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A Review on the Mechanism Removal of Pesticides and Heavy Metal from Agricultural Runoff in Treatment Train

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***Abstract*—**Pesticides have been used widely over the world in agriculture to protect from pests and reduce crop losses. However, it affects the environment with toxic chemicals. Exceed of toxic constituents in the ecosystem will result in bad side effects. The hydrological cycle is related to the existence of pesticides and heavy metal which it can penetrate through varieties of sources into the soil or water bodies, especially runoff. Therefore, proper mechanisms of pesticide and heavy metal removal should be studied to improve the quality of ecosystem free or reduce from unwanted substances. This paper reviews the use of treatment train and its mechanisms to minimize pesticides and heavy metal from agricultural runoff. Organochlorine (OCL) is a common pesticide that was found in the agricultural runoff. OCL is one of the toxic chemicals that can disturb the ecosystem such as inhibiting plants' growth and harm human health by having symptoms as asthma, active cancer cell, vomit, diarrhea, etc. Thus, this unwanted contaminant gives disadvantages to the environment and needs treatment system. Hence, treatment train by bioretention system is suitable because removal efficiency achieves until 90% of pesticide removal with selected vegetated plant and additive.

***Keywords*—**Pesticides, heavy metal, agricultural runoff, bioretention, mechanism removal, treatment train.

I. Introduction

AGRICULTURE has become one of the biggest industries that contribute to nation development. Many lands were explored to fulfill the aggressive needs to support the demand. Despite that, it results in the environment being polluted due to uncontrolled agriculture activities. The development of agricultural lands has led the pollution entering water bodies by agricultural runoff. This problem arises when most of the agriculture agencies use pesticides to control losses from crop yields devastation. Many farmers were interested in using pesticides rather than implementing organic plantation as it gives more profit and saves time to control pests. The usage of pesticides became widespread worldwide to maintain the high quality product fruits and vegetables [1].

Pesticides usage gives benefits to crop production as it increases the percentage production and reduces the crop losses. However, it leads to pollution in the environment due to the chemical ingredients [2]. Those ingredients increased the toxicity towards the environment and affected human health. Farmers have high possibility of being affected by the toxicity of pesticide because of agricultural practices such as pesticide spray techniques. The techniques require the farmers to spray the pesticides towards crop. Once it was exposed into the air, some of the chemicals evaporated while farmers also indirectly inhale the air that mixes with unwanted chemicals. As the pesticides are commonly applied through spray techniques, chemical ingredients from pesticides are absorbed into soil and water bodies [3]. Then, the polluted water flows from the agricultural area and enters the swale that contaminates the soil and water. Nevertheless, this pollution could be not only pesticides but all pollutants that flow from the agricultural area such as sediments, nutrients or heavy metal mixing up together and flowing until final destination. Hence, bad effects such as algae bloom, animal defect and even diseases to human could happen once they are absorbed into the environment since water is essential chain in the hydrologic cycle [4]. Furthermore, it has been reported that river pollution in Malaysia is becoming worse every year. According to Health Impact of River Water Pollution in Malaysia by [5], about 49% of rivers in Malaysia was polluted and contaminated due to agriculture, industries and farming. Besides, most of the contributors to river pollution at Klang river basin are from agro-farm sources when 34 rivers were categorized as polluted and some of the rivers are having eutrophication phenomena because of excessive nutrients. It is proving that agriculture gives a big impact on the environment. Usually, runoff that flows from agriculture area consists of high concentration of nutrients and pesticides from agriculture practices. Therefore, Best Management Practices (BMPs) and Low Impact Development (LID) are applied to reduce the pollution and manage the runoff from agriculture area before it flows into the water bodies. These approaches may be used to overcome the problem but on the other hand, it has low ability to cater the pollutant removal consistency [6].

Agriculture pollution is one of the issues that needed to be concerned since it initiates harmful effects to humans and environment. Many agencies and researchers have created awareness towards this pollution. Moreover, the government also created environmental department to control this issue. BMPs are one of the efforts to help reduce pollution by giving practices in the agricultural system such as control the usage of pesticides in agriculture. In this practice, the farmers should

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follow all the procedures to protect the environment in reducing pollution. After a certain period, water quality will be improved with sustainability approach by applying those BMP practices [7]. The usage of chemicals in farming activities was controlled by Agricultural and Environment Department. Only certain pesticides are banned from being used in the pesticides application such as Aldrin, Dieldrin, HCH, etc. [8]. In addition, LID is another alternative that helps this issue by creating a few ideas to develop innovative removal system and ecology that suit the agriculture environment. LID also brings new ideas that can give advantages of low impact pollution to environmental quality. Bioretention is one of the systems in LID that can support agriculture runoff from infecting the environment. Many researchers have practised this system to create a better solution in removing the pollutant from water runoff. Most of the researchers admit the effectiveness to treat water pollution [9]. However, the concept between LID and BMP are the same, capable of reducing pollution in the agricultural area. Both alternatives give the same impact to the environmental condition.

Treatment train is one of the solutions from BMP and LID that effectively treat water pollution that contains sediment, heavy metal, nutrients etc. It is designed to meet the standards of environmental quality by having a sequence or multiple treatment channels. It is also used to capture the first runoff event and reduce pollutants that mix in the runoff. The treatment train consists of components such as pretreatment, storage, and filtration. All the features could be different based on the design that needs to meet the criteria of each runoff problem. Some of the runoffs are having another type of impurities: gross pollutants, sediments, etc. [10]. So, the designer needs to consider the treatment train design based on the nature of the runoff. The final effluent of runoff should follow the cleanliness in water quality standards. However, there is no implementation of treatment train in agricultural runoff. In this research, the researcher will focus on treatment train that acts as a mechanism of pesticide and heavy metal removal.

