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Research Paper

The Effect of Turkish Coffee and Cadmium Acetate on *Drosophila melanogaster*

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Abstract: In the study, Cadmium (Cd), which is a environmentally polluting toxic heavy metal, was added to the diet of model organism *Drosophila melanogaster* Meigen through water and food, and it was tried to determine the effect on life-development and sex ratio by using dry commercial Turkish coffee (TK). The female and male individuals fed with the Cd acetate (0-30 ppm) and TK (2%) used also had a long life span. It was determined that the decreasing survival rate with Cd acetate may increase with the addition of TK to the food, the duration of puberty may be shortened with TK, and the sex ratio in favor of men even though there is no difference in nutrition. In addition, it was determined that the use of Cd acetate shortens the life span of adult individuals, while feeding with TK does not affect this negative effect much.

Keywords: *Drosophila melanogaster, sex ratio, developmental period, Cadmium acetate, Turkish coffee, longevity.*

Introduction

Many substances that cause pollution in nature cannot be destroyed due to the developing industry and the waste materials released accordingly. This situation brings pollution with it and affects all living things negatively. Environment, soil, water and air pollution caused by heavy metals are seen as a very important problem. These contaminating metals affect all organisms directly or indirectly through the food chain / respiration. Cd is the symbol of Cadmium, which is a dangerous and toxic heavy metal, and it is a white colored element. The atomic number is 48, the atomic weight is 112.4, and its valence is + 2. The biological half-life is on average 29 years (Asri et al., 2007; Çoşan et al., 2017). The effect of cadmium acetate [Cd (CH3COO) 2.2H20] on living things has not been fully proven, and research is ongoing (Güner & Kavlak, 2017). The organs first affected by cadmium and its components are kidneys and liver. Cd accumulating in tissues; high blood pressure, anemia, bone loss, and even lung cancer can cause important illnesses (Demir et al., 2002, Asar et al., 2004). In addition, it has been reported to cause toxicity in the urinary, cardiovascular, gastrointestinal and central nervous systems (Asri et al., 2007; Çoşan et al., 2017). The possible effect of cd acetate especially on the reproductive system is the main purpose of this study. Because Cd acetate taken indirectly with water and nutrients; It causes the reproduction, survival and development of the species in nature and the change of the sex. This situation causes species to be endangered or populations change and another process begins.

The toxic effects of chemical compounds used in industry should be thoroughly tested in rodents, rabbits or monkeys such as rats or mice. However, it is not possible to test every chemical compound. Therefore, alternative screening methods, which are cheap and fast, are used in which the possible effects of a chemical compound in mammals can be accurately defined. For this purpose, some in vivo and in vitro test systems with non-mammalian animal species are used in the studies. *Drosophila melanogaster* Meigen, one of these test systems; It is one of the organisms used in modeling metabolic disorders, neurodegenerative diseases and cancer (Bilen & Bonini, 2005; Gonzalez, 2013; Owusu-Ansah & Perrimon, 2014; Hirabayashi, 2016). However it is used, in toxicity studies (Pappus & Mishra, 2018; Amorim et al., 2019; Rand et al., 2019) and environmental impact studies (Van Straalen and Roelofs, 2005; Wiman et al., 2016; Ko et al. (2017). Based on the information obtained from model insects, inferences are made for mammalian models (Brumby and Richardson, 2005; Hariharan and Bilder, 2006; Miles et al., 2011; Gonzalez, 2013; Hirabayashi, 2016).

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Coffee is the most consumed beverage in the world and has attracted the attention of researchers due to its carcinogenic, genotoxic and antioxidant effects (Duarte et al., 1999; Abraham & Stopper, 2004; Araque et al., 2007; Arab, 2010; Trinh et al., 2010; Wang et al. 2016; Ko et al., 2017; Nagpal & Abraham, 2019). It is known that beverages such as wine, coffee and tea can reduce Cd accumulation in tissues (Winiarska-Mieczan, 2013). However, the effect of Turkish coffee (TK) against heavy metals such as Cd acetate taken with our daily diet has not been tested in terms of model organisms. Nowadays, researches on the use of natural ingredients in treatment have gained importance. Therefore, in our study; It is aimed to investigate the effect of TK, which has a high flavonoid content and antioxidant effect on heavy metal chelating, on some biological properties of *D. melanogaster* against foodborne Cd toxicity.

Materials and Methods

Wild-type (W^{1118}) adult flies of *D. melanogaster* have been cultured in Necmettin Erbakan University Research Laboratories (Turkey). *D. melanogaster* was kept in a standard nutrient medium containing mashed potatoes, agar, sucrose, dry yeast, ascorbic acid, and nipagin at 60-70% humidity, constant temperature of 25 ± 2° C and dark by Nüve cooled, ES 120.

Cd acetate was obtained from Dr. Mehmet Okan ERDAL (Meram Vocational School, Necmettin Erbakan University, Konya, Turkey). Cd acetate (0-30 ppm) was dissolved in distile water was added to standard insect nutrient, TK (added to 2% of the nutrient) were purchased commercially in October 2019, and the experiment was set up with pre-feeding experiments and previous studies (Cheng, 1980; Abraham & Graf, 1996; Nagpal & Abraham, 2019). The first stage larvae obtained from the culture were transferred to this experimental nutritents (Figure 1) by means of a fine tip brush. All experiments were carried out on four replicates and 100 larvae were used in each replicate.

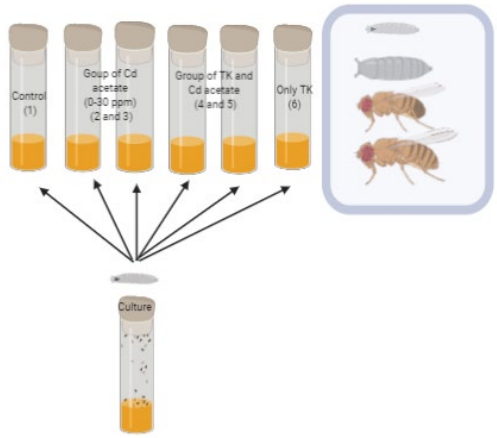

Figure 1. Experimental design with stock culture (create in BioRender.com)

Newly hatched larvae were feed with extracts until adult stage, and biological traits (survivorship, development, sex ratio, longevity) of 3rd instar larvae, puparium, female and male were investigated. In calculating the life expectancy of individuals, the rate of survival was calculated by determining the non-mature individuals. In mature individuals, they were fed the same food during their survival. Adults in the control and administration groups were checked and died at the specified time each day and recorded. The living individuals were transferred to new containers containing food (from the beginning).

The effects of Cd acetat and TK on insect survival and development were evaluated considering the percentage of individuals reaching the 3rd larval stage, pup and adult stage and the average time (days) to reach this stage. Experimental data were expressed as means ± S.E. The data were subjected to statistical analysis (SPSS Inc., Chicago, IL, USA) by one-way analysis of variance (ANOVA) was followed by lest significant difference (LSD) test to determine significant differences between means. Mann Whitney U test was used to determine the changes occurring between male and female adult stages. Data on survivorship were compared by Chi-square test (Snedecor and Cochran, 1967). A values of $p<0.05$ was considered significant.

Results

Commercial TK, which was determined to cause contamination, was sterilized in powder form and added to the food. According to Table 1, by using Cd acetate and TK in nutrition;

- Feeding the insect with 30 ppm Cd acetate in the larval stage shows lethal effect (Lc_{50}); It was determined that the rate of larval survival increased from 50% to 60% with TK added to the food. In Pupal survival rates, TK; While it was not effective in those who fed low doses of Cd acetate, it was found that the insects fed with high doses of Cd acetate caused a statistically significant increase in survival rates (from 34% to 50%). In adult individuals; It has been determined that TK affects the survival rate, but even the low amount of Cd acetate allows half of 100 individuals to survive. It has been observed that the decrease in adult life repair observed in individuals fed with nutrients supplemented with Cd acetate increased with the addition of TK to the fattening medium. While the larval development time in *Drosophila* can be between 3-4 days, it has been determined that TK increases this period by 7 days and Cd acetate by 9 days. No statistically significant difference was observed in the larvae fed with the increased dose of Cd acetate, although shortening the larval development time with the two substances (Cd acetate + TK) used together. 4-5 days of pupal development can be extended with Cd acetate approximately 4 times, and adding TK to the food can decrease this period up to 5 days (from 16 days to 11 days). Although the use of cd acetate causes the insect to complete its maturation time in about 19 days, this time can be shortened by 4 days with the use of TK. Although it is statistically low in female and male ratios; firstly it can be said to be equal or in favor of men
- It has been identified with the use of Cd acetate, the life span of individuals is reduced by approximately half; male individuals live longer and adding TK to the nutrient medium does not affect this negative situation much (Figure 1, LSD Test). When the groups are evaluated among themselves; There is a statistically significant difference in the life span of females and males in the group where 10 ppm Cd acetate and TK are added to the food medium (Table 2, $p < 0.05$, Mann whitney U Test).

Table 1. Effect of Turkish coffee and Cadmium acetate in insects on survival, development and sex ratio on insect

ppm	Survival to the 3rd larval stage (%) (M* ± SE)†	Time to the 3rd larval stage (days) (M* ± SE)†	Survival to pupal stage (%) (M* ± SE)†	Time to pupal stage (day) (M* ± SE)†	Survival to adult stage (%) (M* ± SE)†	Time to adult stage (day) (M* ± SE)†	Sex ratio (%) Female /Male (M* ± SE)†
0.0[a]	98.0 ± 0.1a	3.8 ± 0.2a	97.5 ± 0.1a	4.8 ± 0.2a	96.0 ± 0.2a	7.3 ± 0.1a	25/75 ± 0.1a
2%TK	90.1 ± 0.1a	11.1 ± 0.1b	88.0 ± 0.1b	12.0 ± 0.1b	70.0 ± 0.1b	15.5 ± 0.1b	55/45 ±0.1d
10 Cd acetate	65.0 ± 0.1b	13.0 ± 0.2c	62.0 ± 0.1c	14.1 ± 0.2c	50.0 ± 0.1c	17.4 ± 0.2c	40/60±0.5bc
30 Cd acetate	50.0 ± 0.2c	13.2 ± 0.2c	34.0 ± 0.2d	16.0 ± 0.2d	22.0 ± 0.2d	19.3 ± 0.2d	45/55 ± 0.5c
10 Cd acetate +2% TK	62.5 ± 0.2b	10.0 ± 0.3b	60.0 ± 0.2c	11.1 ± 0.3b	56.0 ± 0.2c	15.8 ± 0.3b	35/65 ±0.2b
30 Cd acetate + 2% TK	60.2 ± 0.2b	13.0 ± 0.3c	59.0 ± 0.2c	15.0 ± 0.3c	48.0 ± 0.2c	19.0 ± 0.3d	48/52 ± 0.2c

*Mean of four repetitions † Values containing the same lower case in the same column are not different from each other, $p > 0,05$ (χ^2 test, LSD Test); [a]Control, **TK**: Turkish Coffee, **Cd acetate**: Cadmium acetate **M:** mean, **Standart Error:** SE

Table 2. Effect of nutrition groups created with Turkish coffee and Cadmium acetate on *Drosophila melanogaster* life span

ppm	Max. Life span/Female (N=100)	Female life span (day) (M* ± SE)†	Max. Life span/Male (N=100)	Male life span (day) (M* ± SE)†
0.0[a]	62.5	60.0 ± 0.2A	65.0	62.0 ± 0.2A
TK 2%	66.0	65.0 ± 0.8A	63.0	65.0 ± 0.8A
10 Cd acetate	42.2	40.0 ± 1.2A	48.1	45.2 ± 1.2B
30 Cd acetate	39.5	39.0 ± 1.2A	38.5	40.0 ± 1.2A
10 Cd acetate + TK 2%	43.4	39.0 ± 0.5A	43.0	41.0 ± 0.5B
30 Cd acetate + TK 2%	41.7	39.5 ± 0.5A	40.7	40.5 ± 0.5A

† Values containing the same capital letter in the same line are not different from each other, $p< 0.05$ (χ^2 test, Mann whitney U Test)

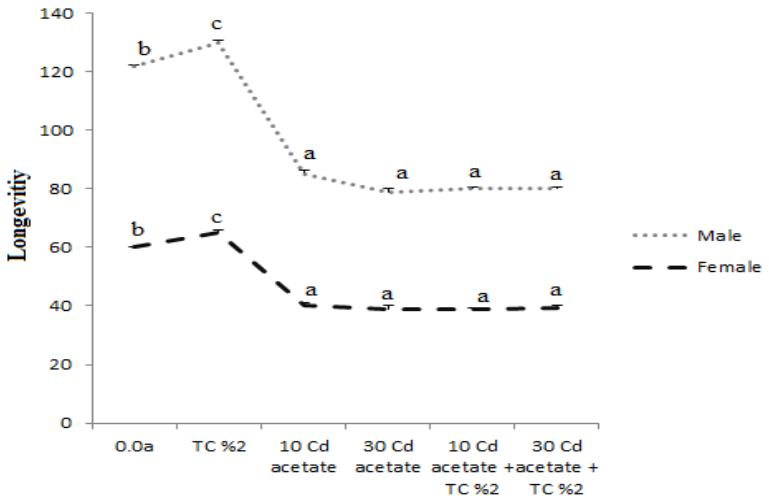

Figure 1. Effect of nutrition groups created with Turkish Coffee and Cadmium acetate on *Drosophila melanogaster* life span ($p< 0.05$; LSD Test)

Discussion

In the literature; there are studies in which the biological parameters are tested on *Drosophila* in a dirty and clean environment created using a single dose of a heavy metal (Posthuma and Van Straalen 1993; Shirley & Sibly, 1999). In these studies, individuals with and without resistance to the environment are tested. Food chain or respiratory substances affect all organisms. Environmental impact determination can be easily done in insects, but invertebrates (especially the Diptera group) that exhibit heavy metal resistance can provide metal homeostasis by forming a resistance protein (metallotionein) to heavy metals during development (Morgan et al., 2007). Metallotionein, which is important in heavy metal resistance, is found in *Drosophila* as it can be found in many creatures (Maroni & Watson 1985; Sterenborg & Roelofs, 2003; Nguyen et al., 2014). In our study, the culture of living was prepared with non-Cd water in order to eliminate resistance in living and a clean environment was created in terms of Cd acetet and generations were grown in this clean environment.

While *D. melanogaster* larvae have 98% survival rate under constant and normal conditions, this rate can decrease up to 80% during adulthood. Development period can different between 7-8 days in total, from larvae to adolescents (Güneş et al., 2017). Foods and their contents can change the rate of living (Güneş, 2016). For example, it is known that the resistant *Drosophila* individuals in the area contaminated with Cd chlorite (80 µg) increase the survival rate by 62% and the development time by

40% from 13 days (Shirley & Sibly, 1999). In the study, the rate of survival in the groups formed with 10 ppm Cd acetate (larva-adult) decreased 1.5-1.9, respectively. In order to reduce the toxicity, it was found that while the rate of 2% TK added to the food remained the same in the larva, it decreased by 1.7 in adulthood. There is tannic acid in the diet used in TK. Tanic acid is also found in beverages such as tea and fruit. Tanic acid is involved in protecting from heavy metals and reduces Cd accumulation in tissues (Graf & Würgler, 1986; Winiarska-Mieczan, 2013; Çoşan et al., 2017; Çalış et al., 2019). This information supports our work. In the study, it was determined that feeding the insect with TK slightly decreased the rate of living in pup and adolescent. In insects with 30 ppm Cd acetate and TK added to the medium; It was observed that TK decreased the 1.9% decrease in the larval stage and the 1.6 decrease in the rate of living. In the process of adulthood; It was determined that the survival rate of insects fed with Cd acetate decreased by 4.3 compared to the control group. It was determined that adding TK to the food of these insects caused the relative improvement by reducing the survival rate by half. Thus, it has been observed that TK has a positive effect on survival rate. For survival flies, a dose-related decline is responded (Nguyen et al., 2014). In experiments with Cd nitrate, it has been stated that the substance given from the larval stage is not effective, and the rate of maturation decreases depending on the concentration after adulthood (Gelegen & Yeşilada, 2000). While lethal effect was 900 ppm Cd nitrate in the same study, the same effect was observed in our study with 30 ppm Cd acetate. In our study, it was determined that adding Cd acetate to the food did not reduce the effect of Cd acetate, although the development period of the insect was extended from 7 days to 19 days with the use of Cd acetate. In fact, it was observed that the development, which extended to 13 days in the larval period, completed 13 days despite the high amount of Cd acetate and TK. In previous studies, it has been reported that 0.15% µg / ml coffee added to the food shortens the development period of the insect (Trinh et al., 2010). It is known that, in terms of Cd content, the rate of living of flies at 80 ppm can decrease significantly (Callaghan & Denny, 2002; Nguyen et al., 2014). In fact, flies for Cd chloride have been reported to have a maximum tolerance of 10 µM (Christie et al., 1985; Debec et al., 1985). In our study, it was determined that the flies tolerated a maximum of 30 ppm Cd acetate. As in other studies (Maroni & Watson 1985; Balamurugan et al., 2007), liveliness is reduced and development time is extended due to Cd acetate exposure.

