Polish Journal of Environmental Studies Vol. 15, No. 1 (2006), 111-119

Original Research

A New Approach to Air Pollution Determination Using Annual Rings: Dendro-Chemical Elemental Analysis of Annual Rings by SEM-EDS

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Received: November 14, 2003
Accepted: August 4, 2005

Abstract

This paper presents a new approach to air pollution determined through the use of elemental analysis of the annual tree rings (ATRs) of Turkish red pine (*Pinus brutia* Ten.). For this aim, every annual ring width was measured on the cross-section wheels of Turkish red pine supplied from ten research points around the Kemerköy (Gökova) thermal power plant (KTPP). The fly ash collected from the surfaces of the needles and the annual growth ring of Turkish red pine in the polluted points were investigated by energy dispersive spectrometer (EDS). The elemental analysis of the annual rings were performed considering the fly ash elemental composition because the main pollutant source was the fly ash emitted from KTPP chimney smoke.

With EDS analyses, some elements such as Al, Si, Mg, K, Fe, Ca, S, Zn, Ti, and Nb were determined in the fly ash. These elements accumulated in ATRs from the KTPP fly ash. They not only accumulated in annual rings formed after KTPP began operation but also accumulated in ATRs formed before KTPP started. It was confirmed that these elements accumulated in the annual rings affected by KTPP much more than the control ATRs. This paper proved that SEM-EDS, a new approach/analytical method to air pollution determination through ATRs, has been successfully applied to dendro-chemical elemental analysis of annual tree rings.

Keywords: thermal power plant, air pollution, annual ring, SEM-EDS analyses.

Abbreviations

TPP - Thermal power plant.
KTPP - The Kemerköy (Gökova) thermal power plant.
HI - The hindering-effect index of air pollutants on the growth of annual tree rings.
ATR - Annual tree ring or annual tree-growth ring.

Introduction

Annual tree rings (ATR), indicate diameter growth of poly-annual woody trees in temperate and arctic regions, characterized by a period of rapid growth in spring which produced light brown wood, followed by a period of slower growth in summer of dark brown wood in the identical year. The differences of light and dark brown wood in annual tree ring stem from the morphology of tracheid cells which make up about 90-95% of pine-tree woods [1].

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The diameter of ATR depends on endogenous and exogenous factors. Endogenous factors include tree age and inherited specifications, which affect the growth of a single tree. Exogenous factors, which affect a whole stand, identified two main groups such as natural environmental factors, including climate, soil type, forest canopy-closure class, topographical structure etc. and anthropogenic factors, including especially air pollution and forest maintenance works [2]. The four of these factors are especially efficient in annual tree ring width that they are tree age, forest canopy-closure class, climate and air pollution. The determination of air pollution effects on annual rings is easy to affect other factors in some times. Several researches have demonstrated that air pollutants can alter annual tree ring growth and total volume production in forests [3-7]. If plant height reduction is not taken into consideration, one-time decrease of annual ring width can cause a two-times decrease of volume production, and if it is taken into consideration, the decrease of volume production also is excessive [8].

Air pollutants such as sulfur dioxide, nitrogen oxides, carbon monoxide, unburned hydrocarbons, hydrogen fluoride and particles appearing as a result of the burning of fossil fuels in thermal power plants spread in the atmosphere, and can effect nearby vegetation [9-12]. Sulfur dioxide and nitrogen oxides form the main constituents of thermal power plants, in addition to carbon dioxide, carbon monoxide, hydrogen fluoride, fly ash etc. are emitted from power plant chimnies to the environment [13, 14]. Particulate matter and the majority of fly ash is trapped by cyclonic and electrostatic precipitators but a considerable amount of fly ash escapes precipitation and is emitted into the atmosphere, then deposited on the soil and vegetation around power plants. Although the elemental composition of fly ash may vary widely, it usually contains higher concentrations of essential plant nutrients such as Ca, Mg, Mn, Fe, Cu, Zn, B, S, K, except nitrogen and available phosphorus besides toxic elements such as Pb, Cr, Ni, (Fe, Cu), B, As, Al, Ti, Co and radioactive elements such as Pu, U [15]. The low concentrations of fly ash have beneficial effects, but the high concentrations of its can cause reduction of plant growth.

