



UNIVERSITÀ DEGLI STUDI DI SASSARI

# DOCTORAL RESEARCH IN AGRICULTURAL SCIENCES DEPARTMENT OF AGRICULTURE CYCLE XXXI

# AGRICULTURE POLLUTION IN LEBANESE RIVERS: INFLUENCE OF SOIL AND SEDIMENT PROPERTIES ON PESTICIDE PERSISTENCE

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I would like to dedicate this PhD thesis to my parents Talal and Manal and to my dear husband Naji.

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#### Abstract

The Beqaa region, crossed by Litani river, represents 47% of Lebanon's agricultural economy. The Litani, the largest river of Lebanon, suffers from different kinds of pollution including that caused by widely used pesticides in Beqaa valley. The herbicides fluazifop (FLP), terbuthylazine (TBZ) and triclopyr (TCP) are the most frequently used in Litani basin, therefore their sorption on sediment and soil samples taken from four sites along Litani river Berdaouni, Joub Jannine, Ammiq and Qaraoun, respectively, was investigated. The sorption data obtained for the three herbicides fitted well to Freundlich logarithmic equation both on sediment and soil samples, showing very low sorption coefficient (Kads) values. At pH values of sediments and soils (7.7 < pH < 7.9 and 7.9 < pH < 8.2 respectively), their colloidal component is negatively charged similarly to the FLP and TCP herbicides, therefore the very low sorption measured is attributable to negative sorption due to the repulsion between species with the same charge. TBZ instead at measured pH values of sediments and soils is in neutral form, therefore, the greatest adsorption observed for TBZ is probably due to a lipophilic effect that is more active for TBZ than for the other two herbicides. This agrees with the higher Kads values observed on samples more rich in organic matter. The low sorption and FLP, TBZ and TCP low degradability make them herbicides at high risk of leaching. The addition of biochar (BC) from coppiced woodlands, to soils and sediments increased considerably Kads values for all three herbicides. The BC effect was more evident on poorer samples in organic matter. These findings suggest that BC addition to Litani basin soil may be considered as an useful tool to prevent FLP, TBZ and TCP leaching in water.

#### **Chapter 1: Introduction**

## 1.1 Pesticides and environment

#### **1.1.1 Definition and classification of pesticides**

The term pesticide includes the words "pest" and "cide". The word "cide", which originates from the Latin word "cida", means "killer". Thus, pesticides can be defined as killer of pests. According to the United Nations Organization for Food and Agriculture (FAO, 2002) "a pesticide is any substance or mixture of substances intended for preventing, destroying, or controlling any pest including vectors of human or animal diseases, unwanted species of plants or animals causing harm during, or otherwise interfering with, the production, processing, storage, or marketing of food, agricultural commodities, wood and wood products, or animal feedstuffs, or which may be administered to animals for the control of insects, arachnids or other pests in or on their bodies".

A pesticide formulation is necessary to make the chemical substance suitable for pest control. Pesticides are a mixture of several chemicals mixed together and consist of active ingredients, which are responsible for controlling the target pest and inert ingredients such as the carrier, stabilizers, and dyes which improve pesticide activity.

The three most common ways of classifying pesticides are based on the mode of action, the targeted pest species, and the pesticide chemical composition (Zacharia, 2011). Pesticides, when classified by their mode of action, are categorized as contact (non-systemic) and systemic pesticides. Contact pesticides do not enter the plant tissues and require a physical contact with the target pest to get the desired effect. Systemic pesticides, after being absorbed by the roots or foliage, are translocated through the vascular system of the plant to get the desired effect. When pesticides are classified based on the type of targeted pest, three main families can be identified. Herbicides, the most widely used pesticides in the world, are intended to eliminate plants that compete with the crops to be protected. Herbicides have different modes of action, e.g. they can be photosynthesis and regulator hormones disruptors, inhibitors of cell division or inhibitors of lipid, cellulose or amino acids synthesis. Fungicides are used to control the proliferation of plant diseases caused by fungi. They can act differently on plants either by inhibiting the respiratory system or cell division, or by disturbing the biosynthesis of sterols, amino acids, proteins or carbohydrate metabolism. Insecticides, neurotoxic, growth regulators or those acting on cellular respiration, used to protect plants against insects, intervene by eliminating or preventing their reproduction. In addition to these three main families, others can be cited such as the following examples: acaricides, against mites; nematicides, against worms of the nematode group; rodenticides, against rodents; molluscicides, against mollusks. Based on the chemical nature of the active ingredients, the chemical classification of pesticides is the most used by scientific researchers to understand their fate in the environment. The variability in pesticide chemical structure is considered as a key factor to recognize their environmental behaviour (Gavrilescu, 2005). chemical families of pesticides available Among the on the market, aryloxyphenoxypropionates, triazines, and picolinic acids are the most used in Lebanon.

Aryloxyphenoxypropionates are lipid synthesis inhibitors through the inhibition of acetyl-coa carboxylase, an enzyme responsible for cell membrane integrity. Acetyl-coa carboxylase catalyzes the formation of malonyl-coa carboxylase, which is a precursor of fatty acids (Gronwald, 1991). Aryloxyphenoxypropionates are the most effective herbicides applied to almost all perennial and annual grasses. Among those, Fluazifop, fenoxaprop and quizalofop are the main herbicides used in post emergence. These herbicides are absorbed by the foliage and

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translocated through the phloem. Symptoms develop slowly and it can take 1-2 weeks for plant death (Gunsolus and Curran, 2002). Fluazifop-p-butyl (trade name: Fusilade max), which is widely used in Lebanon, is a herbicide used for post-emergent application of graminaceous weeds for example in potatoes, fodders, vegetables, pome fruit, stone fruit, vineyards, and other broad-leaved crops (Negre et al., 1988; FAO, 2000). In soil, fluazifop-p-butyl is quickly hydrolysed to fluazifop acid, the effective phytotoxic moiety of fluazifop-butyl (Carr, 1986). Fluazifop-p-butyl is slightly toxic to birds and mammals but highly toxic to fish and aquatic invertebrates 2001). Fluazifop acid (RS-2-[4-[[(5-trifluoromethyl)-2-(Tu et al.. piridinyl]oxy]phenoxy]propanoic acid; FLP) was registered by the Lebanese Ministry of Agriculture on 5th August 2013. Figure 1 shows the chemical structure of FLP.



Figure 1. Fluazifop (FLP) chemical structure.

Triazines are photosynthesis inhibitors through their binding on proteins of the photosynthetic electron transport chain (Gunsolus and Curran, 2002). The first triazine was discovered more than 50 years ago. Nowadays, some triazine herbicides are used in more than a hundred countries around the world (LeBaron et al., 2008). Triazine herbicides, which are weak bases, are selective herbicides used to control a wide spectrum of annual and perennial grass and broadleaf weeds. Atrazine (banned by the European Union in 2007), propazine, cyanazin, metribuzin, terbuthylazine and simazine are all triazines. Triazine classes include

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methoxytriazines, methylthiotriazines, chlorotriazines and asymmetrical triazines. They are translocated in the xylem to plant leaves. The injury symptoms appeared as yellowing of foliage followed by necrosis (Gunsolus and Curran, 2002). Triazines herbicides were used a lot in Lebanon although they had been banned by the Lebanese Ministry of Agriculture (atrazine and simazine: decision of use prohibition number 309/1 on 24/6/2010). A water monitoring study detected the presence of triazines herbicides in Lebanese water resources (Al Ashi, 2015). The herbicide terbuthylazine (6-chloro-N2-ethyl-N4-tert-butyl-1,3,5 triazine-2,4-diamine; TBZ) is a broad spectrum triazine used as selective herbicide in pre-post emergent treatments of maize, potatoes, fruit trees, citrus, vines, olives, and so on. (WHO, 2003; Gous, 2005; EFSA, 2017). Figure 2 shows the chemical structure of TBZ. It is absorbed by plant roots to block CO<sub>2</sub> sorption in the chlorophyll function and, therefore, inhibits the photosynthesis at photosystem II (Canero et al., 2011). The environmental fate of TBZ, which is used since 2007 as alternative for atrazine banned by European Union (Sass, 2006), is a result of several factors including the uncontrolled use of this herbicide, agricultural practices, TBZ physicochemical properties (solubility, hydrophobicity, soil sorption and its half-life) and hydrogeological properties of the field (Bottoni et al., 2013). TBZ can undergo both biotic and abiotic degradation processes (photolysis, oxidation and hydrolysis) that lead to de-alkylation of the amine groups, dechlorination, and later to hydroxylation (Papadopoulos et al., 2007). The degradation is strongly influenced by temperature, microbial activity, moisture levels, aeration, and pH (WHO, 2003). TBZ and its main degradation products are a real concern in environmental compartments, the substitution of a chlorine in the triazine ring with a methyl/ethyl group keeps its toxicological effect on target and non-target species. In fact TBZ herbicide causes high risks for mammals, earthworms, aquatic organisms, and non-target plants (EFSA, 2011). De-alkylated

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metabolites are more persistent in the environment and more soluble than the parent molecule TBZ (Bottoni et al., 2013).



Figure 2. Terbuthylazine (TBZ) chemical structure.

Picolinic acids (pyridine carboxylic acids) are aromatic acid herbicides. The first pyridine derivative was  $\alpha$ -picoline- $\gamma$ -carboxylic acid (Shreiner and Shorey, 1908). These herbicides are growth regulators through the mimicking of auxin (plant growth hormone) and lead to plant growth abnormalities and, thereby, its death (Tu et al., 2001). They were developed to control a wide range of broadleaf weeds and, due to their persistence, can be effective for several months (Bezdicek et al., 2011). These herbicides are absorbed by the foliage and roots to be translocated through the phloem and xylem (Gunsolus and Curran, 2002). The injury symptoms are poor seed germination, abnormal growth, malformed fruit, reduced yields, and plant death (Hagood et al., 2012). Picloram, clopyralid, triclopyr and fluroxypyr all belong to this class. Triclopyr (trade name: Garlon 4), registered by the Ministry of Agriculture in Lebanon on 4th September 2012, is a pyridine-based herbicide (3, 5, 6-trichloro-2pyridinyloxyacetic acid; TCP) used in post-emergence as broadleaf-weed control (Byrd et al., 1980). Figure 3 shows the chemical structure of TCP. It is an auxin mimic herbicide. After its absorption by the foliage and roots of plant, cell division and plant growth are disrupted leading to plant death. In soil, triclopyr rapidly is

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hydrolysed to triclopyr acid, which is responsible for its phytotoxicity (Lewer and Owen, 1990). Aquatic toxicity of triclopyr depends strongly on its formulation. The butoxyethyl ester (the active ingredient of Garlon 4) is moderate to high acutely toxic to fish, aquatic invertebrates and aquatic plants and moderate acutely toxic to amphibians (Kegley et al., 2010).



