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Chlorpyrifos – Methyl Degradation in Soil and Human Exposure

Environment

KEYWORDS : pesticide, chlorpyrifos-methyl, degradation in soil, exposure dose

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ABSTRACT

Synthetic pesticides are one of the most widespread methods used for pest control in agriculture. Chlorpyrifos-methyl is commonly used in Romania, and it is classified as an organophosphorus non-carcinogenic substance used to control insects, by inhibiting the activity of acetylcholinesterase. This study's aim was to monitor the degradation of chlorpyrifos-methyl pesticide after spraying directly on vegetation-free soil, under natural conditions, and to calculate the exposure dose through ingestion and dermal contact. The presence of pesticides in the vegetation-free soil was detectable even after 133 days following the time of use. After 49 days, significant chlorpyrifos-methyl concentration differences ($p<0.05$) had been recorded for the two soil depths (0-5 cm and 30 cm), suggesting a high degree of retention in the soil surface in question. After this period of time, the concentration's trend was to equalize. No significant differences between chlorpyrifos-methyl concentrations collected from 0-5 cm and 30 cm depths had been found after 133 days. The calculated oral and dermal exposure doses, as well as the cumulative dose, were significantly lower than ADI for adults and children.

INTRODUCTION

Chlorpyrifos-methyl (O,O-dimethyl O-3,5,6-trichloro-2-pyridinyl phosphorothioate) is an organophosphatic pesticide used to control insects on fruits, vegetables and cereal plants. Abiotic factors (temperature, moisture, soil pH, etc.), plant species and/or microbial community, pesticide characteristics (hydrophilicity, pKa/b, etc.), biological and chemical reactions determine the pesticides metabolic fate. (Kazemi et al., 2012, Topp et al., 1997). Among others, the soil properties that affect the pesticide movement are: structure, texture, amount of organic matter or clay minerals, etc. These factors will affect both the soil's ability to retain water and its degradation. Sandy soils retain less water than clay or organic soils. The heavier the soil is, the lower the leaching potential will be. (Brady & Weil, 1999).

Chlorpyrifos-methyl is susceptible to aqueous hydrolysis (half-lives of 27 to 13 days at pH 4 through pH 9) (MacBean, 2008-2010), therefore it is assumed that abiotic hydrolysis of moist soils is an important process linked to its fate in the environment. The half-life degradation (both abiotic and biotic) of chlorpyrifos-methyl was measured in soils incubated in a greenhouse at 23-26°C; degradation results consist in 7, 6, 6, and 11 days in sandy and agricultural soils, organic-rich orchard soils and volcanic ones. (HSDB).

Chlorpyrifos-methyl is classified as an organophosphorus non-carcinogenic substance used to control insects, which inhibit the activity of acetylcholinesterase. The Acceptable Daily Intake (ADI) of chlorpyrifos-methyl is of 0-0.01 mg/kg body weight (b.w.), agreed at the joint FAO/WHO (WHO) Conference on Pesticide Residues (JMPR), where the compound was evaluated in 1975, 1991 and 1992. (WHO, 2009).

This study's aim was to monitor chlorpyrifos-methyl pesticide degradation after spraying directly on vegetation-free soil, under natural conditions, and to calculate the exposure dose through ingestion and dermal contact.

MATERIALS AND METHODS

The experiment of chlorpyrifos-methyl pesticide degradation in soil was performed in a rural agricultural range of 225 m^2, outside the built-up area of Sâncraiu village, where no pesticide had been used for more than 10 years. On this area, five sampling points, of 1m^2 each, had been chosen, and the vegetation was removed the day before the soil was dug up to about 20 cm. Before spraying with chlorpyrifos-methyl, the first set of soil sample was collected out of the five sampling points, from 0-5 cm and 30 cm depth.

In order to monitor the pesticide degradation in soil, a hand-pump spraying RELDAN EC 22 insecticide, having 225 g/l chlorpyrifos-methyl as active substance (we used 100 ml RELDAN 22 EC with 10 l water), was performed from 30 cm height, with the nozzles oriented downwards.

The second set of soil samples was collected 30 minutes (day 0) after spraying the pesticide on the five sampling points, from 0-5 cm and 30 cm depths, namely a total of 10 soil samples. In order to follow the chlorpyrifos-methyl degradation in soil, the samples were collected after 7, 21, 49 and 133 days following the pesticide use. A total of 60 soil samples had been collected during the experiment and transported in insulated boxes to the laboratory and stored in a refrigerator until analysis.

