Supporting Information

Field-deployable Measurement of Soil Extracellular Enzyme Activity Using Surface-enhanced Raman Spectroscopy

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Text S1. AuNP synthesis

The gold seeds were first prepared based on the Frens' method.[1] Briefly, gold precursor ($HAuCl_4$, 1 mM) was reduced by sodium citrate (3.88 mM) at 100 °C. AuNPs in larger size were subsequently synthesized based on seed-mediated growth as follows. One hundred milliliter of $HAuCl_4$ solution (0.254 mM) was heated to boil with magnetic stirring and refluxing condensation to avoid volume loss due to water evaporation. As the $HAuCl_4$ solution started to boil, aliquots of 818-μL seed colloid and 440-μL sodium citrate solution (38.8 mM) were pipetted into the flask successively. The color of the mixture immediately changed to light blue, which then turned murky blue within 2 min, and the endpoint of the reaction was indicated by a pink color after around 4 min. The flask was then removed from the heating mantle, followed by turning off the condensation equipment until the the colloid was cooled down to room temperature.

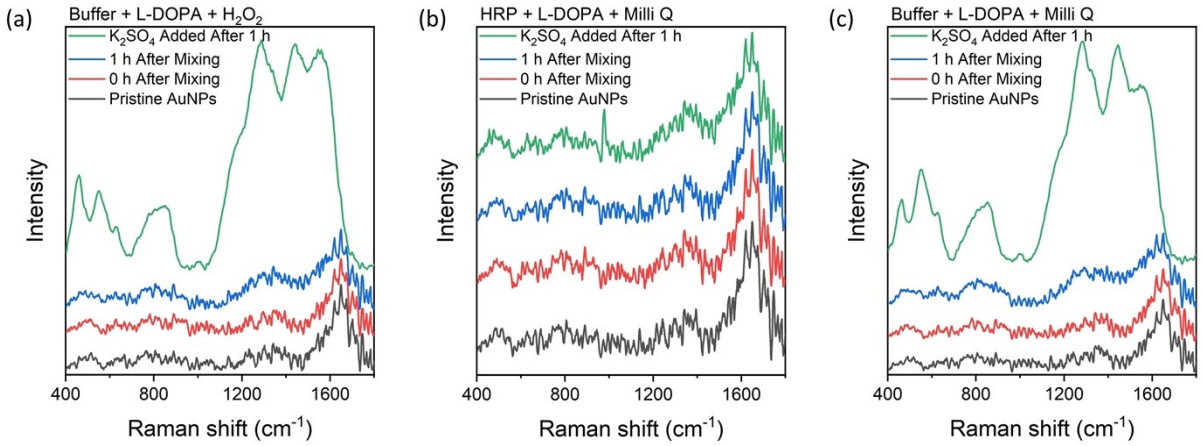

Figure S1. Variation of Raman spectra of AuNP colloid containing (a) acetate buffer, L-DOPA, and H_2O_2; (b) HRP, L-DOPA, and Milli Q; (c) acetate buffer, L-DOPA, and Milli Q over 1 hr. Potassium sulfate was added to induce SERS after 1 hr.

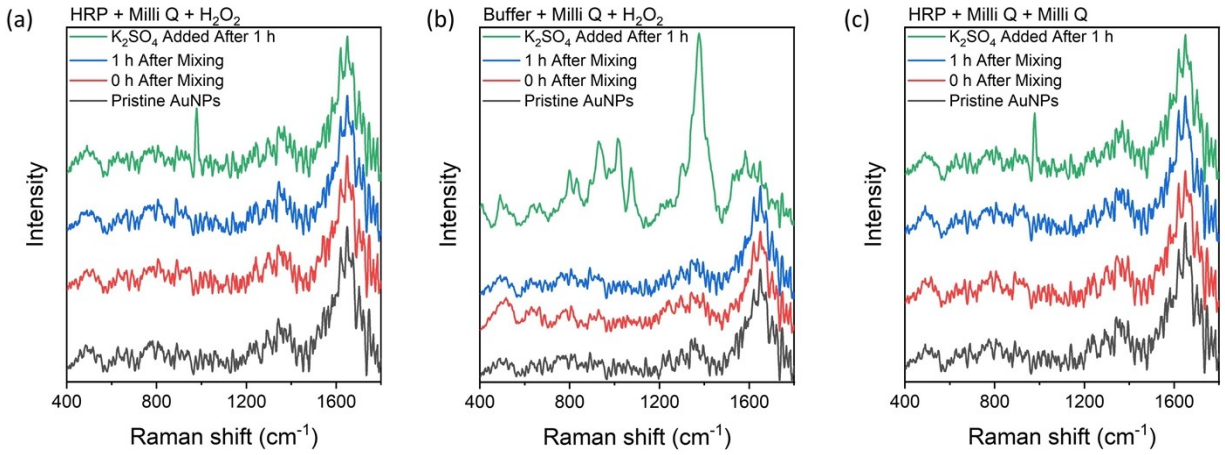

Figure S2. Variation of Raman spectra of AuNP colloid containing (a) HRP, Milli Q, and H_2O_2; (b) acetate buffer, Milli Q, and H_2O_2; (c) HRP, Milli Q, and Milli Q over 1 hr. Potassium sulfate was added to induce SERS after 1 hr.

