Determination of Redox Behavior in Vitro of Nitrodiphenyl Ether Herbicides Using Cyclic Voltammetry

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Redox behavior of nitrodiphenyl ether (nitroDPE) herbicides was examined by using cyclic voltammetry. The following nitroDPEs were analyzed: acifluorfen, sodium 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoate; acifluorfen-methyl (AFM), methyl 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoate; bifenox, methyl 5-(2,4-dichlorophenoxy)-2-nitrobenzoate; nitrofen, 2,4-dichlorophenyl *p*-nitrophenyl ether; nitrofluorfen, 2-chloro-1-(4-nitrophenoxy)-4-(trifluoromethyl)benzene; oxyfluorfen, 2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl)benzene; MC-7783, potassium 5-(2,4-dichlorophenoxy)-2-nitrobenzoate; MC-10982, ethyl 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoate. Voltammograms of nitroDPEs in protic media were indicative of an electrochemically irreversible electrode reaction. In the absence of protons, the electrode reaction of nonpolar nitroDPEs was characteristic of a quasi-reversible electron transfer process. Redox chemistry of polar nitroDPEs in aprotic solvent was more complex.

NitroDPE herbicides with an ortho substituent on one of the benzene rings induce injury only in foliar tissue that has been exposed to light following herbicide application (Matsunaka, 1969a,b; Yih and Swithenbank, 1975; Fadayomi and Warren, 1976; Vanstone and Stobbe, 1979). Orr and Hess (1981) studied the structure–activity relationships of eight nitroDPEs in excised cucumber (*Cucumis sativus* L.) cotyledons. The following decreasing order of relative activities was observed: AFM > MC-10982 > bifenox > oxyfluorfen. Nitrofen, nitrofluorfen, acifluorfen, and MC-7783 had no herbicidal effect. The reason for inactivity was not determined. However, since all compounds show herbicidal properties in the proper formulation (Bahr, 1978), inactivity may have been due to lack of penetration.

It has been proposed that nitroDPEs exert their herbicidal effect through various toxic products (e.g., free radicals) formed following photoactivation (Fadayomi and Warren, 1976; Pritchard et al., 1980; Orr and Hess, 1982a,b). Orr and Hess (1982b) suggested that the relative activity differences of nitroDPEs may be related to the effect various chemical substituents have on the molecules' ability to readily form highly reactive free radicals (i.e., the nitroDPE radical anion). Hence, we decided it was important to examine the redox behavior of these compounds. The experiments reported here were conducted to study the voltammetric properties of several permutations of chemical design built around the nitroDPE moiety.

MATERIALS AND METHODS

Chemicals and Solvents. Electrochemical measurements made in aqueous protolytic solvent included 50% (v/v) ethanol (ETOH) buffered at pH 7.0 with 0.1 M potassium phosphate (KH_2PO_4/K_2HPO_4) buffer (KPO₄). Reagents were used without further purification. Measurements made in an aprotic environment used tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte at 0.1 M in dimethylformamide (DMF). TBAPF₆ was prepared by metathesis of NH₄PF₆ and *n*-Bu₄NI in aqueous solution followed by two recrystallizations from ETOH and finally vacuum-dried. DMF ("Distilled in Glass" grade, Burdick and Jackson, Muskegan, MI) was used without further purification. Care

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should be exercised when handling DMF.