This review reports pesticides and heavy metal pollution that occur around the world, especially in Malaysia. As agriculture needs are increasing, the usage of pesticides also increases. This situation triggered high possibility of unwanted chemical exposure to the environment and accelerated the pollution [11]. Moreover, this review also addresses water quality management that consists of treatment system from BMP and LID practices including treatment train used to treat polluted runoff. The crucial part in this review discusses about the mechanisms removal of pesticides and heavy metal in treatment train system as well as the process during removal. Since the treatment system is new for agricultural runoff, future works of this research area are also noted in order to detail out the new implementation towards the research.

II. Pesticides and Heavy Metal Pollution

Pesticides are commonly used in protecting crops from pest and enhancing productivity. It is a toxic chemical substance that purposely exposed into air using spray applications in order to control and demolish the population of harmful insects, pests, fungi or weeds. Some of the pesticides also contain heavy metals that can inhibit the natural process of habitats [12]. Moreover, rapid activity in agriculture has led to increase disposal of heavy metals and radionuclide into the environment. In fact, heavy metals have become a hazard due to agriculture practices and categorized as agricultural pollution for the recent past [13]. In agriculture practices, spray applications are most relevant method which contains more than one active ingredient that has the ability to kill organisms. According to the data, worldwide crop production has loss of 20% to 40% due to pest attack and disease [1]. Due to that, the usage has increased for the past few decades. Based on estimation, worldwide pesticides are used about five point two billion pounds per year [14]. Intensive usage of pesticides has resulted crops comprise high residue chemical pollutant and involve the environment through the process of leaching, erosion, runoff or volatilization of pesticides [2]. Furthermore, the issue regarding water pollution from agriculture has increased as there are many negative impacts on human health. The pollutants that flow in the runoff such as nutrients, heavy metal and pesticides have ride human health to be in a perilous situation which lead to diseases once human drank the contaminated water. In addition, the disease such as blue-baby syndrome has resulted to Methaemoglobinemia, a symptom that potentially leads to fatal illness in infants due to high levels of nitrate in aqueous solution which affects child growth. Other than that, any type of cancer happens to the farmers because they are exposed to toxic chemicals in pesticides through spray techniques. But, pesticides can also be absorbed into water and accumulated. Since many illness cases were reported, some of the toxic pesticides were banned at certain broad-spectrum but certain countries still use as it is cheaper [15]. Furthermore, aquatic ecosystems are also affected when eutrophication happens because of accumulation of nutrients in water bodies. Hence, the pollution could diminish through leaking of nutrients then affect biodiversity and fishery.

Pollution of pesticides and heavy metal in agricultural runoff was tested by many researchers to prove the existence in the environment. Tables VI and VII summarize pesticides and heavy metal pollution exist in the agricultural area.

A. Pesticides in Agriculture

Pesticides usually used to kill the pest that affects the crop productivity. Pest attack had caused lost big amount of crops and also lead to income reduction to the farmers. To solve the problem, farmers had to use chemical to kill the pest by using pesticides that considered as a successful approach for pest reduction in agricultural area [12], [13]. There are many types of pesticides application method such as spraying, dusting, granular application, seed dressing and etc. Commonly application that used by farmers are spray application since it was the easiest way to perform [12], [13], [16], [17]. However, pesticides contain toxic chemicals substances since its purpose was used to kill harmful pests or insects. Besides, spray applications contain more than one active ingredient that has

the ability to kill organisms [17]. Even though it was a good choice in demolish the pest, the toxic chemical can disturb the environment once it flows into the ecosystem. The environment will be toxic if the acidic chemical was not controlled from the first stage. Hence, many effects will occur and arise in future.

Pesticides are well known in agricultural consumption. There are many types of pesticides produced. Each category shows different function to destroy unwanted organisms in agriculture product. Basically, pesticides were categorized into few types which are bactericide, fungicide, herbicide, insecticide, moiluscicides, nematicides, and veterinary. The common pesticides that are found in agricultural practices are herbicides and insecticides [18], [19]. Those pesticides bring significant influence in the agricultural area since the main problem that destroys the crop comes from insect and weeds itself. In order to elaborate more regarding pesticides, Fig. 1 represents the categories of pesticides product while Table III indicates the function for each pesticide [1], [14], [20], [21].

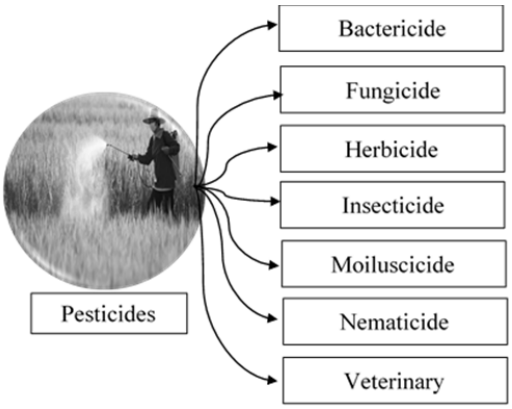

Fig. 1 Types of pesticides

TABLE I
PURPOSE OF PESTICIDES [1], [14]

Type of pesticides	Target organisms	Example of active ingredients
Bactericide	Bacteria	Metiram, Difolatan
Fungicide	Fungi	Phenylamides, Dicarboxamides
Herbicide (paraquat, glyphosphate and propanil)	Plants	Atrazine, 2.4-D, Acifluerfen
Insecticide (OCL, organophosphate, and carbamates)	Insects	Dimethoate, Permethrin
Moiluscicide	Snails and sludge	Methiocarb,Carbaryl
Nematicide	Nermatodes	Aldicarb, Dibromochloropropane
Veterinary	Animal parasites	Fenthion, Flumethrin

Chemicals in pesticides are dangerous to human health and the environment. Exposure of pesticides toxicity can defect human health risk based on the chemical. Most of pesticide ingredients can irritate human if it was exposed for a certain period. It also can cause even cancer to human if the pesticides contain higher toxic chemical concentrations. To discuss more on the effect of pesticides, Table II explains its side effects.