In order to determine the chlorpyrifos-methyl pesticide in soil, the Sánchez-Brunete C et al (2004) method was adapted. The columns for polypropylene extraction were prepared by placing two circles of filter paper at basis, the lower orifice was obstructed and 5 g of soil sample sieved through the 2 mm sieve were added. The soil samples were extracted with 4 ml of ethyl acetate for 15 minutes in an ultrasonic water bath at room temperature. After extraction, the solvent was filtered and collected in tubes. The soil samples were extracted once again with another 4 ml of ethyl acetate (15 min.). The extraction solvent was filtered and the soil samples were washed with 1 ml of additional solvent. The total extracts collected in tubes were concentrated with a weak nitrogen flow to a volume of 1 ml and stored at 4°C until analysis by GC-MS. The analysis by GC-MS was performed with a gas chromatograph equipped with an automatic split/splitless injector and a mass spectrometer with detector Shimadzu GCMS-QP2010 Plus NCI. Separation of compounds was performed in a fused silica capillary column (TG-5MS), 5% phenyl polysiloxane as non-polar stationary phase (30 m, 0.25 mm internal diameter and 0.25 µm film thickness).

Quality control was performed with blank samples analysis and control sample analysis of known concentration for each set of tests. The blank samples were below the method's determination limit (0.005 µg/ml) while the control samples were within the range of $X_{0 \pm 2*s}$, where X_0 is the average standard solution determinations of 3.0 µg/ml performed in days and s is their standard deviation.

In addition to chlorpyrifos-methyl pesticide, the following indicators were determined from the soil samples: pH in accordance with SR 7184-13/2001 and humidity (dry matter) in accordance with ISO 11465/1998; physical properties: bulk density (STAS 1913/3-76), grain-size (STAS 1913/5-85), adsorption capacity (STAS 1913/2-88) and organic matter (STAS 7107/1-76).

The daily intake and the doses of oral and dermal exposure (hands) for chlorpyrifos-methyl in soil were calculated with the Exposure Dose Calculator program, developed by ATSDR within the Center for Disease Control and Prevention, for a target population: children between 1 and 6 years old with a body weight of 16 kg and adults between 19 and 65 years old and a body weight of 70 kg. For children with Pica disorder, ages 1 to 6 and a body weight of 16 kg, only oral exposure doses were calculated.

The standard soil intake rates predetermined by the ATSDR program were used in the calculation model (100 mg/day - adult, 200 mg/day - child and 5000 mg/day - child with pica behavior). The exposure factor represents how often and for how long a population is exposed to contaminated soil and takes into consideration the frequency, duration and time of exposure (ATSDR, 2005). In this case, the exposure factor is equal to 1, representing a daily exposure. The body weight is used in the equation for calculating the exposure dose, because when exposed to the same amount of a substance, people with a lower body weight will receive a relatively higher dose of substance in comparison to people with a higher body weight.

The total attached soil depends on the exposed skin surface, which is different for each age group. The current study took into consideration that hands are the most likely and frequent skin surface that may come in contact with chlorpyrifos-methyl.

The bioavailability factor represents the amount of the substance absorbed in a person's body and it is a percentage of the total amount of the substance that actually enters into the blood and is available to affect a person. In this case, the bioavailability factor is equal to 1, representing 100% of the total amount.

The exposure factor depends on the frequency and duration of exposure and for this study it has been estimated that the population is exposed to chlorpyrifos-methyl 20 days during one year.

Student's t-test and Pearson's R Correlation Test were used for ANOVA statistical processing.

RESULTS

In the very first part of the experiment, the initial soil status regarding the presence of chlorpyrifos-methyl pesticide, was characterized by a concentration below the detection limit of the analytical method (<0.02 mg/kg dry matter).

After using Reldan 22EC pesticide, Chlorpyrifos-methyl, concentrations in soils (collected from 0-5 cm and 30 cm) decreased in time. (Figure 1).

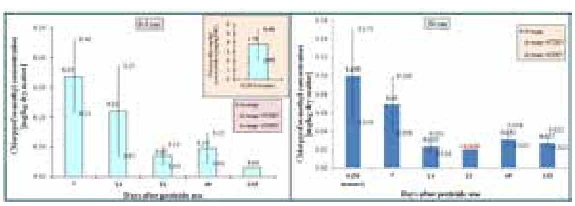

Figure 1. Average concentrations +/- SD of chlorpyrifos-methyl in soil (0-5 cm and 30 cm) after pesticide spraying

Most of chlorpyrifos-methyl pesticide in soil samples collected at 0-5 cm degraded within the first 7 days, from an average concentration of 3.781 mg/kg DM, it reached an average of 0.338 mg/kg DM after 7 days, that is a concentration eleven times lower (t=4.53, p=0.01), while after 133 days it reached an average of chlorpyrifos-methyl concentrations 120 times lower (t=4.95, p=0.008).

