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## The Effect of the Addition of Biodiesel in the Fossil Diesel to Its Characterizing Parameters

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**Abstract:** Nowadays it is clear that all the scientific efforts are directed of finding the alternative resources for the fuels, in all national and international levels of different countries, as well as in our country. Due to its importance, there have been a lot of literature survey and are established some experimental set-up to try profiting biodiesel using different feedstocks usually form the wastes. As it can be understandable, there are a lot of processes to reach the required quality of the biodiesel in order to be ready to use for operation in internal combustion engines. One of the reasons for this resistance is a certain lack of knowledge about the effect of biofuels on engine emissions. This paper presents environmental and economic benefits from the use of biodiesel, and the impact on the improvement of qualitative indicators of the amount of biodiesel added to fossil diesel. The purpose is to maintain constant engine performance, due to changes beginning with the influence of the quantity of fuel to power motor, fuel consumption and thermal efficiency. Which is the most important and what should be emphasized more in this scenario, it is fact that the comparisons between environment biodiesel emissions and fossil diesel. There are closely related come presence in the burning gases the following material such as nitric oxides and particulate matter, the latter not only in mass and composition, but also in size distributions.

**Keywords:** *biodiesel, diesel, emissions, environment, characterization*

### Introduction

Energy sources are classified as renewable and non-renewable. Energy obtained by hydro, solar, wind, biomass and wastes are renewable energy sources, while fossil fuels are non-renewable energy sources as was mentioned in (Roy, 2004).

The issues of energy availability and its security have caused serious concerns around the world and prompted researchers to look for better alternatives to reduce the dependency on petroleum products. Fossil fuels have a negative effect on environment, by emitting CO<sub>2</sub>, CO, SO<sub>x</sub>, NO<sub>x</sub> and smoke emissions when used as fuel in combustion devices. NO<sub>x</sub> and CO<sub>2</sub> cause greenhouse effect and SO<sub>x</sub> cause acid rains as was mentioned in (Kalam *et al.*, 2003). Biofuels produced from lignocellulosic materials and vegetable oils provide a feasible solution to the twin crises of fossil fuel depletion and environmental degradation. Biodiesel is considered as a promising alternative fuel for diesel engines. It is an oxygenated fuel made from vegetable oils and animal fats by the conversion of the triglycerides to esters (primarily methyl esters) via various esterification processes as was mentioned in (Ramadhas *et al.*, 2005). The fuel characteristics of biodiesel are similar to that of fossil diesel fuel and it permits the biodiesel to use as an alternative fuel for diesel engines without any major modification. Its additional advantages include outstanding lubricity, excellent biodegradability, superior combustion efficiency and low toxicity, among other fuels as was mentioned in (Balat *et al.*, 2010). Many studies show that unburned hydrocarbons (HC), carbon monoxide (CO) and sulfur levels are significantly less in the exhaust gas, while using biodiesel as fuel. However, a noticeable increase in the oxides of the nitrogen (NO<sub>x</sub>) levels is reported with biodiesel as was mentioned in (Sahoo *et al.*, 2009), (Demirbas *et al.*, 2011), (Lapuerta *et al.*, 2008), (Narayana *et al.*, 2008). Although biodiesel is considered as a potential alternative fuel, it has some demerits like poor cold flow properties and lower oxidation stability than petroleum fuels as was mentioned in (Knothe, 2005; Dunn 2005). Saturated compounds are responsible for the unfavourable cold flow properties observed in biodiesel, and the unsaturated esters are mainly responsible for the reduced oxidation stability as was mentioned in

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(Dunn, 2005). Treatment with oxidation inhibitors containing hindered phenols is the most common approach to increase the oxidative stability of biodiesel.

A growing concern over the environmental effects of diesel and diminishing natural resources has led to the development of biodiesel. Biodiesel has promising potential as eventually replacing most of the diesel used in automobiles. Currently, a significant amount of air pollution is contributed by pollutants from car exhaust and fuel emissions. This then leads to the question of how does exhaust and emissions from biodiesel differ from diesel. Would using biodiesel improve fuel emissions or will this new fuel have no substantial effect on the environment? Petroleum diesel has many combustion products such as: carbon dioxide, carbon monoxide, nitrogen oxides, Sulphur dioxide, polycyclic aromatic hydrocarbons, and particles of soot, dust, smoke, and aerosols (particulate matter). Carbon dioxide contributes to global warming by acting as a “greenhouse gas” and keeps heat from escaping into the atmosphere. Nitrogen oxides lead to formation of ozone along with hydrocarbons and accounts for the ground level smog present in major cities. Hydrocarbons are also suspected of being carcinogenic and particulate matter can lead to complications in health and the respiratory system as was mentioned in (Demirbas, 2005). Long term diesel emission is harming the environment, so if biodiesel does produce a significantly lower amount of air pollution then the incentive for everyday use is even stronger.

The definition of biodiesel is the mono alkyl esters of the fatty acids derived from vegetable oils. Alcohol and a catalyst are mixed with vegetable oil producing glycerin and methyl esters, the biodiesel component, through transesterification as was mentioned in (Lue et al., 2001). This process is necessary in order to lower the viscosity of the oil and increase fuel efficiency. It is also important to remember that there are multiple types of biodiesel based on the type of oil used. Palm seed, soybean, and peanut oil are all commonly used for biodiesel as was mentioned in (Chen et al., 2007). Different types of oil may lead to slightly different emission results. Based on current research the most popular and most successful way of collecting and analyzing car exhaust and emissions is by using a dilution tunnel for the initial collection (Chen *et al.*, 2007). A dilution tunnel is a large tube or tunnel that provides space where the gases from car exhaust can mix and become diluted enough for later analysis. In order to determine the differences between petroleum and biodiesel emission, car exhaust will be collected and analyzed with a dilution tunnel. Car exhaust is a logical source for fuel emissions because the exhaust is a mixture of gases, vapors, and solids providing a source for multiple emission products as was mentioned in (Aulich *et al.*, 2005).

## **Biodiesel as a Fuel and as a Blending Component**

### **As a Fuel**

Biodiesel (B100) is defined as “a fuel comprised of monoalkyl esters of long-chain fatty acids derived from vegetable oils or animal fats.” In addition, it must meet all of the parameters as defined within the ASTM specification D6751, “Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels” as was mentioned in (Harris 2005). Biodiesel is a fuel designed as a blendstock for use in blending with petroleum diesel fuel. It is not intended for use with gasoline. Biodiesel has been proven to reduce the emissions of hydrocarbons, carbon monoxide and particulates when used alone or with blends that include petroleum diesel. Biodiesel has excellent lubricity properties and is typically low in sulphur content, thus meeting the needs of the EPA and new generation fuels.

### **As a Fuel Additive**

Nearly every Original Equipment Manufacturer (OEM) approves the use of up to 5% biodiesel (B5) when blended with diesel fuel that meets its appropriate specifications as found within ASTM D975. These specifications are not dependent upon the oil or fat used to produce the biodiesel, or the specific process employed. However, it is critical to understand that the results, and some performance criteria, may vary based upon the feedstock used. The conformance of the product to the ASTM specifications is a requirement for any and all tax incentives and credits. Due to the handling of hazardous materials and large quantities of flammable chemicals during the reaction, the production of biodiesel should only be undertaken by trained professionals. Federal, state and local laws may exist that require special permits for the production and handling of fatty acid methyl esters and the components used to manufacture such as standard put in the Table 1.

**Table 1.** Standard Specification for Biodiesel Fuel Blend Stock (B100) For Middle Distillate Fuels

	<i>Test Method</i>	<i>Limits</i>	<i>Units</i>
Water and Sediment	ASTM D2709	0.05 max	% volume
Kinematic Viscosity 40 °C	ASTM D445	1.9 – 6.0	mm <sup>2</sup> /s
Sulfated Ash	ASTM D874	0.02 max	% mass
Sulfur			
S 15 Grande	ASTM D5453	0.0015 max	% mass
S 500 Grade	ASTM D5453	0.05 max	% mass
Copper Strip Corrosion	ASTM D130	No 3 max	
Alcohol Content (One of the following must be met)			
Methanol Content	EN 14110	0.20 max	% volume
Flash Point, Closed Cup	D93	130 min	°C
Cetane Number	ASTM D613	47 min	
Cloud Point	ASTM D2500	Raport to Customer	°C
Carbon Residue	ASTM D4530	0.05 max	% mass
Acid Number	ASTM D664	0.50 max	mg KOH/g
Free Glycerin	ASTM D6584	0.02	% mass
Total Glycerin	ASTM D6584	0.24	% mass
Phosphorus	ASTM D4951	10 max	ppm
Vacuum Distillation End Point	ASTM D1160	360 °C max	°C
Oxidative Stability	EN 14112	3 min	hours
Cold Soak Filtration	Annex to D6751	360 max	seconds
Calcium & Magnesium (combined)	EN 14538	5 max	ppm
Sodium & Potassium (combined)	EN 14538	5 max	ppm

Each of the parameters listed within the specifications is designed, and limits set accordingly, to ensure that the product is fit for purpose. Each result must conform to the specifications to help ensure that biodiesel may be used as a fuel without causing harm. If any parameters are found to not meet these specifications, that fuel is technically not biodiesel and is in jeopardy of losing any applicable tax credits. The following have been some characteristics already studied and considered for the characterization of the impact to the resulting biodiesel property:

*Relationship of Properties to Performance*

*Cloud Point:* While the Cloud Point must be reported, there are no minimum or maximum requirements. It is vital to understand the importance of this value in relation to the performance and handling of B100 at low ambient temperatures. The Cloud Point is the most conservative temperature at which components begin to precipitate from the fuel that may cause operability issues. Cloud Point results will vary significantly depending upon the feedstock from which the methyl ester was created.

*Monoglycerides* are partially converted fats and oils found within biodiesel. While not reported separately in the U.S., they are accounted for as part of the total glycerin. The monoglycerides formed as the result of different feedstocks have inherently different properties. They all have somewhat higher melting and Cloud Points, as opposed to the methyl esters. This may lead to the appearance of precipitates just above the reported Cloud Point. It has been shown that the presence of even small amounts of saturated monoglycerides will significantly raise the Cloud Point of biodiesel, while unsaturated monoglycerides will not. These saturated monoglycerides are one of the more common culprits in filter plugging. This material will appear as a thick, waxy coating. The monoglycerides formed from tallow or palm, or those that are saturated by nature, have significantly higher melting points that will require more diligence and more energy to dissolve back into solution. The monoglycerides derived from soy and canola are much less saturated, leading to considerably less impact on filterability.

*Corrosion and Deposits:* *Acid Number* the Acid Number is a relative indicator of the acidic impurities, degradation and/or oxidation of the fuel. Free fatty acids arise in part through the hydrolysis of the feedstock fats and oils. Improper processing or oxidation may also lead to higher values. These oxidative products are associated with fuel system deposits and corrosion. Unfortunately, organic acids vary widely in corrosion properties, and the results cannot be used to predict failures.

*Free and Total Glycerin* the Free Glycerin value records the level of by-product glycerin that remains in B100. The Total Glycerin result measures the amounts of unconverted and partially converted fats and oils. Excessive levels of these components may lead to storage tank and fuel system filter plugging, along with engine fouling.

*Oxidative Stability* The oxidative stability of the fuel is related in part to the Acid Number results. As the biodiesel degrades, or oxidizes, organic acids or polymers are created as a by-product which may lead to corrosion or filter plugging. The Oxidation Stability result is an accelerated test used to predict the fuel's stability for longer-term storage, possibly up to six months.

*Combustion: Cetane Number* for diesel fuel is a rough equivalent to Octane Rating for gasoline. The value provides a measure of the ignition characteristics of the fuel in compression ignition engines. The lowest value for typical biodiesel is the same as a "premium petroleum diesel" at 47.

*Flash Point* the Flash Point is used in shipping and safety regulations to define flammable and combustible materials. This result is used to determine the classification for the Department of Transportation (DOT) regulations. It is important to note that a typical result of 130° C for biodiesel is almost twice that of petroleum diesel (approximately 70° C) and therefore much safer to handle and transport. The Flash Point is also used to ensure the residual methanol left in the fuel after biodiesel processing will not negatively affect combustion and other fuel system components.

*Visual Appearance* While there is no correlation between the colour of biodiesel and its performance as a fuel, it is critical that the sample be free of undissolved water, sediment and suspended matter. At room temperature, the sample should be clear and transparent. Any cloudiness or haze may be an indication of impurities or excess water that may be present.

## Material and Methods

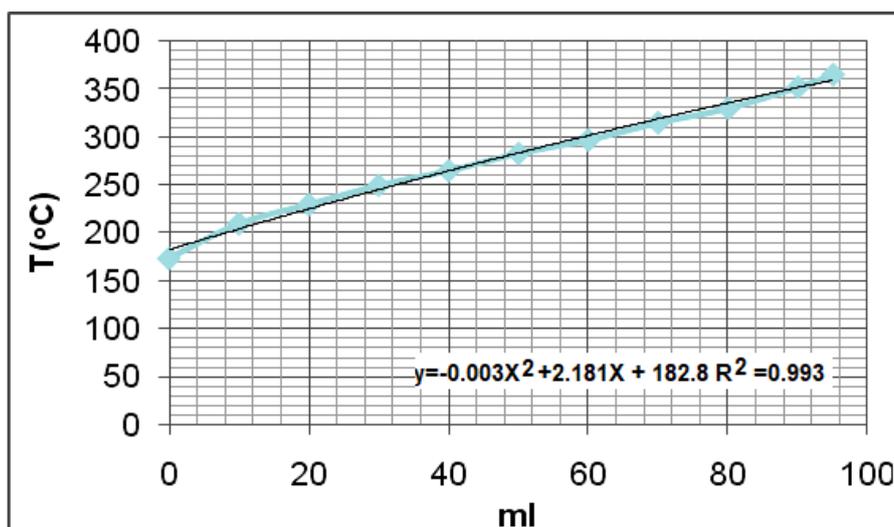
Entry on the part of this paper is devoted with more attention to Biodiesel. In other papers of the nowadays specialized literature, there are more information for the way of its production, how to make it suitable for handling and other settings. These parameters will be compared with those of biodiesel, and from the resultant acts will see which of these parameters used to change with the addition of diesel to biodiesel in different quantities. In total 300ml product was analysed where we add biodiesel to diesel were mixed in different ratios, samples differed by addition of 15 ml biodiesel more than previous sample as can be seen in the table 1. Each parameter was defined by different analytical and instrumental methods.

## Results and Discussion

The following table 1 are provided qualitative characteristics of mixtures in various ratios according to a preliminary plan of mixing. Biodiesel produced were mixed with fossil diesel traditional, where in this case we have used only one-party diesel. Interesting part of this study was to determine Sulphur content because for the results achieved, we see clearly important influence of biodiesel to reduce the amount of sulphur in fuel and different property characterization was determined as shown in the Table 2. In the Figure 1 it is shown the graphical presentations of the standard distillation curve for B5 type mixture.

