

Ferric Ethylenediamine-tetraacetic Acid (FeEDTA) Photodegradation in Commercially Produced Soluble Fertilizers

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SUMMARY. Irradiation of ferric ethylenediaminetetraacetic acid (FeEDTA, iron chelate)-containing commercial fertilizer solutions by fluorescent plus incandescent lamps resulted in the loss of both FeEDTA and soluble iron (Fe), and the formation of a yellow-tan precipitate that was mostly composed of Fe. The ratio of soluble Fe:manganese (Mn) was altered due to FeEDTA photodegradation from 2:1 in the nonirradiated solutions to 1:4 in the irradiated solutions, respectively. Storing fertilizer solutions in containers that were impervious to light prevented FeEDTA photodegradation.

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The application of fertilizers is a necessary part of greenhouse and nursery plant production to maintain plant growth under optimal conditions in a container that provides a minimal root medium volume. Water-soluble fertilizers used in greenhouse and nursery operations are often prepared as a concentrated stock solution, and applied with irrigation water via inline-injection by a proportioner. Such fertilizers commonly supply Fe as a chelate with ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentacetic acid (DTPA), hydroxyethylene-diaminetriacetic acid (HEDTA) and/or ethylenediamine-di-o-hydroxy-phenylacetic acid (EDDHA); and the micronutrients Mn, zinc (Zn), and copper (Cu) as chelates with EDTA. Chelating agents through multiple coordinate bonding with the metallic ion, are capable of maintaining the metal in a soluble form in chemical environments (i.e., pH) where the metal would otherwise precipitate (Kolthoff et al., 1969; Reed, 1996). For example, EDTA has a high affinity for Fe and will form a stable complex with the metal across a pH range from 4.0 to 6.3. Iron chelated with EDTA will remain soluble within a pH range from 4.0 to 6.3 (Norvell, 1971). When these chelating agents bind Fe, however, the metal-chelate complex absorbs UV and blue radiation that causes the photodegradation of the chelating agent, rendering Fe insoluble (Albano and Miller, 2001; Frisell et al., 1959; Hamaker, 1956; Wallace et al., 1967). When complexed with Fe and exposed to UV and blue radiation, the chelating agent EDTA photodegrades into glyoxylic acid, carbon dioxide (CO_2), formaldehyde, and amine residue(s) (Frisell et al., 1959; Hamaker, 1956). The objective of this study was to document FeEDTA photodegradation in commercial fertilizer solutions.