The average of chlorpyrifos-methyl concentration in soil samples collected from 30 cm depth, after 30 minutes (day 0) following the pesticide use, was 0.10 mg/kg DM and reached a concentration 1.6 times lower (0.07 mg/kg DM) after 7 days from the pesticide use and 3.3 times lower after 133 days. Chlorpyrifos-methyl concentrations were lower at 30 cm depth than the soil samples collected at 0-5 cm depth.

Student's "t" test showed significant differences between the average concentrations of chlorpyrifos-methyl pesticide dependent on the sampling depth at 30 minutes (t=4.85, p=0.008), 7 days (t=4.69, p=0.005) and smaller differences at 14 (t=2.48, p=0.05), 21 (t=3.23, p=0.032) and 49 (t=2.78, p=0.05) days. For samples collected after 133 days, there were no significant differences dependent on the sampling depth (t=1.73, p=0.14).

Figure 2 shows the degradation rate of chlorpyrifos-methyl pesticide dependent on the sampling time. The zero value is regarded as the initial concentration (i.e. the pesticide concentration in soil at 30 minutes). During the study period, a decrease in concentrations was observed, in the case of the maximum measured concentrations being more pronounced than in the case of average and minimum values.

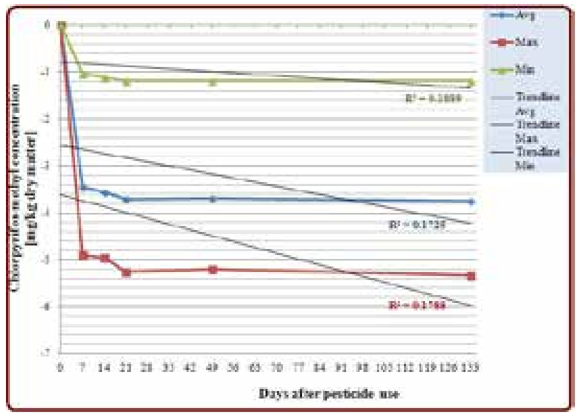

Figure 2. Degradation rate of chlorpyrifos-methyl pesticide in soil (0-5 cm)

According to FAO 2000, chlorpyrifos-methyl pesticide is classified as an easily degradable pesticide (DT50<20 days) (FAO 2000). In this study, although the first measurement was performed after a week, the estimated half-life is less than 7 days, most likely about 3 days.

Figure 3 shows the relationship between chlorpyrifos-methyl concentrations and soil properties (R^2=0.04-0.085) after 7, 14 and 21 days following pesticide use. In these situations, soils (from 0-5 cm) with high clay content had higher pesticide concentrations, while the soil with higher sand content, had lower concentrations of chlorpyrifos-methyl.

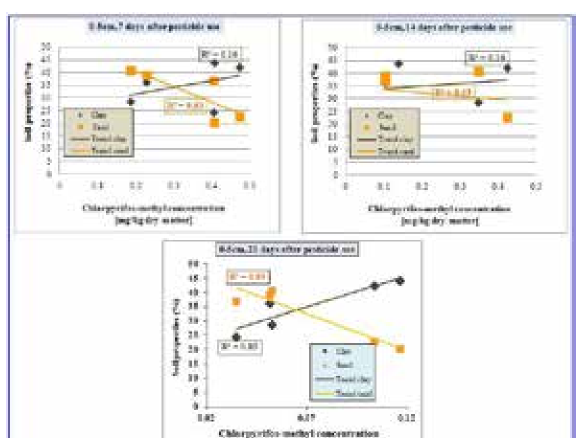

Figure 3. Regression line between chlorpyrifos-methyl concentrations and soil properties (% clay, % sand) in soil samples collected from 0-5 cm depth after 7, 14 and 21 days

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following pesticide use.

After 0, 49 and 133 days following pesticide use, soil samples (from 0-5 cm) with high clay content had lower pesticide concentrations, while soils with higher sand content had higher concentrations of chlorpyrifos-methyl.

