



Research Article

DETERMINATION OF CARBAMATE RESIDUES IN WATER BY GAS CHROMATOGRAPHY WITH ELECTRON CAPTURE DETECTOR (GC-ECD): A CASE STUDY IN TALATA IBOAKA, FIANARANTSOA, MADAGASCAR**Andry Harinaina Rabearisoa^{1*}, Hajandrainy Rabearisoa¹, Nasolo Sedravola, Randimbiarison²**¹Université de Fianarantsoa, Ecole Normale Supérieure : Sciences et technologies, Fianarantsoa, Madagascar.²Université de Fianarantsoa, Faculté des Lettres et Sciences Humaines, Fianarantsoa, Madagascar.

ARTICLE INFO

Article History:Received 16th November, 2023Received in revised form 22nd November, 2023Accepted 18th December, 2023Published online 28th December, 2023**Key words:**

Keywords: Carbamate Residues, Water, Gas Chromatography

ABSTRACT

Research concerning the residue of carbamate in water from central production samples from Talata Iboaka, Fianarantsoa province has been conducted. The aim of this study was to analyze, identify and evaluate carbamate insecticides in water. Water samples were extracted using separator funnel with 15% (v/v) dichloromethane/n-hexane. Clean up was done using a chromatography column with florisil, and the residues were derivatized with 1-fluoro-2,4-dinitrobenzene. The derivatives were determined by gas chromatography with Electron Capture Detector (GC-ECD). The results of the study revealed that the average concentration of carbamate pesticides in all carbamate residues in water samples ranged from 0.001 to 2.508ppm in all samples investigated. Except for methonyl and carbaryl, the water sample taken from the white cabbage field was below the established water standard. The results of this study indicated that, in spite of more careful usages, of pesticides especially carbamate residues still pollute the environment resulting in contamination of these white cabbage fields.

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INTRODUCTION

Pesticides are chemicals used by farmers to help them produce their crops. These chemicals are always designed to control disease or prevent economic loss but at the same time they are frequently associated with deleterious influence on living organisms and the environment (Cooper, J. et al., 2007). Carbamates are a group of organic compounds that share a common functional group with the general structure -NH (CO) O- (Ghosh, A.K and Brindisi M., 2020) and it will be discussed in this research those are mainly use in agriculture, as insecticides, fungicides, herbicides, nematocides, or sprout inhibitors. They are also used as biocides for industrial or other applications and in household products. 90% of the Malagasy farmers used more than eight types of pesticides to control plant diseases, while for herbicides they used more than two (2) kinds and would then just mix them together. Fungicides and herbicides were rarely used for white cabbage plants. The dosages and intervals used show that the users did not follow the specified levels and intervals usage of the pesticides. Instead, farmers based the dosages and intervals of use on the level of plant disease in the fields. The spraying instruments used by the farmers were hand sprayers. While using the spraying instruments, none of the respondents wore complete safety equipment (face mask, hand socks, boots shoes, closed clothes). All respondents mixed more than six kinds of insecticides to be particular, they use nine kinds of insecticides

(i.e., Carbosulfan, Aldicarb-sulfone, Aldicarb, Methomyl, Carbaryl, Carbofuran, Propoxur, Dioxycarb) and more than three (3) kinds of fungicides (Probineb, Propiconazol, Mancozeb) for their white cabbage planting. Moreover, they only had a two to five-days interval time for spraying. All of the respondents added adhesive materials such as washing soap or porcelain cleaner to the insecticides, fungicides, or herbicides. This was done to minimize the loss of pesticides and protect them from the rain and wind. Carbamate insecticides are mainly applied to the plants and reach the soil, while carbamate nematocides and herbicides are applied directly to the soil (Sahoo, A., et al., 1990). The objective of this research is to determine carbamate residues in water by means of gas chromatography techniques. The test is devised for the main types of carbamate pesticides that are commonly used in agriculture or plantation. It is also intended to further the discussion on how to meet the difficulties in pesticide residue analysis and the future trends in chemical analysis related to pesticides.

MATERIALS AND METHODS**Time and Location of Research**

The research was conducted from March to September 2023 to study the residues of carbamate insecticide in white cabbage fields that are grown by different farmers plots in the province of Fianarantsoa, specifically in the villages of Talata Iboaka.

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Gas Chromatography was the method used to analyze the carbamate residues.

Materials and Equipments

The materials which were needed for the analysis are as follows: Acetone, Petroleum Ether, KOH 0,5 N, Na₂SO₄ anhydrous, Celite 545- magnesium, distilled water, n-hexane, silica gel, filter papers, glass wool, florisil, activated carbon, standard solution pesticide carbamate (methomyl, carbaryl, 3hydroxycarbofuran, carbofuran, dioxycarb, propoxur, aldicarb sulfone, and aldicarb), and water samples. The equipment consisted of a Buchner funnel, measuring cylinders, stand ring, separator funnel, shaker, rotary vacuum evaporator, micro tubes, refrigerator, pipette, mortar, Buchner Filter, hairdryer, digital balance, homogenizer, rotary evaporator, micropipette, and a set of gas Chromatography.

Sampling Method

Three samples were taken during the Harvest time from three sites in Talata Iboaka as mentioned above. Farmers in the site of observation applied carbamate insecticides on white cabbage crop during dry season. Three samples of 1kg water samples were taken from the same locations and the samples were taken from different areas. Water samples were taken randomly.

Water sample

The water sample was taken from underground 0-100 cm depth next to the white cabbage field. Each sample was mixed and then approximately 500-1000 ml was collected, placed into a container and labelled with its code, date, time and place of collection.

Procedures for Carbamate Residues Analysis

100 ml of the prepared water sample was inserted into separation funnels, then added with 50 ml of mixture of 15 % dichloromethane and n-hexane (DH) and shaken strongly for two minutes. After shaking, the solution formed two layers, aqueous in the lower layer and DH in the upper layer. The lower layer was poured into Erlenmeyer; meanwhile the upper layer is placed in a tube. The upper layer liquid is poured back into the separating funnel and extracted three times. The upper layer as the result from extraction is purified by passing it through the chromatography column which is filled with anhydrous sodium sulphate. Afterwards, the tube is rinsed with 10 ml of n-hexane and then reinserted into the chromatography column. The Rinsing procedure was repeated three times and the sample had to be reheated for evaporation until the amount of the solution becomes 1 ml. After performing the rinsing procedure, the tube had to be washed with acetone. The acetone from the tube which was used in rinsing was poured into the experiment bulb with the volume of 10 ml, 50 ml of n-hexane was applied afterwards. After that procedure, the solution is evaporated again until 1 ml remains then the tube is rinsed gradually by acetone and the rinsing result is taken as water sample by extraction method into the test tube until 10 ml of it remains. The solution sample is ready to be injected into the GC after derivatization process.

