Detection of Dichlorvos Residue in Cowpea Grains, Six Months after Application Using High Performance Liquid Chromatography

ABSTRACT

In Kano State Nigeria, especially at the famous Dawanau grains market, dichlorvos (DDVP: 2, 2-dichlorovinyl dimethyl phosphate), which is a synthetic organophosphate insecticide is being widely used against stored insect pests of cowpea grains by traders and merchants alike. High Performance Liquid Chromatography (HPLC) screening using commercially available brand of such an organophosphate insecticide was carried out in a Chemistry Laboratory at Bayero University Kano in 2014. This was aimed at determining the presence or absence of the insecticide in the treated and untreated grains of cowpea before, day one and six months after application. The analysis was carried out using an Agilent 1260 Quadpump HPLC, equipped with diode array detector, autosampler and thermostetted column compartment. The result was processed using Agilent Chemstation software. Dichlorvos detection was achieved at 214 nm, while the overlaid chromatograms suggested the presence of DDVP: 2, 2-dichlorovinyl dimethyl phosphate in the test sample relative to the chromatogram of the standard commercial sample at a retention time of 2.163 and 2.283 minutes, respectively. The peak of the target compound was visibly not present in the control chromatogram at the stated retention time. In conclusion, detection of dichlorvos in grains six months after application highlights among others, the dangers and/or disadvantages associated with the use of the chemicals for the protection of stored cowpea grains against insect pests especially by the personnel lacking requisite knowledge on the appropriate ways of handling/application of such synthetic products for both human and environmental safety.

Keywords: [Dichlorvos, Organophosphate, Agilent 1260 Quadpump HPLC, chromatogram, autosampler, DDVP: 2, 2-dichlorovinyl dimethyl phosphate and diode array detector}

1. INTRODUCTION

Food security in sub-Saharan Africa largely depends upon improved food productivity through the use of sustainable agricultural practices and the reduction of post-harvest losses caused by pests and diseases [1, 2]. According to [3] pests and diseases pose the greatest threat to increased food production during storage and handling. Before harvest, insects cause about 15 – 100% crop damage, while storage losses in food grain range between 10 – 60%. Storage insect pests cause substantial damage to the stored grain [4]. However, [5] pointed out that to ensure high food quality and standards acceptable to the consumer, quality control, including good storage and handling practices must be observed at all stages. Managing stored grains requires the use of various techniques to ensure that the quality of the stored grains does not deteriorate over time. These measures include: the use of sanitation; storing sound, whole and dry grain; managing temperature and aeration; including the use of chemical protectants, regular sampling, and fumigation [6].

Pesticide usage in developing nations like Africa has increased dramatically in recent times with adverse effects on humans and other non-target organisms [7]. Misuse of highly toxic pesticides, coupled with a weak or a totally absent legislative framework in the use of pesticides are reasons for the high incidence of pesticide poisoning in developing countries [8]. Unintended exposure to pesticides can occur during their manufacturing, formulation and application or from environmental residues after application [9]. The use of pesticides in grains storage becomes more intensive in the Northern part of Nigeria especially at Dawanau grains market in Kano State, which is viewed as the largest grain market in West Africa. The cowpea grain farmers and traders' ignorance about pesticide toxicity led to its misuse: abusive application, inadequate usage, etc. [10].

Dichlorvos (2, 3-dichlorovinyl dimethyl phosphate) is one of the classes of insecticides referred to as organophosphates used to control households and stored products insects. It is effective against mushroom flies, aphids, spider mites, caterpillars, thrips, and white flies in greenhouse, outdoor fruits, and vegetable crops [11, 12]. Therapeutically, dichlorvos is used as a fumigant or to treat a variety of parasitic worm infections in dogs, livestock and humans. It acts against insects as a contact and stomach poison [11]. Dichlorvos pesticide self-poisoning is an important clinical problem in the developing world, and kills an estimated 200,000 people every year [13]. Concentrates of dichlorvos is mildly irritating to skin and may cause localized sweating, involuntary muscle contractions and burning sensations or actual burns [14]. When inhaled, the first effects are usually respiratory and may include bloody or runny nose, coughing, chest discomfort, difficult or short breath, and wheezing due to constriction or excess fluid in the bronchial tubes. When in contact with eyes will cause pain, bleeding, tears, pupil constriction, and blurred vision [12]. The objective of this study is to determine the presence or absence of dichlorvos in treated cowpea grains six months after storage.

