	**0.80**	0.11	−0.04
Cu	**0.77**	0.05	0.07
Cr	**0.96**	−0.09	0.02
Fe	**0.92**	−0.09	0.01
Ni	**0.93**	0.06	0.10
Zn	0.49	0.05	−0.04
V	**0.96**	−0.05	0.09
K^+	0.25	−0.35	0.09
Na^+	−0.07	0.30	**−0.88**
Ca^{2+}	0.05	**0.64**	0.08
Mg^{2+}	−0.08	−0.25	**−0.78**
SO_4^{2-}	0.11	**0.65**	0.17
Cl^-	0.02	**0.79**	0.07
NO_3-N	−0.14	**0.72**	−0.32
NO_2-N	−0.06	−0.10	−0.37
N_{tot}	−0.12	**0.69**	−0.36
Explained variance			
60.9 %	32.9 %	17.7 %	10.4 %

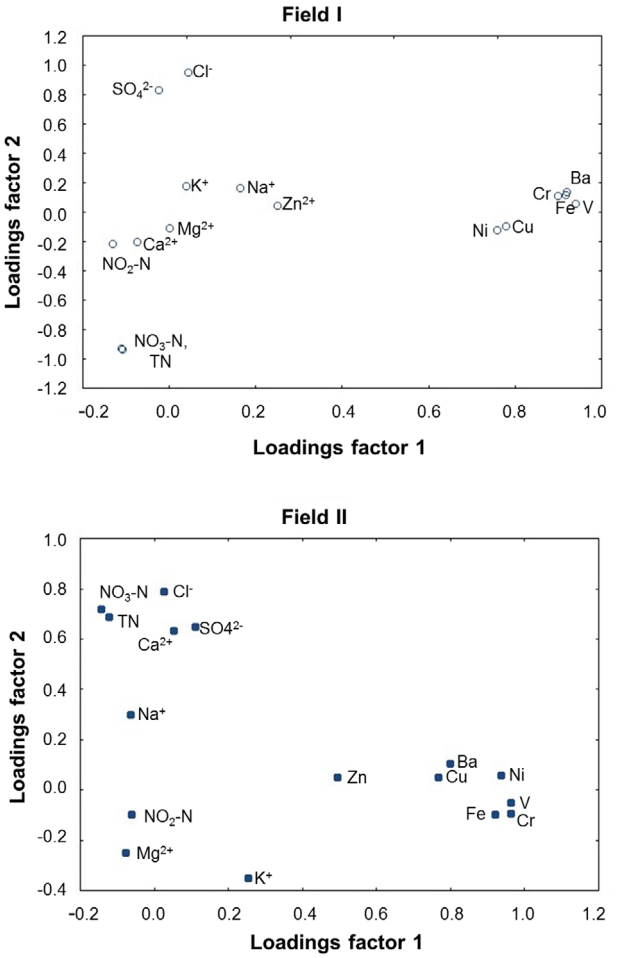

Figure 3. Factor loadings of FA for field I and field II; factor 1 versus factor 2.

Likewise, the higher amount of Zn in slurry than in mineral fertilizer may explain higher Zn concentrations in drainage water of field II in 2013.

With regard to the differences in concentration levels and time-dependent occurrence of metals peaks in both fields, characteristics of the drainage waters of the fields can be summarized by the following main groups of elements.

(I) As, Ba, Fe, and Mn belong to the first group. Here, the highest peak concentrations occurred in autumn 2013. The peaks were higher at field I in contrast to field II, especially for Fe and Mn (Table 4, Figure 4). Iron and Mn are abundant elements in soils and ingredients of mineral fertilizers. High As, Ba, Fe, and Mn concentrations are in line with ochre depositions at field I.[35] Ochre as natural earth pigment contains hydrated iron oxide. Large amounts of iron hydroxide deposits presuppose the solution of Fe(II) in oxygen-free soil water.[47] Due to site conditions of field I, the development of subsoil zones with confined groundwater may occur[35] which leads to anoxic conditions with low redox potential. Upon contact with oxygen (air may enter the collection drain at the outlet), precipitation of brown Fe(III) hydroxides (ochre flakes) occurs. Increased Fe concentrations of field I drainage can, therefore, be attributed to the dissolution of iron minerals in reductive soil zones. With the participation of aerobic manganese-oxidizing bacteria, oxidation of Mn(II) leads to the precipitation of insoluble Mn(IV) oxide hydrates. Other ions can be deposited by adsorption. At the sites studied this was especially the case for As and Ba. Beside Fe, high precipitation rates of As were reported during methodical work on metal precipitation in conveying hoses.[48] Denitrification

