Supplementary Information to:

Glyphosate is a transformation product of a widely used aminopolyphosphonate complexing agent

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RESULTS AND DISCUSSION

DTPMP stability in the absence of manganese

In the absence of MnO_2 and Mn^{2+} no DTPMP transformation could be detected by means of IC-PAD. Using LC-MS (samples diluted 1:2), no glyphosate and 0.321 ± 0.008 µM (corresponding to 0.03 mol-%) AMPA were detected after 168 hours. The AMPA concentrations detected in the control are negligible compared to the AMPA concentrations quantified at the end of the respective manganese experiments (30 to 200 µM), especially since for all those AMPA measurements the samples were diluted 1:100.

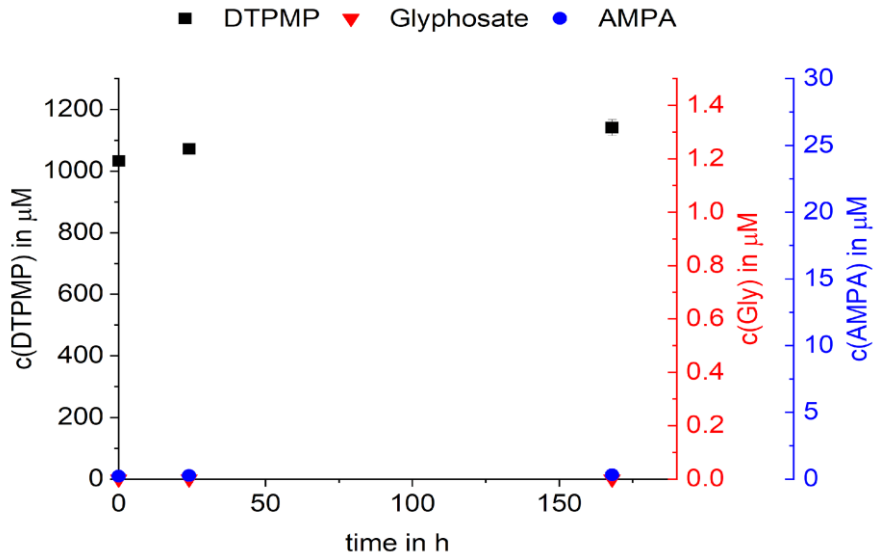

Figure S 1: DTPMP, AMPA and glyphosate concentrations over the course of the control experiment without MnO_2 or Mn^{2+}. Y-axis ranges were chosen according to those of the MnO_2 experiments displayed in the text. Error bars represent absolute errors between experimental duplicates.

