Technical challenges in soil photolysis studies using SETAC 1995 and/or draft OECD guideline

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Introduction

For the registration of plant protection products (PPP), data on photolysis of chemicals in soil are required by Commission Regulation EU 283/2013. The SETAC (1995) guideline is the regulatory relevant guideline, while the OECD draft guideline on soil photolysis (2002) has never been implemented. A key difference between the two guidelines is that the SETAC guideline uses air-dried soils, while the OECD draft guideline recommends air dried or moist soils (about 75% of the field capacity). Also, recent EFSA guidance (2022) discusses differences of using air-dried and moist soils in soil photolysis studies.

The objectives of this study were 1) Identify the technical challenges associated to the performance of soil photolysis study using SETAC and /or OECD guideline 2) to perform a literature review followed by lab experiments comparing the extent of photodegradation when dry or moist soil is used.

Materials and Methods

Soil used: 13.1% sand, 62.7% silt, 24.2% clay and OC content 4.45% according to DIN norm.

Sample preparation: Soil slurry was prepared using 10g (dry weight) soil mixed with distilled water and transferred into the test vessel i.e. a quartz glass tray (18 cm x 3.5 cm; height: 1 cm). The soil slurry was dried in an oven at ~35°C. The moist soil was prepared by adding distilled water to maintain at 45% WHC (water holding capacity) equivalent to ~70% of the field capacity. The soil thickness in the test vessel was ~2 mm.

Test item application: Non-labelled cypermethrin was spiked homogeneously in the soil sample using 0.5mL co-solvent (acetonitrile). The starting test concentration of the test item was 0.4mg/kg (dry soil).

Incubation conditions: The spiked soil was closed and incubated in an irradiation unit (Suntest CPS+, ATLAS Material Testing Technology GmbH) with continuous irradiation of 75W/m² (300-400nm). To maintain the soil temperature at 20±2°C, a cooling unit (cryostat) was placed under the test vessel to cool the soil (see Figure 1b). Additionally, to prevent fluctuations in soil temperature resulting from surrounding temperature, the irradiation unit was placed inside a climatic chamber at 12°C. The soil temperature was measured using a thin and flat temperature sensor (See Figure 1a) which was covered and placed beneath the soil layer. The dark control samples were incubated separately in a dark chamber.

Sampling, sample processing and analysis: The samples were sacrificed at 0d, 2d, 5d and 7d. Soil samples were extracted three times (30min shaking) using 40mL acetonitrile. The combined extract was analyzed using LCMS.

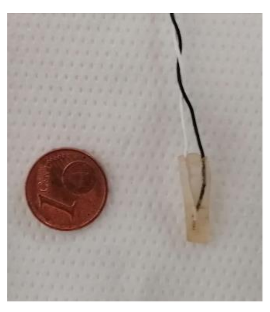

Figure 1a: A Photo of a thin and flat temperature sensor used for soil temperature measurements during this study.

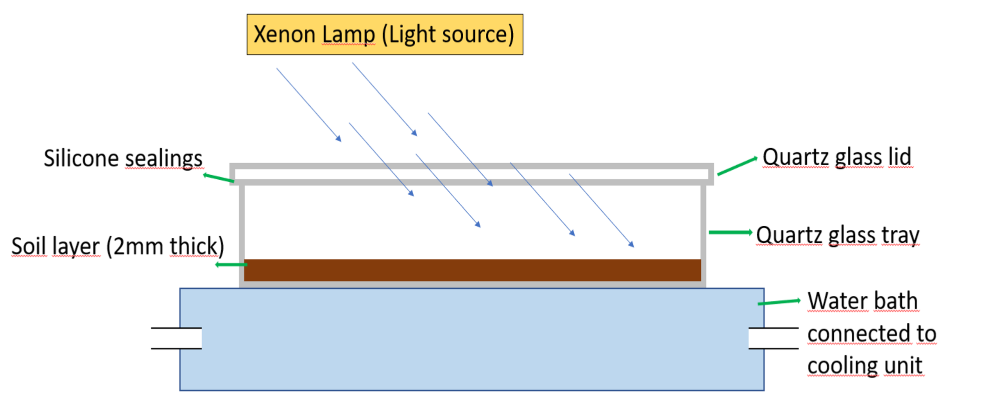

Figure 1b: A graphical representation of soil sample (air dried or moistened) placed in a quartz glass tray (test vessel) incubated in irradiation conditions during a soil photolysis study.

Results and Discussion

Technical challenges and issues

The soil temperature measured during the test was 20±2°C. However, the position and geometry of the temperature sensor are key parameters for the soil temperature measured. Hence, measured soil temperature did not accurately reflect the temperature gradient across different soil layers. As the upper soil surface receiving the direct irradiation is heated (>>20°C) while the bottom soil layer which is directly connected to the cooling unit is cooled to 2-3°C or lower (see Figure 1b).

