IJEGEO

International Journal of Environment and Geoinformatics 10(2):061-069 (2023)

Research Article

Determination of the distribution and sources of inorganic pollutants in particular material in the atmosphere of Istanbul

Cemil Çelen[1], Nuray Çağlar[2], Bircan Gençer Balkıs[1], Abdullah Aksu[2]

[1] Istanbul Metropolitan Municipality, Environmental Protection and Control Department, Anatolian Environment Laboratory Istanbul, TURKIYE
[2] Istanbul University, Institute of Marine Science and Management, Department of Chemical Oceanography, 34134 Istanbul, TURKIYE

* Corresponding author: C. Çelen
* E-mail: cemilcelen@gmail.com

Received: 22.12.2022
Accepted 21.04.2023

How to cite: Çelen, et al., (2023). Determination of the distribution and sources of inorganic pollutants in particular material in the atmosphere of Istanbul, *International Journal of Environment and Geoinformatics (IJEGEO)*, 10(2): 061-069. doi. 10.30897/ijegeo.1222756

Abstract

In this study, metal analyzes were made on filtered samples belonging to different periods of 2017 and 2018 at the air quality stations in Yenibosna, Aksaray and Kadıköy in Istanbul, and were evaluated together with sulfate, nitrogen oxides, carbon monoxide and ozone parameters published by the Istanbul Metropolitan Municipality. Correlations among the metals and among gases were calculated. Considering all the data, the heavy metals with the highest correlation were Fe-Cu (0.93) and Mn-Zn (0.80). In order to determine whether the metal analysis results are at the level of pollution, the enrichment factor was calculated by taking the aluminum element as a reference. The elements that was seen enrichment in all stations are Cd, Zn, Cu and Pb. In addition, the ratios of the average enrichment factors to each other were calculated in order to determine the changes in the compared periods (summer-winter or months) at the stations. In the Aksaray station, where summer-winter comparison was made, the metals with the highest enrichment in winter were Pb and Ni. In order to see the effect of the quarantines applied periodically throughout the country due to the Covid-19 pandemic on the air pollution in Istanbul, the pollutant gas data shared by the IMM AQMC for 2019, 2020 and 2021 years were evaluated and seen that different situations at each station. At Kadıköy station, both the lowest CO and the highest NO and NO_x (although they decreased significantly) emissions were determined in 2021.

Keywords: Air pollution, environmental pollution, metal, Istanbul, seasonal variations

Introduction

Air pollution is one of the biggest environmental problems especially in metropolitan cities due to industrialization, increasing population and unplanned urbanization in recent years. Urban air pollution is caused by the relationship between pollutant concentrations (emissions) and the dispersion, advection and deposition processes that reduce and eliminate them (Goodsite et al., 2021). The local contribution to air pollution in cities depends on demographic/geographical factors, such as the size of the city area and the intensity of pollutant emissions within the area (Hylander and Goodsite, 2006). One of the most important sources of urban air pollution is mobile pollutants (i.e. vehicle traffic) (Goodsite et al., 2021; Kodak, 2022).

Aluminum (Al), iron (Fe) and manganese (Mn) are crustal elements; sodium (Na) is element that come from marine aerosols (FAO, 2022; Saltzman, 2009). The most important sources of heavy metals spreading to the environment are industrial activities such as the use of fossil fuels (solid-liquid), mining enterprises, chemical and paint industry, cement production, iron and steel industry, thermal power plants, glass production, garbage and waste sludge incineration plants (EEA, 2020; EEA, 2022). Due to these activities, metals such as cadmium, lead, arsenic, iron, nickel and chromium are emitted into the environment (EC, 2002). Air pollutants can be classified into four groups; particulate matter (PM), heavy metals (lead, mercury, cadmium, nickel etc.), gas pollutants (CO, SO_x, NO_x, O_3, HC) and persistent organic pollutants (dioxin/furan, PCB etc.) (EMEP, 2021). There are three main sources of heavy metals in street dust: Cu, Pb, Zn and Sb elements are caused by traffic emissions; As, Cr, Mn and Ni elements are of natural origin; Fe, Cd and Hg elements are of both natural and anthropological origin (Keshavarzi et al., 2015). Metal pollutants do not decompose biologically or chemically like organic pollutants, they just turn from one compound to another compound, form; however, they are never lost (Taylan and Özkoç, 2007; Rainbow, 1995).

Ships are an important source of pollutants for both the sea and the atmosphere. Sources of marine pollution from ships are due to ship accidents, mixing of fuel into the sea, wastewater and ballast-water discharged from ships, solid waste, and accidental spillage. Ships release various pollutants into the atmosphere, because transport ships are powered by heavy fuel oil. Maritime transport causes 10-15% of global anthropogenic SO_x and NO_x emissions, and about 3% of global CO_2 emissions (Bayırhan et al., 2019; IMO, 2015; Ülker et al., 2021; Nusa and Kodak, 2023).

The enrichment factor (EF) is the approach to characterize the chemical composition of the particulate matter in the air and is the ratio of the element and normalization metal concentration ratio to be measured to that of the amount in the air in the reference ambient and material (Balkıs et al., 2009). It is used to determine both the source of the pollution (Aksu, 2015). When crust is selected as the reference ambient (EF_{crust}), enrichment from crust to air can be calculated, and when sea is selected (EF_{sea}), enrichment from sea to air can be calculated. Elements such as Al and Fe, which can be found in abundance in the soil structure, can be selected as normalization elements. There is no clear evaluation of the enrichment factor from crust and sea to air. Chester (1990) stated that enrichment factor values can be evaluated as follows: If the EF value is less than 10, there is no enrichment pollution originates from crust or sea. If the EF value is greater than 10, there is normal or excessive enrichment and the pollution source is of anthropogenic origin.