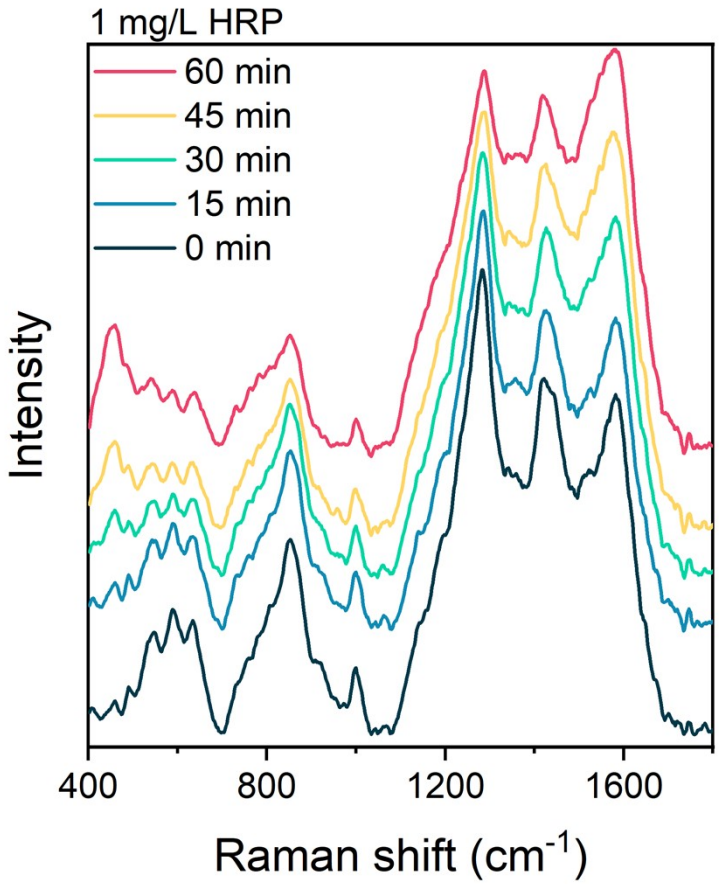

Figure S3. Variation of Raman spectra of L-DOPA over 1 hr, acquired from AuNP colloid containing acetate buffer, L-DOPA, H_2O_2, and 1 mg/L HRP.

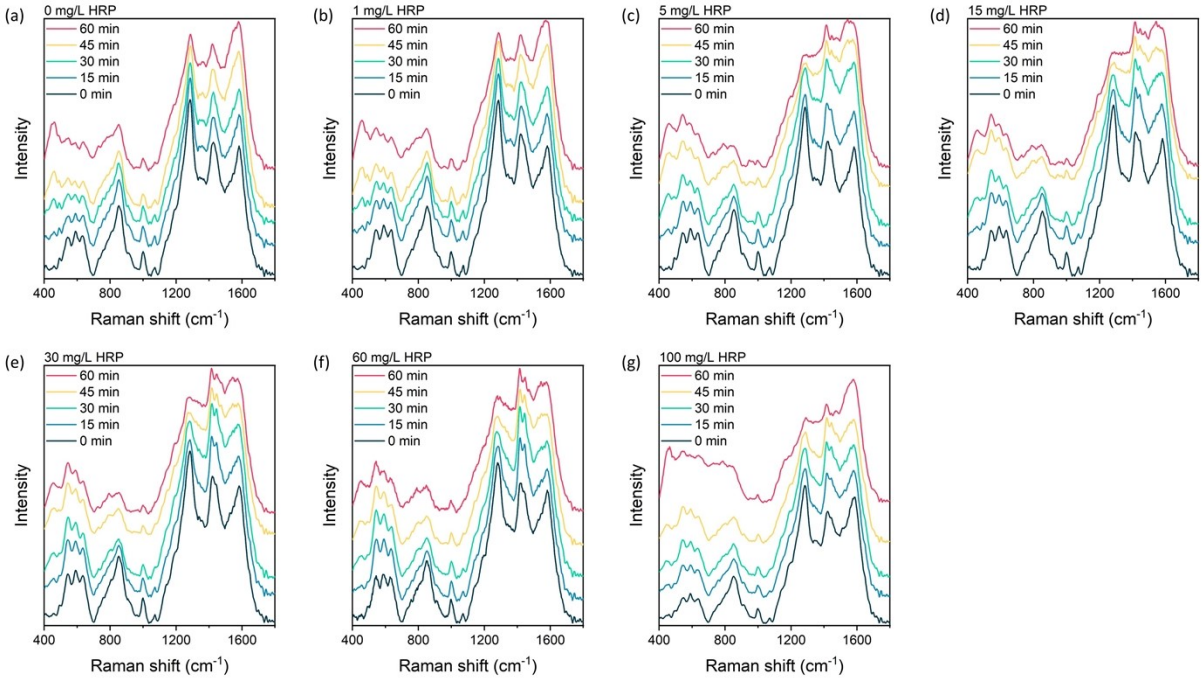

Figure S4. Replication #2 – Variation of SERS spectra of L-DOPA over 1 hr, acquired from AuNP colloid containing acetate buffer, L-DOPA, H_2O_2, with varying concentrations of HRP: (a) 0, (b) 1, (c) 5, (d) 15, (e) 30, (f) 60 mg/L, and (g) 100 mg/L.