© 2021 The Authors. CLEAN – Soil, Air, Water published by Wiley-VCH GmbH

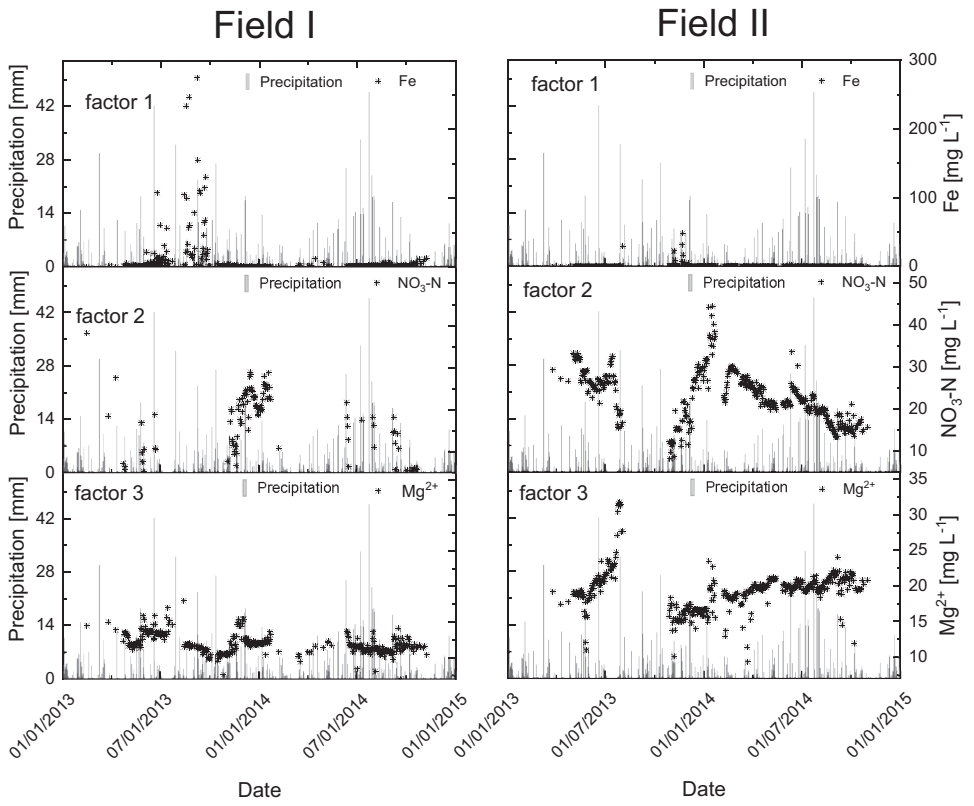

Figure 4. Trend of Fe, NO_3-N and Mg^{2+} concentrations as well as precipitation in drain water of field I and II.

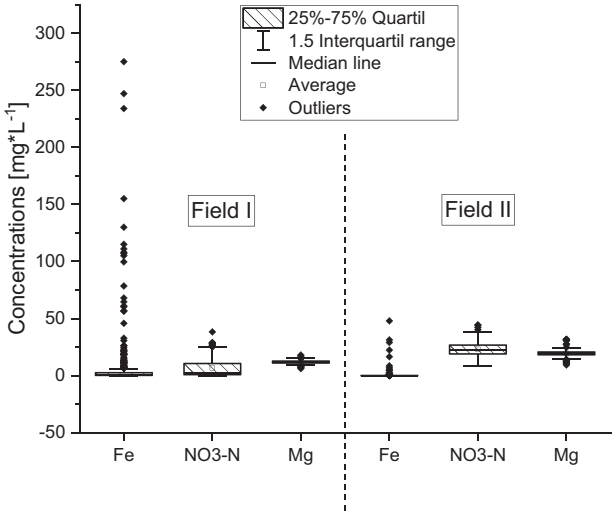

Figure 5. Box plots of NO_3-N, Mg^{2+}, and Fe concentrations in drain water of fields I and II; (2013–2014).

