# Uptake of 3,3′,4,4′-Tetrachloroazobenzene (TCAB) Soil Residues by Rice (*Oryza sativa* L.)[†]

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Bioavailability of soil residues of 3,3′,4,4′-tetrachloroazobenzene (TCAB) to rice (*Oryza sativa* L.) was examined using [$^{14}$C]TCAB. Rice plants were grown on soil treated with TCAB after aging for 0, 3, and 6 months. The $^{14}CO_2$ evolved during the 3- and 6-month aging periods was only 0.04 and 0.13%, respectively, of the applied [$^{14}$C]TCAB. Mineralization of [$^{14}$C]TCAB to $^{14}CO_2$ during the 42-d growth period of rice plants ranged from 0.04 to 0.07%, without differences among treatments ($p < 0.05$). The range of concentrations of TCAB detected in shoots and roots of rice plants at harvest ranged from 0.07 to 0.08 and from 2.60 to 2.67 mg/kg, respectively. Presence of growing plants accelerated conversion of TCAB to bound residues, especially in the humin and humic acid fractions.

**Keywords:** *3,3′,4,4′-Tetrachloroazobenzene; aged residues; mineralization; bioavailability to rice*

## INTRODUCTION

3,3′,4,4′-Tetrachloroazobenzene (TCAB) is a contaminant formed both from the manufacturing processes of 3,4-dichloroaniline (3,4-DCA) and its derivative herbicides and from the degradation of these herbicides belonging to the classes of phenylcarbamates, phenylureas, and acylanilides in the environment. Propanil (3′,4′-dichloropropionanilide), which represents acylanilides, has been used in rice paddy fields against weeds including barnyard grass (*Echinochloa crus-galli*) in Korea. Linuron [3-(3,4-dichlorophenyl)-1-methoxy-1-methylurea], belonging to the phenylurea herbicide, has also been in wide use for weed control in most crops including maize, potato, garlic, barley, onion, soybean, and carrot. TCAB, structurally and toxicologically similar to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), produces chloracne among chemical workers handling 3,4-DCA-derived herbicides (Hill et al., 1981; Poland et al., 1976), and it is a potent inducer of aryl hydrocarbon hydroxylase (Poland et al., 1976). In addition, TCAB is mutagenic (Hsia et al., 1977; Gilbert et al., 1980; Prasad, 1970), potentially carcinogenic, and quite toxic to mammalian cells, all of which may be correlated with observable cytological changes (Hsia et al., 1977).

TCAB shows strong porphyrinogenic potential in chick embryo liver cell cultures, over the same exposure concentration range as TCDD (Mensink and Strik, 1982). Moreover, TCAB causes thymic atrophy in rats (Hsia et al., 1982). Carey et al. (1980) detected TCAB in the range of 0.01–0.05 ppm in soil samples collected from rice-growing areas in the United States. TCAB is absorbed from soil by plant roots and translocated into shoots and grains, suggesting the possibility of the eventual consumption by animals, including human beings (Still, 1969).

Viswanathan et al. (1978) identified TCAB in all parts including grain (<0.005 µg/g) of barley (*Hordeum vulgare* L.) plants grown in soil treated with 3,4-DCA. Worobey (1984) grew soybean (*Glycine soja* L.) in soil

treated with TCAB and showed translocation of the azo compound into plant shoots via roots. Only 0.05–0.20% of the original radioactivity of [$^{14}$C]TCAB incubated in French soils was evolved as $^{14}CO_2$ during 3 months (Lee and Fournier, 1978), and only 0.41% was evolved as $^{14}CO_2$ in a Korean soil during 15 months (Lee and Kyung, 1991). Most of the chemical remained intact. Bound residues increased gradually with aging, especially those portions incorporated in the humin and humic acid fractions (Lee and Kyung, 1991).

The present investigation was aimed at elucidating the bioavailability of fresh and aged residues of TCAB in soil to rice plants and at seeking possible biodegradation and biorelease in the presence of the rhizosphere in relation to the former because this azo compound is extremely stable in our environment (Lee and Fournier, 1978; Lee and Kyung, 1991).

