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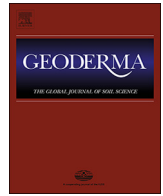
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Erosional effects on distribution and bioavailability of soil nitrogen fractions in Belgian Loess Belt

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ABSTRACT

Soil erosion strongly influences the transport and fate of carbon (C) and nitrogen (N) in hillslope soils. However, in dynamic landscapes, erosional effects on soil N cycling and primary controls on N bioavailability are not well understood: particularly with respect to differences between topsoil and subsoil. Here we aim to explore the influence of erosion on (i) spatial distributions of soil N fractions and (ii) controls on N bioavailability in eroding vs. depositional sites within the Belgian Loess Belt. Soil samples were fractionated by aggregate size and density. In addition, intact soil samples were incubated to determine the influence of oxygen status (0, 5, and 20%) and labile organic matter on mineralization and nitrification of N in the context of erosion. The results showed that the deposition of eroded upslope soil materials led to N enrichment throughout entire soil profiles. Across both eroding and depositional sites, more than 93% of the total N was associated with minerals. Increased macro-aggregate- and mineral-associated N at the depositional site indicated that aggregation and N stabilized by minerals contribute to N enrichment in the depositional soils. Inorganic N, mostly NO_3^- -N, was also larger at the depositional site. Oxygen concentrations were positively related to net N nitrification and mineralization rates regardless of geomorphic position. Glucose addition significantly reduced net N mineralization and nitrification rates. In conclusion, our results indicate that soil erosion might not only lead to spatial variations of N pools but also potentially affect the transformation and bioavailability of N along eroding hillslopes. Future research should consider the fate of different N species in eroding landscapes and consequences for both carbon sequestration and N leaching.

1. Introduction

Soil erosion and subsequent deposition significantly regulate biogeochemical cycling of carbon (C) and nitrogen (N) across soil-mantled hillslopes (Berhe et al., 2018; Quinton et al., 2010). Globally, soil erosion laterally redistributes a sediment flux of about $35 \pm 10 \text{ Pg yr}^{-1}$, of which water erosion is responsible for approximately 28 Pg yr^{-1} (Quinton et al., 2010). In the past, many studies have focused on quantifying the magnitude of erosion rates and transport of organic matter and vertical C exchange (Berhe et al., 2018). Over the past two decades, researchers have started exploring the fate of eroded soil organic C and its stabilization mechanisms as a function of topographic positions (e.g. Berhe et al., 2012; Doetterl et al., 2016; Wang et al., 2013, 2014, 2018; Wiaux et al., 2014). In comparison, there has been limited focus on how erosion and subsequent deposition affect redistribution and bioavailability of N in eroding landscapes (Berhe et al.,

2018; Berhe and Torn, 2017; Liu et al., 2018) despite growing knowledge that soil erosion exerts an important control on spatial patterns of nutrient availability, soil fertility and plant productivity (Berhe et al., 2018; Doetterl et al., 2016).

Nitrogen is one of the essential soil nutrients and its bioavailability strongly limits plant productivity (Jilling et al., 2018; van Breemen et al., 2002). Most process-level studies on soil N cycling and transformation have focused on flat, stable landscapes that experience minimal soil erosion and deposition (Bimüller et al., 2016; Verchot et al., 2001; Vitousek and Matson, 1988). On hillslopes, the soil N cycle can be strongly affected by erosion and the transport of soil mass (Berhe and Torn, 2017). Globally about 23–42 Tg of N per year is thought to be transported by erosion (Quinton et al., 2010). These erosion-induced lateral N fluxes are on the same order of magnitude as N applied in the form of agricultural chemical fertilizers (<http://www.fao.org/faostat/>). In addition, recent estimates suggest that the erosional soil N loss

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corresponds to between 7 and 25% of the N inputs into eroding landscapes (Berhe and Torn, 2017). Soil erosion leads to the breakdown of aggregates and release of previously protected organic matter, transport of labile and particulate N (unprotected, not associated to minerals) and alterations to N availability in soil organic matter for microbial decomposers (Hilton et al., 2013; Wang et al., 2014). This erosion-induced microbial process is a primary regulator of the N mineralization-immobilization balance (Jilling et al., 2018; Weintraub et al., 2015).

Soil N transformation, from organic N into inorganic forms (nitrate and ammonium), is directly related to microbial activity, which in turn regulates N availability, and subsequently plant growth (Buchkowski et al., 2018; Li et al., 2013; Vitousek and Matson, 1988). In addition, inorganic N is a dynamic and mobile specie that can be easily leached to the subsoil, and eventually groundwater. Excessive N losses to groundwater cause severe environmental and contamination problems (Davidson et al., 1992; Jia et al., 2018; van Breemen et al., 2002). Within a catchment, mobilization of nitrate and ammonium N are sensitive to erosional processes (Taylor et al., 2015). N-containing organic matter can be immobilized by microbes or adsorbed by clay-sized minerals (Kögel-Knabner et al., 2008; Vitousek and Matson, 1988). The transformation of soil N is either directly or indirectly mediated by soil microbes. Soil microbes are sensitive to environmental conditions, such as availability of labile C and nutrients as well as oxygen (O₂) status (Cirimo and McDonnell, 1997; Turner et al., 2017; Yuan et al., 2018). Therefore, the amount of available soil N strongly depends on environmental variables that influence the composition and abundance of microbial communities, such as soil erosion and land use management (Berhe and Torn, 2017; Davidson et al., 1992; Vitousek and Matson, 1988; Weintraub et al., 2015).

In a sloping landscape, the N cycle in soils is closely related to erosion (Berhe and Torn, 2017; Weintraub et al., 2015). During erosion, soil N in upper hillslope positions is redistributed to lower-lying positions, where soil N can be rendered unstable (Berhe and Torn, 2017; Weintraub et al., 2015). Soil N experiences continuous transformation and losses during transport through the soil conveyor belt via nitrification and denitrification, leaching, and runoff (Neill et al., 1997; Owen et al., 2010; Taylor et al., 2015; Weintraub et al., 2015). Deposition of eroded soil particles is often accompanied by changes in soil environmental conditions, such as temperature, moisture, and O₂ availability (Hilton et al., 2013; Turner et al., 2017; Weintraub et al., 2015). In turn, these changes can affect the transformation and mineralization of organic N (Li et al., 2013). Recent studies have demonstrated that, contrary to our expectations, mineral-associated N is highly bioavailable and acts as an important N source for soil microbes (Jilling et al., 2018; Turner et al., 2017), which can be strongly redistributed by erosion. During erosion and transport, increased rates of organic N mineralization contributed to the formation of more inorganic N, leading to increased N losses in particulate and dissolved form (Quinton et al., 2010). Despite the importance of N transformations during erosion, the mechanisms controlling soil N transformations in eroding landscapes remain poorly understood.

