

Loss of trace elements from agricultural soil

S. D. W. Comber, R. J. Schindler, M. S. A. Blackwell & T. Darch

To cite this article: S. D. W. Comber, R. J. Schindler, M. S. A. Blackwell & T. Darch (03 Dec 2024): Loss of trace elements from agricultural soil, Environmental Technology, DOI: [10.1080/09593330.2024.2423907](https://doi.org/10.1080/09593330.2024.2423907)

To link to this article: <https://doi.org/10.1080/09593330.2024.2423907>



© 2024 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group



[View supplementary material](#)



Published online: 03 Dec 2024.



[Submit your article to this journal](#)



Article views: 100



[View related articles](#)



[View Crossmark data](#)

Loss of trace elements from agricultural soil

S. D. W. Comber^a, R. J. Schindler ^a, M. S. A. Blackwell^b and T. Darch^b

^aSchool of Geography, Earth & Environmental Science, Plymouth University, Plymouth, UK; ^bRothamsted Research, N Wyke, Devon, UK

ABSTRACT

Soil erosion is a world-wide issue driven by land management and climate change. Research has focussed on soil loss rates from agricultural land. However, the loss of trace elements essential for soil and plant health, or potentially toxic elements that occur as impurities in fertilisers and manures, is poorly understood. This study reports on the loads and forms of copper, cadmium, manganese, nickel, selenium and zinc lost from three types of agricultural systems at Rothamsted Research's North Wyke Farm Platform over five individual storm events. Loads reflected a combination of concentrations in the soil, annual additions from fertilisers, the ability to leach from the soil and rainfall intensity. Arable fields demonstrated an order of magnitude greater loss of soil compared to pasture. Consequently, particulate-bound losses were higher, and the proportion of losses in solution were 29% lower on average, compared with pasture. Overall losses for each element were statistically similar for pastures. In comparison, arable fields showed greater average losses for five essential elements (15.3%) compared to pasture (9.7%). Nickel exhibited the greatest average loss (27% overall; 39% for arable) and zinc the lowest (2% overall; 3% for arable). The predominant loss of cadmium was in the dissolved phase (96% overall; 92% arable), followed by selenium (81%/63%), nickel (64%/35%) and copper (61%/34%). Conversely, dissolved losses of manganese (38%/21%) and zinc (28%/8%) were lower than particulate losses. We conclude that overall loss, and form of the loss, varies significantly between arable and pastoral systems, and the physico-chemical properties of the element itself.

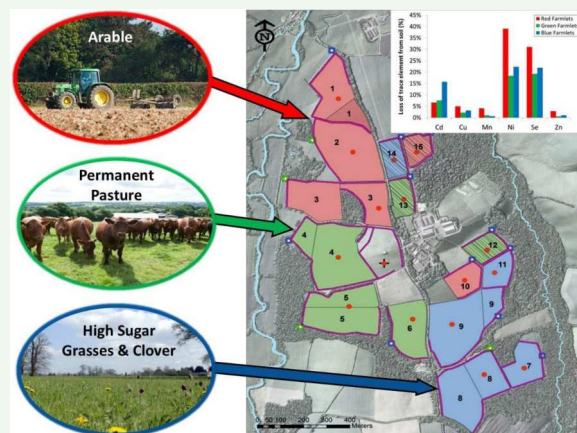
ARTICLE HISTORY

Received 23 July 2024

Accepted 14 October 2024

KEYWORDS

Trace elements; agricultural soil; leaching; erosion; partitioning




Highlights

- (1) Soil loss from arable land is up to 10 times that of pasture.
- (2) Trace elements are strongly associated with sediment in runoff from arable fields.
- (3) Dissolved trace element concentration is relatively stable across a rain event.

- (4) Relative losses of dissolved versus particulate-bound metals varied between elements. Up to 40% of nickel applied to soil is leached.

1. Introduction

Efficient and environmentally friendly use of chemicals within the agricultural sector is essential in the modern

CONTACT S. D. W. Comber  sean.comber@plymouth.ac.uk  School of Geography, Earth & Environmental Science, Plymouth University, Plymouth, UK
 Supplemental data for this article can be accessed online at <https://doi.org/10.1080/09593330.2024.2423907>.

© 2024 The Author(s). Published by Informa UK Limited, trading as Taylor & Francis Group
This is an Open Access article distributed under the terms of the Creative Commons Attribution-NonCommercial-NoDerivatives License (<http://creativecommons.org/licenses/by-nc-nd/4.0/>), which permits non-commercial re-use, distribution, and reproduction in any medium, provided the original work is properly cited, and is not altered, transformed, or built upon in any way. The terms on which this article has been published allow the posting of the Accepted Manuscript in a repository by the author(s) or with their consent.

world to ensure maximum efficiency and minimal environment impacts. Metal micronutrient deficiency is a significant concern and impacts on productivity and health of agricultural systems [1]. Furthermore, transfer from soils to surface waters of Priority Hazardous Pollutants such as cadmium is a concern regarding the ecology of the receiving water [2].

Sources of metals in freshwater catchments are environmentally ubiquitous and naturally occurring, as well as driven by human activity. Efforts to develop common methodologies in source apportionment models have shown that sources are very broad and geographically varied. The largest inputs to freshwaters within the EU are associated with soil loss containing naturally derived metals from agricultural land and forestry, followed by anthropogenically derived metals in runoff from agricultural land originating from fertiliser and biocides, run off from roads and roofs, sewage effluent, atmospheric deposition and industry, particularly abandoned mines [3]. For instance, Comber [4] determined that 11,904 tonnes per annum (tpa) of Zinc are emitted to freshwater bodies in the EU, principally through soil loss (7208 tpa) but with substantial contributions via runoff (3150 tpa), sewage effluent (1767 tpa), atmospheric deposition (1250 tpa) and abandoned mines and industry (63 tpa).

In rural areas, anthropogenic sources are primarily dependent on agricultural land use type. For instance, ~40% of copper inputs in the EU are from animal manure and ~50% from pesticide and biocides, with smaller inputs from inorganic fertiliser and runoff from industry and transport networks [3]. Emissions to freshwater may occur in the particulate form through soil loss or in soluble form as runoff or groundwater. Consequently, both inputs and losses are expected to vary between forested, pasture or arable land use types. There is scant literature data on the loss of trace elements from agricultural land, either in the dissolved phase or associated with soil erosion, which is a prerequisite for improved management of metals within agricultural systems [5]. There are some limited data for crops that use copper based biocides to treat fungal infections in vineyards [6]. Sadovnikova et al. [7] undertook a mass balance of copper fluxes into and out of soil including the main sources, uptake into crops or livestock and leaching. This was completed for grass and arable crops for sand, sand-calcareous, clay, clay-calcareous, loess and peat soils. A mean of 8.8% loss for copper was calculated (median = 10.8%, $n = 13$, 95% confidence interval = 2.95%). A second study [8] undertook a practical study which measured copper and zinc fluxes across different soil types (silty, loam, clay, sand) in the UK and reported a 9% and

10.1% loss respectively of dissolved material. The measured 9% loss of cadmium was significantly lower than the values reported elsewhere using partitioning models suggesting between 40 and 100% of cadmium may be lost via leaching [9]. DeVries et al. [10] undertook a similar survey in the Netherlands across most types of soil used for grass and arable and reported zinc loss of 1.8% to 36%, with the greatest leaching from sandy (poor sorption) and peat (acidic) soils. The EU RAR [11] reports 240 g/ha/yr of zinc leached from soil against 1222 g/ha/yr inputs, equating to a 20% loss to water (including groundwater).

Trace elements are associated with soil particles, either as part of the underlying mineralogy, or adsorbed. Climate change resulting in more intense rain events, means soil erosion from arable land is of increasing concern across the world [12]. Bulk loss of soil from agricultural land therefore is a pathway for trace element loss to water [5].

Furthermore, the UK has undertaken a major project to generate a source apportionment model for chemicals entering the aquatic environment [5]. Although the model currently includes nutrient losses from arable and livestock agriculture, there is currently no reliable data for loss of metals from agriculture (dissolved or particulate).

This research therefore aimed to fill in these gaps for trace element retention and loss from soil by utilising Rothamsted Research's North Wyke Farm Platform (NWFP), in Devon, UK [13] to generate a trace element mass balance loss from agricultural land. Although there is published literature on soil metal runoff and some data on soil micronutrient deficiency, none offers the degree of comprehensiveness offered with using the North Wyke Farm Platform, a UKRI National Bioscience Research Infrastructure (NBRI), owing to all of the supporting data available (flow, suspended solids, nutrient management, land use, agricultural practice) which serves to enhance the dataset.