According to European Environment Agency (EEA, 2022) key primary air pollutants are particulate matter (PM), black carbon (BC), sulphur oxides (SO_2), nitrogen oxides (NO_x) (including nitrogen monoxide and nitrogen dioxide, NO_2), ammonia (NH_3), carbon monoxide (CO), methane (CH_4). Sulfur and nitrogen are the most important air pollutants affecting the aquatic ecosystem, the source of which is largely air (Sonwani and Maurya, 2019). Air pollution (especially sulfur oxides, nitrogen oxides and ozone) affects diverse ecosystems and biodiversity by changing its physical components. Oxides of sulfur and nitrogen react together to form acid rain and increase the acidity of the soil. Increased acidity negatively affects nutrient cycling, reproduction and climate regulation in the ecosystem (Sonwani and Maurya, 2019). The gases that trap the infrared rays coming to the world and convert them into heat by forming a layer between the atmosphere and the earth, absorb the rays reflected from the earth and regulate the heat balance of the world are called greenhouse gases (Bayraç and Emrah, 2016). Carbon dioxide (CO_2), chlorofluorocarbon (CFC), methane (CH_4), ozone (O_3), nitrous oxide (N_2O) and water vapor are defined as greenhouse gases. Greenhouse gas emissions, which have increased more in recent years, cause global warming, climate change, warming and rising sea water, drought and flood events by disrupting the radiation balance of the world and its atmosphere through both natural and human activities (Pachauri and Meyer, 2015). In Fig 1, it is seen that the increase in CO_2, CH_4 and N_2O emissions has accelerated in recent years since 1850.

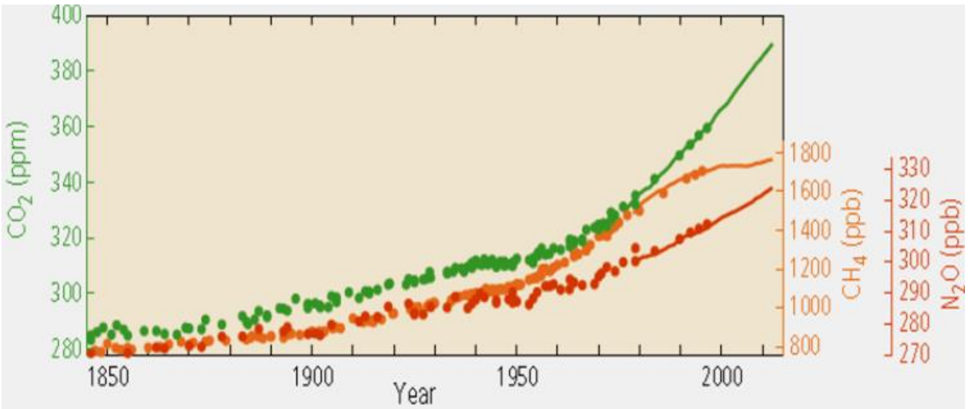

Fig. 1. Global annual average greenhouse gas concentrations (Pachauri and Meyer, 2015).

Particulate matter (PM) in the atmosphere, which has an important place among air pollutants, can cause serious environmental problems. The size of the particles; Identification of pollutant sources is very important in terms of understanding health effects, effects on climate, residence time in the atmosphere and precipitation from the atmosphere (Arslan and Akyürek, 2018; Manisalidis et al., 2020). Air pollution increases pre-existing health problems such as diabetes, lung diseases, asthma, heart diseases and cancer, which make Covid-19 more serious and fatal (CREA, 2020). Wu et al. (2020) did the first important study on the relationship between air pollution and Covid-19. According to the study, it has been determined that people who are exposed to long term air pollution are much more affected by Covid-19, and 1 $\mu g/m^3$ increase in the amount of $PM_{2.5}$ in the air causes an 8% increase in the death rate from Covid-19.

The aims of this study were:

i. Determination of metal concentrations by analyzing PM10 samples from different periods in 2017-2018 at Kadıköy, Aksaray and Yenibosna stations.
ii. Calculation of the enrichment factor (EF) according to the metal analysis result for the interpretation of the pollution source.
iii. Evaluation of pollutant gas data for the same period shared by Istanbul Metropolitan Municipality Air Quality Monitoring Center (IMM AQMC).
iv. To evaluate the impact of the pandemic on air pollution by using the monthly average pollutant gas data shared by IMM AQMC between the years 2019-2021.

Materials and Methods

Chemicals

Nitric Acid (65%) purchased from Tekkim (Bursa, Türkiye). Hydrogen Peroxide (30%) purchased from Merck (Darmstadt, Germany). For ICP analysis, ICP multi-element standard solution (Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl, Zn) purchased from Merck (Darmstadt, Germany).

Study Area and sampling

Although the sources of air pollution are generally known, they can vary in every region of Istanbul. This is because meteorological conditions (rain, temperature, etc.), wind directions and emissions (heavy traffic, oscillations in industrial areas, etc) affect air pollution. Thus, the sources of pollutants can be determined as a result of air quality sampling and their analysis in a designated area.

The Marmara Region and especially Istanbul, hosting and leading the development of many sectors of Türkiye, being the market place, and can be considered as its capital, not political but industrial, economic, cultural, etc. This situation is both a direct source of air pollution (in a broader expression, environmental pollution), but also indirectly causes an increase in pollution (heating systems, traffic, etc.) with the increase in population. Pollution caused by heavy and less mobile traffic is one of the most important problems of Istanbul. Traffic-induced pollution parameters are CO, NO_x, SO_x PM and heavy metals. Due to the use of fossil fuels in vehicles, Cd, Ni, Cr; Cu, Sb, Ba due to brake pads; Zn, Cd due to tire wear; Ni, Cr elements are emitted into the environment due to the rubber coating (Hjortenkrans, 2008). Traffic density in Istanbul increases in the winter months and decreases periodically in the summer months. Metal analysis studies in PM carried out previously in Istanbul are shown in Table 1.

Istanbul has two airports with direct and connecting flights to many destinations in Türkiye and the world. According to 2017 data, the total number of passengers at these two airports is approximately 49% of the total number of passengers in Türkiye (DHMİ, 2018). Exhaust emissions created by airplanes during flight are CO_2 (Carbon dioxide), H_2O (water vapor), NO_x (nitrogen oxides), SO_x (sulfur oxides), CO (carbon monoxide), HC (hydrocarbons) gases and Al, Cr, Fe, Ni elements. (Kesgin, 2006; Starik, 2008).