The main objective of this study is to (i) compare the distribution of N in different fractions (aggregate size and density fractions), and (ii) examine the controls (e.g. oxygen status and the availability of labile organic matter) on N mineralization and transformation in eroding vs. depositional positions along an eroding hillslope in the Belgian Loess Belt. This experimental site has been previously studied to constrain how erosion processes and soil C stabilization mechanisms respond to geomorphic variations (Doetterl et al., 2012; Wang et al., 2013, 2014; Wiaux et al., 2014).

2. Materials and methods

2.1. Site description and soil sampling

Soil samples were collected from an upslope (eroding) and a

downslope (depositional) position of a terraced hillslope in the Belgian Loess Belt, Belgium. Slope percentages in the study area range between 4 and 16%. Agriculture in the area started at least 1000 years ago (van Oost et al., 2005) with significant changes over the last 250 years (van Rompaey et al., 2002) but we have no record of field specific agricultural use. Soils were classified as Haplic Cambisols at the eroding site and Colluvic Regosols at the depositional site (WRB, 2006). Within the study area, the primary crops are wheat (*Triticum aestivum* L.), maize (*Zea mays* L.), potato (*Solanum tuberosum* L.), sugar beet (*Beta vulgaris* L.), and chicory (*Cichorium intybus* L.). Deposition rates in the study area were estimated to be approximately 0.73 cm year⁻¹ using ¹³⁷Cs tracer techniques (Wang, 2011). Mean annual temperature is 9–10 °C and mean annual precipitation is 750–800 mm. Samples were taken under wet conditions in early spring representing almost field capacity.

At each site, five 0–200 cm soil cores were collected by depth increment. Soil samples were separated at 5 cm increments between the 0–50 cm, at 10 cm increments between 50 and 100 cm, and at 20 cm increments between 100 and 200 cm, respectively. Separates of soil samples were stored at 4 °C under field moist conditions and the other aliquot was air-dried before further analysis. In the 5–10 cm intervals, soil pH was 5.5 ± 0.1 and 7.0 ± 0.1 at the eroding and depositional sites, respectively. Soil organic carbon contents were 8.2 ± 1.0 and 10.8 ± 0.7 g kg⁻¹ at the eroding and depositional sites, respectively. Within the 0–20 cm intervals, soil moisture was similar between depositional (23.3 ± 1.5%) and eroding (22.9 ± 1.2%) sites. More detailed information on the sites and sampling approach can be found in Wang et al. (2013, 2014).

2.2. Aggregate size fractionation

Samples representing topsoil (0–5 and 5–10 cm) and subsoil (45–70 and 160–200 cm) from eroding and depositional sites were selected for aggregate size fractionation using the dry-sieving method (Cammaraat and Imeson, 1998). Briefly, 170–200 g of air-dried samples were fractionated using nine mesh sieves, including 16, 8, 5, 4, 2, 1, 0.5, 0.25 and 0.125 mm, allowing ten size fractions to be obtained. All size fractions were weighed to determine their proportion relative to the total soil mass. The N contents within each aggregate fraction were determined with a C/N analyzer (Elementar Vario EL, Hannau, Germany). Large macro-aggregates were defined as aggregates being > 2 mm. The average recovery of the total soil mass was 99.4 ± 3.7% (SD).

2.3. Soil density fractionation

We fractionated the topsoil (5–10 cm) and subsoil (45–70 and 160–200 cm) from both the eroding and depositional sites by density using a sodium polytungstate (SPT) solution with a density of 1.6 g cm⁻³ (Cerli et al., 2012; Golchin et al., 1994). The bulk soil (< 2 mm) was separated into three operationally defined soil fractions: the free light fraction (fLF; < 1.6 g cm⁻³), the occluded light fraction (oLF), and the heavy fraction (> 1.6 g cm⁻³). All density fractions were freeze-dried, homogenized and used for the determination of C and N with a C/N analyzer (Wang et al., 2014). The mean recovery of the soil mass was 95.6 ± 2.3% (SD).

2.4. Incubation experiments

In order to eliminate disturbance effects on aggregates and dry-wetting effects, we directly incubated the intact soil cores, which were immediately transferred to the laboratory and stored at 4 °C, in order to examine controls on the mineralization of soil nitrogen in topsoils and subsoils across the studied hillslope. The controls included oxygen availability and addition of labile substrate, which were sensitive to erosional and depositional processes. Soil samples from the 5–10 cm (topsoil), as well as 45–70 and 160–200 cm (subsoil) were selected from both eroding and depositional sites. For the incubations, 20 g of moist

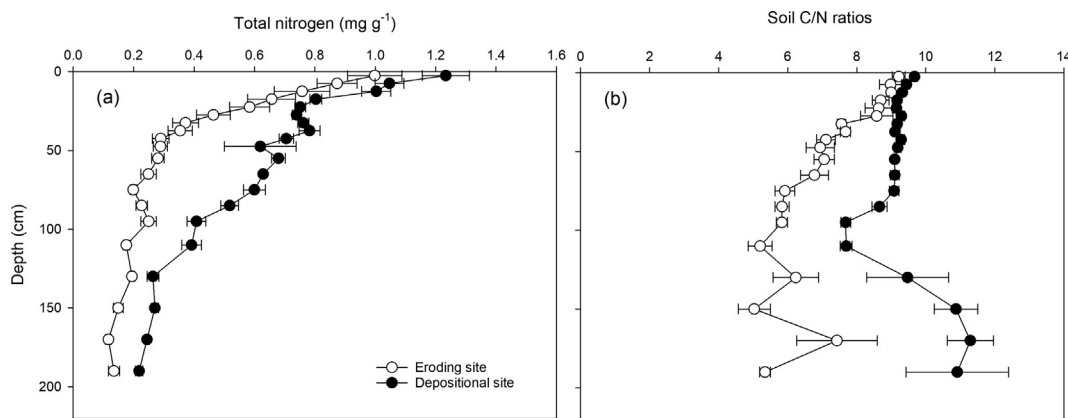


Fig. 1. Depth distribution of (a) total nitrogen (N) contents (mg g^{-1}) and (b) C/N ratios from eroding and depositional sites (mean \pm standard error; $n = 3-5$).

soil (oven-dried basis) were incubated at 20°C in the dark for 28 days in two sets of triplicates. The incubations were carried out at three O_2 levels: the control (20% oxygen, laboratory atmosphere), no oxygen (N_2 atmosphere) and low oxygen (5% O_2 in an N_2 atmosphere; Praxair, Vlaardingen, the Netherlands), as well as with and without glucose (labile substrate) addition. For half of the incubated sample sets, 15 mg glucose-C per g soil C (1 ml solution) was added after the first 14 days pre-incubation, following Hartley et al. (2010). For comparison, the same amount of distilled water (1 ml) was added to all other flasks. Concentrations of CO_2 and CH_4 were determined by gas chromatography (Varian STAR 3600, Palo Alto, California, USA) and reported in detail in Wang et al. (2013). After 28 days of incubation, soil samples were frozen and stored at -18°C for subsequent determination of soil microbial biomass N (SMBN), dissolved organic C (DOC), dissolved total N (DTN), and $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$.

