A Thesis Presented to

The Faculty of Alfred University

A Qualitative Analysis and Quantitative Methodology Used to Examine Crumb Rubber Pellets from Artificial Turf Fields for the Presence of Lead

by

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Abstract:

University of Washington's Associate Women's Head Soccer Coach, Amy Griffin, has created a list of 268 athletes that have been diagnosed with cancer after playing on an artificial turf field at some point in their athletic career. Griffin believes that crumb rubber pellets that are a component of the artificial turf fields could be the reason behind why so many of her past athletes have developed cancer. Numerous investigations have been published in the literature that discuss possible components of crumb rubber pellets that could be carcinogenic to humans. Heavy metals are one of the groups of substances that have been researched in past studies. The purpose of this investigation was to quantitatively and qualitatively analyze the amount of lead present in three different samples of crumb rubber pellets collected from various colleges' artificial turf fields. The three samples were collected from Alfred University's, Alfred State College's, and Brockport State College's athletic fields. The samples were qualitatively analyzed by means of scanning electron microscopy, and quantitatively analyzed by means of flame atomic absorption spectroscopy. Both the quantitative analysis of the Alfred University sample and the qualitative analyses of all three of the three school's samples showed there to be no lead present within the crumb rubber pellets. Further investigations are warranted, as only a small sample of pellets from the artificial turf fields were analyzed, and the samples did indicate that there were trace amounts of other heavy metals present.

1. Introduction:

Associate Head Coach for the University of Washington's women's soccer team, Amy Griffin, has coached women's soccer players for over 24 years (Tuhus, 2019). In this time, she has worked through various challenges and obstacles with each one of her athletes (Tuhus, 2019). As any successful college coach should, Griffin has offered help to these athletes in so many different aspects of their lives, whether it be encouraging them to seek academic help, easing the transition that comes with trying out a new position, or even helping the athlete battle the grueling process of recovering from a sports injury. Although Griffin's coaching experience seems relatively normal, there is one aspect of her life that definitely stands out in comparison to other collegiate coach's experiences. Instead of having to help athletes through the processes of rehabilitating a strained hamstring, torn ACL, or other relatively common athletic injury, Griffin has had to support several of her past athletes in their battles against cancer.

Griffin's first experience with cancer occurred in 2009, when she received a call that one of her previous athletes was in the hospital, and had just received a Non-Hodgkin's Lymphoma diagnosis, which is a relatively rare type of blood cancer (Tuhus, 2019). Griffin reported that in her first 15 years of coaching she had never known any of her previous athletes to have had cancer (Public Employees for Environmental Responsibility [PEER], 2021). This changed very quickly for Griffin in 2009. When visiting the athlete that was diagnosed with Non-Hodgkin's Lymphoma in the hospital, Griffin heard news that another one of her athletes had also been diagnosed with the same exact condition (PEER, 2021). Interestingly, both of the athletes had played as goalkeepers in their past soccer careers (PEER, 2021). The goalkeepers looked to the other for support and began questioning what environmental factors were present in each of their lives that could have possibly been responsible for causing the development of the cancer

(PEER, 2021). The girls and Griffin came to the realization that the crumb rubber pellets that are a component of the artificial turf fields that they had played on in their soccer career may be the culprit. The goalkeepers shared with Amy that they had a lot of contact with these tiny black pellets in their soccer careers, and it was not uncommon for them to find the pellets in open wounds, swallow the pellets, inhale the pellets, or even get the pellets stuck in their eyes (PEER, 2021).

Griffin decided to look into the crumb rubber turf pellets a little bit further and investigate the potential toxicity of the pellets, which are a large component of artificial turf fields (Tuhus, 2019). Several types of artificial turf fields (like the ones that Griffin's athletes played on) use crumb rubber as an infill material that is deposited between blades of artificial grass attached to a backing material (Lim, 2008). Early on in her investigation, she discovered that these crumb rubber turf pellets are created by grinding up old tires (Tuhus, 2019). Before the tires are ground up into these small pellets- which typically are about one-sixteenth of an inch to one quarter of an inch in diameter- the tires must go through a process in which the tire components and steel are removed. (Lim, 2008). After this process the tires are ground up, and then deposited on to the field at a rate of 2-3 lbs/ft^2 of field surface (Lim, 2008).

Within a couple of months, Amy had made some very profound discoveries. She learned about an organization called the Environmental Protection Agency (EPA), that is in charge of keeping humans safe from environmental factors (Tuhus, 2019). This agency claims tires are toxic, and a tax should be placed on tires so there is money available to collect old tires, and properly dispose of the tires in a way that is not harmful to the environment. The EPA has placed a tax on tires and created an agreement in which they are held responsible to collect all old tires so they can be properly disposed of (Tuhus, 2019). It is illegal to throw away, burn, or bury old

tires, so individuals that are purchasing a tire must pay an additional fee that will go to the EPA (Tuhus, 2019). Griffin discovered the EPA had nowhere to dispose of the tires they had collected, and this agency ended up sponsoring the growth of crumb rubber to solve their tire overflow problem (Tuhus, 2019). Griffin was horrified to learn the government actually subsidizes communities that use crumb rubber fields (Tuhus, 2019). She found out California had received 6.1 million dollars from the government in 2015 to help facilitate a revitalization of various parks and recreational facilities by installing additional crumb rubber turf fields (Tuhus, 2009).

Griffin also discovered the existence of the Resource Conservation Recovery Act (RCRA), which is an act responsible for regulating the amount of waste that humans put into the environment (Tuhus, 2009). There is a law from the RCRA that makes it illegal to throw a tire away because it is toxic waste. Although disposing of a complete tire is illegal, disposing of these tires in tiny shredded up pieces is not illegal, because they are technically no longer a tire (Tuhus, 2009). The New York State Department of Environmental Conservation claims that in 2004, about 22.5 percent of NYS generated scrap tires were used to produce ground rubber (Lim, 2008). Under the Environmental Conservation Law (ECL), crumb rubber is not considered a solid waste product, and therefore is not regulated as a solid waste under the DEC solid waste regulations or the ECL (Lim, 2008).

This realization caused Amy Griffin to become hypervigilant when it came to the possible relationship between athletes being diagnosed with cancer and crumb rubber pellets used as infill on synthetic turf fields (Tuhus, 2009). Because there is no current law in place that regulates the chemical constituents of crumb rubber infill, Griffin became concerned that her athletes had been playing on artificial turf fields that contained toxic, possibly carcinogenic chemicals. She started

performing her own research on the potential toxicity of crumb rubber infill made from old tires and created a list of athletes that had been diagnosed with cancer who had also played on an artificial turf field at some point in their lives. The two athletes Amy met in the hospital were first and second on her list, which was originally created in 2009 (Tuhus, 2009). In 2020, Amy claimed her list of athletes contained two hundred and sixty-eight people (Environment & Human Health, Inc. [EHHI], n.d.). Of the 268 athletes, 209 of them were soccer players (EHHI, n.d.). The additional 59 athletes came from football, lacrosse and baseball teams (EHHI, n.d.). Of the 268 athletes included on Amy Griffin's List, 73 of the athletes had been diagnosed with Hodgkin's Lymphoma, 35 of the athletes had been diagnosed with Non-Hodgkin's Lymphoma, 58 of the athletes had been diagnosed with Leukemia, 33 had been diagnosed with a Sarcoma, 17 had been diagnosed with testicular cancer, 12 had been diagnosed with thyroid cancer, 10 had been diagnosed with brain cancer, and 3 had been diagnosed with lung cancer (EHHI, n.d.).

Interestingly, Amy Griffin also discovered an additional correlation when analyzing the information she had collected over the years of creating her list. Of the 268 athletes on Amy Griffin's List, sixty percent of the athletes were goalkeepers (EHHI, n.d.). When Amy addressed the public about her findings, she urged the scientific community to perform additional scientific studies that investigate the potential carcinogenicity of these artificial crumb rubber pellets (Tuhus, 2019). She also brought up her concerns over the goalkeepers and stated that these individuals were more likely to swallow the pellets or breathe the pellets in comparison to other players playing in different positions. Goalies are constantly diving to save balls, they often experience a spray of these pellets into their face, which causes unintentional inhalation or ingestion. Amy Griffin thought this may be one reason such a large percentage of people on her list of past athletes that had been diagnosed with cancer were goalies.

