

# Slow Release of *S*-Ethyl Dipropylcarbamothioate from Clay Surfaces†

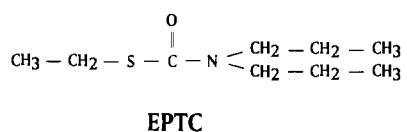
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The adsorption/desorption behavior of the volatile herbicide *S*-ethyl dipropylcarbamothioate (EPTC) to/from montmorillonite and sepiolite was studied. The clays were used as such or with their surface properties modified by adsorption of the cationic dye methyl green (MG). At 30 °C, the half-life time ( $T_{1/2}$ ) of the herbicide in its free form was 10 h, whereas when adsorbed to montmorillonite the  $T_{1/2}$  was more than 5 days. When EPTC was incorporated into the soil, the  $T_{1/2}$  values were 4 and 9 days for the free and adsorbed forms, respectively. The interactions between EPTC and clay surface were studied by Fourier-transform infrared spectroscopy. Vibrational spectra revealed two different populations of EPTC in the clay-organic complexes: one in which the molecules are adsorbed, interacting with the clay surface, and another in which they do not interact with the clay, their spectrum being almost identical to that of free EPTC. Coadsorbed MG impairs the EPTC-clay interactions, causing an increase in free EPTC, indicating that free EPTC is released from the organoclay at a rate higher than that of adsorbed EPTC. Oat bioassays showed that the herbicidal activity of clay-complexed EPTC was extended by more than 1 week. These data indicate that clay-EPTC interactions can be employed to improve herbicidal performance of EPTC and to control its release to the environment.

## INTRODUCTION

Volatilization is a major factor limiting the lifetime of carbamothioate herbicides in the field (Wilkinson, 1988). That is the case for the important and widely used *S*-ethyl dipropylcarbamothioate (EPTC). It has been shown that



its volatilization from soils strongly depends on the content of clay, organic matter, and moisture (Ashton and Sheets, 1959; Cliath, 1980; Fang et al., 1961; Gray, 1965; Gray and Weierich, 1968; Koren et al., 1969; Sheets, 1959; Upchurch and Mason, 1962). Using infrared spectroscopy, Mortland (1968) and Mortland and Meggitt (1966) studied the interactions between EPTC and montmorillonite, and the effect of water, heat, and coadsorption of an organic cation (pyridinium) on volatilization of the herbicide from the clay surface. Using oat bioassay, Ashton and Sheets (1959) reported that higher concentrations of EPTC were needed in heavy soil (80% clay) as compared to light soil (16% clay). Experiments on slow release of pesticides from clays to an aqueous phase have been reported (Gerstl and Yaron, 1980; Saltzman and Mingelgrin, 1980). The possibility of using sepiolite (a clay having a fibrous structure with channels in the direction of the fiber and a high adsorptivity) as a pesticide carrier has also been suggested (Alvarez, 1984).

In this paper we report a study, using both analytical techniques and bioassays, on the release of EPTC from montmorillonite and from sepiolite in two different situations: (a) unmodified clays; (b) clays whose surface

properties were modified by adsorption of the organic cation methyl green (MG).

## MATERIALS AND METHODS

**Materials.** The clays used were sodium montmorillonite SWy-1 (Mont) obtained from the Source Clay Repository, Clay Minerals Society, and sepiolite (Sep) obtained from Tolsa SA, Spain. EPTC (analytical grade) and MG were obtained from ICI America and Fluka AG, respectively, and used without further purification. Sandy soil (85% sand, 8% silt, 7% clay, 0.45% organic matter, and pH 6.9) was used throughout this study.