with iron sulfides (esp. FeS_2) as an electron donor is important in anoxic environments and mediated by bacteria.[49] The main reaction products are gaseous nitrogen, sulfate and ferrous iron. High sulfate concentrations in field I (Table 3), but also in field II support this denitrification process. Increasing sulfate concentrations in a reducing aquifer as a consequence of denitrification have already been reported.[40] In fact, this is currently a rising problem in some aquifers of the North German Plain. Denitrification by iron sulfides is favored by high pH value[40] as they were found in the study area (Table 3). These pH values are typical for the carbonic acid/carbonate buffer range (6.2–8.6).[39] Boundary conditions such as soil texture, soil utilization and hydrological situation are also important. Relative soil moisture content Θ_{rel} was used to distinguish between aerobic and anaerobic conditions.[44] It was assumed that at a relative soil moisture content of $\Theta_{rel} > 0.61$ aerobic microorganisms are strongly impaired in their activity, while the activity of anaerobes increases. In our study, the mean relative moisture content of the soil Θ_{rel} was 1.01 for field I and 0.90 for field II, respectively (March to December 2014, $n = 928$, depth 85 cm, close to the drain; data not shown). This indicates that denitrification is possible in both fields.

(II) Al, Co, Cr, Pb, and V belong to a second group. Peak concentrations of these elements were higher in field II compared to field I, with maximum values in 2013 (Table 4). The metals are ingredients of mineral and organic fertilizers. Here, the main source is soil erosion, because concentrations in the investigated soils were clearly higher than in the applied fertilizer (**Table 6**). Due to the slope of the terrain from field I to field II, surface erosion during heavy rain can be expected. On the basis of local conditions, eroded material can enter the manhole and increase the concentration of fine particulate matter with typical regional soil constituents like Al, Co, Cr, Pb, and V. Due to the applied microwave digestion, elements from this fine material were detected in the drainage water beside solutes. Applying particle size measurements of eroded sediment and soil material in

© 2021 The Authors. CLEAN – Soil, Air, Water published by Wiley-VCH GmbH

Table 6. Metal content of selected fertilizers applied to the study fields and of the investigated soils in comparison with literature data and regional geogenic background values for soils (all data in mg kg^{-1}, values marked with *) in % of dry mass).

Metal	Fertilizers, applied to the study fields					Selected fertilizer, applied in Germany (mean values)[29]					Soils investigated			
	CAN, 2012	Granulated urea, 2012	ASN, 2014	CAN, 2015	Organic slurry, 2017	Straight P	PK	NP	NPK	Organo-mineral NP	Organo-mineral NPK	Topsoil field I, 12/2015	Topsoil field II, 12/2015	Precaution values soils[45] ***)	Geogr. background[53] ***)
Al	550	<160	642	453	884	4934	3432	1531	1204	na	1950	23 740	19 740	ne	ne
As	<2	<2	<2	<2	0.7	10.4	4.2	8.8	3.0	4.2	4.1	2	<2	ne	8
Cd	<2	<2	<2	<2	0.2	20.5	6.7	15.2	2.3	<LOQ	1.7	<2	<2	1.0	0.1
Co	<10	<10	<10	<10	1.3	1.8	0.83	1.5	2.6	na	0.74	<10	<10	ne	11
Cr	<10	<10	<10	<10	3.4	135	144	136	30.7	43.1	14.4	37	32	60	47
Cu	<2	<2	<35	<2	0.01*)	42.7	16.8	41.5	39	na	41.1	4	5	40	19
Fe	560	<70	<300	653	1380	7289	12 443	3094	2037	na	3043	9300	6990	ne	ne
Mn	45	<10	78	52	0.03*)	138	1263	144	126	na	116	340	286	ne	373
Mo	12	30	<5	<2	1.9	9.1	6.5	3.9	9.2	na	13.0	<2	<2	ne	ne
Ni	<5	<5	<5	<5	3.4	33.8	20.2	21.9	12.7	63	7.1	8	6	50	26
Pb	<2	<2	<2	1.3	1.4	4.7	4.3	1.2	1.5	7.5	3	19	21	70	25
Sb	2	2	8	<2	—	1.7	0.99	1.3	0.31	na	0.46	<2	<2	ne	ne
U	<2	4	<2	<2	—	110	79	62	14.3	1.5	9.7	<2	<2	ne	ne
V	<10	<10	<10	<10	<LOQ	58	128	72	26.0	na	15.8	24	16	ne	58
Zn	3	<2	<13	<2	0.04*)	354	173	238	111	na	105	36	32	150	55