Derivatization

During the derivatization, a stock solution was prepared. This was 2, 4 Fluoro- dinitro-benzene (FDNB) 6 % v/v of about 6

ml in a tube. FNDP dissolved in 94 ml acetone p.a. The Stock solution of KOH 0.5 N was obtained by weighing 28,05 g of KOH and dissolved in 400 ml Aquades in glass goblet then stirred by using magnetic rod. After being dissolved, adjust the volume until 500 ml with aquades. Stock solution Borax 5% by weighing 25 g borax and was dissolved in 450 ml of aquades then stirred by using magnetic stirrer. After dissolving the volume was adjusted to 500 ml. Mixture of stock solutions with n-Hexane and petroleum ether was prepared with the comparison 45:3 (v/v) with a quantity of 200 ml according to the need. After preparing the stock solutions, derivatization was conducted by dissolving solid extract from 10 ml test tube which was put into 300 ml round bulb then the 20 ml experiment tube was rinsed up with acetone as the sample was placed in the same bulb. The evaporation procedure was conducted in with the dissolvent in the bulb by evaporating it until 1 ml remains then respectively 100 ml aquades was added, 1 ml FDNB 6%, and 2ml KOH 0,5 N, then shaken using shaker for 20 minutes. After that, 10 ml borax 5% was added, and then the extract was heated at 80 degrees Celsius for 20 minutes. After that, the solution was cooled in a cooler container. As it cools, the extract solution was move from the bulb to the funnel separator, added with 10 ml n-Hexane mixture and Petroleum ether and shaken for three minutes. Having shaken, the funnel separator was lifted and the stative iron was placed, and then a complete separation took place. The fraction of n-Hexane mixture and petroleum ether are shown at the top area, whereas the water fraction is at the bottom area. The water fraction was poured in up to the limit mark along with n-Hexane fraction and petroleum ether filtered through filter paper plus a spoon (more or less 2 g) of anhydrous sodium sulphate then 10 ml of it was spilled into the test tube and sample solution then was ready to be injected into the GC.

Determination OF Carbamate Residues

Carbamate residues concentrations were determined by direct comparison with a single standard manually or electronically when injection volume and response are within ten per cent of those of the sample pesticide of interest. The carbamate concentration was calculated using the following formula and the results in microgram per liter ($\mu\text{g/L}$) of the extract can be presented as follows:

$$\text{Concentration} = \frac{A \times B \times C \times D}{E \times F \times G} \text{----- (1)}$$

Where: A is the mass of standard pesticide in nanograms (ng); B is the peak height of sample, mm, or peak area, mm²; C is the extract volume μL ; D is the dilution factor, if there was no clean-up, then the dilution factor is 1; if a portion of the extract solution was concentrated after clean-up process. Then the dilution factor is a decimal; if it was diluted, the dilution factor exceeds 1; E is the peak height of standard, mm, or peak area, mm²; F is the volume of extract injected, μL ; G is the volume of sample extracted, ml.

RESULTS AND DISCUSSION

The samples were analyzed by Gas Chromatography – Electron Capture Detector after extraction (water sample was extracted with separation funnel extraction and, clean up and derivatization). Gas chromatography measurements were performed on a Shimadzu 2014 gas chromatograph equipped

Table1.Result of Carbamate Residues Analysis

Active Ingredients	Samples					
	Water 1A	W 1B	Water 1C	Water 3	Water 4	Water 5
Aldicarb Sulfone Aldicarb	0.433	0.368	0.444	0.370	0.290	0.374
Methomyl	0.536	0.144	0.550	0.548	0.553	0.561
Carbaryl	1.901	1.272	1.923	2.077	2.508	2.135
3-hydroxycarbofuran	0.738	0.625	0.883	0.903	0.879	0.904
Carbofuran	0.067	0.049	0.074	0.075	0.080	0.084
Dioxy carb	0.541	0.331	0.577	0.593	0.621	0.601
Propoxur	0.011	0.007	0.012	0.010	0.001	0.002
	0.010	0.005	0.004	0.003	0.006	0.007

with an electron capture detector (ECD) operated at 230°C. The rate of data acquisition was set to 50 Hz. The splitless injector operated at 250°C.

Injections were carried out by an auto sampler using a 1 µL syringe. A 30m x 0.25mm i.d. Rtx-1 fused silica capillary column with 100% dimethylpolysiloxane stationary phase was used for the experiments. Carrier gas N₂ flow programming was used 22ml/minute with pressure 65 kPa as a mobile phase.

The results obtained in the application of the method for analysis of water samples indicate the presence of carbamate residues. Although these pesticides are highly toxic, they are frequently used for the control of infestations in white cabbage cultivation (Tongzhang, Z et al., 2001). From Carbamate compound detection, Methomyl residue is the highest amount concentration in the all samples analyzed in the range from 1.272 ppm to 2.508 ppm, while dioxycarb is the lowest value.

The residues of dioxycarb were found in all samples of water next to white cabbage fields in very low levels; however, in very low levels. The range of the concentration of dioxycarb in all water samples varied from 0.001 ppm to 0.012 ppm. The mean concentration of aldicarb and aldicarb sulphone residues in this study from water samples were achieved at a range of levels from 0.144 ppm–0.561 ppm. Ritter, W.F. (1990) found that the Aldicarb is persist in groundwater, but it degrades to non-toxic products with a span that ranges from a few weeks to as long as several years under typical conditions. The primary mode of degradation is chemical hydrolysis, although there may also be some microbial decay in shallow groundwater. In addition, US EPA (1988) Aldicarb sulphoxide and aldicarb sulphone residues were found in approximately a 1:1 ratio in groundwater and the pH including the temperature were the factors affecting the rate of disappearance in water.

The Propoxur residue was present in 100% of the water samples analyzed. The range of concentration in the samples water varied from 0.003 ppm–0.01 ppm. Propoxur is compatible with most insecticides and fungicides except alkaline, and may be found in combination with azinphosmethyl, chlorpyrifos, cyfluthrin, dichlorvos, disulfoton, or methiocarb. It is used on a variety of insect pests such as chewing and sucking insects, ants, cockroaches, crickets, flies, and mosquitoes, and can be used for control of these in agricultural or (as Baygon) in non-agricultural applications (Kovacic, P et al., 2012). In the environment, propoxur is subject to degradation via hydrolysis and microbial action. It is also very volatile, technical propoxur has a vapor pressure of 2.78 mPa and a half-life of thirteen days at 25°C (Wei, W et al., 2018).