Table 1. Metal analysis studies in PM carried out previously in Istanbul

Studier	Period	PM	Station	Results	Unit
Izladıoğlu, 2019	2017	$PM_{2.5}$	Aksaray	Cd: 0.15-0.44; Co: 0.03-1.29; Cr: 5.15-10.73; Cu: 2.52-79.45; Ni: 3.67-118.86	ng/m³
Onat et al., 2012	2005-2006	PM_{10}	Yenibosna (average)	Cd: 4.5; Co: 4.8; Cr: 62.2; Cu: 49.2; Ni: 13.2; Pb: 105.4	ng/m³
Aksu, 2015	2010	PM_{10}	Tuzla	Al: 14-248; Cd: 0.001-0.41; Cr: 0.004-0.28; Cu: 0.04-2.68; Fe: 5.48-74; Pb: 0.01-0.77; Zn: 0.01-0.65	ng/m³
Şahin et al., 2016	2008-2010	PM_{10}	Beşiktaş (average)	Cd: 0.7; Co: 0.4; Cr: 7.9; Cu: 15; Ni: 4.3; Pb: 7.3; Mn: 13.6; Zn: 216; Fe: 1034.9	µg/m³

In this study, the air quality data of three different stations belonging to the Istanbul Metropolitan Municipality Environmental Protection Directorate, located in the west, middle and east of Istanbul, were evaluated. These are Yenibosna, Aksaray and Kadıköy stations. Station locations, types and sampling dates expressed in Table 2 and shown on the map in Fig. 2. Kadıköy is the densest region of the Anatolian side in terms of both population (481.983 people in 2020) and traffic. For this reason, it has been considered as a suitable place to examine the pollution parameters originating from traffic and population density. This station is located adjacent to the open car park and expressed as urban station type by IMM. 50 m away, Söğütlüçeşme Street is an area with very heavy traffic. In addition, sea-sourced inputs were also examined and ship emissions were evaluated due to its near to Kadıköy and Haydarpaşa Ports. Hundreds of domestic passenger transportation trips are organized from Kadıköy Port per day, Haydarpaşa port is one of the international cargo transportation centers.

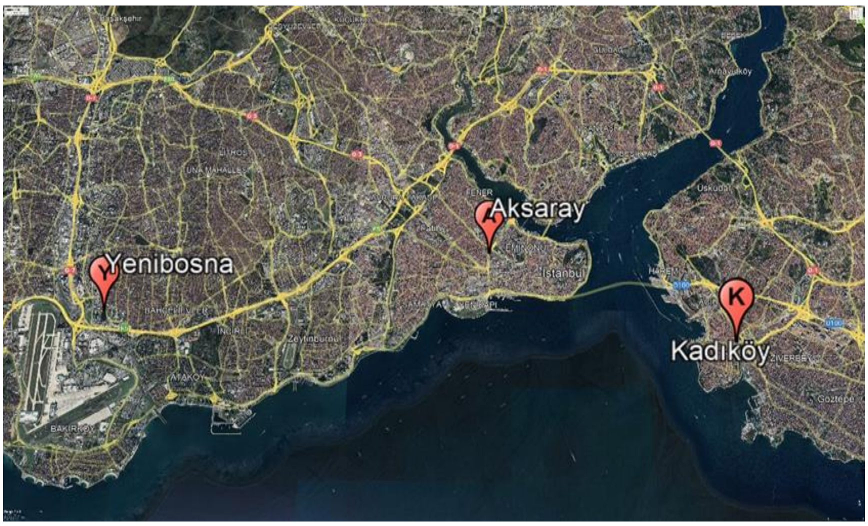

Fig. 2. Locations of sample collection from Istanbul, Türkiye.

Aksaray is the both a tourist center and one of the regions with heavy traffic and population (Fatih district 2020 population is 396.594 people), located in the geographically central part of Istanbul on the European side, in Fatih district. Located next to Haşim İşcan Passage, where traffic is heavily all day long, the station has been accepted as a traffic station type by IMM. It was preferred in order to examine the effect of traffic on air pollution in a different region from the literature. Yenibosna is located in Bahçelievler district (2020 population 592.371) on the European side, north of the D-100 highway (500 m away), near Atatürk Airport and the highway connection road (E6) (600 m away). For this reason, this location where traffic is always heavy. It is also a residential area and has been accepted as an urban station type by IMM.

Table 2. Sampling station, locations and sampling dates

Station and Type	Latitude (N)	Longitude (E)	Date Range
Kadıköy (Urban)	40.990800	29.033336	26.01.2017 06.02.2017 17.10.2017 20.10.2017
Aksaray (Traffic)	41.014361	28.953942	06.06.2017 17.06.2017 14.01.2018 18.01.2018
Yenibosna (Urban)	40.997489	28.827225	23.05.2017 27.05.2017 28.02.2018 04.03.2018

Digestion and Preparation Method

PM10 filter papers were accepted as homogeneous and were divided into two parts in the middle for parallel analysis and weighed on a Precisa/XB 220A brand precision balance. 8 ml of HNO_3 (nitric acid) and 2 ml of H_2O_2 (hydrogen peroxide) were added to the filter papers placed in the microwave tubes and they were kept in the fume hood for a minimum of 30 minutes for the reaction to take place. The digestion process was carried out in the Anton Paar/Multiwave Go microwave device. The program applied in the microwave is shown in Table 3. The digestion sample was diluted to 30 ml by filtration with a syringe.

Table 3. Microwave device program stages

Step	Ramp	Temp.	Hold	Power
1	10 min	160 °C	15 min	800 W
2	10 min	195 °C	10 min	800 W
3	Cooling	40 °C		

Preparation of calibration standards

Merck Multi Standard solution was used for the calibration of the ICP OES device. A small amount of standard solution was weighed and diluted with nitric acid solution and Standard 4 (Std 4) was prepared. Std 3 and other calibration standards were prepared by making approximately 4 times dilution from Std 4, and the concentration of each element of each standard was calculated considering the stock concentrations specified in the certificate (Table 4).