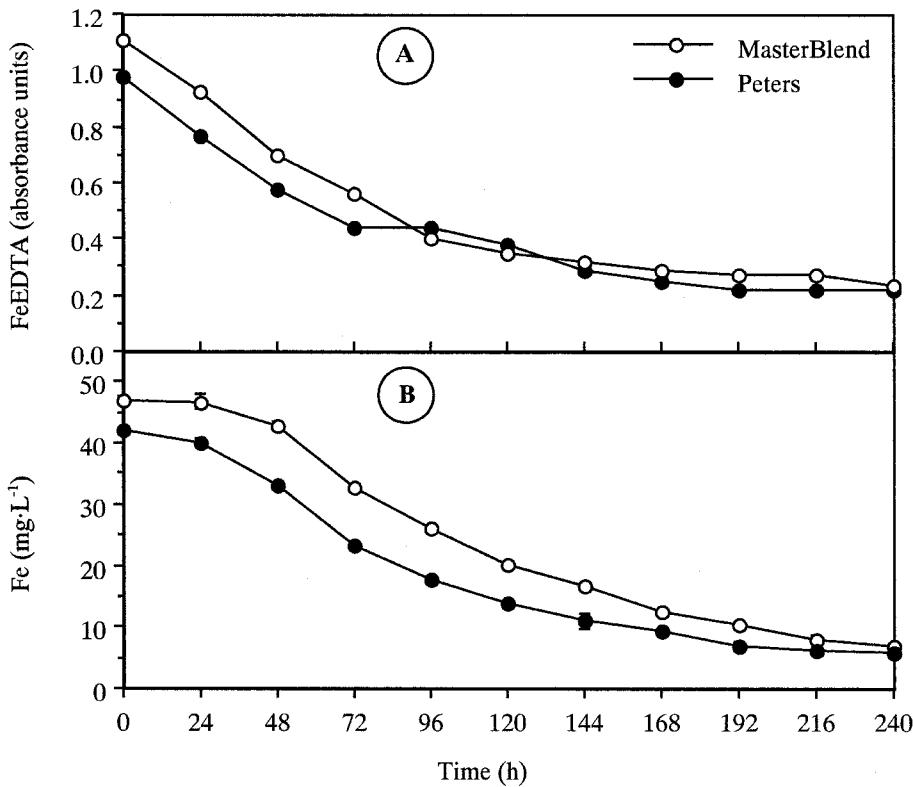


Fig. 1. Loss of the iron chelate, ferric ethylenediaminetetraacetic acid (FeEDTA) (A) and soluble iron (Fe) (B) from FeEDTA-containing Peters or Masterblend 20-10-20 (20N-4.3P-16.6K) fertilizer solutions formulated as a 100_(XtimesX) stock based on a 100 mg·L⁻¹ (100 ppm) nitrogen 1_(XtimesX) concentration. Fertilizer solutions were irradiated or nonirradiated with 500 $\mu\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ (330-800 nm) from a fluorescent plus incandescent light source for 10 d. FeEDTA was measured spectrophotometrically at 258 nm and soluble Fe was measured by atomic absorption spectrophotometry. Vertical bars indicate SE (n = 3). If none are shown, they fall within the dimensions of the plotting symbol; 1 mg·L⁻¹ = 1 ppm.

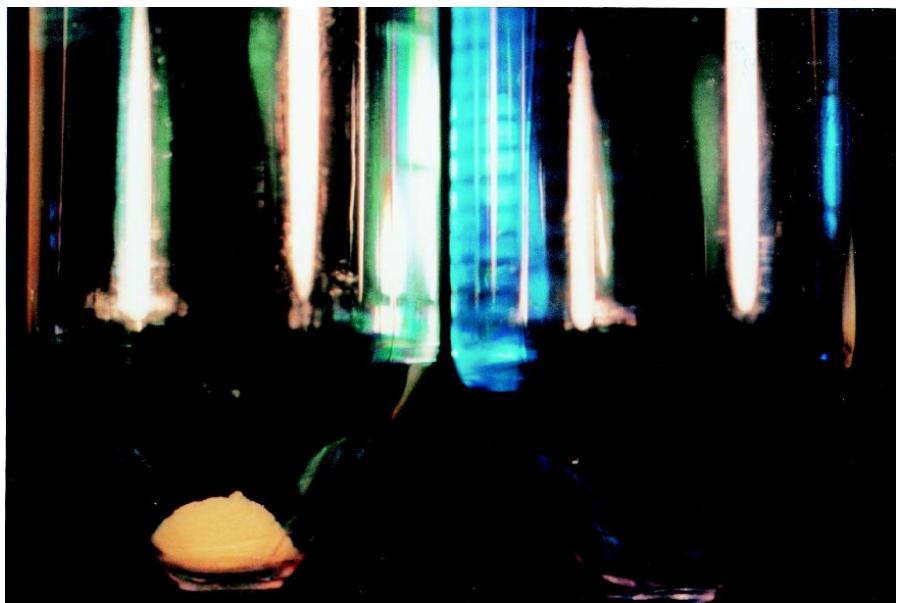


Fig. 2. Precipitate that formed when Peters or Masterblend 20-10-20 (20N-4.3P-16.6K) fertilizer solutions were irradiated (left). No precipitate formed in Peters or Masterblend fertilizer solutions that were nonirradiated (right). Fertilizer solutions were formulated as a 100_(XtimesX) stock based on a 100 mg·L⁻¹ (100 ppm) nitrogen 1_(XtimesX) concentration and were irradiated or nonirradiated with 500 μmol·m⁻²·s⁻¹ (330-800 nm) from a fluorescent plus incandescent light source for 10 d.