Table2 Standards for Maximum Residue Limits (MRLs) in Water

Carbamate compounds	Maximum Residue Limits (ppm)
	Water
Aldicarb Sulfone	0.50*
Aldicarb	0.50*
Methomyl	0.50*
Carbaryl	0.50*
3-hydroxycarbofuran	0.70*
Carbofuran	0.70*
Propoxur	1**
Dioxy carb	0.50***

Sources: * EPA 8081A

**Japan food chemical research foundation

***Database on pesticide residue limits Austria

In order to be able to set a maximum level, not only do the health risks have to be assessed but the residues must also be analytically determinable. Suitable analytical methods for the detection of carbamate residues in water and also methods for pesticide detection in all environmental compartments must be provided by the applicant (as rule the producer of an agent) within the framework of the pesticide approval procedure.

The average concentration of methomyl and carbaryl recorded for water samples are higher than the maximum level recommended by EPA, Japan food chemical research foundation, and Database on pesticide residue limits Austria Table.2. Aldicarb sulfon, aldicarb, 3-hydroxycarbofuran, dioxycarb and propoxur were also in almost all the samples at concentrations well below the Japan food chemical research foundation and EPA limits.

This result indicated by Lightfoot et al., (1987), when Aldicarb sulfon, aldicarb residues move downward into the saturated zone or groundwater, degradation of the residues continues and the degradation mechanism appears to be mainly chemical hydrolysis catalyzed by soil surfaces, it means aldicarb residue disappears rapidly in the sample. Jianqiang, L., (2020) also observed that the 3-hydroxycarbofuran detected in water and degrade rapidly depend on the pH of the soil and ground water. In addition Paul, R. (2005) reported that the Propoxur is used for the control of insects and it is highly in water soluble and thus has potential for leaching into groundwater and easily to degrade. We can say that all carbamate residues except Methomyl and carbaryl could degrade rapidly and be good for the plant in the fields.

In the water samples, methomyl and carbaryl were present in 100% of the samples analyzed and the samples showed the residues above maximum residue limits, while Aldicarb sulfone, aldicarb, 3- hydroxycarbofuran, dioxycarb, carbofuran, and propoxur were lower than the maximum residue limits (MRLs), so the bioaccumulation of these residues is likely to pose health problems in higher organisms such as human.

In general, the carbaryl confirmed by our result does not readily volatilize into the atmosphere and it is unlikely to volatilize from water to air. Carbaryl moderately binds to soil and has potential to leach to groundwater (LaFleur, K.S., 1976). April, R.V.S (2013) and Sonia,C (2004) also reported respectively, the methomyl is unlikely to persist in complex soils and groundwater.

This study has shown that agricultural chemicals could be detected in white cabbage fields from water at the levels around the guideline values that represent risk of adverse health effect. Our study showed that the farmers are at significant risk of acute carbamate residues poisoning when spraying their crops. Spray frequency, use of a greater number of hazardous pesticides, and skin exposure tended to occur together. While the results shown, so many samples below the detection limit due to the non-persistence carbamates residue. The low level of translocation, though important for protection against burrowing insects, mites and nematodes, would imply lack of threat to the users of the harvested materials so long as there is a reasonable time lapse between application and harvesting and the safety of these insecticides is assured. Therefore, they are low persistence carbamates. It is suggested that a waiting periods between the last application and the harvest must be around 14 days or more for both insecticides in the white cabbage field and the farmers could not use the water during this period, since the total detectable amounts in the five days were 1.272 ppm-5.759 ppm for methomyl and carbaryl were 0.557 ppm to 0.904 ppm respectively because of maximum residue levels (MRLs), that were set were exceeded by samples. This means that there is not an appropriate level of concern in obeying good agricultural practices on the part of some growers, causing occupational exposure and toxic residues in white cabbage fields appearing in the environment.

CONCLUSION

This study was initiated to determine what residues of eight carbamate insecticides (Aldicarb Sulfone, Aldicarb, Methomyl, Carbaryl, 3- hydroxycarbofuran, Carbofuran, Dioxycarb, Propoxur) remained on raw agricultural commodities after harvest.

The GC-ECD method for the determination of Aldicarb Sulfone, Aldicarb, Methomyl, Carbaryl, 3- hydroxycarbofuran, Carbofuran, Dioxycarb, Propoxur in water samples without pretreatment was shown to be specific, precise and accurate. The chromatograms generated were ideal for the identification of individual peaks with significant correlation and reproducibility regarding their readings of standard solutions.

From the analysis water samples it can be concluded that:

1. Out of the eight carbamate pesticides analyzed in the water samples, Aldicarb Sulfone, Aldicarb, Methomyl, Carbaryl, 3-hydroxycarbofuran,

Carbofuran, Dioxycarb, Propoxur were detected in all of the samples tested.

2. A total of water samples carbamate residues were tested in the range of: methomyl (1.272-2.508 ppm), carbaryl (0.625-0.904 ppm), 3-hydroxycarbofuran (0,049-0.084 ppm), carbofuran (0.331-0.621 ppm), dioxycarb(0,001-0.011 ppm), propoxur (0.003-0.010 ppm), aldicarb sulfone (0.290-0.444 ppm), and aldicarb (0.144-0.561 ppm). Methomyl and carbaryl were above the maximum residue limits
3. For farmers in the tropics, fully protective garb is too hot and too costly to maintain; farmers thus accept illness as a necessity. Integrated pest management has previously been demonstrated to reduce carbamate insecticide use with no loss of crop yield. The frequency of spraying should be reduced through widespread training in integrated pest management, and also the licensing and sale of the most hazardous pesticides should be regulated.

Acknowledgements

The author acknowledges the immense help received from the scholars whose articles are cited and included in references of this manuscript.

Conflict of Interest Statement

All the authors confirm that they have no conflicts of interest regarding the present work.

