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Research

ANALYSIS OF FLUORIDE POLLUTION FROM FERTILIZER INDUSTRY AND PHOSPHOGYPSUM PILES IN AGRICULTURAL AREA

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ABSTRACT

Soil fluoride pollution due to small and large scale industrial plants and phosphogypsum (PG) as a by-product of a chemical fertilizer production plant (CFPP) in Bandırma district in Turkey was studied. The soil fluoride concentrations of the samples varied in the range of 75 mg/kg to 884 mg/kg with an average of 300 mg/kg ± 195 mg/kg. The average fluoride amount in the soils around the world has been exceeded in many areas in prevailing wind directions, varying in 394 mg/kg ± 884 mg/kg, while it was lower (30 mg/kg to 380 mg/kg) in other directions. Spatial soil fluoride map showed that the fluoride has been transported up to 15 km away by atmospheric transportation under the influence of prevailing winds. High fluoride concentrations measured in PG samples varied in the range of 2320 mg/kg to 3400 mg/kg. We conclude that atmospheric transportation of PG and fluoride containing emissions of CFPP may be the cause of fluoride accumulation and the pollution in the soils located around.

INTRODUCTION

The fluoride in the atmosphere is in a cycling process among the organisms living in the air, water and soil via biochemical activities. It is formed in the water and soil naturally with the chemical degradation of the minerals containing F^-. High soil fluoride concentration affects the fertile structure of the soil by preventing decomposition of organic substances (Zhu, *et al.* 2007). The production of steel, glass, ceramic and glue, the processing of copper, nickel and phosphate, production and use of phosphate fertilizer and pesticide, and burning of coal are all industrial sources of fluoride compounds (Fordyce, 2011). Fluorine is widely regarded as the third most important air pollutant after SO_3 and O_3 (Jha, *et al.*, 2008). The fluorine compounds emitted by these industries can reach the soil by dry deposition, rainfall, through fall or decomposition of plant residues contaminated by fluorine (Gago, *et al.*, 2012). Fluoride distribution in the environment is controlled by physical-chemical parameters of emission, rain intensity and soil properties. Fluorides thus might be existed in the atmosphere in gaseous form or adsorbed to particles. The gaseous fluoride compounds pose more risks than those of the particles. The fluoride containing aerosols can be transported to long distances from the source by wind or atmospherical turbulence. The deposition speed of both gaseous hydrogen fluoride and fluoride aerosols are considered in determining how far fluorides can move in the air. Transportation of the particles those are bigger than 10 μm in diameter is defined by its deposition speed and the spread of these particles is generally limited around the area close to their source, but the smaller particles can be transported to farther distances by meteorological factors because their deposition speed is less effective (WHO, 2002).

Fluoride accumulates at top soil layer because, it is retained by the iron, aluminium hydroxide, oxide and silicate compounds in the soil (Luther, *et al.*, 1996). Fluoride doesn't easily migrate from the soil to other media. The availability of most soil fluorides by vegetation is limited because they are insoluble.

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However, low pH and/or clay increases the fluoride level of the soil, and so its uptake by the plants' roots, as well. Fluoride is kept on the surface of clay minerals or organic substances and precipitates in one or more minerals. When fluoride gets into the soil, firstly a quick exchange reaction occurs following by slower reactions like the precipitation of fluorite (CaF_2) and fluorapatite ($Ca_5(PO_4)_3F$). Most of the fluoride in soil is relatively inactive because it has no tendency to dissolve and to be exchangeable (WHO, 2002). It was declared that the optimum range of soil fluoride is 200 ppm to 300 ppm, recommended safety limit for F^- in water is 1.0 mg/l varying in 0.7 mg/l to 1.2 mg/l, acceptable maximum concentration is 1.5 mg/l in water and 0.2 mg/l to 2.0 mg/m^3 in the air by World Health Organization (WHO) (Newman, 1984). Fluoride is dangerous for the health of the living things when it reaches to underground waters by departing the soil whose its fluoride concentration is high. Taking excessive amount of fluoride chronically causes permanent, irreversible and untreatable bone and skeleton deformation (Zhu, *et al*., 2007). Fluoride damages not only human beings but also microorganisms, insects, aquatic creatures and plants. In the leaves of plants, fluoride may exists in higher concentrations (Fordyce, 2011). Fluoride, as an air pollutant, causes leaf burning even in low concentrations (Luther, *et al*., 1996). Excessive accumulation of fluoride in plants causes the leaves to spoil, fruits to get damaged and adverse effects in crops (Mishra, *et al*., 2009). The accumulation in the surface soil with subsequently high amounts of soluble F^- indicate that continued F^- deposition will keep or increase the availability for plants and soil organisms (Arnesen and Krogstad, 1998).