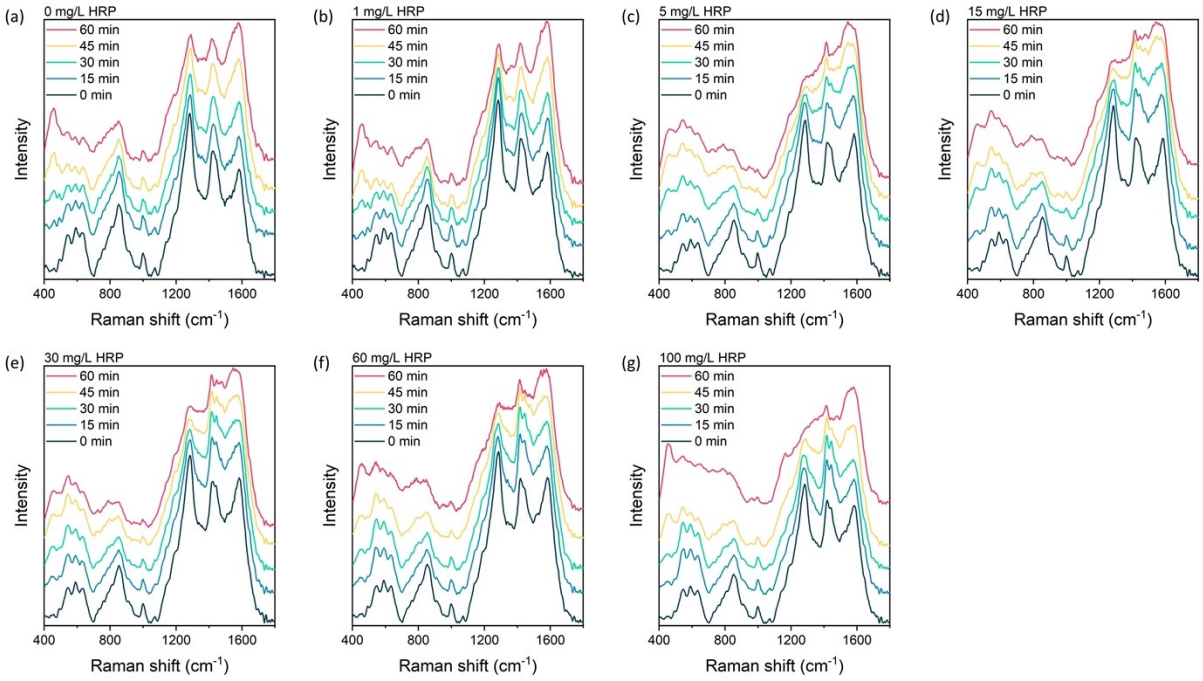

Figure S5. Replication #3 – Variation of SERS spectra of L-DOPA over 1 hr, acquired from AuNP colloid containing acetate buffer, L-DOPA, H_2O_2, with varying concentrations of HRP: (a) 0, (b) 1, (c) 5, (d) 15, (e) 30, (f) 60 mg/L, and (g) 100 mg/L.

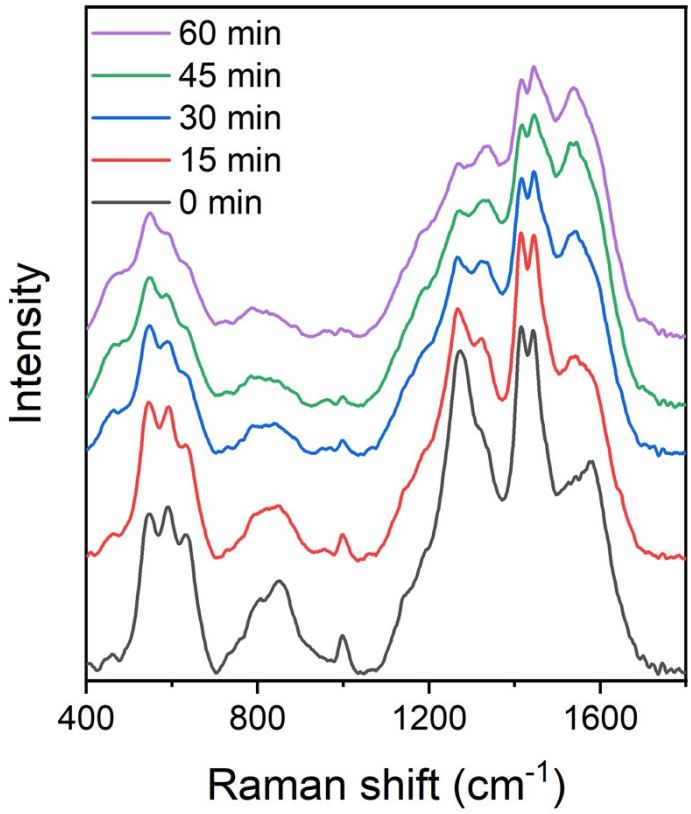

Figure S6. Variation of Raman spectra of L-DOPA over 1 hr, acquired from AuNP colloid containing L-DOPA, H_2O_2, and 0.1 mM $FeSO_4$. The "0 min" was marked after the addition of 0.1 mM $FeSO_4$.