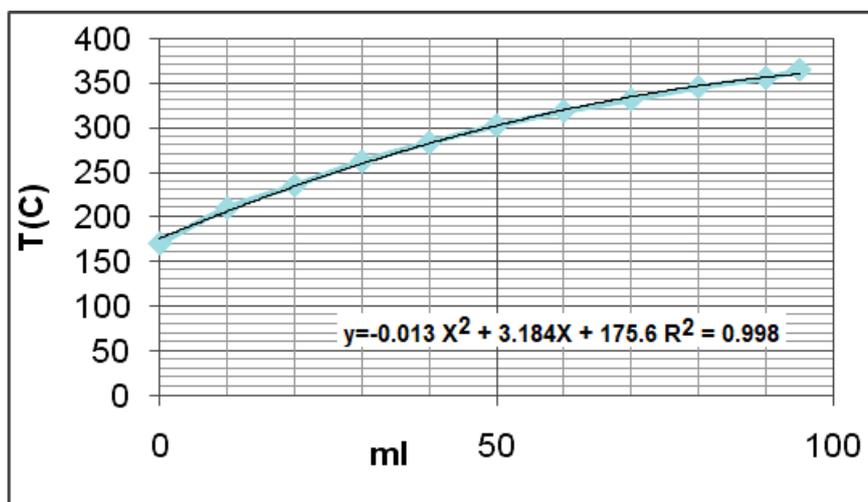
**Table 2.** Qualitative characteristics of compounds in various reports

Nr	BD + Diesel (300ml)	Temp (°C)	d <sub>t</sub> <sup>4</sup> (gr/cm <sup>3</sup> )	d <sub>4</sub> <sup>20</sup> (gr/cm <sup>3</sup> )	n <sub>D</sub> <sup>t</sup>	n <sub>D</sub> <sup>20</sup>	P <sub>f</sub> (°C)	P (°C)
1	15+285	25	0.82	0.832	1.461	1.459	58	75
2	30+270	25	0.82	0.832	1.462	1.460	73	95
3	45+255	25	0.822	0.832	1.462	1.460	76	89
4	60+240	25	0.824	0.832	1.462	1.460	64	71
5	75+225	25	0.824	0.832	1.462	1.460	64	70



**Figure 1.** Distillation curve for B5

In the Figure 2 it is shown the graphical presentation of the experimental standard distillation curve for B25 type mixture.



**Figure 2.** Distillation curve for B25

For both type of mixing we have statistically treated all data from the standard experimental distillation curve, realized in our laboratory, and we have calculated the best fit regression coefficients which was shown in both graphs. In the Table 3 we have shown the experimental evaluation of the Sulphur content depending on the ratio of the mixture

**Table 3:** Sulphur content depending on the ratio of the mixture

Nr.	Type	Sulphur content	
		(mg/l) apparatus Multi EA 3100 Standard ISO 20846:2011	(ppm) Apparatus XRF Standard ASTM D 7220
1	B5	7.77	8.7
2	B10	7.35	8.3
3	B15	7.76	8.12
4	B20	7.05	7.4
5	B25	7.12	6.8

## Conclusions

This paper presents the effects of biodiesel produced by us, as additive in petroleum diesel. The properties of diesel, biodiesel and their mixtures, were compared.

The development of biodiesel is a positive sign of the growing concern for the environment and the impact we are leaving on it. Searching the effects of biodiesel emission is a forward step because it begins to look at what other consequences the daily use of this new fuel might bring. There are some recommendations from the international research done on biodiesel and has suggested that the use of biodiesel in main city traffic has few negative impacts on the environment.

Some by-products with the exception of nitrogen oxide are less than those from petroleum diesel. Producing this fuel is also more friendly to the environment in some points, and certainly, more responsible than diesel. The main reason why biodiesel has yet to become widely available is due to the fact that producing the fuel is still much more expensive than the cheaper petroleum.

Hopefully research will continue to be done, to reach more effectiveness of biodiesel produced with different feed stock, as well as other alternative fuels and in the near future scientists intend to find the best way of producing biodiesel from organic wastes.

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## Physical-chemical Characterization of Drinking Water around a mining Industrial Region in the North of Kosovo

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**Abstract:** Zvecan is a mining industrial region in the north of Kosovo. In addition, other industrial sectors have developed. Unfortunately, the region is very much polluted. The source is industrial activity (exploitation of mineral resources and ferrous metallurgy, and other chemical industry). The present paper aims to investigate pollution level in Zvecan and raise public awareness. In the end recommendations regarding pollution monitoring process and other measures are made. Some water samples have been collected from 2014 to 2015 and analyzed. The results reported contaminated water. As it can be seen, the main purpose of this study was to identify physical and chemical characteristics of drinking water in some villages in the municipality of Zvecan. On the other hand, local authority needs to take urgent measures to improve situation and to offer for the exposed population living in the vicinity of the pollution source, other source of drinking water for personal and community usage.

**Keywords:** *pollution, contamination, monitoring, mining, industry,*

### Introduction

It is estimated that nearly half of Kosovo's mineral reserves, 49.7% is concentrated in the vicinity of Mitrovica, and so, in the past an intensive development of ferrous metallurgy has been the main industrial activity of the area, except other chemical plants and manufactures. Due to such a concentration industry which has used old facilities and outdated technology brought about this resulted situation.

Other reasons of this pollution have been also installation of such facilities in a relatively small area, caused a high rate of exploitation, wrong configuration of the terrain with wind rose, inadequate urban choice, etc., which has led to extremely high levels of water pollution.

Being the most common substance on earth, water is not only necessary for life, but also indispensable for development and sustainability in our planet. The role and importance of water is very large as physiological, hygienic, economic and ecological means of usage. According to specific reports the World Health Organization, every year, as a result of unsanitary water use, about 500 million people get sick.

In Kosovo, 44% of resident population are connected to the network pipeline for water supply, while 28% of them have sanitation, and some 62% of rural population used to get their water from unhygienic wells, being drilled close to the septic dams. Kosovo is the country in Europe with no perfect water supply network and sanitation.

Supplying the population with drinking water, poses very specific requirements and criteria, ranging from water quality, construction and purification technology, various operations of preparation, supervision and supply reservoirs to distribution customers. Therefore, continuous physical-chemical and bacteriological tests and analysis are more than necessary, even obligatory.

The presence of some chemical substances in drinking water is naturally imposed because they influence in certain amount the organoleptic and sensorial characteristics. Drinking water should be firstly clean, which means biological and bacteriological purity need to be ensured, then to be clear,

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having a pleasant taste, and no smell and of course no fever, which ensure the refreshing taste. Above mentioned properties and desirable taste of the water are reflection of presence of some gases dissolved in water (oxygen and carbon dioxide) and small amount<sup>3</sup> of calcium bicarbonate. The concentration of oxygen in water depends, not only by the temperature and partial pressure, but also from the degree of water pollution (WHO 2001; Voznaya, 1991). The presence of the reducing substances such as: ammonia, iron (II), nitrites and other substances, which being oxidized, can easily disrupt this balance, thereby diminishing the amount of dissolved oxygen, so that the concentration of dissolved oxygen can be related to the presence of various impurities in the water (Krasniqi & Nushi-Latifi, 2002; Oxfam Delagua, 1993; Vitaku *et al.*, 2013).

One of the more important parameters which indicates the degree of purity of the water, is chemical oxygen consumption (GO) or oxidization, which shows the necessary amount of oxidizing reagent for oxidation of colloidal substances, belonging to the organic or inorganic structure. The greater value of GO's, the more water pollution we have, deriving in an urgent measure to be taken for its cleaning (Hernea & Tenche-Constantinescu, 2013) The products of the disintegration of organic substances under the influence of special bacteria, can produce to water an unpleasant odor, and make it unsuitable for drinking purpose.

## **Material and Methods**

For this research work, samples have been taken in different sites, and analysed strictly for the indicators responsible for water quality. Sampling points have been located close to the water wells opened in some villages, and also taken in locations immediately after the so-called disk of "Trepca" mine.

Measurements have been performed for determining such parameters (Standard Methods, 1995; Catranguiu *et al.*, 2015; URL-1) as smell, colour, turbidity, temperature, pH value, chloride and thermo tolerant Coliform bacteria presence of faecal origin, employing an instrument such as "Portals Water Testing Kit", while other parameters like specific conductivity, consumption of  $\text{KMnO}_4$ , dry residue without filter, dry residue after filtration, suspended substances, nitrites, iron and manganese, which have been determined in the laboratories of the Regional Public Health Institute in Mitrovica.

Measuring the temperature, the amount of chlorine, turbidity and pH value was made on site, but the presence of thermo tolerant Coliform bacteria of faecal origin, was done in the special laboratory setup. Analyses of chlorine and pH value were performed in comparator, which is part of the instrumental device (Voznaya, 1991).

Water samples were taken with the clean container, but not sterile (part of the apparatus) (Voznaya, 1991). The vessel was rinsed several times with water that was taken for analysis. Comparator cells rinsed several times with water to be tested, filled with water and then to introduce the tablet right cell DPD - 1 for testing of chlorine, while the left cell comparator introduce phenol red tablet for testing pH value. Values of free chlorine residual and pH, was read during daylight, having the opportunity to compare the sample's colour with standard set of colours in the central part of comparator.

Total residual chlorine content has been analysed according to the standard procedure or protocol. Turbidity was determined in turbidity pipes, which were scalable from 2 to 5 TU. Their scaling was done on a logarithmic scale with higher critical values. The result was the value of the line that is closest to the water level.

Evaluation of electrical conductivity was done using the conductometer, while the the oxygen content, was evaluated by Winkler's bottle. Nitrites were defined in the Helligenit comparator, while other parameters were determined according to standard methods (URL-2; URL-3).

## **Results and Discussion**

The experimental research has been performed for the characterization of the drinking water and its quality in some villages of the municipality of Zvecan, mainly to those water samples taken directly after the disk Trepca Mine, and the respective results of analysis are presented in the Tables 1-3.

In order to simplify the presentation of the results and not repeating values, we have been referred to the selected time for experiments. During the experiment is worth mentioning that all experiments were performed in the field conditions.

**Table 1.** Physical and chemical analysis of drinking water in village Mazhiq

<b>Parameters</b>	<b>Units</b>	<b>Standards</b>	<b>Actual Value</b>
Temperature	°K/°C	281.16 - 285 (8-12)	9
Wind		n.a	n.a
Taste		n.a	n.a
Blur	NTU	1.2 - 2.4	0.21
Color	Scale Co- Pt	10.0 - 20.0	n.a
Value of pH	pH	6.8 - 8.5/6.5 - 9.5	5.02
Wastage of KMnO <sub>4</sub>	mg/l O <sub>2</sub>	8*12**	2.16
Free Chlorine DPD1/DPD4	mg/l Cl <sub>2</sub>	0.2 - 0.5	n.a
Chloride	mg/l Cl	200	230
Ammonia	mg/l N	0.1	0.03
Nitrites	mg/l N	0.005	0.006
Nitrates	mg/l N	10	0.8
Iron	mg/l Fe	0.3	n.a
Manganese	mg/l Mn	0.05	n.a
Residue after evaporation	mg/l	800 - 1000	n.a
Electrical conductivity	ms/cm	1500	315
Lead	mg/Pb	0.01	n.a
Sulphates	mg/SO <sub>4</sub>	200	56.22
Hardness	dH	30	4.6
Phenol	mg/l	0.001	n.a
Detergents	mg/l	0.1	n.a

**Table 2.** Physical and chemical analysis of drinking water in the village Vllahi

<b>Parameters</b>	<b>Units</b>	<b>Standards</b>	<b>Actual Value</b>
Temperature	°K/°C	281.16 - 285 (8-12)	11.2
Wind		n.a	n.a
Taste		n.a	n.a
Blur	NTU	1.2 - 2.4	0.25
Color	Scale Co- Pt	10.0 - 20.0	n.a
Value of pH	pH	6.8 - 8.5/6.5 - 9.5	3.61
Wastage of KMnO <sub>4</sub>	mg/l O <sub>2</sub>	8*12**	3.67
Free Chlorine DPD1/DPD4	mg/l Cl <sub>2</sub>	0.2 - 0.5	n.a
Chloride	mg/l Cl	200	270
Ammonia	mg/l N	0.1	0.04
Nitrites	mg/l N	0.005	0.017
Nitrates	mg/l N	10	8.6
Iron	mg/l Fe	0.3	n.a
Manganese	mg/l Mn	0.05	n.a
Residue after evaporation	mg/l	800 - 1000	n.a
Electrical conductivity	ms/cm	15000	860
Lead	mg/Pb	0.01	n.a
Sulphates	mg/SO <sub>4</sub>	200	74.30
Hardness	dH	30	5.48
Phenol	mg/l	0.001	n.a
Detergents	mg/l	0.1	n.a

**Table 3.** Physical and chemical analysis of drinking water in village Zhazhë.

<b>Parameters</b>	<b>Units</b>	<b>Standards</b>	<b>Actual Value</b>
Temperature	°K/°C	281.16 - 285 (8-12)	6.5
Wind		n.a	n.a
Taste		n.a	n.a
Blur	NTU	1.2-2.4	0.10
Colour	Scale Co- Pt	10.0 - 20.0	n.a
Value of pH	pH	6.8 - 8.5/6.5 - 9.5	3.9
Wastage of KMnO4	mg/l O <sub>2</sub>	8*12**	3.76
Free Chlorine DPD1/DPD4	mg/l Cl <sub>2</sub>	0.2 - 0.5	n.a
Chloride	mg/l Cl	200	250
Ammonia	mg/l N	0.1	0.01
Nitrites	mg/l N	0.005	0.004
Nitrates	mg/l N	10	0.47
Iron	mg/l Fe	0.3	n.a
Manganese	mg/l Mn	0.05	n.a
Residue after evaporation	mg/l	800 - 1000	n.a
Electrical conductivity	ms/cm	15000	257
Lead	mg/Pb	0.01	n.a
Sulphates	mg/SO <sub>4</sub>	200	64.7
Hardness	dH	30	2.35
Phenol	mg/l	0.001	n.a
Detergents	mg/l	0.1	n.a

### Conclusion and Recommendation

Based on the physical and chemical analyses, it can be drawn this conclusion:

From all analysed samples of drinking water fountains and water wells, can be derived some results that most of them were characterized to be in normal range according to the allowed limits, but there was a case of sampling water which exceed the level of chemical contents and higher value of other physical indicators that the values of approved standards established by regulations of the country and international allowable values. This was the case of the water sample taken from wells drilled within the territory the village Crohn Mazhiq, which represent a high value for the nitrites ions to be 0.006 mg/l N, which is much higher than the recommended standard.

Except this case, all the analysed samples showed characteristics within the allowed limits and the water quality seems to be suitable for usage as drinking water, although no bacteriological characterization has been made to set the presence of the bacteria colonies.

Considering the water as a universal solvent, it can be distinguished that in all water samples analysed, there is a high value of acidity with a low pH, indicating the fact that Trepca mine minerals affected groundwater, increasing its acidity (lower the pH value).

This phenomenon has been observed only in this region of Kosovo, which is the most impacted area from Trepca mines and its mineral industry.