## MATERIALS AND METHODS

**Synthesis and Purification of [$^{14}$C]TCAB.** Before the synthesis of [$^{14}$C]TCAB, impurities in the [$^{14}$C]-3,4-DCA (Figure 1A; Amersham, Arlington Heights, IL); specific activity, 226.44 MBq/mM) were removed using an $Al_2O_3$-packed column activated at 110 °C for 3 h and a mixture of *n*-hexane—benzene (1:1 v/v) as the eluent at a rate of 0.5 mL/min.

[$^{14}$C]TCAB was synthesized by the method of Lee et al. (1977). The purified [$^{14}$C]-3,4-DCA (13.6 mg) was put into a Pyrex test tube and 20 mg of CuCl and 1 mL of pyridine were added to it. The mixture was then reacted at 60 °C in a water bath for 10 h under a constant stream of air. When the reaction was complete, residual pyridine was evaporated to dryness. The dry reaction mixture was dissolved in a small volume of *n*-hexane—benzene (7:3 v/v) and passed through a silicic acid column using the same solvent as the eluent. The purity of the synthesized [$^{14}$C]TCAB (Figure 1B; specific activity, 193.23 MBq/mM) was confirmed by autoradiography and cochromatography (Figure 2A).

**Thin-Layer Chromatography (TLC) and Autoradiography.** Thin-layer chromatography (TLC) followed by autoradiography using Fuji Medical X-ray film (Fuji Photo Film Co., Ltd, Japan) was used for elucidation of degradation products of TCAB. TLC was performed using precoated aluminum plates and developed using the *n*-hexane—benzene (7:3 v/v) mixture and/or the benzene—dichloromethane (1:1 v/v) mixture. The spots were visualized under a UV lamp (254 nm; Mineral Light Model UV GL-58).

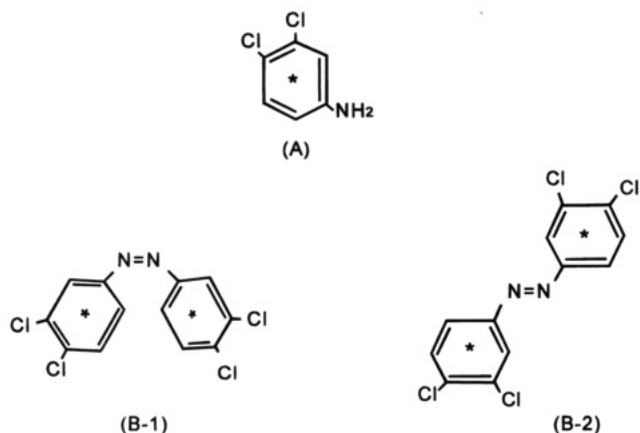* Author to whom correspondence should be addressed [fax (0431)69-2549].

**Figure 1.** Structural formulas and labeled positions (*) of 3,4-dichloroaniline (DCA; A) and 3,3′,4,4′-tetrachloroazobenzene (TCAB; B-1, cis isomer, and B-2, trans isomer).
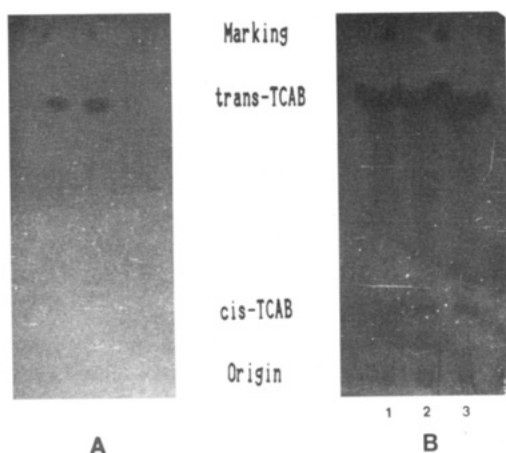


**Figure 2.** Autoradiograms of [$^{14}$C]TCAB purified (A) and extracts of soils which were treated with [$^{14}$C]TCAB (B). B: (1) freshly treated and 42-day rice planting, (2) 3-month aging prior to 42-day rice planting, and (3) 6-month aging prior to 42-day rice planting. Developing solvent: n-hexane−benzene (7:3 v/v).