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S1. Determination of carbamate residues

Gas Chromatography Conditions

Gas chromatography Type: Gas Chromatography Mark Shimadzu type GC-2014 Made in Japan with the 63Ni Selective Electron-Capture Detectors

Column type: Rtx-1 (30 m × 0.53 mm i.d)

Column temperature: 270°C

Injector temperature: 230°C

Mobile phase: gas N₂ was used as detector make-up at 22 mL min⁻¹

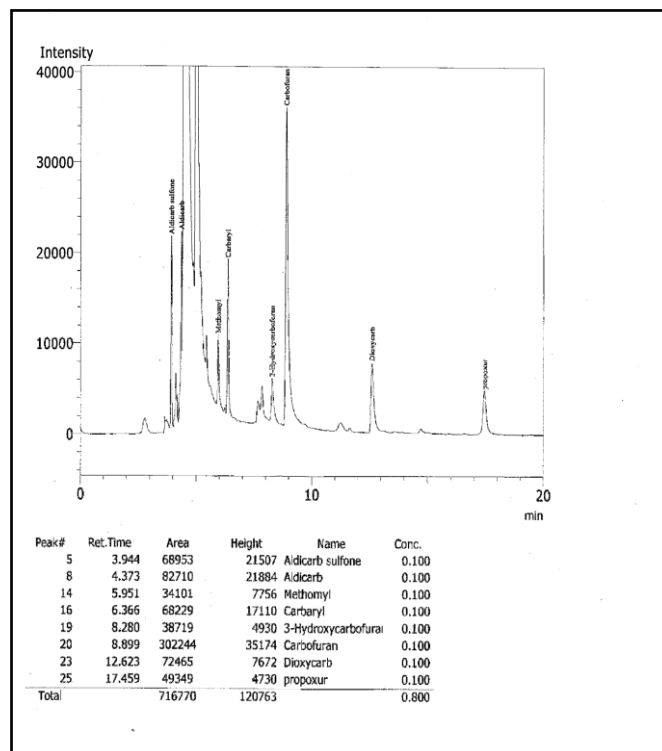
S2. Sensitivity of Analytical Method

Limit of detection. The LOD of a method of analysis is the lowest concentration of analyte in a sample that can be detected and confirmed, but not necessarily quantified, under the stated conditions of the test. For instrumental methods, a signal-to-noise ratio of 3:1 is generally acceptable for reliably establishing this limit. However, this is only guidance and can be adversely affected by baseline interference caused by co-extractives from the matrix. With a limit of detection one intends to characterize the capability of a method or instrument to detect the analyte of interest. A related misconception is that it is impossible to detect the analyte when the actual level is below the limit of detection.

Table S1. Analytical Sensitivity

Compound	Correlation Coefficient	Slope	Detection Limit (Ppm)
Aldicarb Sulfon	0.979592	226530.6	0.092
Aldicarb	0.987938	63979.59	0.107
Methomyl	0.981162	20408.16	0.272
Carbaryl	0.998019	51233	0.008
Carbofuran	0.997813	226530.6	0.092
3-Hydroxycarbofuran	0.997005	32244.9	0.107
Propoxur	0.999194	43571.43	0.055
Dioxy carb	0.906944	37933.76	0.630

Appendix 1. Chromatogram of standard solution of Carbamate residues (1ppm)



Analytical conditions

Gas chromatography Type: Gas Chromatography Mark Shimadzu type GC-2014 with the 63Ni Selective Electron-Capture Detectors

Column type: Rtx-1 (30 m × 0.53 mm i.d)

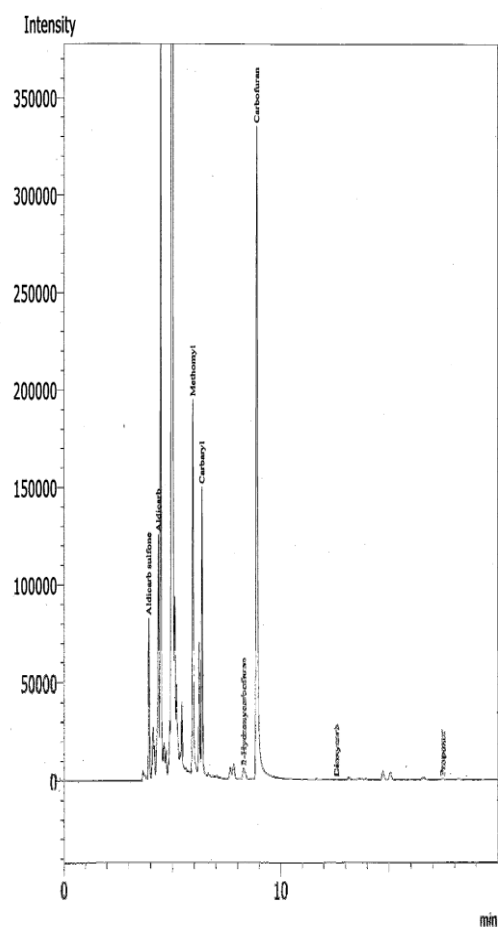
Column temperature: 270°C

Injector temperature: 230°C

Mobile phase: gas N₂ was used as detector make-up at 22 mL min⁻¹ with pressure 65kpa

Stationary Phase: 100% methyl substituted polysilox

Appendix2. Chromatogram of Carbamate residues in Water sample (W5)