2.5. Nitrogen analytical methods

Soil microbial biomass N was determined before and after the incubation using the chloroform fumigation-extraction method (Chevallier et al., 2010; Joergensen, 1996). Dissolved organic C and DTN were extracted using 0.05 M K_2SO_4 and concentrations of the soil extracts were determined using a TOC analyzer (TOC-VCPH, Shimadzu). Soil microbial biomass N was calculated by dividing the difference between the extracted DTN in fumigated and non-fumigated soil samples by a conversion factor of 0.54, which is defined as the extractable part of the microbial biomass after fumigation (Brookes et al., 1985). The concentrations of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ in the soil extracts were determined by an automated wet chemistry analyzer-continuous flow (Skalar SAN++ System, Breda, The Netherlands). We calculated the total inorganic N as the sum of $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$. We calculated net ammonification, net nitrification and net N mineralization over the course of the incubation.

The net cumulative N nitrification (N_n), ammonification (N_a) and mineralization (N_m) were calculated as followed:

$$N_n = \text{NO}_3^-_{28} - \text{NO}_3^-_0 \quad (1)$$

$$N_a = \text{NH}_4^+_{28} - \text{NH}_4^+_0 \quad (2)$$

$$N_m = N_n + N_a \quad (3)$$

where $\text{NO}_3^-_{30}$ and $\text{NH}_4^+_{40}$ are the NO_3^- and NH_4^+ contents in the samples before the incubation, while $\text{NO}_3^-_{328}$ and $\text{NH}_4^+_{428}$ are the NO_3^- and NH_4^+ contents after 28 days of incubation, respectively. The units of N_n , N_a , and N_m are $\mu\text{g g}^{-1}$ soil.

2.6. Statistical analysis

The mass content of N in each fraction is calculated as:

$$\begin{aligned} N \text{ in each fraction } (\text{mgg}^{-1}) \\ = \frac{N \text{ content per fraction} \times \text{mass of each fraction}}{\text{mass of bulk soil}} \end{aligned} \quad (4)$$

The proportion of N in each fraction relative to soil total N is calculated as:

$$\begin{aligned} N \text{ in each fraction } (\% \text{total } N) \\ = \frac{N \text{ content per fraction} \times \text{mass of each fraction}}{\text{mass of bulk soil} \times N \text{ content in bulk soil}} \times 100\% \end{aligned} \quad (5)$$

A multi-way analysis of variance (ANOVA) was conducted to examine the direct and interactive effects of erosion, depth, O_2 levels (0, 5 and 20% O_2) and glucose addition on the rates of net N mineralization, nitrification, and ammonification. Differences between eroding and depositional sites were tested using one-way ANOVA. In all cases, we considered differences to be statistically significant at $P < 0.05$. All results are expressed as the mean of three replicates. All data were analyzed with JMP 13.2 (SAS Institute, Cary, USA).

3. Results

3.1. Depth distribution of total nitrogen

Soil total N contents exponentially decreased with depths at both sites (Fig. 1a). At comparable depths, the depositional site had significantly larger total N contents than the eroding site throughout the entire soil profiles (Fig. 1a). The difference of total N between the two sites was smaller in the topsoil and sharply increased with depth, resulting in approximately threefold greater N contents in depositional soils at 30–80 cm depth (about 0.5 mg g^{-1} soil). Below 100 cm, the difference in total N content between the two sites remained relatively constant.

Soil C/N ratios in the eroding soil decreased from the surface to 100 cm depth, while at the depositional site, these ratios were relatively constant within the upper 80 cm, with the lowest values appearing at ~ 100 cm depth (Fig. 1b). Soil C/N ratios were higher at depositional than eroding sites. The difference in C/N ratios between the two sites was smaller in the surface soil and increased with depth. Below ~ 150 cm depth, soil C/N ratios showed larger variations at both sites.

3.2. Aggregate associated nitrogen distribution

The large macro-aggregates ($> 2 \text{ mm}$) contained more than 67% of the total N at the two sites (Fig. 2). Large macroaggregates contributed significantly more to total N in depositional soils than in eroding soils. The 8–16 mm fraction contained most of the N at the two sites, primary owing to its large mass abundance. The N distribution over the ten