Instrumental Analysis

Analysis of the samples was done on PerkinElmer Optima 2100 ICP OES instrument. The metals have been analyzed are Al, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn. First, the elements to be analyzed were calibrated, and then the calibration control was done. Since the samples were studied by dividing into two parts, the average of the analysis results obtained from the ICP OES device was multiplied by two. The result obtained as a result of the multiplication was converted into µg/m3 by dividing the sampler's average collection volume (55.2 m^3).

Table 4. Standard preparation table (mg/l)

Stock Cons.	***Metal***	**Std 4**	**Std 3**	**Std 2**	**Std 1**
1002	*Cd*	1.1844	0.1969	0.0337	0.0055
1003	*Cr*	1.1856	0.1971	0.0338	0.0055
999	*Cu*	1.1809	0.1964	0.0336	0.0055
1005	*Fe*	1.1880	0.1975	0.0338	0.0055
1008	*Mn*	1.1915	0.1981	0.0339	0.0055
1001	*Na*	1.1832	0.1968	0.0337	0.0055
999	*Ni*	1.1809	0.1964	0.0336	0.0055
1001	*Pb*	1.1832	0.1968	0.0337	0.0055
1001	*Zn*	1.1832	0.1968	0.0337	0.0055
999	*Co*	1.1809	0.1964	0.0336	0.0055
1001	*Al*	1.1832	0.1968	0.0337	0.0055

Results and Discussion

After metal analysis of the samples in order to evaluate the amount of terrestrial pollution belonging to three stations, the enrichment factor was calculated by using Al metal. Since Kadıköy station is near to the sea, the enrichment factor was calculated with Na metal in order to calculate the marine pollution of this environment. The crustal (for EF_{crust}) and sea water (EF_{sea}) values of Krauskopf (1979) were used as reference values. The evaluation of the enrichment factor was made according to Chester (1990).

Kadıköy

It was aimed to examine the 9-month changes in the parameters with the samples from January-February 2017 (12 days) and October 2017 (4 days). With the data of both periods, first the enrichment factor (EF_{crust}) and then the average of the periodic enrichment factors were calculated and the average of the October period was compared to the average of the January-February period. Thus, it was aimed to determine the elements where enrichment (or change) occurs in the 9-month period. Metals result range; Cd (0.010-0.054), Co (0.014-0.093), Cr (0.198-2.96), Cu (0.498-4.46), Fe (7.68-146.7), Mn (0.202-3.13), Ni (0.124-0.872), Pb (0.246-1.39), Zn (0.849-5.99). According to the January-February period metal data of Kadıköy station, the periodical highest concentrations were observed in Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn elements on February 1, 2017. In the October period, Cd, Cr, Cu, Mn elements reached the highest concentration on 17 October.

EF_{crust} values range; Cd (87.60-3544), Co (1.5-15.79), Cr (5.68-76.72), Cu (27-171.8), Fe (0.32-3.21), Mn (0.82-3.01), Ni (2.07-96.22), Pb (17.37-323.6), Zn (32.22-141.6). Enrichment was observed in Cd, Cu, Pb and Zn elements on all days. The elements that were enriched on all days are Cd, Cu, Zn, and it can be said that the pollution is anthropogenic. EF_{crust} data at Kadıköy station belong to two periods, January-February and October 2017. It has been understood that there was a periodic decrease in all elements. The elements whose amount changes the most were Cd, Ni, Pb, while the least changing element was Fe.

According to these data, heavy metal pollution in the atmosphere of Kadıköy in the January-February period decreased significantly in October. It can be thought that the biggest reason for this was that the pollution load caused by heating may not have shown its full effect in October. Due to its near to the sea, the high values (EF_{sea}>10) in all elements according to the EF_{sea} data calculated to detect marine pollution only at Kadıköy station (by taking the Na element as a reference) show that there is no enrichment from the sea, and the anthropogenic contribution is very high.

The highest were observed in both NO, NO_2, NO_x, PM_{10}, SO_2 parameters and Cr, Cu, Ni, Pb, Zn elements on February 2, 2017, in the January-February period at Kadıköy station. Although this station is actually accepted as an urban area, NO, NO_x and CO concentrations are similar to Aksaray, which is accepted as a traffic area. It can be thought that maritime transport is effective as the source of pollution in this area.

Aksaray

Samples from June 2017 (13 days) and January 2018 (4 days) were analyzed. With the metal analysis data of the summer and winter periods, first the enrichment factor and then the average of the enrichment factor for the period were calculated and the winter period average was compared to the summer period average. Thus, it was aimed to determine the elements with enrichment specific to the winter period. Metals result range; Cd (0.009-0.069), Co (0.018-0.078), Cr (0.247-1.76), Cu (0.657-2.91), Fe (13.63-65.04), Mn (0.014-2.16), Ni (0-0.733), Pb (under the measuring limits of the device-0.954), Zn (1.92-6.18).

EF_{crust} values range; Cd (63.06- 977.5), Co (0.83-7.94), Cr (2.37-16.26), Cu (14.49-55.77), Fe (0.28-1.16), Mn (0.01-1.70), Ni (0-15.43). Pb (0-108.4), Zn (31.97-95.60). High enrichment was observed in heavy metals (Cd, Co, Cr, Cu, Ni, Pb, Zn) in the winter period on January 14, 2018. Cd, Cu, Zn were the elements that are enriched on all days, and it could be said that the contribution of anthropogenic pollution is very high. Elements with enrichment on some days were Cr, Ni, and Pb. Elements with no enrichment Co, Fe and Mn. Although the highest metal concentrations were observed on January 16, the highest enrichment was observed on January 14. This situation could be explained by the fact that the amount of Aluminum was low and other elements were high on January 14 due to non-soil pollution, and as a result, the enrichment rate increased. The metals with the highest enrichment increase from summer to winter were Pb (4.82 multiple), Cd (3.86 multiple) and Ni (2.99 multiple). On the other hand, no increase in periodic enrichment was observed in Fe element. Periodic enrichment is observed for each element except Fe in the winter period compared to the summer period. The most enriched elements in winter are Pb, Cd and Ni, and these three elements were traffic-related. It can be thought that the reason for the increase in these elements is the heavy traffic.