Griffin's claims led to an influx of scientific studies that investigated the composition of artificial crumb rubber turf pellets. From the early 2000s up to the present day, scientists from around the world have worked to conduct various experiments in which they try and analyze some of the components of crumb rubber pellets used as infill on artificial turf fields and determine whether or not there are substances present in these pellets that could be harmful to human health. To date, the substances that have raised the most alarm in the scientific community, and have appeared most in the literature include volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), polyaromatic hydrocarbons (PAHs), and various heavy metals (Ahrar, 2017; Boeglin et al, 2006; Bocca et al., 2009; Canepari et al., 2018; Cheng et al., 2014; Li et al., 2010; Perkins et al., 2019; Peterson et al., 2018; Pronk et al., 2018; Schiliro et al., 2012; Simcox et al, 2011; Zhang et. al, 2008). Heavy metals that have been investigated in past studies within the scientific literature include antimony, arsenic, barium, cadmium, chromium, cobalt, copper, lithium, lead, mercury, molybdenum, nickel, selenium, thallium, tin, titanium, vanadium, and zinc (Ahrar 2017; Bocca et al., 2009; Canepari et al., 2018; Li et al., 2010; Peterson et al., 2018; Pronk et al., 2008; Schiliro et al., 2012; Simcox et al., 2011; Zhang et al., 2008).

For the purpose of this investigation, a special focus will be placed on the presence of lead in crumb rubber pellets found on artificial turf fields. Lead is a naturally occurring heavy metal that is found in abundant amounts throughout the earth (National Institute of Environmental Health Sciences [NIH], n.d.). Although lead is naturally occurring, it has been found to be quite hazardous to humans' overall health and well-being. In 1973, due to health concerns, the federal government began to slowly decrease the allowable amount of lead in gasoline and eliminated it completely by 1996 (NIH, n.d.). In 1986 the federal government made the decision to restrict the

amount of lead in bonding material used in welding (i.e., solders), faucets, pipes, and similar materials (NIH, n.d.). Lead exposure is still thought to be a significant public health concern because of the persistent lead hazards in the environment (EIH, n.d.).

Lead is thought to be mutagenic and genotoxic and elicits a positive response in tests for enzyme inhibition, fidelity of DNA synthesis, mutations, chromosomal aberrations, cancer, and birth defects (Valverde et al., 2002). Lead also inhibits DNA repair and acts synergistically with other mutagens in vitro (Steenland & Boffetta, 2000). In a study conducted on rodents, when lead acetate was administered orally, cutaneously and intraperitoneally, the rodents ended up developing kidney cancer, brain cancer (gliomas), and lung cancer (Steenland & Boffetta, 2000). Although none of the athletes on Amy Griffin's list were diagnosed with kidney cancer, there were several that received diagnoses of either brain cancer or lung cancer (EHHI, n.d.). As stated previously, the vast majority of the athletes on Amy Griffin's list were diagnosed with Non-Hodgkin's lymphoma (NHL), or leukemia. According to the American Cancer Society [ACS], gene changes related to NHL are usually acquired during life, rather than being inherited, and these acquired changes can result from prolonged exposure to cancer-causing chemicals (ACS, n.d.). The American Cancer Society also states DNA mutations can increase an individual's chances for developing Leukemia. These gene mutations can be acquired throughout an individual's lifetime and can result from exposure to radiation or cancer-causing chemicals (ACS, n.d.). It has been proven that lead is a carcinogen, and past studies have found small amounts of lead within crumb rubber pellets that are a huge component of artificial turf fields. The possibility cannot be ruled out that the reason the athletes developed cancer was due to exposure to lead within the crumb rubber pellets.

It is important to remember that all of the names of the athletes included on Amy Griffin's list were collected in a purely anecdotal manner (Tuhus, 2019). The claims Amy Griffin has made about the carcinogenic nature of crumb rubber turf pellets were based off of her own observations and experiences (Tuhus, 2019). Even Amy Griffin has admitted that correlation does not necessarily equal causation, and that further research is necessary to back up her claims (Tuhus, 2019). Although there has been an increase in publications on the topic of the carcinogenic nature of artificial crumb rubber turf, there has still yet to be a conclusive study that has been published that proves or disproves whether crumb rubber pellets contain a hazardous amount of lead that could cause cancer if the athletes are exposed to these pellets while playing on artificial turf fields. Therefore, the purpose of this investigation is to both qualitatively and quantitatively analyze these crumb rubber pellets for lead.

2. Materials:

Three different samples of crumb rubber pellets were collected from various artificial turf fields. The samples were collected from Alfred University's athletic field, Brockport State College's athletic field, and Alfred State College's athletic field. The Brockport State College turf sample was collected on November 16th, 2021. The sample was collected from the sideline near the 50-yard line on the visiting team's side of the field. The Alfred State College turf sample was collected on January 30th, 2022. The sample was collected near the endzone on the north side of the field, on the home team's sideline. The Alfred University turf sample was collected on January 30th, 2022. This sample was collected near the endzone on the south side of the field, on the visiting team's sideline. Each of the samples were collected by gloved hand. The individual crumb rubber pellets were picked up and placed in glass vials with a plastic top. Before any work was completed with the crumb rubber pellets, the pellets were lightly rinsed with water, and then laid out on a paper towel to dry. This step was taken to separate the crumb rubber pellets from any extra material that was accidentally obtained during the collection process (e.g., pieces of synthetic grass, organic matter, small pebbles). After the crumb rubber turf pellets dried out on the paper towels, they were placed back in their respective labeled glass vials.

3. Methods:

Part 1- Qualitative Analysis of Crumb Rubber Specimen's for Lead:

To qualitatively analyze the different chemical compositions of the crumb rubber turf pellets, a scanning electron microscope (SEM) was used. The instrument that was utilized is the JSM-6010PLUS/LA InTouchScope™.

Three different crumb rubber sample specimens from each of the respective athletic fields (Alfred University, Alfred State, and Brockport) were prepared. Several of the crumb rubber pellets that were collected were mounted on a metal stub using a conductive carbon-based glue. The three samples were then sputter coated with silver, which is a conductive metal. The samples were sputter coated with silver in order to prevent charge build up on the specimen's surface from the electron beam of the SEM.

High resolution micrographs were taken of each of the three turf sample specimens in the secondary electron mode (SEI) and the backscattered electron mode (BEC). The secondary electron images that were taken show the topography of the surface of the crumb rubber pellets. The backscatter electron images that were taken show compositional differences of the turf. Areas on a backscattered image that appear brighter tend to be areas that house higher atomic number elements.

The SEM microscope is also equipped with X-ray microanalysis system called EDS. EDS stands for "Energy Dispersive Spectroscopy", and it is based on electrons emitted from a sample during electron irradiation. The machine is can pick up on various x-rays that are emitted from a sample that has just been hit with the electron beam. Each of the x-rays that are emitted are characteristic of a different element. The qualitative analysis aspect of the EDS mode of an SEM would be able to detect if there was any lead within each of the prepared crumb rubber

pellet samples. A point analysis was also performed for each of the three turf specimens. Four spots were chosen at random on each of the turf samples, and then a compositional analysis was performed for each of the four respective spots on the three separate turf samples. An elemental spectral map was also generated for each of the three samples using the EDS mode of the SEM.

Part 2- Quantitative Methodology to Determine Amount of Lead in Crumb Rubber Samples:

The amount of lead that was present in the Alfred University crumb rubber sample was determined by using flame atomic absorption spectroscopy, an analytical chemistry technique. The following steps were taken.

A. A 1000ppm lead stock solution was made to create different standards to be used during the flame atomic absorption spectrometry procedure.

1. Measured out 1.6021 grams of $Pb(NO_2)_2$ and added the solute to a 1000ml volumetric flask
2. Added 10 ml of HNO_3 to that volumetric flask 1000ml volumetric flask
3. Filled the rest of the flask with deionized water up to the 1000ml line
4. Calculated the exact amount of lead in ppm within the stock solution (see calculations below)

1.6021 g of Pb x 207.19 u (atomic mass of Pb) /331.39 u (atomic mass of $Pb(NO_2)_2$) = 1.002 g of Pb

207.19 (Pb) + 14.01 (N) + 16.00 (O) = 331.39 (atomic mass of $Pb(NO_2)_2$

B. A microwave digestion procedure was developed. Once the lead is in solution, a quantitative analysis can be performed by means of flame atomic absorption spectrometry. The flame atomic absorption spectrometry will be able to provide the amount of lead in ppm within this solution. Used the CEM Discover 2.0 microwave. Attempted multiple different trials and methods to find acceptable parameters that worked best to get the lead into solution. The parameters used in trial 3 were thought to be the most successful.

