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Posted Date: 25 July 2023

doi: 10.20944/preprints202307.1537.v1

Keywords: Long-term Observations; Trace Elements; Seasonal variation; Atmospheric pollutants doi:10.20944/preprints202307.1537.v1

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Trace Elements Concentrations in Urban Air at Helsinki, Finland, during a 44 Year Period

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Abstract: The atmospheric concentrations of sodium, aluminum, silicon, sulphur, chlorine, potassium, calcium, titanium, vanadium, chromium, manganese, iron, nickel, copper, zinc, bromine and lead were measured in air filters at the Finnish Meteorological Institute station, in Helsinki, Finland, during a period of 44 years (1962-2005). The mean annual concentrations were calculated and are presented from the lowest values to the highest ones Cr<Ni<Ti<Br<V<Mn<Cu<Zn<Cl<Al<Fe<K<Ca<Na<Pb<Si<S. Most of the elements (Fe, Si, Ti, K, Ca, Zn, Br, Pb, V, Ni, S, Cr, Na, Al, Cl) present higher values during spring and winter season while in summer the elements (Ti, Ca, S, Na) are found in higher concentrations. There is a strong correlation between the elements (V-Ni, Si-Pb, Fe-Ca, V-Cr, Si-K, K-Ca, Fe-Ti, K-Na, Si-Ca, V-S), indicating their common source. The identification of the sources of trace elements was performed based on positive matrix factorization analysis, using SoFi software. Four PM sources were identified: road dust (due to usage of leaded fuel), heavy oil combustion/secondary sulfates, traffic emissions and natural dust (soil). For the total of 44 years studied, significant decreases in concentrations were observed for all trace elements, most of which were over 50%: Na (-74%), Al (-86%), Si (-88%), S (-82%), K (-82%), Ca (-89%), Ti (-80%), V (-89%), Cr (-82%), Mn (-77%), Fe (-77%), Ni (-61%), Zn (-72%), Pb (-95%). The current data are consistent with previous air studies covering the whole territory of Finland. Finally, a significant decline has been observed in the majority of the elemental concentrations since the end of 70s, underlying the effectiveness of different environmental policies that have been applied during the last decades.

Keywords: long-term observations; trace elements; seasonal variation; atmospheric pollutants

1. Introduction

Air pollution is an environmental and human health issue that continuously concerns worldwide [1]. A lot of deaths globally attributed to air pollution exposure [2]. Suspended Particulate Matter (PM) is an important atmospheric pollutant with severe public health effects particularly in metropolitan areas which are heavily affected by emissions from vehicles, industry and other sources of urban pollution [3-5]. The inhalation of small sized particles of atmospheric aerosols is responsible of numerous health problems [6]. Different studies have correlated particles with severe respiratory diseases, such as lung cancer, chronic obstructive pulmonary disease, asthma [4,5,7,8] as well as with cardiovascular diseases such as stroke, deep vein thrombosis, coronary events, myocardial infractions, atherosclerosis [8,9] and with other physical and mental health disorders [10,11,12]. In order to fully understand the impact of particles on human health and the environment, a comprehensive characterization of the atmospheric aerosol in needed.

Aerosol particles are a complex mixture of chemical species coming from different sources, either anthropogenic (traffic, industry and combustion processes in general), or natural (sea-salt, windblow dust, forest fires and volcanic eruptions) [13]. For example, the resuspended soil dust contributes to the total emission of specific trace elements (e.g. Cr, Mn, V, Ni) to the atmosphere [14]. Some elements like As, Cd, Ni are linked with both natural and anthropogenic sources [15]. Some of them are released to the atmosphere through the combustion of fossil fuels for the production of heat and electricity (e.g. As, Cd, Cr, Mn, Ni, V), on non-ferrous metal production (e.g. As, Cd, Cu, Zn) [4,16] and of waste incineration (As, Cl, Cd, Co, Cu, Cr, Mo, Ni, Pb and Zn) [17,18]. The atmospheric elements Pb, Fe, Cu, Ni and Cd are usually emitted due to traffic while Zn comes from vehicle tire rubber abrasion [14]. Leaded gasoline combustion was considered to be traditionally the major source of Pb [16], but nowadays the industrial processes and the energy sector are responsible for most of the Pb emissions in Europe [19]. In EU, the road transport still generates 20% of Pb emissions, as the residual Pb in fuel, engine lubricants and parts, as well as tires and break wears still contribute to the emissions [19]. The elemental content of the aerosol particles and their association with different sources in crucial especially for the environmental legislation, showing the future efforts need to be focused on specific sources in order to be successful and effective [14,20].

There are several factors that affect the aerosol's characteristics and their deposition to ecosystem even in distances far away from their source, like the particle size, speed and temperature of exhaust fumes, height of release, prevailing winds, precipitation conditions, topography and soil cover [21,22]. A lot of trace elements in particles are also influenced by the long-range transport, giving the advantage of identifying even distant sources just by knowing the elemental composition of the particles. Thus, trace elements can be used as tracers of possible transports of atmospheric pollutants even in far distances [14,23].

In Europe, during the last decades a declining trend has been observed in the majority of trace elements concentrations but there is still a potential for further reduction [4,14,24]. From 1990 to 2017, the emissions of Cd, Pb and Hg have been decreased by 64%, 93% and 72%, respectively, while in Finland, Cd has been reduced by 86%, Pb by 95% and Hg by 47% [19]. Since the beginning of the 20th century and the beginning of the 21st century, EU has established different directives (e.g. Directives 92/72/EEC, 96/62/EC, 1999/30/EC, 2000/69/EC, 2002/3/EC) in order to reduce air pollution to levels that minimize harmful effects on human health and the environment as a whole and has thus set limits and target values for different elemental concentrations in aerosols (e.g., As, Cd, Ni and Pb) [25-28] as well as in sulphur and other organic compounds. Different national inventories have been established for tracking possible pollution emission sources and the emitted quantities such as EMEP (European Monitoring and Evaluation Program), NEI (National Emissions Inventory, USA), NPRI (National Pollutant Release Inventories; Canada) [29].