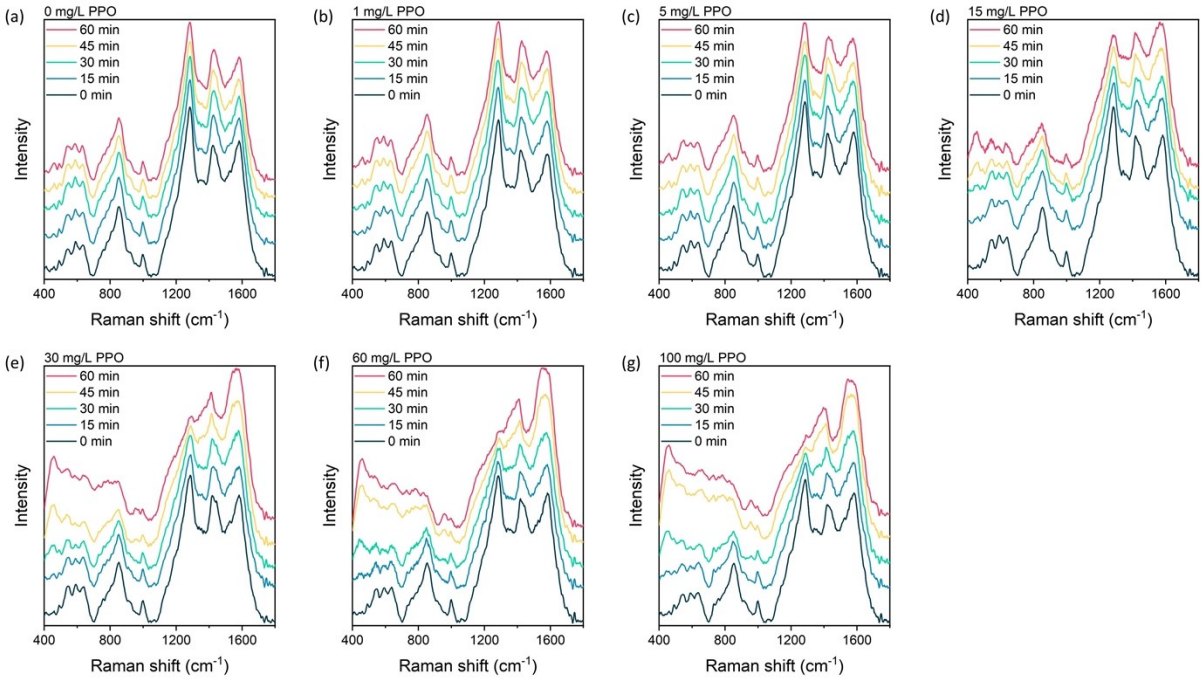

Figure S7. Replication #1 – Variation of SERS spectra of L-DOPA over 1 hr, acquired from AuNP colloid containing acetate buffer, L-DOPA, with varying concentrations of PPO: (a) 0, (b) 1, (c) 5, (d) 15, (e) 30, (f) 60 mg/L, and (g) 100 mg/L.

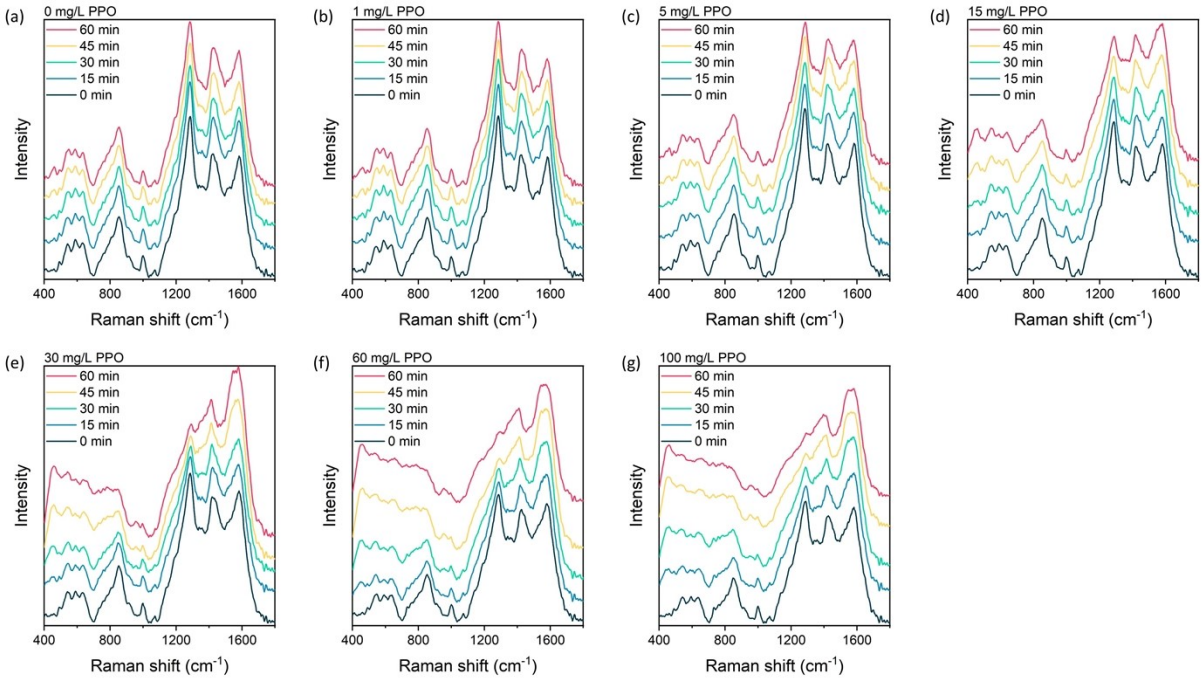

Figure S8. Replication #2 – Variation of SERS spectra of L-DOPA over 1 hr, acquired from AuNP colloid containing acetate buffer, L-DOPA, with varying concentrations of PPO: (a) 0, (b) 1, (c) 5, (d) 15, (e) 30, (f) 60 mg/L, and (g) 100 mg/L.