Trial One:

1. Weighed out .4967 g of crumb rubber turf from Alfred University field. Placed the turf in a 35 mL microwave vessel.
2. Added 10ml of pre-made 2M HNO_3 to the crumb rubber turf.

3. Added a stir bar to the microwave vessel, capped the vessel off and placed it in the microwave
4. Digested in the microwave with the following parameters:
    a. 250˚C
    b. 200 W
    c. 10 minutes
5. Stopped the microwave digestion because the pressure reached over 300psi.
6. Filtered remaining crumb rubber from the solution using coarse filter paper. Used a 25ml volumetric flask to catch the solution.
7. Brought the solution up to volume using DI water.

Trial Two:

1. Weighed out .5041g of crumb rubber pellets from Alfred University's field. Placed the turf in a 35 mL microwave vessel
2. Added 10 mL of pre-made 2M HNO_3 to the crumb rubber turf in the microwave vessel.
3. Added a stir bar to the microwave vessel, capped the vessel off and placed it in the microwave
4. Digested in the microwave with the following parameters:
    a. 200 ˚C
    b. 300 W
    c. 10 minutes
5. Stopped the microwave digestion because the pressure of the apparatus reached over 300 psi.
6. Filtered remaining crumb rubber from the solution using coarse filer paper. Used a 25ml volumetric flask to catch the solution
7. Brought the solution up to volume using DI water.

Trial Three:

1. Weighed out .5036g of crumb rubber turf from Alfred University's field. Placed the turf in a 35 mL microwave vessel.
2. Added 10mL of 2 M HNO_3 to the crumb rubber turf in the microwave vessel.
3. Added a stir bar to the microwave vessel, capped the vessel off and placed it in the microwave
4. Digested the turf in the microwave with the following parameters:
    a. 150 ˚C
    b. 300 W
    c. 5 minutes
5. Let the microwave run for the full 5 minutes, the pressure of the apparatus did not reach over 300 psi for this trial. The parameters used in this trial should be used in trials to come because the digestion was able to run for the full 5 minutes.

6. Filtered remaining crumb rubber from the solution using coarse filter paper. Used a 25ml volumetric flask to catch the solution.
7. Brought the solution up to volume using DI water.

C. The amount of lead within the solutions that were created from the three microwave digestion trials was analyzed. A calibration curve was created on the Flame Atomic Absorption Spectroscopy (AAS) Machine using a blank, a 5 mg/L lead standard and a 20 mg/L lead standard. To calibrate the AAS, a blank was first measured. The blank that was used was diluted 2M HNO_3. The baseline absorption measurement for the blank was 0. Next, the absorptions of the lead standard solutions were measured. The baseline absorption measurement for the 5 mg/L lead standard was .006. The baseline absorption measurement for the 20mg/L lead standard was .037. From this data, a calibration curve was created. The calibration curve determines the relationship between the absorbance of light and the concentration of the element (lead) in the solution. Finally, the absorption measurement for the solutions made from the microwave digestion procedures were collected. These absorption measurements were then used to determine the concentration of the lead within the solutions that were made by digesting the crumb rubber. All three trials run on the flame aa gave readings below 0.0ppm. These absorption measurements suggest that there is no lead present within any of the three solutions that were made from the microwave digestion procedures using crumb rubber from Alfred University's artificial turf field

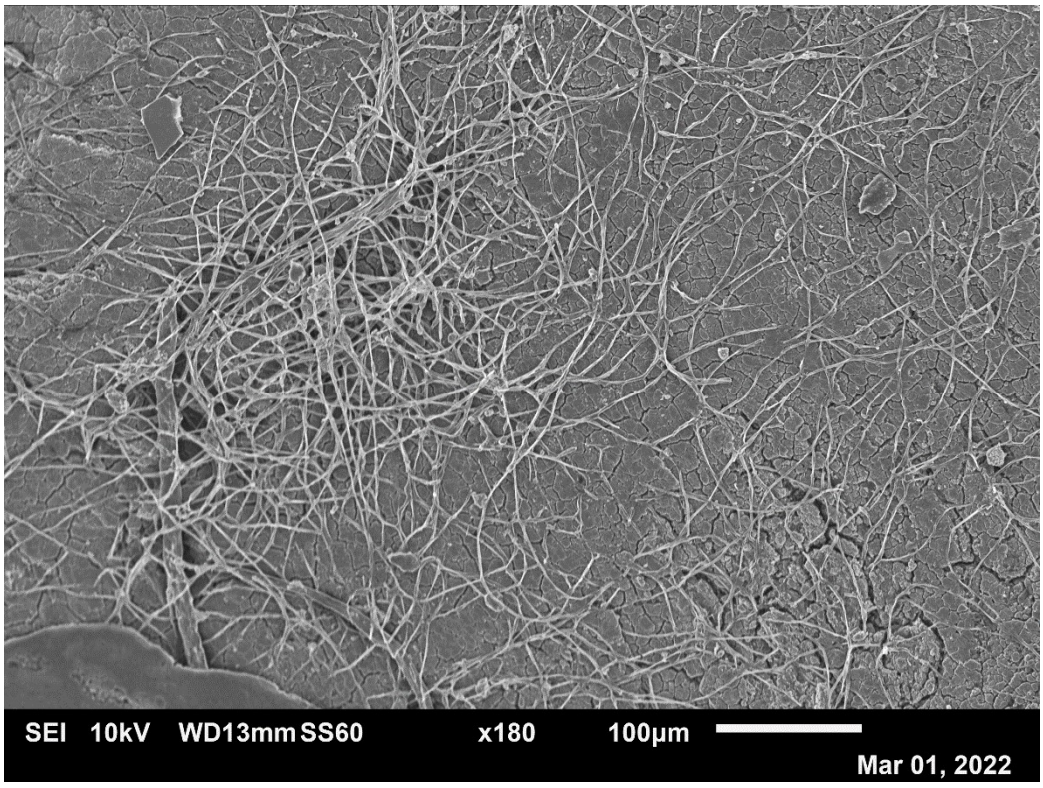
4. Results:

Qualitative Analysis of Specimen 1- Alfred University's Crumb Rubber Pellets:

The provided chemical analyses are shown in the forms of secondary and backscatter micrographs, as well as elemental maps, spot analyses and spectral maps that were created in EDS mode. Figure 1 is a secondary micrograph of the crumb rubber that was collected from Alfred University's athletic field. Figure 2 is a backscatter micrograph of the crumb rubber pellets that were collected from Alfred University's athletic field. Both figures 1 and 2 were taken at 180x magnification. Figure 3 is a secondary micrograph of the crumb rubber pellets that were collected from Alfred University's athletic field. Figure 4 is a backscatter micrograph that was taken of the crumb rubber pellets collected from Alfred University's field. Both figures 3 and 4 were taken at 600x magnification. Figure 5 is a secondary micrograph of the crumb rubber pellets that were collected from Alfred University's athletic field. Figure 6 is a backscatter micrograph of the crumb rubber pellets that were collected from Alfred University. Figure 7 contains the data from the point analyses that were ran in EDS mode. Figure 8 contains the elemental spectra of each of the separate points on the specimen that were analyzed. Figure 9 shows an elemental mapping by energy-dispersive X-ray analysis. Figure 10 shows the elemental spectra that was generated from the specimen.

None of the point analyses taken from Alfred University crumb rubber specimen indicate the presence of any lead (Figure 7). There is also no peak for lead included in the spectra for this sample (Figure 8, Figure 10). From a qualitative standpoint, this data shows us that there is no lead in this sample of the crumb rubber pellets collected from Alfred University's artificial turf field.

