# Effects of tannins on soil carbon, cation exchange capacity, and metal solubility

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**Problem:** Tannins are common plant-derived polyphenolic compounds that sorb to soil and affect the solubility of soil nitrogen and chemical processes that may be important for the formation of soil organic matter and nutrient cycling. However, studies are needed that a) compare different classes of tannins and related compounds; b) determine if soils have a maximum storage capacity for phenolics; and c) examine the effects of tannins on the solubility/mobility of metals and important soil properties like cation exchange capacity.

**Approach:** Repeated (8) applications of chemically well-defined hydrolyzable and condensed tannins (polymers) and related non-tannin phenolic substances (monomers) to soil samples followed by extractions with cool (23 °C) and hot water (16 hours, 80 °C).

**Sorption of phenolic-C:** Treatment solutions (10 mg of compound $g^{-1}$ soil) were added to soil samples (2.5 g). After shaking for 1 hour, samples were centrifuged, decanted, and the supernatants analyzed. Soluble-C was analyzed with a Shimadzu TOC-VCPN.

$$\text{Sorption} = \text{Trt-}C_{added} - (\text{Sol-}C_{trt} - \text{Sol-}C_{control}),$$

where Trt-$C_{added}$ is the soluble-C added in treatment solutions and Sol-$C_{trt}$ and Sol-$C_{control}$ are soluble-C in supernatants from treated and control samples respectively.

**Elemental analysis** of supernatants was performed using a Spectro ICP spectrometer.

**Total soil-C & Cation Exchange Capacity:** Soil remaining after the last water extraction was dried (55 °C) and assayed for total soil-C content with a FlashEA 1112 NC Analyzer (CE Elantech, Lakewood, NJ). Cation exchange capacity (CEC) was measured at the soil pH by exchange with cobalt hexamine trichloride (ISO 23470:2007).

| Land Use | Depth (cm) | $pH_{H2O}$ (1:1) | Total-C (mg $g^{-1}$) | Total-N (mg $g^{-1}$) | CEC (cmolc $kg^{-1}$) |
|---|---|---|---|---|---|
| Forest | 0-5 | 4.47 | 56.0 | 4.0 | 9.8 |
| | 10-20 | 3.97 | 17.3 | 1.7 | 4.3 |
| | | | | | |
| Pasture | 0-5 | 5.27 | 42.9 | 4.5 | 10.1 |
| | 10-20 | 5.24 | 15.7 | 1.8 | 5.1 |

**Treatments:** Soil from paired pasture and forest sites in West Virginia, USA, was treated with deionized water (Control) or with solutions containing model tannins or non-tannin phenolic compounds selected to represent a range of phenolic compounds of varying complexity in the plant-soil continuum.