The aim of the present study is to investigate the elemental concentrations in aerosol filters collected in the capital of Finland, Helsinki during the years 1962-2005. Since the beginning of the 60's, there is a routine monitoring data system located in the Helsinki metropolitan area which in combination with extended measurements and modeling research projects gives valuable information about trace elements in aerosols particles, their emission sources and their flying paths before their deposition to ecosystem. The study of the elemental concentrations of a 44-year time series can give details about the factors that affect their concentrations (for example urban pollution, transboundary pollution and others), any seasonal variations that may exist and finally, it can show how the reduced emissions, after the application of EU regulations, have affected the concentration trends of different elements at this central location.

2. Materials and Methods

2.1. Study area, sampling and measurements

The capital of Helsinki and its surrounding are situated on a coastal region by the Baltic Sea at 60,2° latitude. The metropolitan area of Helsinki consists of four cities (Helsinki, Espoo, Vantaa and Kauniainen) covering an area of 743 km^2 with a population of more than one and half million inhabitants [30]. The current survey focused only on the Helsinki city and specifically on the Finnish Meteorological Institute (FMI) facilities.

Between 1962 and 1966 the aerosol sampling system was operated in the district of Sörnäinen (60º11′N, 24º57′E, Figure 1). The building was situated beside a main street and the sampling took place on the roof of the building 30 m above the street level and 49 m above the sea level [a.s.l.]. From 1967 to 2005 the aerosol samples were collected on the roof of the FMI's main building in the district of Kaisaniemi (60°10′N, 24°57′E). The air inlet was located 21 m above the street level and 30 m a.s.l. the building was located adjacent to a botanical garden and a park with a main road being about 100m east of the building.

Weekly aerosol samples (air filters) were collected by means of an aerosol beta radioactivity monitoring system [31]. For this purpose, Whatman 42 paper filters were used. The filters were changed every Monday at 06 UTC, assayed in the radioactivity laboratory, and archived for future use [32]. In this study filters belonging to the whole period of 1962-2005 were chosen from the sample archive for analysis.

Air filters retrieved from the sample archive were analyzed for 17 elements (Na, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Pb) using a high-resolution energy dispersive X-ray fluorescence spectrometer with 3-D optics and secondary targets (PANalytical Epsilon 5) at the Institute of Nuclear and Radiological Sciences and Technology, Energy and Safety, N.C.S.R. Demokritos, in Athens, Greece. The concentrations of field blanks were determined and subtracted from every reported value of each sample (Calculated limits of detection, LOD, are shown in Table 1). More details about XRF analysis and quantification can be found in Manousakas et al. (2017) [33].

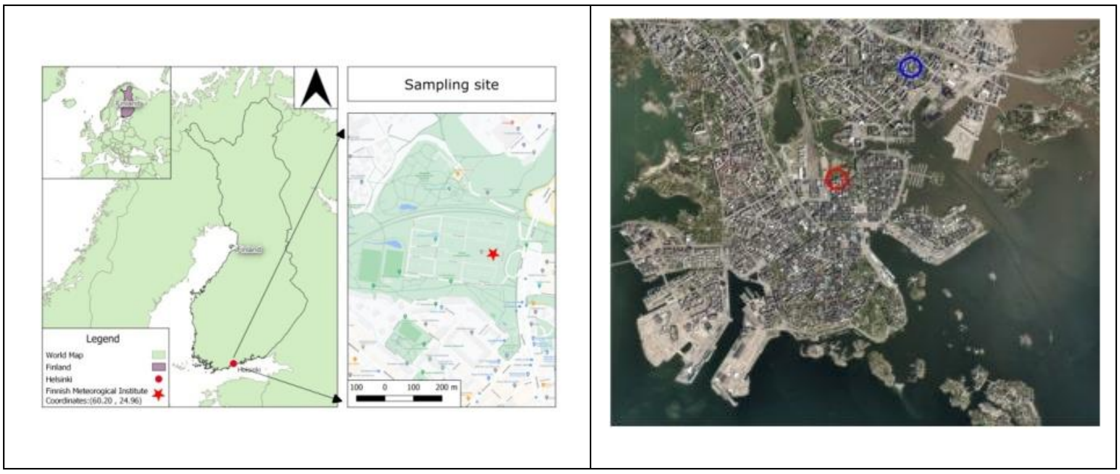

Figure 1. Location of the measurement sites, Finnish Meteorological Institute, in Helsinki. Blue circle: 1962-1966, Red circle: 1967-2005 (Aerial photo: National Land Survey of Finland, CC BY 4.0).

Table 1. The expanded measurement uncertainties (MU) and limits of detections in μg m^{-3} of trace elements measured by the ED-XRF spectrometer.