TABLE II
EFFECT OF PESTICIDES [29]

Type of diseases	Effect	Chemical causes
Irritation	• Redness and pain • Respiratory irritation can produce nasal, laryngeal, or pulmonary effects • Upper and lower respiratory tract irritation	Most of pesticides
Allergic sensitization	• Redness and pain • Dermal and ocular irritation • Asthma	Fungicides
Enzyme inhibition	• Cholinesterase activity is decreased by exposure to organophosphorus compounds and carbamates. • Cholinergic crisis	Cholinesterase, OPs and Carbamates.
Oxidative damage	• Promoter of superoxide radical • Caustic lesions and pulmonary fibrosis	Paraquat
Inhibition of neurotransmission	• Calcium homeostasis alteration • Gamma-aminobutyric acid (GABA) inhibition	OCLs

Most used pesticides are herbicides and insecticides. This chemical is very toxic once it is exposed to the environment. Table III shows pesticides chemical compounds for mostly used pesticides which are OCL, Organophosphate, Paraquat, Carbamates [5], [30], [31].

TABLE III
COMPOUND OF PESTICIDES

Types of Pesticides	Types of Compound	Chemical contain
Insecticides	OCL	DDT, Dieldrin, Heptachlor, Chlordane, Endosulfan and Dicofol.
Insecticides	Organophosphate	Malathion, Parathion, Diazinon, Fenthion, Dichlorvos, Chlorpyrifos, and Ethion
Insecticides	Carbamates	Originally in single chemical or known as Ester Ethyl Carbamate
Herbicides	Paraquat	Originally in single chemical known as Methyl Viologen

OCL pesticides are the synthetic chemical solutions that are extensively used in agriculture around the world. They were commonly used and considered as chlorinated hydrocarbon derivatives which have vast potentials to kill the pest. These agents also belong to the persistent organic pollutants class. The compounds are recognized as high toxicity, slow degradation and bioaccumulation [14], [32], [33]. A certain developed country such as China has banned the usage due to its toxicity to the environment but the application has been rising since the market offers low cost [2]. In understanding the OC pesticides, Table VIII shows the toxicity of OC pesticides.

B. Heavy Metal in Agricultural

Agriculture activities give advantage in crop production. However, the movements caused contamination to the environment. High usage of pesticides and fertilizer are one of the main sources that cause contamination. The chemicals in the pesticides and fertilizer can exhibit the contamination of heavy metal whether in soil or runoff [34]. Heavy metal usually exists in nature but it can cause harm if it exceeds

certain amount of concentration [35]. In addition, heavy metals are considered as a metal of relatively high density and have metallic properties. Some of them were poisonous due to the high relative of atomic weight. Among all heavy metals, Copper (Cu), Cadmium (Cd), Zinc (Zn), Arsenic (As), Mercury (Hg), Chromium (Cr), Lead (Pb) and Antimony (Sb) are categorized as high risk of contamination especially in agricultural soil [36]. Based on the researchers, there were four types of heavy metal usually found in soil that lead to heavy metal contamination in soil which are Cu, Zn, Cd and Pb [34], [37].

Soil contamination with heavy metal happened in the world and became a major environmental problem. This problem was reported by many researchers for several times as discussed in Table II. Nevertheless, heavy metal could be not easily removed from soil due to high toxicity [38]. The contamination could exist from many sources such as mining, industrial nor agricultural practices [34], [39]. Those sources give the result of having anthropogenic causes. Anthropogenic is defined as causes made by human activities to nature [13], [35], [37], [40]-[42]. The causes may come from fertilizer, pesticides or any chemicals from agricultural practices that accumulated in the system which disturbed the natural equilibrium. High-level concentrations of heavy metal in soil present the consequence to the quality growth of the plant, soil biological process through bio magnification once toxic chemicals enter the human body [40].

Heavy metal can come from many places but the concern was when it enters into the water bodies such as river. This can be even worse when the water carries heavy metal elements flowed to the agricultural area. Somehow the water was used for irrigation purpose by farmers and the toxicity percolated into the ground and caused the pollution [41]. Moreover, crops cultivated from contaminated soil may cause profound health effect to human once the elements get through into the body [43], [44]. Meanwhile, children were easy in the exposure of heavy metal toxicity side effect when dealing with the toxicity. The effect of heavy metal toxicity could disturb the first development stage of child growth and human will be expose to cancer [45]-[47]. Cr, Cu, Ar, Cd, Pb were of a particular concern because of much known detrimental health effects on humans through extra amounts of food consumption [48], [49]. Higher concentration of heavy metal contamination could harm humans and other animals [41], [50], [51]. In contrast, Cr and Cu cause non-carcinogenic health hazards which involve within neurological involvement, vomit, headache with liver disease if exceeds a certain amount of concentrations [50]. In fact, the contamination had long terms negative effect on human or the ecology [52]-[54].

III. Water Quality Management for Agricultural Runoff

Water is very crucial for agricultural development. In the process agriculture activity, water is being used to perform the agricultural production. On the global scale, agricultural production uses more lands rather than any other economic purpose [11], [59]. Since agricultural activities increased, water usage will be increased. In world view, it has been reported total of water withdrawal about 70% for agricultural sector [60]. As more of agriculture land development occurs, the water usage also will increase. Besides, the environment could have exposed to pollution without proper practices as usually the developer will dump all unwanted waste or pollutants into the river and that will lead to sedimentation. Then, the pollution that already exists in the land with fertilizers and pesticide will flow together and into water bodies through the percolation process as this situation will continue to contaminate the environment. Irrigation canals are one of the water channels that affect pollution. Due to that, pesticides and nitrate residues are mostly found in an irrigation canal at paddy fields [61]. Thus, water quality management practices are relevant to apply in the agricultural runoff to reduce pollution.