Although Cd nitrate does not differ between sex ratios in flies (Yeşilada & Gelegen, 2000), feeding can affect the sex ratios. While some foods increase the ratio of females (Güneş et al., 2019), sometimes an increase in the ratio of males can be observed (Arıca et al., 2017). Even coffee added to food is known to be more effective in males (Nagpal & Abraham, 2019). Because the sex ratio in insects is important for determining the population density (Yeşim & Gülel, 2006). Factors such as the amount and type of nutrients affect the survival-breeding-egg release status of the species. This causes an increase in the population. This situation may endanger the continuation of the species. Study; Although adding Cd acetate and TK to the medium of insects does not ensure that the gender ratios are equal, it has been found to affect the male part in favor.

The lifetime that differs between species may not be the same even on different sexes of the same species. It may even differ between different nutritional and environmental conditions and populations of the same genotype (Kızılet & Uysal, 2012). Nutritional factors such as diet, regimen or intake of specific nutrients have been shown to alter animal life (Le Bourg 2001; Page et al., 2010; Altun et al., 2011). Flies can live 60-78 days under constant conditions (Yeşilada & Gelegen, 2000; Uysal & Semendöken, 2011). However, heavy metals such as Cd nitrate shorten the adult lifetime of flies (Balamurugan et al., 2007). In our study; add Cd acetate in nutrition, it has been observed that the life span of individuals is shortened by approximately half, males live longer and feeding with TK has no effect. Coffee is a substance that contains phytochemicals with effective activity against compounds such as ethyl methanesulfonate and has a known protective effect (Prakash et al., 2014). Coffee taken up to 2% of the food has been reported to have a positive effect and reduce genotoxicity and mutagenicity (Abraham & Graf, 1996; Nagpal & Abraham, 2019). It can be said that this situation supports our study. In another study, it was stated that males individuals live longer than females similar to this situation (Yeşim & Gülel, 2006). In another study with coffee; It has been reported that coffee has no effect on lifetime (approximately 60 days) without discrimination between females and males, but decaffeinated coffee reduces the life span (Trinh et al., 2010). Especially the mutations seen in males individuals have been reported to decrease significantly with coffee (Nagpal & Abraham,

2019). This situation can be shown as evidence for long-lasting male individuals to get rid of the effect more quickly, as in our study.

Conclusion

In this study; It has been determined that using TK against exposure to CD acetate has some effect on the survival rate of the insect, but not on the life span. In the following studies, it is suggested to study the relationship between female reproduction and aging, biochemical parameters and metal detoxification.

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Analysis of the Influence of Adriatic Sea Level on Buna River Flow

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Abstract: The water system of Shkodra Lake, Buna River, and Drini River with a total surface area of 19580 km^2, is the largest in Albania and in Adriatic cost of Balkan Peninsula in terms of watershed and water discharge. Buna River has a total length of around 44 km and an average discharge of 680 m^3/s. Around 1.5 km from flowing out of Shkodra Lake, Buna River joins Drini River, and then after meandering in a low land area Buna River discharges into the Adriatic Sea all the waters of the water system. To study the influence of Adriatic Sea level on Buna River flow, a mathematical model is set-up using SOBEK software developed from Deltares Institute, the Netherlands. The mathematical model is based on topographic survey carried out in the study area. Around 400 cross sections are used to represent the riverbed topography of Buna River and lower part of Drini River. Different sea water levels are analysed, and their effect is evaluated along Buna River for a period of low flow and high flow. Mathematical model results indicate that high water levels of Adriatic Sea due to meteorological and astronomic tide affect Buna River water levels until 21.6 km upstream for the period of high flow, and 37.5 km upstream for the period of low flow. Buna River water levels upstream of the junction with Drini River are not affected from the Adriatic Sea levels.

Keywords: *Buna River, water level, mathematical model, tide, upstream*

Introduction

Buna River is part of the water system of Shkodra Lake, Drini and Buna River. This water system is the largest in Albania and also the largest in Adriatic cost of Balkan Peninsula in terms of watershed and water discharge. The water system of Shkodra Lake, Drini and Buna River has a watershed with significant amounts of annual precipitation ranging from 1600 mm to 4000 mm (IHM, 1975). The water system of Shkodra Lake, Drini and Buna River collects the waters from a total surface of 19580 km^2. The drainage area of this water system is extended in different countries such as: Albania, Montenegro, Kosovo, and North Macedonia. Drini River with its branches Kiri and Gjadri has a total drainage area of 14400 km^2. Shkodra Lake has total drainage area of 5180 km^2 (IHM, 1984). All the waters of this water system are discharged into the Adriatic Sea through Buna River bed. Buna River has an average discharge of 680 m^3/s and total length of 44 km. After 1.5 km away from its source out of Shkodra Lake, Buna River has a junction with Drini River. Buna River is a lowland river with a lot of meanders along its course. Before flowing into the Adriatic Sea, River Buna is divided into two branches. One of the branches flows in the territory of Albania and the other one in Montenegro. Figure 1 shows the location of the study area.

In the case of rivers flowing into the sea, sea level fluctuations have an impact on the water flow regime in the lower part of the rivers. Sea level fluctuations occur due to astronomical tides and meteorological tides. The astronomical tide is caused by the gravitational actions of the Moon and the Sun, and the rotation of the Earth. The astronomical tide has a cycle of rising and falling of water sea levels every day. The meteorological tide represents the changes in water level caused by local meteorological conditions. Meteorological phenomena such as wind, barometric pressure, and precipitation can cause an increase in sea water level. The meteorological tide depends on daily or seasonal changes in weather conditions.

In order to study the influence of Adriatic Sea level on Buna River flow, a mathematical model is set-up for the study area based on the topographic survey made from both countries Albania and Montenegro in their national coordinate systems.

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Figure 1. Location of the study area (*Source: Google Streets)*

Materials and Methods

The mathematical model built in SOBEK software is used to study the influence of Adriatic Sea level on Buna River flow. This software is provided in the framework of IPA Cross border Albania-Montenegro project. SOBEK software is developed from the Deltares Institute in Delft, Netherland. This software is designed to perform one-dimensional hydraulic calculations for a full network of natural or constructed channels, and also 2Dimensional hydraulic calculations on two-dimensional (2D) horizontal grids (Deltares, 2013). SOBEK is based on high performance computer technology that means it can handle water networks of any size - big or small. In order to build the mathematical model for the water system of Shkodra Lake, Drini and Buna River, the 1DFLOW module in SOBEK is applied. The 1DFLOW module consists of a network of reaches connected to each other at connection nodes. In each reach a number of calculation points are defined. These calculation points represent the spatial numerical grid to be used in the simulation (Deltares, 2013).

Model equations for 1Dimensional flow

The water flow is computed in SOBEK software by solving the full 1Dimensional Saint-Venant equations. These equations are derived from the Navier–Stokes equations. The 1D Saint-Venant equations are derived from equations of conservation of mass (Eq.1) and conservation of momentum (Eq.2) (Cunge, *et al.,* 1980). The Saint-Venant equations expressed in their non-conservative form are as follow:

$$\frac{\partial \zeta}{\partial t} + \frac{\partial (uh)}{\partial x} = 0 \qquad \text{[Eq.1]}$$

$$\frac{\partial u}{\partial t} + u\frac{\partial u}{\partial x} + g\frac{\partial \zeta}{\partial x} + c_f \frac{u|u|}{h} = 0 \qquad \text{[Eq.2]}$$

where: ζ water level (with respect to the reference level) defined as $\zeta = h + z_b$ [m]
h local water depth [m]
z_b the local bottom level [m]
u flow velocity [m/s]
c_f friction coefficient

In SOBEK software the Saint-Venant equations are solved numerically using a robust numerical scheme proposed by Stelling called Delft Scheme. This scheme solves the continuity and momentum

equation by means of a staggered grid and implicit integration scheme. In this staggered grid the water levels are defined at the connection nodes and calculation points (1D nodes), while the discharges are defined at the intermediate reach segments (Deltares, 2013). The momentum equation and continuity equation will be solved numerically on this grid, which results in the hydraulic states at the calculation points and the reach segments. According to Stelling and Duinmeijer (Stelling & Duinmeijer, 2003), in the case of gradually varied flow or in flow expansion, the momentum conservation equation is applied, whereas for strong flow contraction the energy head formula should be applied.

Setting up the Mathematical Model in SOBEK

The 1D mathematical model using SOBEK software is set-up based on the digital terrain model developed from the topographic survey made in the study area during the period 2005-2006, from the Albanian Academy of Sciences and the Academy of Sciences and Arts of Montenegro (ASA & AASM, 2006). The topography survey was carried out for around 400 cross sections in Buna River and lower part of Drini River (1 Km before the joining with Buna River). Cross sections are measured at intervals of around 100 m from each–other, which gives a good representation of river bathymetry. The mathematical model built in SOBEK software for the water system of Lake Shkodra Lake, Drini and Buna River is presented in Figure 2.

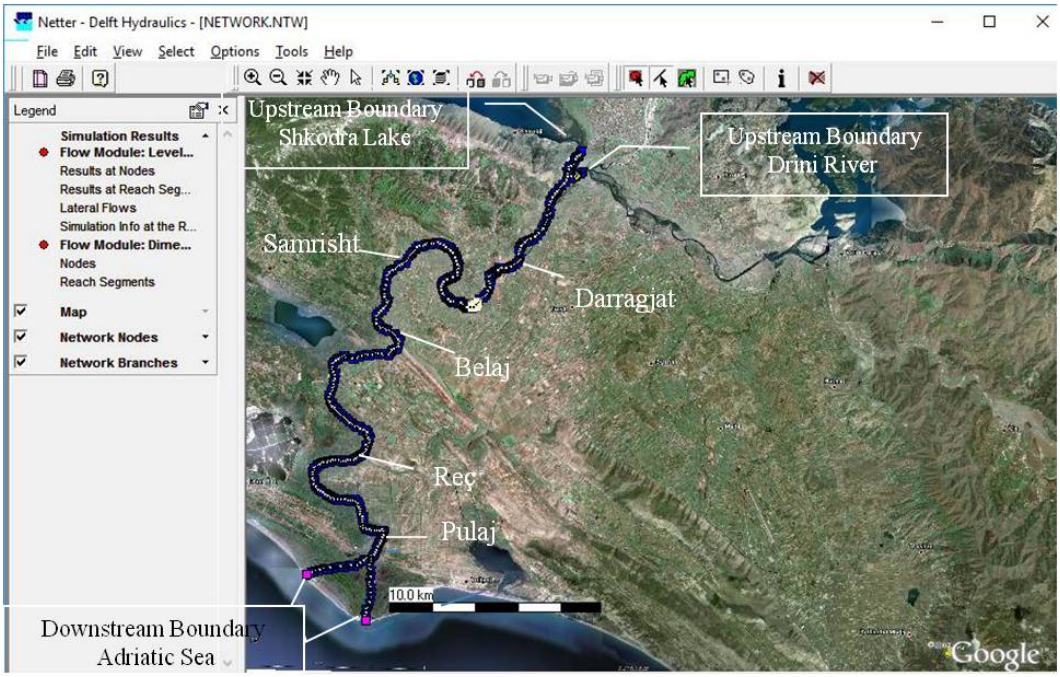

Figure 2. The 1D mathematical model built in SOBEK software for the study area

One of the major steps in setting up a mathematical model is entering the cross section data. For this reason, it is very important to have available a large number of cross sections to describe the geometry of the river system. The quality of the mathematical model depends on the accuracy of the terrain data. Another important element, which describes the river cross sections, is the roughness coefficient. For the river cross sections in SOBEK, which are Y-Z profiles, are used different roughness coefficients for the left overbank, main channel, and the right overbank. Figure 3 represents Manning's *n* values for a given cross section in SOBEK.

Roughness coefficient values for the main channel (n_1) and for the overbank area (n_2) are given preliminary values based on tables and figures compiled by Ven Te Chow (1959). During the calibration process different values of Manning roughness coefficient n_1 and n_2 are tested. The calibration of the mathematical model built in SOBEK software it is accomplished using the traditional method of Trial-and-error (Vidal *et al.,* 2007). For the calibration of the mathematical model hourly data of water level measurements form the Dajç on-line station were used. After the

calibration process, the roughness coefficient values which give the best match between the measured water levels and model outputs are accepted.

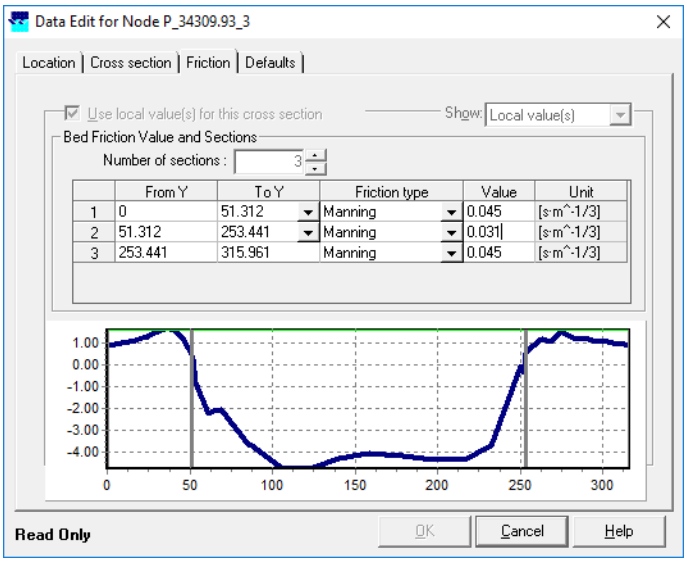

Figure 3. Representation of roughness coefficient for the model built in SOBEK

Results and Discussions

Buna River flow is influenced by the fluctuations of the Adriatic Sea levels. In order to analyse the impact of the Adriatic Sea levels on Buna River flow, average sea levels due to meteorological tide of 0m, 0.5 m, 1.0 m and 1.5 m are considered. The values of average sea level are based on the data of meteorological tides from the observations (IHM, 1984). The study area experiences semidiurnal astronomic tides, which have a cycle with two nearly equal high tides and low tides every day. The astronomic tide has amplitude of 40 cm based on the observations (IHM, 1984). The values of semidiurnal astronomic tides were superimposed to the values of mean sea level from meteorological tide. The effect of Adriatic Sea levels on Buna River regime is analysed for the cross sections in the vicinity of the villages: Pulaj, Reç, Belaj, Samrisht, and Darragjat presented in figure 2.

The mathematical model built in SOBEK software was used to analyse the effect of Adriatic Sea water level on Buna River flow for the period of low flow (5- 18 November 2014) and high flow (25 January-27 February 2015). The inflow (discharge) hydrographs at Buna Bridge (River Buna) and Bahçellëk Bridge (Drini River) for the selected periods are used as upstream boundary conditions (figure 4 and 5). The inflow hydrographs at Buna Bridge used in the 1D model built in SOBEK takes into account the flows coming out of Shkodra Lake into the Buna River. Whereas the inflow hydrographs at Bahçellëk Bridge takes into account the flows coming into Buna River from Drini River. Drini River is a tributary of Buna River, but with a strong influence on Buna River flow. The water flow regime of Drini River, at the downstream part before the junction with Buna River is influenced from the operation of the Vau Dejës hydropower. The discharge hydrographs are calculated based on hourly water level measurements at Buna Bridge and Bahçellëk Bridge stations. Hourly water level measurements at these stations are converted into discharges based on the stage–discharge relationship. Stage–discharge relationship is created based on discharge measurements done in Buna Bridge and Bahçellëk Bridge for the period 1992-2001, and 2010 (GIZ, 2018). As downstream boundary condition it is used the hydrograph of sea water level at Buna River mouth in Albanian and Montenegro for the values: ± 0 m, ± 0 m and tide 40 cm (± 0.2 m), 0.5 m and tide 40 cm (± 0.2 m), 1.0 m and tide 40 cm (± 0.2 m), 1.5 m and tide 40 cm (± 0.2 m).

