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Measurements of Heavy Elements and Radioactivity Concentration Levels in Types of Fertilizers and Pesticides Commonly Used in Sana'a Yemen

Ahmed Khalid Abdul-Rahim[1] * and Bassam Mohammed Mughalles Hijab[1]

[1]**Department of Physics, Faculty of Science, University of Sana'a, Sana'a, Yemen**

*Corresponding author: a.qubati@su.edu.ye, aabdulra@gmail.com

Abstract

This study aims to measure heavy metals (HMs) concentration and radioactivity concentration levels in fertilizer and pesticide samples collected from local markets in Sana'a, Yemen. Gamma spectroscopy employing a Survey Sodium Iodide NaI (Tl) RIIDEYM-G detector was used for radiation and dose assessments. As for heavy metal analyses, this study used Inductively Coupled Optical Emission Spectroscopy (ICP-OES). Thirty samples were collected from local markets in Sana'a, Yemen. Radioactivity measurements show low levels of radioactivity concentration. The average dose rates due to fertilizer and pesticide samples were 1.14 and 1.07 mSv/y, respectively. These values are nearly equal to the recommended annual radiation dose rate limit (1 mSv/y) recommended by the International Commission on Radiological Protection (ICRP). For heavy metal analysis, it was found that the average concentrations of heavy metals (HMs) (cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), nickel (Ni), lead (Pb), and zinc (Zn)) in the fertilizer samples were 1.08 mg/kg, 4.944 mg/kg, 13.8495 mg/kg, 274.371 mg/kg, 3.30446 mg/kg, 15.35686 mg/kg, and 24.4547 mg/kg, respectively. Heavy metal concentrations in fertilizer samples were mainly less than European (EU) guideline limits, with the exception of a few samples. The average concentrations of heavy metals (Cd, Cr, Cu, Fe, Ni, Pb, and Zn) in the pesticide samples were 0.8 mg/kg, 0.5784 mg/kg, 52.280 mg/kg, 73.4651 mg/kg, 2.4482 mg/kg, 3.199 mg/kg, and 1.1309 mg/kg, respectively. The heavy metal concentrations in pesticide samples were less than the corresponding values in fertilizer samples.

Article Info

Keywords:
Radioactivity, Dose Rate,Heavy Metals, Gamma Spectroscopy, Inductively Coupled Optical Emission spectroscopy (ICP-OES).

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1. INTRODUCTION

Fertilizer is the term used to describe any natural or artificial material that is added to soil or plant tissues to provide nutrients to plants. Fertilizers might be made from a range of natural and industrial sources. Fertilization is generally based on the three essential macronutrients: nitrogen (N), potassium (K), and phosphorus (P). Although fertilizers can significantly increase agricultural yields, they can also cause pollution and harm the nutrient balance of the soil [1]. During the production of fertilizers, masses of heavy metals may transfer to fertilizers, and then to soil, which finally enters the food chain. Fruits, vegetables, and crops may absorb heavy metals from contaminated soil, which leads to health problems in both humans and animals that consume them [1]. One of the biggest issues facing modern human society is environmental pollution. A significant cause of contamination in the environment is heavy metals. Although heavy metals are naturally found elements throughout the earth's crust, most environmental pollution and human exposure are the result of man-made activities such as mining and smelting, industrial production, and metal-containing compounds in household products and agriculture [2]. A heavy metal is a metal with a high atomic mass and a density greater than 5 g/cm^3. Heavy metal concentrations at high levels have various effects on plants and soil, depending on the type of heavy metal. It was reported that metals with higher permissible limits are safer. Lead (Pb) has the highest permissible limit in soil, followed by Zn and Cu, while Cd has the lowest permissible limit. Thus, the buildup of Cd in the soil is more hazardous than Cu, Zn, and Pb. However, Cu has the highest permissible limit in plants, followed by Pb, Zn, and Cd. Therefore, Cu is the least toxic in plants, followed by Pb, Zn, and Cd [3]. Because of their toxicity, heavy metals cause a range of health issues and contaminate food chains. Long-lasting exposure to heavy metals in the environment creates a significant risk to living creatures. Heavy metals can accumulate in particular organs, such as the kidneys, liver, brain, and bones can cause serious health hazards . Furthermore, heavy metal concentrations beyond threshold levels have an effect on soil microbiology and may decrease its fertility [4, 5]. Depending on the type of fertilizer and its origin, fertilizers may contain some concentrations of radioactive elements. Phosphate ores contain about 1500 Bq/kg of uranium and radium. In general, phosphate ores of sedimentary origin have high concentrations of uranium series [6]. Volcanic, phosphate, granite, and salt rocks all may contain large amounts of naturally occurring radioactive nuclei. Moreover, it was reported that chemical fertilizers used in agriculture are one cause of the rise in natural radiation [6]. Fertilizers used in agriculture typically contain amounts of naturally occurring radionuclides and residues of heavy metals. One major anthropogenic source of uranium entry into the environment is the use of such fertilizers [7]. The concentrations of the naturally occurring radionuclides in phosphate fertilizers are mostly determined by their concentrations in the phosphate rock (PR) from which they are originated [8, 9]. It was reported that phosphate fertilizers contain a range of radioactive elements and heavy metals that may pose risks to human health [9]. Pesticides are synthetic chemical compounds that are used to control pests in various fields, including agriculture [3]. Plant production requires the use of pesticides, particularly for commercially significant crop species. Studies indicate that almost one-third of all agricultural crops globally are protected by pesticides [3]. Pesticide overuse leads to their buildup in food chains, which may expose animals and humans to serious health hazards [3, 10]. Moreover, pesticide use may cause heavy metals to accumulate in agricultural soils. It was noted in studies that heavy metal buildup is a direct result of atmospheric deposition as well as overuse of fertilizers and pesticides [11]. Due to the quick growth of technology, environments and people have been exposed to a variety of toxic chemicals, particularly pesticides. There is strong evidence connecting pesticides to a host of illnesses, including hormone imbalances, cancer, asthma, and hypersensitivity. They also have the potential to cause birth defects, lower birth weight, and even death. Furthermore, pesticides may harm human endocrine glands and destroy the body's hormonal equilibrium [3]. In this study, Inductively Coupled Optical Emission spectroscopy (ICP-OES) was used in heavy metals analysis. The ICP-OES is an analytical technique used to determine how much of certain elements are in a sample. The ICP-OES principle uses the fact that atoms and ions can absorb energy to move electrons from the ground state to an excited state. The ICP-OES principle relies on those exited atoms releasing light at specific wavelengths. As an electron returns from a higher energy level to a lower energy level, it emits light of a very specific wavelength. As a result, the photons' wavelengths can be utilized to determine the elements from which they are originated. The concentration of the originating element in the sample is directly related to the total quantity of photons [12]. For radioactive analysis, gamma spectroscopy was used. Gamma spectroscopy is the qualitative analysis of gamma-ray sources' energy spectra. Gamma rays are produced by most radioactive sources and come in a range of intensities and energies. A gamma-ray energy spectrum can be detected using a spectroscopic device to detect and analyze these emissions [13]. In this study, the Gamma spectrometer NaI (Tl) Thermo Scientific RIIDEYM-G was used. The RIIDEYM-G is a portable and reliable device for accurate and timely assessment of gamma radiation and dose rate measurements [14]. The problem of heavy metal and pesticide contamination has become serious, and in order to minimize the risks as much as possible, innovative and feasible solutions are required. Human health is seriously impacted by the spread of heavy metals and pesticides throughout the food chain. Despite the consequences of such contamination, there is currently insufficient information to offer a trustworthy assessment of the true scope of the issue globally [15]. Thus, the goal of this research is to assess the contamination due to heavy metals and the radioactivity concentration levels in fertilizer and pesticide samples. The collected samples represent the most common types of fertilizers and pesticides that are often used in Yemen. Our study is a significant contribution to efforts to monitor and control the usage of such materials for the sake of the protection of people and the environment.