**Preparation of Clay Complexes.** The clay-dye complexes Mont-MG and Sep-MG were prepared by dropwise addition of aliquots of a 10 mM aqueous solution of MG to a 1% (w/v) aqueous suspension of the clay under continuous stirring (Margulies et al., 1992). After a 30-min centrifugation (16000g), the precipitate was washed three times with distilled water, freeze-dried, and ground to <50 μm. The Mont-EPTC, Mont-MG-EPTC, Sep-EPTC, and Sep-MG-EPTC complexes were prepared by adding the appropriate amount of EPTC in hexane to the corresponding powdered clay or clay-MG and evaporating the solvent under gentle reduced pressure as described previously (Margulies et al., 1988, 1992).

**Volatilization of EPTC.** One-milliliter samples of a hexane solution containing 7.5 mg/mL of EPTC were evaporated in glass Petri dishes (5-cm diameter). After the films of EPTC were incubated at 30 °C for different periods of time, 10 mL of hexane was added to each Petri dish and the amount of remaining EPTC was determined by gas chromatography (GC).

EPTC-containing powdered clay complexes prepared as described above, with levels of 0.2, 0.5, and 0.8 mmol of EPTC/g of clay, were evenly spread in a <1-mm layer on the bottom of glass Petri dishes and incubated at 30 °C for different periods of time. Powdered clay sample (50 mg) was treated with 10 mL of hexane, shaken for 1 h, and filtered to separate the clay particles; EPTC in the filtrate was quantitated by GC.

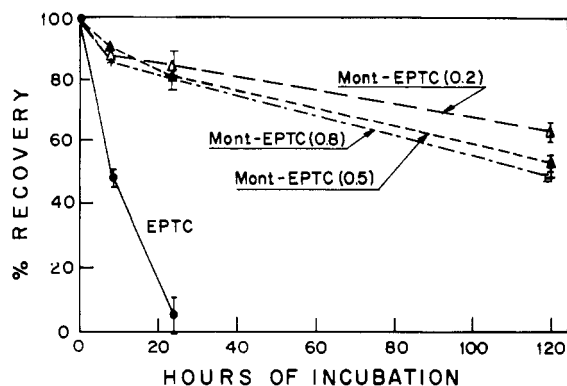
The rate of volatilization of EPTC from soil was determined using the following procedure: EPTC (alone or as a Mont-EPTC complex containing 0.8 mmol/g of clay) was thoroughly mixed with sandy soil at a concentration of 10 ppmw. Soil sample (32 g) was put in a plastic Petri dish (5-cm diameter) and moistened to field capacity (10% w/w). After incubation at 30 °C for different periods of time, EPTC was extracted from the soil by shaking the content of each Petri dish with 25 mL of hexane for 1 h. The extract was filtered and analyzed by GC. Experiments were repeated at least twice and carried out in five replicates.

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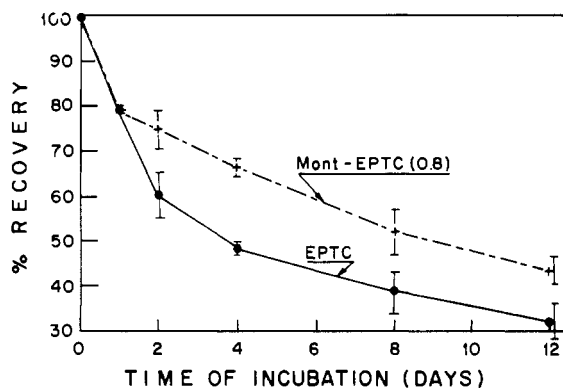
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**Figure 1.** Volatilization of EPTC in its free form and adsorbed to montmorillonite, at different loads. Numbers in parentheses refer to concentrations of EPTC in millimoles per gram of clay. Bars indicate SD.