Ammonia (NH_3), ammonium salt aerosols, nitrous oxide and nitrogen oxides (N_2O ve NOx), flour in the form of SiF_4 and HF, sulfur oxides (SOx), fertilizer particles, acidic emissions and the radiation caused by PG is among the atmospheric pollutants spreading from fertilizer industry (UNEP, 1998). Fluoride emissions released as silicon tetrafluoride (SiF_4) or hydrogen fluoride (HF) into the air (EFMA, 2000). Air pollution due to fluoride compounds thus indirectly affects the soils by wet and dry deposition close the fertilizer plants.

Phosphogypsum, which is a byproduct of chemical fertilizer industry, stacked in deposition areas on the soil without undergoing any treatment, causes serious environmental pollution in soil, water and air due to accumulation (Bolivar, *et al*., 2009; Aoun, *et al*., 2010). Al-Attar conducted a study in Syria in which soil samples were analyzed taken from adjacent areas close to PG stacks produced by phosphate industry (Al Attar, *et al*., 2012). A recent study, investigated potential environmental contamination with heavy metals and fluorides in the vicinity of PG stockpiles. In contrast, little information is available about the pollution generated by the atmospheric dry deposition of phosphate and PG particulates in the vicinity of fertilizer plants (Kassir, *et al*., 2012). Researchers showed that the concentration of the soil fluoride as a result of the erosion of PG has increased, a significant decrease in crop yields of the agricultural products and also the bones of the bovine animals in the area have broken easily and their teeth have dappled unexpectedly. Mirlean and Roisenberg analyzed fluoride levels in rain water, groundwater and surface soil samples those taken from around the phosphatic fertilizer industry in Rio Grande, South Brazil within their survey. It's published that during the fertilizer production, fluoride containing emissions released into the air and accumulated on the surface soil due to deposition, with the highest fluoride concentrations at a distance of up to 2 km from the factory (Mirlean and Roisenberg, 2007).

In this study, fluoride concenrations in the soils of Bandırma region and fluoride levels of PG that is stacked in an open deposition area, have been analyzed and spatial soil fluoride distributions has been produced. The soil fluoride contamination as a result of the emissions released from a large-scale CFPP located in the study area, and stacked PG piles and its transportation to deposition area, was revealed by analyzing many soil and PG samples collected by considering the distance to the phosphogypsum deposition area (PGDA) and prevailing wind directions. According to spatial distribution map, the higher soil fluoride levels occured in the southwest and southeast directions, decreasing with the distance from CFPP and PGDA. In the study area, up to a 15 km distance from PGDA, soil fluoride level was still high as a consequence of atmospheric transportation, corresponding with prevailing wind directions.

MATERIALS AND METHODS

Study area

This study was carried out in and around intensely farmed Bandırma district of Balıkesir province (Fig. 1). 65% part of the province consists of arable soil. The average annual wind speed of the region is 4.13 m/s (max: 22.45 m/s), temperature is 14.4°C, soil temperature is 16.0°C and average rain fall is 702.1 mm (RTMFAL, 2005). There are different soil types that have various qualities