Additional concentration profiles of transformation experiments

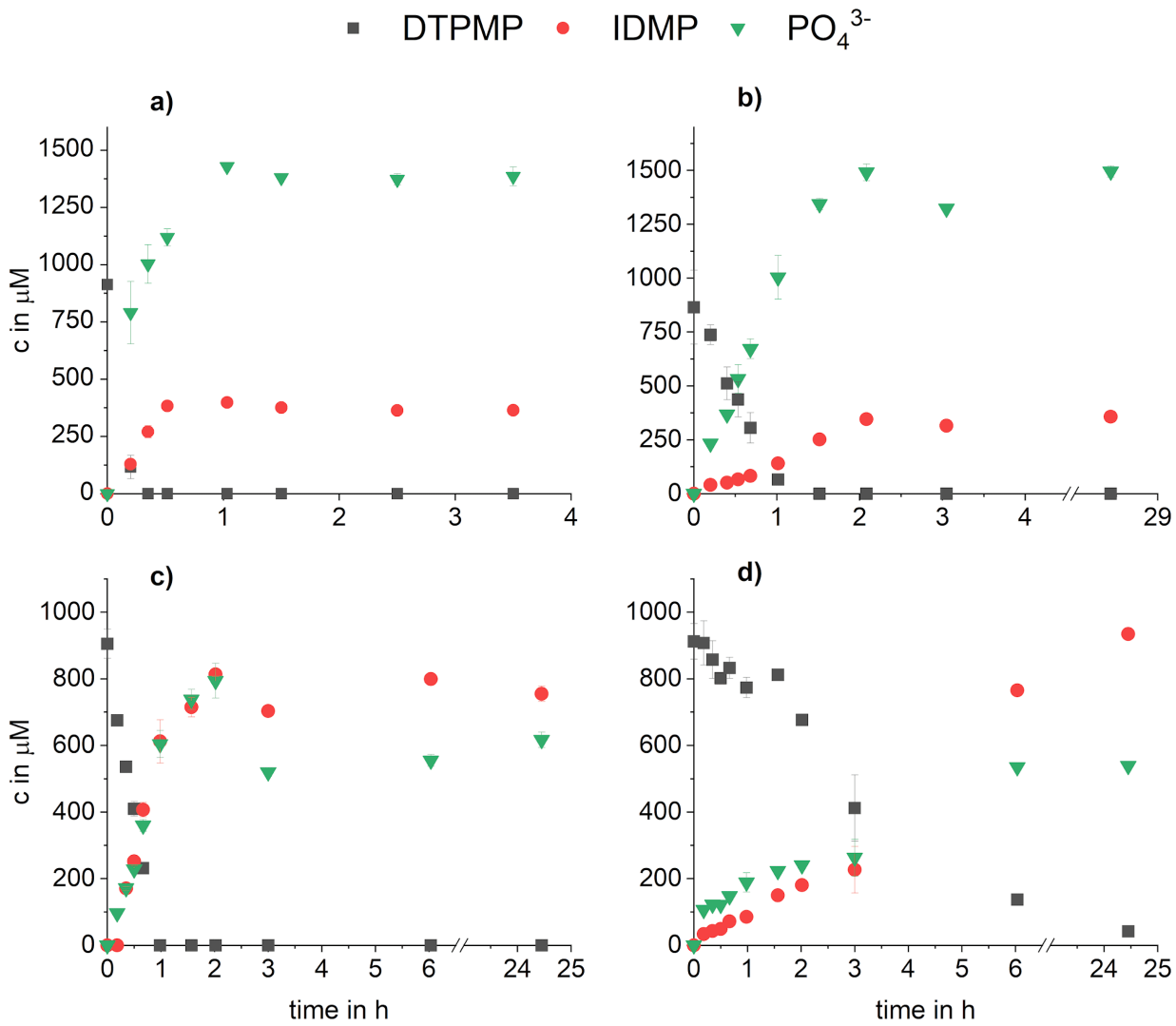

Figure S 2: Aqueous DTPMP, IDMP and PO_4^{3-} concentrations quantified using IC-ICP-MS ($^{31}P^{16}O^+$) during DTPMP oxidation by MnO_2 in four different experiments. a) 1.0 g/L MnO_2 oxic, b) 0.1 g/L MnO_2 oxic, c) 1.0 g/L MnO_2 anoxic, d) 0.1 g/L MnO_2 anoxic. Error bars represent absolute errors between experimental duplicates.

