



Hypoxic and acidic – Soils on mofette fields



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ABSTRACT

Mofette fields are areas characterized by CO₂ that ascends from the earth mantle to the surface owing to volcanic activities. Geogenic CO₂ may almost completely make up the soil atmosphere on mofette fields, inducing fundamental effects on both the vegetation and soils. Mofette fields are thus a natural laboratory to study the effects of increased CO₂ concentrations in the soil atmosphere. Plants adapt physiologically or anatomically to the specific gas budget on mofette fields, forming a typical, often azonal, mofette vegetation. Soil formation and development are similarly controlled by the gas budget. The acidifying effect of CO₂ induces low soil pH, accelerated silicate weathering and leaching of base cations. Formation of secondary Fe and Mn oxides is decreased under partial to total O₂ exclusion, and the oxides remain poorly crystalline. Reduced Fe minerals may be stable in a CO₂ atmosphere. Soil organic matter accumulates on mofette fields and stays in unaltered and less decomposed state, as bioturbation is diminished and microbial communities shift to anaerobic and acidophilic ones, utilizing geogenic CO₂ instead of plant-derived C. Several soil properties and functions are controlled by CO₂ that acts as a soil-forming factor. Thus, we suggest to emphasize its effects more distinctly in soil classification by a 'mofettic' qualifier applicable to all soil reference groups of the WRB classification.

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1. Introduction

Soil gas emissions are common in seismic and volcanic areas. Apart from CO₂ (mofettes), also SO₂ and H₂S (solfatares), CH₄ (mud volcanoes) and hot water vapour (fumaroles) are the most common soil gases (Etiope et al., 2004a, 2004b; Heinicke et al., 2009; Martinelli and Panahi, 2003; Pfanz et al., 2004), with Ar, H₂, He and N₂ at trace levels (Bräuer et al., 2011). The gases are released from ascending magma

owing to temperature and pressure release and find their way to the surface through cracks and fissures. Aside from water vapour, CO₂ is the most important gas occurring in volcanic exhalations. Carbon dioxide dissolves out of the ascending magma, and on its way upward, gas molecules coalesce to form larger bubbles. Depending on the path length, pressure and temperature, the flux of CO₂ can be large (Sparks, 1978). In some cases, CO₂ is dissolved in ascending water and reaches the surface together with the water phase, a system called a mineral spring (i.e., a wet mofette). Carbon dioxide diffusing upward in dry, undissolved state, forms so-called dry mofettes independent of whether it degasses through dry soil or through a water body.

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In general, geogenic CO₂ emanations can be spotted either by a modified vegetation (Pfanz et al., 2004, 2007; Vodnik et al., 2002a, 2002b), by corpses of dead animals (Pfanz, 2008) or by atmospheric abnormalities (Kies et al., 2015). Vegetation is either much smaller than in control areas, more chlorotic, with less flowers and viable seeds, or is defined by its azonal character. In the latter case, plants grow far outside their normal growth distribution patterns. Swamp or mire species may thus be found within fertilized fodder meadows. Their anatomical or physiological ability to compete with hypoxia or even anoxia gives them a decisive competitive advantage.

Mofettes co-occur worldwide with seismic structures and in pre- and post-volcanic areas. In Europe, they can be found in Germany (Eifel, Rhön, Teutoburg Forest, Neckar valley, NW Franconia), in the Czech Republic (Cheb basin), Slovenia (Radenci area), Italy (Toscany), Iceland, Greece, Hungary, Romania (Hargitha Mountains) and France (Massif Central). Worldwide they are found for instance within the caldera of the Yellowstone volcano or in the Inyo crater range, in the Cascades range (USA), in geothermal fields of New Zealand, Kamchatka and Indonesia (Djeng Plateau).

Apart from other soil-forming factors, soils on mofette fields are at first affected by increased CO₂ concentrations in the soil atmosphere. Generally and irrespective of mofette fields, the soil atmosphere is enriched in CO₂, relative to the above-ground atmosphere. This is a consequence of biological processes such as root respiration, rhizomicrobial respiration, decomposition of plant residues, the priming effect induced by root exudation or by addition of plant residues, and basal respiration by microbial decomposition of soil organic matter (SOM) (Kuzyakov, 2006). The CO₂ concentration in the soil atmosphere commonly amounts to <5% (w/v), but it may rise up to >10% (Geisler, 1973), depending on soil texture, depth, temperature, compaction and water saturation. However, the soil atmosphere in mofette fields may be almost completely composed of (geogenic) CO₂. This is partially considered in the classification system of the World Reference Base for Soil Resources (IUSS Working Group WRB, 2014) by the 'reductive' qualifier, which is on the second level of categorical detail. The 'reductive' qualifier applies for soils "having reducing conditions, in ≥25% of the volume of the fine earth within 100 cm of the soil surface, caused by gaseous emissions, e.g. methane or carbon dioxide, or caused by liquid intrusions, e.g. gasoline" (IUSS Working Group WRB, 2014). Thus, the qualifier is not exclusive for soils with a CO₂ atmosphere. In the definition of the qualifier, no differentiation is made between the chemically rather passive geogenic CO₂, which displaces O₂ in the soil atmosphere, and substances actively involved in redox reactions such as CH₄, H₂S and hydrocarbons.