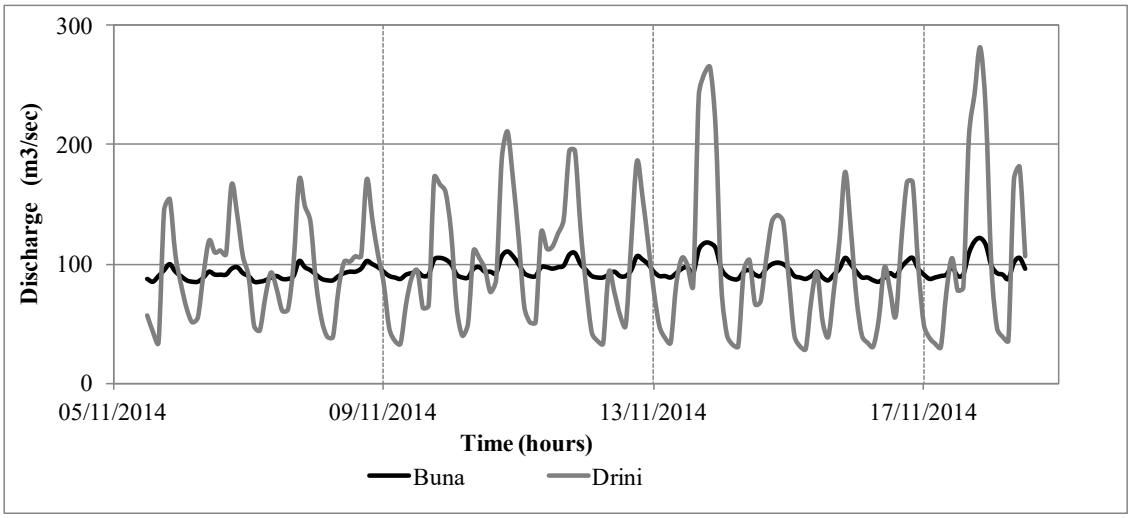

Figure 4. The inflow hydrographs at Buna and Drini River for the low flow period

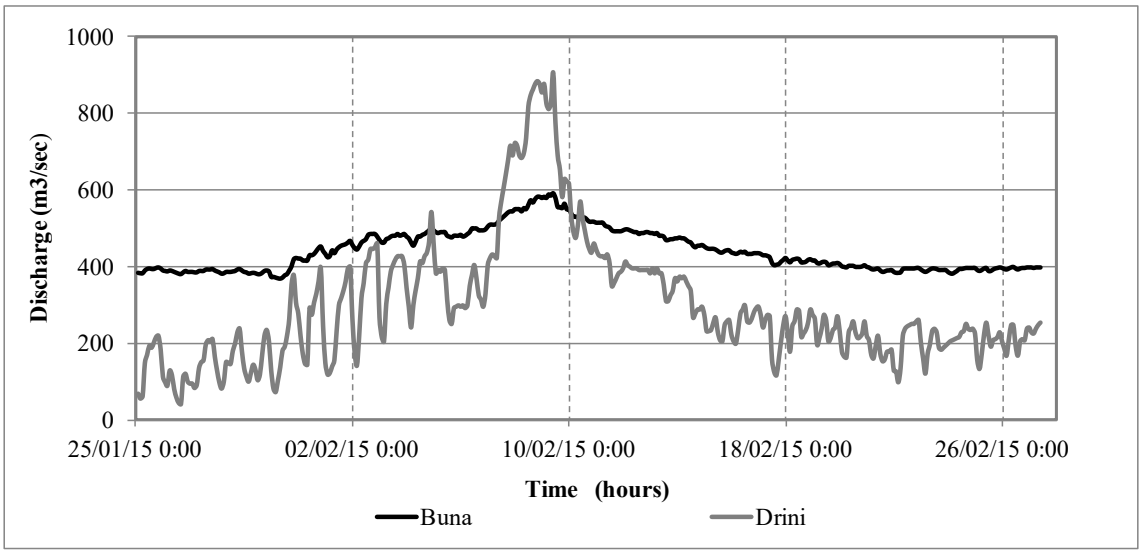

Figure 5. The inflow hydrographs at Buna and Drini River for the high flow period

Impact of Adriatic Sea level on Buna River for the period of low flow

The fluctuations of water levels along Buna River for the period of low flow (5- 18 November 2014) are based on mathematical model results for the study area. Adriatic Sea water level effects are analysed for the cross sections along Buna River in the vicinity of the villages: Pulaj, Reç, Belaj, Samrisht, and Darragjat at respectively distance from the sea (3.4 km, 11.6 km, 21.6 km, 27 km, and 37.5 km).

The figures 6 to 10 show that Adriatic Sea level fluctuations have an impact on the flow regime of Buna River for the period of low flow. The impact is very significant in the profile close to Pulaj village, where Buna River water levels follow the sea level fluctuations. At the profile close to Reç village the impact is still strong, Buna River water level follow the sea level fluctuations especially for high sea water levels. The impact of sea level fluctuations starts to decrease at profile close to Belaj and Samrisht village. At the profile close to Darragjat village the impact of sea level fluctuations on Buna River water levels is small, even in the case of high sea water levels. Water levels of Buna River are not affected from sea level fluctuations for the profiles upstream of Darragjat.

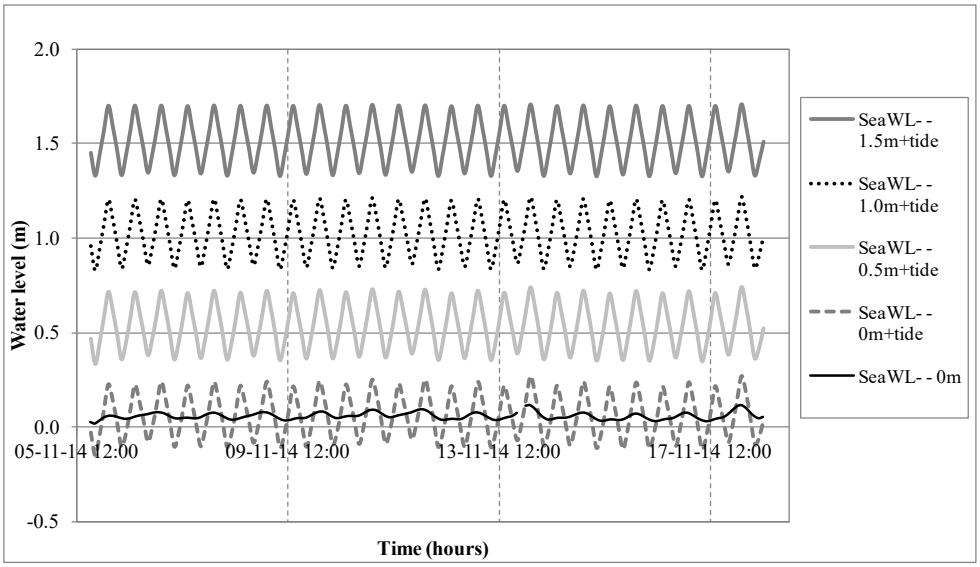

Figure 6. Water level close to Pulaj for different sea level for the low-flow period

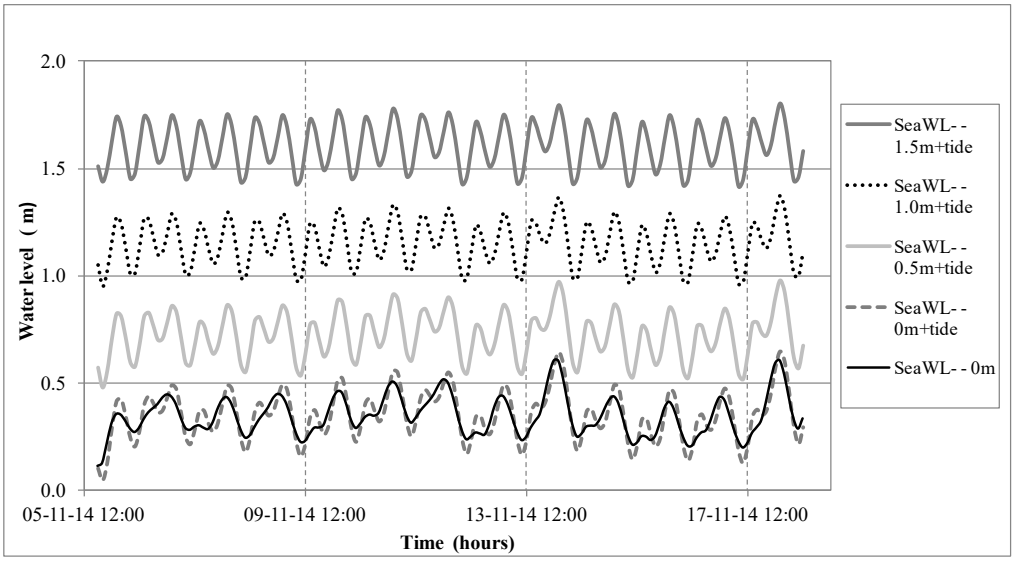

Figure 7. Water level close to Reç for different sea level for the low-flow period

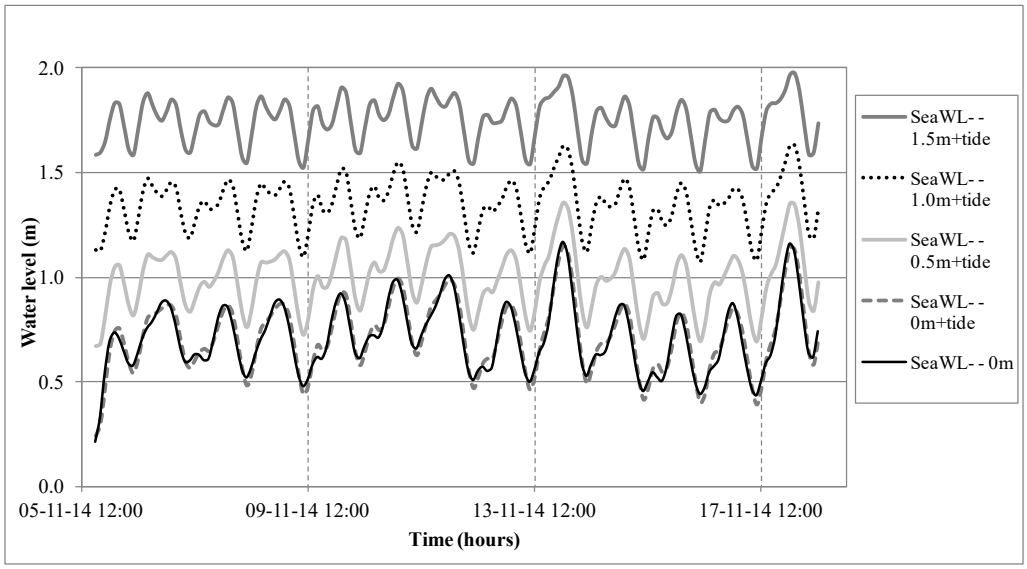

Figure 8. Water level close to Belaj for different sea level for the low-flow period

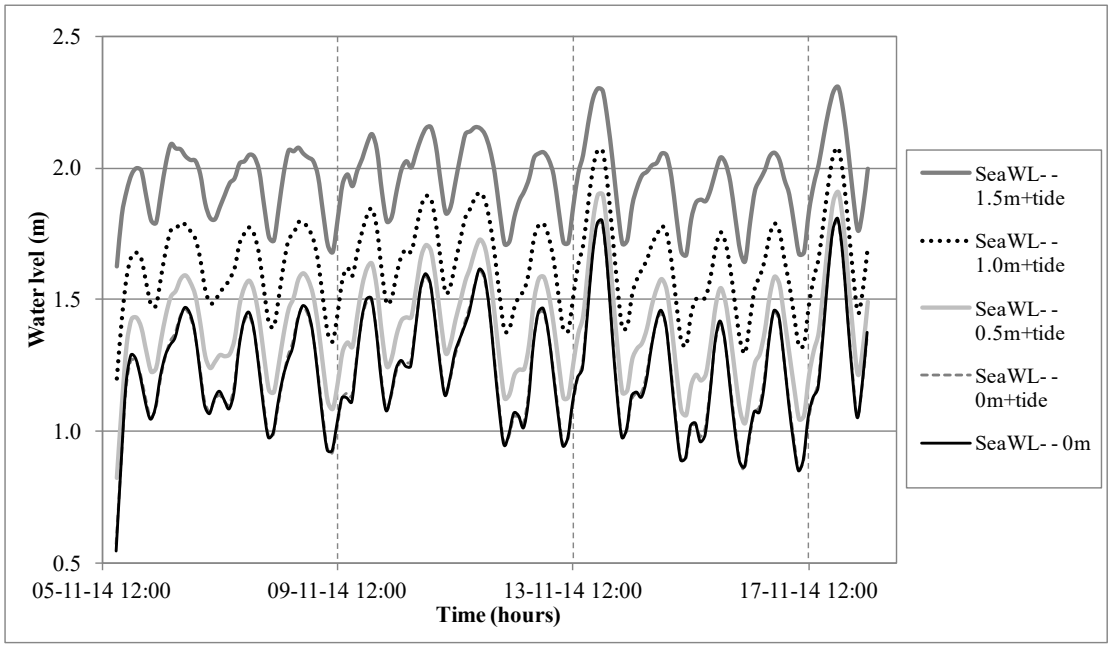

Figure 9. Water level close to Samrisht for different sea level for the low-flow period

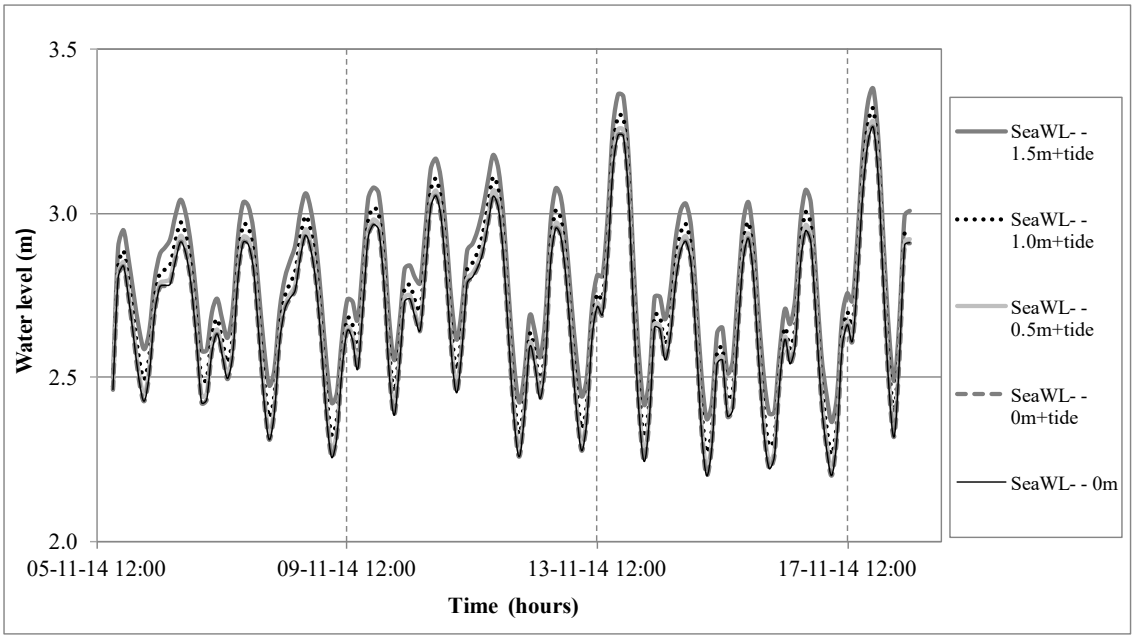

Figure 10. Water level close to Darragjat for different sea level for the low-flow period

Impact of Adriatic Sea level on Buna River for the period of high flow

The following figures 11, 12, 13, 14, and 15 show the fluctuations of water levels for the period of high flow (25 January -27 February 2015) based on mathematical model results. Adriatic Sea water level effects are analysed for the cross sections along Buna River in the vicinity of the villages: Pulaj, Reç, Belaj, Samrisht, and Darragjat at respectively distance from the sea (3.4 km, 11.6 km, 21.6 km, 27 km, and 37.5 km).