Water quality management could reduce pollution and improve environmental health. To support the quality, government should take serious attention into health issue after cases regarding excessive toxic contaminants in water and soil [62]. Standard amounts of contaminant for water quality are introduced to control the chemical concentrations in the environment. Somehow, there are still pollutions occurred in the runoff because people are not aware of the pollution. Besides, expensive chemical usage in agricultural practices is barrier in changing the environmental and sustainable concepts. The problems have created more initiative by having BMP and LID practices. There are few treatment systems that were designed to solve the problem regarding pollutant in surface runoff which suitable to control the excessive amount in water and soil.

A. Treatment Train System in BMP and LID

Treatment system for runoff is designed to cater polluted runoff and reduce volume runoff in a sustainable approach. Many systems are used to solve the arising problem which reduces the pollutant in runoff through infiltration process. Infiltration process is crucial as it is expected to have a few advantages including groundwater recharge, runoff volume reduction, low stream flow augmentation, and water quality enhancement [63]. Among systems applied in BMP and LID are Riparian Buffer Zone, Permeable Conveyance System, Wetland, Infiltration Basin, Runoff Treatment Train, Bioretention, etc. Riparian Buffer Zone is a zone that acts as a buffer with the planted area along with water bodies which prevent polluted runoff flow into the riparian zone, as shown in Fig. 2. At the same time, infiltration basin and wetland are one area that allows the water to percolate into the ground.

In urban areas, permeable conveyance system is usually applied as the surrounding area paved on the surface. Moreover, the paved area inhibits the percolation process that can cause flood. Thus, this practice helps the runoff permits into the soil at permeable area and water can flow through conveyance drain as illustrated in Fig. 3. Another practice that usually gets attention by the researchers is the treatment train by using bioretention system. The system improves the water quality when runoff percolates into the soil while the polluted

particles are trapped within filter media and deposits onto the surface (soil and vegetated plant) via adsorption process [6], [30]-[33].

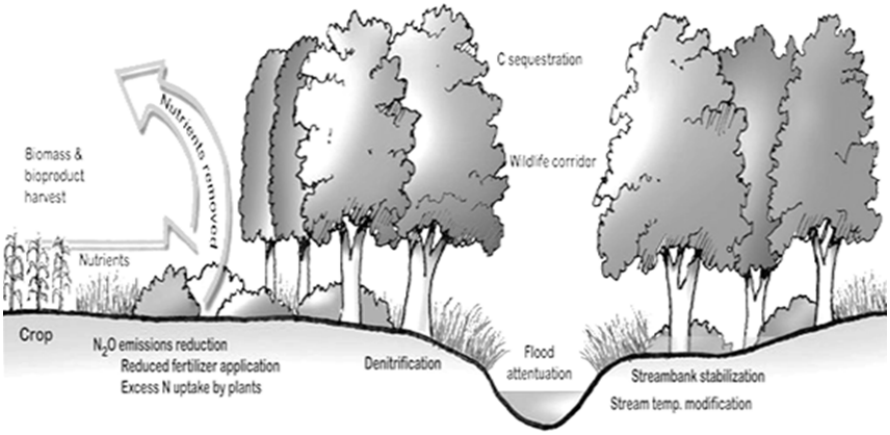

Fig. 2 Riparian Buffer Zone [66]

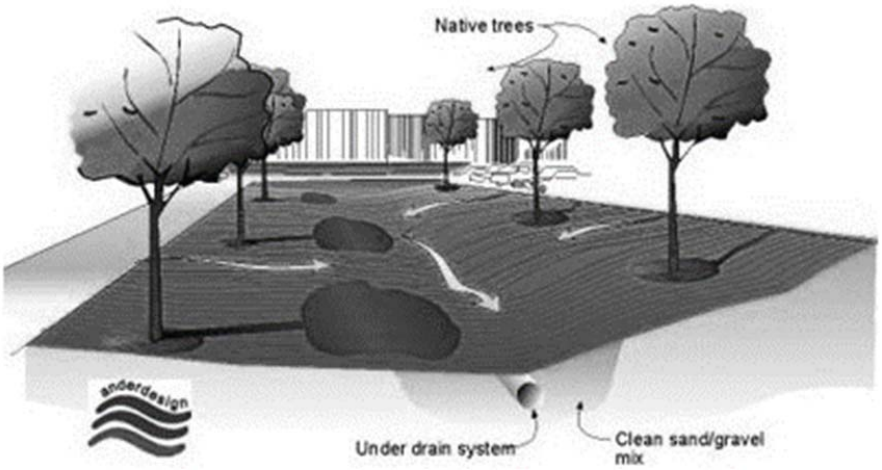

Fig. 3 Permeable Conveyance System [64]

B. Details Concepts of Treatment Train in Runoff

Treatment train is defined as a sequence of runoff treatments in a train that are designed to meet standards and needs of particular environment [6], [68]. Treatment train is mostly applied in stormwater runoff. It is important when a treatment measure needs pretreatments to remove pollutants, such as nutrients and fine sediments that would otherwise impact its performance. The design was included with few treatment stages to filter the pollutant throughout the runoff. At the first stage, gross pollutant was filtered by the physical screening process. Then, filtration techniques are utilized when the water flows into swales or bioretention system. Some fine pollutants such as sediments, pesticides, or heavy metals are absorbed into soil, vegetated plant and additives. Indirectly, it enhances the performance of system to improve the water quality [34]-[37], [69].

Some studies have demonstrated that the treatment train was effective for stormwater quantity and quality control [33], [41], [63], [69]. A field test of the selected treatment train conducted in China resulted in that peak flow rate and runoff reduction of stormwater of a bioretention cell were more than swale. For water quality, the bioretention in general showed better removal of pesticides and nutrient efficiency than swale as this paper focuses removal of chemical toxicity [41]. Bioretention system indeed is the best alternative in reducing chemical pollutant. However, the approach is still not being implemented for agricultural runoff.