2 Methodology

2.1 The farm platform

The North Wyke Farm Platform is explained in detail elsewhere [14]. The hydrologically isolated fields within the Farm Platform are designated in one of three distinct areas, or farm systems, each of which is managed under a different operational philosophy (Figure 1). The core hypothesis reflects this via the calculation of 'sustainability metrics' that can accurately predict the long-term performance of each treatment. Metrics are directly calculated from the platform's fine resolution data

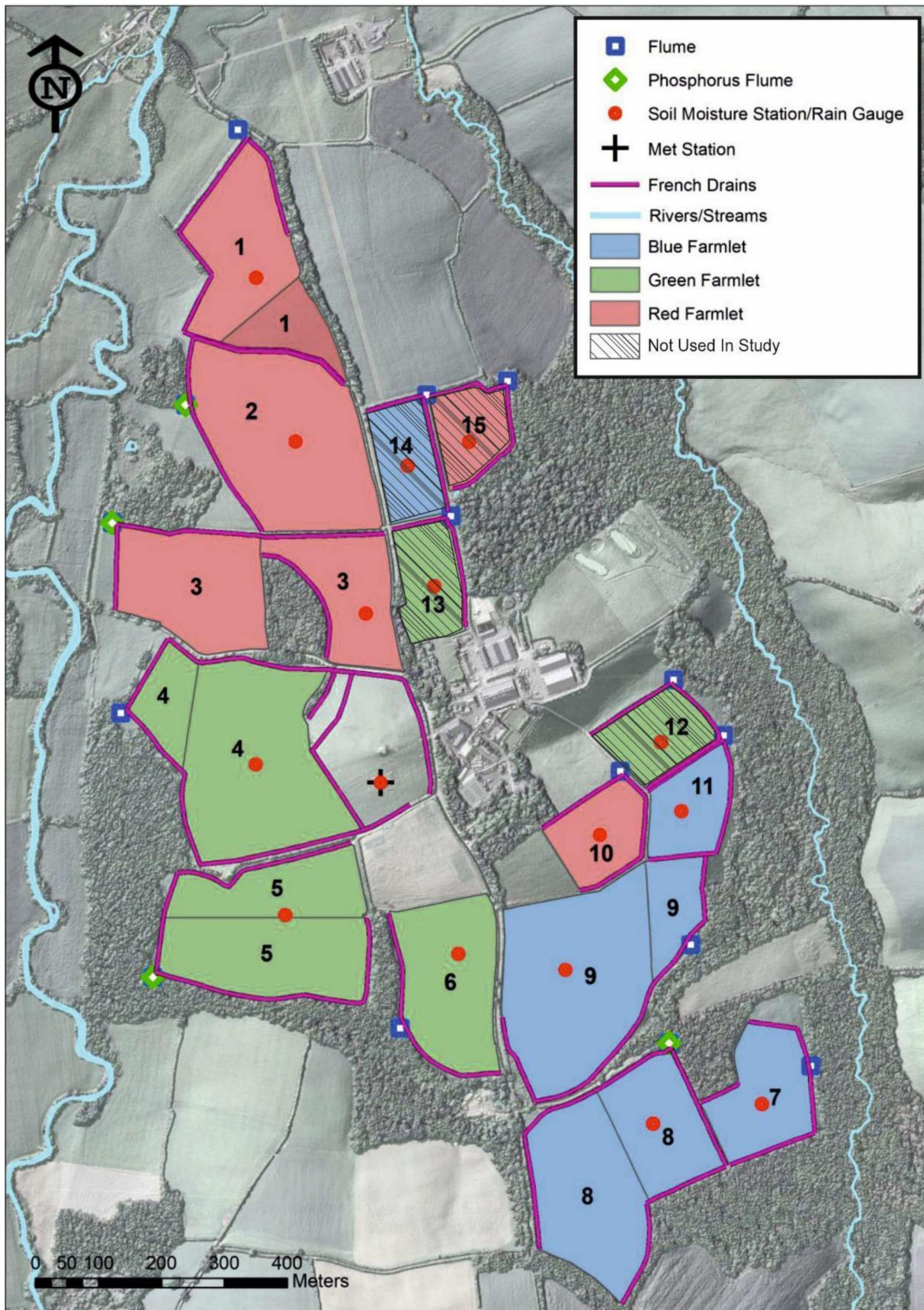


Figure 1. Map of the North Wyke Farm Platform, showing designation of catchments within each field system, French drain system, and locations of flumes and meteorological station. Note that some catchments were not used in this study.

collections, and are carefully chosen to be transferrable to other farming systems, across the UK and the world. In this way, outputs from the platform directly influence sustainable land use both nationally and internationally.

The farming systems each consist of five component catchments over 21 ha. Catchments comprise single or multiple fields that are heavily monitored to provide fine-resolution data on all inputs, outputs and events. All of the catchments are hydrologically isolated: water, sediments and nutrients run to a series of French drains, which connect to individual flumes and cabin laboratories (Figure S1) for automated and physical sampling [15]. Online and off-line sampling and analysis is principally designed around determining fluxes of macro-nutrients (nitrogen and phosphorus) suspended sediment and carbon. However, frozen water samples were used in this study to determine soluble concentrations of key trace metals as micronutrients. Automated records of discharge and turbidity, combined with measured soil concentrations, were used to determine particulate metal losses. In addition, a meteorological station at the centre of the site (Figure 1) provides a suite of weather variables, including rainfall measurements used in this study.

The timeline of each system's treatment are as follows:

- From April 2011 to March 2013, all three pasture-based livestock farming systems were as one (permanent pasture) with no separate treatments in operation.
- From April 2013 to September 2015 then on to April 2019, two of three systems were gradually transitioned, one re-sown with high sugar grasses (Red system), the other re-sown with high sugar grass, white clover mix (Blue system). The remaining (Green) system continued as permanent pasture with a wide variety of plant species (including *Agrostis stolonifera*, *Alopecurus geniculatus*, *Dactylis glomerata*, *Holcus lanatus*, *Lolium perenne*, *Phleum pratense*, *Poa annua*, *Poa trivialis*, *Cardamine pratensis*, *Cerastium fontanum*, *Cirsium arvense*, *Juncus effusus*, *Ranunculus repens*, *Rumex crispus*, *Rumex obtusifolius*, *Veronica serpyllifolia*, *Taraxacum officinale*, *Trifolium repens*).
- From April 2019, the Red system transitioned to an arable system growing human edible crops, initially winter wheat.

The data used in this research covered late 2019 to early 2020, and therefore captures the switch from pasture to

arable for the Red system and offered the opportunity to assess the impact of ploughing of grassland on loss of particulate and dissolved trace elements from agricultural soils.

A combination of runoff samples already collected during wet weather events and soil and fertiliser sampling across a number of soil types was used to generate a trace metal micronutrient mass balance. Based on known crop and animal nutrition requirements, the data is assessed to determine whether the soils are deficient in these key micronutrients.

2.2. Selection of micronutrients

A large number of trace elements were analysed as part of the work, too many to assess in detail within a single manuscript. Based on data quality and levels of interest, cadmium, copper, manganese, nickel, selenium and zinc were selected for the mass balance assessment (Table S1). Copper, nickel, selenium, zinc and manganese are all essential elements [16]; whereas cadmium is a Water Framework Directive Priority Hazardous Pollutant where discharges to water are required to be reduced and eliminated. There is also significant interest in understanding the wider source apportionment of trace elements entering the aquatic environment via diffuse sources [5].

2.3. Catchment selection

Analyses were restricted to 11 of the 15 catchments due to a combination of poor quality of automated data for some catchments during the study period, and limitations in the resources allocated to undertake water sample analyses. However, the combined area of catchments contributing to each Field System was similar ($18.8 > \text{ha} < 20.5$; Table S2).

2.4. Period of study and rainfall events

This study examines the flux of selected micronutrient metals over the winter of 2019–2020. This period was selected as it facilitates the examination of the effects of the Red system's transition from pastoral to arable land, and a direct comparison with the pastoral Blue and Green systems. Sampled storms are numbered sequentially (starting from 2017). We focus on five storm events, from Storm 17 in October 2019 to Storm 21 in February 2020 which offered a range of intensities, but with similar durations (Table S3). Total rainfall during each storm event ranged (Table S3, Figure 2) from 15.6 mm (Storm 19) to 48.6 mm (Storm 21).

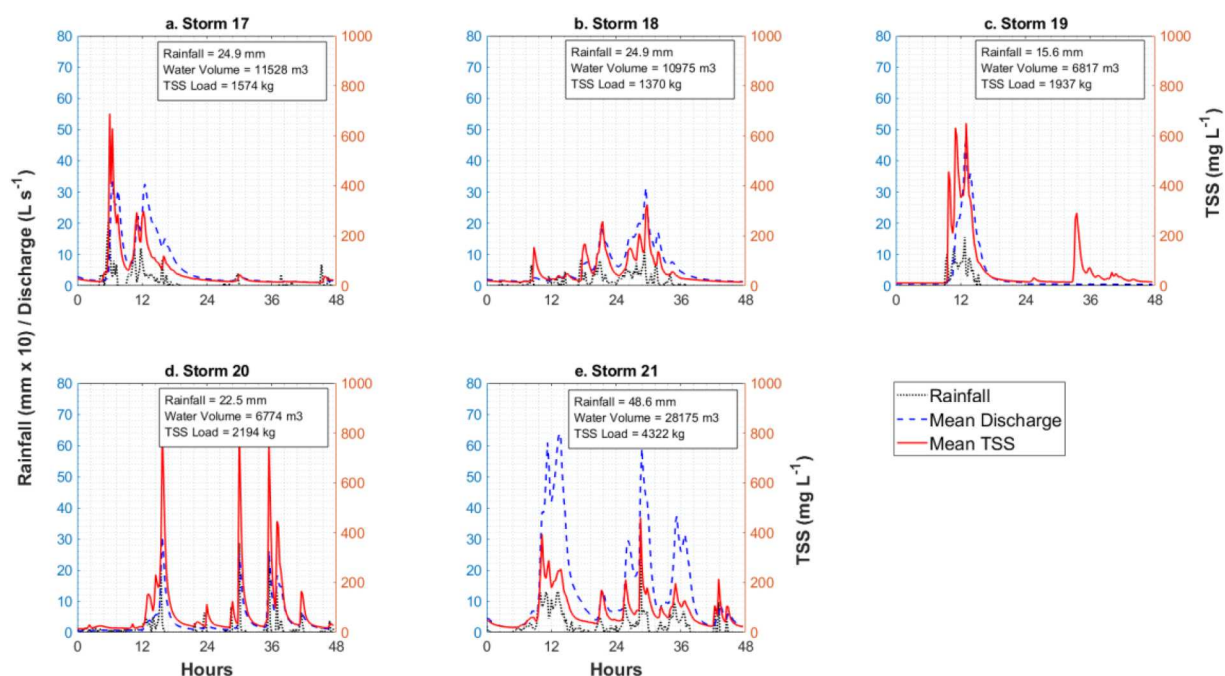


Figure 2. Rainfall, total suspended solids concentrations and mean discharge for all catchments per storm.

