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*Full Length Research Paper*

# Loss of Chlorpyrifos from Plastic Bags used in Commercial Banana Production

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Abstract

**Chlorpyrifos is an organophosphate pesticide used in Costa Rica and other countries around the world for banana and plantain production. In Costa Rica, chlorpyrifos is impregnated into blue plastic bags that are placed around ripening fruit to prevent insect damage to fruit skin. Much is known about chlorpyrifos movement and degradation rates from soils and foliage, but no studies are known on the movement and dissipation of chlorpyrifos from plastic bags. Our objective was to determine the rate of chlorpyrifos loss from plastic bags used in banana production, and to estimate the potential amount chlorpyrifos lost through volatilization or degradation annually in banana production in Costa Rica. Although chlorpyrifos bags were found to be very heterogeneous in chlorpyrifos concentration, approximately 90% of the chlorpyrifos was lost within the first 10 days during 3 replicated experiments, under average daily temperature regimes between 19°C and 30°C. As the vast majority of chlorpyrifos is lost from plastic bags under these conditions, it is estimated than 22.5 metric tonnes of chlorpyrifos and degradation products may lost to the environment, annually during banana and plantain production in Costa Rica.**

**Keywords:** Pesticides, Costa Rica, Agriculture, Latin America, Plantain.

## INTRODUCTION

Chlorpyrifos an organophosphate pesticide registered for use in various fruits and plants cultivation in over 98 countries around the world (Ulrichs et al., 2003). In Costa Rica, and much of Latin America, the pesticide chlorpyrifos is used primarily for both commercial and small-scaled banana and plantain production (Polidoro et al., 2008; Castillo et al., 2012; de la Cruz et al., 2014). Several studies have documented chlorpyrifos in Costa Rican surface waters near banana and plantain production (Polidoro et al., 2008; Castillo et al., 2000; Carvalho et al., 2002).

In many rural areas in Costa Rica, surface waters are used by residents for drinking and other household uses. Van Wendel de Joode et al. (2012) found that 50% of children living near banana plantations had exceeding amounts of chlorpyrifos in their body systems, surpassing the U.S. EPA chronic population adjusted dose. Chlorpyrifos is a neurotoxicant that blocks the red blood cell and plasma acetylcholinesterase (Van Wendelde Joode et al., 2012; Coulston et al., 1972; Kisciki et al., 1999; McCollister et al., 1974; Nolan et al., 1984). Through a metabolic reaction, the production of the chlorpyrifosoxon and inactivation of acetylcholinesterase enzyme drives the overstimulation of the peripheral nerve system leading to muscle weakness and even paralysis in extreme situations (Ulrichs et al., 2003; Giesy et al., 1999).

Eleven major countries import bananas (including the U.S., Japan, Belgium, Luxembourg, France, Germany, the Netherlands, the U.K., Canada, New Zealand, and Switzerland) from 21 banana-exporting countries worldwide (Wilson and Otsuki, 2004).

Australia, South Africa and Spain apply chlorpyrifos as a direct foliar spray on banana plants, while Colombia, Ecuador, Costa Rica, Honduras, and the Philippines use chlorpyrifos-impregnated plastic, generally blue, bags (World Health Organization and Food and Agriculture Organization, 2000). In these latter countries, chlorpyrifos-impregnated plastic bags are kept

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over the ripening fruits for three months to protect the banana skins from cosmetic damage caused by insects, primarily thrips (*Chaetanaphothrips orchidii* Moulton and *C. signipennis* Bagnall, Order Thysanoptera: Family Thripidae). In general, farmers receive a better price for export quality fruit, if the bananas do not appear cosmetically damaged by insects or various animals (Polidoro et al., 2008).

As a pesticide that has been in use for several decades, the toxicity and environmental behavior of chlorpyrifos are fairly well-known (Barron and Woodburn, 1995; Racke, 1993; Giesy and Solomon, 2014). With a relatively high octanol-water partition coefficient ($K_{ow}$) chlorpyrifos is relatively slowest to dissipate and degrade in the soil environment, with half-lives reported from 2 weeks to over a year depending on soil type and climate (Racke 1993; Giesy and Solomon, 2014; Das and Adhya, 2015). Possible degradation pathways in soils include photo-induced reactions on the surface (Howard, 1989), hydrolysis, de-chlorination, and oxidation (Walia et al., 1988). The products of chlorpyrifos oxidation and de-chlorination undergo photolysis to form the main degradation product known as the chlorpyrifosoxon. Chlorpyrifos degradation may be delayed in soils with history of chlorpyrifos applications due to resistance to enhanced degradation by microbes (Racke and Coats, 1988).