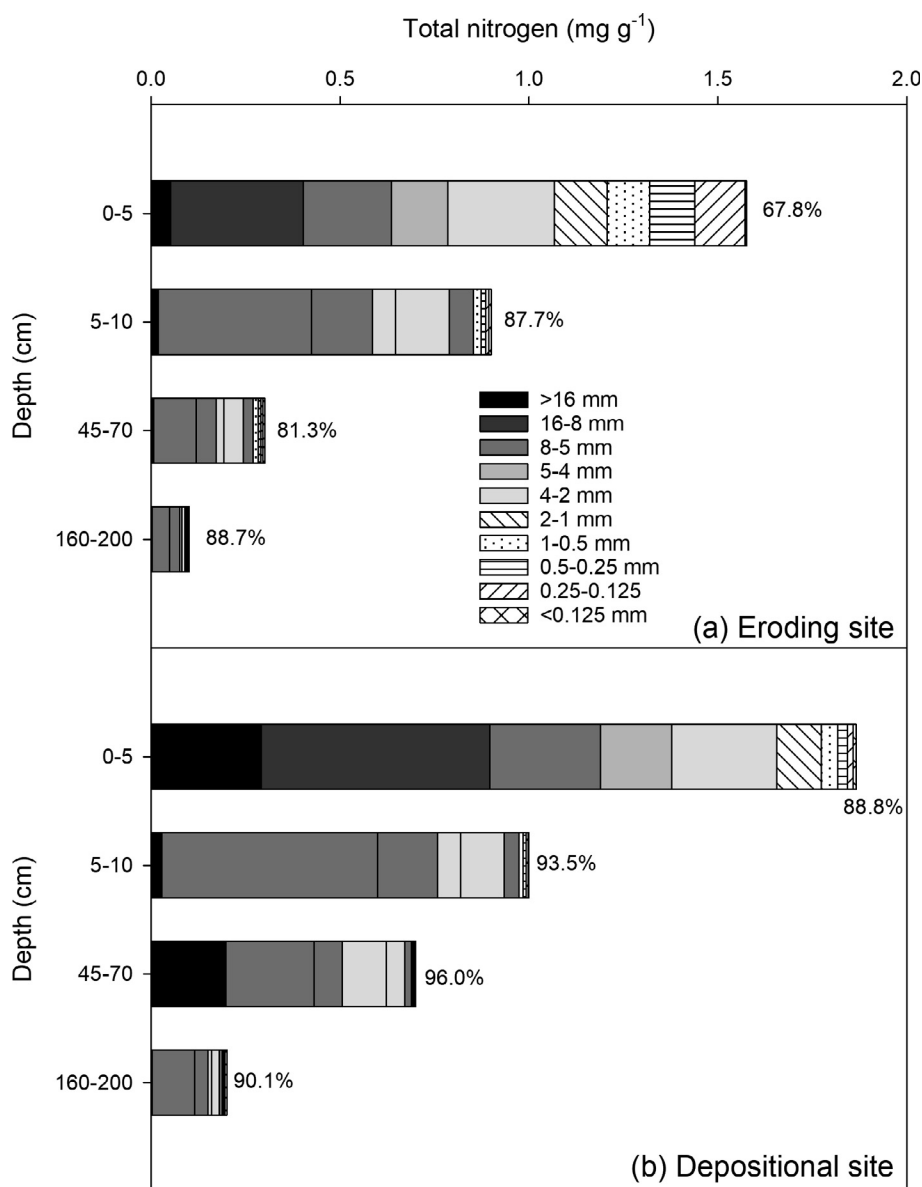


Fig. 2. Distribution of total nitrogen (N; mg g⁻¹) in the ten aggregate size fractions at eroding (a) and depositional (b) sites. Data were calculated by multiplying the N per aggregate size fraction with the corresponding mass of the fractions. The numbers in the figure (percentages) refer to the contributions of large macro-aggregates (> 2 mm) to total N (total N = 100%) at four representative soil depths.

aggregate size fractions generally mirrored the mass distribution of the aggregate classes.

The depositional site had significantly higher N contents in the bulk soil (mg g⁻¹; Fig. 1) and within most aggregates of the same size (mg g⁻¹ fraction) than the eroding site, except for the 5–10 cm depth interval (Table 1). For the 0–5 cm depth, the 0.125–0.25 mm aggregates had the largest N contents per aggregate among all aggregate sizes, while no specific patterns were observed for other depths.

Over 93% of the total soil N was associated with minerals (heavy fraction), followed by occluded N and particulate N (N in the free light fraction) (Fig. 3). At the depositional site, we found more N contained within the occluded and heavy fractions than at the eroding site for comparable depths.

In the free light fraction, the N content per fraction was significantly higher in the 45–70 cm and 160–200 cm depths, while they were similar in the 5–10 cm depth at both sites (Table 2). In the occluded light fraction, the N content per fraction was significantly higher at the depositional site. In the heavy fraction, the N contents were similar at both sites except for 45–70 cm depth, where with higher N contents are

found at the depositional site.

3.3. Inorganic nitrogen

At the two sites, inorganic N concentrations showed a decreasing trend with depth (Table 3). Inorganic N constituted 0.2 to 1.2% of the total N, which was dominated by NO₃-N at both sites. Depositional soils had significantly larger inorganic N and NO₃-N contents at 5–10 cm and 45–70 cm depths. At 160–200 cm depths, inorganic N concentrations did not differ significantly between the two sites. At 5–10 cm depth, soil microbial biomass N was approximately twice as much at the eroding sites.

3.4. Net nitrogen nitrification, and mineralization

Net N mineralization and net N nitrification rates showed a similar trend at the two sites (Figs. 4 and 5). Erosion, depths, and oxygen concentrations significantly affected net N mineralization and net N nitrification rates (Figs. 4–6). The net N mineralization and net N

Table 1 Nitrogen (N) content (mg g^{-1} fraction) of ten aggregate size fractions (mean \pm standard error; n = 3; except for 160–200 cm depth). The different small letters indicated the significant differences between the eroding and the depositional sites.

Site	Depth (cm)	Aggregate size										Average
		> 16	16–8	8–5	5–4	4–2	2–1	1–0.5	0.5–0.25	0.25–0.125	< 0.125	
Eroding site	0–5	1.60 \pm 0.33a	1.43 \pm 0.28a	1.36 \pm 0.13b	1.47 \pm 0.21a	1.57 \pm 0.27a	1.68 \pm 0.24a	1.76 \pm 0.31a	1.95 \pm 0.35a	2.25 \pm 0.38a	1.42 \pm 0.17a	1.65
	5–10	1.55 \pm 0.58a	1.06 \pm 0.05b	1.19 \pm 0.19a	1.17 \pm 0.22a	1.30 \pm 0.38a	1.57 \pm 0.37a	1.57 \pm 0.35a	1.75 \pm 0.40a	1.99 \pm 0.42a	1.32 \pm 0.14a	1.45
	45–70	0.43 \pm 0.02a	0.42 \pm 0.03b	0.40 \pm 0.02b	0.45 \pm 0.03b	0.46 \pm 0.03b	0.44 \pm 0.01b	0.49 \pm 0.03b	0.46 \pm 0.04b	0.42 \pm 0.03b	0.43 \pm 0.01b	0.44
Depositional site	160–200	0	0.18	0.33	0.27	0.23	0.21	0.26	0.26	0.31	0.30	0.23
	0–5	1.60 \pm 0.09a	1.85 \pm 0.06a	1.89 \pm 0.10a	1.82 \pm 0.18a	2.06 \pm 0.25a	2.07 \pm 0.22a	2.20 \pm 0.18a	2.46 \pm 0.26a	2.5 \pm 0.26a	1.68 \pm 0.04a	2.01
	5–10	1.40 \pm 0.47a	1.43 \pm 0.02a	1.32 \pm 0.02a	1.29 \pm 0.06a	1.32 \pm 0.01a	1.31 \pm 0.05a	1.40 \pm 0.04a	1.63 \pm 0.08a	1.57 \pm 0.11a	1.07 \pm 0.05a	1.37
160–200	45–70	0.85 \pm 0.09a	0.81 \pm 0.08a	0.82 \pm 0.02a	0.8 \pm 0.01a	0.88 \pm 0.04a	0.88 \pm 0.01a	0.84 \pm 0.02a	0.81 \pm 0.02a	0.79 \pm 0.08a	0.61 \pm 0.04a	0.81
	160–200	0	0.32	0.37	0.37	0.40	0.35	0.47	0.40	0.35	0.43	0.35