Cyclic Voltammetry. Electrochemical measurements were made using a Princeton Applied Research (PARC) Model 173 potentiostat/galvanostat coupled to a PARC Model 175 universal programmer (Elliott et al., 1981). Voltammograms [i.e., current–voltage (*i–E*) diagrams] were recorded on a Houston Omnigraph 2000 X-Y recorder. A three-electrode, glass electrochemical cell was used with a stationary, glassy carbon (Atomergic Chemetals Corp., Plainview, NY) working (area = 7 mm²), a platinum wire auxiliary, and a saturated calomel (SCE) reference electrode. All potentials are reported as *E* (V) vs. SCE. Solutions in the electrochemical cell were deaerated with purified nitrogen. Measurements were made in unstirred solutions at room temperature. All solutions were freshly prepared prior to each experiment. End point potentials were typically 0.5 and –1.3 to –2.0 V. Scans were initiated at 0.5 V in the negative direction. Scan rate was 100 mV/s. For aqueous solutions electrochemical breakdown of the solvent/supporting electrolyte occurred starting at –1.5 V. This phenomenon was not observed for the aprotic solvent system within the potential range used for the experiments reported here.
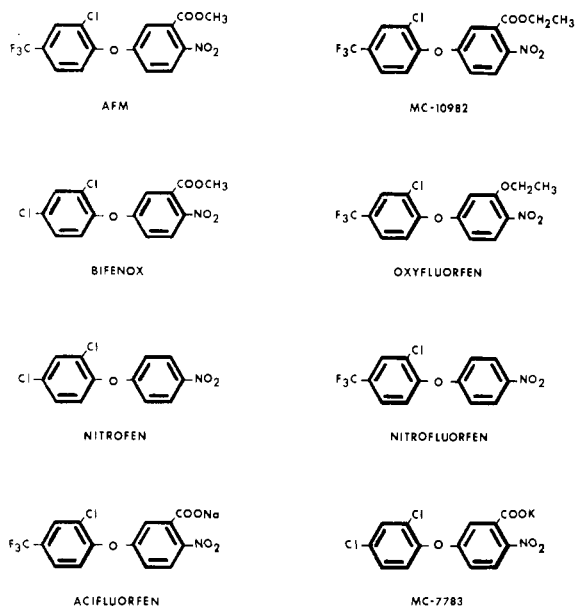
Herbicides. NitroDPE compounds were gifts from the Rhône-Poulenc Chemical Co., Monmouth Junction, NJ. The chemical coded name for MC-7783 now designated by the manufacturer is LS 83.5002.

RESULTS AND DISCUSSION

The redox states of eight different nitroDPE herbicides were examined. The chemical structures of these compounds are shown in Figure 1. All compounds have in common a chlorine atom and nitro group at the 2- and 4′-position, respectively. They differ with respect to the presence or absence of an R group at the 3′-position and the nature of that R group when present. These analogues also made it possible to study the electrochemical effect of replacing the chlorine atom at the 4-position with a trifluoromethyl group. The voltammetric properties of each nitroDPE were examined in both protolytic and aprotic solvent.

The cyclic voltammograms of all eight nitroDPEs in 0.1 M KPO₄ (pH 7.0)/50% (v/v) ETOH are presented in Figure 2. The voltammograms were obtained by measuring the current *i* at the working electrode as a function of the potential *E* (V) vs. SCE. A scan of the potential was initiated at 0.5 V in the negative direction at 100 mV/s. The overall shape of each of these curves is similar. One

Redox Behavior of Nitrodiphenyl Ether Herbicides

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Figure 1. Chemical structures of nitroDPE compounds. Below each structure is the common name, abbreviated name, or coded chemical name originally designated by the manufacturer (Rhône-Poulenc Chemical Co).
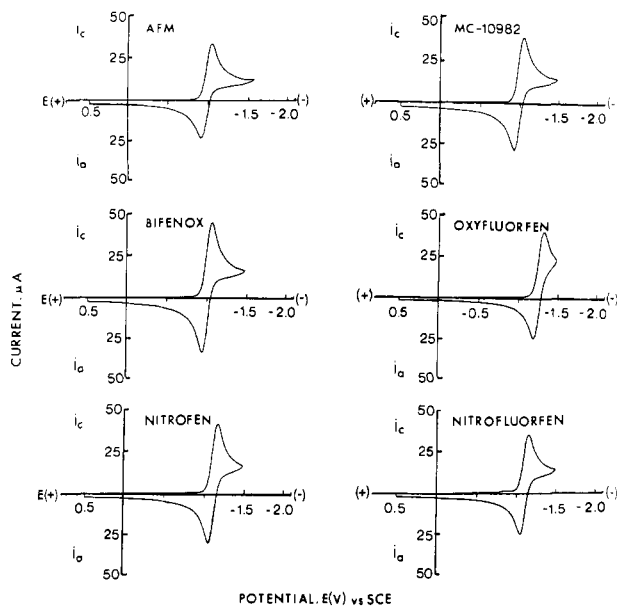