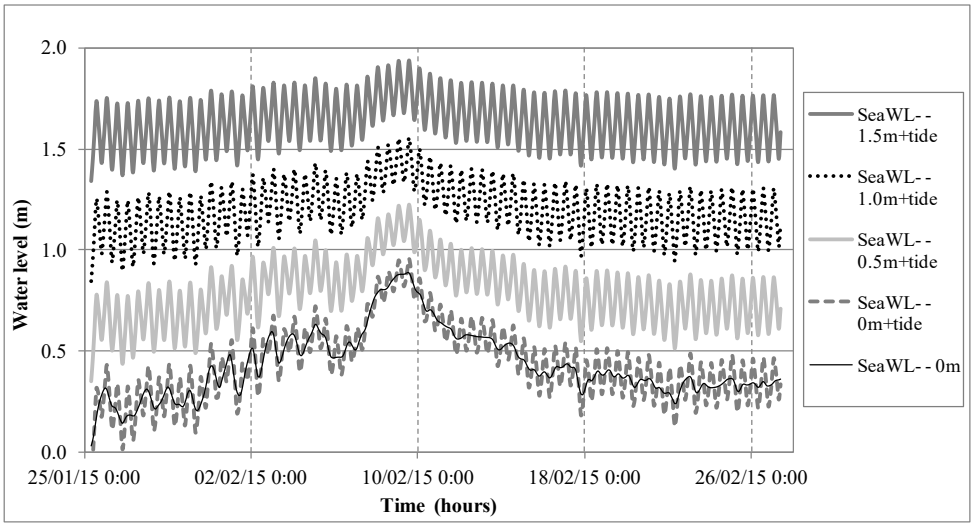

Figure 11. Water level close to Pulaj for different sea level for the high-flow period

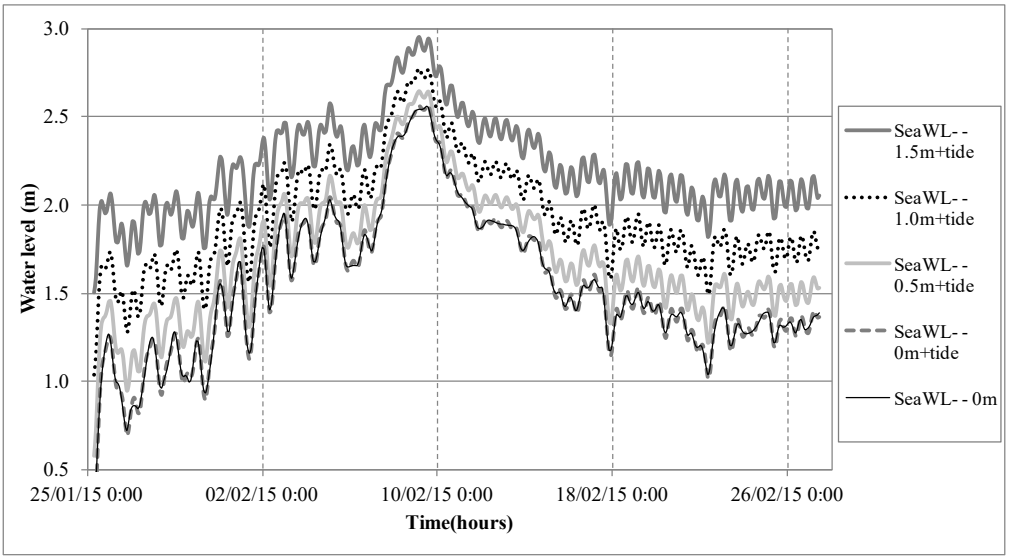

Figure 12. Water level close to Reç for different sea level for the high-flow period

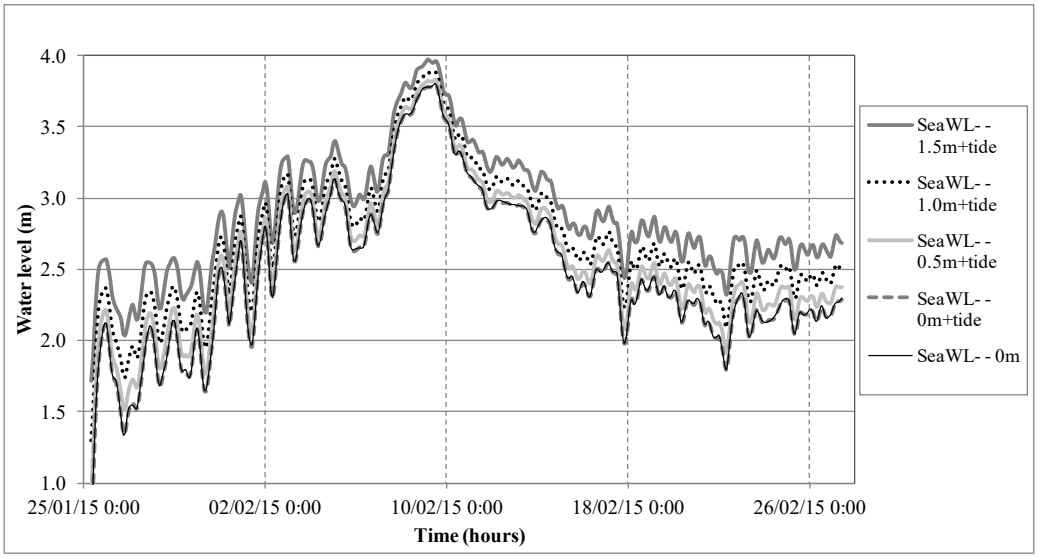

Figure 13. Water level close to Belaj for different sea level for the high-flow period

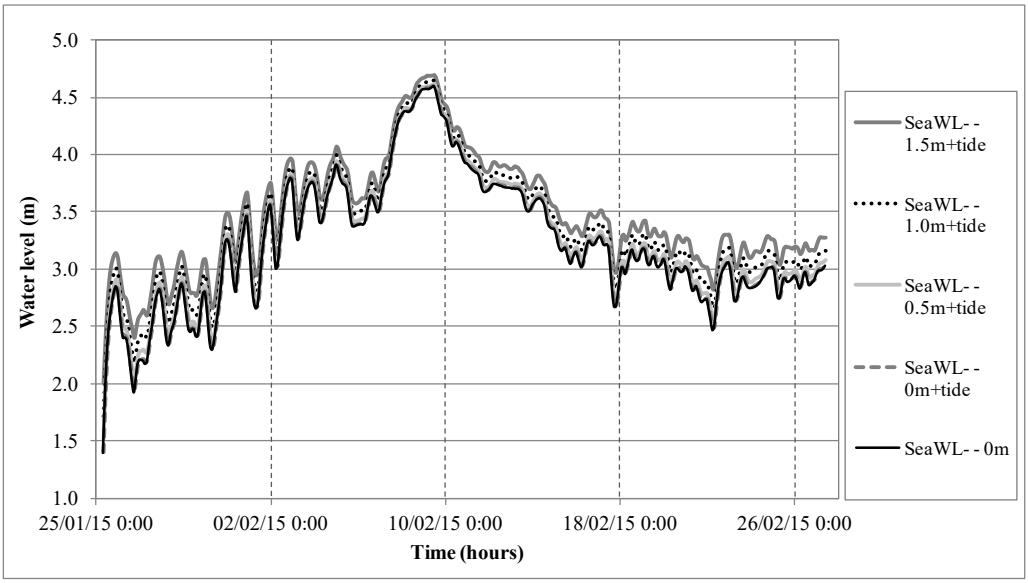

Figure 14. Water level near Samrisht for different sea level for the high-flow period

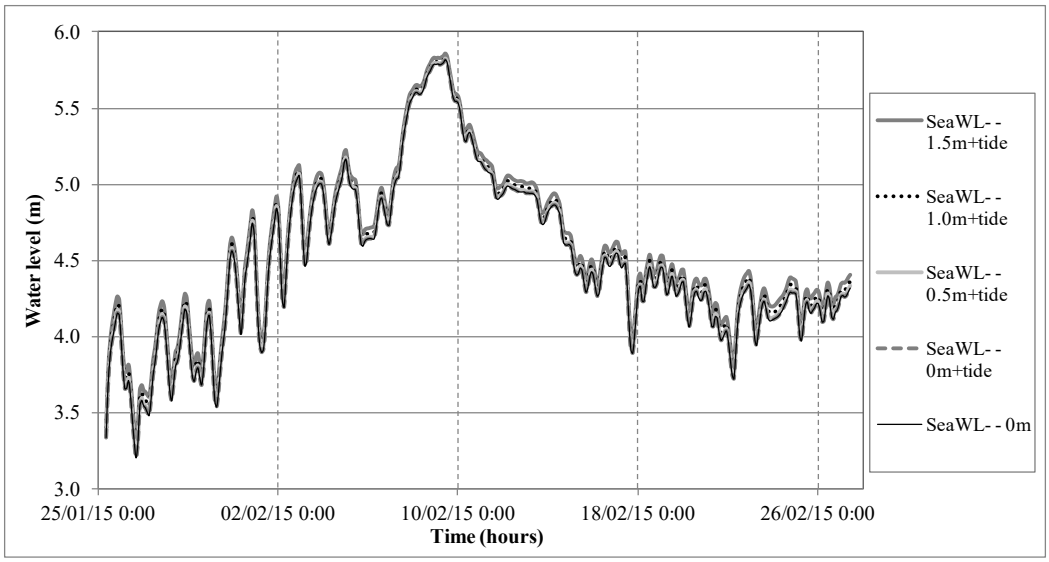

Figure 15. Water level near Darragjat for different sea level for the high-flow period

From the above figures 11 to 15, we can see that for the period of high flow, water level at profile close to Pulaj village follow the Drini River fluctuations superimposing the effect of the sea level fluctuations. At the profile close to Reç village, Buna River water levels follow the fluctuations of Drin River superimposing the effect of sea level fluctuations, but in a smaller degree than in Pulaj. At the profile close to Belaj and Samrisht, water levels of Buna River follow the fluctuations of Drin River superimposing the effect of sea level fluctuations, especially for high sea water levels. At the profile close to Darragjat village only high sea water levels have a small impact on Buna river water levels. Water levels of Buna River are not affected by the sea level fluctuations for the profiles upstream of the junction with Drini River.

Conclusions

The impact of the Adriatic Sea levels on Buna River flow is analysed through a mathematical model built in SOBEK software for average sea levels of meteorological tide 0 m, 0.5 m, 1.0 m, and 1.5 m. The values of astronomic tide with amplitude of 40 cm were superimposed to the values of mean sea level from meteorological tide.

Mathematical model results indicate that the increase of Adriatic Sea level due to meteorological and astronomic tide leads to the increase of Buna water levels for the period of high flow, and especially low flow. The effect of Adriatic Sea level on Buna River flow can reach many kilometres upstream because of low bottom slope of Buna River.

- For average sea level of 0.0 m plus the astronomic tide 40cm the impact on Buna River water levels can reach upstream until Reç for the period of low flow. Maximum increase of Buna water level for this period near Reç is 9 cm. For the period of high flow the impact on Buna River water levels can reach upstream until Pulaj, where the increase of Buna water level for the peak event is 7 cm.
- For average sea level of 0.5 m due to meteorological tide plus the astronomic tide 40 cm the impact on Buna River water levels can reach upstream until Samrisht for the period of low flow. Maximum increase of Buna water level for this period near Samrisht is 20 cm. For the period of high flow the impact on Buna River water levels can reach upstream until Belaj, where the increase of Buna water level for the peak event is 5 cm.
- For average sea level of 1.0 m due to meteorological tide plus the astronomic tide 40cm the impact on Buna River water levels can reach upstream until Darragjat for the period of low flow and high flow. Maximum increase of Buna water level for the period of low flow is 7 cm. For the period of high flow the increase of Buna water level in Darragjat for the peak event is 2 cm.
- For average sea level of 1.5 m due to meteorological tide plus the astronomic tide 40 cm the impact on Buna River water levels can reach upstream until Darragjat for the period of low flow and high flow. Maximum increase of Buna water level for the period of low flow is 17 cm. For the period of high flow the increase of Buna water level in Darragjat for the peak event is 4 cm.

The Adriatic Sea level fluctuations do not affect the flow of Buna River upstream of the junction with Drini River. Buna River water level fluctuations upstream of the junction are affected from the Drini River fluctuations caused from the operation of the Vau Dejës hydropower.

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The Relationship Between the Adorability of Urban Landscapes and Their Users Demographic Variables: The Case of Edremit, Van/Turkey[#]

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Abstract: It is shown in the literature that people want to be more in preferred places and spend their time better when they are in the preferred place. User input is needed for evidence-based design that has developed in recent years. The determination of user preferences containing demographic information about urban landscapes creates important inputs for landscape architects and city planners. Van / Edremit district, which is considered rich in landscape assets, has made the distinction between the new settlement and the old settlement in terms of urbanization in recent years. In this study, the attitudes of different social groups towards the space were investigated in determining the preferences of Edremit for urban landscape and it was aimed to make suggestions for the improvement of the urban landscape. For this purpose, analyzes were carried out to understand what demographic information affecting likes. Visual survey technique, which is applied with visuals and used to determine the perception of the user towards the space, is the main method of the study. The questionnaire was applied to 400 people, and according to the results of the analysis, it was seen that the level of education and income increased and the likes of the senior occupational groups significantly decreased.

Keywords*: Demographic variables, urban landscape, user preference, Edremit, Van*

Introduction

Landscape is a whole where we spend an important part of our daily life while we are working, traveling, eating or relaxing, even if we are watching from a distance, we feel. People want to stay in preferred places more than non-preferred places (Nasar, 1992; Kaplan *et al.,* 1998; Gulgun *et al.,* 2014; Surat, 2017). Sometimes in preferred places, users can explicitly reject the changes that are considered to be made by the administrators. However, in spaces that appeal to different users, it is one of the designers' duties to predict possible conflicts between users and managers, and to prevent these conflicts with space planning and design. Therefore, understanding the preferences regarding the spaces is important for the designers and planners who are the creators of the space (Aşur and Alphan, 2017; Oktay, 2017; Benliay and Altuntaş, 2019; Sezen *et al.,* 2019).

In fact, preferences are related with liking, which is closely related to the aesthetic doctrine that produces thoughts on liking. Urban landscapes are perceived differently by people with their values (Ekşioğlu, 2010; Yazıcı and Kiper, 2019). Many variables are effective in users' visual perceptions and preferences. Most of our perception is based on visual perception. Most of the people perceive the world by seeing. In addition, one third of the brain consists of nerves that work with respect to the eyesight. Perception, which is defined as the process of obtaining various information from the environment, varies according to individuals, its demographic characteristics (age, gender, occupation, education, income, etc.), culture, environment and the social group in which it lives affect the perception (Bozhüyük, 2007; Eagleman, 2013). Therefore, photographs, slides or images in various formats are used in environmental studies. This requires sampling of the environments and landscapes. In the evolutionary based theory developed from landscape choice theories that stand out in landscape aesthetics, information processing theory (Kaplan and Kaplan, 1989) stands out.

The province of Van has a rich landscape in terms of cultural, natural and historical heritage. It can be defined as a period in which the urban development dynamics of Van City changed after the

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period of Van earthquakes in 2011. Edremit district has been shaped under the influence of many civilizations and cultures for centuries. Edremit district is under the influence of processes such as population growth, natural disasters, internal and external migration, security, economic deficiencies, insufficient human resources, ignoring the value and sustainability of the natural, cultural landscape of short-term economic development efforts. The aim of this study, which has been carried out in Edremit district, one of the central districts of Van, which has been experiencing a rapid urbanization process in recent years, is to question whether there is a meaningful difference in likes for urban landscapes according to demographic characteristics among users. The data obtained will contribute to professional disciplines such as landscape architects, city planners and architects in sustainable urban landscape planning and design studies. In addition, municipalities and other city stakeholders will have the ability to predict new urban developments based on the findings from this study.

Material and Method

The main material of the study is Edremit district in Van province in Eastern Anatolia Region/Turkey. The district has a hilly land form rising to the south from Van Lake. Edremit has a settlement starting from the Van Central border to the Gevaş district along the Van Lake coastline (Anonymous, 2019). The location of the district follows the coastline and the length of the district center varies between 24 km and the width between 16-18 km (Figure 1). In this study, various old and new settlements in the district and natural and structured landscapes of their close surroundings are discussed. In addition, the census data related to the area, literature on landscape and environmental aesthetics, photographs taken in the area, survey data are the main materials of the research.