Element	(MU) (%)	Number of samples	LOD (μg m^{-3})
Na	30.2	599	0.0307
Al	16.0	599	0.0098
Si	15.8	599	0.0028
S	9.1	599	0.0009
Cl	15.8	599	0.0009
K	9.1	599	0.0009
Ca	10.4	599	0.0068
Ti	10.9	599	0.0025
V	13.2	599	0.0015
Cr	21.2	599	0.0025
Mn	16.8	599	0.0012
Fe	10.4	599	0.0012
Ni	17.8	599	0.0009
Cu	11.2	599	0.0012
Zn	12.1	599	0.0015
Br	18.0	599	0.0012
Pb	13.5	599	0.0022

2.2. *Source apportionment methodology*

Source apportionment was implemented through the multilinear engine-2 (ME-2) solver and controlled via SoFi (Source Finder) 8 Pro, which allows for a systematic PMF analysis [34]. Receptor modeling is based on the mass conservation principle:

$$\text{xij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij}$$

where xij is the concentration of the jth species in the ith sample, gik is the contribution of the kth source in the ith sample, fkj is the concentration of the jth species in the kth source k, and eij is the residual of each individual measurement result. Data below the limit of detection (LOD) were substituted by half of the LOD and the uncertainties were set to 5/6 of the LOD. Missing data were substituted by the geometric mean of the measured concentrations and the corresponding uncertainties were set as 4 times these geometric mean [35]. Chemical species with high noise were down-weighted based on their signal-to-noise (S/N) ratio to reduce the influence of poor variables on the analysis, and species with S/N between 0.5 and 1 were defined as weak variables and down-weighted by increasing the uncertainty.

Modeling errors were investigated by examining the residuals of the solution. The residuals were normally distributed, unstructured over time, and variables [36]. The rotational ambiguity was investigated using the methodology described by Francesco Canonaco et al. (2021) [37]. All mathematical indicators suggest source apportionment solution with low uncertainty. The optimum number of factors was decided by monitoring the evolution of mathematical indicators (Q/Qexp, scaled residuals, structure of the residuals, unexplained variation), as well as the physical meaning of the factors.

All data were used in one dataset and PMF runs included all the years. The disadvantage of using many years for a single run is that it is assumed that the sources remain the same as far as their number and their chemical fingerprint are concerned. Before using the entire dataset, we investigated using smaller batches of the data, but the results were very similar or worst (factor mixing) when compared to results over the entire dataset.

3. Results

3.1. Atmospheric concentration levels

The concentrations of seventeen elements were determined using the XRF technique. The results of the descriptive statistical analysis of the elemental concentrations in air filters (multiannual, minimum, maximum, median, mean, standard deviation and total percentage of decrease) are presented in Table 2. Figure 2 reveals the annual average concentrations (in μg m^{-3}) for specific elements (Si, S, V, Cr, Ni, Pb) measured at the FMI station. The majority of the elements present a declining trend over the years. On a percentage basis, trace element concentrations decreased greatly (Figure 3). The lowest decrease was shown for the elements Cu, Br and Cl. In contrast, the highest decrease was observed for Pb, on percentage 95% (Table 2). The higher annual mean concentrations of K, Ca, Na and Zn are observed in the years of 1962-1963, while in the next four years; Pb, Fe and Al show their higher values. In the late 60’s and early beginning of 70’s, the highest peaks of Si, Ti, Ni, V, Cr, S and Br can be distinguished. More than a decade later, the elements Mn, Cu and Cl present their highest concentrations. To be more precise, the elemental concentrations follow the below order (from lower to higher ones) during a 40-yeartime series: Cr<Ni<Ti<Br<V<Mn<Cu<Zn<Cl<Al<Fe<K<Ca<Na<Pb<Si<S. for some pairs of trace elements a strong correlation was observed between them, which proves that they may have a common source of origin: V-Ni ($R^2 = 0.93$, $r = 0.96$), Si-Pb ($R^2 = 0.92$, $r = 0.96$), Fe-Ca ($R^2 = 0.88$, $r = 0.94$), V-Cr ($R^2 = 0.86$, $r = 0.93$), Si-K ($R^2 = 0.86$, $r = 0.93$), K-Ca ($R^2 = 0.84$, $r = 0.92$), Fe-Ti ($R^2 = 0.83$, $r = 0.91$), K-Na ($R^2 = 0.83$, $r = 0.91$), Si-Ca ($R^2 = 0.81$, $r = 0.90$), V-S ($R^2 = 0.81$, $r = 0.90$). The sample correlation coefficient is expressed by r, and R^2 is the square of the correlation. It measures the proportion of variation in the dependent variable that can be attributed to the independent variable (in this case, denotes the variation between the two elements, in each pair of them). Table 3 presents the correlations of all possible combinations of trace elements. It is noteworthy that most of the elements show lower concentrations no longer than 1980, which coincides with the introduction of different regulations for controlling and reducing air pollution.

Table 2. The multiannual minimum, maximum, median, mean concentrations, standard deviation (in μg m^{-3}) and total percentage decrease in trace elements concentrations, for the studied period (1962-2005), obtained from the FMI station.

Element	Min	Max	Median	Mean	St. Dev.	Total decrease
			(μg m^{-3})			(%)
Na	0.07	1.37	0.26	0.30	0.19	-74.0
Al	<0.01	1.04	0.09	0.13	0.13	-86.0
Si	0.03	3.84	0.38	0.55	0.58	-88.0
S	0.09	5.12	0.84	1.02	0.71	-82.0
Cl	<0.01	0.49	0.02	0.03	0.06	-22.0
K	<0.01	1.21	0.17	0.22	0.15	-82.0
Ca	0.01	1.76	0.17	0.21	0.19	-89.0
Ti	<0.01	0.15	0.01	0.02	0.01	-80.0
V	<0.01	0.14	0.01	0.02	0.02	-89.0

Cr	<0.01	0.05	0.01	0.01	0.01	-82.0
Mn	<0.01	0.18	0.01	0.01	0.01	-77.0
Fe	0.01	1.56	0.18	0.21	0.15	-77.0
Ni	<0.01	0.04	0.00	0.01	0.01	-61.0
Cu	<0.01	0.44	0.02	0.03	0.04	-37.0
Zn	<0.01	0.44	0.04	0.06	0.05	-72.0
Br	<0.01	0.11	0.01	0.01	0.02	-32.0
Pb	<0.01	1.96	0.10	0.17	0.23	-95.0