na, not analyzed; ne, not existing; LOQ, limit of quantification; **) soil type loam/silt; ***) subsoil boulder clay.

© 2021 The Authors. CLEAN – Soil, Air, Water published by Wiley-VCH GmbH

river water[50] it was shown that up to 98 % of the cumulative particle fraction of the fine material was smaller than 20 µm, 86 % < 10 µm, 56 % < 5 µm, and 48 % <2 µm. For atmospheric deposition of metals, the particulate matter fraction PM_{10} is relevant. In the study area, metals in the fraction <10 µm are negligible as source of fine particulate matter for the fields.[51]

(III) Cd, Cu, Mo, Sb, U, and Zn are part of the third group, which separates from the group I and II by a lack of outstanding concentration peaks. Concentrations varied more diffusely with lower amplitudes compared to the other two groups. Their contents were higher in the slurry than in the mineral fertilizer. Some elements showed similarities to group I (Mo and Cd) and group II (Cu and Zn) behavior. Molybdenum, Sb, Cd, and U are ingredients of inorganic fertilizers. Increasing concentrations of Cu and Zn in soils are discussed as a result of spreading pig slurry on crop fields, which is a common practice of fertilization.[33] However, the initially expected influence of fertilization was not clearly seen for the elements of this group.

Boron is known as possible ingredient of inorganic fertilizers, Ni as possible ingredient of livestock waste. Furthermore, B is suitable as indicator to track the impact of land applications of treated municipal wastewater and other sources on ground water quality.[52] Concentrations of both B and Ni were lower than expected. They reveal no signs of significant inputs of these metals from fertilizers or other sources into drain water.

3.3. Metal Contents in Fertilizers and Soils

Both, results of randomly investigated fertilizers applied by the agricultural cooperative as well as results of randomly investigated soils at the end of the studied period are in line with results of drainage water analysis.

Metal contents of fertilizers were significantly lower compared to other fertilizers applied in Germany,[29] except for Mo in 2012 (Table 6).

Metal contents in the two investigated soils (Table 6) were also below precaution values for soils according to the Federal Soil Protection and Contaminated Site Ordinance[45] and below regional geogenic background values for subsoils of boulder clay, a characteristic feature of the investigated area.[53] For Cd, the applied method was not sensitive enough to allow a statement regarding the precaution value of soils.

Analyses of the mineral fertilizer applied at long-term observation areas in Saxony-Anhalt between 2009 and 2015 (State Institute for Agriculture and Horticulture Saxony-Anhalt, unpublished) were within the range presented in Table 6. Their mean values were 1.5 mg kg^{-1} for Cu, 72 mg kg^{-1} for Mn, and 48.3 mg kg^{-1} for Zn. This is important because element concentrations in drainage water measured in 2013 and 2014 might originate from fertilizers applied in previous years, depending on their residence time in soil. Compared to mineral fertilizer, the metal contents of slurries applied at the long-term observation areas in Saxony-Anhalt (mean values 2009–2015, State Institute for Agriculture and Horticulture Saxony-Anhalt, unpublished) were higher for Cu (16.8 mg kg^{-1}) and Zn (22.4 mg kg^{-1}) but lower for Mn (20.9 mg kg^{-1}).

Metal content in cattle slurry applied to the studied fields was low compared to reference values, specified in the German Fertilizer Ordinance (DüMV).[54] All values were below existing labelling thresholds/permitted limits (20/40 mg kg^{-1} for As, 1.0/1.5 mg kg^{-1} for Cd, 300 mg kg^{-1}/not defined for Cr, 40/80 mg kg^{-1} for Ni and 100/150 mg kg^{-1} for Pb). Other thresholds refer to the percent dry mass of slurry (below 0.004 % for Co, 0.07 % for Cu, and 0.5 % for Zn). These values were also not exceeded in the slurry tested in 2017.