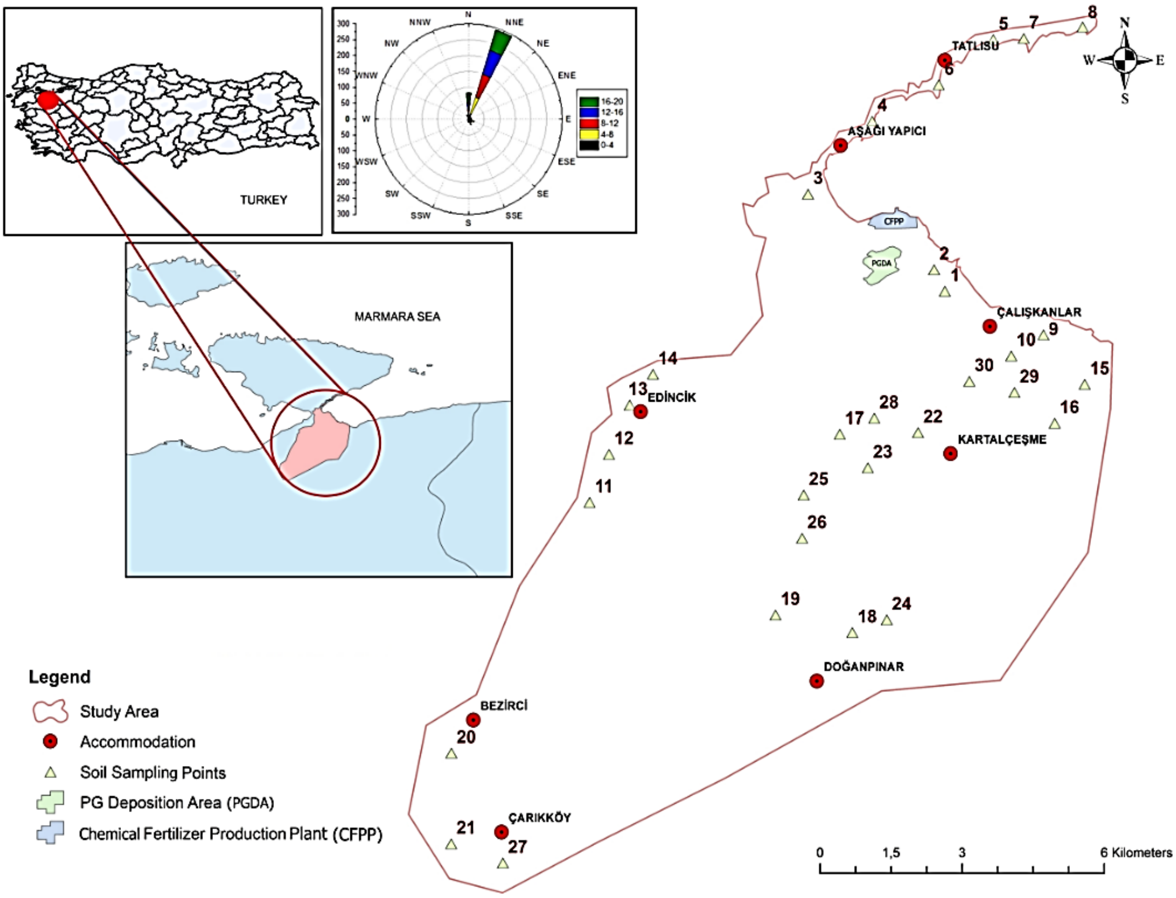

Fig. 1 Map of the sampling points and the vicinity of Bandırma.

in Bandırma. In the region, non-calcareous brown soils, vertisol soils, non-calcareous brown forest soils and brown forest soils are dominant (Report-1 1971, Report-2 1971). As it can be seen from the wind rose in Fig. 1, the prevailing winds in the research area blow in the directions of 51.18% NNE and 11.27% N, 5.90% ESE, 5.77% SSE and 4.32% NNW (Akdağ, *et al.*, 2007). The prevailing winds in the region that are in the directions of NNE and N will move polluted air to the directions of SSW and S. Considering prevailing wind directions controlling most of air movements, many soil samples were taken at increasing intervals within July, 2012. In the region, there are many different small and large scale industries such as the production of sulfuric acid and phosphoric acid used in chemical fertilizers, technical grade phosphoric acid, organic fertilizer, phosphate salt used in detergent and ceramic industry, and marble industry, boric acid and sulphuric acid production plants, and production of rice, flour, sauce, yeast and animal feed.