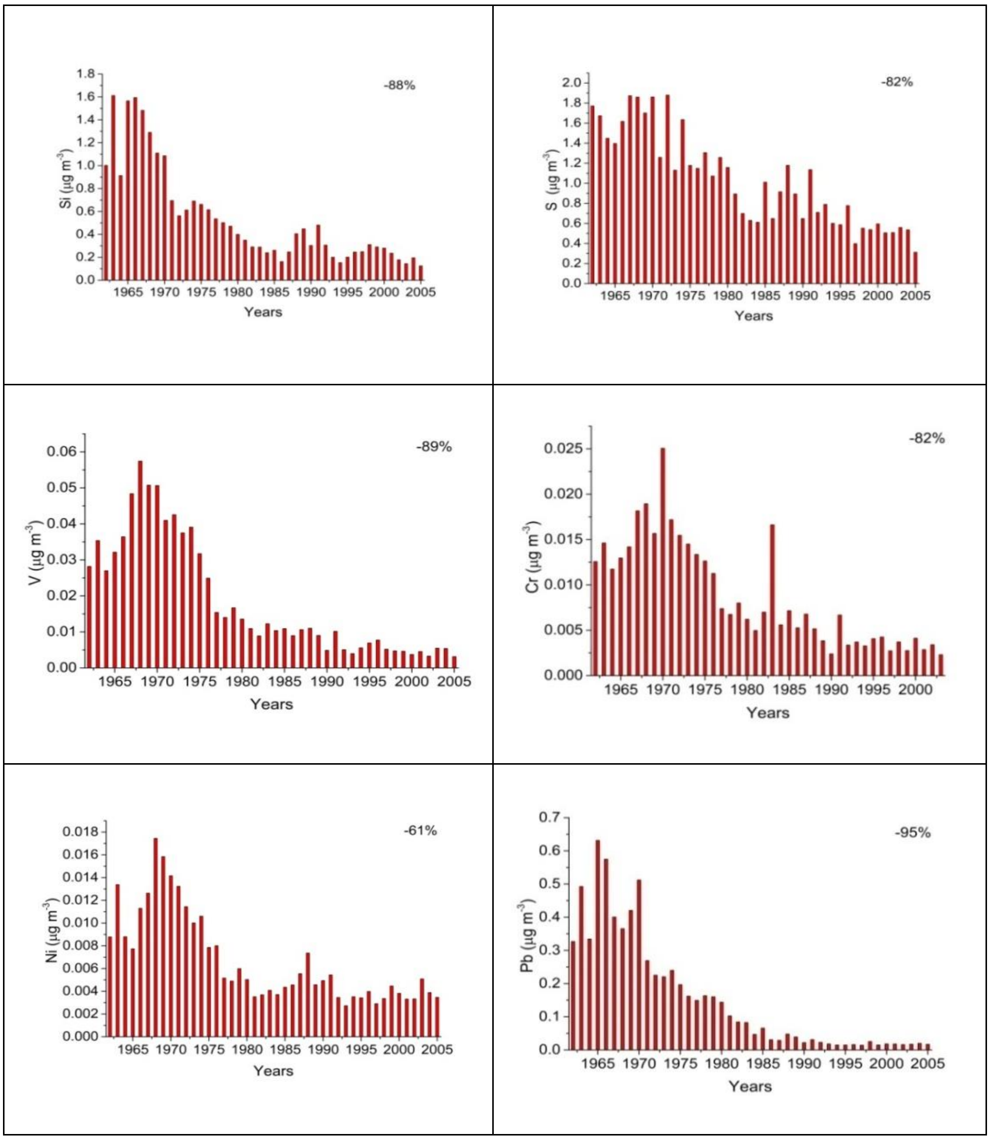

Figure 2. The annual average concentrations of Si, S, V, Cr, Ni, Pb elements (in µg m^{-3}) at Helsinki station (FMI). In the right corner of each diagram, the percentage reduction of each trace elements is noted.

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Table 3. Correlation coefficients between the trace elements.

	Na	Al	Si	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Br	Pb
Na	1																
Al	0.87	1															
Si	0.89	0.86	1														
S	0.81	0.83	0.84	1													
Cl	-0.24	-0.32	-0.21	-0.30	1												
K	0.91	0.81	0.93	0.85	-0.13	1											
Ca	0.85	0.83	0.90	0.79	-0.18	0.92	1										
Ti	0.88	0.89	0.81	0.82	-0.21	0.86	0.84	1									
V	0.80	0.83	0.83	0.90	-0.31	0.78	0.69	0.80	1								
Cr	0.76	0.72	0.76	0.83	-0.34	0.68	0.59	0.67	0.93	1							
Mn	0.34	0.61	0.45	0.31	-0.13	0.42	0.44	0.44	0.26	0.18	1						
Fe	0.87	0.89	0.88	0.81	-0.15	0.89	0.94	0.91	0.77	0.67	0.42	1					
Ni	0.82	0.83	0.82	0.87	-0.28	0.78	0.70	0.83	0.96	0.87	0.26	0.79	1				
Cu	0.51	0.43	0.38	0.29	-0.11	0.43	0.40	0.48	0.34	0.40	0.08	0.50	0.38	1			
Zn	0.86	0.70	0.84	0.68	-0.12	0.89	0.81	0.76	0.66	0.60	0.29	0.81	0.72	0.62	1		
Br	0.50	0.54	0.33	0.43	-0.02	0.36	0.35	0.40	0.42	0.32	0.19	0.40	0.40	0.21	0.22	1	
Pb	0.81	0.77	0.96	0.84	-0.26	0.87	0.78	0.69	0.86	0.82	0.37	0.75	0.82	0.28	0.77	0.29	1