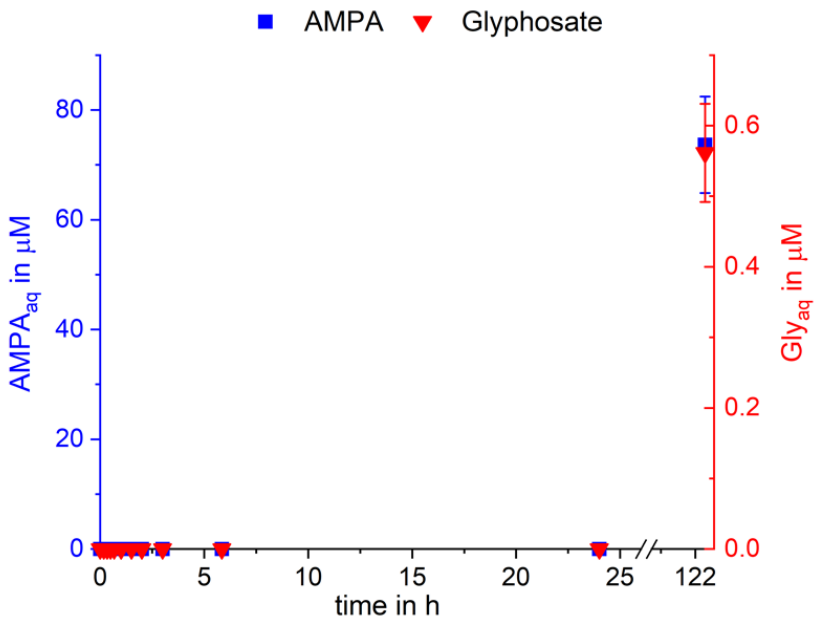

Figure S 3: Glyphosate and AMPA concentrations in the experiment with 1 mM DTPMP and 1 mM Mn^{2+} under oxic conditions until 120 hours. Error bars represent absolute errors between experimental duplicates.

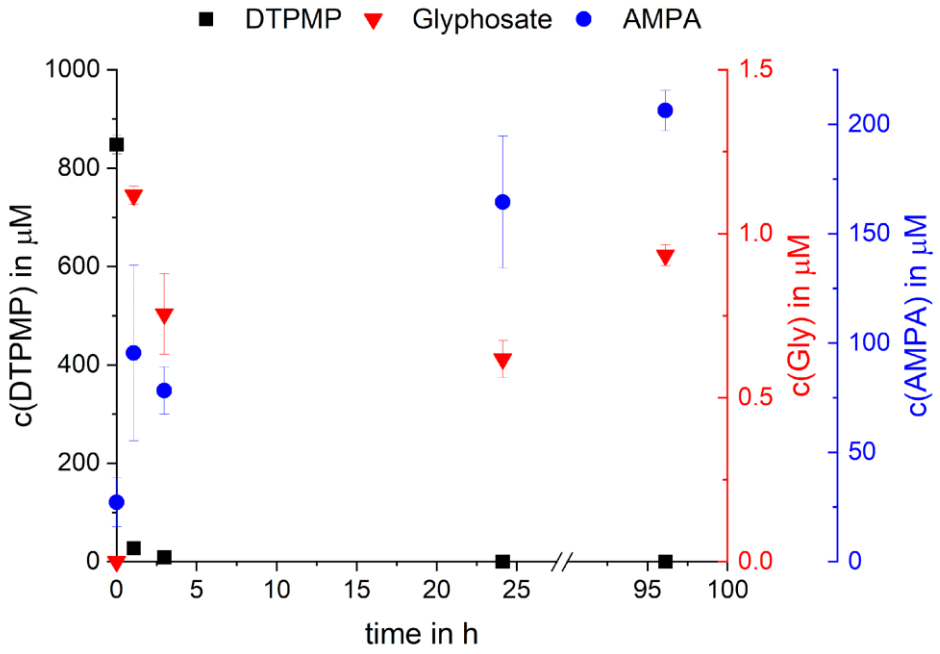

Figure S 4: Aqueous concentration of DTPMP quantified by means of IC-ICP-MS and total concentrations of glyphosate and AMPA quantified by means of LC-QQQ after derivatization in the longtime replica of 1.0 g/L MnO_2 under oxic conditions. Error bars represent absolute errors between experimental duplicates.

