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STUDY #288: EVALUATING PESTICIDE MOVEMENT IN COARSE-TEXTURED SOILS IN THE PRESENCE OF NANOPARTICLES.

I. INTRODUCTION

Nanotechnology is defined as relating to materials, systems and processes that exist or operate at a scale of 100 nanometers (nm) or less. Due to their small size, nanoparticles have a very large surface area relative to their volume, which results in greater chemical reactivity and biological activity compared to larger particles of the same chemical composition (Garnett and Kallinteri 2006; Limbach et al. 2007; Nel et al. 2006). Nanoscale materials are increasingly being used in a wide range of applications, including medicine and public health, energy, electronics, pharmaceuticals, pollution reduction and environmental cleanup, and in product improvement such as for stronger, lighter, and more durable or conductive materials. Nanoparticles with their high relative surface area may minimize pesticide leaching by increasing adsorption, reducing runoff and decreasing release kinetics (Gogos et al. 2012). In 2007, USEPA acknowledged that it has been contacted by several manufacturers interested in releasing nanoscale pesticides (U.S. EPA 2007), and recently (December 2011) conditionally registered such a pesticide, HeiQ AGS-20. Many of the world's leading agrochemical companies have active nanotechnology research and development programs. A number of commercially available chemicals, such as fungicides and plant growth regulators have emulsions that contain nanoparticles (Scrinis and Lyons, 2007).

The objective of this study is to evaluate the effect of nanoparticles on the mobility of two pesticides that are regulated as ground water contaminants. Zero-tension lysimeters will be used to characterize leaching of pesticide solute in the presence of nanoparticles. Experience from using lysimeters in a previous field study (Clayton and Aggarwal, 2012) has indicated that lysimeters provide benefits over soil coring for investigating the persistence and mobility of pesticides and their degradates. Lysimeters with collection reservoirs address several limitations inherent with soil coring, such as:

1) collection of all leachate irrespective of the magnitude of water applications, potential for residue movement, or characteristics of the soil;
2) ease and cost effectiveness of sampling, only requiring extraction of the solute by pump with the frequency of sampling unrestricted;
3) interception and accumulation of leaching residues of transformation products, which have been elusive in previous soil coring studies conducted by DPR possibly due to their slow rate of formation coupled to a high potential for movement in soil;

4) enhanced chemical analytical sensitivity for residues in solution compared to residues bound to soil;
5) direct measure of the flux of water and residues leached beyond the bottom of a soil core.

For this study, our hypothesis is that nanoparticles will increase the soil-adsorption capacity of pesticides, thus reducing the mobility of pesticides in the soil and mitigate some risk of their potential to contaminate ground water.

II. STUDY OBJECTIVE

The objective of this study is to compare the movement and persistence of two pesticides and their degradates when co-applied with nanoparticles under an irrigation regime known to produce percolating water in a leaching-vulnerable soil.

III. PERSONNEL

The study will be conducted by staff from the CDPR's Environmental Monitoring Branch under the general direction of Lisa Quagliaroli, Senior Environmental Scientist (Supervisor). Key personnel are listed below:

Project Leaders:	Vaneet Aggarwal and Murray Clayton
Field Coordinator:	Alfredo DaSilva
Senior Scientist:	John Troiano
Laboratory Liaison:	Sue Peoples for analyses conducted by CDFA
Cooperators:	University of California Kearney Agricultural and Extension Center
Contact Person:	Vaneet Aggarwal, phone: 916-445-5393, email: vaggarwal@cdpr.ca.gov, FAX: 916-324-4088

IV. STUDY PLAN

This study will be conducted on a bare, coarse textured, sandy loam soil. University of California Kearney Agricultural Research and Extension Center (KARE) will be responsible for designating the location for the experiment, installation and testing of irrigation systems, application of chemicals via chemigation along with obtaining any necessary pesticide application permits and/or notifications to the County Agricultural Commissioner, maintenance, and irrigation of plots for the duration of the experiment. KARE will assist with installation of the lysimeters. DPR staff will be responsible for the construction and installation of lysimeters, providing nanoparticles, incorporation of nanoparticles into soil matrix before chemigation, soil coring activities, solute sampling from lysimeters, chemical analysis, data analysis and reporting of results.

