CONTAMINATION OF ORGANIC PESTICIDES IN SURFACE WATER OF CHATTOGRAM METROPOLITAN AREA AND PHOTOMETRIC EFFECTS IN REMOVING THESE SUBSTANCES

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The Author

June 2020

DEDICATION

DEDICATED TO MY BELOVED FAMILY AND RESPECTED TEACHERS

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List of Abbreviations

Abbreviation	Elaboration
ACh	Acetylcholine
AChE	Acetylcholinesterase
BARI	Bangladesh Agricultural Research Institute
BCPA	Bangladesh Crop Protection Association
BPH	Brown planthopper
Ch	Choline
CNS	Central Nervous System
CPS	Chlorpyrifos
CWA	Clean Water Act
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethylene
DDT	Dichlorodiphenyltrichloroethane
DETP	Diethyl thiophosphate
EPA	Environmental Protection Agency
EEC	European Economic Commission
EU	European Union
GC	Gas Chromatography
GC-ECD	Gas Chromatography Electron Capture Detector
GCMS	Gas Chromatography Mass Spectrometry
GmbH	Gesellschaft mit beschränkter Haftung
HPLC	High Performance Liquid Chromatography
MRL	Maximum Residue Level
MS	Mass Spectrometer
NASS	National Agricultural Statistics Service
NMFS	National Marine Fisheries Service
OPE	Organophosphate
ppb	parts per billion

ppm	parts per million
ppt	parts per trillion
TCP	Trichloropyridinol
UV	Ultraviolet
WHO	World Health Organization

Abstract

Organic pesticides applied to agricultural lands and the wash water of fruits and vegetables have strong capacity to contaminate surface water resources. Regular use of contaminated ground and surface water make the natural attenuation of these pesticides more complex and people are directly affecting through use and consumption of water containing higher level of toxic pesticides. This research aimed to detect the concentration of chlorpyrifos and carbaryl, pesticides belonged to the organophosphate and carbamate pesticide groups respectively, in surface water sources collected from different locations of Chattogram Metropolitan Area and observe photometric effects on their concentration by exposing the water samples to sodium light. Gas Chromatography Mass Spectrometry (GCMS) technique was used to detect and measure the concentration of chlorpyrifos and carbaryl pesticides in the treated water samples. 08 out of 12 water samples contained carbaryl ranging from 61.11 ppb to 216.1 ppb, which are above the WHO guideline value. Only 04 water samples contained carbaryl below the WHO guideline value which is still alarming. Chlorpyrifos was not detected in any of the water samples. Disc polarimeter with 589.44 nm wavelength was used as a source of light to observe whether exposure to specific light intensity has any effect on the concentration of the pesticides. After 10 minutes exposure to the 589.44 nm wavelength light, on an average, 95.35% of the carbaryl contents were removed from every water sample contaminated with carbaryl. The lowest percentage removal of carbaryl from water sample was 87.92% while the highest carbaryl removal percentage from water sample was 98.40%. Specific regulation guidelines must be introduced to limit the use of carbaryl in Bangladesh to assure safe water for people.

Keywords: Organophosphate, carbamate, chlorpyrifos, carbaryl, surface water, GCMS, photo-treatment

Chapter-1: Introduction

Any material that is applied to plants, harvested crops, water, soil, structures, clothing and furnishings, or animals so as to draw in, repel, kill or regulate or to interrupt the expansion and reproduction of pests, or to regulate the growth of plants, is known as a pesticide (Randall *et al*., 2014)). Pesticides can be applied directly or sprayed over the fields of crops. Therefore, they are easily released to the environment, especially in water (Bagchi *et al*., 2009). In pest management programs, pesticides often play a key role. Sometimes for a given pest, application of pesticide may be the only known control method. There are many pest-control options such as, biological, mechanical, cultural, regulatory control of pests. But the major benefits associated with the use of pesticides are their effectiveness, the speed and ease of controlling pests, and their comparative reasonable cost (Randall *et al*., 2014).

Classification of pesticides can be done based on their chemical structures or their target organisms or physical state. Based on chemical structure, pesticides are classified into organic, inorganic, synthetic, or biological pesticide. Based on target organisms, pesticides are divided into different types such as herbicides, insecticides, fungicides, rodenticides. Pesticides such as organochlorines, organophosphates, and carbamates fall under the prominent insecticide families. DDT, being one of the organochlorine pesticides, have varying degree of toxicities. But due to their persistence and potential to bioaccumulate, DDT and many other organochlorine pesticides have been phased out already. Organochlorines were largely replaced by organophosphate (e.g., chlorpyrifos) and carbamates (e.g., carbaryl, carbofuran). Carbamates, being less toxic to vertebrates, have replaced the more toxic organophosphorus pesticides in many cases (Kamrin, 1997).

Organophosphate (OPE) are a group of organic compounds derived from phosphate esters and are used widely as insecticides, herbicides, nerve agents and flame retardants (Van der Veen *et al*., 2012). Commonly used organophosphate pesticides are parathion, malathion, methyl parathion, chlorpyrifos (Registered pesticide list, BCPA).

Carbamate is a group of organic compounds derived from carbamic acid (NH_2COOH). The carbamate ester functional group is responsible for its activity as a pesticide. The most commonly used carbamate pesticides are carbaryl, carbofuran, adicarb, ethienocarb, fenobucarb, oxamyl, and methomyl (Fukuto,1990).

Both organophosphorus and carbamate insecticides are toxic to insects and mammals. The toxicity of insecticidally active organophosphate and carbamate esters to animals is attributed to their ability to inhibit acetylcholinesterase (AChE), which is a class of enzymes that catalyzes the hydrolysis of the neurotransmitting agent acetylcholine (ACh). Although organophosphate pesticide inhibits AChE irreversibly while carbamate pesticide inhibits the enzyme reversibly, which makes the former pesticide more toxic to insects and mammals (Fukuto,1990).

The enzyme AChE catalyzes the breakdown of acetylcholine (Ach) into choline (Ch) and acetic acid (A), thus reducing the concentration of ACh in the synaptic junction. AChE is a regulating agent of nervous transmission. When an organophosphorus or carbamate ester pesticide inactivates AChE enzyme present in the target insect group's brain, the enzyme is no longer able to hydrolyze ACh; the concentration of ACh in the synaptic junction remains high, and continuous stimulation of the muscle or nerve fiber occurs, resulting eventually in exhaustion and tetany and ultimately kills the insect (Fukuto,1990).

Chlorpyrifos (CPS) is an organophosphate pesticide, IUPAC name- O, O-Diethyl O-3,5,6-trichloropyridin-2-yl phosphorothioate, chemical formula- $C_9H_{11}Cl_3NO_3PS$, a colorless crystal, used on crops, animals, and buildings, and for other places, to kill different types of pests, which includes insects and worms. Nervous systems of insects are affected by the pesticide. It inhibits the acetylcholinesterase enzyme of the nervous system (Muller and Franz, 2000). Chlorpyrifos is widely used in crops like corn, cotton, almonds, and fruit trees, such as bananas, oranges and apples (NASS Agricultural Chemical Database, 2011). In Bangladesh, Chlorpyrifos is regularly being used in the fields of tea, cotton, potato, rice, sugarcane to control pests e.g., Stemborer, Hispa, Termite, Aphid, Cutworm and BPH (Registered pesticide list, BCPA). According to WHO, chlorpyrifos is moderately toxic to humans based on its acute toxicity. Exposure to CPS beyond recommended levels may bring autoimmune disorders, neurological effects and persistent developmental disorders (WHO, 2010; Israel, 2012).

Carbaryl, IUPAC name- 1-naphthyl methylcarbamate, chemical formula- $C_{12}H_{11}NO_2$, a colorless crystalline solid, is an insecticide in the carbamate family, used for the control of structural and agricultural pests. It is also used as a molluscicide (Robert, 2002). In the United States, carbaryl is still among the most commonly applied pesticides for many types of grain crops, fruits and vegetables, cut flowers, turf, nursery and ornamentals, green houses, oyster beds and golf courses. Apart from agricultural sector, carbaryl is also used on gardens, ornamentals, residential sites, and turf grass. Carbaryl continues to be used in Canada, Australia, the United States, and developing countries although it has been phased out in the European Union (Koshlukova *et al*., 2014). In Bangladesh, carbaryl (trade name- Sevin), is used under different brand names in different crops and fruits such as jute, rice, mango and tea to control pests such as Leaf roller, Case worm, Thrips, Hispa, Rice bug, Leaf eating caterpillar, BPH, Hoppers (Registered pesticide list, BCPA). Exposure to carbaryl occurs through inhaling vapors, ingesting residues in food, and skin contact. Carbaryl is also used as a veterinary drug and as an active ingredient in different lotion and shampoo to treat head and pubic lice infection (Jolley *et al*., 1991). In food samples and in surface water samples carbaryl has been detected at low levels (EPA, 1984). Acute occupational carbaryl exposure of humans has been linked to cause cholinesterase inhibition, due to which the function of central nervous system (CNS) is impaired. This damage to the nervous system results in nausea, vomiting, blurred vision, bronchoconstriction, convulsions, and respiratory failure (Sittig, 1985).

Just like how the majority of the aquatic and terrestrial life forms are sensitive to the variation of the quality of the fresh water supply, human beings are no different. The mortality of aquatic life is highly affected by the changes in properties of fresh water quality. In addition, the organisms who live in the contaminated water and the organisms who drink water from contaminated source are in great danger.

The dynamics of both natural weathering processes and anthropogenic activities (pesticide residue, pharmaceutical and different toxic chemical residue) can have a significant impact on water quality. For the transport and subsequent contamination of water bodies, two mechanisms are primarily responsible: diffusion and advection. The property of molecules to move from high concentration zones to low concentration zones is diffusion while the movement of water due to gravity or in response to pressure forces is advection. To put it simply into words, let's see what will happen if a barrel of pesticide is dumped into a water body. The process of diffusion will cause the chemical to move away from its initial location to be spread throughout the water body. Also forces of advection such as waves and currents will move the chemicals in the direction of the water flow. These two processes will ultimately cause a relatively uniform distribution of pesticide concentration throughout the water body (Artiola *et al*., 2004).

Most pesticides are organic compounds. They are often applied in much smaller quantities than fertilizers in the agricultural systems. However, synthetic pesticides may have deleterious effects at very low concentrations as they are designed to be very toxic to plants and pests. Although most pesticides are solids, to facilitate their handling and application they are usually dissolved in water or oil. The chemical structure controls the action and extent of usage of the organic pesticides. The fate and transport, environmental persistence, mobility, water solubility and toxicity of organic pesticides depend on their chemical structure (Brusseau *et al*., 2004).

Results of a recent study indicate some pond water samples contaminated by organochlorine and carbamate pesticide (carbaryl and carofuran) (Bagchi *et al*., 2009). Slight contamination of some of the water samples, collected from Meherpur region, was reported with residues of diazinon, chlorpyriphos (organophosphorus insecticide) and carbofuran (carbamate insecticide) (Uddin *et al*., 2013). Another study indicated the presence of organophosphorus (Malathion) pesticide in surface water samples collected from Rangpur district using High Performance Liquid Chromatography (HPLC) while organochlorine pesticides were absent in all of the collected water samples (Ara *et al*., 2014). The results of these study conducted in Bangladesh indicate that the presence of organic pesticide in surface water samples is becoming an issue of great concern day by day.

1.1. Objectives of this study:

I. To detect the presence of chlorpyrifos and carbaryl pesticide in surface water sample

II. To quantify the amount of chlorpyrifos and carbaryl present in the surface water sample using Gas Chromatography–Mass Spectrometry

III. To measure the effect of photo-treatment on the concentration of the mentioned pesticides in the water sample

IV. To suggest ways to minimize the pesticide contamination of surface water

Chapter-2: Review of Literature

2.1. History of early pesticide use

Human civilizations have tried the most effective and less time-consuming approaches to cultivate and preserve their food resources since ancient times. For example, due to the shielding effect of toxic plants for insect elimination, they have cultivated venomous and nutritious vegetation in the same place. Another initial method for removing pests was the use of elemental sulfur for several millennia. One of the oldest still existing documents 'Ebers papyrus' contain some preparation techniques for the removal of insects from foods. Primitive sulfides were also used in traditional Chinese medicines. The use of 'para-pesticides', such as mercury and arsenic, began around the year 1500 (Abubakar *et al*., 2020).

Different written documents from ancient Greece and Rome show that for the control of plant diseases, weeds, insects and animal pests, the ancient people used religion, folk magic and different chemical methods. The chemical products used as insecticide were either from easily available animal source or from plant source as there was no chemical industry back then. Different records suggest the use of smoke against mildew and blights. Straw, chaff, hedge clippings, crabs, fish, dung, ox or other animal horn to windward were burnt to spread malodorous smoke throughout the orchard, crop or vineyard. Apart from smoke, various plant extracts like bitter lupin or wild cucumber were also used against insect. To trap crawling insects tar was also used on tree trunks. Salt water or sea water was also used to control weeds. Over 2000 years, 'Pyrethrum daisies' – a type of flower was dried to form Pyrethrum powder to protect stored grains. Inorganic chemicals were very popular as pesticide in ancient times. A mixture of copper sulphate and lime, known as Bordeaux Mixture, is a popular fungicide till this day (Smith *et al*., 1975; Laura, 2010).

Inorganic chemicals such as sodium chlorate and sulphuric acid or naturally derived organic chemicals were widely used as pesticides up until the start of synthetic pesticide era, 1940 and beyond. Initially these substances were used for the destruction of food reserves during the World War II which later on became a very useful tool for the cultivation of foods in day-to-day life. Although the long-term adverse effects of pesticide usage and exposure to pesticide were highlighted by several scientists repeatedly, the usage of pesticide never seemed to decrease.

2.2. History of organic pesticides: Organochlorines

To control fungal growth and insect, some of the early used organics were by-products of coal gas production or other industrial processes, such as nitrophenols, chlorophenols, creosote, naphthalene and petroleum oils. Likewise, from a similar source, ammonium sulphate and sodium arsenate were derived to be used as herbicide. But the high application rates, lack of selectivity and toxicity towards plant species were some of the major drawbacks of these chemicals. Thus, the need for synthetic pesticides became a major discussion (Unsworth, 2010).

In the year 1940, the application of synthetic pesticides increased drastically as different organics such as DDT, aldrin, endrin, BHC, dieldrin, parathion, chlordane, captan and 2,4-D got discovered. All of the mentioned synthetic organic pesticides of chlorinated hydrocarbon group were effective and inexpensive and soon became very popular. Dichlorodiphenyltrichloroethane or DDT, the first important synthetic organic pesticide, was discovered in 1939. Paul Muller, a Swiss chemist discovered the pesticidal action of DDT. He also received Nobel Prize in medicine for his discovery in 1948. DDT was very popular for many reasons such as budget friendly, ease of application, low toxicity to mammals, broad spectrum activity, insoluble in water and persistent to the environment in which it was applied to. To control the spread of insect borne diseases like malaria and typhus, DDT became the only solution during the second half of World War II (Muir, 1998).

However, the success story of DDT came to end with the publication of Rachel Carson’s ‘Silent spring’. Published in 1962, this best-selling book highlighted major sings and warnings about pesticide use. The writer also predicted the unimaginable destruction caused by the uncontrolled and wide-spread use of chlorinated pesticides or in her words- by the ‘rain of chemicals’. In her book she linked the death of non-target organisms with the excessive use of chlorinated hydrocarbons (DDT) due to direct toxicity (fish and crabs) or indirect toxicity related to persistence (mammals, birds). DDT is fat soluble and so it can be accumulated in the fatty tissues of an organism exposed to the chemical, a property known as bioaccumulation. DDT content also increase as we go upwards of a food chain, a property known as biomagnification. DDT also damages the reproductive system of animals and due to its persistence, it can be found in the tissues of many marine aquatic animals and in the mammalian milk even though the mentioned animals were examined far away from the source of the application of DDT (NPIC DDT technical fact sheet, 2000). As it is persistent, organisms can easily take it up from the environment. A study report shows the extent of bioaccumulation and biomagnification of the concentrations of DDT in the estuarine ecosystem which is next to Long Island Sound. The summary of the report is presented in the following figure (Muir, 1998).

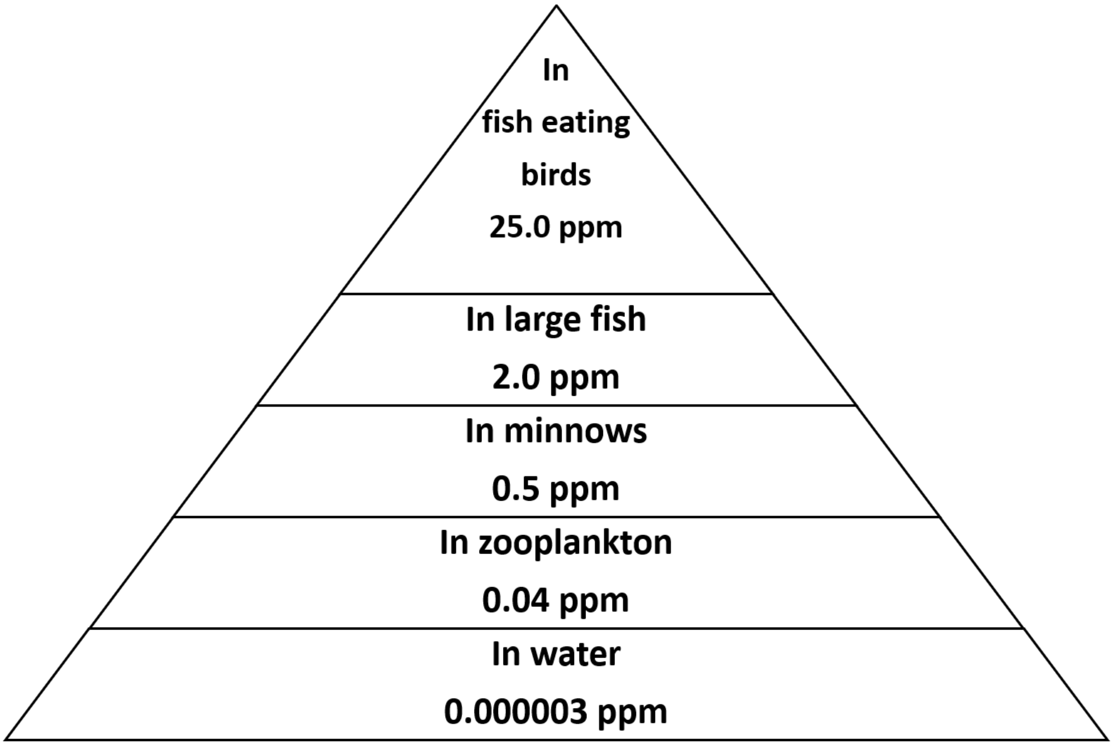

Figure 1. Biomagnification of DDT in an estuarine ecosystem

DDT was reported to be carcinogenic and cause disruption in the endocrine and reproductive systems. Experimental studies suggest that DDT and DDE (a breakdown product of DDT) are attributed to be immunotoxic, carcinogenic and neurotoxic to nontarget animals (Turusov *et al*. 2002). Although DDT production and usage is banned worldwide, India, North Korea and China are the only three countries where production of DDT still continues (van den Berg, 2009). The acute and chronic health effects and destructive ecological effects of DDT and other organochlorines ultimately brought the need of alternative pesticides such as organophosphorus and carbamates into discussion.

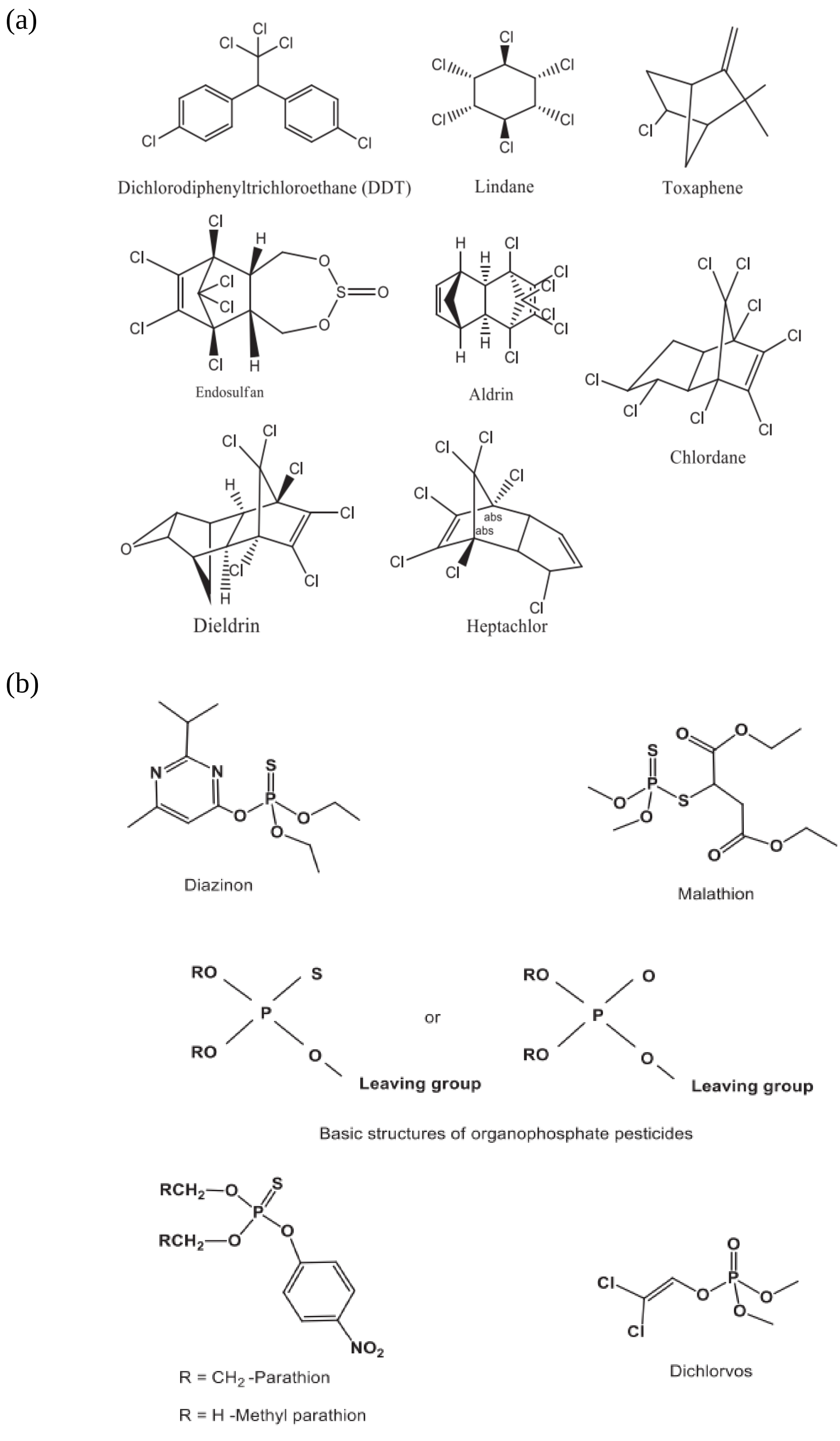

Figure 2. Chemical structures of some synthetic (a) organochlorine and organophosphate pesticides (Abubakar *et al*., 2020)

2.3. Use of Organophosphorus pesticides

In 1854, Frenchman Philippe de Clermont first successfully synthesized an ester of phosphoric acid, also known as organophosphate. He described the chemical as a sticky liquid with a peculiar odor and with a burning taste. Later in 1932, Willy Lange, a German chemist and one of his students, Gerde von Krueger shaded light on the toxic properties of organophosphates. Upon inhaling the fumes of phosphoric esters at a very small amount, they faced breathing difficulties, disturbance in consciousness, painful oversensitivity to eyes, dimming of vision and all of these feelings continued for several hours. Thus, they reported this chemical as nerve agent with cholinergic effects due to the presence of ester functional group (Petroianu, 2010).

After the properties of organophosphates were discovered, German chemist Gerhard Schrader started experiments with these chemicals to observe its ability as insecticides. He realized that this could be used as an agent of chemical warfare and so he was appointed as the in-charge of the development of organophosphates as nerve agents by the Nazi government. The government produced a bulk amount of organophosphates but they did not use these nerve agents in World War II as it was intended. Soon after the war, American scientists got the information about the production of organophosphates and they started to produce it in large quantities. Parathion, malathion became popular replacement of organochlorine pesticides. After the ban of DDT and other organochlorine pesticides, the organophosphorus compounds became very handy (Hayes, 2000).

2.3.1. The mode of action of Organophosphorus pesticides

There is a synaptic gap between the two nerve cells of the insects and mammals, known as synaptic cleft that prevents direct message or signal transfer from one nerve cells to the other. Acetylcholine, a neurotransmitter, is mediated to bridge this gap. This chemical is released from the presynaptic nerve cells to bridge this gap and to pass information across nerve cells. When the transfer of signals across nerve cells is completed, then the neurotransmitter acetylcholine is converted into inactive forms by an enzyme named acetylcholinesterase. This way the receptors of acetylcholine gets free to transfer the next signal or stimulus.

The organophosphorus pesticides disrupt this process of neurotransmission. They act like the neurotransmitter acetylcholine and binds with the enzyme acetylcholinesterase before the enzyme can bind with the usual chemical acetylcholine. Organophosphorus compounds create a complex with the enzyme and so the enzyme is unavailable to convert the acetylcholine into inactive form to terminate the stimulus. The vital process of discharging and transferring the neural signals remain incomplete due to the disturbance created by the pesticide. The nervous system stops working as the message transfer ceases due to the accumulation of the enzyme in the areas of neural signal by the synapses. Overstimulation of nervous system results into the paralysis of respiratory system for mammals and paralysis of nervous system of the insects, ultimately causing death (Satoh *et al*., 2011).

2.3.2. Health effects of Organophosphorus pesticides

Organophosphorus, being a potent nerve agent, can be absorbed via all routes such as inhalation, ingestion and skin contact. This poisonous chemical has effects on brain development of different organisms as it disrupts the function of neurotransmitter which is key to brain development. Sometimes the metabolites of the organophosphorus pesticides are more toxic than the original pesticides. Parathion, one of the organophosphates, is carcinogenic, according to the United States Environmental Protection Agency The pesticide also has cognitive and behavioral effects on neonates, toddlers or children. A review article showed direct relation of deleterious health effects of children of different ages. Prenatal exposure was assessed in studies and cognitive deficits were found in 7-year-old child, attention deficit problems were found in toddlers and abnormal motor reflexes were found in newborns (Muñoz-Quezada *et al*., 2013). U.S. Department of Agriculture tested a representative sample of produce and found detectable traces of organophosphates. In frozen blueberries, celery, green beans, peaches, broccoli, and strawberries the amount of organophosphates found were 28%, 20%, 27%, 17%, 8% and 25% respectively (Sarah Klein, 2010). Even at low levels of exposure, these pesticides can be very detrimental to fetuses and young children as their brain development depends on the sequences of biological processes.

2.4. Chlorpyrifos- An organophosphate pesticide

Being an organophosphate, chlorpyrifos (CPS) is used as insecticide, acaricide and miticide. CPS is used on a variety of food and feed crops primarily to control foliage and soil-borne insect pests. Since 1965, CPS has been used in both agricultural and non-agricultural areas as a pesticide. In terms of total pounds of active ingredient, the largest agricultural market for chlorpyrifos is corn. CPS is also used on soybeans, fruit and nut trees. Application of CPS as pesticide on cranberries, cauliflower, broccoli, Brussels sprouts as well as other row crops is also very common. It has some non-agricultural uses such as on turf, green houses, golf courses, fence posts and utility poles. It is also used as mosquito adulticide (U.S. EPA, 2002).

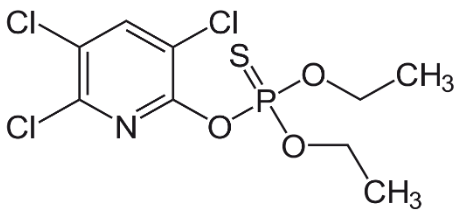

Figure 3. Chemical structure of Chlorpyrifos (CPS)

Chlorpyrifos was patented by Dow chemical company in 1966 (US patent). CPS has a broad-spectrum insecticidal activity, high efficacy, fast knockdown, flexible application timing and method, easy to handle, moderate mammalian toxicity. It is active on foliar-feeding and soil-dwelling insect pests. It is effective primarily by contact but the efficiency increases if taken through ingestion. On plant foliage, it exhibits short residual activity. Several attempts were made to ban the use of CPS in the United States but all attempts were failed as CPS is one of the most important tools for Integrated Pest Management (Nelson *et al.*, 2016).

