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EVALUATION OF ENVIRONMENTAL POLLUTION CAUSED BY THE BLACK SEA COASTAL HIGHWAY USING CHEMICAL ANALYSIS OF SCOTS PINE (*PINUS SYLVESTRIS* L.) NEEDLES AS BIOINDICATOR IN SURMENE CAMBURNU NATURE PARK, TURKEY

UFUK FATIH KUCUKALI

Department of Architecture, Istanbul Aydin University, Istanbul, Turkey
**Corresponding author's email: ufkucukali@aydin.edu.tr*

Abstract

Black Sea coastal highway is one of the busiest roads in the north of Turkey. With this study, it has been determined that sulfur dioxide (SO_2) originating from the Black Sea coastal highway causes multifaceted environmental problems including degradation of habitat and natural landscape on the flora of Sürmene Çamburnu Nature Park. Pollution concentrations of lead (Pb), zinc (Zn) and copper (Cu) were obtained by chemical analyzes of Scots pine (*P. sylvestris* L.) needles collected from sampling points in 2019, 2020 and 2021. When *P. sylvestris* L. needles, which is an important bioindicator in monitoring these environmental degradations and one of the natural plant species of the area, were examined in the laboratory, it was determined that the Pb and Cu values were above the limit values of World Health Organization (WHO), the Food and Agriculture Organization of the United Nations (FAO) and U.S. Environmental Protection Agency (EPA), but the Zn value was within the limit values. These results indicate that Pb and Cu values, which are above the limit values, tend to decrease towards the upper limit values, especially in 2019 and 2020, as a result of the decrease in vehicle traffic on the highway due to the Covid 19 pandemic. However, it was determined that Cu, Pb, and Zn values started to increase in 2021 due to the increase in vehicle density due to the post pandemic time.

Key words: Air Pollution; Heavy metals; Scots pine needles; Çamburnu Nature Park.

Introduction

One of the most important problems experienced by cities is environmental pollution caused by pollutants discharged into the atmosphere from transportation and heavy metals, along with urbanization and industrialization. The use of biological materials as indicators in the detection and monitoring of these pollutions is a very reliable method. A significant number of studies have been conducted evaluating the issue from a wide variety of perspectives regarding the negative effects of air pollution on the entire urban ecosystem (Krämer *et al*., 2000; Schwela, 2000; Zhang *et al*., 2007). In addition to studies evaluating the relationship of air pollution in cities with the transportation system (Ambarwati *et al*., 2016; Borrego *et al*., 2006; Cariolet *et al*., 2018), there are many studies investigating the relationship between the Covid 19 pandemic and air pollution (Berman & Ebisu, 2020; Contini & Costabile, 2020; Krecl *et al*., 2020).

In addition, when the examples of some coastal megacities and the studies on monitoring their pollution profile and discussing the effect of pollution on plant species/vegetation are examined, changes in different plant species can be observed by different chemical sources according to different geographical parameters. In order to observe these changes, the pathological and physiological responses of plants to pathogens are discussed using methods such as the ANOVA statistical method (Alamgir *et al*., 2019; Shaukat & Khan, 2009). Moreover, when studies revealing the accumulation mechanisms of pollutants in soil sediments, water and vegetation are examined, it has been determined that toxic metals and pathogenic microorganisms vary according to various socio-economic activities such as agricultural activities (Alamgir *et al*., 2016). For example, in a study (Khan *et al*., 2020) on the accumulation mechanisms of heavy metals transmitted to plants, water and soils by various sources of pollution, microbiological and heavy metal loads in vegetables irrigated with wastewater were revealed.

Coal, a fossil resource used in residential heating, is one of the main pollutants that cause an increase in SO_2 emissions in the atmosphere. In terms of the degree of impact, power plants, industry and transportation functions should also be considered as SO_2 sources (Adame *et al*., 2020; Karplus *et al*., 2018; Kaygusuz, 2021; Sun *et al*., 2019). When Trabzon's Sürmene district is evaluated from this point of view, coal heating and the Black Sea coastal road can be seen as the main sources of pollutants. In addition to the multifaceted health problems such as respiratory disorders, lung diseases, asthma, cystic fibrosis, emphysema, lung cancer, mesothelioma, pulmonary hypertension, tuberculosis and irritation of the eyes (Kampa & Castanas, 2008; Türk & Kavraz, 2011) caused by SO_2 on humans, it also has negative effects on animals and plants. The visible symptoms on plants are very diverse. For example; SO_2 can cause needles yellowing and injury, reduce photosynthetic activity, destroy pigments, cause stomatal damage, interfere with membrane permeability, and reduce plant growth and yield. (Alçı *et al*., 2017; Otoide & Kayode, 2016) General characteristics of the plant, leaf age, photosynthesis intensity, moisture degree, depending on the SO_2 density and duration of action, the degree of damage to plants from SO_2 gas varies. In general, SO_2 concentrations between 0.05-10 ppm are harmful to plants (Levit, 1980).