In surface waters, chlorpyrifos undergoes abiotic hydrolysis and photosensitized oxidation to produce thiophosphate (TCP) and other degradation products (Howard, 1989; Macalady and Wolfe, 1983; Schimmel et al., 1983). Its relatively low solubility and moderate vapor pressure promotes relatively rapid volatilization of non-sediment bound chlorpyrifos from water surfaces. Although increased temperature plays a major role in the increased degradation rates of chlorpyrifos, the amount of sunlight does not appear to have a significant effect (Frank et al., 1991). Once in the air, chlorpyrifos can degrade rapidly through photo-oxidation to form the chlorpyrifosoxon.Once in the vapor phase, the half-life of chlorpyrifos may be 2.6 days or less (Atkinson, 1987; Fontaine and Teere, 1987). Although little is known on the environmental behavior of the two primary degradation products of chlorpyrifos, TCP and the chlorpyrifos-oxon, the chlorpyrifos-oxon is estimated to be more toxic than the parent form (Tiwari and Guha, 2014; Wang et al., 2010; Sparling and Fellers, 2007).

Understanding pesticide movement and degradation rates from the point of application is necessary for calculating the overall mass balance and environmental load of pesticides in surrounding soil, water and air resources that can impact public and ecosystem health (Lacher and Goldstein, 1997; Dinham and Malik, 2003; Maroni et al., 2006).Thus, as no studies are known to have examined loss rates of chlorpyrifos impregnated in plastic bags, our overall objectives were to: 1) to determine the rate of chlorpyrifos loss at various temperatures from plastic bags used in commercial banana production throughout Latin America, and 2) to estimate the potential environmental emissions of chlorpyrifos (including potential degradation products) to the atmosphere in banana production in Costa Rica.

## MATERIAL AND METHODS

Chlorpyrifos-impregnated plastic bags used in banana production were obtained from a commercial agrochemical distributor in San Jose, Costa Rica. Bags were sub-sampled in 1 $cm^2$ sections in a horizontal (n=9) and vertical (n=9) transect to determine the average amount of chlorpyrifos present in a single bag. Three experiments were conducted in an outside gated area at Arizona State University, in Phoenix, Arizona (September 2014, November 2014, and February 2015). For each experiment, between 3 and 6 bags were hung on clotheslines, and secured with clothespins. Bags were sampled daily or bi-weekly for up to 4 weeks. Sampling consisted of cutting replicate 2 $cm^2$ randomly selected subsamples of each bag. Daily temperatures, windspeed and precipitation were obtained from National Oceanic and Atmospheric Administration (2015) (Figure 1). In September 2014, outside temperatures averaged 30$^oC$, with a maximum high of 39$^oC$ and low of 25$^oC$.In November 2014, the daily average temperature was 21°C, with a high of 27$^oC$ and a low of 15$^oC$, and in February 2015 the average temperature was 19 °C, with a high of 25$^oC$ and a low of 10$^oC$. There was approximately 0.25 cm of precipitation during the September 2014 experiment, and no precipitation recorded during the November 2014 and February 2015 experiments.

All plastic bag subsamples were submerged in 20mL of a 1:1 mixture of acetone and hexane, and placed on a mixing rotary for 48 hours. The surrogate p-terphenyl was added to each bag sample to allow for quantification of method recoveries (90-92%). After rotary mixing, each sample was blown down to a volume of 1 mL using nitrogen gas, and passed through sodium sulfate to remove any polar compounds. Several laboratory blanks were included for each experiment, and decacosaned50 was added to all final extracts as an internal standard to standardize final extract volumes. All sample extracts were analyzed by GC-MS, and quantification results confirmed using a pure standard of Chlorpyrifos, with detection limits of approximately 0.1 µg/mL. It is important to note that key degradation products (such as the chlorpyrifosoxon as it is likely the main degradation product from photodegradation) are not available as pure standards for confirmation and quantification. However, based on chlorpyrifos molecular weight (350.6 g/mol) and the primary quantification ions (258 and 97) confirmed by pure chlorpyrifos standard in the mass spectra, the potential presence of the chlorpyrifos oxon (molecular weight 334 g/mol) was not detected. This suggests that the dominant mechanism of chlorpyrifos