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## Evaluation of the Irrigation Waters of Çaycuma District in Terms of Certain Water Parameters

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**Abstract:** This study was conducted in the Çaycuma district of the Zonguldak Province, which is the district with the highest density of agricultural activities in the city. Water is the basic resource needed for life and is one of the most important factors that influence yield and quality in agricultural productions. In the present study, five locations were randomly selected amongst the irrigated fields of the district, and the irrigation water samples collected from these fields were analyzed to determine their pH and electrical conductivity, and their anion, cation, and boron contents. The relationships between all the measured properties were tested for statistical relevance with two-tailed Pearson correlation analysis. Boron content is an important parameter for growing the boron-susceptible plant species, and a positive relationship between boron (B) content and pH also Pearson correlation coefficient ( $r=0,992$ ) was found statistically significant at the level of  $p<0.01$ . On the other hand, a negative relationship between the electric conductivity and boron content was also determined ( $r=-0.929$ ) with the level of  $p<0.05$ . Evaluation of the analysis results reveals that the tested waters are appropriate even for growing the boron-susceptible plants and that it is possible to introduce a wide range of new products as an addition to the ones already grown in the region.

**Keywords:** *Irrigation water, Çaycuma, agricultural production, water quality, pH*

### Introduction

Due to the rapid increase of the world population, it becomes ever more difficult to provide enough food and water for the humankind. For the agriculturally intense areas, low-quality waters or the lack of ample amounts of water in nature represents a particularly important problem (Gülgün et al., 2013; Yazici et al., 2013; Aşur, 2017) As the natural resources in this regard grow scarce every day and as they become more polluted, the saline content of the soil increases and the waters become unsuitable for agricultural activities, forcing the plant growers to use low-quality waters for their irrigation purposes (Yeter and Yurtseven, 2015; Kıymaz et al., 2016; Sancak et al., 2017).

Even though our country holds a strong position in terms of agriculture and agriculture-based industries, the amounts of harvested products fail to reach the desired levels due to unconscious irrigation, enriching, and pest control methods involved with the agricultural sector in the country (Arslan et al., 2007). The primary objective in agricultural activities is to obtain the highest possible yield per unit area in a sustainable manner. In that regard, water represents one of the most important limiting factors for this goal. When this problem is evaluated with the perspective of future generations, the preservation of water resources become even more important (Howell and Tolck, 2001). Effective use of water is also important for proper and high-quality plant growth (Yudelman, 1994; Şimşek et al., 2017; Gülgün et al., 2015).

The quality of the water source, and its effects on the soil and plant development may show significant variation based on the water's physical and chemical properties. Furthermore, the salinity tolerance of the plants also varies based on the climate properties of the location, the amount of water used, and irrigation period and method. In order to be able to reach the desired levels of production, it is necessary to evaluate these quality properties in the irrigated locations (Rhoades, 1972; Şimşek et al., 2017). In the near future, it is possible that the water presence will become even scarcer and that there will be problems regarding the quality of the existing water (WWAP, 2012). For this reason, it is of utmost importance to identify and monitor the quality components of the water sources used for

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irrigation purposes in order to ensure the sustainability of the water presence and of agricultural activities (Kıymaz et al., 2016).

In Pakistan, used lake for to investigate biological, chemical and physical characteristics of drinking and irrigation waters. This study which in Pakistan have show a detailed review of drinking-water quality in the country and the consequent health impacts. The parameters analyzed in irrigation waters are respectively: pH, sulfates (mg/L), faecal coliform, electrical conductivity (mµmhos/ cm) total dissolved solids (mg/L), chlorides (mg/L), suspended solids (mg/L), magnesium (mg/L), dissolved oxygen (mg/L), nitrates (mg/L), biochemical oxygen demand (mg/L), calcium (mg/L), chemical oxygen demand (mg/L). This study have suggested that there is need to launch public awareness for educate people about the importance of safe irrigation water supplies (Aziz, 2005). In the studies Bafra Plain on the quality of groundwater water parameters like EC, pH, Na<sup>+</sup>, Ca<sup>+2</sup>, K<sup>+</sup>, Mg<sup>+2</sup>, CO<sub>3</sub><sup>-2</sup>, HCO<sub>3</sub><sup>-</sup>, Cl and SO<sub>4</sub><sup>-2</sup> was determined very significant changes and so have suggested that the irrigation should not be done (Arslan et al. 2007). In the study performed in Kırşehir province, samples were collected from 40 regions used in irrigation. In the study, it was observed that the waters had neutral or alkaline properties and was determined the sulphate concentrations varied between 1.49 and 299.7 ppm (Şimşek *et al.*, 2017).

Çaycuma district is located within the Zonguldak province, which in turn is located in the Black Sea Region of Turkey. The district is positioned between the two shoulders of the Filyos Valley. Çaycuma has a wide range of agricultural products, and besides the vegetables, fruits, and feed plants produced in the city, ornamental plants are also gaining popularity in the region. The fact that numerous types of agricultural activities are conducted in the province makes the irrigation water quality even a more important property.

Analysis of irrigation water to determine the content beforehand; with this water can be prevented the increase of salinity in the land irrigated with time, with the use of fertilizers can ensure the continuity of soil fertility. The awareness of the need to analyze the irrigation water in our region will increase the efficiency of the fertilizer used, the correct use of water resources, soil fertility.

Zonguldak city is not suitable for agricultural production especially due to have thermal power plants and uneven terrain sourced from the geographical structure of the city center. For this reason, in this study it is aimed to determine chemical properties of irrigation water samples taken from 5 different locations and take required measures at Çaycuma region where agricultural production is dense.

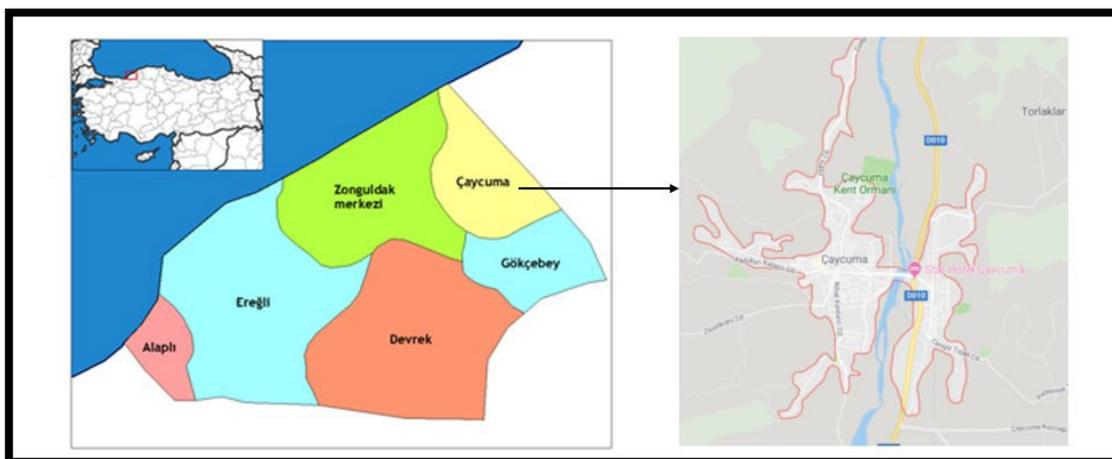
## Materials and Methods

Çaycuma district of Zonguldak is quite prominent in terms of agricultural activities. The fertile plains along the Filyos Valley constitute the agricultural power of the district, which is also its economic cornerstone. The mild climate of the Black Sea Region is predominant in the region, and the annual average precipitation is between 1250 and 1500 kg/m<sup>2</sup>, most of which occurs during the spring and the fall (Anonymous, 2019; Figure 1).

The samples for the study were collected from 5 different locations in Çaycuma. The selected regions have different environmental impacts and are also areas where agricultural activities are generally concentrated. The water samples analyzed were taken from three different locations which are rivers, taps and wells. Table 1 represents the locations from which the samples were taken, along with each location's distance to district centrum.

**Table 1.** Locations from which the water samples were collected from.

Sample Locations	GPS coordinates	Distance to center (km)
Çaycuma River	41° 25' 43.1112" Northand 32° 4' 37.9416" East gps	0
Çaycuma Drinking Water	41° 25' 43.1112" Northand 32° 4' 37.9416" East gps	0
Perşembe Municipality	41° 24' 50.8860" Northand 32° 9' 29.6532" East gps	7
Kayıkçılar Village	41° 21' 42.3072" Northand ve 32° 10' 37.4664" East gps	5
Kayıkçılar Wells Water	41° 21' 42.3072" Northand ve 32° 10' 37.4664" East gps	5



**Figure 1.** Location of the research area

During the sampling, the criterions defined by Ayyıldız (1990) were taken as a basis. When collecting the samples from rivers, the sampling was made from a depth of 30 to 40 cm. Considering the hydrodynamic properties of the water, parameters like temperature, pH, and electrical conductivity were measured in a laboratory right after the collection of the sample. High-density polyethylene sample jars were used to store the samples. When collecting samples from taps, the water was run for a few minutes first. Furthermore, the vicinity of the tap and the tap itself was cleaned with alcohol before sample collection. When collecting samples from wells, samples were taken into the containers after a certain period of water pumping.

The collected samples were transported to Bülent Ecevit University (BEU) Çaycuma Food and Agriculture Vocational High School Chemical Technologies Laboratory for analysis, except for anion and cation measurements, which were performed in BEU Central Laboratories. For anion-cation analysis was used ion chromatography. Carbonate-bicarbonate analysis was determined by titration method by using digital burette. Boron was determined by spectrophotometric method.

## Results and Discussions

### Correlation Analysis

The results of the analysis were evaluated in SPSS 22 software. All the relationships between the measured water properties were determined using the two-tailed Pearson correlation analysis and given Table 2. A strong and positive relationship between was determined between the boron content and pH ( $r= 0.992$ ) with significance level  $p<0.01$ . On the other hand, a strong negative relationship between the boron content and electric conductivity was also determined ( $r=- 0.929$ ) with significance level  $p<0.05$ . Other positive and meaningful relationships were between: Ca and Na content ( $r=0.925$ ), Ca and Sulphate ( $r = 0.885$ ), Ca and Mg ( $r = 0.945$ ), and Na and Chloride ( $r = 0.912$ ).

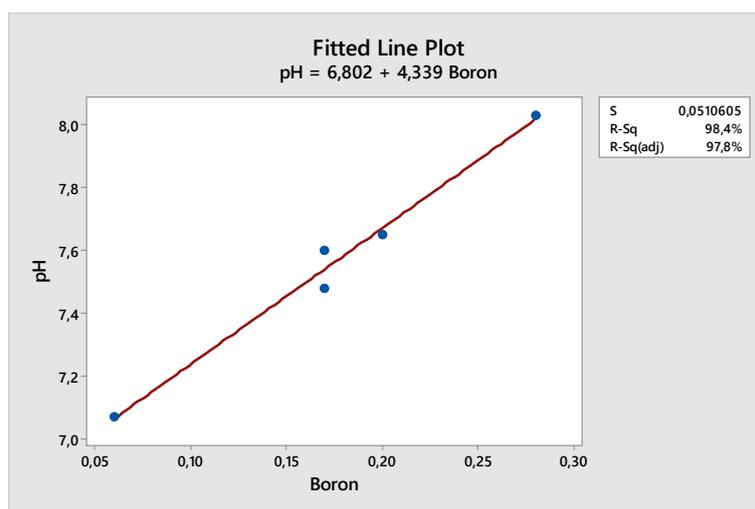
**Table 2.** The relationships between the measured water properties.

	pH	EC	C	HCO <sub>3</sub>	Bor	Klorür	Sülfat	Nitrat	Na	K	Ca	Mg	%Na
pH	1												
EC	-.874	1											
C	-.785	.785	1										
HCO <sub>3</sub>	-.836	.935*	.588	1									
Bor	.992**	-.929*	-.805	-.880*	1								
Klorür	.021	-.176	-.626	.047	.062	1							
Suphat	.138	.171	-.388	.227	.058	.515	1						
Nitrat	.360	-.580	-.719	-.263	.432	.607	-.094	1					
Na	.377	-.382	-.851	-.152	.388	.912*	.662	.635	1				
K	.706	-.667	-.954*	-.400	.717	.599	.376	.808	.831	1			
Ca	.321	-.149	-.718	.040	.284	.775	.885*	.375	.925*	.729	1		
Mg	.264	-.063	-.656	.193	.220	.690	.797	.475	.852	.765	.945*	1	
%Na	.726	-.960**	-.695	-.931*	.805	.242	-.254	.534	.348	.526	.060	-.081	1

\*\* values for  $p<0.01$  (double-tailed), \* values for  $p<0.05$  (double-tailed)

**The Regression Between the Boron Content and pH**

The boron content of the irrigation water is very influential in product growth and its quality (Brown et al., 2002; Hilal et al., 2011). This study is therefore quite relevant, as the investigation of the toxicity of the boron content is quite important for the Çaycuma district in which vegetables and fruits are the products grown the most. As the boron content of the water increases, the plants’ capability of performing photosynthesis drops, slowing down the plants’ growth and shortening their lives (Wei et al., 2001; Parks and Edwards, 2005). A regression analysis of boron content was performed in the present study and it shows high correlation with pH, and the regression equation and the corresponding graph is presented in Figure 2.



**Figure 2.** The regression graph between the boron versus pH.

Inspection of Figure 2 reveals that as the boron content increases, the pH also increases. At Table 3 given the regression analysis results parameters with F and p values. The results of  $R^2 = 98.4\%$  and  $R^2 \text{ linear} = 97.8\%$  are clear indicators that the pH value of a given water source can be used to determine if the water can be used for irrigation, considering the boron-accumulation problems.

**Table 3.** The regression analysis results for boron and pH.

Analysis of Variance					
Source	DF	SS	MS	F	p
Regression	1	0.0245113	0.0245113	179.93	0.001
Error	3	0.0004087	0.0001362		
Total	4	0.0249200			

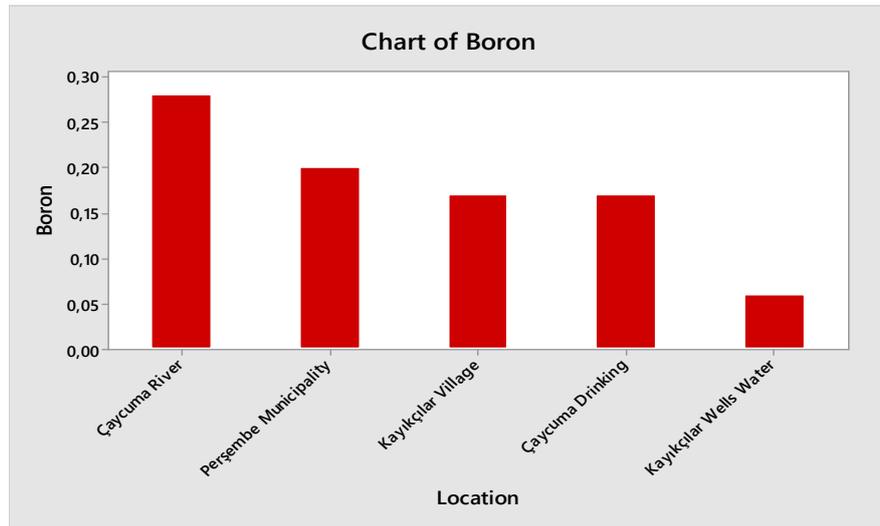
The location-based distribution of boron content in the region is given in Figure 3. As can be seen, Çaycuma River has the most content with 0.28 ppm, while the lowest boron content is in Kayıkçılar Well waters with 0.06 ppm. The boron content is lower than 0.3 ppm in all locations. The boron content limit for the susceptible plants is between 1 and 1.25 ppm. The results clearly indicate that the waters of our district can be used for irrigation of even the boron-susceptible plants.