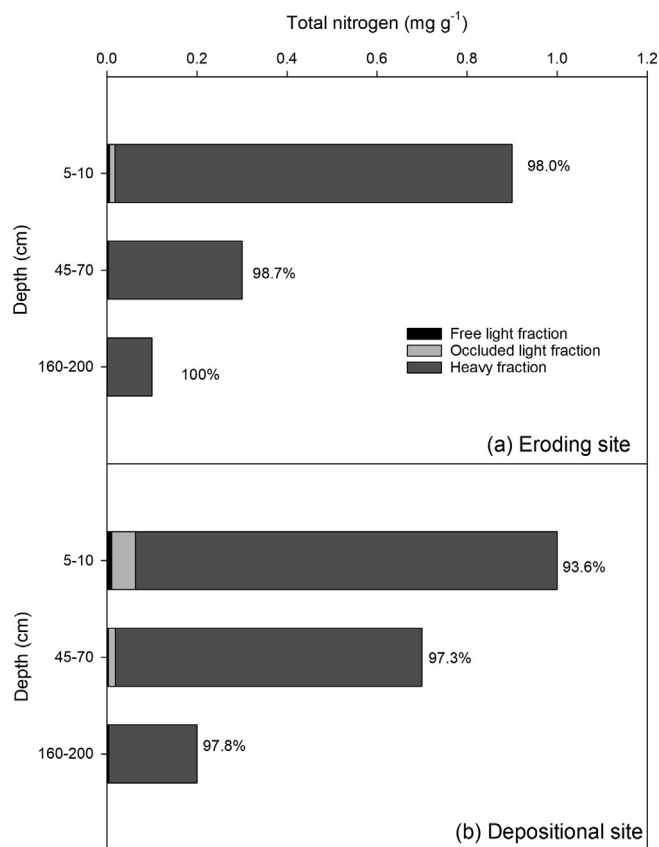


Fig. 3. Nitrogen (N) contents in the three density fractions (free light fraction, occluded light fraction, and heavy fraction) from the eroding (a) and depositional (b) sites. Percentages in the figures refer to the contribution of the heavy fraction to total nitrogen at the three soil depths.

nitrification rates showed positive values and decreased with depth at the two sites under 5% and 20% O₂ conditions. Under anaerobic conditions, all soils exhibited negative net N mineralization and net N nitrification rates. The depositional site had lower average net N nitrification rates and net N mineralization rates, but higher average net ammonification rates (Fig. 6). Oxygen concentrations increased net nitrification and mineralization rates but tended to decrease net ammonification rates. In addition, glucose additions decreased net nitrification and mineralization rates but increased ammonification.

4. Discussion

4.1. Erosional redistribution of soil N fractions

Our results suggest that the deposition of the eroded upslope soil material leads to N enrichment throughout the depositional profiles, with the largest difference in total N between the two sites at 35–80 cm depth (Fig. 1a). The N enrichment at the depositional site may be attributed to preferential transport and deposition of N-enriched soil materials. This assumption is supported by a significant larger N content of the occluded light fractions in the depositional site compared with the eroding site (Table 2 and Fig. 4) and often higher N contents in the eroded sediment (McCorkle et al., 2016; Ritchie et al., 2005). The occluded light fraction represented the relative finer organic particles of similar composition as the free light fraction (mainly plant-derived debris), which can be easily transported due to low density, but which is slightly more altered (Golchin et al., 1994; Cerli et al., 2012). Our results indicate that erosion exerts an important control on the depth distribution of soil N in eroding landscapes. The results are in line with previous studies showing erosional effects on N contents and storage

Table 2

Nitrogen (N) content per fraction (mg g^{-1} fraction) of the free light fraction, occluded light fraction, and heavy fraction from three representative depths at the eroding and depositional sites (mean \pm standard error; “np” represents “not present”). The different small letters indicated the significant differences between the eroding and the depositional sites.

Sites	Depth (cm)	Free light fraction N (mg g^{-1} fraction)	Occluded light fraction N (mg g^{-1} fraction)	Heavy fraction N (mg g^{-1} fraction)
Eroding site	5–10	12.45 \pm 0.46 a	19.16 \pm 0.98b	0.82 \pm 0.02a
	45–70	3.96 \pm 0.23a	10.29 \pm 1.39b	0.18 \pm 0.02b
	160–200	np	np	0.11 \pm 0.01b
Depositional site	5–10	12.74 \pm 0.83a	28.63 \pm 0.66a	0.81 \pm 0.10a
	45–70	6.84 \pm 2.26 a	21.96 \pm 0.30a	0.50 \pm 0.03a
	160–200	9.88 \pm 3.71	17.94 \pm 2.42	0.18 \pm 0.01a

Table 3

Concentrations of ammonium ($\text{NH}_4\text{-N}$), nitrate ($\text{NO}_3\text{-N}$), inorganic N ($\mu\text{g g}^{-1}$ soil), and soil microbial N in three selected depths from the eroding and depositional sites (mean \pm SE; n = 3 and “n.d” means “not detectable”). The different small letters indicated the significant differences between the eroding and the depositional sites.

Sites	Depths (cm)	$\text{NH}_4\text{-N}$ ($\mu\text{g g}^{-1}$ soil)	$\text{NO}_3\text{-N}$ ($\mu\text{g g}^{-1}$ soil)	Inorganic N ($\mu\text{g g}^{-1}$ soil)	Inorganic N (%TN)	Soil microbial biomass N ($\mu\text{g g}^{-1}$ soil)
Eroding site	5–10	1.86 \pm 0.24a	8.42 \pm 0.56b	10.28 \pm 0.43b	0.88	10.47
	45–70	0.67 \pm 0.20a	0.96 \pm 0.04b	1.63 \pm 0.17b	0.38	n.d
	160–200	0.59 \pm 0.26a	0.43 \pm 0.26a	1.02 \pm 0.52a	0.44	n.d
Depositional site	5–10	0.34 \pm 0.01b	15.62 \pm 1.13a	15.96 \pm 1.14a	1.17	30.44
	45–70	0.97 \pm 0.03a	2.46 \pm 0.06a	3.43 \pm 0.03a	0.41	1.02
	160–200	0.34 \pm 0.11a	0.40 \pm 0.03a	0.74 \pm 0.14a	0.21	n.d

(Berhe and Torn, 2017; Weintraub et al., 2015). In an eroding landscape at Tennessee Valley, California, depositional soils stored up to three times more N than eroding soils (Berhe and Torn, 2017).