IV. Removal Mechanism in Treatment Train

A. Relation of Pesticide in Hydrological Cycle

Pollution that occurred in agricultural runoff can be categorized as non-point sources pollution. The sources could be from many places and it was tied closely with hydrologic cycle that is present in our environment [13], [71]-[74]. Hydrologic cycle process could be sources that determined water quality in agricultural runoff. For example, the cycle process starts with precipitation from rainfall. As the water absorbs into groundwater through infiltration and percolation process, it flows together with an unwanted chemical substance, thus enters the water bodies. Hence, unwanted

substances affect water bodies to be polluted. The mobilization of pollutant such as pesticides through agricultural runoff related with the process in hydrological cycle is called as pesticide cycle. The cycle begins with agriculture practices once it was exposed into the environment such as practices by spray techniques. Pesticides and heavy metals were percolated into the ground and leached into water bodies. Some of the pollutants could be degraded into the air, absorbed into the crop or transported by runoff [11], [24], [39], [40]. Pesticide cycle is illustrated in Fig. 4.

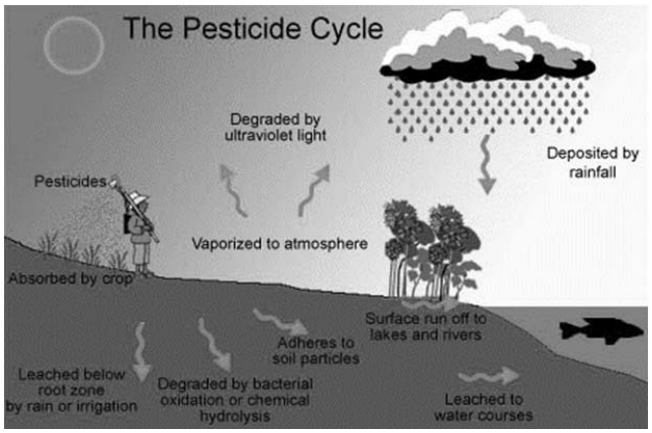

Fig. 4 Pesticides Cycle [4]

B. Processes Involved in Bioretention

The concept of removal by bioretention system involves few processes. Once runoff flows into the system, the water undergoes the process of infiltration, plant uptake, and filtration. Lastly, the treated runoff flows out from the bioretention system in the drain zone [65], [67], [75]-[78]. The processes are discussed more as shown in Fig. 5 and Table IV.

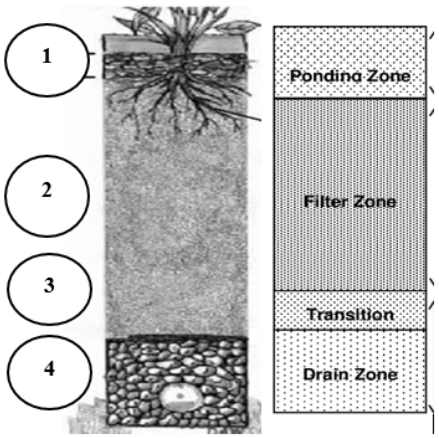

Fig. 5 Zone of bioretention system [67]

Plant uptake was an important part in the pollutant removal process. Plant uptake process is also called as phytoremediation in which plant cell has the ability to absorb pollutant with the root, stems, etc. Some pollutants could be exposed into the air when the plant was going through evapotranspiration process [43], [44]. Each part of the plant has their own process to reduce the pollutant from water. Details of phytoremediation process are discussed in Table V.

TABLE IV
POLLUTANT REMOVAL PROCESS IN BIORETENTION SYSTEM

Stages/Zone	Process	Description
1 (Ponding Zone)	Infiltration	The water flows into the system and starts to infiltrate into the soil.
2 (Filter Zone)	• Infiltration • Adsorption • Plant uptake	• The water infiltrates deeper into the soil and absorbs by soil particle. • Pollutant in the water such as pesticides and heavy metal are going process of adsorption which is the particle absorbs into soil media. • Some of the pollutants were absorbed into the plant through root system
3 (Transition)	Filtration	Water percolates and filters through geotextile as filter media before passing through next level.
4 (Drain Zone)	Runoff	Excess treated water flows out from the system through drain.

TABLE V
PHYTOREMEDIATION PROCESS IN PLANTS [40], [43]-[45], [82]-[84]

Process	Description
Phytoextraction	Uptake and concentration of substances from the environment into the plant biomass.
Phytostabilization	Reducing the mobility of substances in the environment, for example by limiting the leaching of substances from the soil.
Phytotransformation	Chemical modification of environmental substances as a direct result of plant metabolism, often resulting in their inactivation, degradation (phytodegradation) or immobilization (phytostabilization).
Phytostimulation	Enhancement of soil microbial activity for the degradation of contaminants, typically by organisms that associate with roots. This process is also known as rhizosphere degradation.
Phytovolatilization	Removal of substances from soil or water with release into the air, sometimes as a result of phytotransformation to more volatile and / or less polluting substances.
Rhizofiltration	Filtering water through a mass of roots to remove toxic substances or excess nutrients. The pollutants remain absorbed in or adsorbed to the roots.

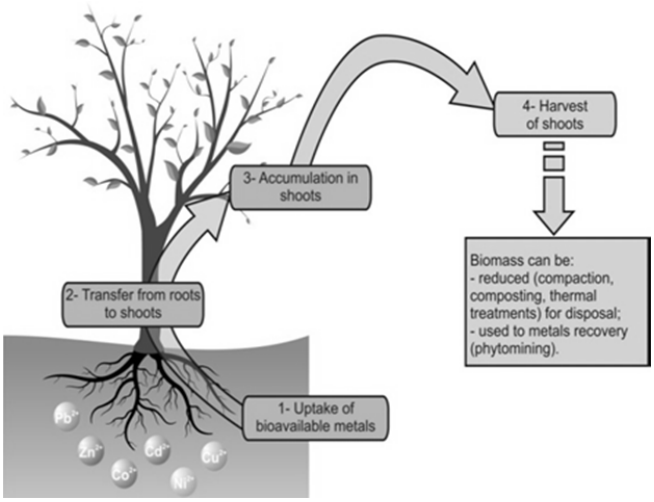

Fig. 6 Phytoremediation process [82]

In treatment train concepts, the process to treat runoff was repeated within three stages by having three bioretention columns as shown in Fig. 7. It can be considered the water was treated in the bioretention system for three times. This concept was designed to filter the runoff from pollutant with an efficient method in the single treatment train. At the same time, series treatment train is implemented to improvise the consistency of treatment train to treat runoff within several periods.