2.5. Sample collection

Through the analysis of stored water and soil samples and existing raw data, combined with a collection of manure and soil samples, a mass balance for each farm system was generated, yielding estimates of the flux of trace metals through the different farming systems in response to different storm events.

- (1) Soil samples were collected at 20 locations based on an evenly spaced 5×4 m grid (Figure S2) within each of the fields on the Farm Platform. Where catchments spanned two fields, a mean value for the catchment was used in analysis. Areas near gateways, water troughs, hedgerows, or areas where supplementary feeding may have occurred, or livestock congregate were avoided. Samples were collected using a 10 cm deep soil pot corer. The total soil collected from each field weighed at least 600 g fresh weight.
- (2) Water samples were collected from flumes using stage-triggered ISCO autosamplers. Samples were retrieved within 48 hrs of the start of the storm event and frozen at -18 °C. The flow-triggering allowed samples to be collected when the discharge either increased or decreased by a pre-set amount, either on the rising or falling limbs. Sampling continued until all 24 bottles in the automated sampler were filled or the sampler was collected, which was typically over a 48 h period. Flux was examined across the period for each storm to ensure the whole

rainfall event and response was captured. Stored runoff samples were analysed to determine the concentration and total mass of soluble trace metals lost during each storm. Five water samples were selected across the storm event, corresponding to first flush, rising limb, peak, falling limb and base flow after the storm (Figure S3).

- (3) Particulate trace metal losses were indirectly measured using a combination of automated turbidity measurements taken across the storm events at 15-min intervals (data retrieved from the North Wyke Farm Platform data portal), and measured soil metal concentrations in each connected field. Turbidity time series were converted into total suspended sediment concentration (TSS – mg/l) with relationships developed using 100 mL samples of runoff from the flumes sampled over a range of flow conditions [17].
- (4) Samples of farmyard manure (cattle and sheep) associated with the pasture systems were collected along with inorganic phosphate fertiliser used in all the systems. Five sheep and five cow samples of excreta were collected in each case ($n=20$) and their contribution to trace metal supply established.

Data were collated and a mass balance undertaken to estimate flux of trace metals through the different farming systems. Based on the data analysis it was possible to determine the impact of farming practices on the

application, retention and loss of selected trace metal micronutrients.

2.6. Sample analysis

All solid samples (soil, manure, inorganic fertiliser) were dried at 40°C for 72 h and sieved through a 2 mm plastic sieve to remove gravel-sized materials before storing until analysis. Prior to analysis all solid samples were digested with *aqua regia* to solubilise their trace elements. All equipment was washed in a 24-hour 10% Nitric Acid (Ultra-pure) bath and then rinsed out with deionised water and Milli-Q (>18 MΩ.cm) water and left to air dry.

With each batch of digestions, blank replicates and a certified reference material (certified reference material EnvironMat Contaminated Soil SS-2) were analysed to ensure analytical quality control. Each sample (0.5 g ± 0.05 g) was weighed into 50 ml glass beakers. Following the methodology described by Chen and Ma [18], 6 ml of *aqua regia* was added to each sample with a ratio of 3:1 of Fisher Scientific analytical grade, 39% hydrochloric acid and 70% nitric acid. Samples were left for cold digest for 1 h with a glass watch glass placed on top of each beaker. Each batch was then placed on a hot plate and heated to boiling point for one hour with subsequent rotations to maximise heating and prevent drying out.

Once cooled, samples were transferred into 25 ml volumetric flasks through a Sartorius 388, folded, acid resistant, quantitative filter paper. The flasks were made up to 25 ml using milli-Q water, capped and stored in a cool dry place until analysis. *Aqua regia* is an effective acid-based extraction method, accepted to leach all available trace elements from soil, though may not dissolve some mineralogical material, but was considered appropriate for agriculturally relevant trace element loss [19,20].

For aqueous matrices, frozen samples previously collected from the North Wyke Farm Platform flumes were defrosted and sub-samples were stored in 50 ml acid-cleaned polythene centrifuge tubes. Prior to analysis, samples were filtered through 0.4 µm polycarbonate membranes.

All samples were analysed using high resolution inductively coupled plasma optical emission spectroscopy (ICP-OES; digests) and/or inductively coupled plasma spectrometry (ICP-MS; aqueous samples). The instruments were calibrated using Labkings quality control standard 26 and iron stock standard PlasmCal grade from QMx and then checked every 10th sample during analysis. Analysis was carried out in

triplicate using indium for internal calibration of the ICP signal [21].

2.7. Data analysis

The drainage from each catchment passed over a flume with a flow gauge to allow discharges from each catchment to be measured for each storm event. The total discharges were multiplied by the trace element concentration to generate a load per event. All calculations were across 48 h to provide consistency. It was not possible to integrate loads over time, owing to a lack of discrete samples. However, there appeared to be no obvious trends in the trace element concentrations across the storm events, and so a mean concentration for each event was used to generate the overall load (Figures S4 to S8 and Tables S4). Loads were normalised by dividing the hydrological area of the field (in hectares) and converted to per day to allow for varying durations of the rain events and facilitate comparison with other studies.

Turbidity data were converted to total suspended solids using the calculation noted above. The loading for particulate metals could then be calculated by multiplying the mean soil concentration for each of the 11 catchments by the calculated suspended solids concentration. As with the dissolved loads, normalisation to per hectare per day allowed cross-comparison of data.

Annual loadings of the trace elements from atmospheric deposition were calculated based on concentrations in nearby rainfall [22] multiplied by the annual rainfall per hectare. Loadings of trace elements from animal manure were calculated from annual average animal numbers (sheep, lambs and cattle) per type of farm system multiplied by the measured trace element concentration in the manure for direct voiding onto the soil. For additional farm yard manure loads, data are collected by Rothamsted for application rates which were then multiplied by the observed concentrations. To calculate the likely additions of trace elements to the soil, that would be available as part of the runoff load, applications and livestock numbers were aggregated across the February 2019–2020 period. This covered the transition of the Red farm system from pasture to arable where the grass was sprayed off in August of 2019. Consequently, although the Red system is classified as arable, there are trace elements from livestock manures and fertilisers attributed to these fields from before August 2019 when the fields were still pasture.

Losses of dissolved and particulate trace elements were calculated based on the analytical data detailed

Table 1. Summary of mean discharge, total suspended solid (TSS) concentrations and total sediment loads for each catchment for each storm.

Storm	17	18	19	20	21
Dates	2-3/11/2019	22-23/11/2019	16-17/01/2020	9-10/02/2020	15-16/02/2020
Total rainfall (mm)	24.9	24.9	15.6	22.5	48.6
Water volume (m ³)	11,528	10,975	6817	6774	28,175
Flume (catchment area, ha)					
			Mean discharge (l/s)		
1 (5.0)	6.8	5.0	3.4	3.2	13.5
2 (6.79)	7.3	6.4	4.2	4.0	17.6
3 (6.83)	7.6	10.9	5.4	6.3	17.3
4 (8.08)	11.3	10.0	6.1	6.5	25.3
5 (6.73)	9.4	7.6	4.9	4.8	20.7
6 (3.95)	3.1	2.6	2.2	1.3	9.7
7 (2.71)	3.0	2.9	1.8	1.6	7.9
8 (7.33)	No data	8.6	5.1	6.1	21.6
9 (7.91)	8.9	6.7	4.5	4.0	22.3
10 (1.91)	1.5	1.5	1.1	0.8	3.8
11 (1.85)	1.7	1.4	0.7	0.7	4.4
Flume (catchment area, ha)					
			Mean Total suspended solids (TSS, mg/l)		
1 (5.0)	74	76	89	112	123
2 (6.79)	132	184	233	290	321
3 (6.83)	194	210	141	191	204
4 (8.08)	21	16	63	22	24
5 (6.73)	29	28	25	36	34
6 (3.95)	29	11	19	23	24
7 (2.71)	32	27	39	46	53
8 (7.33)	No data	18	28	36	31
9 (7.91)	22	37	26	33	30
10 (1.91)	72	108	86	99	95
11 (1.85)	20	28	23	21	30
Flume (catchment area, ha)					
			Total sediment load (kg)		
1 (5.0)	176	136	218	209	511
2 (6.79)	355	400	768	823	1799
3 (6.83)	937	888	586	839	1099
4 (8.08)	60	36	314	37	134
5 (6.73)	87	54	66	61	178
6 (3.95)	27	9	25	12	60
7 (2.71)	26	18	42	25	96
8 (7.33)	No data	36	80	80	144
9 (7.91)	54	51	59	45	148
10 (1.91)	44	63	75	58	122
11 (1.85)	11	14	12	5	32

above, but multiplied up from the 137 mm of total rainfall across the five studied events to the total annual rainfall of 979 mm per year.

All statistics were generated using MatLab statistical software.