The reductive qualifier can be combined with only 4 of 32 reference soil groups, Andosols (as supplementary qualifier), Gleysols, Stagnosols and Technosols (as principal qualifier). While there is no consideration of the influence of CO₂ or other gases on soil development in the US Soil Taxonomy, the German soil classification (Ad-hoc Arbeitsgruppe Boden, 2005) defines the soil type 'Reduktosol' similar to the 'reductive' qualifier. Again, the soil type comprises soils characterized by gases such as CH₄, H₂S and CO₂ without considering the differing effects of the respective gases. The 'Reduktosol' has a diagnostic Y horizon, which may feature an oxidized Yo horizon, coloured by secondary Fe oxides and with temporary CH₄ and CO₂ in the soil atmosphere (≥10%), and/or a reduced Yr horizon with an O₂-free, CH₄- or CO₂-rich soil atmosphere and white, grey, grey-green, blue-green and black colours.

Soils on mofette fields are a natural laboratory to study the effects of high CO₂ concentrations in the soil atmosphere on the dynamics of SOM, weathering and mineral formation, which might be transferrable to soil development at increased biogenic and/or atmospheric CO₂ concentrations in soil. The aim of this review is to summarize the recently growing knowledge on soil formation and properties on mofette fields and to identify gaps in knowledge, especially regarding the role of CO₂ as a soil-forming factor.

2. Composition and fluxes of gases in mofette fields

At mofettes sites, gases from deep magma chambers in the earth mantle or from seismic fraction zones reach the soil surface. Depending on the local characteristics of the lithosphere, CO₂, after being dissolved out, diffuses upward to the soil surface. Unevenly distributed cracks and fissures within the lithosphere and soil, permeable and impermeable soil zones and the presence of soil water strongly influence the upward penetration of geogenic gases. Less permeable to impermeable (loamy, clayey) soil zones block the way of the permeating gas, while highly permeable (sandy) zones facilitate upward diffusion. This leads to a very inhomogeneous degassing pattern that is observed in nearly all mofette areas. At highly degassing sites, soil CO₂ concentrations ([CO₂]) in the upper 0.8 m of soil can reach very high values. Several authors already published soil [CO₂] and CO₂ efflux rates (e.g., Kämpf et al., 2013; Pfanz et al., 2004; Saßmannshausen, 2010; Thomalla, 2015; Vodnik et al., 2006, 2009). Despite the relatively large heterogeneity of the degassing regime in different areas, the obvious degassing patterns have been found to be fairly stable over longer time periods (Thomalla, 2015; Vodnik et al., 2006).

Data on CO₂ concentration and flux (Figs. 1 and 2) were collected on a mofette field in the Czech Plesná valley (Saßmannshausen, 2010; Thomalla, 2015) along lengthwise (15 m) and crosswise (9 m) transects.

The spatial heterogeneity of geogenic [CO₂] at different soil depths is demonstrated in Fig. 1. Fig. 1a shows [CO₂] at 10 cm soil depth that is at control levels at the upper part of the mofette field, whereas the lower right part of Fig. 1a already shows high [CO₂] in a very shallow soil horizon. From 10 to 60 cm soil depth, [CO₂] increases, although the surface concentrations are still mirrored at 20 cm (Fig. 1b). At 60 cm soil depth, >30% of the area shows [CO₂] >70% (Fig. 1d). As CO₂ displaces O₂ in the soil atmosphere of mofette fields, the concentrations of these gases are commonly strongly negatively correlated ($r^2 > 0.8$; e.g., Saßmannshausen, 2010; Thomalla, 2015).

Soil CO₂ fluxes mirror the measured CO₂ concentrations (Fig. 2). As gas fluxes were measured in chambers attached to the soil surface, the best accordance is between CO₂ flux and CO₂ concentrations of the upper soil layers (Figs. 1, 2). In control plots, CO₂ fluxes ranged from 0.2 to 10 mol m⁻² d⁻¹, while at highly degassing spots, fluxes reach values of 250 to 750 mol m⁻² d⁻¹. At one single spot, even 10,320 mol CO₂ m⁻² d⁻¹ were determined. These data are in accordance with fluxes published by Chiodini (2008) and Mörner and Etiope (2002). Soil CO₂ diffuse degassing from non-volcanic sites ranged from 0.1 to 5 kg CO₂ m⁻² a⁻¹ (Fort Sulphurdale, USA; Klusman et al., 2000) via 208 kg CO₂ m⁻² a⁻¹ (Dixie Valley; Bergfeld et al., 2001) and 3285 kg CO₂ m⁻² a⁻¹ (Selvana, Italy; Rogie et al., 2000) to 11,900 kg CO₂ m⁻² a⁻¹ at a mud volcano in the Yellowstone National Park (Werner et al., 2000).

3. Vegetation on mofette fields

In mofette fields, plants adapt physiologically or anatomically to the very special mofette situation. Aside from this morpho-physiological adaption, there is also a kind of floristic adaptation: the occurrence of a very typical mofette vegetation. According to Pfanz (2008), plants in mofette fields can be grouped into three categories. Plants that strictly avoid geogenic CO₂ at concentrations above 2–3% are called *mofettophobic* (Fig. 3a), whereas those that grow directly above strong CO₂ emanations are *mofettophilic* (Fig. 3b). Plants that occur in degassing as well as in control areas are named *mofettovague* (see also Saßmannshausen, 2010; Thomalla, 2015). At sites, where both the soil CO₂ concentration and the CO₂ flux are large, plants do not grow at all (Fig. 4). There seems to be no adaptation mechanism in plants able to cope the excess of CO₂, which was similarly found for collembolans and nematodes in CO₂ high-flux areas of the Italian mofette Il Bossoleto (Pfanz, Hohberg, Schulz, unpublished results).

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