**Preparation and Aging of Soil**. Soil was collected from a rice paddy, air-dried, and passed through a 2-mm sieve. Soil characteristics are as follows: pH (KCl, 1:5), 5.1; organic matter, 1.8%; cation exchange capacity, 96 mmol(+)/kg of soil; sand, 38.1%; silt, 37.6%; clay, 24.3%; texture, loam. Soil was treated with a mixture of $^{14}$C-labeled and nonlabeled TCAB. To ensure homogeneity, TCAB dissolved in benzene was added dropwise to about 200 g of soil and benzene was allowed to evaporate under a weak stream of N$_2$. After benzene was removed, the soil was combined with the remaining soil (about 6.3 kg) and mixed in a ballmill. Treated soil was then aged at 21 ± 1 °C for 3 and 6 months.

The radioactivities of [$^{14}$C]TCAB added to the soil (6.5 kg, on a dry weight basis) for aging for 3 and 6 months were 785.9 and 749.3 kBq, respectively, at a total TCAB concentration of 5 mg/kg of soil in each treatment. During aging, moisture was replenished weekly and kept at 50% of the maximum water-holding capacity of the soil. The $^{14}$CO$_2$ evolved during aging was absorbed in 1 N NaOH and measured every other week. At the completion of the aging, the soil was air-dried and the $^{14}$C radioactivity was measured on a subsample with a liquid scintillation counter (Philips PW 4700 LSC) following combustion with a biological oxidizer (R. J. Harvey Instrument Corp., NJ).

**Cultivation and Sampling of Rice Plant**. The soil samples containing TCAB residues were put into stainless steel pots (17 cm i.d. × 10 cm height) into which 45-day-old rice seedlings (Oryza sativa cv. Akibare, Japan) were transplanted. The root portion was separated from the aerial portions of the plant by seals of poly(vinyl acetate) for a root

chamber aerated with CO$_2$-free air. $^{14}$CO$_2$ from TCAB mineralization and CO$_2$ from root and soil respiration were absorbed in 1 N NaOH. In each pot eight seedlings were grown with 2 seedlings/hill.

Soil moisture lost by transpiration of rice plants was replenished daily. During the growing period, the moisture content was kept at about 60% of the maximum water-holding capacity of the soil. Rice plants were then grown for 42 days.

At harvest, shoots were separated from roots. Roots were collected and rinsed with tap water to remove soil. Immediately after obtaining fresh weights, shoots and roots were freeze-dried and pulverized, and dry weights were determined. Soil was air-dried, and a portion was ground in a mortar and mixed before combustion for radioactivity measurement.

**Extraction and Analysis of Soil and Plant Samples**. Twenty grams of air-dried soil (dry weight basis) was shaken with 50 mL of acetone for 4 h and then centrifuged at 27000g for 10 min to collect the supernatant. After three repetitions with acetone, benzene extraction was continued until the radioactivity of the extract was not greater than the background level.

Five grams of the soil samples was extracted again with 5 mL of 0.1 M sodium pyrophosphate. Insoluble material, humin, was separated by centrifugation at 16000g for 10 min. The humic acid fraction was flocculated by acidification of the supernatant with concentrated HCl. The fulvic acid fraction remained in solution and was separated from humic acid by centrifugation. The humic acid precipitate was redissolved in 1 N NaOH. Radioactivity was measured using Aquasol (DuPont, NEN Research Products) as the cocktail. Radioactivity in the humin fraction was measured as $^{14}$CO$_2$ following combustion.

To compare the extraction efficiency of benzene, acetone, and BF$_3$·methanol complex (about 14% BF$_3$ in methanol, w/w), root samples (about 1 g) which had been freeze-dried and pulverized were extracted with 10 mL of each solvent for 2 h in an ultrasonicator. The mixture was then centrifuged at 10000g for 15 min. This procedure was repeated until radioactivity of the extracts was diminished to the background level. Supernatants from each solvent were combined and concentrated for analysis; three replicate extractions were performed for each solvent.

**Partitioning Radioactivity of Soil Extracts between Aqueous Phase and Organic Phase**. Soil extracts which had been combined and concentrated to dryness were dissolved in 15 mL of acetone, and 5 mL was evaporated to dryness with a stream of air. Residue was dissolved in 5 mL of benzene, 5 mL of distilled water was added, and the tube was shaken vigorously and allowed to stand. After phase separation, the benzene phase was dehydrated over anhydrous Na$_2$SO$_4$, and 2 mL of each phase was taken separately into scintillation vials. Benzene was evaporated before adding the toluene cocktail. Aquasol was added to the aqueous phase for radioactivity measurements. Radioactivity was counted for 10 min and corrected for background and quenching.