Figure 3. Triclopyr (TCP) chemical structure.

#### **1.1.2** Pesticides persistence in the environment

Persistence is expressed in terms of pesticide half-life ( $t_{1/2}$ ), which is the time required to reduce by half the amount of pesticide after its application in the field. As the pesticide  $t_{1/2}$ increases, the time the molecule remains in the environment increases and, therefore, the pesticide exposure of the population and the risk or harmful effects could have serious significance (Navarro et al., 2007). Based on their  $t_{1/2}$ , pesticides can be classified into three main groups: non persistent pesticides with a soil  $t_{1/2}$  of less than 30 days, moderately persistent pesticides with a soil  $t_{1/2}$  of 30 to 100 days, or persistent pesticides with a soil  $t_{1/2}$  of more than 100 days. Once applied, pesticides can undergo many processes, including degradation, soil sorption, volatilization, leaching to groundwater, runoff to surface water, and plant uptake

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(Figure 4). These processes are influenced by the physicochemical properties of pesticides, environmental conditions, soil characteristics and microbial activity (Tiryaki and Temur, 2010).



Figure 4. Pesticide pathways in the environment.

A comprehensive review of pesticide physicochemical properties, based on the review by Pereira et al. (2016), is necessary to understand the main aspects regarding their behaviour and their potential impact on the environment. Water solubility and volatility are the two main properties related to the mobility of the pesticides applied. Water solubility (mg/L) refers to the maximum amount of a given pesticide that can dissolve in a given amount of water. It is influenced by temperature, pH and hydrophobicity/lipophilicity of the pesticide. Regarding pesticide behaviour, a polar pesticide that is highly soluble in water has a tendency to be moved to surface water or to ground water by runoff or leaching respectively. Moreover, the pesticide vapour pressure can predict its possibility to reach the atmosphere. Generally, high pesticide vapour pressure can cause vapour drift and consequently, increases environmental pollution risk. Henry's law constant ( $K_H$ ) defines the pesticide ability to volatilize and is estimated by the ratio of the pesticide concentration in air by its concentration in water. Regarding the environmental significance, the pesticide is more likely to volatilize when the value of  $K_H$  is more than  $10^2$ . Octanol/water partitioning coefficient ( $K_{ow}$ ), which is related to pesticide bioaccumulation, measures the pesticide's differential solubility in organic and aqueous solutions at equilibrium. The  $K_{ow}$  values provide an indication of a pesticide tendency to bio accumulate. Pesticides with a high  $K_{ow}$  are hydrophobic, attach to lipids, and consequently bio accumulate in the fatty tissues of organisms. Distribution coefficient ( $K_d$ ) and soil organic partition coefficient ( $K_{oc}$ ) are fundamental parameters that can identify the strength of pesticide sorption on soil particles and ascertain its environmental fate. A large value of  $K_d$ , defined as the ratio of pesticide solid phase concentration to solution phase concentration, at equilibrium, indicates that soil sorption is favored. This value is often expressed in the form of  $K_{oc}$  by carrying out a normalization of  $K_d$  with respect to the organic carbon content of the soil ( $K_{oc} = (K_d \times 100)/\%$  soil organic carbon). The higher the  $K_{oc}$  value, the more likely the pesticide is adsorbed on soil, and therefore, the less mobile it is.

Sorption is a fundamental process that controls pesticide behaviour in the environment by influencing its degradation, mobility and plant uptake. It is principally regulated by the soil texture and organic matter (OM) content (Weber, 1982). Usually, a soil containing more clay and/or OM can adsorb more pesticide (Sánchez-Jiméneza et al., 2012). Sorption can occur through the adhesion of pesticide, present in the soil solution phase, on the surface of adsorbent in soil solid phase (OM, clay and iron or aluminum oxides). It depends on both physical and chemical properties of particular soil and specific pesticides (Calvet, 1989). The OM is considered as the principal adsorbent of pesticides in soil, especially of non-polar ones. The extent of pesticide sorption depends both on the OM in soil (Ahmad et al., 2001) and on its

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chemical structure (Dutta, 2015). The heterogeneity in the chemical nature of OM must be considered while determining the soil sorption capacities (Ahmad et al., 2001). It has been observed that changes in OM aromaticity cause a variations in the herbicide Koc values (Parolo et al., 2017). In addition, carboxylic and phenolic functional groups of OM constitute a set of variable charges, from acidic medium to neutral or slightly alkaline medium, which can influence the strength of sorption (Stevenson, 1972). In soils with low OM, the sorption of pesticides often depends on the clay fraction. An increase in clay content increases sorption especially of polar pesticides (Đurović et al., 2009). The pesticide sorption on clay depends on the clay surface charge density, surface exchangeable cations, and clay hydration status (Besse-Hoggan et al., 2009). Pesticide sorption by clays varies considerably between the various combinations of clay types and pesticide physicochemical parameters (Sheng et al., 2001). The sorption of pesticides on clay minerals, which are constituted by the superposing of aluminosilicates sheet structure, occurs preferentially on the external surfaces rather than in the inter lamellar spaces (Calvet, 1989). Among the factors that control pesticide sorption on soil organic and mineral constituents, pH is one of the most important. Soil pH influences the sorption of many ionisable pesticides and could have minor effects on non-ionic pesticides (At, 1990). The pH-dependence of pesticide sorption originates from the different proportions of pesticide ionic and neutral forms present at a given pH value. Generally, sorption of ionisable pesticides is stronger in soils at lower pH values and high organic carbon (Kah and Brown, 2007). A possible explanation is the contribution of electrostatic interactions related to pesticide ionization degree (Vitoratos et al., 2016). At pH values greater than their pK<sub>a</sub> (acid dissociation constant at logarithmic scale), Acidic pesticides, exist predominantly in the anionic form and could be adsorbed weakly even though they are repelled by the negative charge of soil

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constituents. With decreasing pH, the neutral form is more strongly adsorbed than the anionic one (Kah and Brown, 2007). Basic pesticides are mainly present as cations at pH values below their  $pK_a$  (Green and Karickhoff, 1990) and are attracted by the negatively-charged soils particles (Nicholls and Evans, 1991).

Pesticide sorption in soil can be well described by the sorption isotherms. Sorption isotherms are curves obtained by plotting Cs (amount of pesticide adsorbed) vs Ce (concentration of the pesticide at equilibrium) (Hinz, 2001). The most commonly mathematical model used to describe these isotherms is the logarithmic form of the Freundlich equation:  $\log C_s = \log K_{ads} +$  $1/n_{ads}$  log C<sub>e</sub> (where K<sub>ads</sub> and  $1/n_{ads}$  are empirical constants representing the intercept and the slope of the isotherm, respectively). Giles et al (1960) classified sorption isotherms (Figure 5), based on their slopes, into four isotherm shapes reflecting the affinity between adsorbate and adsorbent. When the slope  $(1/n_{ads} \text{ value})$  is greater than 1, the sigmoidal curve is defined as Stype isotherm. S-type curve indicates a low pesticide/soil affinity at low concentration, but the sorption becomes easier as the pesticide concentration increases. This condition may be due to cooperative interactions that favour the assembling of adsorbate molecules at the sorbent surface, because they can bind on each other more strongly (Hinz, 2001). The concave curve, which has  $1/n_{ads}$  value < 1, is called L-type isotherm and indicates that there is high affinity between the adsorbate and the adsorbent. This curve suggests a progressive saturation of sorbent. When the curve reaches a plateau it means that the sorbent has a limited sorption capacity. The H-type isotherm is an extreme case of L-type isotherm where the initial slope is very high. It is indicative of a very high pesticide affinity to sorbent, thus suggesting a strong adsorbateadsorbent interaction. The curve is a C-type isotherm when the  $1/n_{ads}$  value = 1. The C-type isotherm means that the K<sub>d</sub> of the pesticide sorption on soil is the same at any concentration and

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suggests that the adsorbate has a constant relative affinity for the adsorbent. This is often used for very low levels of sorption (Limousin et al., 2007).



Figure 5. Sorption isotherms (Limousin et al., 2007).

## 1.1.3 Exposition for pesticides and related diseases

Pesticides are poisons and, unfortunately, they can have harm effects on human health. The World Health Organization (WHO) estimates that there are 3 million cases of pesticide poisoning yearly and more than 220,000 deaths. WHO (2004) classified pesticides by hazard based on the acute oral and dermal toxicity to the rat (Table 1).

WHO Class	LD <sub>50</sub> <sup>a</sup> for the rat (mg/kg body weight)		
VIIIO Ciuss	Oral	Dermal	
Extremely hazardous	< 5	< 50	
Highly hazardous	5 - 50	50 - 200	
Moderately hazardous	50 - 2000	200 - 2000	
Slightly hazardous	Over 2000	Over 2000	
Unlikely to present acute hazard	5000 or more	5000 or more	

Table 1. Classification of pesticide hazard according to WHO (2004).

<sup>a</sup> The LD50 value estimates the number of mg of toxicant per kg of bodyweight required to kill 50% of the population of animals tested.

Several studies have confirmed the effects of pesticides on human health. For example, organochlorine pesticides (OCs) were detected in all breast milk samples of Tanzanian women, which suggests that the mothers had been exposed to different sources of OCs. Additionally, when cases of Tunisian women with breast cancer were inspected and blood samples were taken and analysed, a potential link was found between serum concentrations of OCs pesticides and breast cancer (Arrebola et al., 2015). In addition, DNA damage in lymphocytes and a circulation of cell-free DNA in blood of greenhouse workers exposed to pesticide proves the genotoxicity impact of pesticides (Ayir, 2018). Moreover, in a systematic review performed to find a link between diabetes risk and pesticides exposure, Evangelou et al. (2016) was found that pesticide exposure increased the risk of diabetes type 2, which was attributed to a reduction in the insulin hormone after the accumulation of pesticides in human tissues. Furthermore, a study conducted in the south of Brazil on 99 rural and 36 urban young men reported that agricultural exposure to pesticides, especially herbicides and fungicides, could disturb male fertility by altering sperm

quality and influencing the reproductive hormone levels (Cremonesea et al., 2017). Another study was conducted on a random sample of farmers and farm family members in the south of Brazil by completing questionnaires and analysing blood samples for each person investigated aiming to assess the endocrine effects of pesticides on agricultural workers. This study suggested that chronic exposure to pesticides, especially herbicides and dithiocarbamate fungicides, may disturb male thyroid function through a decrease in circulating levels of thyroid hormones (Piccoli et al., 2016).