Trees and especially coniferous trees may accumulate environmental pollutants directly from the atmosphere, by deposition on the leaves or bark, or indirectly following deposition on the soil and subsequent root uptake [7, 16, 17]. In the case of foliar deposition, pollutants may be transported to the ATRs via the phloem whilst deposits on the bark may be transported by diffusion [18]. Stand throughfall and plant litter increase the load of heavy metals and sulfur on the forest floor [19]. Accumulation via the soil to the ATRs is strongly influenced by soil chemistry and the solubility and form of the pollutant. There may be a substantial delay between deposition and uptake, depending on the rate of migration through the soil to root depth. Elements dissolved in the soil solution are adsorbed by the root and may be transported to the ATRs in the transpiration stream which may pass through more than one ATR, depending on the species [7, 20].

Following deposition in the ATR, radial translocation of elements across ring boundaries can occur, particularly via rays [21]. The radial distribution of elements has also shown to change seasonally [22] and follow re-sampling after 10 years [23]. The accumulation of environmental pollutants by annual rings is thus an indirect and complex process and highly dependent on water solubility, tree species and other environmental factors [20]. Furthermore, the concentration of many trace elements of environmental concern in the ATRs is relatively low with regard to their concentration in the environment, particularly those with low solubility. Analysis of ATRs has, however, provided valuable information, with a number of studies accurately reflecting known changes in environmental pollution [7].

Materials and Methods

The Kemerköy Thermal Power Plant and Surrounding Forests

KTPP is in the Gökova (Kerme) gulf (37º 02´ N, 27º 54´ E), 98 km from Mugla in the south Aegean Region of Turkey (Fig. 1).

It began operation in 1992. It is part of the triplet/thermal power plant complex in Mugla, made up of three (and optional plus one) units having the power per unit of 210 MW. It produces electricity by burning 5000 t/d of lignite per unit. The calorific degree of the lignite is 1550-2400 cal/g and its includes about 33% moisture, 32% ash, 21.5% carbon, 1.5% hydrogen, 9.4% nitrogen+oxygen and 2.6% combustible sulfur [24].

KTPP releases 10^6 m^3/h chimney smoke per unit into the atmosphere. The smoke consists of about 9000 mg/m^3 sulfur dioxide, 800 mg/m^3 nitrogen oxides, 600 mg/m^3 fly ash, 600 mg/m^3 carbon monoxide, 12 % carbon dioxide, 5 % oxygen and others [25].

The natural forest consists of 25-80 year-old Turkish red pines [26], a tree that produces 23% of the total allowable cut of the forests and covers 3,096,064 hectares in Turkey [27]. There are *Platanus orient*alis L., *Salix alba* L., *Juglans regia* L. and *Ulmus minor* L. in valleys and by streams. A characteristic scrubby (macchie) flora makes up of more than 40 species of small trees in the undergrowth. Parts of these stands are labeled as production forests while the other parts of them as protection. The soils are red-brown, brown and redzina. Soil depth is generally 30-300 cm. The forest is generally closed and rarely light as canopy closure [28]. There are a number of villages and fields close to the forested points.

Methods

Ten research points (and one research tree in all of the points) around the KTPP were chosen (Fig. 1), and the

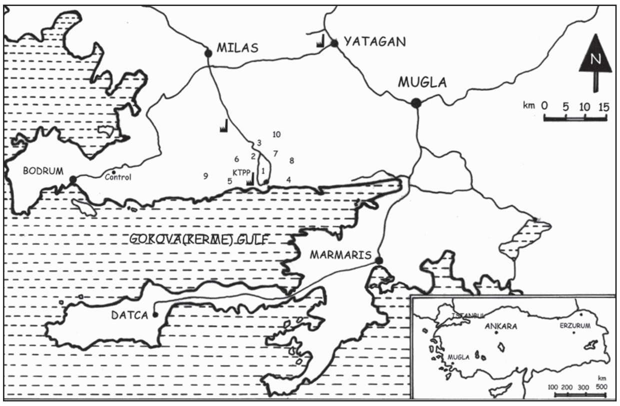

Fig. 1. The position of the KTPP and the research points.

cross-section wheels of Turkish red pines at chest height ($d_{1.30}$) were supplied from about 30-40 year-old trees in September 2002. The cross-sectioned wheels of the Turkish red pine were ground with an emery wheel and photographs were taken. Every annual-ring width was measured with a scale loupe in 0.01-mm units from the outer ATR (belonging to 2002) to central ATR. All of the ATR width belonging to the every research plant were measured as consisting of right angle to four direction from the center, and annual-ring width calculated as mean value of the four measurements. The mean value of the four measurements was recorded in the table as annual-ring width.