**Irrigation Water Analysis Results based on Location**

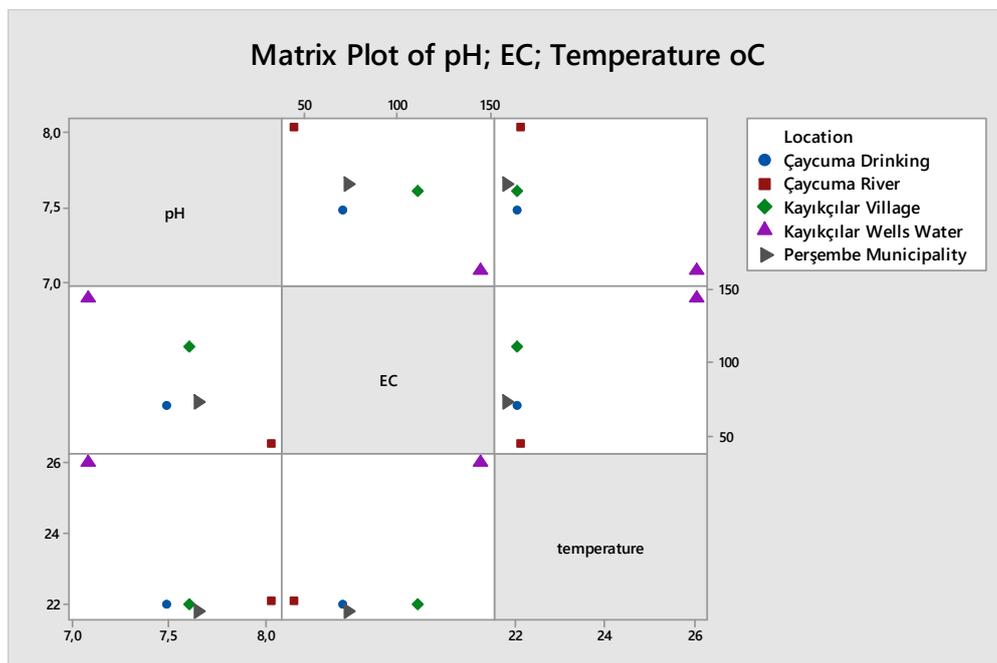
Minitab 15 software was used to prepare the graphical illustrations of analysis results. Figures 4 and 5 represent the anion, cation, pH, electric conductivity, and temperature parameters in matrix graphs. pH values between 6.5 and 8.4 are considered to be normal for irrigation waters, and inspection of Figure 3 reveals that the lowest pH value in our region is in the Kayıkçılar Village with pH 7.07, and highest in the Çaycuma River with pH 8.03. All locations had lower than 145 µmhos/cm electrical conductivity, which meets the “very good quality” criteria of Schofield System that is <145 µmhos/cm.

Inspection of Figure 5 the lowest nitrate, sulphate, chloride, sodium, potassium, and calcium levels were determined to be in the well waters of the Kayıkçılar Village used particularly in greenhouse and field irrigation with 0, 2.57, 0.24, 6.54, 0.13, and 12.57 ppm levels, respectively. Even

though sulphate is less toxic than chloride, it is still relevant for irrigation waters as it causes the sedimentation of calcium. The highest sulphate content was observed in the Kayıkçılar village with 223.82 ppm, and the well-water sulphate content of that particular region was found to be 2.57 ppm, which is the lowest observed amongst our samples. For this reason, in order to prevent the soil from getting harmed with sulphate accumulation, the waters of that particular well should be used for the irrigation of the region. Ministry of Forestry and Water Affairs General Directorate of Water Management has determined the limit chloride level as 4 me/l, and the chloride concentration in our region varies between 0.035 - 0.618 me/l.

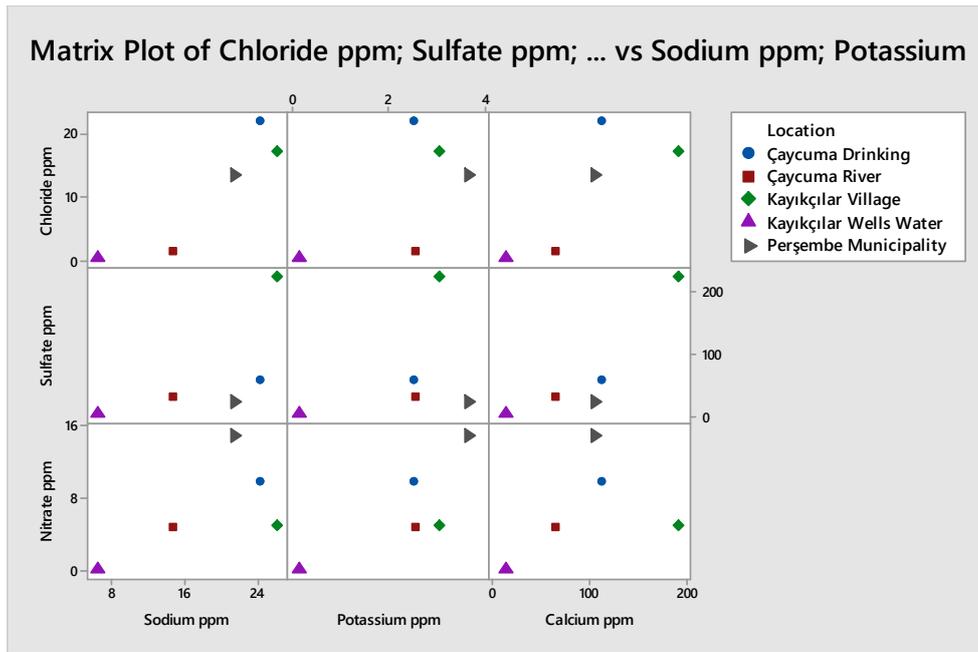


**Figure 3.** Distribution of boron content

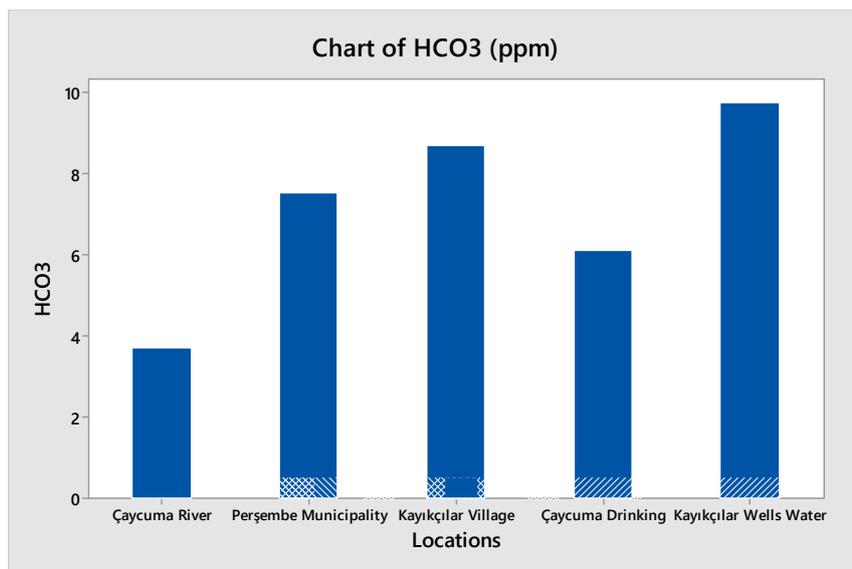


**Figure 4.** Matrix-graph of pH, electrical conductivity, and temperature parameters

Waters with bio-carbonate content can increase the sodium level variable of the agricultural soils. The carbonate concentration in all locations in our region is 0, while the lowest bio-carbonate levels were determined in the Çaycuma river with 3.72 ppm, and the highest in Kayıkçılar village well water with 9.77 ppm (Figure 6). These values are ideal for all kinds of irrigations.



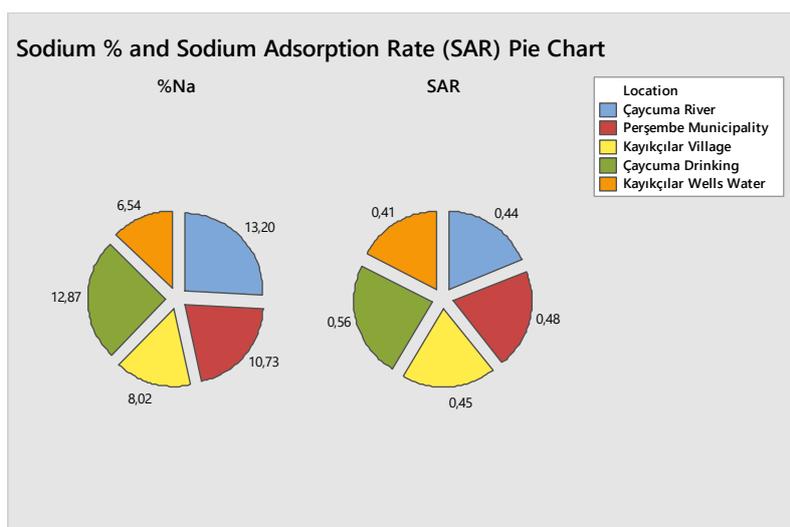
**Figure 5.** Matrix-graph of anion and cation parameters



**Figure 6.** Distribution of bio-carbonate levels based on locations

As the sodium concentration increases, the Sodium Adsorption Rate (SAR) also increases. SAR is an important parameter for alkalinity, and if it's between 0 and 10 in a water source, that water can be used for all kinds of irrigation purposes. The SAR values in our region vary between 0.41 and 0.56 and its chance of creating alkalinity is quite low. According to Schofield System, Na% value considered "very good" is <20. As can be seen in Figure 7, the highest Na% level in our region was found to be in Çaycuma River with 13.20 ppm, which meets the <20 requirements. Table 4 represents the salinity and alkalinity classifications for the studied locations. T1 is the low salty and T4 is in very high salt water class. Also A1 is located in the class of low sodium and A4 very high sodium water. T3 is the class of high salt water and it can be used in irrigation of salt resistant plants. T2 is a medium-salt water class and can be used to irrigate all plants except saline-sensitive plants.

When Table 4 is examined, the wells water in the Perşembe municipality and Kayıkçılar village is in the high salt water class and the other locations are classified as medium salt water. The alkalinity class has been involved in all classes less sodium salt.



**Figure 7.** Na% and SAR distribution based on locations.

**Table 4.** Classifications of the Irrigation Waters

Locationlar	Irrigation water class
Çaycuma River	T2A1
Çaycuma Drinking Water	T2A1
Perşembe Municipality	T3A1
Kayıkçılar Village	T2A1
Kayıkçılar Wells Water	T3A1

*T: Salinity A: Alkalinity*

## Results

The water sample collected from the Kayıkçılar Village Wells water and Perşembe Municipality irrigation system were found to be of high quality and salinity and to have low sodium content. Çaycuma River and tap water samples, and Kayıkçılar Village irrigation waters were found to be of medium salinity and to have low sodium content. From the boron content perspective, all of the water samples were determined to be proper to use in irrigation, even for the growing of boron-susceptible species. pH values of the water samples vary between 7.4 and 8.3, and a statistically relevant positive correlation was determined between the pH value and boron content. The fact that the minimum pH value of our waters was found as 7.4 indicates that our waters are relatively soft, as they can't meet the  $pH < 7$  requirements to dissolve minerals like calcium carbonate, magnesium and sulphate. Evaluation of the anion contents reveals that the Kayıkçılar Village is at the limit level in terms of sulphate content.

The highest pH in our region was found in Çaycuma River with 8.03. This pH value is close to the maximum portion of the pH values (6,5-8,4) for the regions where Çaycuma River is used. Since the soil has high buffering capacity, it takes a long time to be affected by irrigation water. However, if the soil is affected, different preventions should be taken instead of trying to correct the pH of the water. In routine measure of pH of irrigation waters, should be add to lime for low pH and add sulfur and other acid based formulations to correct high pH. Awareness should be made about this issue. The routine controls of the pH value in the irrigation water and taking necessary measures will contribute to the economic activities as well.

The most important parameters affecting the intake of boron by plants are irrigation water and soil pH (Bartleta ve Picarelli, 1973; Bennett ve Mathias, 1973; Demirtaş, 2005). High levels of boron in irrigation water or soil can cause product losses. Boron element is usually carried by water in plants makes the boron content of irrigation water important. The regression between boron and pH was found to be statistically significant at  $F = 179,93$  and  $p = 0,001$ , which enabled the monitoring of the effect of boron mineral, which damages sensitive plants, for our region by pH analysis and to take measures against possible increase. The salinity results of the Perşembe municipality and Kayıkçılar well water were found T3 and the irrigation water of these regions contain a large amount of salt.

In Kayıkçılar village, where the maximum amount of sulphate is 223,82 ppm, have recommended to use well water ortouse it in times of high pH in order not to damage the soil. In general, we suggest that excellent quality parameters of irrigation Water and the availability of favorable, flat lands in Çaycuma allow this region to be used in agricultural tourism activities.

Kayıkçılar village residents generally use the well water in the garden, greenhouse and fields, so that they do not create salinity problems in case they are used continuously, it is necessary to raise awareness about the necessity of applying some washing water together with each irrigation water and the necessity of growing the plant to be salt resistant.

Literature studies have shown that high-quality water allows higher yields when used in good soil and water practices (Şimşek et al., 2017). For this reason, the irrigation water quality of the regions that depend on agriculture to sustain their economies should be determined and monitored in order to help take precautions against changes that may occur in the parameters that influence the yields.

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## Determination of Heavy Metals in the Lumbardhi River, Prizren - Kosovo

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**Abstract** - This paper elaborates the monitoring of surface water pollution in the River Lumbardhi of Prizren town, from the source of the river to the discharge into the other river known as Drini i Bardhë, monitoring the flow of the river both in rural and urban areas. The biggest problem in environmental protection is the quality of surface water. A number of chemical-physical parameters and some heavy metals have been analysed. Heavy metals analysis was done through the technique known as FAAS (Flame Atomic Absorption Spectroscopy), and the results show that concentration is within the permissible levels and as such do not pose a risk in the future for human health.

**Keywords:** *FAAS, Copper (Cu), Iron (Fe), Zinc (Zn), Nickel (Ni), Chromium (Cr)*

### Introduction

The natural concentration of metals in raw water which has not been treated or purified varies from state to state, country to country. It depends on many factors such as geological structures, the soil, the acidity of the water and the particulate matter concentration. Most metal species in natural fresh water occur in organic compounds, organic complexes or colloids (Nalatambi, 2009). Major industrial sources include surface treatment processes with elements such as Cd, Pb, Mn, Cu, Zn, Cr, Hg, As, Fe and Ni, as well as industrial products that, at the end of their life, are discharged in wastes (Baysal *et al.*, 2012). Therefore, World Health Organization (WHO) and European Community recommend controlling toxic metal ions in food sources in order to guarantee food safety and Flame Atomic Absorption Spectrometry (FAAS) is widely used and preferred for determination of toxic elements (Alpdoğan *et al.*, 2016).