Farmers are at greater risk from exposure to pesticides by inhalation or dermal absorption and their unprotected behavior during crop treatment makes them even more susceptible. Young children and fetus are vulnerable to pesticide effects due to their weak immune system. Additionally, contaminated food chain (such as vegetables, fruit, meat, eggs, milk and milk products) and water resources can increase the risk of human exposure to pesticides. The ability of a pesticide to accumulate in plant tissues and animal fat is generally linked to the physicochemical properties of the pesticide used (Kibria, 2016).

### **1.1.4 Soil remediation techniques**

Pesticide removal from soil matrices can be performed by several remediation techniques such as biological remediation, which uses microorganisms (fungi, bacteria, yeast) to degrade pollutants, including pesticides, into less harmful products (Singh, 2008), phytoremediation, which uses vegetation for remediation purposes by low molecular weight contaminants uptake, chemical treatments, for example oxidation processes, and physical processes exploiting the adsorbing capabilities of inorganic, carbonaceous, and polymeric materials (Marican and Durán-Lara, 2018). The choice of the remediation technique depends on numerous factors related to the

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physicochemical characteristics of the contaminated site, the environmental conditions, the level of pollution, the type of pesticides, the cost assessment and the end use of contaminated media.

However, although for biological and chemical treatments the remediation achievement was reported in literature, they suffer from drawbacks. Biological processes require more time for land restoration and can fail under some environmental conditions. Moreover, some pesticides can break down into more toxic products. Chemical processes are expensive and may pose some environmental risks through the use of chemicals. Instead, physical processes, based on the use of adsorbents able to immobilize pesticides in soil and prevent their leaching and moving to water surface, are a promising technique in terms of cost assessment compared to biological and chemical techniques. Further, adsorption processes are ecofriendly and do not generate any harmful product.

Extensive literature reported the use of adsorbents based on inorganic (clay minerals and zeolites), carbonaceous, and polymeric materials. Clay minerals, which are negatively charged and have a hydrophilic character, are used to adsorb positively charged pesticides (polar ones). Clay minerals can be modified in the presence of alkylammonium cations or natural organic cations to improve their performance as barriers against hydrophobic pesticides. Added organic cations increase the organic carbon content of the modified clays. So, this will rise their adsorptive capacities. The adsorptive capacities of modified clays depends on several factors including the type of natural clay before modification, the chemical structure of organic cations and the physicochemical characteristics of pesticides (Marín-Benito et al., 2018; Marican and Durán-Lara, 2018). Zeolites are hydrated aluminosilicates minerals intended to adsorb pesticides from water. They have high chemical and thermal stability and interconnected micropores that display a narrow pore-size distribution and possess a cage structure. They could be regenerated

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while maintaining their original properties. The mobility of pesticides decreases, as the pesticides tend to be associated with zeolites (Pucarevic et al., 2017; Marican and Durán-Lara, 2018). Between polymeric materials, cyclodextrins, dendrimers and hyper-cross linked polymers are the most used as organic adsorbent (Marican and Durán-Lara, 2018).

Recently, the remediation techniques based on sorption, have been extended to exogenous OM (Marín-Benito et al., 2018) such as manure, compost, sewage sludge, bio solids and biochar. Particularly, the use of biochar is a very promising method to overcome the pollution problem by low-cost and ecofriendly materials (Cara and Jitareanu, 2015). Biochar is a carbon-rich by-product produced by thermo-chemical decomposition of biomass at high temperature in absence of oxygen (Tang et al., 2013). In comparison to other soil treatments, the high surface area, the density of surface functional groups and the porosity of biochar enable it to adsorb organic and inorganic pollutants efficiently. In addition to its adsorption capacities for remediation purposes, the following four complementary values may persuade to the use of biochar and could distinguish it from other remediation sorbents (Figure 6). Biochar could mitigate climate change through carbon sequestration and reduction of the emissions of greenhouse gases (Brassard et al., 2016), enhance soil fertility (Tang et al., 2013), help dealing with the waste management by recycling the organic waste using pyrolysis and contribute partially, as a green energy, to a global energy demand. All these social, environmental and financial benefits favors the application of biochar for pollution remediation as low-cost, environmental-friendly and effective solution.

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Figure 6. Benefits of biochar (Lehmann and Joseph, 2009).