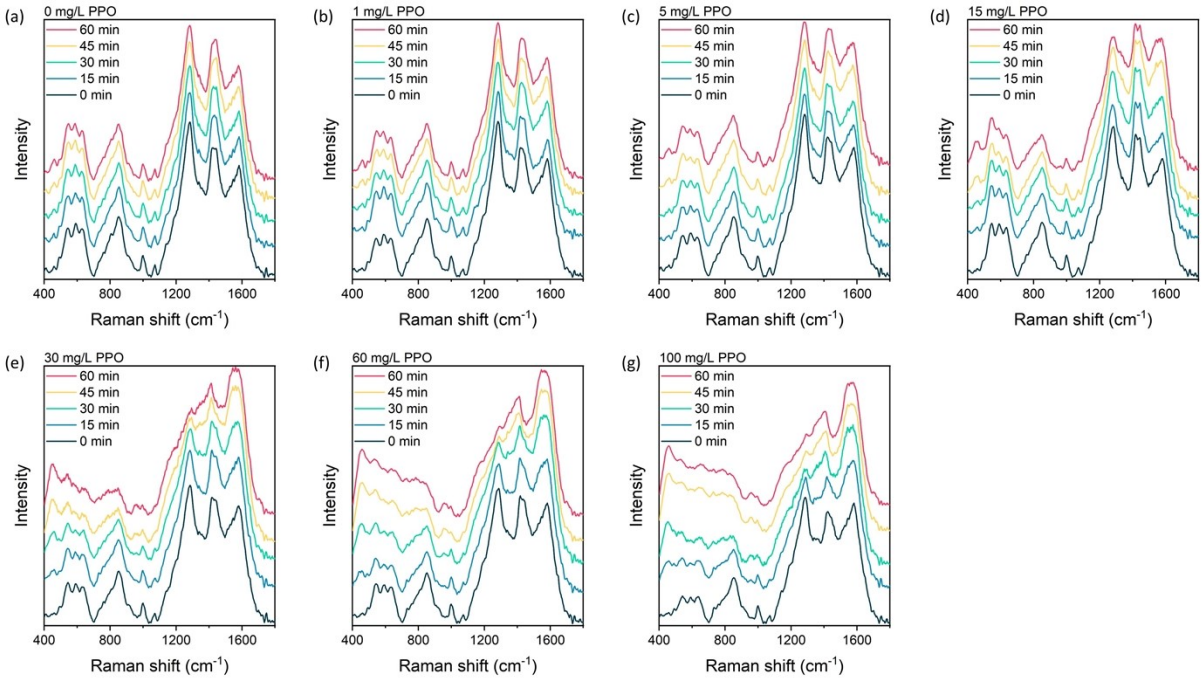

Figure S9. Replication #3 – Variation of SERS spectra of L-DOPA over 1 hr, acquired from AuNP colloid containing acetate buffer, L-DOPA, with varying concentrations of PPO: (a) 0, (b) 1, (c) 5, (d) 15, (e) 30, (f) 60 mg/L, and (g) 100 mg/L.

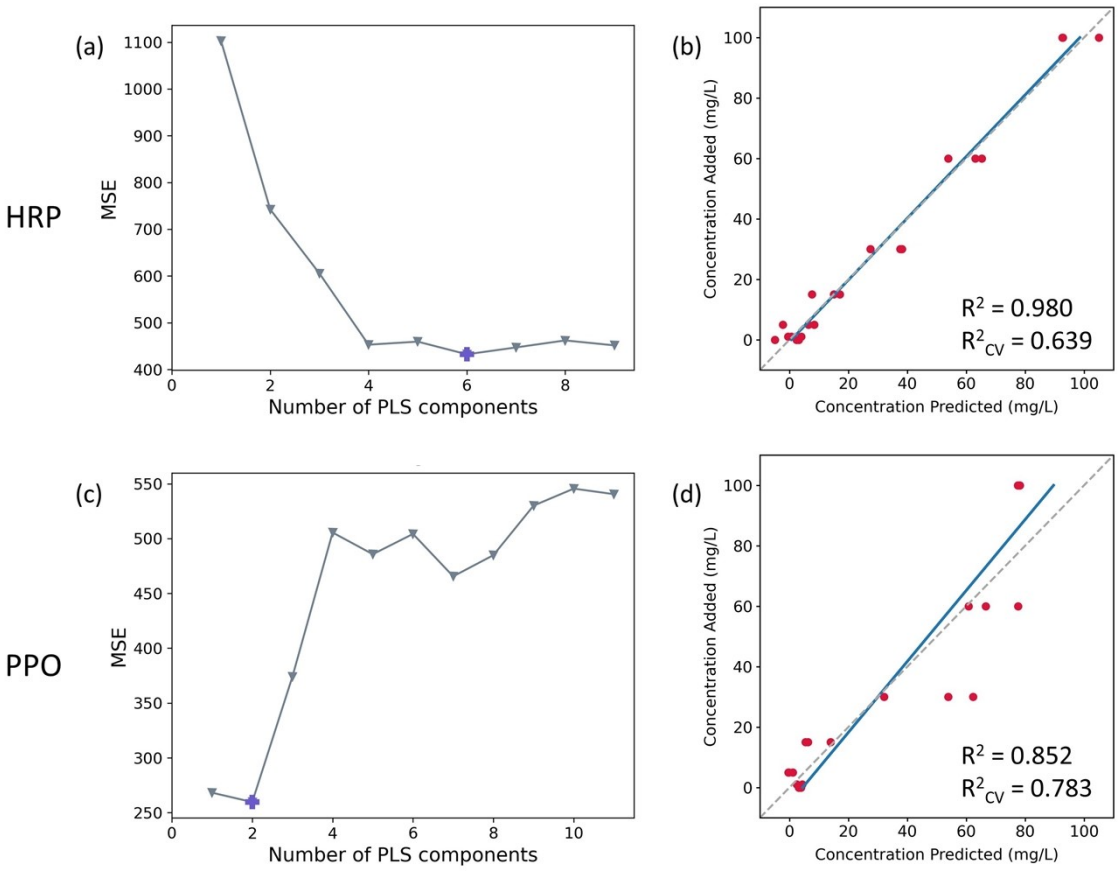

Figure S10. Error analysis for determining the optimal number of PLS components for (a) HRP and (c) PPO at 60 min; PLS regression results of (b) HRP and (d) PPO experiments using the respective optimal component numbers (6 for HRP, 2 for PPO). "CV" refers to cross validation.