Soil sampling

As shown in Fig. 1, 30 soil sampling points have been determined. Representative samples have been collected from the area to be able to reflect the soil character, taking them from the 25 cm depth by cleaning the plant cover on the surface of the top layer of the soil and digging a V-shaped area. At least almost 700 g soil samples from each point, and 2 kg in total, have been taken and stored in special polyethylene cups in a dark environment. They have been dried on large filter papers under open room conditions and cleaned for 2-3 days after the stones and unwanted materials in the samples have been removed (Fig. 1).

Fluoride analysis of soil samples

Samples have been ground to homogenize them and to crumble the bigger particles in them and they have been sieved through a steel sieve in 2 mm diameter after having been dried in a drying oven set to 105°C for 24 hr. During the research, the soil samples have been kept in a dark and dry environment to protect them from external factors. To determine the total fluoride level in the soil samples, alkali fusion-selective ion electrode technique McQuaker and Gurney has been used. 6 ml 17 N NaOH is added to 0.5 g soil sample taken into a 130 ml Ni crucible, ground, dried at 105°C, sieved and heated with distilled water. Then, the leaching solution is gradually heated to 600°C for decomposition of soil samples by fusion with NaOH for 30 min at that temperature. The fused samples were dissolved

Table 1. The average soil fluoride content of the soil samples and the distance to the PGDA

Sampling point	Average soil fluoride concentration (mg/kg)	Std. Dev. (mg/kg)	Distance (km)
1	457.2	135.1	0.5
2	884	253.13	0.7
3	133.6	32.17	1.92
4	256.6	37.55	2.72
5	202.4	50.14	5.1
6	311.2	42.04	4.12
7	187.6	48.07	5.1
8	380.4	22.82	5.8
9	605.2	32.91	2.6
10	394	13.19	2.1
11	226	13.78	6.25
12	234	15.3	5.4
13	638	51.94	4.1
14	792.8	63.16	4.5
15	207.4	49.78	4.4
16	181	48.2	3.8
17	194.4	44.55	3.86
18	135.6	24.16	8.5
19	213.8	18.74	8.5
20	168.6	31.01	13.2
21	338.8	34.48	14.7
22	224.8	21.43	3.6
23	282	63.42	4.2
24	256	17.44	7.8
25	217.6	40.23	6.1
26	200.8	7.98	6.6
27	248.8	22.48	14.1
28	227.6	58.05	3.5
29	93.4	79.75	3.2
30	74.8	23.21	2.8

with deionized water and mixed with TISAB buffer solution before electropotential measurement. The extraction with water (soil:water ratio 1:1, with occasional stirring, followed with vacuum pump filter method), was applied for the determination of available F in the soil samples. In the filtrate aliquot, pH was adjusted to 8-9 with suprapure HCl buffer solution and potentiometric measurement of fluorine content by ion-selective electrode was carried out. Before measuring the total F in the sample with Thermo ORION 4-Star pH/ion analyzer, calibration of the device has been done with 0.1, 1.0 and 10 ppm F standard. After the calibration, the total F in the solution was measured in mg/l and transformed to mg/kg for each soil sample.

Determination of the fluoride concentration in phosphogypsum samples

One of the major pollutants except from the heavy metals in PG and radioactive substances is fluoride. The fluoride amount in PG may change in time depending on the origin of the phosphate rock used as a raw material in chemical fertilizer production industry and the operating conditions of the production process. Moreover, the pollutants in PG will also vary considering the content of phosphate rock used in the process obtained from different countries. The study area covers a large-scale CFPP and PGDA. Therefore, many PG samples have been also analyzed according to alkali fusion selective ion electrode technique (McQuaker and Henryk, 1977). The total fluoride amount of 18 dried PG samples collected around the PGDA has been measured with ORION-4 Star ion analyzer by using 0.1 M (1900 ppm) fluoride standard and calibrating the device with 1.9, 19 and 190 ppm standard solutions. The analysis for each of the samples has been repeated 3 times and the average of total fluoride amount (mg/kg) in PG has been calculated.