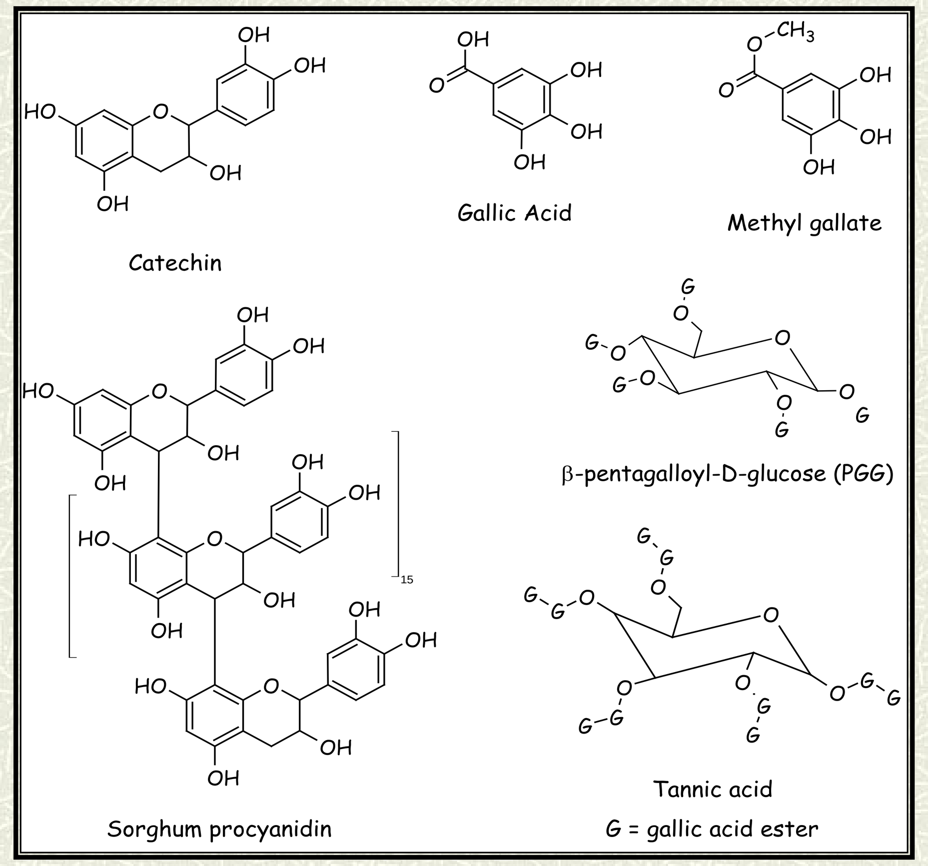



**Fig. 1.** Our representative condensed tannin was a polymeric flavonoid-based proanthocyanidin isolated from sorghum grain (SOR). We also evaluated tannic acid (TA), a mixture of galloyl esters, and β-1,2,3,4,6-penta-*O*-galloyl-D-glucose, (PGG), a well defined gallotannin purified from the tannic acid. Non-tannin phenolics included the flavonoid catechin (CAT), the phenolic acid, gallic acid (GA), and its ester, methyl gallate, (MG).

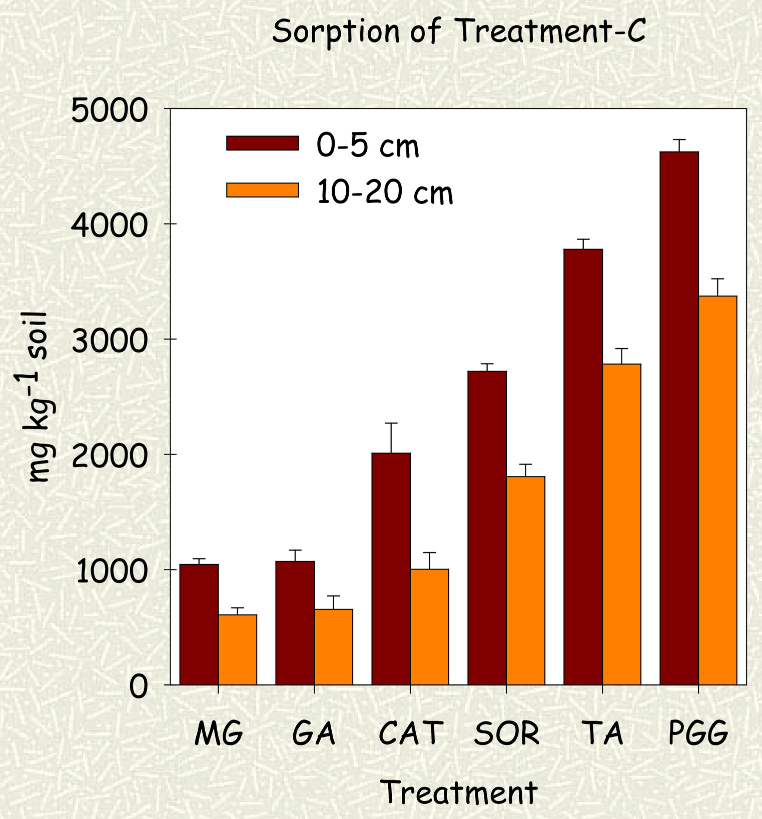



**Fig. 2.** Varying fractions of the soluble-C in the **first application of the phenolic treatments** were sorbed by the soil. The greatest average sorption was observed for PGG (3998 ± 184) > TA (3280 ± 150) > SOR (2263 ± 133) > CAT (1506 ± 194) > GA (862 ± 91) = MG (826 ± 68 mg $kg^{-1}$ soil). These were equivalent to about 79, 65, 44, 25, 18, and 16 % of added treatment-C respectively. Unlike the others, sorption did not vary with depth for GA and MG treatments (Tukey's HSD).

