

A NEW METHOD FOR ULTRA-LOW SULFATE EXTRACTION
AND A PILOT STUDY IN ARID SOILS

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DEDICATION

This thesis is dedicated to my husband, Jorge, my parents, Aurelio, and María and my siblings Blanca and Osvaldo. The reason I am where I am right now, is because of you. You have and continue to motivate me in continuing on this educational path. Even though sometimes it seems too much, I know you will always be there for me. Thank you for being you!

PREVIEW

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by

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THESIS

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ABSTRACT

Sulfur in soils is a crucial nutrient for all organisms including plants. Sulfate (SO_4^{2-}), a water soluble anion, is a good source of this important element. Because of the importance of sulfur for agriculture, the use of sulfate has been well studied in temperate climate zones, and it is generally accepted that microbes play a critical role in controlling the availability of sulfate. Organically bound sulfur, such as sulfate esters and carbon-bonded sulfur, compounds that are generated and decomposed by microbes, are essential sulfur sources for plants under these conditions. For arid environments, knowledge of sulfate turnover in soils by microbes and plants is much more limited. It is not known whether sulfate turnover by microbes in desert soils is more or less critical than in temperate climates.

El Paso, Texas is located in the Chihuahuan Desert, an arid environment. It is also surrounded by agricultural areas, which receive sulfate through application of fertilizers and irrigation waters; is located in proximity of White Sands National Park, a source of gypsum dust; and receives water from two aquifers, Mesilla and Hueco Bolson that have relatively high sulfate concentrations. These contrasts make El Paso a unique site for sulfur cycling studies.

Theoretically, it is possible to trace the sulfate turnover by measuring changes in the sulfur and oxygen isotope of sulfate. The challenge for this approach is that sulfate in arid soils exists only in low concentration, which renders accurate determination of isotope compositions difficult. The objectives of this study were 1) to develop a new method to extract low sulfate from soils for isotope analysis and 2) to carry out a pilot study on microbial turnover of sulfate in soils from nearby White Sands National Park, El Paso Texas and the Indio Mountains.

So far, methods for the extraction of sulfate from solutions with low sulfate concentrations relied on techniques that employed ion exchange resins. This approach requires large volumes of the

solution from which sulfate is to be extracted, and only works for solutions with low ion strength. Thus, sulfate extraction from high-chloride, low-sulfate solutions was not possible. My now proven technique uses the classical approach of collecting sulfate as barium sulfate, followed by a chelator-assisted dissolution-precipitation step which returns a pure barium sulfate sample. The method can be used on solutions with high chloride levels, up to the equivalent of chloride encountered in seawater (>500 mM), and enables extraction of sulfate from samples with sulfate concentrations as low as 0.03 μM and volumes below of 50 ml.

The application of the developed technique to soils from a site on the ‘Lost Dog Trail’ (El Paso), and a location in the Indio Mountains revealed that arid soils have indeed extremely low sulfate content. The observed values for the Indio Mountains are $\sim 0.5 \mu\text{mol}$ of sulfate per gram of soil. No sulfate was recovered from the Lost Dog Trail samples, suggesting a sulfate content of less than $0.1 \mu\text{mol}$ of sulfate per gram of soil for this site. The sulfur isotope composition of the sulfate obtained from the Indio Mountains is almost identical to the isotope composition of sulfate found near the White Sands National Park, indicating that transport of dust from this site could be a major sulfur source to this region. This input could be in form of dry deposition, or happen during rain events. In order to obtain insight if biological sulfur cycling takes place in the investigated arid soils, a strong rainfall event was mimicked. The soils were covered with water that was amended with sulfate ($\sim 210 \mu\text{M}$, approximately 3 times the typical value for rainwater over North America) and labeled with ^{18}O -enriched water. Decreasing sulfate concentrations and an enrichment in ^{18}O of sulfate revealed that microbial sulfur cycling takes place after rainfall events, and that oxygen isotopes of sulfate can be successfully applied to trace soil sulfur cycling in arid soils.

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1. BACKGROUND AND MOTIVATION

1.1 SULFUR AS BIO-ESSENTIAL NUTRIENT

Sulfur (S) is an essential nutrient for all living organisms. For plants, sulfur is one of the four most important macro-nutrients, including nitrogen, phosphorus, and potassium (Eriksen et al., 1998). Sulfur is instrumental for nitrogen fixation and the synthesis of amino acids such as cysteine and methionine, coenzymes (A, biotin, thiamine, glutathione), chlorophyll and other secondary sulfur compounds (Figure 1; Eriksen et al., 1998).