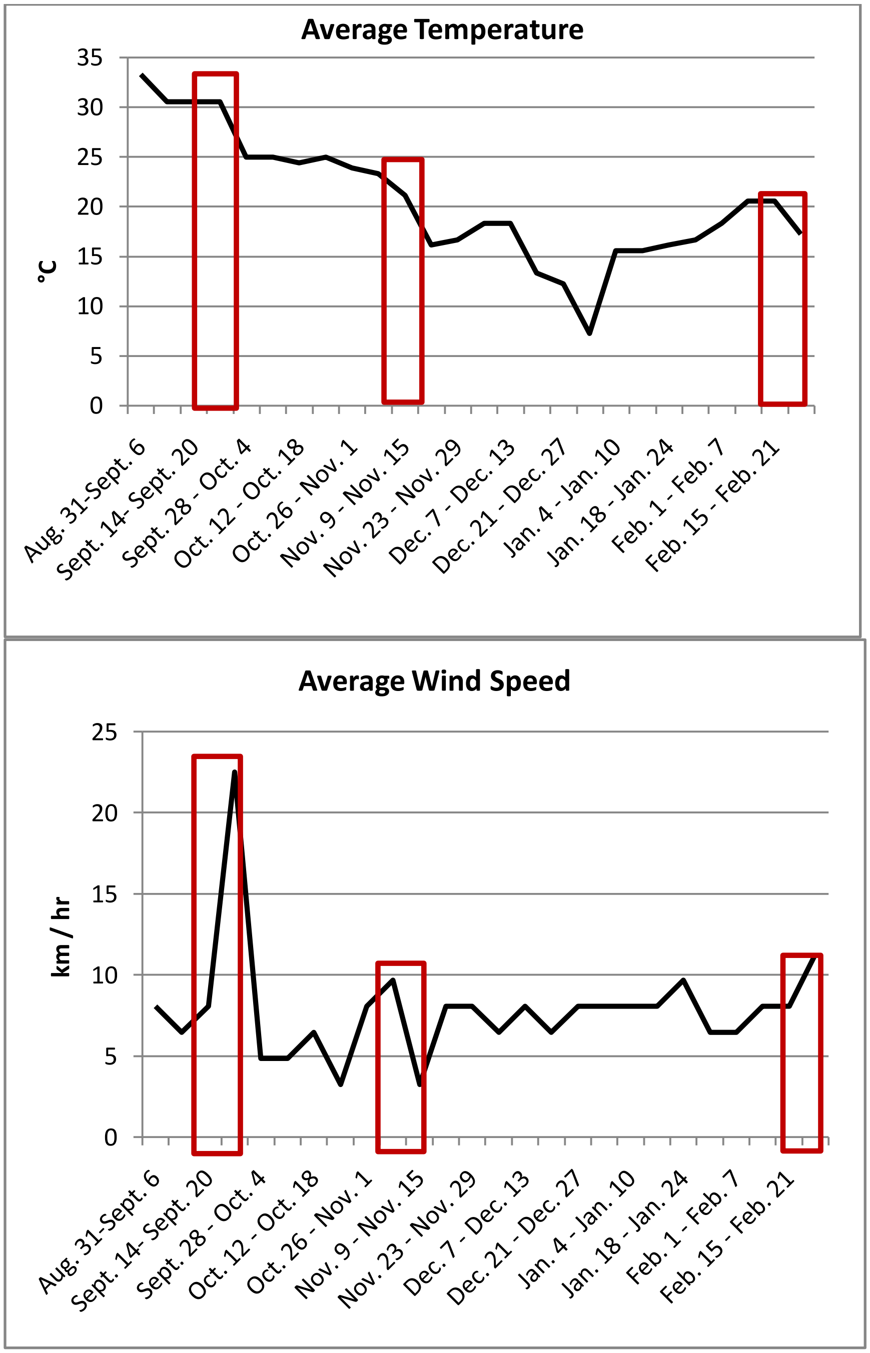


**Figure 1.** Climatic conditions during field experiments that demonstrate the average temperatures, precipitation and wind speed. Boxes indicate the real time of the experiments against the full months

loss in these experiments may be volatilization from the bags, rather than photo degradation on the bags.