The Lumbardhi River emanates into the Sharri Mountains and flows into the White Drini. It runs through the middle of the city of Prizren (Abdullahu Sh., 1979). There are discharges of rural and urban waters without any prior treatment. Urban discharge waters originate from households, municipal services, industrial discharges, anthropogenic factors, agricultural waste, *etc.* (Çullaj, 2011). Unlike the municipal wastewater, whose composition is known, it is difficult to know the origin of discharge waters from different industries, pollutants and their specific components. Based on the samples taken in the field and the analyses carried out in the laboratory, the quality of surface water in the Lumbardhi River was assessed by pollutants, concentrations of some heavy metals, for the period February-March 2019. The aim of monitoring the quality of the Lumbardhi River surface water is to analyse its quality, the dynamics of change during water flows (melting of snow, rains, *etc.*). This is especially important in the Lumbardhi River where industrial, urban discharges take place, because pollution has a great impact on the quality of surface water and the environment.

### Material and Methods

Physical and chemical parameter analyses have been done at the Laboratory of the Department of Food Science and Biotechnology at UBT Prishtina, in order to evaluate the real situation of the Lumbardhi River. Research has been carried out in six sampling points: Lumbardhi source - Prevalla (L1); Sredska (L2), Andrra (L3), City Park (L4), Vlashnje (L5), Drini i Bardhë (L6).

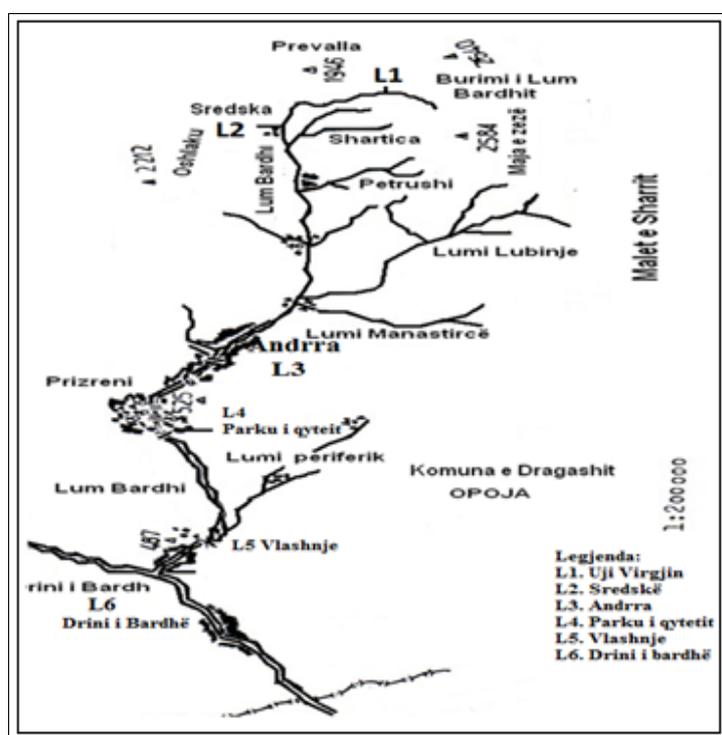
During the study, we have monitored the entire Lumbardhi River flow from its source to its joining with the River Drini i Bardhë. We think that there are still no measures taken by the municipal bodies for wastewater treatment, industrial ones and other recipients to make our river cleaner. The waterfall as an element of particular importance varies from season to season. This also causes the

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change of contaminants during the seasons of the year. The following physicochemical parameters are presented, as shown in the following tables as well as heavy metals: Copper, Iron, Zinc, Nickel and Chromium data are collected and recorded according to standardized methods. The above-mentioned metal concentration has been analysed using the analytical technique known as Flame Atomic Absorption Spectroscopy (FAAS) - Model Perkin Elmer AA300.

### Sampling and sample preparation

The taking of Samples was done in the intervals of time: February, March 2019, in six sampling points. Taking the water sample for laboratory analysis is done according to the known standards, concretely according to the standard methods based on ISO 5667-5 of 2006, for standard sampling rules. Nitric acid (HNO<sub>3</sub>) is added in water samples for heavy metal analysis during the sampling of water. For each metal we have prepared a series of standards with known concentrations from stock solutions with a concentration of 1000 mg/l (ppm) and then constructed calibration curves for each of them. Sampling points for monitoring the pollution of Lumbardhi are shown in Figure 1.



**Figure 1.** Sampling points map (Shukri, 1979)

### Results and Discussion

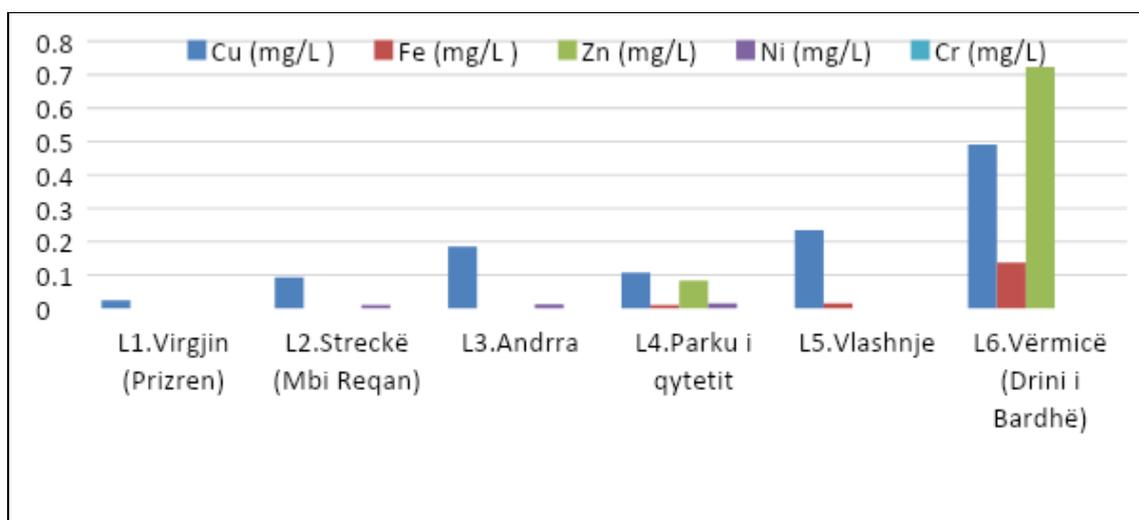
**Table 1.** Some physico-chemical parameters in the Lumbardhi River for the period February - March 2019.

Sampling points	pH	Temp.	Saturation with O <sub>2</sub> (%)	O <sub>2</sub> mg/l (ppm)	Conductivity (µs/cm)	Time of sampling
L1. Virgin (Prizren)	8.26	13.3	88	8.4	173.6	11:00
L2. Streckë (Above Reqan)	8.44	8.5	88	9.1	223	12:05
L3. Andrra	8.24	9.1	89.2	9.2	218	12:50
L4. City Park	8.2	10.6	82.5	8.5	255	13:15
L5. Vlashnje	8.2	9.9	76.6	7.7	303	13:50
L6. Vërmicë (Drini i Bardhë)	8.58	13.8	93.5	9.0	433	15:00

**Table 2.** Concentrations of some heavy metals in the Lumbardhi River for the period February - March 2019.

Sampling points	Cu (mg/L)	Fe (mg/L)	Zn (mg/L)	Ni (mg/L)	Cr (mg/L)
L1. Virgin (Prizren)	0.024	< LOD	< LOD	0	< LOD
L2. Streckë (Above Reqan)	0.093	<LOD	< LOD	0.01	< LOD
L3. Andrra	0.185	< LOD	< LOD	0.012	< LOD
L4. City Park	0.107	0.01	0.083	0.015	< LOD
L5. Vlashnje	0.234	0.015	< LOD	0.017	< LOD
L6. Vërmicë (Drini i Bardhë)	0.490	0.137	0.723	0.015	< LOD

*LOD- Limit of Detection*



**Figure 2.** Graphic presentation of some heavy metals of the River Lumbardhi for the period February - March 2019.

### Discussion

From tab. 2 and fig. 2 we can see that some heavy metals are present in the analysed water, but within permissible levels set by EU, WHO and FAO. Based on the methodology of the study we think that we have managed to qualitatively analyse the pollution of the Lumbardhi River in six locations during the interval February-March 2019. During the physical-chemical analysis of the surface water quality, the samples taken at the sampling points have variations regarding the concentrations of Copper (Cu.), Iron (Fe), Zinc (Zn) and Nickel (Ni). From the table 2 we can see that in all the analysed samples we have the presence of Cu though within permissible levels. From the sampling points regarding the Fe concentration, we can see that in three of them we have detected the presence of Fe, even though like with other metals the Fe concentration it was within the permissible levels. Zinc is detected only in the two analysed samples, although in one of them this metal exhibits higher values compared to other metals, probably as a result of the slightly larger pollution at this sampling point. According to the Ni concentration, we can see that almost in all analysed samples we have detected this heavy metal, and it is believed that this comes as a result that this heavy metal (mineral) is present in our region, given these that have been introduced since the eighties (Pula Xh. & Beqiri L., 1985). From the obtained results we can see that in all the analysed samples the concentration of Cr was not detected.

### Conclusions

Based on the data presented in this article we can conclude that concentrations of analysed heavy metals in the water of Lumbardhi River are within the permissible levels and as such these heavy metals do not pose a risk to human health in the future.

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## Protective effects of humic acid against chromium stress in wheat (*Triticum aestivum* L. cv. Delabrad-2)

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**Abstract:** Wheat (*T. aestivum*) is the world's most widely cereal crop and is a staple food for a over 50 % world's population. Soils contaminated with heavy metals may cause deleterious effects on human health. However, humic substances (humic acid and fulvic acid) might benefit plant growth by improving nutrient uptake and the activation of biomass production. Hence, the objective of the current study was to investigate the effects of humic acid (HA) on photosynthetic pigment and malondialdehyde content (MDA) against chromium stress in *Triticum aestivum* L. cv. Delabrad-2. For this purpose, four Cr treatments (0.10, 0.20, 0.30, 0.50 mM) were applied to wheat seedlings and the liquid humic acid sprayed on the leaves at 1.5 mg L<sup>-1</sup> dose alone or in combination with chromium stress for 21 days. According to our results, the higher concentration of Cr was found in the leaves in comparison with roots and stems of wheat plants. The treatment with 0.6 mM Cr concentration was the most effective for wheat. Total carotenoid, total chlorophyll, chlorophyll a and b contents decreased in groups only chromium compared to HA+Cr groups depending on the increased chromium dose. However, the application of HA increased the chlorophyll a/b ratio and MDA content in plants as compared with Cr treatment alone. We conclude that HA application eliminated the toxicity of Cr stress by modulating the photosynthetic activities in wheat.

**Keywords:** *Wheat, Heavy metal stress, Humic acid, photosynthetic pigment,*

### Introduction

In recent years, rapid grown in the agricultural and industrial sectors has also led to an increase in the levels of various heavy metals in soil and aquatic environment (Sohail et al., 2016). Soils polluted with heavy metals have threatened living organisms including plants and animals (Ali et al., 2015; Adrees et al., 2015). Chromium (Cr) is one of the 18 core hazardous air pollutants and causes serious environmental contamination in soil and groundwater (Shankar et al., 2005). In plants, Cr is found in the forms of trivalent and hexavalent and Cr (III) is relatively stable and less toxic than Cr (IV) (Chattopadhyay et al., 2010; Oliveira, 2012). This toxicity of Cr(IV) includes reduced plant growth and development, the inhibition of photosynthesis and enzymatic activities, chlorosis and ultimately plant death (Gill et al., 2015; Bukhari et al., 2016).

Bioaccumulation and toxicity of Cr has been reported in various crops (Mishra et al., 1997; Singh, 2001; Shanker, 2003). It is known that Cr is toxic to most higher plants at about 0.5 to 5.0 mg mL<sup>-1</sup> in nutrient solution and 5 to 100 mg g<sup>-1</sup> in soil (Davies et al., 2002; Oliveira, 2012). Chromium eventually accumulates in crops from contaminated soils and is mainly retained in the root tissues (Ahmed et al., 2016; Jaison and Muthukumar, 2016). Studies also reported that Cr stress affects photosynthesis in terms of carbon assimilation, electron transport and photophosphorylation in plants (Barbosa et al., 2007; Rodriguez et al., 2012). Decrease in photosynthetic pigments by chromium can be ascribed to the inhibition of the electron transport processes and to the disorder of ultrastructure of chloroplasts (Pandey and Sharma, 2003; Shanker et al., 2005). Moreover, it was found that Cr toxicity caused the ultrastructural changes in the form of lamellar system (Ali et al., 2013). The reduction in the content of photosynthetic pigments due to Cr toxicity has been reported in many plants (Sharma and Sharma, 1996; Nichols et al, 2000; Shanker, 2003).

Exposure of plants to high levels of Cr also leads to enhanced production of reactive oxygen species (ROS) (Islam et al, 2014; Gill et al., 2015). Lipid peroxidation is the most deleterious influence caused

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by Cr and heavy metals induced ROS (Mithofer et al., 2004). Malondialdehyde (MDA) is one of the cytotoxic products of lipid peroxidation and an indicator of free radical production and tissue damage (Ohkawa et al., 1979). It was also reported that over production of ROS in plants under stress conditions can damage in selective permeability of biological membrane structure. Absorption of Cr is facilitated by a carrier membrane, the cell membrane stability are very important (Maiti et al., 2012).

Humic substances (fulvic acid and humic acid) are the main components of soil organic matter (Chen and Aviad, 1990). Humic acids (HA) are characterized as having high molecular weight and a heterogenous natural resource (Larcher, 2003). It has been reported that humic substances in the soil caused to increase the uptake of mineral elements and the weights of crop plants (Kausar et al., 1985; Chen et al., 2004). Eyheraguibel et al. (2008) showed that humic acid application increased the length and dry weight of maize plant roots. Furthermore, it was reported that humic acid leads to increased biological yield through increasing nitrogen content of the plant (Ayas and Gülser, 2005). According to Tufail et al. (2014), humic acid stimulated the growth of root and shoot of wheat plants. Studies on the effects of humic substances on plant growth showed that the promoting effects of humic acid was associated with increasing cell membrane permeability, oxygen and phosphate uptake, respiration and photosynthesis and root cell elongation (Tan, 2003; Türkmen et al., 2004). Recently, it has been reported that humic substances is used for effectively removal of heavy metals from aqueous media. (Tang et al., 2014). However, little information is available on the effects of humic acid against Cr stress. The aim of this study was to determine the effects of humic acid in terms of photosynthetic pigments and malondialdehyde content against Cr stress on wheat plants.

## **Materials and Methods**

### *Plant Material and Experimental Design*

The wheat seedlings (*Triticum aestivum* cv. Delabrad-2), which grown as bread wheat in Amasya (Suluova), were used in this study. Germinated wheat seedlings were transferred to plastic pots each containing sand and soil and were grown under controlled conditions (light/dark regime of 16/8 h at 25 °C, relative humidity of 70 %). The seedlings were grown for four weeks and 2.0 mg/L humic acid were treated alone or in combination with various concentrations chromium stress (0.20, 0.40 and 0.60mM).

