

Rapid Formation of Abiotic CO₂ Results from Additions of a Simple Phenolic, Gallic Acid, to Soil

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Abstract

Abiotic efflux of CO₂ from soil is often attributed to dissolution of carbonates, and therefore not expected to occur in soils with a low pH. However, another abiotic source of CO₂, less constrained by pH, may arise from reactions that oxidize natural soil organic matter and reduce metal oxides. Studies of redox reactions between phenolic compounds and Fe and Mn oxides in soil have been focused mainly on the environmental fate of both oxidants and reductants and formation of organic matter. We measured CO₂ formed during 3-hour, room temperature (22±2 °C), incubations of samples of archived soils and from an ongoing crop diversity study. Subsamples (8 g. ODE) of each soil, were treated (5 ml) with water, or solutions of glucose (0.029 M), or gallic acid (0.025 M). For each soil, subsamples amended with H₂O or with the glucose solution produced little CO₂ and were nearly identical to each other, while CO₂ quickly formed after treatment with gallic acid regardless of pH. The net increase in CO₂ due to gallic acid, observed from the 18 archived soils, ranged from less than 0.5 to more than 80 mg CO₂-C kg⁻¹ soil. Significant treatment effects were observed in samples from the crop diversity study with more (Tukey's P[?]0.05) net CO₂ from a small grain-fallow treatment compared a 5-year rotation treatment, 19.04 and 15.77 mg CO₂-C kg⁻¹ soil, respectively. This study suggests abiotic reactions capable of rapidly producing a burst of CO₂ can occur in a wide range of soils following inputs of simple phenolic compounds and be impacted by management regimes. We suggest these are redox reactions in soil linked to Mn or Fe metal oxides and when considered together with fluctuations of carbon inputs to soil and redox cycling, might be a larger contributor to C emissions than previously accounted for.

Rapid Formation of Abiotic CO₂ Results from Additions of a Simple Phenolic, Gallic Acid, to Soil

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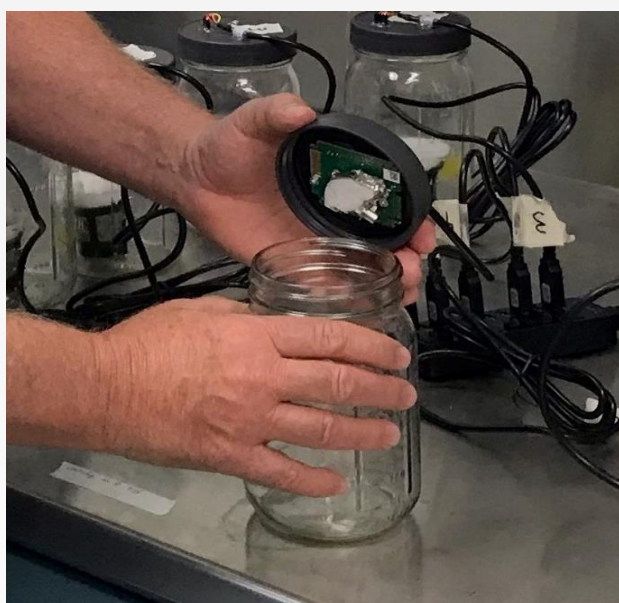
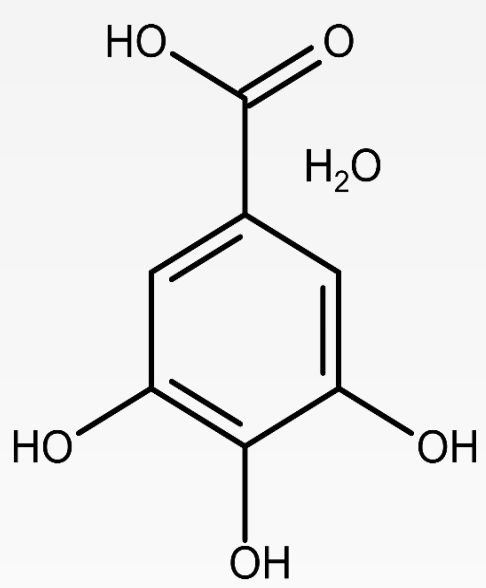
Context: Phenolic compounds including hydroxybenzoic or hydroxycinnamic acids are present in many crops and forages. They are believed to serve a variety of purposes related to protection from herbivores and both abiotic and biotic environmental stresses. Below ground they are a component of root exudates that influence soil microorganisms, fertility and soil organic matter. As part of the above-ground biomass, they directly influence human and animal health when consumed, and have also been indirectly linked to environmental benefits such as reductions in greenhouse gas formation. Recently, USDA scientists observed the rapid formation of CO₂ from soils amended with gallic acid (GA), a common simple phenolic compound typical of those found in many plants (**Fig. 1a**).