The special evaluation way was developed for hindering effects of air pollutants on annual tree ring growth. The hindering effects of the air pollutants on annual tree ring growth were developed as HI index (The hindering index of air pollutants on annual tree ring growth). The HI index is shown in eq. (1).

$$\mathrm{HI} = \frac{a/b}{c/d} \qquad (1)$$

where a/b is the average of the 11 ATR width before KTPP began operation, c/d is the average of the 11 ATR width after KTPP began operation, a is total ATR width 11 years before KTPP began operation, b is total years of ATRs before KTPP (11 years), c is total ATR width (belonging to 11 years, from 1992 to 2002) after KTPP began operation, d is total years of ATRs after KTPP began operation (11 years).

By this way, the hindering effects of air pollutants emitted from the KTPP on annual tree ring growth was determined as the times of obstruction of annual tree ring growth. HI index belonging to control and all of the research points are given in Table 1. Because of the fact that the prior ATRs had excess growth, the HI index ought to become bigger than the control. Thence the real HI can be calculated by deducting excess values.

T-test for dependent samples was performed by STATISTICA 6.0 on the mean annual ring width at all research points. In addition, 'The box and whiskers plot for all variables' were performed by descriptive statistics for determining the differences of the control and all the research points (Fig. 3).

By this way, the 1st and the 7th research points determined the excessive affected research points from air pollution. The cross-section wheels belonging to the 1st and the 7th research and the control (unpolluted) points were about 2 mm apart as EDS-investigating samples from bark to center through radial direction. Their surfaces were shined with emery wheel cleaned with fabric. They were dried at 80°C for one day. Then, conductivity was provided by sputtering with Au-Pd target using a sputter-coater and thus the samples brought on a state to able to examine in JEOL 6400 SEM-EDS combined system energy dispersive spectrometer. The sputter-coater procedure was repeated three times for 10 seconds after the samples were cooled to room temperature. After the samples coated in nanometer degree were attached in the holder of SEM, they were placed into a vacuum chamber for elemental analysis (EDS). Energy-dispersive spectrums obtained 20 keV energy levels on the annual tree ring. T-test for dependent samples was performed on the comparison of the average elemental composition between control and the 1st and the 7th research points.

On the other hand, the needles of terminal twigs on branches of the Turkish red pines that are about 1.5 meters tall were cut with gardening shears and the dust on the surface of the needles was kept from falling in the 1st and 7th research points. Then the needles were washed thoroughly in a container with distilled water and the dust was released into the water for elemental analysis of the fly ash. The collected dust in the distilled water were filtered on filter paper and dried at 80^0C. Then, the fly ashes were mixed thoroughly. Because the main heavy-metal source was the fly ash of KTPP chimney smoke, it was analyzed elementally in a JEOL-6400 SEM-EDS combined system energy dispersive spectrometry at 20 keV energy level.

Results and Discussion

The Visual and Statistical Evaluation of Annual Growth-Ring Measurements

The hindering effects of air pollution on ATR growth has been seen very easy on the cross-section wheels taken from the control, the 1st, the 2nd, the 7th and the 9th research points (Fig. 2). The ATR width belonging to the last 11 years in the 1st, 2nd, and 7th research points were constricted because of nearness to KTPP. The last period of the 8 years of ATRs in the 9th research point were restricted by KTPP.

The hindering index of air pollution on ATR growth for all research points (HI index) is given in Table 1.

Table 1 shows that air pollutants emitted from KTPP hindered annual ring growth in the polluted points. HI was determined as 5.36, 4.68, 3.23, 3.18, 3.15, 3.01, 2.98 in the 1st, the 7th, the 2nd, the 6th, the 3rd, the 8th and 4th research

Table 1. The HI index belonging to the control and all of the research points.