2. MATERIAL AND METHODS

The study was carried out at the Laboratory of the Department of Pure and Industrial Chemistry, Faculty of Science, Bayero University Kano (110 58' N, 80 25' E) in 2014. Five kg of untreated cowpea grain (Dan Misra) was obtained from the Kano Agricultural and Rural Development Authority (KNARDA) this was divided into two i.e 4kg which was treated with dichlorvos (4ml/4kg) and 1kg (untreated control), simulating the dose of dichlovors used by cowpea merchants at Dawanau market for the protection of cowpea grains while in storage.

Six months after, 50g of the dichlorvos treated and untreated cowpea seeds were measured and each put in a 250ml conical flask after which 100ml of methanol was added in each flask, the treated cowpea was washed using the methanol to extract the expected dichlorvos residues from the cowpea. The mixture was then used for the screening exercise. Qualitative screening of treated and untreated cowpea samples for the detection of presence of Dichlovors insecticide was made using the high performance liquid chromatography and commercially available brand of dichlorvos was used as a guide. A 20 minutes program was carried out using water/acetonitrile gradient on Zorbax high definition 3.5µ-C18-column (RP), at 20℃, 20 µL was injected from a solution of 10mg/ml in HPLC grade methanol. Analysis was run at 1ml per minute and detection was achieved at 214 nm. The analysis was conducted with Agilent 1260 Quadpump HPLC, with diode array detector, autosampler and thermostetted column compartment. The result was processed using Agilent Chemstation software.

3. RESULTS

Figure 1 reveals the presence of the target insecticide (dichlorvos) in the protected cowpea stored for the duration of six months in the store and the detection was made at 214 nm. The overlaid chromatograms suggested the presence of DDVP: 2, 2-dichlorovinyl dimethyl phosphate in the test sample relative to the chromatogram of the standard commercial sample (Fig. 2) at a retention time of 2.163 and 2.283 minutes, respectively. The peak of target compound was visibly not present in the control chromatogram at the stated retention times (Fig. 3).

DISCUSSION

Results of the study indicated the presence of the dichlorvos six months post application in the treated cowpea grain. The detection of dichlorvos in the treated grains could be attributed to the inappropriate application such as over dosing of the said pesticide done indiscriminately to achieve set goals [13]. Most farmers (especially grain marketers) exposed cowpea grains to dangerous chemicals especially organophosphates which are normally higher or above normal approved doses by the governments/or international organizations such as FAO, WHO etc [13]. This improper use of pesticides may lead to the emergence of resistant pest populations, which would be insensitive to normal pesticide dosages [13, 14

and 15]. In cowpea, the mean concentration ranged from 0.001 to 0.108 mg/kg^{-1} for organochlorine pesticides, 0.002 to 0.015mg/kg^{-1} for organophosphorus pesticides and 0.001–0.039mg/kg^{-1} for pyrethroids pesticides [16].

A study in Zimbabwe have indicated that illiteracy, poor or bad attitudes of farmers on dangers of pesticides contributed to higher levels of dichlorvos in vegetables in Zimbabwe [13] and such could be a similar trend happening at Dawanau market in Kano State. Higher dosages of Dichlovos are being used irrespective of the recommended dosage in grains storage in the sub Saharan Africa especially in Dawanau grains Market each year as both farmers and traders alike await better prices. It is equally a common practice that calendar application of such pesticides are widely practiced by both farmers and traders, this particular practice is capable of increasing pesticide residue accumulation in such stored grains [2]. The grain traders/merchants are directly mixing grains with higher dosages of chemical insecticides in order to have maximum and long term protection against insect pest damage. The detected levels of dichlorvos on the treated cowpea grain could be due to shortening of the recommended withdrawal period, which is the minimum time one must wait between pesticide application and usage by the ultimate consumers of any insecticide treated commodity. Organophosphorous pesticides are widely applied in agriculture because their degradation elsewhere is known to be rapid [17]. However, in this study Dichlovos is said to persist for six months after application. This could be attributed to the higher dosage of the pesticide applied.

In Nigeria, especially in the northern part, dichlorvors is traded under different names such as Nuvan, Sniper or Pia-pia and is handled and used as a household insecticide indiscriminately. Moreover, excessive or higher dosages of Dichlovos applied by traders and farmers in Dawanau market have probably caused the persistence and possibly pest resistance in stored grains protected using dichlovos. This has been reported by several researchers including [18] that the stored product insects pests were found to be resistant against different insecticides including the dichlorovos, cyclodienes, chlorpyrifos, cyanophos, carbamates, carbaryl, cypermethrin, dichlorodiphenyltrichloroethane, deltamethrin, diazinon, ethylene bromide, ethyl formate organophosphates, permethrin, pyrethrins, and propoxur. More so, [19] reported that resistance to pesticides used to protect grain and other stored food stuffs is widespread and involves all groups of pesticides and most of the important pests. The residue of dichlorvos found in the stored cowpea grains may lead to various health issues that are unknown by the grain marketers or the final consumers. This might expose the final consumer to different diseases such as impaired memory and concentration, disorientation, severe depressions, irritability, confusion, headache, speech difficulties, delayed reaction times, nightmares, sleepwalking and drowsiness or insomnia. An influenza-like condition with headache, nausea, weakness, loss of appetite, and malaise has also been reported [20, 13]. In a similar study by [21], results clearly indicated that inhalation of chlorpyrifos, dichlorvos and alphacypermethrin for eight weeks caused a slight decrease in the average body weight gain in test mice.