Objectives: a) establish that rapid CO₂ evolution is not simply the result of soil microbial activity (biotic CO₂ formation) or pH (carbonates), b) develop hypotheses for possible mechanisms and management implications.

Approach: Patterns of CO₂ formation were monitored using a K30 CO₂ sensor (CO2Meter.com, Ormond Beach, FL) with static (closed jar) incubations of soil (**Fig. 1b**). During initial studies we evaluated samples collected in June 2021 from an ongoing crop diversity study near Mandan, ND and archived samples of 18 benchmark soils from locations throughout the United States, stored since their collection in 1983-84. Archived samples represented: Arizona, (Mohave, AZ), California, (Yolo, CA), Colorado (Fort Collins, CO), Hawaii, (Kolekole, HI(K)), Hawaii, (Wahaiwa, HI(W)), Indiana, (Miami, IN), Iowa, (Clarion, IA), Kentucky, (Crider, KY), Maine, (Caribou, ME), Nebraska, (Sharpsburg, NE(S)), Nebraska, (Valentine, NE(V)), North Carolina, (Cecil, NC), North Dakota, (Barnes, ND), Oregon, (Walla Walla, OR), South Carolina, (Rains, SC), Texas, (Houston Black, TX(HB)), Texas, (Pullman, TX(P)), and Virginia, (Frederick, VA).

For each incubation, subsamples (8 g.) of oven dry (105 °C) soil were treated (5 mL) with water, or solutions of glucose (0.029 M), or GA (0.025 M) and incubated at room temperature (22±2 °C). The solutions of GA and glucose were intended to supply equivalent amount of C to the soils.

Figure 1. a) Gallic acid or 3,4,5-trihydroxybenzoic acid monohydrate and b) a K30 CO₂ sensor affixed to the inner lid of a 950 mL jar with data acquisition via a laptop computer.



A common pattern emerged during incubation of each oven dry soil. Subsamples amended with H₂O or with the glucose solution produced little CO₂ and were nearly identical to each other. Conversely, greater amounts of CO₂ quickly formed following treatment with gallic acid even when the pH was less than 7.