Figure 1 (top); Figure 2 (bottom)



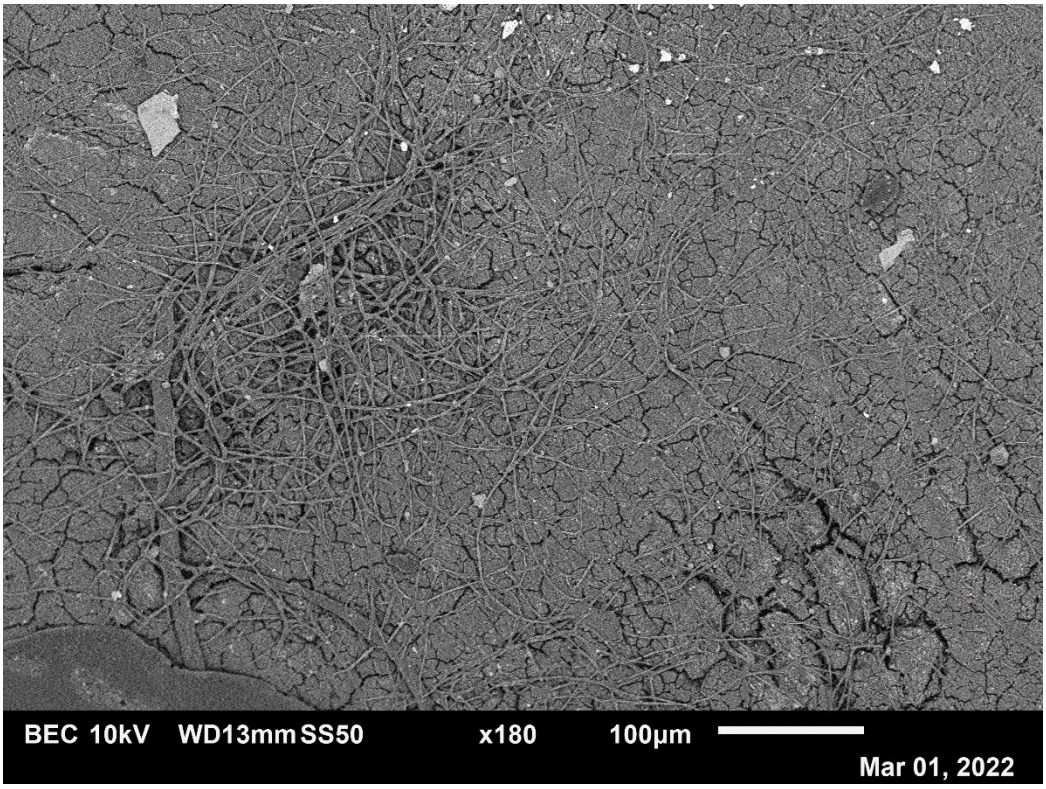
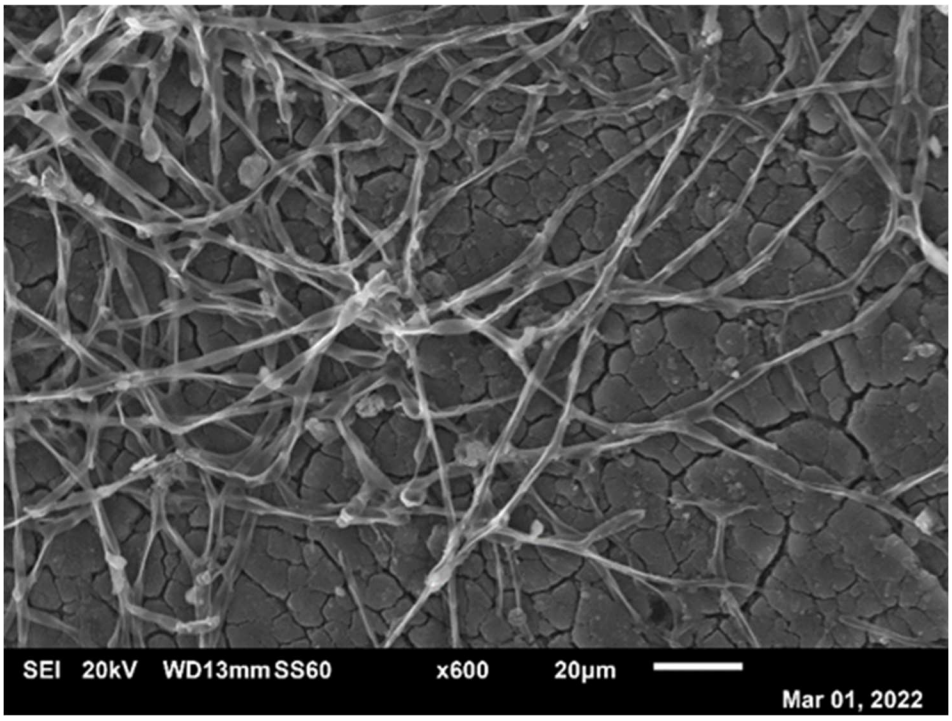


Figure 3 (top); Figure 4 (bottom)



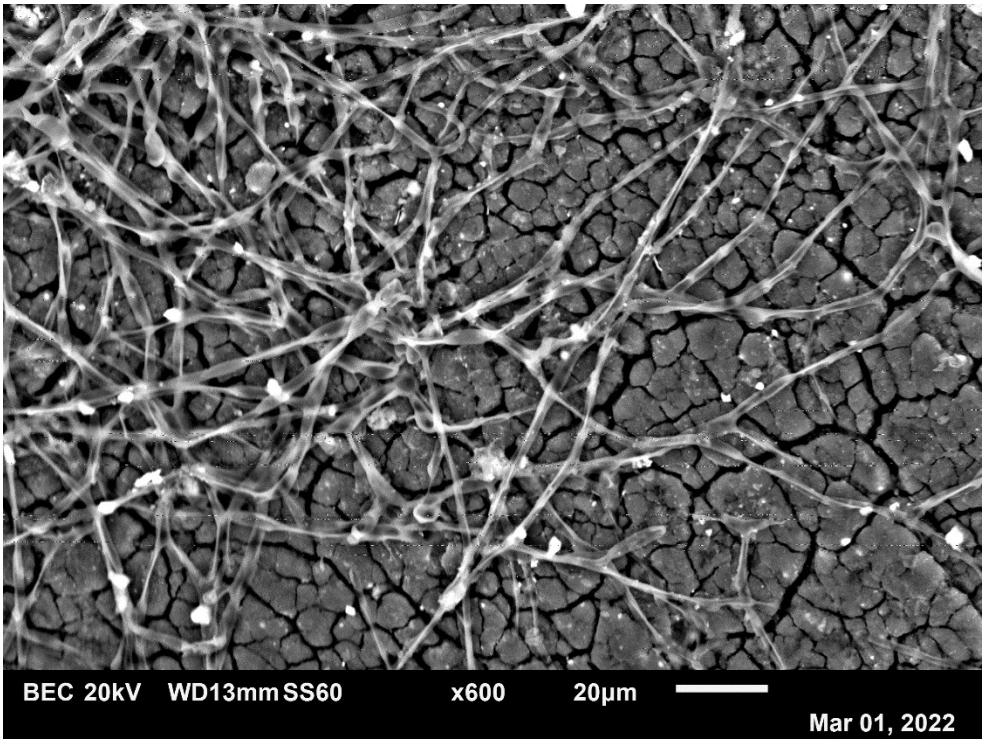
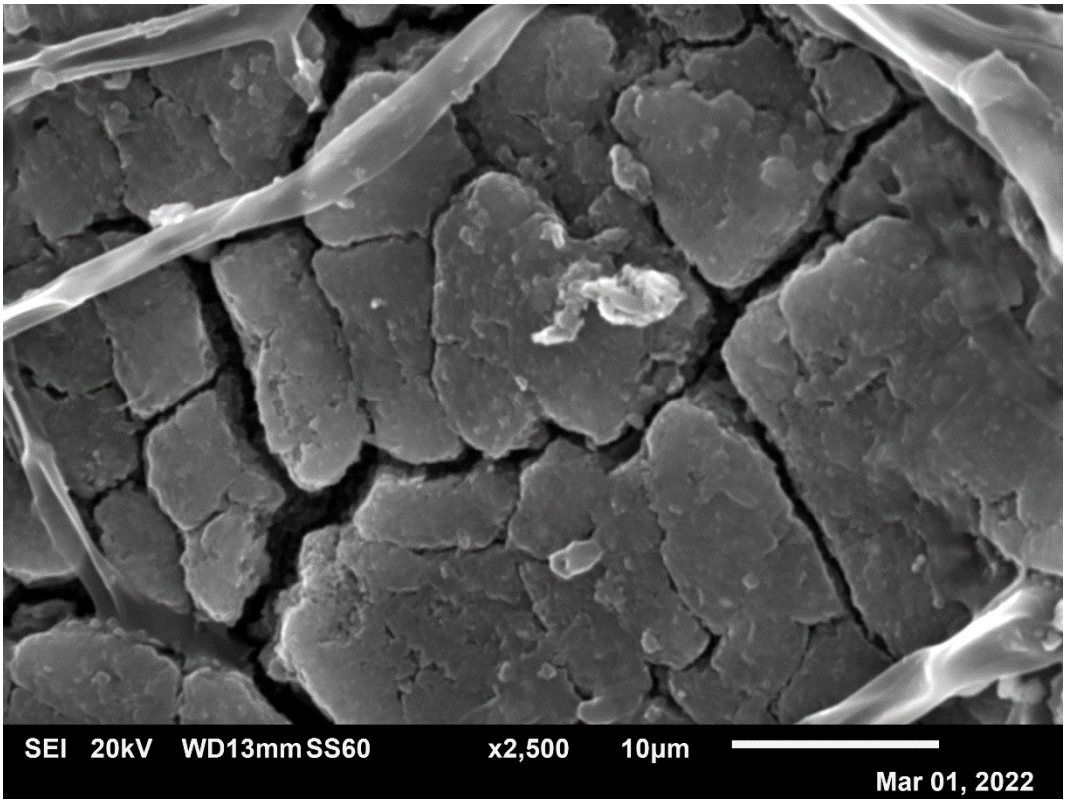