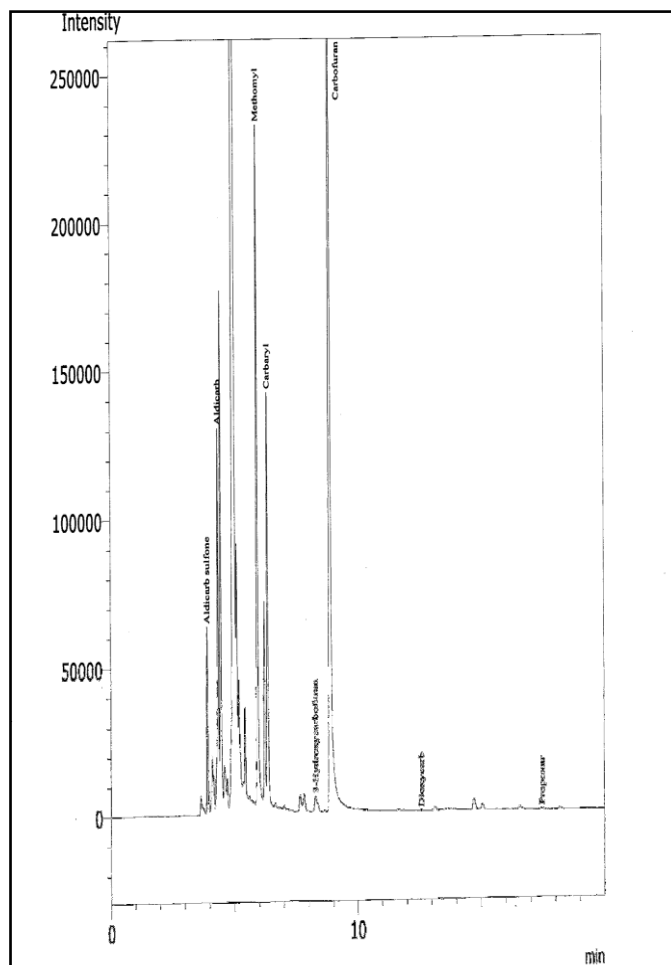


Peak#	Ret.Time	Area	Height	Name	Conc.
3	3.929	257816	82624	Aldicarb sulfone	0.374
6	4.364	463747	124132	Aldicarb	0.561
19	5.943	728191	194353	Methomyl	2.135
21	6.360	616769	149387	Carbaryl	0.904
27	8.288	32615	5322	3-Hydroxycarbofura	0.084
30	8.891	1815402	333932	Carbofuran	0.601
32	12.597	1260	182	Dioxycarb	0.002
41	17.473	3365	491	Propoxur	0.007
Total		3919165	890483		4.667

Analytical conditions

Gas chromatography Type : Gas Chromatography Mark Shimadzu type GC-2014 with the 63Ni Selective Electron-Capture Detectors
 Column type : Rtx-1 (30 m × 0.53 mm i.d)
 Column temperature : 270°C
 Injector temperature : 230°C
 Mobile phase : gas N2 was used as detector make-up at 22mL min⁻¹ with pressure 65 kpa
 Stationary Phase : 100% methyl substituted polysiloxane

Appendix3. Chromatogram of carbamate residues in well Water sample

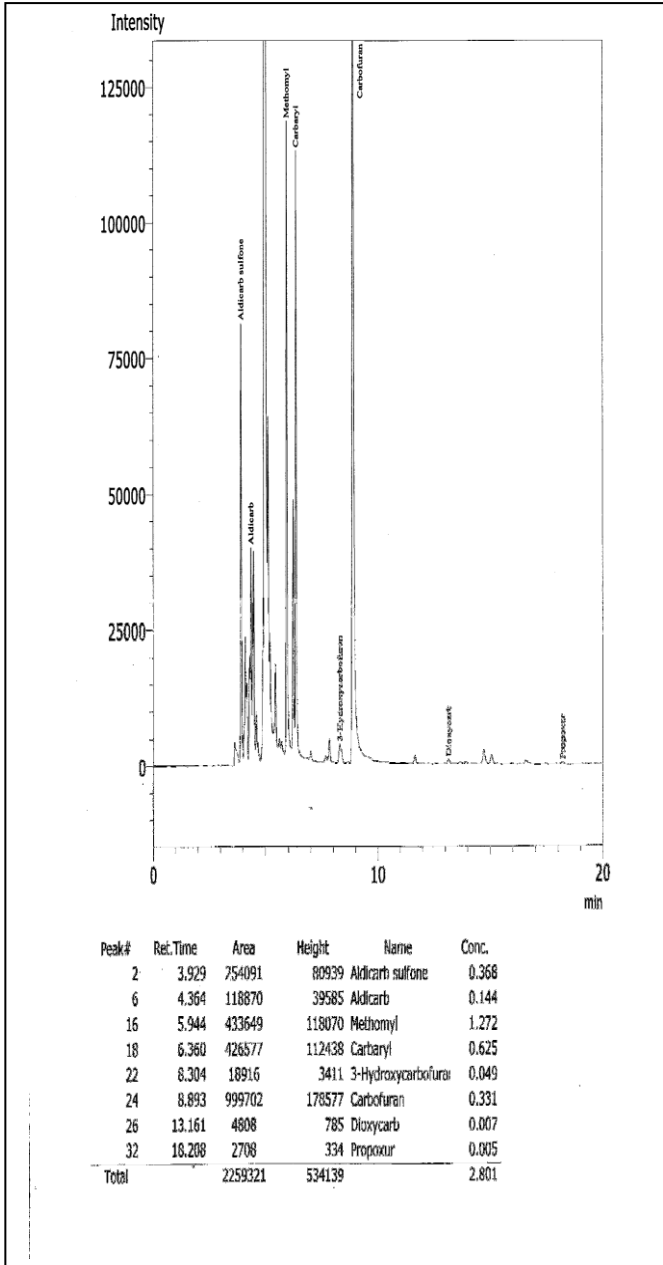


Peak#	Ret.Time	Area	Height	Name	Conc.
2	3.929	200179	63216	Aldicarb sulfone	0.290
5	4.364	457361	129288	Aldicarb	0.553
18	5.944	855306	232056	Methomyl	2.508
20	6.359	599859	141794	Carbaryl	0.879
26	8.289	30992	5116	3-Hydroxycarbofura	0.080
29	8.892	1877010	343912	Carbofuran	0.621
31	12.602	1078	152	Dioxycarb	0.001
39	17.472	3044	436	Propoxur	0.006
Total		4024779	915970		4.939