2.4.1 Mode of action of CPS and its toxicity

The mechanism of CPS as a pesticide is no different than any other organophosphate pesticide. It kills the insects by affecting the nervous system. It binds with the AChE enzyme on its active site. As a result, the breakdown of Ach is prevented in the synaptic cleft. This causes overstimulation of nerve cells leading to neurotoxicity and eventually death. The mechanism of toxicity of CPS to non-target organisms such as mammals is also similar to the mechanism to target ones. Within minutes to hours after an exposure to CPS, typical signs and symptoms start to develop in humans. Tearing of eyes, increased saliva production, increased sweat production, runny nose, dizziness, nausea and headache are some of the common signs and symptoms after acute exposure to CPS. Weakness or tremors, muscle twitching, abdominal cramps, diarrhea, vomiting, lack of coordination, blurred vision are some signs of progression (Christensen *et al.*, 2009).

Table 1. Crops and Target pests on which Chlorpyrifos acts upon (Nelson et al., 2016)

Crop	Target Pests
Alfalfa	Alfalfa weevil, armyworms, aphids, potato leafhoppers.
Brassica vegetables	Cabbage maggot, aphids
Citrus	Scale insects, mealybug, Asian citrus psyllid, rust mite, citrus leaf miner, katydids.
Corn, Field	European corn borer, Corn rootworm, cutworm, white grub
Corn, Sweet	corn earworm, armyworms, corn rootworm (larvae and adult), cutworms, seed corn maggot, wireworms
Cotton	Cotton aphid, Lygus bug, armyworms, pink bollworm
Grapes	Mealybugs, cutworms, ants
Mint	mint root borer
Onions	Onion maggot
Peanuts	Lesser cornstalk borer, corn rootworms, white mold
Apples, Pears	San Jose scale, rosy apple aphid, pandemis leafroller, oblique-banded leafroller, climbing cutworms
Soybeans	Soybean aphid, bean leaf beetle, grasshoppers, spider mites
Stone Fruits	San Jose scale, peach twig borer, peach twig borer, peach tree borer, lesser peach tree borer, American plum borer
Sugar Beets	cutworm, wireworm, sugar beet root maggot, armyworms
Sweet Potatoes	Wireworms, southern corn rootworm, flea beetles
Tree nuts	San Jose scale, peach twig borer, navel orange worm, codling moth, walnut husk fly, walnut aphid
Wheat	Aphids, grasshoppers, orange wheat blossom midge

Chlorpyrifos undergoes rapid hydrolysis to form primary metabolite and other intermediate derivates which are more toxic chemicals compared to the parent chemical CPS. The common primary metabolite of CPS is 3,5,6-trichloropyridinol (TCP). Some intermediate metabolites of CPS are CPS oxon, diethyl thiophosphate (DETP) and 3,5,6-trichloro-2 methoxypyrimidine. CPS is less toxic than TCP and CPS oxon. Excess use and spread of CPS pesticide to crops may cause leaching into water bodies and may contaminate the surface water far away from the source of application (Dar *et al*., 2019).

2.4.2. Chlorpyrifos in surface water

The Federal Water Pollution Control Act, section 311(b)(2)(A) and the CWA amendments of 1977 and 1978 clearly states that chlorpyrifos in waterways is a hazardous substance. All isomers and hydrates of chlorpyrifos in any solution or mixture are included in this regulation. There is no chlorpyrifos regulatory standard set for drinking water by EPA. Although a drinking water guideline of 2 ug/L (2 ppb) was established by EPA (US, EPA). To protect steelhead and salmon under CWA and ESA, a limit on the use of CPS was recommended by EPA and NMFS (National Marine Fisheries Service) in different water bodies of the United States.

In Argentina, 42% of the 26 surface water samples collected contained a detectable and alarming levels of chlorpyrifos. Most of the water samples were collected from the water bodies near soyabean crop fields (Marino *et al*., 2005). Wash water of cauliflower, grapes, coriander leaves, brinjal and bitter guard were tested for the presence of chlorpyrifos pesticides in India in a recent study and almost all the samples were tested positive for the presence of the pesticide (Karthikumar *et al*., 2020).

In Bangladesh, CPS is persistently found at alarming levels in a number of domestic vegetables and surface and groundwater sources (Tanvir *et al*., 2015). In a study conducted in the coastal area of Bangladesh, the residue of chlorpyriphos was detected in only one pond water sample, from Feni at a concentration of 3.80 microgram per liter. The water samples were analyzed by HPLC (Uddin *et al*., 2013). Two samples collected from two different pond from Meherpur region, contained residue of CPS at ppm level (Uddin *et al*., 2013).

2.5. Carbamate Pesticides

The history of discovery and development of carbamate pesticides is very colorful and interesting. During the mid-nineteenth century, to reveal the guilt or innocence of people accused of witchcraft in West Africa oral administration of calabar bean paste was used. Calabar bean paste was rich in carbamate alkaloids. After the forceful ingestion of calabar bean paste if the alleged person died, then the accusation was confirmed. If the person did not die, then he was declared innocent. The West African word for calabar bean is esere. The active carbamate present in the bean was named eserine in the local language while we know it as 'physostigmine'. Apart from this natural carbamate source, there was attempt to synthesize carbamate compounds to develop new insect repellent in the mid to late 1940s. But the insecticidal properties of the newly synthesized carbamate compounds got quick recognition and appreciation (Stephanie, 2005).

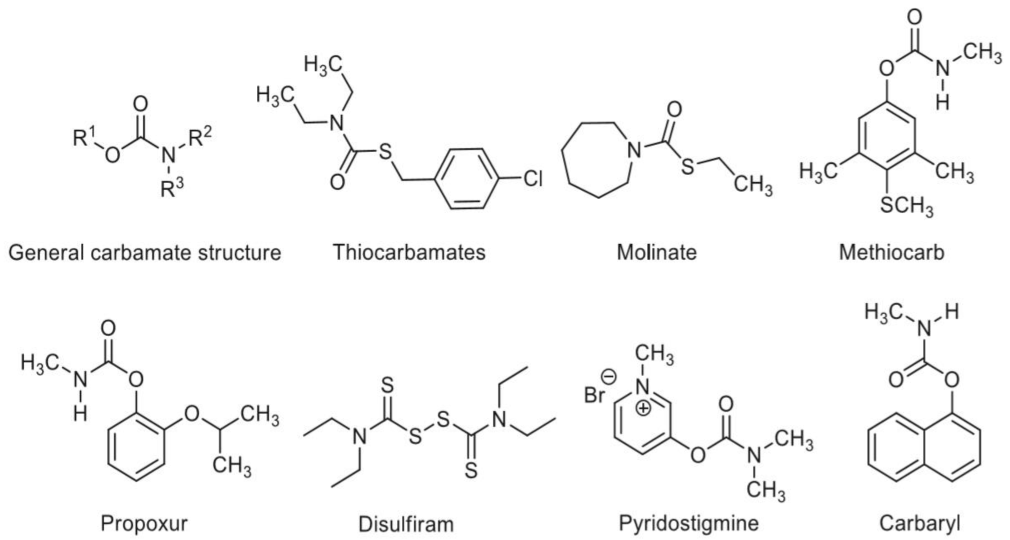

Figure 4. Chemical structures of some Carbamate compounds (Hassaan *et al*., 2020)

Carbamate, thiocarbamate and dithiocarbamate are three main groups of carbamate pesticides. Carbamates are derived from carbamic acid. The carbamate ester functional group is responsible for the insecticidal properties of carbamate compounds. The first synthesized carbamate pesticide was carbaryl, followed by aldicarb. N-methyl-carbamates such as bendiocarb, carbaryl, aldicarb, carbofuran, propoxur, methomyl, oxamyl are powerful insecticides (Gupta, 2014).

2.5.1. The mode of action of Carbamate pesticides and its toxicity

In the brain and neuromuscular junctions in skeletal muscles. the inhibition of acetylcholinesterase (AChE) at synapses are the clinical signs of the toxicity of N-methylcarbamate insecticides. Apart from AChE, carbamate compounds can bind to other receptors, enzymes and proteins. Due to the carbamylation, the activity of AChE is inhibited by carbamates. So, at the nerve endings of all cholinergic nerves acetylcholine (ACh) accumulates and causes an overstimulation of electrical activity. Carbamates interact with the enzyme AChE in the same manner as the natural substrate Ach. But the rates of hydrolysis and reactivation of AChE (decarbamylation) appear to be drastically slower than for the hydrolysis of the acetylated enzyme (Gupta, 2014).

A variety of toxicologic effects on the central nervous system, peripheral nervous system, musculoskeletal, cardiovascular, ocular, immunologic, reproductive, and other body systems are known to be produced by AChE inhibiting carbamates. In addition to these, oxidative stress, apoptosis, endocrine disruption, and carcinogenesis are also reported to be linked with AChE inhibiting carbamates. Some of them are extremely toxic to mammals and birds. High dosage carbamate exposure leads to several symptoms of CNS origin such as tremors, convulsions, incoordination, partial or generalized seizure, mental disturbance, cyanosis and coma. Within a few hours, due to cardiac and respiratory failure, the person might die. Clinical signs of acute poisoning usually resolve within a few hours of exposure. But some symptoms of a neuro-psychological nature appear to persist for a longer period. In general, carbamates are degraded into metabolites of lesser toxicity. In terms of environmental persistence, they are of lesser concern compared to organophosphorus pesticides (Gupta, 2014).

2.6. Carbaryl- an N-methyl carbamate pesticide

1-naphthyl methylcarbamate is commonly sold under the brand name Sevin of Bayer company. In 1958, carbaryl was discovered by Union Carbide and was introduced commercially to be used as an insecticide. Union Carbide pesticide operations was included in the purchase of Aventis Crop Science by Bayer company in 2002. In the US, carbaryl is that the third most used insecticide for commercial agriculture, home gardens, forestry and rangeland protection. It is not concentrated in fatty tissues nor it is secreted in mammalian milk (Robert, 2002). Carbaryl kills both target and non-target organisms which disturbs ecological balance. Malaria carrying mosquitos or other disease-causing insects are killed by the application of carbaryl. But in addition to this, carbaryl also kills beneficial insects such as honeybees as well as crustaceans (Bond *et al*., 2016).

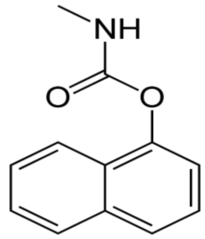

Figure 5. Chemical structure of carbaryl

2.6.1. Mode of action of carbaryl and its toxicity

Carbaryl exposure can be through inhalation, ingestion or contact. When insects are exposed to carbaryl, their nervous system is overstimulated. Using the signaling chemical, ACh, nerves transfer signals to other nerves. The enzyme AChE quickly breaks this ACh chemical to resting condition. Carbaryl disrupts the functioning of the enzyme by binding with the enzyme. The affected nerve stimulation becomes continuous resulting into the malfunctioning of the breathing muscles, ultimately causing death. The mechanism of toxicity of carbaryl is no different than the other pesticides of carbamate group (Bond *et al*., 2016).

Acute toxicity of carbaryl results in cholinergic syndromes from overstimulation of the muscarinic and nicotinic receptors. These include hypersalivation, respiratory distress, miosis, muscular twitches, tremors, ataxia, diarrhea, and vomiting. There are some nonlethal effects. Among them hematological and liver enzyme changes, alterations in brain enzymes and neurotransmitter levels, changes in catecholamine metabolism, renal effects, hypothermia, and body weight decreases are common. Reproductive and developmental toxicity, genotoxicity, immunotoxicity, carcinogenicity are some of the outcomes of chronic exposure to carbaryl pesticides (Koshlukova, 2014).

Table 2. List of registered carbaryl pesticides available in Bangladesh with their trade names, registration holder company, recommended crops and recommended pests (Registered pesticide list, BCPA)

<table>
<tr><th>Trade name</th><th>Registration holder company</th><th>Recommended crops</th><th>Recommended pests</th></tr>
<tr><td>Sevin 85 SP</td><td>Bayer Crop Science Limited</td><td rowspan="2">Rice, jute, vegetables, mango</td><td rowspan="2">Leaf eating caterpillar, hoppers, Hispa, rice bugs, leaf roller</td></tr>
<tr><td>Vitabryl 85 WP</td><td>McDonald Bangladesh (Pvt) Limited</td></tr>
<tr><td>Reflex 85 WP</td><td>Bangladesh Agricultural Industries</td><td>Rice</td><td>BPH</td></tr>
<tr><td>Coral 85 WP</td><td>Agro Continent Bangladesh</td><td>Rice</td><td>BPH</td></tr>
<tr><td>Acicarb 85 WP</td><td>ACI Formulations Limited</td><td>Rice, Tea</td><td>BPH, Termite</td></tr>
<tr><td>Sarkking 85 WP</td><td>SARK Bangladesh</td><td>Rice, Jute</td><td>Hairy caterpillar, BPH</td></tr>
<tr><td>Kubrayl 85 WP</td><td>Asia Trade International</td><td>Mango, Rice</td><td>BPH, Hopper</td></tr>
<tr><td>Durbin 85 WP</td><td>S I Agro International</td><td>Jute</td><td>Hairy caterpillar</td></tr>
<tr><td>Kalvin 85 WP</td><td>King Tech Corporation Bangladesh</td><td>Tea, Rice, Jute</td><td>Helopeltis, BPH, Hairy caterpillar</td></tr>
<tr><td>Ravin 85 WP</td><td>Sea Trade Fertilizer Limited</td><td>Jute, Rice</td><td>Hairy caterpillar, BPH</td></tr>
<tr><td>Aristoryl 85 WP</td><td>A M Traders</td><td>Tea</td><td>Helopeltis</td></tr>
</table>

2.6.2. Carbaryl in surface water

A significant number of water samples collected from different sources of a cotton growing area in Southern Malawi, were contaminated with carbaryl residues beyond the Maximum Residue Level (MRL). The concentration of carbaryl in surface water samples were recorded to be ranging from 0.083 mg/L to 0.254 mg/L during rainy seasons which were above the recommended limits. The concentration of carbaryl in ground water samples were ranging from 0.165 mg/L to 0.492 mg/L which were also above recommended limits. Concentration of carbaryl were recorded to be higher during the rainy season than the dry season. This coincides with heavy fertilizer and insecticide application as opposed to the dry season. The WHO MRL of carbaryl in water is 0.05 mg/L (Kanyika-Mbewe *et al*., 2020).

Carbaryl was detected in the surface water sample of the coastal region of Bangladesh in a study. Two water samples collected from two ponds, one from Nobipur and another one from Senbag upazila of Noakhali district tested positive for the pesticide. The concentration level of Carbaryl was 1.32µg/L in Nobipur sample and 6.40µg/L in Senbag sample (Uddin *et al*., 2013). Pesticides of carbamate origin are rapidly taken up by plants from soil and water through the roots. Then they are translocated mainly into the leaves and they sue to chemical degradation, metabolites are found in the tissues of plants. In water, the carbamate pesticides are degraded by microbial decomposition, hydrolysis and photolysis (Thapar *et al*., 1995).

2.7. Pesticide contamination in water bodies

To improve crop productivity and yield, the use of pesticides is very helpful for the agricultural sector. But the indiscriminate use of pesticides comes with negative consequences. Environmental pollution, especially water pollution caused by pesticide residue are major concerns. Water pollution simply means the presence of chemicals that are not suitable or desirable to be in water bodies in the first place. It makes the water contaminated and also unsuitable for use. Pesticides applied to the land areas may be flushed away by wind or rainfall into the water bodies, making it contaminated. These events alter the physicochemical and biological properties of water and make it toxic and unsuitable. Contamination of water due to the presence of pesticides, disturbs the ecosystem as it affects the living organisms that are dependent on the water bodies.

Any body of water found on the surface above the ground is known as surface water. It includes the saltwater in the ocean as well as the freshwater sources. Rivers, streams, lakes, wetlands, ponds, reservoirs, and creeks are some sources of freshwater. Water runoff and precipitation of water involved in the water cycle are the source of the water in the surface water bodies. While the evaporation of water from the surface of the water bodies and the seepage of water into the ground cause the loss of water from the surface water bodies. Water cycle connects the surface water and ground water supplies. Groundwater can resurface on land to supply surface water. Seepage of surface water into the ground feeds the ground water reservoir.

Surface water is easily accessible by humans for regular use compared to ground water. It is used for drinking, irrigation and for many other purposes. It is also important as many habitats and aquatic life depends on this source of water. Monitoring the earth's surface water is very important. The flow rates of streams and the tracking of vegetation around surface water bodies can be monitored by surface measurements and satellite imagery. Flow rates of streams helps to determine the impact on the availability of surface water due to human activities and climate change. On the other hand, increased surface runoff is caused by the loss of vegetation near the surface water bodies resulting in floods.

The pollution of water can be due to direct application of pesticides or due to indirect contact. To control aquatic plants direct application of pesticides into the water bodies is seen. On the other hand, due to the air flow or surface water runoff, indirect pollution of surface water bodies is seen. Pesticide seepage through soil is the major reason behind groundwater pollution since DDT era. Widespread use of the pesticides in agricultural and non-agricultural lands made the water pollution due to pesticides more of a common issue worldwide. Either the pesticide itself or the degraded form or pesticide residue is causing the water pollution (Sullivan, 2005).

2.7.1. Origin of pesticide entry into water bodies

Entrance of pesticides into water resources could be due to point sources or diffuse sources. A point source of water pollution due to pesticide can be explained as a single restricted source of pesticide that is the only source from which the water resources are being affected. The diffuse sources of pesticide contamination in water are spray drift, surface runoff and leaching. If pesticide is sprayed to any agricultural field which is very near to surface water bodies, spray drift may occur. Instead of infiltrating on the soil, due to excessive rainfall or any other reason, the overflow of water may cause water pollution as waterflow carries away the pesticides from one place to another. This phenomenon is known as surface water runoff. Leaching may contaminate the groundwater sources directly or may contaminate the surface water laterally as well. Organic pesticides are soluble to water to some extent. If a pesticide is more water soluble than soil, leaching into water bodies will contaminate the water resources (Srivastava *et al*., 2019).

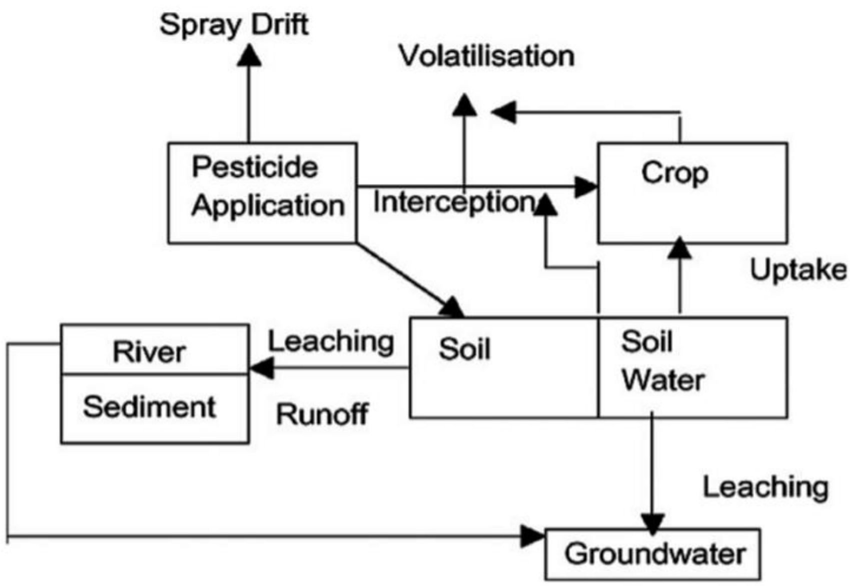

Figure 6. Pathways of a pesticide applied to a crop and how it is contaminating the water bodies (Srivastava *et al*., 2019)

2.7.2. Factors that increase pesticide movement toward water

Pesticides, when reaches to the soil, may be absorbed by the plant or destroyed by the degradation process. If not the case, it may be absorbed to the soil particles or leaching may occur through the soil. The fate of pesticide depends on several factors such as application method of pesticide, the properties of soil, the conditions of the application site and most importantly the cumulative effects of pesticide. The immigration of pesticides through the soil onto the water is controlled by the absorptivity of pesticides, solubility, volatility and degradation rate. If the absorptivity of pesticides is strong, it does not affect the water bodies that much. But if the absorptivity of pesticide by the soil is weak, then it leaches into the water resources leaving the soil, contaminating the water. Solubility is another important parameter as a pesticide which is more soluble in water will be easily carried away by the waterflow compared to a less soluble one. Volatility of an organic pesticide also controls its leaching potential as a highly volatile pesticide will transfer into the air instead of water thus leaching into the water will be reduced for that pesticide. Pesticide is degraded by hydrolysis, photolysis or microbial degradation. Some pesticides react with water as in hydrolysis and produce harmless or more harmful chemicals. Photolysis causes the breakdown of pesticides into simpler version due to the action of light. Soil bacteria and fungi also help in the degradation of pesticides near the root zone of a plant. If a pesticide takes less time to degrade in any process, it is less likely to cause water pollution by leaching. On the other hand, if the pesticide is persistent and takes more time to degrade, it can be potential source of pesticide contamination in water. Although degradation of pesticides sometimes creates more disturbing and toxic chemicals and they cause serious water pollution (Khalid, 2019).

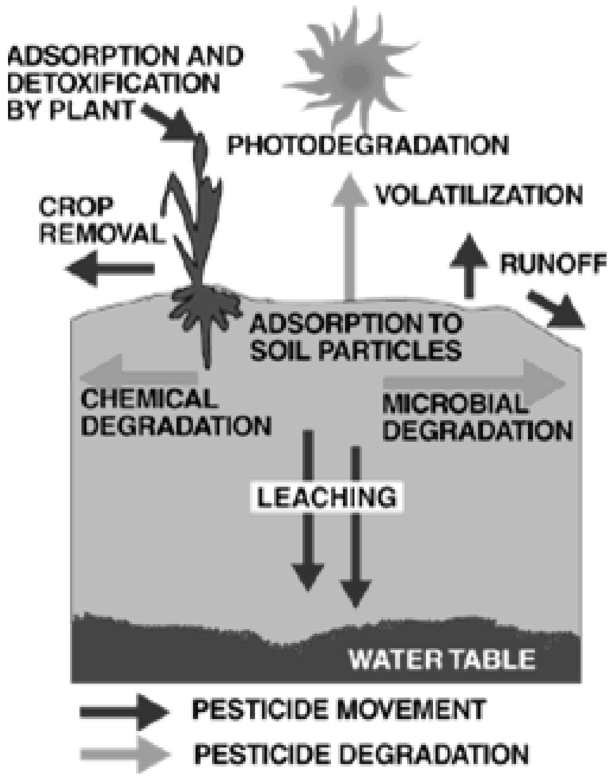

Figure 7. Pesticide contamination in water (Source: agriculture.wy.gov/pesticide/)

2.7.3. Organochlorine, organophosphorus and carbamate pesticides in water

Different studies conducted all over the world show the presence of organochlorine, organophosphorus and carbamate pesticides is surface water and groundwater samples. Despite the banning of many organochlorine pesticides, the presence of those pesticides in water samples till this date is very alarming.

Carbaryl is moderately soluble in water. The solubility of carbaryl in water increases with the increase of temperature. In 42 states, carbaryl and its residue was detected in surface water samples near agricultural and non-agricultural lands. Although the concentration of carbaryl was higher near agricultural lands compared to other types of lands. Carbaryl is detected in water in microgram per liter or ppb concentration.

Table 3. Detection of carbaryl in U.S. surface waters (Whitacre, 2008).

State	**Type of land use**	**Surface water detections (no.)**	**Concentration range (ppb)**
Alabama	Urban	61	0.002–0.422
	Agriculture	19	
	Mixed	41	
California	Urban	166	0.0005–5.20
	Agriculture	251	
	Mixed	432	
Florida	Urban	39	0.003–0.441
	Agriculture	21	
	Mixed	39	
Washington	Urban	46	0.002–0.267
	Agriculture	267	
	Mixed	106	
Texas	Urban	164	0.002–2.0
	Agriculture	13	
	Mixed	138	

In Egypt, the Nile River water samples were contaminated with different types of pesticides. In the studied area, organochlorine pesticides such as endosulfan, heptachlor, dicofol, p,p´-DDT, aldrin were found in the river water samples. Also, organophosphorus pesticides namely chlorpyrifos, triazophos, diazinon and carbamate pesticide carbofuran were also detected in the Nile water samples. 60% of the water samples were contaminated with pesticides according to the study. The most detected pesticide was Chlorpyrifos. The pesticides were also detected in the aquatic fish samples from the Nile River. (Shalaby *et al*., 2018).

In Savar and Dhamrai Upazilas in Bangladesh, water samples collected from both paddy and vegetable fields were contaminated by several organophosphorus and carbamate pesticides. Organophosphorus pesticide- Malathion and diazinon, carbamate pesticide- carbaryl and carbofuran were detected in the water samples while chlorpyrifos was not detected in any of the water samples (Chowdhury *et al*., 2012). In pond water samples collected from Feni and Meherpur region, chlorpyrifos pesticide was detected. Carbaryl was also detected in pond water samples collected from Nobipur and Senbag Upazilla (Uddin *et al*., 2013). Pond water samples collected from different locations of Bangladesh were analyzed to quantify the levels of pesticide residues and DDD, DDE, DDT, heptachlor (organochlorines), carbaryl, carbofuran (carbamate pesticides) were detected in different pond water samples in this study (Bagchi *et al*., 2009).

2.8. Analysis of pesticides using Gas Chromatography-Mass Spectrometry (GC-MS)

GCMS is an analytical method which has a broad range of applications covering many scientific disciplines. In environmental science subjects, GC-MS is commonly used to quantify the levels of organic contaminants. GCMS is highly specific to identify sample even of small volume. This is why GCMS is widely used in forensic analysis. The features of gas-chromatography and mass spectrometry are combined in GCMS to spot different substances within a test sample. This method gives more specific and accurate results compared to other chromatographic techniques available.

Gas chromatography has a mobile phase and a stationary phase to separate different molecules from a sample for identification. The mobile phase of GC contains a carrier gas, usually helium, nitrogen or hydrogen. A microscopic layer of liquid or polymer is used as a stationary phase. This microscopic layer is on an inert solid support inside a column. A column is usually a glass or metal capillary tubing. Within the column the gaseous sample being analyzed interacts with the stationary phase. As a result of which each constituent in the mobile phase gets exposed to the stationary phase. The dimension and properties of the column plays a very important role in the separation process. Each constituent in the mobile phase will travel through the length of the column and will be retained by the stationary phase and then elute from the column at different times, known as the retention time.

The mass spectrometer is composed of three parts- an ion source, mass analyzer and a detector. The sample is ionized by the bombardment of electrons. As a result of which the sample molecules become charged. The ionized charged molecules may become fragmented or non-fragmented. These molecules are separated based on their mass to charge ratio by subjecting them to an electric or magnetic field. The charged molecules are deflected and their deflected path is captured by a detector and then calculated. The signal intensity of detected ions makes the resulted spectrum. The signal intensity is the function of the mass to charge ratio of the charged ions. The masses of fragments or non-fragmented molecules are determined and the chemical structures are also elucidated.

So, in the GC portion of the GCMS, the injected sample is swept by the carrier gas flow though the column and the motion are inhibited by the adsorption of molecules into the stationary phase and so the molecules are separated based on their different retention times. This allows the MS portion of the GCMS, to capture the molecules to ionize and to detect and measure the deflected path of the ionized molecules separately based on their mass to charge ratio. Results are displayed as spectra. The spectra are of the signal intensity of detected ions as a function of the mass-to-charge ratio. Identification of the atoms or non-fragmented molecules in the sample is done by correlating known masses of an entire molecule to the identified masses. The fragmented molecules are identified through a characteristic fragmentation pattern. GC and MS together allow more accurate identification of molecules present in the sample (Sparkman *et al*., 2011).