Figure 5 (top); Figure 6 (bottom)



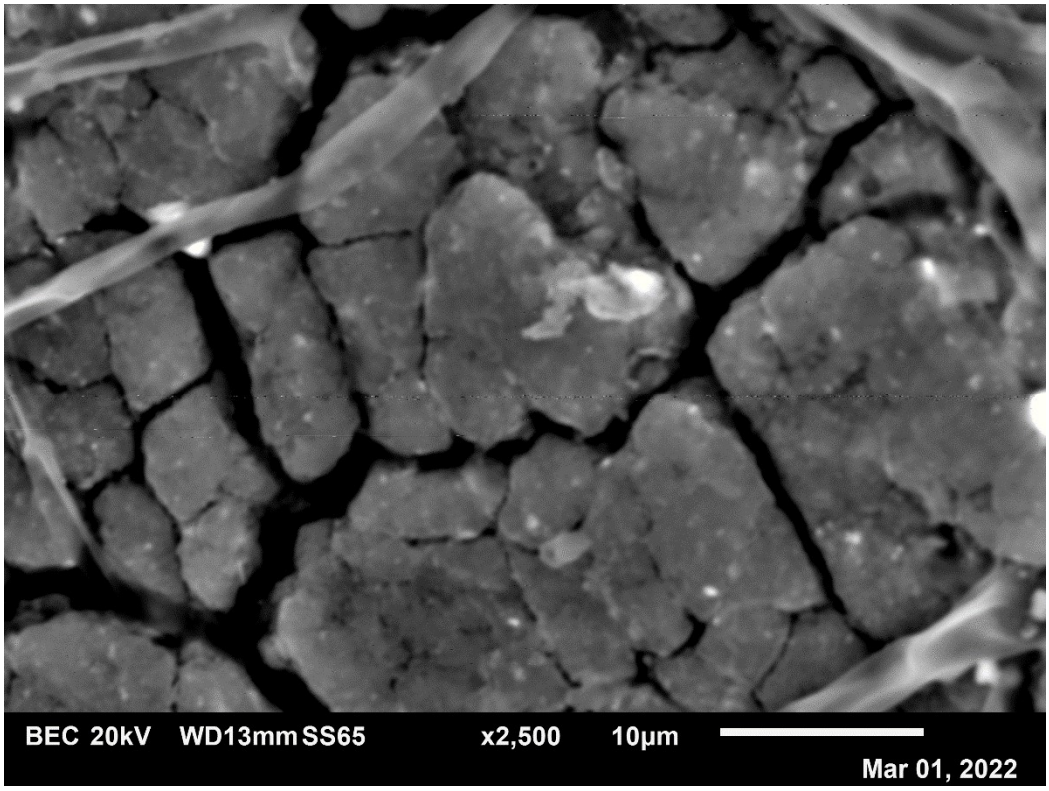


Figure 7 (top); Figure 8 (bottom)

Point 1:

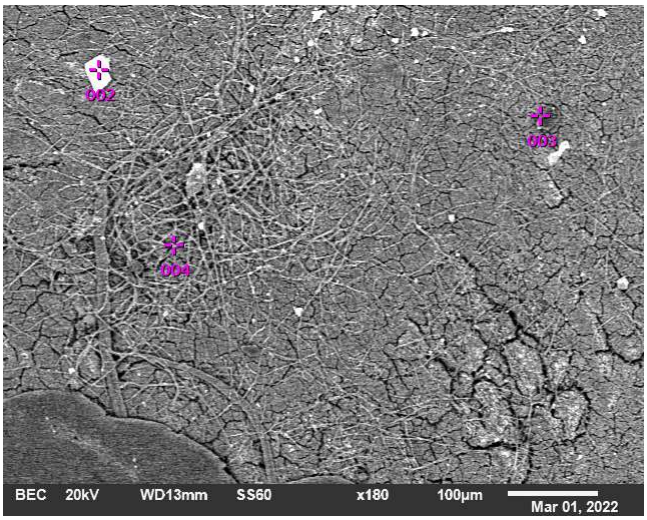
Formula	mass%	Atom%	Sigma	Net	K ratio	Line
C	73.26	80.45	0.03	234214	0.1920376	K
O	21.25	17.52	0.07	39308	0.1094563	K
Al	0.70	0.34	0.01	15603	0.0139445	K
Si	1.32	0.62	0.02	31068	0.0310799	K
S	1.42	0.59	0.01	32841	0.0396454	K
K	0.29	0.10	0.01	5474	0.0084740	K
Fe	0.85	0.20	0.02	6008	0.0214245	K
Zn	0.91	0.18	0.04	3135	0.0214789	K
Total	100.00	100.00				

Point 2:

Formula	mass%	Atom%	Sigma	Net	K ratio	Line
C	63.72	73.07	0.02	270678	0.2219353	K
O	25.96	22.35	0.06	93479	0.2602963	K
Na	0.29	0.17	0.01	5809	0.0086154	K
Mg	0.32	0.18	0.01	9747	0.0088795	K
Al	2.76	1.41	0.01	105035	0.0938677	K
Si	3.52	1.73	0.02	137014	0.1370654	K
S	0.85	0.37	0.01	32342	0.0390432	K
K	1.04	0.36	0.01	32839	0.0508344	K
Fe	0.97	0.24	0.01	11840	0.0422248	K
Zn	0.57	0.12	0.02	3433	0.0235219	K
Total	100.00	100.00				

Point 3:

Formula	mass%	Atom%	Sigma	Net	K ratio	Line
C	96.46	99.52	0.02	1046583	0.8581170	K
Al	0.12	0.05	0.01	5259	0.0046998	K
S	0.12	0.05	0.00	5207	0.0062862	K
Ag	3.30	0.38	0.02	76851	0.1475731	L
Total	100.00	100.00				



Point 4:

Formula	mass%	Atom%	Sigma	Net	K ratio	Line
C	53.53	61.07	0.02	334559	0.2743129	K
N	21.64	21.17	0.10	16616	0.1827094	K
O	18.34	15.71	0.06	52939	0.1474110	K
Na	0.17	0.10	0.01	3618	0.0053649	K
Mg	0.10	0.06	0.01	3193	0.0029086	K
Al	0.51	0.26	0.01	20847	0.0186306	K
Si	0.85	0.42	0.01	37311	0.0373246	K
P	0.23	0.10	0.01	8736	0.0120497	K
S	0.77	0.33	0.01	33748	0.0407416	K
Cl	0.13	0.05	0.00	5300	0.0070024	K
K	0.42	0.15	0.01	15036	0.0232766	K
Ti	0.12	0.03	0.01	2683	0.0055271	K
Fe	0.90	0.22	0.01	12113	0.0431969	K
Zn	0.62	0.13	0.02	4075	0.0279180	K
Ag	1.67	0.21	0.02	39249	0.0753675	L
Total	100.00	100.00				