The study will consist of a single site with treatment plots arranged as a completely randomized design. The site will contain a total of nine plots consisting of three treatments each with three replicate plots. The three treatments will include a control (no soil-incorporated nanoparticles) and two levels of soil-incorporated nanoparticles at 2% w/v and at 10% w/v, respectively. Treatment plots will be 1-m^2, each with a zero-tension column lysimeter installed at the center (Figure 1). Adjacent plots will be separated by 1 m. The lysimeter design and study soil properties will reflect characteristics that minimize potential for preferential flow and saturated lower boundary conditions. Lysimeter features will include the containment of undisturbed soil as opposed to repacked soil and a graduated fine-to-coarse-textured sand filtration barrier at the base of the soil core to improve drainage (Figure 2). After installation of the lysimeters the irrigation system will be installed and verified for uniformity of water application. Frequent irrigations will be conducted across the sites until drainage water is extracted from all lysimeters to confirm their functionality and to standardize each plot's initial soil-water content. The top 7.6 cm of soil will then be removed from six lysimeters, thoroughly mixed with nanoparticles at either 2% or 10% w/v and added back to the top of the devices. The control lysimeters – those without nanoparticles – will have the top 7.6 cm of soil removed, mixed and replaced in a manner consistent with those devices containing the nanoparticles.

Atrazine and bromacil will be applied to the plots at a rate of 3.4 kg/ha approximately four to six weeks after installation of the lysimeters and irrigation system. Potassium bromide also will be applied at a rate of 100 kg Br/ha as a tracer for water movement. These chemicals will be applied by chemigation simultaneously into the soil with a total of 1 inch of water. Irrigation will be applied to the sites at 7-day intervals for a period of approximately 60 days. The site will receive water applications at 160% of cumulative ETo, which represents inefficient water applications that are typical of unpressurized surface delivery systems used in California, such as furrow (California Agricultural Technology Institute, 1988; Snyder et al., 1986) Irrigation will be indexed to ETo, determined from a nearby CIMIS weather station. Collection of daily weather station data will include ETo; mean, maximum and minimum air temperature; and rainfall.

Following irrigation and lysimeter installation soil cores will be collected at several locations within the study site. These soil samples will be used to characterize background pesticide residues, textural composition, total organic carbon content, bulk density and initial soil moisture content. Their locations will be centered between plots to ensure that the soil in each plot remains undisturbed. The samples will also be used to characterize background bromide levels.

Solute will be extracted from lysimeter reservoirs at 7-day intervals, occurring on the same day, but just prior to the weekly water applications. The water samples will be measured for total volume and analyzed for bromide and pesticide residues. At the end of the study soil cores will be collected from within the lysimeters for bromide and pesticide analysis (detailed methodology provided in Protocol Section V).

V. SAMPLING METHODS

- Soil to be analyzed for background pesticide and bromide residues will be sampled using methods in soil sampling protocol FSSO002.00 (Garretson, 1999). These cores will be sampled to a depth of 3 feet at 6-inch increments. Upon extraction each 6-inch subsample to be analyzed for pesticide residues will be placed in a sealed jar on dried ice and maintained in frozen storage until chemical analysis. Samples to be analyzed for bromide residues will be sealed in plastic bags and transferred to refrigerated storage prior to analysis.

- Soil within the lysimeters to be analyzed for pesticide and bromide residues will be sampled using the general methodology in soil sampling protocol FSSO002.00 (Garretson, 1999). These cores will be sampled to a depth of 3 feet at 6-inch increments. Each 6-inch sub-core will be 12-inches in diameter (inside diameter of lysimeters) and extracted using trowels and shovels. Sanitizing of the soil extraction equipment will be consistent with those methods used for bucket augers as stated in sampling protocol FSSO002.00 (Garretson, 1999). Soil from each 6-inch sub-core will be thoroughly mixed inside a plastic bag and one of two subsamples of approximately 500 g transferred to a sealed jar on dry ice and maintained in frozen storage until chemical analysis. The remaining subsample will be transferred to a second plastic bag and sealed to be later placed in cold storage prior to its analyses for bromide residues using protocol METH007.00 (Pinera-Pasquino, 2008).

  Soil to be analyzed for textural composition using protocol METH004.00 (Dietrich, 2005), total organic carbon content using protocol METH005.00 (Gunasekara, 2006), and background bromide residues using protocol METH007.00 (Pinera-Pasquino, 2008) will be sampled to a depth of 3 feet at 6-inch increments with standard bucket augers using soil sampling protocol FSSO002.00 (Garretson, 1999). Soil to be analyzed for bulk density and initial soil moisture content will be collected using a sample ring kit designed to obtain undisturbed soil samples using methods specified by the equipment manufacturer (Soil Moisture Equipment Corp., Santa Barbara, California, USA).