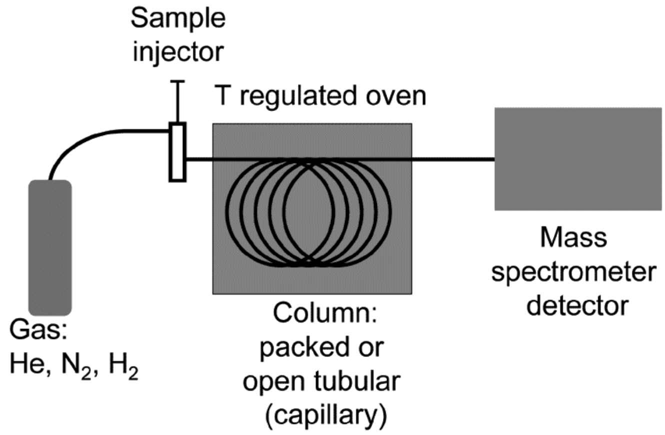

Figure 8. Schematic diagram of GCMS (Source: Wikipedia)

2.8.1. Pesticide analysis using GC and GCMS

Different studies were conducted in different places to detect and measure the concentration of pesticides using GC alone or using the GCMS. In a study conducted in India, GC was used to analyze organophosphorus and organochlorine pesticide concentration in fish samples collected from Ganga River (Wasim *et al.*, 2009). GC was also used to analyze organochlorine, organophosphorus, and carbamate pesticides in fish samples collected from the Nile River, Egypt (Shalaby *et al.*, 2018). GC-ECD was used to analyze organochlorine and organophosphorus pesticides in surface and ground water samples in a study conducted in Kanpur, Uttar Pradesh, India (Sankararamakrishnan *et al.*, 2005). Using gas chromatography–tandem mass spectrometry, carbofuran and carbaryl was determined in human blood plasma samples in a study conducted in Greece (Petropoulou *et al.*, 2006). Chlorpyrifos was also detected using GC-MS in ground water samples, surface water samples and drinking water samples in a study conducted in Madrid, Spain (Mauriz *et al.*, 2006). Using GC, Chlorpyrifos was detected in surface and ground water samples from Naushahro Feroze district, Pakistan (Arain *et al.*, 2018). GC-MS was also used to detect residues of nineteen pesticides in fresh vegetable samples collected from different markets of Dhaka city, Bangladesh (Chowdhury *et al.*, 2013).

2.9. Removal of pesticides from surface water and ground water

Removal or degradation of organic pesticides from water bodies largely depends on their chemical structure. Two common ways by which the parent organic pesticides are degraded to form less or more toxic compounds are hydrolysis and photolysis. Another method in nature to dissipate the parent organic compound is microbial degradation which depends on the bioavailability of the pesticide compound. Change in temperature and in pH values also have major effect in pesticide concentration. Chlorpyrifos concentration reduced drastically in water samples at temperature 40 degrees Celsius compared to 22 degrees Celsius according to the study. Also, in alkaline pH (pH 8) the breakdown of chlorpyrifos was notable than acidic pH (pH 6) (Marouane *et al*., 2015). Hydrolysis of carbaryl in water was studied by Rajagopal et al. in 1984. According to them, at alkaline condition with pH 8 and at temperature 20 degrees Celsius, there is a 50 percent reduction in the carbaryl concentration in water in four days due to hydrolysis of carbaryl to produce a major degradation product namely 1-napthol (Rajagopal *et al*., 1984). To reduce the pesticide contents from surface water samples different physical, biological and chemical treatment methods are used. A good result is seen in the reduction of organic pesticide amount by photochemical processes. The presence of titanium dioxide or different transitional metal oxides as catalysts, according to different studies, improves the result (Kundu *et al*., 2005).

2.9.1. Effect of UV-visible light in the concentration of chlorpyrifos and carbaryl pesticides

Degradation of pesticides due to the exposure to different intensity of light largely depends on the duration of light exposure and the type of pesticide. Chlorpyrifos was successfully reduced from different water samples using natural sunlight. Exposure of water samples to sunlight directly for 6 hours every day till day 12 resulted in a notable degradation of the pesticide chlorpyrifos. The study highlighted the significant relation of sunlight and organic pesticide content in water bodies. (Chowdhury *et al*. 2013). Another study showed that the use of titanium dioxide with UV light exposure to water samples increases the efficiency of chlorpyrifos removal from the water samples. And treating water with UV light gave more positive result compared to the use of visible light or sunlight treatment (Gafar, 2010). In Morocco, water samples contaminated with chlorpyrifos were subjected to UV light exposure using UV photometer in presence of different metal catalysts in a study. The concentration of chlorpyrifos reduced notably (Marouane *et al*., 2015).

According to Brahmia and Richard, carbaryl can be photolyzed to form naphthoquinone or hydroxynaphthoquinone products such as 1,2-naphthoquione, 1,4-naphthoquinone, 2-hydroxy-1,4-naphthoquinone, and 7-hydroxy-1,4-naphthoquinone (Brahmia and Richard, 2003). The concentration of carbaryl in water drops after phototreatment as carbaryl is degraded into simpler compounds such as 1-naphthol and 1,4-naphthoquinone due to photolysis.

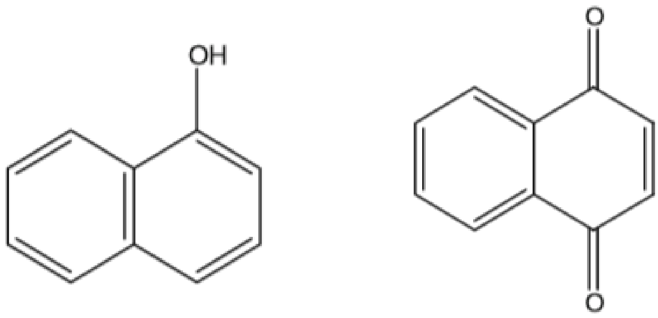

Figure 9. Structure of 1-naphthol and 1,4-naphthoquinone

Effect of photolytic reaction to remove carbaryl from water samples was also studied using UV lamp. UV light of 250 nm wavelength was used in the experiment for different duration of time to see the comparative results of the reduction of carbaryl concentration. 1 minute of exposure resulted in 80.27% degradation of carbaryl while 8 minutes of UV light exposure resulted in 100% removal of carbaryl pesticide from the water samples. UV irradiation technique brought a comparatively better result than ultrasound treatment of water samples in the same study (Khoobdel *et al*., 2010).

Chapter-3: Materials and methods

3.1. Study area and period

The present study 'Contamination of organic pesticides in surface water of Chattogram Metropolitan Area and photometric effects in removing these substances' was conducted from July to December, 2020 at Chattogram Veterinary and Animal Sciences University. The surface water samples were collected from different areas of the Chattogram Metropolitan Area. The collected surface water samples were transported to the laboratory under the Department of Applied Chemistry and Chemical Technology for storage and various experimental procedures were completed in the same laboratory. While the analysis of water samples using GCMS machine was done in the laboratory under the Department of Applied Food Science and Nutrition. The study consists of collection of surface water samples, pretreatment of surface water samples, extraction of pesticides from the water samples, storage of extracted samples, photo treatment of sample extract using polarimeter, and analysis of pesticides using GCMS.

3.2. Collection of surface water sample

Surface water samples were collected from 12 different ponds of 5 different areas of Chattogram. Four samples from Khulshi, 4 samples from Pahartoli, 2 from Kornelhat, 1 from Agrabad and 1 from Boubazar, in total 12 samples were collected.

Table 4. Sample number and location

Sample no	Sample location
01	Khulshi (BARI pond 1)
02	Khulshi (BARI pond 2)
03	Khulshi (BARI pond 3)
04	Khulshi (Poultry farm)
05	Agrabad (Agrabad deba)
06	Kornel hat (Pond 1)
07	Kornel hat (Pond 2)
08	Kaibalyadham (Dham 1)
09	Kaibalyadham (Dham 2)
10	Pahartali (Pahartali bazar)
11	Pahartali (Kali mandir)
12	Boubazar (Eidgah boubazar)

3.3. Reagents and standards

95% pure HPLC grade n-hexane, purchased from Fisher scientific USA, was used for the extraction of pesticides from water samples. HPLC grade methanol (99.9% pure) was purchased from Fisher scientific USA and was used for the preparation of standard solutions of chlorpyrifos and carbaryl pesticides.

250 mg 98.9% pure carbaryl and 100 mg 99.4% pure chlorpyrifos were purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany) for the analysis of these pesticides in water samples using GCMS.

3.4. Surface water sampling procedure

Plastic bottles with tight lid were used to collect water samples from the aforementioned areas. The bottles were thoroughly washed with distilled water before collecting the water samples. Then each bottle was rinsed with the respective surface water sample and then water samples were collected into those bottles. Small volume of water from different corners of the ponds were mixed and collected in the sampling bottles.

3.5. Storage of water samples

The water samples were transported to the laboratory immediately after collection. In the laboratory the water samples were stored in the refrigerator at 4 degrees Celsius temperature until the pretreatment of the water samples for analysis.

3.6. Pretreatment of the water samples

The water samples were filtered using 'Double rings 102 qualitative filter paper of medium speed with 12.5 cm diameter' to clarify the water samples. The process was slow and all the water samples were filtered and stored again in the plastic bottles at 4 degrees Celsius temperature.

3.7. Extraction of pesticide carbaryl and chlorpyrifos from the water samples

Extraction of Carbaryl and chlorpyrifos pesticides from water samples was done by following the 'US EPA standard method 3510C separatory funnel liquid-liquid extraction' guidelines. As an extraction solvent, in this liquid-liquid extraction process, n-hexane was used. Using a graduated measuring cylinder, 100 ml water sample was taken in a separatory funnel. For every 100 ml of water sample, 6 ml of n-hexane was added to the separatory funnel. The mixture was shaken for 1 to 2 minutes with periodic venting. Shaking the contents in the separatory funnel creates excess pressure and so periodic venting was done repeatedly to release the excess pressure. Then the contents of the separatory funnel were allowed to separate for 10 minutes. After 10 minutes the organic layer was separated in the upper layer of the separatory funnel. The upper layer was collected and the entire process was repeated. Finally, the organic pesticide extracts were collected in vials with appropriate labeling for further analysis (Arian *et al*., 2018).

3.8. Preparation of standard solution and calibration curve of carbaryl and chlorpyrifos

Standard solutions of 9 ppb, 18 ppb and 180 ppb carbaryl were prepared from the purchased 250g carbaryl standard from Dr. Ehrenstorfer GmbH (Germany). HPLC grade 99.9% pure methanol was used as solvent for carbaryl. The standards were run in the GCMS and a calibration curve was prepared from GCMS.

Standard solutions of 100 ppb, 200 ppb and 500 ppb chlorpyrifos were prepared from 100g chlorpyrifos standard, purchased from Dr. Ehrenstorfer GmbH (Germany), using HPLC grade 99.9% pure methanol as solvent. The prepared standard solutions were used to prepare the calibration curve of chlorpyrifos.

3.9. Analysis of chlorpyrifos and carbaryl using GCMS

Gas Chromatography-Mass Spectrometry is one of the most precise and accurate methods available for quantitative analysis of organic pesticides. The SCION (SQ) 456-GC from the laboratory under the Department of Applied Food Science and Nutrition was used for the analytical purpose. MSWS8: System Control Software and SCION MS-40 Software were used throughout the analysis. Helium was used as the carrier gas here. Manifold, transfer line and EI temperature were set to 40º C, 250º C and 250º C respectively. The machine is equipped with 8400 autosampler with 10 µL syringe and a split-splitless injector. For cleaning the GCMS sample source or autosampler, the steps that were followed are: 2 to 3 times pre-injection solvent flush, 2 to 3 times pre-injection sample flush, 2 to 3 times post injection solvent flush and lastly cleaning of the solvent source.

Column flow rate was 1.8 ml/min. The column temperature program was as follows: 80º C for 1 min; increase 10º C/min to 240º C; increase temperature up to 265º C and hold for 10 min. The Mass Spectrometer system was operated in the full-scan mode. MS scan time was 200 milliseconds. The MS was operated with a mass range from m/z 50 to 550. By comparing with the retention time of authentic standards and mass spectra of those standards, the chromatographic peaks of analytes were identified.

The analysis of carbaryl and chlorpyrifos pesticides in the water samples was carried out by running standards of carbaryl and chlorpyrifos respectively on Scion 456 GC machine at first. Calibration curves of carbaryl and chlorpyrifos were drawn from the data of standard sample run. After calibration, the prepared samples were taken into vials and were injected to the GCMS. Using linear equation $y= mx+C$, the concentration of carbaryl and chlorpyrifos in the water samples were measured.

3.10. Exposure of water samples to sodium light using polarimeter

A disk polarimeter, model WXG-4, manufacturer VTSYIQI, China, was used to expose the extracted water samples in visible spectrum of light. The light source of this polarimeter was a sodium lamp with 589.44 nm wavelength. All the extracted labelled water samples that showed a positive result for the presence of pesticides were exposed in sodium light for 10 minutes each to observe the photodegradation of pesticides in water samples. Then the treated water samples were sent to analyze the pesticide contents using the GCMS machine.

3.11. Data analysis

MSWS8: system control software and SCION MS-40 software were used to analyze the data received from the GCMS machine. The final results were analyzed using Microsoft Excel 2016.

Chapter-4: Results

4.1. Concentration of carbaryl in water samples

Twelve surface water samples collected from different regions of Chattogram Metropolitan Area were analyzed for the presence of carbaryl pesticides using GCMS. The location of the collection of water samples were limited to Khulshi, Agrabad, Eidgah boubazar, Kornel hut, Pahartali and Kaibalyadham. Among the samples collected from different regions, all tested positive for the presence of carbaryl in ppb (micrograms per liter) concentration. The results were compared with WHO guideline value of water quality. The lowest concentration of carbaryl was 34.65 ppb, detected in the water sample collected from a pond near Pahartali bazar (sample no 10). While the highest concentration of carbaryl was 216.1 ppb, detected in the water sample collected from a pond near Pahartali kali mandir (sample no 11). The WHO MRL of carbaryl in drinking water is 0.05 mg/L or 50 ppb. Eight out of twelve water samples contained carbaryl above the WHO guideline value.

Table 5. Carbaryl in twelve surface water samples from Chattogram

Sample no	Location	Carbaryl concentration (ppb)	
01	Khulshi (BARI pond 1)	94.92	**WHO MRL of carbaryl in drinking water is 50 ppb**
02	Khulshi (BARI pond 2)	113.7	
03	Khulshi (BARI pond 3)	77.28	
04	Khulshi (Poultry farm)	87.00	
05	Agrabad (Agrabad deba)	106.8	
06	Kornel hat (Pond 1)	61.11	
07	Kornel hat (Pond 2)	39.61	
08	Kaibalyadham (Dham 1)	35.06	
09	Kaibalyadham (Dham 2)	36.22	
10	Pahartali (Pahartali bazar)	34.65	
11	Pahartali (Kali mandir)	216.1	
12	Eidgah boubazar	201.6	

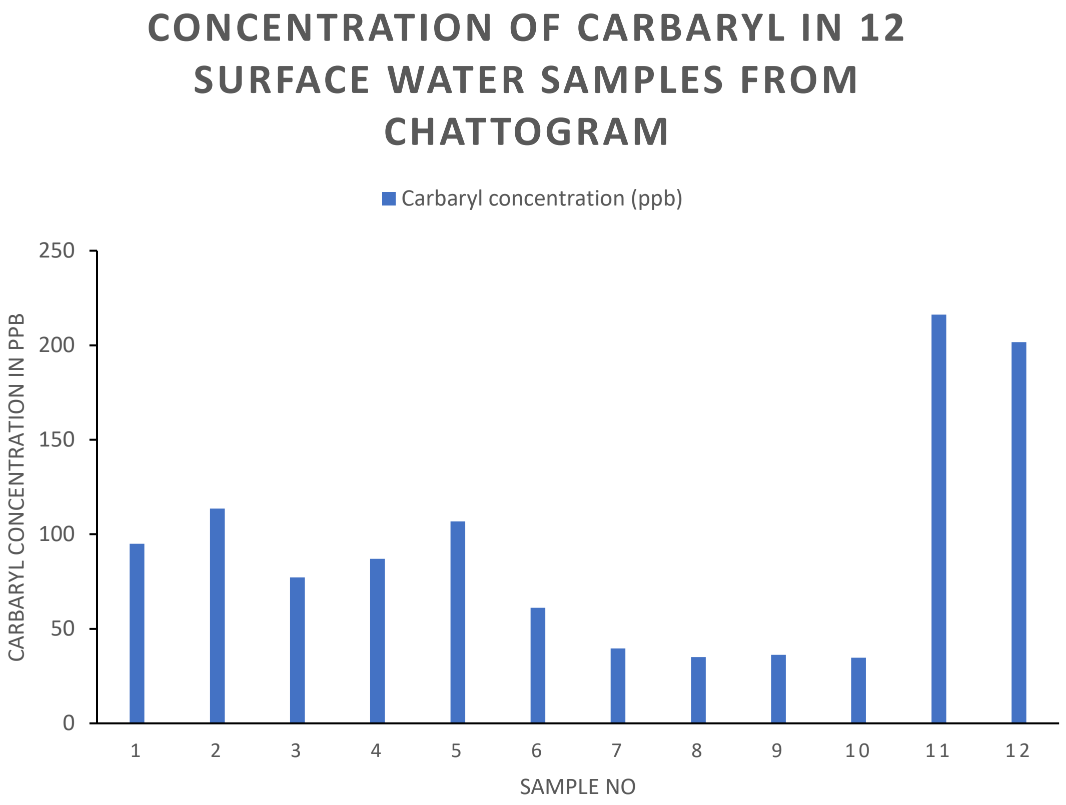

Figure 10. Concentration of carbaryl pesticide in 12 surface water samples in Chattogram

4.2.Effect of photo-treatment on the concentration of carbaryl in water samples

Each of the twelve surface water samples were treated with 589.44 nm wavelength sodium light using a disk polarimeter. After 10 minutes of light exposure, all the water samples were again analyzed in the GCMS to observe the photometric effects on the pesticide concentration. The concentration of carbaryl in the water samples dropped significantly after the photo-treatment. On an average, 95.35% of the carbaryl contents were removed from the water samples (Table 6).

Table 6. Effect of photo-treatment on the concentration of carbaryl in water samples

Sample no	Location	Initial Carbaryl concentration (ppb)	Carbaryl concentration (ppb) after photo-treatment	Percentage (%) removal of carbaryl from water samples by photo-treatment
01	Khulshi (BARI pond 1)	94.92	3.755	96.04
02	Khulshi (BARI pond 2)	113.7	5.025	95.58
03	Khulshi (BARI pond 3)	77.28	1.233	98.40
04	Khulshi (Poultry farm)	87.00	1.524	98.25
05	Agrabad (Agrabad deba)	106.8	3.489	96.73
06	Kornel hat (Pond 1)	61.11	7.380	87.92
07	Kornel hat (Pond 2)	39.61	3.032	92.35
08	Kaibalyadham (Dham 1)	35.06	1.978	94.36
09	Kaibalyadham (Dham 2)	36.22	0.820	97.74
10	Pahartali (Pahartali bazar)	34.65	2.169	93.74
11	Pahartali (Kali mandir)	216.1	7.753	96.41
12	Boubazar (Eidgah boubazar)	201.6	6.733	96.66
				Average 95.35

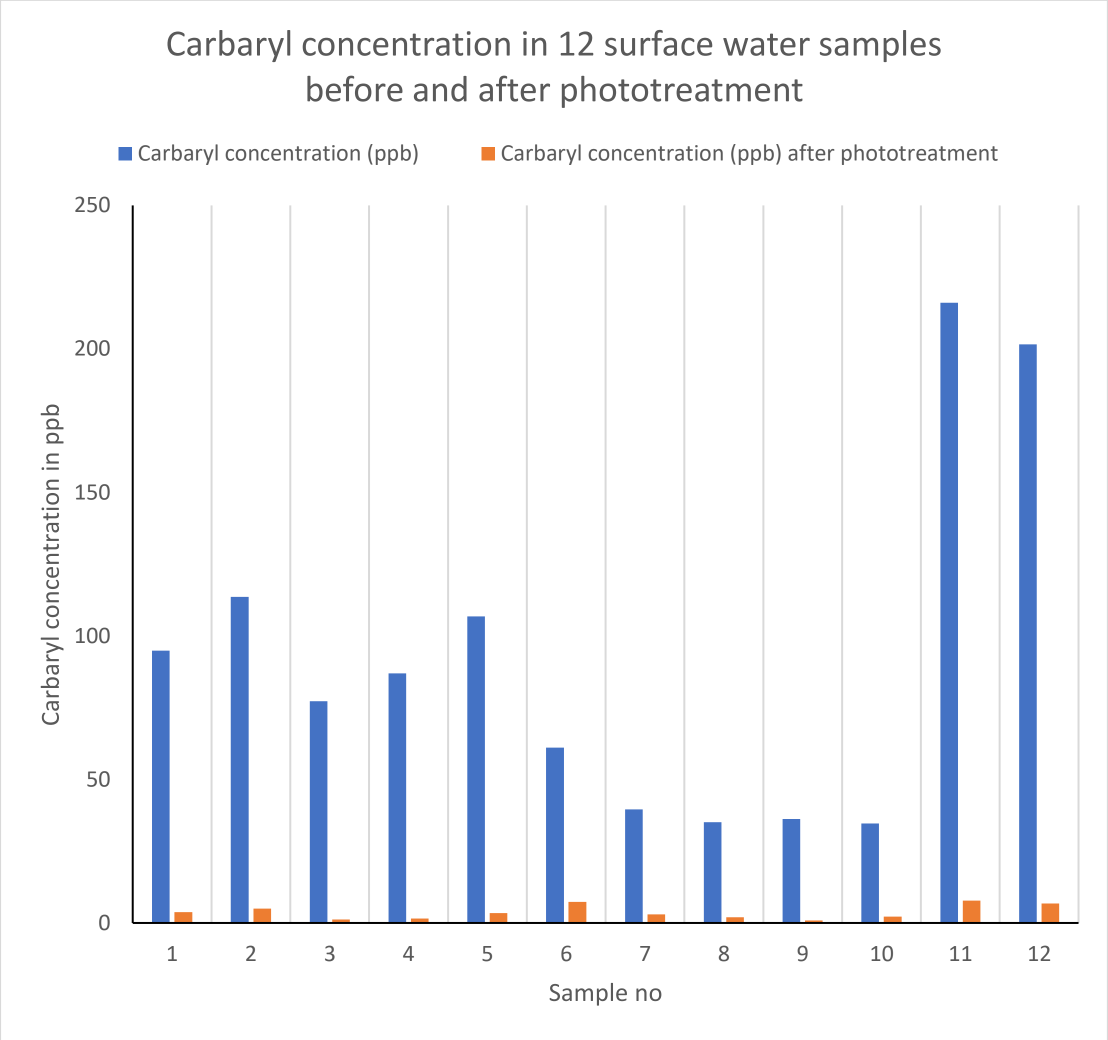

Figure 11. Concentration of carbaryl pesticide in 12 surface water samples before and after phototreatment

4.3. Concentration of chlorpyrifos in water samples

The water samples were also analyzed for the presence of chlorpyrifos. Chlorpyrifos was not detected in any of the water samples collected from different regions of Chattogram Metropolitan Area.

Chapter-5: Discussions

The present study was conducted for investigating the presence of organophosphorus and carbamate pesticides, mainly chlorpyrifos and carbaryl respectively, in surface water samples collected from different regions of Chattogram Metropolitan Area and the effect of photo-treatment of those water samples on the concentration of the pesticides.

The presence of organic pesticides in surface water bodies is always a matter of concern. Moreover, increase of textile dyes, organic & inorganic chemicals in wastewater are making the natural water systems more vulnerable. Different studies were conducted all over the world to address this issue. Very few research works had been done so far in this issue in Bangladesh. Unfortunately, there is no data available till this date to address the organic pesticide contamination level of surface water resources in Chattogram Metropolitan Area. In this study, the results show that all the collected water samples were contaminated with a carbamate pesticide namely carbaryl. The WHO maximum residue limit of carbaryl in drinking water is 50 ppb. Eight out of twelve water samples contained carbaryl ranging from 61.11 ppb to 216.1 ppb, which are above the WHO guideline value. Only four water samples contained carbaryl below the WHO guideline value which is still alarming. According to EEC, for drinking water, the total pesticide level should not exceed 0.5 ppb and individual pesticide not greater than 0.1 ppb (EEC Directive 80/778/EEC). All 12 water samples crossed the EEC borderline in the present study.

The sources of the water samples were chosen very carefully. Ponds that are very close to the agricultural farm or that are widely used by public for washing their food items, utensils and many other uses. Some specific sample locations were targeted as in Agrabad deba and Eidgah boubazar boropukur because here people regularly wash their vegetables which could be a source of the pesticides in the water bodies. On the other hand, the presence of carbaryl in water bodies could be due to surface water runoff.

In a study conducted in Southern Malawi, the concentration of carbaryl in surface water samples were recorded to be ranging from 83 ppb to 254 ppb (Kanyika-Mbewe *et al.*, 2020). In 42 states of the United States, carbaryl and its residue was detected in surface water samples near agricultural and non-agricultural lands in ppb concentration (Whitacre, 2008). In Noakhali district, two water samples were reported to contain carbaryl, one sample contained 1.32 ppb carbaryl and the other one contained 6.40 ppb carbaryl (Uddin *et al*., 2013). In the present study, the results showed that the lowest carbaryl concentration was 34.65 ppb, detected in the water sample collected from a pond near Pahartali bazar (sample no 10). While the highest concentration of carbaryl was 216.1 ppb, detected in the water sample collected from a pond near Pahartali kali mandir (sample no 11).

Pesticides of carbamate origin such as carbaryl are rapidly taken up by plants from soil and water through the roots. Then they are translocated mainly into the leaves and they sue to chemical degradation, metabolites are found in the tissues of plants. So, washing those plant tissues or food from plant sources that were subjected to carbaryl exposure during cultivation could retain the pesticide and later contaminate the water bodies where they are being washed off (Thapar *et al*., 1995). Wash water of different vegetables were tested for the presence of organic pesticides in India in a recent study and almost all the samples were tested positive for the presence of pesticide (Karthikumar *et al*., 2020).

Chlorpyrifos, an organophosphorus pesticide, was not detected in any of the water samples in the present study. In a similar study conducted in Argentina, 42% of the 26 surface water samples collected contained a detectable and alarming levels of chlorpyrifos (Marino *et al*., 2005). In India, a recent study showed the presence of chlorpyrifos pesticides in the wash water of cauliflower, grapes, coriander leaves, brinjal and bitter guard which clearly shows the importance of testing the water bodies for the presence of this pesticide where vegetables are regularly washed off by general people (Sankar *et al*., 2020).

In Bangladesh, CPS is persistently found at alarming levels in a number of domestic vegetables and surface and groundwater sources (Tanvir *et al*., 2015). In a study conducted in the coastal area of Bangladesh, the residue of chlorpyriphos was detected in only one pond water sample, from Feni at a concentration of 3.80 ppb (Uddin *et al*., 2013). In another study conducted in Meherpur region, two samples collected from two different pond, contained residue of CPS at ppm level (Uddin *et al*., 2013). In a study conducted in Taragong Thana of Rangpur district in Bangladesh, CPS was not detected in any of surface water samples collected for the study. And the author concluded that may be the farmers in that region do not use that pesticide anymore (Ara *et al*, 2014).

In the present study, CPS was not detected in any of the surface water samples. The result suggests that may be the farmers in Chattogram metropolitan area do not use CPS as a pesticide or may be the usage is very limited.

According to Thapar, one of the ways by which the carbamate pesticides (carbaryl) in water are degraded is photolysis (Thapar *et al*., 1995). The effect of photolytic reaction to remove carbaryl from water samples was investigated using UV light of 250 nm wavelength where 1 minute of exposure resulted in 80.27% degradation of carbaryl while 8 minutes of UV light exposure resulted in 100% removal of carbaryl pesticide from the water samples (Khoobdel *et al*., 2010).

Chlorpyrifos was successfully reduced from different water samples using natural sunlight. Exposure of water samples to sunlight directly for 6 hours every day till day 12 resulted in a notable degradation of the pesticide chlorpyrifos. The study highlighted the significant relation of sunlight and organic pesticide content in water bodies. (Chowdhury *et al*., 2013). Treating water with UV light gave more positive result compared to the use of visible light or sunlight treatment to remove chlorpyrifos pesticide from water samples (Gafar, 2010).

In the present study, a disk polarimeter with sodium lamp having 589.44 nm wavelength light was used. After 10 minutes exposure to the 589.44 nm wavelength light, on an average, 95.35% of the carbaryl contents were removed from the water samples. The lowest removal percentage of carbaryl in water sample was 87.92% from Kornel hut pond (sample no 6) while the highest carbaryl removal percentage from water samples was 98.40% from Khulshi (sample no 3). Due to photolytic degradation carbaryl might have been broken down into simpler compounds such as 1-naphthol or 1,4-naphthoquinone.

The level of contamination of metropolitan area's surface water by organic pesticides should be less than the rural areas as majority of the animal farms, agricultural farms and lands are in the rural areas. Therefore, the chances of pesticide contamination of surface water resources are higher in the rural areas compared to the metropolitan area. Our study result showed a significant level of organic pesticide contamination of surface water resources collected from Chattogram Metropolitan Area and the chances are high that the level of contamination might be more alarming in the rural areas.