## 1.1.5 Biochar

Biochar is produced by thermo-chemical decomposition of biomass at high temperature in the absence of oxygen (Tang et al., 2013). This reaction gives also a gas product named syngas and a liquid product called bio-oil which are alternative energy resources to fossil fuel combustion. The following chemical equation (1) summarizes the thermo-chemical conversion of biomass:

```
Biomass + Heat \longrightarrow Syngas + Bio-oil + Biochar (1)
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Biomass derived from different feedstocks, such as woodchips, animal manure, sewagesludge, crop residues and solid waste, can have different physico-chemical properties. These properties, particularly bulk density, particle size, ash content, moisture content, percentage of

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inorganic substances, volatile substances, lignin, cellulose, hemicellulose and the fraction of fixed carbon, are important for the identification of the biochar properties produced (Nartey and Zhao, 2014).



Figure 7. Characteristics of pyrolysis, gasification and hydrothermal carbonization processes.

The Figure 7 (adapted from Cha et al., 2016) summarizes the characteristics of the main carbonization processes used for char production (pyrolysis, gasification and hydrothermal carbonization). The most effective carbonization process for biochar production is slow pyrolysis. However, this process is not suitable for wet biomass due to the necessity of feedstock drying before the reaction. In contrast, hydrothermal carbonization provide the thermo-chemical decomposition of wet biomass without the need for drying minimizing the energy required comparing for other carbonization processes (Malghani et al., 2013). Biochar yield, which is related to the biomass content of cellulose and lignin in the biomass (Tan et al., 2017), could also vary according to the carbonization processes. It could be 25%-35% end of slow pyrolysis, 40%-70% end of hydrothermal carbonization and only 10% end of gasification (Kambo and Dutta,

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2015). It was reviewed that biochar yield decreases slightly at high pyrolytic temperature due to the volatilization of other substances of the biomass (Nartey and Zhao, 2014).

The biochar obtained through slow pyrolysis reveals an increase in ash content percentage while biochar produced by the use of hydrothermal carbonization process shows significant reduction in the ash content due to the demineralization of biomass ash composition (Kambo and Dutta, 2015). Ash contains many alkaline ions, so a biochar with high ash content increases the soil pH (Tan et al., 2017). Additionally, biomass polymers (principally hemicellulose) will be decomposed in hydrothermal carbonization more than in slow pyrolysis (Kambo and Dutta, 2015). It was suggested, by comparing the char elemental analysis (H/C – O/C ratios), that in hydrothermal carbonization the ratio of decarboxylation to dehydration reaction rates is more than that of the slow-pyrolysis process (Kambo and Dutta, 2015). The H/C value reveals the OM aromatization while biochar content of superficial polar functional groups and its hydrophilicity are reflected by O/C value (Tan et al., 2017).

Specific environmental and agronomic applications of biochar require specific biochar production conditions (Ippolito et al., 2012). Two most important factors that governs the properties of biochar production are the temperature chosen (pyrolytic conditions) and the biomass (parent matter). The biochar properties investigated under slow pyrolysis conditions reveals that biochar originating from different biomass has different physical and chemical properties (Lee et al., 2014). It has been observed that the type of biomass affect biochar yield, its thermal stability, and its elemental composition (Sun et al., 2014). Additionally, effect of pyrolytic conditions on sorptive capacities of biochar have been reported, it was found that the surface area, bulk properties and hydrophobicity of biochar were influenced with increasing of pyrolytic temperature (Cha et al., 2016). Also, it has been observed that micro pore volumes

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were enhanced and the concentration of total acidic surface functional groups (e.g. lactonic, phenolic and carboxylic) decreases as the pyrolytic temperature increases. These findings were significantly correlated with biochar elemental analysis showing the decrease of oxygen amount in biochar as pyrolytic temperature increases (Suliman et al., 2016). Concerning biochar bulk properties, it has been observed that when the pyrolytic temperature increases from 300 to 500 °C, the degree of carbonization increase in contrast to hydrogen and oxygen content, and ash content increase due to mineral content remaining after carbonization (Kim et al., 2012). Moreover, it has been observed that biochar produced at high temperature has the highest values of alkalinity and salinity and the yield of biochar decreases due both to hemicellulose, cellulose and lignin degradation which occurs at 220, 315 and 400 °C, respectively and to the loss of volatile fraction (Al-Wabel et al., 2013).

Biochar production has increased recently so that according to Grand View Research in U.S. (2017) its global market size reaches 353.4 kilotons in 2017 and agriculture sector has the largest share (70.91 %). The effectiveness of biochar can vary depending on its application way. The biochar application technique depends upon the purposes of applying biochar. It also depends on the field characteristics and the available machinery. Biochar can be applied alone or by mixing it with composts or manures. Generally, there are three main biochar application methods: top-dressing, top soil incorporation and deep-banded application (Verheijen et al., 2009; Blackwell et al., 2009). Top-dressing of biochar is the application of biochar by hand or by spreader to the field where mechanical access is not possible (such as no-till systems, forests, perennial cropping system and grasslands). The incorporation is the application of biochar using conventional tillage systems. It leads to more topsoil homogenization and the biochar will

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generally reach 0-30 cm in topsoil depth. Otherwise, deep-banded application is the biochar application in the rhizosphere. It can be done either by pneumatic systems which are used in industrialized agriculture or by putting it in furrows or trenches followed by land levelling to ensure a uniform slope. Using pelleted biochar or taking personal protective measures could resolve the problem caused by the biochar dust fraction during handling, storage and application. Additionally, left crop residues on land would maintain a protective soil surface cover and reduce the removing of biochar by water and wind erosion because of its low density. Otherwise, mixing biochar with manure or compost could have the same result.

Biochar is considered as sorbent material and has several environmental benefits in terms of sorbent of pollutants and environmental waste management (Cha et al., 2016). It is known as a cost-effective way compared to another remediation techniques (Safaei Khorram et al., 2016). Biochar added to soil enhances the sorption of some herbicides (Cabrera et al., 2014). Several studies revealed that pesticide sorption to biochar tends to be 5 - 2500 times stronger than BCfree soil (Yang and Sheng, 2003; Yu et al., 2006). Studies on pesticides sorption-desorption in soil amended with biochar show high irreversible sorption, which could alter their mobility through the entrapment and accumulation of pesticides in the biochar micro pores (Yu et al., 2011; Marín-Benito et al., 2017). Consequently, pesticides leaching (Li et al., 2013) and plant uptake decreases markedly in biochar-amended soil (Yu et al., 2009). Once applied, biochar influences strongly pesticide behavior in the environment and its effects depend on both biochar and pesticide properties. Biochar produced from different types of biomass (maize straw, pine wood dust and swine manure) at different pyrolytic conditions led to a change in sorption capacity for hydrophobic compounds such as Acetochlor (Wang et al., 2016). Cederlund et al. (2016) studied the sorption affinity of wood-based biochar for several pesticides with different

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properties and revealed that Freundlich K<sub>ads</sub> value decreased in the following order: diuron > chlorpyrifos > MCPA > bentazone > glyphosate this means that sorptive capacities of biochar vary according to the physico-chemical properties of pesticides. On another hand, while studying the effect of beech wood biochar on several herbicides, it was shown that the sorption of neutral herbicide (methyl-desphenyl- chloradizon) increased on soils treated with biochar compared to biochar-free soil, whereas the sorption of negatively-charged herbicides (imazamox, metazachlor oxalic acid and metazachlor sulfonic acid) was not affected by biochar (Dechene et al., 2014). Similarly, another study showed that biochar has strong sorption capacity for non-polar pesticides and moderately sorption capacity for polar pesticides (Kookana, 2010). The sorption of pesticides in soils treated with biochar may vary depending on the different dose of biochar used, indicating that the use of a suitable dose of biochar may favor pesticide sorption. It has been recommended a proper screening for the chemical and physical properties of biochar and herbicides before the soil amendment to maximize pesticide efficacy and minimize environmental impacts (Gamiz et al., 2017). Moreover, biochar could be an alternative low-cost method to purify water from herbicides (Essandoh et al., 2016).

#### 1.2 Soil and pesticides use in Lebanon

### **1.2.1 General overview**

Lebanon is a Middle Eastern country located on the Mediterranean Sea. It occupies about 10,452 km<sup>2</sup>. It stretches between latitudes 33°03' and 34°45' and longitudes 35°05' and 36°30'. In geomorphological terms, Lebanon is divided into five regions (Figure 8) which are the coastal zone (region 1), the south of Lebanon (region 5), the Beqaa valley (region 3) which is a land depression separating the Mount Lebanon (region 2) and Anti-Lebanon (region 4) parallel Mountains. Beqaa valley is about 120 km from north to south and is a synclinal extending the African rift that represents 14% of the territory. This high region of an altitude of 850 - 1000 m in average draws a corridor with a width varying between 5 and 20 km. It is devoted mainly for agriculture.



Figure 8. Topography of Lebanon (MoE, 2009).

Lebanon has 17 perennial rivers, including the Litani river. This river flows in the Beqaa valley to form the Qaraoun lake (Figure 9) then it moves southward until its discharges in the Mediterranean Sea (south of Lebanon). Litani river, which is the largest one in Lebanon (length 170 km; average annual discharge 335 million m<sup>3</sup>/year), is considered as the "lifeline" of the Beqaa and south regions. In fact, 246 cities, towns and villages belonging to four Mohafazats (i.e. administrative governorates) are located within the Litani river basin (LRB). In LRB there are the Qaraoun reservoir (capacity of about 220 million m<sup>3</sup>) and different wetlands, with the most famous being the Ammiq wetland (2.8 km), with naturally freshwater ponds in the carbonate rocks.



Figure 9. Flows of Litani river in the Beqaa plain (Storey, 2003).

The importance of this river is demonstrated by its impact on the socioeconomic sector in Lebanon. It has the ability to ensure irrigation for thousands of hectares of agricultural land in Beqaa and south Lebanon, to produce electricity through three electricity plants (Qaraoun, Markaba, and Al-Awali stations) that can generate about 190 megawatts (~10% - 12% of Lebanese requirement). LRB has become recently a subject of numerous studies on pollution and hydrology. Due to its pollution, the number of disease rate has increased dramatically among the living population (more than 370,000 people). Additionally, several studies revealed a severe pollution of Qaraoun lake. In Lebanon, the mass of pesticides imported in 1990 was 1,530 tons and the amount of pesticides used in 2002 was 170 tons as reported by "Asplante", a non-profit association of importers and distributors of agricultural production materials. Table 2 shows the amounts of pesticides by types imported to Lebanon (thousands kg/year) (MoE, 2005). Fungicides and insecticides were the most important pesticides imported to Lebanon followed by herbicides. On the whole, pesticide importation increased throughout the 4 investigated years (1996 - 2000). An assessment conducted by the Lebanese Ministry of Environment in a recent report reveals that Lebanon no longer imports a whole range of persistent pesticides from 1996 to 2000 (MoE, 2006).