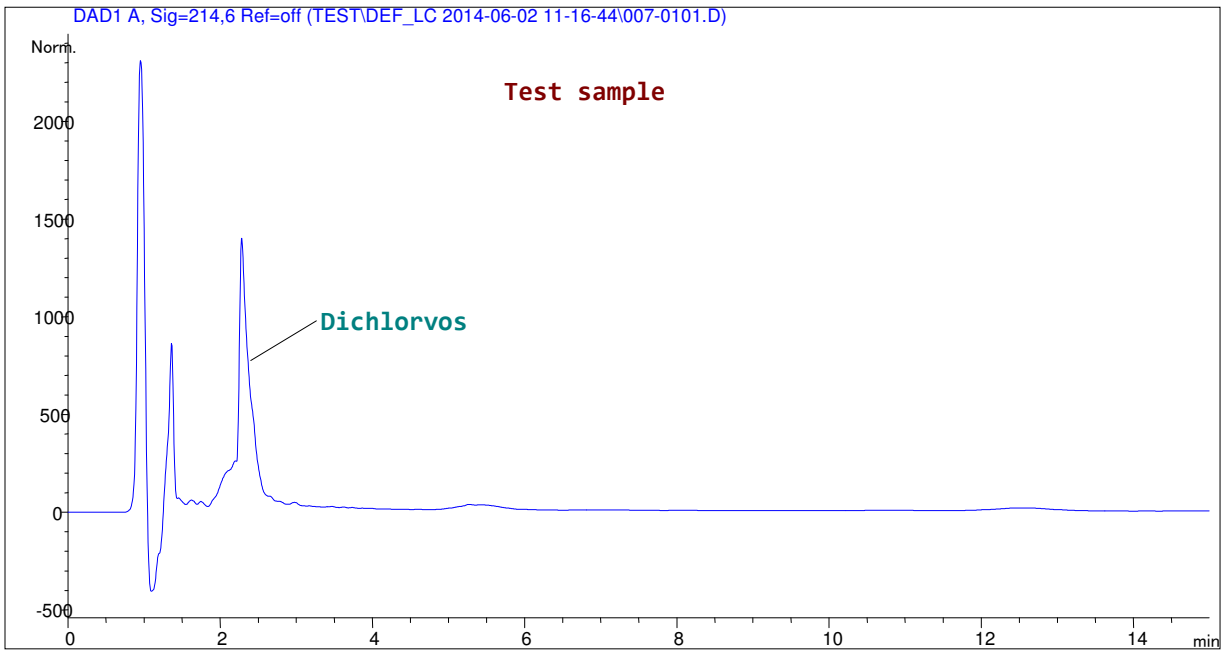

Figure 1: Chromatogram of the Dichlovos protected cowpea grains

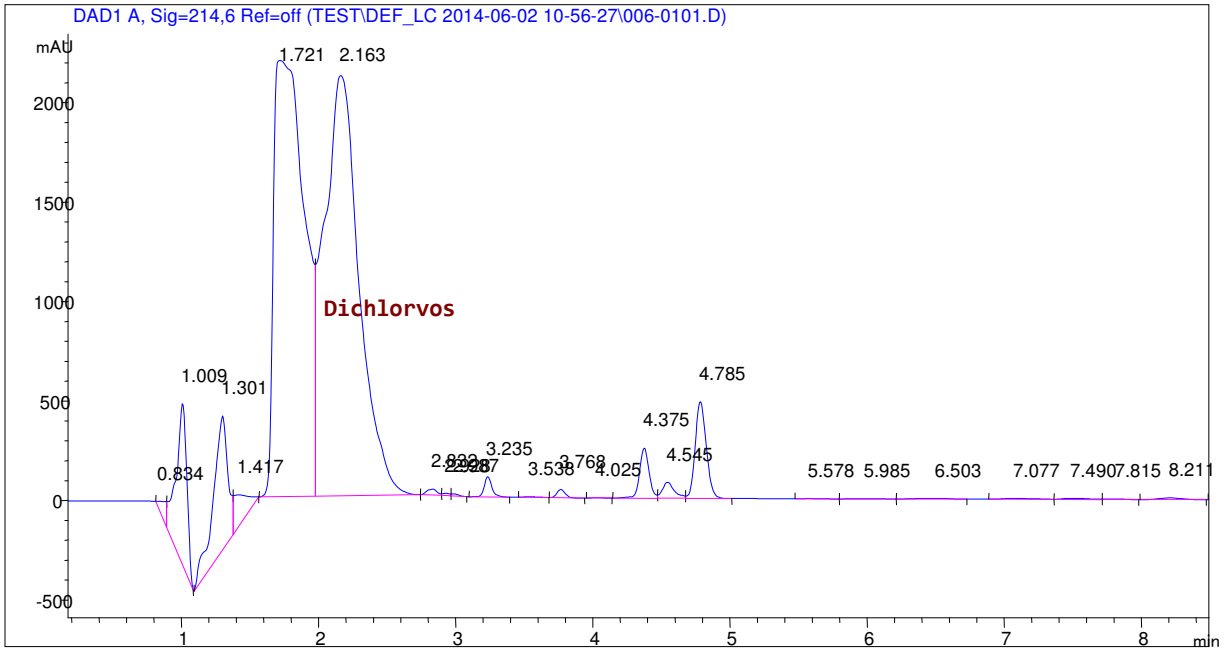

Figure 2: Chromatogram of a commercially available brand of dichlorvos used as standard

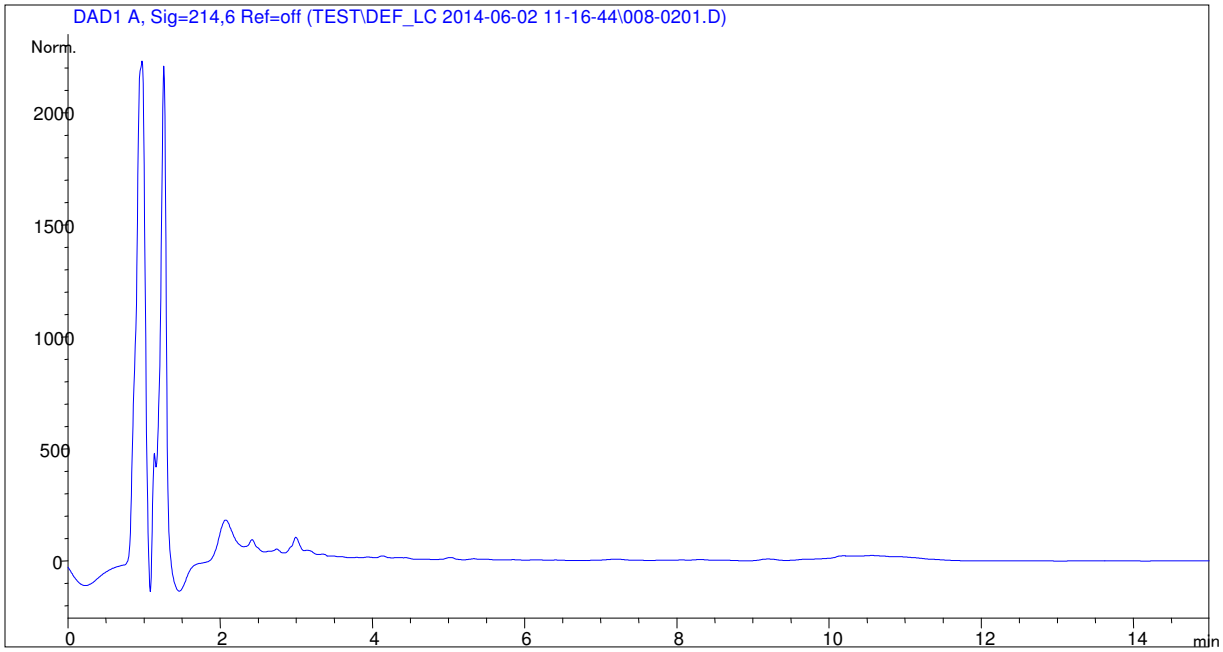

Figure 3: Chromatogram of the unprotected cowpea grains used as control

4. CONCLUSION

The present investigation clearly indicated the presence of dichlorvos (i.e. an organophophate insecticide) in cowpea grains six months after application and this situation highlights among others, the dangers and/or disadvantages associated with the use of synthetic chemicals used for the protection of stored cowpea grains against insect pests especially by the personnel lacking requisite knowledge on the appropriate ways of handling/application of such products. Owing to the serious implication of the inappropriate use of synthetic chemicals on humans and environment there is therefore, the need for the regulatory authorities to target places like Dawanau market with a campaign on best practices in the use of such chemicals on agricultural commodities.

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