Chapter-6: Conclusion

The results from this study revealed that the surface water sources of Chattogram Metropolitan Area are contaminated with an organic pesticide carbaryl. Eight out of twelve water samples contained carbaryl above the WHO guideline value. All twelve water samples crossed the borderline proposed by EEC for any individual pesticide in drinking water. There was no presence of the organophosphorus pesticide chlorpyrifos in any of the water samples. This study was conducted to observe the effect of sodium light of visible spectrum with 589.44 nm wavelength to reduce the pesticide concentration from the surface water samples. After 10 minutes exposure to sodium light, on an average there was around 95.35% reduction of carbaryl concentration from all of the water samples. The result of this study suggested that treating water with sodium light could reduce the concentration of organic pesticide carbaryl present in water.

Chapter-7: Recommendations

In the present study only two organic pesticides were analyzed with a limited sample size due to budget shortage and also due to the ongoing crisis of COVID-19 pandemic. Analysis of other organophosphorus and carbamate pesticides is suggested, such as carbofuran. Carbofuran was initially included in our study plan but due to different limitations the analysis was not completed. Also, the sample size needs to be increased and a broader sampling area needs to be covered to get the real picture of pesticide contamination. Surface water samples from the rural areas could also be analyzed to observe the level of pesticide contamination.

Further studies need to be carried out to check the effect of changing other parameters of water samples such as changing the pH, temperature, treating the water samples with appropriate catalyst. Also, to see the effect of sodium light of 589.44 nm wavelength, the duration of exposure could be of different ranges. The wavelength of light could also be of different ranges. Further studies are also suggested to observe the seasonal effect on pesticide contamination in surface water bodies.

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Appendix A: Experimental Data 1

Carbaryl calibration curve in GCMS

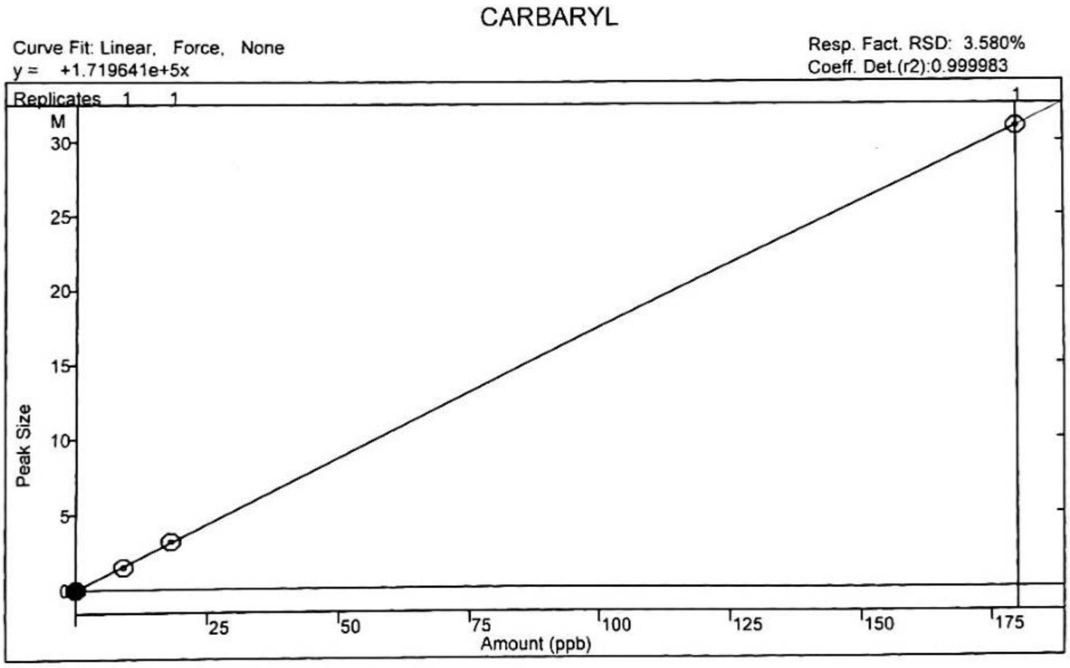
Print Date: 19 Oct 2020 13:26:35 — Compound Summary for CARBARYL

Compound Summary Report

Instrument ID:	GC-MS
Method:	c:\brukerws\methods\pesticide_run_method_final_14.10.2020.mth
Last Calibration:	10/15/2020 11:11 AM
Data Path:	C:\BrukerWS\data\13.10.2020\14.10.2020\

1) CARBARYL

Level	File	Conc. ppb	RT	Response Ion: 115.1	RF
1	std_1_6_ppm.xms				
2	std_2_12_ppm.xms				
3	std_3_24_ppm.xms				
1	Std_1_100ppb.xms				
2	Std_2_200ppb.xms				
3	Std_3_500ppb.xms				
1	Std_1_200_ppb.xms				
1	carbanyl_18_ppm.xms				
1	Carbaryl_std_9ppb.XMS				
1	Carbaryl_std_9ppb.xms				
1	Carbaryl_std_18ppb				
1	arbaryl_std_180ppb				
1	std_1_9_ppb.xms	8.594	13.950	1.478e+6	164209.141
2	std_2_18_ppb.xms	18.452	13.948	3.173e+6	176281.500
3	std_3_180_ppb.xms	179.975	13.948	3.095e+7	171940.328
1	std_1_9_ppb.XMS				
1	std_2_18_ppb.XMS				
1	std_3_180_ppb.XMS				
1	std_1_9_ppb.XMS				
1	std_2_18_ppb.XMS				
1	std_3_180_ppb.XMS				
	Average:		2.989		170810.313
	RF Range:				136648.250 - 204972.375



Concentration of carbaryl (Chromatogram & Mass spectrum for sample no 01)

Print Date: 19 Oct 2020 13:28:39

Target Compound Report for #1 from sample_1.xms

Sample ID:	sample_1	Operator:	Jewel
Instrument ID:	GC-MS	Last Calibration:	10/19/2020 1:22 PM
Measurement Type:	Area	Calibration Type:	External Standard
Acquisition Date:	10/19/2020 1:28 AM	Data File:	... violet\sample_1.xms
Calculation Date:	10/19/2020 1:22 PM	Method:	...final_15.10.2020.mth
Sample Type:	Analysis		
Inj. Sample Notes:	None		

Compound Information

Peak Name: CARBARYL

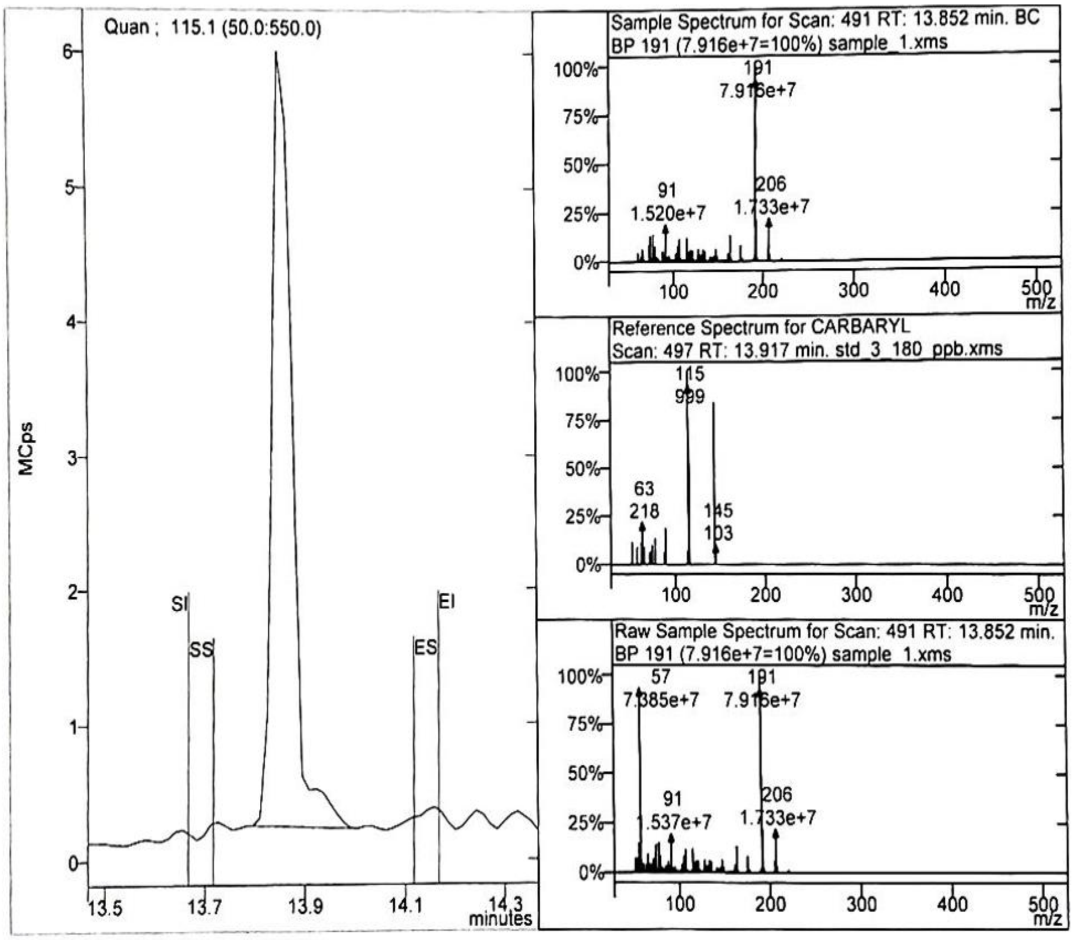
Result Index: 1 Compound Number: 1 CAS Number: None Identified

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	13.917 +/- 0.200	13.856 min.	Pass
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	115.1		
Calibration Equation	Linear, Force, None	y = +1.7196e+5x	
Area	>=500	1.632e+7	Pass
Height		5.769e+6	
Amount	>= 0.000 ppb	94.920 ppb	Pass



Concentration of carbaryl (Chromatogram & Mass spectrum for sample no 02)

Print Date: 19 Oct 2020 13:32:43

Target Compound Report for #1 from sample_2.xms

Sample ID:	sample_2	Operator:	Jewel
Instrument ID:	GC-MS	Last Calibration:	10/19/2020 1:22 PM
Measurement Type:	Area	Calibration Type:	External Standard
Acquisition Date:	10/19/2020 1:53 AM	Data File:	... violet\sample_2.xms
Calculation Date:	10/19/2020 1:22 PM	Method:	...final_15.10.2020.mth
Sample Type:	Analysis		
Inj. Sample Notes:	None		

Compound Information

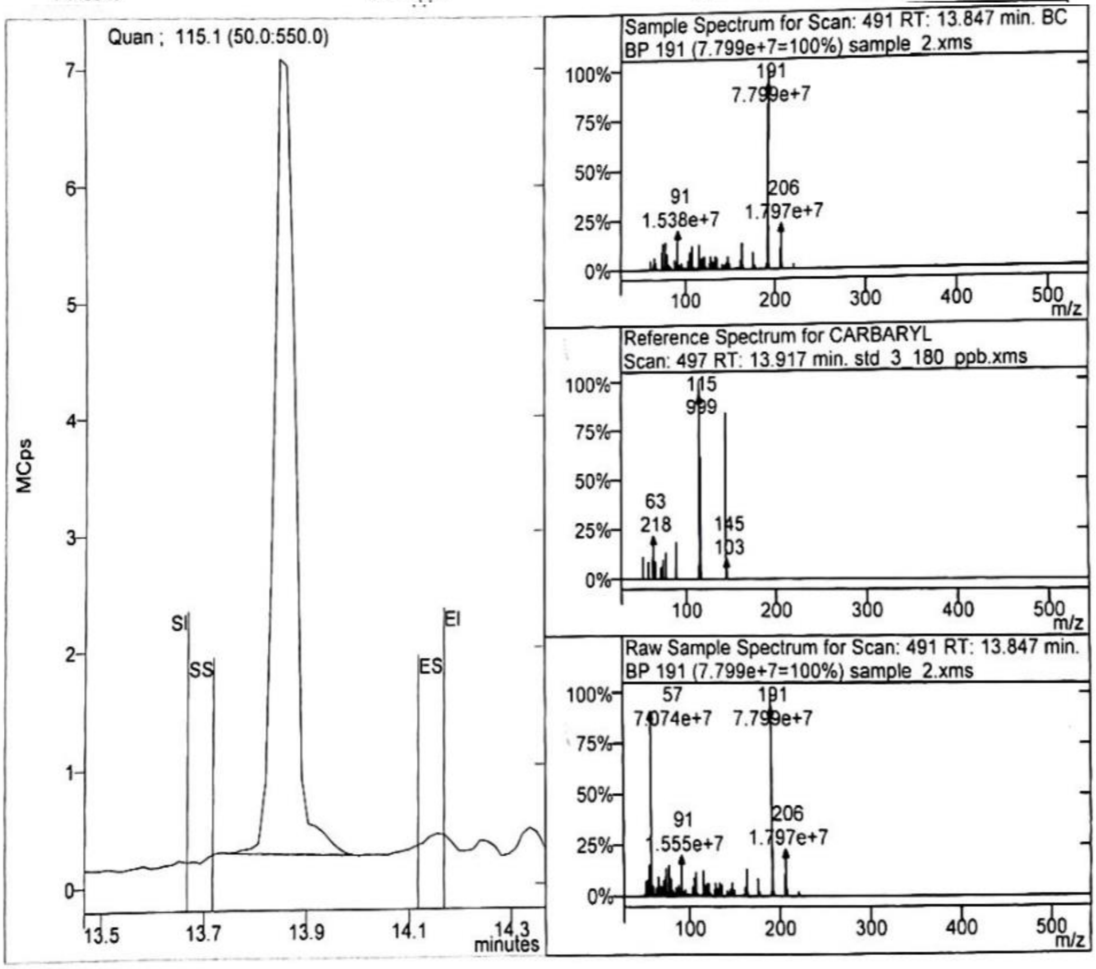
Peak Name:	CARBARYL	CAS Number: None	Identified
Result Index:	1 Compound Number: 1		

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	13.917 +/- 0.200	13.854 min.	Pass
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	115.1		
Calibration Equation	Linear, Force, None	y = +1.7196e+5x	
Area	>=500	1.954e+7	Pass
Height		6.820e+6	
Amount	>= 0.000 ppb	113.653 ppb	Pass



Concentration of carbaryl (Chromatogram & Mass spectrum for sample no 03)

Print Date: 19 Oct 2020 13:35:32

Target Compound Report for #1 from sample_3.xms

Sample ID:	sample_3	Operator:	Jewel
Instrument ID:	GC-MS	Last Calibration:	10/19/2020 1:22 PM
Measurement Type:	Area	Calibration Type:	External Standard
Acquisition Date:	10/19/2020 2:17 AM	Data File:	... violet\sample_3.xms
Calculation Date:	10/19/2020 1:22 PM	Method:	...final_15.10.2020.mth
Sample Type:	Analysis		
Inj. Sample Notes:	None		

Compound Information

Peak Name: CARBARYL

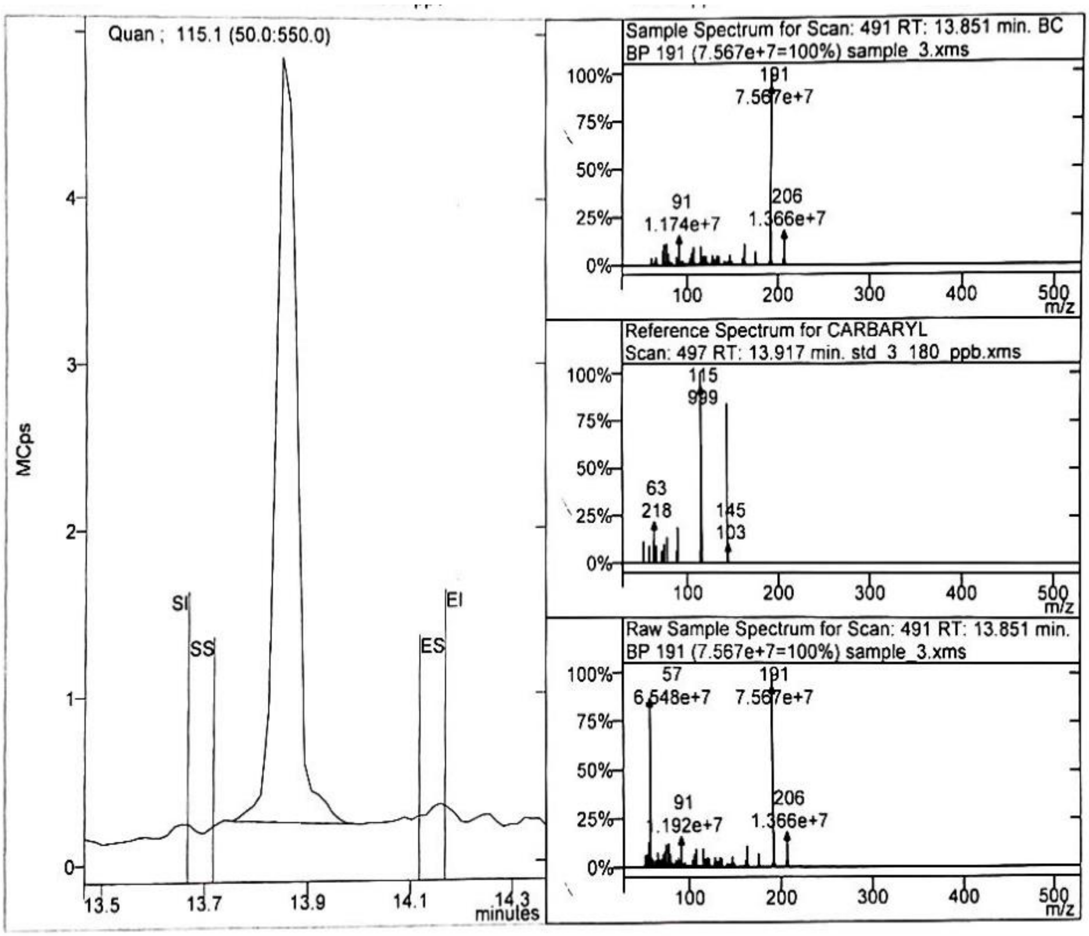
Result Index: 1 Compound Number: 1 CAS Number: None Identified

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	13.917 +/- 0.200	13.856 min.	Pass
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	115.1		
Calibration Equation	Linear, Force, None	y = +1.7196e+5x	
Area	>=500	1.329e+7	Pass
Height		4.607e+6	
Amount	>= 0.000 ppb	77.284 ppb	Pass



Concentration of carbaryl (Chromatogram & Mass spectrum for sample no 04)

Print Date: 19 Oct 2020 13:38:09

Target Compound Report for #1 from sample_4.xms

Sample ID:	sample_4	Operator:	Jewel
Instrument ID:	GC-MS	Last Calibration:	10/19/2020 1:22 PM
Measurement Type:	Area	Calibration Type:	External Standard
Acquisition Date:	10/19/2020 2:42 AM	Data File:	... violet\sample_4.xms
Calculation Date:	10/19/2020 1:22 PM	Method:	...final_15.10.2020.mth
Sample Type:	Analysis		
Inj. Sample Notes:	None		

Compound Information

Peak Name: CARBARYL

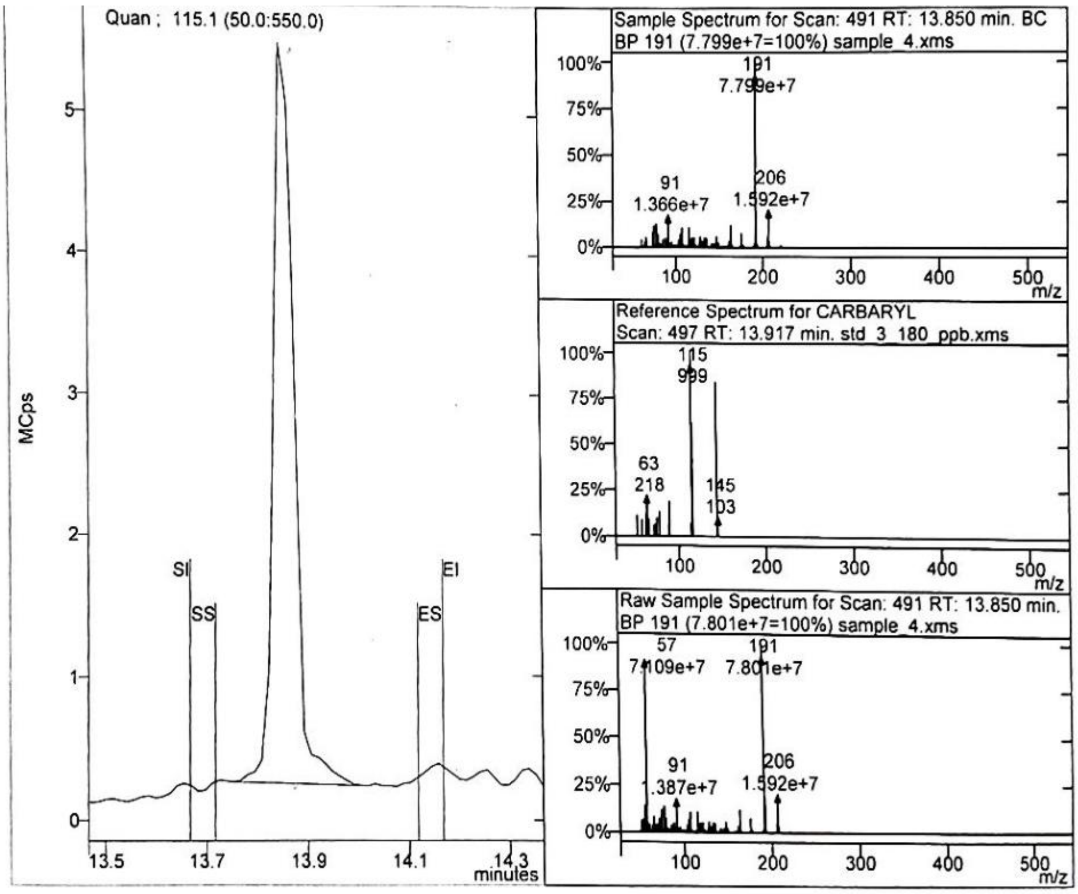
Result Index: 1 Compound Number: 1 CAS Number: None Identified

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	13.917 +/- 0.200	13.854 min.	Pass
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	115.1		
Calibration Equation	Linear, Force, None	y = +1.7196e+5x	
Area	>=500	1.496e+7	Pass
Height		5.247e+6	
Amount	>= 0.000 ppb	87.003 ppb	Pass



Concentration of carbaryl (Chromatogram & Mass spectrum for sample no 05)

Print Date: 19 Oct 2020 13:43:54

Target Compound Report for #1 from sample_5.xms

Sample ID:	sample_5	Operator:	Jewel
Instrument ID:	GC-MS	Last Calibration:	10/19/2020 1:22 PM
Measurement Type:	Area	Calibration Type:	External Standard
Acquisition Date:	10/19/2020 3:06 AM	Data File:	... violet\sample_5.xms
Calculation Date:	10/19/2020 1:22 PM	Method:	...final_15.10.2020.mth
Sample Type:	Analysis		
Inj. Sample Notes:	None		

Compound Information

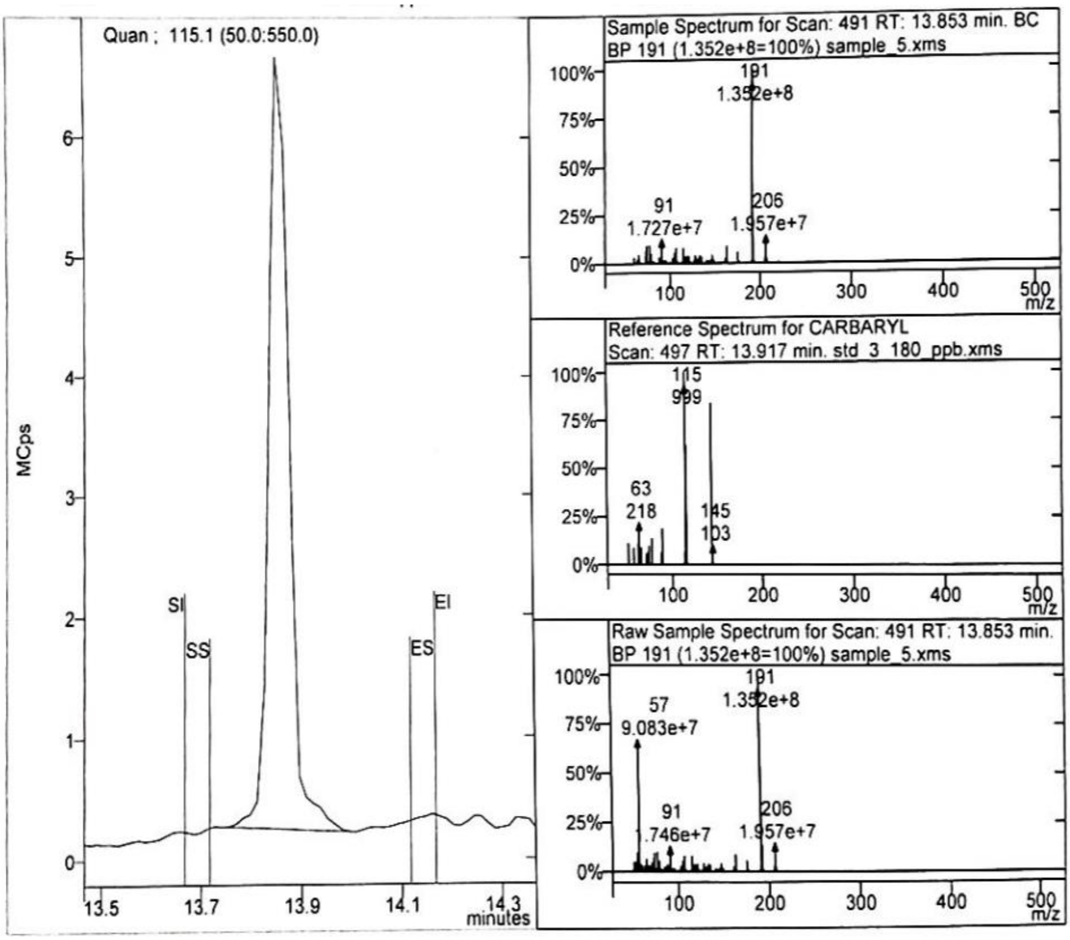
Peak Name:	CARBARYL		
Result Index:	1 Compound Number: 1	CAS Number: None	Identified

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	13.917 +/- 0.200	13.856 min.	Pass
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	115.1		
Calibration Equation	Linear, Force, None	y = +1.7196e+5x	
Area	>=500	1.836e+7	Pass
Height		6.422e+6	
Amount	>= 0.000 ppb	106.783 ppb	Pass



Concentration of carbaryl (Chromatogram & Mass spectrum for sample no 06)

Print Date 19 Oct 2020 14 30 07 — Target Compound Report for #1 from sample_6 xms

Sample ID	sample_6	Operator	Jewel
Instrument ID	GC-MS	Last Calibration	10/19/2020 1 22 PM
Measurement Type	Area	Calibration Type	External Standard
Acquisition Date	10/18/2020 11 26 PM	Data File	... violet\sample_6 xms
Calculation Date	10/19/2020 1 22 PM	Method	...final_15 10 2020 mth
Sample Type	Analysis		
Inj Sample Notes	None		