Year	Fungicides	Insecticides	Acaricides	Herbicides	Nematicides
1996	723	873	66	318	25
1997	988	845	179	534	23
1998	1424	1312	183	964	265
1999	661	535	213	509	28
2000	953	719	250	456	45

Table 2. Amounts of pesticides imported to Lebanon (thousands kg/year) (MoE, 2005).

Table 3 indicates the amount of pesticide active ingredient used per type of culture in Lebanon in 2000 (MoE, 2001). This data show that vegetables receive the highest quantity of pesticides (16.7 kg/ha) is about 45,232 ha of the area cultivated in Lebanon. Lebanese Ministry of Agriculture has established a well-equipped laboratory in Kfarchima (near Beirut) to evaluate pesticide residues in harvests and the composition of imported pesticides to Lebanon before retail.

Type of culture	Cultivated area (ha)	Kg/ha in year 2000
Stone fruits	59,515	7.9
Citrus	59,515	5.9 - 6.2
Olive	52,421	5.0
Tobacco	24,730	10.7
Sugar beet	24,730	8.6
Vineyards	24,730	1.2
Banana	N/a	1.1
Vegetables	45,232	16.7

Table 3. Pesticide use reported in kg / ha of active ingredient per type of culture (MoE, 2001).

The business plan for combating the pollution of the Qaraoun lake (MoE, 2011) made two surveys in the villages of the Beqaa region to identify the types of pesticides used and the quantities applied per crop. The farmers and the major agricultural input suppliers in the Beqaa region were the targets of the two surveys. A total of five small providers and 105 farmers cultivating 21 types of crops were interviewed in 7 villages in Beqaa: Barr Elias, El Mansoura, El Marej, Qaraoun, Hawch El Rafqa, Jeb Jannine and Temnin El Tahta. The results of these surveys revealed the high pesticide use in Beqaa (applying twice the recommended dose) without any respect for applications time intervals. Also, it detected that some farmers were not respecting pre and post-harvest intervals, thus increase the risk of harvest residues pesticides. This is due to the farmer's weak knowledge about using and handling pesticides according to necessary directives. The business plan issued a list of traded pesticides in the Beqaa market and its active ingredient by pesticides types can be found in Table 4.

Table 4. Active ingredient of insecticides, herbicides and fungicides used in Beqaa (MoE, 2011).

Insecticides Abamectin, Acetamiprid, Alpha-cypermethrin, Amitraz, Chlorpyriphos + Cypermethrin, Cyhexatin, Cypermethrin, Deltamethrin, Diazinon, Dimethoate, Emamectin benzoate, Endosulfon, Etoxazole, Flufenoxuron, Imidacloprid, Indoxacarb, Lufenuron, Methamidiphos, Methiocarb, Methomyl, Mevinphos, Propargite, Thiamethoxam.

Herbicides 2.4D amine salt, Glyphosate, Fluazifop-p-butyl, Metribuzin, Oxyfluorfen, Paraquat, Simazine, Triclopyr, Quizalofop-p-ethyl, Trifluralin.

 Fungicides Azoxystrobin, Azoxystrobin + Difenoconazole, Benomyl, Carbendazin, Chlorothalonil, Copper hydroxide, Copper oxychloride, Cyproconazole, Fenarimol, Hexaconazole, Hymexazol, Mancozeb, Mancozeb + Metalaxyl, Myclobutanil, Procymidon, Sulphur, Triadimenol, Trifloxystrobin, Zineb, Ziram.

In Lebanon, a statistical study done among 206 individuals (agriculture workers and distributors) found that only 25% of them used gloves, masks and required clothing during pesticide application. Far worse, only 2.4% of them used empty containers of pesticides to store water and food. Certainly, this predispose them to high intoxication risk (Salameh et al., 2004). A recent study on the assessment of dietary exposure to 47 pesticides residues in an urban city Beirut and a semi-rural city Keserwan found that 18 residues were detected on at least one sample, including dimethoate, chlorpyrifos methyl, gamma HCH, primiphos methyl, procymidone, alpha endosulfan, beta endosulfan, endosulfan sulfate, fenithrion, malathion, dieldrin, chlorpyrifos and diazinon. Moreover, the estimated mean daily exposure ranged between 7.33 and 55.35  $\mu$ g/day (Nasreddine, 2016). Chronic bronchitis in Lebanese adults was related to pesticide exposure as a result of a survey conducted in 10 hospitals (Salameh, 2006).

#### 1.2.2 Land use and agriculture in the Beqaa region

According to the results of the agriculture census done by the Ministry of Agriculture in Lebanon in 2010 (MoA, 2010), the overall agricultural area in the Beqaa region was almost 42% of the total exploitable agricultural land in Lebanon and would reach 47% in 2015 (MoA, 2015). On the whole, the land use for agriculture in Beqaa is increasing and agriculture is still the dominant economic activity. In terms of irrigation from surface water, the Beqaa region holds the largest share with 43% respecting to the irrigated area in Lebanon. The distribution of land use (including all crop types) showed that the Beqaa in 2010 and 2015 maintains its rank in Lebanon without marked change. Seasonal crops include the following: cereals, vegetables, legumes, forage crops, industrial crops, flowers and ornamental plants. The distribution of seasonal crops in 2010 was in Beqaa 31% of the overall seasonal crops in Lebanon. In 2015, it remained

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approximately the same (32%). Permanent cropland is land occupied for a long period by crops with a vegetation cycle of more than one year and therefore grown for several years before replanting. These are fruit trees (clumps, peppercorn fruits, stone fruits, bananas, exotic fruits), walnut trees (walnuts, chestnuts...), pines, olive trees and grapes. Wooded lands and forests are excluded from this category. The distribution of permanent crops in 2010 shows that Beqaa is gaining 29 % overall permanent croplands in Lebanon while, in 2015, it slightly decreased about 3 % to become 26 %. Protected crops include greenhouses (modern and traditional) and tunnels. In 2010, the Beqaa represent the lowest rates of the total area of protected crops (2 %). In 2015, it declined to 1 %. Table 5 shows the distribution of different types of crops in Beqaa in 2010 and 2015. Cereals and vegetables are the most important indispensable food crops. The average area covered by cereals and vegetables increased to reach in 2015 about 19,076 ha and 16,505 ha, respectively.

	Temporary crops (ha)					Permanent crops (ha)			
Year	Fodder	Pulses	Cereals	Vegetables		Grape	Olive	Stone-	Pome-
i cai	crops	1 41505	Cercuis		Grupe		fruits	fruit	
2010	875	1,955	15,723	13,646	-	3,899	2,682	3,474	1,716
2015	1,129	2,411	19,076	16,505		4,355	2,050	2,880	1,479

**Table 5.** Distribution of different types of crops in Beqaa in 2010 and 2015.

# 1.2.3 Pollution pressure in the Beqaa region

The negative influence of anthropogenic activities could affect the hydrologic trend of Litani river (Shaban and Nassif, 2007) as well as its water quality. Intensive agriculture like the

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overuse of fertilizers and pesticides, farms (poultry, cows and sheep), industrial activity and urban expansion in Beqaa region are the main cause which could increase the pressure on soil, water surface (Litani river and Qaraoun reservoir) and groundwater quality (Jurdi et al., 2002; Darwish et al., 2008). The final business plan for combating pollution of the Qaraoun lake (MoE, 2011). lists several dumpsites which are located near the Litani river receiving different kind of wastes such as municipal, industry, slaughter house and medical waste and characterize their susceptibility to affect water resources quality. Figure 10 shows a summary of the global strength of pressures from different sectors in each zone. Shaban and Nassif (2007) have revealed the sources of pollution of the Qaraoun lake by satellite image analysis. Irregular values of the physiochemical and microbiological parameters have been superimposed on the land use map to extract a possible link between the location of the pollution and the closest land area that may contribute to pollution by using the physical characteristics of the area (slope, steam...), which in turn may play a role in transferring chemicals and wastes. Many villages in Beqaa are not connected to sewer system, as well as, most of the wastewater treatment plants in this area are currently inoperative or marginally working. Thus, the releasing of untreated wastewater directly to the Litani river could exert significant pressure by increasing the contamination of water surfaces (MoE, 2011). Several studies on Litani watercourses and Qaraoun reservoir revealed that they are severely affected by domestic wastewater discharge. This is apparent from the high levels of organic matter, measured as Chemical Oxygen Demand (COD) or Total Organic Carbon (TOC), from the concentrations of ammonia (NH<sub>3</sub>), the conductivity of the water and the bacteriological analysis (Amacha et al., 2017).



Figure 10. Summary of the global strength of pressures from different sectors in Beqaa region (MoE, 2011).

Nutrients refers to nitrogen and phosphorus in a water pollution context due to the use of fertilizers. Several studies have shown a seasonal pattern for nutrients in Litani river. Figure 11 shows a comparative analysis of nutrient levels in dry season from 1995 to 2015 adapted from (Jurdi et al., 2002; Shaban and Nassif, 2007; Abou-Hamdan et al., 2014; Diab et al., 2014; Amacha et al., 2017). Reviewed nutrients are sulphate, nitrite, nitrate and phosphate. The values of the measured nutrients at the Litani inflow into Qaraoun lake were almost higher than acceptable guidelines and they have been increased during the last 10 years.



Figure 11. Inflow of nutrients from Litani river into Qaraoun reservoir (1995 - 2015).

The excessive use of pesticides without any regulation and due to lack of awareness and education among the farmers and runoff of agricultural wastes in the river increase the total pesticides concentration in the environment. Although the Lebanese Ministry of Agriculture has forbidden some type of pesticides, farmers still using them by illegal means (Abou Fakhr et al., 1995). Recently, the only study which monitored the pesticide occurrence in Litani river and Qaraoun lake surface water throughout one whole year, detected the maximum levels of fenpropathrin (220.1 ng/L), chlorpropham (33.7 ng/L) and bifenthrin (34.6 ng/L), in addition to endosulfan sulfate, chlorpyrifos, alachlor which are included in the European priority pollutant

list, diazinon, methoxychlor, tetradifon, DDE and DDD, pendimethalin, bromopropylate, procymidone, and lindane. As well, this study noticed a high pesticide risk for aquatic organisms which could affects fishes and invertebrates (Kouzayha et al., 2013).

Concerning the metallic pollution in Beqaa region, it has been revealed that heavy metals (Cu, Cd, Cr, Ni, Pb, Zn and Co) accumulated at the soil surface (0 - 20 cm) are the result of two factors which could be erosion sedimentation or direct input of sewage water (Darwish et al., 2008). Cr, Ni and Pb exceeded the Canadian guideline for agricultural use while Cd, Cu, Zn and Co were within acceptable limits (Figure 12).



Figure 12. Heavy metal analysis result of soil depth 0 - 20 cm in Beqaa region.

Huge number of studies showed the amplification levels of heavy metals concentrations in surface water and sediments of Litani river and Qaraoun reservoir which are typical proof for pollution caused by local industrial discharges and progressive urbanization (Jurdi et al., 2002; Saad et al., 2006; Korfali and Jurdi, 2006; Diab et al., 2014; Haydar et al., 2014) reported during a screening for several sites along Litani river, that metallic pollution is affected by seasonal variations. Thus, the depletion of water quality increases during the dry season. The total metal

concentrations (dry season of 2013 and 2014) in the reservoir sediments at the inflow of Litani river, adapted from Haydar et al. (2014) and Wazne and Korfali (2016), are shown in Table 6. The influx site collects pollutants form Litani valley north of Qaraoun reservoir and consequently possible types of pollutants could enter the reservoir. According to guideline proposed by US EPA, influx site is characterized by moderate pollution by Cu and Zn, heavy pollution for Cr and Ni while Pb concentration is not so far below the threshold level. According to the sediment quality guidelines of New York State Department of Environmental Conservation and Washington State Department of Ecology, Pb is not so far below to effect range low level (ISQG-L) whereas Cu, Cd and Zn are lower than effect range high level (ISQG-H) and higher than ISQG-L level which indicates these elements probably have adverse effects on organisms that live in sediment while Cr is higher than ISQG-L level which means that this element certainly has adverse effect on aquatic organisms. Otherwise, the United States Agency for International Development (USAID) detected Cr, Cd and Pb in all fish samples taken from Qaraoun reservoir and revealed that cadmium and lead levels exceed the Food and Drug Administration (FDA) levels for Toxic Elements in Fish (USAID, 2005).