2. METHODOLOGY

2.1. Heavy metals analysis

Samples preparation and classification

Fifteen samples of phosphate fertilizers and fifteen pesticide samples were collected from agricultural markets and stores of the most commonly used types in Sana'a, Yemen. After collecting the samples, they were cleaned, dried, numbered, coded, and weighed. The samples were grinded, sieved, and placed in plastic containers with a capacity of 250 grams. An electric balance (FISHER EMD-3100, serial number P0108837) with a range of up to 220 g and an accuracy of 0.01 mg was used for weighing samples. Grinding samples was done using an electric powder grinder (model DE-100 grams, voltage 220V/50-60 Hz, power capacity 650 watts, accuracy 30-300 MB, and 25000 revolutions/min). The instrument used is at the laboratories of the Yemeni Organization for Standardization, Metrology, and Quality Control. The sieving process of the samples was carried out using a sieve with multiple sizes $(125\mu m, 150\mu m, 212\mu m, 500\mu m,\ 1mm)$ to obtain a homogeneous powder. Samples were digested and converted from powder to liquid using a microwave digestive system (Model Number 206, Part Number 9110637, Serial Number 0600196, 120 Volts, 50/60 Hz, 3.3 Amps, and, 400 Watts). The device used is at the General Directorate of Plant Protection, Ministry of Agriculture Laboratories, Sana'a, Yemen. Heavy metals (HMs) measurements were carried out using an Inductively Coupled Optical Emission Spectrometer (ICP-OES) (model MPX VISTA). Once more, the device used is located at the Yemen Organization for Standardization, Metrology, and Quality Control, Sana'a, Yemen. The fertilizer and pesticide sample data sheets are presented in Tables (1and2). Figures (1–6) show images of the following devices used in analysis : an electric balance, an electrical powder grinder, a multiple-range sieve, a microwave digestion system, a heavy metal measuring system (ICP - OES) device, and a Gamma spectrometer NaI (Tl) Thermo Scientific RIIDEYM-G.

HMs Measurements Procedure

1. Before measuring HMs concentrations in samples, HMs concentrations in blank samples that contain only solvent were measured to eliminate any effect of the impurities that may exist in the solution used in the digestion of the samples.
2. Before measuring samples, the ICP-OES device was calibrated to read the correct measurement readings. Calibration standard samples with specific concentrations were used to obtain the calibration curves. The calibration curve determines the relationship between the intensity of the light emitted and the concentration of the standard sample for each heavy metal. For correct measurement readings, calibration curves should be straight lines.
3. The fertilizer and pesticide samples were grinded and passed through multiple - range size sieves.
4. The homogenized powder samples were stored in volumetric plastic cups (150 g) that were tightly closed.
5. All the samples were weighed and digested. Next, 7 mm of concentrated nitric acid (HNO_3) at a concentration of 1% and 2 mm of hydroxide (H_2O_2) at a concentration of 30% were added to accelerate the process of dissolution and digestion. Samples were then covered and kept at a temperature of 550 degrees Celsius.
6. The samples were left for a period of two days (48 hours), so that the samples were converted from a powder to a liquid form by the digestion device (microwave) and the soluble acids.
7. After digestion, the samples were transferred to a 50-mL plastic tube, and then deionized water was added for dilution.
8. After the digestion process, the filtration process using filter papers was used for only four fertilizer samples.
9. Finally, an ICP-OES spectrometer was used to measure the heavy metal concentration in the sample.

2.2. Radioactive measurement analysis

Apparatus

Gamma Spectrometer Detector NaI (Tl):

The process of measuring radioactivity in samples was achieved using a NaI (Tl) gamma spectrometer with crystal dimensions' detector (2"x2") NaI (Tl), type Thermo Scientific (RIIDEYM-G), model (RIIdeye -1.65 SNS), PN (42508170-160), and S.N. (10333), a voltage of 220 volts. The measurement time taken for each sample was 180 seconds. The device used is at the Directorate of Plant Protection, Ministry of Agriculture Laboratories, Sana'a, Yemen. The instrument output shows a report containing instrument information, spectrum information, and a result description. Specifically, the report includes the gamma spectrum, measuring period time, total counts, and total dose.

Radioactivity Concentration Measurements procedure

1. Thirty study samples, 15 fertilizer samples, and 15 pesticide samples, were crushed and passed through sieves.

2. The homogenized powder form of the samples was stored in plastic containers and covered tightly.

3. The samples were kept for one month before they were measured so that they reached radiation equilibrium.

4. Finally, Gamma Spectroscopy using (RIIDEYM-G) was used to measure the radioactive concentration levels and radiation doses due to the samples.

3. RESULTS

Table 3 shows the average concentrations of heavy metals in blank samples (containing the solvent only). The HMs concentration results in blank samples were used to find the net samples' concentrations. The concentrations in blank samples were subtracted from the measured heavy metal concentrations in the collected samples to find the net results of heavy metal concentration.

Table 1. Fertilizer samples data sheet

S.C	F.T	Supplier
F1	FU +HU	Brandt, Spain
F2	SW	Ecuaf ortaf, Turkey
F3	NS	Shijazhanglen and chmicals, China
F4	Fe	Jaer, Spain
F5	NS	Syngneta , Italia
F6	MGO	Heaching, China
F7	PK	Fabbrica cooperotic aperfcs , Italia
F8	OM	Green has, China
F9	NPK	Zenagro, Spain
F10	NPK + TE	Euro chem, Belgium
F11	HU + K	Glopal traeina, China
F12	UREA	Sabic, Saudi Arabia
F13	TE + Fe	Green has, China
F14	KS	Shanxi beacon technology, China
F15	NPK +TE	Total astra Industrial, Saudi Arabia
S.C: Sample Code, FT: Fertilizer Type, FU: Fulvic acid HU: Humic acid ; Fe: Iron ; SW: Solid Waste; NS: Nitrogen Sulfate; MGO: Magnesium Oxide: OM: Organic Metter; PK: Phosphorus Potassium; NPK: Nitrogen Phosphorus Potassium; TE: Tellurium; KS: Poly Sulfide		

Table 2. Pesticide samples data sheet

S. C	pesticides Type	pesticides Group	Supplier
P1	Acetamiprid	Insecticide	Montaget, China
P2	Carbendazim	Fungicide	Sega Scieces, China
P3	Thiocyclam hydrogen	Insecticide	Hebei Guon, China
P4	Hydrochloride	Insecticide	Hebei Guon, China
P5	Imidacloprid	Insecticide	CAC Nantong, China
P6	Metalaxyl + Copper Oxychloride	Fungicide	Modern, China
P7	Famoxadone – Cymoxanil	Fungicide	Keagro Shandone, China
P8	Pyraclostrobin + boscalid (Thiumethoxam)	Fungicide	United Phosphorus, India
P9	Iprodione	Fungicide	Qingdao Xin RUN Bio CO- Ltd, China
P10	Trifloxystrobin	Fungicide	Red Sun, China
P11	Pyraclastrobin	Fungicide	Modern, China
P12	Thiophanate – Methyl	Fungicide	Keagro Shandone, China
P13	Lambda Cyhalothrin	Insecticide	United Phosphorus, India
P14	Hymexazole	Fungicide	Qingdao Xin RUN Bio CO- Ltd, China
P15	Kresoxim Methyl	Fungicide	Red Sun, China

Table 3. Average HMs concentrations in blank samples.