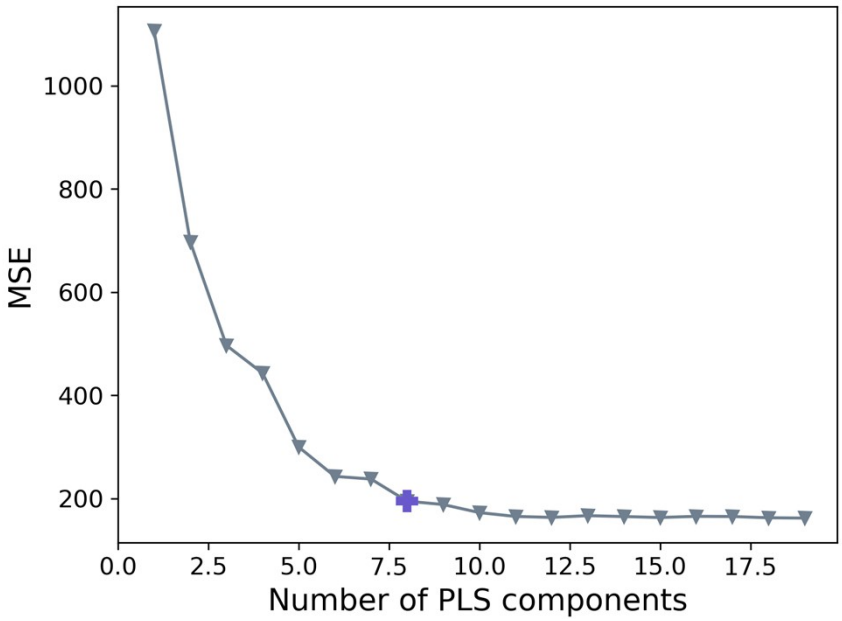

Figure S11. Error analysis for determining the optimal number of PLS components for HRP, using data collected at 60 and 45 min. The smallest error occurred at 19 components, but component number of 8 was selected for PLS modeling to prevent overfitting. "CV" refers to cross validation.

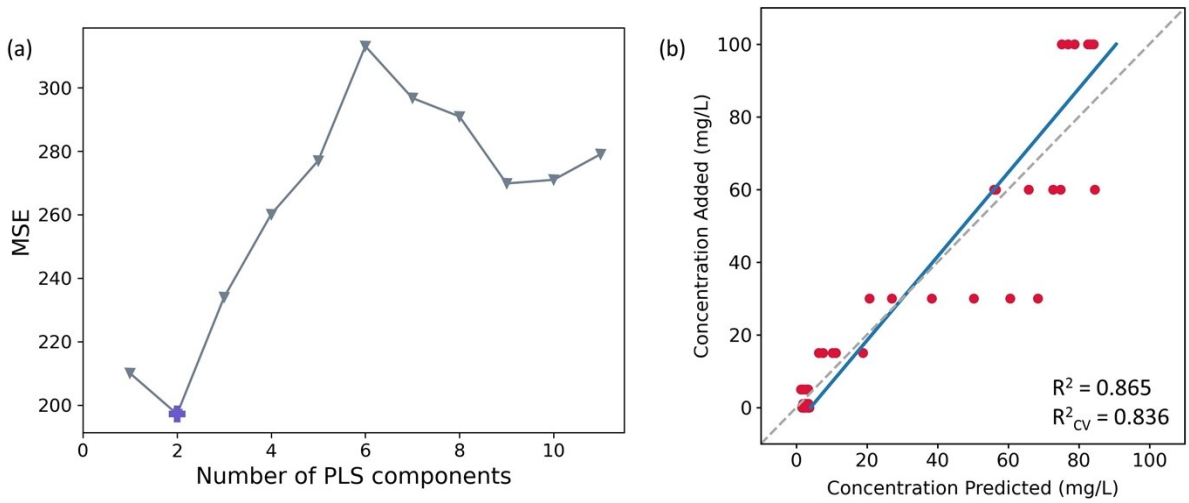

Figure S12. (a) Error analysis for determining the optimal number of PLS components for PPO, using data collected at 60 and 45 min. (b) PLS regression results of PPO experiments using the optimal component number of 2. "CV" refers to cross validation.

