Catena 171 (2018) 426–439

Contents lists available at ScienceDirect

Catena

journal homepage: www.elsevier.com/locate/catena

The response of metal leaching from soils to climate change and land management in a temperate lowland catchment

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ARTICLE INFO

Keywords:
CENTURY model
Climate change
Leaching
Heavy metals
Soil organic matter
Spatial modelling

ABSTRACT

Changes in soil hydrology as a result of climate change or changes in land management may affect metal release and leaching from soils. The aim of this study is to assess the cascading response of SOM and DOC levels and metal leaching to climate change in the medium-sized lowland Dommel catchment in the southern part of the Netherlands. We implemented the CENTURY model in a spatial setting to simulate SOM, DOC, and water dynamics in topsoils of the Dutch portion of the Dommel catchment under various climate and land management scenarios. These CENTURY model outputs were subsequently used to calculate changes in the topsoil concentrations, solubility, and leaching of cadmium (Cd) and zinc (Zn) for current (1991–2010) and future (2081–2100) conditions using empirical partition-relations. Since the metal leaching model could not be evaluated quantitatively against measured values, we focus mainly on the trends in the projected metal concentrations and leaching rates for the different scenarios. Our results show that under all climate and land management scenarios, the SOM contents in the topsoil of the Dommel catchment are projected to increase by about 10% and the DOC concentrations to decrease by about 20% in the period from present to 2100. These changes in SOM and DOC only have a minor influence on metal concentrations and leaching rates under the climate change scenarios. Our scenario calculations show a considerable decrease in topsoil Cd concentrations in the next century as a result of increased percolation rates. Zinc, however, shows an increase due to agricultural inputs to soil via manure application. These trends are primarily controlled by the balance between atmospheric and agricultural inputs and output via leaching. While SOM and DOC are important controls on the spatial variation in metal mobility and leaching rates, climate-induced changes in SOM and DOC only have a minor influence on metal concentrations and leaching rates. The climate-induced changes in metal concentrations in both the topsoil and the soil leachate are primarily driven by changes in precipitation and associated water percolation rates.

1. Introduction

In many parts of the world, anthropogenic activities have led to soil contamination by heavy metals (Xue et al., 2003; Azimi et al., 2004; Peng et al., 2009). Apart from local soil contamination by waste dumps and mining activities, soils have become enriched with metals by diffuse inputs via atmospheric deposition or application of manure, fertilisers, sewage sludge or other agrochemicals. Leaching of heavy metals from diffusively contaminated soils can be a major source of metals in surface waters (Bonten et al., 2008b; Wijngaard et al., 2017).

Changes in soil hydrology as a result of climate change or changes in land management may accelerate or reduce metal release and leaching. For example, Visser et al. (2012) projected reduced future metal leaching rates in response to reduced precipitation in a small metal-contaminated catchment in the southern part of the Netherlands. In contrast, Joris et al. (2014) predicted a climate-induced increase in metal fluxes in northern Belgium.

Furthermore, lowering of the soil pH due to, for example, acid deposition or a raise in the soil redox potential due to, for example, soil drainage may cause an accelerated release of bound metals into the soil solution of metal-contaminated soils. During the early 1990s this phenomenon was referred to as ‘chemical time bombs’ (Stigliani, 1991).

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https://doi.org/10.1016/j.catena.2018.07.034
Received 23 October 2017; Received in revised form 11 July 2018; Accepted 24 July 2018
Available online 31 July 2018

Climate change or changes in land management may contribute to such changes in environmental soil conditions. Initially, it was argued that climate-change induced losses of SOM in European soils could cause a reduction in the cation exchange capacity, thereby promoting the mobilisation of metals (Ter Meulen-Smidt, 1995). The response of SOM content to climate change is however not unambiguous as besides negative responses (Cramer et al., 2001; Smith et al., 2005; Stergiadi et al., 2016), positive responses have also been reported (Liski et al., 2002; Álvaro-Fuentes et al., 2012; Gottschalk et al., 2012; Smith, 2012). Moreover, climate change affects the DOC concentrations in soil and these changes are mainly associated with changes in precipitation and evapotranspiration patterns (Harrison et al., 2008; Stergiadi et al., 2016). An increase in precipitation has been suggested to result in enhanced DOC concentrations and leaching rates (Whitehead et al., 2009), whereas a decrease in net precipitation is predicted to result in reduced DOC concentrations and leaching rates (Stergiadi et al., 2016).

The above-mentioned studies indicate that the response to climate change of the solid-solution partitioning, mobility and leaching of metals is equivocal and involves many feedback processes. Quantification of these responses is essential for a proper assessment of leaching to groundwater and surface water and related risks to ecosystems and humans. The most common approaches for such quantifications that consider changing soil properties involve the use of process-based multi-surface models describing solution chemistry and binding to reactive surfaces (Weng et al., 2002; Bonten et al., 2008a; Dijkstra et al., 2009; Groenenberg et al., 2012) or empirical partition-relations that relate the distribution of metals to soil properties (McBride et al., 1997; Sauvé et al., 2000; Tipping et al., 2003; Rodrigues et al., 2010; Groenenberg et al., 2012).

The aim of this study is to assess the cascading response of SOM and DOC levels and metal leaching to climate change in a medium-sized lowland catchment in the southern part of the Netherlands (Dommel). For this purpose, we implemented the CENTURY model (Parton et al., 1987, 1988, 1993) in a spatial setting to model SOM, DOC, and water dynamics in topsoils of the Dommel catchment under various climate and land management scenarios. These CENTURY model outputs were subsequently used to predict changes in the topsoil concentrations, solubility, and leaching of cadmium (Cd) and zinc (Zn) for current (1991–2010) and future (2081–2100) conditions using the empirical metal partition relations developed by Römkens et al. (2004) and Groenenberg et al. (2012). As the metal leaching model could not be evaluated quantitatively against measured values, the model results are subject to an unknown degree of uncertainty. Therefore, we focus the results description and discussion on the trends in the projected metal concentrations and leaching rates and their differences between the climate and land management scenarios.

2. Methods

2.1. Study area

We modelled metal leaching in the Dutch portion of the Dommel catchment, which covers an area of approximately 1500 km^2 (Fig. 1). The Dommel River is a 146 km long lowland tributary river to the river Meuse. It rises on the Kempen plateau in the northeastern part of Belgium at an altitude of about 80 m above mean sea level and confluences with the Meuse near the city of 's-Hertogenbosch at about sea level (Bleeker and van Gestel, 2007; De Jonge et al., 2008). The climate is temperate with an average temperature of 10.3 °C and an average annual precipitation of 750 mm y^{-1} over the period 1981–2010 (KNMI, 2011).

The soils consist mainly of Pleistocene fluvial and aeolian sands and loamy sands. (De Mulder et al., 2003) with generally low topsoil pH values between 3.6 and 5. Land use in the Dommel catchment consists of intensively used agricultural land (27% arable land, 23% pastures), natural and semi-natural areas (22% forest, 7% grassland, 3% heather) and urban areas (14%).

The predominantly sandy soils of the Dommel catchment naturally contain relatively small amounts of heavy metals. The background concentration of Zn and Cd depend on the clay content is generally around 20 mg kg^{-1} for Zn and around 0.14 mg kg^{-1} for Cd (Bonten et al., 2007). However, the area is considerably polluted by Zn and Cd originating from the historical operation of four zinc-ore smelters in both the Dutch and Belgian part of the catchment and the application of artificial fertilisers and manure on agricultural land (Bonten et al., 2012). Emissions from the zinc ore smelters in the region caused atmospheric deposition of Zn and Cd during about one century, especially in the southern part of the catchment. Since the early 1970s, the atmospheric metal emissions have been greatly reduced as a result of the switchover to the cleaner electrometallurgical ore processing. In addition, the use of ore slags in road constructions and gardens' paving contributed to further dispersal of metals in the area (Copius Peereboom-Stegeman and Copius Peereboom, 1989; Bonten et al., 2012), although the pollution derived from ore slags has a more local character than the pollution due to diffuse atmospheric deposition. Intensive livestock farming in the catchment has led and leads to additional metal loads to soil, including Zn and Cd to agricultural land. However, in the study area, the agricultural load of metals is relatively small compared to the historic atmospheric deposition. For instance, the cumulative Zn load to soil from atmospheric deposition between 1880 and 2000 is estimated to be 435 kg ha^{-1} while the cumulative Zn load from agricultural sources equals 95 kg ha^{-1} (Bonten et al., 2012). The present-day topsoil concentrations amount to between 20 mg kg^{-1} and > 200 mg kg^{-1} for zinc between 0.1 mg kg^{-1} and > 5 mg kg^{-1} for cadmium (Mol et al., 2012). These high levels of diffuse metal contamination has led to the degradation of soil ecosystems and potential health risks related to the uptake of these metals by arable crops (Copius Peereboom-Stegeman and Copius Peereboom, 1989). Furthermore, leaching to groundwater and surface water potentially affect drinking water resources (Pedroli et al., 1990; Crommentuijn et al., 2000).