- Sampling from lysimeter reservoirs will consist of extracting all solute from each lysimeter using a self-priming electric pump. Each extraction will be measured for total volume then partitioned into two vessels for pesticide and bromide analysis. The samples will be placed on ice then transferred to refrigerated storage until chemical analysis. Between each solute extraction the pump and its tubing will be flushed with cleansing liquids identical to those used for soil sampling equipment in protocol FSSO002.00 (Garretson, 1999).

VI. CHEMICAL ANALYSIS AND QUALITY CONTROL

Pesticide analysis will be conducted by the CDFA Center for Analytical Chemistry. A multi-analyte method is current for soil-bound and water solubilized simazine, atrazine, diuron, bromacil, norflurazon, hexazinone, the degradates of simazine and atrazine deethylsimazine (ACET), deisopropylatrazine (also ACET), didealkylated triazine (DACT), and the primary norflurazon degradate desmethyl norflurazon (DSMN) (CDFA, 1999). Analytical quality control procedures for these chemicals will follow recommendations from chemistry laboratory quality control protocol QAQC001.00 (Segawa, 1995). Quality control procedures for the analysis of bromide in soil and water will follow those recommended in protocol METH007.00 (Pinera-Pasquino, 2008).

VII. DATA ANALYSIS

The statistical analysis will compare the effect of nanoparticles on the movement of the pesticide residues. For comparing the time course of residues measured in water samples collected from the lysimeters, the statistical model will be a repeated measures mixed model where time and nanoparticle treatment are fixed effects, time is a repeated measure, and soil core is a random variable. Soil core is a random variable because this site represents a subsite of all possible sites. For comparing the soil distribution of residues between treatments, a repeated measures mixed model will again be used where nanoparticle treatment and soil depth are fixed effects, soil depth within each lysimeters is a repeated measure because concentrations between depths are highly correlated, and soil core is again a random variable as previously explained. The SAS procedure PROC MIXED will be used to provide analysis for the models specified in Tables 1 and 2.

Table 1. Mixed Model Table for Lysimeter Soil Core Analysis

Source of Variation	Degrees of Freedom
Treatment (nanoparticles vs control)	2
Soil Depth	5
Treatment x Soil Depth	10
Error	36
Total	53

Table 2. Mixed Model Table for Lysimeter Solute Analysis

Source of Variation	Degrees of Freedom
Treatment (nanoparticles vs control)	2
Time	8
Treatment x Time	16
Error	54
Total	80

VIII. TIMETABLE OF ACTIVITIES

September / October 2013:

- Finalization of nanoparticle study protocol.

July / September 2013:

- Finalization of contract amendment.

September / October 2013:

- Chemical analysis of soil cores for background pesticide and bromide residues.

September / October 2013:

- Installation of irrigation system and verification of uniformity of water application.
- Installation of lysimeters.
- Incorporation of nanoparticles into lysimeter soil.
- Conduct frequent irrigations over study plots (lysimeter and control plots) until all lysimeter reservoirs experience drainage to ensure their functionality and to standardize the soil-water content across all plots.
- Soil coring to characterize soil initial moisture content, bulk density, textural composition, and total organic carbon content.
- Laboratory analysis of soil samples to characterize soil initial soil moisture content, bulk density, textural composition, and total organic carbon content.
- Chemigation of pesticides and potassium bromide.
- First irrigation.

October / November 2013:

- First solute extraction from lysimeters.
- Second irrigation.
- Weekly solute extraction from lysimeters.
- Weekly irrigations.

December 2013:

- Ninth and final solute extraction.
- Soil sampling within study plots for chemical and bromide residues.

January / June 2014:

- Chemical analysis – by DPR.
- Data analysis – by DPR.

March 2014

- Submission of irrigation system report by cooperator

July 2014 / December 2014:

- Preparation of scientific report and research papers for publication – by DPR.