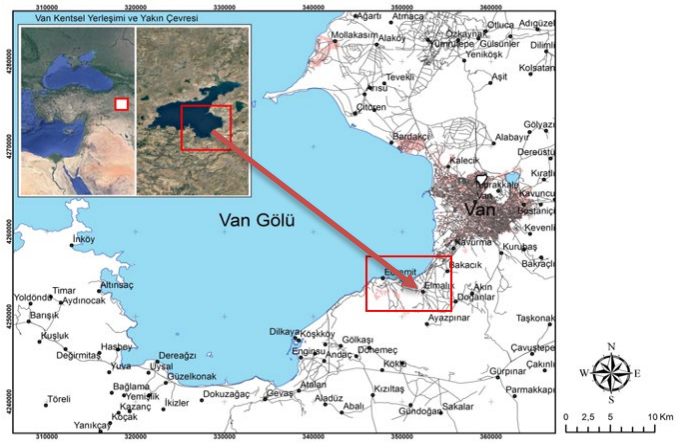

Figure 1. Location of the study area (Edremit/Van)

This study has been tried to be realized with visual landscape evaluation techniques. The main method of the research is the visual survey technique, which is applied with visuals and used to determine the perception of the user towards the space. In this context, based on the information processing theory, four features that are effective in environmental preference; In terms of consistency, complexity, legibility and mystery (Kaplan *et al.*, 1998), visual preferences of the users were determined in the urban areas of Edremit district. According to the results of the address-based census, Edremit district's population in 2017 consisted of 124.375 people. According to the sampling calculation made for p = 0.5 q = 0.5 with a simple random sampling method of ± 0.05 sampling error, it is foreseen that at least 400 surveys will represent the district within the specified deficiencies. In the study, photography was used as a valid method in visual landscape assessment (Hall, 2001; Clay and Smidt, 2004; Kalın, 2004; Çakcı, 2007). Different photographs were taken by taking the views of the city's urban and urban green areas at different rates. The 1012 photographs obtained were classified according to their content and 258 photographs were selected for the sampling survey as a result of the elimination carried out in the context of their contents. The sampling questionnaire was sent to experts on the internet in five parts and 5 experts were asked to score 5 items under the titles of likes, consistency, complexity, legibility and mystery for each photograph in the context of 5-point likert scale formal aesthetic variables. When the experts completed the scoring, the data matrix obtained by taking the average of the points given was coded into the SPSS program and hierarchical cluster

analysis was performed. One-way Anova, correlation and regression tests were applied on the data collected in the survey. With the regression models to be created, formal aesthetic variables that are significant predictors in the preferences regarding the urban area were determined.

RESULT

Users' rating of photos

51 photos selected from the photographs taken from the urban landscape area of Edremit / Van were presented to 400 users with the photo survey method. As a result of the analysis, 5 most liked photos were revealed (Figure 2). In this study, it is revealed that the most admired images are areas that are rich in vegetative terms.

Figure 2. The top five visuals according to the users' rating points

Photo 48 of the images used in the study is the most liked visual by the users with an average score of 4.24 as a result of the users' rating. The scores of the 5 most liked images are given in Table 1.

Table 1. Scores of the most liked photos as a result of the survey

Edremit/Van Urban Landscape Areas					
Photo No	48	31	41	23	18
Average Score	4.24	4.16	4.12	4.00	3.99

Demographic information in the evaluation of user surveys: The demographic information of 400 users surveyed is given in Table 2. Accordingly, 66% of the participants are women and 33% of them are men. One user did not answer the gender question. Considering the age distribution of the participants, it is seen that 37% of the participants are between the ages of 15-18, 38% are in the age range of 19-29 and 14.0% are between the ages of 30-49. Participants between the ages of 50-65 constitute 8.3%, while 10 (2.5%) of the participants are over 65 years of age. One user did not specify his age. In terms of education while 10 users (2.5%) of the respondents are in primary school, 134 users (33.5%) are at the undergraduate level, 28 users (7%) are at the graduate level, and 16 users (4%) are at the doctorate level. In terms of job one user (0.3%) of the participants worked in the

private sector, 14 users (3.5%) worked in the private sector, 5 users (1.3%) self-employed, 39 users (9.8%) civil servants, 3 users (0.8%) tradesmen, 13 users (3.3%) retired, 285 users (71.3%) students, 17 users (4.3%) housewives, 2 users (0.5%) while unemployed, 18 users are in the other category. Considering the monthly income of the participants, it was observed that 250 users (62.5%) had a minimum wage and below, 38 users (9.5%) had an income of 4501 TL and above it and 43 participants could not report on monthly income.

Table 2. Demographic distribution of users surveyed

Gender	Female	Male	Other							
N	267	132	1							
%	66.8	33.0	0.3							
Age	15-18	19-29	30-49	50-65	65 and above		Other			
N	148	152	56	33	10		1			
%	37.0	38.0	14.0	8.3	2.5		0.3			
Educational Status	Readers / Writers	Elementary School	Secondary Education	High School	Associate Degree	Bachelor graduates		Master	Doctorate	Other
N	0	10	11	165	34	134	28		16	2
%	0.0	2.5	2.8	41.3	8.5	33.5	7.0		4.0	0.5
Job	Worker	Private sector	Self-employment	Officer	tradesman	Retired	Teacher	Housewife	unemployed	Other	lost
N	1	14	5	39	3	13	285	17	2	18	3
%	0.3	3.5	1.3	9.8	0.8	3.3	71.3	4.3	0.5	4.5	0.8
Monthly Income	Minimum wage and below	950-1,500 TL.	1,501-2,500 TL.	2,501-3500 TL.	3,501-4500 TL.	4,501 TL. and above	Other			
N	250	16	18	16	19	38	43			
%	62.5	4.0	4.5	4.0	4.8	9.5	10.8			

Relation of demographic variables and all rating scores

In this study, a regression model was tried to be established in order to measure the differences among the subgroups of likes. For this, all the likes scores and the demographic variables opposite are written one after the other and a data matrix with 20400x5 porosity is created. In this regression model, liking scores are defined as dependent variables. With the sequential scale data (such as age, education level, monthly income), the variable of being a woman and being a student is defined as a dummy variable as 1-0, and a stepwise regression model was created with 5 independent variables in total. The results of the analysis are shown in Table 2.

Accordingly, the stepwise regression analysis, which was conducted to find out what demographic information affecting the likes, was completed in 3 stages. It is seen that occupation, education level and monthly income, which are 3 demographic features, are important factors in terms of their contribution to appreciation of the space shown in the photograph. In the first step of the analysis, the occupation variable, which explains 1.8% of the variance of the liking of the place in the photo, was taken. When the regression coefficient sign of the profession variable is examined, it is seen that it is negative. In other words, the increase in the upper occupational group causes a decrease in likes. If this variable is considered as the dummy variable, it is concluded that the students significantly liked the places less than the other profession groups. In the second stage, the educational status variable that makes a significant contribution to the explained variance is taken. The educational status variable contributed 0.3% to the explanation of the variance related to the liking of the place shown in the photograph. When the regression coefficient sign of the educational status variable is examined, it is seen that it is negative. In other words, as the education level increases, the level of appreciation decreases. In this context, it can be said that those who received higher education significantly liked the place shown in the photo. In the third stage of the analysis, monthly income variable was included in the analysis. The monthly income variable made a 0.01% contribution to the explanation of the variance related to the liking of the place shown in the photograph. Regarding the sign of the regression coefficient, it is seen that it is negative. Although the monthly income variable makes little contribution (0.01%) in explaining the variance related to the liking of the place shown in the photograph, it still appears as a significant variable in explaining the appreciation. When the regression coefficient of the monthly income variable is analyzed, it is seen that the coefficient takes

negative value. In other words, individuals from the upper income group significantly like the space shown in the photographs.

Accordingly, three demographic features (Profession, Education, Monthly income) are seen as a significant factor in the regression model. In other words, the demographic characteristics of the subjects that affect the liking of a place created with plants are Profession, Education and monthly income (Table 3). As a result of this analysis, the liking of a place can be achieved with the following formula;

User Likes = 3.601 (Fixed) -0.523 (Profession) -0.046 (Educational Status) – 0.023 (Monthly Income).

Table 3. Demographic variables that significantly affect users' likes overall rating

Demographic variables	R	ΔR^2	B	SH_β	β	T	p
1.Job	0.136	0.018	-0.523	0.042	-0.171	-12.502	0.000
2.Education Status	0.144	0.003	-0.046	0.009	-0.044	-5.260	0.000
3. Monthly Income	0.145	0.000	-0.023	0.011	0.029	-2.021	0.043
Fixed	-	-	3.601	0.057	-	63.586	0.000
R^2 = 0.021 F (3. 18201)= 130.186 P=0.000							

Theories about landscaping preferences are not only evolutionary in origin, but there are also cultural theories. One of these is the Topophilia (Love to Space) theory developed by Tuan (1974). According to this theory, preferences regarding the landscape are affected by variables such as age, gender, and educational status (Tveit *et al*., 2006). In this study, it was found that cultural variables such as monthly income, education level, profession significantly affect the preference of landscapes. For example, as the senior profession group, education level and monthly income increase, the appreciation decreases significantly. Based on these data, it can be said that the findings of the study support the theory of Topophilia. According to the study done, it shows that the most preferred images are rich in plant existence. The reason for this can be shown as the importance given by educated and conscious people to plant assets in urban areas.

Conclusions and Recommendations

In the evaluation studies on aesthetic preferences, the measurement of the relationship between landscape and the demographic characteristics of the sensors is an important issue that should be emphasized (Sevenant and Antrop, 2009). In their study of Junker and Buchecker (2008) stated that demographic characteristics such as age, monthly income, profession and education level have a significant impact on human environmental values and aesthetic preferences. In the statistical inquiries, it was revealed that individuals with high educational status liked the places shown in the photos significantly less. This finding supports the study of Oktay (2017). Also, according to the results of this study, the level of appreciation decreases as the income level increases. However, Polat *et al.* (2012) found that in their study in the recreation areas of Konya city and Oktay (2017) in their study in Konyaaltı, the increase in revenue increased significantly, but the reason for the result of the Edremit example is that the higher income group is more social compared to the lower income groups. It is predictable that he may have the opportunity and therefore be more fortunate to travel. From this point of view, it is meaningful that the upper income group, which has the chance to compare with the landscape arrangements in other cities, likes the Edremit urban landscape less. In addition, it was concluded that the gender and age factors of the users are not related to the like of the urban landscape.

Acar *et al*. (2002), Güngör and Aslan (2004), Todorova *et al*. (2004) and Sezen *et al*. (2011) as stated by plants as living and living entities are different objects from classical inanimate design objects that indicate different seasons and different times of the day and have different spatial expressions. Urban designs, supported by the green texture presented in this study, are more appreciated by the users in terms of visual landscape. In line with these results, it is revealed that the green texture deficiency in the perspective view of mass housing areas, especially from the new settlements, should be eliminated in order to improve the urban landscape image revealed by the general settlement of Edremit district/Van. Studies on the demographic characteristics of the users will enable the revealing of user profiles for urban landscape areas of a particular region. The findings to be obtained will be important bases in their work for the relevant planners and managers. In the light of the results of the study, in line with the environmental preferences of the users, it is necessary to

take these concepts into consideration by the municipalities and other city stakeholders on the basis of sustainable urban landscape planning and design.

Acknowledgements: *We would like to thank Dr. H.E. Oktay for helping us in the statistical analysis of this study.*

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Use of EURO-CORDEX Models for Analyses of the Future Water Resources in Bovilla Catchment

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Abstract: Bovilla catchment is part of the Ishëm River. The artificial lake created in 1998 from the Bovilla dam is one of the most important water resources in Albania because is used as the main source from the Tirana Municipality water supply system. About 60% of Bovilla catchment is covered by forest (both broad-leaved and coniferous) and 5% of the area is bare or only barely wooded. Grasslands and pastures cover about 8-9% of the area, while 18% are dedicated to agriculture. Climate change, growing population, unsustainable development, and inappropriate land use threaten to induce or intensify natural hazards' exposure and vulnerability with disastrous consequences for the environment and societies. The performance and the spatial resolution of General Circulation Models (GCMs) have continuously improved in the recent years, but the typical state of the art spatial scale is still too coarse to realistically reproduce present climate and project climate change signals on local scales, especially in the presence of complex orography. In order to provide seasonal and annual water balance with different climate change scenarios for Bovilla catchment, the hydrological rainfall-runoff model HEC-HMS was implemented. In the absence of measured data, the parameters' values of the hydrological model were assigned based on acceptable data ranges from the manual, from literature, and on the expert experience. The parameters have been finalized in order to well match the simulated and observed data.

Keywords*:* climate change, general circulation models, hydrological model, rainfall-runoff

Introduction

Bovilla catchment is part of the Ishëm River. The artificial lake created in 1998 from the Bovilla dam is one of the most important water resources in Albania because is used as the main source from the Tirana ++Municipality water supply system. About 60% of Bovilla catchment is covered by forest (both broad-leaved and coniferous) and 5% of the area is bare or only barely wooded. Grasslands and pastures cover about 8-9% of the area, while 18% are dedicated to agriculture. Climate change, growing population, unsustainable development, and inappropriate land use threaten to induce or intensify natural hazards' exposure and vulnerability with disastrous consequences for the environment and societies (Cardona *et al*. 2012). The performance and the spatial resolution of General Circulation Models (GCMs) have continuously improved in the recent years, but the typical state of the art spatial scale is still too coarse to realistically reproduce present climate and project climate change signals on local scales, especially in the presence of complex orography (Scoccimarro *et al*. 2013). In order to provide seasonal and annual water balance with different climate change scenarios for Bovilla catchment, the hydrological rainfall-runoff model HEC-HMS was implemented. In the absence of measured data, the parameters' values of the hydrological model were assigned based on acceptable data ranges from the manual, from literature, and on the expert experience. The parameters have been finalized in order to well match the simulated and observed data.

Materials and Methods

In order to perform analyses of the climate change in Bovilla catchment are needed assessment of the model's bias and application of the bias correction techniques as a preliminary step for simulated weather variables to be corrected. In the present paragraph, the main checks performed to test the quality of the available observations are described, before using them for model bias correction.

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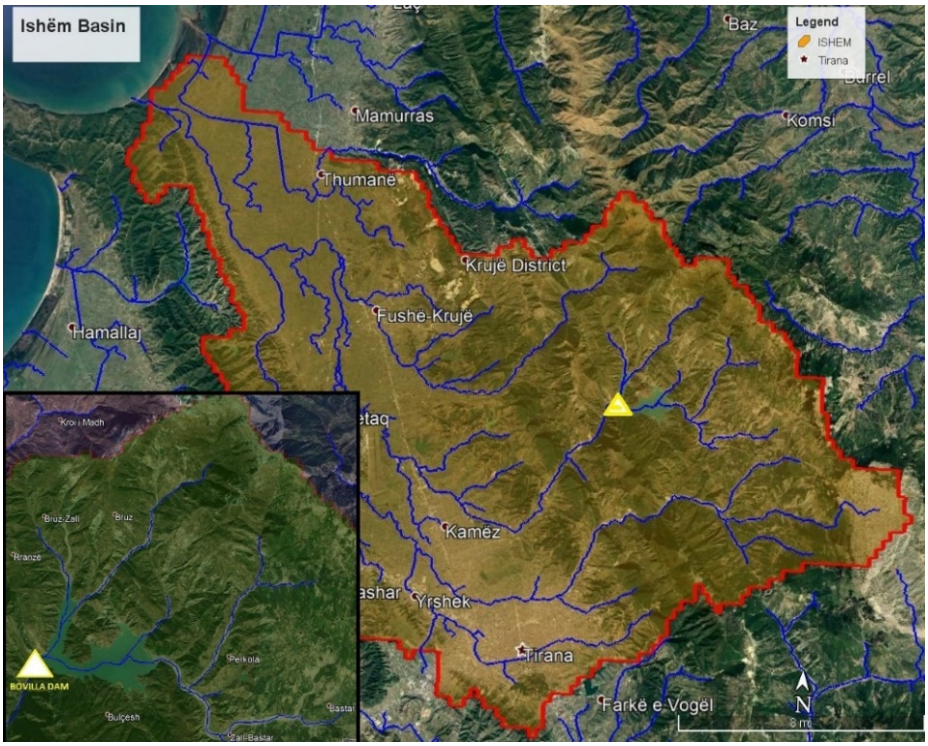


Figure 1 Ishëm river basin and Bovilla catchment

The available observational data are:
Daily precipitation:
period 2002-2011 (stations Shengjergj, Linze, and Dajt Fshat);
period 1960-1990 (station Zallmner);
Daily maximum and minimum temperature:
period 2002-2011 (stations Bulqize, Shengjergj, Linze, Tirana and Dajt Fshat);
period 1960-1990 (station Kruje)

The application of the bias-correction methods based on the observed dataset shorter than 30 years period doesn't permit to completely remove the bias, in particular for what concerns the values in the tails of the distributions. Based on this concept, the observed data was validated through a basic integrity test for the identification of anomalous values (Ray *et al*. 2016).

On the base of these tests, the initial dataset was reduced. However, the completeness test over the whole period considered was passed (at least 75% of data are available) for both periods 2002-2011 and 1971-1990, for each variable and station examined. This preliminary phase is essential for the evaluation of the bias and the following bias correction application. In order to verify how many observational data are not available, the percentage per year of the missing data for each station is calculated, for each variable, considering the observed period 2002-2011. No missing values are detected considering the observed period 1960-1990. The yearly precipitation and maximum and minimum temperature values for the different stations are reported. A high value of the annual maximum and minimum temperature for Tirana station in 2010 and above all in 2011 with respect to the other stations is reported. In fact, in those years, both variables are characterized respectively by about 25% of missing data (generally in February, November, and December) in 2010 and 28% of missing data (from January to the middle of April) in 2011.