2.2. Model description

2.2.1. Spatial implementation of the CENTURY model

To assess the effects of climate change and land management on SOM and DOC, we implemented the CENTURY 4.6 model (Parton et al., 1987, 1988, 1993) in a spatial setting using the PCRaster-Python framework (Karssenberg et al., 2010). The CENTURY model simulates the dynamics of carbon (C), nitrogen (N), phosphorus (P), and sulphur (S) in the top 20 cm of the soil profile on a monthly time step. The model has different plant production submodels for grassland, agricultural land, and forests, which are linked to a common soil organic matter submodel. It also includes a straightforward water budget submodel that calculates soil moisture content and drainage from the topsoil.

The concepts, variables, and parameters of the various submodels that constitute the CENTURY model have been described in detail by Parton et al. (1987, 1988, 1993) and Metherell et al. (1993). Below, we describe in brief the model setup and for details about the CENTURY model we refer to these references. In the CENTURY model, plant residues and soil organic carbon (SOC) are apportioned to various conceptual pools with different potential decomposition rates. Soil surface and root litter are classified into structural and metabolic material based on their lignin to nitrogen ratio. The first category represents material resistant to decomposition and the second category easily decomposable material. Likewise, the SOC is classified into three pools with different potential decomposition rates (an active pool with a turnover time of several years, a slow pool with a turnover time of 20–50 years, and a passive pool, with a turnover time of 400–2000 years). Decomposition products of each litter or SOC pool flows successively into one or two SOC pools with longer turnover times. The actual turnover rates of the various litter and SOC pools and

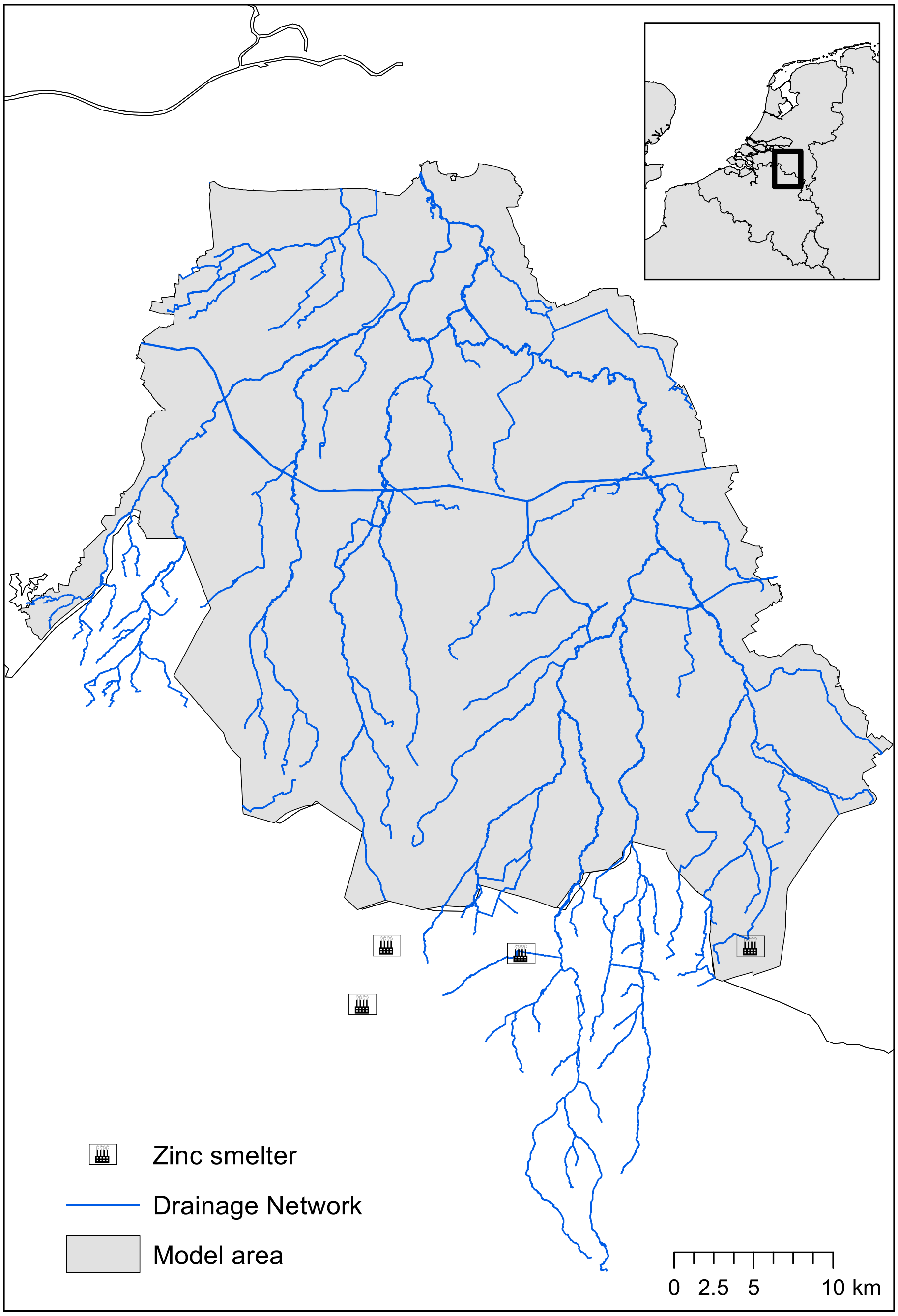

Fig. 1. Location of the Dommel catchment.

the partitioning of the decomposition products between the pools depend on soil temperature, soil moisture, soil pH, soil texture, and cultivation. Part of the decomposition products from the active SOC pool is lost as leached DOC. The leaching rate increases with the actual turnover rate of active SOC and the water drainage rate from the soil profile, and decreases with clay content.

The CENTURY model requires input on climate (temperature and precipitation), soil properties (soil texture, bulk density, field capacity, wilting point, soil pH, initial organic and mineral soil C, N, P, and S), land cover (crop type and vegetation), plant chemistry characteristics (e.g. lignin content, nutrient content), and land management practices (e.g. fertilisation, cultivation, harvest, grazing, irrigation). The primary output of the CENTURY model are the total average SOC levels, SOC fractionation in different pools in the top 20 cm of the soil profile, and the water drainage and DOC leaching rate from this soil layer. The monthly CENTURY model outputs were aggregated to annual average SOM contents (assuming the SOM content to be twice the SOC content) and water fluxes and flow-weighted annual average DOC concentrations in the soil leachate for further calculations in the metal leaching submodel.

2.2.2. Metal leaching submodel

The metal leaching model simulates the time-varying Cd and Zn concentrations in the soil solution based on soil and solution composition and the soil metal concentrations in the top 20 cm of the soil. The model considers the "reactive" metal concentration, rather than the "total" soil metal concentration (which includes metals occluded in soil minerals), based on the premise that only the reactive metal concentration contributes to metal partitioning with the soil solution and subsequent leaching (e.g. Römkens et al., 2004). We assumed equilibrium between the reactive metal concentrations and the soil solution, which is a common approach in regional modelling studies of metal leaching (e.g. Bonten et al., 2012; Joris et al., 2014).

First, the reactive metal contents, (i.e. the soil metal contents extracted with 0.43 M HNO_3) are calculated using the following regression equations reported by Römkens et al. (2004) which were obtained by analysing a large set of soil samples, including all major Dutch soil types and land uses:

$$\log Q_{Zn} = 0.428 + 0.183 \log SOM - 0.298 \log clay + 1.235 \log TM_{Zn}$$

$$\log Q_{Cd} = 0.289 + 0.022 \log SOM - 0.062 \log clay + 1.075 \log TM_{Cd}$$

where Q is the reactive soil metal concentration (mol kg^{-1}), *SOM* is annual average total soil organic matter content (%), *clay* is clay content (%) and *TM* is total soil metal concentration (mol kg^{-1}).

Second, the Cd and Zn concentration in solution are calculated using the empirical partition-relations developed by Groenenberg et al. (2012), based on 118 soil samples from the Netherlands, including various soil types (sandy, clay, peat and loess) and degrees of metal contamination:

$$\log C_{Zn} = 0.93 + 0.99 \log Q_{Zn} - 0.43 \log SOM - 0.22 \log clay - 0.14 \log AlFe_{ox} + 0.12 \log DOC - 0.46pH$$

$$\log C_{Cd} = 1.60 + 1.11 \log Q_{Cd} - 0.62 \log SOM - 0.39 \log AlFe_{ox} + 0.29 \log DOC - 0.41pH$$

where C is the metal concentration in solution (mol L^{-1}), $AlFe_{ox}$ is the sum of oxalate extractable aluminium and iron (mmol kg^{-1}), and *DOC* is the flow-weighted annual average DOC concentration (mg L^{-1}) as calculated by the CENTURY model.