Figure 2: A picture of moist soil sample incubated under irradiation condition after 5d of incubation. Visual observation shows condensation of water in the inner walls of the test vessel.

Especially for the samples where moist soil was used, condensation was observed in the inner walls of the test setup (see Figure 2). No significant losses in water (except one sample where air leakage was suspected) were observed in the moist soil samples. Airtight, closed system setup was established by the use of silicone sealings. However, for the testing of volatiles, silicon sealings should be avoided.

Degradation of cypermethrin in air-dried vs moist soil

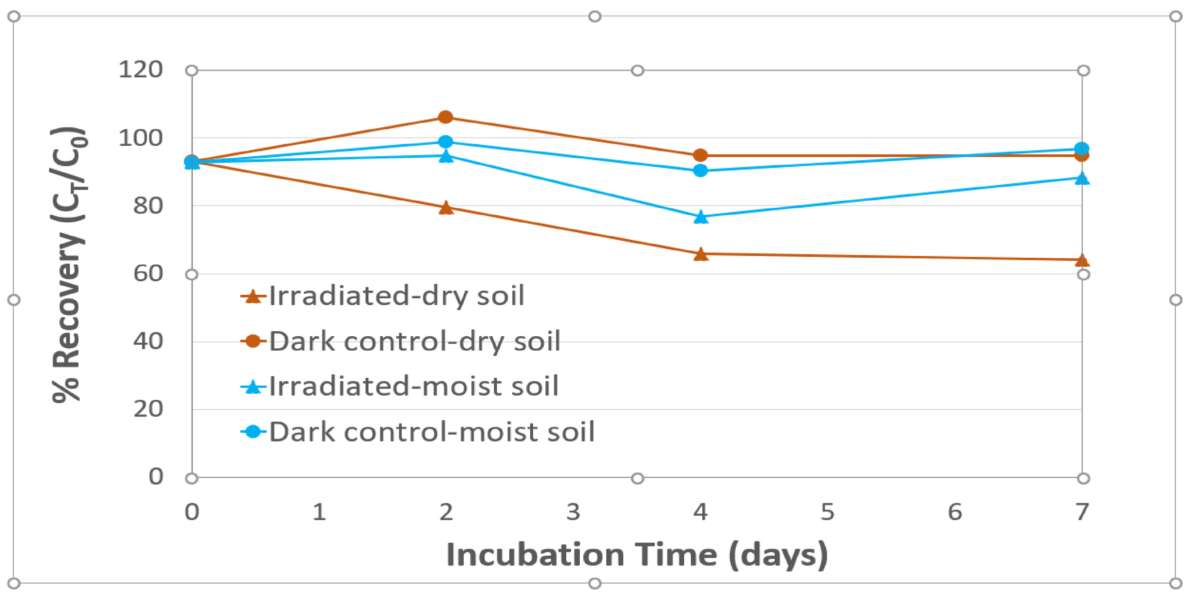

Figure 3: Under continuous irradiation (75W/m2, wavelength 300-400nm), cypermethrin degraded slower in moist soil than in air dried soil. After 7d, 64.3%±8.5% of the test item was recovered in air-dried soil, compared to 88.4%±6.9% in moist soil. The effects of water droplets from moist soil (Figure 2) on irradiation were not evaluated. The impact of using moist soil on photodegradation of test item is not clear. Dark control recovery from air dried and moist samples was 93-106% and 90.4 -98.7%, respectively. Results for dry soil indicate that soil photolysis is a possible route of degradation of cypermethrin (see also RAR (2018)).

Literature review on soil photolysis using air dried vs moist soil

An informal review of ~40 recent EU active substance dossiers showed substantial heterogeneity in the test method used for soil photolysis studies. Test methods varied between SETAC (1995), OPPTS 835.2410 (2008) and/or draft OECD (2002) and was commonly dependent on the age of the study, with a shift towards draft OECD in more recent studies. No studies were found where both air dried and moist soils were used, and several of the studies where moist soils were used referred to challenges maintaining soil moisture. A review of soil photolysis studies on PPP available in open literature indicated that compared to dry soil, maintenance of soil moisture almost exclusively results in faster degradation. Across the several compounds evaluated (e.g. dimethoate, mecoprop, chlorpyrifos, etc.) soil moisture was a key parameter impacting the outcome of soil photolysis studies.

Conclusions

Maintaining reproducible test parameters (soil moisture, soil temperature) is a main issue in soil photolysis studies due to the high amount of heat generated by the xenon light source. Literature review and our experimental data suggest differences in photodegradation in air-dried versus moist soil. If the difference in degradation of cypermethrin was due to the technical issues while using moist soil was not clear.

References

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Acknowledgement: We would like to thank Fraunhofer internal house project for funding the experimental part of the study. Sincere thanks to Dieter Struwe from Fraunhofer IME for supporting in technical and enginnering aspects during the study.