POTENTIAL, E(V) vs SCE
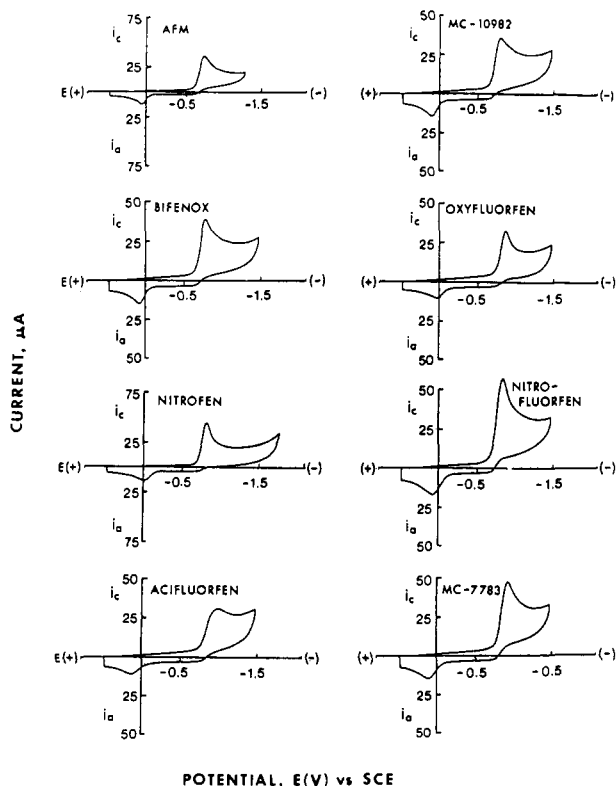
Figure 2. Cyclic voltammograms of 1 mM nitroDPE compounds in 0.1 M KPO₄ (pH 7.0)/50% (v/v) ETOH. Scans were initiated at 0.5 V in the negative direction at 100 mV/s.

cathodic peak was observed during the initial forward scan and a smaller, single anodic peak was seen during the reverse scan. These voltammograms are indicative of an electrochemically irreversible electrode reaction (Bard and Faulkner, 1980). Cathodic E_{pc} and anodic E_{pa} peak potentials range from −0.75 to −1.0 V and from −0.01 to −0.15 V, respectively. The large separations between anodic and cathodic processes (peak potential separations $\Delta E_p = E_{pa} - E_{pc} \cong 0.8$ V) and the differences in the magnitudes of the cathodic i_{pc} and anodic i_{pa} peak currents ($i_{pc}/i_{pa} \gg 1$) are clear indications of the chemical instability of the initial

Potential, E(V) vs SCE
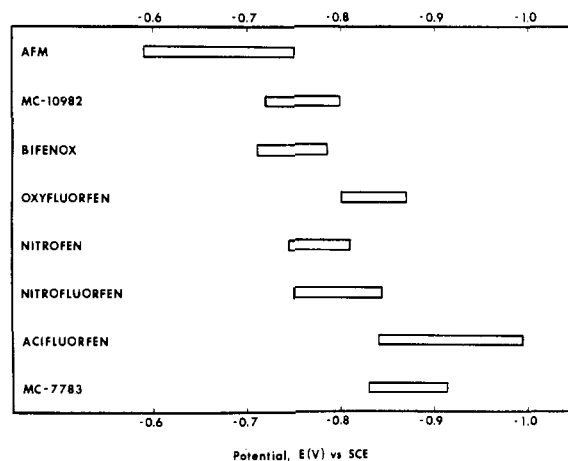
Figure 3. Voltammetric properties of nitroDPE compounds obtained from Figure 2 presented in a Kissinger Chart (Miner et al., 1981). See the text for methods used to display this voltammetric information.

POTENTIAL, E(V) vs SCE

Figure 4. Cyclic voltammograms of 2 mM nonpolar nitroDPE compounds in DMF. The supporting electrolyte was 0.1 M TBAPF₆ in DMF. Scans were initiated at 0.5 V in the negative direction at 100 mV/s.

reduction products. The irreversible nature of the reactions does not permit the direct calculation of any thermodynamic parameters (e.g., formal reduction potential $E^{0'}$ or electron stoichiometry n) from these voltammograms.