The accumulation of SO_2 and heavy metals in the tissues of plants depending on the years, especially in high concentrations, can reduce plant growth and development, and in extreme cases, may cause the death of plants. The way heavy metals reach terrestrial ecosystems is mainly by precipitation. The damage level of SO_2 on terrestrial ecosystems is determined by evaluating the level of discoloration and defoliation of autosynthetic tissues. In this study, an evaluation was made with the measurements of macro and micro-elements in Scots pine needles.

Chemical analysis of various plants like mosses (Chakrabortty & Paratkar, 2006; Gerdol *et al*., 2014); lichens (Henderson, 2000); agricultural crops and ornamental plants (Stevens *et al*., 2020) and coniferous trees (Aliyar *et al*., 2020; Likus-Cieślik *et al*., 2020) have been used as bioindicators for air pollution monitoring studies. Located in Sürmene Çamburnu Nature Park, Scots pine (*P. sylvestris* L.) meets many of the requirements of a good bioindicator plant.

Although many international studies have been carried out in recent years (Dmuchowski & Bytnerowicz, 1995; Figas *et al*., 2021; Sut-Lohmann, 2020; Opekunova *et al*., 2021) examining the relationship between Pb, Cu and Zn concentrations in Scots pine (*P. sylvestris* L.) needles and air quality monitoring, there are very few studies in Turkey (Aricak *et al*., 2020; Yılmaz & Zengin, 2004).

The aim of this study is to evaluate transportation-related air pollution caused by the Black Sea coastal highway by analyzing the SO_2 and heavy metal accumulations in Scots pine (*Pinus sylvestris* L.). Thus, the relationship between transportation and air pollution is put forward through a bioindicator and to reveal the necessity of urbanization with correct planning methods.

Material and Methods

Working steps consisting of literature review, research design, data collection, data analysis and conclusion are seen in detail in the flow diagram (Fig. 1).

Besides, one-way ANOVA test, which is a tool used to test whether there is a statistically significant difference between the means of independent groups, was used. All the analyzes were performed using STATISTICA 10 computer program. In order to compare concentration of the heavy metals in the Scots pine (*P. sylvestris* L.) needles, average, minimum and maximum values, standard deviations and coefficients of variation were calculated (CV). Besides, coefficients of correlation of Spearman rank of the needles of Scots pine in heavy metals were calculated. While evaluating the suitability of the one-way ANOVA test for this study, the main determinant was that the data comply with the normal distribution and that the group variances were equal.