Heavy metal	concentration (mg/kg)
Cd	0.004081
Cr	0
Cu	0.013902
Fe	0.025798
Ni	0.009093
Pb	0
Zn	0.079235

Before measuring HMs, we calibrate the ICP-OES device. Calibration standard samples of heavy metal elements (Cd, Cr, Cu, Fe, Ni, Pb, and Zn) with concentrations of 0.1, 0.5, 1.00, and 5.00 mg/kg, respectively, were used to obtain the calibration curves. The results of the calibration curve are demonstrated in Table 4 and Figure 7. Table 5 and Figure 8 present the heavy metal concentrations in fertilizer samples. Heavy metal concentrations in pesticide samples are demonstrated in Table 6 and Figure 9. The average and maximum values of HMs concentration in collected fertilizer samples, as well as the European guideline 2019 HMs limits and Texas, U.S.A. limits, are shown in Table 8. Table 9 shows the comparison between the average and maximum values of HMs concentration in pesticide samples and fertilizer samples. Table 7 demonstrates the radioactive concentrations in counts per second (cps) in fertilizer and pesticide samples. It also demonstrates the resultant dose rates. Figures (10,11) demonstrate the gamma spectrum for the radioactive concentrations in fertilizer and pesticide samples. Tables (10,11) presents the correlation coefficients of heavy metals concentration with radiation dose for fertilizer and pesticide samples.

4. DISCUSSION

As demonstrated in Table 4 and Figure 7, the calibration curves were straight lines. Obtaining straight lines indicates that the ICP-OES device was calibrated to read the correct measurement readings. As demonstrated in Table 5 and Figure 8, the average values of HMs in the fertilizer samples are: Cd (1.08 mg/kg), Cr (4.944 mg/kg), Cu (13.8495 mg/kg), Fe (274.371 mg/kg), Ni

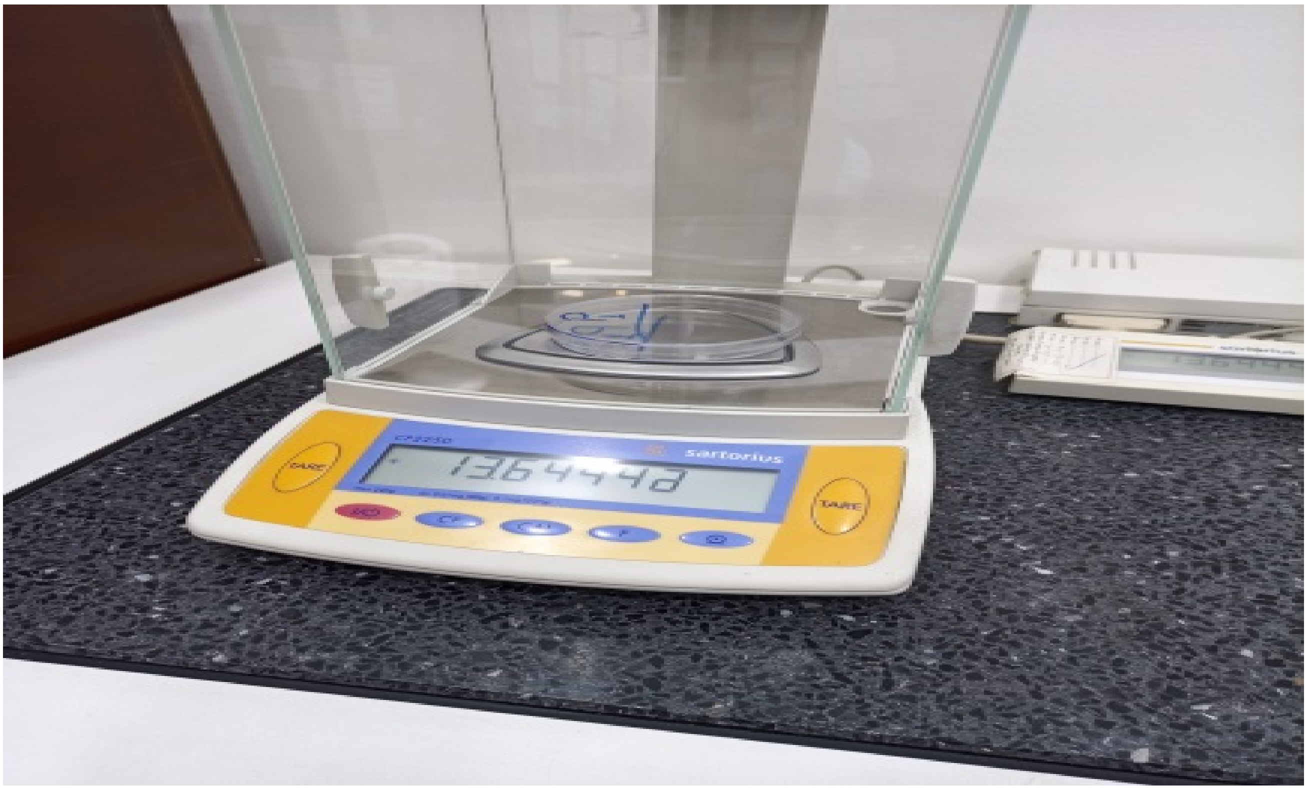


Figure 1. Electric balance : FISHER, EMD-3100, serial no. P0108837

Figure 2. Electrical powder grinder

Figure 3. precision test sieves

(3.30446 mg/kg), Pb (15.3569 mg/kg), and Zn (24.4547 mg/kg). In addition, the maximum values of HMs in fertilizer samples are: Cd (2.5 mg/kg), Cr (40.54 mg/kg), Cu (2394.3 mg/kg), Fe (5939.8 mg/kg), Ni (13.144 mg/kg),

Figure 4. Microwave digestion system

Figure 5. (ICP - OES) device for heavy metal concentration analysis.

