World Journal of Advanced Research and Reviews

eISSN: 2581-9615 CODEN (USA): WJARAI

Cross Ref DOI: 10.30574/wjarr

Journal homepage: https://wjarr.com/

(Research Article)

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Change of Mg and K concentrations for 40 years in the Düzce atmosphere by *Pinus pinaster* annual rings

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World Journal of Advanced Research and Reviews, 2022, 16(03), 560–567

Publication history: Received on 08 November 2022; revised on 16 December 2022; accepted on 18 December 2022

Article DOI: https://doi.org/10.30574/wjarr.2022.16.3.1372

Abstract

Air is one of the most essential elements that living things need to survive. Air pollution has become even more important due to reasons such as population growth and the difficulties brought by global warming and war. The factors that make up air pollution are also one of the most important factors of environmental pollution and cause serious pollution problems. While some metals in the air positively affect plant growth as nutrient elements in agricultural activities, they cause deterioration of plant development due to the accumulation of high concentrations in plant organs. This study, as an indicator of the time-dependent variation of Mg and K concentrations with atmospheric accumulation, reveals the variation and year-related amounts of *Pinus pinaster* species in Düzce province.

Keywords: Accumulation; Environmental; Trace metal; Indicator; Nutrient; Wood

1. Introduction

Very few of the lands on earth are suitable for agriculture, and the lands cultivated in limited areas are under pollution pressure for various reasons today [1-9]. On existing agricultural lands; Developing industrial activities, fertilizers and pesticides used in agricultural production, exhaust gases and zoning problems have caused pollution problems in agricultural lands [10-17]. In order to benefit from annual ring effectively, it is necessary to know the sources of metals, which are indicators of air pollution, and then to find a solution for them [18-27].

Population growth, which gained momentum with urbanization, also caused various environmental problems [28-36]. Industrial activities developed in our country due to technological developments have triggered migration from villages to cities and cause unplanned population growth [37-40]. High population growth rate, industrial facilities, exhaust gases from vehicles and mineral fuels cause air pollution [41-46]. Industrial plants, mineral fuels and vehicle exhaust emissions are the most important air pollutants in our country and worldwide, and they significantly threaten human health [47-55]. Today, many factors cause environmental pollution [56-64]. These; Agricultural fertilizers and pesticides used for agricultural purposes, industrialization, and human-induced, heavy metal-sourced waste [64-68]. When these factors are evaluated, atmospheric heavy metals are emphasized as the most critical air pollutant [69-73]. It is very important to evaluate trees in terms of heavy metal pollution, which is one of the most critical threats to human and environmental health [74-78].

This study aimed to determine the time-dependent change of K and Mg concentration of *Pinus pinaster* located in Düzce, which is among the cities with the most polluted air among European cities, on a regional basis.

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2. Material and methods

2.1. Sample preparation

The study will be carried out on a *Pinus pinaster* tree grown in Düzce. The ring samples to be used within the scope of the study were obtained during the cutting made in Düzce City Cemetery in February 2022, by marking the north direction on the log and taking its coordinates. The log provided was examined and determined to be 40 years old. If the experiment is approved, the upper surface of the log will be smoothed by sanding so that the annual rings can be seen more clearly in the laboratory. Within the scope of the study, considering the annual ring widths, they will be grouped between 1 and 8 from the outside to the inside, each 5 years. After the wood surface is divided into groups and the age ranges are determined, samples will be taken from wood in every age range with the help of a steel-tipped drill and placed in glass petri dishes. The wood samples to be taken will be shredded and turned into sawdust. During these processes, care will be taken not to use tools made of metals that are the subject of the study.

