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Soil Research

Supplementary Material

Copper speciation and mobility in glyphosate co-contaminated soils: a microcosm and X-ray absorption spectroscopy study

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Supplementary material

Table S1. Recommend Application rates of commercial herbicide, Glyphosate, isopropylamine sale 48% w/v

| Weeds | | Application Rate | |
|-------------------------|------------------|-------------------------------------|--------------------|
| | | cc. rai ⁻¹ ^{1/} | L ha ⁻¹ |
| Annual weeds | | 225 - 250 | 1.41 – 1.56 |
| Perennial weeds, shaded | | 500 | 3.13 |
| Perennial weeds, sunny | Cogon grass | 750 | 4.88 |
| | Purple nut sedge | 600 – 700 | 3.75- 4.38 |
| | Giant mimosa | 1500 - 3000 | 9.38 – 18.75 |
| Others | | 500 – 1,000 | 3.13 – 6.25 |

Division of Agricultural Regulation. (1994) Thailand Pesticide Registration Book. THAI AGRO BUSINESS ASSOCIATION

^{1/} National unit for land area equivalent to 6.25 ha.

Table S2. Calculation of glyphosate concentration in soil from literature and the recommend application rate.

| | Glyphosate | Soil | Concentration of glyphosate in soil based on the calculation |
|---------------------------|---|--|--|
| Wang (2009) | 5 mL of 0.1 mM | 1.0 g | 0.5 mmol kg ⁻¹ |
| Wang (2009) | 10 mL of 0.1 mM | 1.0 g | 1.0 mmol kg ⁻¹ |
| Recommend Rate | 7 L ha ⁻¹ of 48% (w/v) commercial product | 1 cm depth, bulk density 1.33 g cm ⁻³ | 0.11 mmol kg ⁻¹ |
| Recommend Rate | 7 L ha ⁻¹ of commercial product (48% w/v) | 2 cm depth, bulk density 1.33 g cm ⁻³ | 0.06 mmol kg ⁻¹ |
| 10 time of Recommend Rate | 10 x 7 L ha ⁻¹ of commercial product (48% w/v) | 1 cm depth, bulk density 1.33 g cm ⁻³ | 1.12 mmol kg ⁻¹ |
| 10 time of Recommend Rate | 10 x 7 L ha ⁻¹ of commercial product (48% w/v) | 2 cm depth, bulk density 1.33 g cm ⁻³ | 0.56 mmol kg ⁻¹ |

Table S3. Peak differences between the main edge peaks, α and β , from the 1st derivative spectra of copper reference compounds.

| Reference compounds | Pre-edge, eV | White line, eV | α , eV | β , eV | Δ , eV |
|---|--------------|----------------|---------------|--------------|---------------|
| Cu(CH ₃ COO) ₂ | 8975.9 | 8997.4 | 8983.8 | 8989.9 | 6.11 |
| CuCO ₃ | 8975.7 | 8996.7 | 8985.8 | 8990.5 | 4.68 |
| CuSO ₄ | 8975.4 | 8995.2 | 8987.1 | 8993.0 | 5.96 |
| Cu ₃ (PO ₄) ₂ | 8975.6 | 8996.2 | 8985.0 | 8991.0 | 5.96 |
| Cu(NO ₃) ₂ | 8975.6 | 8994.5 | 8985.7 | 8991.7 | 6.0 |
| Cu(OH) ₂ | 8975.8 | 8996.0 | 8986.0 | 8992.0 | 6.0 |

Table S4. Least Significant Difference (LSD) comparison of mean of total copper content in soils between soil without and with glyphosate within the same soil layer on day 1, day14 and day 40.