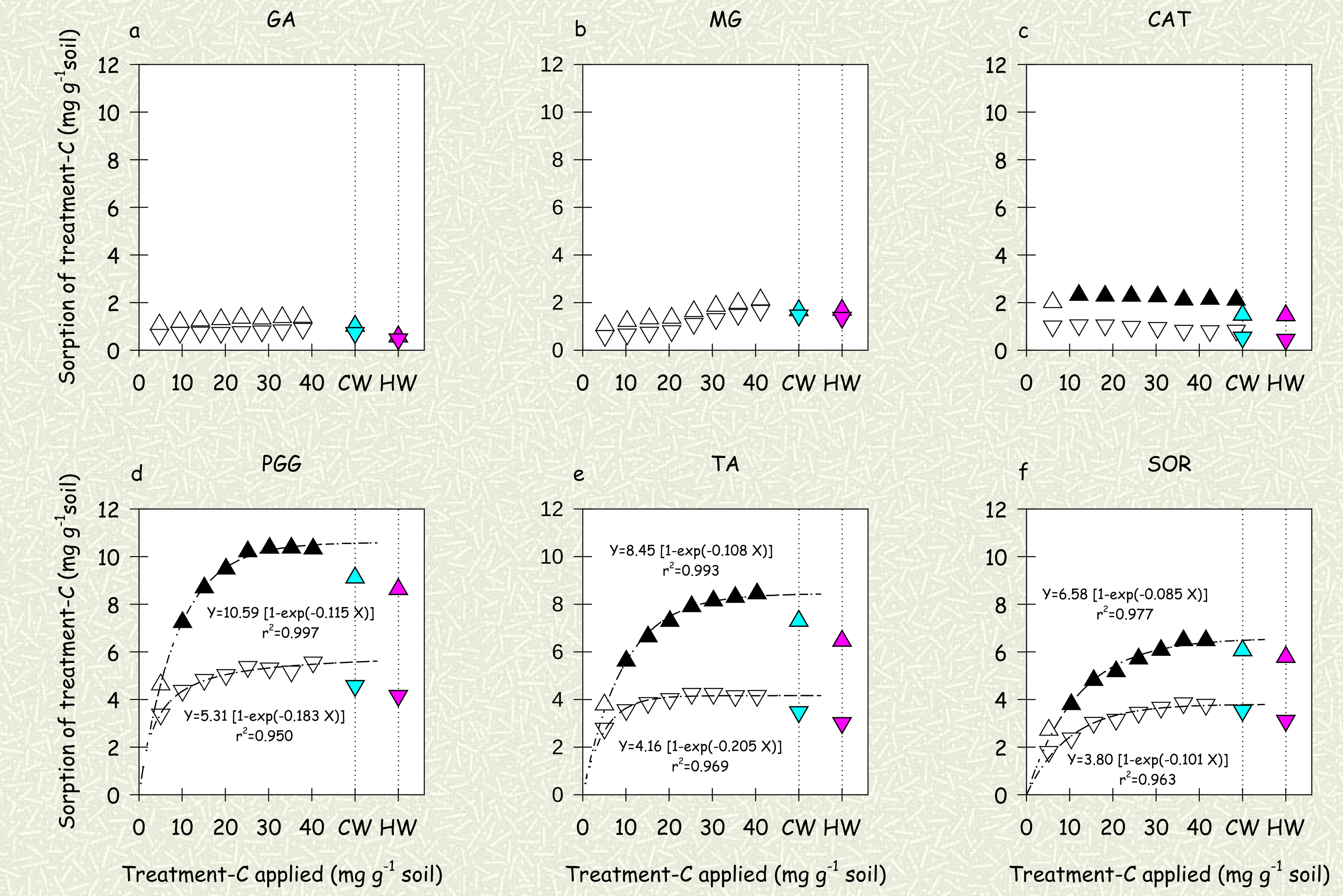



**Fig. 3.** Initial patterns persisted throughout seven subsequent treatment applications with **greatest cumulative sorption of tannin-C**, PGG, TA and SOR, compared to other phenolic compounds and less sorption with depth for all treatments except GA and MG. Little incremental sorption of non-tannin phenolics occurred after the first application of treatments (a-c) while repeated applications of tannins resulted in patterns that were closely described with a simple sorption equation (d-f). **Soluble-C was extracted from "loaded" soils** with cool water (CW) indicating some sorbed treatment-C was only weakly held on the soil matrix. Hot water (HW) removed more soluble-C from treated and control samples (not shown) than CW indicating it was partially from native soil organic matter. More than 85% of cumulative sorbed SOR-C remained in soil, compared to 81% of MG, 79% of PGG, 74% of TA, 50% of CAT, and 40% of the GA.