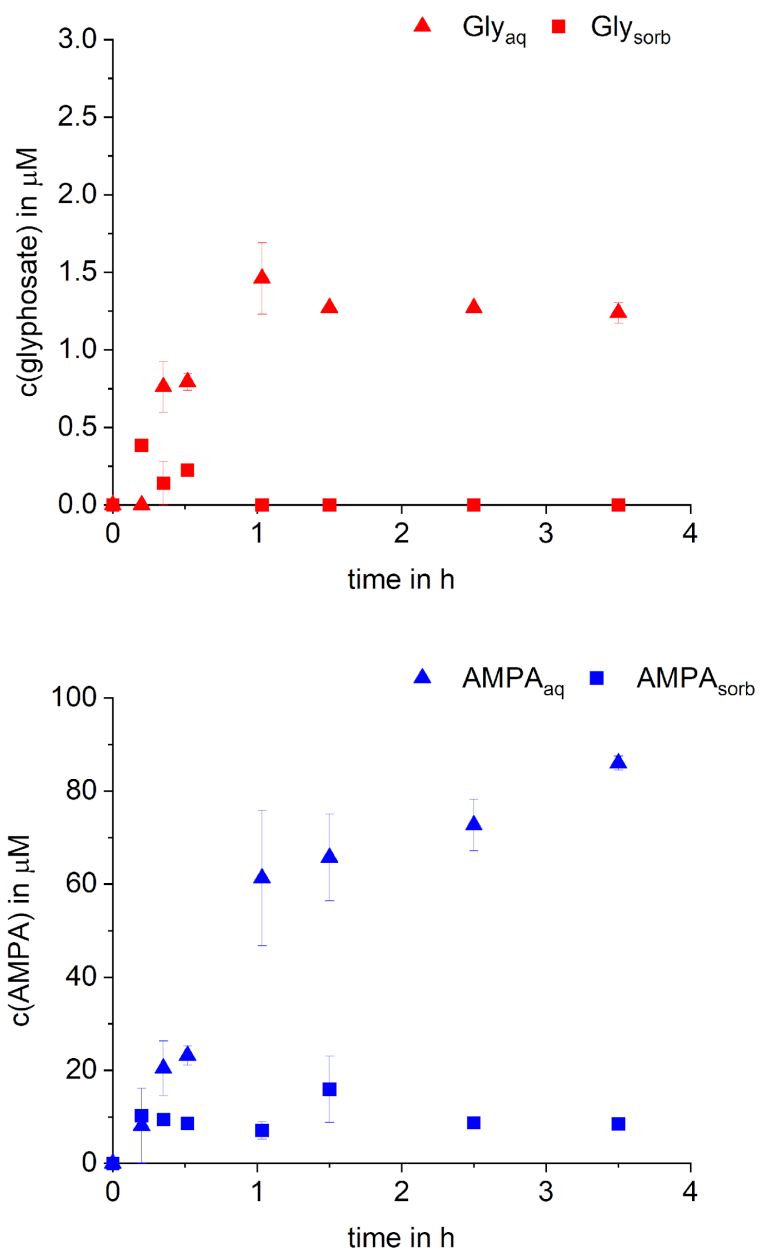

Figure S 5: Aqueous and sorbed AMPA and glyphosate concentrations in the experiment with 1.0 g/L MnO_2 under oxic conditions. Error bars represent absolute errors between experimental duplicates.

Nuclear Magnetic Resonance Spectroscopy (NMR)