3. Results and discussion

The data above could therefore be translated into loads for each element generated for each catchment for each storm event. This allowed the comparison of rain intensity and duration with loads of trace elements lost from the field (total and dissolved).

Figure 2 provides a summary of the mean discharge from the 11 catchments for each of the storm events. As is generally the case, storm events vary considerably in their duration and intensity. As can be seen, Storm 17 started with some intense rain followed by three further showers between 24 and 48 h. Storm 18 had relatively consistent rain between 10 and 36 h, whereas storm 19 was characterised by a short duration heavy downpour after

around 12 h. Storm 20 exhibited heavy spates of rain after 14, 30, 36 and 40 h and finally storm 21 showed the most persistent rain, almost twice the next highest in terms of total accumulation over 48 h (Table 1). Although the patterns of rainfall varied for storms 17–20, the overall accumulated mm of rain were similar (Table 1).

Summing the total rainfall across each storm examined shows that the five events accounted for 15% of the annual mean average rainfall since records began in 2012 (887 mm/yr \pm SE 62.3 mm), and 14% of both 2019 (988 mm) and 2020 (999 mm) total rainfall. Scaling up the soil loss rate to one year provides a mean average across all field systems of 4.1 kg/ha/day (Table 2). This is in line with reported values of 4.4 kg/ha/day for the UK [23]. However, soil loss from the Red System, which was converted to arable in the spring prior to the study period, was 9.7 kg/ha/day – more than twice this UK mean value. This is 13% higher than the maximum soil loss rate reported by Pulley & Collins [17] on ploughed fields within the Farm Platform over 2013–2015, but similar to typical erosion rates on

Table 2. Summary of soil erosion rates by field management system.

	All	Red	Green	Blue
Total soil loss (kg)	12,245	10,105	1161	979
Catchment area (ha)	59	20.5	18.8	19.8
Calculation period (hour)	48	48	48	48
Total rainfall (mm)	137	137	137	137
Annual rainfall (mm)	979	979	979	979
Soil loss (kg/ha/mm rain)	1.5	3.6	0.5	0.4
Soil loss rate (kg/ha/day)	4.1	9.7	1.2	1.0
UK average (kg/ha/day)	4.4			

https://ec.europa.eu/eurostat/statistics-explained/index.php/Agri-environmental_indicator_-_soil_erosion

arable land of ~10 kg/ha/day reported by van Oost et al. [24]. Arable crops have been shown to be responsible for soil loss of up to 60 kg/ha/day for carrots grown in Turkey [12]. Conversely, soil losses for the Green (1.2 kg/ha/day) and Blue (1.0 kg/ha/day) systems were notably lower than the UK average for all agricultural systems but within typical rates for grassland of 0.46–3.78 kg/ha/day [25–27]

When trace metals enter soils they undergo a range of possible reactions that depend up on the original form of the metal being added and the physico-chemical characteristics of the receiving soil. The form of these main reactions is illustrated in Figure S9. The fraction of the trace metal that is potentially bioavailable to organisms in the soil is present in the soil solution and also that proportion held on surface exchange sites of soil particulate material. This 'labile' fraction of trace metal has been shown to vary greatly in uncontaminated soils as a proportion of the total (strong acid extractable) concentration from <2% to 99% [28–29]. The variability in ambient soil quality parameters which control the partitioning and mobility of trace elements means there is limited relationship between trace element concentrations in soil solution and the total levels in the soil from geogenic sources or in material added to soil. Geogenic trace elements are subjected to the same reactions as shown in Figure S9. Sorption and precipitation move metals from the solution to the solid phase (soil surfaces); ageing moves metals from soil particulate surfaces to deeper and more strongly binding locations within the solid phase through (a) surface pore diffusion, (b) solid-state diffusion, (c) occlusion of metals through precipitation of other phases, (d) precipitation of new metal solid phases and (e) occlusion in organic matter [30].

The large variation between the amount of bioavailable trace element compared with the total metal has been shown to be dependent on two key factors:

- (1) Soil type (such as pH, organic carbon content, cation exchange capacity, clay content), and;
- (2) The time between the addition of a soluble form of the trace element to soil and tests, also called ageing [31].

Consequently, there is significant variability in the proportion of the total soil trace element that is present in the exchangeable pool [29]. Krishnamurti and Naidu [32] measured total copper and soil solution copper concentrations in 11 South Australian soils and noted ranges of between 3.8 and 18.8 mg/kg and 0.05 and 0.4 mg/l, respectively (1.3–2.1% of copper in solution). McGrath et al. [33] investigated the influence of organic matter, in a copper (and manganese and zinc) amended peat soil on the concentrations of copper in soil solution as extracted using 0.01 M CaCl₂ solution. The highest percentage of soil solution copper was extracted from soils amended with up to 20 mg/kg of copper, but this was only 0.1% of the total.

For this study, mean concentrations of the trace elements in the soil (Table 3), were generally of a similar magnitude to one another, with a few exceptions, for example for the Green system, there were elevated cadmium concentrations in two of three fields studied and manganese in one of the three. For the Blue system, there was elevated zinc concentration in one of the fields and for the Red system, high zinc concentration was measured in one of the fields. These variations of up to typically a factor of 2, and may reflect some inconsistencies in the field soil profiles and/or variations in applications of fertilisers and manures. Soil data

Table 3. Mean soil concentrations for the trace elements of interest (gray cells are less than the limit of detection).

Field	Soil trace element (mg/kg)					
	Cd	Cu	Mn	Ni	Se	Zn
1	0.004	33.3	386	27.0	1.07	125
2	0.002	34.2	437	28.6	0.76	76
3	0.072	30.4	641	24.8	1.06	74
4	0.086	33.3	1244	23.7	1.03	69
5	0.082	35.2	455	24.5	1.06	68
6	0.004	36.2	323	24.0	0.65	75
7	0.002	37.6	417	26.8	0.74	79
8	0.002	33.1	536	23.0	0.93	77
9	0.021	38.3	458	24.8	1.00	67
10	0.029	28.2	316	24.2	0.99	70
11	0.011	38.4	483	26.0	0.92	181
Red	0.03	31.5	445	26.1	0.97	86
Green	0.06	34.9	674	24.1	0.91	71
Blue	0.01	36.9	474	25.1	0.89	101

were collected from the pasture systems in 2017 when the blue system was high-sugar grass + legume mix without use of nitrogen fertiliser, the Green system was permanent pasture with N fertiliser and the Red system (prior to turning to arable) was high-sugar grass with fertiliser [1]. Comparison with the Blue and Green systems was possible, but not the Red owing to very different management. Mean zinc concentrations for high and low micro-nutrient areas within the fields were 61–85 mg/kg for the Blue system and 73–92 mg/kg Green system; here the Blue system soil zinc was 101 mg/kg (± 52 mg/kg – 95% confidence range) and the Green system 71 mg/kg (± 4 mg/kg – 95% confidence range). The wide variability in places meant there was no significant difference in the soil zinc concentration.

Copper soil concentrations for this survey was 37 mg/kg (± 2.5 mg/kg – 95% confidence interval) for the Blue system, 35 mg/kg (± 1.7 mg/kg – 95% confidence interval) for the Green system and 31.5 mg/kg (± 2.7 mg/kg – 95% confidence interval) for the Red system. These compared well with the previous data of 14–36 mg/kg; 23–30 mg/kg and 13–27 mg/kg for the Blue, Green and Red systems respectively.

Manganese concentrations in the soil varied significantly within the two surveys. This study generated means and 95% confidence intervals of 474 (± 49 mg/kg) for the Blue system, 674 \pm 564 mg/kg for the Green system and 445 \pm 137 mg/kg for the Red system, compared with 313–852 mg/kg, 342–802 mg/kg and 235–983 mg/kg for the Blue, Green and Red systems respectively in the study by Thomas et al. [1]. The wide variations in observed concentrations meant there were no significant differences between data from 2017 and 2020.

Selenium is much less abundant than copper and zinc for example, and was present at concentrations of 0.89 mg/kg (± 0.11 mg/kg – 95% confidence interval) for the Blue system, 0.91 mg/kg (± 0.26 mg/kg – 95% confidence interval) for the Green system and 0.97 mg/kg (± 0.14 mg/kg – 95% confidence interval) for the Red. These values were very similar to the previous study that reported 0.9–1.2 mg/kg, 0.9–1.2 mg/kg and 1–1.3 mg/kg for the Blue, Green and Red systems respectively [1].

Cadmium may be found as an impurity in inorganic phosphate fertilisers [34] and zinc and manganese are essential elements present in fertilisers and feeds [35]. A survey of almost 5700 UK soils generated mean concentrations of Cadmium 0.8 mg/kg; Copper 23.1 mg/kg; Nickel 24.5 mg/kg, and; Zinc 97.1 mg/kg [35]. These are in line with those reported from the North Wyke Farm Platform for copper, nickel and zinc, but higher

than values measured for cadmium. This may reflect the older data in the EA survey when cadmium, as Priority Hazardous Substance, was not as well controlled as it is now. Furthermore, Cd detection limits for the EA dataset were only 0.2 mg/kg which may have contributed the reported higher mean concentrations. The North Wyke Farm Platform soils are typically clay-loam, which can have higher trace element concentrations owing to finer particulates having a stronger affinity for metals than sandier soils [36]. It may therefore be concluded that concentrations for the trace elements are not atypical of those found in the UK in general.