## RESULTS AND DISCUSSION

**Stability of [$^{14}$C]TCAB in Soil**. Mineralization of [$^{14}$C]TCAB to $^{14}$CO$_2$ during the aging periods of 3 and 6 months accounts for 0.04 and 0.13% of the applied radioactivity, respectively. Thus, TCAB is extremely stable, chemically and microbiologically. This confirms the report of Lee and Fournier (1978) that [$^{14}$C]TCAB incubated for 6 months in French soils with different pH's and organic matter contents evolved only 0.05−0.20% as $^{14}$CO$_2$; more than 93% was recovered intact in all soils. Amounts of $^{14}$CO$_2$ evolved during growth of rice plants are unaffected by the rhizosphere of rice plants (Table 1). In fact, it is known that various kinds of sugars, amino acids, and organic acids are accumulated in the rhizosphere of rice plants (Kimura et al., 1977). Miskovic et al. (1977) reported that a higher activity of dehydrogenase was observed in the rhizosphere of corn than in root-free soil. In general, the

**Table 1. Fate of [$^{14}$C]TCAB Residues in Soil after Growing Rice Plants for 42 Days**

| treatment | at planting (kBq) | $^{14}CO_2$ (%) | roots (%) | shoots (%) | soil (%) | recovery (%) |
|---|---|---|---|---|---|---|
| | | | | radioactivity from TCAB | | |
| freshly treated | 187.4 | 0.06 | 0.72 (2.60)[a] | 0.02 (0.08)[a] | 97.90 | 98.70 |
| 3-month aged | 179.3 | 0.04 | 0.92 (2.67)[a] | 0.02 (0.08)[a] | 98.00 | 98.98 |
| 6-month aged | 176.1 | 0.07 | 0.97 (2.62)[a] | 0.02 (0.07)[a] | 96.80 | 97.86 |

[a] Amounts of TCAB (mg/kg) in parentheses are calculated on the basis of specific $^{14}$C activity of the TCAB applied.

rhizosphere is a zone of intense microbiological activity due to its higher concentration of carbohydrates, amino acids, vitamins, and other growth-promoting substances (Nicholas et al., 1965).

As an additional proof for the stability of TCAB, TLC of the postharvest soil extract of each treatment obtained by successive acetone—benzene extraction shows that most of the TCAB remained as the trans isomer (Figure 2B). Similar trace amounts of the cis isomer were formed in all treatments. Earlier, Lee et al. (1977) encountered occurrence of the cis—trans isomerism during [$^{14}$C]TCAB synthesis. The chromatographic results suggest that, except for the change in geometrical isomerism, TCAB remains intact for months in soil.

**Absorption and Translocation of [$^{14}$C]TCAB by Rice Plants.** No difference in absorption and translocation of $^{14}$C activity was found among treatments (Table 1), that is, bioavailability of TCAB residues in soil to rice plants was unaffected by aging. Usually, when pesticides with polar functional groups are aged in soil, their bioavailability to plants decreases considerably (Lee et al., 1988, 1989, 1991). The extremely nonpolar characteristics of TCAB are directly related to this different result. Very little translocation of $^{14}$C activity was observed. The amounts of $^{14}$C from labeled TCAB absorbed by rice plants, calculated as TCAB equivalents, ranged from 2.60 to 2.67 mg/kg of dry roots. The amounts found in shoots ranged from 0.07 to 0.08 mg/kg.

Worobey (1984) reported that TCAB residue levels in plants varied with the organic matter content of soil where crops were grown; levels as high as 58.4 ppm were detected in roots of soybean grown in 1.7% organic matter soil and 0.62 ppm in shoots from 0% organic matter soil after 12 days of exposure. Only 5.6% of the total TCAB present in nutrient solution was absorbed by intact rice plants, and only 3.2% of the absorbed TCAB was translocated to the shoots after 12 days of exposure (Still, 1969).