At our sites, soil C/N ratios did not follow the patterns of soil N depth distribution: We observed almost no decrease of depositional soil C/N ratios until ~ 80 cm depth, whereas C/N ratios decreased systematically with depth in the eroding soils (Fig. 1b). Unchanged and relatively higher soil C/N ratios with depth at the depositional site might indicate less intensive decomposition of organic matter than at the eroding site due to (macro)aggregation (Fig. 2) and sorption on the mineral surfaces (Fig. 3). At the depositional site, re-aggregation and sorption of organic matter on the mineral surfaces can protect organic matter, making it less favorable for decomposition which explains the

C/N ratio values. As erosion occurred, deposition and burial of the eroded materials moved the surface soil into the subsurface soil, which contributed to the relatively unchanged C/N ratios with depth. This is also supported by smaller N mineralization and net nitrification rates at the depositional site (Fig. 6), which may be constrained by the labile substrates, i.e., dissolved organic carbon, for the soil microbes (cf. Section 4.2). These results are in line with significantly reduced organic C mineralization at the depositional site relative to the eroding site (Wang et al., 2013).

Mineral associated N, i.e. N in the heavy fraction, dominated the total N inventory (Fig. 3). N-containing compounds form chemical bonds with reactive mineral surfaces, such as clay minerals and poorly crystalline Fe and Al oxides (Kleber et al., 2015; Kögel-Knabner et al.,

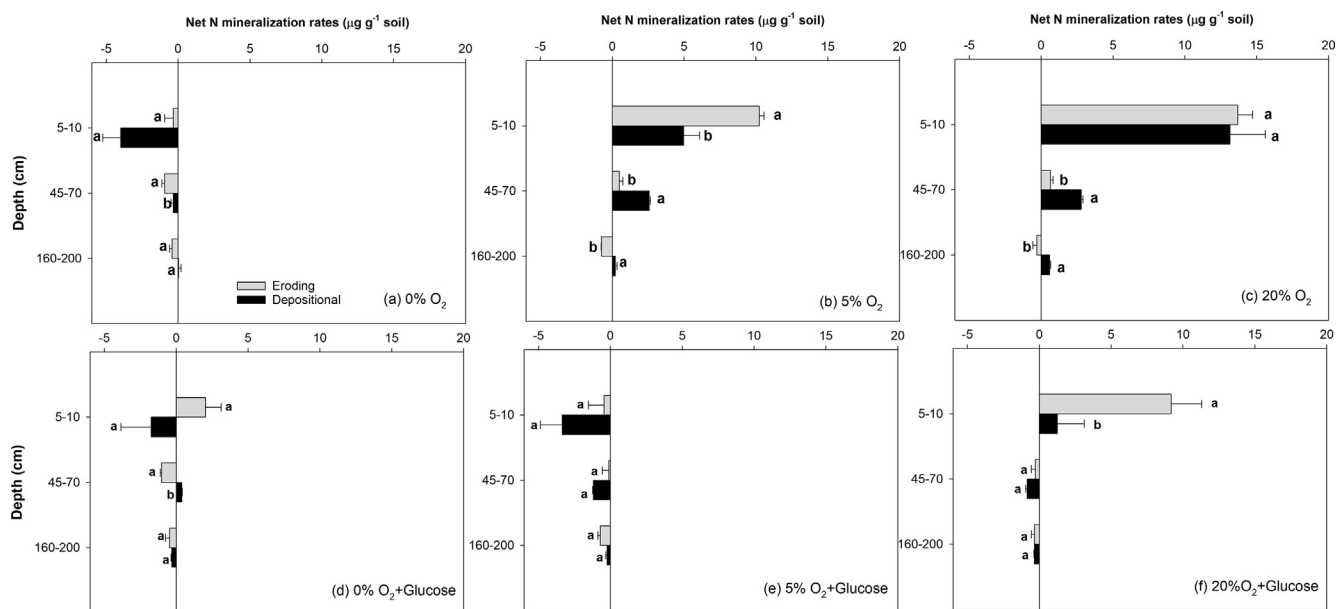


Fig. 4. Net nitrogen (N) mineralization rates for three selected depths at the eroding and depositional sites under three O_2 conditions (0%, 5%, and 20%) and with and without glucose addition. Different letters represent a significant difference between eroding and depositional sites ($p < 0.05$). Error bars represent the standard errors ($n = 3$).