The aim is to define a high-resolution climate projection data for impact analysis on the Bovilla catchment, to be used as input in the hydrological model in order to estimate the impacts on the hydrological process. Selection of the model among those currently available within the EURO-CORDEX project (Coordinated Downscaling Experiment - European Domain) at the maximum resolution (about 12 km) on the Bovilla catchment. The selection highlights the simulations having the best performances in terms of precipitation and temperature (the performances are evaluated using all the weather data available over the area).

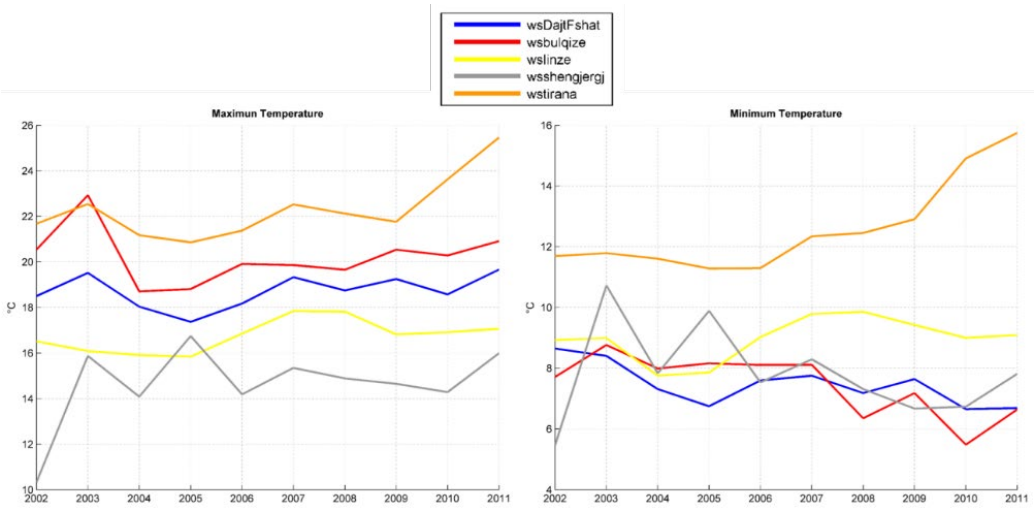


Figure 2 Annual distribution of observational maximum and minimum temperature data for stations, considering the observed period 2002-2011.

Definition of bias-corrected climate data, using the selected model for the 3 periods:

a. on the period 1981-2010 (historical);
b. on the period 2011-2100 under IPCC RCP4.5 scenario;
c. on the period 2011-2100 under IPCC RCP8.5 scenario.

EURO-CORDEX simulations were used at the spatial resolution of 0.11 degrees (about 12 km), forced by different GCM. In particular, the "best" model was selected on the base of a comparison between the observed precipitation and temperature data, available, and all the currently available EURO-CORDEX simulations over the area of interest of the project. After this phase, permitting the selection of the RCM having the lowest bias in the area with respect to the selected variables a bias correction (BC) statistical approach was used (Gudmundsson *et al*. 2012) in order to overcome the existing bias and make these climate data suitable to be input for the hydrological model.

It is worth noting that bias correction performed over a period shorter than 30 years does not allow a whole bias removal, as the observations are available on a time period lower than the one considered necessary by the WMO to represent the climate of the area. Before making the bias correction of the climate data, a completeness test was performed for each case study, in order to ensure that each of them contains a satisfying percentage of valid data (at least 75%). Afterward, the bias correction of the selected model was performed by using 2002-2011 or 1971-1990 as a control period, according to the availability of the observational data. As a further analysis, the annual values of the EURO-CORDEX models for the observed period (2002-2011) were compared with the observed ones.

Generally, the selected model reproduces better the annual trend of the observed values than the other models, especially concerning the annual cumulative precipitation (prcptot) and the average annual minimum temperature (tasmin). As expected, the selected bias correction method (QUANT) reduces the error for all three variables.

Results and Discussions

Timespan 2002-2011 and 1971-1990 are respectively assumed as reference period according to with data availability in Figure 3, observed (black line), modeled (blue line) and bias-corrected data (red line) of monthly values respectively for precipitation, maximum temperature, and minimum temperature are displayed for each case study. It is worth noting that, in all cases considered, bias-corrected data (red line) fit very well with observed data (black line). Therefore, the selected bias correction method (QUANT) removes the systematic error of the climate model (blue line) on the control period.

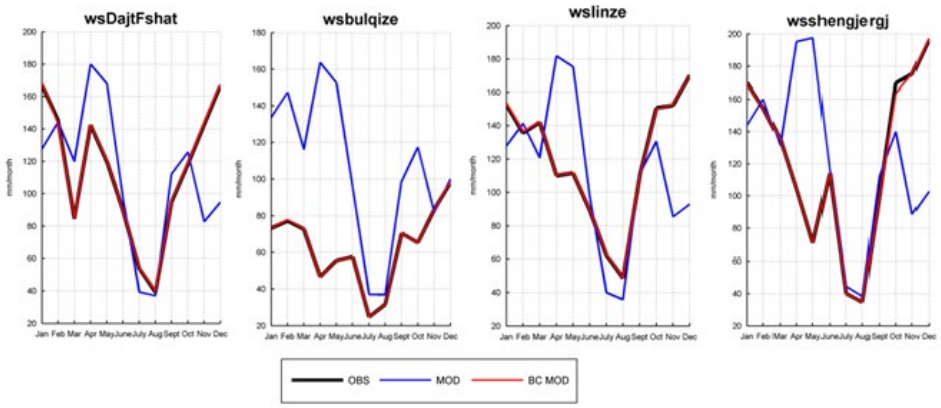


Figure 3 The annual cycle of monthly values for precipitation over the calibration period 2002-2011.

Figure 4 shows the comparison between measures and bias-corrected modeled data considering the calibration period 2002-2011.

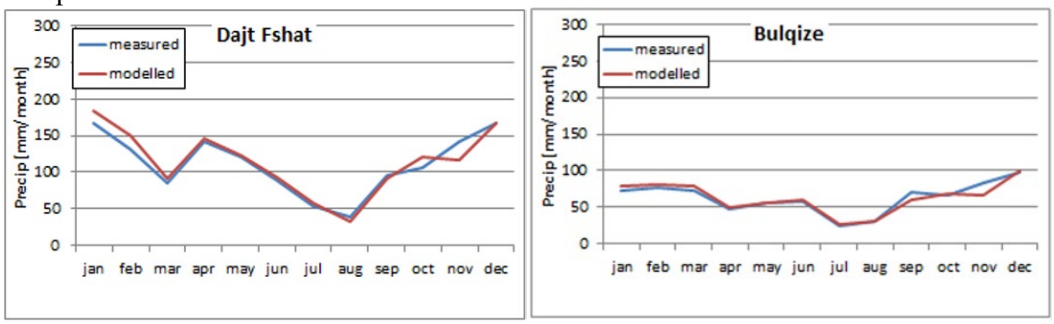


Figure 4 Monthly precipitation in the observed period 2002-2011: comparison between measures and bias-corrected modeled data.

Figure 5 shows the comparison between the datasets 2002-2011 and 1981-2010 of the monthly precipitation obtained from the bias-corrected model.

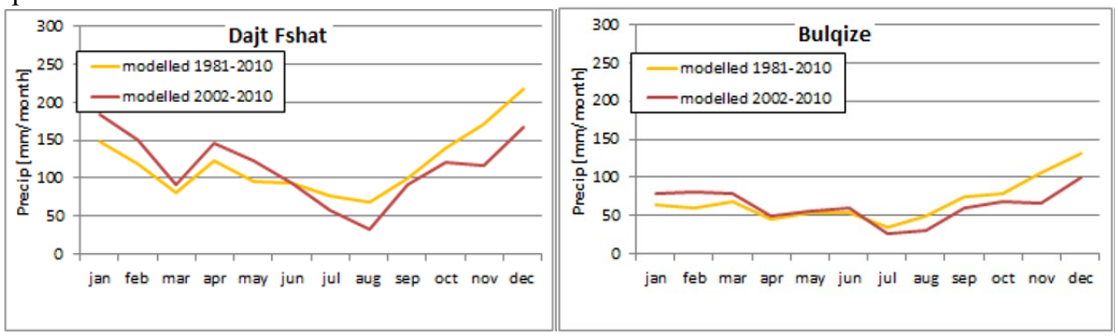


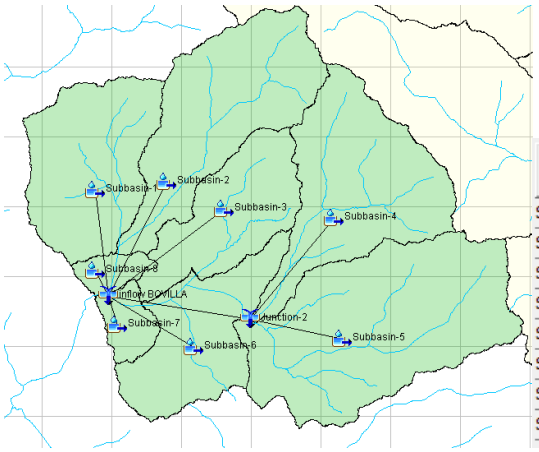
Figure 5 Monthly precipitation from the bias-corrected model: period 2002-2010 (red line) and the period 1981-2010 (orange line).

It is necessary to be aware that one of the problematic aspects related to bias correction methods is that the climate change signal might be altered (Teutschbein & Seibert, 2012).

Therefore, it is important to assess whether the bias correction method can preserve the climate change signal of the selected regional climate model. To this aim, annual time series and trend of observed, modeled and bias-corrected data were evaluated.

These analyses were performed for precipitation calibration for the period 2002-2011 and for calibration period 1971-1990, and for maximum and minimum temperature for calibration period 2002-2011 and for calibration period 1971-1990 under RCP4.5 and RCP8.5 scenarios.

Considering the calibration period 2002-2011, under RCP4.5 the trend is properly preserved by bias-corrected model for temperature variables, while for precipitation slight differences in trend values are recorded. Under RCP8.5 trend is generally well preserved for each variable and for each case. Considering the calibration period 1971-1990, under both scenarios, the trend is well preserved by the bias-corrected model for each variable and case considered.



Subbasin	Area (KM2)
Subbasin-1	13.47
Subbasin-2	16.2
Subbasin-3	9.9
Subbasin-4	16.72
Subbasin-5	24.5
Subbasin-6	10.73
Subbasin-7	2.32
Subbasin-8	1.61

Figure 6 Basin model of Bovilla in HEC HMS.

In general, from the results obtained, the climate change signal is well preserved when the calibration period 1971-1990 is considered because it contains more data, vice versa when the calibration period 2002-2011 is used a slight worst agreement is obtained. All this climatological database needs to be implemented as input data in the hydrological model HEC HMS that is chosen. Bovilla basin was divided into many subbasins in order to better calculate the inflow at the reservoir. Figure 6 shows the basin model of Bovilla in HEC HMS divided into 8 subbasin areas. The lack of water level and discharge data excludes the possibility of the model calibration. So, the model was implemented using parameters suggested in the literature, except for the morphological ones (time lag, slopes, *etc*.) and covers factor USACE (2000). The rainfall and temperature 120-year pattern of the RCP4.5 and RCP8.5 scenarios were entered as input data in the hydrological model HEC HMS for Bovilla. The dataset was divided in the following four 30-year series for computational reasons:

a. period 1981-2010 (historical);
b. period 2011-2040;
c. period 2041-2070;
d. period 2071-2100.

The results were processed and statistically analyzed with regard to:

- flow peak value and frequency,
- flow-duration curve,
- seasonal water balance,

Figure 7 and Figure 8 show the analysis of the hydrological model results for the Bovilla basin in terms of simulated maximum annual flow (daily values) using rainfall and temperature dataset of RCP4.5 and RCP8.5 scenarios.

From the results, it can be observed that:

- there is a slightly increasing trend, more evident for RCP8.5 scenario, of the flow peaks with highest return periods (i.e. 100 years return period);
- Figure 7 shows a different behaviour of the two CC scenarios in terms of flow peaks mean value: the RCP8.5 scenario results show more flow peaks in the range from 105 to 140 m^3/s than RCP4.5 scenario results;
- the probability density distribution (Gaussian) of simulated maximum annual flow shows a change in the distribution of medium-high flow peaks: it is that while in the historical period the flows with a peak in the range 45-60 m^3/s are more frequent, in the CC scenarios, the flows with a peak in the range 60-75 m^3/s become more frequent (Figure 8).

In order to analyze the frequency of flow peaks, the results were firstly split in two 50-year series, one from 2001 to 2050 and one from 2051 to 2100 and ordered increasingly. It can be observed that:

- the runoff calculated using RCP4.5 scenario generates a peak with return period (RP) of 50 years equal to 134 m^3/s in 2001-2050, and to 153 m^3/s in 2051-2100 (+14%);
- in 2051-2100 the 50-year RP flow peak of the first 50 years is exceeded twice, indicating an increasing trend of the flood's frequency;
- the runoff calculated using RCP8.5 scenario generates a peak with a return period of 50 years equal

to 131 m³/s in 2001-2050, and to 159 m³/s in 2051-2100 (+21%), indicating an increase of the 2001-2050 50-year RP peak frequency;

- both the scenarios, and the RCP8.5 scenario, generate higher maximum annual flows with considering the same return period values.

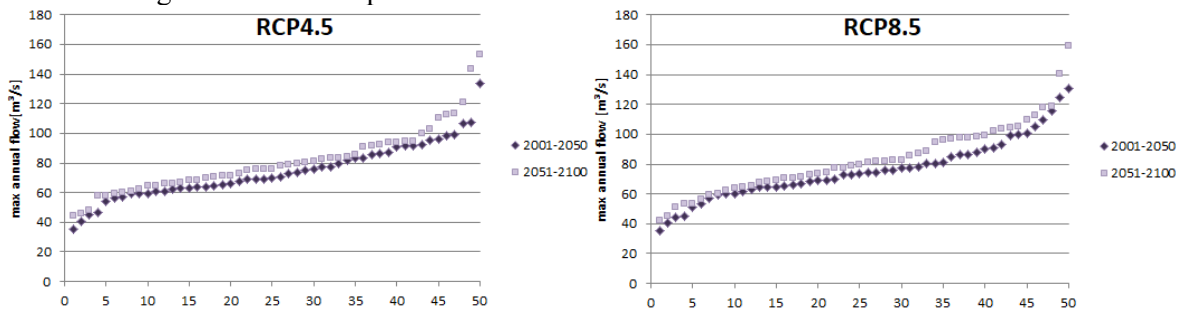


Figure 7 Hydrological model results for Bovilla basin: simulated maximum annual flow covering the periods 2001-2050 and 2051-2100, on a decreasing scale, using rainfall and temperature dataset of RCP4.5 and RCP8.5 scenarios.

The same analysis was done with the 30-year periods, including the historical one (1981-2010, 2011-2040, 2041-2070, 2071-2100), and it confirms the increasing term of flood peaks, more regular in case of the RCP8.5 scenario.

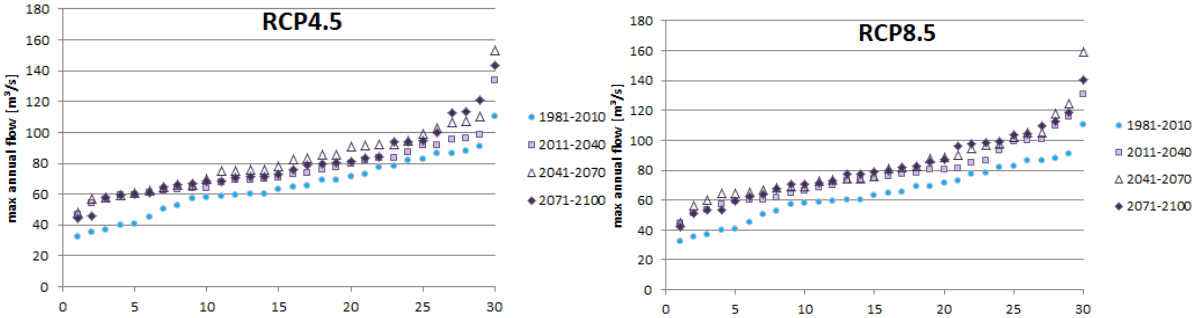


Figure 8 Hydrological model results for Bovilla basin: simulated maximum annual flow covering the 30-year periods 1981-2010, 2011-2040, 2041-2070, 2071-2100, on a decreasing scale, using rainfall and temperature dataset of RCP4.5 and RCP8.5 scenarios.

The results were processed to calculate the flow-duration curves for the same 30-year periods (1981-2010, 2011-2040, 2041-2070, 2071-2100). The flow duration curves show the torrential regime of the rivers in the Bovilla basin. Figure 9 shows the comparison of the calculated flow-duration curves, in logarithmic scale, using rainfall and temperature dataset of RCP4.5 and RCP8.5 scenarios respectively. It can be observed that climate change scenarios affect the ordinary flows that decrease over time, more visible in the RCP8.5 scenario case.