The inclusion of the voltammograms of Figure 2 is important in that the shapes of the i–E curves illustrate the nature of the electrode reaction with nitroDPEs in protolytic solvent. However, it is helpful to present specific voltammetric data in the more organized fashion of Figure 3. Figure 3 is a so-called Kissinger chart (Miner et al., 1981). The right edge of each bar represents the cathodic peak potential E_{pc} obtained during the initial forward scan and the left edge defines the cathodic peak potential $E_{pc/2}$ at half the cathodic peak current $i_{pc/2}$. Thus, the width of the rectangle is indicative of the relative rate of reduction (i.e., the electron transfer rate from the electrode to nitroDPE is inversely related to rectangle width).

Cyclic voltammograms for the six nonpolar nitroDPEs, AFM, MC-10982, bifenox, oxyfluorfen, nitrofen, and nitrofluorfen, in DMF are shown in Figure 4. The supporting electrolyte was 0.1 M TBAPF₆ in DMF. Scans

Table I. Voltammetric Data for Nonpolar NitroDPE Compounds in DMF[c]

compounds[a]	E_{pc},[b] V	i_{pc}, μA	E_{pa}, V	i_{pa}, μA	ΔE_p, V	$E_{1/2}$, V	$E_{pc/2}$, V	$E_{pa/2}$, V
AFM	−1.05	33.5	−0.940	29.2	0.110	−0.995	−0.985	−1.04
MC-10982	−1.03	39.0	−0.925	36.0	0.105	−0.978	−0.970	−1.00
bifenox	−1.05	45.0	−0.935	42.0	0.115	−0.993	−0.985	−1.01
oxyfluorfen	−1.32	39.5	−1.19	29.0	0.130	−1.26	−1.24	−1.23
nitrofen	−1.16	41.0	−1.05	39.5	0.110	−1.11	−1.08	−1.12
nitrofluorfen	−1.15	35.0	−1.04	30.5	0.110	−1.10	−1.08	−1.11

[a] All compounds were 2 mM. [b] Abbreviations: E_{pc}, cathodic peak potential; i_{pc}, cathodic peak current; E_{pa}, anodic peak potential; i_{pa}, anodic peak current; ΔE_p, $E_{pa} - E_{pc}$; $E_{pc/2}$, cathodic potential at half i_{pc}; $E_{pa/2}$, anodic potential at half i_{pa}. [c] Note: voltammetric parameters as indicated in Figure 4.

Table II. Voltammetric Data for Polar NitroDPE Compounds in DMF[d]

compounds[b]	peak I[a]			peak II		
	E_{pc},[c] V	i_{pc}, μA	$E_{pc/2}$, V	E_{pc}, V	i_{pc}, μA	$E_{pc/2}$, V
acifluorfen	−1.34	14.5	−1.24	−1.67	6.5	−1.50
MC-7783	−1.36	8.25	−1.28	−1.81	26.5	−1.67

[a] Peak I and peak II as indicated in Figure 5. [b] Compounds were 2 mM. [c] Abbreviations: as indicated in Table I.
[d] Note: voltammetric parameters as indicated in Figure 4.

were initiated at 0.5 V in the negative direction at 100 mV/s. The shape of each of these voltammograms is similar and characteristic of a quasi-reversible electrode reaction (Bard and Faulkner, 1980). A single cathodic peak was observed during the initial forward scan, and a single anodic peak of equal size ($i_{pc} \cong i_{pa}$) was seen during the reverse scan. The reduction products were chemically stable on the time scale of the experiment; $i_{pc}/i_{pa} \cong 1.0$. The separation in peak potentials ΔE_p is greater than 59 mV (Table I). The reduction of these compounds was shifted to more negative potentials relative to the respective reduction under protic conditions.