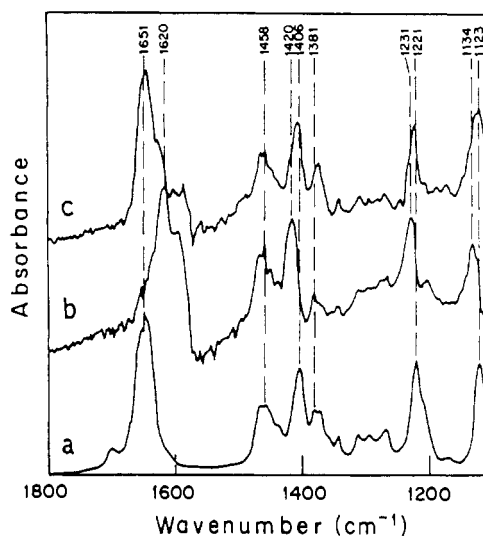
**Figure 2.** Volatilization of EPTC incorporated in soil in its free form and adsorbed on montmorillonite at a load of 0.8 mmol/g of clay. Bars indicate SD.

The gas chromatograph used was a HP 5890 instrument equipped with a flame ionization detector. A HP1 methyl silicone column (5 m, 0.53 mm i.d.) was operated with temperature programming (110–145 °C, 10 °C/min) using nitrogen as carrier gas at 20 mL/min. The adsorption interactions between EPTC and two different clays (Mont and Sep), with surface properties modified by adsorption of MG, were studied by Fourier-transform infrared (FTIR) spectroscopy. EPTC was adsorbed to the clay or clay–MG at a load of 0.8 mmol/g of clay and incubated in open Petri dishes at 30 °C, and small samples were periodically taken for FTIR measurements. Infrared spectra were obtained using KBr pellets with a Nicolet MX-S Fourier-transform infrared spectrophotometer interfaced to an Elite Star 16-bit PC and a Goerz SE284 digital plotter.

**Bioassay.** Soil activities of EPTC and clay–EPTC complexes were estimated using oat (*Avena sativa* var. Saya-3, Hazera, Israel) seeds. The herbicide (alone or adsorbed to clay) was thoroughly mixed with sandy soil at a concentration of 5 ppmw. Either pots (7.5-cm diameter) or Petri dishes (5.0-cm diameter) were filled with the soil, watered to field capacity, and incubated at 28 °C in a greenhouse. At weekly intervals (up to 5 consecutive weeks), 10 and 7 oat seeds were sown in each pot or Petri dish, respectively. One week after sowing, the oat seedlings were removed from the soil in the Petri dish and washed, and their root length was measured. Shoot fresh weight of the oat plants grown in pots was determined 2 weeks after emergence.

## RESULTS AND DISCUSSION

**Release of EPTC from Montmorillonite.** Figures 1 and 2 present the results of analytical experiments aimed at testing the effect of adsorption to montmorillonite on the rate of EPTC loss by volatilization when EPTC is exposed to air or incorporated in soil, respectively. Figure 1 shows that free EPTC volatilized almost completely (5% recovery) after 1 day of incubation at 30 °C, whereas when

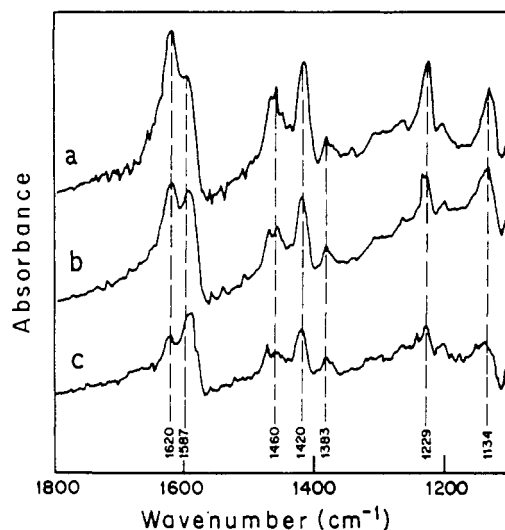


**Figure 3.** Fourier-transform infrared absorption spectra of EPTC: (a) in its free form; (b) adsorbed on montmorillonite (after the spectrum of montmorillonite was subtracted); (c) adsorbed to a Mont–MG complex containing 0.8 mmol of MG/g of clay (after subtraction of the spectrum of Mont–MG).