References	Sampling year	Matrix	Cu	Cd	Cr	Zn	Pb
Wazne et al., 2016	2013	Sediment	40	-	-	160	30
Haydar et al., 2014	2014	Sediment	36.1	1.9	134	145.2	29.7

Table 6. Heavy metals (mg/kg) in Litani river sediments at its inflow in Qaraoun.

Particularly in a site known for a warm climate (Slim et al., 2012), the influx of nutrients due to agricultural activities from Litani into Qaraoun reservoir amplify the eutrophication and the development of cyanobacteria which produce toxins that can be harmful for livestock, fauna and humans (Atoui et al., 2013; Fadel et al., 2016). During the period 2000 - 2001, it has been reported 98 species of microscopic algae on which cyanobacteria can develop in Qaraoun reservoir (Saad et al., 2005). In spring 2009, it has been detected for the first time the contamination of Qaraoun lake by cyanobacteria (Slim et al., 2012). Atoui et al (2013) monitored the eutrophication in Qaraoun lake from May 2009 to June 2011 and realized the appearance of several types of cyanobacteria harmful bloom. During 2012 - 2013, Fadel et al. (2014) has been observed that Cyanobacteria bloomed in summer and early autumn, and therefore, it has been observed that the trophic state of the reservoir is found to be eutrophic to hypereutrophic (Fadel et al., 2015). Recently, macrophytic species as bio indicators for water quality were investigated along overall LRB. Both 35 submersed and emergent macrophytic species were identified to show a spatial variability. It has been concluded that water quality and the level of nutrients in each site influenced the macrophytic community (Baydoun et al., 2016). Therefore, it become necessary to reduce the influents of nutrients from villages in the upper part of LRB to the Qaraoun reservoir.

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# **Aims and Objectives**

Recently, pollution monitoring of water resources in Lebanon had gained much concern as many pesticides can be detected in surface, ground, raining and potable waters. In particular, the Litani river, the largest in Lebanon, suffers from different kind of pollution including that caused by pesticides widely used in Beqaa Valley. Among herbicides, Fluazifop (FLP), Terbuthylazine (TBZ) and Triclopyr (TCP) are the most used. Due to their water solubility and resistance to degradation, these herbicides may cause an environmental threat to the Litani basin. However, although these herbicides have been found in large quantities in the water bodies, to our knowledge there is no information available in the literature on the behaviour of FLP, TBZ and TCP on sediment and soil of Litani river basin.

Thus, in this PhD work, the FLP, TBZ and TCP sorption behaviour on sediment and soil samples from four sites along Litani river basin (Berdaouni, Joub Jannine, Aammiq and Qaraoun), will be studied with the aim of highlighting how the different chemical-physical properties of the three herbicides and sediments and soils can influence the mobility of active ingredients.

Moreover, taking into account that many literature data show the effect of biochar on the environmental fate of organic pollutants in soils, particularly its effectiveness in controlling the release and leaching of herbicides, the study will be extended to sediments and soils added with biochar, obtained from coppiced woodlands at pyrolysis temperatures of 550 - 600 °C, in order to assess whether the biochar effect on the sorption processes of herbicides allows a possible suppression of the FLP, TBZ and TCP movement in the Litani river basin.

The results obtained will lead to further research on herbicide sorption capacities of biochar from different feedstocks and obtained at different pyrolytic temperatures in order to compare the different biochar efficiencies and choose the suitable one.

Furthermore, considering the high presence of pollutant agrochemicals in Lebanese water resources, the study can be carried out both on different pesticides and on soil and sediment samples from other areas of Lebanon in order to suggest possible pollution mitigation strategies.

## **Chapter 2: Materials and Methods**

#### 2.1 Study area

# 2.1.1 Geographical importance

The Litani river basin (LRB, 210 km<sup>2</sup>  $\approx$  20 % of Lebanon's area) is located across the major part of the Lebanese territory between 33° 06′ 25″N and 34° 04′ 05″N and 35° 14′ 40″E and 36° 22′ 44″E. LRB is divided into upper Litani river basin (ULRB), where the river is stretched between two parallel mountain chains (Anti-Lebanon and Mount Lebanon) in the Beqaa region and the Lower Litani river basin (LLRB), where the river flows to the southwest towards the Mediterranean Sea (Shaban et al., 2018). ULRB is the area of study of this research work (Figure 13). Due to its topographical characteristics, ULRB is characterized by areas of different slope gradient which varies from very steep lands (> 60%) to steep lands (30% - 60%), sloping lands (15% - 30%), rolling land (8 - 15%), and flat area (0 - 8%) in the Beqaa valley (Darwish et al., 2006). The altitude decreases gradually from the mountain chains to the Beqaa plain (Table 7) (Shaban et al., 2018).

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Elevation (m)	Area (km²)	Ratio of the catchment area (%)	Major localities
2000	104	5	Partially on the crests of Mount-
			Lebanon and Anti-Lebanon
2000 - 1500	232	11	Elongated stretches parallel to the
2000 1200			Beqaa plain
			Elongated stretches parallel to the
1500 - 1000	723	34	Beqaa plain till the contact
			between ULRB and LLRB
1000 500	0.4.4	40	Extension along the maximum
1000 - 500	844	40	length of the catchment

**Table 7.** Slope gradient of Litani river basin (LRB) (Shaban et al., 2018).



Figure 13. Overview map of the upper Litani river basin (ULRB) (USAID, 2005).

### **2.1.2 Physical characteristics**

### Geology

In Lebanon, the geology plays an important role in the water flow or the storage regime. The Beqaa valley, where the ULRB is stretched, is a depressed block located between the two elevated mountain chains forming a graben structure characterized by U-shape. It is bordered in its western side by Yammouneh fault and in its eastern side by Serghaya fault. The exposed strata reveals rocks dating back to Middle Jurassic up to the quaternary geologic periods (Shaban et al., 2018). The geologic formation of ULRB is shown in Figure 14. In Lebanon, the present rock formation is characterized by different lithological aspects that allow them to store, transfer or slow down the flow of ground water (Shaban et al., 2018). According to Amacha and Baydoun (2018) the aquifer (rock mass or stratum that is able to store water) systems of the ULRB comprise four main hydro geological units that are presented, from older to younger, as follows:

- Jurassic Aquifer has a thickness of about 1000 m. It is considered the main karstic formation in the ULRB composed of dolomitic limestone and has high infiltration rates in recharge areas;
- Cenomanian–Turonian Aquifer has a thickness of 900 m. It is composed of dolomitic and marly limestone and has high infiltration rates in recharge areas. It outcrops at the high altitude of the eastern slopes in the northern part of Mount Lebanon and the western slopes of the Anti-Lebanon Mountain chains;

- Eocene Aquifer has a thickness of 800 900 m. It is composed of marly limestones and has a high infiltration rate. It outcrops at the borders of the Beqaa valley on the eastern and western sides;
- Quaternary–Neogene Aquifer is composed of two formations: the Quaternary deposits and the Miocene formation. It has a thickness range from 0 to >700 m. It is composed of conglomerate alluviums. It is an unconsolidated aquifer where groundwater flow is relatively low. It is found in the central part of the Beqaa plain.



Figure 14. Geologic map of the upper Litani river basin (ULRB) (USAID ,2003).

#### Drainage morphometry and catchment hydrology

The morphometry of the Litani river was studied by Shaban et al. (2018) to evaluate the primary watercourse behavior. Table 8 shows different drainage morphometric parameters of the Litani river. LRB has a soft topographic terrain and displays low to moderate channel slope, which could influence its discharge rate and shows a low density rate, which means a high infiltration rate and a low meandering ratio, which could influence the runoff and the sedimentation.

Channel slope	1.06		
Drainage density	$0.68 \text{ km/km}^2$		
Meandering ratio	1.28		
Texture topography	0.54		

Table 8. Drainage morphometric parameters of the Litani river (Shaban et al., 2018).

The ULRB area includes about 132 km of the river and flows in the upper part of the basin. The upper Litani river (ULR) has a gentle slope that influences the water flow-regime. It shows a slow runoff rate which decreases the water flow velocity and thus increases sedimentation. Table 9 shows the major hydrological characteristics of ULR (Shaban et al., 2018).

 Table 9. Major hydrological characteristics of the upper Litani river basin (ULRB) (Shaban et al., 2018).

Areal extent	$1602 \text{ km}^2$
Prevailing flow direction	NNE-SSW
Slope gradient	5 - 8 m/km
Runoff rate	22 - 25 (%)
Infiltration rate	25 - 28 (%)
Runoff velocity	5 - 10 (km/h)
Volume of discharged water	410 (mm <sup>3</sup> /year)

## **2.1.3 Climatic conditions**

The Litani river is characterized by two main subclimates which are humid in the coastal region and sub-humid in the Beqaa region. The rainfall extends over 60 - 70 days per year between October and March and reaches an average of about 875 mm. In winter, the humidity is between 60 - 80% and then decreases in summer to reach 40 - 60%. The altitude affects temperature variation in the LRB. The average minimal temperature is 12 °C, while the average maximal temperature ranges between 15 and 28 °C. The snow, which is the main source for water resources, occurs at 1200 m for a maximum of one month per year (Shaban et al., 2018).

## 2.2 Sampling sites

The sampling sites are shown in Figure 15:

Berdaouni: The basin of the Berdaouni river, a tributary of the Litani river with a source at an altitude of 1236 m, is located in the region of the central Beqaa. The Berdaouni river flows from the east side of Mount Sannine (Qaa Er Rim springs) through a narrow canyon into the city of Zahle, then it turns southwards down the Beqaa plain and flows into the Litani river after a course of 12 km at an altitude of 890 m (Ismaïl et al., 2015). In 2015, the annual discharge of the Berdaouni River was 35 million m<sup>3</sup>/year and the dryness period occurred from July to September (Nassif et al., 2015). The Berdaouni river is impacted by urban, agricultural, and industrial discharges (USAID, 2012). Sediment samples were collected at the conjunction of the Berdaouni and Litani rivers (sampling B1: 33°81'24.13"N 35°89'42.24"E), whereas soil samples were taken from an

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agricultural land (sampling B2: 33°81'37.070"N 35°93'99.790"E) cultivated by wheat parallel to the river.

- Joub Jannine: The Joub Jannine river is located on the left side of Joub Jannine city (altitude: 872 m) approximately 7 km northeast of Qaraoun lake. The stream gauging station at the Joub Jannine bridge registered from 1999 to 2009 a very high flows from January to April (peaks occurred in February: 24.1 m<sup>3</sup>/s) with almost no flow between July and October (lowest average flow occurred in August of 0.2 m<sup>3</sup>/s) (USAID, 2012). Sediment samples were collected from the Litani river under the Joub Jannine bridge (sampling J1: 33°38'19.9"N 35°46'47.1"E), whereas soil samples were taken from agricultural land (sampling J2: 33°63'94.11"N, 35°78'23.12"E) near the bridge cultivated by wheat. This area collects domestic sewage during the dry season and wet season and agricultural pollutants by runoff.