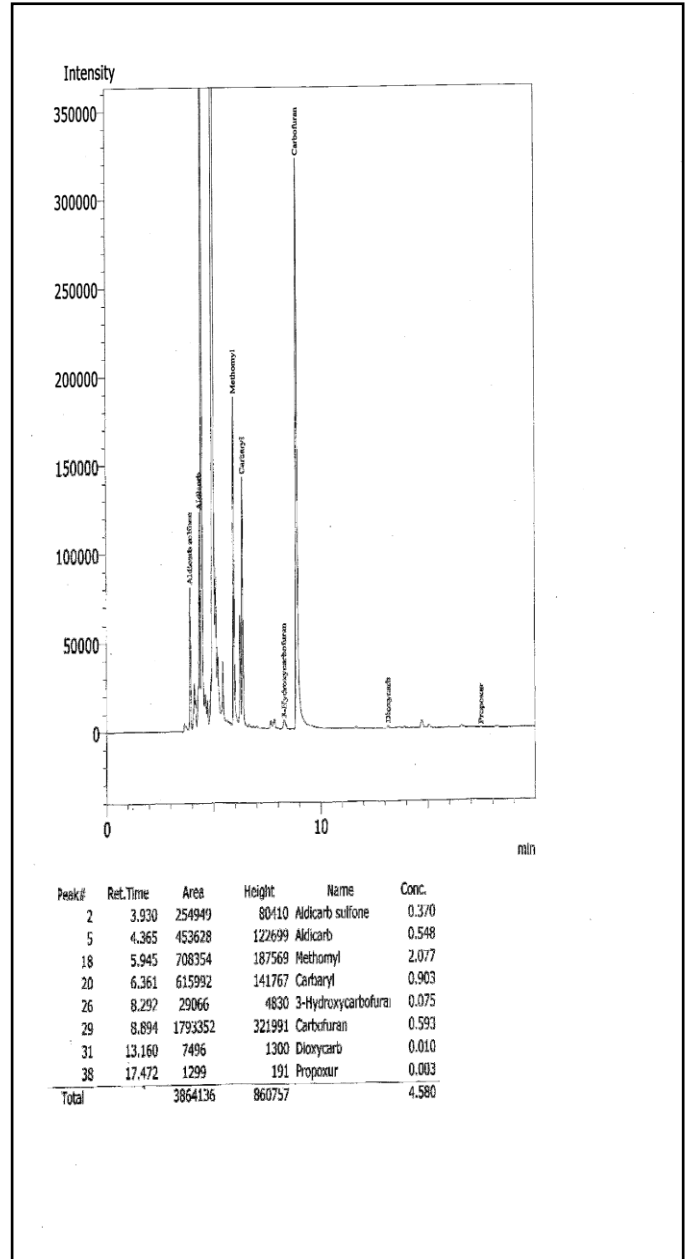
Analytical conditions

Gas chromatography Type : Gas Chromatography Mark Shimadzu type GC-2014 with the 63Ni Selective Electron-Capture Detectors
 Column type : Rtx-1 (30 m × 0.53 mm i.d)
 Column temperature : 270°C
 Injector temperature : 230°C
 Mobile phase : gas N2 was used as detector make-up at 22mL min⁻¹ with pressure 65kpa
 Stationary Phase : 100% methyl substituted polysiloxane

Appendix4. Chromatogram of Carbamate residues in well Water sample (W1A1)



Appendix5. Chromatogram of Carbamate residues in water sample (W1C)



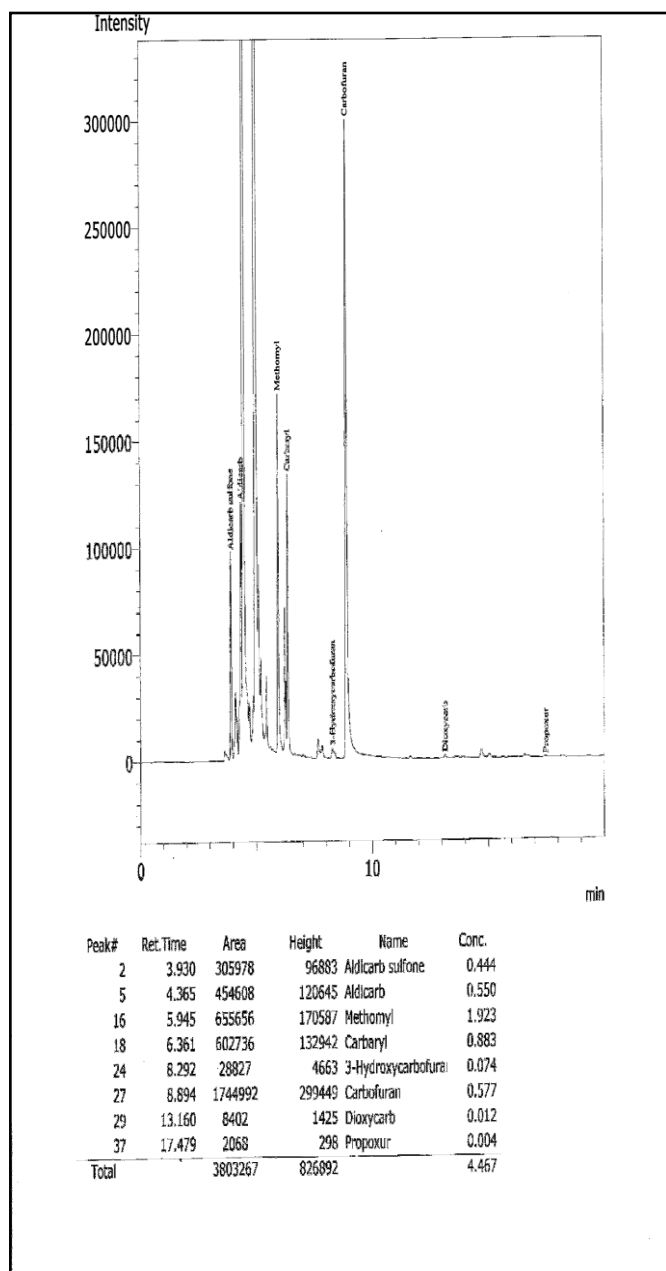
Analytical conditions

Gas chromatography Type : Gas Chromatography Mark Shimadzu type GC-2014 with the 63Ni Selective Electron-Capture Detectors
 Column type : Rtx-1 (30 m × 0.53 mm i.d)
 Column temperature : 270°C
 Injector temperature : 230°C
 Mobile phase : gas N2 was used as detector make-up at 22mL min⁻¹ with pressure 65 kpa

Analytical conditions

Gas chromatography Type : Gas Chromatography Mark Shimadzu type GC-2014 with the 63Ni Selective Electron-Capture Detectors
 Column type : Rtx-1 (30 m × 0.53 mm i.d)
 Column temperature : 270°C
 Injector temperature : 230°C
 Mobile phase : gas N2 was used as detector make-up at 22mL min⁻¹ with pressure 65 kpa

