



Metal mobilization in soil by two structurally defined polyphenols

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HIGHLIGHTS

- ▶ The larger polyphenol (oenothein B) binds more Fe and Al than the smaller EGCg.
- ▶ Oenothein B mobilized a significant amount of Fe and Al from soil.
- ▶ Micelle-mediated separation was utilized to study tannin-metal binding.
- ▶ Langmuir model for competitive binding was used to predict multiple metal binding.

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ABSTRACT

Polyphenols including tannins comprise a large percentage of plant detritus such as leaf litter, and affect soil processes including metal dynamics. We tested the effects of tannins on soil metal mobilization by determining the binding stoichiometries of two model polyphenols to Al(III) and Fe(III) using micelle-mediated separation and inductively coupled plasma optical emission spectroscopy (ICP-OES). By fitting the data to the Langmuir model we found the higher molecular weight polyphenol (oenothein B) was able to bind more metal than the smaller polyphenol (epigallocatechin gallate, EGCg). For example, oenothein B bound 9.43 mol Fe mol⁻¹, while EGCg bound 4.41 mol of Fe mol⁻¹. Using the parameters from the binding model, we applied the Langmuir model for competitive binding to predict binding for mixtures of Al(III) and Fe(III). Using the parameters from the single metal experiments and information about polyphenol sorption to soils we built a model to predict metal mobilization from soils amended with polyphenols. We tested the model with three natural soils and found that it predicted mobilization of Fe and Al with $r^2 = 0.92$ and $r^2 = 0.88$, respectively. The amount of metal that was mobilized was directly proportional to the maximum amount of metal bound to the polyphenol. The secondary parameter in each model was the amount of weak organically chelated Fe or Al that was in the soil. This study provides the first compound-specific information about how natural polyphenols interact with metals in the environment. We propose a model that is applicable to developing phytochelation agents for metal detoxification, and we discuss how tannins may play a role in metal mobilization from soils.

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1. Introduction

Metals accumulate in soils by natural, industrial, or agricultural activity (Galloway et al., 1982; Bradford et al., 2008; Ngh and Hanafiah, 2008). After oxygen and silicon, iron and aluminum are the most abundant elements in soils, comprising about 3% and 7%, respectively (Sposito, 1989), and mainly found in the primary

and secondary minerals. Natural sources of metals in soil include weathering of the underlying bedrock, soil dust, and volcanic ash (Galloway et al., 1982; Schutzendubel and Polle, 2002). Agricultural practices are also potential sources of metal input into soils. Fertilization with animal manure from livestock fed diets enriched in heavy metals can increase metal concentrations in wastewater and soil (Bradford et al., 2008). Industrialization and fossil fuel utilization have increased the amount of metal released into the atmosphere, which increases atmospheric deposition to soil (Galloway et al., 1982). Anthropogenic inputs of metals from the atmosphere account for large portions of the total yearly input with the two highest metals being Fe and Al (Lantzy and Mackenzie, 1979).

Abbreviations: EGCg, epigallocatechin gallate; X_m , maximum amount of metal bound; b, isotherm model parameter; HPLC, high performance liquid chromatography; ICP-OES, inductively coupled plasma optical emission spectroscopy; TFA, trifluoroacetic acid.

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Whether or not a metal is mobile or immobile depends on factors including the fractions sorbed to soil surfaces or complexed to organic compounds (Schutzendubel and Polle, 2002). Soil microorganism and plants modify the bioavailability and toxicity of metals in part by influencing metal speciation (Ernst, 1996). Plants control metal speciation in soils either by acidifying the soil through proton exudation or by releasing organic compounds that chelate metals (Ernst, 1996). Plants produce many different organic compounds that bind metals including phytochelatin, simple phenols, and polyphenols including tannins (Slabbert, 1992; Suresh and Ravishankar, 2004; Michalak, 2006). Phenols and polyphenols comprise about 15% of the total dissolved organic carbon in a typical forest (Suominen et al., 2003).

Polyphenols are among the most common and abundant plant secondary metabolites, and enter soil systems by several different pathways, including root exudation and leaf litter decomposition (Bertin et al., 2003; Kraus et al., 2003). Tannins, which are defined as high molecular weight polyphenols that precipitate protein, are abundant and widespread among higher plants (Quideau et al., 2011). Chemically tannins comprise two distinct structural classes, the flavan-3-ol derived condensed tannins and the hydrolyzable tannins (Yoshida et al., 2005). Plants accumulate complex mixtures of polyphenols, which may include hydrolyzable and/or condensed tannins, based on interactions between environmental and genetic factors (Salminen, 2004; Schweitzer et al., 2008; Scioneaux et al., 2011). While tannins are well-known for their protein binding activity (Hagerman, 2012), and are of interest to the food and health sciences because of their antioxidant activity (Scalbert et al., 2005), there has been relatively little investigation of the importance of metal binding by tannins. Tannins form complexes with metals through *ortho*-dihydroxyl groups (Slabbert, 1992). The resulting complexes can be mono-, bi-, or tri-dentate (Slabbert, 1992). Tannins are also highly aromatic compounds and thus provide many different pi-cation binding sites for metal ions (Ma and Dougherty, 1997; Zaric et al., 2000).