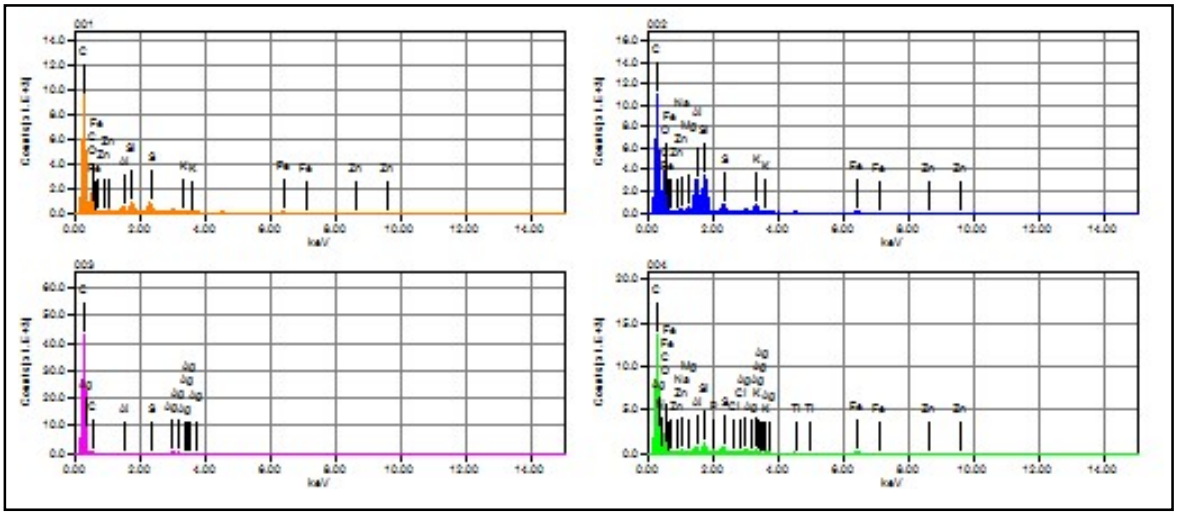


Figure 9

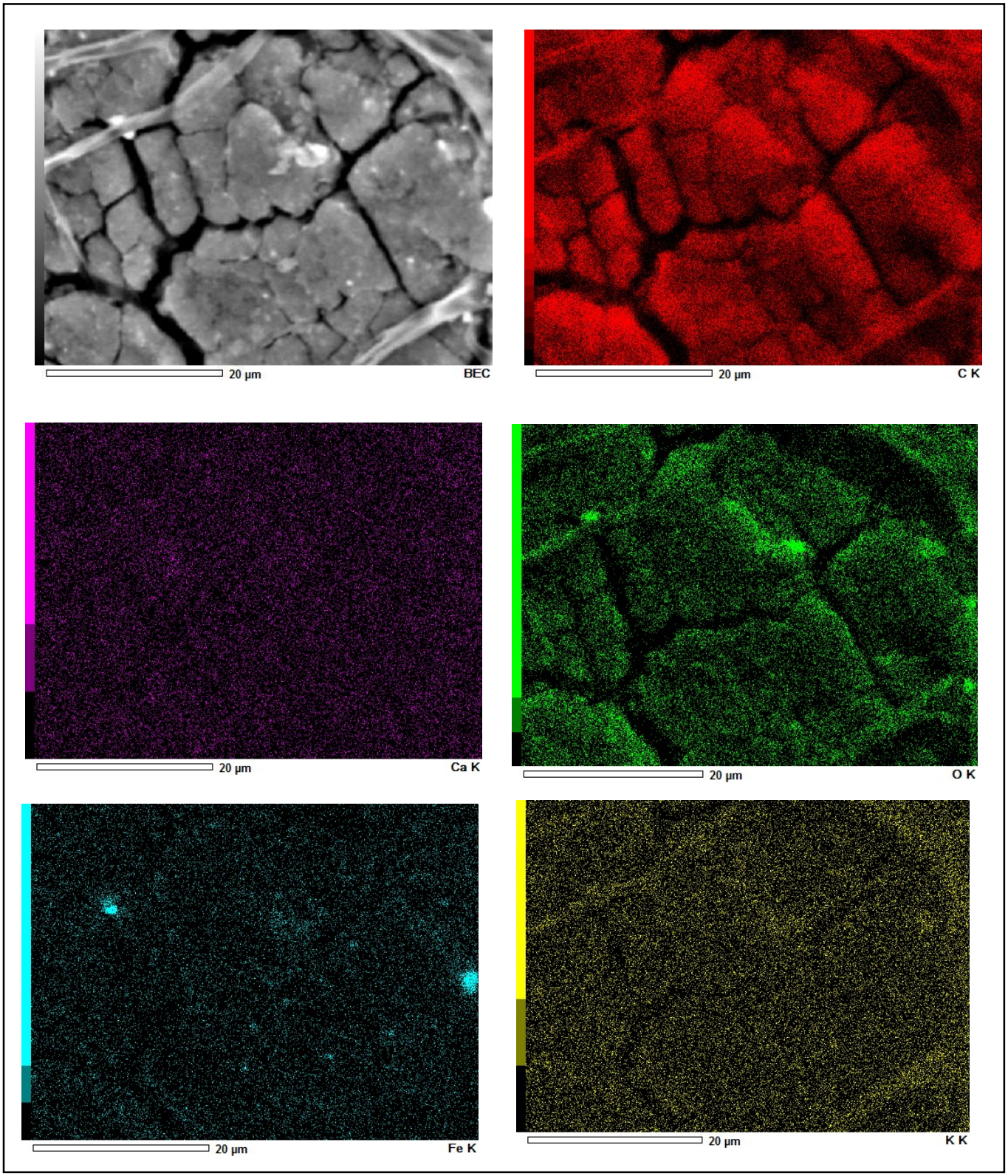
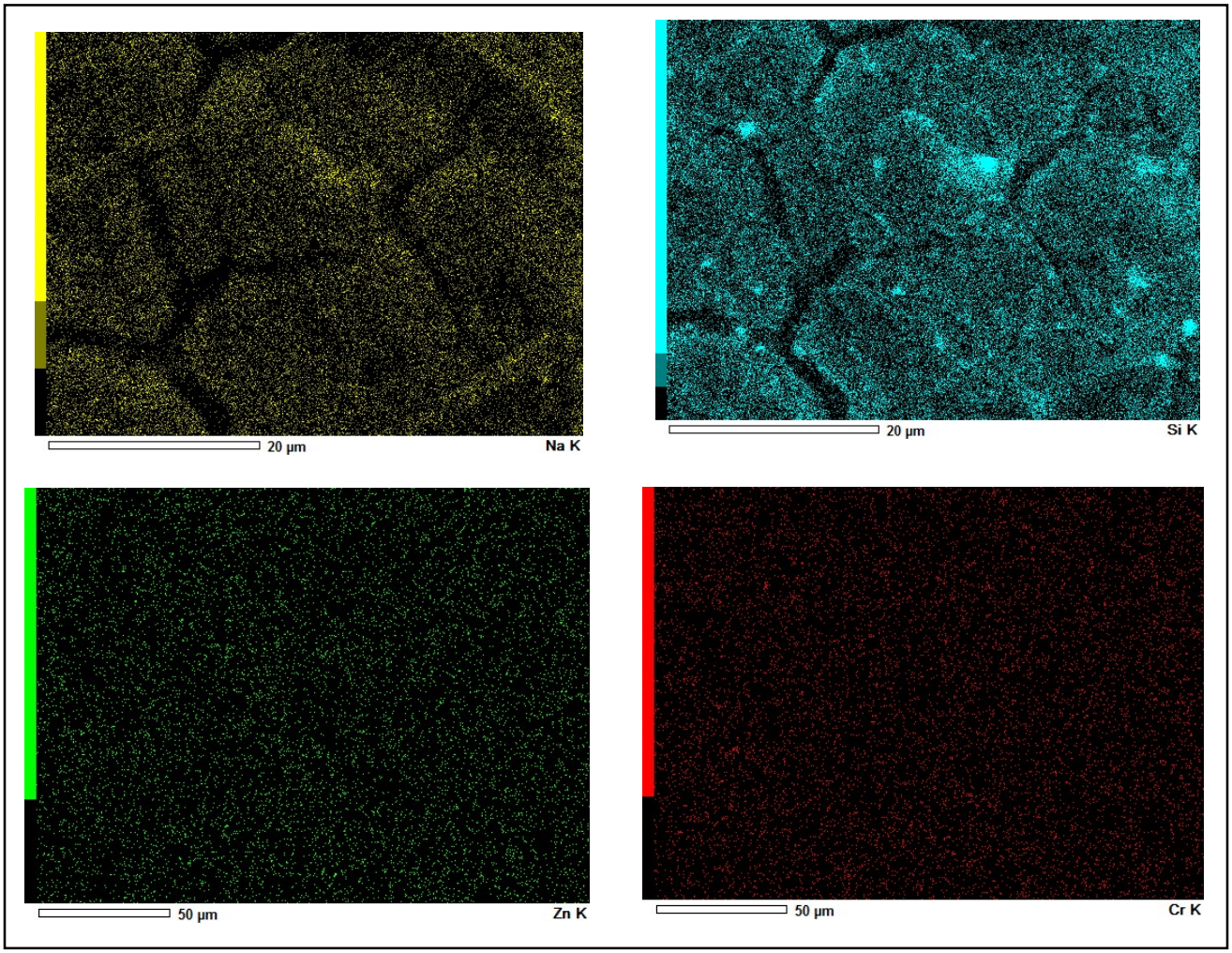
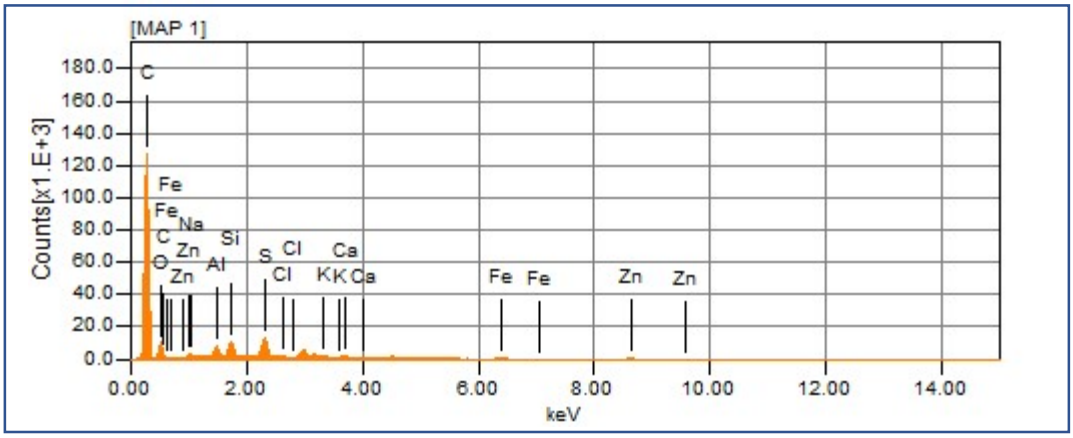