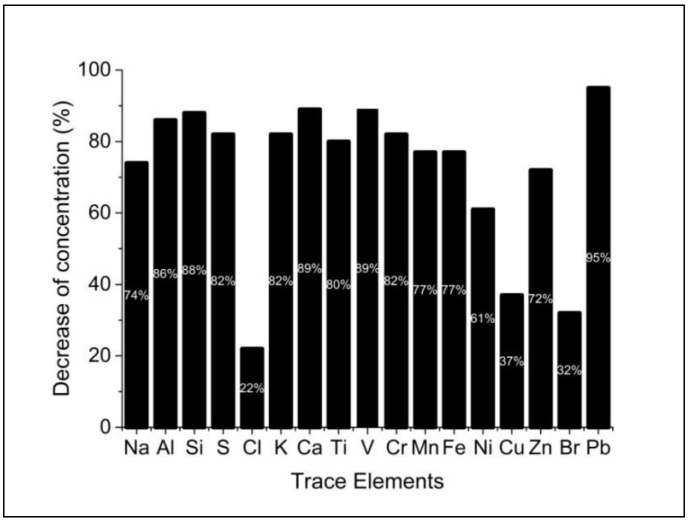


Figure 3. Total percentage decrease of trace elements concentrations.

Various sources may emit the above elements, including natural and anthropogenic ones. Wind-borne soil particles, volcanoes, biogenic sources (e.g. non-sea salt marine), wild forest fires and sea salt spray can be recognized as the principal natural sources of trace elements [38]. One of the most important natural factors that are influencing the elemental concentrations in aerosols is the wind-blown soil particles. Some elements are tightly connected with the soil-derived dust such as Cr, Mn, Pb, V, Fe, Al, Si and Zn, and their distribution is favored by the dry conditions during the warm season [20,39]. Cu and Ni might be associated with another natural source, volcanic eruptions. In addition, Na and Cl are probably observed in aerosol particles due to sea salt spray [20, 40-43] but unfortunately there are not enough data for the specific two elements in order to extract a precise conclusion.

Traffic, industrial and mining activities, oil combustion, argiculture, energy combustion, are the main anthropogenic sources of trace elements. It should be noticed that some elements might originate from multiple sources (natural and anthropogenic), such as Fe, Zn, Cu, Mn, Cr, Ni, V. For example, the element Fe in combination with Zn and Cu can also be related to anthropogenic activities and more specifically to traffic emissions, due to tires, brakes and vehicle body wear (Cu, Fe, Zn), as well as due to the road surface wear (Si, Ti, Fe, Al, Ca) and combustion of lubricating oil (Ca and Zn) [20,44,45]. The elements Cr, Mn, Ni and V are emitted to the atmosphere probably due to fossil fuel combustion [16,46]. Metal industry might also play a role in the concentrations of Mn, Cu and Zn [16,47]. Long-range transport of air pollutants to Finland do occur. For example, S, Ni and Cu emissions from the metallurgical industry in North-West Russia have been detected in Finland [48].

Furthermore, one of the most important anthropogenic pollutants, Pb, which has been decreased since the beginning of the 1970's, is strongly correlated with the lead smelters north of Helsinki, the on-site incinerators and the lead gasoline and fuel combustion for heat and electricity productions, as well as with the wear of vehicles parts [49,50]. Before 1975 the incineration of unsorted household waste in Helsinki caused significant Pb emissions because of the lead foil capsules of wine bottles [51].

3.2. Seasonal variation

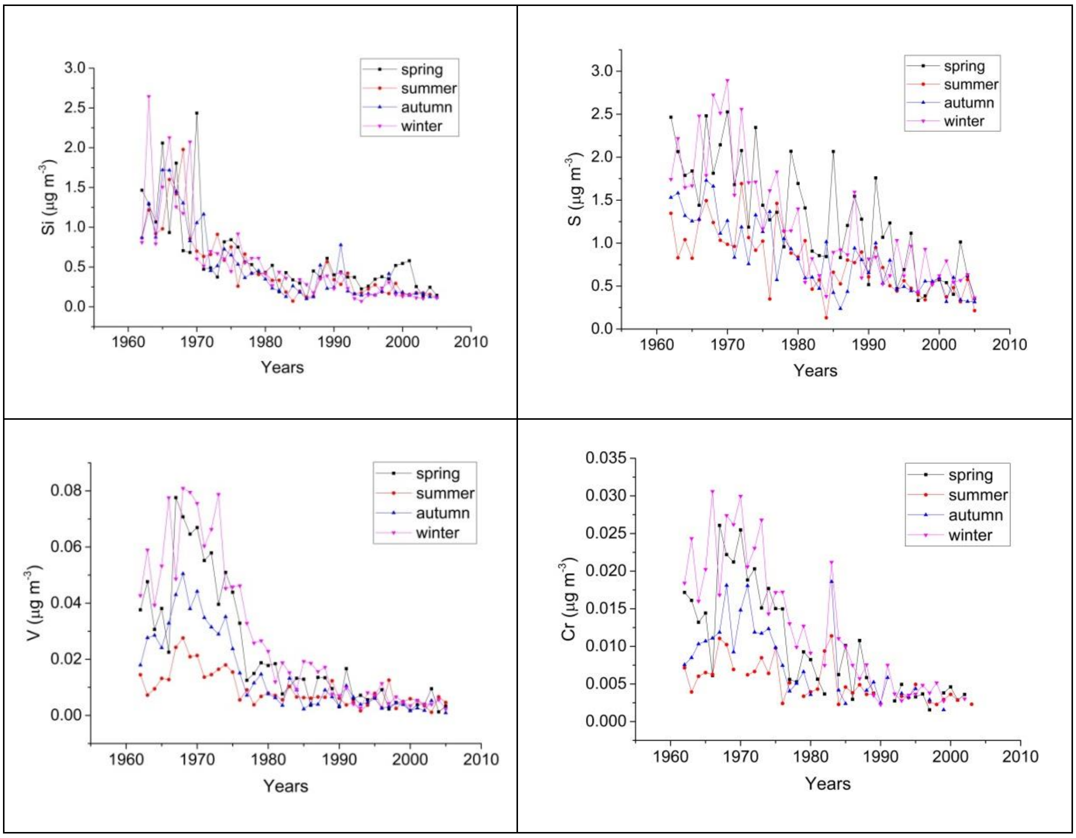
Seasonal differences can cause significant changes in elemental concentrations. Temporal patterns of mean seasonal concentrations have been plotted as a function of time in Figure 4. Most of the elements present higher concentrations during spring and winter period. For wxample, the elements Fe, Si, K, Ca, Cu, V, Ni, S, Cr, Cl and Al have higher concentrations during the cold months, rather than in summer and autumn. In winter the emissions from energy production are at their seasonal maximum. Also, in winter the lower troposphere becomes stratisfied in the absence of solar heating causing convective air flows. Thus, emitted air pollutants stay close to the ground and are not diluted upwards in the atmosphere. Some elements present intense fluctuations in their concentrations like