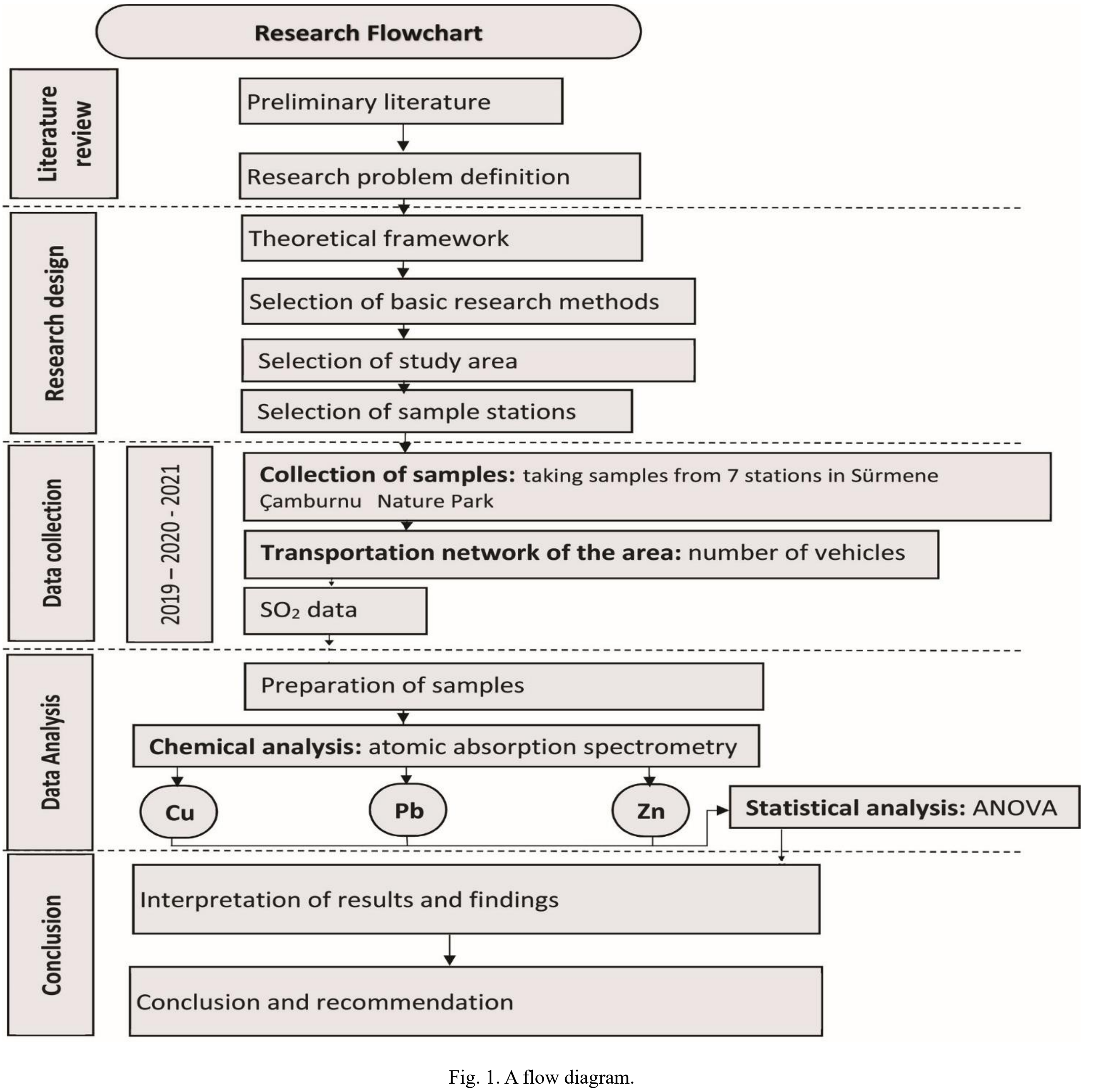

Fig. 1. A flow diagram.

Study area: The study area is located in Sürmene district of Trabzon province in the Eastern Black Sea Region of Turkey (Fig. 3). The study area is located at a distance of 8.7 km from Sürmene district center and covers an area of approximately 0.05 km^2 (Davis, 1965). The study area is also one of the rare regions where Scots pine (*P. sylvestris* L.) grows at sea level.

The research area receives high precipitation in all months and is compatible with the Eastern Black Sea climate zone, which has a hot summer and mild winter climate. Annual average temperatures are 15°C, the highest temperature is 31.8°C in August, and the lowest temperature is -2.6°C in January. The annual average total precipitation amount is 1668.6 mm. The highest precipitation was measured at 274.9 mm in October 2018. The annual average relative humidity value is 81.8%, the highest in autumn and the lowest in winter. The highest relative humidity was measured in October 2015 with 86.3%, and the lowest relative humidity was measured in February 2011 at 77.2%. Speed and direction of the wind; It affects the factors such as precipitation, temperature, evaporation, humidity and drought of the area, as well as the spread of air pollution. The fastest wind in the research area is 28.4 m/sec from the WNW direction in March and the lowest wind is 13.0 m/sec from the W direction in October (Tezel-Oguz *et al*., 2020).

This research was carried out by taking samples from 7 stations in Sürmene Çamburnu Nature Park (Fig. 3). In the selection of the station locations, non-industrialized natural area were chosen due to the methodology of the study. In order to determine air pollution caused by transportation, the areas on the Black Sea coastal highway and its impact areas were chosen as stations. In addition, depending on the natural morphology and microclimatic characteristics of the study area, areas that can be effective in the distribution and precipitation processes of air pollution have been determined.

The Black Sea Coastal Road (Fig. 2) is not only an international road connecting Turkey to Central Asia, but also one of the important infrastructure investments that connects all Black Sea coastal cities to each other on a local scale and to big cities on a national scale. The highway between the Samsun and Sarp (Hopa) border-gate measures 542 km, passes from 5 cities and 30 towns and directly serves to about 1.5 million people (Tezel-Oguz *et al*., 2020).

Transportation is very important socially and economically in the Black Sea Region, where settlements are mostly located on the coastline. With the creation of divided roads on the Black Sea Coastal Road, it is aimed to create uninterrupted transportation conditions by separating the city - district centers and transit traffic. In addition, it is aimed to turn the Black Sea Coastal Road into a safe, fast and high standard divided road that can respond to the growing trade and port transportation volume and contribute to its development. Thus, it is aimed to shorten travel time, reduce maintenance, fuel, depreciation and vehicle operating expenses, and emissions that cause air pollution. However, studies (Tezel-Oguz *et al*., 2020) indicate an increase in air pollution and heavy metal emissions, especially due to heavy traffic volume (Aricak *et al*., 2020).

In addition, the changes in the number of daily vehicle crossings of the Black Sea coastal road in 2019, 2020 and 2021 from the General Directorate of Highways were examined. The number of daily vehicle passes from the Black Sea coastal road, on which the study area is located, was determined as 50,750 in 2019, in line with the transportation statistics of previous years. Then, when the restrictions were implemented due to the pandemic in 2020, the number of daily vehicle passes decreased to 23,230. In the post-pandemic period, it increased to 48,650. In the 2019 - 2020 periods, the decrease in the number of vehicle passes was calculated as 45.77% (Gokce, 2015).

Station 1 is located at the East entrance of Çamburnu District, Station 2 in the district center, Stations 3 in the southern part of Maritime Faculty campus area, Stations 4 and 5 in the Sürmene Çamburnu Nature Park, Station 6 around Çamburnu waste facilities and Station 7 around forestry management directorate about 2 km from the Black Sea coastal highway (Table 1).