RESULTS

The average fluoride concentrations for each of the 30 soil samples have been obtained from the average of 5 repetitions of each sample. The distance of the samples to the PGDA covered an area of 30 km in diameter as shown in Fig. 1. The average total soil

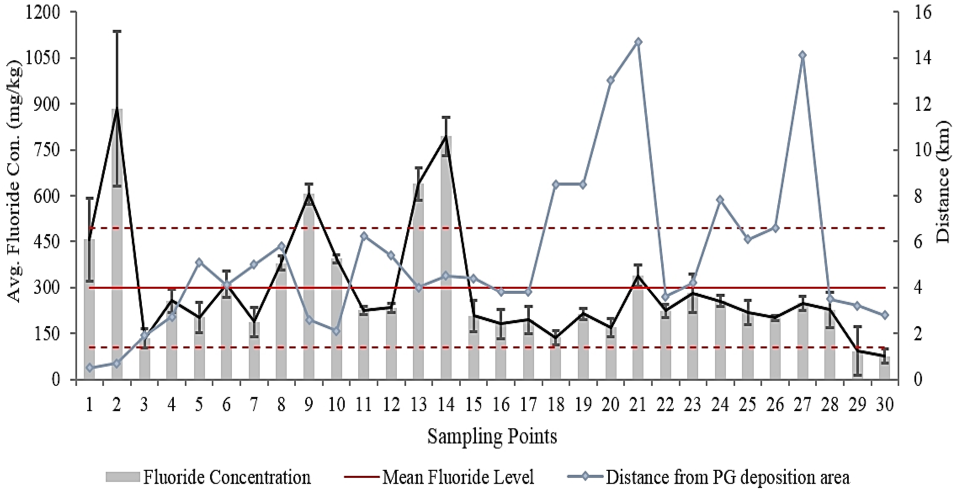

Fig. 2 The average soil fluoride concentrations with the distance to PGDA by sampling points.

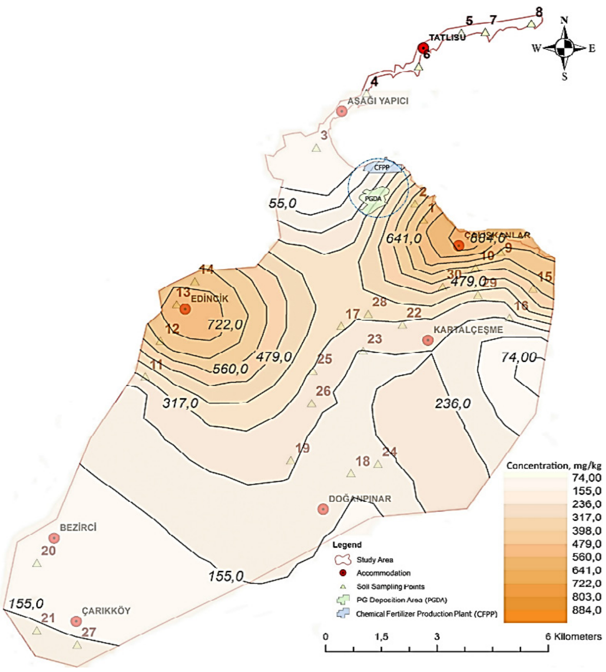

Fig. 3 Spatial fluoride concentrations in the soils over the study area.

fluoride concentrations of all samples varied between 75 mg/kg to 884 mg/kg with the overall average of 300 mg/kg ± 195 mg/kg. The average soil fluoride concentrations with their standard deviations (mg/kg) and the distance (km) of sampling point to the PGDA have been given in Table 1 which demonstrate the variations in soil fluoride levels according to the distance.

