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Calcium oxalate contribution to calcium cycling in forests of contrasting nutrient status

Jenny M. Dauer [a,*], Steven S. Perakis [b]

[a] Department of Forest Ecosystems and Society, Oregon State University, 321 Richardson Hall, Corvallis, OR 97331, USA
[b] U.S. Geological Survey, Forest and Rangeland Ecosystem Science Center, 3200 SW Jefferson Way, Corvallis, OR 97331, USA

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ABSTRACT

Calcium oxalate (Ca oxalate) is an insoluble biomineral that forms in plants and fungi, and occurs in soils across many types of ecosystems. Assessing how Ca oxalate may shape ecosystem Ca cycling requires information on the distribution of Ca oxalate among plant biomass, detritus, and mineral soil, and how it varies with ecosystem Ca status. We compared two Douglas-fir forests of contrasting ecosystem Ca availability, and found that Ca oxalate was partitioned similarly among plant biomass, detritus and mineral soil major ecosystem compartments at both sites, and total pools of Ca oxalate were greater in the high-Ca forest. However, the proportional importance of Ca oxalate was greater in the low-Ca than high-Ca forest (18% versus 4% of actively cycling ecosystem Ca, respectively). And calcium oxalate in mineral soil, which is of particular interest as a potential long-term Ca reservoir, was a larger portion of total available Ca (exchangeable Ca plus Ca oxalate Ca) in the low-Ca site than the high-Ca site (9% versus 1% of available soil Ca, respectively). Calcium oxalate was the dominant form of Ca returned from plants to soil as leaf litterfall at the high-Ca site, yet calcium oxalate disappeared rapidly from decomposing litter (0.28 yr^{-1} or faster) at both sites. We conclude that accumulation of Ca oxalate in forest ecosystems appears most closely related to overall Ca supply for live biomass pools, and that the accumulation of Ca oxalate in forest floor and mineral soil is limited by rapid microbial degradation of putatively unavailable Ca oxalate.

1. Introduction

Calcium (Ca) is an essential macronutrient that is increasingly recognized as a biogeochemical factor that influences ecosystem structure and function (Schaberg et al., 2001; Lautner and Fromm, 2010). In some forests Ca from mineral weathering may be insufficient for plant growth particularly on soils that are highly weathered (Cuevas and Medina, 1988; Bockheim and Langley-Turnbaugh, 1997), subject to chronic acid rain or nitrogen deposition (Driscoll et al., 2001; Bigelow and Canham, 2007; Liu et al., 2011), or in stands undergoing sequential whole-tree harvests (Perakis et al., 2006; Siemion et al., 2011). Progress in understanding the sustainability of ecosystem Ca supply has been hampered by a lack of information on the various forms and pools of Ca in forest ecosystems. For example, while there has been considerable interest and methodological development in understanding how various chemical forms of other macronutrients such as nitrogen and phosphorous are distributed in plants and soils, comparable approaches for investigating Ca forms and partitioning in plant–soil systems are poorly developed (Sparks, 1996). In fact, nearly all ecosystem and nutrition studies measure plant tissues as bulk-Ca and in forest floor and soils via exchangeable Ca (Mead, 1984; Sparks, 1996), which makes it difficult to identify specific biogeochemical and physiological processes that influence Ca dynamics.

Calcium-oxalate (Ca oxalate) is a biomineral form of Ca that may play an important ecosystem role, but its contribution to pools of Ca in forests is poorly understood. Calcium oxalate is created by nearly all plants (Franceschi and Nakata, 2005) and by both mycorrhizal and saprophitic fungi (Cromack et al., 1979; Arnott, 1995; Dutton and Evans, 1996). Both plants and fungi internally create Ca oxalate crystals to sequester Ca away from the cytoplasm, where ionic Ca is kept in micromolar concentrations (Arnott, 1995; Franceschi and Nakata, 2005). Plants and fungi also release oxalic acids into soil or detritus to regulate pH and

* Corresponding author. Present address: School of Natural Resources, University of Nebraska-Lincoln, 3310 Holdrege Street, Lincoln, NE 68583-0995, USA. Tel.: +1 402 472 8784; fax: +1 402 472 2946.
E-mail address: jenny.dauer@unl.edu (J.M. Dauer).

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cation–anion balance of their external microenvironment (Jellison et al., 1997) or to enhance mineral weathering or decomposition for nutrient uptake, especially phosphorous (Ryan et al., 2001; Arvieu et al., 2003). Oxalic acid can subsequently bind to free soil Ca ions forming highly insoluble Ca oxalate crystals (K_{sp} 2.57×10^{-9}; Ringbom, 1963), whereas other metal-oxalate complexes are more soluble (Baran and Monje, 2008; Echigo and Kimata, 2011). Concentrations of crystalline Ca oxalate are rarely quantified in soil, yet Ca oxalate is often present where examined (Graustein et al., 1977; Cromack et al., 1979), particularly associated with decomposing leaf litter (Arnott, 1982; Horner et al., 1995), ectomycorrhizal fungal mats (Cromack et al., 1979; Entry et al., 1991) and lichen (Fujii et al., 2013). Despite progress in identifying mechanisms and controls on Ca oxalate formation in plants (Franceschi and Nakata, 2005), understanding the significance of Ca oxalate occurrence at the ecosystem-scale requires more detailed information on Ca oxalate contribution to vegetation, detritus and mineral soil Ca pools.