In the summer period, on 8 June 2017, when the CO, NO, NO_2, NO_x, PM_{10} parameters reached the highest concentration, it was observed that the O_3 amount was the lowest, the air temperature was high, and the wind speed was low. In the metal data, the highest concentrations were reached for Al, Cd and Zn elements on the same date. In the winter period, on January 16, 2018, when CO, NO, NO_x, PM_{10}, SO_2 and humidity values reached the highest values, the lowest concentration was observed for O_3. In the metal data of the same date, the periodic highest concentrations were observed in all of the elements.

Yenibosna

In order to examine the change in the periods of May 2017 (5 days) and February-March (3 days), metal analyzes were made and the enrichment factor was calculated. In order to see the periodic change, the period averages were proportioned to each other. Metals result range; Cd (0.010-0.030), Co (0.007-0.048), Cr (1.07-1.84), Cu (0.809-2.31), Fe (7.58-47.83), Mn (0.271-1.44), Ni (0.230-0.502), Pb (0.164-1.37), Zn (1.54-4.15).

EF_{crust} values range; Cd (139.3- 696.2), Co (1.75-4.33), Cr (16.12-66.46), Cu (24.30-139.4), Fe (0.48-2.81), Mn (1.43-3.12), Ni (4.78-21.75), Pb (45.36-163), Zn (55.86-128.1). The highest EF_{crust} values were seen on 26 May 2017. In the February- March period of 2018, compared to the May 2017 period, there was an average of 1,03-multiple and 1,08-multiple increase in enrichment in Co and Pb elements, respectively, while there was a decrease in other elements, and the elements that decreased the most were Cu and Fe. The elements that were enriched on all days are Cd, Cu and Zn, and the source of pollution is anthropogenic. Elements with enrichment on some days were Cr, Ni, Pb. Elements with no enrichment were Co, Fe and Mn, and the pollution is of natural origin.

At Yenibosna Station, the highest concentrations were determined in each elements at the same time on the day when the PM_{10} parameter was the highest. This means that increasing the amount of PM_{10} increases the pollutant load. On the day with the highest PM_{10} parameter (May 25, 2017), it was observed that the rain rate and temperature were the highest and the humidity was the lowest.

Conclusion

When each metal parameter was evaluated together, the elements that enriched in each period in three stations were Cd, Cu and Zn. This shows that three stations were exposed to traffic-related pollution. In addition, the correlation coefficients of the metals with each other were calculated (Table 5). The highest correlation coefficient is between Fe-Cu and Al-Zn. The high correlation between the elements may mean that their emission sources may be the same or similar. Common sources of air pollutants for Fe and Cu elements are industry and traffic, for Al and Zn elements are soil and dust (Fang et al., 2015; FAO, 2022). The lowest correlation coefficient is between Na-Fe and Na-Cr. These elements are among the most abundant elements in the soil and in the sea. Periodic comparisons were made in order to determine the pollutants specific to the analyzed periods (Table 6). Pb, Cd, Ni concentrations increased significantly at Aksaray and Kadıköy stations. These elements are traffic related emission sources. At Yenibosna station decreased Cu, Fe, and Cr emissions.

Pandemic Period

In order to understand whether there is a decrease in air pollutant emissions during the pandemic period, the pollutant parameters for the years 2019, 2020 (first year of the pandemic), 2021 (second year of the pandemic) shared by the IMM AQMC were evaluated. Year 2019 is used for background. Data for some periods have not been published. Pandemic restrictions were carried out in Türkiye in March 2020 firstly. Restrictions increased and decreased from time to time and removed (almost completely) as of July 2021. The averages of polluting gas emissions in 2019, 2020 and 2021 are shown in Table 7. With this table, it was aimed that each station can be evaluated separately. In addition, air quality limit values are specified according to the Air Quality Assessment and Management Regulation (AQAMR) dated 06.06.2008 applied in Türkiye.

At Kadıköy station CO, NO, NO_2, NO_x and SO_2 parameters increased in 2020 and decreased in 2021. In CO, NO_2, NO_x, O_3 and SO_2 parameters, the highest concentrations were determined in the three-year average. On the contrary, the annual average ozone amount decreased in the first year and increased in the second year. The most important reason for this situation is that while these parameters generally increase in winter, ozone is inversely proportional to the temperature. In addition, NO_x can participate in ozone formation (EPA, 1999). NO and NO_x emissions decreased significantly, nevertheless annual average NO_2 and NO_x data exceeded the AQAMR limit value every year.

Table 5. Correlation of PM_{10} metal data (three stations).

Metal	*Al*	*Cd*	*Co*	*Cr*	*Cu*	*Fe*	*Mn*	*Na*	*Ni*	*Pb*	*Zn*
Al	1	0.21	0.79	0.44	0.72	0.76	0.78	0.49	0.18	0.18	0.84
Cd		1	0.35	0.17	0.39	0.31	0.35	-0.20	0.72	0.43	0.27
Co			1	0.32	0.52	0.50	0.60	0.54	0.29	0.22	0.72
Cr				1	0.52	0.55	0.62	-0.01	0.36	0.36	0.49
Cu					1	0.93	0.76	0.04	0.54	0.39	0.71
Fe						1	0.77	0.01	0.47	0.38	0.76
Mn							1	0.23	0.39	0.44	0.80
Na								1	-0.38	-0.23	0.37
Ni									1	0.62	0.33
Pb										1	0.38
Zn											1

Table 6. Periodic investigation of metal concentrations of three stations

Station	Period	Finding	Estimation
Aksaray	Summer⇨Winter	Significant increase in Pb, Cd, Ni concentrations	The increase can be thought to be due to traffic.
Kadıköy	January ⇨November	Significant decrease in Cd, Ni, Pb concentrations	The increase can be thought to be due to traffic.
Yenibosna	2017 May⇨2018 March	Decrease in Cu, Fe, Cr concentrations	It may be due to seasonal temperature changes or PM transport by wind in May.