In general, plants grown in small pots have a tendency to take up greater amounts of chemical residues than those grown in lysimeters and/or fields under the same physical and physiological conditions. For example, Führ and Mittelstaedt (1982) reported that sugar beets grown in a microecosystem (0.9 kg of soil/pot) absorbed 50 times more [*ethylene*-$^{14}C_2$]isocarbamide treated in soil than in a lysimeter (0.76 m$^2$). Furthermore, Lee et al. (1991) found greater levels of chemical residue were detected in rice straw than in hulled grains. When rice plants were grown on soils treated once in the first year with the herbicide [$^{14}$C]bentazon (log $K_{ow}$: −0.46) and the systemic insecticide [$^{14}$C]-carbofuran (log $K_{ow}$: 1.23−1.42), respectively, in lysi-

meters, the straw contained 86 and 26 times more bentazon and 95 and 22 times more carbofuran than hulled grains in the first and second year of harvest, respectively, on a concentration (ppm) basis. Detection of large amounts of TCAB and/or its metabolites in rice hulled grains is unlikely. By comparing TCAB with these chemicals in terms of the *n*-octanol—water partition coefficient, log $K_{ow}$ of TCAB was calculated as about 4.71 on the basis of the solubility of TCAB in water (3.13 × 10$^{-1}$ ppm; Still, 1969). On the basis of these results, it is quite reasonable to believe that the small uptake and translocation of TCAB by rice plants are correlated with its rather large log $K_{ow}$ value.

**Fate of [$^{14}$C]TCAB Residues in Soil with Rice Cultivation.** Table 1 presents the fate of the [$^{14}$C]-TCAB residues in soil 42 days after transplanting of rice, expressed as the percentage of [$^{14}$C]TCAB radioactivity applied originally to the soil. Most of the $^{14}$C radioactivity from TCAB (96.8−98.0%) remained in the soil as extractable and nonextractable bound residues. Mineralization to $^{14}CO_2$ during that period ranged only from 0.04 to 0.07%, suggesting no effect of the rhizosphere and aging.

In Table 2, the partitioning between aqueous phase and organic phase of the extractable residues of [$^{14}$C]-TCAB from the soils of various treatments indicates the chemical structure of TCAB was unchanged either by aging or in response to rice plant growth. In fact, it was expected that dechlorination of any chlorine atoms in the molecular structure, followed by hydroxylation and further oxidation, would increase its polarity. The only change, however, could be the isomerization of the usual *trans*-TCAB into its geometrical isomer *cis*-TCAB which is more polar than the former (Lee and Fournier, 1978), even if it was not partitioned to the aqueous phase (Figure 1, B-1 and B-2).

Although changes in uptake and metabolism of TCAB by plants were largely unaffected, changes in bound residues of [$^{14}$C]TCAB in soil depend on the extent of aging and the presence of rice plants, as shown in Table 2. The amount of bound residues increased with growth of rice from 1.4 to 19.5% in the freshly treated pots. This result could originate both from the aging (the 42-day growing period) and from the presence of rice plant roots. Nevertheless, considering changes from 8.9 (3-month aged) to 21.5% (3-month aged + 42-day planting) and from 15.9 (6-month aged) to 21.9% (6-month aged + 42-day planting), and the comparison of bound residues of freshly treated, 3-month aged and 6-month aged treatments, it is clear that the rhizosphere of rice plants greatly enhanced formation of bound residues of TCAB in soil, presumably due to exudates from roots (Curl and Truelove, 1986).

Most of the nonextractable bound residues of [$^{14}$C]-TCAB in soil were incorporated into the humin fraction (about 59−77%). On the basis of this result, it is clear that as the aging period increases, less $^{14}$C radioactivity is incorporated into the fulvic acid fraction. In addition, $^{14}$C radioactivities incorporated into the fulvic acid fraction decreased remarkably after rice was grown for 42 days, especially showing a noticeable decrease from 21.8 (freshly treated) to 3.7% (freshly treated + 42-day planting). The $^{14}$C radioactivities in the humic acid fraction, however, increased during the same period.