The model runs on an annual time step. The annual metal leaching rate is calculated as the product of the metal concentration in solution and the annual average water flux as calculated by the CENTURY model. The metal leaching rates are reported in g m^{-2} y^{-1}. The total soil metal concentrations are updated each time step according to a mass balance calculation taking into account the metal losses due to leaching and gains due to metal emissions to the soil from agriculture or atmospheric deposition and soil bulk density.

2.3. Model input and calculation

2.3.1. General

For our model calculations, we used the spatial schematization of the STONE database (Van Bakel et al., 2008), which corresponds to a grid cell size of 250 m × 250 m. The STONE database served as a major source of model input for soil properties (soil texture, pH, drainage class, iron/aluminium hydroxides, bulk density) for both the CENTURY model and the metal leaching submodel. A land use map was derived from the LGN6 dataset (*Landelijk Grondgebruiksbestand Nederland* version 6) (Hazeu et al., 2010). The model was run for the agricultural land use classes (grasslands: grazed and non-grazed, and arable land), deciduous and coniferous forests, and heather in the Dommel catchment. Built-up areas and open water were omitted from the model calculations. We modelled the metal concentrations and leaching rates for the current (1991–2010 period) and future conditions (2081–2100 period) under the various climate and land management scenarios. The methods and additional data sources for model initialisation and scenario calculations are described below.

2.3.2. CENTURY model

For the CENTURY model calculations, we pursued a similar approach as reported by Stergiadi et al. (2016). We modelled the simultaneous cycles of C, N and P. The values of the plant or crop specific model parameters were adopted from the default parameter values for a range of crop and forest types, which were provided with the CENTURY model (see Metherell et al., 1993).

It has long been known that the response of SOM and DOC to climate and land use change is slow and takes place at the time scale of centuries (Post and Kwon, 2000; Schulp and Verburg, 2009). Like in the study by Stergiadi et al. (2016), we simulated the current SOM levels instead of using existing SOM measurements or SOM estimations from the STONE database to prevent spurious trends in the scenario calculations arising from possible inconsistencies amongst the initial SOM and DOC levels on the one hand and the spatial model input of other soil characteristics and land use on the other hand. To take the effects of land use history on the current and future SOM and DOC levels into account and to ensure a sufficiently long model spin-up period, the CENTURY model was run for the period from 800 CE onwards. Details about the CENTURY model calculations during this spin-up period are given in Appendix A.

Meteorological input data (minimum and maximum monthly temperatures, monthly precipitation rates) were based on data from the Royal Dutch Meteorological Institute (KNMI) Eindhoven weather station (period after 1950) located in the centre of the Dommel catchment, and the De Bilt weather station (1901–1950 period) located about 70 km north from Eindhoven. The climate reconstruction for the model initialization (before 800 CE), as well as for the model simulations for the period 800–1905, was based on scaling factors calculated by data reported by Brandsma and Buishand (1996) and Van Engelen et al. (2001). For the period before 1906, the model was forced by repeated mean minimum and maximum temperatures for every year and stochastically generated precipitation from a skewed distribution. For the period 1906–2012, actual weather data from the KNMI was used.

The simulated SOM levels were validated by comparing the averaged outcomes of CENTURY model aggregated for the different land use classes in the catchment for the 1991–2010 period to the SOM contents as reported in the STONE database (Van Bakel et al., 2008).

2.3.3. Climate and land management scenarios

To assess the impacts of climate change on metal concentrations and leaching, we adopted the two future climate scenarios developed for the Netherlands by the Royal Dutch Meteorological Institute (Van den Hurk et al., 2014; KNMI, 2015a). We used the G_H and the W_H scenarios in our model calculations, which represent the 'Moderate' (G) and 'Warm' (W) scenarios for the global temperature increase with a 'High value' (H) for the change in air circulation pattern (KNMI, 2015a). These scenarios are characterised by milder and wetter winters, and hotter and dryer summers with increased intensity of extreme rainfall events (Table 1). To obtain continuous time series of mean monthly temperature and

Table 1
Annual and seasonal changes in temperature and precipitation and annual changes in potential evapotranspiration between the reference period 1981–2010 and the 2071–2100 period for the different GH and WH climate change scenarios (KNMI, 2014a).

Season	Variable	Climate 1981–2010	Scenario changes 2071–2100	
		Reference period	GH	WH
Year	Temperature	10,1 °C	+1,7 °C	+3,7 °C
	Precipitation	851 mm	+5%	+7%
	Potential evapotranspiration (Makkink)	559 mm	+5,5%	+10%
Winter	Temperature	3,4 °C	+2,0 °C	+4,1 °C
	Precipitation	211 mm	+12%	+30%
Spring	Temperature	9,5 °C	+1,5 °C	+3,1 °C
	Precipitation	173 mm	+7,5%	+12%
Summer	Temperature	17,0 °C	+1,7 °C	+3,7 °C
	Precipitation	224 mm	−8%	−23%
Autumn	Temperature	10,0 °C	+1,6 °C	+3,8 °C
	Precipitation	214 mm	+9%	+12%

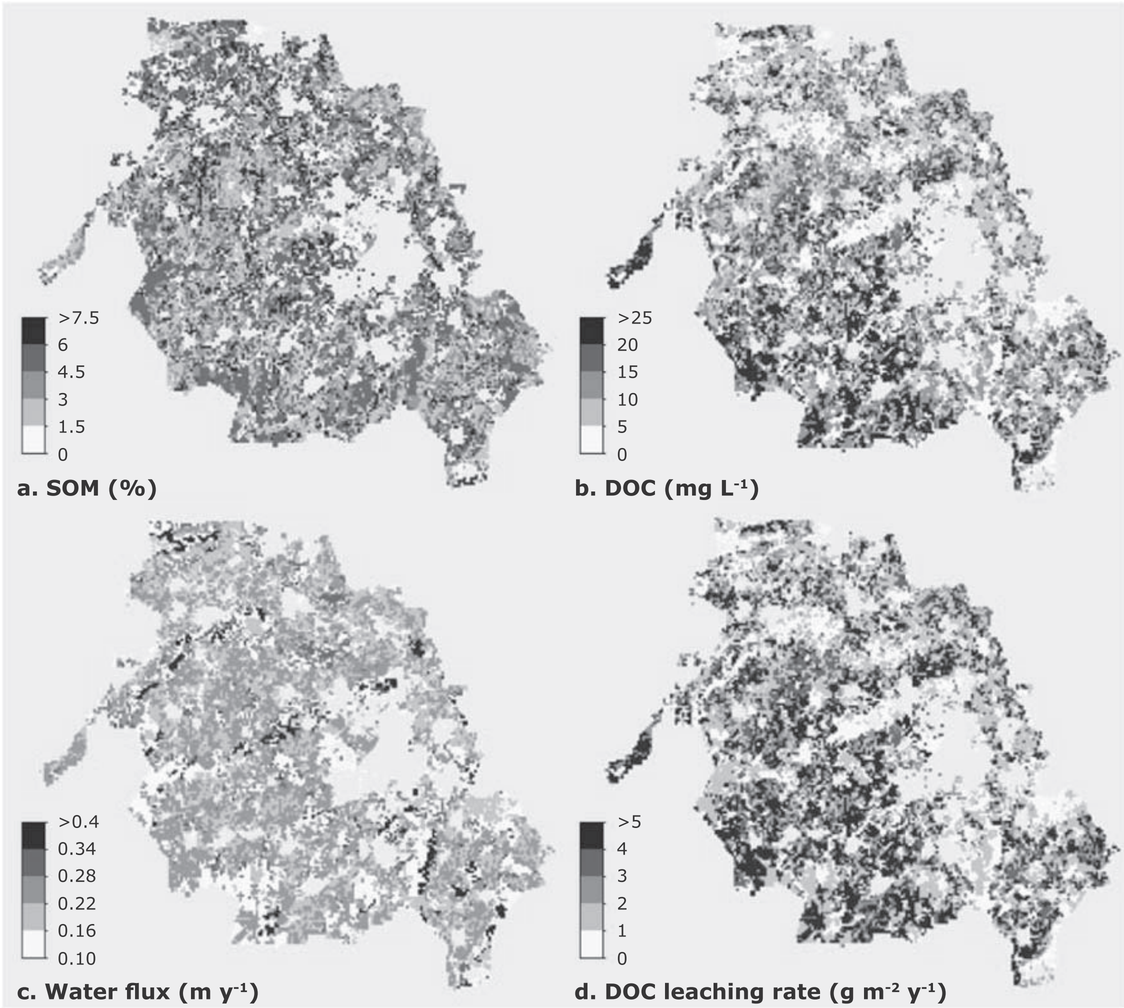

Fig. 2. Spatial distribution of a) simulated SOM (%), b) DOC concentrations (mg L^{-1}), c) water fluxes (mm y^{-1}), and d) DOC leaching rates (g m^{-2}) for the present (1991–2010) in the Dutch portion of the Dommel catchment.

precipitation for the Eindhoven weather station for the period 2013–2100, the historic time series for the 10-year period around 1990 (1985–1994) was transformed according to the G_H and W_H climate scenarios for successive 10-year periods from 2010 to 2100 using the KNMI time series transformation tool (KNMI, 2015b). In addition, data for a no-climate-change reference scenario were derived by transforming the 10-year time series around 1990 to 2010 using the no climate change option and using this time series for the subsequent decades until 2100. The mean monthly temperatures were subsequently transformed into mean monthly minimum and maximum temperatures using a regression relation established for the period 1990–2012. In the scenario calculations, the effects of increased atmospheric CO_2 concentrations on biomass production were not taken into account.