Figure 6. Gamma spectrometer NaI (Tl) Thermo Scientific RIIDEYM-G

Table 4. Intensities of HMs of standard samples

Conc. (mg/kg)	Intensity (cps)						
	Cd	Cr	Cu	Fe	Ni	Pb	Zn
0.1	80.844	176.968	247.714	172.436	29.236	9.816	193.741
0.5	350.126	792.146	1172.53	683.021	116.624	31.705	833.283
1	705.62	1578.46	2345.6	1350.31	234.339	59.593	1660.24
5	3574.78	7807.77	11931.5	6629.23	1158.52	271.338	8226.06

Pb (184.24 mg/kg), and Zn (2460.08 mg/kg). The European guideline 2019 HMs limits of heavy metal in inorganic fertilizers are: Cd (3 mg/kg), Cr (200 mg/kg), Cu (600 mg/kg), Ni (100 mg/kg), Pb (120 mg/kg), and Zn (1500 mg/kg) [10]. In the United States, the state of Texas sets regulations to limit the concentration of heavy

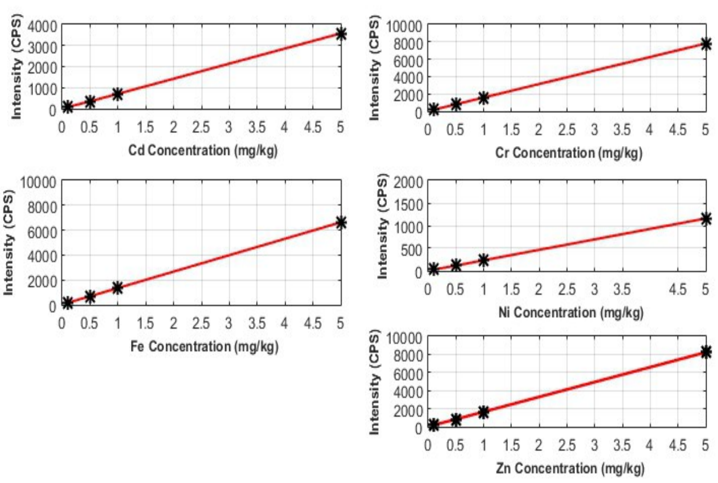


Figure 7. Calibration curves of the standard samples.

Table 5. Heavy metal concentration in phosphate fertilizer samples.

S.C.	F. T.	F. G.	Cd conc. (mg/kg)	Cr conc. (mg/kg)	Cu conc. (mg/kg)	Fe conc. (mg/kg)	Ni. conc. (mg/kg)	Pb conc. (mg/kg)	Zn conc. (mg/kg)
F1	FU +HU	SSP	0.99108	1.238	42.864	528.49	4.212	7.214	3.468
F4	Fe		0.7371	40.540	0	36.609	0	184.245	0
F3	NS	DAP	0.97128	1.456	1.4569	98.584	0	12.383	0
F5	NS		0.998	0.499	1.746	69.111	0	12.724	0
F6	MG O	MAP	0.9828	0	2.948	160.687	0	0	0
F8	OM		2.5	0	15.75	459.25	8.25	0	8
F12	Urea	UREA	1.699	0	10.436	32.523	0	0	12.135
F2	SW	NPK	0.74331	1.2388	17.839	5939.8	0	0	7.928
F7	PK		0.98036	14.950	21.322	979.624	7.842	4.901	106.61
F9	NPK		0.48332	3.382	24.407	102.222	0	0	192.36
F10	NPK+TE TE		1.2195	1.707	3.414	58.779	0	2.439	3.414
F11	HU + K		1.988	0	19.383	568.568	12.673	0	4.97
F13	TE + FE		0.49236	3.938	2394.3	2479.77	3.446	1.723	2460.08
F14	KS		0.995	2.985	29.352	225.118	0	3.98	3.482
F15	NPK + TE		0.49602	2.232	2.976	247.265	13.144	0.744	0
Maximum			2.5	40.540	2394.3	5939.8	13.144	184.24	2460.08
Average			1.08514	4.944	13.8495	274.371	3.5405	15.356	24.4547

The average values were calculated after excluding the outliers. The excluded values are : Cu in sample 13, Fe in samples 2 and 11, Zn in sample 13

S.C.: Sample Code, F.T.: Fertilizer Type, F.G.: Fertilizer Group; SSP: single super phosphate, DAP: Di-ammonium Phosphate, MAP mono ammonium phosphate FU: Fulvic acid HU: Humic acid ; Fe: Iron ; SW: Solid Waste; NS: Nitrogen Sulfate; MGO: Magnesium Oxide: OM: Organic Metter; PK: Phosphorus Potassium; NPK: Nitrogen Phosphorus Potassium; TE: Tellurium; KS: Poly Sulfide

metals. The regulation states that the maximum permissible concentrations of heavy metals in phosphate micronutrient fertilizers are: Cd (39 mg/kg), Ni (420 mg/kg), Pb (300 mg/kg), and Zn (2800 mg/kg) [16]. In addition, the global average concentration of HMs in soils varies for Cd (0.00–0.06 mg/kg), Pb (10–150 mg/kg), and Zn (10–300 mg/kg) [17]. With the exception of samples 4, and 13, the heavy metal concentrations in fertilizer