IX. BUDGET

Budget component	Units	Expense/unit ($)	Total expense ($)
Contracted cooperator	1	29,000	29,000
Pesticide soil analysis of background residues	9	864	7,776
QA/QC for background residues	1	864	864
Pesticide soil analysis	54	864	46,656
QA/QC for pesticide soil analysis	5	864	4,320
Pesticide analysis of chemigation solute	1	864	864
QA/QC for pesticide analysis of chemigation solute	1	864	864
Pesticide analysis of lysimeter reservoir solute	81	864	69,984
QA/QC for pesticide analysis of lysimeter reservoir solute	10	864	8,640
Equipment & supplies	1	4,000	4,000
Travel (days)	50	135	6,750
PY	0.25	100,000	25,000
Total			204,718

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Figure 1. Randomized layout of control and lysimeter plots in each experimental site.

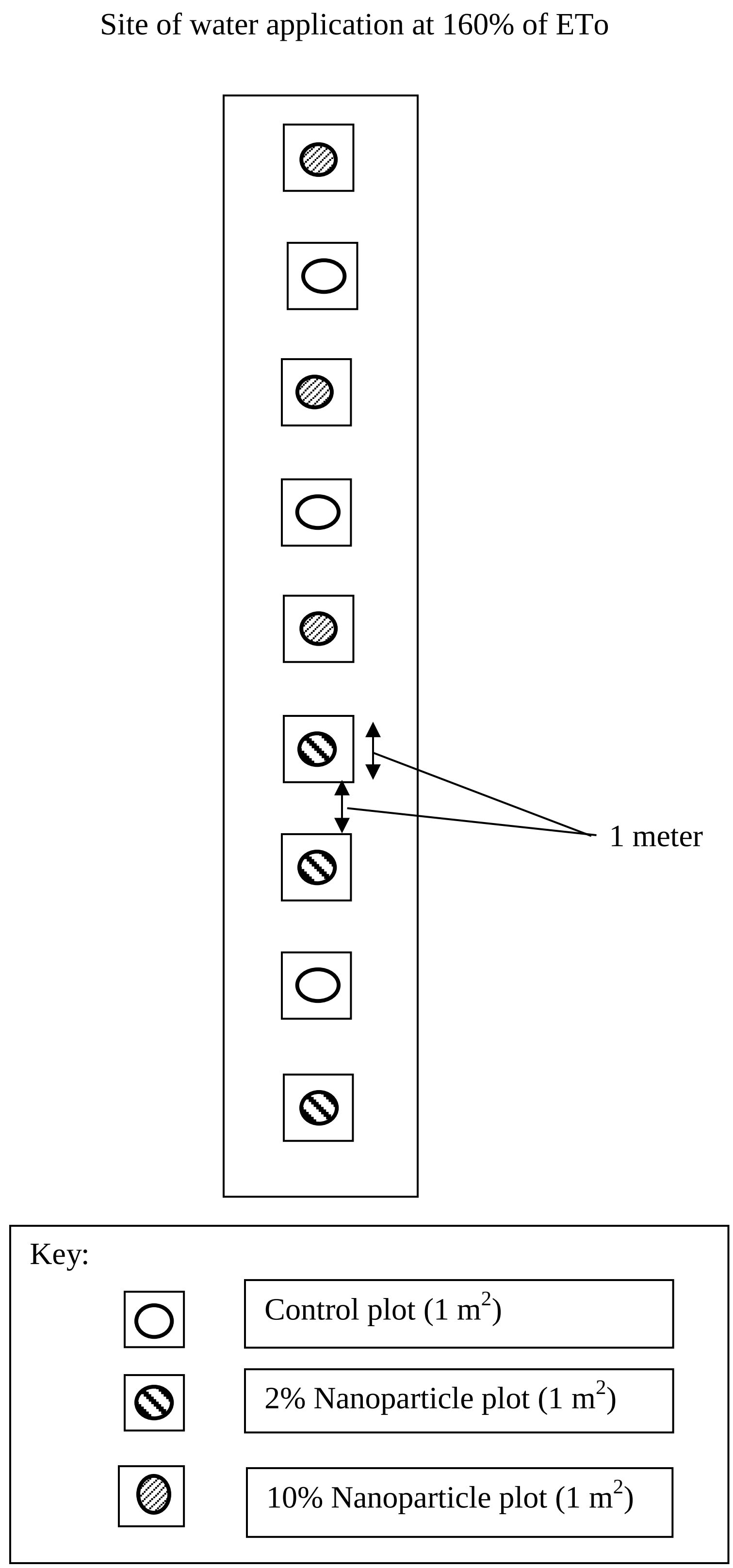

Figure 2. Lysimeter design.