Specific voltammetric data for the six nonpolar nitroD-PEs was obtained from the voltammograms of Figure 4 and presented in Table I. Cathodic E_{pc} and anodic E_{pa} peak potentials for these compounds in DMF range from −1.03 to −1.32 V and from −0.925 to −1.19 V, respectively. The measured half-wave potentials $E_{1/2} = (E_{pa} - E_{pc})/2$ were also determined (Table I). Our linear sweep voltammetry experiments employing a rotating disk electrode indicated the electron stoichiometry n for the reduction of nitrofen in aprotic solvent is 1 (to be reported elsewhere). On the basis of comparisons with nitrofen and other nitroaromatics (Smith and Bard, 1975), the reduction of nonpolar nitroDPEs in aprotic solvent is most likely a one-electron transfer reaction yielding the chemically stable radical anion. Thus, $E_{1/2}$ is a good approximation of the formal reduction potential $E^{0\prime}$ for the quasi-reversible one-electron reduction process of nonpolar nitroDPEs in DMF. On the basis of the information in Figure 4 and Table I there appears to be three distinct groups of nonpolar nitroDPEs: (a) AFM, MC-10982, and bifenox [average $E_{1/2}$ = −0.989 ± 0.009 (SD)V); (b) oxyfluorfen ($E_{1/2}$ = −1.26 V); (c) nitrofen and nitrofluorfen [average $E_{1/2}$ = −1.105 ± 0.007 (SD) V].

The voltammograms of the two polar nitroDPEs, acifluorfen and MC-7783, in DMF are more complex (Figure 5). These reactions are chemically irreversible (Bard and Faulkner, 1980). Two peaks were seen during the first forward scan. Two switching potentials E_λ ($E_{\lambda 1}$ = −1.5 V and $E_{\lambda 2}$ = −1.7 V) were used in the cyclic voltammetry experiment with acifluorfen. The solid line represents the scan with switching potential $E_{\lambda 2}$. During this scan two cathodic peaks and a broad anodic peak were observed. A second scan represented by the dotted line had a switching potential $E_{\lambda 1}$ of −1.5 V. This scan was performed in an attempt to isolate the first cathodic peak I and, if present, its associated anodic peak. A small anodic peak
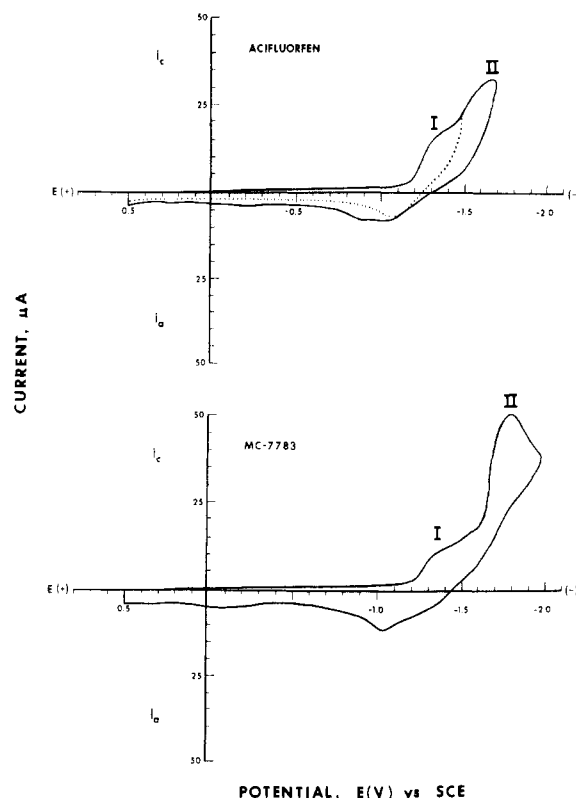

Figure 5. Cyclic voltammograms of 2 mM acifluorfen and MC-7783 in DMF. Voltammetric parameters are identical with those described in Figure 4.

was observed during the reverse scan. There is also a small anodic peak associated with peak II.