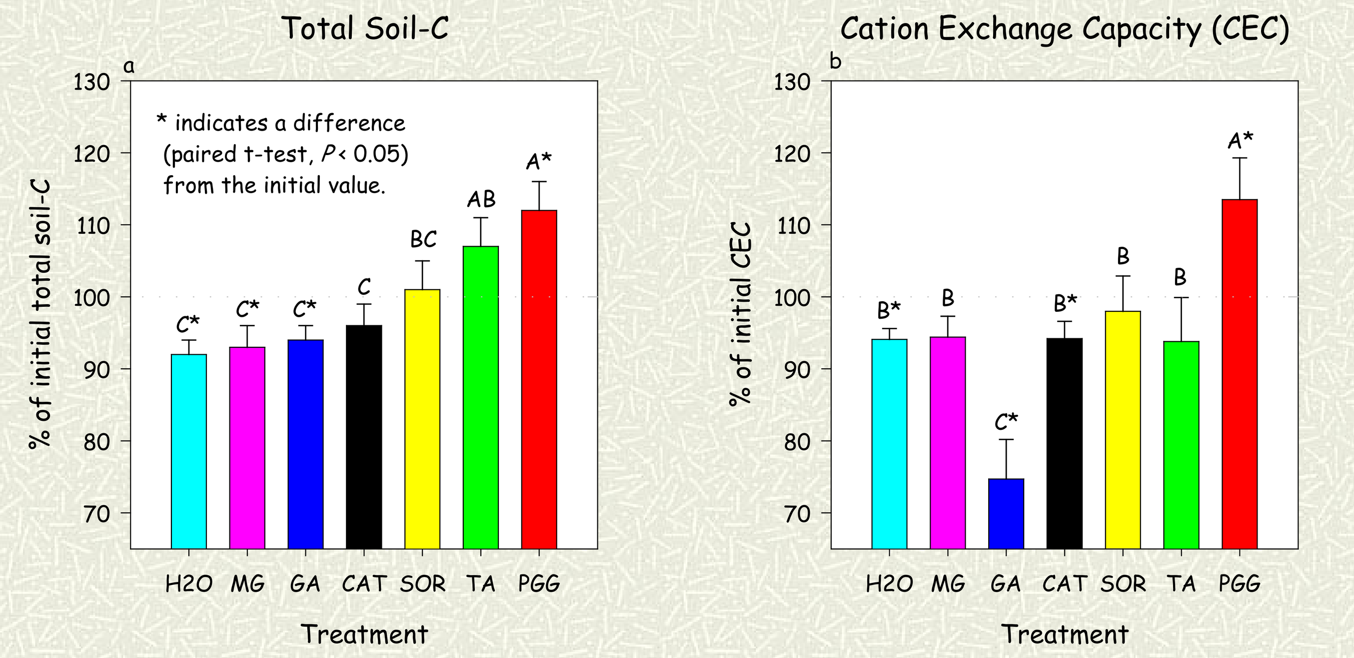
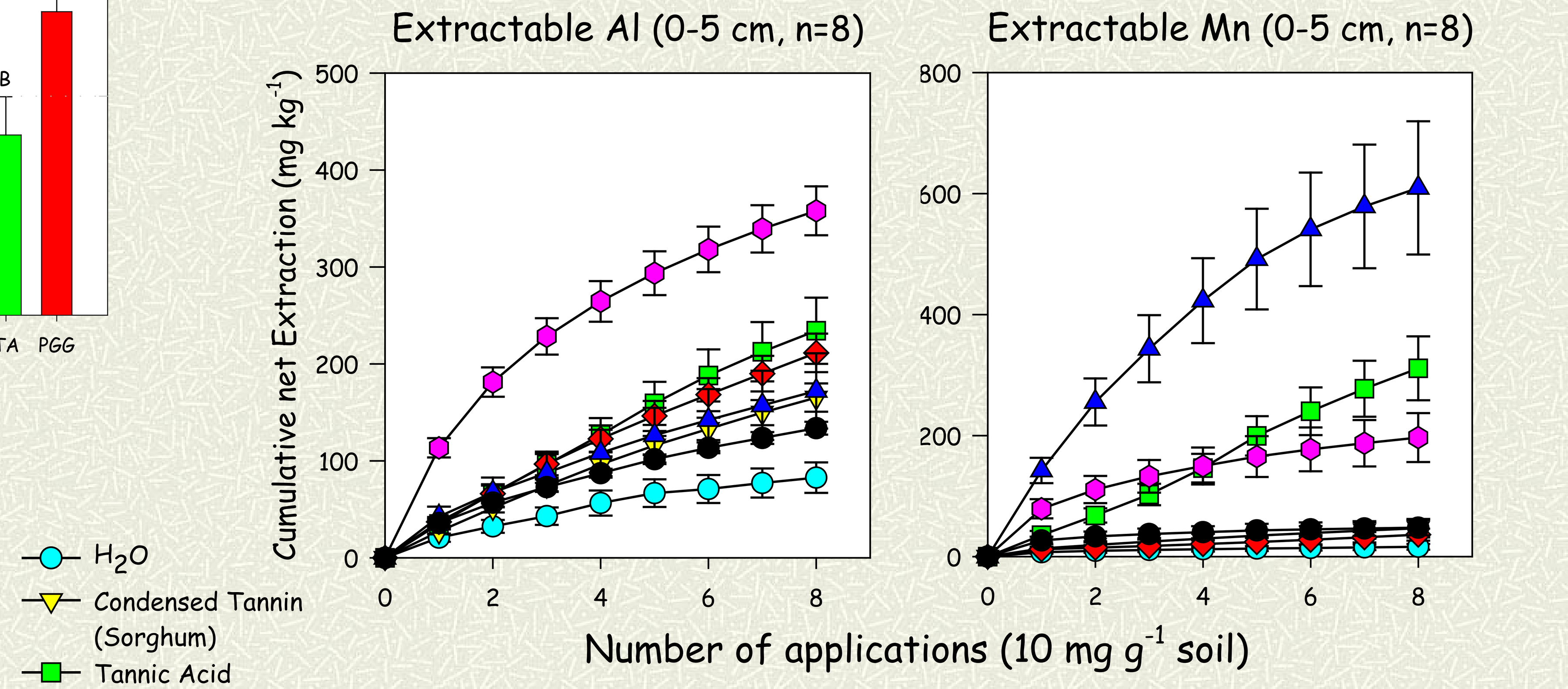
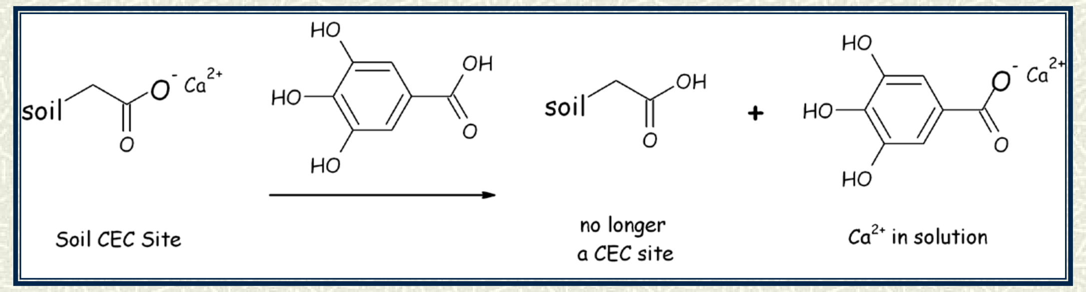