EPTC was adsorbed to montmorillonite at different loads in the range 0.2–0.8 mmol of EPTC/g of clay, the recovery at the same time was about 80%. The half-life time of herbicide (50% recovery) in its free state was 10 h and that of the adsorbed samples more than 5 days. Since no significant differences were observed between the montmorillonite samples with different loads of EPTC, and to minimize the amount of clay required and increase the content of the active ingredient, all further experiments were carried out using a load of 0.8 mmol/g of clay (13% w/w).

The results presented in Figure 2 show that incorporation of the herbicide into the soil reduces the rate of volatilization. This is in accordance with the results of King and Evans (1982) and can be attributed to adsorption interactions between EPTC molecules and the clay or organic matter constituents of the soil. Again, the recovery of clay-adsorbed EPTC from soil was considerably higher than that of free EPTC. The half-life time of EPTC was increased from 4 days when it was in the free state to 9 days when adsorbed to montmorillonite. Since water molecules compete with EPTC for the adsorption sites on the clay surface (Mortland and Meggitt, 1966), the release of the pesticide from the soil strongly depends on the moisture content. To avoid variability due to this effect, the herbicide was incorporated into a dry soil and then water was added to the soil up to its field capacity.

**Clay–EPTC Interactions.** In Figure 3 the FTIR spectra of free EPTC (a), EPTC adsorbed to Mont (b), and EPTC adsorbed to Mont–MG (c) are shown. Curves b and c are difference spectra obtained by subtracting from the spectra of the complexes containing EPTC the spectra of the corresponding materials without EPTC. A prominent shift of the strong absorption corresponding to the C=O stretching vibration of EPTC as a result of adsorption to montmorillonite is observed. In free EPTC this vibration is at 1651 cm<sup>-1</sup>, whereas in the adsorbed state it is shifted to lower energies appearing as a broad band with a maximum at 1620 cm<sup>-1</sup> and a shoulder at 1597 cm<sup>-1</sup>. This suggests that there are two different adsorption sites on the Mont surface where the EPTC molecules interact differently, the strongest interaction being reflected by the absorption at 1597 cm<sup>-1</sup>.



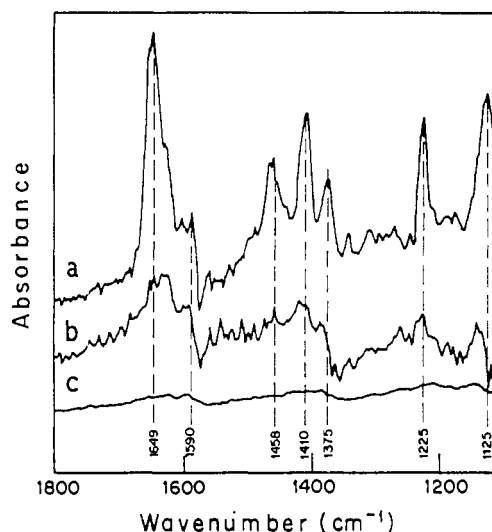
**Figure 4.** Fourier-transform infrared absorption spectra of EPTC adsorbed on montmorillonite (0.8 mmol/g of clay) after (a) 0, (b) 3, and (c) 7 days of incubation at 30 °C.

In accordance with Mortland and Meggitt (1966), adsorption of EPTC to the clay through the carbonyl group induces a certain double-bond character to the C–N bond. This may explain the observed shift of C–N stretching vibrations at 1123 and 1221  $\text{cm}^{-1}$  (Nakanishi and Solomon, 1977) to 1134 and 1231  $\text{cm}^{-1}$ , respectively. From the C–H bending vibrations in the 1350–1470- $\text{cm}^{-1}$  region, only the peak at 1406  $\text{cm}^{-1}$ , which probably corresponds to the methylene linked to the sulfur atom (Nakanishi and Solomon, 1977), is modified by adsorption and shifted to 1420  $\text{cm}^{-1}$ .