Heavy metal concentrations of needles were determined from Scots pine needles collected from 7 stations. Besides, the measurement of the monthly average SO_2 concentration was carried out in predominantly cloudless sky and calm wind conditions during the 2019–2021 period. For this purpose, a modified version of Amay-Sugiur method, which is the passive sampling technique used by Krochmal & Gorski (1991) to determine nitrogen in ambient air, was applied.

As a result of the measurements made, SO_2 differences emerged between November and April at 7 stations (Table 2). Although the concentration of SO_2 released into the atmosphere demonstrated prominent seasonal variation, it is more common especially in winter months. In this context, it was meaningful to evaluate a pattern that reveals spatial differences within the study area. These patterns were evaluated by associating them with three main land uses; residential areas and green areas, which under the influence of air pollution on the Black Sea coastal highway, near the solid waste storage area, and biorepaired areas after forest fire. These areas are: Çamburnu district west entrance point (Station 1), Çamburnu city center (Station 2), Maritime Faculty campus area (Station 3) and Çamburnu nature park (Stations 4 and 5) is a green area that is directly affected by the air pollution caused by the Black Sea coastal highway. Apart from these, Çamburnu waste facilities (station 6), which has a reduced rate of being affected by air pollution caused by transportation, but is under the influence of other heavy metals and air pollution sources as a solid waste storage area. Around forestry management directorate (Station 7), which is the forest fire area that broke out on January 7, 2017 and damaged approximately 25 hectares of Scots pine (*P. sylvestris* L.). These land use patterns express different characteristics according to their physical geography characteristics and their exposure to air pollution.

Fig. 2. Transportation network of the area.

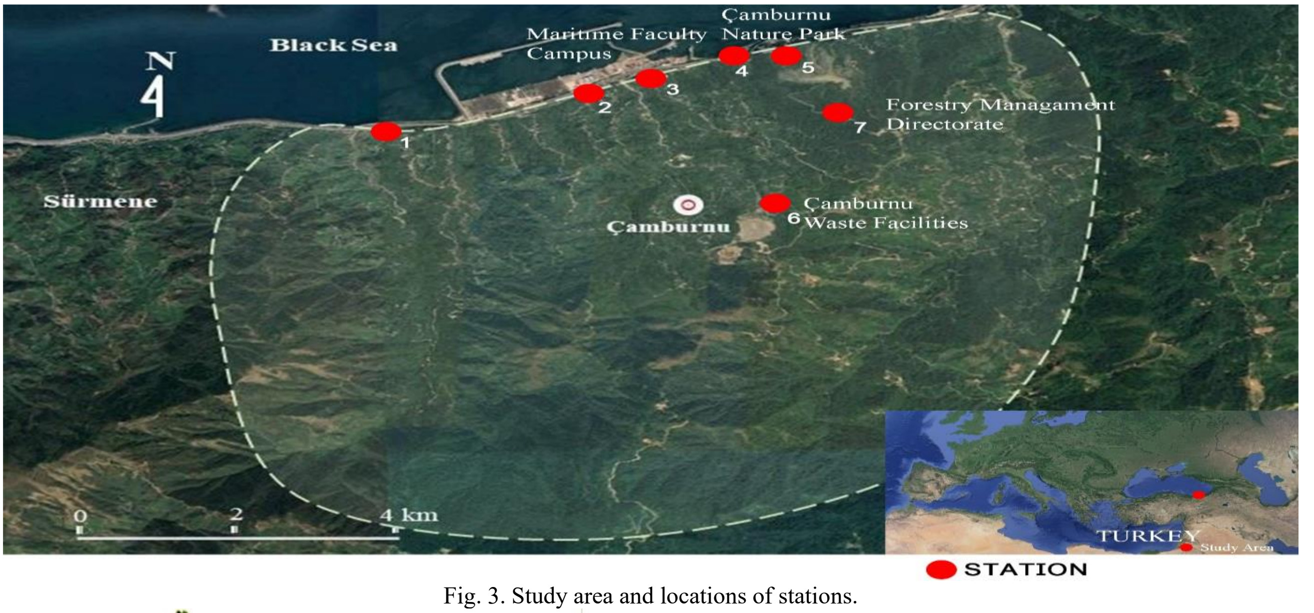

Fig. 3. Study area and locations of stations.

Fig. 4. Needles samples.

Table 1. The number, name, coordinate and altitude value of the sampling stations.

Station Nos.	Station name	Coordinates	Altitude (m)
1	East entrance of Çamburnu district	N 40°55.534′; E 40°13.390′	18
2	Çamburnu district center	N 40°54.887′; E 40°12.097′	18
3	Southern part of Maritime Faculty campus	N 40°55.287′; E 40°12.714′	18
4	Northern part of Çamburnu Nature Park	N 40°55.483′; E 40°12.952′	19
5	Western part of Çamburnu Nature Park	N 40°55.580′; E 40°12.711′	40
6	Around Çamburnu waste facilities	N 40°53.692′; E 40°12.661′	433
7	Around forestry management directorate	N 40°55.121′; E 40°12.895′	127

Table 2. SO2 emission averages for November and April 2019, 2020 and 2021.