## RESULTS

Results from the bag transects, found that the concentration of chlorpyrifos is highly variable both horizontally and vertically across the bags. Average chlorpyrifos concentration was determined to be 38.5µg/cm$^2$ (+/- 15.7) (Figure 2). Based on standard bag dimensions (89cm x132 cm), overall average chlorpyrifos concentration per bag was calculated to be about 450 mg (+/- 183 mg). Considering there are approximately 1,000 plants per hectare cultivated in more than 50,000 hectares of production (Polidoro et al.,

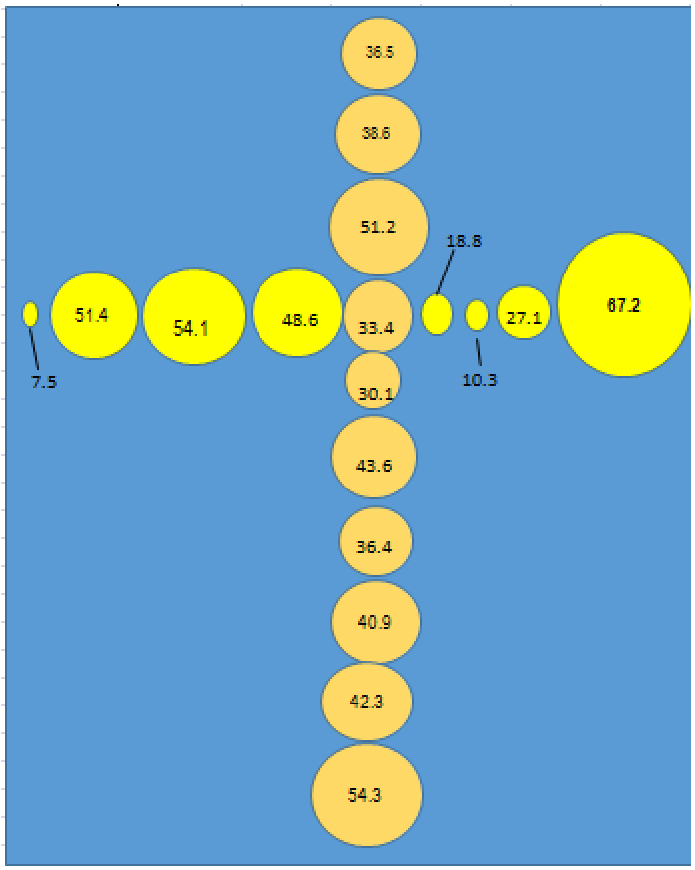


**Figure 2**. Example of variation in chlorpyrifos concentration (µg/cm$^2$) in a vertical and horizontal transect in a chlorpyrifos-impregnated plastic bag.

2008), about 22.5 metric tons of chlorpyrifos (including degradation products) is potentially emitted annually from banana production in Costa Rica.

In each of the three experiments conducted, all chlorpyrifos was found to have been lost from the bags within the first 10 days (Figure 3). During the hottest experimental period (September 2014) chlorpyrifos appeared to have been lost to volatilization (or completely degraded to chlorpyrifosoxon or other products) in the first five days. During the coolest period (February 2015) the rate of chlorpyrifos loss was slower, but showed complete loss within 10 days.

## DISCUSSION

As chlorpyrifos-impregnated bags are placed over ripening banana fruits for a period of 3 months, it was hypothesized that the chlorpyrifos would remain effective in protecting against insect damage over the entire time period. With its relatively high $K_{ow}$ and affinity for hydrophobic regions of organic matter in soils and sediments (Racke 1993), it was assumed that chlorpyrifos in plastic bags (which are also hydrophobic) may also exhibit relatively slower volatilization and degradation rates than chlorpyrifos found on water surfaces. However, rates of chlorpyrifos loss observed during these experiments were similar to volatilization rates that have been observed from surface waters (i.e. 3.5 to 20 days, Racke, 1993), likely due to relatively rapid volatilization and/or photodegradation upon atmospheric exposure.