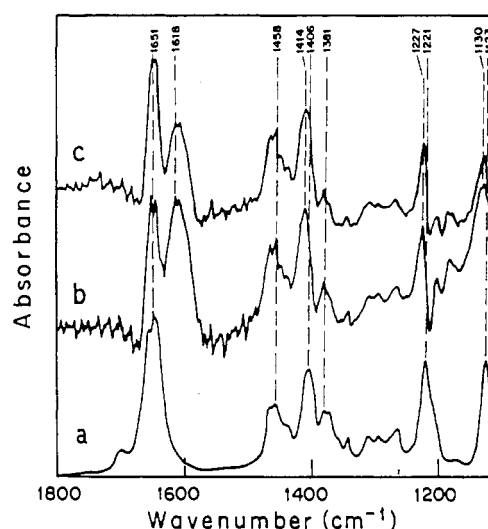
Complete coverage of the clay surface by MG prevents EPTC–clay interactions, and the FTIR spectrum resembles that of the free compound (Figure 3c). This is in contrast to the results reported for the adsorption of EPTC to a montmorillonite–pyridinium complex (Mortland, 1968). In that case, the infrared spectrum was practically unchanged by the presence of the organic cation, and a hydrogen bond linked between EPTC and pyridinium was suggested. In our case it seems that EPTC is adsorbed to the clay–MG complex by much weaker hydrophobic bonds.

The FTIR spectra of EPTC adsorbed to montmorillonite and to Mont–MG after 3 and 7 days of incubation at 30 °C are shown in Figures 4 and 5, respectively. When adsorbed to Mont, a considerable amount of EPTC still remains adsorbed even after 7 days. The fraction which was volatilized is mainly that which interacts weakly with the clay surface and which has the carbonyl absorption at 1620  $\text{cm}^{-1}$ . On the other hand, in the case of the Mont–MG–EPTC complex (Figure 5), EPTC was released much more quickly, and after 3 days of incubation the spectrum of the herbicide was hardly measurable.

The same experimental approach (FTIR) described above was used to study the interactions between EPTC and sepiolite. Figure 6 shows the FTIR spectra of EPTC adsorbed to Sep (Figure 6b) and adsorbed to a Sep–MG complex containing 0.2 mmol of MG/g of clay (Figure 6c). These are difference spectra obtained by subtraction of the spectra of Sep and Sep–MG from the spectra of EPTC-containing complexes Sep–EPTC and Sep–MG–EPTC, respectively. The spectrum of EPTC in its free state, previously shown in Figure 3, is reproduced again here (Figure 6a) for comparison. In the spectrum of EPTC adsorbed to sepiolite (Figure 6b) a splitting of the C=O stretching vibration into two separate bands is observed. One band appears at 1651  $\text{cm}^{-1}$ , as in free EPTC, and



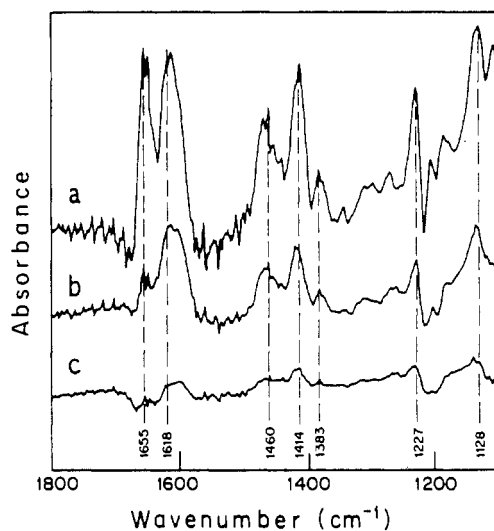
**Figure 5.** Fourier-transform infrared absorption spectra of EPTC adsorbed at a load of 0.8 mmol/g of clay, on a Mont–MG complex containing 0.8 mmol of MG/g of clay, after (a) 0, (b) 3, and (c) 7 days of incubation at 30 °C.