### *Determination of Pigment and Malondialdehyde Content (MDA)*

Carotenoid and chlorophyll contents were extracted from the uppermost leaves of wheat plants. Concentrations of chlorophyll a, chlorophyll b and carotenoids were calculated using the method of Lichtenthaler and Welburn (1983). MDA content was determined spectrophotometrically as described by Heath and Packer (1968). The absorbance of supernatant was recorded at 532, 600 and 450 nm. The MDA content was calculated by using its molar extinction coefficient of 155 mM<sup>-1</sup> cm<sup>-1</sup>.

### *Determination of Cr Contents*

After washing, the samples were divided into root, stem and leaves. Then all samples are washed with 2% HCl and with tap and distilled water. The samples were dried in an oven at 105 °C. This process was continued until a constant weight was reached. Plant samples (1/2 g dry weight) were transferred to pyrex tubes. Heavy metals were digested for (7.5 mL) 65% HNO<sub>3</sub> and (2.5 mL) 36% HCl at 25 °C for 12 hours. Then, the samples were heated at 105 °C in the incubator for 2 hours. Chromium contents in samples were determined by using atomic absorption spectrometry (Thermo scientific ice 3000 series) using the method by Lamhamdi et al. (2013).

### *Statistical Analysis*

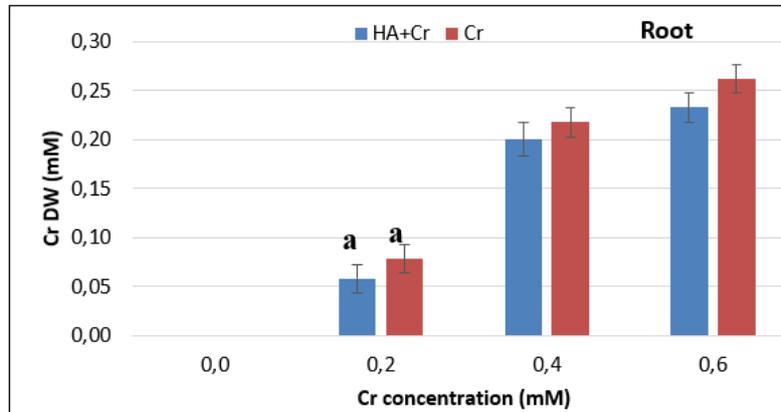
All values in results are mean of at least three replicates±standard deviation (SD). The data were analysed using SPSS version 12.0. Tukey's post-test (at a significance level of p< 0.05) was used to compare the treatment groups.

## **Results and Discussion**

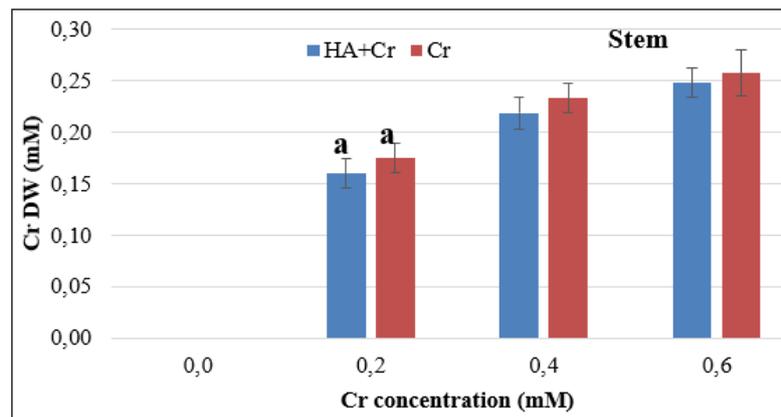
### **Effect of HA on Cr Uptake by Wheat Plants**

In this study, the amount of Cr in the root, stem and leaf parts increased significantly with increasing Cr levels (Figures 1-3). The higher concentration of Cr was found in the leaves in comparison with roots and stems of wheat plants. The treatment with 0.6 mM Cr concentration was the most effective for wheat

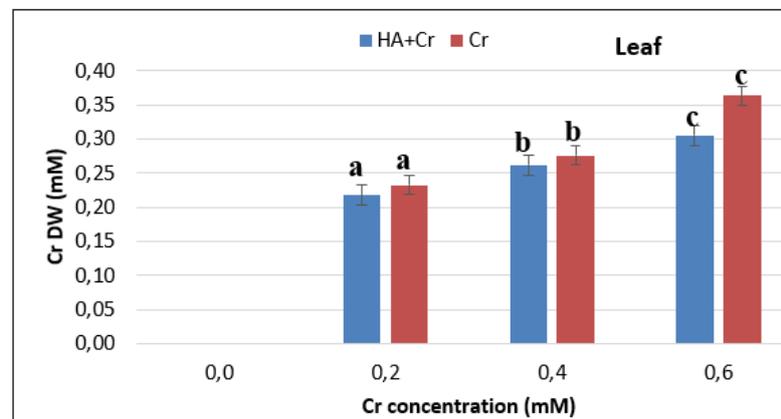
(Figure 3). However, it was found that the Cr toxicity is more predominant in root compared to leaf and shoot in many plant species such as wheat in the previous study (Ali et al., 2013; Dotaniya et al., 2014; Gill et al., 2015). Ali et al. (2018) also reported that the accumulation of Cr in roots was significantly higher than both stem and leaves in wheat plants. In this study, higher Cr amounts in leaves might be due to fast translocation and more accumulation of Cr in leaves compared to root and stem.



**Figure 1.** Effects of HA on Cr accumulation in root of wheat plants under Cr stress. Values are means of three replicates. Different letters indicate significant difference at  $p < 0.05$  (Tukey's multiple range test).



**Figure 2.** Effects of HA on Cr accumulation in stem of wheat plants under Cr stress. Values are means of three replicates. Different letters indicate significant difference at  $p < 0.05$  (Tukey's multiple range test).

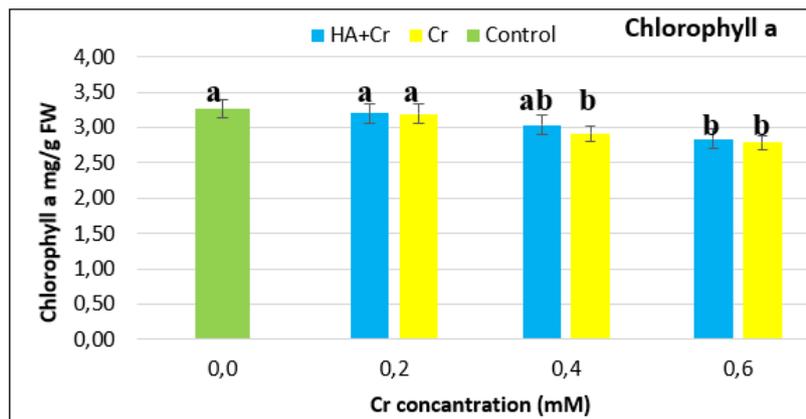


**Figure 3.** Effects of HA on Cr accumulation in leaves of wheat plants under Cr stress. Values are means of three replicates. Different letters indicate significant difference at  $p < 0.05$  (Tukey's multiple range test).

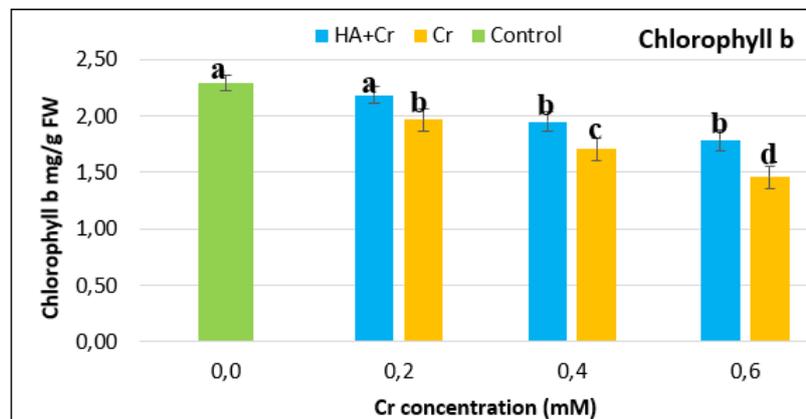
Application of HA markedly ( $p < 0.05$ ) decreased Cr toxicity compared to Cr-treated groups only. (Figures 1-3). The role of humic acid in reducing heavy metal stress in soil has been reported earlier by some researchers (Harter and Naidu, 2001; Billingham, 2015). Chen and Aviad (1990) reported that humic substances have more profound effects in growth, plant height and dry weight. Similarly, root and shoot weight were increased in response to foliar application of humic acid to tomato plants (Yildirim, 2007). A remarkable reduction in Cr uptake was reported in the treatment with fulvic acid (FA) in *Triticum aestivum* L (Ali et al., 2015). Decreased Cr uptake with FA might be caused by competition between other essential nutrients and Cr in the soil (Matysiak et al., 2011; Ali et al., 2013).

Effect of HA on Photosynthetic pigments and MDA

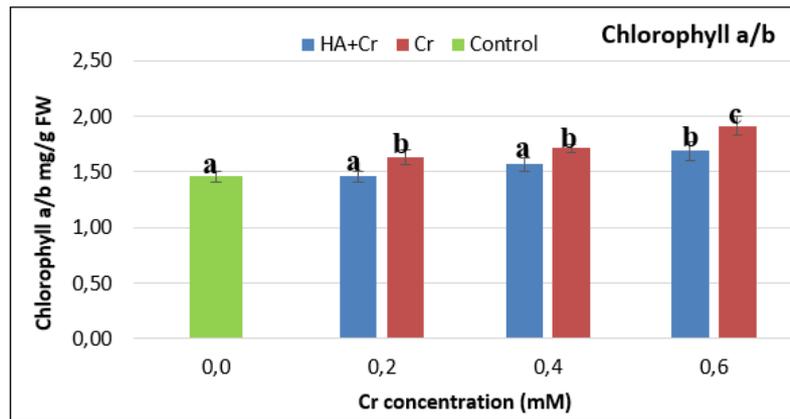
Total Chlorophyll, total carotenoid, chlorophyll a and chlorophyll b, concentrations were decreased with the application of Cr alone. This reduction in photosynthetic pigments was more higher especially under highest Cr stress (Figures 4- 8). Decreased chlorophyll content associated with Cr stress in various plant was also previously reported by some researchers (Sharma and Sharma, 1993; Nichols et al., 2000; Zengin and Munzuroğlu, 2006). The reduction of photosynthetic pigments induced by Cr was attributed to disorganizations in the chloroplast membranes and to the inhibition of gas exchange parameters and electron transport (Vazquez et al., 1987; Ali et al., 2011; Gill et al., 2015). Ehsan et al. (2013) was also reported that ROS generation under metal stress caused reduction in chlorophyll pigments. In earlier studies, chromium also caused a reduction in the chlorophyll concentration of wheat plants (Sharma et al., 1995; Subrahmanyam, 2008). In our study, increase in chlorophyll a/b ratio indicates that chlorophyll b is more sensitive to Cr toxicity than chlorophyll a in *Triticum aestivum* cv. Delabrad-2 (Figure 6). These findings are in agreement with the findings of Zengin and Munzuroğlu (2005) and Subrahmanyam (2008).



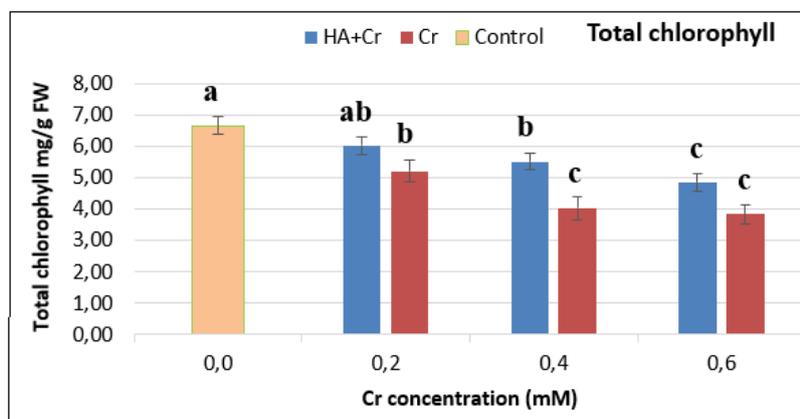
**Figure 4.** Effects of HA on the content of chlorophyll a of wheat plants under Cr stress. Values are means of three replicates. Different letters indicate significant difference at  $p < 0.05$  (Tukey's multiple range test).



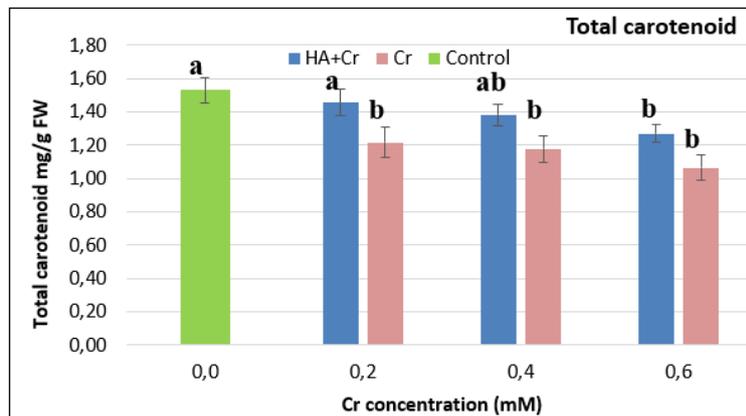
**Figure 5.** Effects of HA on the content of chlorophyll b of wheat plants under Cr stress. Values are means of three replicates. Different letters indicate significant difference at  $p < 0.05$  (Tukey's multiple range test).



**Figure 6.** Effects of HA on the content of Chlorophyll a/b of wheat plants under Cr stress. Values are means of three replicates. Different letters indicate significant difference at  $p < 0.05$  (Tukey's multiple range test).



**Figure 7.** Effects of HA on the content of total chlorophyll of wheat plants under Cr stress. Values are means of three replicates. Different letters indicate significant difference at  $p < 0.05$  (Tukey's multiple range test).

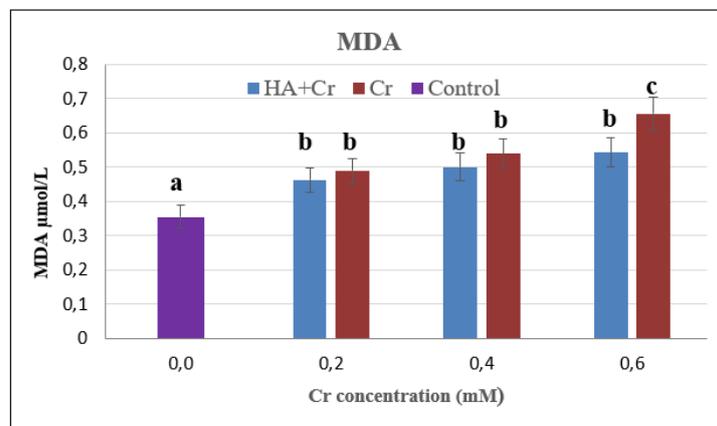


**Figure 8.** Effects of HA on the content of total carotenoid of wheat plants under Cr stress. Values are means of three replicates. Different letters indicate significant difference at  $p < 0.05$  (Tukey's multiple range test).