4. Concluding Remarks

Resulting from a two-year study under real conditions, metal concentrations in drainage waters from the investigated fields only occasionally posed a risk for groundwater or downstream water bodies. The findings are supported by the low pollutant load of the applied fertilizers but are not yet fully understood. With respect to the residence time of fertilizers in soil and resulting possible build-up processes of trace elements in the soils, longer investigation periods are needed for a comprehensive understanding of the hydrological cause-and-effect relationship. This is especially important against the background of climate change with increasing dry periods, as the study was carried out under average precipitation conditions. For example, rainfall during extreme dry weather in 2018 and 2019 was much lower compared to the studied period. Regarding the associated impact on the soil–water balance, a change in the relationship between precipitation and leachate generation in the study area cannot be ruled out.

Export of metals from the agricultural fields into the drainage waters was predominantly driven by pedo-hydrological conditions leading to ochre precipitation and denitrification. To avoid or minimize these influences, measures to protect against erosion and to reduce nitrate entries should supplement the careful use of fertilizers. Measures to reduce soil erosion can be catch crop cultivation, soil vegetation over the whole year and reduced soil tillage. To reduce the influence of denitrification on the mobility of metals, a fertilizer management adapted to seasonal plant requirements would be important.

More detailed seasonal investigations on metal mobility with focus on the influence of pyrite weathering and varying nitrate entries are also recommended.

Acknowledgements

The authors would like to thank K. Muhs and R. Lüdtke (Department Soil System Science, UFZ) for their support in fieldwork and analysis. Trace element analyses in water were performed by C. Hoffmeister, U. Block, and M. Mehrens (Department River Ecology, UFZ), analyses of soil and fertilizer by A. Rämmler (Department Analytical Chemistry, UFZ). The authors thank B. Matzke (laboratory of the State Institute for Agriculture and Horticulture Saxony Anhalt) for slurry analyses. The support of the Chairman of the Management Board of agricultural cooperative "Altmärkische Höhe," e.G., Lückstedt (F. Wiese) was greatly appreciated. The investigations were performed within a project (No. 31086), funded by the German Federal Environmental Foundation (DBU). The manuscript has benefited considerably from valuable discussions on statistics with J. Kraft. Two anonymous reviewers were acknowledged for carefully reading the manuscript and providing constructive comments.

Conflict of Interest

The authors declare no conflict of interest.

© 2021 The Authors. CLEAN – Soil, Air, Water published by Wiley-VCH GmbH

Author Contributions

M.B.: Conceptualization, data curation, investigation, methodology, supervision, validation, writing-original draft, writing-review and editing. H.R.: Conceptualization, data curation, investigation, methodology, validation, writing-original draft, writing-review and editing. K.W.-P.: Conceptualization, data curation, investigation, methodology, validation, writing-original draft, writing-review and editing. N.T.: Conceptualization, data curation, investigation, methodology, validation, writing-original draft, writing-review and editing. R.M.: Conceptualization, data curation, investigation, methodology, project administration, validation, writing-original draft, writing-review and editing.

Keywords

drainage water, fertilizer, metal concentrations, North German Plain, pedo-hydrological conditions

Received: September 16, 2020
Revised: February 4, 2021
Published online: May 6, 2021