	Research points										
	Control	1	2	3	4	5	6	7	8	9	10
HI index	1.20	5.36	3.23	3.15	2.98	2.56	3.18	4.68	3.01	1.95	2.72
Real HI index	1.00	5.12	3.03	2.95	2.78	2.36	2.98	4.48	2.81	1.75	2.52

points, respectively. The fact that the HI belonging to the control point is 1.20 can be attributed to rapid growth of the prior ATRs. The real HI can be determined as the deduction of the 0.20 value (1.20-1.0 = 0.20) from the HI in Table 1. Consequently, the real HI was calculated.

The box and whisker plot for all research points performed by descriptive statistics for determining the differences of the control and all of the research points is shown in Fig. 3.

Fig.3 shows that air pollutants emitted from the chimney of KTPP hindered to growth of the ATRs by descending way towards the 1st, the 7th, the 4th, the 8th, the 2nd, the 9th, the 5th, the 3rd, the 6th and the 10th.

At the same time, t-test for dependent samples was performed using statistical analysis to compare mean ATR widths in the control and all of the research points. It recorded significant differences at $p < 0.05$ between control and all of the research points.

Because the annual ring width measurements of Turkish red pine in all of the research points were selected to facilitate in SEM-EDS analysis, the results of these works were not extensively discussed. Fig. 2, Table 1 and Fig. 3, show that ATR width in the 1st and 7th research points are most affected by air pollutants.

Dendro-Chemical Elemental Analysis of Annual Tree Rings by SEM-EDS

Fly ash on surfaces of Turkish red pine needles and the ATRs of Turkish red pine in the polluted point were analyzed using EDS. The elemental analysis of ATRs have been performed considering the fly ash elemental composition because the main heavy-metal source is the fly ash of KTPP chimney smoke. With EDS analyses, some elements such as Al, Si, Mg, K, Fe, Ca, S, Zn, Ti and Nb were determined in fly ash on the surfaces of Turkish red pine needles. The elemental analysis results of the fly ash collected from the surfaces of Turkish red pine needles are given in Table 2.

Certain amounts of these elements can accumulate in ATRs through roots, bark and leaves [5]. Related to this aim, the elemental analysis and EDS spectrums of the ATRs were performed. The elemental analysis results of the ATRs belonging to the control point are given in Table 3, the 1st and the 7th research point are given in Tables 4 and 5, respectively.

Once metals enter trees, they are not necessarily restricted to tree rings formed during the current year [16]. It was determined from Tables 4 and 5 that the elements/heavy metals in annual rings of Turkish red pine formed after KTPP began to operation were transported in annual rings prior to the pollution episode. Most tree species, including Turkish red pine, contain an outer band of living sapwood that surrounds an inner core of dead heartwood. Water transporting trace metals from the roots may be conducted in several adjacent sapwood tree rings and, in some cases, translocation of trace metals across the width of the sapwood has been reported. The major pathway of radial transport through xylem tissue is via ray cells, which are strands of living cells extending in a radial direction from the cambium, toward the pith as in the Turkish red pine [5, 29].

Examinations of Tables 3, 4 and 5 show that all of the average values of elements/heavy metals in the pol-

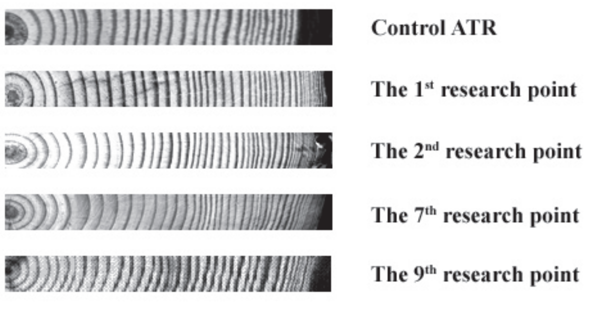

Fig. 2. Cross-sections of Turkish red pine belonging to the control, the 1st, the 2nd, the 7th and the 9th research points.

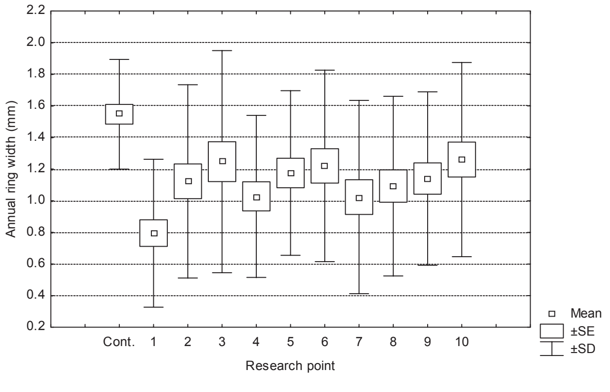

Fig. 3. The box and whiskers plot for all research points as descriptive statistics.