Compound Information

Peak Name: CARBARYL

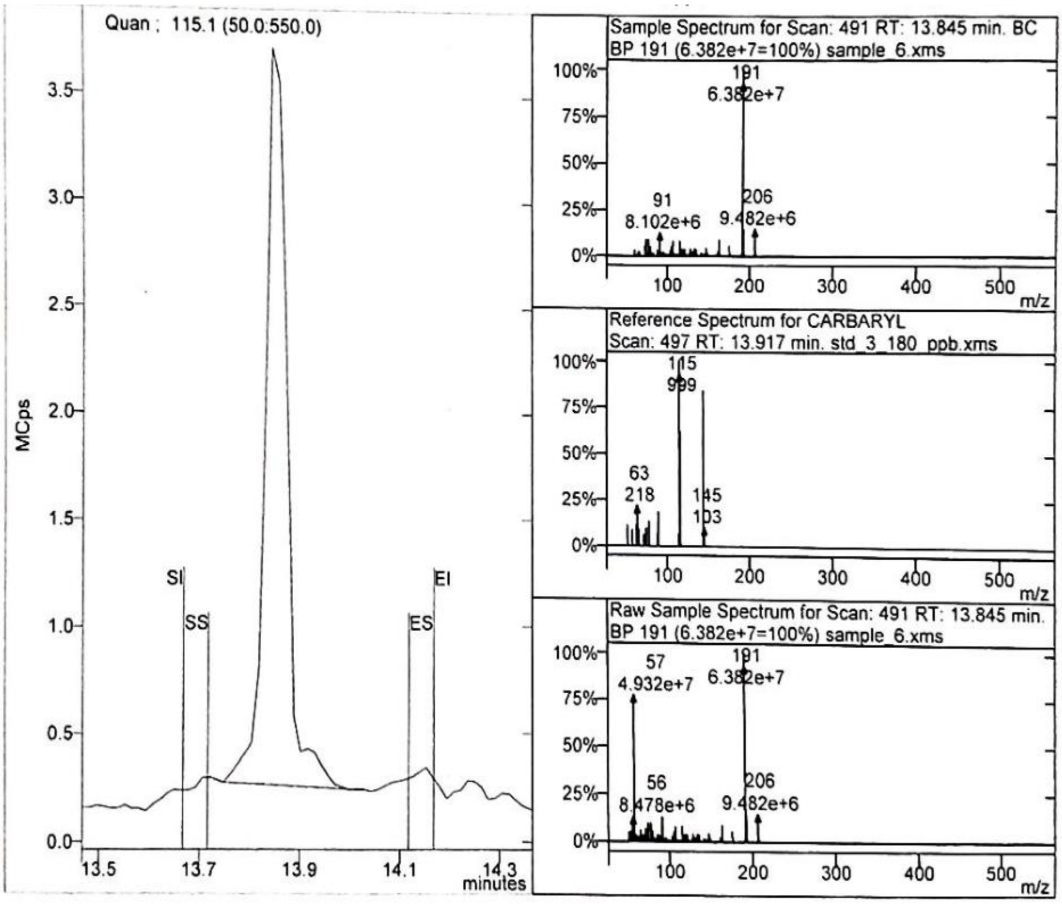
Result Index: 1 Compound Number: 1 CAS Number: None Identified

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	13 917 +/- 0 200	13.851 min.	Pass
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	115.1		
Calibration Equation	Linear, Force, None	y = +1.7196e+5x	
Area	>=500	1.051e+7	Pass
Height		3.456e+6	
Amount	>= 0.000 ppb	61.113 ppb	Pass



Concentration of carbaryl (Chromatogram & Mass spectrum for sample no 07)

Print Date: 19 Oct 2020 14:32:30 | Target Compound Report for #1 from sample_7.xms

Sample ID:	sample_7	Operator:	Jewel
Instrument ID:	GC-MS	Last Calibration:	10/19/2020 1:22 PM
Measurement Type:	Area	Calibration Type:	External Standard
Acquisition Date:	10/18/2020 11:51 PM	Data File:	... violet\sample_7.xms
Calculation Date:	10/19/2020 1:22 PM	Method:	...final_15.10.2020.mth
Sample Type:	Analysis		
Inj. Sample Notes:	None		

Compound Information

Peak Name: CARBARYL

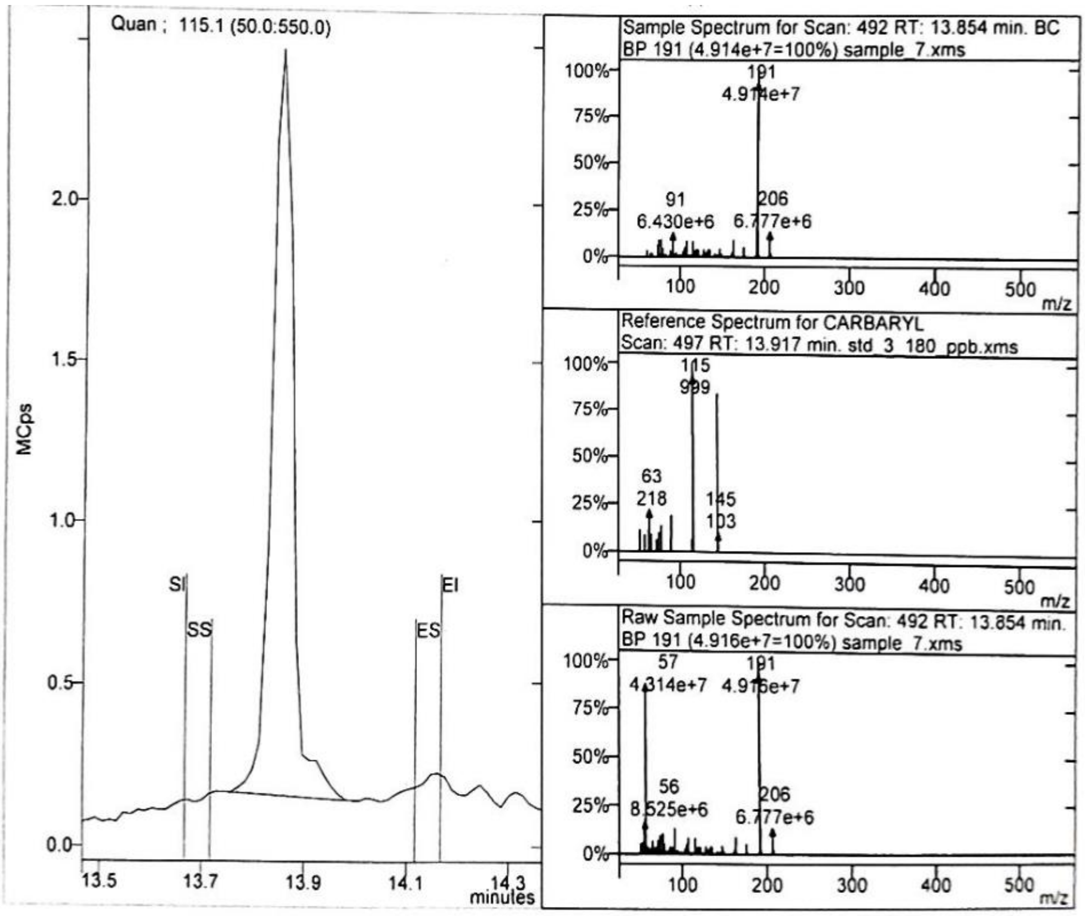
Result Index: 1 Compound Number: 1 CAS Number: None Identified

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	13.917 +/- 0.200	13.852 min.	Pass
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	115.1		
Calibration Equation	Linear, Force, None	y = +1.7196e+5x	
Area	>=500	6.812e+6	Pass
Height		2.328e+6	
Amount	>= 0.000 ppb	39.613 ppb	Pass



Concentration of carbaryl (Chromatogram & Mass spectrum for sample no 08)

Print Date: 19 Oct 2020 14:35:48

Target Compound Report for #1 from sample_8.xms

Sample ID:	sample_8	Operator:	Jewel
Instrument ID:	GC-MS	Last Calibration:	10/19/2020 1:22 PM
Measurement Type:	Area	Calibration Type:	External Standard
Acquisition Date:	10/19/2020 12:15 AM	Data File:	... violet\sample_8.xms
Calculation Date:	10/19/2020 1:22 PM	Method:	...final_15.10.2020.mth
Sample Type:	Analysis		
Inj. Sample Notes:	None		

Compound Information

Peak Name: CARBARYL

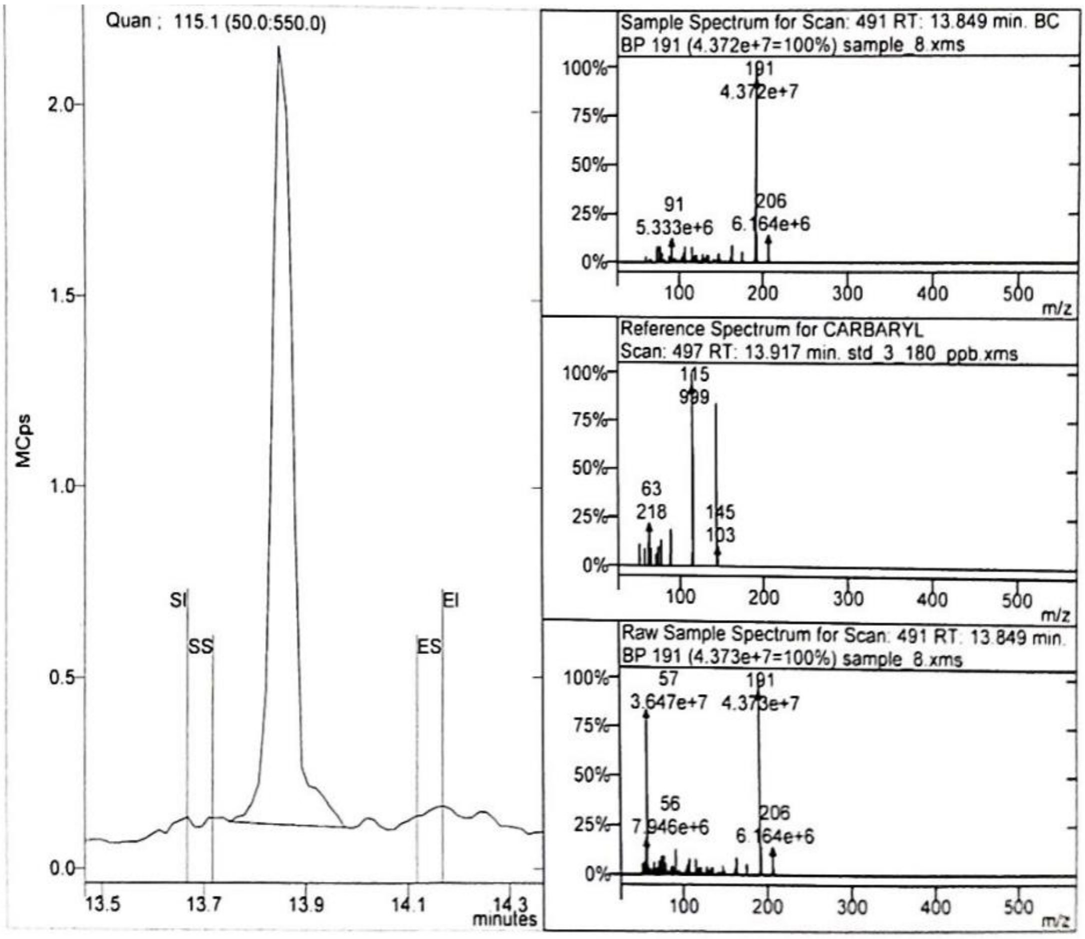
Result Index: 1 Compound Number: 1 CAS Number: None Identified

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	13.917 +/- 0.200	13.853 min.	Pass
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	115.1		
Calibration Equation	Linear, Force, None	y = +1.7196e+5x	
Area	>=500	6.030e+6	Pass
Height		2.049e+6	
Amount	>= 0.000 ppb	35.064 ppb	Pass



Concentration of carbaryl (Chromatogram & Mass spectrum for sample no 09)

Print Date 19 Oct 2020 14 38 39

Target Compound Report for #1 from sample_9.xms

Sample ID	sample_9	Operator:	Jewel
Instrument ID	GC-MS	Last Calibration	10/19/2020 1 22 PM
Measurement Type	Area	Calibration Type	External Standard
Acquisition Date	10/19/2020 12 40 AM	Data File	... violet\sample_9 xms
Calculation Date	10/19/2020 1 22 PM	Method	...final_15 10 2020 mth
Sample Type	Analysis		
Inj. Sample Notes	None		

Compound Information

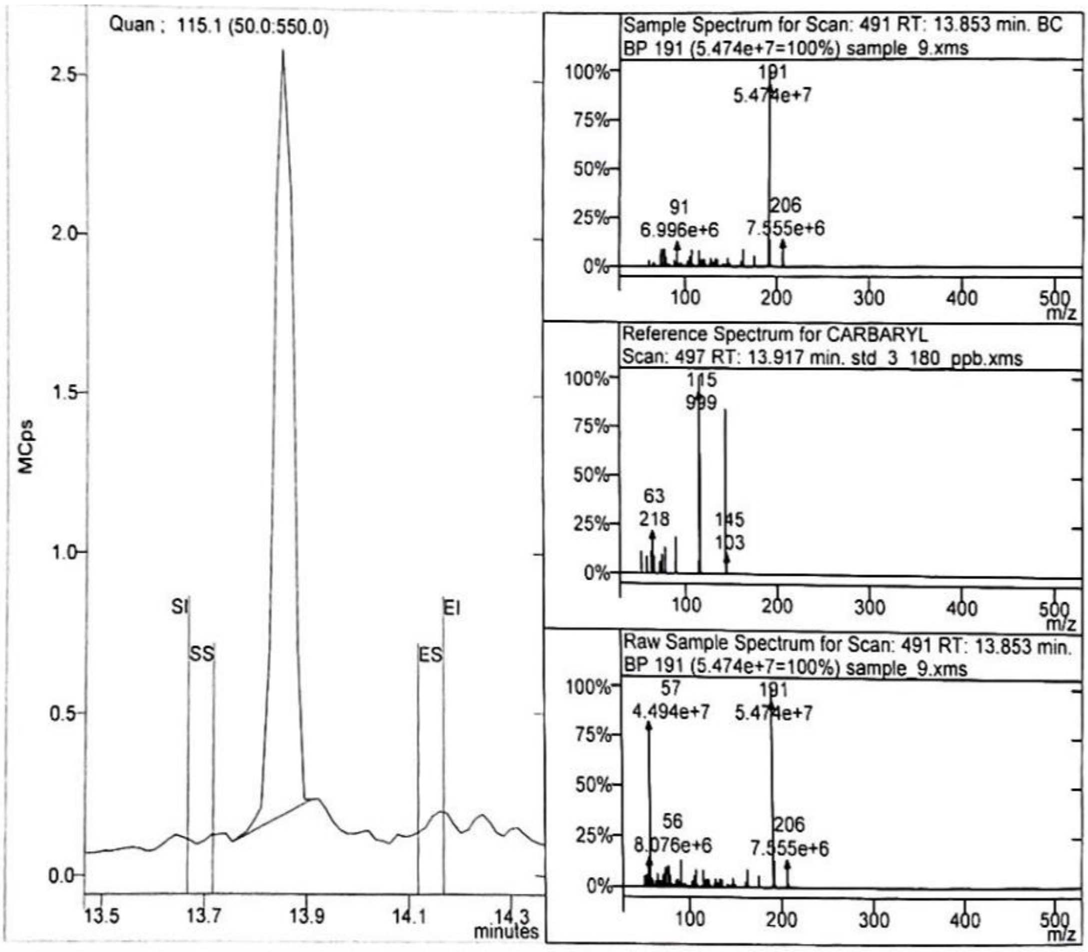
Peak Name:	CARBARYL			
Result Index:	1	Compound Number: 1	CAS Number: None	Identified

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	13.917 +/- 0.200	13.853 min.	Pass
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	115.1		
Calibration Equation	Linear, Force, None	y = +1.7196e+5x	
Area	>=500	6.229e+6	Pass
Height		2.405e+6	
Amount	>= 0.000 ppb	36.220 ppb	Pass



Concentration of carbaryl (Chromatogram & Mass spectrum for sample no 10)

Print Date: 19 Oct 2020 13:30:58

Target Compound Report for #1 from sample_10.xms

Sample ID:	sample_10	Operator:	Jewel
Instrument ID:	GC-MS	Last Calibration:	10/19/2020 1:22 PM
Measurement Type:	Area	Calibration Type:	External Standard
Acquisition Date:	10/19/2020 1:04 AM	Data File:	...violet\sample_10.xms
Calculation Date:	10/19/2020 1:22 PM	Method:	...final_15.10.2020.mth
Sample Type:	Analysis		
Inj. Sample Notes:	None		

Compound Information

Peak Name: CARBARYL

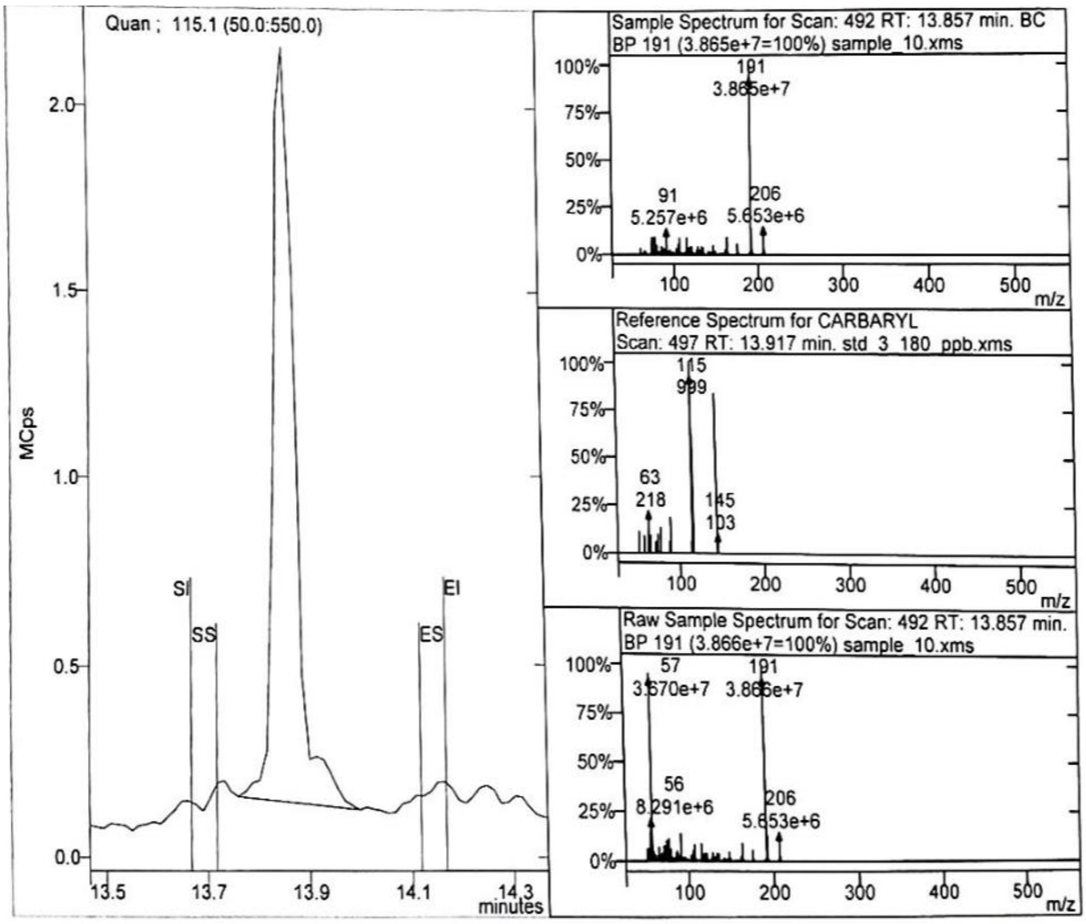
Result Index: 1 Compound Number: 1 CAS Number: None Identified

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	13.917 +/- 0.200	13.853 min.	Pass
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	115.1		
Calibration Equation	Linear, Force, None	y = +1.7196e+5x	
Area	>=500	5.959e+6	Pass
Height		2.020e+6	
Amount	>= 0.000 ppb	34.653 ppb	Pass



Concentration of carbaryl (Chromatogram & Mass spectrum for sample no 11)

Print Date: 19 Oct 2020 14:40:29

Target Compound Report for #1 from sample_kl.xms

Sample ID:	sample_kl	Operator:	Jewel
Instrument ID:	GC-MS	Last Calibration:	10/19/2020 1:22 PM
Measurement Type:	Area	Calibration Type:	External Standard
Acquisition Date:	10/18/2020 10:38 PM	Data File:	...violet\sample_kl.xms
Calculation Date:	10/19/2020 1:22 PM	Method:	...final_15.10.2020.mth
Sample Type:	Analysis		
Inj. Sample Notes:	None		

Compound Information

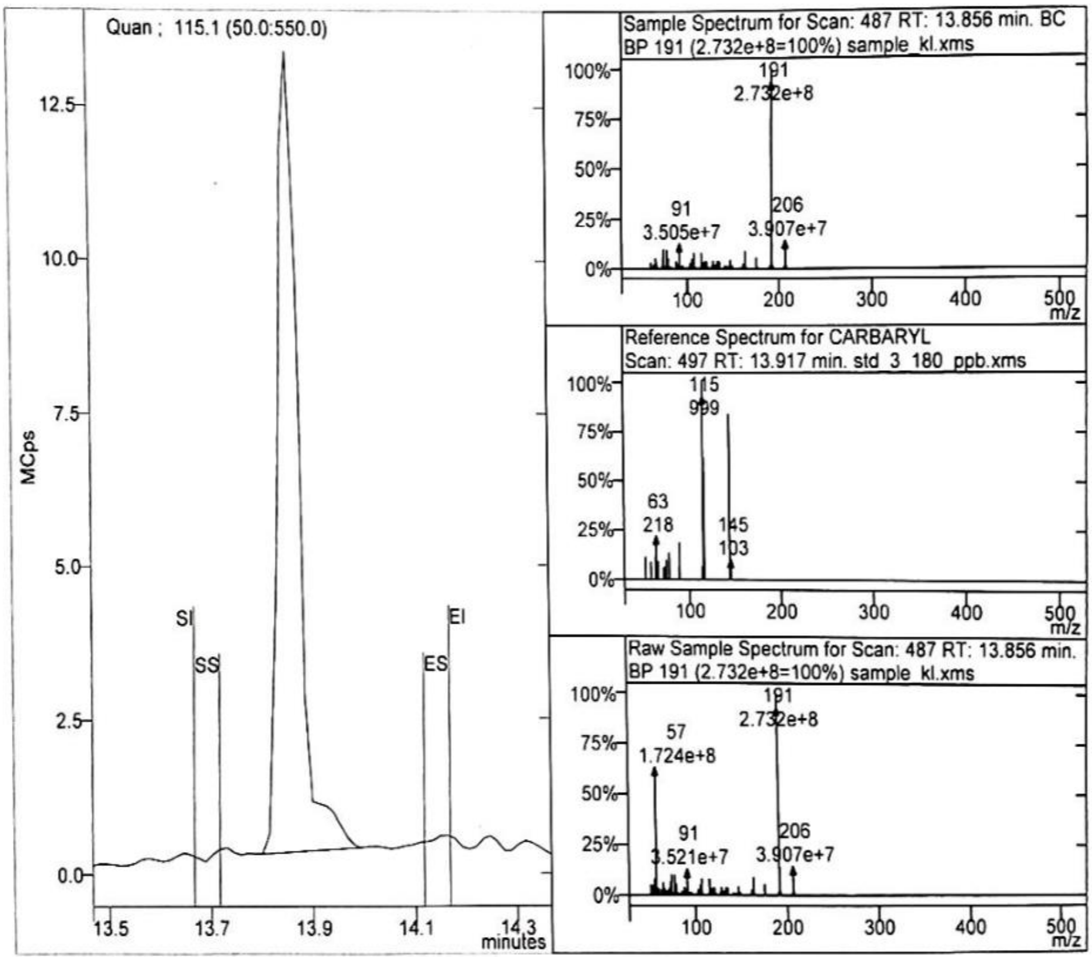
Peak Name:	CARBARYL		
Result Index:	1 Compound Number: 1	CAS Number: None	Identified

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	13.917 +/- 0.200	13.853 min.	Pass
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	115.1		
Calibration Equation	Linear, Force, None	y = +1.7196e+5x	
Area	>=500	3.717e+7	Pass
Height		1.304e+7	
Amount	>= 0.000 ppb	216.121 ppb	Pass



Concentration of carbaryl (Chromatogram & Mass spectrum for sample no 12)

Print Date: 19 Oct 2020 13:41:24 Target Compound Report for #1 from sample_4_kl.xms

Sample ID:	sample_4_kl	Operator:	Jewel
Instrument ID:	GC-MS	Last Calibration:	10/19/2020 1:22 PM
Measurement Type:	Area	Calibration Type:	External Standard
Acquisition Date:	10/18/2020 11:02 PM	Data File:	...olet\sample_4_kl.xms
Calculation Date:	10/19/2020 1:22 PM	Method:	...final_15.10.2020.mth
Sample Type:	Analysis		
Inj. Sample Notes:	None		

Compound Information

Peak Name: CARBARYL

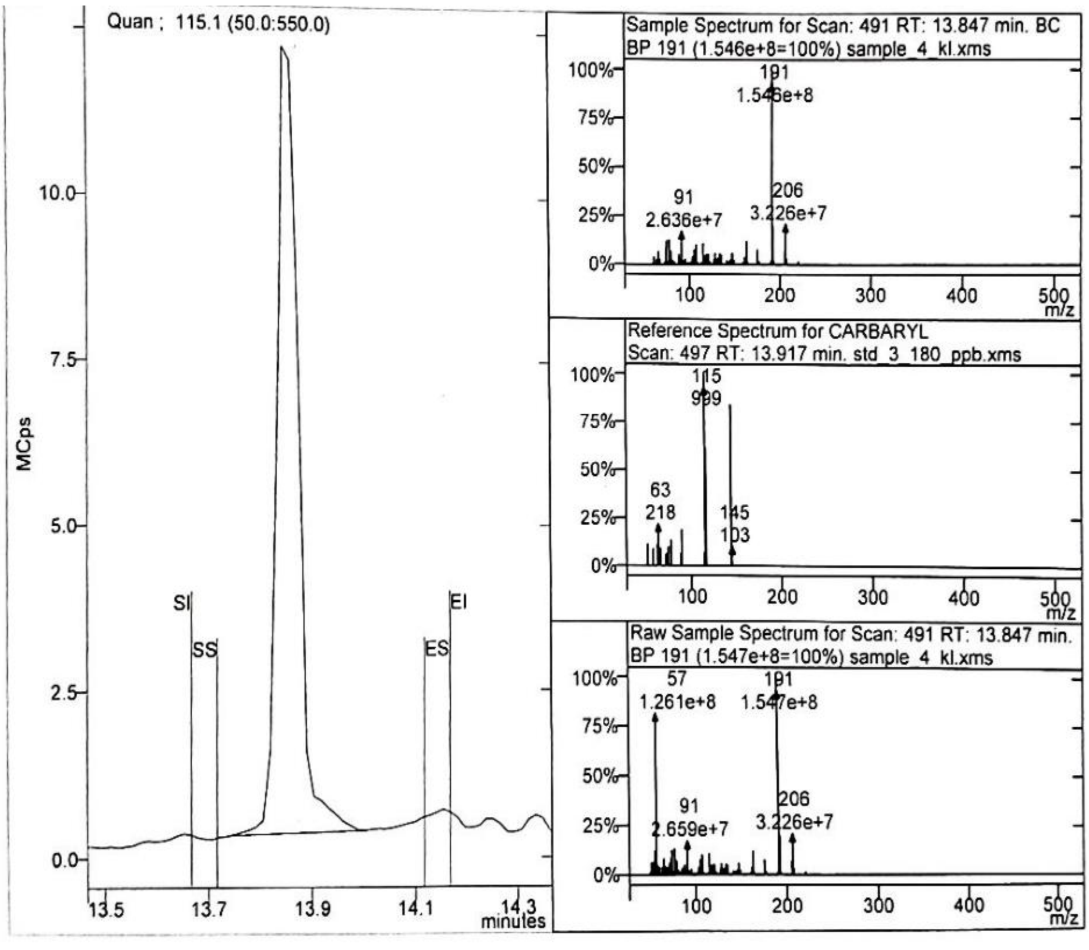
Result Index: 1 Compound Number: 1 CAS Number: None Identified

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	13.917 +/- 0.200	13.853 min.	Pass
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	115.1		
Calibration Equation	Linear, Force, None	y = +1.7196e+5x	
Area	>=500	3.467e+7	Pass
Height		1.188e+7	
Amount	>= 0.000 ppb	201.608 ppb	Pass



Appendix A: Experimental Data 2

Carbaryl calibration curve

Print Date: 17 Oct 2020 15:42:38 Compound Summary for CARBARYL

Compound Summary Report

Instrument ID:	GC-MS
Method:	c:\brukerws\methods\pesticide_run_method_final_14.10.2020.mth
Last Calibration:	10/15/2020 11:11 AM
Data Path:	C:\BrukerWS\data\13.10.2020\14.10.2020\