| | Soil Depth (cm) | Mean of total copper in soil (mg kg ⁻¹) | | Absolute value of mean difference | Standard Error | <i>p</i> -value |
|-------|-----------------|---|-----------------|-----------------------------------|----------------|-----------------|
| | | Without glyphosate | With glyphosate | | | |
| Day1 | 0-2 | 193.90±15.0 2 | 194.81±4.64 | 0.9138 | 5.3162 | 0.8670 |
| | 2-4 | 11.88±0.84 | 8.47±1.01 | 3.4053 | 5.3162 | 0.5362 |
| | 4-6 | 7.34±0.27 | 7.73±3.54 | 0.3897 | 5.3162 | 0.9430 |
| | 6-8 | 5.97±2.26 | 6.91±2.59 | 0.9359 | 5.3162 | 0.8638 |
| | 8-10 | 8.27±1.62 | 6.74±2.62 | 1.5310 | 5.3162 | 0.7792 |
| Day14 | 0-2 | 228.65±13.7 1 | 220.63±8.83 | 8.0179 | 5.4912 | 0.1749 |
| | 2-4 | 10.38±1.84 | 10.50±0.10 | 0.1188 | 5.4912 | 0.9832 |
| | 4-6 | 5.23±1.21 | 5.37±1.40 | 0.1369 | 5.4912 | 0.9806 |
| | 6-8 | 5.50±2.11 | 6.94±3.33 | 1.4384 | 5.4912 | 0.7987 |
| | 8-10 | 5.73±0.75 | 8.58±3.57 | 2.8419 | 5.4912 | 0.6160 |
| Day40 | 0-2 | 234.75±37.6 3 | 226.94±4.16 | 7.8185 | 2.3374 | 0.0074 |
| | 2-4 | 12.70±3.82 | 16.11±2.92 | 3.4111 | 2.3374 | 0.1752 |
| | 4-6 | 8.18±2.63 | 8.53±0.48 | 0.3488 | 2.3374 | 0.8843 |
| | 6-8 | 7.24±1.95 | 7.35±1.10 | 0.1142 | 2.3374 | 0.9620 |
| | 8-10 | 7.59±1.40 | 7.06±0.17 | 0.5251 | 2.3374 | 0.8268 |

Table S5. Least Significant Difference (LSD) comparison of mean of copper fraction in the 0-2 cm depth soils between soil without and with glyphosate within the same fraction at day 1, day14 and day40.

| Day | Fraction | Mean of copper fraction in soil (%) | | Absolute value of mean difference | Standard Error | <i>p</i> -value |
|-------|----------|-------------------------------------|-----------------|-----------------------------------|----------------|-----------------|
| | | Without glyphosate | With glyphosate | | | |
| Day1 | F1 | 0.45±0.09 | 20.25±0.66 | 19.80 | 0.393114 | 4.0971E-09 |
| | F2 | 6.76±1.47 | 11.93±1.18 | 5.17 | 0.949621 | 0.0016 |
| | F3 | 21.84±1.45 | 11.32±0.03 | 10.52 | 1.434313 | 0.0003 |
| | F4 | 16.97±2.43 | 11.95±0.09 | 5.02 | 1.16026 | 0.0049 |
| | F5 | 51.68±5.10 | 42.43±2.36 | 9.25 | 3.164499 | 0.0265 |
| | F6 | 2.30±0.35 | 2.12±0.46 | 0.18 | 0.787818 | 0.8212 |
| Day14 | F1 | 0.38±0.04 | 3.81±0.68 | 3.43 | 0.393114 | 0.0001 |
| | F2 | 2.82±0.17 | 4.89±1.28 | 2.07 | 0.949621 | 0.0724 |
| | F3 | 17.13±0.88 | 17.63±2.90 | 0.50 | 1.434313 | 0.7371 |
| | F4 | 13.94±0.25 | 12.09±0.69 | 1.85 | 1.16026 | 0.1621 |
| | F5 | 61.67±0.43 | 58.95±5.21 | 2.72 | 3.164499 | 0.4230 |
| | F6 | 4.06±0.49 | 2.63±0.33 | 1.43 | 0.787818 | 0.1196 |
| Day40 | F1 | 0.33±0.12 | 0.53±0.07 | 0.20 | 0.393114 | 0.6299 |
| | F2 | 3.20±0.25 | 3.65±0.35 | 0.45 | 0.949621 | 0.6516 |
| | F3 | 11.84±1.02 | 13.06±0.03 | 1.222 | 1.434313 | 0.4267 |
| | F4 | 13.78±1.28 | 12.29±0.07 | 1.49 | 1.16026 | 0.2450 |
| | F5 | 64.68±0.87 | 53.67±0.65 | 11.00 | 3.164499 | 0.0132 |
| | F6 | 6.17±1.49 | 16.80±0.90 | 10.63 | 0.787818 | 1.0309E-05 |