Figure 9, continued (top); Figure 10 (bottom)



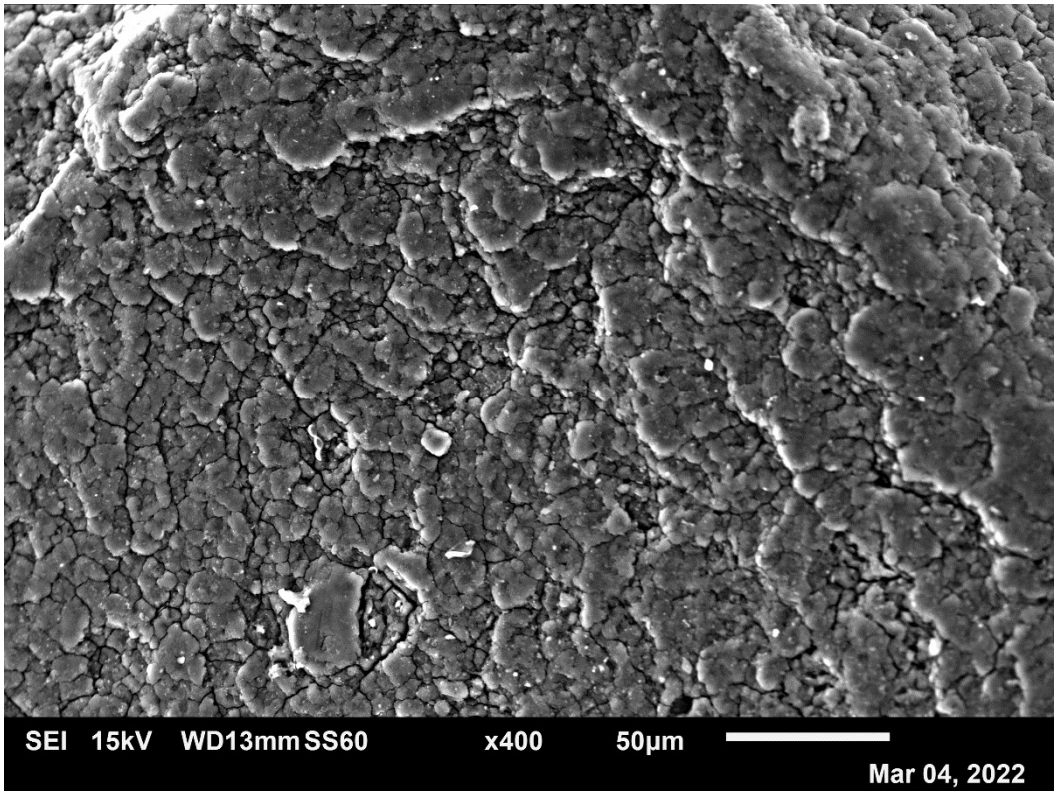


Qualitative Analysis of Specimen 2- Alfred State's Crumb Rubber Pellets:

The provided chemical analyses are shown in the forms of secondary and backscatter micrographs, as well as spot analyses, spectral maps, and elemental maps that were created in EDS mode. Figure 11 is a secondary micrograph of the crumb rubber that was collected from Alfred States College's athletic field. Figure 12 is a backscatter micrograph of the crumb rubber pellets that were collected from Alfred State College's athletic field. Both figures 11 and 12 were taken at 400x magnification. Figure 13 contains the data from the point analyses that were performed in EDS mode. Figure 14 shows an elemental mapping created by energy-dispersive X-ray analysis. Figure 15 is the elemental spectra that was generated from the specimen.

None of the point analyses taken from Alfred State's crumb rubber specimen indicate the presence of any lead (Figure 13). There is also no peak for lead included in the spectra for this sample (Figure 13, Figure 15). No lead x-rays were detected when the elemental mapping was performed (Figure 14). From a qualitative standpoint, this data shows us that there is no lead in this particular sample of the crumb rubber pellets collected from Alfred State College's artificial turf field.

Figure 11 (top), Figure 12 (bottom)



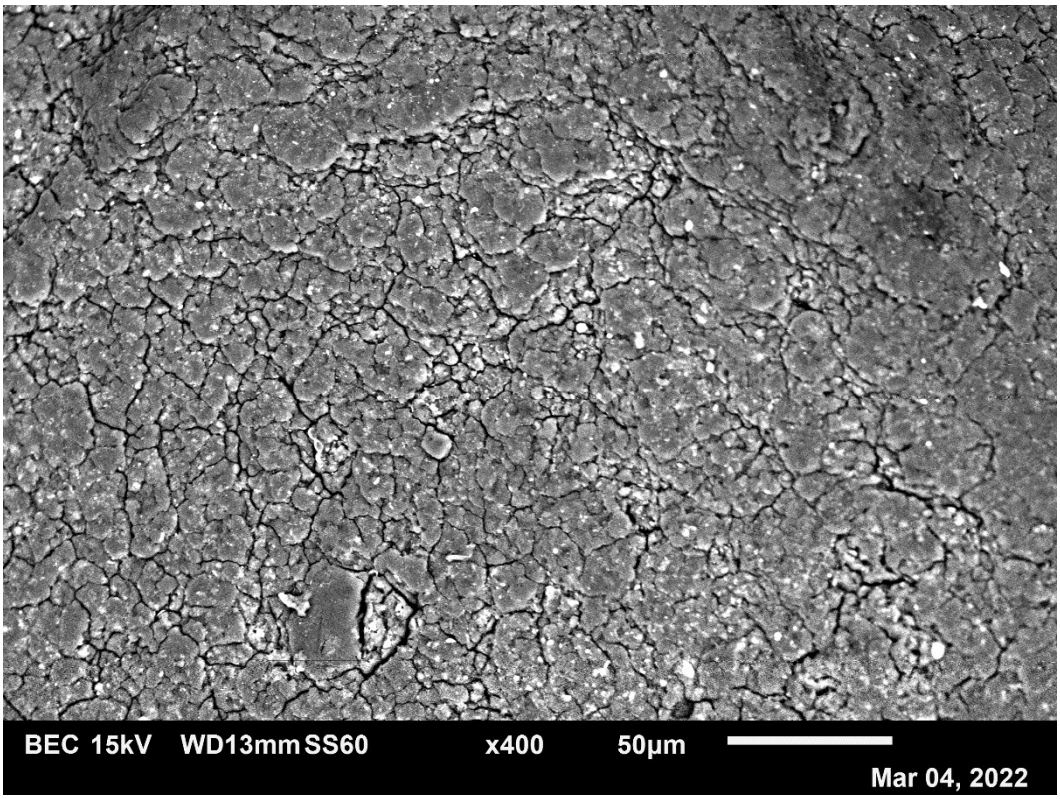
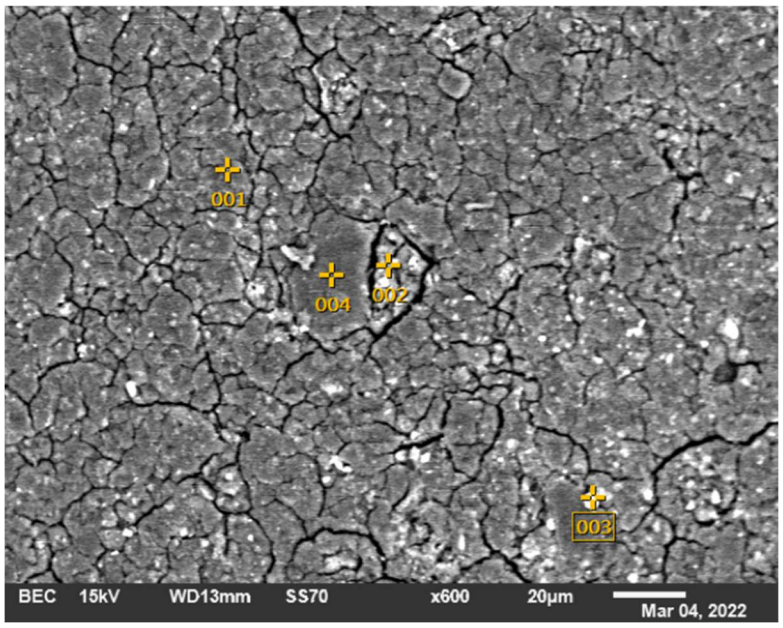


