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# Mineral N stock and nitrate accumulation in the 50 to 200 m profile on the Loess Plateau

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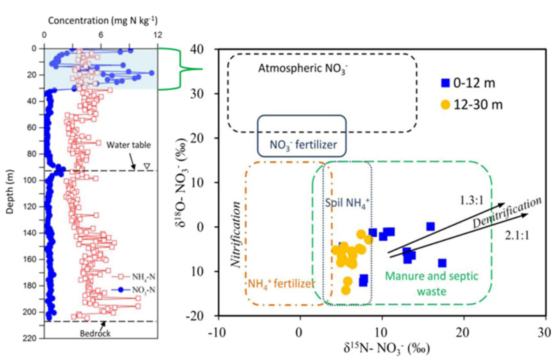
## HIGHLIGHTS

- Sediments were taken from land surface to bedrock on the Loess Plateau.
- Vertical patterns of $NO_3$-N and $NH_4$-N content and mineral N stock were determined.
- Significant nitrate accumulation was observed to 30–50 m depth at two sites.
- Soil $\delta^{15}N$ and $\delta^{18}O$ of nitrate indicate different causes for accumulated nitrate.
- A low denitrification potential in the lower part of the vadose zone

## GRAPHICAL ABSTRACT

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## ABSTRACT

Nitrogen (N) stored in deep profiles is important in assessing regional and/or global N stocks and nitrate leaching risk to groundwater. The Chinese Loess Plateau, which is characterized by significantly thick loess deposits, potentially stores immense stocks of mineral N, posing future threats to groundwater quality. In order to determine the vertical distributions of nitrate and ammonium content in the region, as well as to characterize the potential accumulation of nitrate in the deep loess profile, we study loess samples collected at five sites (Yangling, Changwu, Fuxian, An'sai and Shenmu) through a 50 to 200 m loess profile. The estimated storage of mineral N varied significantly among the five sites, ranging from 0.46 to 2.43 × $10^4$ kg N $ha^{-1}$. Ammonium exhibited fluctuations and dominated mineral N stocks within the whole profile at the sites, except for the upper 20–30 m at Yangling and Changwu. Measured nitrate content in the entire profile at Fuxian, An'sai and Shenmu is low, but significant accumulations were observed to 30–50 m depth at the other two sites. Analysis of $\delta^{15}N$ and $\delta^{18}O$ of nitrate indicates different causes for accumulated nitrate at these two sites. Mineralization and nitrification of manure and organic N respectively contribute nitrate to the 0–12 and 12–30 m profile at Changwu; while nitrification of $NH_4^+$ fertilizer, $NO_3^-$ fertilizer and nitrification of organic N control the nitrate distribution in the 0–3, 3–7 and 7–10 m layer at Yangling, respectively. Furthermore, our analysis illustrates the low denitrification

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potential in the lower part of the vadose zone. The accumulated nitrate introduced by human activities is thus mainly distributed in the upper vadose zone (above 30 m), indicating, currently, a low nitrate leaching risk to groundwater due to a high storage capacity of the thick vadose zone in the region.



## 1. Introduction

Over use of synthetic nitrogen (N) fertilizer (and/or manure) as well as increased deposition of atmospheric N have adversely and chronically affected soil and water quality, human health, biodiversity and ecosystem functions around the world (Vitousek et al., 1997, 2009; Galloway et al., 2003; Walvoord et al., 2003; Zhu et al., 2005; Guo et al., 2010). To understand and manage the environmental impacts of mineral nitrogen, N reservoirs, sources and cycling rates have been studied at a wide range of scales to quantify N budgets (Cleveland et al., 1999; Galloway et al., 2003; Jin et al., 2015; Quan et al., 2016). Investigations of soil N within the upper 1 m soil depth, defined operationally as the biologically active soil zone or the root zone in most agricultural systems, where N turnover is rapid (Schlesinger et al., 1990), as well as lower vadose zone beyond the root zone, have been conducted around the world (Mercado, 1976; Walvoord et al., 2003; Izbicki et al., 2015; Turkeltaub et al., 2015; Huang et al., 2016). However, the scarcity of measured deep N data still limits the regional and/or global estimation of N stock, especially for some regions with thick sedimentary deposits. For example, consideration of desert subsoil N storage could raise estimates of vadose zone N inventory by 14 to 71% for warm deserts and arid shrublands worldwide and by 3 to 16% globally (Walvoord et al., 2003). In a recent study, Ascott et al. (2017) estimate 605–1814 Tg of nitrate stored in pore waters in the vadose zone across the globe.