Table 7. Annual averages of polluting gas emissions in 2019, 2020 and 2021 by stations.

Station	Year (average)	CO (µg/m³)	NO (µg/m³)	NO_2 (µg/m³)	NO_x (µg/m³)	O_3 (µg/m³)	PM_{10} (µg/m³)	SO_2 (µg/m³)
Kadıköy	2019	550.8	140.7	52.3	280.9	20.8	36.6	3.7
	2020	666	172.5	61.9	338.3	16.3	32.3	3.9
	2021	531.8	34.9	47.6	102.7	19.7	32.1	2.8
Aksaray	2019	504.2	84.8	97.2	226.6	15.7	48	3.7
	2020	511,3	62.5	87	183.8	18.6	40.7	2.7
	2021	604,6	55.8	80.7	166.8	16.6	40	3.6
Yenibosna	2019	784	36	47.3	102.3	No data	35.5	4.1
	2020	789.8	36.6	41.8	97.5		39.5	2.9
	2021	898.9	39.2	45.7	106.6		34.6	2.7
AQAMR Value (Annual)		-	-	44	30	-	40	20

The average of NO_x emissions for December 2019 is 832.1, and the average for December 2021 is 111.2 (there is no data for December 2020) (Fig. 3). It was observed that CO emission decreased only at Kadıköy station (in 2021) (Fig. 4). This situation may be an indication that the effect of traffic-related pollutants in the region has decreased. The most important reasons for the high emissions at this station can be considered as a parking lot adjacent to the station and heavy traffic around it. It can be thought that the effect of the pandemic restrictions on this station is seen in the second year, not in the first year. PM_{10} amount generally decreased with restrictions, increased in winter.

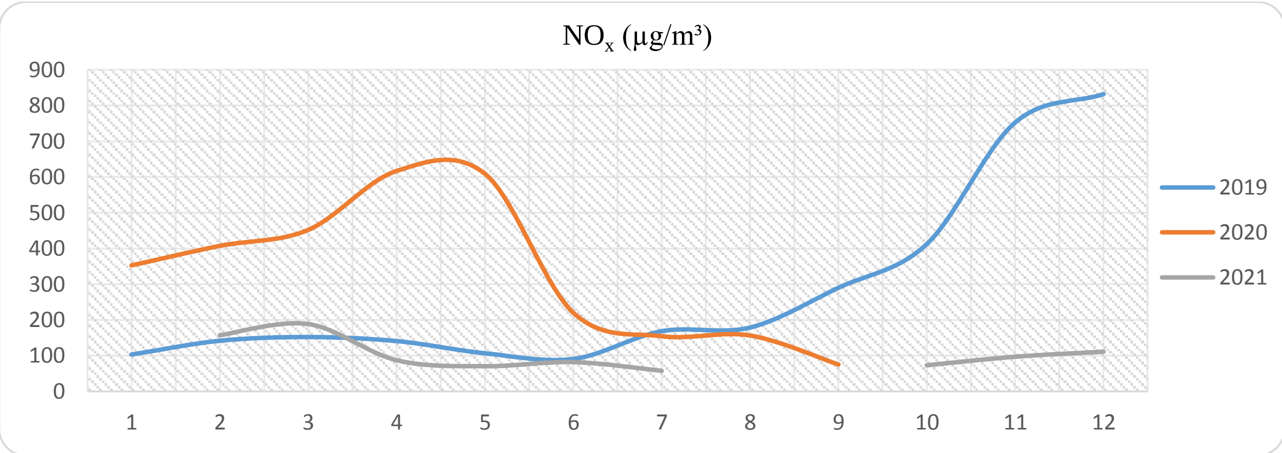

Fig. 3. Monthly average NO_x emissions by years at Kadıköy station (data for some periods have not been published).

At Aksaray station NO, NO_2, NO_x and PM_{10} parameters decreased but the most emissions were at this station, CO increased every year. This situation can be explained by the decrease in the number of vehicles in traffic due to restrictions. The highest NO_2 and PM_{10} concentrations were detected at this station. In 2021, PM_{10} data decreased to limit value. The highest NO_2 concentration was detected in August 2021 (131.7 µg/m³) and the lowest concentration in December 2021 (60.5 µg/m³). The highest PM_{10} concentration was detected in November 2019 (69.7 µg/m³) and the lowest concentration in August 2020 (31.4 µg/m³). Emissions at this station (excluding CO) generally tend to decrease from year to year due to pandemic restrictions.

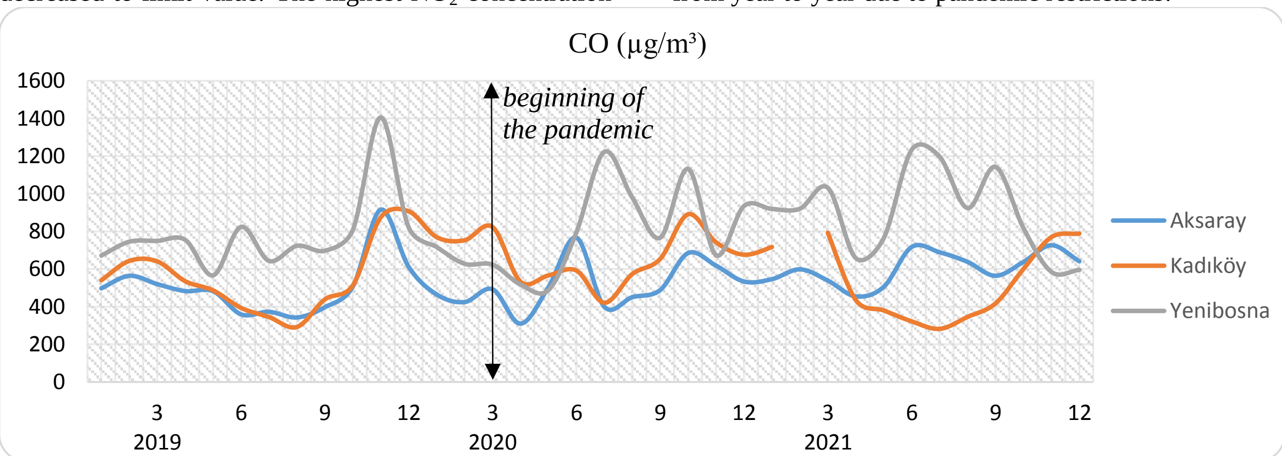

Fig. 4. Monthly average CO emissions at Aksaray, Kadıköy and Yenibosna stations in 2019, 2020, 2021 (data for some periods have not been published).