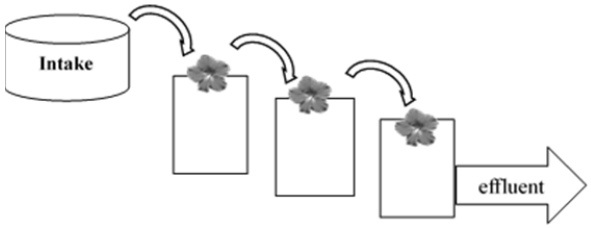

Fig. 7 Single treatment train

C. Pollutant Removal in Bioretention System

In the treatment train, plant and additive help remove more pesticides and heavy metals from the agricultural runoff rather than depending on soil in bioretention system itself. A suitable plant that can be used in removal pesticides according to the weather in Malaysia that can be considered as hot and humid condition was Hibiscus plant [67], [81], [85]-[87]. In other hands, flower plants such as Phlox, Coreopsis were used as they were suitable in bioretention system [88]-[90]. However, any types of plant also can improve the adsorption process of pesticides but it causes to have minimized result. While for additive, coconut husk, rice husk, durian peel and oil palm fruit have the ability in absorbing more pesticides which reduce the concentration percentage in water runoff [91]-[94]. Moreover, hibiscus was the most suitable for heavy metal removal and it can reduce the concentration of Cd, Pb, Zn or even As [95]-[98]. After that, any fruit peel was suitable for additive removal of heavy metals [99]. In contrast, heavy metals were hard to remove totally from water due to their high chemical toxicity [38]. More details were discussed more on the efficiency of pollutant removal in bioretention system in Table IX.

TABLE VI
PESTICIDE POLLUTION IN AGRICULTURE

Pollution occurred	Details	Type of pollutant	Amount of pollutant	Limitations	Ref
Pesticides residues were found in the irrigation canals at Sungai Muda, Kedah (Malaysia).	• The residue is present in two seasons: wet and dry season. Detection of residue is done by extraction method according to types of pesticides and gas chromatography. • The insecticides, namely: α-endosulfan, β-endosulfan, endosulfan sulphate, cypermethrin and chlorpyrifos were found in the surface water of the irrigation canals.	Insecticides: i. OCL α-endosulfan • β-endosulfan • Endosulfan Sulphate ii. Organophosphate • Chlorpyrifos iii. Pyrethroid • Cypermethrin	The insecticide concentration was monitored from September (9) 2010 to March (3) 2011. • Highest concentration: i. Cypermethrin: 3.97μg/mL ii. Chlorpyrifos :4.42 μg/mL • Lowest Concentration: iii. α-endosulfan: 0.26 μg/mL iv. Chlorpyrifos: 0.13 μg/mL	• Involve complex procedure (extraction and gas cromatography to get concentration amount in water). • Have to monitored within two seasons.	[3]
OCL compound residue in three places of Malaysia's paddy fields: i. Tanjong Karang, Selangor. ii. Sekinchan, Selangor. iii. Felcra, Seberang Perak, Perak	1) Found in fish sample: i. Puyu (Anabas Testudineus) ii. Haruan (Channa Striatus) iii. Sepat (Tricogaster Pectoralis) • Water samples from the irrigation channel were also analyzed.	Pesticides: 1) Only conducted detection of the OCL compound in the fish sample: i. Aldrin ii. Dieldrin iii. Endrin iv. Endosulfan v. O, p-DDT vi. P, p-DDT Endosulfan found in water samples from an irrigation channel.	1) OCL compound in irrigation canals: i. Tanjong Karang (OC residue: 0.04 mg/kg) ii. Sekinchan (OC residue: 0.04 mg/kg) *. Ecxeed limit: 0.03 mg/kg 2) BDL in fish sample at Seberang, Perak and Sekinchan: i. Haruan: < 0.02 mg/kg ii. Sepat: < 0.02 mg/kg iii. Puyu: < 0.02 mg/kg BDL: Below detection level observations	• Endosulfan is a chemical in the hydrophobic compound which results in higher concentration more in soil rather than water. Thus, it has led to low bioaccumulation of pesticides residue in fish sample. Future research needs to be done regarding bioaccumulation of endosulfan pesticide residue in water.	[5]
OCL pesticides were observed at paddy field of Machang, Kelantan (Malaysia)	The sample was taken in the soil of lowland paddy field by collecting soil sample at 5 different locations. After concentration residue tests were analyzed, pesticides residue was present in the sample. All samples taken showed similar characteristics which are slightly acidic, low organic carbon	OCL compound: i. α HCH ii. β HCH iii. γ HCH iv. δ HCH v. 4-40-DDT vi. Endosulfan Sulphate	Highest concentration during low of water at first sampling which is: i. α HCH: 7.34 μg/kg ii. β HCH: 3.12 μg/kg iii. γ HCH: 3.73 μg/kg iv. δ HCH: 1.95 μg/kg v. 4-40-DDT: 5.24 μg/kg vi. Endosulfan Sulphate: 0.03 μg/kg	• Limitations of compound residue detection. • Involve complex procedure to get the concentration of residue amount in water.	[1], [2] [22]