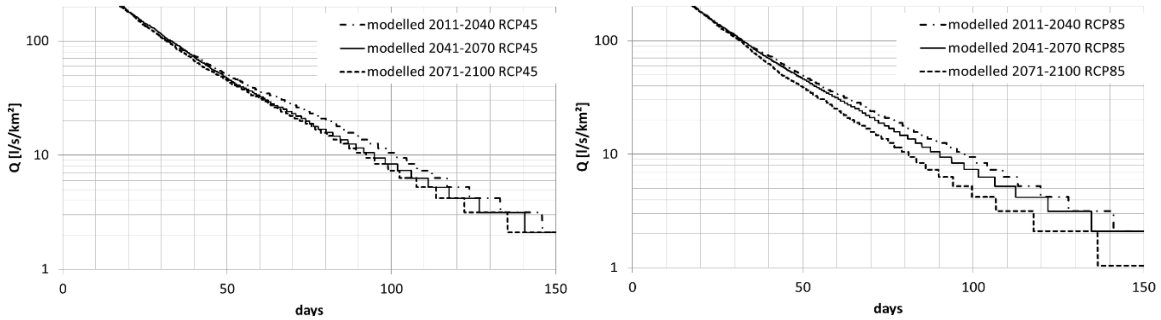


Figure 9 Hydrological model results for Bovilla basin: comparison of the flow-duration curves obtained by the simulation of the 30-year periods 1981-2010, 2011-2040, 2041-2070, 2071-2100, in logarithmic scale, using rainfall and temperature dataset of RCP4.5 and RCP8.5 scenarios. At the bottom: zoom in the range of 0-150 days. The hydrological model results were processed to analyze the seasonal trend.

In this case study, the following simulated daily time-series were considered:

- historical, time series from 1981 to 2010;
- RCP4.5 scenario, time series from 2011 to 2100 (last 30-year period simulated);
- RCP8.5 scenario, time series from 2011 to 2100(last 30-year period simulated).

The seasonal components were identified using the Seasonal Trend decomposition based on LOESS (STL) method. The results obtained for Bovilla basin in terms of the simulated mean daily flow for RCP4.5 (red line) and RCP8.5 (green line) scenarios compared to the simulated mean daily flow of the historical period (blue line).

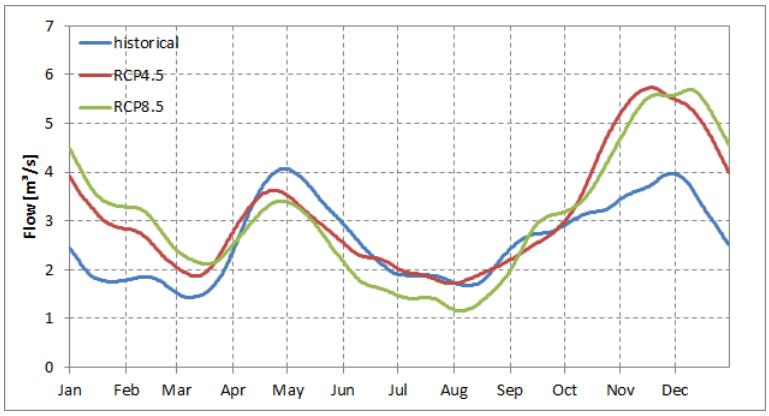


Figure 10 Model results for Bovilla basin: simulated mean daily flow for RCP4.5 and RCP8.5 scenarios

In the CC scenarios, a 20% increase of the annual mean flow is calculated, as compared to the historical period results: the mean flow grows from 2.6 m^3/s (historical) to 3.1 and 3.0 m^3/s, respectively for RCP4.5 and RCO8.5 scenarios. The climate change scenarios lead to more rainy winter and more droughts in spring and summer:

- considering rainfall events, the more significant variations are expected in November and December, with a 50% increase of monthly mean flow;
- a longer duration of winter rainy period is to be expected, followed by a less rainy spring when a 15% flow reduction for both CC scenarios is to be expected;
- considering the dry period, the RCP4.5 scenario doesn't show any variation for the summer when the RCP8.5 scenario shows a 30% reduction of the expected flow instead.

The increasing rain precipitation to be expected in the CC scenarios allows having a positive water balance that can increase water volume in the reservoir.

Conclusions

The first results of the high-resolution (EUR-11) future climate simulations from EURO-CORDEX were presented in the literature in 2013 (Jacob et al. 2014). The analysis carried out was directed towards regional climatic changes in Europe, addressing the differences between mean changes in annual mean temperature and total precipitation for the IPCC RCP4.5 and RCP8.5 scenarios. The results obtained in this study are consistent with the analysis reported in the mentioned paper. More specifically, under RCP8.5, (Jacob *et al.* 2014) report for large parts of Southern Europe warming of the mean annual temperature of more than 4 °C, for the period 2071-2100 compared to 1971-2000, and of about 4.5°C, over Albania. Similar results for the warming trend are reported in the present work, also if minimum and maximum daily temperature are analyzed and not mean daily temperature. Instead, under the RCP4.5 scenario, the warming for the long-term period (2071-2100) compared with the control period (1971-2000) is in the range [2°C; 2.5°C] over Albania, in agreement with the temperature change found in this work. In terms of precipitation, the paper reports a similar expected pattern between RCP4.5 and RCP8.5; in particular, the ensemble projects, for both scenarios, a substantial steady signal with slight changes in annual precipitation in the range [-5%; 5%]. Similar results, also if in the present work the precipitation results are expressed in mm, are reported. Under RCP4.5, the model project a substantial steady signal, while, under RCP8.5 a slight decrease in annual precipitation is projected. The climate change scenarios lead to more rainy winter and more droughts in spring and summer. The results

obtained for the Bovilla basin in terms of the simulated mean yearly flow are showing a relative increase in the total volume of the water. The monthly distribution is expected to be with a bigger difference from wet to dry season. This means that in term of the water management will be more difficult to use the water in the dry season and also this will be related to higher flood possibility in the wet season.

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Colour and COD Removal from Real Textile Wastewater by Using Diatomite

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Abstract The aim of this study was to investigate the adsorption performance of a low-cost adsorbent, diatomite, for the treatment of real textile wastewater. Effect of adsorbent dosage, contact time and particle size on colour and COD removal was investigated. The results showed that colour removals were achieved within a relatively short time and while COD removals increased with increasing contact time. Diatomite dosage was found to be a critical parameter especially for the COD removal. COD removal increased from 37% to 57% with an increase in diatomite dosage from 10 g/L to 150 g/L. Particle size, on the other hand, presented different removal trends. As colour removal was slightly increased (<5%) with decreasing particle size, a higher COD removal (70%) was observed for the smallest particles size (<425 mm). The influence of thermal and acid/alkaline pre-treatments on the performance of the natural diatomite was also evaluated. Thermal treatments significantly decreased the medium EC, while colour and COD removals were not significantly changed. Similarly, acid and alkaline pre-treatments seem not to increase the adsorption performance of natural diatomite.

Key words: *textile industry, wastewater, treatment, diatomite, adsorption*

Introduction

The textile industry is one of the major industrial activities that consumes large amounts of water and produces highly polluted wastewaters. Textile industry uses different amounts of water, dyes, chemicals and surfactants in various processes in order to produce high quality textile products (Kamaruddin *et al*., 2013). The treatment of textile wastewater poses considerable difficulties due to the presence of dyes and persistent organic and inorganic compounds. The methods used in the treatment of textile effluents include biological treatment, coagulation-flocculation, ozone oxidation, adsorption and membrane processes (Kausar *et al*., 2018; Özacar & Şengil, 2003). Adsorption is one of the effective treatment processes for the removal of dyes from textile wastewater. A great number of low-cost adsorbents have been used for the removal of textile dyes (Özcan & Özcan, 2004; Doğan *et al.,* 2006; Lin *et al*., 2007; Patra *et al*., 2015).

Diatomite is a siliceous rock composed of the fossilised skeletal remains of aquatic plants called diatoms (Erdem *et al*., 2005). Diatomite has been used for the adsorption of various pollutants from water and wastewaters, either in natural or modified form obtained by chemical or thermal modifications (Reza et al., 2015; Calıskan et al., 2011). The surface of diatomite contains silanol groups that spreading over the silica matrix (Figure 1). The silanol groups are very active groups and can react with various polar organic compounds (Al-Ghouti *et al*., 2003).

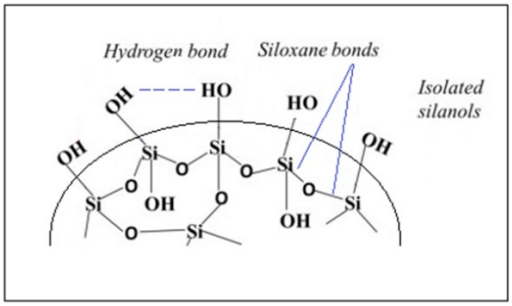

Figure 1. Structure of silica surface involving bonds types and silanol groups (Al-Ghouti et al., 2003)

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In this study, colour and chemical oxygen demand (COD) removal from real textile wastewater using diatomite was investigated by varying the contact time, diatomite dosage and particle size. The influence of thermal, acid and alkaline treatments on the performance of natural diatomite was also evaluated.

Materials and Methods

Textile Wastewater

The raw textile wastewater samples were obtained from a textile industry located in Kayseri Turkey. Different reactive dyes and various chemicals were used during various treatment stages resulting in the complex composition of textile wastewater. The wastewater is directly discharged into the wastewater collection system of industrial zone without any pre-treatment. Sample collection has been done several times during this study. All samples have been kept at 4°C and have been used without any pre-treatment. The characteristics of raw textile wastewater are presented in Table 1.

Table 1. Textile wastewater characteristics

Parameters	Raw textile wastewater	
	Range	Average
COD (mg/L)	101-687	378.7
TOC (mg/L)	12-202	95.1
Colour (Pt-Co)	394-1126	734.1
Conductivity (mS/cm)	3.36-3.56	3.42
pH	7.12-8.60	7.85

Adsorption Studies

Diatomite used in the experimental studies was obtained from Kazan-Ankara. Before use in the adsorption experiments, it was crushed and sieved into different particle sizes. SEM image and XRD spectra of natural diatomite were shown in Figure 2. SEM image shows high porous structure of diatomite and XRD spectra shows the amorphous nature of diatomite. Batch adsorption experiments were conducted using natural diatomite and real textile wastewater on Julabo SW23 mechanical shaker. The influence of contact time (5-1440 min; diatomite <425 mm), adsorbent dosage (10-150 g/L; diatomite <425 mm) and particle size (<425, 425-600 and 600-1180 nm) was determined. All adsorption experiments were carried out in 250 mL flasks with 100 mL of wastewater at 30±2°C without any other adjustment.

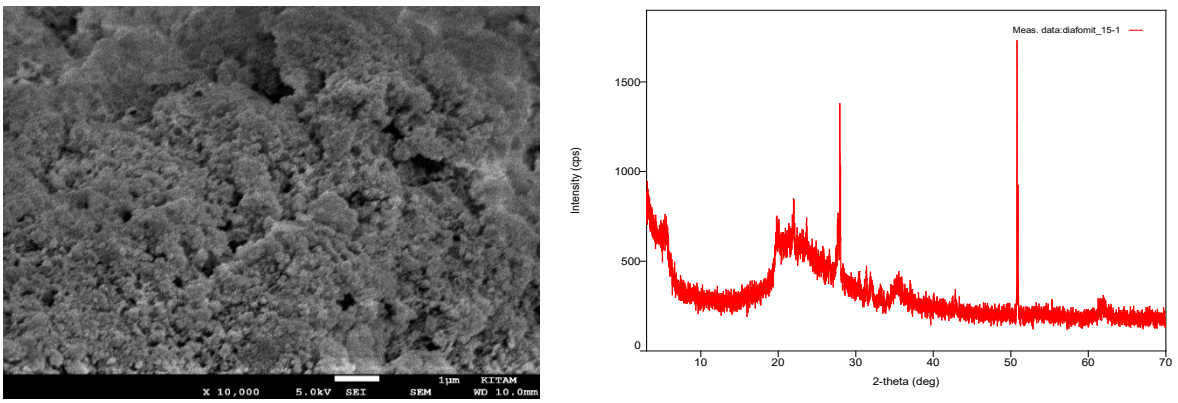

Figure 2. SEM image and XRD spectra of natural diatomite

The adsorbent performance of natural diatomite has been investigated by thermal and acid/alkaline treatments. Thermal treatments were done by keeping the natural diatomite with a particle size below 425 mm at temperatures varying between 300 and 900°C for one hour. Acid and alkaline treatments were performed by keeping the adsorbent (diatomite <425 mm) at 30°C in 2 M H_2SO_4 or NaOH solutions for one hour followed by a washing step with distilled water and a drying step (24 h at 70°C). The performance of adsorbent after all experiments was evaluated by differences in COD, colour (Pt-

Co unit), electrical conductivity (EC) and pH. COD experiments were carried out according to APHA-AWWA-WPCF (1998).

The pseudo-second order model was used for the modelling of the kinetic data obtained for the colour and COD removals. The linearized form of pseudo second-order kinetic model is given by Eq. (1) as:

$$\frac{t}{qt} = \frac{1}{k.qe^2} + \frac{1}{qe}t \qquad (1)$$

where k is the rate constant (g/mg min), qe is the sorption capacity at equilibrium (mg/g). The values of k and qe were obtained from the slope and intercept of the plots of t/q_t against t (Zhanga et al, 2018).

Results and Discussion

Effect of Contact Time

The influence of contact time on the adsorption of textile wastewater constituents and medium conditions was investigated using natural diatomite with a particle size below 425 mm. As can be seen from Figure 3, variation of colour and COD removal with contact time revealed different trends within time. An initial fast colour removal of approximately 60% was observed within 5 min. An additional increase of only 7% was achieved at the end of 1440 min. On the other hand, the initial COD removal was about 40% but increased with time, reaching a value of 78% at the end of 1440 min. These results show that the sorption sites on diatomite have different affinities for different constituents present in the textile wastewater. It can be seen from Figure 3 that; EC and pH of medium revealed an insignificant change (± 0.1) implying that the interaction of textile wastewater with diatomite didn't cause to a release of ionic constituents from the adsorbent.

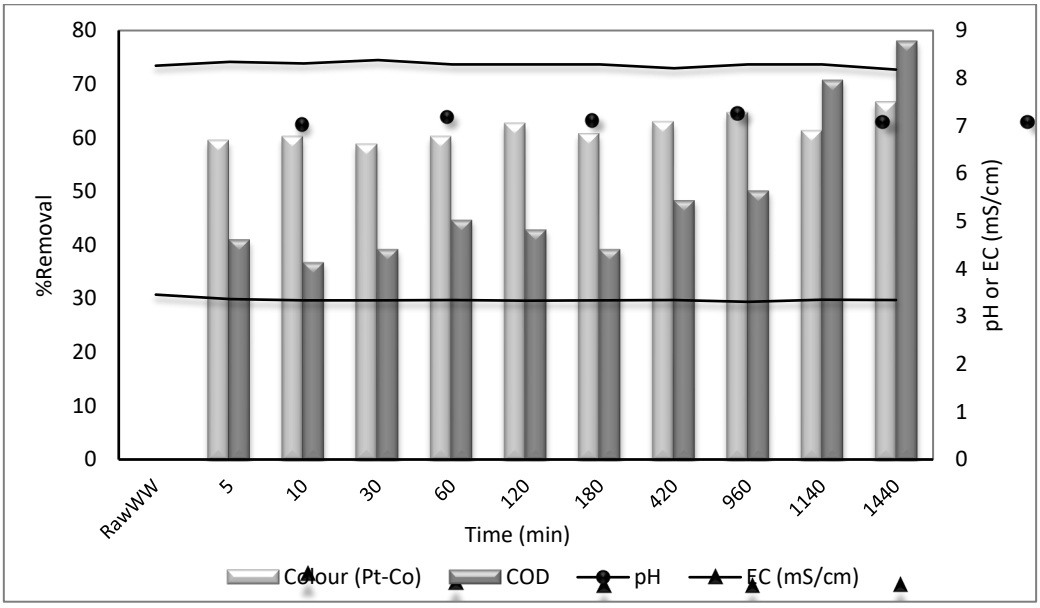

Figure 3. The effect of contact time on EC, pH, colour and COD removal

Effect of Adsorbent Dosage

It can be observed from Figure 4 that colour and COD values that the removal of both parameters represented an increase with increasing diatomite dosage. When the adsorbent dosage increased from 10 to 100 g/L colour removal increased from 37% to 57% and COD removal increased from 49% to 63%. These results showed that the reactive sites of diatomite have a higher affinity to reactive dyes present in the textile wastewater than other organic constituents. The influence of diatomite concentration on the medium conditions can also be seen in Figure 4. Both EC and pH represented a slightly decreasing trend with increased adsorbent dosage. When the spectra of treated wastewater were analysed it can be seen from Figure 5 that the absorbance at 292 nm decreased with an increase in

diatomite concentration from 10 to 150 g/L. This result showed that the aromatic moieties of dyes in the textile wastewater were adsorbed on the diatomite surface.