Material and methods

SOLUTION COMPOSITION AND PHOTODEGRADATION CONDITIONS: Peters Peat-Lite Special (The Scotts Co., Marysville, Ohio) and MasterBlend (for soilless growing media, Masterblend International, Chicago) 20N-4.3P-16.6K (20-10-20) fertilizers that contain FeEDTA were prepared as 100_(XtimesX) stock solutions based on a 1_(XtimesX) concentration of 100 mg·L⁻¹ (ppm) of nitrogen (N). The product-label information for these fertilizers indicate that a 100 mg·L⁻¹ N formulation should have an Fe concentration of 0.50 mg·L⁻¹. The actual 1_(XtimesX) Fe concentration of the Peters and Masterblend solutions were 0.43 mg·L⁻¹ and 0.48 mg·L⁻¹ Fe, respectively. Fertilizer solutions [900 mL (30.44 fl oz)] were contained in 1-L (0.264-gal) high-density polyethylene (HDPE) bottles (Nalgene Co., Rochester, N.Y.). Solutions were irradiated or nonirradiated for 10 d with 500 μmol·m⁻²·s⁻¹ (330 to 800 nm), measured at the external container surface with a spectroradiometer (LI-1800; LI-COR, Lincoln, Nebr.). Containers were placed on their side for irradiation and nonirradiated containers were covered with aluminum foil. Irradiance intensity was varied by adjusting lamp-bank distance from solution con-

tainers. The radiation source was fluorescent plus incandescent lamps. The study was conducted in a controlled environment growth chamber and solution temperature was maintained at 20 °C (72 °F) by adjusting air temperature. Three replications of each treatment were made and the study was arranged as a completely randomized design within a single growth chamber.

FERTILIZER SOLUTION ANALYSIS: At 24-h intervals, a 20 mL aliquot was drawn from each container after agitation. Samples were then centrifuged at 6,000 g_n for 20 min in a Sorvall SA-600 angle-head rotor (DuPont Instruments, Wilmington, Del.) at 22 °C (68 °F) and the supernatant was retained for analysis. The pellet derived from day-10 samples was dissolved in 20 mL of 1 N HCl. The supernatant and pellet fractions were analyzed for Fe, Mn, Cu, and Zn by atomic absorption spectrophotometry (AA). FeEDTA was monitored in supernatant fractions spectrophotometrically at 258 nm as described by Hill-Cottingham (1957). Absorbance of FeEDTA standard solutions was linear ($r^2 = 0.99$) from 0.1 to 5.0 mg·L⁻¹ (data not shown). Peters and Masterblend fertilizers supply Mn, Zn, and Cu as EDTA-chelates. Manganese

and Cu ions and chelates can be a source of interference for detecting FeEDTA spectrophotometrically at 258 nm.

STATISTICS: Data were analyzed by analysis of variance (ANOVA) to determine the effect of irradiation. Calculations were performed with the general linear model (GLM) procedure of SAS (SAS Institute, Inc., Cary, N.C.). Means were separated and planned comparisons were made using a LSD or pairwise *t* tests.

Results and discussion

FeEDTA PHOTODEGRADATION IN COMMERCIAL FERTILIZER SOLUTIONS: Irradiating Peters or Masterblend fertilizer solutions with 500 μmol·m⁻²·s⁻¹ (330 to 800 nm) from a fluorescent plus incandescent light source for 10 d, resulted in the loss of FeEDTA (Fig. 1A), the loss of soluble Fe (Fig. 1B), and the formation of a yellow-tan colored precipitate (Fig. 2). Solutions that were nonirradiated did not lose FeEDTA or soluble Fe (data not shown), and no precipitate formed (Fig. 2). These data are in agreement with what was observed to occur when FeDTPA- or FeEDTA-containing lab-prepared nutrient solutions were irradiated under similar light and solution temperature conditions (Albano and Miller, 2001).