Voltammetric data for the polar nitroDPEs in DMF are presented in Table II. The cathodic peak potential E_{pc}, peak current i_{pc}, and potential $E_{pc/2}$ at half the peak current $i_{pc/2}$ were obtained for both peaks of each compound. The cathodic peak potential E_{pc} of acifluorfen and MC-7783 are nearly equal for peak I although the magnitude of the peak height i_{pc} for acifluorfen is greater than that of MC-7783. The reduction represented by the second peak II of MC-7783 occurred at a more negative potential than was observed for peak II of acifluorfen. Peak II of MC-7783 had a greater i_{pc} value.

Further electrochemical characterization of the simplest nitroDPE nitrofen is in progress and will be presented elsewhere. Linear sweep voltammetry employing a rotating

disk electrode has been used to determine the electron stoichiometry *n*. Information concerning the voltammetric properties and electron stoichiometry of nitrofen and knowledge of the redox behavior of other nitroaromatic compounds should permit us to propose a reasonable mechanism for the oxidation–reduction of nitrofen in protolytic and aprotic solvents.

Registry No. Acifluorfen, 50594-6-6; AFM, 50594-67-7; bifenox, 42576-02-3; nitrofen, 1836-75-5; nitrofluorfen, 42874-01-1; oxyfluorfen, 42874-03-3; MC-7783, 74434-43-8; MC-10982, 74315-61-0.

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Distribution of Butylate, Heptachlor, Lindane, and Dieldrin Emulsifiable Concentrated and Butylate Microencapsulated Formulations in Microagroecosystem Chambers

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The comparative distribution of butylate herbicide and heptachlor, lindane, and dieldrin insecticides as emulsifiable concentrated (EC) and butylate microencapsulated (ME) formulations in microagroecosystem chambers was determined. [^{14}C]Butylate EC at 5.5 and ME at 5.2 and the insecticides at 2 kg ha^{-1} were sprayed onto soil. One treatment set was immediately incorporated and a second set was incorporated 24 h later. Corn was planted, and soil, air, and corn samples were taken periodically for pesticide assay. For butylate ME and the insecticides, the distribution in percent of applied after 52 days in soil was 65–69% for immediate incorporation and 58–63% for delayed incorporation and in corn and weeds <1% for insecticides and 5% for butylate (^{14}C equiv). Loss by vaporization for heptachlor, lindane, and dieldrin, respectively, was 15, 12, and 3% from immediate incorporation and 38, 26, and 4% from delayed incorporation. Butylate EC (^{14}C equiv) immediate and delayed incorporation, respectively, resulted in 18 and 6% remaining in soil and 5 and 1% in corn and weeds.

A farm practice that is becoming more popular is that of minimum till, because erosion, energy, and costs usually are reduced. One aspect for successful minimum-till practices will, in many cases, involve use of chemical pesticides applied to soil surfaces rather than soil incorporation. Depending upon a pesticide's vapor pressure and formulation, considerable pesticide losses may occur. The body of information on vapor losses of pesticides with time under various soil and plant conditions is small and limited to a few pesticides, primarily chlorinated hydrocarbon insecticides.

S-Ethyl diisobutylthiocarbamate (butylate) is a preemergent herbicide used to control grasses and some broadleaf weeds. Because butylate has a high vapor pressure (1735 mPa or 13 × 10^{-3} mmHg at 25 °C) (Mullison et al., 1979)

and consequent high losses through volatilization, it must be incorporated into the soil in <1 h after application according to labeled instructions. An alternative has been the development of microencapsulation to reduce butylate losses through volatilization.

Atallah et al. (1979) in a comparative volatilization study of liquid (EC) and granular (G) formulations of 1,2,4,5,6,7,8,8-octachloro-3a,4,7,7a-tetrahydro-4,7-methanoindan (chlordane) and 1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene (heptachlor) mixed in laboratory soil found chlordane EC formulations were 20 times more volatile than the corresponding G formulation. Heptachlor EC formulations was 5–10 times more volatile than the G formulation.

This paper compares the distribution of microencapsulated (ME) butylate with emulsifiable concentrated (EC) butylate, heptachlor, the γ-isomer of 1,2,3,4,5,6-hexachlorocyclohexane (lindane), and 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo,exo*-5,8-dimethanonaphthalene (dieldrin) formulations in microagroecosystem chambers.

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