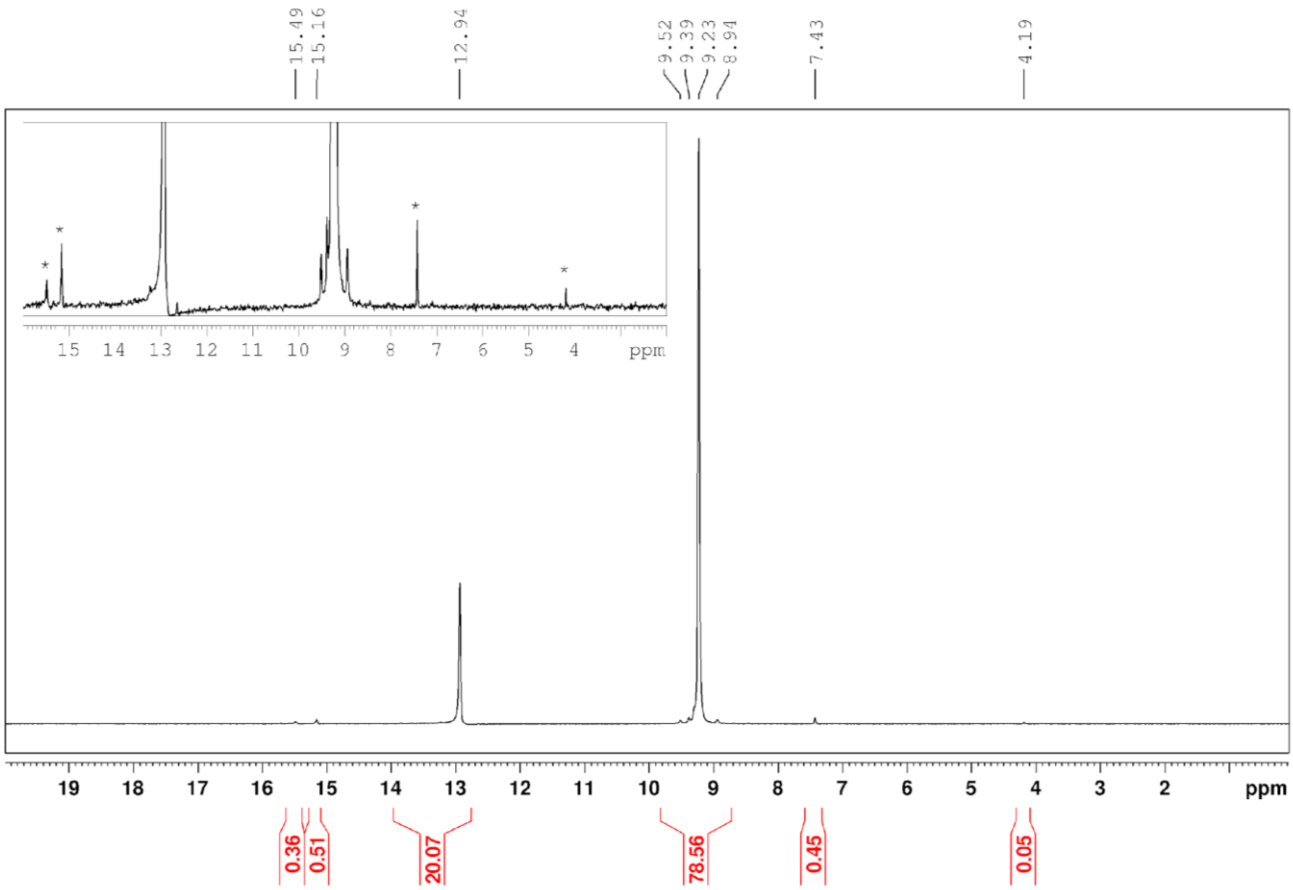

Figure S 6: ^{31}P-{^{1}H}-NMR-spectrum of DTPMP in D_2O measured as stated in the Materials & Methods section. δ (ppm): 9.23, 12.94. Impurities are marked with an asterisk. The sum of integrals is normalized to 100.

Mineral Characterization

Point of zero charge (pH_{PZC})

The pH_{PZC} of the MnO_2 used in this study has been analyzed via ζ-potential measurements using Zetasizer Nano ZSP (Malvern Pananalytical, Malvern, United Kingdom) in folded capillary zeta cells at 20 °C. Measurements were conducted in triplicates with 10 to 15 runs, each. For analysis, 50 mg/L MnO_2 suspensions were prepared in 10 mM NaCl + 10 mM MES buffer and the pH was adjusted by 0.1 M or 1 M NaOH and HCl. The point of zero charge was determined by plotting the zeta potential as function of the adjusted pH and subsequent regression of the linear part of the data sets. pH_{PZC} was defined at 5.6 ± 0.1.