To assess the effects of changes in land management practices on metal concentrations and leaching, a land management scenario was defined according to the land management scenario reported by Stergiadi et al. (2016). This scenario involves changes in the application rates of organic and inorganic fertilisers. For grassland and arable land systems, the future (2013 − 2100) application rate for nitrogen via manure was kept the same as in the period 1951–2012, while the application rate for phosphorus was reduced by 20% due to declining phosphorus levels in fodder (LTO, 2013). Compared to the fertilisation rates in the period 1951–2012, inorganic nitrogen fertilisation rates were reduced by nearly 60% in the grassland systems and by nearly 20% in the arable land systems for the period 2013–2100 in order to comply with the nitrogen application standards provided by the Dutch Ministry of Economic Affairs, Agriculture and Innovation (2011), which are based on the EU Nitrates Directive (Commission of the European Communities, 1991). The future total phosphorus application rates on agricultural land were based on the EU Common Agricultural Policy (Alterra, 2011) and were set to equal the amount of phosphorus that is removed by grazing or harvest. For this reason, the future amount of phosphorus added to grasslands via inorganic fertilisers was set to zero and the future phosphorus addition to arable land was reduced by almost 80% (Stergiadi et al., 2016). The land management scenario was combined with both climate change scenarios, which resulted in the two additional G_H-FERT and W_H-FERT scenarios. The climate and land management scenarios do not take account of changes in soil pH as a result of precipitation, atmospheric deposition, land management and changes therein.

2.3.4. *Metal leaching submodel*

For modelling the soil metal concentrations and leaching, new maps of total Zn and Cd concentrations in the topsoil were created by combining geo-referenced concentration data from various data sources: North Brabant provincial soil monitoring network (n = 167; sampling depth = 0.1 m; sampling year 1995), RIVM (2016) (n = 96; sampling depth = 0.1 m; sampling period 1993–2011), Geochemical Soil Atlas of the Netherlands (Van der Veer, 2006; Mol et al., 2012) (n = 13; sampling depth = 0.2 m; sampling period 2002–2003), and data from municipal soil information systems ($n = 4829$; sampling depth up to 0.5 m; sampling period 1993–2002). The log-transformed metal concentrations were interpolated using universal block-kriging to a 250 m resolution grid and subsequently back-transformed and bias-corrected to obtain block mean concentrations. The resulting interpolated metal concentrations were assumed to refer to the year 1995, as the majority of the samples dated from that year. The future agricultural metal emissions to arable land and grassland were based on current values of agricultural metal loads from manure and artificial fertilisers (Van der Grift et al., 2008) and were set to $2\,g\,Cd\,ha^{-1}\,y^{-1}$ and $2170\,g\,Zn\,ha^{-1}\,y^{-1}$ for the G_H and W_H scenarios. For the G_H-FERT and W_H-FERT, the Cd loading to soil was reduced to $1.5\,g\,Cd\,ha^{-1}\,y^{-1}$ based on the projected reductions in the application rates of artificial fertilisers. As these scenarios project neither reductions in manure application rates nor in Zn concentrations in manure, the Zn loads to soil were assumed to remain $2170\,g\,Zn\,ha^{-1}\,y^{-1}$.

As mentioned above, the values of SOM and DOC for the empirical partition-relations were derived from the CENTURY model output, whereas the values of the other soil chemical parameters (pH, clay content, and $AlFe_{ox}$ content) were based on the STONE database (Van Bakel et al., 2008) and were kept constant throughout the simulation period.

3. Results

3.1. SOM and DOC levels

Fig. 2 shows the simulated spatial distribution of the current (1991–2010 period) SOM and DOC levels and water fluxes. Fig. 3 summarises the CENTURY model outcomes in terms of the average SOM and DOC levels and water fluxes for the present (1991–2010) and the projected situation in the 2081–2100 period under the various climate land management scenarios aggregated for the entire catchment and for the different land use classes in the catchment. In addition, the results are summarised for the most contaminated part of the catchment, i.e. the area where the current total Cd concentration exceeds $0.5\,mg\,kg^{-1}$. For comparison, the SOM contents as reported by the STONE database (Van Bakel et al., 2008) are plotted.

The simulated current, overall average SOM content in the study area is 4.25% with the highest values in grazed grasslands. Compared to the SOM contents reported in the STONE database, the CENTURY model slightly underestimates the overall average SOM content, but slightly overestimates the average SOM content in the contaminated part of the catchment. At the gridcell level, the simulated SOM contents correlate only weakly with the STONE SOM contents ($r = 0.17$ for gridcell with SOM $< 10\%$; $n = 17{,}680$). This rather weak correlation can be largely attributed to the weak or even negative correlation between simulated and 'observed' SOM contents in the agricultural land use classes ($r = -0.25$ for grazed grassland; $r = 0.00$ for non-grazed grassland; and $r = -0.10$ for arable land). Nevertheless, the CENTURY model predicts the average SOM content in grazed grasslands rather well, but slightly overestimates the average SOM content in non-grazed grasslands and slightly underestimates the average SOM content in arable land (Fig. 2). Despite the average SOM contents are considerably underestimated for heathland and deciduous forests and slightly underestimated for coniferous forests, the predicted and observed SOM contents for these semi-natural areas are significantly positively correlated ($r = 0.25$ for deciduous forest; $r = 0.84$ for coniferous forest; and $r = 0.68$ for heather).

Compared to the present situation, the average SOM contents are projected to increase for all scenarios. Compared to the no-climate-change scenario, the climate change scenarios lead to a slight decrease of $< 0.1\%$ SOM, which indicates that the simulated future trends in SOM content are primarily autonomous. The DOC concentration decreases by approximately $2\,mg\,L^{-1}$ on average for all scenarios compared to the present situation. Compared to the no-climate-change scenario, the climate change scenarios show a slight increase in DOC concentration by up to $0.5\,mg\,L^{-1}$. The DOC leaching rates for the no-climate-change scenario increase compared to the present situation, mainly due to the increased water fluxes from the soil profile. The climate change scenarios show a further increase in DOC leaching rates by up to 32%. The increase is most prominent for coniferous forests. The catchment-scale SOM contents and DOC concentrations and leaching rates are barely affected by changes in land management.

3.2. Metal leaching

Figs. 4 and 5 show the respective average Cd and Zn concentrations in the topsoil and soil leachate and leaching rates for the 1991–2010 period and the 2081–2100 period under the W_H scenario, which represents the most extreme scenario. Although the absolute values differ slightly for the other scenarios, the concentration and leaching rate patterns are similar. Figs. 4a and 5a show the current soil contamination based on the spatial interpolation of the measured topsoil Cd and Zn concentrations. The current soil contamination is concentrated in the southern Dutch part of the catchment near the Belgian-Dutch border, with the highest Cd concentrations located more to the west than the highest Zn concentration. A similar pattern is found for the metal concentrations in the leachate (Figs. 4c and 5c) and the metal leaching rates (Figs. 4e and 5e). In the 2081–2100 period, the contamination hotspots in the southern part of the study area have virtually vanished. The Cd concentrations and leaching rates have diminished across the study area, whereas the Zn concentrations and leaching rates have increased in large parts of the catchment.

Fig. 6 summarises the metal leaching model outcomes aggregated for the different land use classes for the present situation (1991–2010) period and for the various scenarios (2081–2100 period). Compared to the 1991–2010 period, the Cd concentrations in the topsoil across the study area decrease for all scenarios. The decline in Cd concentrations is slightly greater for the W_H and G_H scenarios than for the no-climate change scenario. The decline in Cd concentrations in the topsoil is especially pronounced in the natural and semi-natural forest and heathland systems as these systems do not receive agricultural Cd inputs. Furthermore, the pH is generally lower in these systems, which promotes the leaching of Cd (see Fig. 6e). The decline in Cd concentrations in grazed grasslands is greater than in non-grazed grasslands, which can be primarily attributed to the lower SOM contents and associated greater leaching rates in grazed grassland soils. The G_H-FERT and W_H-FERT scenarios show a slightly greater decline in Cd concentrations on grassland soils than the respective G_H and W_H scenarios, because of the reduced artificial fertiliser inputs. In the contaminated area, the Cd concentration in the topsoil decreases considerably, because Cd leaching is predominant over the agricultural Cd inputs in this area.