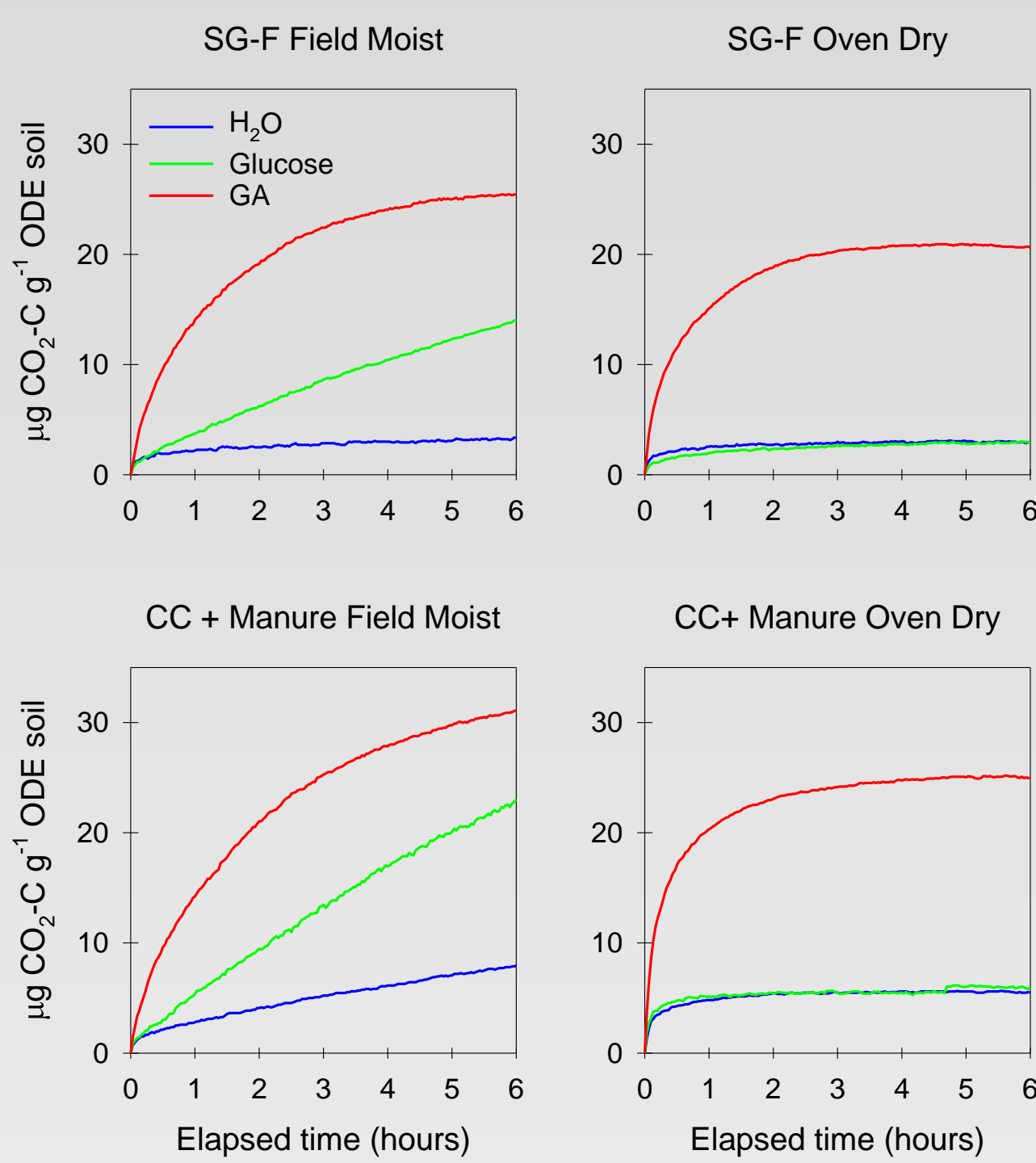