The results presented here indicate that under similar warm-weather conditions in Costa Rica or other banana producing nations in Latin America, the protective nature of the chlorpyrifos-impregnated bags to prevent cosmetic fruit skin damage may be more related to the physical barrier presented by the plastic bag itself, rather than the efficacy of the pesticide over the 3 months. In fact, in organic banana production, clear plastic bags (without pesticides) are placed over ripening fruit for 3 months to achieve relatively the same effect (Polidoro 2007). Damage to organic banana skins may occur at later stages during packing and transportation, in the absence of post-harvesting fungicides or insecticides.

As weather conditions in Arizona are certainly drier and sometimes warmer than in Costa Rica, similar in-

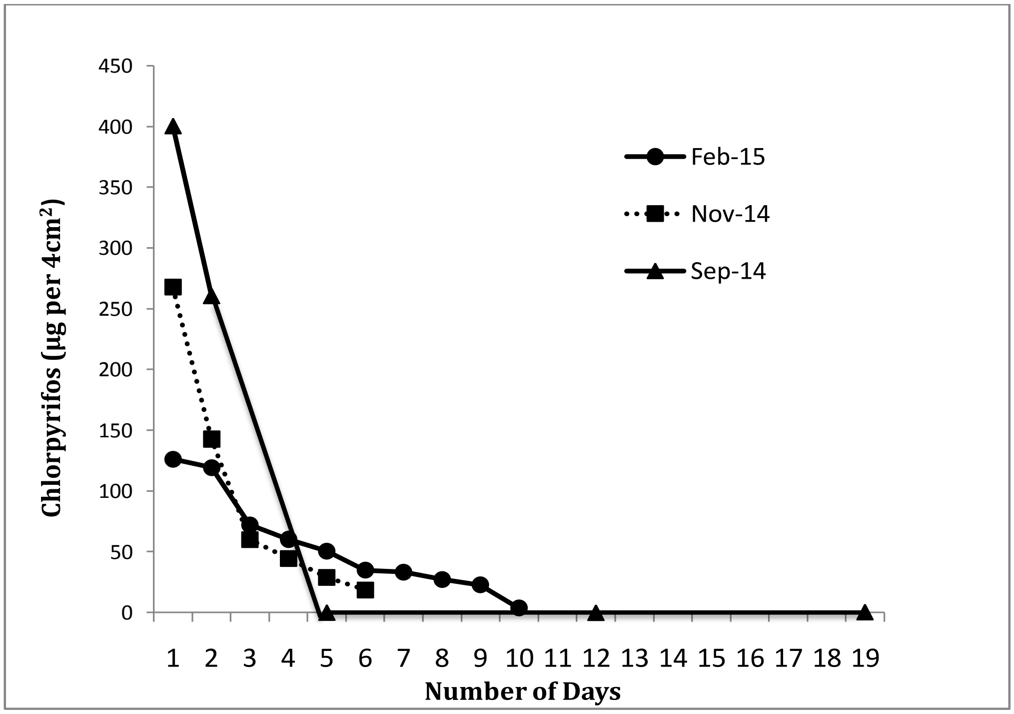


**Figure 3.** Average amount of chlorpyrifos(µg/4cm$^2$) in sampled plastic bags over experimental days.

situ experiments should be conducted in Costa Rica to further validate results. Given that approximately 22.5 metric tons of chlorpyrifos (including degradation products) are potentially emitted into the environment annually in commercial banana production in Costa Rica and all parent chlorpyrifos appears to be lost from the plastic bags in less than 10 days, more studies are needed to determine if the bags themselves (or an alternative) can provide physical protection from insects without pesticide impregnation in commercial grade fruit. Finally, as the skin itself is not consumed and is only important for cosmetic or aesthetic value, global consumers should be made more aware of the potential environmental and human health impacts of pesticides such as chlorpyrifos that are used in conventional banana production.

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