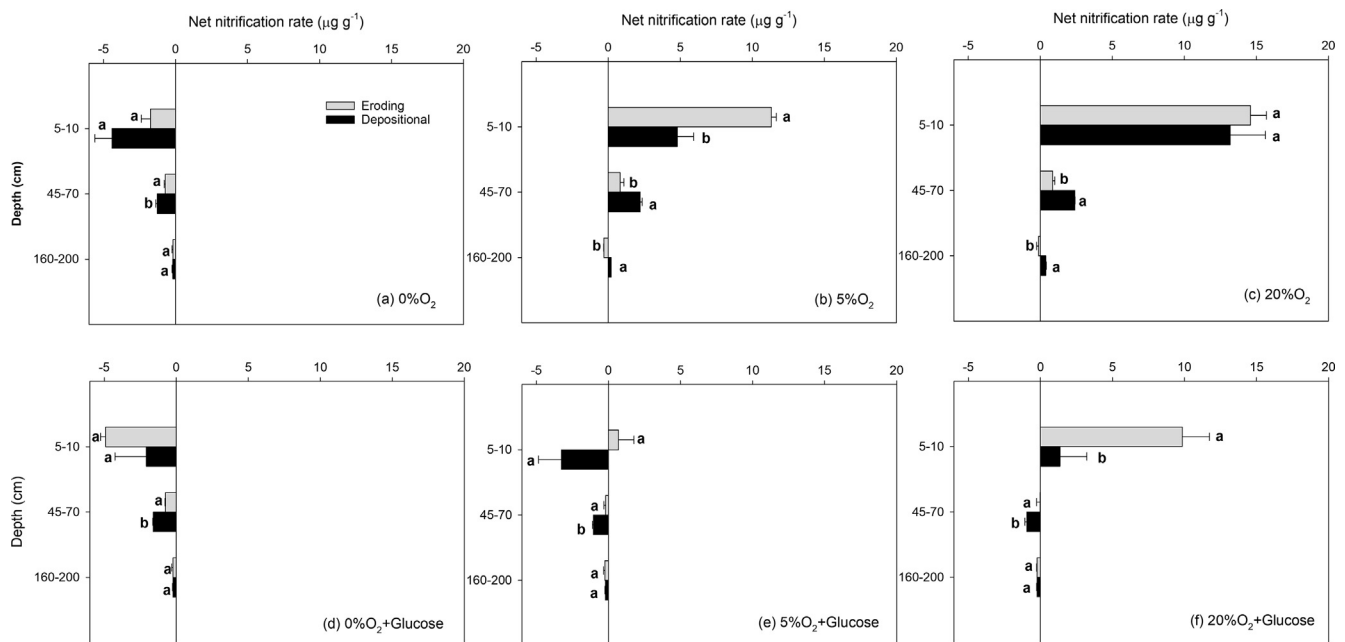


Fig. 5. Net nitrogen (N) nitrification rates for three depths at the eroding and depositional sites with different O₂ availabilities (0%, 5%, and 20%) and with and without glucose addition. Different letters represent a significant difference between eroding and depositional sites ($p < 0.05$). Error bars represented standard error ($n = 3$).

2008). In the recent review of Jilling et al. (2018), mineral associated N comprised between 34.8 and 94.5% of total N. In addition, Berhe and Torn, (2017) suggested that more than 90% of soil N is associated with relatively recalcitrant and stable forms of organic matter, which is an important control on long-term stabilization of organic matter in soils (Berhe and Torn, 2017; Kleber et al., 2007; Schlesinger, 1997).

The high contribution of N in large macroaggregates (> 2 mm) to the total N at the eroding site (67.8%) increased to more than 88.8% at the depositional site (Fig. 2). These results indicate that re-aggregation and burial of transported soil particles in depositional soil likely protect fresh N inputs from subsequent gaseous and dissolution losses. Since organic N forms accounted for more than 98.8% of the total N at the two sites (Table 3), N associated with minerals is likely to closely associated with soil organic matter (Wang et al., 2013, 2014). At the depositional site, the increased macro-aggregate and mineral associated N could be derived from: (i) the preferential removal and transport of N-enriched surface soils from the eroding to depositional positions (Berhe and Torn, 2017; Kuhn et al., 2009); and (ii) dissolved N forms (i.e. inorganic N) and other readily soluble components generated by the breakdown of aggregates, which could be leached and transported via overland or subsurface flow, and subsequently placed in contact with reactive mineral surfaces to enable sorptive protection (Craine et al., 2015; Kaiser and Kalbitz, 2012; Taylor et al., 2015) and/or (iii) *in-situ* biological N fixation and burial of plant-derived N input (Berhe et al., 2012; Wang et al., 2013, 2014; Weintraub et al., 2015; Yoo et al., 2006). The latter may be reflected by the largest contribution of particulate N to total N in topsoils at the depositional site (Fig. 3).

In depositional subsoils, N contents per fraction in the free light and occluded light fractions were significantly higher than in eroding soils (Table 3). In contrast, at eroding positions, erosion removes the nutrient-enriched topsoil and exposes the subsurface soil with small C loadings but more available mineral surfaces, which have a large capacity to stabilize N-containing compounds (Berhe and Torn, 2017; Kleber et al., 2015). In addition to the preferential transport of particulate N from upslope positions, these exhumed mineral surfaces provide available sorption sites for N-containing compounds, which may explain the larger proportion of mineral associated N relative to total soil N in eroding soils (Fig. 3).

4.2. Erosional effects on transformation and bioavailability of soil nitrogen

Erosion and transport of surface soil and associated organic matter not only redistribute N over different fractions both laterally and vertically but also significantly influence the bioavailability of soil N (Table 3). At the depositional site, inorganic N concentrations were significantly higher in the 5–10 cm and 45–70 cm depth intervals than at the eroding site (Table 3). The difference in inorganic N between the two sites was driven by NO₃-N (Table 3). Our results were comparable with previous studies that show erosion exerts an important control on soil N availability wherein they compare inorganic N pools, net mineralization and nitrification rates in the ridge, shoulder and slope position of a soil mantled hillslope (Hilton et al., 2013; Weintraub et al., 2015). Our results also emphasize that soil erosion strongly controls the distribution of inorganic N in dynamic eroding landscapes.

Averaged across all the variables, net N mineralization (1.68 vs. 0.47 $\mu\text{g g}^{-1}$) and net nitrification rates (1.59 vs. 0.22 $\mu\text{g g}^{-1}$) were significantly higher at the eroding site (Fig. 6). Previous studies have suggested that erosion is a critical landscape-level control that influences factors regulating N bioavailability, such as soil moisture and nutrient availability (Stewart et al., 2014; Weintraub et al., 2015). Our results appear contradictory to this, at least with respect to greater proportions of mineral associated N detected at the eroding site (Fig. 3). In the studied soil, the free light fraction likely plays a relatively minor role in N mineralization because this fraction represents a small proportion of the total N ($< 5\%$). One possible explanation for this counterintuitive observation could be that although mineral-associated organic matter has historically been considered a relatively passive N reservoir, recent studies suggested a strong potential for destabilization of mineral-organic associations under favorable conditions (Jilling et al., 2018; Keiluweit et al., 2015).