Table 2. Elemental composition of fly ash collected from the surfaces of Turkish red pine needles at the 1st and the 7th research points.

Research point	Elemental Analysis Results (Weight%)										
	Mg	Si	Al	Nb	Ca	K	S	Fe	Zn	Ti	Others*
The 1st	0.47	6.56	3.98	0.78	35.06	1.20	9.31	1.22	1.74	0.38	39.68
The 7th	0.81	5.69	4.10	0.54	38.28	1.14	8.64	2.50	0.40	0.60	37.90

*These elements are carbon, oxygen and the other non-detectable elements.

Table 3. Elemental analysis of the ATRs belonging to the control point.

Specifications of annual rings		Elemental Analysis Results (Weight%)										
The number	Corresponding year*	Mg	Si	Al	Nb	Ca	K	S	Fe	Zn	Ti	Others**
1	2002	0.00	0.59	0.14	2.75	1.29	0.36	0.00	0.35	3.36	0.24	90.92
5	1998	0.09	0.59	0.76	3.03	0.86	1.33	0.00	0.51	1.50	0.10	91.23
9	1994	0.00	0.19	0.00	2.26	2.30	1.53	0.00	0.00	0.00	0.06	93.66
13	1990	1.04	0.31	0.00	4.96	0.53	1.07	0.00	0.29	7.76	0.13	83.91
17	1986	0.00	0.90	0.19	3.70	1.10	0.56	0.00	0.00	1.18	0.02	92.35
21	1982	0.00	0.23	0.49	2.64	2.26	0.99	0.04	0.00	0.00	0.00	93.35
25	1978	0.00	0.09	0.34	3.61	0.84	0.31	0.01	0.00	0.00	0.00	94.80
29	1974	0.00	0.41	0.00	3.93	0.98	1.13	0.00	0.00	1.03	0.16	92.36
The core	1973	0.28	0.43	0.40	4.78	1.00	0.78	0.00	0.00	0.32	0.03	91.98
Average value		0.15	0.41	0.25	3.51	1.24	0.89	0.005	0.12	1.68	0.08	91.61

*From the outer annual ring to the interior annual ring (pith).
** These elements are carbon, oxygen and the other non-detectable elements.

luted areas were more than the control point. The variation of elemental composition of ATRs may have been non-uniform distribution in some points from the outer ATR to the interior ATR (sap) because of wood defect, but the average amounts of elements/heavy metals into annual rings in the polluted areas were greater than the control point. The average elemental composition value between the control and the 1st and the 7th research points were significant at $p < 0.05$, according to t-test. By this way, the increments of the elements/heavy metals in the annual rings stem from air pollution were tested by quantitative and statistical analysis. Elemental distribution of ATRs in the control, the 1st and the 7th research points were given in Figure 4. Even if it was seen more or less amount in excess the other elements between control with the 1st and the 7th research points, the excess of Mg, Si, Nb, Ca, K and Zn were seen more clearly. These elements present in the composition of lignite and fly ash. It is seen that the fly ash, the main constituent of chimney smoke of the KTPP, has emitted into the atmosphere and then it has deposited on the soil and vegetation around the power plants.

At the same time, the SEM-EDS spectra of the ATRs belonging to the control and the 1st research point were given in Figs. 5a and 5b respectively. Examinations of the peaks of Figs. 5a and 5b, the excess of elemental composition between the control and 1st research points was seen more clearly as a different presentation way. The peaks of elements/heavy metals of the annual rings belonging to the polluted point were larger than the control point. These differences were tested by EDS analyses as quantitatively in Table 3 and 4.

The objective of this work was to evaluate the influence of power plant emissions on every annual ring width in the polluted and control points. SEM-EDS analyses obtained the following results:

1. All of the elements/heavy metals found in fly ash of KTPP chimney smoke were determined in the ATRs.
2. The analyzing procedure was performed on the border annual rings which formed before and after KTPP began operation, but it didn't determine distinctive differences for the elemental composition between ATRs before and after KTPP began operation.
3. There were no differences for the elemental composition in the spring-wood and the summer-wood belonging to identical ATRs.