With soil loss loads calculated, the amount of particulate trace elements carried with it may be calculated (Figure 3). Unsurprisingly, the arable (Red system) leads to greater suspended solids loss and therefore associated trace elements. Loads per hectare varied across the different storm events, with Storm 21 having the highest, reflecting the more intense rainfall over the 48 h period. The high sugar grass/white clover sown Blue system seems to retain solids and trace elements more effectively than the Green, permanent pasture system with a larger variety of species present. Higher manganese and cadmium loads from the Green system reflects the soil concentrations rather than the sediment loading.

From a soil health point of view, the dissolved trace element loading is potentially of more importance owing to its bioavailability for uptake into plants. The slightly acidic nature of the soils (typically 6.8 for all of the three systems (Table S6). would increase bioavailability but also solubility and therefore mobility. It was therefore important to also calculate the loads of dissolved trace elements being lost from the different systems. Samples were taken at 5 points during each rain event: base flow, first flush, the rising limb, peak flow and falling limb (Figure S3). The dissolved metal concentrations observed would be expected to follow a trend determined by the soil-water partition coefficient (K_p), the rainfall which would act as a diluent, the discharge flow from the catchment, linked to the rain intensity and water holding capacity of the soil and the kinetics of exchange. The data are summarised for field flumes 1 and 2 (Red system), 6 (Green) and 7 (Blue) as examples below (Figure 4) with the full dataset plotted against discharge volume in Figure S4 to S8).

Overall, there is relatively little variation in concentrations of the dissolved trace elements across any given flume for each of the rain events, which is surprising. Concentrations of all of the trace elements of interest were generally elevated for Storm 18 at Catchment 7 during the peak flow, but not for the more intense Storm 21. Most of the trace elements show a decreasing trend

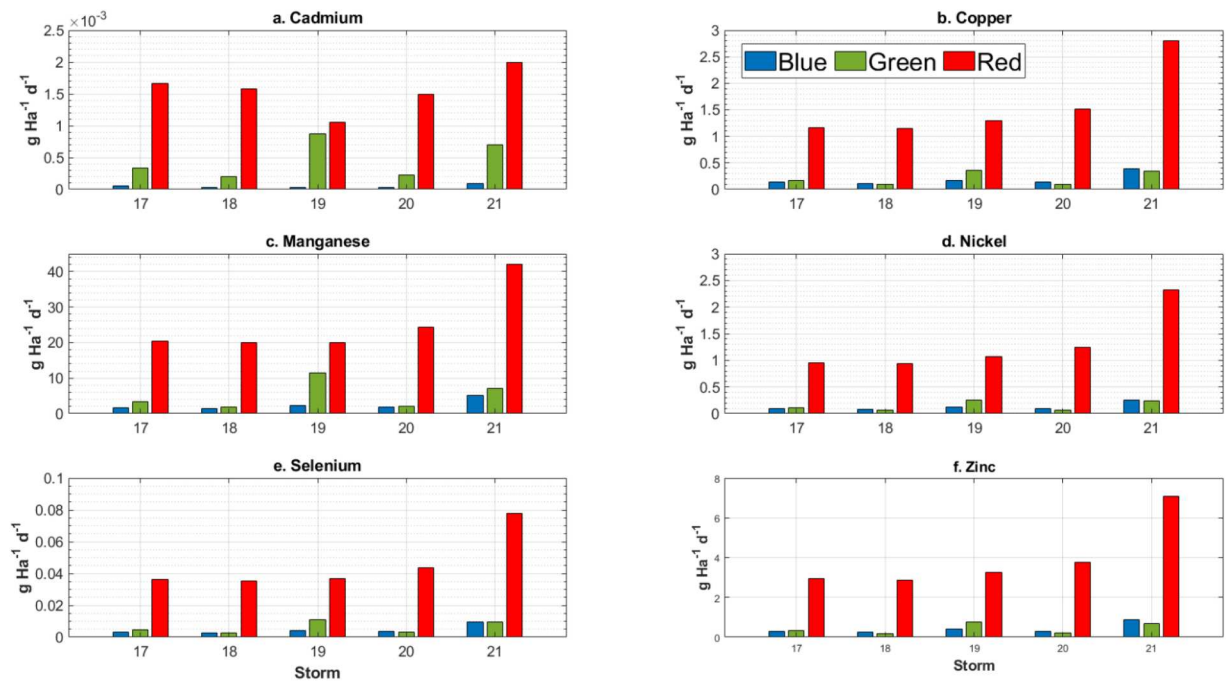


Figure 3. Mean loads of particulate trace elements discharged for the 11 flumes for the five storm events.

in concentrations during Storm 18 for Catchment 1 (unlike Storm 21) which may reflect less dilution from the less intense rainfall. The profile of the Storm 18 storm event was also quite different, with initially only a small amount of discharge which may explain the reduced dilution and hence higher concentration observed. The relatively constant concentration of trace elements across the storm events meant that a mean concentration could be used to multiply by the volume of water discharged to calculate a load, with which to compare with particulate loads.

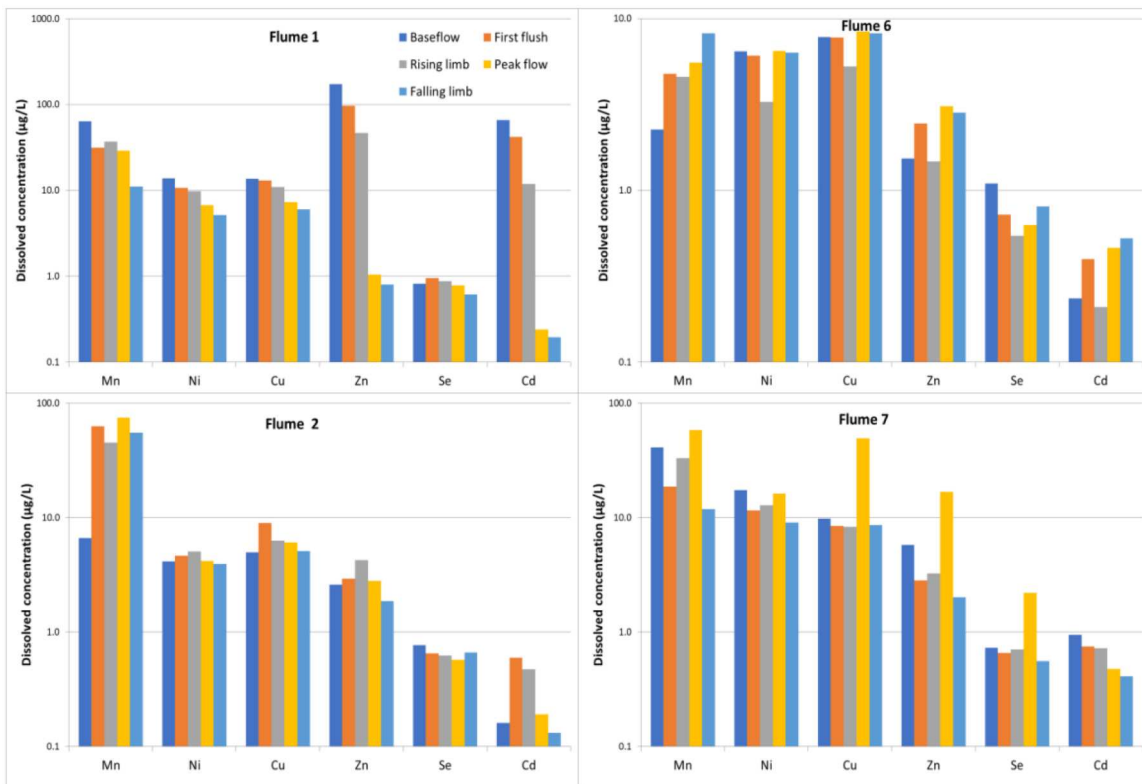
There are, however, significant differences in observed concentrations when aggregating the different catchments into the three different management methods (Table 4). Concentrations varied between a factor of approximately 2.5 (Ni and Se) and almost 10 (for Mn) and did not reflect the amount of particulate material being lost from the fields (i.e. the change to arable farming in the Red system did not lead to higher dissolved concentrations).

Owing to the dissolved concentrations being relatively independent of the discharge volume, the dissolved loads tend to reflect the magnitude of the rain events, hence Storm 21 generating significantly higher loads (Figure 5, Table S5). The figure below shows that almost all of the cadmium lost from all of the catchments is in the dissolved phase (>90%), compared with less than 10% of zinc for the Red (arable) field systems. There is a clear difference between the permanent pastures (Green and Blue systems) and

the red arable ones, where for all of the elements, the percentage dissolved is significantly lower (other than for cadmium). This difference in proportions was driven by relatively low dissolved concentrations (zinc), higher particulate loads (zinc, nickel) or higher dissolved concentrations (manganese, copper to a degree) or a combination of these.