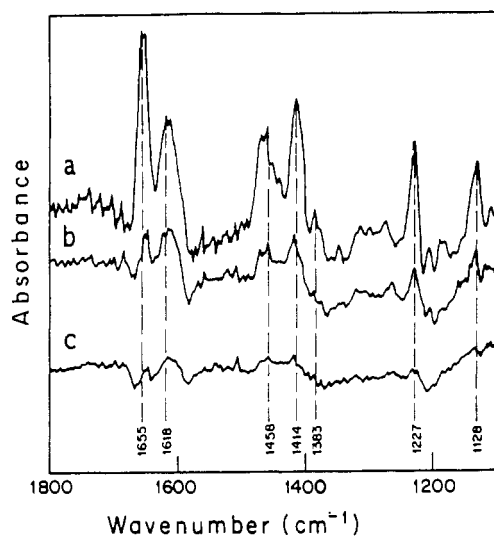
**Figure 6.** Fourier-transform infrared absorption spectra of EPTC: (a) in its free form; (b) adsorbed on sepiolite (after the spectrum of sepiolite was subtracted); (c) adsorbed to a Sep–MG complex containing 0.2 mmol of MG/g clay (after the spectrum of Sep–MG was subtracted).

another at lower frequencies (1618  $\text{cm}^{-1}$ ), which can be assigned to EPTC molecules interacting with the clay surface through the carbonyl group. This spectrum suggests that there are two different populations of EPTC molecules in the complex with sepiolite. In one population the organic molecules do not interact with the clay, whereas in the second one they are adsorbed on the mineral surface, probably to the OH of the silanoyl groups at the external surfaces of the clay or to the coordinate water.

According to Serna and Vanscoyoc (1978), only small and very polar organic molecules such as methanol or ethanol could penetrate to a certain extent into the channels of sepiolite, exchanging the zeolitic water. The relatively bulky EPTC molecules might not be able to enter these small channels and should, therefore, be adsorbed on the external surfaces. The same authors indicated also that, due to crystallographic defects, micropores of dimensions much larger than those of the channels are present in sepiolite. Inside these pores, new silanoyl groups are exposed and they might well be efficient adsorption sites for EPTC.



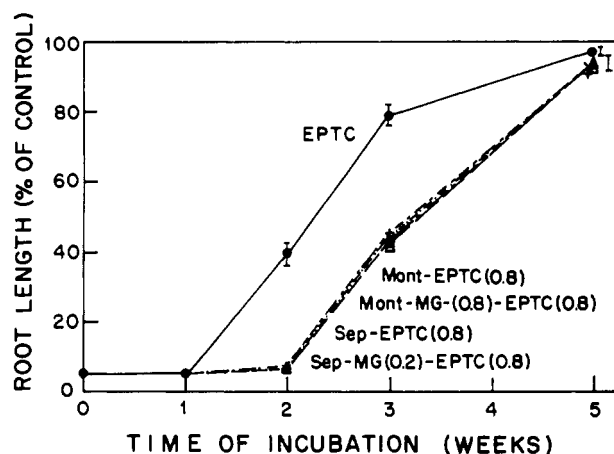
**Figure 7.** Fourier-transform infrared absorption spectra of EPTC adsorbed on sepiolite (0.8 mmol/g of clay) after (a) 0, (b) 3, and (c) 7 days of incubation at 30 °C.