Years	Station numbers							Average SO_2 ($\mu g/m^3$)
	1	2	3	4	5	6	7	
2019	105	171	127	98	85	60	63	101
2020	58	78	62	61	46	42	40	55
2021	118	189	134	103	98	63	68	110

Collection of samples: Samples collected from 7 stations were collected by a team at the same time on the same day and delivered to the laboratory in airtight transport bags. Needles were obtained from 10 Scotch pine trees with similar physical characteristics in the sample collection areas in November and April in 2019 - 2020 and 2021. As a result of the analysis of long-term measurements; the periods with the highest SO_2 rates in the research area were determined as November and April. For this reason, these months were preferred for the collection of Scots pine (*Pinus sylvestris* L.) needles. There is no extreme meteorological change in the study area during the years and months of research (Fig. 4).

The needles were obtained from approximately 2 to 3 meters from the ground level. An average of 100 needles were collected from 10 shoots from each tree. The needles obtained from the shoots of Scots pines that have grown in the east and west directions were mixed homogeneously. Afterwards, needle samples were separated into 1-year and 2-year forms and stored in polyethylene bags in a compartment at 5 °C for chemical analysis (Rautio *et al*., 1998).

Preparation of samples: The needles were washed with distilled water for about 1 minute to remove foreign matter such as dust. Then, the needles, which were taken to the drying oven at 68°C for 24 hours, took the form of fine powder particles and were stored in plastic vials to be used in chemical analysis (Cotrozzi, 2020).

Chemical analysis

A composite sample was formed by mixing the small dust particles formed by drying the needles obtained from 10 Scots pines from each of the sample areas in the same amount. Dry digestion was applied to copper (Cu) and zinc (Zn) using a muffle furnace. Then, copper (Cu) and zinc (Zn) diluted in a solution of sulphuric acid and atomized in an acetylene air flame. Lead (Pb) was atomized in the acetylene flame after having been digested in a mixture of nitric, perchloric ($HClO_4$) and sulphuric acid (H_2SO_4) and condensed with purity: 99.04% Ammonium pyrrolidine dithiocarbamate - $C_5H_9NS_2$ NH_3 (Allen, 1974). Afterwards, Perkin-Elmer Model 4110 ZL Atomic Absorption Spectrometer Aanalyts-700 was used to determine metal concentrations (Tüzen, 2003). One part per million (ppm) of the dry matter obtained from the needles was used as the evaluation unit and was used in all analyzes and evaluations.

Results and Discussion

SO_2: SO_2 concentration levels vary seasonally and it has been observed that they reach their maximum values in winter months. Likewise, studies on air pollution in the province of Trabzon, where the study area is located, support a similar trend (Türk & Kavraz, 2011). In later studies, low quality coal used for heating purposes in residential areas is indicated as the main reason for this phenomenon (Kara *et al*., 2020; Kose *et al*., 2022). SO_2 concentrations have also demonstrated substantial variation among stations, with the minimum level observed in the Station 7 (around forestry management directorate), and highest in the Station 2 (Çamburnu district center). Compared to other stations, the highest SO_2 concentrations were detected in Station 2, with 171 $\mu g/m^3$ in 2019, 78 $\mu g/m^3$ in 2020, and 189 $\mu g/m^3$ in 2021. In addition, when the averages of all stations were examined in the same year, the values were determined as 101 $\mu g/m^3$ in 2019, 55 $\mu g/m^3$ in 2020, and 110 $\mu g/m^3$ in 2021 (Table 2).

Cu: Cu pollution is caused by emissions and atmospheric deposits resulting from human activity, pesticide use, the use of sewage waste as fertilizer, coal and mineral deposits (Nriagu, 1996). Cu concentrations in pine needles demonstrate significant variations between different stations with different land uses. While Cu levels are below 5 ppm in Stations 6 and 7, Cu concentration values range between 10.90 to 16.51 in Stations 4 and 5. Besides Cu concentration values ranged between 15.68 and 25.12 in Stations 1, 2 and 3 (Table 3). Higher Cu values caused by the transportation connected to the Black Sea coastal road at stations close to the shore are also supported by other studies (Mendil *et al*., 2005; Kucuk & Topcu, 2017) carried out near the study area.

Pb: The transport and mobilization of Pb depends on regional and seasonal differences and depending on atmospheric flows, it can reach and affect regions spatially distant from emission sources. While the anthropogenic activities that caused Pb in the atmosphere in the 1750s were caused by the burning of Pb-containing coal, today one of the main indicators of pollution due to transportation can be seen as the Pb value in the atmosphere (Hou *et al*., 2019).

As a result of the analyzes (Table 4), there are Pb values varying between 12.84 and 41.56 ppm in Scots pine needles. It was observed that the internationally accepted Pb limit value of 30 ppm was exceeded at stations 1, 2, and 3. It can be said that the highest Pb value is observed at stations 2 and 3, based on all years within the sampling points. Finally, stations 4, 5, 6 and 7 are relatively less polluted stations with a Pb value of 14-30 ppm.