Such variations are best described via the partition coefficients, calculated by dividing the particulate concentrations by the dissolved ones (K_p). The partition coefficients range from approximately 100 l/kg for cadmium to 10's of thousands for zinc. Assuming the partitioning comes to an equilibrium (rarely actually the case outside of a laboratory) then the K_p should be relatively constant across a range of aqueous and particulate concentrations, which is largely demonstrated in Figure 6. Despite there being significant variations in dissolved and particulate concentrations the K_p s remain closely aligned, with the exception of cadmium for the Blue system which exhibited relatively high dissolved cadmium concentrations. These observed K_p 's are in line with previously reported values for soil:water. Log K_p values for cadmium range from 0.1 to 5, with a median of 2.9; copper from 0.1 to 3.6 with a median of 2.7; nickel 1 to 3.8 with a median of 3.1; selenium -0.3 to 2.4, median of 1.0; zinc -1.0 to 5 with a median of 3.1 [37]. The wide variations are driven by differences in soil pH, organic carbon concentration, ionic strength and particle size distribution. K_p for zinc and nickel for example varies from 10 to 10,000 l/kg between a pH of

Storm 18



Storm 21

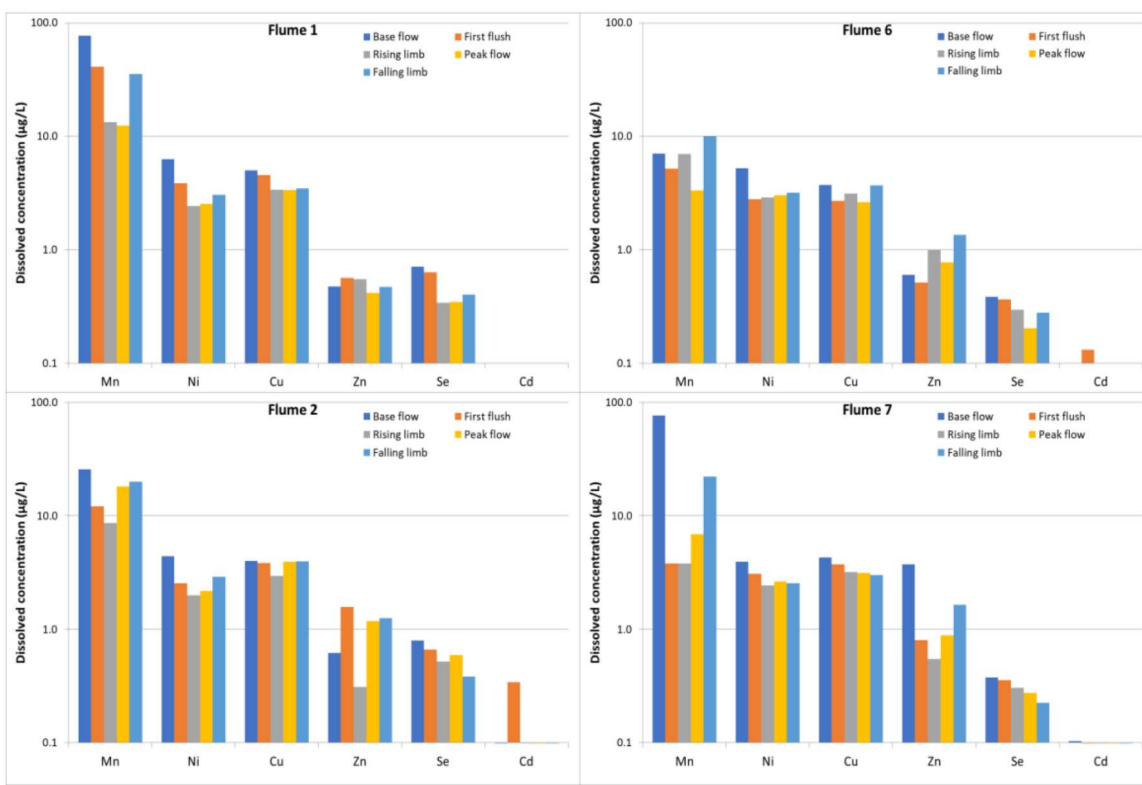


Figure 4. Concentrations of trace elements across the storm events for selected catchments (Flumes 1, 2, 6 and 7) for significantly different storms (Storm 18 (top) and Storm 21 (bottom)).

Table 4. Summary of dissolved concentrations across the five storm events.

Storm	Cd	Cu	Mn	Ni	Se	Zn
17						
Red	0.13	9	18.6	8	0.5	3.9
Green	0.14	10.7	27.8	7.4	0.4	6
Blue	0.15	9.3	30.7	8	0.4	9.2
18						
Red	0.3	7.2	37.9	6	0.7	1.8
Green	0.26	7.6	10	5.8	0.7	2.6
Blue	0.67	8.8	21.5	9.8	0.8	3
19						
Red	0.14	6.6	84.1	5.1	0.8	2.1
Green	0.13	4.9	16.4	4	0.6	1.9
Blue	0.18	5.4	24.1	5.5	0.6	2.4
20						
Red	0.28	6.9	133.3	7.4	1	2.6
Green	0.17	7.3	66.3	6.2	0.7	2.8
Blue	0.21	7.1	57.7	8.6	0.6	3.4
21						
Red	0.07	3.3	22.9	2.8	0.5	0.6
Green	0.13	4	28.5	2.5	0.4	1.7
Blue	0.08	3.2	11.2	2.7	0.3	1.1

4 and 8. Copper on the other hand had a more narrow range of 100–10,000 across a pH of 5–8, but was more influenced by organic carbon content, which was relatively consistent across the field systems but present at concentrations in excess of the dissolved copper concentrations therefore likely indicating the occurrence of a degree of complexation, stabilising copper in the dissolved phase (Table S6) [38]. Cadmium K_p has been reported to have a similar range (10–8000 l/g) between a pH of 4 and 8 [39,40].

For slightly acidic soils such as those in this study, slightly lower K_p would be expected for elements such as cadmium, zinc, nickel and copper. Selenium will be present as anions and so would be expected to respond differently to pH changes, with less solubility and bioavailability at lower pH [1].

Manganese K_p has been reported to vary between 130 (clay, high organic carbon) to 22,000 l/kg (clay till) in Swedish soils [41]; the latter being similar in soil type and K_p to this study. A similar value of 3000 l/kg was reported for nickel for clay till. Selenium K_p for the Swedish soils ranged from 10 (clay till) to

140 (high organic carbon – 33% loss on ignition) l/kg; lower than the ~1000 l/kg observed in this study. Soil amended with sewage sludge then monitored for leaching reported percentage of nickel and copper in the dissolved phase as approximately 70%, similar to the green and blue field systems in this study, but the per cent dissolved for zinc was 80%, which was higher than reported here, potentially owing to high concentrations of zinc present in sewage sludge [42].

The partitioning with the soil is time dependent, particularly for elements such as selenium which may occur in more than one form and be present in anionic forms such as selenate (VI). Experimental data show that the transfer towards less labile phases is controlled by slow processes (potentially decades) limiting the overall sorption of selenium in soils [43]. Consequently, short term laboratory partitioning experiments would result in underestimation of selenium sorbed over time, which puts emphasis on field-based data. For example, the K_p of field based measurements ranged from 797 to 1325 l/kg, for slightly acidic grassland soils, which is

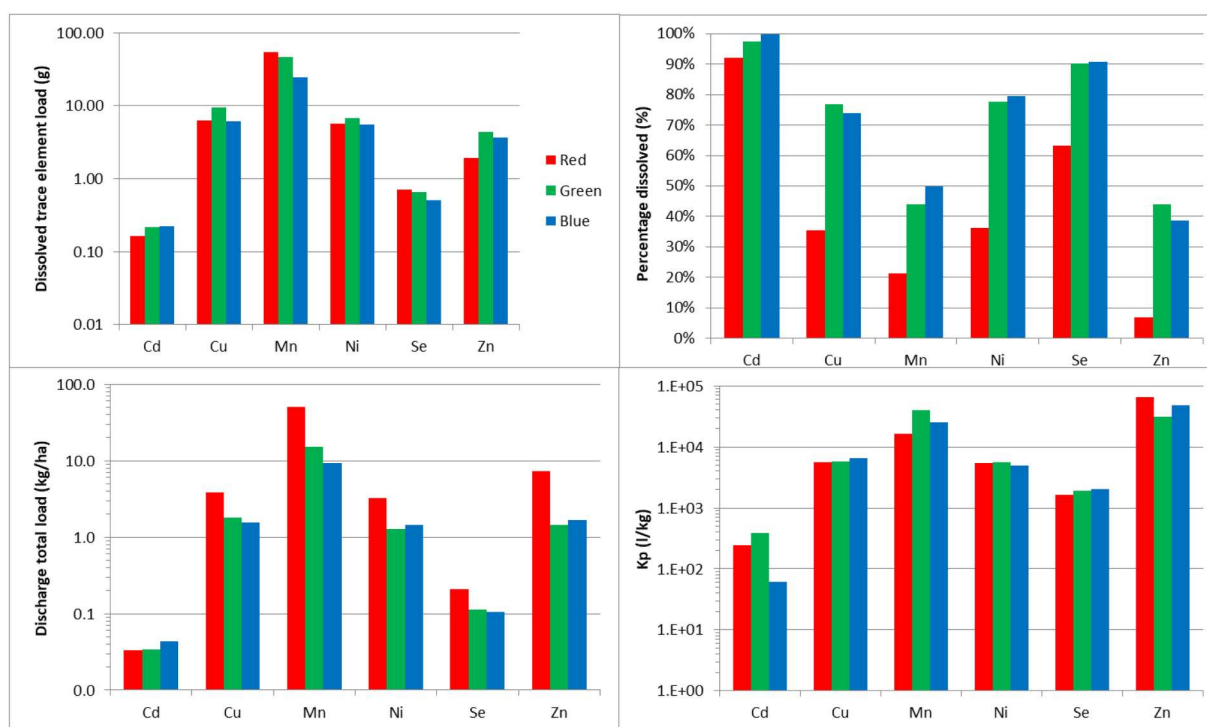


Figure 5. Total dissolved load (top left), percentage of load discharged as dissolved (top right), total load of trace element discharged per hectare (bottom left), and partition coefficients (bottom right) for the three different systems across all of the five storm events.

very similar to the Kps measured in this study for similar soil type.