Effect of Particle Size

Figure 6 shows the variation of colour and COD removals and pH and EC with particle size. It can be stated that particle size has not an important influence on colour removal (4%). In the study by Ngulube *et al*. (2017) on the adsorption of textile dyes, it was similarly reported that the particle size of diatomite had little effect on the removal of dyes. COD removal data reveals a different trend with particle size. The highest removal was observed for the smallest particles size (<425 mm). The lowest COD removal was observed for the 425-600 mm fraction, for which the highest pH rises and lowest EC drop was observed.

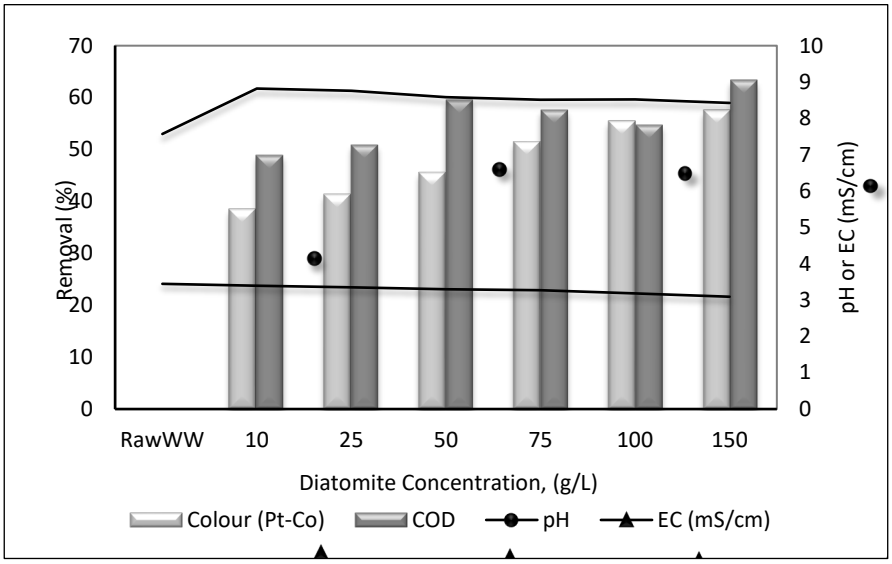

Figure 4. The effect of diatomite dosage on EC, pH, colour and COD removal

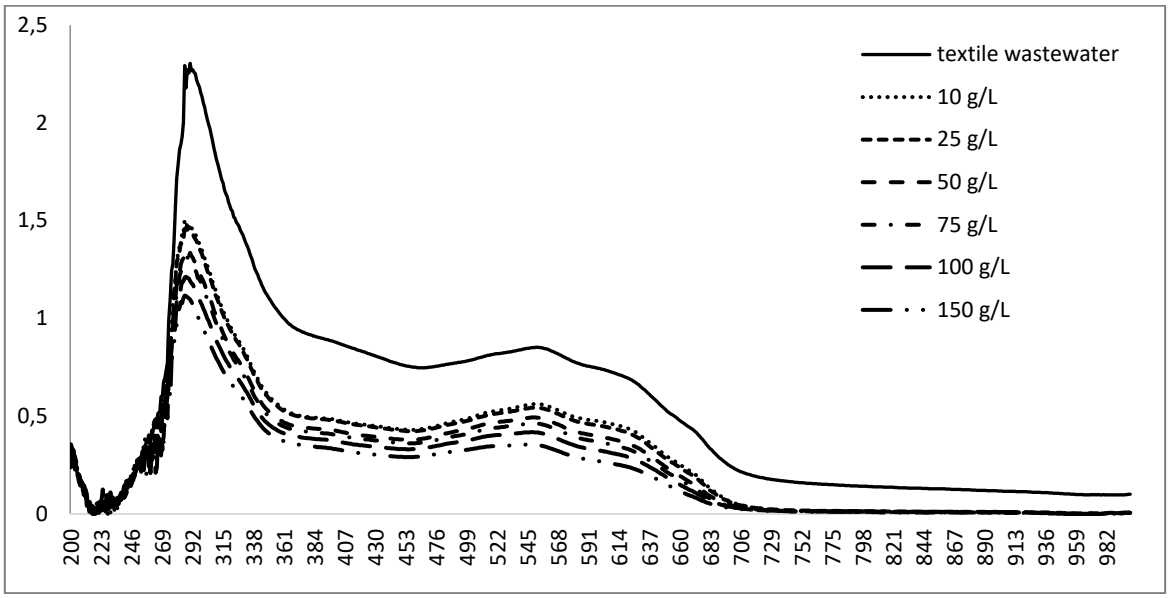

Figure 5. Spectra of dye before and after adsorption on diatomite

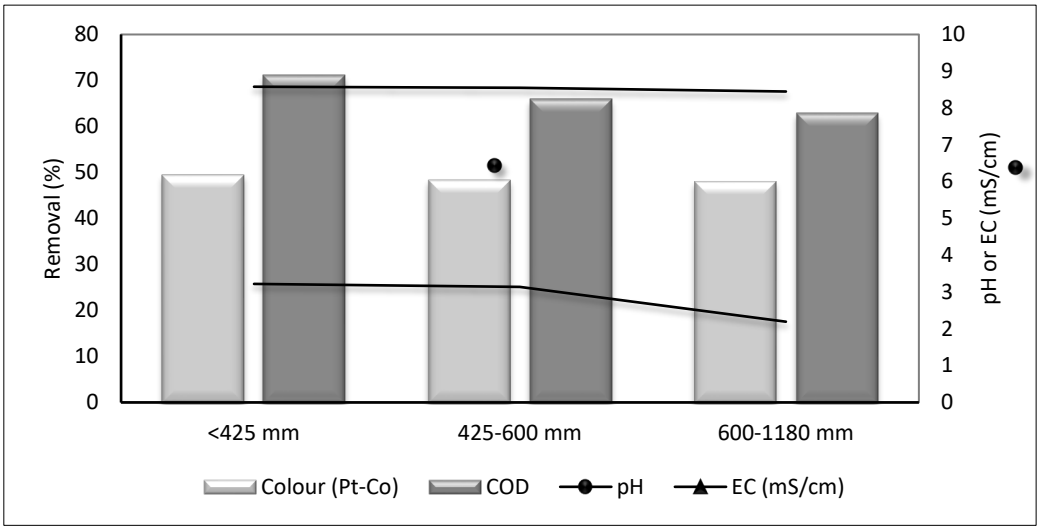

Figure 6. The effect of particle size on pH, EC, colour and COD removal

Effect of Thermal Treatment

It is assumed that thermal treatment causes desorption of adsorbed water in the crystal structure of the diatomite by formation of active hydroxyl groups. Generally, thermal treatment affects the type, distribution, content of hydrated species such as water, H-bonded and isolated silanol groups, and reactive sites for various surface reactions (Reza et al. 2015).

In order to investigate the effect of thermal treatment, adsorption experiments were performed with thermally pre-treated diatomite (<425 mm). It can be seen from Figure 7 that, the EC values of textile wastewater decreased for diatomite pre-treated at higher temperatures. The EC of textile wastewater dropped from 3.37 mS/cm to 3.09 mS/cm for 500 °C and to 1.68 mS/cm for 900 °C. These results imply that thermal treatment activates sorption sites on diatomite resulting in elevated ion sorption. The pH levels measured reflected a different trend for increased thermal pre-treatment temperatures. The pH of textile wastewater dropped from 7.49 to 7.02 for 500 °C and increased to 7.83 for 900 °C.

Considering the results for the removal of colour and COD, it can be stated that thermal pre-treatments had insignificant influence on the sorption of textile dyes and organic constituents. Changes in the removal of colour and COD were only ±4% and ±5%, respectively (Figure 7). In general, it can be concluded that the thermal pre-treatment increased the affinity of diatomite towards ionic constituents rather than dyes and organic constituents present in the textile wastewater.

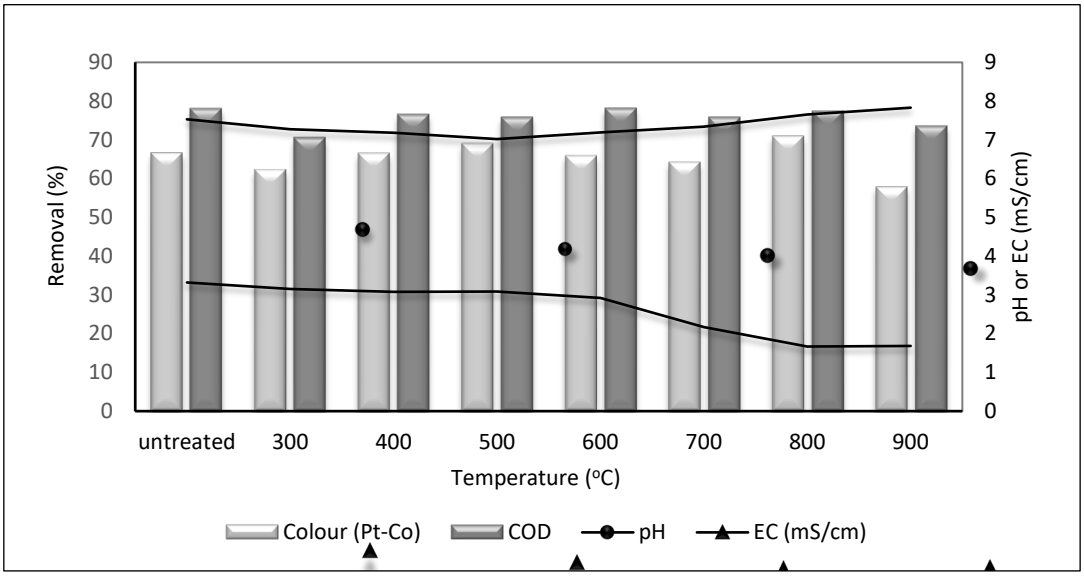

Figure 7. The effect of thermal treatment on EC, pH, colour and COD removal

3.4. Effect of Acid/Alkaline Treatment

Chemical treatment is widely used for purification of diatomite and alteration of its surface properties. Acid treatment is expected to reduce or remove the other oxides of diatomite in proportion to SiO_2 and to increase its surface area and adsorption capacity. The acid activators used for modification of diatomite include hydrochloric acid, nitric acid, sulfuric acid, sulfuric acid/H_2O_2 and phosphorous acid. The alkaline activators include sodium hydroxide, potassium hydroxide and sodium carbonate. These activators are used for purification diatomite, removal of impurities and chemically formation of finer pores (Reza et al. 2015).

In order to improve the performance of adsorbent, diatomite was treated with 2 M H_2SO_4 or NaOH solutions. These pre-treatments presented different effects on colour and COD removals. Acid treatments seem to have increased the colour removal efficiency from approximately 50% to 88%, whereas COD removal efficiencies decreased from about 65% to 23% (Figure 8). On the contrary, alkaline treatments seem to have an opposite influence on colour. NaOH treatments caused to an increase in colour, implying that some constituents have been released during the interaction of textile wastewater and diatomite. The COD removal efficiency, on the other hand, decreased to approximately 40%. Thus, both treatments did not increase the COD removal efficiency.

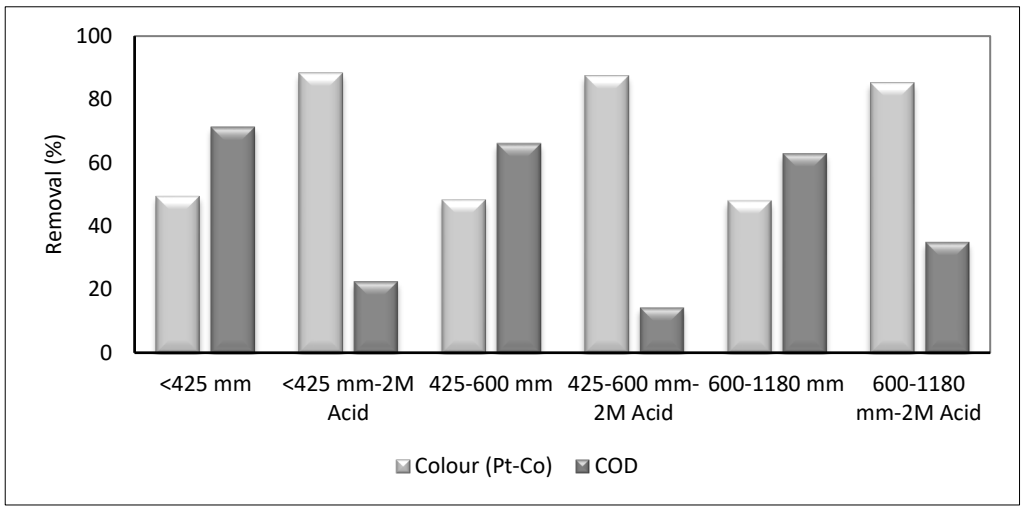

Figure 8. The effect of acid treatment on colour and COD removal

Adsorption Kinetics

Kinetic studies are important to analyse the controlling mechanism of adsorption process. The kinetic parameters provide information about mechanism and rate of adsorption process. Pseudo-second-order model was found to fit well the experiment data. The pseudo-second order kinetic plots obtained for colour and COD removal are presented in Figure 9 and the kinetic parameters are given in Table 2. The conformity of data to pseudo-second order kinetic model suggested that the chemisorption is the dominant mechanism controlling the rate of the adsorption process. Similar results were observed in previous studies (Kehinde & Aziz, 2016).

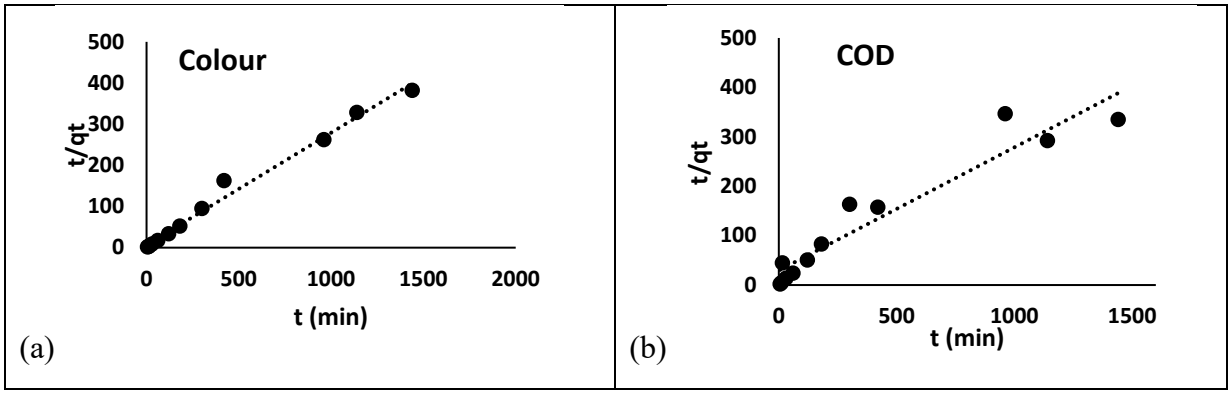

Figure 9. The plots of the pseudo second-order kinetics (a) Colour, (b) COD

Table 2. Parameters of the pseudo-second order model

	$q_{e\,(cal)}$ mg/g	k (min^{-1})	R^2
COD (mg/L)	4.011	0.0021	0.9141
Colour (Pt-Co)	3.664	0.0119	0.9883

Conclusion

In this study the adsorption performance of natural diatomite for the removal of colour and COD from real textile wastewater has been investigated. The effect of time, adsorbent dosage, particle size on colour and COD removals and medium EC and pH were analysed. Contact time has an insignificant effect on EC and colour removal, while significant effect on COD removal. Diatomite concentration, on the other hand, seems to have reduced the medium EC and increased the colour and COD removals. Particle size has been found to influence colour and COD removals differently; as smaller particle sizes seem to increase COD removal; bigger sizes seem to increase colour removal. Thermal pre-treatment was found to mainly influence EC by revealing half levels. Acid and alkaline treatments of diatomite, on the other hand, did not change the adsorbent performance to the desired levels. Overall it can be concluded that natural diatomite was effective in the treatment of raw textile wastewater, removing mainly dyes and organic compounds and inorganic ions at a lower degree.

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