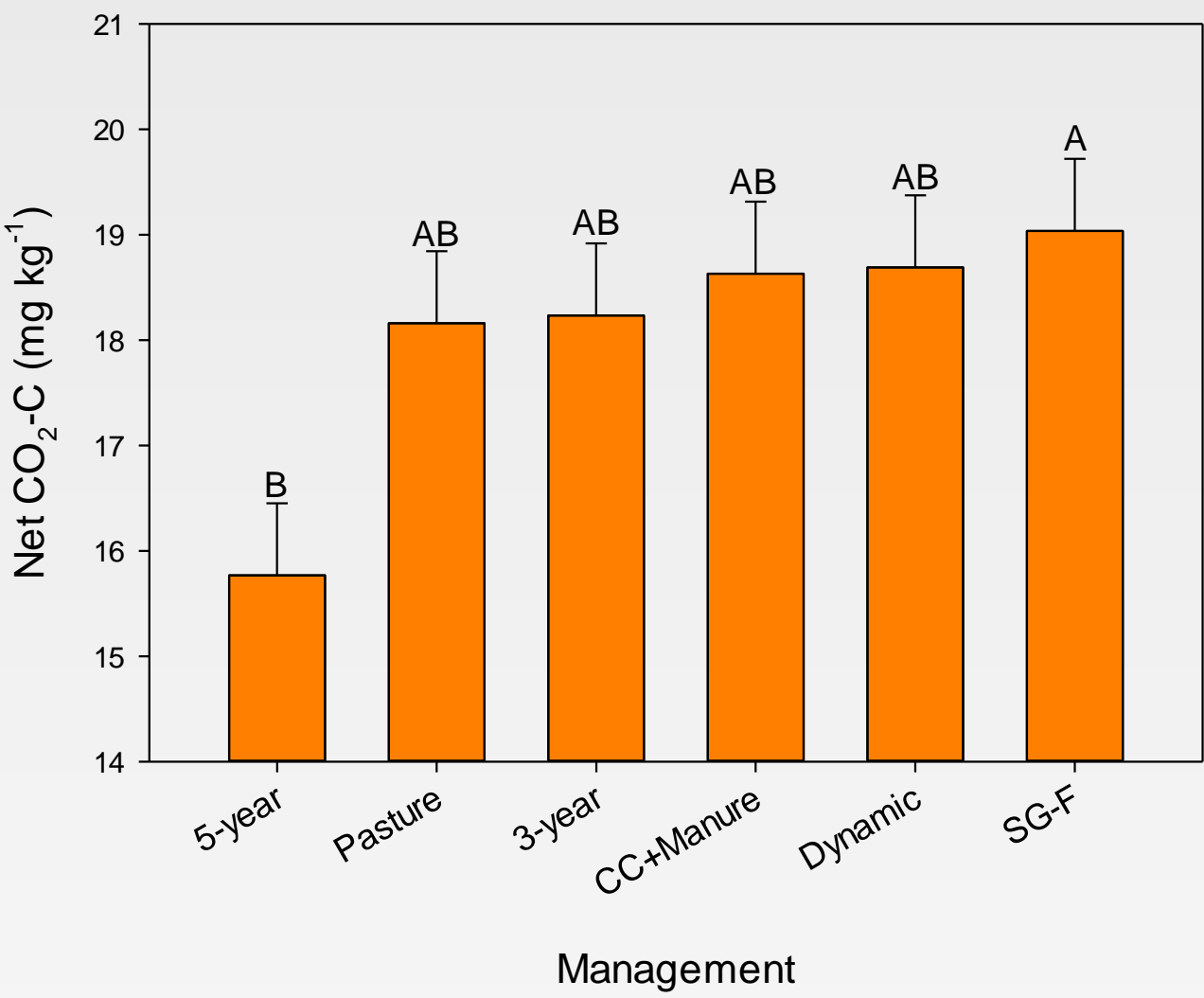