The Zn concentrations in topsoil on agricultural land show an overall increase for all scenarios due to the Zn inputs via manure. The Zn concentrations in grassland soils increase in particular by about 50% to 75%. In contrast, the Zn concentrations in forest and heather systems decrease by about 70% for all scenarios, again because these systems do not receive additional Zn inputs via fertilisers. Like for Cd, the Zn concentrations in the topsoil of the contaminated area decrease considerably between 1991 and 2010 and 2081–2100.

Like the concentrations in the topsoil, the Cd leaching rates and concentrations in the soil leachate decrease for all scenarios between 1991 and 2010 and 2081–2100 and the Zn leaching rates and concentrations in the leachate increase in the agricultural soils and decrease in the forest and heather systems. The metal leaching rates are slightly greater for the G_H and W_H scenarios than for the no-climate-change scenario. This is primarily due to the enhanced precipitation and thus, the water flux in the climate change scenarios, which are greater under the W_H scenarios than under the G_H scenarios. This effect of the water flux on the metal leaching rate is attenuated due to the

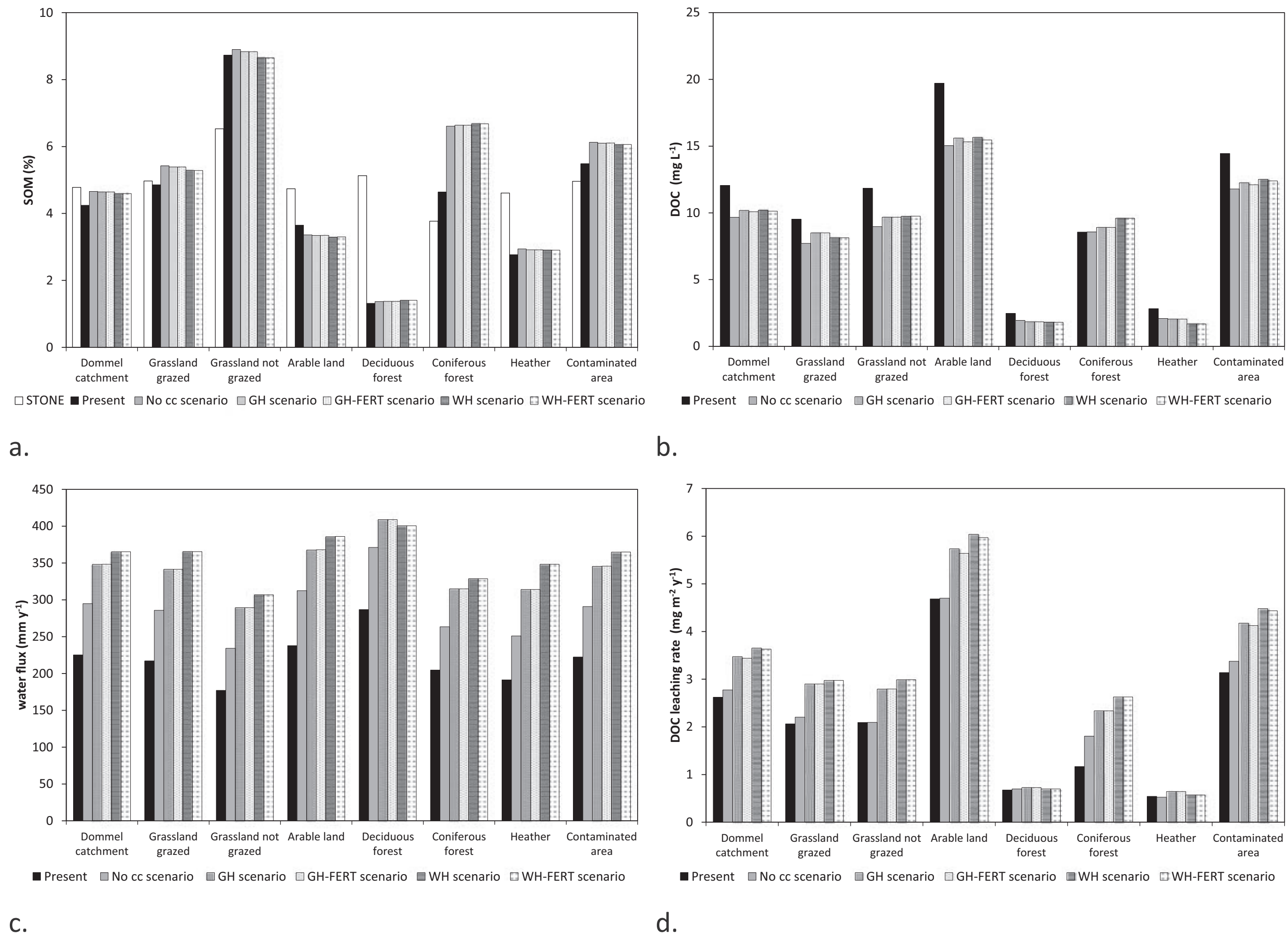

Fig. 3. a) 'Observed' SOM(%) according to the STONE database and simulated SOM (%), b) DOC concentrations (mg L^{-1}), c) water fluxes (mm y^{-1}), and d) DOC leaching rates (g m^{-2} y^{-1}) for the present (1991–2010) and climate and land management scenarios (2081–2100).

feedback of the enhanced decline of the metal concentrations in the topsoil as a result of the enhanced leaching rates. Under the G_H and W_H scenarios, this effect is further attenuated due to the effects of decreased SOM content and increased DOC concentrations relative to the no-climate-change scenario, which promote the loss of the metals from the topsoil. However, additional scenario calculations in which the effect of declining topsoil metal concentrations were not taken into account (results not shown in Fig. 6) show that, compared to the no-climate scenario, the changes in SOM and DOC under the G_H and W_H scenarios alone cause an increase of the area-averaged metal concentration in the leachate by only 1% (Zn) to 3% (Cd).

4. Discussion

In this study, we attempted to quantify the response of metal concentration and leaching rates in a lowland Dommel catchment in the Netherlands to climate and land management change. This was achieved by using a spatial implementation of the CENTURY model coupled with a metal leaching submodel based on metal partitioning relations. The model results with respect to the SOM content were evaluated using SOM contents as reported in the STONE database. At the aggregated scale of the land use classes, the average SOM contents in the agricultural parts of the Dommel catchment were simulated reasonably well. However, at the gridcell scale, the simulated SOM contents correlate weakly or even negatively with the STONE SOM contents. This may be attributed to variation in land use history and application of organic fertiliser between the agricultural fields which was likely insufficiently accounted for in the CENTURY model, mainly because data on this variation are lacking. The model results should therefore not be interpreted at the scale of individual fields. The absolute values of the simulated SOM contents for the semi-natural and natural land use classes were slightly (coniferous forest) to considerably (deciduous forest and heather) underestimated, but showed better correlations with the STONE SOM contents.

The model results with respect to metal concentrations and leaching rates could not be evaluated quantitatively against measured values as measurements of metal concentrations in the soil leachate are lacking for the Dommel catchment. The model outcomes could also not be evaluated using changes in topsoil metal concentrations observed in the framework the National Soil Monitoring Network (Wattel-Koekkoek et al., 2012). Wattel-Koekkoek et al. (2012) concluded that it is not possible to attribute changes in observed soil composition between the mid-1990s and the late 2000s to real changes, as they could just as well be artefacts as a result of short-range spatial variability or changes in the procedures of soil sampling and analysis.

Nevertheless, a qualitative assessment of the validity and reliability of the model results can be made based on an evaluation of the model inputs and comparison to results from previous studies reported in the literature. Both the CENTURY model and the set of metal partitioning relations have been applied and tested for Dutch soils (Stergiadi et al., 2016; Groenenberg et al., 2012) and in our simulations for the Dommel catchment, we adopted the model parameters from these studies.