Table 4. Elemental analysis of ATRs belonging to the 1st research point.

Specifications of annual rings		Elemental Analysis Results (Weight%)										
The number	Corresponding year *	Mg	Si	Al	Nb	Ca	K	S	Fe	Zn	Ti	Others**
1	2002	0.00	1.10	0.28	5.51	1.89	1.95	0.03	0.38	3.56	0.04	85.26
5	1998	0.20	0.93	0.17	3.25	1.14	1.68	0.06	0.53	1.51	0.17	90.36
9	1994	0.38	0.56	0.75	4.34	1.55	1.57	0.21	0.42	3.95	0.20	86.07
13	1990	0.32	0.53	0.00	4.07	1.49	1.63	0.00	0.00	0.76	0.90	90.30
17	1986	0.00	0.40	0.59	2.98	1.28	2.10	0.00	0.01	9.68	0.19	82.77
21	1982	0.36	0.30	0.31	3.00	1.06	1.96	0.00	0.00	0.00	0.44	92.57
25	1978	0.00	0.08	0.76	3.07	1.28	2.02	0.00	0.00	1.33	0.00	91.46
29	1974	0.24	0.32	0.22	4.38	1.87	1.34	0.00	0.01	1.51	0.03	90.08
33	1973	0.88	0.87	0.18	0.65	7.20	1.13	0.37	0.14	0.68	0.15	87.75
37	1966	1.21	0.99	0.20	5.98	7.28	1.74	0.63	0.41	1.59	0.00	79.97
41	1962	0.72	0.74	0.31	4.56	4.90	0.82	0.00	0.24	0.00	0.39	87.32
The core	1960	0.65	0.67	0.37	5.67	4.21	0.36	0.00	0.18	0.00	0.11	87.78
Average value		0.41	0.62	0.34	3.95	2.92	1.52	0.10	0.15	2.04	0.21	87.64

*From the outer annual ring to the interior annual ring (pith).

** These elements are carbon, oxygen and the other non-detectable elements.

Table 5. Elemental analysis of the ATRs belonging to the 7th research point.

Specifications of annual rings		Elemental Analysis Results (Weight%)										
The number	Corresponding year *	Mg	Si	Al	Nb	Ca	K	S	Fe	Zn	Ti	Others**
1	2002	0.00	1.21	0.67	4.09	0.82	2.16	0.15	0.12	0.00	0.00	90.78
5	1998	0.54	0.00	0.74	2.74	0.81	1.64	0.15	1.02	7.77	0.12	84.47
9	1994	0.00	0.26	0.40	3.71	1.43	2.47	0.00	0.05	9.68	0.24	81.76
13	1990	0.00	0.97	0.22	4.57	1.50	1.36	0.00	0.00	0.00	1.88	89.47
17	1986	0.77	0.78	0.31	5.07	2.43	0.00	0.00	0.33	6.13	0.00	84.18
21	1982	0.97	0.37	0.00	7.78	1.98	0.94	0.00	0.00	3.95	0.23	83.78
25	1978	1.13	0.00	0.50	3.71	0.99	1.08	0.00	0.00	2.77	0.00	89.82
29	1974	0.00	0.48	0.27	4.37	1.55	1.20	0.05	0.40	0.98	0.03	90.67
33	1973	0.00	0.45	0.25	4.98	1.85	0.00	0.00	0.00	0.68	0.00	91.79
37	1966	0.45	0.34	0.47	3.78	0.65	1.60	0.00	0.00	0.00	0.00	92.71
41	1962	0.00	0.23	0.37	2.68	3.92	0.72	0.01	1.90	0.00	0.56	89.61
The core	1960	0.00	0.35	0.00	4.51	1.53	0.00	0.00	0.00	0.32	0.05	93.24
Average value		0.32	0.45	0.35	4.33	1.62	1.09	0.03	0.28	2.69	0.25	88.52

*From the outer annual ring to the interior annual ring (pith).