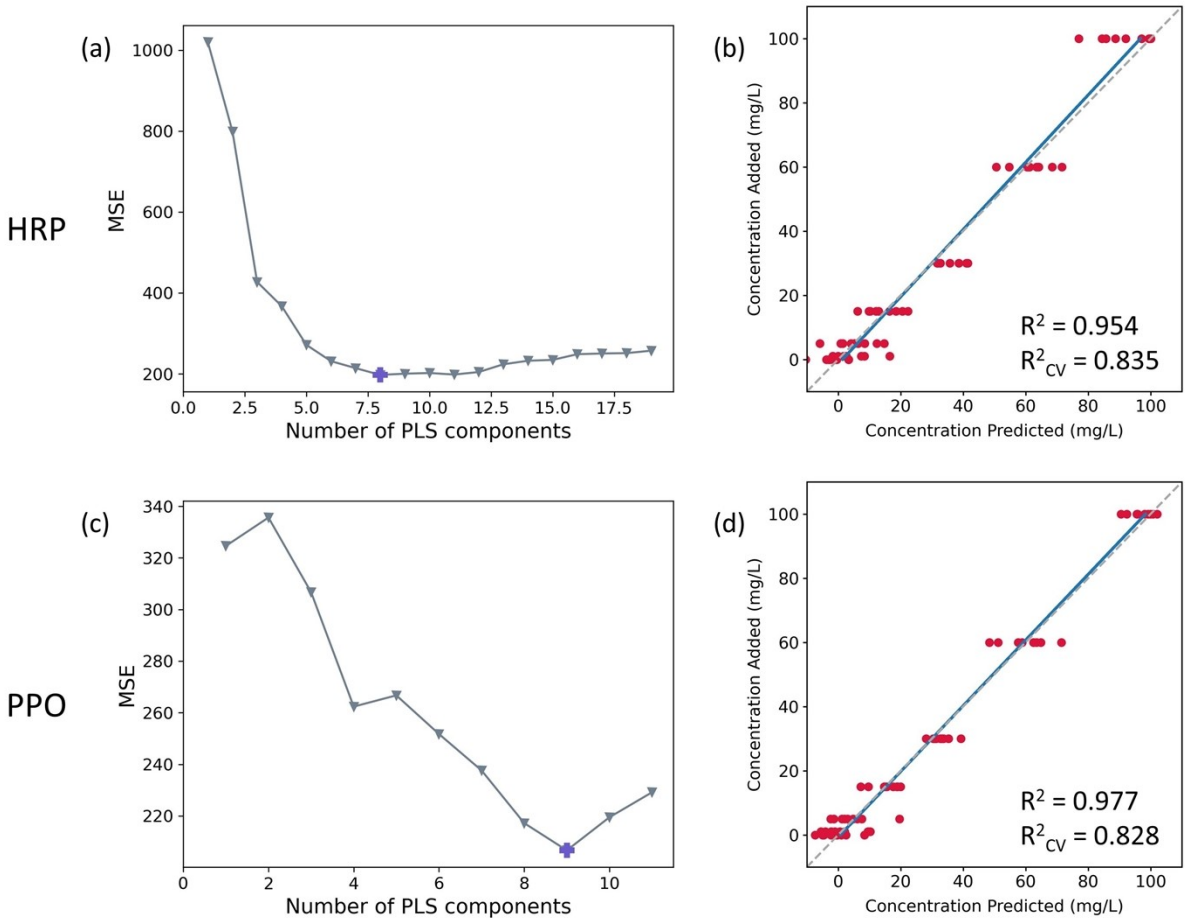

Figure S13. Error analysis for determining the optimal number of PLS components for (a) HRP and (c) PPO, using data collected at 60, 45, and 30 min; PLS regression results of (b) HRP and (d) PPO experiments using the respective optimal component numbers (8 for HRP, 9 for PPO). "CV" refers to cross validation.

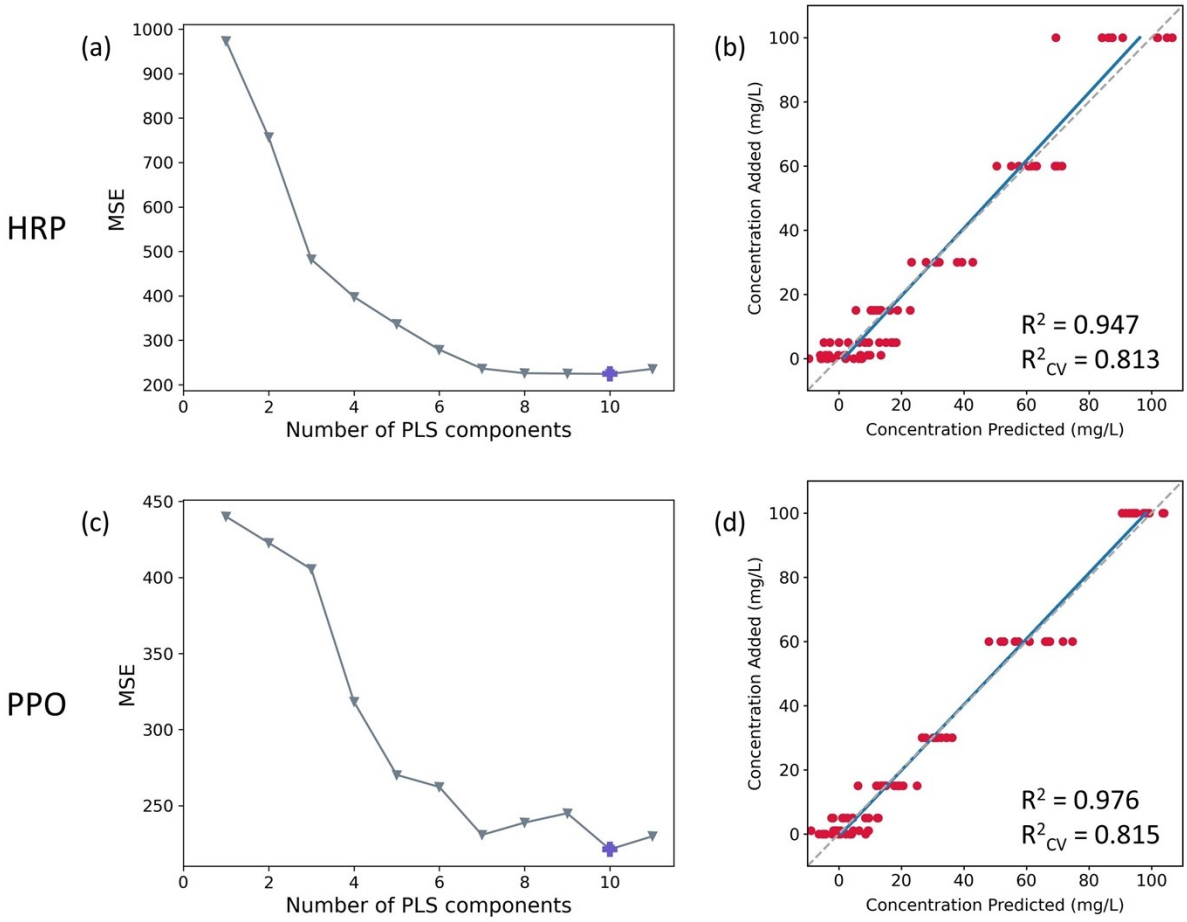

Figure S14. Error analysis for determining the optimal number of PLS components for (a) HRP and (c) PPO, using data collected at 60, 45, 30, and 15 min; PLS regression results of (b) HRP and (d) PPO experiments using the respective optimal component numbers (10 for both HRP and PPO). "CV" refers to cross validation.