Over the last two decades an increase in sulfur deficiency has been recorded in many regions of the world (Eriksen, 2009). This sulfur deficiency is mainly caused by the decrease of acid rain due to environmental policies to reduce sulfur dioxide (SO_2) emissions, the increased use of low-sulfur fertilizers and a decrease in the use of pesticides and fungicides that contain sulfur (Eriksen, 2009). For example, as a side effect of the industrial revolution, sulfur deposition in Denmark rose since 1800, reaching a peak in 1970 followed by a sharp decrease due to environmental policies to reduce sulfur dioxide emissions (Figure 2; Eriksen, 2009). A similar pattern is observed in the United States (Figure 3). The decrease in sulfate input has led to a renewed interest in soil sulfur cycling, as sulfate deficiency could negatively impact crop yields.

1.2 MOBILITY OF SULFATE-SULFUR, A CRITICAL NUTRIENT FOR PLANTS

In soils, sulfur is commonly found as organically bound sulfur accounting for approximately 95% of the total sulfur (Eriksen et al., 1998). Sulfate (SO_4^{2-}) or inorganically bound sulfur accounts for approximately 5% of the total sulfur (Scherer, 2009). Sulfate is a crucial sulfur source for plants, because organically bound sulfur must first be liberated from the organic compounds and converted into sulfate before it can be taken up by the root system (Eriksen et al., 1998; Scherer,

2009). In soils, inorganic sulfate can be found in three different forms; sulfate in soil solution (i.e. aqueous sulfate), adsorbed sulfate, and mineral sulfate (Scherer, 2001). The content of sulfate in soils usually depends on plant uptake, contribution from external sulfate sources such as fertilizers, sulfate on dust particles or sulfate in rainwater (acid rain), sulfate immobilization through processes such as adsorption or precipitation, re-mobilization of sulfate by the same processes operating in the opposite direction, formation of organically bound sulfur as well as the mineralization of these compounds, and removal of sulfate by aqueous or wind transport (Scherer, 2009). The ability of soils to retain sulfate by adsorption is controlled by the concentration of anions and cations including the pH-dependent abundance of protons and hydroxide ions that compete with sulfate for adsorption sites on minerals (e.g. clays, iron oxides), soil organic matter, and colloids (Scherer, 2009). Presence of organic compounds in solution (dissolved organic carbon, DOC) also can strongly affect sulfate adsorption via occupation of charged mineral surfaces or as chelators that decrease the activity of cations in solution (e.g. calcium). The soil pH also strongly affects the sequestration or release of sulfate by controlling the precipitation or dissolution of minerals that can trap sulfate, either as coprecipitates (e.g. in carbonates) or as minerals like gypsum or anhydrite (Mayer et al., 1995b). Moreover, the pH plays a critical role in the mineralization of organically bound sulfur, as the activity of the enzymes that catalyze these processes are pH dependent (Ganeshamurthy and Nielsen, 1990; Klose et al., 1999; Kertesz, 2000).

1.3 DYNAMICS BETWEEN ORGANIC SULFUR AND INORGANIC SULFUR

Organically bound sulfur is likely to play a key role in the sulfur cycle of soils, because it constitutes 95% to 98% of the total soil sulfur (Ghani et al., 1993; Kertesz and Mirleau, 2004; Scherer, 2009). The dominance of organically bound sulfur in soils is probably owed to two facts. First, in soils, organically bound sulfur is typically less mobile than sulfate (Scherer, 2001; Scherer,

2009), and second, microbial conversion of inorganic sulfate to organically bound sulfur appears to be very efficient (Eriksen, 2009). As organic sulfur is unavailable for plants the transformation of abundant organically bound sulfur to inorganic sulfur becomes a critical process for plant access and uptake (Castellano and Dick, 1991; Scherer, 2001).

Organically bound sulfur is a heterogeneous mixture of compounds derived from organisms in the soil, including microbes, plants, and animals (Eriksen, 2009). There are two major groups of sulfur compounds that can be identified within this complexity, namely ester sulfates (C-O-S) and carbon-bonded sulfur (C-S) (Scherer, 2009). Microbes play a key role both in the conversion of sulfate into ester sulfates and carbon-bonded sulfur and in the mineralization of these compounds (Ghani et al., 1993). Microbial mineralization of carbon-bound sulfur compounds is probably driven by energetic needs. This means that the reduced carbon moiety of the compound is oxidized to carbon dioxide in order to gain energy, with sulfate being released as a metabolic by-product (Ghani et al., 1993). In contrast, mineralization of ester sulfates is driven by the need for inorganic sulfate. When the supply with inorganic sulfate does not cover the microbial sulfate demand in the soil, enzymes called sulfatases are produced or activated (Scherer, 2009). These sulfatases act as catalysts for the hydrolysis of ester sulfates (C-O-S). One group of sulfatases, the S-O cleaving sulfatases (aryl sulfate monoesters) have been found to be among the most powerful biological catalysts known (Edwards et al., 2012). The two reasons for mineralization of organically bound sulfur are similar to the reasons for mineralization of organically bound phosphorus, where phosphate is either released to the environment because of phosphorous limitation or during the breakdown of organic compounds for dissimilatory processes.