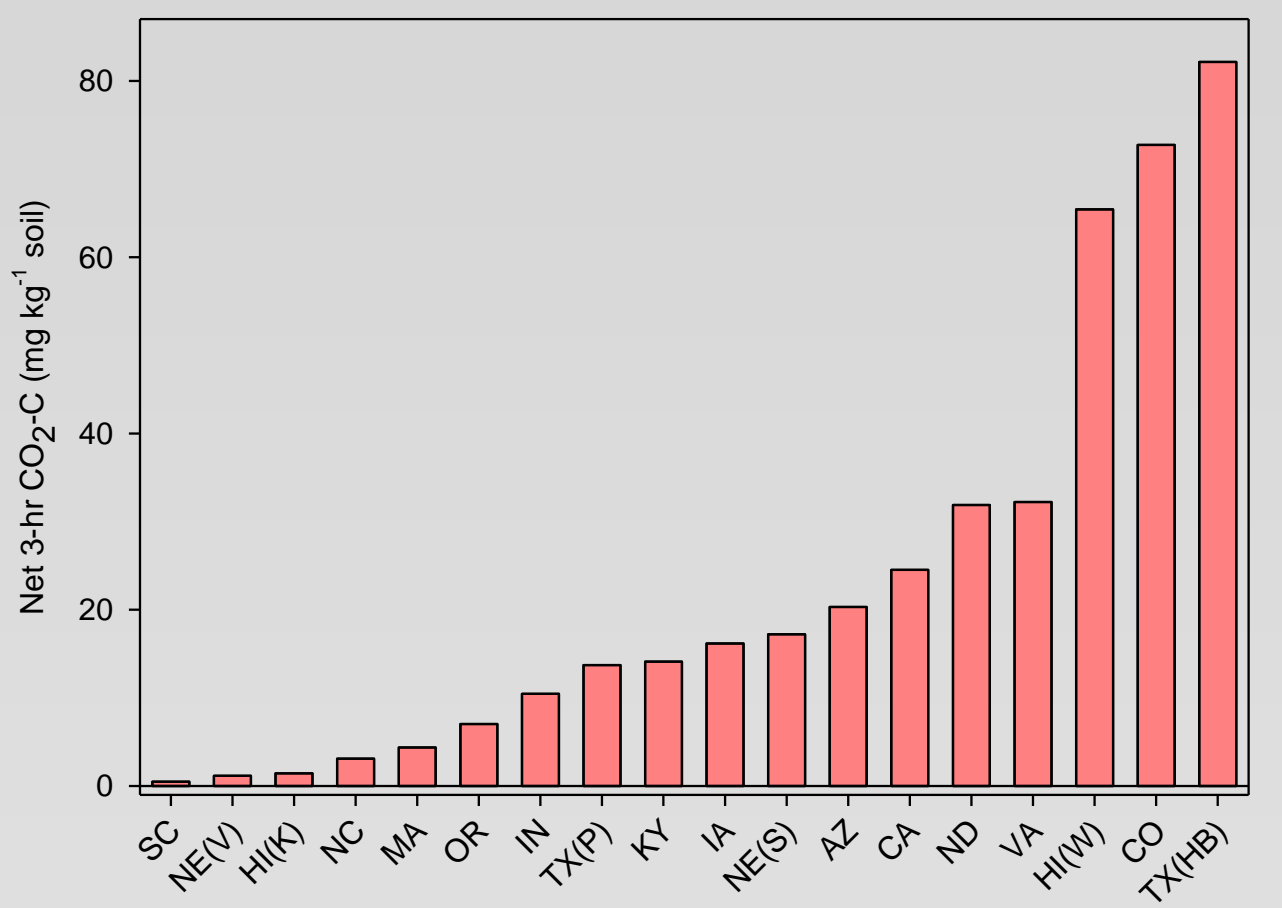