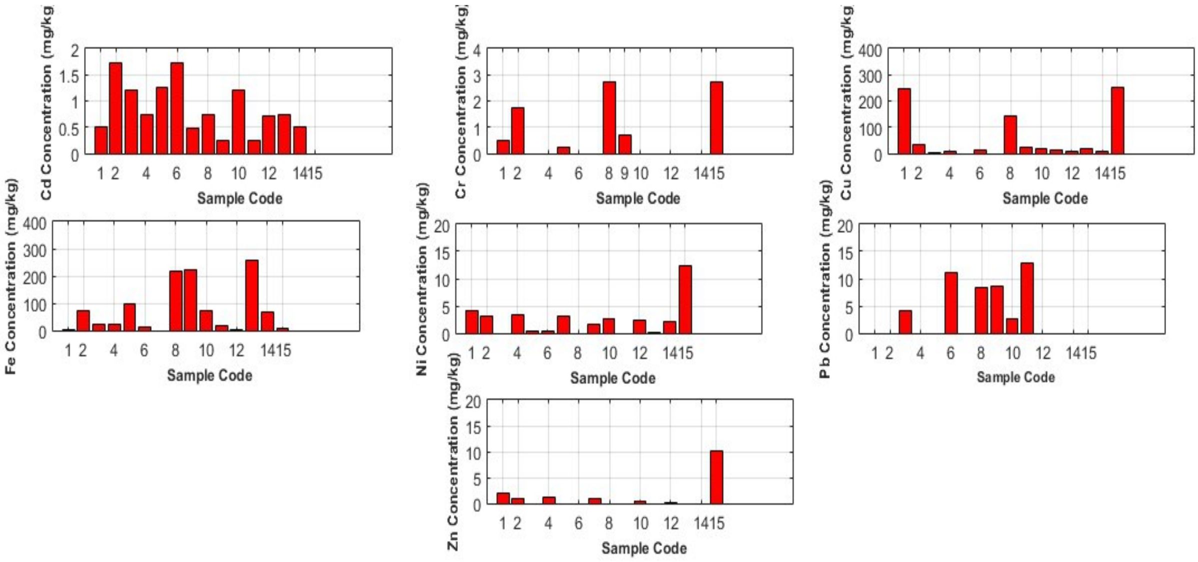


Figure 8. Heavy metal concentrations in fertilizer samples

Table 6. Heavy metal concentrations in pesticide samples

S.C.	P.T.	P.G.	Cd conc. (mg/kg)	Cr conc. (mg/kg)	Cu conc. (mg/kg)	Fe conc. (mg/kg)	Ni conc. (mg/kg)	Pb conc. (mg/kg)	Zn conc. (mg/kg)
1	Acetamiprid	Ins.	0.495	0.495	248.47	0.991	4.212	0	1.982
13	Lambda Gyhlothrin		0.738	0	16.494	258.48	0.246	0	0
3	Thiocyclam Hydrogen		1.214	0	2.428	21.125	0	4.128	0
4	Cartap Hydrochloride		0.737	0	7.862	24.324	3.439	0	1.228
5	Imidacloprid		1.247	0.249	0	97.305	0.499	0	0
6	Metalaxyl + Copper Oxychloride	Fung.	1.719	0	11.056	14.250	0.491	11.056	0
7	Famoxadone – Cymoxanil		0.490	0	0	0	3.186	0	0.980
8	Pyraclostrobin + boscaid (Thiumethoxam)		0.75	2.75	142.5	219	0	8.5	0
9	Iprodione		0.241	0.724	25.373	224.50	1.691	8.699	0
10	Trifloxystrobin		1.219	0	16.098	73.413	2.682	2.682	0.487
11	Pyraclasonn		0.248	0	14.91	17.64	0	12.92	0
12	Thiophanate – Methyl		0.72	0	10.193	2.184	2.427	0	0. 242
2	Carbendazim		1.730	1.730	32.129	71.179	3.212	0	0.988
14	Hymexazole		0.497	0	5.97	69.65	2.238	0	0.000
15	Kresoxim – Methyl		0	2.728	250.73	7.936	12.40	0	10.168
Maximum			1.730	2.75	250.73	258.48	12.40	12.92	10.168
Average			0.803	0.5784	52.2809	73.4651	2.4482	3.199	1.130929

S.C.: sample code, P.T.: Pesticide Type, P.G.: Pesticide Group, Ins.: Inseticide, Fung.:Fungicide, P.G: Pesticide Group

samples were less than EU guideline limits. Specifically, it was found that the Pb concentration in sample 4 (184.24 mg/kg) exceeds the EU guideline limit (120 mg/kg). The Cu concentration in sample 13 (2394.3 mg/kg) exceeds the EU guideline limit (600 mg/kg). The Zn concentration in sample 13 (2460 mg/kg) exceeds

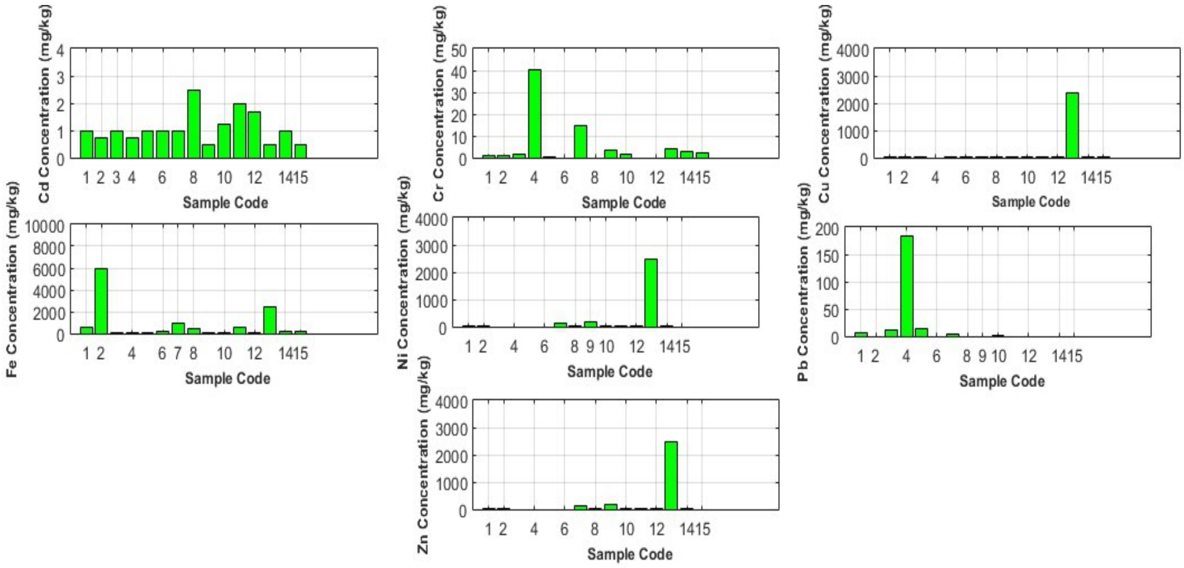


Figure 9. Heavy metals concentration in pesticide samples

the EU guideline limit for Zn (1500 mg/kg). However, results for HMs concentrations (Cd, Pb, and Zn) in all fertilizer samples were less than the Texas U.S.A. regulations [16]. So, it was found that there were only two contaminated samples (4 and 13) according to EU guideline limits. Sample 4, which belongs to the SSP fertilizer group, has a high concentration of Pb (184.24 mg/kg), and sample 13, which belongs to the PNK fertilizer group, has a high concentration of Cu (2394.3 mg/kg) and Zn (2460 m/kg). Moreover, it was noted that the average and maximum concentrations of iron (Fe) were 247.265 mg/kg and 5939.8 mg/kg, respectively. We were not able to compare Fe concentrations with global limits since no reported limit values were found in the available literature. Furthermore, Cd, Pb, and Zn concentrations in most fertilizer samples exceed the global values of these HMs in soil [17]. Additionally, no reported limits were found in the available literature on heavy metal concentrations for pesticides. However, comparing the average values and maximum values of the concentrations of HVs in pesticide samples and in fertilizer samples, we can see that the average and maximum concentrations in pesticide samples were less than the corresponding values in fertilizer samples for all measured heavy elements. Table 7 and Figures (10 and 11) show low radioactivity concentrations in fertilizer and pesticide samples. The Gamma spectra for samples show K-40 peaks at energy 1462 Kev. In addition, it was found that fertilizer samples 2 and 14 contain uranium-233 with dose rates of 0.000352 mrem/h, and 0.000351756 mrem/h, respectively. The existence of uranium-233 could be due to contamination during production or to the raw material that was used to produce that type of fertilizer. Finally, the average dose rate due to fertilizer samples was 0.012979 mrem/h (1.14 mSv/y), and the average dose rate due to pesticide samples was 0.012267 mrem/h (1.07 mSv/y). These values are slightly close to the recommended annual radiation dose rate limit of 1 mSv/y recommended by the ICRP [18].

Statistical analysis

For correlation analysis, SPSS Spearman's rank statistics method was used. For fertilizer samples, correlation coefficients (r) of heavy metals (Cd, Cr, Cu, Fe, Ni, Pb, Fe, and Zn) with radiation doses equal - 0.61, 0.622, 0.132, -0.264, -0.383, 0.476, and 0.098, respectively, with significant levels (P-values) of 0.567, 0.013, 0.639, 0.341, 0.159, 0.073, and 0.728, respectively. Analysis shows that for fertilizer samples, a positive significant medium correlation was observed between concentration of Cr and radiation dose at 0.01 level. No correlation was observed between concentrations of HMs Cu, Fe, Ni, and Zn with radiation doses. Furthermore, for the elements Cd and Ni, insignificant correlations with radiation dose were observed.