Pollution occurred	Details	Type of pollutant	Amount of pollutant	Limitations	Ref
	content, high water content and sandy texture type.				
Pesticides found at two places in the paddy field, Selangor (drain, soil, irrigation canal): i. Sungai Burung ii. Sawah Sempadan	Found in the water sample and soil from the study area. Location of water sample: i. Small drain ii. End of the field iii. Amid of the field	Diagnosed the pesticide in lab. Type of pesticide in the sample: i. Paraquat ii. 2, 4-D	Total pesticides concentration found in the sample for five days: i. Paraquat: 18 mg/kg ii. 2, 4-D: 5.6 mg/kg	The sample needs to be taken according to the paddy planting season for the higher concentration of residue in water and plant.	[23]
There is the existence of OCL pesticides residue in rice paddies field at Krian District, Perak.	Sampling was taken total of 332 paddy fish at 5 locations in the Krian district which is: i. Tanjong Piandang- Paddy field (36 fish) ii. Sungai Kota-Paddy field (98 fish) iii. Jalan Bharu-sump pond (83 fish) iv. Sungai Burong-irrigation (56 fish) v. Parit Tanjong Piandang-irrigation (59fish)	OCL pesticides: i. Dieldrin ii. α – chlordane iii. β –chlordane iv. β HCH v. γ –HCH vi. p,p'-DDT vii. p,p'-DDE viii. p,p'-DDD ix. Aldrin	• Highest concentration at Paddy field Tanjung Piandang: i. Dieldrin: 24.9 µg/kg ii. α –chlordane: 15.1 µg/kg iii. β –chlordane: 12.7 µg/kg iv. β HCH: 8.2 µg/kg v. γ –HCH: 3.5 µg/kg vi. p,p'-DDT: 6.0 µg/kg vii. p,p'-DDE: 4.4 µg/kg viii. p, p'-DDD: 3.9 µg/kg ix. Aldrin: 0.5 µg/kg	• Limitations of compound residue detection. • Involve complex procedure to get the concentration of residue amount in water sample and fish.	[24]
OCL residue in paddy crops taken between two different types of cultivation. The sample was taken at MARDI paddy fields and farmers' paddy field that did not follow the scheduled practice from MARDI.	The sample taken was to compare concentration level of OCL pesticides in leaves, stems and rice grains from paddy plant. Every sample has proven the existence of residue. Two different locations of paddy field were taken as a site study.	OCL pesticides: i. α -endosulfan ii. β - endosulfan iii. Endosulfan- sulfate iv. Aldrin v. Heptachlor	• More toxic compound of OCL pesticides was found at paddy field cultivated by farmers. Only few and less toxic amount of pesticides was found in MARDI cultivation of paddy field. • Highest concentration is detected within Endosulfan sulfate compound at outlet intake. • Endosulfan-sulfate concentration: i. Leaves: 547.67 µg/kg. ii. Stem: 368.93 µg/kg. iii. Rice: 22.37 µg/kg.	Limitation of this study is found when higher amount of water can disturb the concentration of pesticides residue.	[25]
OCL pesticides and polychlorinated biphenyl (PCB) are detected in the river due to pesticides application at paddy field from agricultural runoff (Vietnam)	An investigation was carried out to determine the current levels of OCL and PCB compounds in the aquatic ecosystems of the Red River Delta. The study area encompasses the delta of the Red River and the coastal area of the Thai Binh province, the most important rice-producing region in North Vietnam.	There are two types of pesticides existence: i. OCL pesticides ii. PCB	The highest concentration found in river from marine sample was OCL pesticides which are: i. p,p'-DDE: 109.7 µg/kg. ii. p, p'-DDD: 42.6 µg/kg. iii. p,p'-DDT: 27.5 6 µg/kg.	Seasonal fluctuation disturbs the sample taken and the concentrations were low.	[26]
OCL pesticides and PCB are detected in paddy field ecosystem. (China)	A series of environmental samples and biological samples was collected in rice fields, including sediments, paddy soils, mitten-handed crabs, loaches and frog. A method by gas chromatography was used to detect the residue.	There are two types of pesticides existence: i. OCL pesticides ii. PCB	The highest concentration of p, p'- DDT (OCL pesticides) compound was resulted by the sample: i. Crab: 177.81 µg/kg. ii. Loach: 711.64 µg/kg. iii. Frog: 164.92 µg/kg.	Future research of PCB should be done since lack of the previous study.	[27]
This study was focused on OCL pesticides at paddy fields since it was commonly used during the process of growing rice (India)	Concentrations of HCH and DDT were determined in 175 surface soil samples from different agricultural fields, fallow and urban lands of districts Nagaon and Dibrugarh, Assam, India.	OCL pesticides: i. Hexachlorocyclohexane (HCH) ii. dichlorodiphenyltrichloroethane (DDT)	The mean concentrations of total HCH and total DDT were 825 ng/g (range: 98–1945 ng/g) and 903 ng/g (range: 166–2288 ng/g) in district Nagaon while 705 ng/g (range: 178–1701 ng/g) and 757 ng/g (range: 75–2296 ng/g) in district Dibrugarh. The soils from paddy fields contained the highest amounts of HCH and DDT residues.	• Large scale of site study. • The analytical procedure was complicated.	[28]