Figure 2. Typical patterns of cumulative CO₂ evolution after adding 5 mL of deionized water (blue) or solutions containing glucose (green) or gallic acid (red) to 8 g. of field-moist or oven dry soil. Soil pH (1:1 water) in the small grain (spring wheat)-fallow and cover crops-manure plots averaged 5.06 and 6.15, respectively.

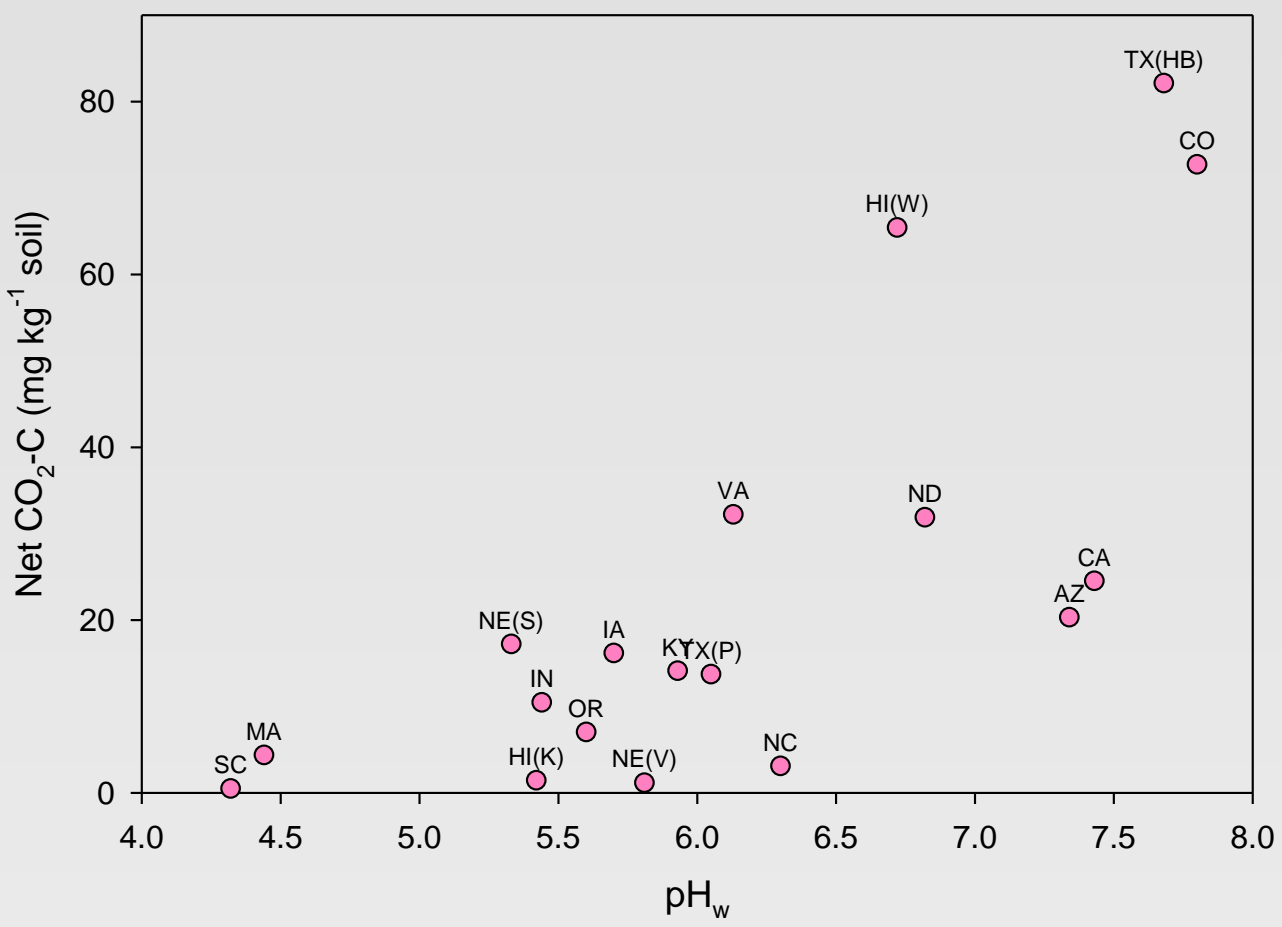
Figure 3. Average estimated net CO₂-C measured for soil samples collected in 2021 from a crop diversity study at Mandan ND. Net CO₂-C was determined as the difference between values for gallic acid and the glucose solutions after 3 hours of incubation at 22±2 °C.