- Ammiq: It is a region in a private property (altitude: 865 m) situated approximately 10 km northeast of Qaraoun lake. The marsh (2.8 km<sup>2</sup>) is bordered by the Barouk mountain on its western side and the Litani river on its eastern side. The Ammiq wetland (1km from the Ammiq village), which is made of several natural ponds of freshwater in the carbonate rocks, is the largest in Lebanon and benefits from the Ramsar convention. It is considered the most important migratory bird route. The agricultural activities practiced at Ammiq are mainly cereal culture, fodder culture and vegetable/legume culture (MoE, 2004; Hajar et al., 2008). Sediment samples were collected from the Litani river (sampling A1: 33°69'95.45"N 35°83'01.91"E), whereas soil samples were taken from agricultural soil (sampling A2: 33°42'01.0"N 35°49'12.2"E).

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Qaraoun: Qaraoun lake, situated in the southern part of the Beqaa valley at an altitude of 800 - 850 m between the two Lebanese mountain chains, is the largest freshwater body in Lebanon and was constructed in 1965. It has an area of about 12 km<sup>2</sup>, maximum depth of about 60 m, a water residence time of 0.77 year, and a capacity of around 225 million m<sup>3</sup>. This artificial lake was primarily built for irrigation purposes and electricity production. It now serves for commercial fishing, recreation and tourism. The Litani river inflow in the Qaraoun lake occurs mainly from October to April. The climate is semi-arid and the average annual precipitation is about 700 mm (Fadel et al., 2014). Sediment samples were collected from Qaraoun Lake (sampling Q1: 33°34'41.8"N 35°41'21.0"E) whereas, soil samples were taken from agricultural soil (sampling Q2: 33°58'68.260"N 35°72'53.020"E).

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**Figure 15.** The sampling sites in the upper Litani river basin (ULRB): Berdaouni (B1: sediment, B2: soil), Joub Jannine (J1: sediment, J2: soil), Ammiq (A1: sediment, A2: soil), and Qaraoun

(Q1: sediment, Q2: soil).

## 2.3 Materials

The soil and sediment samples were taken from the four sites as follows (Figure 15): Ammiq, river sediment (A1) and agricultural soil (A2); Berdaouni, river sediment (B1) and agricultural soil (B2); Joub Jannine, river sediment (J1) and agricultural soil (J2); and Qaraoun, river sediment (Q1) and agricultural soil (Q2).

The sediment and soil samples were collected at a depth of 20 cm from each site. The samples were air-dried and sieved to < 2 mm. The particle size distribution was determined by the Purdue University Soil Testing Laboratory using the pipet method (Day, 1965). The organic carbon content was measured according to the modified Walkley-Black method (Jackson, 1958). The sediment and the soil suspension pH values were determined on slurries with a sediment/water or soil/water ratio of 1:2.5.

Three herbicides, fluazifop (FLP), terbuthylazine (TBZ), and triclopyr (TCP) were used in the study (Table 10).

Herbicide	Water solubility	Vapor pressure	Log K <sub>ow</sub>	pKa
	(mg/L)	(mPa)		
FLP <sup>a</sup>	780	0.055	3.18 (pH = 7)	2.98
$TBZ^{b}$	8.5	0.09	3.40	1.90
TCP <sup>c</sup>	440	0.17	0.42 (pH = 5)	2.93

 Table 10. Selected physicochemical properties of studied herbicides.

a b Fluazifop, Terbuthylazine, C Triclopyr.

Solid biochar (BC) was a commercial charcoal provided by Lakeland Coppice Products (UK) obtained from coppiced woodlands (maple and oak). The BC was obtained at pyrolysis temperatures of 550 - 600 °C in a transportable ring kiln (2.15 m in diameter and holding around 2 t of hardwood). Carbon and Nitrogen BC contents were determined using a CHN Elemental Analyzer (Carlo Erba Instruments, mod 1500 series 2). Samples of BC (screened by means of a 2 mm sieve) were oven dried at 105 °C for 24 h. The dry samples were acid digested with a microwave oven (CEM, MARSXpress) according to the EPA method 3052. The solutions obtained after the mineralization were filtered (0.45 µm PTFE) and diluted. Total element contents of BC were determined by an ICP optical spectrometer (Varian Inc., Vista MPX) using scandium as internal standard. The pH value was measured in the BC/water suspension at a 1:2.5 ratio. The main characteristics of BC are reported in Table 11. The solvents of HPLC grade (Carlo Erba Reagenti, Milano, Italy) were used without any additional purification.

**Table 11.** Some chemical properties of biochar (BC).

Sample	"II	С	Ν	C/N	Al	Ca	Fe	K	Mg	Na	Р
	рн	%	%	C/N	g/kg						
BC	9.8	75.81	0.90	84.23	268	24.5	0.33	11.8	27.8	11.9	23.3

# 2.3.1 Sorption on soils, sediments, biochar and soils and sediments added with biochar

FLP, TBZ and TCP sorption isotherms were obtained on sediment and soil, on BC, and on sediment + BC and soil + BC, using a batch equilibrium method. In general, 2.5 g samples of sediment or soil or 25 mg of BC were equilibrated in polyallomer centrifuge tubes with 5 mL of aqueous herbicide solution. In a successive test, 25 mg of BC were added to 2.5 g of sediment or soil, and were equilibrated in polyallomer centrifuge tubes with 5 mL of aqueous herbicide solution. The tubes were previously checked to verify that they did not adsorb the herbicides. The initial concentration of herbicide solutions ranged between 130 and 520  $\mu$ M for FLP, between 9 and 33  $\mu$ M for TBZ and 133 and 522  $\mu$ M for TCP. The tubes were shaken in an endover-end shaker (70 rpm) at 25 ± 2 °C until equilibrium was reached. Preliminary kinetic batch studies indicated that the equilibrium was reached within 6 h for FLP, 2 h for TBZ, and 5 h for TCP. No degradation took place within the afore mentioned times. After equilibration, the suspensions were centrifuged at 3500 rpm for 10 min and the supernatant was pipetted off and analyzed immediately. The herbicide amount adsorbed was calculated from the difference between the initial and final concentrations of herbicide in solution.

Sorption data were fit to the logarithmic form of the Freundlich equation,  $\log C_s = \log K_{ads} + 1/n_{ads} \log C_e$ , where  $C_s$  (in µmol kg<sup>-1</sup> units) is the amount of herbicide adsorbed,  $C_e$  (in µM units) is the equilibrium concentration in solution, and  $\log K_{ads}$  and  $1/n_{ads}$  are empirical constants representing the intercept and the slope of the isotherm, respectively.

# 2.3.2 Analytical techniques

The concentration of FLP, TBZ and TCP was determined by HPLC. The analytical system was assembled as follows: a Waters 1515 pump equipped with a Waters 2487 UV/VIS programmable detector operating at a specific wavelength (nm) for each herbicide, Breeze chromatography software and an end-capped  $\mu$  Bondapak C<sub>18</sub> analytical column (10  $\mu$ m, 3.9 x 300 mm). Acetonitrile plus water, previously brought to pH 2.7 with phosphoric acid, were the mobile phase. The details of analytical procedures are reported in Table 12.

Herbicide	Eluent	Wavelength	Flow rate	Retention time
	(H <sub>2</sub> O / CH <sub>3</sub> CN)	(nm)	(mL/min)	(min)
<b>FLP</b> <sup>a</sup>	50 / 50	270	0.6	8.8
TBZ <sup>b</sup>	30 / 70	240	0.5	7.0
TCP <sup>c</sup>	50 / 50	295	0.5	9.2

Table 12. Analytical procedures.

a b c Triclopyr.

### **Chapter 3: Results and Discussion**

## **3.1** Physicochemical parameters of sediment and soil samples

The physicochemical characteristics of the sediments and soils collected along the Litani river are shown in Table 13. The texture variability showed that the amount of the clay increases successively from the North of the watercourse in the following order Berdaouni (B1) < Ammig (A1) < Joub Jannine (J1) and accumulates in the artificial Qaraoun Lake (Q1), where the Litani river is embedded. Differently, the amount of sand decreases from  $B1 \approx A1$  to Q1. The spatial variability of the texture of the sediments allows to identify three zones in the river catchment: A1 and B1 as sandy silt loam sediment, J1 as silty clay loam sediment and Q1 as clay sediment. This is well-matched with the drainage morphometry of the Litani river basin, which displays low to moderate channel slope and low meandering ratio, which could influence the river discharge and the sedimentation process (Shaban et al., 2018). Instead, the texture of all soils neighboring to their respective sediments can be defined as clay soil in agreement with Darwish et al (2006), who found that all soils of the Beqaa plain were mainly of clay texture. Additionally, the pH values of sediment and soil samples ranged from 7.8 (slightly alkaline) to 8.2 (moderate alkaline). The weakly alkaline pH in the Beqaa region is generally affected by the parent material of basic rocks, composed mainly of calcium carbonate rocks. Finally, the OM content was always higher in soil than in sediment samples. This difference is attributable to agricultural activities and to other causes such as spillage of waste water of industries and municipalities, and presence of dumpsites.

Sample	pН	OM (%)	Clay (%)	Sand (%)	Silt (%)
A1	7.8	1.8	17.5	37.4	45.1
B1	7.9	2.1	7.8	44.8	47.4
J1	7.9	4.1	26.9	16.3	56.8
Q1	7.7	2.8	52.4	19.0	28.6
A2	7.9	7.2	64.3	30.7	5.0
B2	8.1	6.7	58.5	38.5	3.0
J2	8.2	6.9	46.9	40.6	12.5
Q2	7.9	7.2	83.5	11.2	5.2

**Table 13**. Selected physical and chemical properties of investigated samples: Berdaouni (B1: sediment, B2: soil), Joub Jannine (J1: sediment, J2: soil), Ammiq (A1: sediment, A2: soil), and Qaraoun (Q1: sediment, Q2: soil).

## **3.2 Fluazifop**

The FLP sorption isotherms on sediments and the relative Freundlich parameters are shown in Figure 16 and Table 14, respectively. The isotherms were of the S-type, with slope  $1/n_{ads}$  values > 1, indicating that the FLP sorption on sediment becomes increasingly favoured as the herbicide concentration increases (Figure 16). In the sorption of organic compounds, an Stype isotherm is generally due to cooperative interactions among adsorbed organic species that stabilize the sorbate and enhance its affinity for the surface (Sposito, 1984). The observed K<sub>ads</sub> values on the sediments showed that the FLP sorption was generally scarce.

At pH values measured for sediment samples (Table 14), both FLP ( $pK_a$  2.98) and sediment colloids are negatively charged, therefore negative sorption would be expected. Nevertheless, a slight sorption was observed, suggesting that probably a lipophilic effect was

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acting (Walter et al., 2000). This agrees with the highest  $K_{ads}$  value observed on sample J1 among sediment samples. In fact, it was the richer in organic matter. On the other hand, the Q1 had a high clay content and likely the formation of organic matter-clay aggregates (Pusino et al., 1992; Mikutta et al., 2007; Mahamat Ahmat et al., 2017), this making the organic matter of Q1 sediment unable to bind FLP. Our results agree with previous data on the FLP sorption on different sediments and soils, in which a negative correlation was found between sorption coefficient and pH values ranging from 4.2 to 8.3 (Rick et al., 1987).



Figure 16. Fluazifop (FLP) sorption isotherms on sediments and sediments + biochar (BC).

System	рН	Kads	1/n <sub>ads</sub>	r
Al	7.8	0.011	1.5	0.9731
B1	7.8	0.046	1.3	0.9870
J1	7.7	0.070	1.3	0.9956
Q1	7.7	0.004	1.6	0.9799
BC	7.9	205.873	0.8	0.9916
A1 + BC	7.8	5.005	0.6	0.9804
B1 + BC	7.9	2.111	0.8	0.9849
J1 + BC	7.9	2.547	0.7	0.9793
Q1 + BC	8.0	0.147	1.2	0.9859

Table 14. Freundlich parameters for the fluazifop (FLP) sorption on sediments,

biochar (BC), and sediments + biochar (BC).

The sorption of FLP on the soils was only slightly higher than that on the sediments, despite the much higher content of soil organic matter. Probably, on soils, only the lipophilic effect plays a key role in FLP retention. As observed for sediments, the soil sorption isotherm shapes were S-type (Table 15, Figure 17).



Figure 17. Fluazifop (FLP) sorption isotherms on soils and soils+ biochar (BC).

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System	рН	Kads	1/nads	r
A2	8.0	0.074	1.1	0.9810
B2	8.1	0.057	1.2	0.9991
J2	8.0	0.078	1.1	0.9972
Q2	7.9	0.079	1.1	0.9776
A2 + BC	8.0	4.921	0.6	0.9899
B2 + BC	8.0	4.969	0.6	0.9662
J2 + BC	8.0	6.557	0.5	0.9952
Q2 + BC	7.9	4.429	0.6	0.9946

Table 15. Freundlich parameters for the fluazifop (FLP) sorption on soils,

and soils + biochar (BC).

Our study is in agreement with the poor sorption capacities for FLP previously observed by Rick et al. (1987) on 15 types of soil and sediment textures (average  $K_d$ : 0.79), by Kah and Brown (2007) on nine types of soils texture ( $K_d$  values range: 0.27 - 1.57), and by Badawi et al. (2015) on loamy soils ( $K_d$  values range: 0.14 - 0.49 mL/g).