Cu. Its variations can be easily identified in the diagram concerning all the seasons. Autumn period is more suitable for studying Cu, as these fluctuations are not so deep. Despite of that, the downward trend of Cu over the years is easily defined (up to two orders of magnitude). As for Fe, it is clear that it has evolved over time to show a reduction of almost one order of magnitude.

Zn also presents increased seasonla and time variability. In the first 20 years (1960s-1980s) there is a noteworthy drop in zinc concentrations, but after the 80s, a minimum plateau (lower concentrations throughout the time series) can be observed. Then, an increase in the concentrations appears, which is stabilized towards the end, at values lower than the ones in the 1960s. No classification of its concentrations can be made depending on the season, as maxima and minima are presented in both warm and cold months.

Pb presents an extremely significant drop in the atmospheric concentrations, almost two orders of magnitude lower, than the 1970s onwards. In the first two decades, fluctuations in Pb concentrations are intense, with thw highest values occurring mainly in the winter and autumn seasons. After the 80s, stabilization in Pb concentrations is observed.

Unfortunately, for some elements ther is a lack in the existing database. For example, there is a sharp fluctuation in Br concentrations during the first 20 years. After the 80’s lower concentrations are observed during winter, while spring and summer have gained the higher values of Br by that time. The same gaps exist in Cr concentrations throughout the time series. Although, a decrease of one order of magnitude can be observed over the years, especially in the first two decades. The cold season favors the emission of Cr in higher values than in summer period. Na and Cl, appear to follow the same behavior as Br and Cr, as the greatest variation in the specific elemental concentrations occurs during the winter months. Although, data of Al concentrations are limited, reaching up to middle of 80’s, some conclusions about seasonal variation can be extracted, with spring and winter being the winners in higher elemental concentrations. Finally, Mn concentrations are mostly influenced during the autumn season.



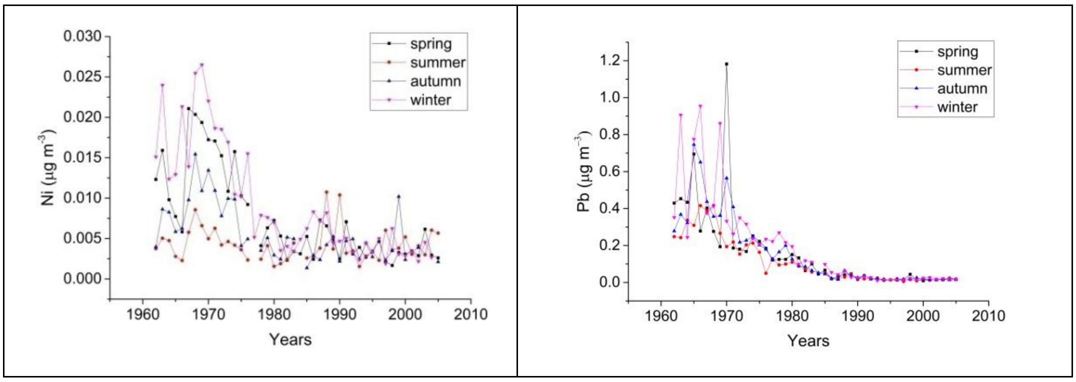


Figure 4. Mean values of seasonal concentrations of trace elements, in µg m-3, through the years.

3.3. Source apportionment

By using the source apportionment approach described in the previous section, we were able to identify four PM sources. Since only elemental tracers were available and the resolution of the samples is very low, it was not possible to identify more (Figure 5).

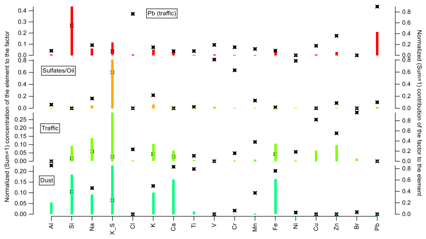


Figure 5. Source profiles. The bars represent the normalized concentrations of the tracers to the factors, while the stars represent the normalized contribution of the factor to the element.