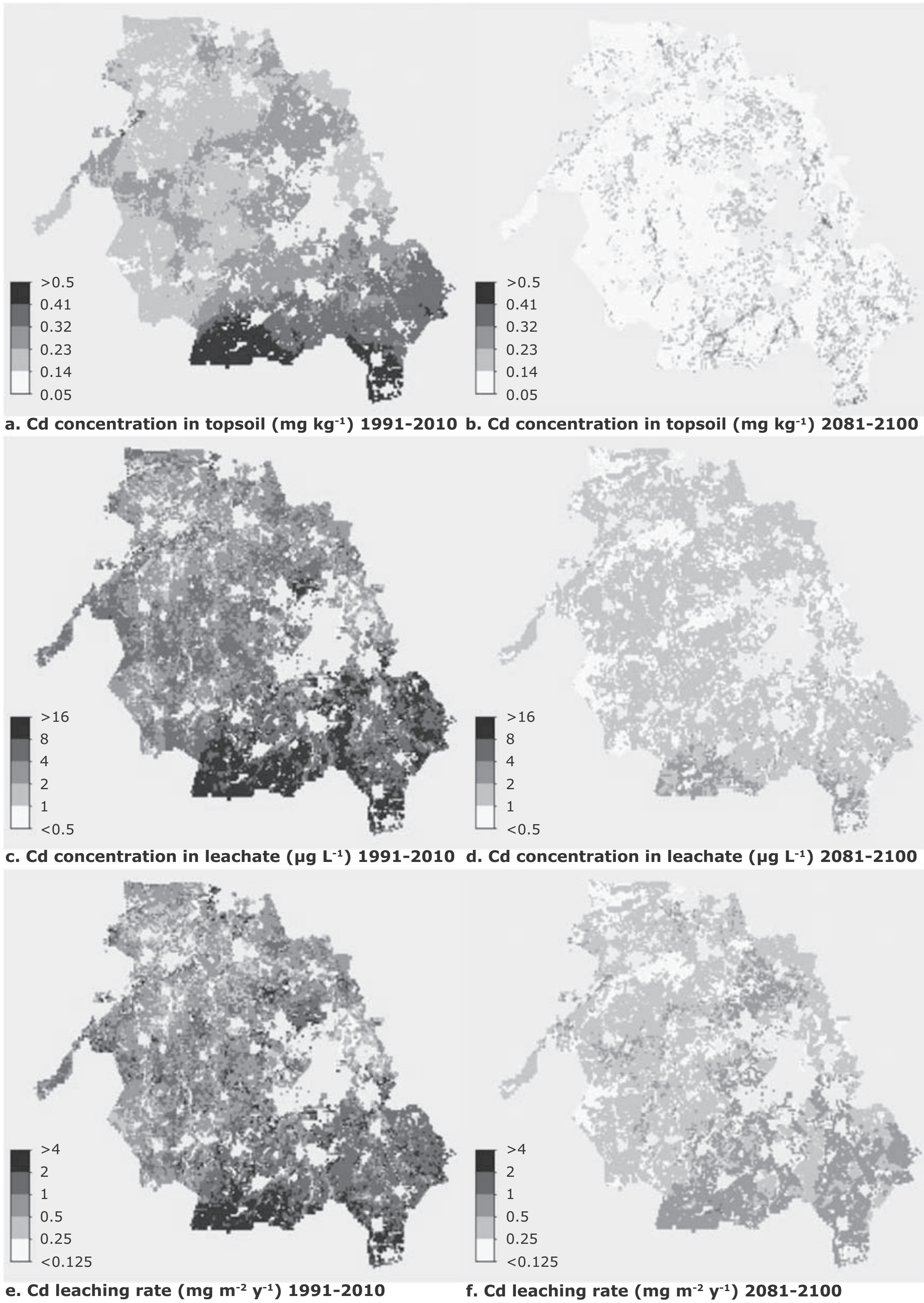

Fig. 4. Simulated Cd concentrations in the topsoil and soil leachate and Cd leaching rate for the present (1991–2010) and under the WH climate change scenario (2081–2100).

Furthermore, we used the STONE database for area-specific model input of soil characteristics. This well-established database has been used for many regional and national assessments in the Netherlands, including metal leaching studies (e.g. Bonten et al., 2008b; Bonten et al., 2012; Visser et al., 2012; Spijker et al., 2013). While previous studies in the Dommel catchment simulated the current topsoil metal concentrations based on estimates of atmospheric deposition and manure and fertiliser application rates (Bonten et al., 2012; Visser et al., 2012), we collated a state-of-the-art data set containing an unprecedented number of > 5000 soil samples to estimate the topsoil

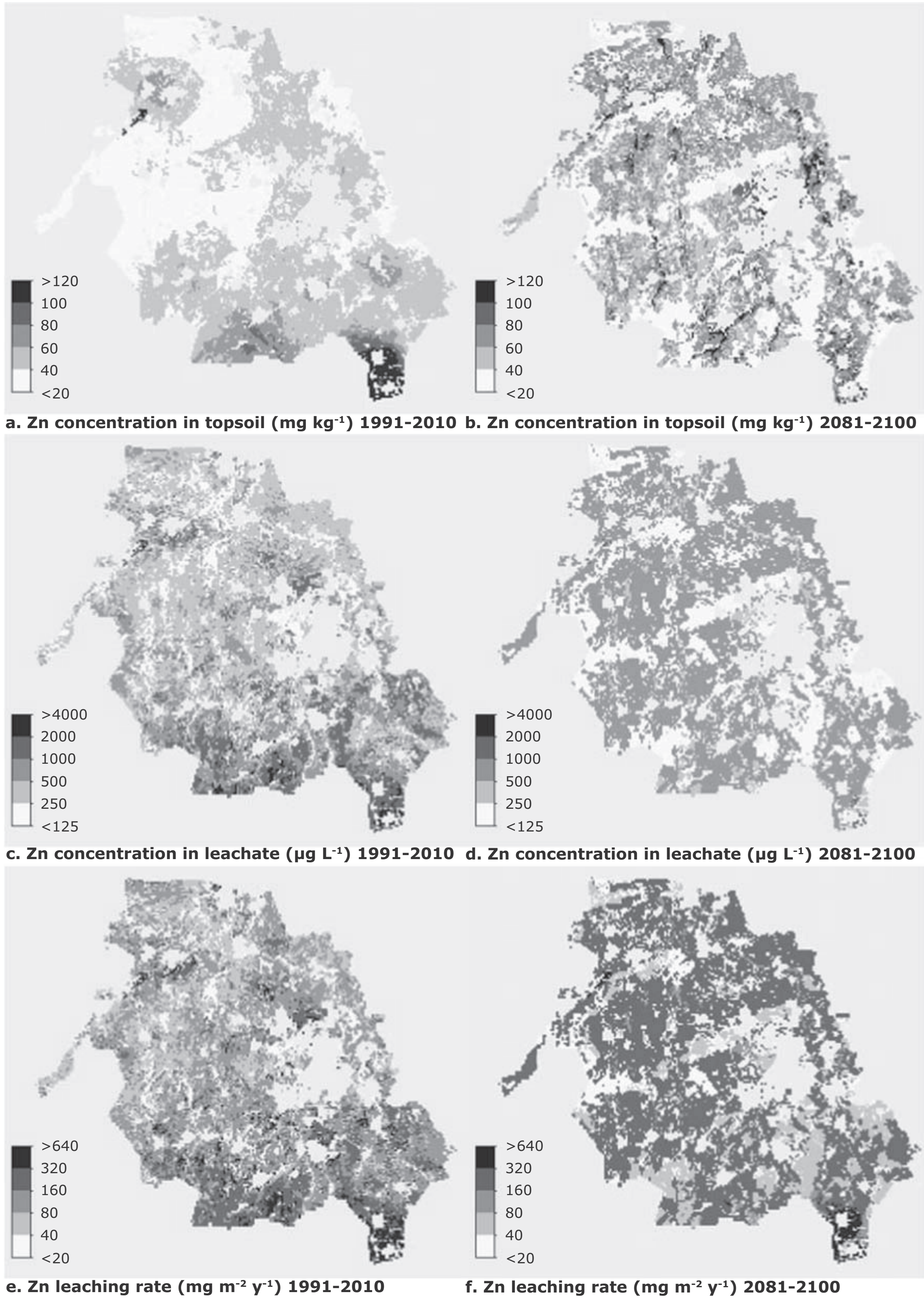

Fig. 5. Simulated Zn concentrations in the topsoil and soil leachate and Zn leaching rate for the present (1991–2010) and under the WH climate change scenario (2081–2100).

metal concentrations in the Dommel catchment in 1995.