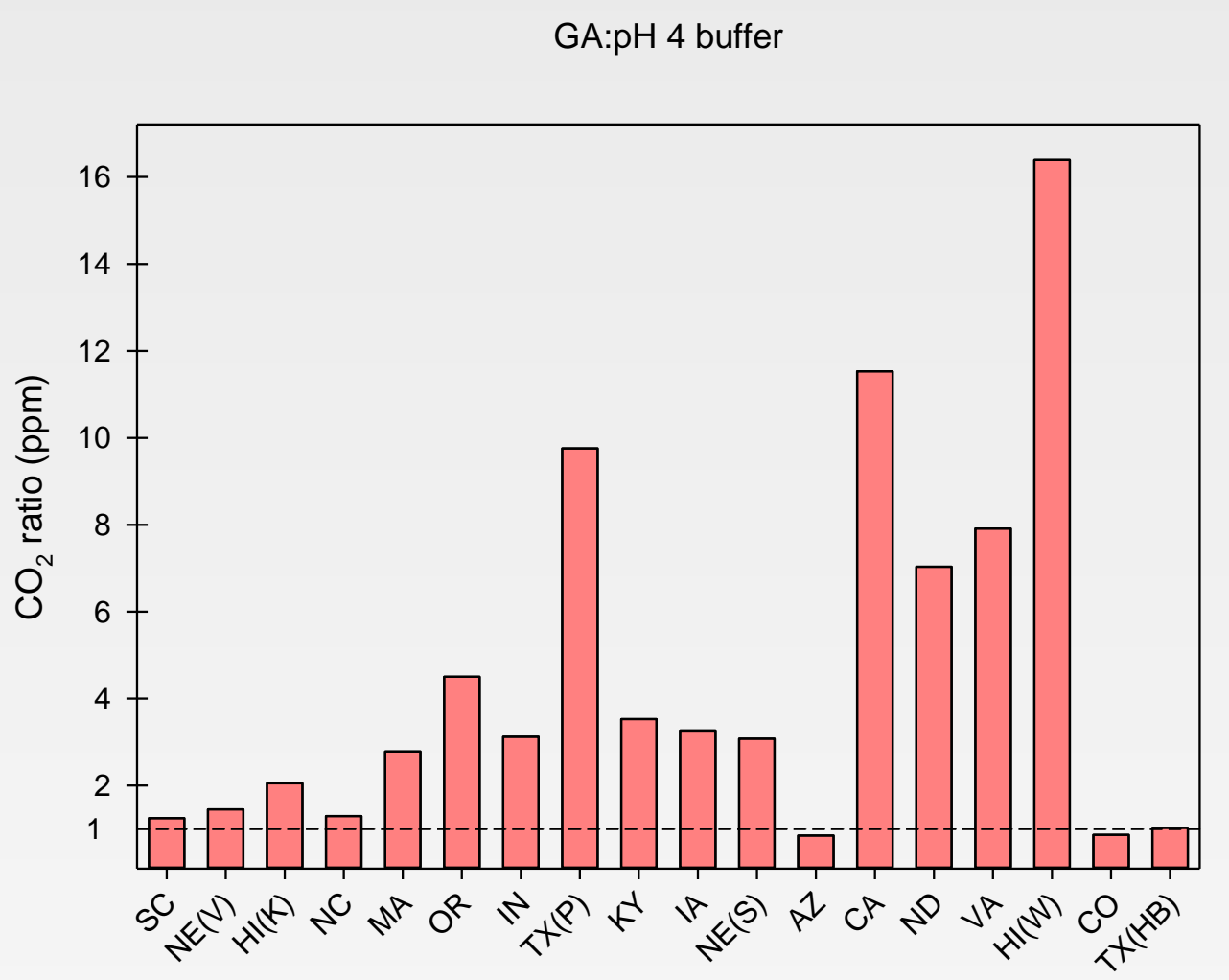
After 3 hours of incubation significant treatment effects for net CO₂-C efflux were observed in samples from the crop diversity study with more (Tukey's $P \leq 0.05$) net CO₂-C from the small grain (spring wheat)-fallow treatment compared to a 5-year rotation regime, an estimated 19.04 and 15.77 mg CO₂-C kg⁻¹ soil, respectively.