The first factor explains the highest variation of Pb, Cl, and Si. Based on the time series of the factor, its emissions were higher before mid-1970s and went to very low concentrations in the mid-1980s onwards (Figures 5 and 6). This time trend follows the use of leaded fuel that started to face out in 1975 and was completely banned starting at the beginning of 90s until the end of the decade in all European countries. Because of concerns over air and soil lead levels and the accumulative neurotoxicity of lead, this leaded fuel has been designated as a Substance of Very High Concern in the European Union. It has been included in the Candidate List for Authorization under the REACH regulation, which involves the Registration, Evaluation, Authorization, and Restriction of Chemicals [52]. Japan became the first country to impose a total ban on leaded gasoline in 1986. From From January 1993 onwards, all gasoline-fueled vehicles sold in the European Union were mandated to use unleaded fuel. Finland followed suit with its ban on leaded fuel in 1994 [53]. Pb was added to the fuel as tetra-ethyl lead ($PbEt_4$) was used until the 90s as an additive in gasoline to prevent the engine from pernature detonation (''knocking''). Leaded gasoline has been banned within the EU from 2000 on, following the Directive 98/70/EC and its amendment (Directive 2003/17/EC) [50]. When $PbEt_4$ burns, it forms not only carbon dioxide and water but also lead, which can oxidize further to form compounds such as lead(II) oxide.

$$(CH_3CH_2)_4Pb + 13O_2 \rightarrow 8CO_2 + 10H_20 + Pb$$

$$2Pb + O_2 \rightarrow 2PbO$$

Pb and PbO could accumulate and destroy the vehicle's engine. To avoid that effect, lead scavengers 1,2-dibromoethane and 1,2-dichloroethane were used together with $PbEt_4$. These additives from volatite lead(II) bromine and lead(II) chloride, respectively, which are flushed from the engine and into the air [54]. The latter can explain the high presence of Cl in the factor.

The factor also explains to a smaller degree the variation of Si, Na, Cu, and Zn. All of these elements are well-known tracers of road dust [55], and their presence in the factor is justified. This factor might also affected by road-salting which could explain the presence of Na.

The second factor is traced by S, Ni, V, and Cr. As allo of these elements are tracers of heavy oil combustion, this factor is identified as heavy oil combustion and secondary sulfates. Combustion of crude oil will produce particles containing V and Ni. Vanadium reacts with the oxygen from the combustion air forming V_2O_5 that creates layers on the heat exchangers and other boiler and stack surfaces. Additionally, V_2O_5 acts as a catalyst in the temperature range 0f 500-800 °C, accelerating the SO_3 formation and greatly increasing its emissions [56]. In the absence of other tracers (e.g. EC), that could help separate a combustion process such as oil combustion to secondary formation of sulfates, it was impossible to separate the factor into two district sources. This factor has a higher contribution during the 70s, most likely due to the higher use of oil during that time (Figure 6).

The third factor is a mixture of anthropogenic (Cu, Zn, Cr, Mn, and Br), and natural elements (Si, Na, K, Ti, and Fe) and it is identified as traffic-related resuspended dust (road dust). Besides the emissions from the exhaust of the vehicles and the emissions of PM precursors from the combustion of fuels and lubricants, vehicles emit substantial amounts of particles through the mechanical abrasion of brakes, clutch, tires, and motor [57]. These are deposited onto the road and the re-suspended together with mineral dust particles and road wear mineral. Br and Cl in the factor might be an indication that the factor is slightly mixed with Pb-related traffic emissions. This is in a way expected as both factors represent traffic-related emissions. The factor has a higher contribution before the 70s and the contribution increases again from the mid-90s onwards (Figure 6). The first might be linked to increased emissions per car in that era (fuel quality might be an important factor here), while the latter with increasing car fleet number. At the end of 2005, there were about 2.8 million cars in traffic in Finland, of which about 2.4 were passenger cars. In 1962 (beginning of the study time series), the number of car fleet was 344,703 (including passenger cars, vans, trucks and buses) [58].

The final factor is mostly composed form natural elements that are major components of soil (Al, Si, Na, S, K, Ca, Mn, and Fe) and is identified as natural dust [59]. The source shows elevated contribution before ths 70s which might be linked to construction activities (Figure 6). As Ca is an important component of the factor, construction activities might also have an effect on the overall source contribution.

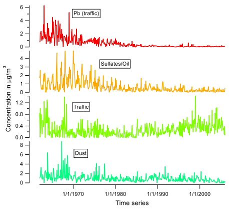


Figure 6. Time series of source contributions. The contribution does not refer to PM mass but to the sun of the species (elements) used as tracers in the source apportionment analysis.

3.4. An overview in the literature

During the last decades, a lot of studies have taken place in the framework of studying air pollution and its impact of human health [60,61], natural ecosystems [62], and even building structures [63,64], either in local [65], regional [66] and global scale [60].

Studies of spatial and temporal patterns of suspended particles have been conducted in different regions of Finland, in order to determine their emission sources and their effects on human lives. For example, Kyllönen et. al. (2009) [67], focused on the deposition of Al, Cr, Cu, Fe, Pb, Mn, Ni, V and Zn elements in bulk deposition at eight background stations in Finland during a ten year period (1998-2007). A south to north decreasing gradient was revealed, due to minor domestic emissions in the north part of Finland, the growing distance from large European source areas and differences in the length of snow-cover period. The annual deposition followed the following order: Cr<Ni<Cu<Pb<Mn<Zn<V<Al<Fe, which is more or less the same rank like in the current survey.