The highest CO concentration seen at Yenibosna station. Furthermore, in the three-year average, the highest CO and the lowest NO_x emissions were detected. The highest CO concentration was detected in November 2019 (1405.4 µg/m³), and the lowest concentration in May 2020 (488.1 µg/m³), which is in the beginning months of the pandemic. There was only a significantly decrease in SO_2 emission as a percentage (Fig. 5), other parameters were not affected by the restrictions or even increased. Although this station type is considered as urban by IMM, there are industrial facilities and the municipal managements around it. These facilities may be the reason why there is no reduction in emissions at this station.

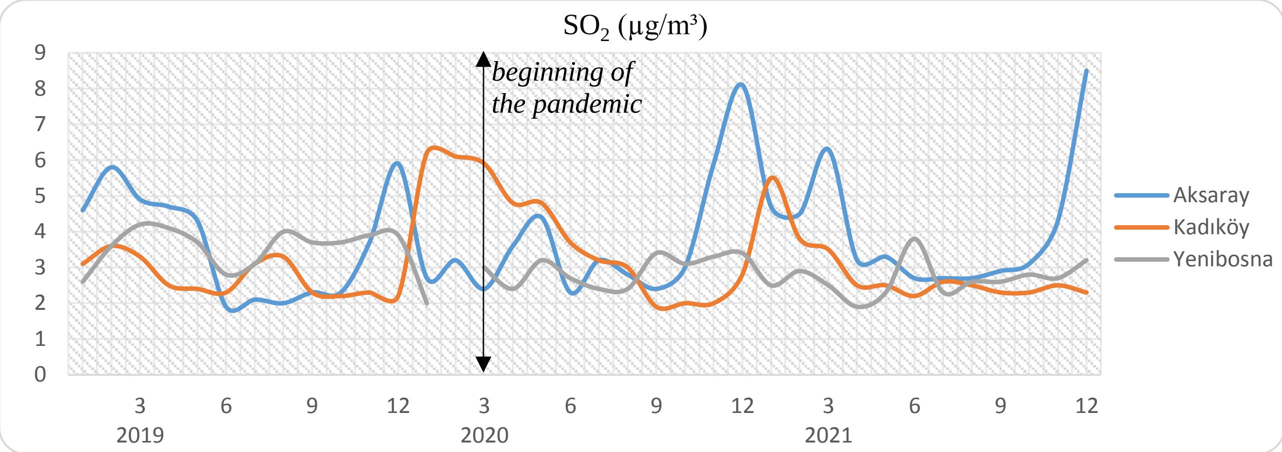

Fig. 5. Monthly average SO_2 emissions at Aksaray, Kadıköy and Yenibosna stations in 2019, 2020, 2021

Impact of Covid-19 restrictions on air pollution

- Since the restrictions were applied from time to time, increases and decreases are seen in the graphs.
- CO emission showed a decreasing trend only at Kadıköy station (in 2021), increased steadily at other stations. The highest annual average value was detected at Yenibosna station.
- Kadıköy station was the station that benefits the most from the restrictions; Except for O_3, each parameters decreased on annual average of 2021. In 2021, compared to 2020, the NO parameter decreased by approximately 80% and NO_x by 70%.
- The reasons for the detection of the highest amount of NO and NO_x at Kadıköy in 2019 and 2020 can be attributed to the car parking lot and heavy traffic.
- At Aksaray station, parameters (excluding CO) generally tend to decrease due to pandemic restrictions. Although the amounts decrease on average every year, the highest NO_2 and PM_{10} concentrations were also seen in this station.
- In 2021, the highest concentrations in NO, NO_2, NO_x, PM_{10} and SO_2 parameters were observed at Aksaray station.
- The highest CO concentration on annual average was seen at Yenibosna station. The lowest CO concentration was observed in May (in 2020) during the first period of the pandemic. SO_2 decreased very significantly as a percentage in 2021 compared to 2019.
- Emissions were generally stable at Yenibosna station, CO tended to increase. Because this station has been affected by pollution from nearby roads even during periods of restriction.
- SO_2 emission was below the AQAMR annual limit value at three stations for three years. Because natural gas is widely used for heating in Istanbul.
- In winter, air pollutant concentrations have generally increased due to heating and heavy traffic.

Acknowledgements

This study was supported by Scientific Research Projects Coordination Unit of Istanbul University (Project No: 35953). We also thank to Istanbul Metropolitan Municipality Environmental Protection and Control Department Air Quality Monitoring Center for using their samples in this study.

References

Aksu, A. (2015). Sources of Metal Pollution in the Urban Atmosphere (A Case Study: Tuzla, Istanbul). *Journal of Environmental Health Science and Engineering*, 13 (1), 1-10

Arslan, O., Akyürek, Ö. (2018). Spatial Modelling of Air Pollution from PM10 and SO2 concentrations during Winter Season in Marmara Region (2013-2014). *International Journal of Environment and Geoinformatics*, 5(1), 1-16. doi.10.30897/ijegeo.412391

Balkıs, N., Aksu, A., Okuş, E., Apak, R. (2009). Heavy metal concentrations in water, suspended matter, and sediment from Gökova Bay, Turkey. *Environmental Monitoring and Assessment*, 167, 359–370.

Bayırhan, İ., Mersin, K., Tokuşlu, A., Gazioğlu, C. (2019). Modelling of Ship Originated Exhaust Gas Emissions in the Strait of Istanbul (Bosphorus). *International Journal of Environment and Geoinformatics*, 6(3), 238-243.