Zn: Zn accumulates in the soil with wastewater discharged from industrial areas and sewage waters. In addition, it can reach the leaves of plants through acid rain (Karatas *et al*., 2006; Hermle *et al*., 2007). Zn concentrations in plant leaves can be seen in the range of 5 -100 ppm. The limit value of Zn causing toxicity is usually above 400 ppm (Vaillant *et al*., 2005).

Table 3. The mean Cu concentrations of needles of Scots pine obtained from the stations in 2019, 2020 and 2021.

Stations number and location information	Needles age	Sampling years and Cu concentrations (November/April) (ppm)			Average Cu (ppm)
		2019	2020	2021	
1. East entrance of Çamburnu district	1	19.35	18.36	19.42	19.04
	2	21.44	19.04	21.56	20.68
2. Çamburnu district center	1	20.38	19.16	20.46	20.00
	2	25.06	23.84	25.12	24.67
3. Southern part of Maritime Faculty Campus	1	17.04	15.68	17.25	16.66
	2	23.02	22.14	23.63	22.93
4. Northern part of Çamburnu Nature Park	1	13.15	12.78	13.40	13.11
	2	16.08	15.77	16.51	16.12
5. Western part of Çamburnu Nature Park	1	11.87	10.90	11.96	11.58
	2	12.98	11.86	13.21	12.68
6. Around Çamburnu waste facilities	1	2.85	2.90	3.12	2.96
	2	3.75	3.95	4.02	3.91
7. Around forestry management directorate	1	1.68	1.60	1.89	1.72
	2	2.78	2.57	2.97	2.77

Table 4. The mean Pb concentrations of needles of Scots pine obtained from the stations in 2019, 2020 and 2021.

Stations number and location information	Needles age	Sampling years and Pb concentrations (November/April) (ppm)			Average Pb (ppm)
		2019	2020	2021	
1. East entrance of Çamburnu district	1	33.48	32.36	33.71	33.18
	2	30.02	29.44	30.78	30.08
2. Çamburnu district center	1	41.38	40.02	41.56	40.99
	2	37.94	37.78	38.94	38.22
3. Southern part of Maritime Faculty Campus	1	35.15	33.94	35.35	34.81
	2	32.36	30.90	32.48	31.91
4. Northern part of Çamburnu Nature Park	1	28.18	26.85	28.41	27.81
	2	23.87	23.02	24.12	23.67
5. Western part of Çamburnu Nature Park	1	26.43	25.88	26.87	26.39
	2	23.14	22.78	23.68	23.20
6. Around Çamburnu waste facilities	1	22.40	21.05	22.75	22.07
	2	20.04	19.66	20.88	20.19
7. Around forestry management directorate	1	15.54	14.89	15.98	15.47
	2	13.14	12.84	13.45	13.14

Table 5. The mean Zn concentrations of needles of Scots pine obtained from the stations in 2019, 2020 and 2021.

Stations number and location information	Needles age	Sampling years and Zn concentrations (November/April) (ppm)			Average Zn (ppm)
		2019	2020	2021	
1. East entrance of Çamburnu district	1	82.45	80.06	83.12	81.88
	2	93.27	90.56	93.45	92.43
2. Çamburnu district center	1	92.44	89.97	93.33	91.91
	2	114.24	109.67	113.78	112.56
3. Southern part of Maritime Faculty Campus	1	86.89	83.90	87.02	85.94
	2	93.22	90.01	94.08	92.43
4. Northern part of Çamburnu Nature Park	1	62.15	60.05	62.89	61.70
	2	66.78	64.67	67.18	66.21
5. Western part of Çamburnu Nature Park	1	62.90	60.98	63.48	62.45
	2	66.88	64.12	68.02	66.34
6. Around Çamburnu waste facilities	1	54.12	52.78	54.35	53.75
	2	59.25	57.02	59.97	58.75
7. Around forestry management directorate	1	53.15	52.60	53.98	53.24
	2	58.89	56.64	60.00	58.61

Table 6. Summary tables of mean Cu, Pb and Zn concentrations detected in Scots pine (*P. sylvestris* L.) needles by station, year and needle age.

Heavy metal			Cu	Pb	Zn
Average (ppm)			13.49 ± 0.48	27.22 ± 0.42	74.15 ± 1.05
Stations	**1**	East entrance of Çamburnu district	19.86 ± 0.42^{a}	31.63 ± 0.62^{a}	87.15 ± 0.74^{a}
	2	Çamburnu district center	22.34 ± 0.48^{b}	39.60 ± 0.28^{d}	102.24 ± 1.65^{c}
	3	Southern part of Maritime Faculty Campus	19.79 ± 0.49^{d}	33.36 ± 0.29^{c}	89.19 ± 0.74^{f}
	4	Northern part of Çamburnu Nature Park	14.61 ± 0.70^{c}	25.74 ± 0.17^{b}	63.95 ± 1.47^{a}
	5	Western part of Çamburnu Nature Park	11.91 ± 0.41^{e}	24.80 ± 0.22^{c}	64.40 ± 1.49^{b}
	6	Around Çamburnu waste facilities	3.43 ± 0.09^{f}	21.13 ± 0.27^{g}	56.25 ± 0.64^{d}
	7	Around forestry management directorate	2.24 ± 0.04^{g}	14.31 ± 0.22^{f}	55.88 ± 0.33^{g}
Sampling year		2019	13.67 ± 0.70^{a}	27.36 ± 0.58^{b}	74.76 ± 1.42^{b}
		2020	12.90 ± 0.61^{b}	26.53 ± 0.52^{a}	72.36 ± 1.18^{a}
		2021	13.95 ± 0.74^{b}	27.78 ± 0.53^{a}	75.33 ± 1.36^{b}
Needle age		1	12.15 ± 0.54^{a}	28.68 ± 0.58^{b}	70.12 ± 1.14^{a}
		2	14.91 ± 0.72^{b}	25.77 ± 0.55^{a}	78.18 ± 1.72^{b}