For pesticide samples, correlation coefficients (r) of heavy meals (Cd, Cr, Cu, Fe, Ni, Pb, and Zn) with radiation doses equal 0.013, 0.137, 0.268, 0.231, - 0.305, 0.655, and -0.249, respectively, with significant levels (P-values) of 0.965, 0.626, 0.334, 0.408, 0.269, 0.008, and 0.392, respectively. For pesticide samples, a positive significant medium correlation was observed between lead and radiation dose. No correlation was observed between HMs (Cd, Cr, Cu, Fe) concentrations with radiation doses. Furthermore, an insignificant medium correlation between Ni and radiation dose was observed.

5. CONCLUSION

In this study, we measured heavy metal (cadmium, chromium, copper, iron, nickel, lead, and zinc) concentrations and radioactivity concentration levels in fertilizer

Table 7. The radioactive concentrations in (cps) in fertilizer and pesticide samples, and the resultant dose rates

S.C.	Radio. Con. (cps)	Dose rate (mrem/h)	S.C.	Radio. Con. (cps)	Dose rate (mrem/h)
F1	112.497	0.01287	P1	110.865	0.01233
F2	118.426	0.01556	P2	110.772	0.012256
F3	112.8	0.01297	P3	110.622	0.012184
F4	107.462	0.01238	P4	111.187	0.012249
F5	107.142	0.011795	P5	111.669	0.012185
F6	108.709	0.012049	P6	111.338	0.01243
F7	112.8	0.012867	P7	111.349	0.012269
F8	111.379	0.012496	P8	112.971	0.012499
F9	112.485	0.013166	P9	114.958	0.01274
F10	112.107	0.0131157	P100	112.154	0.01233
F11	112.8	0.0129734	P11	111.384	0.012298
F12	111.226	0.012381	P12	110.05	0.012149
F13	110.018	0.012315	P13	110.238	0.012152
F14	118.426	0.015561	P14	109.359	0.011924
F15	110.865	0.012191	P15	109.636	0.012016
Ave.	111.94	0.012979		111.2368	0.012267
S.C: Sample Code; Radio. Con. : Radio concentration ; Ave: Average					

Table 8. Comparison between average and maximum values of HM concentrations (mg/kg) in current study fertilizer samples and European and Texas U.S.A limits

Heavy metal concentration (mg/kg)								
		Cd	Cr	Cu	Fe	Ni	Pb	Zn
Av. In F.S.	F. S	1.08	4.94	13.8495	274.371	3.30446	15.3569	24.4547
Max in F.S.	F.S	2.5	40.54	2394.3	5939.8	13.144	184.24	2460.08
HMs limits	EU	3	200	600	-	100	120	1500
HMs limits	Texas USA	39	-	-	-	420	300	2800
Av. : Average values, Max: maximum, F.S : current study fertilizer samples, EU: European guideline,								

Table 9. Comparison between average and maximum values of HM concentrations (mg/kg) in pesticide samples and fertilizer samples

Heavy metal concentration (mg/kg)								
Heavy Element		Cd	Cr	Cu	Fe	Ni	Pb	Zn
Av.	P.S.	0.80	0.578	52.280	73.465	2.4482	3.199	1.1309
Av.	F. S.	1.08	4.944	13.8495	274.371	3.30446	15.3569	24.4547
Max.	P.S.	1.730	2.75	250.73	258.48	12.40	12.92	10.168
Max	F.S.	2.5	40.54	2394.3	5939.8	13.144	184.24	2460.08
Av. : Average, Max. : Maximum, P.S.: Pesticide Samples, F.S: Fertilizer Samples								

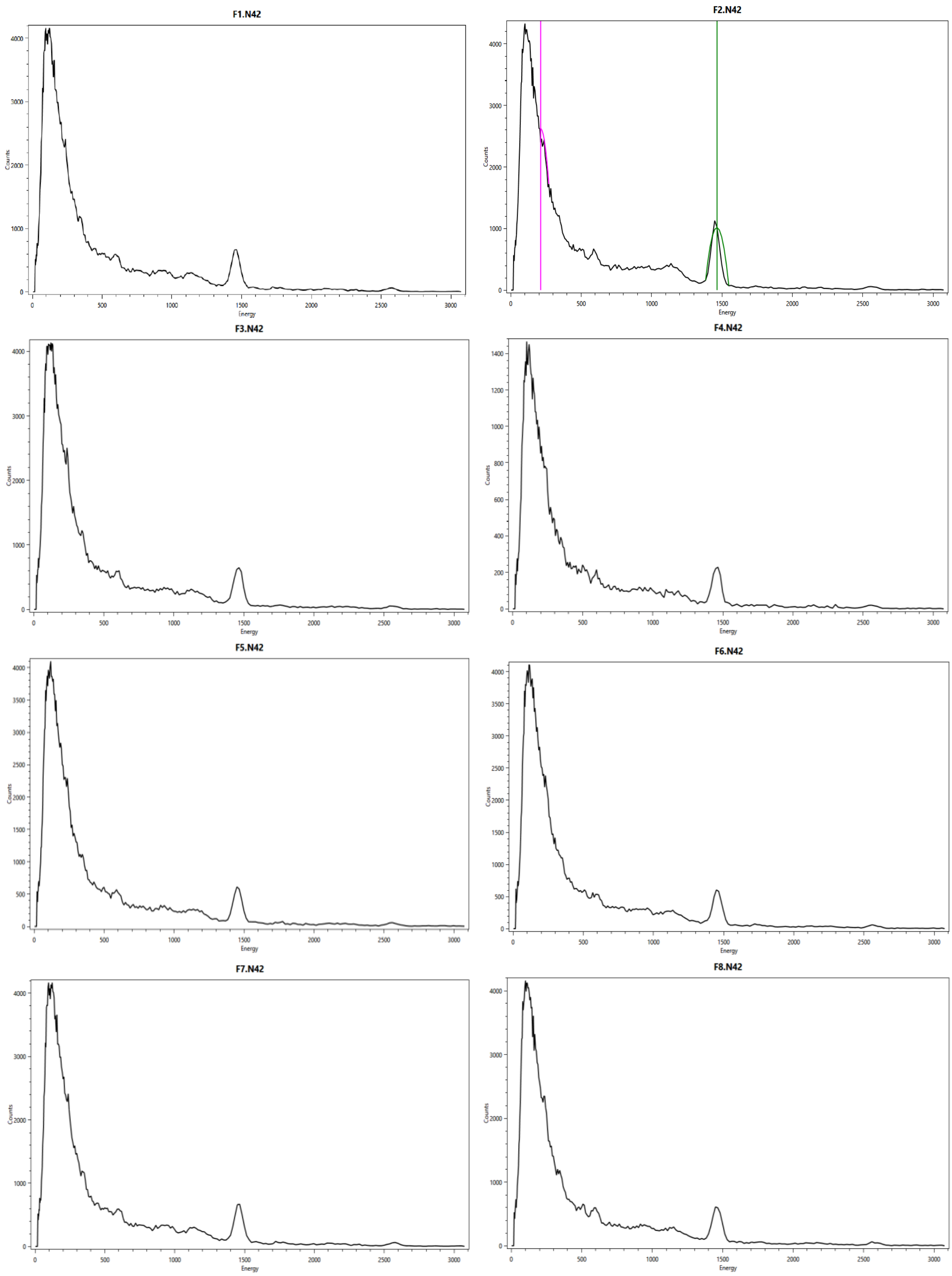
Table 10. Spearman correlation coefficients of heavy metals concentration with radiation dose for fertilizer samples