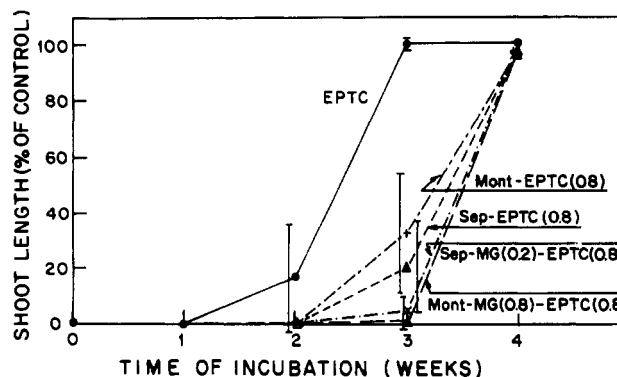
**Figure 8.** Fourier-transform infrared absorption spectra of EPTC adsorbed, at a load of 0.8 mmol/g of clay, on a Sep-MG complex containing 0.8 mmol of MG/g of clay, after (a) 0, (b) 3, and (c) 7 days of incubation at 30 °C.

In the spectrum of EPTC adsorbed to Sep-MG (Figure 6c) it can be observed that the intensities of the 1651- and 1618- $\text{cm}^{-1}$  bands are higher and lower, respectively, than those of the same bands in the spectrum of EPTC adsorbed to sepiolite without MG (Figure 6b). Our interpretation is that MG competes with EPTC for the same adsorption sites (silanols), preventing interactions between the herbicide and the clay surface, hence increasing the population of EPTC molecules which are in the free-like fraction. The fact that the band at 1618  $\text{cm}^{-1}$  is still present in spectrum 6c indicates that the MG molecules do not completely occupy the adsorption sites of EPTC, most probably those Si-OH present in the micropores, which are not accessible for the large dye molecule. This interpretation is supported by the fact that when the spectrum of EPTC adsorbed on Sep (Figure 6b) was subtracted from that of the herbicide adsorbed on Sep-MG (Figure 6c), the resulting spectrum (not shown) was almost identical to that of free EPTC (Figure 6a).

Figures 7 and 8 show the change of the spectra of EPTC adsorbed to sepiolite and to Sep-MG, respectively, after 3 (curves b) and 7 days (curves c) of incubation at 30 °C.



**Figure 9.** Effect of incubation time on the herbicidal activity of EPTC, incorporated in the soil alone or adsorbed on montmorillonite (Mont) and sepiolite (Sep), with and without methyl green (MG). The herbicidal activity was determined by oat root bioassay in Petri dishes. Root length was recorded 7 days after sowing. Numbers in parentheses refer to concentrations of the organic compounds in millimoles per gram of clay.



**Figure 10.** Effect of incubation time on the herbicidal activity of EPTC, incorporated in the soil alone or adsorbed on montmorillonite (Mont) and sepiolite (Sep), with and without methyl green (MG). Herbicidal activity was determined by oat shoot bioassay in pots. Oat shoot was harvested 2 weeks after emergence. Numbers in parentheses refer to concentrations of the organic compounds in millimoles per gram of clay.

The release of the herbicide from its clay complexes is evident from the decrease in the intensities of all absorption bands of EPTC, mainly those corresponding to the free molecules (1655  $\text{cm}^{-1}$ ) which do not interact with the clay surface.

**Bioassay.** The half-life times of free EPTC incorporated into sandy soil were 15.5 and 17 days as determined by root and shoot lengths of oat seedlings, respectively (Figures 9 and 10). These data are in agreement with those reported by Tal et al. (1989) for EPTC behavior in sandy soils. Using either Mont-EPTC or Sep-EPTC, with or without MG, did not change the dissipation pattern of the herbicide but resulted in a half-life time 1 week longer than that of free EPTC. These data indicate that the adsorption of the clay is of major importance in determining the duration of the soil activity of EPTC. Our results demonstrate that in sandy soils with low content of clay, the application of EPTC adsorbed to either montmorillonite or sepiolite results in a significant extension of its biological activity.

#### ACKNOWLEDGMENT

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