2.2. Sample analyses

Samples will be sieved after they are room-dried and placed in glass petri dishes. The samples taken in glass containers will be kept in the laboratory with their mouths open until they become room-dry, and the samples that have become room-dry will be dried in an oven at 45 °C for two weeks. 0.5 g of the samples to be dried will be taken and 6 ml of 65% HNO_3 and 2 ml of 35% H_2O_2 will be added and placed in the microwave oven. The program of the microwave device will be adjusted to go up to 200 °C in 15 minutes and stay at 200 °C for 15 minutes. After the samples are burned in the microwave oven, the samples that have become solution will be taken into scaled balloon test tubes and made up to 50 ml with ultrapure water, metal analyzes will be made with the ICP-OES device. The analysis results will be multiplied by 100 as the samples are taken 0.5 gr and made up to 50 gr with water. According to the analysis results that do not fall into the calibration graph, different calibration graphs will be created at the ppm level and re-reading will be done. The main expense item in the research is service procurement for heavy metal analyzes to be made with the help of the ICP-OES device. Heavy metal analyses will be performed in an accredited central research laboratory. All measurements within the scope of the paper will be made in 3 repetitions. Variance analysis will be applied to the obtained data using SPSS 21.0 package program, Duncan test will be applied for the factors determined as a result of variance analysis that there is statistically significant difference between them at least 95% confidence level ($p<0.05$). The data to be obtained will be interpreted by tabulating, and thus it will be tried to determine how the concentrations of the elements in the study have changed from past to present.

3. Results and discussion

The change of Mg (ppm) concentrations in annual rings by periods and directions and the statistical analysis results are presented in Table 1.

Table 1 Change of Mg (ppm) Concentration by periods and direction in annual rings

Years	North	East	South	West	F Value	Average
2017-2021	308.8 Ce	358.9 De	234.0 Be	162.4 Af	1082.7***	266.0 bc
2012-2016	260.2 Dd	161.9 Bb	189.7 Cc	113.0 Ab	1856.9***	181.2 ab
2007-2011	221.7 Bb	223.7 Bc	150.6 Aa	147.8 Ae	404.3***	186.0 ab
2002-2006	238.6 Cc	287.9 Dd	207.3 Bd	150.0 Ae	1098.4***	221.0 ab
1997-2001	568.0 Dg	459.0 Cg	204.7 Bd	138.0 Ad	15788.6***	342.4 c
1992-1996	45.,2 Cf	521.5 Dh	317.2 Bg	113.3 Ab	11145.9***	351.0 c
1987-1991	30.,9 De	47.0 Aa	156.7 Cb	108.4 Ba	6334.3***	154.8 a
1982-1986	149.5 Ba	382.7 Df	279.8 Cf	129.2 Ac	1527.7***	235.3 ab
F Value	2839.4***	3781.6***	1261.3***	434.7***		5.3***
Average	313.2 C	305.3 C	217.5 B	132.8 A	16.185***	

According to Duncan's test results, the letters a, b, etc., represent the statistical differences between organs. ns: not significant. *** significant at 0.001 level.

When the change of Mg concentration was examined, it was determined that the change was statistically significant (at least p<0.05) on the basis of period in all directions and based on direction in all periods. According to the average values, the lowest Mg concentration was obtained in 1987-1991, while the highest Mg concentrations were obtained in 1992-2001. On the directional basis, the lowest concentrations were obtained in the west and the highest in north and east directions. The Mg concentration changes by organ, and direction and the statistical analysis results are shown in Table 2.

Table 2 Changes in Mg (ppm) concentrations by direction and organs

Organ	North	East	South	West	F Value	Average
Outer Bark	1764.7 Db	460.8 B	662.8 Cb	313.8 Ab	29817.0***	800.5 b
Inner Bark	203.6 Aa	346.8 C	217.5 Ba	355.1 Dc	4956.4***	280.8 a
Wood	313.2 Ca	305.3 C	217.5 Ba	132.8 Aa	16.1***	242.2 a
F Value	204.5***	1.7 ns	103.3***	313.2***		35.6***
Average	447.4 C	325.0 BC	262.0 AB	173.1 A	6.089**	

According to Duncan's test results, the letters a, b, etc., represent the statistical differences between organs. ns: not significant. ** significant at 0.01level, *** significant at 0.001 level.

When the change of Mg concentration on the basis of organ was examined, it was determined that the change on the basis of organ in all directions except the east direction and on the direction basis in all organs was statistically significant (at least p<0.05). According to the average values, the lowest Mg concentrations were obtained in the inner bark and wood, while the highest Mg concentration was obtained in the outer bark. Based on direction, a change is observed in the form of west<south<east<north. The change of K (ppm) concentrations in annual rings by periods and directions and the statistical analysis results are presented in Table 3.