Brunauer-Emmett-Teller method (BET)

The specific surface area (SSA) of the MnO_2 has been determined by nitrogen sorption-desorption isotherms using a Gemini VII 2390 (Micrometrics, Norcross, GA, USA). Samples were degassed before analysis overnight under vacuum at 120 °C. SSA was determined at 64.5 ± 0.2 m^2/g.

Powder X-ray diffraction (XRD)

XRD measurements were performed in Göttingen by Volker Karius using an Orion Comet P2 Powder diffractometer (XRD Eigenmann GmbH, Schneittach-Hormersdorf, Germany) equipped with a Cu–source (Cu-Kα radiation, λ_1 = 1.54060 Å, λ_2 = 1.54443 Å) with a $K\alpha_2/K\alpha_1$ relation of 0.5 and a beam voltage and current of 40 kV and 40 mA, respectively.

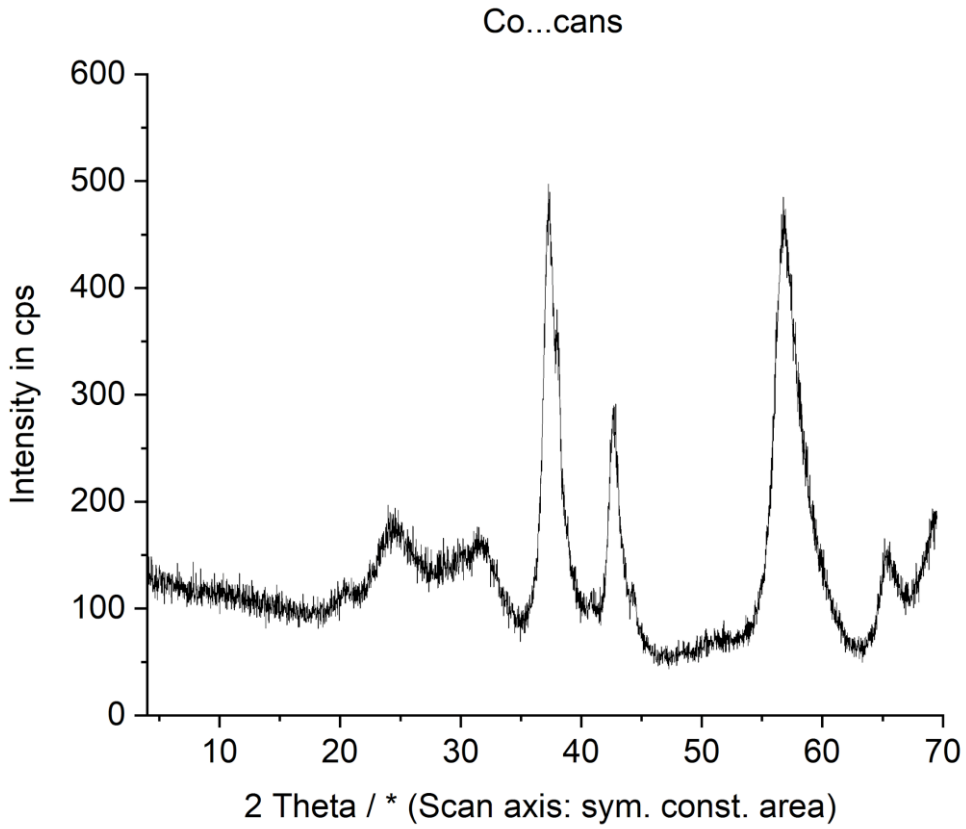

Figure S 7: X-ray diffractogram of the manganese dioxide used in this study. Measurement details are given in the text above.