Trace elements that are lost from the soil may be resupplied into the soil solution from the pool of labile elements present in the soil in order to maintain equilibrium.

A key aspect of the study was to assess the loss of essential elements (copper, manganese, nickel, selenium and zinc) or potentially toxic elements (cadmium) from the soil. Concentrations in atmospheric deposition were available from the literature (Table S7), while concentrations in manures and fertilisers were collected as part of this study (Table S8). The application rates of manure (direct voiding from livestock in the fields plus application of farmyard manure) and inorganic fertiliser were obtained from Rothamsted Research databases (Table S9). The amount of manure produced per animal per day was obtained from literature data [5].

For all of the trace elements, the farmyard manure was the main source, followed by direct voiding, with atmospheric deposition and inorganic fertiliser inputs typically an order of magnitude lower (Figure 6 top and S10). These loadings were compared with the loss rates to generate a percentage loss per annum which showed significant differences (Figure 6 top). As would be expected the calculated losses (of total trace element) reflected the partition coefficients of the trace elements with manganese and

zinc having the lowest losses. Cadmium exhibited the lowest partition coefficients, but the percentage loss ranged from 6% to 16% which was lower than those for nickel and selenium which had higher Kp's (Figure 6 bottom). This is likely due to the fact that although a high percentage of cadmium in the runoff was in the dissolved phase, the lower loading to soil (particularly compared with nickel) meant there was less total loss. A greater percentage loss was observed for cadmium from the blue farm system, reflecting lower loading (particularly from farmyard manure and inorganic fertiliser) rather than higher loss.

For the other elements, the Red system exhibited highest loss from soil, which reflected the higher loss rate associated with the particulate fraction being lost from soil erosion from the arable system. Without measuring the uptake of the trace elements into the arable crops or the permanent grassland, it was not possible to undertake a full mass balance, however, uptake into biomass for the elements has been shown to be significant [7,42].

In terms of ecological impact, the relatively low loss rates of cadmium from each system is a positive outcome regarding impacts on waterbodies receiving runoff, even if what is leached is mostly soluble. Low levels of losses of copper and zinc, often of concern from a deficiency point of view with regard to plant

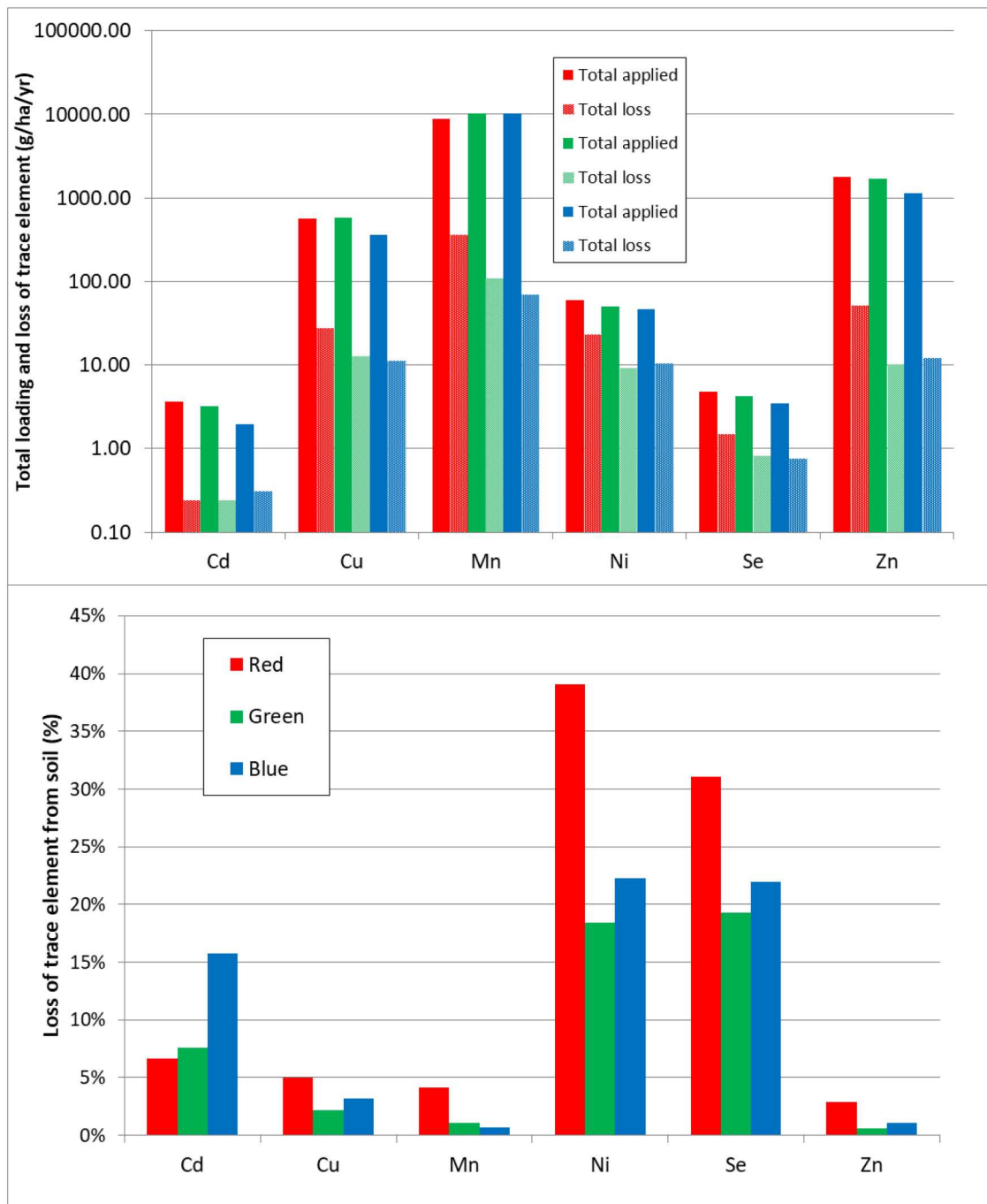


Figure 6. Annual loading of trace elements to soil for the Red system (top) and the loss of trace elements from soil as a percentage of annual loads for all systems (bottom). (Note there were no atmospheric deposition data for manganese and selenium).

and livestock nutrition, also may be considered a positive outcome. Manganese being relatively insoluble under oxic conditions, was only leached up to an estimated 4%. The trace element of most concern was therefore selenium for which up to 31% of that applied was estimated to be lost. Lower selenium concentrations in pastureland forage (compared with concentrated cereal feed) has been shown to lead to deficiency in livestock [44,45]. A 20–30% loss, particularly when it is dominated by the more bioavailable dissolved

fraction (up to 90%) suggests that this element is likely to provide the highest risk of nutritional deficiency.

4. Conclusion

This study has highlighted the importance of considering losses of trace elements from farm systems under different types of management. Soil erosion is an accepted concern world-wide, however, little data exist regarding the magnitude of losses of trace

elements, which may either be essential for crop growth and soil health or potentially toxic elements present as impurities lost to receiving waterbodies. Based on a comparison of inputs and losses from a controlled field environment, it is clear that trace elements are lost from field systems, particularly arable soils during heavy rain events. Elements such as cadmium are associated with the dissolved phase, whereas zinc is predominantly adsorbed to particulate material. The loss of trace elements is controlled by a combination of concentrations in the soil itself, the intensity of the rain, the likely partitioning of the element between the dissolved and particulate phases (driven by the physico-chemical properties of the element itself as well as the ambient conditions) and the soil management. Overall, comparing inputs and outputs, the data suggests that up to 40% of applied nickel is lost in soil runoff from arable fields, compared with less than 1% of zinc from pasture lands. The study highlights the importance of fully understanding the ability of fields to retain their soil as well as trace elements to avoid essential elements or potentially toxic elements being lost to receiving waters.

Acknowledgements

The authors would like to thank Dr Rob Clough for assistance in the analytical aspects of this work. The work was funded by Plymouth University's Seale Hayne Educational Trust. The North Wyke Farm Platform is a UK National Capability supported by the Biotechnology and Biological Sciences Research Council (BBS/E/C/000J0100 and BBS/E/RH/23NB0008). We also acknowledge the interests of the Ecological Continuity Trust (ECT), whose national network of LTEs includes the experiment on which this research was conducted.

Disclosure statement

No potential conflict of interest was reported by the author(s).

Funding

This work was supported by Seale Hayne Educational Trust.

Data availability statement

Data can be made available upon request.