Table 3 Change of K (ppm) concentration by periods and direction in annual rings

Years	North	East	South	West	F Value	Average
2017-2021	446.3 Bg	47.1 Aa	535.9 Cg	631.4 Dg	5408.8***	415.2 b
2012-2016	64.3 Aa	78.9 Ab	460.7 Be	715.5 Ch	4114.6***	329.8 b
2007-2011	58.3 Aa	149.8 Bc	389.2 Cc	611.0 Df	1879.6***	302.0 ab
2002-2006	348.0 Bf	165.2 Ad	430.0 Cd	575.6 De	1233.4***	379.7 b
1997-2001	332.0 Be	53.9 Aa	326.9 Bb	440.2 Cd	4410.0***	288.2 ab
1992-1996	258.7 Cd	58.6 Aa	497.9 Df	237.6 Bc	3028.3***	263.2 ab
1987-1991	137.0 c	UL	UL	137.6 a	0,0 ns	137.3 a
1982-1986	103.0 b	UL	131.4 a	166.9 b	144.7***	133.8 a
F Value	2227.5***	112.1***	1774.1***	1945.3***		2.6*
Average	218.4 B	92.2 A	396.0 C	439.5 C	22.838***	

According to Duncan's test results, the letters a, b, etc., represent the statistical differences between organs. ns: not significant. * significant at 0.05level, *** significant at 0.001 level.

When the change of K concentration on the basis of age was examined, it was determined that the change on the basis of age in all directions and on the basis of direction in all ages was statistically significant (at least p<0.05). According to the average values, the lowest K concentrations were obtained in the period of 1982-1986, while the highest K concentration was obtained in 2012-2021. Based on direction, the lowest K concentration was obtained in the east, and the highest Mg concentrations were obtained in the south and west directions. The K concentration changes by organ, and direction and the statistical analysis results are shown in Table 4.

Table 4 Changes in K (ppm) concentrations by direction and organs

Organ	North	East	South	West	F Value	Average
Outer Bark	675.7 Cb	126.2 Ab	292.4 Bb	1218.5 Db	7604.4***	578.2 b
Inner Bark	104.9 Ba	46.3 Aa	89.7 Ba	651.6 Ca	2433.9***	223.1 a
Wood	218.4 Ba	92.2 Aab	396.0 Cb	439.5 Ca	22.8***	296.2 a
F Value	18.5***	2.4 ns	9.3**	20.3***		8.1**
Average	252.8 B	90.7 A	350.4 B	538.6 C	22.663***	

According to Duncan's test results, the letters a, b, etc., represent the statistical differences between organs. ns: not significant. ** significant at 0,01 level, *** Significant at 0.001 level.

When the change of K concentration based on organs was examined, it was determined that the change on the basis of organ in all directions except the east direction and on the basis of direction in all organs was statistically significant (at least $p<0.05$). According to the average values, the lowest K concentrations were obtained in the inner bark and wood, while the highest K concentration was obtained in the outer bark. On the basis of direction, the lowest value was obtained in the east and the highest value in the west direction, while the north and south directions were in the same group as a result of the Duncan test.

Trace metals have been the subject of many studies in recent years, as they are elements that can be extremely harmful to human and environmental health in high concentrations [79-81]. The study determined the densities of different metals in various tree species depending on air pollution [82-84]. As a result of the evaluation of the analysis results, it has been determined that all heavy metals are in different types and amounts, and it is thought that these amounts are due to the high vehicular traffic of the region in the sampling area [84-86]. When the variation of K and Mg concentrations is examined, it is seen that the changes differ in a statistically significant level. Study has been done. It is aimed to determine the heavy metal pollution concentrations in landscape plants obtained in different cities [87-90].

4. Conclusion

As a result of the research, it was observed that the Zn, Pb, Mn and Ni elements in the samples taken from the points close to the highways were in higher concentrations than the samples taken from the places far from the highways. Although many species are used in biomonitor studies, the accumulation levels of species are still being investigated in terms of their usability as biomonitors. However, suitable climate type and soil structure support this. As a result, annual rings of *Pinus pinaster* tree may also be suitable for other metals and pollutants, as evidence of its usability in measuring air quality.

Compliance with ethical standards

Disclosure of conflict of interest

The authors declare that they no conflict of interest. The none of the authors have any competing interests in the manuscript.

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