[1] K. Dragon, D. Kasztelan, J. Gorski, J. Najman, *Environ. Earth Sci.* **2016**, *75*, 100.
[2] H. Spaling, *Agric. Ecosyst. Environ.* **1995**, *53*, 279.
[3] D. Zak, N. Meyer, A. Cabezas, J. Gelbrecht, R. Mauersberger, B. Tiemeyer, C. Wagner, R. McInnes, *Ecol. Eng.* **2017**, *103*, *Part B*, 488.
[4] B. Tiemeyer, B. Lennartz, P. Kahle, *Agric. Ecosyst. Environ.* **2008**, *123*, 125.
[5] H. Behrendt, A. Bachor, *Water Sci. Technol.* **1998**, *38*, 147.
[6] M. Nausch, J. Woelk, P. Kahle, G. Nausch, T. Leipe, B. Lennartz, *Agric. Water Manage.* **2017**, *187*, 77.
[7] J. C. Rozemeijer, Y. van der Velde, F. C. van Geer, M. F. P. Bierkens, H. P. Broers, *Environ. Pollut.* **2010**, *158*, 3571.
[8] G. Wessolek, B. Kluge, A. Toland, T. Nehls, E. Klingelmann, Y. N. Rim, B. Mekiffer, S. Trinks, in *Perspectives in Urban Ecology—Studies of Ecosystems and Interactions Between Humans and Nature in the Metropolis of Berlin* (Eds: W. Endlicher, P. Hostert, I. Kowarik, E. Kulke, J. Lossau, J. Marzluff, E. van der Meer, H. Mieg, G. Nützmann, M. Schulz, G. Wessolek), Springer, Berlin, Heidelberg, Germany **2011**, pp. 89–133.
[9] P. P. Xue, Y. Carrillo, V. Pino, B. Minasny, A. B. McBratney, *Sci. Rep.* **2018**, *8*, 11725.
[10] K. Kalbitz, R. Wennrich, *Sci. Total Environ.* **1998**, *209*, 27.
[11] M. A. Kashem, B. R. Singh, *Nutr. Cycling. Agroecosyst.* **2001**, *61*, 247.
[12] R. O. Freitas, E. Buscardo, L. Nagy, A. B. dos Santos Maciel, R. Carrenho, R. C. C. Luizao, *Mycorrhiza* **2014**, *24*, 21.
[13] M. M. Palta, J. G. Ehrenfeld, D. Giménez, P. M. Groffman, V. Subroy, *Soil Biol. Biochem.* **2016**, *101*, 237.
[14] M. Delgado-Baquerizo, J. Grinyer, P. B. Reich, B. K. Singh, *Funct. Ecol.* **2016**, *30*, 1862.
[15] H. Xie, L. Chen, Z. Shen, *Water* **2015**, *7*, 1088.
[16] P. K. Kalita, A. S. Algoazany, J. K. Mitchell, R. A. C. Cooke, M. C. Hirschi, *Agric. Ecosyst, Environ.* **2006**, *115*, 183.
[17] B. Tiemeyer, P. Kahle, B. Lennartz, *Agric. Water Manage.* **2006**, *85*, 47.
[18] N. Tauchnitz, J. Bischoff, M. Schrödter, H. Rupp, R. Meissner, *Wasserwirtschaft* **2014**, *104*, 36.
[19] F. Godlinski, P. Leinweber, R. Meissner, J. Seeger, *Nutr. Cycling. Agroecosyst.* **2004**, *68*, 47.
[20] B. Tiemeyer, P. Kahle, B. Lennartz, *Agric. Water Manage.* **2009**, *96*, 677.
[21] B. Ulén, C. von Brömssen, G. Johansson, G. Torstensson, L. S. Forsberg, *Agric. Ecosyst. Environ.* **2012**, *151*, 61.
[22] A. Svanbäck, B. Ulén, A. Etana, *Agric. Ecosyst. Environ.* **2014**, *184*, 124.
[23] M. D. Ruark, S. M. Brouder, R. F. Turco, *J. Environ. Qual.* **2009**, *38*, 1205.
[24] B. Tiemeyer, P. Kahle, *Biogeosciences* **2014**, *11*, 4123.
[25] M. R. Williams, K. W. King, N. R. Fausey, *Agric. Water Manage.* **2017**, *192*, 159.
[26] B. H. Baker, R. Kröger, J. P. Brooks, R. K. Smith, J. M. Prince Czarnecki, *Water Res.* **2015**, *87*, 193.
[27] E. Gimeno-Garćia, V. Andreu, R. Boluda, *Environ. Pollut.* **1996**, *92*, 19.