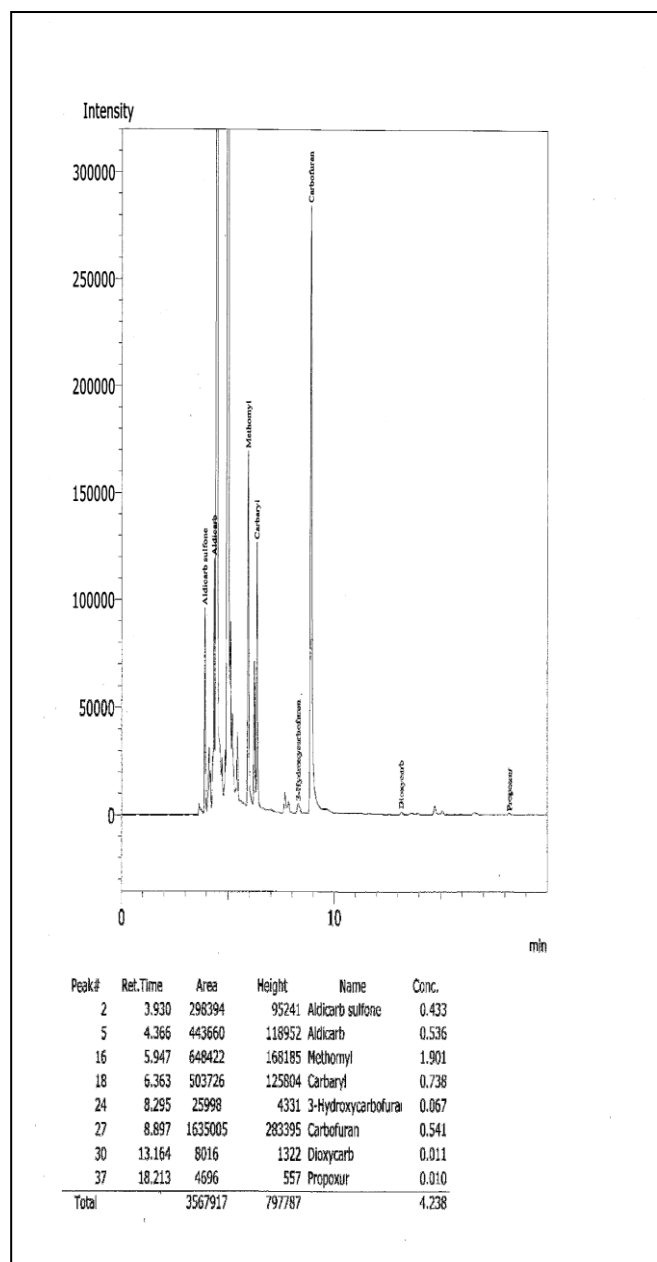
Appendix6. Chromatogram of carbamate residues in water sample (W1B)



Analytical conditions

Gas chromatography Type : Gas Chromatography Mark Shimadzu type GC-2014 with the 63Ni Selective Electron-Capture Detectors
 Column type : Rtx-1 (30 m × 0.53 mm i.d)
 Column temperature : 270°C
 Injector temperature : 230°C
 Mobile phase : gas N2 was used as detector make- up at 22mL min⁻¹ with pressure 65 kpa
 Stationary Phase : 100% methyl substituted polysiloxane

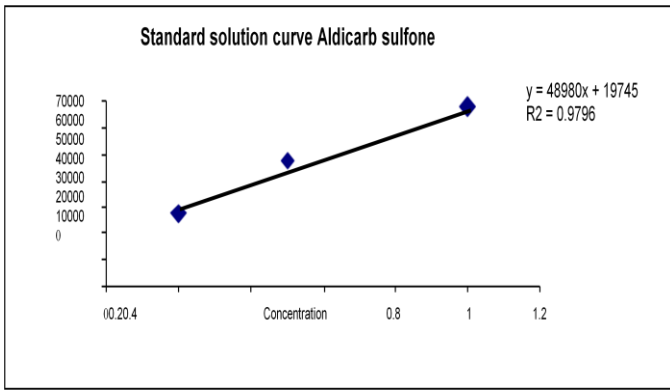
Appendix7. Chromatogram of carbamate residues in water sample (W1A)



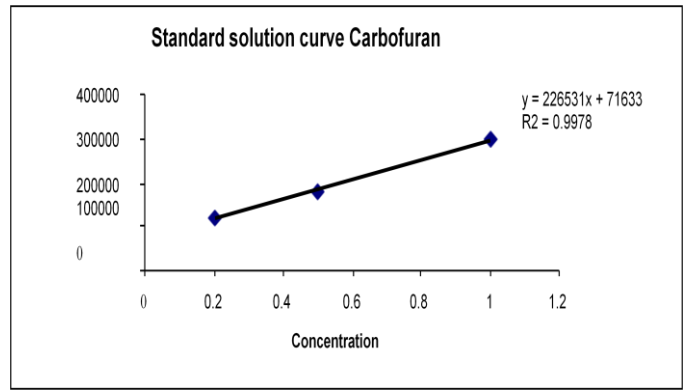
Analytical conditions

Gas chromatography Type: Gas Chromatography Mark Shimadzu type GC-2014 with the 63Ni Selective Electron-Capture Detectors
 Column type : Rtx-1 (30 m × 0.53 mm i.d)
 Column temperature : 270°C
 Injector temperature : 230°C
 Mobile phase : gas N2 was used as detector make- up at 22mL min⁻¹ with pressure 65 kpa
 Stationary Phase : 100% methyl substituted polysiloxane

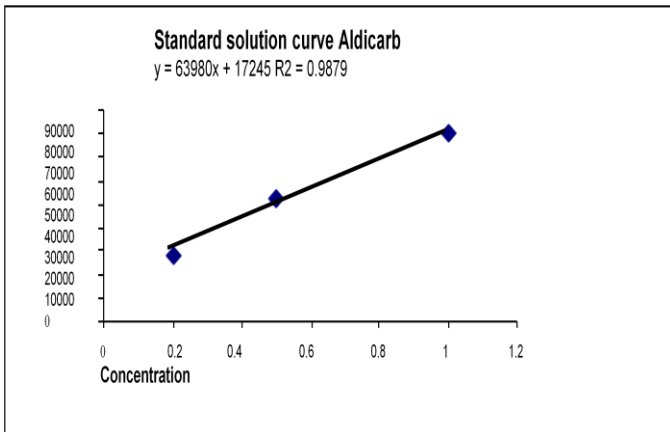
Appendix8. Standard Solution Curve Aldicarb Sulfone



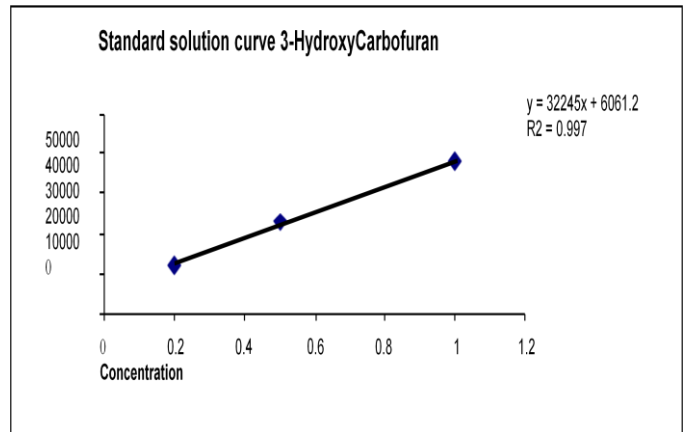
Appendix12. Standard solution curve Carbofuran