Bayraç, H.N., Emrah, D. (2016). Impacts of Climate Change on Agriculture Sector in Turkey. *Journal of Eskişehir Osmangazi University,* 11(1), 23-48.

Chester, R. (1990). *Marine Geochemistry*. London: Unwin Hyman.

CREA (2020). How Air Pollution Worsens the COVID-19 Pandemic. Retrieved 05 December 2022 from https://energyandcleanair.org

DHMI (2018). Türkiye General Directorate of State Airports Authority. *2017 Airline Industry Report*. Retrieved 05 December 2022 from https://www.dhmi.gov.tr

EC (2002). Heavy Metals in Waste Final Report, European Commission, Denmark.

EEA (2020). The challenge of reducing industrial pollution. Retrieved 15 December 2022 from https://www.eea.europa.eu/signals/signals-2020/articles/the-challenge-of-reducing-industrial-pollution

EEA (2022). Europen Environment Agency. Retrieved 15 December 2022 from https://www.eea.europa.eu

EMEP (2021). Air Pollutant Emission Inventory Guidebook. European Environment Agency.

EPA (1999). Nitrogen Oxides (NO_x), Why and How They Are Controlled, Technical Bulletin. Clean Air Technology Center (MD-12).

Fang, T., Guo, H., Verma, V., Peltier, R. E. & Weber, R. J. (2015). PM2.5 water-soluble elements in the southeastern United States: automated analytical method development, spatiotemporal distributions, source apportionment, and implications for heath studies. *Atmos. Chem. Phys*. 15, 11667–11682.

Goodsite, M., E., Hertel, O., Johnson, M.S., Jørgensen, N.R. (2021). Urban Air Quality: Sources and Concentrations. In: Meyers, R.A. (Eds.), *Air Pollution Sources, Statistics and Health Effects* (193-214), New York, NY: Springer.

Hjortenkrans, D. (2008). *Road Traffic Metals–Sources and Emissions* (PhD thesis). University of Kalmar Sweden School of Pure and Applied Natural Sciences Faculty of Natural Sciences and Engineering, Kalmar, Sweeden.

Hylander, L.D., Goodsite, M.E. (2006). Environmental Costs of Mercury Pollution, *Sci Total Environ,* 368, 352-370

IMO (2015). Third IMO GHG Study 2014, Executive Summary and Final Report. London: International Maritime Organization.

Izladıoğlu, S. (2019). *Determination of Metal Content and Health Risk of Fine Particles Sourced from Traffic* (PhD thesis). Istanbul University, İstanbul.

Kesgin, U. (2006). Aircraft Emissions at Turkish Airports. *Energy*, 31 (2), 372-384.

Keshavarzi, B., Tazarvi, Z., Rajabzadeh, M.A., Najmeddin, A. (2015). Chemical Speciation, Human Health Risk Assessment and Pollution Level of Selected Heavy Metals in Urban Street Dust of Shiraz, Iran. *Atmospheric Environment*, 119, 1-10.

Kodak, G. (2022). The Role of International Maritime Traffic on PM10 Pollutant in the Strait of Istanbul (Bosphorus). *International Journal of Environment and Geoinformatics*, 9(3), 36-47, doi.10.30897/ ijegeo.977393

Krauskopf, K. (1979). Introduction to Geochemistry. New York: McGraw-Hill Book Company

Manisalidis, I., Stavropoulou, E., Stavropoulos, A., Bezirtzoglou, E. (2020). Environmental and Health Impacts of Air Pollution: A Review. *Air Pollution Environment and Health,* (8), 14.

Nusa, K., Kodak, G. (2023). Comparison of Maritime and Road Transportations in Emissions Perspective: A Review Article. *International Journal of Environment and Geoinformatics*, 10(2), 48-60. doi.10.30897/ijegeo.1254161

Onat, B., Şahin, Ü.A., Bayat, C. (2012). Assessment of Particulate Matter in the Urban Atmosphere: Size Distribution, Metal Composition and Source Characterization Using Principal Component Analysis. *Journal of Environmental Monitoring*, 14 (5), 1400-1409.

Pachauri, R.K., Meyer, L. (Eds.) (2015). The Intergovernmental Panel on Climate Change. *Climate Change 2014 Synthesis Report*, Cenevre, Switzerland: IPCC

Rainbow, P.S. (1995). Biomonitoring of Heavy Metal Availability in the Marine Environment. *Marine Pollution Bulletin*, 31, 183-192.

Şahin, Ü.A., Polat, G., Onat, B. (2016). Mass Size Distribution and Source Identification of Particulate Matter Metal Components at Four Urban Sites and A Background Site of Istanbul. *Environmental Science and Pollution Research*, 23 (11), 11085-11099.

Saltzman, E.S. (2009) Marine Aerosols. *Surface Ocean-Lower Atmosphere Processes Geophysical Research Series*, 187. American Geophysical Union. 10.1029/2008GM000769.

Sonwani, S., Maurya, V. (2019). Impact of Air Pollution on the Environment and Economy. In: P. Saxena, V. Naik (Eds.), *Air Pollution: Sources, Impacts and Controls* (113-164). Wallingford: CABI.

Starik, A.M. (2008). Gaseous and Particulate Emissions with Jet Engine Exhaust and Atmospheric Pollution. RTO. Retrieved 05 December 2022 from https://www.sto.nato.int.

Taylan, Z.S., Özkoç, H.B. (2007). Bioavailibility of Aquatic Organisms in Determination of Potential Heavy Metal Pollution. Journal of Balıkesir University, 9 (2), 17-33.

Ülker, D., Bayırhan, I., Mersin, K., Gazioğlu, C. (2021). A comparative CO2 emissions analysis and mitigation strategies of short-sea shipping and road transport in the Marmara Region. *Carbon Management*,12,1-12.

Wu, X., Nethery, R.C., Sabath, M.B., Braun, D., Dominici, F. (2020). Exposure to Air Pollution and COVID-19 Mortality in the United States: A Nationwide Cross-Sectional Study. *Science Advances,* 6(45).