ORCID

R. J. Schindler  <http://orcid.org/0000-0001-6870-0845>

References

- [1] Thomas CL, Darch T, Harris P, et al. The distribution of soil micro-nutrients and the effects on herbage micro-nutrient uptake and yield in three different pasture systems. *Agronomy*. 2021;11:1731. doi:10.3390/agronomy11091731
- [2] EC. European Commission. Priority substances daughter directive — Directive 2008/105/EC of the European Parliament and of the Council of 16 December 2008 on environmental quality standards in the field of water policy. 2008 [cited 2012 May 23]. Available from: <http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:348:0084:0097:EN:PDF>.
- [3] Comber S, Deviller G, Wilson I, et al. Sources of copper into the European aquatic environment. *Integr Environ Assess Manag*. 2022;19(4):853–1160. doi:10.1002/ieam.4700
- [4] Comber S. European source appointment of zinc. Water resources associates report. 2023.
- [5] Comber S, Smith R, Daldorph P, et al. Development of a chemical source apportionment decision support framework for catchment management. *Environ Sci Technol*. 2013;47(17):9824–9832. doi:10.1021/es401793e
- [6] Babscanyi I, Chabaux F, Granet M, et al. Copper in soil fractions and runoff in a vineyard catchment: insights from copper stable isotopes. *Sci Total Environ*. 2016;557–558:154–162. doi:10.1016/j.scitotenv.2016.03.037
- [7] Sadovnikova L, Otabbong E, Iakimenko O, et al. Dynamic transformation of sewage sludge and farmyard manure components. 2. Copper, lead and cadmium forms in incubated soils. *Agric Ecosyst Environ*. 1996;58:127–132. doi:10.1016/0167-8809(95)01007-6
- [8] Monteiro SC, Lofts S, Boxall A. Scientific/technical report submitted to EFSA: pre-assessment of environmental impact of zinc and copper used in animal nutrition; 2010 [cited July 2020]. Available from: <https://efsa.onlinelibrary.wiley.com/doi/epdf/10.2903sp.efsa.2010.EN-74>.
- [9] Smolders E, Six L. Revisiting and updating the effect of phosphate fertilizers to cadmium accumulation in European agricultural soils. *Heverlee: Fertilizers Europe*; 2013.
- [10] De Vries W, Römkens PFAM, Voogd JCH. Prediction of the long term accumulation and leaching of zinc in Dutch agricultural soils: a risk assessment study Wageningen, Alterra, Alterra-Report 1030. 2004; 93 p.
- [11] European Union Risk Assessment Report (Zinc Metal). JRC Scientific and Technical Reports, JRC 61245. 2008.
- [12] Quinton JN, Fiener P. Soil erosion on arable land: An unresolved global environmental threat. *Prog Phys Geogr*. 2023;0(0):1–26.
- [13] Rothamsted. North Wyke, Farm Platform, Rothamsted Research, Okehampton, Devon, UK; 2024. Available at: <https://www.rothamsted.ac.uk/national-capability/north-wyke-farm-platform>.
- [14] Hawkins JMB, Griffith BA, Sint HM, et al. The North Wyke Farm platform: design, establishment and development. Rothamsted Research; 2023a. doi:10.23637/rothamsted.98y1x
- [15] Hawkins JMB, Griffith BA, Harris P. The North Wyke Farm Platform: Fine Resolution (15-Minute) Hydrology and Water Quality Data. Rothamsted Research; 2023b. doi:10.23637/rothamsted.98y34

- [16] Tan LL, Nancharaiah YV, van Hullebusch ED, et al. Selenium: environmental significance, pollution, and biological treatment technologies. *Biotechnol Adv.* 2016;34(5):886–907. doi:10.1016/j.biotechadv.2016.05.005
- [17] Pulley S, Collins AL. Sediment loss in response to scheduled pasture ploughing and reseeded: The importance of soil moisture content in controlling risk. *Soil Tillage Res.* 2020;204:104746. doi:10.1016/j.still.2020.104746
- [18] Chen M, Ma LQ. Comparison of three aqua regia digestion methods for twenty florida soils. *Soil Sci Soc Am J.* 2001; 65:491–499.
- [19] Idera F, Omotola O, Paul U, et al. Evaluation of the effectiveness of different acid digestion on sediments. *IOSR J Appl Chem.* 2014;7(12):39–47. doi:10.9790/5736-071213947
- [20] Santoro A, Held A, Linsinger T, et al. Comparison of total and aqua regia extractability of heavy metals in sewage sludge: The case study of a certified reference material. *Trends Anal Chem.* 2017;89:34–40. doi:10.1016/j.trac.2017.01.010
- [21] Tokalioglu S, Clough R, Foulkes M, et al. Bioaccessibility of Cr, Cu, Fe, Mg, Mn, Mo, Se and Zn from nutritional supplements by the unified BARGE method. *Food Chem.* 2014;150:321–327. doi:10.1016/j.foodchem.2013.10.151
- [22] Aas W, Bohlin-Nizzetto P. Heavy metals and POP measurements, 2019. EMEP. Co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe. EMEP/CCC-Report 3/2021. 2021. Ref: O-7726, October 2021, ISBN 978-82-425-3057-8. ISSN 2464-3920.
- [23] Borrelli P, Van Oost K, Meusburger K, et al. A step towards a holistic assessment of soil degradation in Europe: coupling on-site erosion with sediment transfer and carbon fluxes. *Environ Res.* 2018;161:291–298. doi:10.1016/j.envres.2017.11.009
- [24] Van Oost K, Cerdan O, Quine TA. Accelerated sediment fluxes by water and tillage erosion on European agricultural land. *Earth Surf Process Landforms.* 2009;34:1625–1634. doi:10.1002/esp.1852
- [25] Whitmore AP, Rickson RJ, Watts CW, et al. Critical levels of soil organic carbon in surface soils in relation to soil stability, function and infiltration project SP0519 final report. London: Department for Environment, Food and Rural Affairs; 2004.
- [26] Bilotta GS, Krueger T, Brazier RE, et al. Assessing catchment-scale erosion and yields of suspended solids from improved temperate grassland. *J Environ Monit* 2010;12:731–739. doi:10.1039/b921584k
- [27] Evans R, Collins AL, Zhang Y, et al. A comparison of conventional and ¹³⁷Cs based estimates of soil erosion rates on arable and grassland across lowland England and Wales. *Earth-Sci Rev* 2017;173:49–64. doi:10.1016/j.earsci.2017.08.005
- [28] McLaren RG, Crawford DV. Studies on soil copper III. Isotopically exchangeable copper in soils. *Eur J Soil Sci.* 1974;25. doi:10.1111/j.1365-2389.1974.tb01108.x
- [29] Ma Y, Lombi E, Nolan AL, et al. Short-term natural attenuation of copper in soils: effects of time, temperature, and soil characteristics. *Environ Toxicol Chem.* 2006a;25:652–658. doi:10.1897/04-601R.1
- [30] ICMM. MERAG: Metals Environmental Risk Assessment Guidance. ICMM, London. International Organization of Motor Vehicle Manufacturer. 2020. World motor vehicle production by country and type data; 2007.
- [31] Ma Y, Lombi E, Oliver IW, et al. Long-term aging of copper added to soils. *Environ Sci Technol* 2006b;40:6310–6317. doi:10.1021/es060306r
- [32] Krishnamurti GS, Naidu R. Solid-solution speciation and phytoavailability of copper and zinc in soils. *Environ Sci Technol.* 2002;36(12):2645–2651.
- [33] McGrath SP, Sanders JR, Shalaby MH. The effects of soil organic matter levels on soil solution concentrations and extractabilities of manganese, zinc and copper. *Geoderma.* 1988;42:177–188. doi:10.1016/0016-7061(88)90033-X
- [34] Dharma-Wardana MWC. Fertilizer usage and cadmium in soils, crops and food. *Environ Geochem Health.* 2018;40:2739–2759. doi:10.1007/s10653-018-0140-x
- [35] EA. Environment agency report: Ambient background metal concentrations. For soils in England and Wales. Science Report: SC050054/SR. 2006. ISBN: 1844326101.
- [36] Shen JJ, Wang Q, Chen YT, et al. Evolution process of the microstructure of saline soil with different compaction degrees during freeze–thaw cycles. *Eng Geol.* 2022;304:106699. doi:10.1016/j.enggeo.2022.106699
- [37] Allison JD, Allinson TL. Partition coefficients for metals in surface water, soil, and waste. U.S. Washington (DC): Environmental Protection Agency Office of Research and Development; 2005. Contract No. 68-C6-0020.
- [38] Degryse F, Smolders E, Parker DR. Partitioning of metals (Cd, Co, Cu, Ni, Pb, Zn) in soils: concepts, methodologies, prediction and applications – a review. *Eur J Soil Sci.* 2009 Aug;60:590–612. doi:10.1111/j.1365-2389.2009.01142.x
- [39] Allen H, Chen YT, Li Y, et al. Soil partition coefficients for Cd by column desorption and comparison to batch adsorption measurements. *Environ Sci Technol* 1995;29:1887–1891. doi:10.1021/es00008a004
- [40] Lee SZ, Allen H, Huang CP, et al. Predicting soil-water partition coefficients for Cd. *Environ Sci Technol.* 1996;30:3418–3424. doi:10.1021/es9507933
- [41] Sheppard S, Long J, Sanipelli B, et al. Solid/liquid partition coefficients (K_d) for selected soils and sediments at Forsmark and Laxemar-Simpevarp. Svensk Kärnbränslehantering AB Swedish Nuclear Fuel and Waste Management Co; 2009.
- [42] Keller C, McGrath SP, Dunham SJ. Trace metal leaching through a soil–grassland system after sewage sludge application. *J Environ Qual* 2002;31:1550–1560. doi:10.2134/jeq2002.1550a
- [43] Tullo PI, Pannier F, Thiry Y, et al. Field study of time-dependent selenium partitioning in soils using isotopically enriched stable selenite tracer. *Sci Total Environ.* 2016;562:280–288. ISSN 0048-9697, doi:10.1016/j.scitotenv.2016.03.207
- [44] Hefnawy AEG, Tórtora-Pérez JL. The importance of selenium and the effects of its deficiency in animal health. *Small Ruminant Res.* 2010;89(2–3):185–192. doi:10.1016/j.smallrumres.2009.12.042
- [45] Orjales I, Latorre CH, Miranda M, et al. Evaluation of trace element status of organic dairy cattle. *Animal.* 2018;12:1296–1305. doi:10.1017/S1751731117002890