** These elements are carbon, oxygen and the other non-detectable elements.

4. The elements/heavy metals accumulated in all of the ATRs in the polluted points were found out much more than the ATRs in the control point. By this way, it was determined that the elements/heavy metals accumulation into annual ring in the polluted points were discovered to have more excessive amounts than control point. The KTPP chimney was constructed 300 m above the ground for dispersion of the pollutants. Because the height of the mountain chains of the surrounding area of the KTPP is approximately same gradient, there is heavily pollution in this area. It was determined in the modeling study that the concentrations of SO_2, NO_x, and fly ash emissions at ground level were calculated as 310, 62, 20 µg/ m^3 in the 1st and 160, 32, 10 µg/ m^3 in the 7th research point, respectively. [26]. These results confirmed that the metal uptake via foliage and through bark might be a major pathway by which metals enter trees, particularly in heavily polluted areas [16].

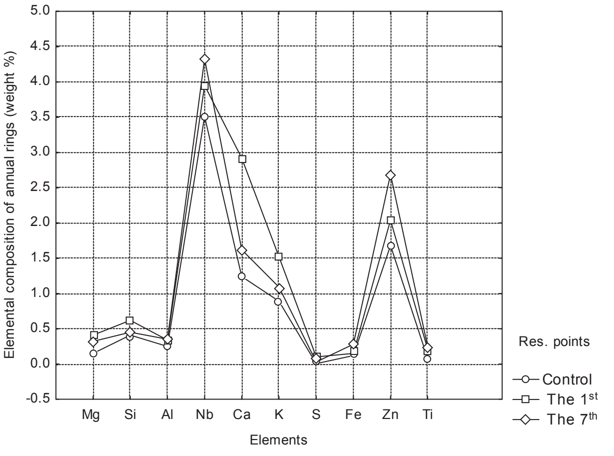

Fig. 4 Elemental distribution of Mg, Si, Al, Nb, Ca, S, Fe, Zn and Ti in ATRs of control, 1st and the 7th research points.

However, uptake of metals by roots is considered to be a major pathway of entry for most elements, metals may enter trees through leaves or bark to become incorporated into ATRs. Metals may also be absorbed by foliage and transported to the internal tissues of plants. Once metals enter trees, they are not necessarily restricted to tree-rings formed during the current year [5, 16]. The amounts of elements in the ATRs after the KTPP began operation could have been much more than the ATR before KTPP began. If there was dead wood (core wood) in the trunks of Turkish red pine before KTPP, the elemental composition of ATRs in these dead woods could have remained partly as unpolluted ATRs for the congestion of transmission corymbs and rays. It was confirmed that the metals emitted by the KTPP chimney accumulated in the ATRs more than control ATRs. Although these elements and/or heavy metals can enter the tree rings intensively after KTPP began operation, they cannot be restricted to the ATRs after KTPP began operation, but they also have passed to ATRs before the KTPP began. This occurrence stems from radial transportation of elements/metals via pith-rays [7, 18]. Clearly, not all tree species are suitable for dendrochemical studies, but if careful sampling strategies are used and suitable tree species are chosen, the chemical analysis of tree-rings can provide information concerning historical changes in soil and atmospheric trace metal levels unavailable from any other source [5]. Although