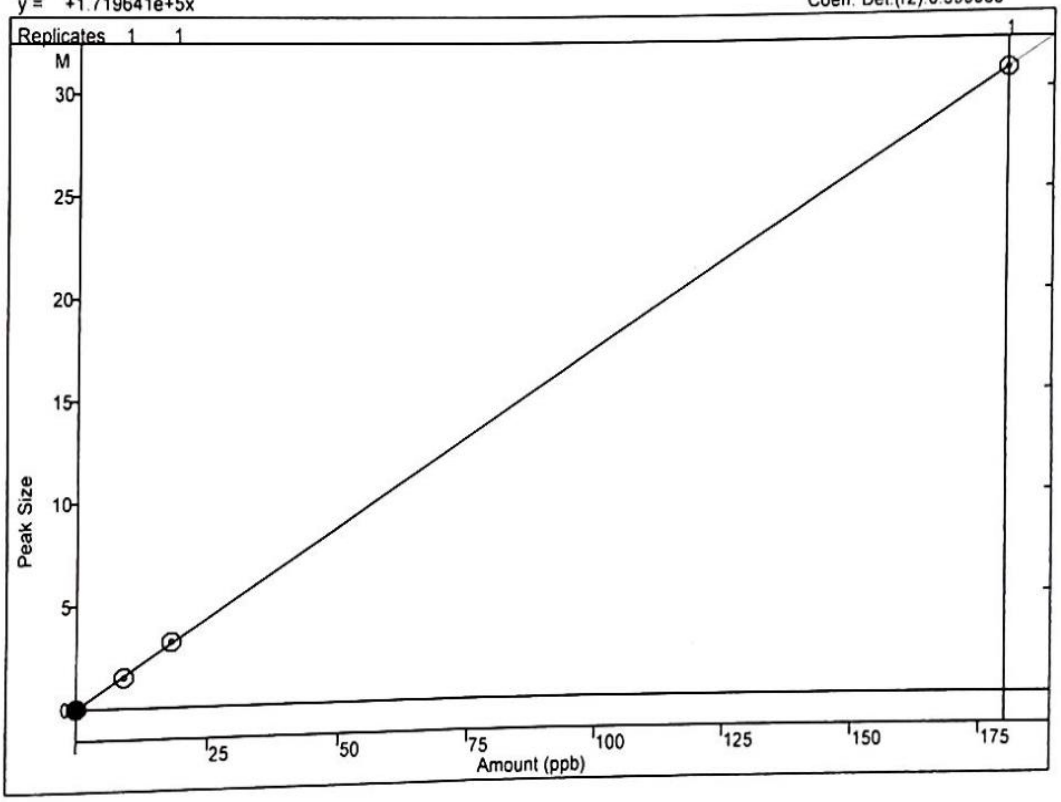
1) CARBARYL

Level	File	Conc. ppb	RT	Response Ion: 115.1	RF
1	std_1_6_ppm.xms				
1	std_2_12_ppm.xms				
1	std_3_24_ppm.xms				
1	Std_1_100ppb.xms				
1	Std_2_200ppb.xms				
1	Std_3_500ppb.xms				
1	Std_1_200_ppb.xms				
1	carbanyl_18_ppm.xms				
1	Carbaryl_std_9ppb.XMS				
1	Carbaryl_std_9ppb.xms				
1	Carbaryl_std_18ppb				
1	arbaryl_std_180ppb				
1	std_1_9_ppb.XMS	8.594	13.950	1.478e+6	164209.141
2	std_2_18_ppb.XMS	18.452	13.948	3.173e+6	176281.500
3	std_3_180_ppb.XMS	179.975	13.948	3.095e+7	171940.328
	Average:		2.790		170810.313
	RF Range:				136648.250 - 204972.375

CARBARYL

Curve Fit: Linear, Force, None Resp. Fact. RSD: 3.580%

y = +1.719641e+5x Coeff. Det.(r2):0.999983



Carbaryl after photo-treatment (Chromatogram & Mass spectrum for S01)

Print Date 17 Oct 2020 15 46 03 | Target Compound Report for #1 from sample_1 xms

Sample ID	sample_1	Operator	Jewel
Instrument ID	GC-MS	Last Calibration	10/17/2020 3 39 PM
Measurement Type	Area	Calibration Type	External Standard
Acquisition Date	10/17/2020 1 10 PM	Data File	..10 2020\sample_1 xms
Calculation Date	10/17/2020 3 39 PM	Method	...final_15 10 2020 mth
Sample Type	Analysis		
Inj Sample Notes	None		

Compound Information

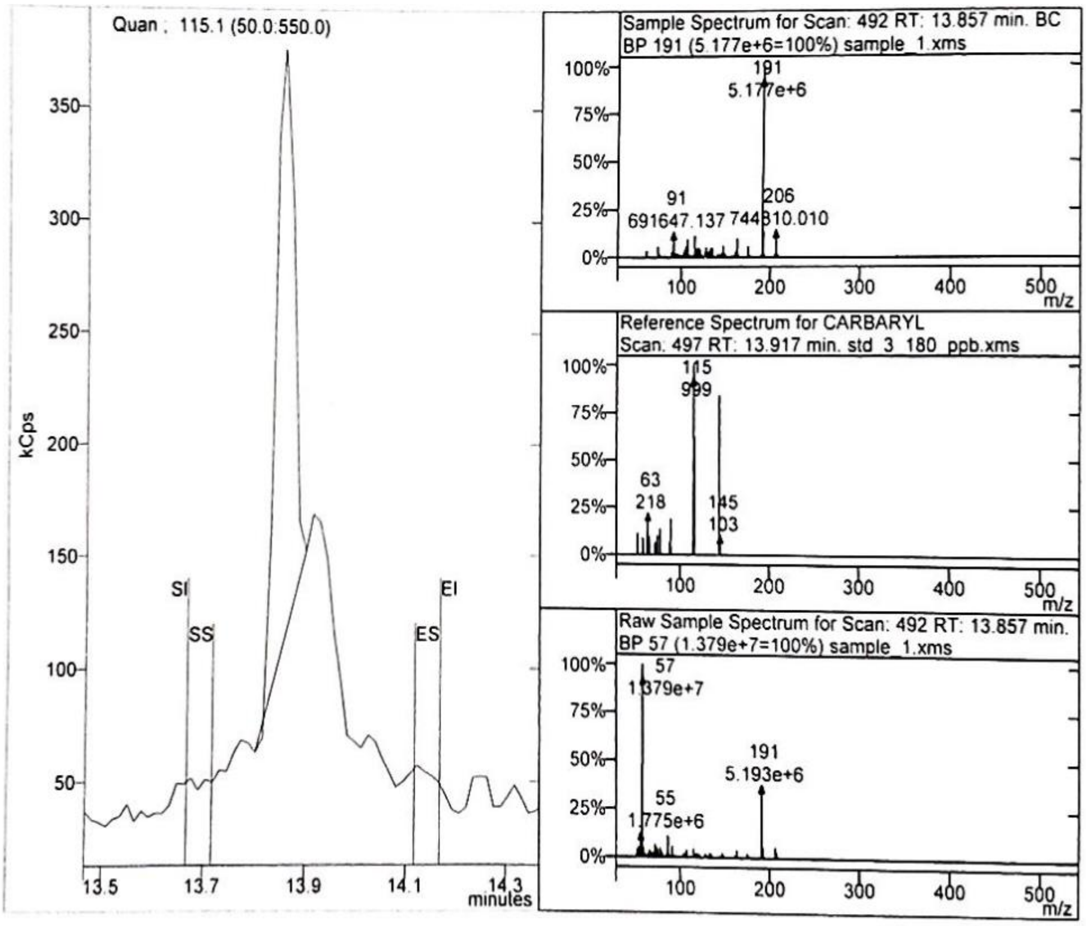
Peak Name	CARBARYL			
Result Index	1	Compound Number: 1	CAS Number: None	Identified

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	13 917 +/- 0.200	13.855 min.	Pass
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	115.1		
Calibration Equation	Linear, Force, None	y = +1.7196e+5x	
Area	>=500	645695	Pass
Height		264401	
Amount	>= 0.000 ppb	3.755 ppb	Pass



Carbaryl after photo-treatment (Chromatogram & Mass spectrum for S02)

Print Date: 17 Oct 2020 15:48:00

Target Compound Report for #1 from sample_2.xms

Sample ID:	sample_2	Operator:	Jewel
Instrument ID:	GC-MS	Last Calibration:	10/17/2020 3:39 PM
Measurement Type:	Area	Calibration Type:	External Standard
Acquisition Date:	10/17/2020 1:35 PM	Data File:	...10.2020\sample_2.xms
Calculation Date:	10/17/2020 3:39 PM	Method:	...final_15.10.2020.mth
Sample Type:	Analysis		
Inj. Sample Notes:	None		

Compound Information

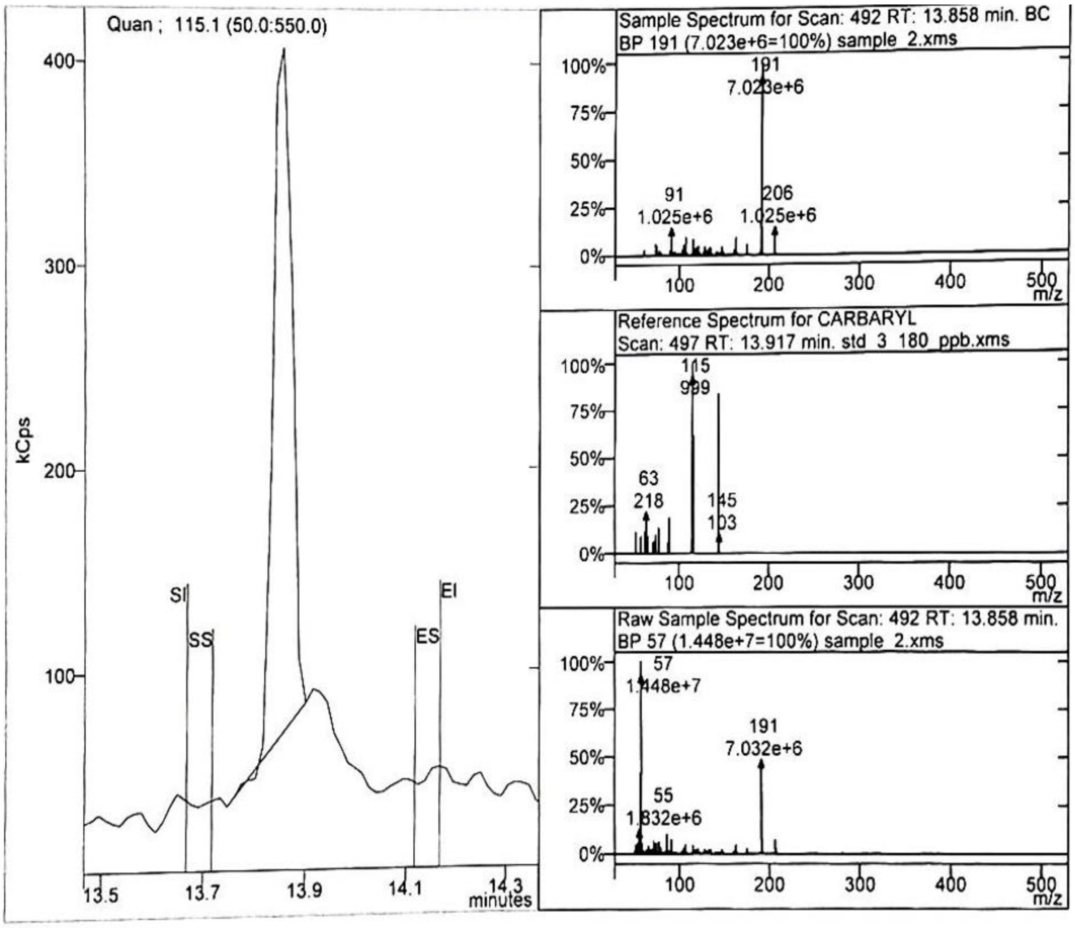
Peak Name:	CARBARYL			
Result Index:	1	Compound Number: 1	CAS Number: None	Identified

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	13.917 +/- 0.200	13.853 min.	Pass
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	115.1		
Calibration Equation	Linear, Force, None	y = +1.7196e+5x	
Area	>=500	864135	Pass
Height		338063	
Amount	>= 0.000 ppb	5.025 ppb	Pass



Carbaryl after photo-treatment (Chromatogram & Mass spectrum for S03)

Print Date: 17 Oct 2020 15:50:34

Target Compound Report for #1 from sample_3.xms

Sample ID:	sample_3	Operator:	Jewel
Instrument ID:	GC-MS	Last Calibration:	10/17/2020 3:39 PM
Measurement Type:	Area	Calibration Type:	External Standard
Acquisition Date:	10/17/2020 1:59 PM	Data File:	...10.2020\sample_3.xms
Calculation Date:	10/17/2020 3:39 PM	Method:	...final_15.10.2020.mth
Sample Type:	Analysis		
Inj. Sample Notes:	None		

Compound Information

Peak Name: CARBARYL

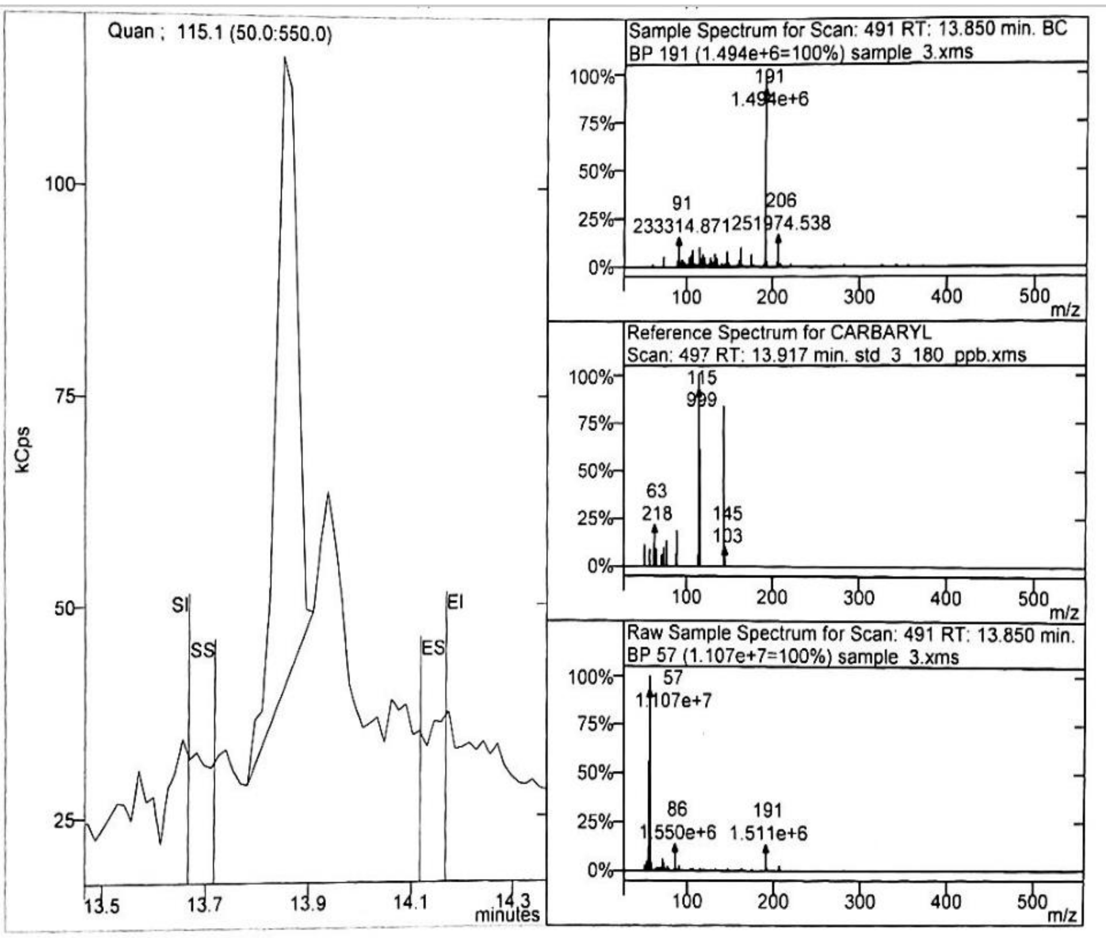
Result Index: 1 Compound Number: 1 CAS Number: None Identified

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	13.917 +/- 0.200	13.856 min.	Pass
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	115.1		
Calibration Equation	Linear, Force, None	y = +1.7196e+5x	
Area	>=500	212098	Pass
Height		74485	
Amount	>= 0.000 ppb	1.233 ppb	Pass



Carbaryl after photo-treatment (Chromatogram & Mass spectrum for S04)

Print Date: 17 Oct 2020 15:52:57

Target Compound Report for #1 from sample_4.xms

Sample ID:	sample_4	Operator:	Jewel
Instrument ID:	GC-MS	Last Calibration:	10/17/2020 3:39 PM
Measurement Type:	Area	Calibration Type:	External Standard
Acquisition Date:	10/17/2020 2:24 PM	Data File:	...10.2020\sample_4.xms
Calculation Date:	10/17/2020 3:39 PM	Method:	...final_15.10.2020.mth
Sample Type:	Analysis		
Inj. Sample Notes:	None		

Compound Information

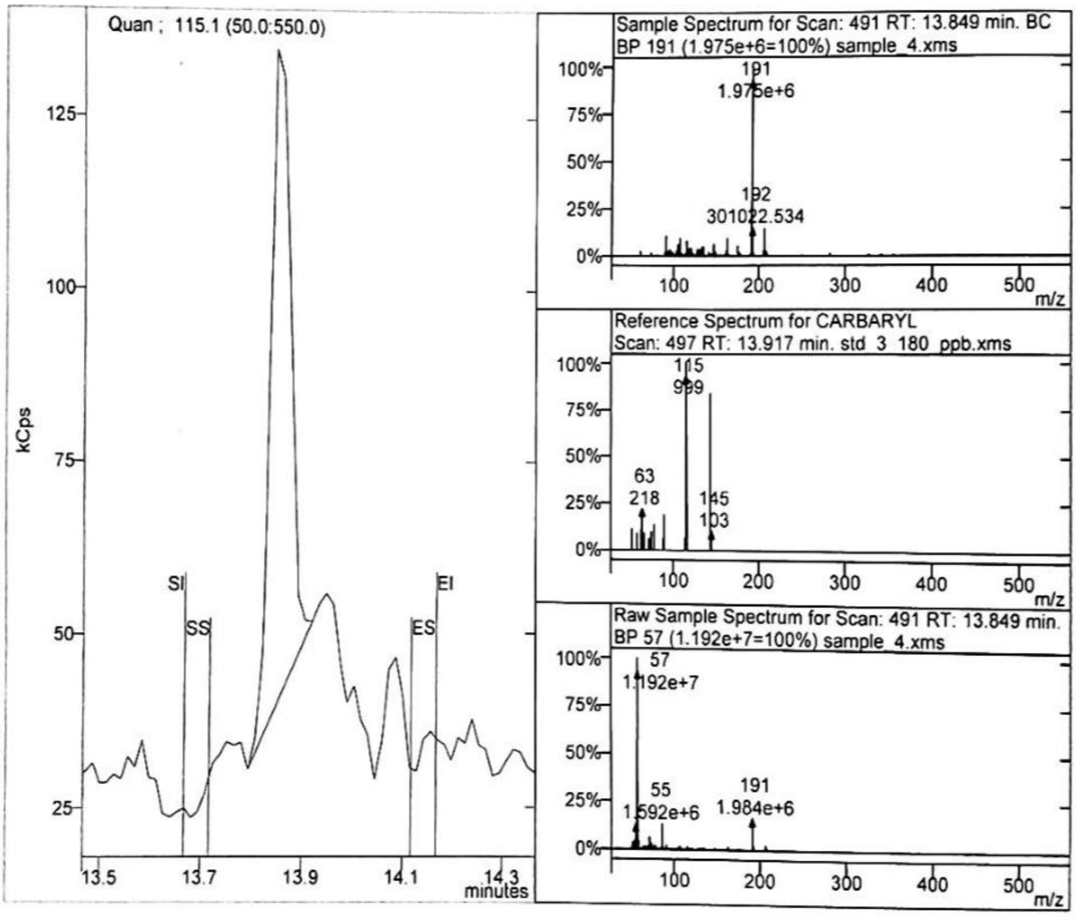
Peak Name:	CARBARYL		
Result Index:	1 Compound Number: 1	CAS Number: None	Identified

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	13.917 +/- 0.200	13.855 min.	Pass
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	115.1		
Calibration Equation	Linear, Force, None	y = +1.7196e+5x	
Area	>=500	262121	Pass
Height		94076	
Amount	>= 0.000 ppb	1.524 ppb	Pass



Carbaryl after photo-treatment (Chromatogram & Mass spectrum for S05)

Print Date: 17 Oct 2020 15:57:01

Target Compound Report for #1 from sample_5.xms

Sample ID:	sample_5	Operator:	Jewel
Instrument ID:	GC-MS	Last Calibration:	10/17/2020 3:39 PM
Measurement Type:	Area	Calibration Type:	External Standard
Acquisition Date:	10/17/2020 2:49 PM	Data File:	...10.2020\sample_5.xms
Calculation Date:	10/17/2020 3:39 PM	Method:	...final_15.10.2020.mth
Sample Type:	Analysis		
Inj. Sample Notes:	None		

Compound Information

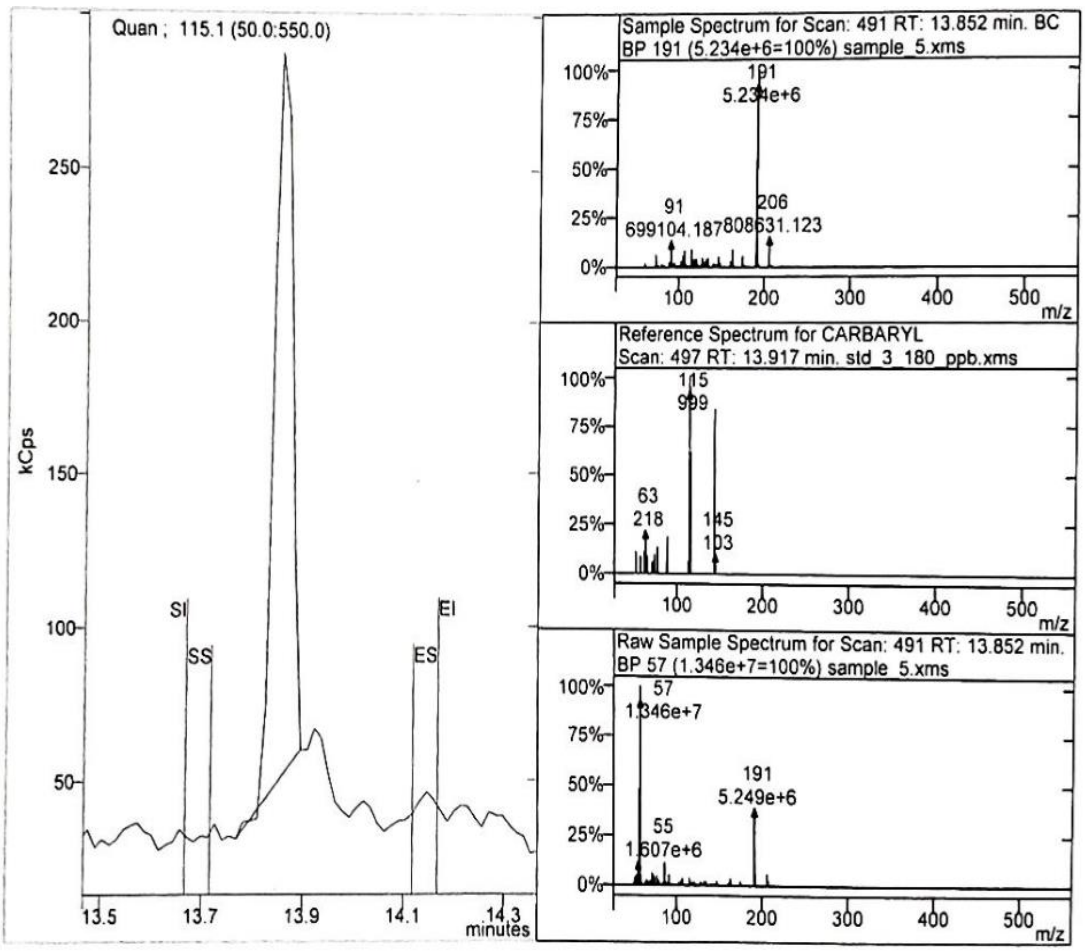
Peak Name:	CARBARYL			
Result Index:	1	Compound Number: 1	CAS Number: None	Identified

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	13.917 +/- 0.200	13.856 min.	Pass
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	115.1		
Calibration Equation	Linear, Force, None	y = +1.7196e+5x	
Area	>=500	599955	Pass
Height		236827	
Amount	>= 0.000 ppb	3.489 ppb	Pass



Carbaryl after photo-treatment (Chromatogram & Mass spectrum for S06)

Print Date: 18 Oct 2020 12:33:04 Target Compound Report for #1 from sample_6.xms

Sample ID:	sample_6	Operator:	Jewel
Instrument ID:	GC-MS	Last Calibration:	10/18/2020 11:18 AM
Measurement Type:	Area	Calibration Type:	External Standard
Acquisition Date:	10/17/2020 7:55 PM	Data File:	...020.new\sample_6.xms
Calculation Date:	10/18/2020 11:18 AM	Method:	...final_15.10.2020.mth
Sample Type:	Analysis		
Inj. Sample Notes:	None		

Compound Information

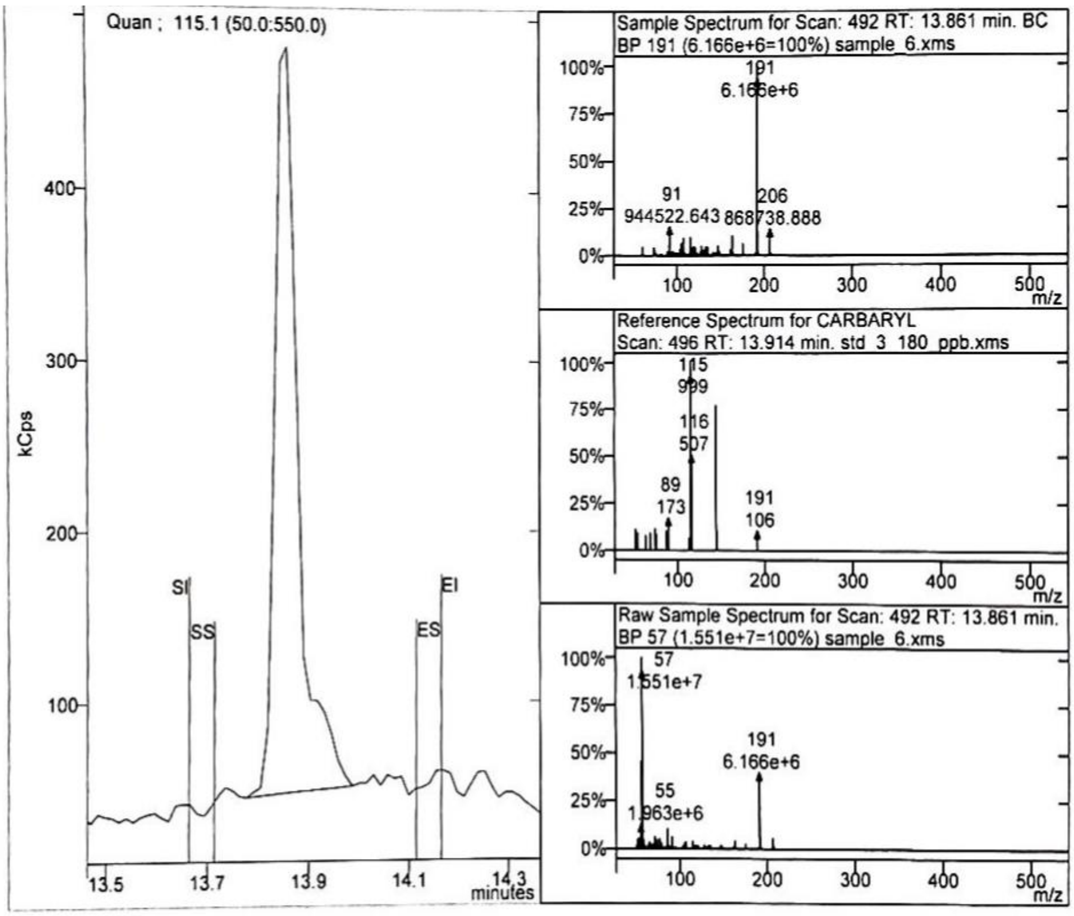
Peak Name:	CARBARYL			
Result Index:	1	Compound Number: 1	CAS Number: None	Identified

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	13.914 +/- 0.200	13.855 min.	Pass
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	115.1		
Calibration Equation	Linear, Force, None	y = +1.9105e+5x	
Area	>=500	1.410e+6	Pass
Height		436373	
Amount	>= 0.000 ppb	7.380 ppb	Pass