As an average of both fertilizers, Fe (88% of total), Mn (12% of total), and Zn (12% of total) were lost following irradiation of the fertilizer solutions. The loss of soluble Fe in the irradiated solutions altered the ratio of soluble Fe:Mn from 2:1 in the nonirradiated solutions to 1:4 in the irradiated solutions (Table 1). In a previous study (Albano and Miller, 2001), similar changes in the Fe:Mn ratio were observed in irradiated nutrient solutions containing FeDTPA. Analysis of the yellow-tan precipitate (Fig. 2) that developed in both fertilizers upon irradiation revealed that it was primarily composed of Fe, accounting for over 80% of the soluble Fe lost due to irradiation, and smaller amounts of Mn and Zn (Table 1).

In conclusion, we have demonstrated that FeEDTA incorporated into commercially-produced water-soluble fertilizers is vulnerable to photodegradation, and that such an occurrence will alter the ratio of soluble micronutrients from that intended by the manufacturer. Growers can easily prevent Fe-chelate photodegradation

Table 1. Iron, manganese, zinc, and copper concentration of supernatant and pellet fractions derived from non-irradiated (NIr) and irradiated (Ir) Peters and Masterblend 20-10-20 (20N-4.3P-16.6K) fertilizer solutions. Fertilizer solutions were formulated as a 100_(XtimesX) stock based on a 100 mg·L⁻¹ (ppm) nitrogen 1_(XtimesX) concentration and were irradiated or nonirradiated with 500 µmol·m⁻²·s⁻¹ (330 to 800 nm) from a fluorescent plus incandescent light source for 10 d.

Element	NIr ^z (mg·L ⁻¹) ^y	Ir (mg·L ⁻¹)	Loss due to irradiation (mg·L ⁻¹)	Loss due to irradiation (%)	Ir-Pellet ^v (mg·L ⁻¹)	Recovered in pellet (%)
Peters						
Iron	43.6 ± 0.6 ^x	04.7 ± 0.2	38.9	89.2	32.0 ± 2.70	82.3
Manganese	20.0 ± 0.0	18.0 ± 0.0	2.0	10.0	2.0 ± 0.0	100.00
Zinc	06.0 ± 0.0	05.3 ± 0.1	0.7	11.6	0.7 ± 0.1	100.00
Copper	03.7 ± 0.1	03.7 ± 0.2	0.0	0.0	0.0	0.0
Fe:Mn ratio	2:1 ^w	1:4	---	---	16:1	---
MasterBlend						
Iron	48.7 ± 0.6	6.7 ± 0.6	42.0	86.2	34.3 ± 4.10	81.7
Manganese	20.0 ± 0.0	17.3 ± 1.6	2.7	13.5	1.7 ± 0.6	63.0
Zinc	6.0 ± 0.0	5.3 ± 0.6	0.7	11.7	0.3 ± 0.1	42.9
Copper	7.7 ± 0.6	8.0 ± 0.0	0.0	0.0	0.0	0.0
Fe:Mn ratio	2:1	1:3	---	---	20:1	---

^zNo precipitate formed in the nonirradiated solution.

^y1 mg·L⁻¹ = 1 ppm.

^xValues are means ± se (n = 3).

^wIron (Fe) and manganese (Mn) values for ratios are rounded off to one significant digit.

^vThe pellet derived from the irradiated solution was resolubilized in 1 N HCl before analysis, therefore data are reported as concentration.

by ensuring that the fertilizer stock tank is impervious to light. Regardless of any influence that Fe-chelate photodegradation has on plant growth and physiology, economics demand that the grower be aware of this phenomenon and minimize its occurrence because, relative to the other fertilizer chemicals, chelates are an expensive component of the product.

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