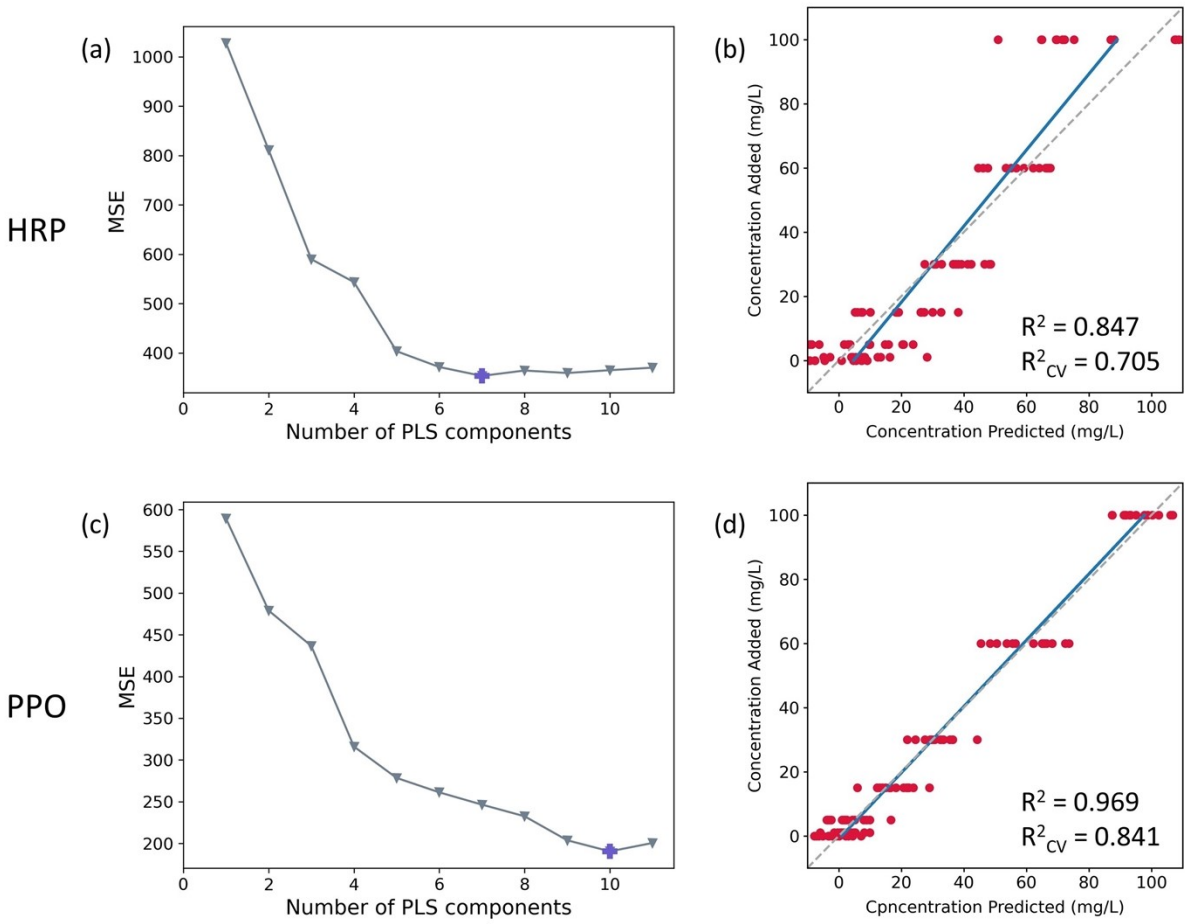

Figure S15. Error analysis for determining the optimal number of PLS components for (a) HRP and (c) PPO, using data collected at 60, 45, 30, 15 and 0 min; PLS regression results of (b) HRP and (d) PPO experiments using the respective optimal component numbers (7 for HRP, 10 for PPO). "CV" refers to cross validation.

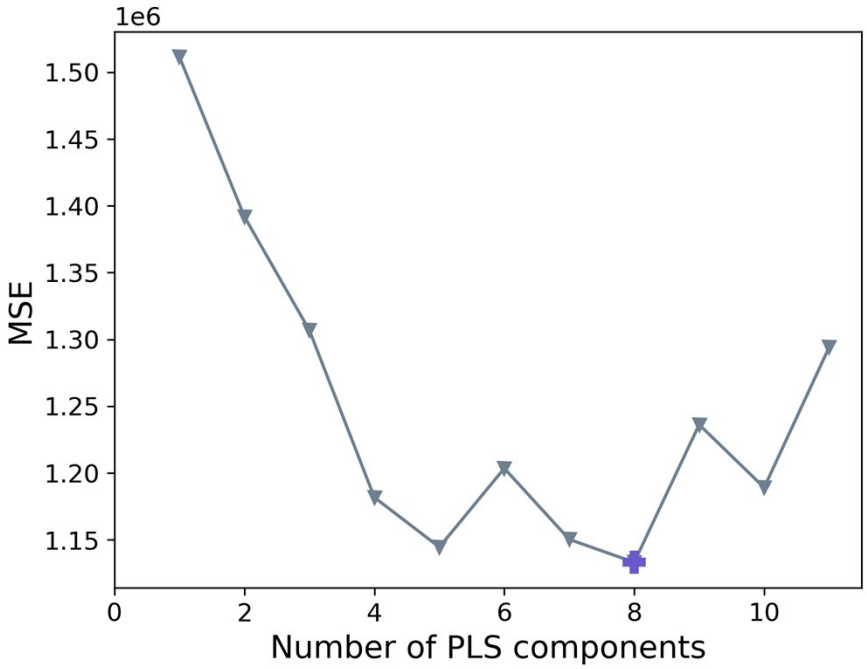

Figure S16. Error analysis for determining the optimal number of PLS components for the regresssion model applied for the real soil samples.