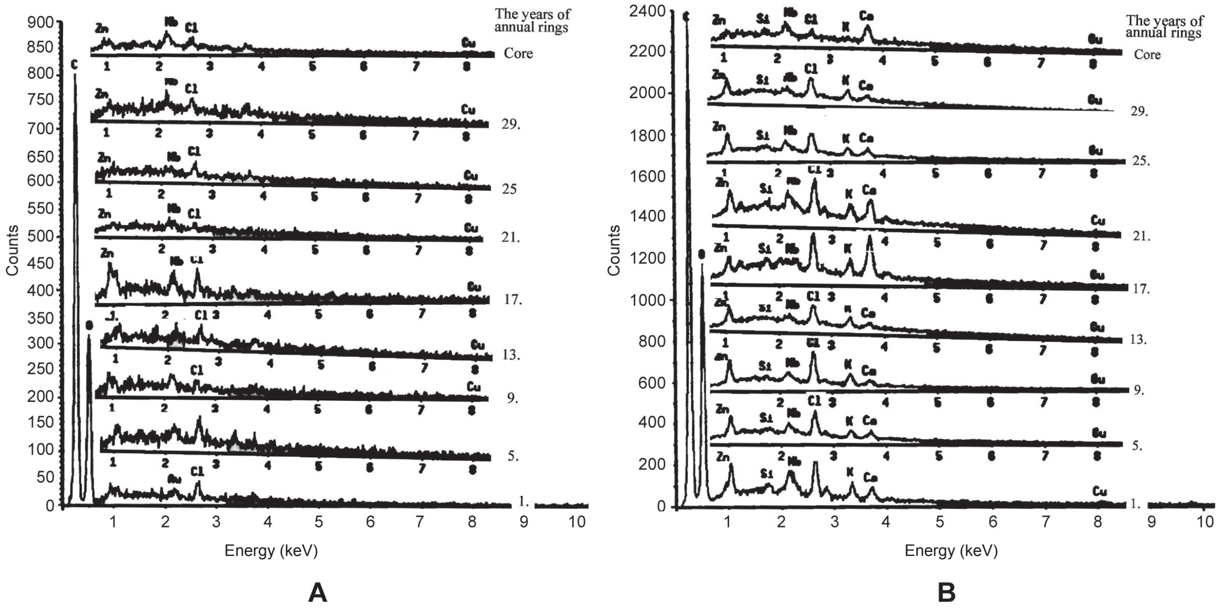

Fig. 5. a) The SEM-EDS spectrums* of the annual rings belonging to the control point; b) The SEM-EDS spectrums* of the annual rings belonging to the 1st research point.

* The spectrums obtained from the outer annual ring (belonging to 2002) to the interior annual ring compatible with Table 3 and 4.

Pinus brutia Ten. may not be a suitable tree species for monitoring temporal historical changes in atmospheric trace metal levels by dendrochemical analysis because of radial transportation of elements/metals via pith-rays into the internal annual rings, it clearly represented that the elements/heavy metals were accumulated to the ATRs of *Pinus brutia* Ten. in all of the polluted areas exposed to high atmospheric concentrations of heavy metals. By this way, the elements/heavy metal accumulation in Turkish red pine trunk stem from the atmospheric pollution of the KTPP were easily determined.

Some techniques for elemental analysis of ATRs are used, such as atomic absorption spectrometry (AAS) [6, 30], neutron activation analysis (NAA) [3], inductively coupled plasma-mass/atomic emission spectrometry (ICP-MS/AES) [5, 31, 32], secondary ion mass spectrometry (SIMS) [33], X-ray fuorescense (XRF) technique [34]. These techniques are more specific and sophisticated methods than SEM-EDS, but numerous processes have been carried out for preparing samples for analyses. Some of these processes are explained, such as preparation of the annual rings/ring-bunches by cutting of the wheel sections to pre-analysis, decomposition of bulk wood, extraction of metals, etc., and then analysis of heavy metals are being applied for annual ring [5, 6, 7, 22]. The energy dispersive spectrometry (EDS) technique is more practical, cheaper, and faster than the others, so energy-dispersive spectrometry has been used for elemental analysis in recent years, even if the results are more approximate than in studies using more specific and sophisticated methods. One significant problem using SEM-EDS for elemental analysis of ATRs may be selecting the suitable energy level for the materials. The 20 keV energy level acquired adequate results at this stage, and the studies and evaluations have been carried out on this subject.

The SEM-EDS analytical method used in dendrochemical elemental analysis of ATR for the first time. This technique is practical and open to new development because the sample of ATRs can be detected by direct investigation. Using SEM-EDS, for instance, the electron beam can be focused onto direct surface of ATR, which enables chemical analysis of the tree-ring or spring and summer wood on identical year. So it becomes easy to directly analyze any annual ring (or spring and summer wood on identical year, and wood defect) onto the wood cross-sectional area of wheel or carotte. This paper confirms that SEM-EDS, a new approach/analytical method to determining air pollution through ATRs, has been successfully applied onto dendro-chemical elemental analysis of ATRs.

Acknowledgements

I would like to thank research assistant Ferhat Bulbul and Professor Dr. Ihsan Efeoglu for long and tiring research during SEM-EDS studies from the Department of Mechanical Engineering at Atatürk University, and also forestry engineer Ertem Unal, who is the chief of Oren Forest Research Office, for his special help.

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