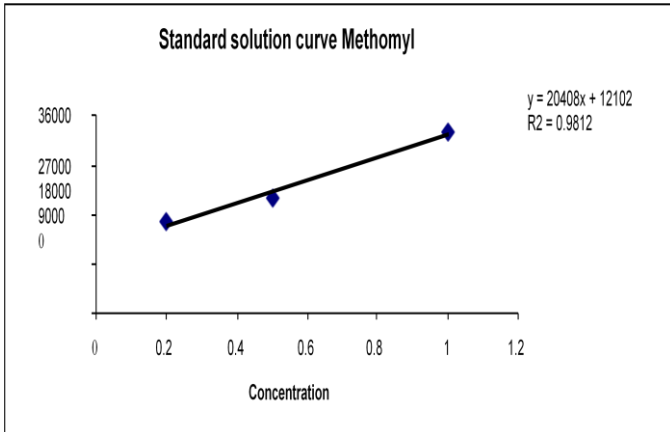
Appendix9. Standard Solution Curve Aldicarb



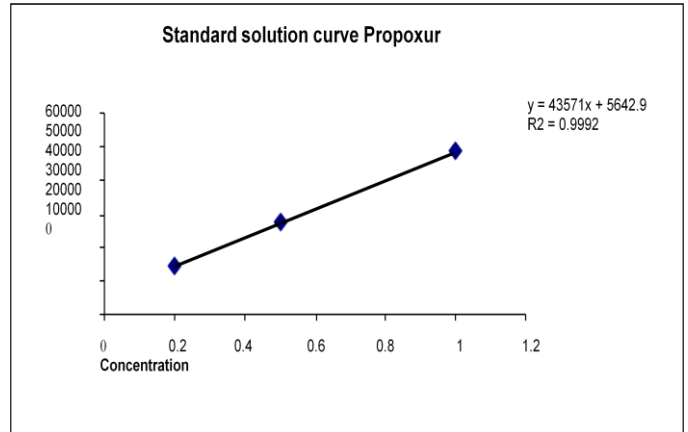
Appendix13. Standard Solution curve 3-HydroxyCarbofuran



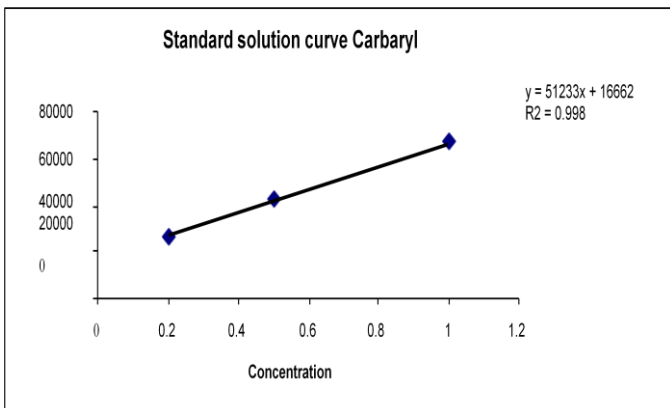
Appendix10. Standard Solution Curve Methomyl



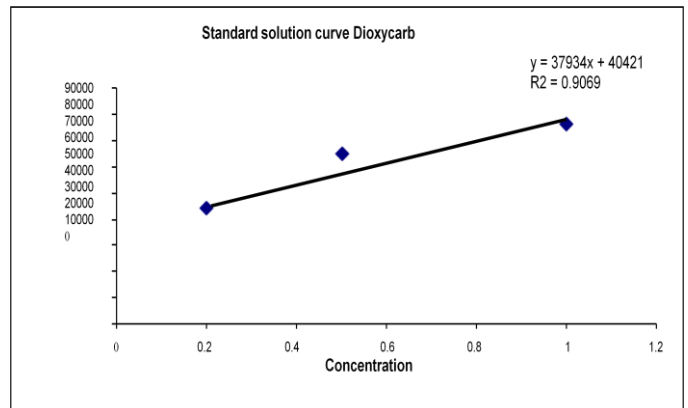
Appendix14. Standard solution curve Propoxur



Appendix11. Standard Solution Curve Carbaryl



Appendix15. Standard solution curve Dioxycarb



Appendix 16. Detection Limit

Calculations Aldicarb Sulfone

Detection Limit = DL Deviation standard= SD

$$DL = \frac{3 \times SD}{Slope}$$

From standard curve equation

$$y = (48979.59 \pm 7069.595)X + (19744.9 \pm 4635.844)$$

$$DL = \frac{3 \times 4635.844}{48979.59} = 0.28394 \text{ ppm}$$

Aldicarb

$$y = (63979.59 \pm 7069.595)X + (17244.9 \pm 4635.844)$$

$$DL = \frac{3 \times 4635.844}{63979.59} = 0.21737 \text{ ppm}$$

Methomyl

$$y = (20408.16 \pm 2827.839)X + (12102.04 \pm 1854.337)$$

$$DL = \frac{3 \times 1854.337}{20408.16} = 0.27258 \text{ ppm}$$

Carbaryl

$$y = (51233 \pm 2282.843)X + (16662.4 \pm 1496.96)$$

$$DL = \frac{3 \times 1496.96}{51233} = 0.00876 \text{ ppm}$$

Carbofuran

$$y = (226530.6 \pm 10604.39)X + (71632.65 \pm 6953.765)$$

$$DL = \frac{3 \times 6953.765}{226530.6} = 0.09209 \text{ ppm}$$

3-Hydroxycarbofuran

$$y = (32244.9 \pm 1767.399)X + (6061.224 \pm 1158.961)$$

$$DL = \frac{3 \times 1158.961}{32244.9} = 0.10782 \text{ ppm}$$

Propoxur

$$y = (43571.43 \pm 1237.119)X + (5642.857 \pm 811.2726)$$

$$DL = \frac{3 \times 811.2726}{43571.43} = 0.05585 \text{ ppm}$$

Dioxy carb

$$y = (37933.67 \pm 12150.87)X + (40420.927 \pm 7967.856)$$

$$DL = \frac{3 \times 7967.856}{37933.76} = 0.63013 \text{ ppm}$$