1.4 SULFUR CYCLING IN SOILS FROM ARID ENVIRONMENTS

Approximately, 41% of the world's land surface is composed of arid and semi-arid ecosystems; regions that are vulnerable to climate change (Reynolds et al., 2007; Luo et al., 2015). Global changes in precipitation and temperature may lead to an increase of arid and semi-arid areas and consequently affect plant nutrition and the ecosystem's function (Reynolds et al., 2007; Knapp et al., 2008; Schimel, 2010; Dai, 2011; Luo et al., 2015). Studies suggest that the increase in aridity can negatively affect the biogeochemical cycle of not just sulfur, but also other nutrients such as nitrogen, phosphorus, and carbon (Luo et al., 2015). Only a few studies have investigated the impact of changing climate on the biogeochemical sulfur cycle in arid and semi-arid region (Luo et al., 2015).

The interest in sulfur cycling in arid and semi-arid soils is driven by the insight that such soils could be sulfur-deficient, an observation that was made as early as 1958 (Ensminger, 1958 *vide* Dracy et al., 2013), and has been corroborated by findings that show that sulfur availability in such systems is tightly coupled to other nutrient cycles (i.e. P and N), and also strongly dependent on water addition. Moreover, there appears to be a threshold in aridity at which the availability of sulfur in soils changes from decreasing availability to increasing availability (Luo et al., 2015). Arid soils from the Southwestern United States appear to harbor microbial communities that rely on the availability of thiosulfate for dissimilatory processes, which raises the question if those communities are important for sulfur and carbon cycling in arid soils (Dracy et al., 2013). The dependence of sulfur cycling in arid and semi-arid soils on the multitude of variables that could drastically change due to climate change, such as different rain patterns in terms of duration, intensity, and seasonality and concomitant change of land use (agriculture, cattle, intensity of irrigation) could heavily impact sulfur availability for plants. For temperate environments, it is

commonly accepted that microbial communities exert a strong control on sulfur availability for the plants, as the microbes play a dominant role in the interconversion of soil sulfur fluxes between inorganic and organically bound sulfur pools. For arid environments, this may not be the case, or, vice versa, may be especially true. Obviously, there is an urgent need to elucidate the role of microbial sulfur cycling in soils from arid and semi-arid environments.

PREVIEW

2. THE CHALLENGE: TRACING MICROBIAL SULFUR CYCLING IN SOILS FROM ARID AND SEMI-ARID ENVIRONMENTS

Based on what is known about arid environments and biogeochemical sulfur cycling in soils, I make the following predictions about soil sulfur cycling in arid environments (Text Box 1).

Text Box 1: Predicions about soil sulfur cycling in arid envrionments

- Arid soils contain diverse inorganic (e.g. mineral-bound sulfate) and organic sulfur sulfur pools, with sulfur inventories that can be very large.
- The spatial distribution of these sulfur pools is highly variable.
- The bio-availabitiy of sulfur stored in these pools varies greatly, and the largest sulfur pools may be the most inaccessible sulfur reservoirs (e.g. sulfate trapped in carbonates such as caliche). As such, there may be vast sulfur pools that can never be tapped into.
- Soil sulfur cycling in arid environments is highly episodic, and tied to precipitation. This means that there are long periods of inactivity, which are interrupted by bursts of activity.

If these presumptions are correct, tracing of sulfur cycling in arid environments faces a suite of challenges. First, bulk analyses of inorganic and organic sulfur and other nutrient (e.g. C, N) inventories are likely not adequate to assess if there is a sulfur deficiency, as presence of sulfur does not indicate availability. And even if plant-available sulfur, such as sulfate, is detected, it is not known what process made the compound available – e.g. mineralization of organically bound sulfur, deposition of sulfate via dust transport, or sulfate in acid rain. Finally, general sulfur availability may not be representative for the sulfur that is bio-available during the burst of activity after precipitation or flooding events. These circumstances highlight the need for tracers of sulfur