	Cd	Cr	Cu	Fe	Ni	Pb	Zn
Dose							
r	-o.61	0.622	0.132	-0.264	-0.383	0.476	0.098
P-value	0.567	0.013	0.639	0.341	0.159	0.073	0.728

Table 11. Spearman correlation coefficients of heavy metals concentration with radiation dose for pesticide samples

	Cd	Cr	Cu	Fe	Ni	Pb	Zn
Dose							
r	0.013	0.137	0.268	0.231	- 0.305	0.655	-0.249
P-value	0.965	0.626	0.334	0.408	0.269	0.008	0.392

and pesticide samples. Inductively Coupled Optical Emission Spectroscopy (ICP-OES) and Gamma Spectroscopy



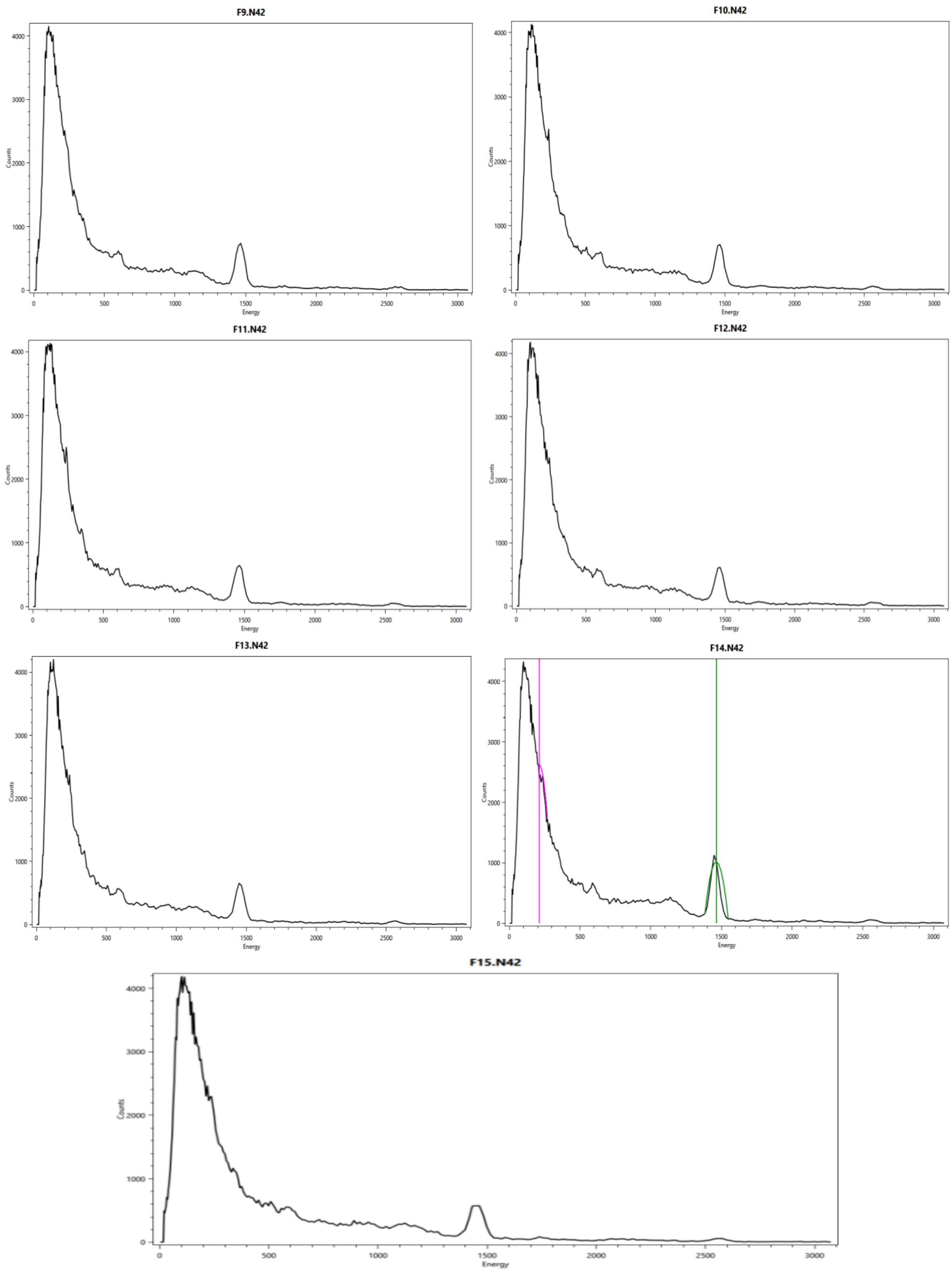


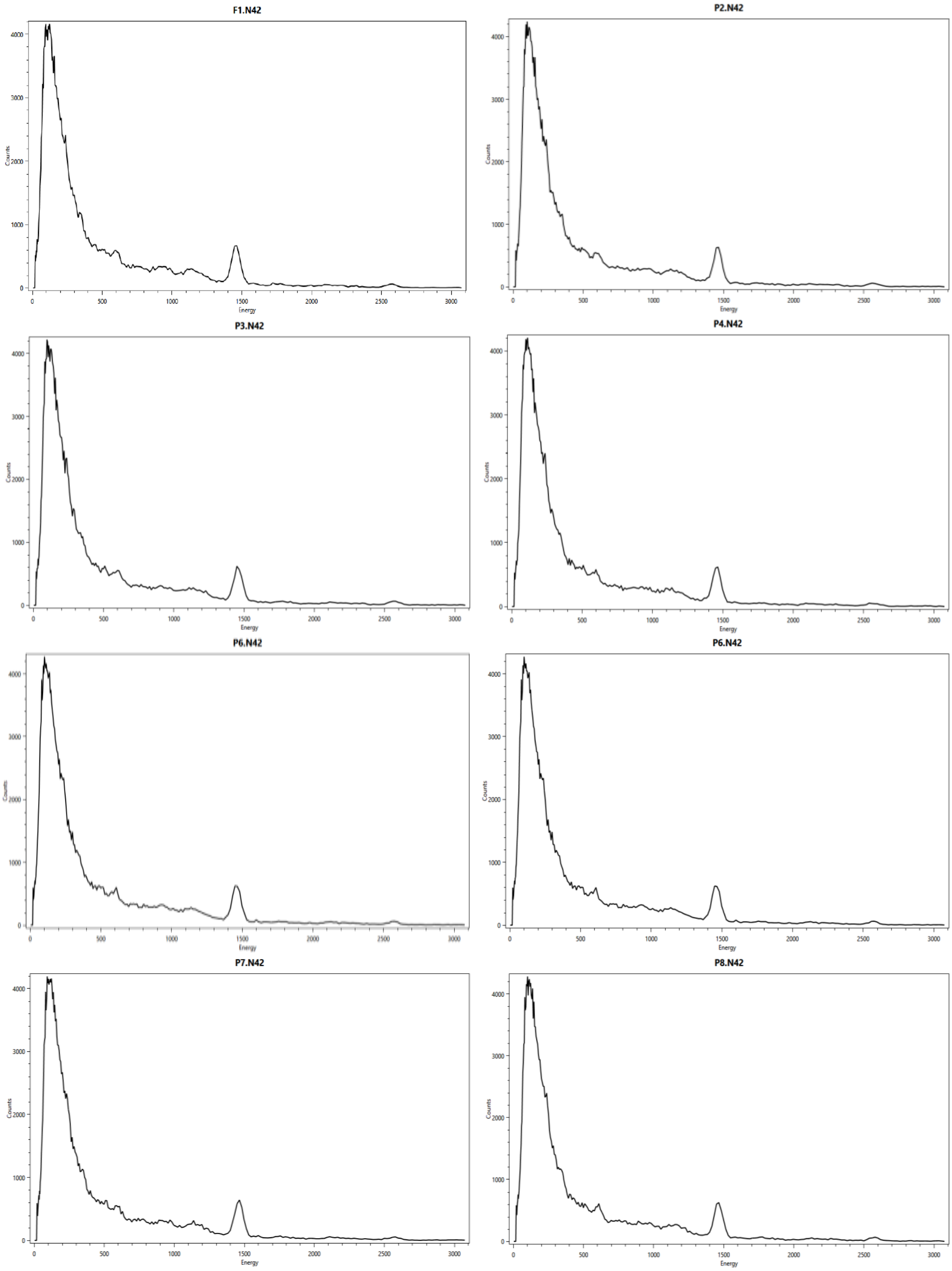
Figure 10. Gamma spectrum of fertilizer samples 1 - 15