After 30 minutes, the pesticide entered quicker in sandy soils, therefore the concentration increased in soils with higher sand content, while in soils with higher clay content, there were lower concentrations, because the substance penetrated slower in it. After 7, 14 and 21 days, higher concentrations were identified in clay soils because they better retain pesticides than sandy soils. After 49 days, in soils with high clay content, there were lower concentrations and after 133 days the concentrations almost reached the detection limit of the device and there was no correlation between pesticide concentrations and percentage of clay and sand in soil.

Also, for the 30 cm depth, the relationship between chlorpyrifos-methyl concentrations and soil type was similar to that described for the surface soil during a period of 7-21 days after use. After 14 and 21 days, chlorpyrifos-methyl concentrations were lower than the detection limit of the method (<0.02 mg/kg dry matter). The substance was measured again after 49 and 133 days, even though the concentrations had been very close to the detection limit. For soil samples collected from 30 cm depth, a negative correlation was found between chlorpyrifos-methyl concentrations and the percentage of clay, but there was a positive one with the percentage of silt content in soil, namely for soils with a higher percentage of clay, there had been lower concentrations of chlorpyrifos-methyl and for a higher percentage of silt, there had been higher concentrations of pesticides, due to the silt's permeability. .

Another factor that interferes in mobility and degradation of substances is the pH. As a result of the measurements performed before pesticide use, the soils analyzed may be characterized as slightly acidic with a pH between 5.87 at the surface and 5.8 at depth. During the experiment, the soil pH had a tendency to decrease, so after 133 days, surface soil pH had an average value of 5.01 and 5.07 at 30 cm depth, soils maintaining the slightly acidic characteristics. This experiment showed that the presence of the pesticide in soils changed the pH. Pearson-Bravais "r" index indicated that only after 14 and 49 days there had been a negative correlation (r=-0.81, r=-0.63, respectively) between chlorpyrifos-methyl concentrations and pH in soil samples collected from 0-5 cm, meaning that there were higher concentrations of pesticides at a lower pH.

The water content in soil samples reported to mass was between 6.91% and 32.47%. A positive Pearson-Bravais correlation between soil moisture and chlorpyrifos-methyl concentration was found only in soil samples collected after 133 days both from 0.5 cm and 30 cm (r=0.52, r=0.85).

Soil samples collected from 0-5 cm had a lower density (0-1.08 g/cm^3) in comparison with soil samples collected from 30 cm (1.08-1.12 g/cm^3). A decrease of chlorpyrifos-methyl concentrations along with increasing soil density in samples collected from 0-5cm after 7, 14 and 21 days were observed. In case of samples collected from 30 cm, this relationship is highlighted only after 30 minutes following the pesticide's use. For soil samples collected from 0-5 cm, after 30 minutes, 49 and 133 days, there was no correlation between concentrations and density because during the first 30 minutes, the pesticide dispersion in soil had been reduced and also after 49 and 133 days there had been only traces of chlorpyrifos-methyl. For soil samples collected from 30 cm on the 14th day and 21st day, concentrations were below the detection limit.

Based on the lowest, highest and average concentrations of chlorpyrifos-methyl measured in soil at different time intervals during the experiment, the daily intake by ingestion and dermal contact was calculated for children, children with Pica disorder and for adults. The daily doses obtained in each case were compared with the acceptable daily intake (ADI) (WHO 2009).

Figure 4 shows that cumulated exposure doses calculated for both oral and dermal pathways decreased for adults and children according to the concentrations considered after 7, 14, 21, 49, and 133 days following pesticide use. Thus, in the case of children, for the pesticide concentrations measured in soil from 0-5 cm, in the last stage of the experiment (133 days), the oral exposure dose was between 3.70E-07 mg/kg/day and 4.11E-07 mg/kg/day, unlike adults for whom the same daily dose ranged from 4.23E-08 mg/kg/day to 4.70E-08 mg/kg/day. Children with Pica disorder recorded the highest exposure doses, ranging between 1.03E-05 mg/kg/day and 9.25E-06 mg/kg/day, representing 0.09% and 0.1% of ADI, and this fact decreases enormously the health risks. Regarding dermal exposure, it laid in the limit of the same magnitude order, both for children and adults (E-09), with differences between 3.28 mg/kg/day and 3.65 mg/kg/day.