(a, b,c, d, e, f, g) In the same column, all means within a particular subclass differ (p<0.01) except those followed by the same superscript

As a result of the analyzes (Table 5), the stations with values above the international limit (Nagajyoti *et al.*, 2010; Hafeez *et al.*, 2013) of Zn 60 ppm in Scots pine needles are 1, 2, 3, 4 and 5, and there are Zn values varying between 60.05 and 114.24 ppm. At stations 6 and 7, the Zn values are below 60 ppm and can be considered as relatively less polluted areas. The highest Zn value was measured at Station 2 as 89.97-114.24 ppm. This is due to the low accumulation of Zn at stations located in less anthropogenic and relatively compact forest areas. In addition, the low Zn values observed around Çamburnu waste facilities are related to the controlled operation of the waste facility. Another factor is the opening of another waste recycling center close to the outer border of the city of Trabzon, thus reducing the waste load at station 6 in the research area. Obtaining high Zn values at other stations located on the coast in the research area is that wastewater may cause higher effects in these areas depending on the geomorphological structure and hydrological structure of the area.

Data analysis

Analysis of variance (ANOVA) was performed in terms of heavy metal content among the data obtained from Scots pine needles. According to the analysis of variance results (p<0.05), there is no significant difference between the locations in terms of Zn, Pb and Cu values.

The highest Cu (25.12 ppm), Pb (41.56 ppm) and Zn (114.24 ppm) concentrations were obtained in the Çamburnu district center (Station 2).

In addition to the changes in Pb, Cu and Zn substances of Scots pine (*P. sylvestris* L.) needles at different stations, significant differences were determined between years. For example, the Cu content of Scots pine needles (13.95 ppm) in 2021 is higher than the Cu content in 2020 (12.90 ppm). Likewise, the averages of Pb value (27.78 ppm) and Zn value (75.33 ppm) in 2021 are higher than the averages of Pb (26.53 ppm) and Zn values (72.36 ppm) in 2020 (Table 6).

When the heavy metal accumulations of Scots pine needles are examined according to their age; It is seen that it causes a considerable variation in terms of Cu substance. Two-year-old Scots pine (*P. sylvestris* L.) needles have a higher Cu content (14.91 ppm) than 1-year-old needles (12.15 ppm). Previous studies indicate that the concentrations of Cu, Pb and Zn vary according to the tissues of the trees.The organ with the highest heavy metal concentration was the Scots pine (*P. sylvestris* L.) needle (Comaklı & Bingol, 2021). In addition, it has been revealed in studies that heavy metal accumulation increases as the age of Scots pine (*P. sylvestris* L.) needles increases (Tzvetkova & Hadjiivanova, 2006). Likewise, Zn content indicated the same characteristic with Cu in terms of accumulation. Zn value (78.18 ppm) in 2-year-old needles is considerably higher than 1-year-old Zn value (70.12). However, it is seen that Pb values indicate lower values in 2-year-old Scotch Pine needles compared to 1-year needles. While the average Pb value of 1-year-old Scots pine needles was 28.68 ppm, it decreased to 25.77 ppm in 2-year needles. This phenomenon may be related to the variable effects of biochemical processes on heavy metal accumulation and movement in plants (Raskin *et al*., 1994).

According to the analyzes made within the scope of the study, it was observed that Cu, Zn, Pb and SO_2 at high concentrations had significant effects on air quality. There are many studies on the effects of air pollution on plants and the detection of heavy metals in plant tissues (Seyyednejad *et al*., 2011; Alamgir, 2016). However, it has been determined that these elements, which are above the World Health Organization (WHO), the Food and Agriculture Organization of the United Nations (FAO) and U.S. Environmental Protection Agency (EPA) limit values in certain stations and in certain research years, have high risks that may cause the death of plants. In 2019, it was determined that the SO_2 concentration measured at stations 1, 2, 3, 4 and 5, which are under the influence of the Black Sea coastal road, started to damage plant tissues and the limit value of 80 $\mu g/m^3$ (Schempp, 2004) was exceeded in these areas. Since SO_2 emission caused by the residential heating in these areas is very limited, the relationship between SO_2 measurements above the limit values and transportation emerges. On the other hand, SO_2 measurements were observed below the limit values at Stations 6 and 7 as areas that were relatively more protected from the effect of the Black Sea coastal highway. In 2020, when it is expected that there will be a decrease in air pollution caused by transportation due to the Covid 19 pandemic, the limit value where the SO_2 concentration started to damage plant tissues was not exceeded, and it was observed that the highest measurement was made at Station 2 as 78 $\mu g/m^3$. In the following year, 2021, with the reduction of the restrictions due to the Covid 19 pandemic, the limit values were exceeded again at Stations 1, 2, 3, 4 and 5, and the highest measurement value was recorded as 189 $\mu g/m^3$ at Station 2 (Table 2).