General evaluation of the soil fluoride levels varying with distance, average fluoride concentrations of the samples (black line), overall average with the standard deviations (dashed lines), a bar diagram which show standard deviations and the distances of each sampling points to the PGDA (gray line, the values arranged for right axis) were given in Fig 2. The average soil fluoride levels at many sampling points, except for points 1, 2, 9, 13 and 14, were found to be lower than the overall average value. Generally, soil fluoride concentrations decreased with the distance to PGDA, which can be explained by reducing air movements containing PG particles from PGDA due to prevailing winds and reducing deposition rate with the distance (Fig. 2).

Spatial soil fluoride distribution over the study area and sampling points are shown in Fig. 3. The spatial soil fluoride map was prepared using semi-variogram parameters through point kriging using a standard software package. Kriging is a geo-statistical gridding method to visualize irregularly spaced data by generating best linear unbiased estimates of an attribute at unmeasured site using known spatial correlation (Jha, 2012). It could be seen that fluoride

Table 2. Comparison of the total soil fluoride levels with the literature data

Location	Total Fluoride (mg/kg)
Canada*	160
Canada*	309
Newfoundland, Canada*	6-11
Newfoundland, Canada*	1138–1915
Newfoundland, Canada*	18.7–26.1
Pennsylvania, USA*	377
Illinois, USA*	271
Montana, USA*	330–1747
Ohio, USA*	353–371
Oklahoma, USA*	121 (117–124)
Oklahoma, USA*	1954
Greece*	823
Greece*	570
Greece*	339
Netherland*	39–679
Guangdong Province, China*	186–387
Bandırma, Turkey**	74.80-884

has distinct geographical distribution with loops and the peaks in the directions of SSW and SE over the study area. As a result of the accumulation of fluoride emissions released from the CFPP and particles from PGDA governed by atmospheric dispersion, high fluoride concentrations have been observed in the samples, particularly taken from close to these areas and transportation route in the prevailing wind directions. The soil fluoride concentrations at the sampling points 1 (457 mg/kg) and 2 (884 mg/kg), very close to CFPP and PGDA within a distance of 0.7 km, were among the highest soil fluoride levels obtained in the study. The fluoride concentration at the sampling point 9 (605 mg/kg) taken from the entrance of Çalışkanlar Village is higher than the level at the point 10 (394 mg/kg).

DISCUSSION

According to spatial distribution map, much lower fluoride levels were observed in the soils in NE direction close to PGDA and CFPP, generally lower than the average soil fluoride level of the world soils (320 mg/kg) (Alina and Henryk 1984), because they were in the opposite direction of prevailing winds and far from the PG transportation route. However, average soil fluoride concentration of 380 mg/kg measured at the point 8 that was about 6 km away from the PGDA was higher than the average fluoride of the world soils. The average soil fluoride concentrations of the samples from the sampling points 11, 12, 13 and 14 in Edincik area where is located on the transportation direction in the southwest have been calculated as 226, 234, 638 and 793 mg/kg, respectively. These highest soil fluoride concentrations in this area showed the accumulation by atmospheric deposition of PG particles undergoing dry or wet deposition implicitly controlled by prevailing winds. In addition, the soil fluoride concentration of 339 mg/kg obtained at the sampling point 21 in southwest direction, where was ~15 km far away from the PGDA, was also higher than the average fluoride of the world soils. The soil fluoride concentration of 249 mg/kg measured at the sampling point 26 in SSW direction, which is ~7 km away from PGDA, was higher than those of the samples taken from the outside of the transportation route in the area (Fig. 3).

As visualized in the spatial map, total soil fluoride concentrations measured in the samples that were taken from the area close to CFPP, PGDA and transportation route were much higher than the average soil fluoride amount of the world-wide soils, decreasing with the distance from PGDA and CFPP. The spatial soil fluoride map also indicated a clear regional spatial variation pattern of F with distinct loops, particularly in Edincik and Çalışkanlar zone, where are located in the prevailing winds. The threshold limit of fluoride in soil has not been declared by any department or authorities, but higher concentration of leachable fluoride in soil may be harmful to ground water as well as to plants through its uptake.