FLP has a great water solubility in water (780 mg/L) and persists in the soil ( $t_{1/2}$  until 168 days), and thus, it is a molecule at high risk of leaching. Therefore, the soil treatment with biochar could represent a useful practice for limiting the FLP mobility and then preventing the pollution of surface and underground waters. When the herbicide sorption study was extended to BC, and to sediments and soils added with 1% BC, FLP showed high affinity for BC ( $K_{ads} \sim 206$ , Table 14), likely due to the great percentage of BC organic carbon ( $\approx 76\%$ ) and to features of the BC used in this study. Indeed, the BC obtained at 500 - 600 °C is mainly composed of aromatic carbon arranged in graphite-like layers thus having elevated porosity and surface area values (Pinna et al., 2016). Presumably, the FLP molecule flatness, due to the extensive conjugation of the two aromatic rings present in its structure, leads to herbicide transfer into BC layers by

lipophilic effect in spite of the negative charge centered on the molecule of the carboxyl group. The Freundlich parameter  $1/n_{ads} <1$  of the FLP + BC suggests an L-type isotherm, indicating a high FLP-BC affinity at low concentration. As the FLP concentration increases, the affinity reduces, because it becomes more difficult for the herbicide to find free sorption sites on BC.

The addition of BC to sediment and soil samples increased considerably the sorption of the herbicide on these substrates. In fact, the mean Kads value measured on BC amended sediments increased about 75 times compared to that of the relative samples without BC and it increased about 72 times in the case of soil samples (Tables 14 and 15). It is noteworthy that the sediment A1, with the lowest organic content, showed the highest K<sub>ads</sub> value when combined with BC. This finding is consistent with several authors (Yu et al., 2011; Wang et al., 2012) who reported that the increase of pesticide sorption in soil amended with biochar was negatively correlated with the initial soil organic matter content, *i.e.* the BC effect was more marked in soils containing a lower organic carbon amount. Once again, the values of K<sub>ads</sub> observed were lower on BC amended samples the richest in clay (Q1 + BC and Q2 + BC), likely due to the presence of clay-organic matter complexes. The BC addition to sediments and soils caused a decrease in  $1/n_{ads}$  values, producing isotherms resembling the L-type (Figures 16 and 17, respectively). In the literature, there is no data concerning the effect of biochar amendment on FLP sorption but these results agree with those described by Yu (Yu et al., 2006) who observed an increase in Kads values and a decrease in  $1/n_{ads}$  values in diuron sorption on biochar-amended soils.

## **3.3** Terbuthylazine

TBZ sorption isotherms on sediment samples are shown in Figure 18 and the relative Freundlich parameters are reported in Table 16. The Freundlich equation described well the experimental data with a coefficient r ranging between 0.961 and 0.973. According to the isotherm classification by Giles (1960), the TBZ adsorption on sediments is described by an Ltype isotherm, slope  $1/n_{ads}$  values < 1, indicating that there is high affinity between TBZ and the sediments. In the sorption of organic compounds, an L-type isotherm suggests a progressive saturation of sorbents. Only B1 showed a 1/n value equal to 0.9, describing an isotherm which diverges slightly from the linearity. The greatest Kads value was obtained for the sorption on sediment J1 (Table 16) suggesting that TBZ sorption is greater on the sediment which has the highest content of organic matter (Table 13). Most probably, the organic matter content of the sediments played the leading role in the TBZ sorption. These results were consistent with that of Wang et al. (2010) that found that the TBZ sorption was also influenced by the presence of OM. The sediments were characterized by pH values  $\geq$  7.7. At these pH values, TBZ (pK<sub>a</sub> 1.9) should behave like neutral compounds (Hornsby et al., 1996). Therefore positive sorption would be expected through hydrophobic interactions with organic matter.



Figure 18. Terbuthylazine (TBZ) sorption isotherms on sediments.

Table 16. Freundlich parameters for the terbuthylazine (TBZ) sorption on sediments.

System	pН	Kads	1/n <sub>ads</sub>	r
A1	8.0	11.334	0.5	0.9610
<b>B</b> 1	8.0	2.451	0.9	0.9891
J1	8.1	20.337	0.6	0.9734
Q1	8.0	8.420	0.6	0.9734

In Figure 19 and Table 17, the Freundlich parameters for the TBZ sorption on soils and the relative isotherms (L-type ) are shown. Because of the high organic matter content of the soil, higher  $K_{ads}$  values would be expected than those observed. Most probably, either a low degree of humification of organic matter (Dousset et al., 1994) or the formation of organic matter-clay aggregates could made the organic matter unable to bind TBZ.



Figure 19. Terbuthylazine (TBZ) sorption isotherms on soils.

Table 17. Freundlich parameters for the terbuthylazine (TBZ) sorption on soils

System	pН	Kads	1/n <sub>ads</sub>	r
A2	7.8	7.890	0.6	0.9913
B2	8.0	6.462	0.7	0.9594
J2	8.0	5.818	0.6	0.9986
Q2	7.8	7.482	0.7	0.9910

The TBZ sorption behavior was studied on BC alone, and on sediment and soil samples after BC addition to evaluate the effect of added biochar. The sorption of TBZ on BC alone was total and immediate, and therefore it was impossible to obtain the Freundlich isotherms and get the  $K_{ads}$  and  $1/n_{ads}$  values. In comparison to the BC-free samples, the addition of BC on sediments and soils enhanced markedly the TBZ sorption, but it was not possible to calculate the value of  $K_{ads}$ . Therefore  $K_d$  values are reported in Table 18. The high affinity of TBZ for BC was probably due to the physical properties of sorbent. In fact, the elevated porosity and surface area values were likely responsible for the observed sorption through the entrapment and accumulation of TBZ in the BC layers.

This finding is consistent with a previous study showing that the TBZ sorption was enhanced in soil amended with biochar derived from *P. radiata* wood (Wang et al., 2010). The high affinity of biochar for TBZ was also reported by several authors. For example, Tejada et al. (2013) observed that soil amended with biochar originating from municipal solid waste adsorbed more TBZ than soil amended with cow manure and poultry manure. Wang et al. (2010) showed that TBZ adsorption on charcoal biochar from high pyrolysis temperature was higher than bio solids in soil with low native organic matter. Additionally, fresh biochar adsorbed more TBZ than aged biochar (Trigo et al., 2014).

System	K <sub>d</sub>
A1+BC	100.26
B1+BC	15.93
J1+BC	41.57
Q1+BC	35.58
A2+BC	30.87
B2+BC	40.63
J2+BC	43.14
Q2+BC	28.57

**Table 18.** Distribution coefficient ( $K_d$ ) for terbuthylazine (TBZ) sorption on sediments + biochar (BC) and soils + biochar (BC).

## 3.4 Triclopyr

The TCP Freundlich parameters for the sorption on sediments are given in Table 19. Generally,  $K_{ads}$  values were very low and the greater sorption was observed in the sample which contained the greatest amount of organic matter. This was consistent with results of Pusino et al. (1994), who found that TCP sorption increased linearly with soil organic matter content. By comparing the sorption of TCP on sediment (table 19) with that of soil (Table 20), we found that  $K_{ads}$  values for TCP sorption on soil were smaller than that of sediment samples. As found for sediments, as the organic matter amount in soil increased, the  $K_{ads}$  values increased. These findings are consistent with Stephenson et al. (1990), who found a 90% of TCP residue in soil organic matter layers even after heavy rainfall. At the pH values of sediments and soil studied (7.6 < pH < 7.9), TCP is in anionic form (pK<sub>a</sub> = 2.93). The low TCP sorption found could be attributed to a repulsion caused by the negative charge of the herbicide and the net negative charge of organic matter and clay minerals in soil and sediment samples. However, TCP sorption

may be induced by a specific hydrophobic mechanism acting between TCP and organic matter (Johnson et al., 1995).



Figure 20. Triclopyr (TCP) sorption isotherms on sediments and sediments + biochar (BC).

Table 19. Freundlich parameters for the triclopyr (TCP) sorption on sediments,

System	pН	Kads	1/n <sub>ads</sub>	r
A1	7.6	0.0157	1.5	0.9696
B1	7.9	0.0011	1.9	0.9745
J1	7.8	0.0718	1.2	0.9868
Q1	7.9	0.0061	1.6	0.9721
BC	8.0	3331.96	0.3	0.9944
A1+BC	7.7	8.1808	0.5	0.9688
B1+BC	8.1	1.6599	0.8	0.9904
J1+BC	7.8	1.5530	0.8	0.9875
Q1+BC	7.9	1.6285	0.7	0.9881

biochar (BC), and sediments + biochar (BC).



Figure 21. Triclopyr (TCP) sorption isotherms on soils and soils + biochar (BC).

TCP sorption isotherms were found to be S-type in sediment (Figure 20) and soil (Figure 21) samples. This indicates that the herbicide sorption on sediment and soils becomes increasingly favored as the herbicide concentration increases. Thus, the cooperative interactions among adsorbed organic species likely stabilize the sorbate and enhance its affinity for the surface.

The TCP sorption on BC experiments showed that TCP has a high affinity for BC (Table 19) with a significant coefficient r equal to 0.994. Craig et al. (2015) took advantage of the high affinity of TCP for biochar to propose a system for water surface purification. Based on Giles et al. (1960), the TCP sorption isotherm shape is L-type isotherm because 1/n equal to 0.3. This indicates a high TCP-BC affinity at low concentration, as the TCP concentration increases, the affinity reduces, because it becomes more difficult for the herbicide to find free sorption sites on BC. In the presence of BC, the TCP sorption on sediment and soil samples was considerably enhanced compared to their relative samples free of BC (Tables 19 and 20). In general, it was noticed that TCP sorption in presence of BC was favored in soil and sediments with low organic

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matter as already observed by our FLP study. Additionally, 1/n values decreased to less than one, so, the sorption isotherm shapes in the presence of BC changed compared to that without BC, thus becoming L-type isotherms (Figures 20 and 21), as already observed in our FLP study and by Yu et al. (2006) for diuron.

**Table 20.** Freundlich parameters for the triclopyr (TCP) sorption on soils,

 and soils + biochar (BC).

System	рН	Kads	1/n <sub>ads</sub>	r
A2	7.6	0.0103	1.5	0.9931
B2	7.8	0.0001	2.2	0.9897
J2	7.8	0.0001	2.1	0.9935
Q2	7.6	0.0120	1.5	0.9955
A2 + BC	8.0	7.5614	0.6	0.9991
B2 + BC	8.0	10.7029	0.5	0.9816
J2 + BC	8.0	13.9508	0.4	0.9995
Q2+BC	7.8	10.678	0.5	0.9961

## **Chapter 4: Conclusions**

The Beqaa region represents 47% of Lebanon's agricultural economy and is crossed by the Litani river. This river, the largest in Lebanon, suffers from different kinds of pollution, including that caused by pesticides widely used in the Beqaa Valley. The intense agricultural activity, the Beqaa topography and, particularly, its physical-chemical properties are the main factors that increase the risk of pollution of ground and surface waters. Nowadays, the situation of the Litani river is getting more disastrous, even because there are no regulations that control the use of pesticides in this area. FLP, TBZ and TCP are among the most used herbicides in the Beqaa Valley and the low sorption measured on the sediment and soil samples collected from this region suggests that these herbicides may cause an environmental threat to the Litani basin. The addition of 1% BC significantly increased herbicide retention on soil and sediments, being effective in reducing the risk of leaching of FLP, TBZ and TCP into the aquatic environment. However, biochar amendment conducted in open field could reduce the bioactivity of the herbicides against weeds. Therefore, this approach should be carried out on soil near the riverside, where there is no intensive cultivation. In this way, soil treated with biochar, acting as a buffer strip, could be useful to limit the pollution of the waters of the Litani river basin. To our knowledge this is the first study carried out on sediment and soil samples from Lebanon concerning the sorption of herbicides and the use of biochar to limit their leaching in the water bodies. Our findings could lead to further research on herbicide sorption capacities of biochar from different feedstocks and obtained at different pyrolytic temperatures in order to compare the different biochar efficiencies and choose the suitable one. Furthermore, considering that the uncontrolled and unregulated pesticide use is becoming matter of concern due to the high presence of these agrochemicals in Lebanese water resources, studies could be conducted on soil

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and sediment samples from other areas of Lebanon in order to suggest possible pollution mitigation strategies.

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