The concentration of Cu, a microelement of vital importance to all organisms, is a determining factor in the biochemical processes of plants. Cu can penetrate plant tissues of acute or chronic origin, as well as point or diffuse air pollution (Ivanov *et al*., 2016). Although the upper limit value of the normal Cu concentration in plants is 20 ppm, this upper limit value is 12 ppm in some plants such as Scots pine (*P. sylvestris* L.) (Dmuchowski & Bytnerowicz, 1995). In addition, Cu value above 30 ppm, which is the phytotoxic level where it is difficult for plants to survive, was not observed in the study area. However, in the study area, the areas where Cu concentrations originating from the Black Sea coastal highway are lower than 12 ppm, which is the upper limit value for Scots pine (*P. sylvestris* L.), are stations 6 and 7. These areas are relatively far from the effects of pollution caused by transportation. When the Cu values at Stations 1,2,3,4, and 5, which are located on the Black Sea coastal highway and in the impact area, were examined, it was determined that the minimum value was 10.90 ppm in the Western part of Çamburnu Nature Park (Station 5) in 2020. It is seen that the relative decrease in the number of motor vehicles and transportation-related pollution caused by the Covid 19 pandemic in 2020 is effective. It was found that the highest Cu value at Stations 1, 2, 3,4, and 5 was 25.12 ppm at station 2 in 2021 in 2-year-old needles (Table 3). In terms of Cu accumulation in Scots pine (*P. sylvestris* L.) needles, it was determined that the Cu values in 2-year needles were higher in all stations.

Pb contamination can originate from a point or diffuse source. Point sources are effective on a local scale and are mostly caused by the discharges from industrial facilities (Holt, 2000). The common Pb pollution source, which is also effective in the study area (Kara *et al*., 2020), is leaded gasoline used in motor vehicles due to its transportation function. It is seen in the literature that (Dmuchowski & Bytnerowicz, 1995). the limit value of Pb detected in plant tissues is 10 ppm. It is considered an extremely toxic level, especially above 30 ppm. In addition, the upper limit value at which the plant cannot survive has been revealed in many studies as 43 ppm (Nazir *et al*., 2015; Albert *et al*., 2021). In terms of international limit values for seven stations in the research area, the values that should normally be below 10 ppm in plants could not be found. When needle samples of all years and ages were examined, it was determined that Pb values were above this limit. Toxic areas with Pb values over 30 ppm are Stations 1,2 and 3. It was observed that 2-year-old needles had less Pb concentration than 1-year-old needles at all stations (Table 4). In this case, it was revealed that the accumulation of Pb in plant tissue followed a course inversely proportional to exposure time. This may be due to the unique morphological structure and microclimate characteristics of the study area.

Zn element has a significant importance in plant physiology besides its importance in all organisms at various rates (Hafeez *et al*., 2013). The acceptable lower and upper limit values of Zn in plants vary between 10 and 100 ppm (Malinowska *et al*., 2015). In the study area, values above 100 ppm were detected in 2-year needles only in Station 2, and the highest Zn measurement was determined as 114.24 ppm in Station 2 in 2019. Since the Zn value is below the limit values of 100 ppm at all stations except for Station 2, Zn pollution in the study area is generally so insignificant that it is out of consideration, but there is a risk of Zn in the coming years, especially for Çamburnu district center (Table 5). It was observed that Zn values decreased in all stations in 2020 due to the Covid 19 pandemic. Similarly, it was seen that it reached the 2019 values again in 2021 and even exceeded the 2019 Zn values in all stations except Station 2. Thus, the relationship between the accumulation of Zn in Scots pine (*P. sylvestris* L.) needles and air pollution caused by transportation could be revealed.

Conclusion

As a result, this study reveals that the Cu, Pb and Zn concentrations detected in Scots pine (*P. sylvestris* L.) needles can be used as a bioindicator that can be used to reveal the relationship between environmental pollution caused by transportation. At the same time, it has been demonstrated in the example of the Çamburnu nature park that the restrictions and lockdown implemented in Turkey due to the Covid 19 pandemic have a positive effect on air pollution in 2020.

Although many international studies have been carried out in recent years examining the relationship between Pb, Cu and Zn concentrations in Scots pine (*P. sylvestris* L.) needles and air quality monitoring, there are very few studies in Turkey. Since there are also very few studies in Turkey on the detection of heavy metal pollutions originating from road transportation as bioindicator, this study can be used for its successors.

Finally, it is recommended for future studies to rescale this study with multiple spatial and temporal variations and to determine the pollution loads caused by transportation by conducting continuous monitoring activities and analyzes.

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