[28] K. W. T. Goulding, L. Blake, *Agric. Ecosyst. Environ.* **1998**, *67*, 135.
[29] S. Kratz, J. Schick, E. Schnug, *Sci. Total Environ.* **2016**, *542 Part B*, 1013.
[30] Z. Ciećko, A. C. Zolnowski, M. Madej, G. Wasiak, J. Lisowski, E. Rolka, *Pol. J. Soil Sci.* **2015**, *48*, 1.
[31] F. A. Nicholson, B. J. Chambers, J. R. Williams, R. J. Unwin, *Bioresour. Technol.* **1999**, *70*, 23.
[32] F. Zhang, Y. Li, M. Yang, W. Li, *Int. J. Environ. Res. Public Health* **2012**, *9*, 2658.
[33] S. Legros, E. Doelsch, F. Feder, G. Moussard, J. Sansoulet, J.-P. Gaudet, S. Rigaud, I. Basile Doelsch, H. Saint Macary, J.-Y. Bottero, *Agric. Ecosyst. Environ.* **2013**, *164*, 70.
[34] A. Sungur, M. Soylak, S. Yilmaz, H. Ozcan, *J. Mater Cycles Waste Manag.* **2016**, *18*, 563.
[35] D. Bednorz, N. Tauchnitz, O. Christen, H. Rupp, R. Meissner, *Water, Air, & Soil Pollut.* **2016**, *227*, 395.
[36] W. Kainz, P. String, M. Weller, K.-J. Hartmann, C. Knauf, A. Möbes, D. Feldhaus, *Bodenatlas Sachsen Anhalt*, LABG, Halle, Germany **1999**.
[37] D. Bednorz, N. Tauchnitz, J. Bischoff, M. Schrödter, B. Koblenz, J. Röcknagel, H. Rupp, F. Wiese, O. Christen, R. Meissner, presented at the 16 Gumpensteiner Lysimetertagung, Raumberg-Gumpenstein, Austria, April **2015**.
[38] M.-O. Aust, S. Thiele-Bruhn, J. Seeger, F. Godlinski, R. Meissner, P. Leineweber, *Water Air Soil Poll.* **2010**, *211*, 143.
[39] B. Ulrich, *Z. Pflanzenernaehr. Bodenkd.* **1981**, *144*, 289.
[40] W. Kölle, P. Werner, O. Strebel, J. Böttcher, *Vom Wasser* **1983**, *61*, 125.
[41] F. Weigold, M. Baborowski, *J. Hydrol.* **2009**, *369*, 296.
[42] P. Morgenstern, L. Brüggemann, R. Wennrich, *Spectrochim. Acta, Part B* **2004**, *59*, 185.
[43] P. Morgenstern, L. Brüggemann, R. Wennrich, *Spectrochim. Acta, Part B* **2005**, *60*, 1373.
[44] J. Onigkeit, *Ph.D. Thesis*, Technische Universität Braunschweig **2006**.
[45] BBodSchV, Bundes Bodenschutzverordnung, BGBl (Federal Law Gazette), Berlin, Germany **1999**.
[46] LAWA, *Ableitung von Geringfügigkeitsschwellenwerten für das Grundwasser*, Kulturbuch-Verlag Berlin, Stuttgart, Germany **2017**.
[47] F. Scheffer, P. Schachtschabel, *Lehrbuch der Bodenkunde*, Enke, Stuttgart, Germany Stuttgart **1989**.
[48] R. Schwartz, G. Miehlich, *Mitt. Dtsch. Bodenkd. Ges.* **1993**, *72*, 457.
[49] W. Kölle, O. Strebel, J. Böttcher, in *Groundwater Monitoring and Management*, IAHS Publication No. 173, IAHS Press, Wallingford, UK **1990**, pp. 23–30.
[50] M. Baborowski, W. von Tümpling, K. Friese, *Hydrol. Earth Syst. Sci.* **2004**, *8*, 135.
[51] Emission control report Saxony-Anhalt 2019, LAU, Halle (Saale), Germany **2020**.
[52] B. G. Katz, D. W. Griffin, *Environ. Geol.* **2008**, *55*, 801.
[53] *Communications on the Geology and Mining of Saxony-Anhalt*, Vol. 18, LABG, Halle (Saale), Germany **2014**.
[54] DüMV, Deutsche Düngemittelverordnung, *BGBl* (Federal Law Gazette), Berlin, Germany December 2012.

© 2021 The Authors. CLEAN – Soil, Air, Water published by Wiley-VCH GmbH