**Fig. 4. Total soil-C,** at the end of the experiment, was higher for tannin treatments than non-tannin phenolics. Samples treated with PGG contained more total-C than the average initial value while those treated with MG, GA, and the Control contained less. **Soil CEC** increased in PGG-treated samples but decreased in GA-treated samples. Increased CEC is attributable to high amounts of PGG-C remaining in soil. Decreased CEC is consistent with differences between soil pH and the GA solution pH (3.3) that affect variable charge components in the soil. Addition of GA decreased soil pH by about 1-2 pH units, presumably protonating CEC sites and mobilizing metals (below).

**Fig. 5.** Multiple applications of methyl gallate increased extraction of Al and Fe (Fe not shown). Similarly, gallic acid increased extraction of Mn and Ca (Ca not shown) compared to the other treatments.




At least two mechanisms may be involved:

1. **Complex formation.**

   Metals in soils bind to organic ligands through H-bonding, coordination (one donor group), and/or chelation. The last two mechanisms form stronger complexes with Al and Fe and also might affect the P cycle since P forms complexes with Al and Fe.

2. **Redox reactions.**

   Phenolic compounds reduce the insoluble Mn(IV) to the soluble Mn(II) form:

   $$Mn(IV)_{(s)} + \text{Phenolics} \Rightarrow Mn(II)_{(aq)} + \text{Quinones}$$

   Redox reactions are common and important in the formation and stabilization of soil organic matter. Quinones are reactive compounds that self-polymerize or co-polymerize with other compounds such as amino-containing compounds to form humic-like substances.

- Soils had a high affinity and a fixed capacity for both hydrolyzable and condensed tannins while related phenolic compounds were less attracted to soil and not affected by depth.
- Sequential washes of tannin "loaded" soil with cool and hot water resulted in the release of some treatment-C indicating it was weakly held however, most of the tannin-C remained on soil.
- Total soil-C confirmed meaningful amounts of tannin-C remained on soil. Soil CEC increased in samples treated with a gallotannin (PGG) but decreased in samples treated with its simple monomeric constituent (GA). **Understanding these differences is important since tannins degrade in soil!**
- Phenolic compounds solubilize and/or mobilize metals in soils and affect important in soil chemical processes.

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