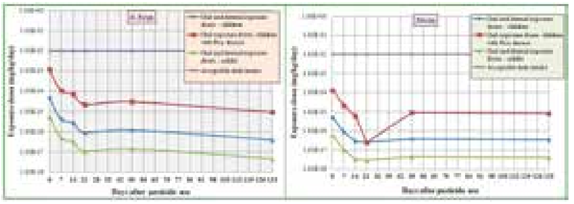

Figure 4. Oral and dermal exposure doses to average concentrations of chlorpyrifos-methyl in soil (0-5 cm and 30 cm) to children, children with Pica disorder and adults - a comparison with the acceptable daily intake

For soil samples collected from 30 cm depth, greater differences were observed between the estimated daily intake and ADI in comparison with soil samples collected from 0-5 cm depth.

CONCLUSIONS

The presence of pesticides in the vegetation-free soil was detectable even after 133 days after their use. In this case, the half-life (DT50) was shorter than 7 days. The chlorpyrifos-methyl concentration after 7 days was 11 times lower in the case of surface soil and only 1.6 times lower in soil depth. Chlorpyrifos-methyl concentrations recorded significant differences (p<0.05) between 0-5 cm and 30 cm after 49 days following pesticide use and this fact suggests the high degree of retention on the soil surface in question, and after this period of time, a tendency to equalize concentrations appeared (surface-depth). No significant differences were found after 133 days between chlorpyrifos-methyl concentrations collected from 0-5 cm and 30 cm depths. In this experiment, the persistence of chlorpyrifos-methyl for a long time was due to the clay soil (high density) and slightly acidic type (pH), which favors retention (adsorption) delaying the degradation process particularly in soil depth.

Considering the soil intake preset through ingestion, the oral exposure dose calculated by ATSDR toxicological model is 1-2 orders of magnitude higher than dermal exposure dose, regardless of the considered pesticide concentration in soil. The calculated oral and dermal exposure doses, as well as the cumulative dose, were significantly lower than ADI for adults and children. Regardless of pesticide concentration in soil, children reached an exposure dose with an order of magnitude higher than adults (expressed as a percentage of ADI).

The highest daily exposure doses were calculated for children with Pica disorder. In their case, only the exposure by this pathway represents up to 16.8 % of ADI.

REFERENCE

[1]ATSDR (Agency for Toxic Substances & Disease Registry), (2005), Public Health Assessment Guidance Manual, U.S. Department of Health and Human Services, Public Health Service Atlanta, Georgia 357, http://www.atsdr.cdc.gov/hac/PHAManual/appg.html. | [2]Brady, N., & Weil, R., (1999), The nature and properties of soils. New Jersey, U.S.A | [2] FAO, (2000), Assessing soil contamination, a reference manual, FAO Pesticide disposal series 8, Rome | [3]HSDB - Hazardous Substances Data Bank [Internet]. CHLORPYRIFOS-METHYL, U.S. National Library of Medicine, Toxicology Data Network (TOXNET), http://toxnet.nlm.nih.gov/cgi-bin/sis/search/a?dbs+hsdb:@term+@DOCNO+6981. | [4]Kazemi, M., Tahmasbi, A. M., Valizadeh, R., Naserian, A. A. and Soni, A. (2012), Organophosphate Oesticides: A General Review. Agric. Sci. Res. J., 2: 512- 522. | [5] MacBean, C. (2008-2010), ed; e-Pesticide Manual. 15th ed., ver. 5.1, Alton, UK; British Crop Protection Council. Chlorpyrifos methyl (5598-13-0) | [6] Sánchez-Brunete, C., Albero, B., Tadeo, JL. (2004), Multiresidue determination of pesticides in soil by gas chromatography-mass spectrometry detection, J Agric Food Chem.; 52(6):1445-51. | [7]SR 7184/13-2001: Soil quality. pH determination. | [8]SR ISO 11465-1998: Soil quality. Determination of the dry matter and water content, reported to mass. Gravimetric method. | [9]STAS 1913/3-76: Determination of soil density. | [10]STAS 1913/5-85: Determination of grain-size. | [11]STAS 1913/2-88: Determination of soils adsorption capacity. | [12]STAS 7107/1- Determination of organic matters. | [13] Topp, E., Vallaeys, T., Soulas, G. (1997), In: van Elsas, J.D., Trevors, J.T.,Wellington, E.M.H. (Eds.), Modern Soil Microbiology. Marcel Dekker, New York, pp. 547–575. | [14] WHO (World Health Organization), (2009), Inventory of evaluations performed by the Joint Meeting on Pesticide Residues (JMPR) CHLORPYRIFOS-METHYL, Pages 155–202. Retrieved from (http://apps.who.int/pesticide-residues-jmpr-database/pesticide?name=CHLORPYRIFOS-METHYL) |