Despite the careful selection of the model input, the model results are subject to considerable yet unquantifiable uncertainty. For example, we note that due to the nonlinear character of both the CENTURY model and the metal partitioning relations, within-grid cell variability of the model inputs leads to bias in the model outcomes. Furthermore, despite the soil pH is an important factor that affects both SOM dynamics (Stergiadi et al., 2016) and metal partitioning (Groenenberg

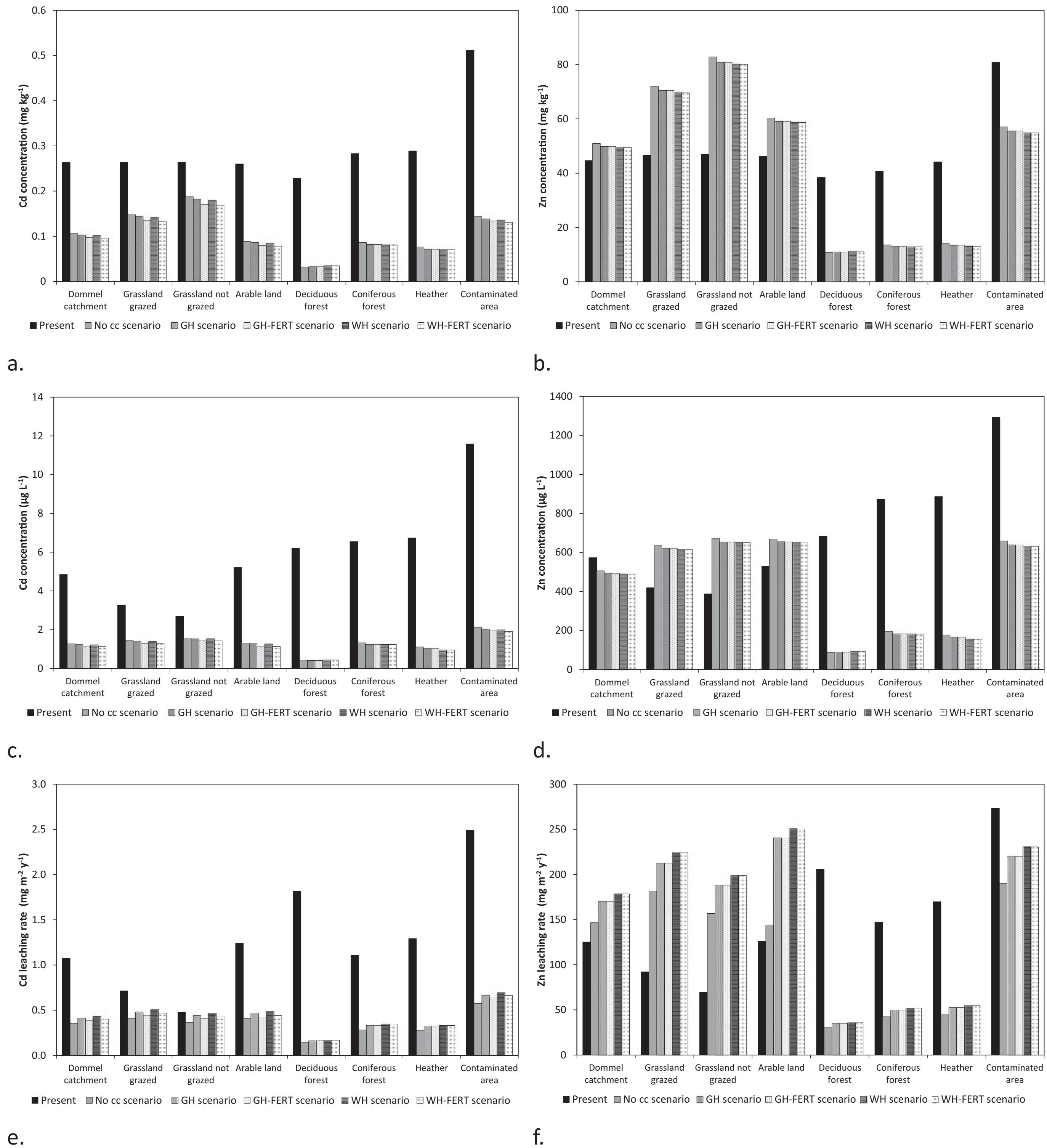

Fig. 6. Simulated a) Cd and b) Zn concentrations in the topsoil, c) Cd and d) Zn concentrations in the soil leachate, and e) Cd and f) Zn leaching rate for the present (1991–2010) and under the WH climate change scenario (2081–2100).

et al., 2012), we did not take the effects of potential changes in soil pH due to for example atmospheric deposition or land management into account in our scenario calculations. The projections for the various scenarios should therefore not be interpreted as absolute future predictions. However, the initial conditions of SOC, DOC, and metal concentrations and the model input of other soil characteristics are the same for all climate and land management scenario calculations. Consequently, the errors in these model inputs are of the same magnitude and point in the same direction, which considerably reduces their effects on the differences between the scenario projections of SOM levels and DOC and metal leaching. The differences between the scenario projections would therefore largely reflect the response to the changes in climate and land management, which was the objective of this study. That is why we focus on the trends in the projected SOM content, DOC and metal concentrations and leaching rates and their differences between the climate and land management scenarios in our interpretations of the model outcomes. Below we discuss the simulated trends and compare them both mutually and with other studies reported in the literature. In addition, we discuss the implications in terms of the major drivers and controls on the metal concentrations and leaching rates.

Our model simulation results indicate that under projected climate change, SOM levels increase in grassland (up to +11% under the WH scenario), forests (up to +44%), and heather (+5%) and decrease in arable land (up to −10%). Our outcomes are in agreement with previous observational studies (Reijneveld et al., 2009; Hanegraaf et al., 2009) and model studies (Vleeshouwers and Verhagen, 2002), which reported on average small SOC decreasing trends for arable lands and small increasing trends for grasslands. Stergiadi et al. (2016), who simulated the effects of climate change on SOC and DOC levels in a generalised sandy soil in northwestern Europe, also found a decrease in SOM content in arable land and an increase in forests. However, Stergiadi et al. (2016) projected the SOM levels under grasslands to decrease by 2% to 5% in 2100. This difference in results is likely due to the different soil pH value used in the simulations: in the Dommel catchment the average pH value of grassland soils is 4.6, which is 0.5 pH units lower than in the simulations for the generalised soil by Stergiadi et al. (2016). A lower soil pH reduces SOM degradation and causes a stronger accumulation of SOM (see also Stergiadi et al. (2016)), especially in soils that have received large inputs of organic matter in the form of manure since the 1950s, as is the case in the study area.

DOC concentrations in the topsoil leachate are simulated to decrease for all land use classes except for coniferous forests. The simulated overall decline of DOC concentrations in the Dommel catchment by about 15% is also in line with the findings of Stergiadi et al. (2016), who projected a decrease in DOC concentrations by about 25% in sandy soils under grassland and arable land. However, the simulated increase in DOC concentrations under coniferous forests by 4% to 12% is in contrast to the projected decline by 10% found by Stergiadi et al. (2016). This difference is likely due to the considerably greater increase in SOM levels in our simulations, as SOM is the source of DOC via the breakdown of the active SOM pool. Like for the differences in the above-mentioned simulated SOM contents in grassland soils, this difference in SOM in coniferous forest soils is likely due to the lower pH values prevailing in the Dommel catchment than in the generalised soil used in the simulations by Stergiadi et al. (2016). In contrast to the results of Stergiadi et al. (2016), we projected the DOC leaching rates to increase under the climate change scenarios, primarily because of the increased projected precipitation rates under the KNMI'14 scenarios. Stergiadi et al. (2016), who used the previous version of the KNMI scenarios (KNMI '06 scenarios), projected a decrease in precipitation rates for the period until 2100. This underlines the findings by Harrison et al. (2008) and Tranvik et al. (2002), who also indicated the importance of climate-induced changes in precipitation for changes in DOC leaching.

Although our study shows that SOM and DOC represent important controls on the spatial variation in metal mobility and leaching rates, our model results also indicate that the climate-induced changes in SOM and DOC affect metal solubility and leaching rates only to a minor extent. Our results show that the future changes in dissolved metal concentrations are primarily controlled by changes in the total soil metal concentrations, which are, in turn, determined by the balance between atmospheric and agricultural inputs and outputs via leaching. Besides the changes in total soil metal concentrations, the changes in metal leaching rates are additionally controlled by changes in water fluxes and associated DOC leaching rates caused by changes in excess precipitation. The difference between the present and the projected dissolved metal concentrations are primarily governed by the interaction of these drivers.

The metal leaching rates are projected to decrease under all scenarios compared to the current situation. However, compared to the no-climate-change scenario, the metal leaching rates are projected to increase under the climate change scenarios in response to increased precipitation rates and DOC leaching rates. This is in accordance with the findings of Joris et al. (2014), who projected a 10% increase in the cumulative Cd leaching flux in northern Belgium (including the Belgian part of the Dommel catchment) after a 100 year period compared to a reference scenario without climate change. The interdependence between metal leaching rate and excess precipitation was also reported by Visser et al. (2012), although they predicted a decrease in metal leaching rates in a small subcatchment of the Dommel River in response to a projected decrease in net precipitation in the climate scenarios that they used. This implies that, as long as climate change scenarios remain inconsistent with respect to changes in precipitation rates, the projected trends in metal leaching rates should be treated with caution.