Soil fluoride contamination in the arable soils of Bandırma was discussed and the analysis results were given so far. Within this scope, in Table 2, the results obtained in this study have been compared to the soil fluoride levels published by WHO (2002) in the literature, which covers many studies on total soil fluoride conducted in many countries, considering the use of soil and the industries in the

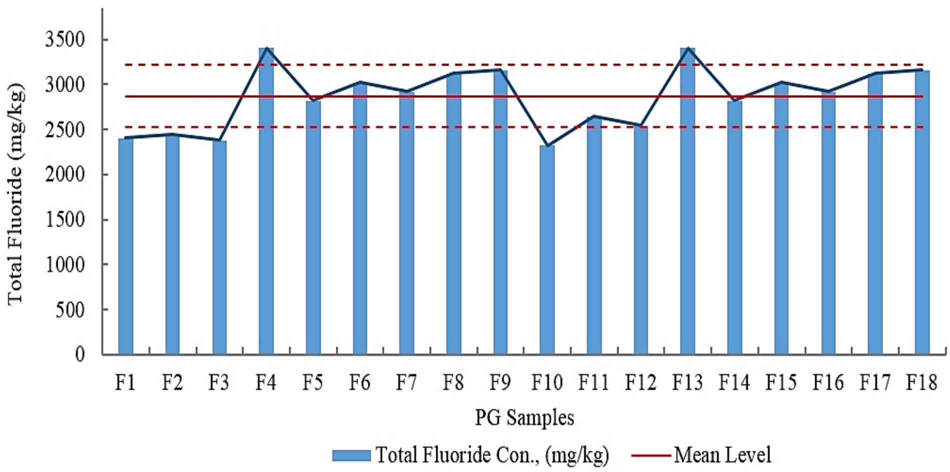

Fig. 4 Average fluoride concentrations of PG samples.

study area as possible source of the fluoride in the soil. According to data given in Table 2, the total fluoride levels obtained in this study can be occurred in the middle of the list in which fluoride levels reach up to 1954 mg/kg that is obtained in Oklahoma, USA. Nevertheless, the soil fluoride levels measured in this study were considerably high compared to the average soil fluoride of worldwide soils.

Fig. 4 a histogram of the averages of total fluoride in PG samples have been shown. The total fluoride concentrations of these samples varied between 2320 mg/kg to 3400 mg/kg with the average of 2867 mg/kg ± 345 mg/kg. In our case, high soil fluoride levels revealed the adverse effect of CFPP and PGDA on the soils around considering reasonably high fluoride concentrations measured in PG samples (Fig. 4).

Soils and phosphogypsum samples were analyzed to determine total fluoride levels in this study. The analysis results of the soils in Bandırma indicated that the soils around the region undergo a serious contamination of fluoride. We concluded that considering long-term wind statistics, the fluoride containing emissions released from a large scale CFPP along with phosphogypsum particles from PGDA have caused the accumulation of the fluoride containing airborne particles on soil by wet and dry deposition over the southern part of the region. In the fluoride analysis of the soil samples, a maximum soil fluoride level about 884 mg/kg has been measured at the sampling point close to CFPP and PGDA whereas the lowest fluoride concentration measured was 75 mg/kg. The average soil fluoride measured in the studied area generally exceeded the average fluoride concentration in worldwide soils. The field sampling considering prevailing wind directions produced a better understanding of soil pollution during the study and pointed out the accumulation of emissions from CFPP and phosphogypsum particles stacked in PGDA. The spatial distribution map indicated the higher soil fluoride levels in the southwest and southeast directions, decreasing with the distance from CFPP and PGDA. In the study area, up to a 15 km distance from PGDA, measured soil fluoride level was still high as a consequence of atmospheric transportation. Therefore, the transfer of PG particles with fluoride ingredients stacked in the open deposition area in piles close to agricultural soils must be avoided, filter systems for gaseous emissions released from CFPP must be improved and health risks of the soil pollution must be studied. In addition to soil fluroride pollution in the region, the pollution due to heavy metals, pesticides and soil radionuclides from industrial activities and cultivation practices must also be examined.

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