In another research, in the subarctic site of Pallas in FInlad (68°00′N, 24°24′E), the elemental concentrations were found to have among the lowest values in Europe [4]. The annual average concentrations during the period 1996-2018 ranged between 0.02 and 20.0 ng m^{-3}, following the order from the lowest values to the highest ones: Cr<V<Ni<Cu<Mn<Pb<Zn<Al<Fe. Directing to an even Nortern part of Finland, in the Arctic zone, in the region of Kevo, long term particle measurements in air filters were conducted between the years 1964-2010 and were analyzed for trace elements content. The concentrations of V, Co, Cu, Pb, Ni, As, Cd were determined and were found to be higher than in other arctic regions. For most elements there was a decreasing trend during the study period, and especially for Pb (-92 %), like in the current study. A season trend was also unveiled, with winter/spring maxima and summer minima to be observed in most of the elements [68,69].

Moreover, in the beginning of the 90's, another research performed by Jalkanen et. al. (2000) [70] revealed the effects of aerosol deposition in the Gulf of Finland. It was noticed that in the eastern part of the Gulf, close to the boarders with Russia, the average annual concentrations of Al, Ca, Fe, K, Si were higher than in the rest region. Finally, in the late 20th century, Anttila, P. & Salmi, T. (2006) [22], examined temporal and spatial patterns of urban PM_{10}, using six years of Finnish monitoring data (1998-2003), at 24 Finnish urban stations. Long term means of PM_{10} ranged between 11 and 24 μg m^{-3}, with traffic having the major impact on the urban PM_{10} concentrations especially in spring season [71-77].

Finland, as a Nordic country, shares boarders with Sweden to northwest, with Norway to north and with Russia to east. It is really interesting to study data from other neighboring countries and identify any possible transboundary transport of elements, as well as to compare the levels of air pollution in Finland with the rest Europe.

Starting with Norway, different studies have been conducted about the elemental deposition during this period. In the beginning of the 90's a Norwegian-Russian survey occurred about local pollution. Ni, Cu and As concentrations were 5 to 10 times higher in the North part of the country (Kirkenes) than in the Southern one (Birkenes), while Cr, Co, Zn and Cd followed the opposite path, probably due to local emission sources and long range transport of air pollutants from continental Europe [78]. Another research was carried out in Norway by Berg et. al (2008) [79], covering a period of 25 years (1980-2005). The concentrations of Pb and Zn were reduced by 97% and 70% respectively (comparable reductions with combination with the wear of vehicle parts [50,80].

A recent effort was performed by Grøntoft (2021) [81], who studied the historical (1835-2020) dry deposition of major air pollutants (SO_2, NO_x, O_3 and $PM_{2.5}$) in the urban background in Oslo, Norway. The annual accumulated dry deposition of the pollutants varied from about 2.3 to 27 g m^{-2}. The maximum concentrations were observed in the 1960s due to high SO_2 emissions from fuel oil combustion, while there was a decrease in the 90's, following the general declining trend in Europe. The same reduction was followed by $PM_{2.5.}$ emissions (relative ones compered to national emissions) due to the replacement of wood with more efficient energy fuels and the reduction of wood burning.

Sweden in another neighboring country of Finland. Victorin (1993) [82], studied the health effects of urban air pollutants and the guideline values and conditions in Sweden. Urban areas were affected more by the use of leaded gasoline, with Pb levels being pretty high until the introduction of unleaded petrol in cars in the 90's. Isakson et. al. (2001) [83] studied the effect of ship emission in Göteborg. The elements V, Ni, Pb and Zn presented a positive correlation with NO emissions from ships, indicating the combustion oil as the main source of V and Ni [16,20].

A lot of studies concerning aerosol particles have been conducted in Russian territory for the same period [84,85]. The majority of them showed the maximal elemental concentrations during winter and spring season, and the association of Pb with the use of leaded gasoline [84]. Fluing ash particles from industrial sources in the regions of Norilsk and the Kola Peninsula were found to be responsible for the higher levels of Fe, Ni, Cu, Cr, Zn, Ca, Mn and Sb in aerosols [85].

4. Conclusions

Forty-four years of weekly and daily air filters have been collected at the roof of the Finnish Meteorological Institute building in the city of Helsinki and analyzed for trace elements concentrations (Na, Al, Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, Br, Pb). The elemental composition of the PM samples was determined using XRF. A declining trend has been noticed in all elemental concentrations, with Pb decline reaching up to 95%. Seasonal variations have been observed, with the maximum concentrations to be appeared during winter and spring season. Strong correlations have been noticed among elements belonging to the same emissions sources. The sources of trace elements were identified using the SoFi software (source apportionment methodology). Four sources were identified: road dust, heavy oil combustion/secondary sulfates, traffic emissions, and natural dust (soil).

A lot of surveys have been conducted for the same period, either in the rest part of Finland or in the neighboring countries (Norway, Sweden and Russia). In the majority of them, the elemental concentrations in aerosols followed the same declines like in the current investigation, showing similar trends over the year. In all of them, Pb is the element with the most important reduction, indicating the severeness and the effectiveness of the different regulations and measurements that had be taken and applied by the European Union since the 70's. Based on the severe impact of air pollution on human health and environment, it is crucial to continuously record the levels of trace elements in the atmosphere both nationally and internationally, apply new regulations about their reduction and strictly control their emission sources for a better future.

Acknowledgments: We acknowledge support of this work by the project CALIBRA/EYIE (MIS 5002799), implemented under Action ''Reinforcement of the Research and Innovation Infrastructures'', funded by the Operational Programme ''Comparativeness, Entrepreneurship and Innovation'' (NSRF 2014-2020) and co-financed by Greece and the European Union (European Regional Development Fund).

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