Zhang et al. (2013) and Lotfi et al. (2015) were also reported that the HA application caused to increase chlorophyll content and photosynthesis rate in heavy metals treated plants. It was also determined that humic acid maintained water content and water uptake by cadmium stress in wheat leaves (Konakçı et al., 2018). In a similar study, humic substances caused a positive role on chlorophyll contents in wheat under Cr stress (Ali et al., 2015). It could be connected with the decrease in chlorophyll degradation and chloroplast damage (Shahid et al., 2012). In addition, absorption of free Cr ions by HA may cause an increase in chlorophyll content (Ali et al., 2015). As shown in Figures 4- 8, a significant decrease in chlorophyll a, chlorophyll b, total chlorophyll and carotenoid pigments was observed at 0.4

and 0.6 mM Cr plus HA as compared to the control. These findings are consistent with the results of Gill et al. (2015) and Ali et al. (2015). Previous studies showed that carotenoid content decreased in wheat and other crops exposed to heavy metal stress. (Ali et al., 2013; Yadav and Singh, 2013). In our study, it was determined a reduction of carotenoid content after Cr stress application. This reduction of carotenoid may be result of a production of ROS (Ghnaya et al., 2009).

MDA is commonly an indicator of lipid peroxidation and oxidative damage to a membrane under heavy metal stress (Chaoui et al., 1997; Dhir et al., 2004). Our study showed that MDA content were significantly enhanced compared to control in wheat plants after exposure to different Cr concentrations (Figure 9). Moreover, the MDA content also increased with increasing doses of Cr. Similar results have already been reported in many earlier studies (Singh et al., 2013; Liu et al., 2014; Gonzales et al., 2017). It was also determined that MDA amounts were increased in wheat and rice under lead stress (Aziz et al., 2015). Furthermore, a similar increase in malondialdehyde content in the maize plants under heavy metal stress was reported (Rizvi and Khan, 2018). In the present study, application of HA reduced the MDA content under Cr stress in wheat seedlings. In addition, the MDA content was reduced with application of HA in wheat plants under Cr stress as compared with Cr alone. This effect might be due to reduction in membrane damage by adsorption of free radicals by humic substances (Ali *et al.*, 2018).



**Figure 9.** Effects of HA on the content of MDA of wheat plants under Cr stress. Values are means of three replicates. Different letters indicate significant difference at  $p < 0.05$  (Tukey's multiple range test).

## Conclusion

This study shows the significant effect of HA on the amount of Cr taken by wheat seedlings. Photosynthetic pigments decreased under Cr stress. However, MDA content were significantly enhanced compared to control in wheat plants after exposure to different Cr concentrations. The HA can reduce the adverse effects of Cr by restricting its uptake and transport by wheat plants. Chromium concentration was larger in leaves and shoots of wheat plants with Cr treatments. From these observations, it was concluded that HA application can improve the Cr stress in the important crops such as wheat. In addition, further studies on the different metal types and tolerance mechanisms of HA should be performed.

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## A Research On Awareness of Zoos: Landscape Architecture Students

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**Abstract:** Nowadays, many environmental organisations are trying to attract attention to the awareness against questioning the goals of zoos. Despite educating, the public about conservation there has been much discussion on how efficient zoos are at doing this. In this context, the main aim of this study is to measure the landscape architecture students' knowledge about conservation and zoos; to query the main role of the zoos and to increase the awareness of the landscape architecture students on zoos who have many lectures on environmental issues during their educational period. The main material of the research is the students who are educating at Ege University Agriculture Faculty Landscape Architecture Department. The University is located in Bornova, which is a metropolitan district of Izmir. The study was considered in four main sections, namely, conceptual framework, data collection, findings, discussion and conclusion. After an initial search of the literature, a questionnaire form was prepared. To compare the awareness level, the questionnaire was conducted to 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup> and 4<sup>th</sup> year students of Landscape Architecture of Ege University Agriculture Faculty where the period of undergraduate study is four years. "Simple Random Sampling Method" was used in the determination of the number of the students on which questionnaire would be conducted, 95 % confidence level and 0.10 sampling error was taken as a basis in the calculations. In the calculation, according to the total number of students which is 391 that the sum of 21 first grade, 18 the second grade, 20 third grade and 26 fourth grade students were used as "Population Size (N)" and the number of students on which the questionnaire would be conducted was determined as 85 at the end. It was aimed at learning each level of the students' opinions and awareness of the subject using these questions. The literature studies on the subject and the information found from the questionnaires were analysed and it was evaluated whether the education of four years on environmental issues has changed the opinions/awareness and the approach of the students to zoos. The approaches of the social and landscape architecture students towards zoos were examined together and the necessity of zoos were questioned. Finally, recommendations to increase the awareness towards zoos were made.

**Keywords:** *Zoo, Landscape architecture, University students' awareness*

### Introduction

The word 'zoo' originated as an abbreviation of the word 'zoological' (Nekolný & Fialová, 2018). According to Blunt (1976), this abbreviation of the term zoological garden was first used in Britain as a popular nickname. It first appeared in print to describe the Clifton Zoo, but was popularized in the famous contemporary music hall song, "Walking in the Zoo on Sunday" (Kisling, 2001).

A zoo is a place where animals live in captivity and are put on display for people to view. The word "zoo" is the short form of "zoological park (URL4). Zoos are public parks which display animals, primarily for the purposes of recreation or education. The first modern zoos were founded in Vienna, Madrid and Paris in the eighteenth century and in London and Berlin in the nineteenth. The first American zoos were established in Philadelphia and Cincinnati in the 1870s (Jamieson, 2017).

Since 1935, the goal of the World Association of Zoos and Aquariums (WAZA) has been to guide, encourage and support the zoos, aquariums and like-minded organisations of the world in animal care and welfare, environmental education and global conservation (URL9).

Many of the larger zoos in the world are close to 100 years old now, and some date back to the 19<sup>th</sup> century. Zoos were often built in public parks, open spaces and lots which had already been vacant, and city governments approved funding for constructing as well as maintaining zoos because zoos bring tourist revenue to the cities. City governments also recognized that zoos would contribute to educating people of all ages about wildlife, biodiversity and natural habitats in other parts of the world. Zoos are

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now playing as much of a role in preserving rare and endangered species of animals, and hence, preserving biodiversity and natural ecosystems throughout the world for the future as gene banks throughout the world are (URL8) (Figure 1).



**Figure 1.** Animal species of wild life

The following is a simple list of the different types of zoos based on exhibit method or function (URL5):

- Ancient Zoos
- Caged Zoos
- Cageless/Barless Zoos
- Children Zoos / Petting Zoos
- Farm in the Zoo
- Travelling Zoo
- Aquatic Zoos
- Wildlife Reserves / Safari Parks
- Wild Animal Parks
- Conservation Parks
- Frozen Zoos

Consequently, zoos are, today, identified as sites of conservation, research, education, and entertainment (Carr & Cohen, 2011). Today there are over 1,000 organized zoos and as many as 10,000 animal collections in the world. In short, zoos are using their unique position to heighten public and political awareness of the interdependence of all life elements on this planet (URL2). There are many arguments against zoos in today's world that bring about a moral dilemma for any free thinking individual (URL7) also there are many articles and some books that make a convincing case for their closure (URL3).

Despite their professed concern for animals, zoos can more accurately be described as "collections" of interesting animals than as actual havens or homes. Even under the best of circumstances at the best of zoos, captivity cannot begin to replicate wild animals' habitats. Animals are often prevented from doing most of the things that are natural and important to them, like running, roaming, flying, climbing, foraging, choosing a partner, and being with others of their own kind. Zoos teach people that it is acceptable to interfere with animals and keep them locked up in captivity, where they are bored, cramped, lonely, deprived of all control over their lives, and far from their natural homes (URL6).

The aims of the study are listed below;

- To learn about the students' awareness of zoos,
- To find out whether the landscape architecture education has effected the opinions / awareness and approach of the students concerning zoos,
- To investigate whether the goals set up are being achieved or not, as parallel to the recent arguments all around the world.

## **Materials and Methods**

The main material of the study is the students who are studying in Ege University Agriculture Faculty Landscape Architecture Department. Ege University, the fourth founded university of Turkey, is established in accordance with the law No. 6595 issued on May 20<sup>th</sup>, 1955 and began its educational life on November 5<sup>th</sup>, 1955. By the year 2019, Ege University includes 17 Faculties, 9 Institutes, 4 Graduate Schools, 1 State Conservatory of Turkish Music, 10 Vocational Schools, 6 Rectorate Units, 37 Application and Research Centres. By the academic year 2017 - 2018, Ege University hosts a total number of 65.587 students, 55.875 of which are undergraduate and associate degree students, and 9.712 are postgraduate students. The university has 3156 academic staff and 6347 administrative staff (URL1). Various publications, internet pages and questionnaire forms are used as research material during the study.

The research method is composed of 4 main phases called as conceptual framework, data collecting, finding and analysis, evaluation and synthesis (Figure 2). After the conceptual framework in which the definition of zoos, the history and current situation in the world of zoos, questionnaire form had been formed. In the calculation of sample size of the questionnaire, the following method of Simple Random Sampling was used (Newbold, 1995) and a 95 % confidence level and 0.10 % sampling error was taken as the basis. Assistance was received from the Instructors of the Department of Agricultural Economy in the Faculty of Agriculture at Ege University in the calculation of sample size of the questionnaire.

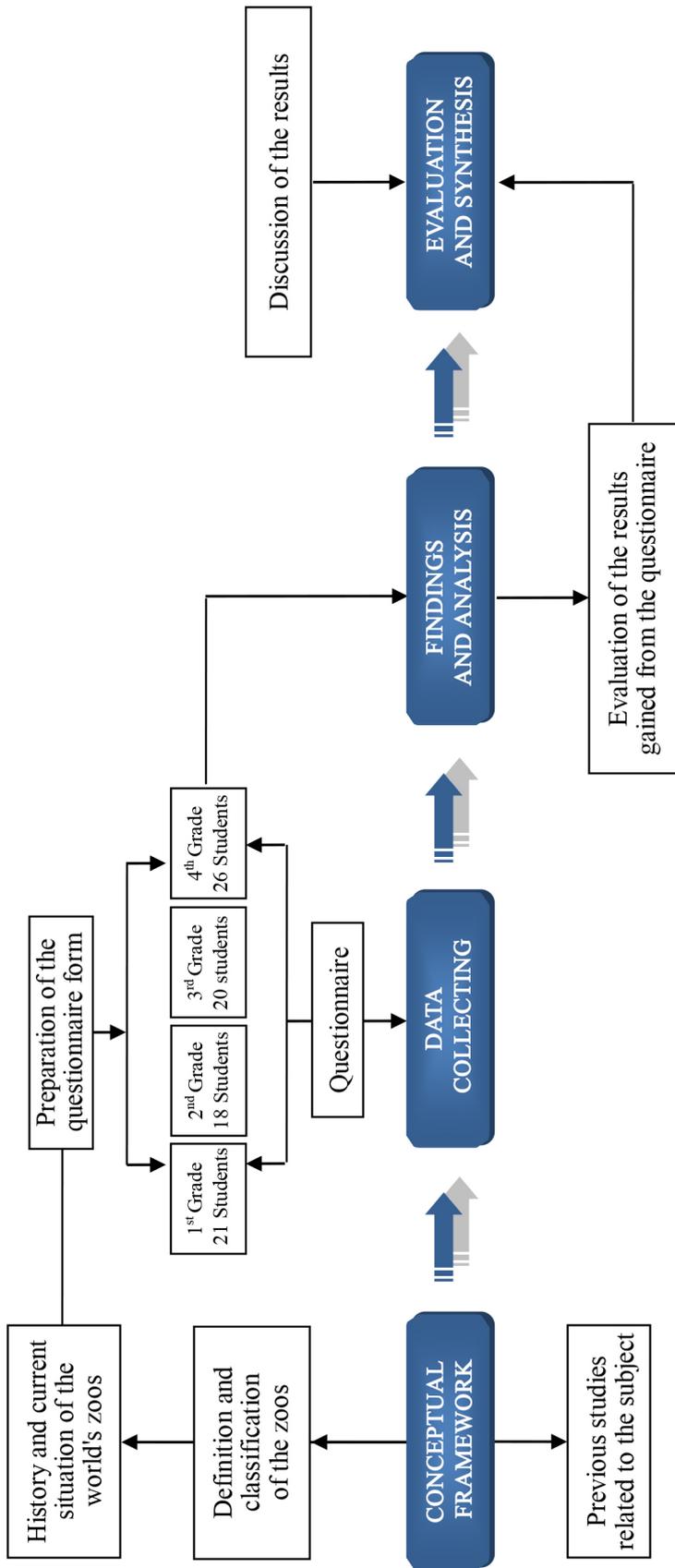
$$n = \frac{[Np(1-p)]}{[(N-1) \sigma^2px + p(1-p)]}$$

The total registered student number of for 2018 - 2019 education period in Ege University Agriculture Faculty Landscape Architecture Department for 2018 - 2019 educational period (391 that the sum of 105 first grade, 92 the second grade, 62 third grade and 132 fourth grade students) was used as the "Population Size (N)" in the calculation, and, at the end of the calculation, the sample size of questionnaire was determined as 85 (21 first grade, 18 the second grade, 20 third grade and 26 fourth grade).

30 closed - ended questions (grading - scale questions, compulsory-elective questions and demographic questions) under 3 headings, namely, **general characteristics of the students, awareness of definitions and concepts, opinions and attitudes** were posed to the respondents.

The aim of performing a questionnaire with four groups (21 students in the first grade, 18 students in the second grade, 20 students in the third grade and 26 students in fourth grade) is to compare the opinions of these students.

The questionnaires were carried out by means of face-to-face interviews with students selected randomly from the Ege University Agriculture Faculty Landscape Architecture Department from 13 to 24 May 2019. The data which are obtained from the questionnaires, in the evaluation stage of the results and there had some suggestions were put forward on the topic in conclusion.



**Figure 2.** Method Flow Diagram

## Results

Questionnaire study was conducted to 85 students of Landscape Architecture Department of Agriculture Faculty in Ege University in order to evaluate the awareness on zoos.

21 first grade, 18 the second grade, 20 third grade and 26 fourth grade students participate to the study. Firstly, demographic structures of the students are determined. It is seen that 80.95 % of 1<sup>st</sup> year students, 44.44 % of 2<sup>nd</sup> year students, 85.00 % of 3<sup>rd</sup> year students and 65.38 % of 4<sup>th</sup> year students are female (Table 1).

**Table 1.** General characteristics of the participants

Class	1		2		3		4		
	%	n	%	n	%	n	%	n	
Sex	Male	19.05	4	55.56	10	15.00	3	34.62	9
	Female	80.95	17	44.44	8	85.00	17	65.38	17
<b>Total</b>		<b>100</b>	<b>21</b>	<b>100</b>	<b>18</b>	<b>100</b>	<b>20</b>	<b>100</b>	<b>26</b>

When the awareness of definitions and concepts related to topic is evaluated, it is seen that 76.19 % of the 1<sup>st</sup> year students, 94.44 % of the 2<sup>nd</sup> year students, 85.00 % of the 3<sup>rd</sup> year students and 92.31 % of the 4<sup>th</sup> year students have been to the zoo. However, most of them partially know the purposes for the establishment of zoos and also partially know the international organizations work relates to zoos. 33.33 % of 1<sup>st</sup> year students, 66.67 % of 2<sup>nd</sup> year students, 75.00 of the 3<sup>rd</sup> year student and 65.38 of the 4<sup>th</sup> year student gives the correct answer to the 6<sup>th</sup> question as “municipality” (Table 2).