Because large amounts of polyphenols are released into soils from plants (Hattenschwiler et al., 2003) and because polyphenols readily bind metals, there is potential for these compounds to significantly influence the mobility and activity of metals in natural systems. Environmental research into tannin–metal interactions has focused on metal solubility in tannin-containing systems (Kaal et al., 2005; Kraal et al., 2006), or biologically relevant chelation of toxic or essential metals (Jung et al., 2003; Chin et al., 2009; Kinraide and Hagerman, 2010). Treatment of goethite or ferrihydrite quartz sand with tannic acid or unfractionated condensed tannin from black pine releases a large amount of Fe(III) from the mineral soil (Kaal et al., 2005). Tannic acid forms complexes with environmentally toxic metals such as Ni(II), Pb(II), Cd(II), and Cr(III) (Ross et al., 2000) and alleviates the toxic effects of Al(III) to wheat roots by forming tannic acid–Al(III) complexes (Kinraide and Hagerman, 2010). Modified quebracho tannin has been proposed as a possible sorbent to remove Pb(II) from wastewater (Yurtsever and Sengil, 2009). However, the effects of polyphenols on environmental metals can be difficult to predict because of their complexity. In aqueous solution, Cu(II) is precipitated by tannic acid at very low metal:organic C ratios, but increasing the amount of copper catalyzes decomposition of the polyphenol and solubilization of the metal (Kraal et al., 2006). In part, this complexity is a consequence of the abundance of research on natural mixtures of polyphenolic compounds instead of purified individual components (Hagerman et al., 1992). It is difficult to extrapolate useful models to predict the nature of tannin–metal interactions in the soil from data obtained from crude mixtures of natural products.

Only a few attempts have been made to establish the stoichiometric ratios of high molecular weight polyphenol–metal complexes (Kennedy and Powell, 1985; Ross et al., 2000). Improved methods

for polyphenol isolation and purification that have been developed over the past decade have made it possible to obtain purified, defined tannins for more careful chemical evaluation (Quideau et al., 2011), allowing us to initiate studies of tannin–metal interactions using two well defined tannins, epigallocatechin gallate (EGCg) and oenothien B (Fig. 1). These two tannins were selected because they include the functional groups of the condensed tannins (epicatechin, the core component of EGCg), of the gallotannins (gallate esters, found in EGCg and oenothien) and of the ellagitannins (hexahydrodiphenic acid, found in oenothien) (Yoshida et al., 2005). These tannins can be purified in large quantity from readily available plants, so were particularly suitable for method development. We chose to investigate Fe(III) and Al(III) because they are the two most abundant metals in soil systems (Jain and Snoeyink, 1973).

We used a novel method, micelle-mediated separation, to establish stoichiometries of binding and the abilities of tannins to mobilize metals from soils. Micelle-mediated separation is a method for removing less polar molecules from aqueous solution or for preconcentrating samples for analysis (Paleologos et al., 2002, 2005; Silva et al., 2006). In this method, the metal and organic ligand are mixed in aqueous solution and allowed to reach equilibrium. The solution is then mixed with a detergent at a temperature that promotes formation of detergent micelles. The organic ligand, and any chelated metal, is partitioned into the detergent phase and is thus separated from free metal. The metal can be determined in either the detergent phase or the aqueous phase. A particular advantage of micelle-mediated separation for our study is its utility even for metals like Al, that do not exhibit spectrophotometric shifts upon ligand binding.

Methods more typically used to speciate environmental metals, such as diffusive gradients in thin films or the Donnan membrane technique (Pesavento et al., 2009) require solid phases for separation of the metal species. Tannins are highly reactive and sorptive compounds, and bind tightly to common membranes, chromatography media, and other supports. Polyacrylamide hydrogels like those used in the diffusive gradient method form strong hydrogen bonds with tannins (Xu et al., 2011). Substrates such as the modified styrene-divinyl-benzene polymers that comprise the membranes for Donnan dialysis (Pyrzynska, 2006) bind a wide range of phenols and polyphenols (Kammerer et al., 2011). While these methods can be used to establish that tannins do bind metals (Kraal et al., 2006), they are not suitable for establishing quantitative trends.

We hypothesize that robust models for predicting the interactions between polyphenols and environmental metals can be constructed based on knowledge of chemical behaviors and structural features of individual compounds. We tested this hypothesis by determining the maximum binding and binding affinities of two model polyphenols to Al(III) and Fe(III) by means of micelle-mediated separation and inductively coupled plasma optical emission spectroscopy (ICP-OES). We used three soils and two model polyphenols (Fig. 1) to develop and test our models of metal mobilization.

2. Materials and methods

2.1. Materials and solutions

Epigallocatechin gallate (EGCg), a gallate ester of a flavan-3-ol, was supplied by Douglas Balentine (Lipton Tea, Englewood Cliffs, NJ). The hydrolyzable tannin oenothien B was prepared from *Epilobium angustifolium* (Zhao, 1995). Aluminum nitrate nonahydrate was purchased from Alfa Aesar (Ward Hill, MA), and ferric nitrate nonahydrate was purchased from Thermo-Fisher Scientific

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