Carbaryl after photo-treatment (Chromatogram & Mass spectrum for S07)

Print Date: 18 Oct 2020 12:35:47

Target Compound Report for #1 from sample_7.xms

Sample ID:	sample_7	Operator:	Jewel
Instrument ID:	GC-MS	Last Calibration:	10/18/2020 11:18 AM
Measurement Type:	Area	Calibration Type:	External Standard
Acquisition Date:	10/17/2020 8:20 PM	Data File:	...020.new\sample_7.xms
Calculation Date:	10/18/2020 11:18 AM	Method:	...final_15.10.2020.mth
Sample Type:	Analysis		
Inj. Sample Notes:	None		

Compound Information

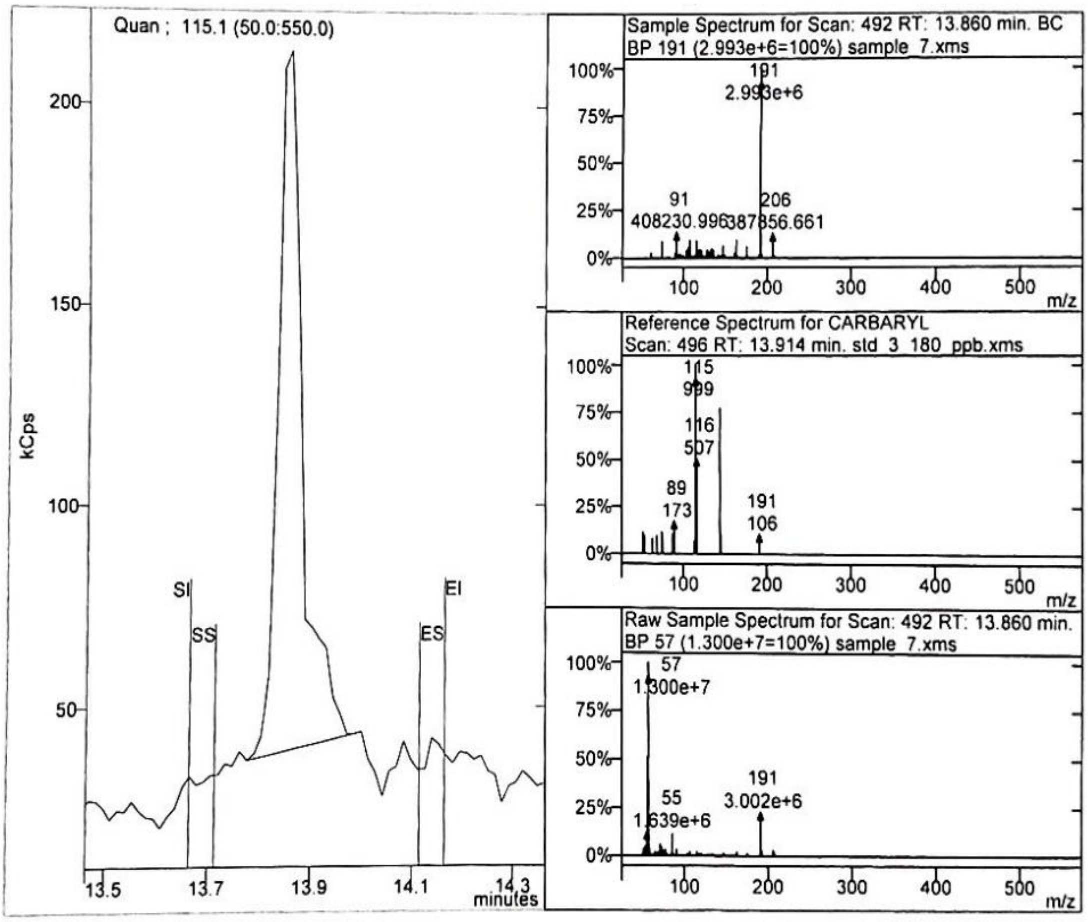
Peak Name:	CARBARYL			
Result Index:	1	Compound Number: 1	CAS Number: None	Identified

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	13.914 +/- 0.200	13.854 min.	Pass
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	115.1		
Calibration Equation	Linear, Force, None	y = +1.9105e+5x	
Area	>=500	579307	Pass
Height		174161	
Amount	>= 0.000 ppb	3.032 ppb	Pass



Carbaryl after photo-treatment (Chromatogram & Mass spectrum for S08)

Print Date: 18 Oct 2020 12:39:07

Target Compound Report for #1 from sample_8.xm

Sample ID:	sample_8	Operator:	Jewel
Instrument ID:	GC-MS	Last Calibration:	10/18/2020 11:18 AM
Measurement Type:	Area	Calibration Type:	External Standard
Acquisition Date:	10/17/2020 8:44 PM	Data File:	...020.new\sample_8.xms
Calculation Date:	10/18/2020 11:18 AM	Method:	...final_15.10.2020.mth
Sample Type:	Analysis		
Inj. Sample Notes:	None		

Compound Information

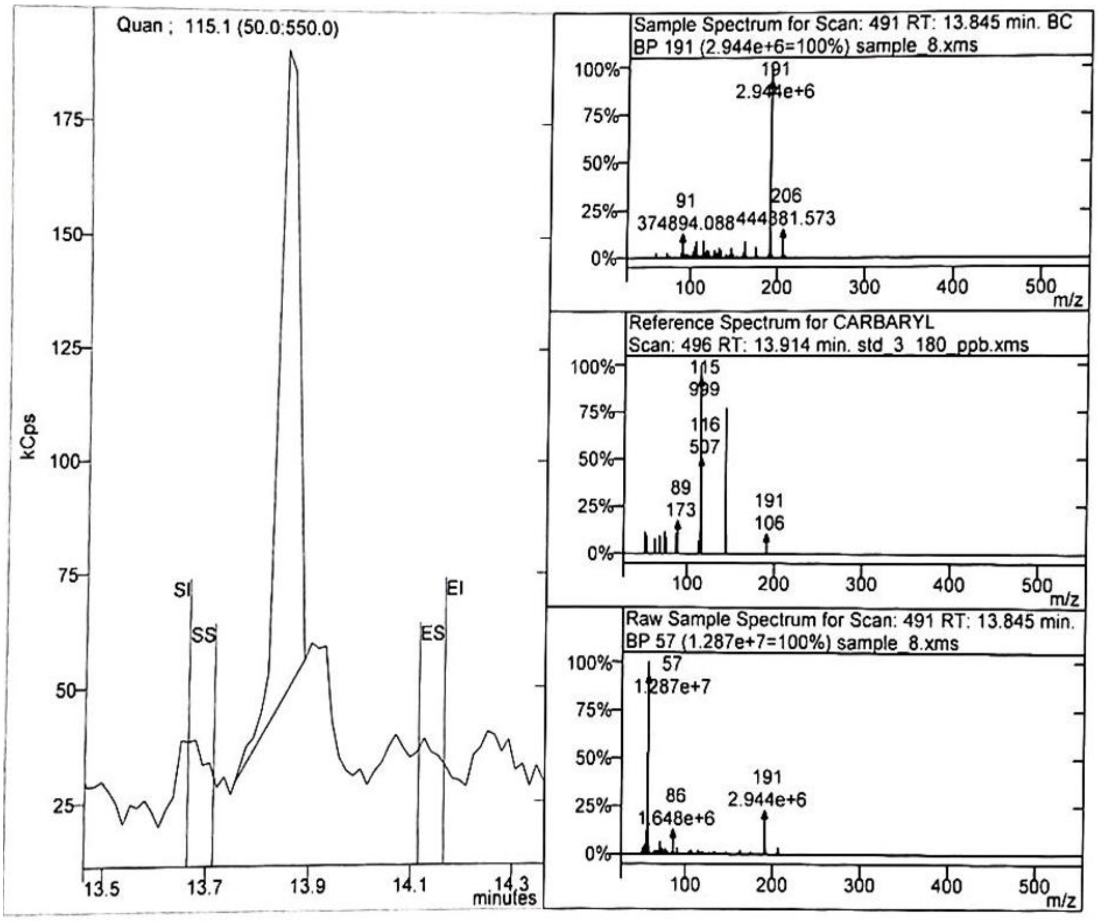
Peak Name:	CARBARYL			
Result Index:	1	Compound Number: 1	CAS Number: None	Identified

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	13.914 +/- 0.200	13.851 min.	Pass
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	115.1		
Calibration Equation	Linear, Force, None	y = +1.9105e+5x	
Area	>=500	377924	Pass
Height		142294	
Amount	>= 0.000 ppb	1.978 ppb	Pass



Carbaryl after photo-treatment (Chromatogram & Mass spectrum for S09)

Print Date: 18 Oct 2020 12:42:16

Target Compound Report for #1 from sample_9.xms

Sample ID:	sample_9	Operator:	Jewel
Instrument ID:	GC-MS	Last Calibration:	10/18/2020 11:18 AM
Measurement Type:	Area	Calibration Type:	External Standard
Acquisition Date:	10/17/2020 9:08 PM	Data File:	...020.new\sample_9.xms
Calculation Date:	10/18/2020 11:18 AM	Method:	...final_15.10.2020.mth
Sample Type:	Analysis		
Inj. Sample Notes:	None		

Compound Information

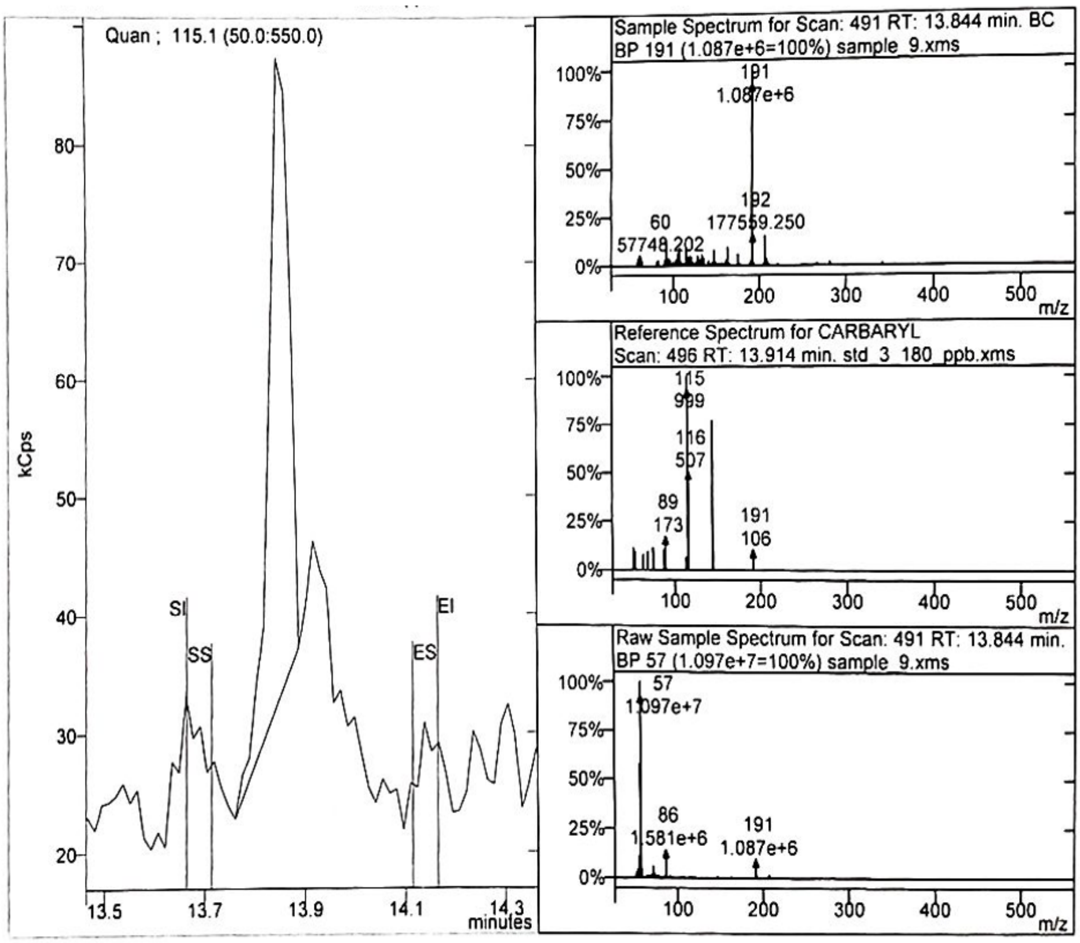
Peak Name:	CARBARYL		Identified
Result Index:	1 Compound Number: 1	CAS Number: None	

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	13.914 +/- 0.200	13.850 min.	Pass
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	115.1		
Calibration Equation	Linear, Force, None	y = +1.9105e+5x	
Area	>=500	156577	Pass
Height		54339	
Amount	>= 0.000 ppb	0.820 ppb	Pass



Carbaryl after photo-treatment (Chromatogram & Mass spectrum for S10)

Print Date: 18 Oct 2020 12:44:45 Target Compound Report for #1 from sample_10.xms

Sample ID:	sample_10	Operator:	Jewel
Instrument ID:	GC-MS	Last Calibration:	10/18/2020 11:18 AM
Measurement Type:	Area	Calibration Type:	External Standard
Acquisition Date:	10/17/2020 9:33 PM	Data File:	...20.new\sample_10.xms
Calculation Date:	10/18/2020 11:18 AM	Method:	...final_15.10.2020.mth
Sample Type:	Analysis		
Inj. Sample Notes:	None		

Compound Information

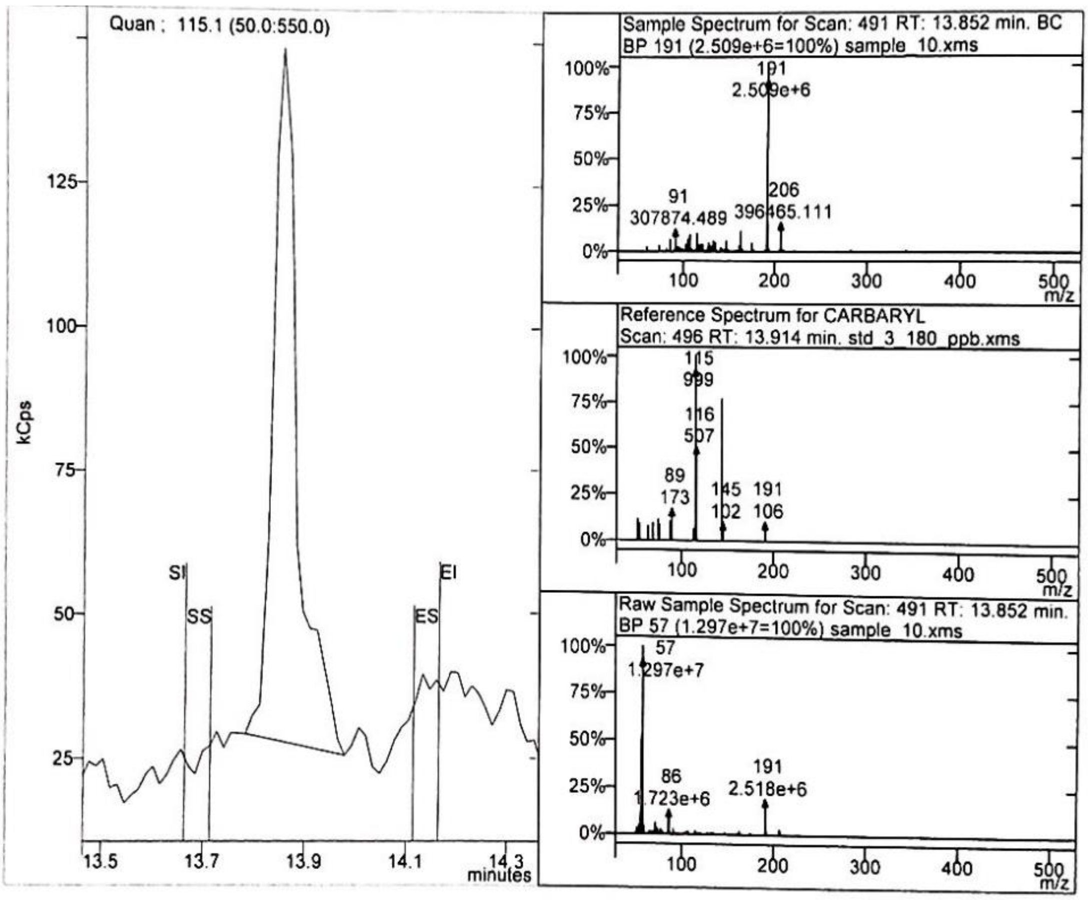
Peak Name:	CARBARYL			
Result Index:	1	Compound Number: 1	CAS Number: None	Identified

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	13.914 +/- 0.200	13.852 min.	Pass
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	115.1		
Calibration Equation	Linear, Force, None	y = +1.9105e+5x	
Area	>=500	414418	Pass
Height		121073	
Amount	>= 0.000 ppb	2.169 ppb	Pass



Carbaryl after photo-treatment (Chromatogram & Mass spectrum for S11)

Print Date: 18 Oct 2020 11:23:18

Target Compound Report for #1 from sample_kl.xms

Sample ID:	sample_kl	Operator:	Jewel
Instrument ID:	GC-MS	Last Calibration:	10/18/2020 11:18 AM
Measurement Type:	Area	Calibration Type:	External Standard
Acquisition Date:	10/17/2020 7:06 PM	Data File:	...20.new\sample_kl.xms
Calculation Date:	10/18/2020 11:18 AM	Method:	...final_15.10.2020.mth
Sample Type:	Analysis		
Inj. Sample Notes:	None		

Compound Information

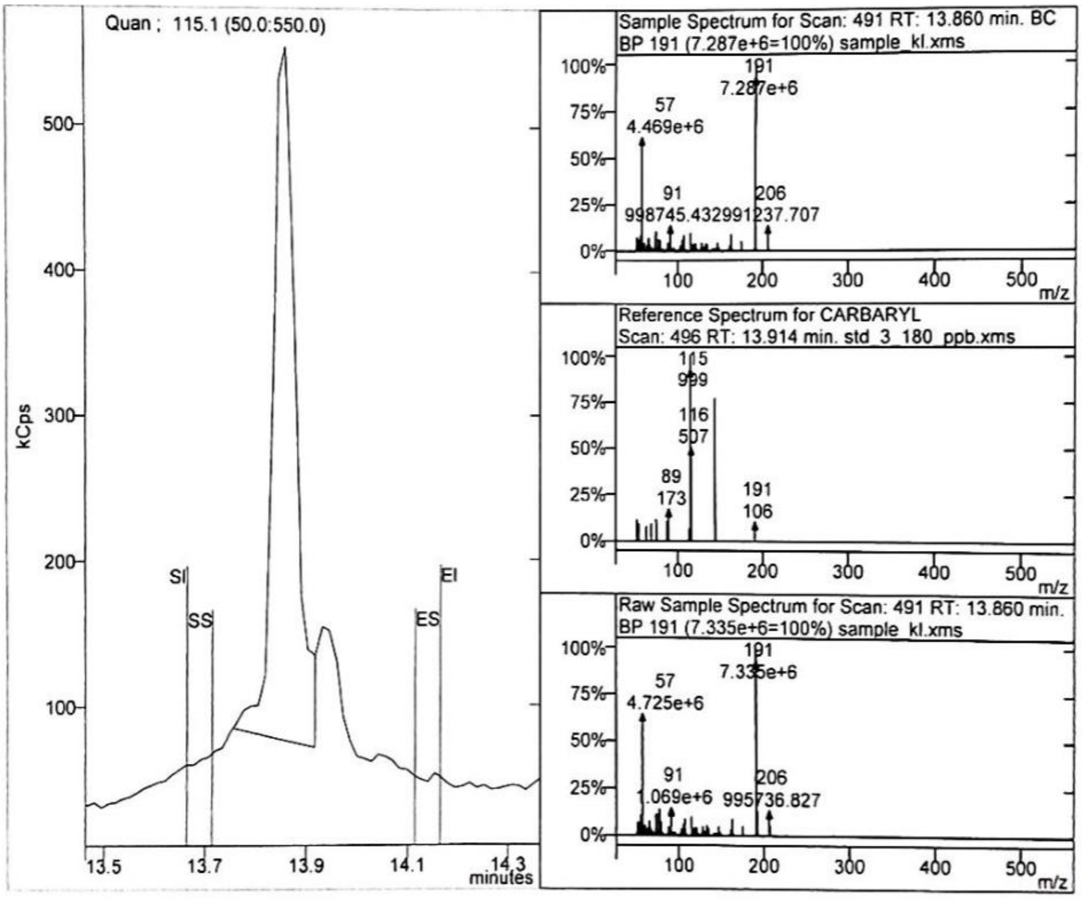
Peak Name:	CARBARYL			
Result Index:	1	Compound Number: 1	CAS Number: None	Identified

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	13.914 +/- 0.200	13.854 min.	Pass
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	115.1		
Calibration Equation	Linear, Force, None	y = +1.9105e+5x	
Area	>=500	1.481e+6	Pass
Height		477315	
Amount	>= 0.000 ppb	7.753 ppb	Pass



Carbaryl after photo-treatment (Chromatogram & Mass spectrum for S12)

Print Date: 18 Oct 2020 12:30:06

Target Compound Report for #1 from sample_4_kl.xms

Sample ID:	sample_4_kl	Operator:	Jewel
Instrument ID:	GC-MS	Last Calibration:	10/18/2020 11:18 AM
Measurement Type:	Area	Calibration Type:	External Standard
Acquisition Date:	10/17/2020 7:31 PM	Data File:	....new\sample_4_kl.xms
Calculation Date:	10/18/2020 11:18 AM	Method:	...final_15.10.2020.mth
Sample Type:	Analysis		
Inj. Sample Notes:	None		

Compound Information

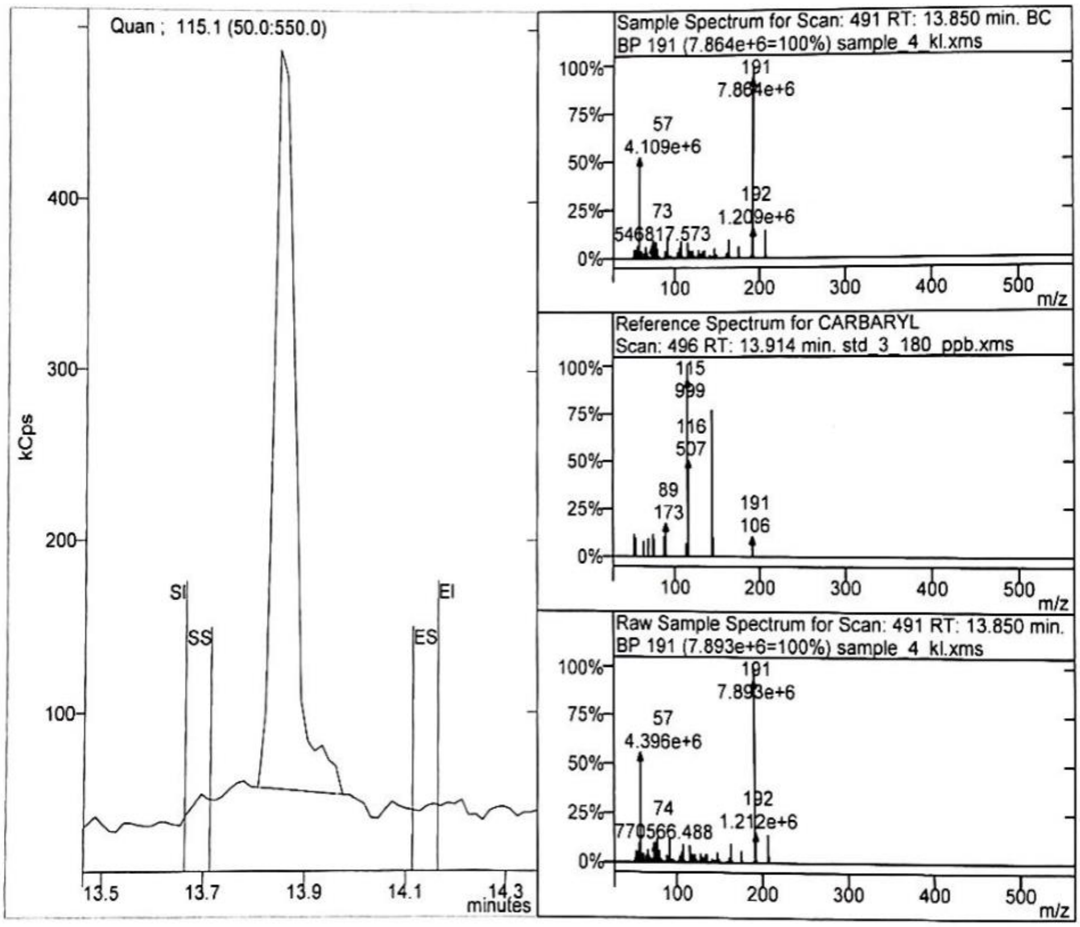
Peak Name:	CARBARYL			
Result Index:	1	Compound Number: 1	CAS Number: None	Identified

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	13.914 +/- 0.200	13.856 min.	Pass
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	115.1		
Calibration Equation	Linear, Force, None	y = +1.9105e+5x	
Area	>=500	1.286e+6	Pass
Height		432441	
Amount	>= 0.000 ppb	6.733 ppb	Pass



Appendix A: Experimental Data 3

Chlorpyrifos calibration curve

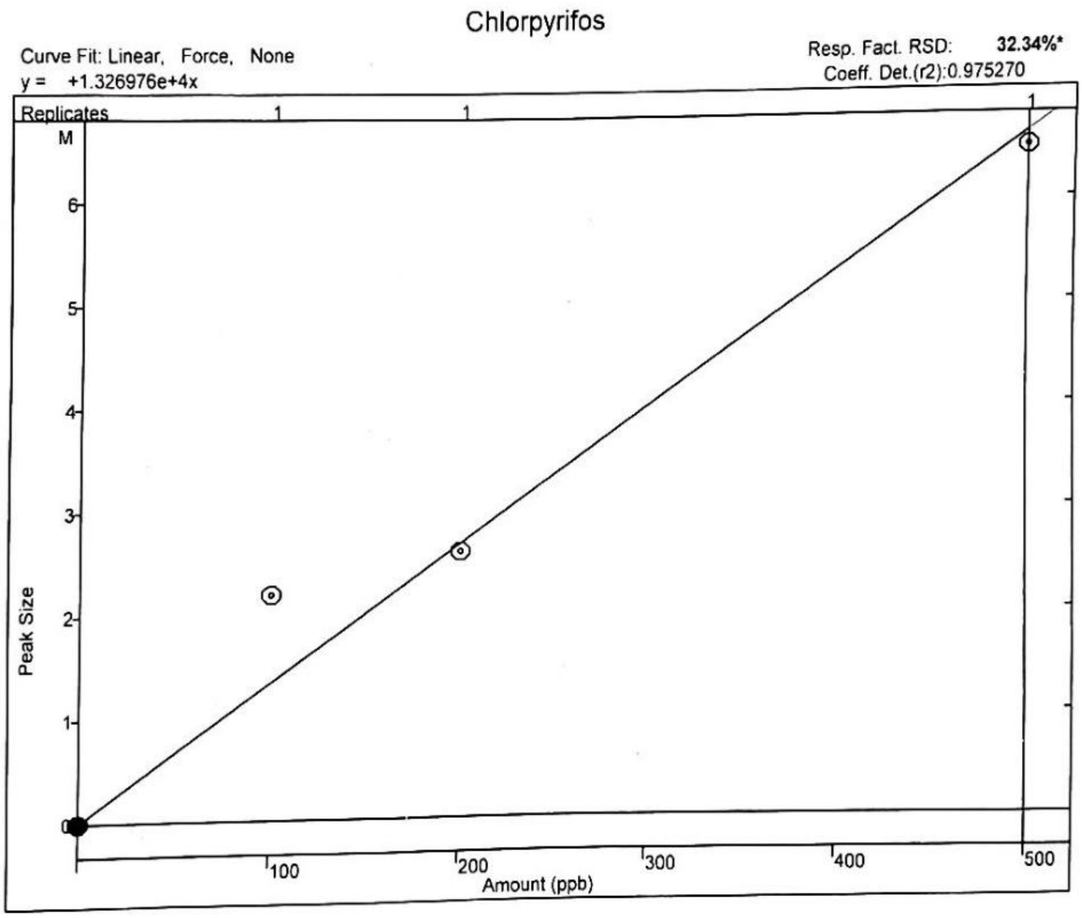
Print Date: 17 Oct 2020 10:47:42 Compound Summary for Chlorpyrifos