5. Conclusions

We simulated the changes in topsoil metal concentrations and leaching rates in response to climate change and change in land management. The results of our scenario calculations show that the average SOM content in the topsoil of the Dommel catchment are projected to increase by about 10% and the DOC concentrations to decrease by about 20% in the period to 2100. These changes depend on soil characteristics and land use and can mainly be attributed to autonomous changes depending on land use history. Climate change will only slightly temper these autonomous changes. Our model results project a considerable decrease in topsoil Cd concentrations in the next century as a result of Cd leaching, despite Cd inputs via fertiliser application. Topsoil Zn concentrations, however, show an increase due to agricultural inputs to soil via manure application. While the current soil contamination by Zn has been primarily caused by historic emissions from the zinc smelters, the primary source of soil contamination by Zn will likely shift towards agricultural inputs during the coming century.

While SOM and DOC are important controls on the spatial variation in metal mobility and leaching rates, climate-induced changes in SOM and DOC only have a minor influence on metal concentrations and leaching rates. Changes in net precipitation and associated water percolation rates are the major driver for projected climate-induced changes in metal leaching rates and the metal concentrations in both the topsoil and the soil leachate.

Acknowledgements

This research was conducted in the framework of the “Climate Cascades” Project, funded by the Dutch National Institute for Public Health and the Environment (RIVM) (S/607021), in collaboration with Utrecht University (The Netherlands), Alterra Wageningen University (The Netherlands), and VITO (Belgium). Drs Kor de Jong (Utrecht University) is thanked for programming and implementing the CENTURY model in the PCRaster-Python framework. We thank Dr Luc T.C. Bonten (formerly Wageningen Environmental Research- Alterra) for providing soil data from the STONE database and Drs Erik Heskes (Province of North Brabant) for providing the dataset of soil metal concentrations from municipal soil information systems. The comments of two anonymous reviewers helped to improve parts of the manuscript.

Appendix A. CENTURY simulation of current SOC levels

To simulate the current SOC levels using the CENTURY model, a long model spin-up period starting from 800 CE was used, similar to the model study by Stergiadi et al. (2016). To initialise the model simulations for the different land use types in 800 CE, the forest submodel was applied for a period of several thousands of years to estimate the equilibrium levels of soil organic matter (C, N, and P) for the native deciduous forest system. Fig. A.1 gives an overview of the land use types and land management events for the three simulated periods of time (blocks) since 800 CE, during which climate, land use and land management practices were kept constant. These blocks represent the history of climate, land use and management typical for the sandy regions in the southern part of the Netherlands (see Stergiadi et al. (2016) for more details). It was assumed that all present-day coniferous forests were heathland systems before 1906 (CBS, 2017a). Portions of the pre-1906 heathland systems were assumed to have been reclaimed to agricultural land (arable land or grassland) since 1906. These areas were selected based on the dominant soil type (non-plaggen soils) according to the STONE database and present-day land use. We assumed that present-day grasslands (grazed or non-grazed) that occur on plaggen soils had been arable land before 1951. The other areas were assumed to have had a constant land use since 800 CE.

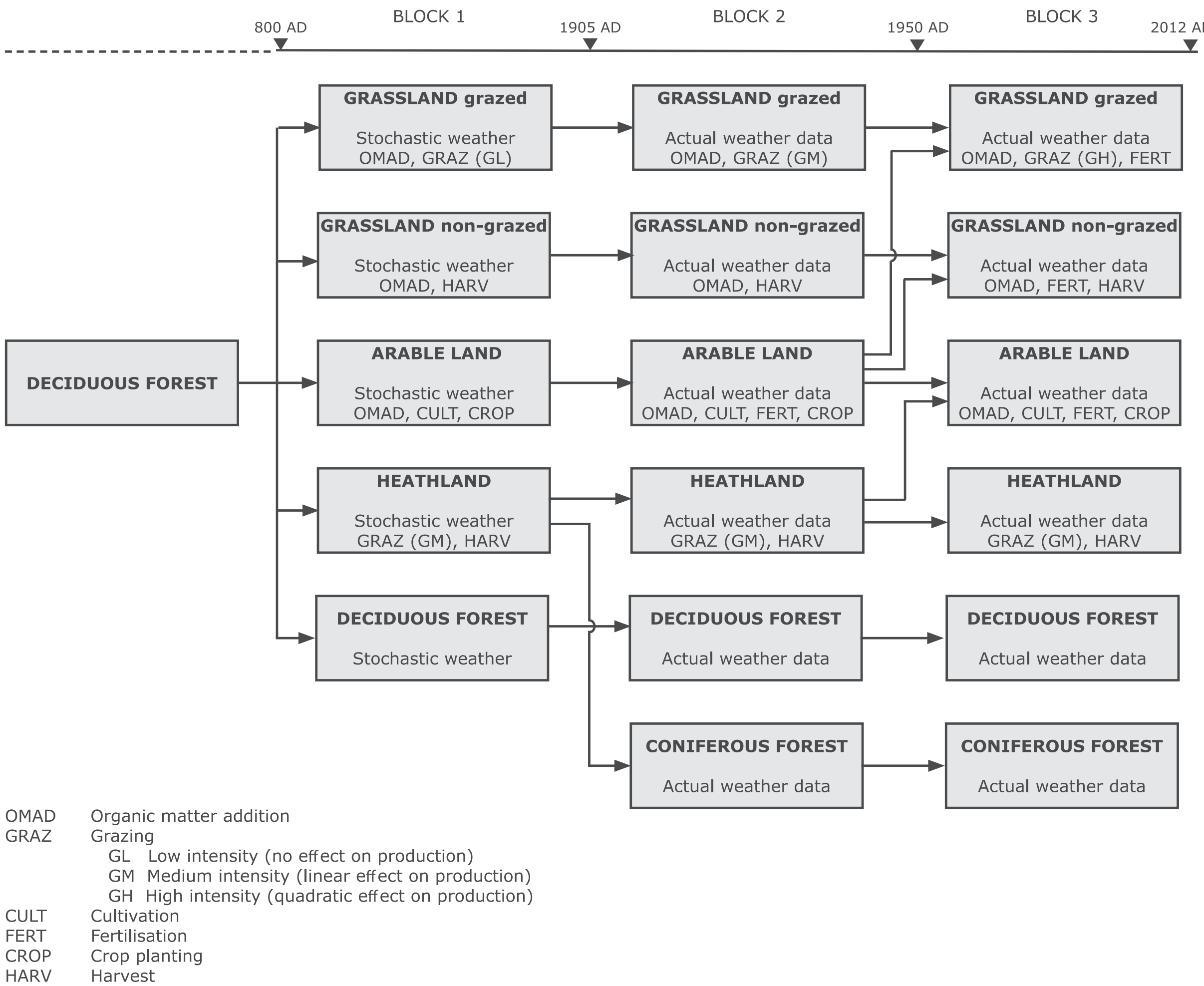

Fig. A.1. Scheme of the CENTURY modelling procedure.

For the pre-1906 heathland system, the event scheduling included grazing and removal of aboveground biomass to be used as fertiliser on arable land. The latter was simulated as harvesting once every 10 year to imitate the litter layer removal, which nevertheless cannot be fully taken into account in the CENTURY model. For the post-1906 heathland system, the event scheduling included grazing and removal of aboveground biomass once every 30 years.

In the grassland systems, organic matter addition was simulated using the default straw manure option with a rate of 300 g m^{-2} y^{-1}. The simulated grazing intensity was simulated to gradually increase in the course of time, being low (no direct effect on biomass production; see Metherell et al., 1993) for the period 800–1905 (block 1), moderate (linear effect on biomass production) for the period 1906–1950 (block 2), and high (quadratic effect on biomass production) for the period 1951–2012 (block 3). After 1950, application of mineral fertilisers was assumed to correspond to an input of 300 kg ha^{-1} y^{-1} nitrogen and 40 kg ha^{-1} y^{-1} phosphorus to the soil.

In the arable land systems, the simulated addition of organic fertilisers for the period 800–1905 (block 1) was simulated as a mixture of straw manure and heath plaggen. Until the beginning of the 20th century, the amount of organic matter added in this system was 520 g m^{-2} y^{-1} (Schulp and Verburg, 2009). Based on the default lignin content of straw manure (25%) and the simulated lignin content of heather litter, the lignin content of the organic mixture was estimated to be 43%. Since 1906, application of mineral fertilisers in the arable systems was introduced, with mineral nitrogen application rates increasing by a factor of 10 after 1950 and mineral phosphorus increasing by a factor of 2, reaching a value of 150 kg ha^{-1} y^{-1} and 40 kg ha^{-1} y^{-1}, respectively (Knibbe, 2000). Since 1906, the simulated manure added on arable land consisted only of straw manure, corresponding to nearly 30% of the amount added in the grassland systems. We simulated a two-year crop rotation schemes consisting of wheat and potatoes until 1951 (blocks 1 and 2). For the period after that (1952–2011), a four-year crop rotation scheme, also including sugar beets and maize, were simulated (CBS, 2017b). Tillage practices in these systems consisted of annual ploughing.

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