Alternatively, the smaller net N mineralization and nitrification rates at the depositional site may be attributed to a lack of labile C, thereby limiting substrates available to soil microbes. At the same study site, Wang et al. (2013) found smaller C mineralization and lower DOC concentrations as well as higher UV absorbance of DOC at the depositional site compared with the eroding site. Coupling of these results may suggest that soil N and C mineralization are closely related to each

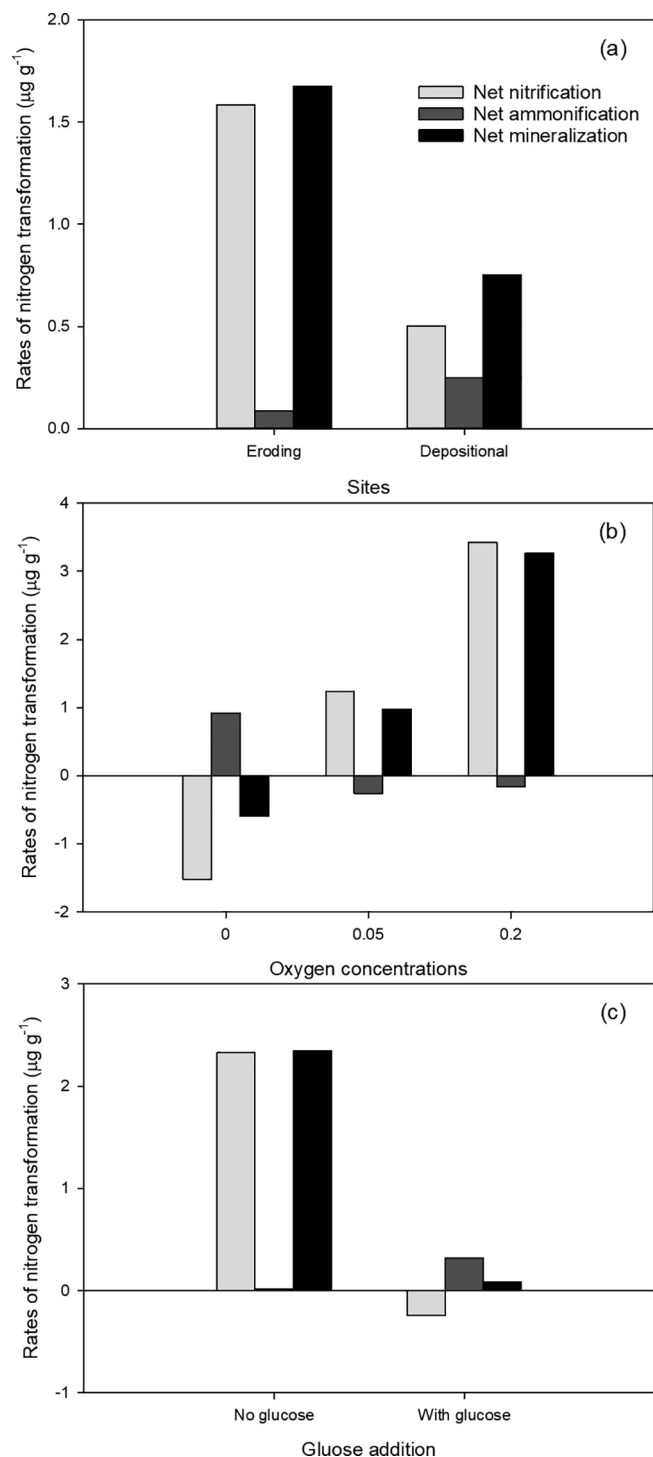


Fig. 6. Averaged net nitrogen (N) mineralization, net nitrification, and net ammonification rates as affected by (a) erosion, (b) oxygen status (0, 5, and 20%), and (c) glucose addition.

other. In addition, N associated with minerals in the depositional site may be more strongly protected against microbial transformation due to different controls governing the stabilization of organic matter between the two sites, such as topographic dependence on the chemical composition of N-containing organic matter bound to reactive mineral surfaces (Berhe et al., 2012; Kleber et al., 2015; Wang et al., 2014).

4.3. Effects of oxygen concentration and glucose addition on N transformation

Soil N mineralization, nitrification and ammonification are microbially mediated processes that depend on the oxygen status and presence of labile organic matter sources (Turner et al., 2017; Yang et al., 2016; Yuan et al., 2018). In our study, glucose addition resulted in smaller net N mineralization and nitrification rates (Fig. 6). These results might be explained by enhanced soil microbial activity and thereby increased organic C mineralization following glucose addition, while the growing population of soil microorganisms utilized a portion of soil N resulting in soil N immobilization (Ma et al., 2016; Yuan et al., 2018). Also, the additions of the rather labile free light fractions ($< 1.6 \text{ g cm}^{-3}$, with averaged organic C concentrations being 11 times higher than the bulk soil) led to N immobilization rather than N mineralization in agricultural and forest soils (Whalen et al., 2000).

We found a positive relationship between O_2 concentrations and net N mineralization and nitrification rates (Fig. 6). This result is in line with previous studies suggesting that O_2 status played a dominant role in the turnover of mineral-associated N under oxic versus anoxic conditions (Turner et al., 2017). However, Yang et al. (2016) found that the change in O_2 concentrations from 20% to 2% did not affect nitrification activities or mineralization rates in paddy soils. They concluded that nitrifiers and microbial communities related to N mineralization might adapt to environments with lower O_2 conditions. Collectively, our results indicate that erosion-induced changes to environmental conditions are an important control on the bioavailability of soil N.

Erosion also changes the pedological properties along the slope (Berhe et al., 2012; Wang et al., 2013), which subsequently exert an important control on the availability, transformation, and immobilization of N in different fractions. These coupled processes, in turn, affect plant productivity, microbial community dynamics, and biogeochemical cycling in soils. However, at our study site, differences in pedogenic oxides between eroding and depositional sites were small (i.e. small pedological change along the slope) (Wang et al., 2013), which may not fully explain the observed differences in mineralization of soil N between eroding and depositional sites. Therefore, we suggest that erosion-induced N transformations and losses can be co-determined by many factors, and further research is required to examine the complex interactions between organic and inorganic substrates, microbes and pedological (mineralogical) variables across the dynamic erosion-deposition continuum.

5. Conclusion

In this study, we explored how erosion affects the vertical and lateral distribution of soil N in bulk soil, aggregate size fractions, and density fractions, as well as their controls on N bioavailability. Our results suggested that the deposition of eroded upslope soil materials led to N enrichment within depositional soil profiles. Total N was dominated by mineral associated N, with more than 93% of soil N found within mineral-associated fractions at both sites. A larger contribution of macroaggregates and mineral-associated N at the depositional site indicates that aggregation and the binding of N-containing compounds with reactive mineral surfaces are important controls on N transformation and stabilization during hillslope transport. In addition, deposition of the eroded soil materials resulted in more inorganic N as well as N enrichments in the microbial biomass, suggesting strong erosional controls on the bioavailability of soil N.

In the context of erosion, O_2 concentrations and the availability of labile C significantly affected N mineralization and nitrification. Our results suggest that local environmental conditions are important factors controlling the bioavailability and transformation of N on soil-mantled hillslopes, with important implications for biogeochemical cycling, soil fertility and agricultural production in sloping landscapes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.geoderma.2020.114231>.

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