Soil N is immobilized by microbes or fixed by clay minerals, but also exists as nitrate ($NO_3$-N) or ammonium ($NH_4$-N) in the soil matrix (Sebilo et al., 2013). Because nitrate is very dynamic and mobile (Gu et al., 2013), subsoil nitrate can leach beyond the reach of roots, eventually leaching to groundwater, causing nitrate contamination and consequently a threat to human health (Babiker et al., 2004). Moreover, nitrate accumulated in the topsoil layer is considered to have very different environmental impacts compared to that leached to the subsoil layer (Zhou et al., 2016). Therefore, quantifying the magnitude and distribution characteristics of subsoil N can provide additional information on understanding of N cycling within thick soil profiles, which will help improving residual N management and assessing the nitrate leaching risk.

The Loess Plateau (LP) is located in the middle reach of the Yellow River in North China and is the deepest and largest loess deposit in the world (Yang et al., 1988). Parts of the region, e.g., the Guanzhong Plain and some tableland areas, have experienced intensive agricultural activities for hundreds of years (Wei et al., 2010). A number of investigations on the plateau have been conducted to investigate the distribution patterns of soil nitrate and ammonium in the profiles and study the loss and accumulation of nitrate in the root zone, which have shown that long-term application of N fertilizer or manure as well as increased nitrate deposition resulting from the rapid development of petroleum and coal industries in this region can significantly increase residual N in the soil and pose a potential threat to groundwater (Lü et al., 1998; Fan et al., 2010; Wei et al., 2010; Jin et al., 2015). However, most of these studies have focused on the top 4 m soil layer. Several studies measured N at depths deeper than 4 m, but usually <20 m (Jin et al., 2015; Zhou et al., 2016). Leakage of nitrate may occur below such depth, gradually moving downward to the deeper vadose zone and to groundwater (Zhou et al., 2016; Huang et al., 2018). Furthermore, the LP is predominantly covered by loessial deposits, which range in thickness from 30 to 200 m (Zhu et al., 2018). This deep deposit means that the LP has high potential for storing nitrogen or other nutrients. Therefore, there is a need for N data to facilitate evaluations of the stock of mineral N and in order to understand N cycles that occur in the deep profiles in the LP. Further research is also needed to determine the depth and extent of leached nitrate, particularly given the environmental sensitivity of the LP region.

We hypothesize that (1) there may be a significant nitrate accumulation in the deep vadose zone, particularly in the southern parts of the region which experience much higher precipitation and more intensive agricultural activities and (2) accumulated nitrate in the deep vadose zone cannot be denitrified due to lack of dissolved organic carbon. To address these hypotheses, loess samples from the land surface to bedrock (approximately 50–200 m) at five sites from the south to the north of the plateau were analyzed to determine nitrate and ammonium concentrations. The specific objectives of this study were (1) to investigate the distribution characteristics of mineral N ($NO_3$-N and $NH_4$-N) between the surface and bedrock on the LP, (2) to assess the size of mineral N stock within thick loess deposits, and (3) to characterize the potential nitrate accumulation in the deeper vadose zone by analyzing natural abundance of nitrate N and O isotopes.

## 2. Materials and methods

### 2.1. Study area

This study was conducted on the Chinese LP (33.72–41.27°N, 100.90–114.55°E and 200–3000 m a.s.l., Fig. 1) that covers a total area of 640,000 $km^2$. The region has a continental monsoon climate with the mean annual precipitation (MAP) ranging from 150 mm in the northwest to 800 mm in the southeast, most (55–78%) of which falls in June through September. The mean annual temperature (MAT) is 3.6 °C in the northwest and increases to 14.3 °C in the southeast (1953–2013 data from 64 weather stations). The thickness of loess deposits ranges from 30 to 200 m, with an average of 92.2 m (Zhu et al., 2018), and sandy in texture in the northwest and more clayey in the southeast. The LP topography is characterized by Yuan (a large flat surface with little or no erosion), Liang (a long narrow range of hills), Mao (an oval-to-round loess hill) and gullies of all shapes and forms (Yang et al., 1988). The plateau can be divided into three sub-regions according to water availability to ecosystems: the Mu Us Desert in the driest northwest sector of the plateau; an area of irrigated agriculture within the main stem of the Yellow River catchment in the southeast plateau; and the rain-fed hilly area in the middle of the plateau (Fig. 1).

### 2.2. Borehole drilling and sediment sample collection

Five boreholes were drilled along a south-north direction on the LP: Yangling (YL), Changwu (CW), Fuxian (FX), An'sai (AS) and Shenmu (SM) (Fig. 1). A single borehole (15 cm in diameter) at each site was drilled from the land surface to bedrock between May and June 2016 using the under-reamer method, also known as the ODEX (Overburden Drilling EXploration) air-hammer drilling method (Izbicki et al., 2000). The drilling depth ranged from 56 to 205 m. A description of each site is shown in Table 1. The croplands at sites FX, AS and SM have been abandoned for natural vegetation restoration since 2000 to control soil erosion.

Entire loess cores were collected at 1 m intervals from the land surface to bedrock at each site. At YL, sediment samples were collected at 0.5 m intervals in the top 10 m depth in order to consider the effect of intensive human activities, and then at 1 m intervals below that. A