Ca oxalate creation in plant tissue and soil, and the subsequent longevity of insoluble Ca oxalate crystals, may influence both short- and long-term Ca supply and biotic recycling in ecosystems. In plants, once Ca^{2+} is deposited in Ca oxalate crystals it becomes unavailable for other physiological processes unless the Ca supply is completely truncated (Franceschi, 1989; Volk et al., 2002). Because general Ca mobility in plant tissue is low, the sequestration of available Ca^{2+} in Ca oxalate crystals may become a limiting process for other plant functions involving Ca such as cell wall formation or cell signaling. As leaves age, Ca oxalate accumulates (Borer et al., 2004; Littke and Zabowski, 2007; Smith et al., 2009). If highly insoluble Ca oxalate from leaf litter, roots and fungi accumulates in soil and then resists degradation, it could potentially reduce soil Ca availability overall for processes such as biotic uptake. The rate of Ca oxalate degradation in soil is unknown; some authors suggest that Ca oxalate is a "slow-release" form of Ca that is retained in soils and an important long-term source in regions where ecosystem Ca inputs are relatively low (Bailey et al., 2003; Smith et al., 2009), while others indicate that Ca oxalate may turnover quickly in leaf litter microcosms (O'Connell et al., 1983). Information on rates of Ca oxalate delivery from plants to soils via leaf litter, on the longevity of Ca oxalate in decaying detritus, and on how these fluxes may vary with site Ca status, are significant unknowns in resolving the importance of Ca oxalate to ecosystem Ca dynamics overall.

Douglas-fir forests of the Oregon Coast Range exhibit wide variation in plant and soil Ca availability due to high nitrogen from symbiotic N fixation and associated Ca loss (Perakis et al., 2006) with Ca limiting growth in some stands (Mainwaring et al., 2014) and provide an opportunity to examine how forest Ca status influences Ca oxalate partitioning and dynamics. The objectives of this study were: (1) to quantify the portion of Ca oxalate in major ecosystem compartments of living biomass, detritus and mineral soil at high and low Ca sites, (2) to examine which factors explain Ca oxalate concentrations across ecosystem pools, and (3) to determine the potential role of foliar Ca oxalate in shaping subsequent Ca dynamics during leaf litter decomposition.

2. Methods

2.1. Study sites

We estimated Ca oxalate in major ecosystem compartments of living biomass, detritus and mineral soil, and sub-compartments (smaller parts of the major compartment e.g., branches, foliage, bark, roots, bole-wood, forest floor, fine woody debris, coarse woody debris, soil at different depth increments) at two sites of contrasting Ca status in the north-central Oregon Coast Range. The two sites are part of a larger study of Ca depletion along a soil nitrogen gradient (Perakis et al., 2006, 2013; Perakis and Sinkhorn, 2011). The high-Ca site (site 5) is located at N44°38′W123°48′; the low-Ca site (site 16) is located at N45°10′W123°55′. Soils at both sites are classified as Andic Dystrudepts, and are derived from Tyee and Yamhill formations, respectively, which are chemically similar and differentiated by the thickness of interbedded sandstone layers. The geology of these sites is described in more detail in Perakis et al. (2013). Both sites experience maritime, temperate climates with cool, wet winters and warm, dry summers. Prior to the current stands, both sites were mixed conifer stands with red alder present. The vegetation at these two sites is dominated by Douglas-fir (*Pseudotsuga menziesii*) planted in 1977 at the high-Ca site and 1980 at the low-Ca site (Table 1). During planting, the sites were clear-cut, broadcast burned, and an initial herbicide treatment was applied to control vegetation competing with Douglas-fir seedlings. There has been no fertilization at the two sites. The two sites have been well documented as having significant differences in Ca cycling, loss, biotic retention and limitation concomitant with differences in soil N content, providing a context to compare site differences in Ca oxalate (Perakis et al., 2006, 2013; Mainwaring et al. 2014).

2.2. Tree tissue sampling and biomass estimation

We collected samples for total Ca and Ca oxalate in live Douglas-fir from previously established 0.5 ha plots at the high and low-Ca sites. Sun-exposed foliage was composited by site from three trees at the end of the growing season (September and October 2007), and separated into age cohorts (5 age cohorts at the high-Ca site and 4 age cohorts at the low-Ca site). Branch samples were collected in 2007 from three trees at each site. Tree cores were collected in May 2010 from three trees at each site using an increment borer, discarding any heart-wood, and separating the remainder into bark and bole-wood tissues. Four additional bark samples were taken with a 2 cm diameter corer. Samples were composited into one bark and one bole-wood sample per site. Root samples were collected in June 2010 by taking a composite of three 6.7 cm diameter soil cores to 10 cm depth, followed by sieving and water washing to isolate fine root samples of <2 mm

Table 1
Site characteristics.

Site	Soil exchangeable Ca 0–10 cm depth	Soil exchangeable Ca 0–100 cm depth	Soil pH (H_2O) 0–10 cm depth	Soil texture (%) 0–10 cm depth			Ca in aboveground plant biomass	Tree age	Total aboveground biomass	ANPP
	kg ha^{-1}	kg ha^{-1}		Sand	Silt	Clay	kg ha^{-1}	years	mg ha^{-1}	mg ha^{-1} yr^{-ha}
High-Ca (5)	853	5680	5.50	53	23	25	172	30	163	21.5
Low-Ca (16)	93	280	4.61	30	31	39	98	27	122	14.3

Characteristics of two sites in the Coast Range of Oregon including soil exchangeable Ca pools to 100 cm depth, soil pH and texture in surface soils, Ca in plant biomass, tree age in 2007 and total aboveground biomass. ANPP calculated as the net annual aboveground in stems, branches, foliage mass plus litterfall (Perakis and Sinkhorn, 2011).