Incubations of the 18 benchmark soil samples produced a wide range of responses, from less than 0.5 to more than 80 mg net CO₂-C kg⁻¹ soil in 3-hours (**Fig. 4a**, left top). This broad range, and instances of variation seen over short distances indicate spatial patterns are likely to be significant and complex.



Greatest net CO₂-C was observed for soils with a pH > 7, suggesting that at least some of the CO₂ was the result of reactions between the relatively low pH (~3.5) gallic acid solution and soil carbonates (**Fig. 4b**, left middle).

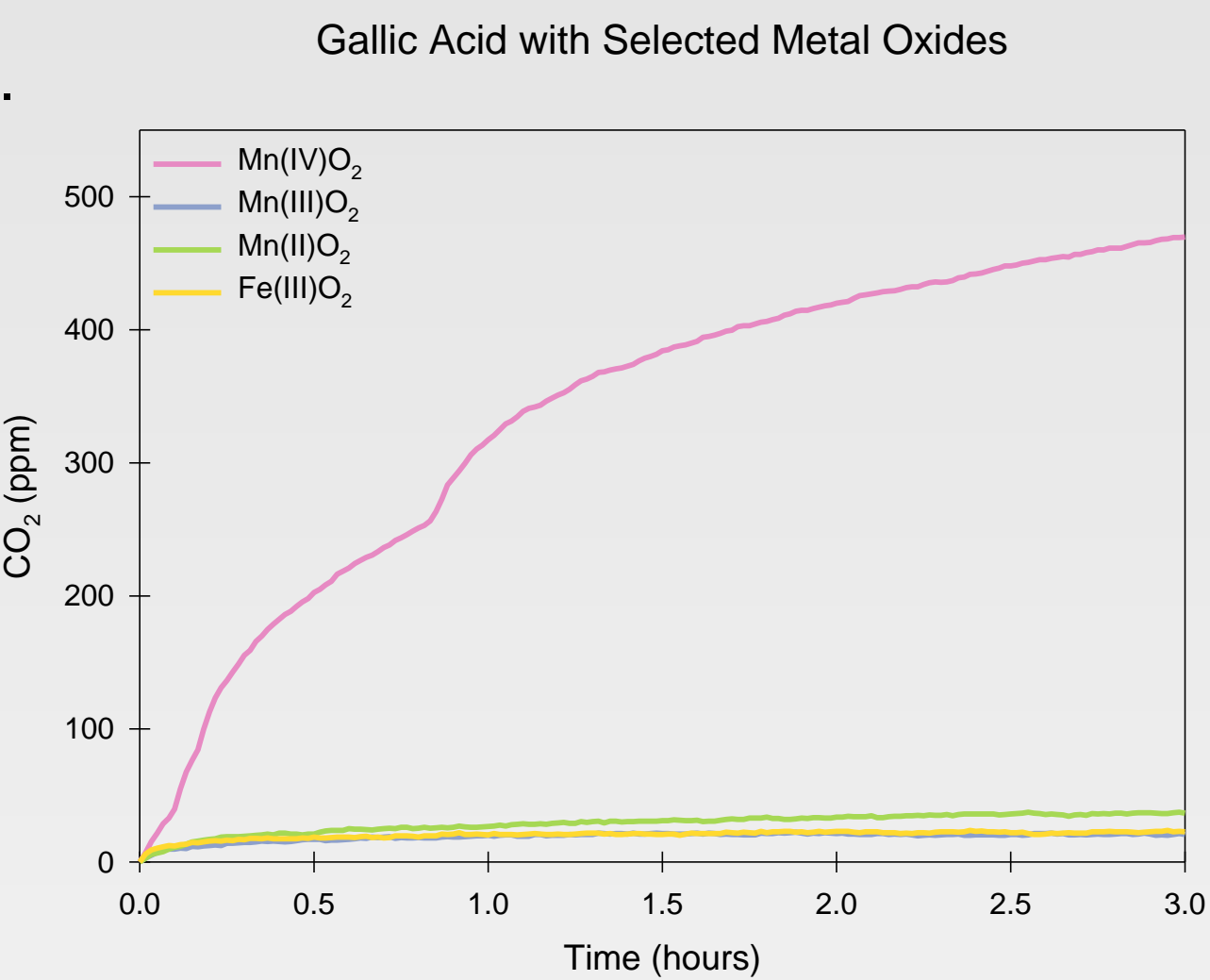


Treating soils with a pH 4 buffer solution revealed carbonates were the major source of CO₂ for TX(HB), CO, and AZ (a ratio ~1, **Fig. 4c** left bottom). However, relatively high amounts of CO₂ were also produced by samples with pH < 7, such as HI(W), ND, VA, TX(P), and OR indicating reactions between soil and the gallic acid. The high ratio (11.5) observed for CA (pH 7.4) infers multiple processes can contribute to short term CO₂ efflux from soil.

Figure 4. Estimated net CO₂-C a) after 3 hours from 18 archived soil samples collected in 1983-84, and b) arrayed against soil pH, and c) ratios of CO₂ produced by soils treated with 5 mL of GA compared to a 5 mL of a pH 4, phthalate buffer (Labchem Inc., Zelenople, PA).

Proposed Mechanism: Abiotic efflux of CO₂ from soil is often attributed to dissolution of carbonates, and thus not expected to occur in soils with a low pH. However, another abiotic source of CO₂, less constrained by pH, may arise from electron transfer reactions that oxidize natural soil organic matter and reduce metal oxides. Studies of these redox reactions between phenolic compounds and Fe and Mn oxides in soil have been focused mainly on the environmental fate of both oxidants and reductants and formation of organic matter.

Figure 5. (below) indicates that CO₂ is rapidly formed when Mn(IV)O₂ is combined with an equimolar quantity of gallic acid.



Take home: Abiotic reactions capable of rapidly producing a burst of CO₂ can occur in a wide range of soils following inputs of some simple phenolic compounds and be impacted by management. We suggest these are redox reactions in soil linked to metal (Mn) oxides and when considered together with fluctuations of carbon inputs to soil and repeated redox cycling, might be a significant contributor to C emissions.