Meanwhile, in view of the extractability of a few solvents, even if TCAB is readily soluble in benzene and acetone, the extraction efficiency of these solvents for [$^{14}$C]TCAB residues incorporated into root tissues are

**Table 2.  Characteristics of [¹⁴C]TCAB Residues in Soil As Affected by Residue Age and the Presence/Absence of Growing Rice Plants**

| treatment | extractable[a] (%) | partitioning of extractable residues (%) between | | distribution of bound residues[b] (%) | | | |
|---|---|---|---|---|---|---|---|
| | | aqueous phase | organic phase | total bound | fulvic acid | humic acid | humin |
| freshly treated | 98.02 | 0.01 | 98.01 | 1.42 | 0.31 (21.84)A | 0.27 (19.01)A | 0.84 (59.15)A |
| 3-month aged | 91.78 | 0.01 | 91.77 | 8.93 | 1.70 (19.04)B | 1.20 (13.43)B | 6.03 (67.53)B |
| 6-month aged | 86.81 | 0.01 | 86.80 | 15.88 | 0.62 (3.91)C | 3.01 (18.95)A | 12.25 (77.14)C |
| freshly treated + 42-day planting | 77.70 | 0.05 | 77.65 | 19.50 | 0.73 (3.74) | 5.07 (26.00) | 13.70 (70.26) |
| 3-month aged + 42-day planting | 75.32 | 0.02 | 75.30 | 21.50 | 0.59 (2.74) | 5.48 (25.49) | 15.43 (71.77) |
| 6-month aged + 42-day planting | 74.68 | 0.01 | 74.68 | 21.91 | 0.71 (3.25) | 6.78 (30.94) | 14.42 (65.81) |

[a] Aqueous phase + organic phase = percent extractable. [b] Fulvic acid + humic acid + humin = percent total bound; in parentheses, fulvic acid + humic acid + humin = 100%.  Numbers followed by the same letter within a column are not significantly different at the 5% levels using Duncan's multiple range test.

**Table 3.  Extraction Efficiency of Various Organic Solvents for [¹⁴C]TCAB Residues Present in the Roots of Rice Plants**

| sample | radioactivity extracted[a] (%) | | |
|---|---|---|---|
| | benzene | acetone | BF₃·methanol[b] |
| freshly treated + 42-day planting | 59.7 ± 2.4 | 75.2 ± 2.0 | 88.7 ± 1.1 |
| 3-month aged + 42-day planting | 62.2 ± 0.9 | 78.9 ± 1.0 | 93.7 ± 0.1 |
| 6-month aged + 42-day planting | 59.8 ± 1.3 | 75.9 ± 1.9 | 89.5 ± 0.5 |

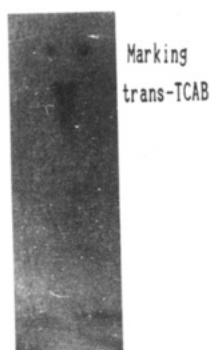[a] Mean of three replications ± standard deviation. [b] About 14% BF₃ (w/w).



**Figure 3.** Autoradiogram of the root extract of rice plants grown in soil treated with [¹⁴C]TCAB. Extracting solvent: boron trifluoride·methanol complex (about 14% BF₃). Developing solvent: benzene–dichloromethane (1:1 v/v).

in the range of 61 and 77%, respectively, of sample radioactivity (Table 3).  However, BF₃·methanol extracted about 91% of the radioactivity.  This solvent has a methylating action on carboxyl groups and is also a strong acid (Worobey, 1984).  Its extraction efficiency is believed to be due to the latter property.  None of the above extracts, however, produced metabolite(s) detectable by autoradiography from the intact [¹⁴C]TCAB (Figure 3).  Results from other solvents are not shown because BF₃·methanol showed far better extraction efficiency.

## CONCLUSIONS

Rice is one of the major crops in Asia, and some herbicides connected directly or indirectly with TCAB are still in wide use.  Hence, the environmental safety of that chemical is extremely important from the viewpoint of public health.  Levels of TCAB detected in shoots of rice plants ranged from 0.06 to 0.09 mg/kg.  Considering the fact that, in general, more chemical residues are absorbed by crops grown in a small pot than in a lysimeter and/or open fields (Führ and Mittelstaedt, 1982), and that hulled rice grains contain much less residue of pesticides absorbed from soil than the straw (Lee et al., 1991), the levels of TCAB residues to be detected in edible rice grains would be negligible and far less than the maximum residue limits (MRL), even if they are not set up for crops, since TCAB in itself is not a pesticide.  Furthermore, aging and the presence of growing plants accelerated conversion of TCAB to a bound form in humin and humic acid fractions, which becomes more difficult for plants to access.

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