**Table 2.** Awareness of definitions and concepts related to topic

	Class	1	2	3	4
		%	%	%	%
<b>Have you ever been to the zoo?</b>	Yes	76.19	94.44	85.00	92.31
	No	23.81	05.56	15.00	07.69
<b>Do you know the purposes for the establishment of zoos?</b>	Yes	14.29	22.22	40.00	42.31
	Partially	76.19	66.67	55.00	42.31
	No	09.52	11.11	05.00	15.38
	Yes	28.57	38.89	20.00	30.77
<b>Do you know organisations whose work relates to zoos?</b>	Partially	38.10	27.78	65.00	34.62
	No	33.33	33.33	15.00	34.62
<b>Which governmental organisation are zoos under the control of?</b>	Municipality	33.33	66.67	75.00	65.38
	Ministry of Forestry and Water Affairs	19.05	05.56	00.00	07.69
	The Council of Ministers	09.52	05.56	00.00	07.69
	Ministry of Food, Agriculture and Livestock	38.10	22.22	25.00	19.23

The opinions to the proposals expressed in the Table 3 are given below:

- *“Zoos aims to protect animal species”*

Participants from each class group were found to be indecisive (respectively 28.57 %, 38.88 %, 15.00 %, 30.77 %). Between the 3<sup>rd</sup> and 4<sup>th</sup> grades, it was seen that the agreement status towards the proposal increased and it was the dominant approach.

- *“Zoos first aims are to protect endangered animal species”*

With a similar approach to the previous proposal; participants at all levels of education remain indecisive about the issue (respectively 33.33 %, 27.78 %, 30.00 % and 38.46 %). Although the instability in grades 3 and 4 persisted, it was seen that the most dominant thought towards the proposal was in agreement status as the level of education progressed.

**Table 3.** Opinions and attitudes - I

Class	1				2				3				4			
	Completely Disagree	Disagree	Undecided	Agree	Completely Agree	Completely Disagree	Disagree	Undecided	Agree	Completely Agree	Completely Disagree	Disagree	Undecided	Agree	Completely Agree	
Please indicate your thoughts on the following propositions	%				%				%				%			
Zoos aims to protect animal species	14.29	23.81	28.57	28.57	04.76	05.56	27.78	38.88	16.67	11.11	10.00	25.00	15.00	35.00	15.00	
Zoos first aims are to protect endangered animal species	04.76	14.29	33.33	28.57	19.05	16.67	27.78	27.78	16.66	11.11	05.00	15.00	30.00	30.00	20.00	
The first aim of the zoos is not making economic profit	19.05	23.81	38.10	19.05	00.00	22.22	16.67	38.88	16.67	05.56	10.00	30.00	40.00	10.00	10.00	
Animal species are happy in zoos	52.38	14.29	33.33	00.00	00.00	27.78	27.78	27.78	11.11	05.55	20.00	50.00	30.00	00.00	00.00	
Zoos provide enough space for the vital needs of animal species	28.57	33.33	28.57	09.52	00.00	11.11	16.67	50.00	22.22	00.00	25.00	30.00	30.00	15.00	00.00	
Zoos only take care of animal species	14.29	38.10	19.05	23.81	04.76	16.67	44.44	22.22	11.11	05.56	20.00	50.00	20.00	10.00	00.00	
Animal species live longer in zoos than in nature	33.33	28.57	38.10	00.00	00.00	22.22	33.33	33.33	05.56	05.56	15.00	20.00	55.00	10.00	00.00	
Zoos are educational places that increase social awareness of animal species and nature	09.52	14.29	38.10	38.10	00.00	05.56	33.33	33.33	27.78	00.00	05.00	10.00	50.00	30.00	05.00	
Animal species in zoos are never collected from the wild	23.81	38.10	33.33	00.00	04.76	33.33	27.78	27.78	11.11	00.00	15.00	15.00	65.00	05.00	00.00	

**Table 3.** Opinions and attitudes - I (Continued)

Class	1				2				3				4							
	Completely Disagree	Disagree	Undecided	Agree	Completely Disagree	Disagree	Undecided	Agree	Completely Agree	Completely Disagree	Disagree	Undecided	Agree	Completely Agree	Completely Disagree	Disagree	Undecided	Agree	Completely Agree	
Please indicate your thoughts on the following propositions	%				%				%				%							
Zoos are also recreation places for visitors	09.52	04.77	52.38	33.33	00.00	05.56	11.11	38.89	33.33	11.11	05.00	00.00	05.00	80.00	10.00	00.00	03.85	19.23	53.84	23.08
Zoos allow scientific research only for the health of animal species	09.52	09.52	61.90	19.06	00.00	05.56	33.33	44.44	16.67	00.00	10.00	35.00	25.00	30.00	00.00	07.69	15.38	57.70	15.38	03.85
Zoos contribute to the city's tourism activities	04.76	04.76	00.00	76.19	14.29	05.56	00.00	22.22	61.11	11.11	00.00	00.00	05.00	80.00	15.00	00.00	00.00	11.54	73.08	15.38
Zoos are one of the most important spaces for visitors to socialize	04.76	14.29	38.10	33.33	09.52	05.56	11.11	22.22	50.00	11.11	10.00	05.00	40.00	30.00	15.00	00.00	15.38	15.38	57.70	11.54

- *“The first aim of the zoos is not making economic profit, Animal species are happy in zoos, Zoos provide enough space for the vital needs of animal species, Zoos only take care of animal species, Animal species live longer in zoos than in nature”*

Indecisiveness includes an important group for these proposals. It is determined that the most dominant thought in all classes for all these proposals is disagreement and the percentages of disagreement status increase as the level of education progressed. 38.46 % of 4<sup>th</sup> year students disagree that the first aim of the zoos is not making economic profit. Also 50.00 % of 2<sup>nd</sup> year students disagree that animal species are happy in zoos.

- *“Zoos are educational places that increase social awareness of animal species and nature”*

In response to this proposal, the percentage of indecisiveness found to be very high in each class (respectively 38.10 %, 33.33 %, 50.00 %, 28.00 %). On the other hand, there was no significant difference between the participants in agreeing and disagreeing with the proposal.

- *“Animal species in zoos are never collected from the wild”*

In response to this proposal, the percentage of indecisiveness found to be very high in each class (respectively 33.33 %, 27.78 %, 65.00 %, 38.46 %). It is determined that the most dominant thought in all classes for all these proposals is disagreement.

- *“Zoos are also recreation places for visitors”*

While the approach to this proposal between the 1st and 2nd grades (respectively 52.38 %, 38.89 %) was indecisive, it was found that the instability between the 3rd and 4th grades decreased considerably and the dominant response became to be in agreement status (respectively 90.00 %, 76.92 %).

- *Zoos allow scientific research only for the health of animal species*

In response to this proposal, the percentage of indecisiveness found to be very high in each class (respectively 61.90 %, 44.44 %, 25.00 %, 57.70 %). On the other hand, there was no significant difference between the participants in agreeing and disagreeing with the proposal.

- *Zoos contribute to the city's tourism activities*

The remarkably dominant approach to this proposal appears to be towards agreement status.

- *Zoos are one of the most important spaces for visitors to socialize*

It was found that there was an indecisive group among the participants at all educational levels for this proposal, besides the dominant response found to be in agreement status.

Undecided group for all the proposals always has a large percentage; It was found out that an important part of the survey participants who had information about zoos because of the education they received could not provide information or opinions about the main aims and objectives of these places.

According to the answers given in Table 3, although the majority of the participants thought that the conservation of the animal species in zoos is one of the aims of zoo construction, also it was seen that majority of the participants' opinion is that the necessary conditions for the animals are not provided, the species do not live longer nor happily in zoos and the zoos also aim to make economic profit.

It was requested that the problems that may be encountered in zoos be graded between 1 (least) and 5 (most) points according to their importance level and the answers given to this question are listed in Table 4.

**Table 4.** Opinions and attitudes – II

Class	1					2					3					4				
	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
What are the most important problems in zoos?	%					%					%					%				
Failure to achieve appropriate natural living standards	00.00	04.76	19.05	09.52	66.67	05.56	00.00	22.22	22.22	50.00	05.00	15.00	10.00	25.00	45.00	03.85	11.54	11.54	19.20	53.85
Not providing the necessary maintenance services to species	00.00	14.29	28.57	28.57	28.57	00.00	11.11	33.33	16.67	38.89	00.00	10.00	30.00	30.00	30.00	00.00	11.54	42.31	23.07	23.08
Lack of quality of the open spaces created for visitors	14.29	14.29	42.85	23.81	04.76	38.89	44.44	05.56	00.00	11.11	20.00	25.00	45.00	05.00	05.00	15.38	15.38	46.15	11.55	11.54
Poor economic power	09.52	09.52	42.86	23.81	14.29	11.76	41.18	17.65	11.76	17.65	05.00	25.00	40.00	20.00	10.00	11.54	38.46	30.77	15.38	03.85
Making an economic profit is the priority aim	04.76	04.76	28.57	00.00	61.91	11.11	05.56	27.78	22.22	33.33	00.00	10.00	20.00	15.00	55.00	03.85	0385	15.38	26.92	50.00
The conduct of scientific research contrary to animal rights	04.76	09.52	14.29	23.81	47.62	16.67	05.56	22.22	22.22	33.33	15.00	25.00	10.00	05.00	45.00	07.69	11.54	30.77	15.38	34.62

\* Please rate as "1" the least important, "5" the most important

**Table 5.** Opinions and attitudes - III

What should be done to improve zoos?	Class																			
	1					2					3					4				
	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5	1	2	3	4	5
%					%					%					%					
Research for the protection of species should be supported by governmental organizations	00.00	00.00	04.76	00.00	95.24	05.56	16.66	00.00	22.22	55.56	00.00	00.00	00.00	00.00	15.00	85.00	00.00	03.85	03.85	03.85
Penal sanctions should be increased for the people who violate animal rights	00.00	00.00	04.76	14.29	80.95	00.00	05.56	05.56	11.11	77.77	00.00	00.00	00.00	00.00	05.00	95.00	00.00	03.85	07.69	07.69
Effective auditing of the establishment, maintenance and management process of zoos	00.00	00.00	14.29	04.76	80.95	05.56	05.56	11.11	16.66	61.11	00.00	00.00	10.00	05.00	85.00	03.85	03.85	11.54	15.38	65.38
Awareness should be created about the importance of the endangered species	00.00	00.00	04.76	14.29	80.95	05.56	11.11	00.00	05.56	77.77	00.00	05.00	00.00	05.00	90.00	00.00	00.00	00.00	15.38	84.62
The importance of the ecological aspects of living species should be better emphasized at all levels of educational planning	00.00	04.76	04.76	23.81	66.67	05.56	11.11	00.00	05.56	77.77	00.00	00.00	15.00	20.00	65.00	00.00	07.69	23.08	00.00	69.23

\* Please rate as "1" the least important, "5" the most important

- The problems of *“Failure to achieve appropriate natural living standards”*, *“Poor economic power”*, *“Making an economic profit is the priority aim”* and *“The conduct of scientific research contrary to animal rights”* received high points from the majority of all grade students.

- None of the participants found the problem of *“not providing the necessary maintenance services to species”* at the least important level.

- Majority of the participants found the problem of *“lack of quality of the open spaces created for visitors”* at the level of 1 and 2 points. The answers showed that meeting the needs of visitors is the least important problem in zoos according to the all grades of students.

- *“Failure to achieve appropriate natural living standards”* was the most important problem for the 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup> grade students and on the other hand *“making an economic profit is the priority aim”* became to be the most important problem for the 4<sup>th</sup> grade students.

It was requested to grade different proposals that will improve zoos, between 1 (least) and 5 (most) points according to their importance level and the answers given to this question are listed in Table 5.

- It has been seen that all the proposals received 4 and 5 points from the majority of all grade students.

- In the 1<sup>st</sup> grade, except for a very limited group, no 1 or 2 points were given to the proposal by the participants and the proposals they supported the most were *“Awareness should be created about the importance of the endangered species”*, *“Penal sanctions should be increased for the people who violate animal rights”* and *“Research for the protection of species should be supported by governmental organizations”*.

- In the 2<sup>nd</sup> grade, it was found that all suggestions could have different values between 1 and 5 points and the proposals they supported the most was *“Penal sanctions should be increased for the people who violate animal rights”*.

- It was seen that 3<sup>rd</sup> grade gave 4 or 5 points predominantly to all proposals and no prominent approach was determined among the participants.

- In the 4<sup>th</sup> grade, it was found that all suggestions could have different values between 2 and 5 points and the proposals they supported the most were *“Awareness should be created about the importance of the endangered species”*, *“Penal sanctions should be increased for the people who violate animal rights”* and *“Research for the protection of species should be supported by governmental organizations”*.

## **Discussion and Conclusion**

Conservation, research, education and entertainment concepts are among the tasks of zoos which are part of urban recreation places. Today, however, the ethical accuracy of these spaces and the necessity of ecology are discussed extensively. Among these discussions, the ideas such as *“Zoos are just for entertainment; Keeping animals in cages and zookeepers are cruel; To see animals, it has to be seen done in wild; Animals in zoos are still taken from the wild, They suffer and die prematurely in zoos”* take place. Another discussed idea is, *“Zoos don’t serve conservation”*. One of the most important tasks of zoos is the protection, reproduction and restoration of animal species and especially the species in danger of extinction. However, according to some experts, the goal of zoos is not to bring the species back to nature, but to create captive new species. It is stated that most species found here are hybrids and therefore have little or no value in terms of protection.

As a result of the survey conducted within the scope of the research, these mentioned controversial ideas were also dominant. Therefore, it was concluded that the students who participated in the survey were undecided about the zoos. According to students who are educated about wildlife, landscape ecology, nature conservation issues as well as urban and rural recreation areas, zoos are important in terms of protection of species, but they are suspicious because of the conditions contrary to animal rights and the inadequacy of the legal mechanism that controls this situation.

In this context, the importance of zoos especially in terms of the protection of endangered species cannot be ignored. However, this aim should be fulfilled in full, the reproduction of the species should be supported and the natural environment should be regained in the continuation of this process. These studies should be supervised through legal processes and related institutions. Besides, zoos should be saved from financial concerns with the support of public or private institutions so that the necessary conditions for the survival of living beings that concern the future of the whole world can be provided.

Another suggestion put forward as a result of this study is to provide a different dimension to the educational purpose expected from zoos. Zoos should be one of the places where children will meet animals, learn to love and protect them and also make physical contact with them. For this purpose, species such as bears, tigers, lions, elephants, giraffes, which are part of the wild nature, do not need to be among the species exhibited to the visitors, as it is not possible to establish physical communication with these species. If necessary, these species should be included in the zoo for protection, but not among humans. In addition, the existence of species that cannot be revived in the zoo is not ethical in terms of animal rights. The educational mission of zoos should be based on instilling animal love, not introducing animal species.

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