Compound Summary Report

Instrument ID: GC-MS
Method: c:\brukerws\methods\pesticide_run_method_final_14.10.2020.mth
Last Calibration: 10/15/2020 11:19 AM
Data Path: c:\BrukerWS\data\13.10.2020\14.10.2020\

1) Chlorpyrifos

Level	File	Conc. ppb	RT	Response Ion: 97.0	RF
1	Std_1_100ppb.xms				
1	Std_2_200ppb.xms				
1	Std_3_500ppb.xms				
1	Std_1_100_ppb.xms				
1	Std_2_200_ppb.xms				
1	Std_3_500_ppb.xms				
1	Carbaryl_std_9ppb.xms				
1	Carbaryl_std_18ppb				
1	arbaryl_std_180ppb				
1	Std_1_100_ppb001.XMS	164.612	19.311	2.184e+6	21843.578*
2	Std_1_200_ppb001.XMS	194.122	19.313	2.576e+6	12879.766
3	Std_1_500_ppb.XMS	489.429	19.313	6.495e+6	12989.201
	Average:		4.828		15904.183
	RF Range:				12723.346 - 19085.019



Chlorpyrifos: Chromatogram & Mass spectrum for Sample no 01

Pnnt Date: 17 Oct 2020 10:52:19

Target Compound Report for #1 from sample_1001.xms

Sample ID:	Sample_1	Operator:	Jewel
Instrument ID:	GC-MS	Last Calibration:	10/17/2020 10:44 AM
Measurement Type:	Area	Calibration Type:	External Standard
Acquisition Date:	10/16/2020 8:19 PM	Data File:	...2020\sample_1001.xms
Calculation Date:	10/17/2020 10:44 AM	Method:	...020 -calibration.mth
Sample Type:	Analysis		
Inj. Sample Notes:	None		

Compound Information

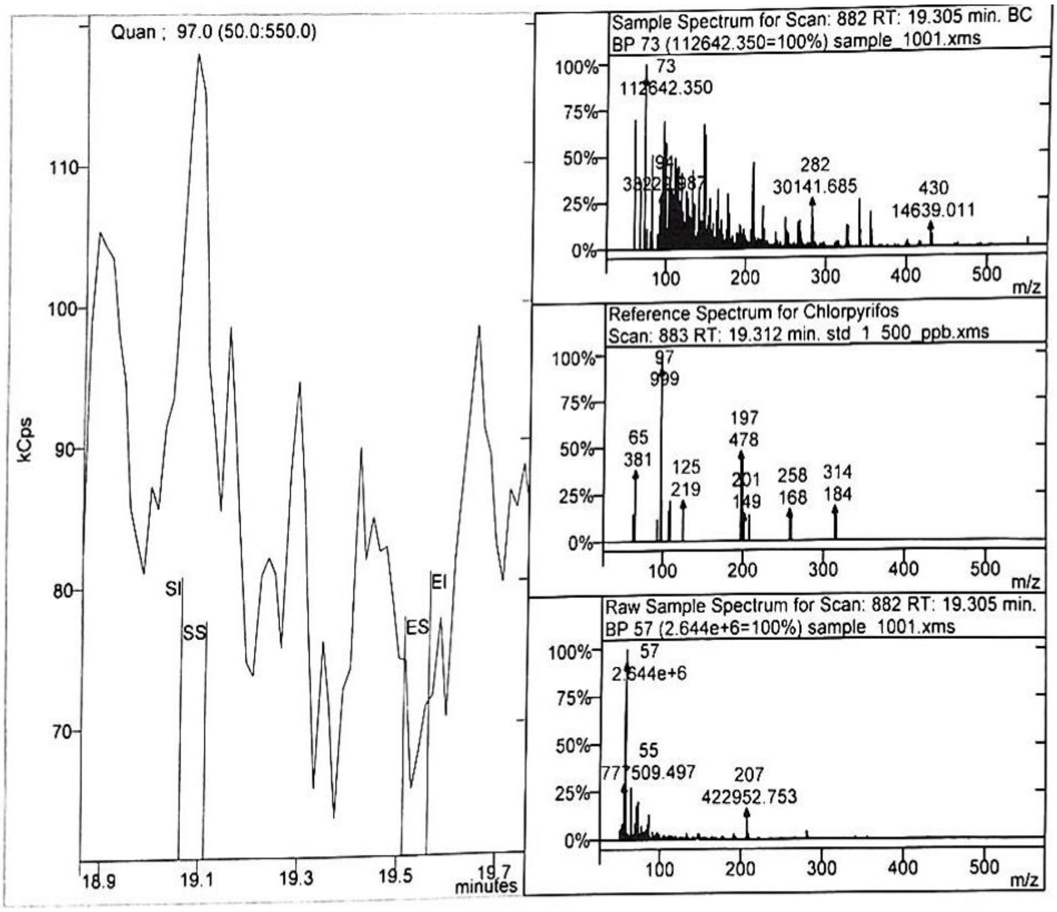
Peak Name:	Chlorpyrifos		
Result Index:	1 Compound Number: 1	CAS Number: 2921-88-2	Missing

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	19.312 +/- 0.200	19.312 min.	Fail
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	97.0		
Calibration Equation	Linear, Force, None	y = +1.3270e+4x	
Area	>=500	0	Fail
Height		0	
Amount	>= 0.000 ppb	0.000 ppb	



Chlorpyrifos: Chromatogram & Mass spectrum for Sample no 02

Print Date: 17 Oct 2020 11:12:42 — Target Compound Report for #1 from sample_2.xms

Sample ID:	Sample_2	Operator:	Jewel
Instrument ID:	GC-MS	Last Calibration:	10/17/2020 11:07 AM
Measurement Type:	Area	Calibration Type:	External Standard
Acquisition Date:	10/16/2020 8:46 PM	Data File:	...10.2020\sample_2.xms
Calculation Date:	10/17/2020 11:07 AM	Method:	...020 -calibration.mth
Sample Type:	Analysis		
Inj. Sample Notes:	None		

Compound Information

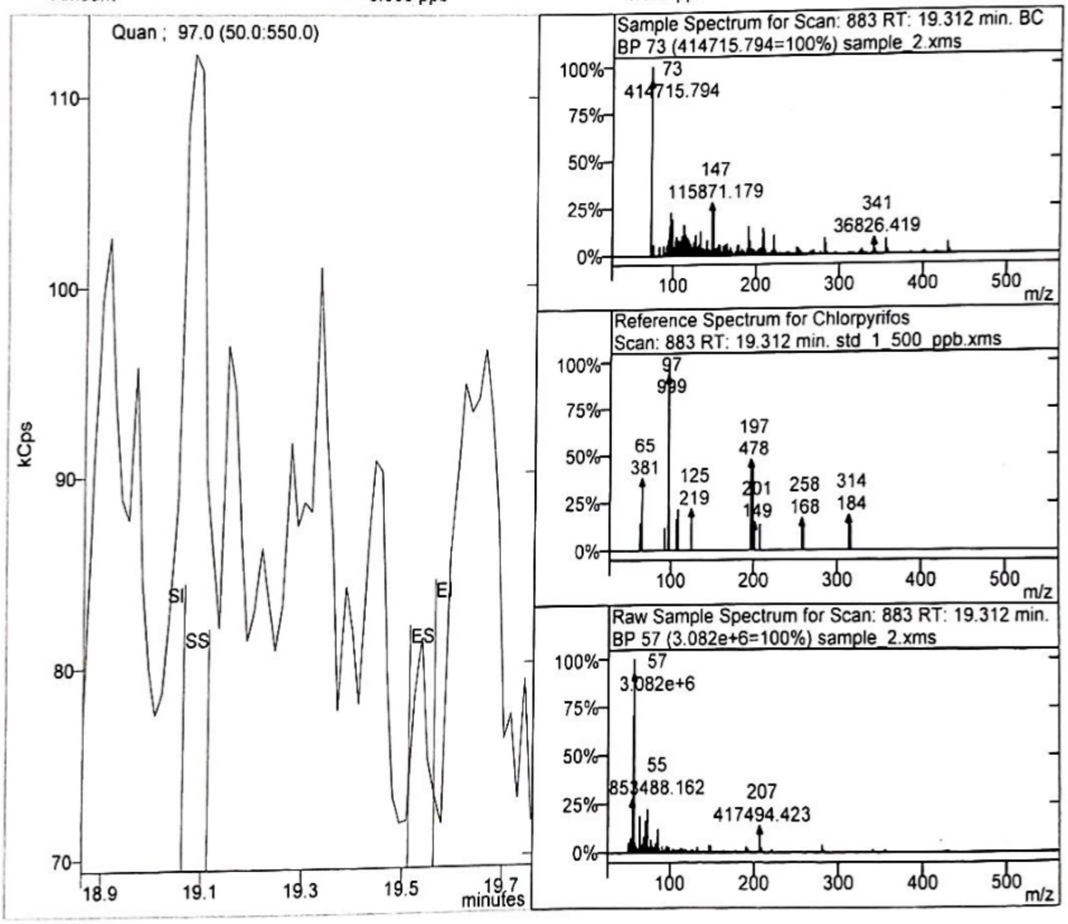
Peak Name:	Chlorpyrifos			
Result Index:	1	Compound Number: 1	CAS Number: 2921-88-2	Missing

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	19.312 +/- 0.200	19.312 min.	Fail
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	97.0		
Calibration Equation	Linear, Force, None	y = +1.3270e+4x	
Area	>=500	0	Fail
Height		0	
Amount	>= 0.000 ppb	0.000 ppb	



Chlorpyrifos: Chromatogram & Mass spectrum for Sample no 03

Print Date: 17 Oct 2020 11:18:02 — Target Compound Report for #1 from sample_3001.xms

Sample ID:	sample_3	Operator:	Jewel
Instrument ID:	GC-MS	Last Calibration:	10/17/2020 11:07 AM
Measurement Type:	Area	Calibration Type:	External Standard
Acquisition Date:	10/16/2020 9:12 PM	Data File:	...2020\sample_3001.xms
Calculation Date:	10/17/2020 11:07 AM	Method:	...020 -calibration.mth
Sample Type:	Analysis		
Inj. Sample Notes:	None		

Compound Information

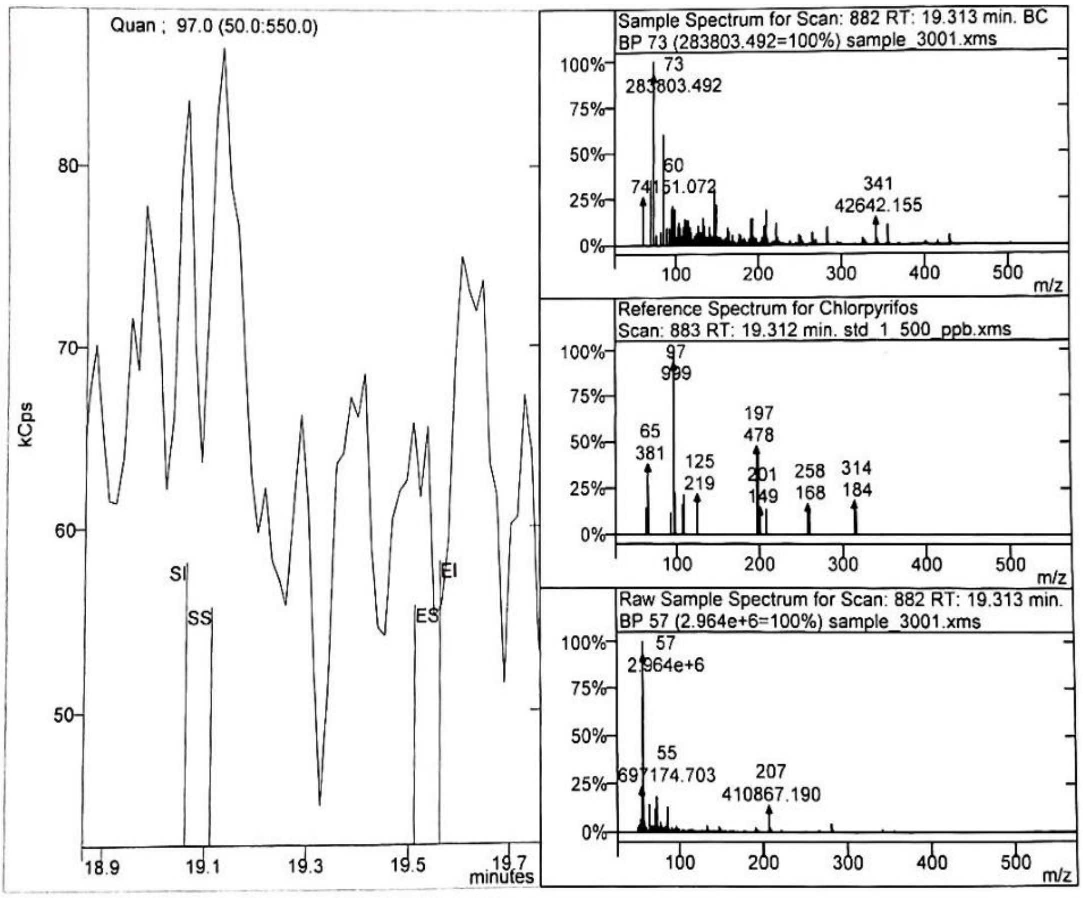
Peak Name:	Chlorpyrifos		
Result Index:	1 Compound Number: 1	CAS Number: 2921-88-2	Missing

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	19.312 +/- 0.200	19.312 min.	Fail
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	97.0		
Calibration Equation	Linear, Force, None	y = +1.3270e+4x	
Area	>=500	0	Fail
Height		0	
Amount	>= 0.000 ppb	0.000 ppb	



Chlorpyrifos: Chromatogram & Mass spectrum for Sample no 04

Print Date: 17 Oct 2020 11:25:56

Target Compound Report for #1 from sample_4001.xms

Sample ID:	sample_4	Operator:	Jewel
Instrument ID:	GC-MS	Last Calibration:	10/17/2020 11:07 AM
Measurement Type:	Area	Calibration Type:	External Standard
Acquisition Date:	10/16/2020 9:39 PM	Data File:	...2020\sample_4001.xms
Calculation Date:	10/17/2020 11:07 AM	Method:	...020 -calibration.mth
Sample Type:	Analysis		
Inj. Sample Notes:	None		

Compound Information

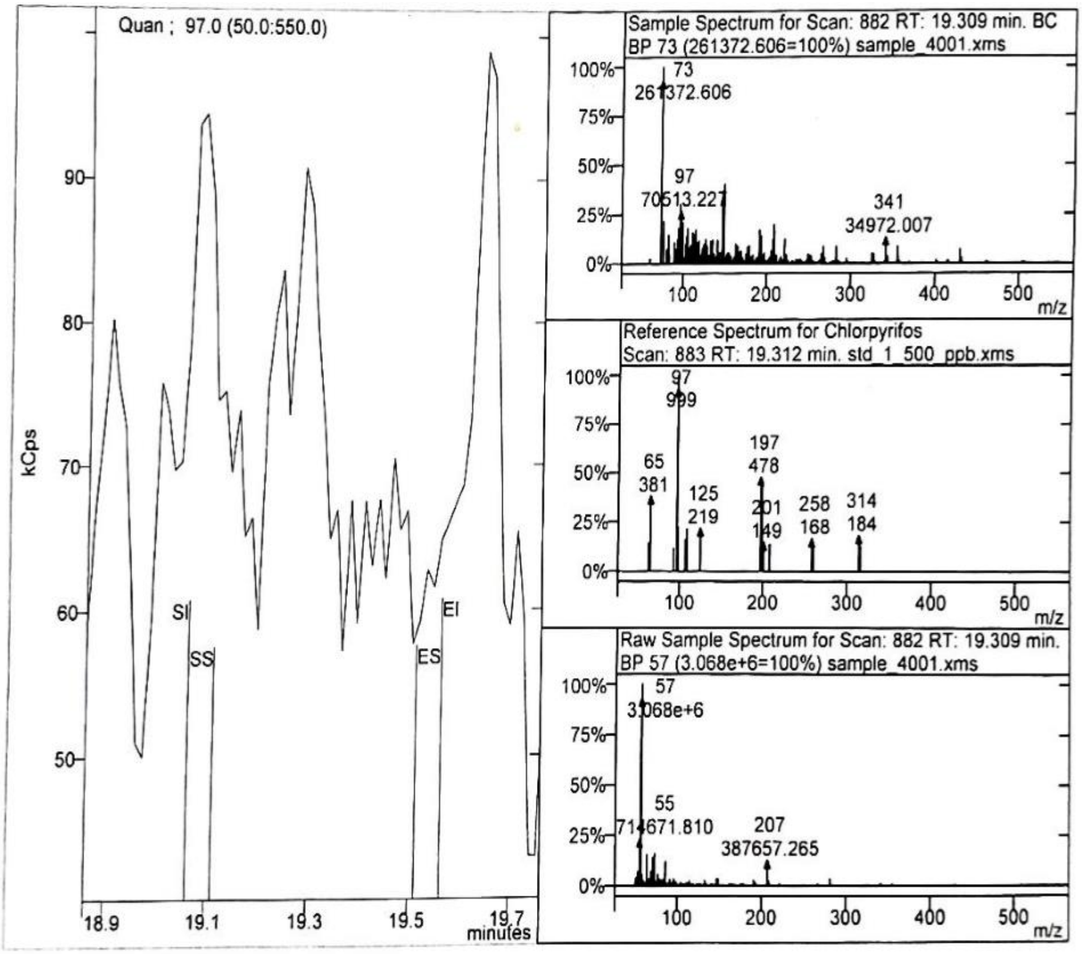
Peak Name:	Chlorpyrifos		
Result Index:	1 Compound Number: 1	CAS Number: 2921-88-2	Missing

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	19.312 +/- 0.200	19.312 min.	Fail
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	97.0		
Calibration Equation	Linear, Force, None	y = +1.3270e+4x	
Area	>=500	0	Fail
Height		0	
Amount	>= 0.000 ppb	0.000 ppb	



Chlorpyrifos: Chromatogram & Mass spectrum for Sample no 05

Print Date 17 Oct 2020 11:29:18 — Target Compound Report for #1 from sample_5.xms

Sample ID:	sample_5	Operator:	Jewel
Instrument ID:	GC-MS	Last Calibration:	10/17/2020 11:07 AM
Measurement Type:	Area	Calibration Type:	External Standard
Acquisition Date:	10/16/2020 10:05 PM	Data File:	...10.2020\sample_5.xms
Calculation Date:	10/17/2020 11:07 AM	Method:	...020 -calibration.mth
Sample Type:	Analysis		
Inj. Sample Notes:	None		

Compound Information

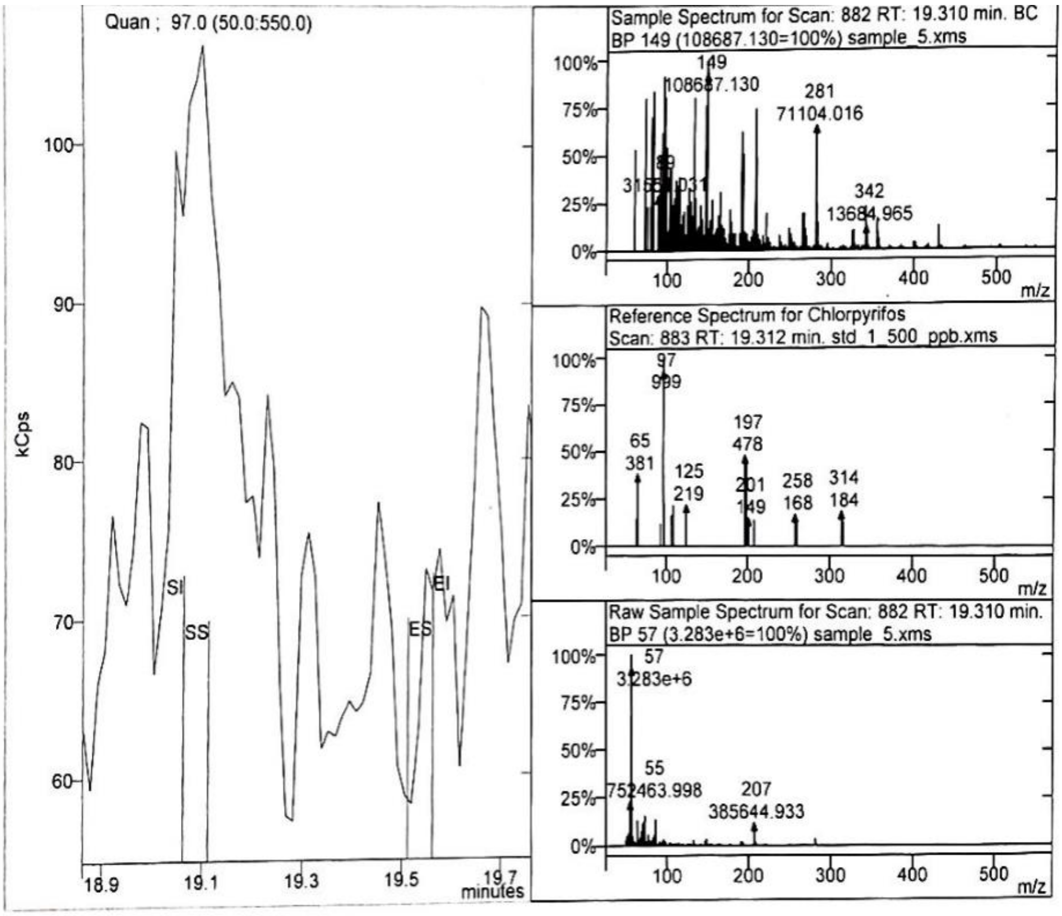
Peak Name:	Chlorpyrifos			
Result Index:	1	Compound Number: 1	CAS Number: 2921-88-2	Missing

Identification

Parameter	Specification	Actual	Status
Search Type	Highest		
Retention Time	19.312 +/- 0.200	19.312 min.	Fail
Match Result		N/A	

Integration and Quantitation

Parameter	Specification	Actual	Status
Quan Ions	97.0		
Calibration Equation	Linear, Force, None	y = +1.3270e+4x	
Area	>=500	0	Fail
Height		0	
Amount	>= 0.000 ppb	0.000 ppb	

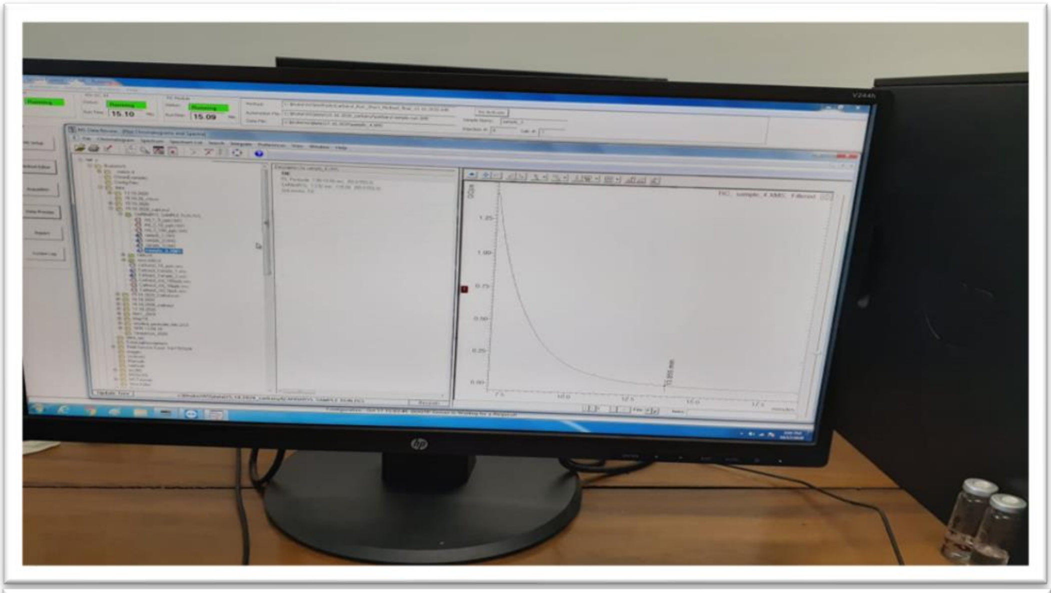


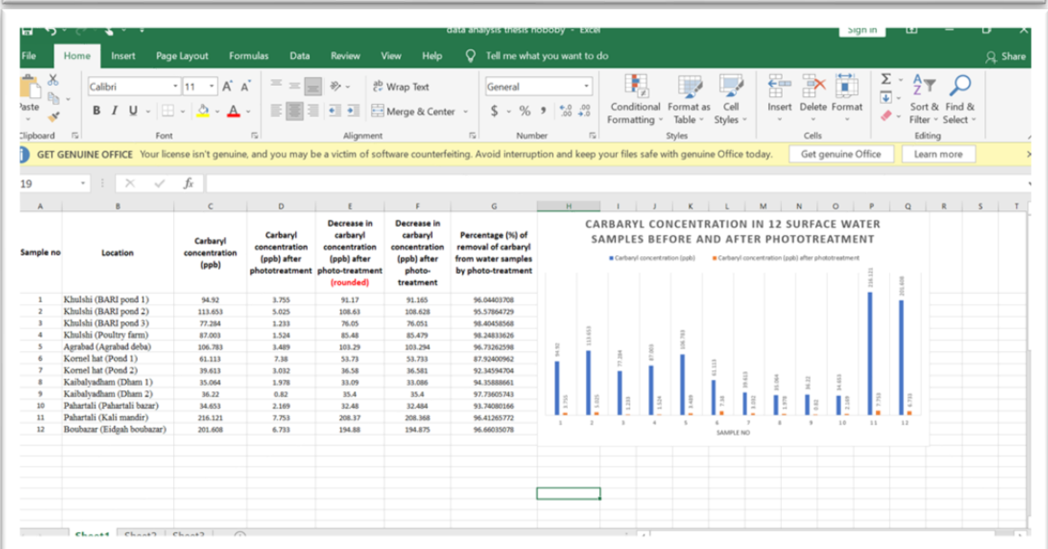
Appendix B: Photo gallery

Fig 12. Sample collection, filtration, sample extraction

Fig 13. Storage of sample extract, Preparation of standard solution of carbaryl and chlorpyrifos

Fig 14. Photo-treatment of water samples using disk polarimeter, Preparation of calibration curve for carbaryl and chlorpyrifos using GCMS





Sample no	Location	Carbaryl concentration (ppb)	Carbaryl concentration (ppb) after phototreatment	Decrease in carbaryl concentration (ppb) after photo-treatment (rounded)	Decrease in carbaryl concentration (ppb) after photo-treatment	Percentage (%) of removal of carbaryl from water samples by photo-treatment
1	Khulshi (BARI pond 1)	94.92	3.755	91.17	91.165	96.04403708
2	Khulshi (BARI pond 2)	113.653	5.025	108.63	108.628	95.57864729
3	Khulshi (BARI pond 3)	77.284	1.233	76.05	76.051	98.40458568
4	Khulshi (Poultry farm)	87.003	1.524	85.48	85.479	98.24833626
5	Agrabad (Agrabad deba)	106.783	3.489	103.29	103.294	96.73262598
6	Kornel hat (Pond 1)	61.113	7.38	53.73	53.733	87.92400962
7	Kornel hat (Pond 2)	39.613	3.032	36.58	36.581	92.34594704
8	Kaibalyadham (Dham 1)	35.064	1.978	33.09	33.086	94.35888661
9	Kaibalyadham (Dham 2)	36.22	0.82	35.4	35.4	97.73605743
10	Pahartali (Pahartali bazar)	34.653	2.169	32.48	32.484	93.74080166
11	Pahartali (Kali mandir)	216.121	7.753	208.37	208.368	96.41265772
12	Boubazar (Eidgah boubazar)	201.608	6.733	194.88	194.875	96.66035078

Fig 15. Sample analysis using GCMS, Data analysis using MS excel

Brief Biography

The author passed the Secondary School Certificate Examination from Dr. Khastagir Government Girls' High School, Chattogram, and then Higher Secondary Certificate Examination from Chattogram College, Chattogram. She obtained her B.Sc. (Hon's) in Food Science and Technology from the Faculty of Food Science and Technology at Chattogram Veterinary and Animal Sciences University, Chattogram, Bangladesh. She was awarded with the prestigious Prime Minister Gold Medal 2017 and the Chancelor Award in the year 2017 for her result in B.Sc. (Hon's). Now, she is a candidate for the degree of Master of Science in Food Chemistry and Quality Assurance under the Department of Applied Chemistry and Chemical Technology, Chattogram Veterinary and Animal Sciences University (CVASU). She has an immense interest to work in improving the quality of food sector through proper guidance and suggestions and to create awareness among people about food safety and quality.