using a survey Sodium Iodide NaI (TI) RIIDEYM-G detector were used to measure heavy metals and radioactive concentration levels, respectively.

Results show that heavy metal concentrations in fertilizer samples were less than the European guideline limits, with the exception of two samples. It was noted that contaminated samples belong to the PNK and SSP fertilizer groups. Moreover, the heavy metal concentrations in pesticide samples were less than the corresponding values in fertilizer samples. In addition, it was found that fertilizer and pesticide samples contain very low radioactive concentration levels, and the average dose rates due to fertilizer and pesticide samples individually were nearly equal to the recommended annual radiation dose rate limit (1 mSv/y) stated by the ICRP.

Statistical correlation analysis of data revealed that there exists a positive significant medium correlation between concentration of Cr and radiation dose for fertilizer samples. For pesticide samples, a positive significant medium correlation was observed between lead and radiation dose.

Finally, we concluded that the fertilizer types that are commonly used in Sana'a, Yemen have acceptable concentrations of heavy metals, with the exception of two types. Specifically, it was found that the Pb concentration in fertilizer sample F4 exceeds the EU guideline limit. Cu and Zn concentrations in fertilizer sample F13 exceed the EU guideline limit. Therefore, the results show that two types of imported fertilizers are contaminated with some heavy metal elements. Exceeding the limits in the mentioned samples suggests that research and monitoring efforts should be continued to ensure that all types of



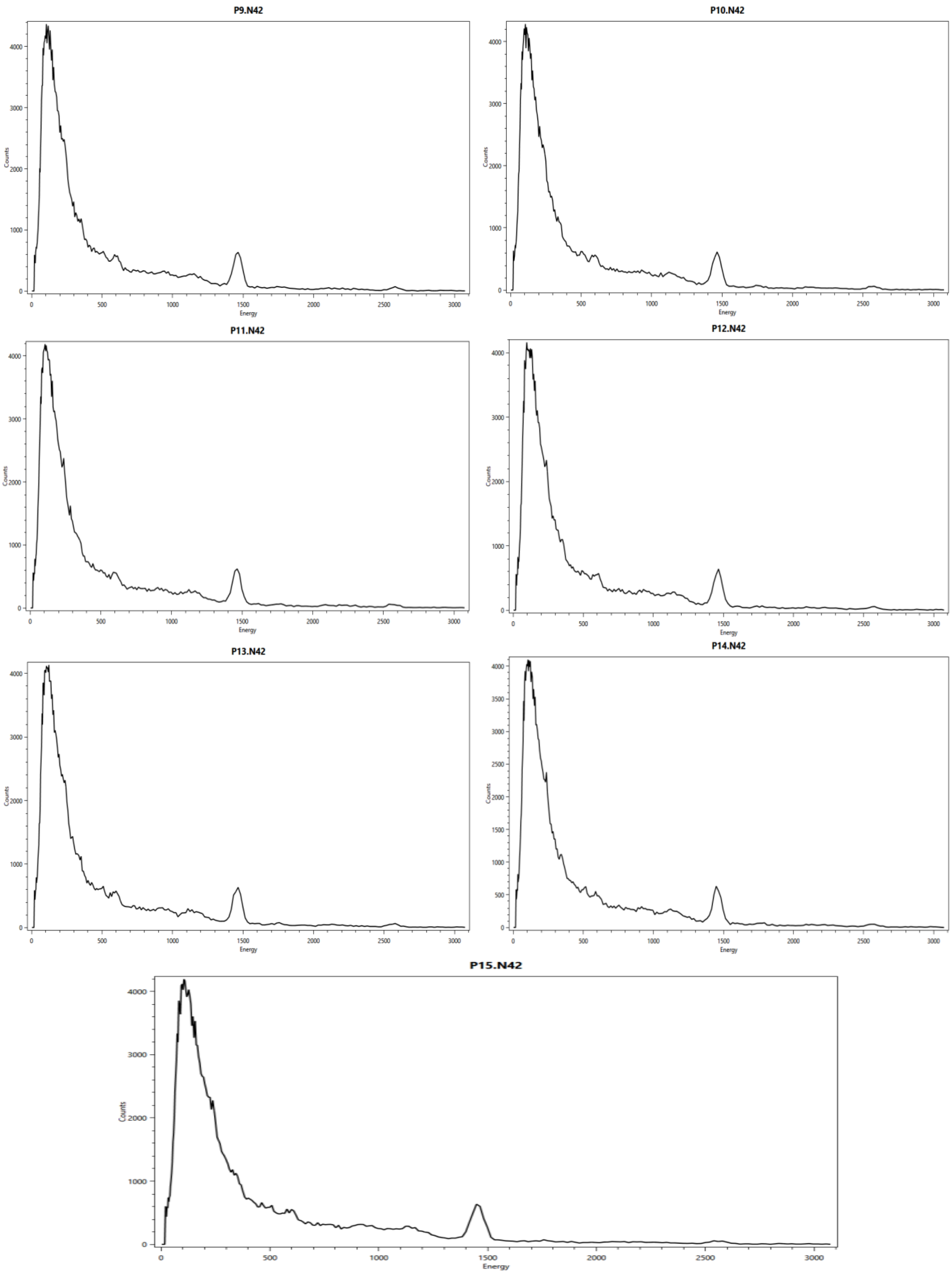


Figure 11. Gamma spectrum of pesticide samples

fertilizers and pesticides are not contaminated and safe.

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