TABLE VII
HEAVY METAL POLLUTION DUE TO AGRICULTURAL ACTIVITIES

Place	Details	Concentration (µg/L)									Limitations	Ref
		Fe	Zn	Mn	Cd	Cr	Pb	Cu	Ni	Hg		
		National Water Quality Standards (NWQS), class II - Raw water										
		1000	5000	100	10	50	50	20	50	1		
Sungai Semenyih	The research was to determine the concentrations of dissolved heavy metals in the river due to municipal activities and agricultural activities. Heavy metal still in the normal range.	441.6	24.78	34.05	0.39	2.37	1.62	7.72	0.79	0.27	Agricultural activities are mostly responsible activity that causes the presence of heavy metal at lower pollution area.	[55]
Kg. Sawah Sempadan	Site sample was collected from paddy field at Tanjong Karang,Selangor. The amount of heavy metals concentrations still in control and indicated that no-carcinogenic dermal health risk to farmers.	-	8.4	-	2.2	4.5	1.6	2.4	2.6	-	The samples are tested from the water sample and not to human. The actual exposure to human cannot be determined.	[56]
Paddy Field, Tumpat, Kelantan	The study investigates the concentrations of heavy metal in soil and plant sample through extraction.	-	6.55	-	0.12	-	9.8	3.93	1.73	-	Few amounts of heavy metal concentration present in the paddy field area. However, monitoring should be done to control heavy toxicity in future.	[57]
Paddy Field, Papar, Sabah	Investigation of heavy metal concentrations at Papar Paddy Field by ICP-OES.	-	1.39	-	0.032	0.42	0.8	0.66	-	-	Heavy metal concentrations still in control but need extensive research for each part of paddy plant.	[58]

TABLE VIII
TOXICITY OF COMMON PESTICIDE COMPOUNDS [32]

Chemical name	Use	Toxicity	Persistence in the environment	WHO classification	Effect to Organism	Biochemical Effect
Dichlorodiphenyltrichloroethane (DDT)	Insecticide	Mice Oral:150-300 mg/kg	High Persistence Half-life: 2-15 years	Moderately hazardous	Mice Birds Fish Rats	Liver tumours, liver changes including hepatocellular hypertrophy, margination and formation of liposheres.
1,1-dichloro-2,2bis (p-chlorophemyl)ethane (DDD)	Insecticide	Mice Oral: 4000 mg/kg	High Persistence Half-life: 5-10 years	Acute hazard is unlikely	Mice	-
Dieldrin	Insecticide	Mice Oral; 38-77 mg/kg	High Persistence Half-life: 9 months	Highly hazardous	Human Mice Dog Rabbit	Neurotoxic, reproductive, developmental, immunological, genotoxic, tumorigenic effects, nausea, vomiting, muscle twitching and aplastic anaemia.
Heptachlor	Insecticide	Mice Oral; 40-220 mg/kg	High Persistence Half-life: 2 years	Highly-moderately hazardous	Mice	-
Endosulfan	Insecticide	Mice Oral; 18-270 mg/kg Dermal: 74 mg/kg	Moderate Persistence Half-Life Alpha Isomer: 35 days Beta Isomer: 150 days	Highly hazardous	Human Mice	Decreases the white blood cell count and macrophage migration, adverse effects on the humoral and cell-mediated immune system. Affects semen quality, sperm count, spermatogonial cells, sperm morphology and other defects in male sex hormones DNA damage and mutation.
Aldrin	Insecticide	Mice Oral; 44 mg/kg	Moderate Persistence Half-Life: 4-7 years	Highly hazardous	Human Mice Dog Rabbit	Neurotoxic, reproductive, developmental, immunological, genotoxic, tumorigenic effects, nausea, vomiting, muscle twitching and aplastic anemia.

V. CONCLUSIONS

According to the discussions, treatment train was able to remove pesticides and heavy metals based on the efficiency percentage. Treatment train system with bioretention column was more effective in water runoff that can reduce pollutant in water about 70% to 100%. This treatment system involves few processes and mechanisms; adsorption, absorption, filtration and phytoremediation. Adsorption process was the most effective in removing pollutants from water runoff and absorbing into soil particle while getting into plant by phytoremediation. However, single treatment train could not achieve the consistency in the removal process due to soil settling and low infiltration [70], [79]. Due to that, in-series treatment train should be used as one of the approaches to remove pollutants in consistent period. In fact, it also can cater huge amount of water runoff in the biorentention system and reduce the velocity of flow before it reaches to the final discharge by having series train. Hence, this study should be analyzed more in getting optimization of treatment train as a new research by conducting experimental work. Indeed, the effort towards this study will contribute Department of

Irrigation and Drainage (DID) for management in treating pollutant especially high toxic chemicals in agricultural runoff [14].

TABLE IX
POLLUTANT REMOVAL EFFICIENCY IN BIORETENTION SYSTEM

Pollution occurred	Pollutant removal with vegetated plant or additives (%)	Pollutant removal with soil (%)	Limitations	Ref
Heavy metals (Pb. Cu, Zn) were removed by bioretention column media composition. Gravel is part of media composition that mostly helps remove the heavy metal concentration from runoff.	92 (Cu), 75 (Zn), 80 (Pb)	23(Cu), 46(Zn),30 (Pb)	Turf with high organic carbon was found to be more effective in heavy metal removal. Further research could be done.	[10]
Investigation was done through hibiscus plant and some additives (coconut husk and cockle shell)	70	65	If vegetated plant was mix with additive, the removal efficiency reduced rather than additive without vegetated plant.	[67]
Analysis on heavy metal (CU, Pb, Cd,Zn) removal was done through bioretention system with additive mixture (coconut husk).	99 (Cu), 100 (Zn), 95 (Cd), 99 (Pb)	-	The purpose of this bioretention system is for the application of pollutant removal in agriculture runoff. However, due to some limitation, this study used synthetic runoff instead. Hence, the results obtained are only applicable for research purpose, not real case study.	[80]
Mevinphos insecticides were analyzed and samples were taken after two weeks.	100	94	-	[100]
Thiacloprid insecticide was reduced by plant named *P. australis*	88	68	Open water part resulted low percentage of residue rather than mesocosms part.	[101]
Endosulfan herbicides were investigated in constructed wetland at Mississippi, USA	76	-	-	[102]
Pesticide concentration was investigated at field study, Norway	91	72	-	[103]
Researcher observed very high absorption of pesticide imidacloprid by *Nymphaea amazonum* with majority of pesticide being found in leaves and shoots.	79	1	Different pesticides reacted different in absorption process. If the pesticides contain many compounds, percentage in plant uptake will reduce.	[104]

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