Figure 13



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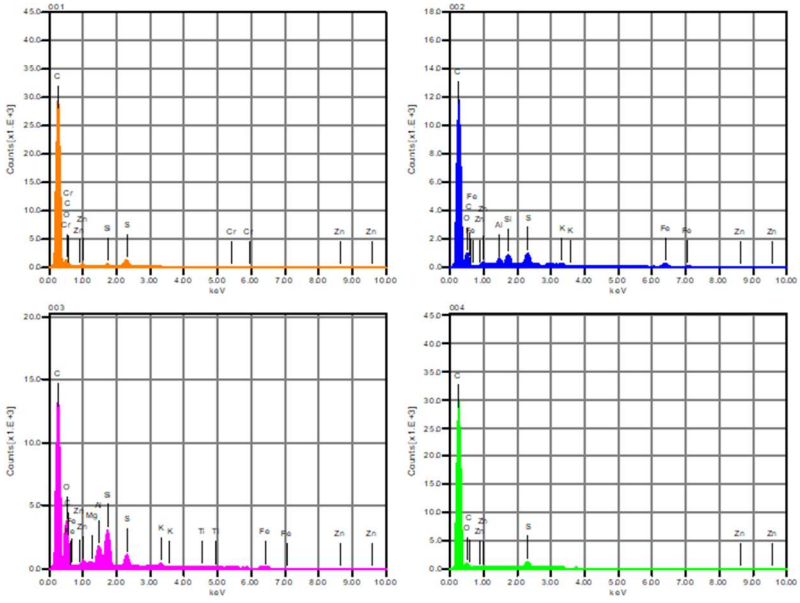
Mag. : x 600
Date : 2022/03/04
Pixel : 640 x 480



Acquisition Condition
Instrument : 6010LA
Volt : 15.00 kV
Current : ---
Process Time : T1
Live time : 30.00 sec.
Real Time : 30.67 sec.
DeadTime : 2.00 %
Count Rate : 10338.00 CPS

	Fe	K	O	C	Mg	Al
	Si	S	Ti	Cr	Zn	
001			8.66	88.28		
	0.31	1.96		nd	0.79	
002	4.53	0.43	10.35	78.25		0.67
	1.42	2.48			1.87	
003	1.49	0.61	22.08	66.23	0.32	2.06
	3.93	1.80	0.38		1.10	
004			7.46	89.40		
		2.07			1.08	
Average	3.01	0.52	12.14	80.54	0.32	1.37
	1.89	2.08	0.38	0.00	1.21	
Deviation	2.15	0.13	6.73	10.77	0.00	0.99
	1.86	0.29	0.00		0.46	

Figure 14

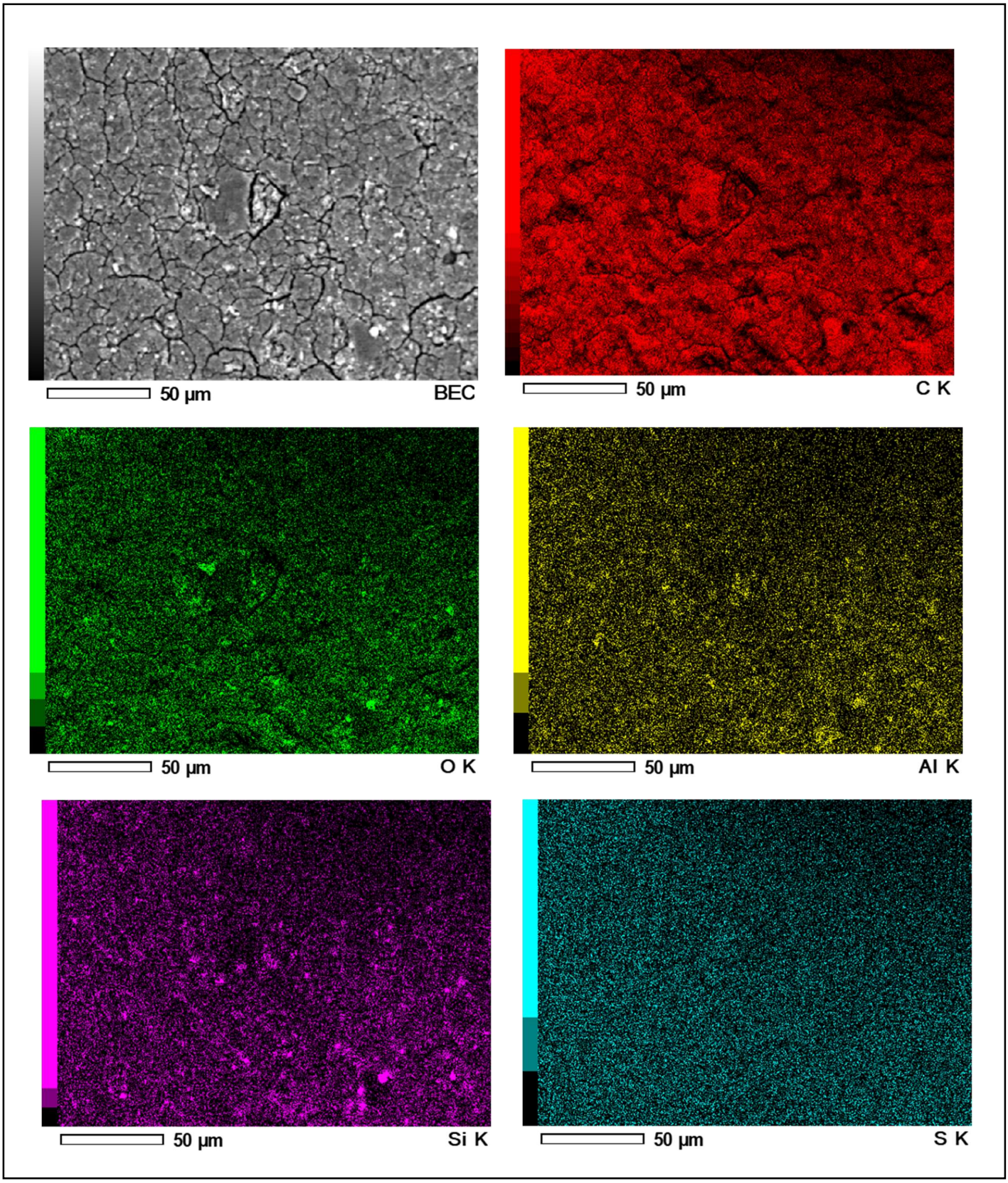
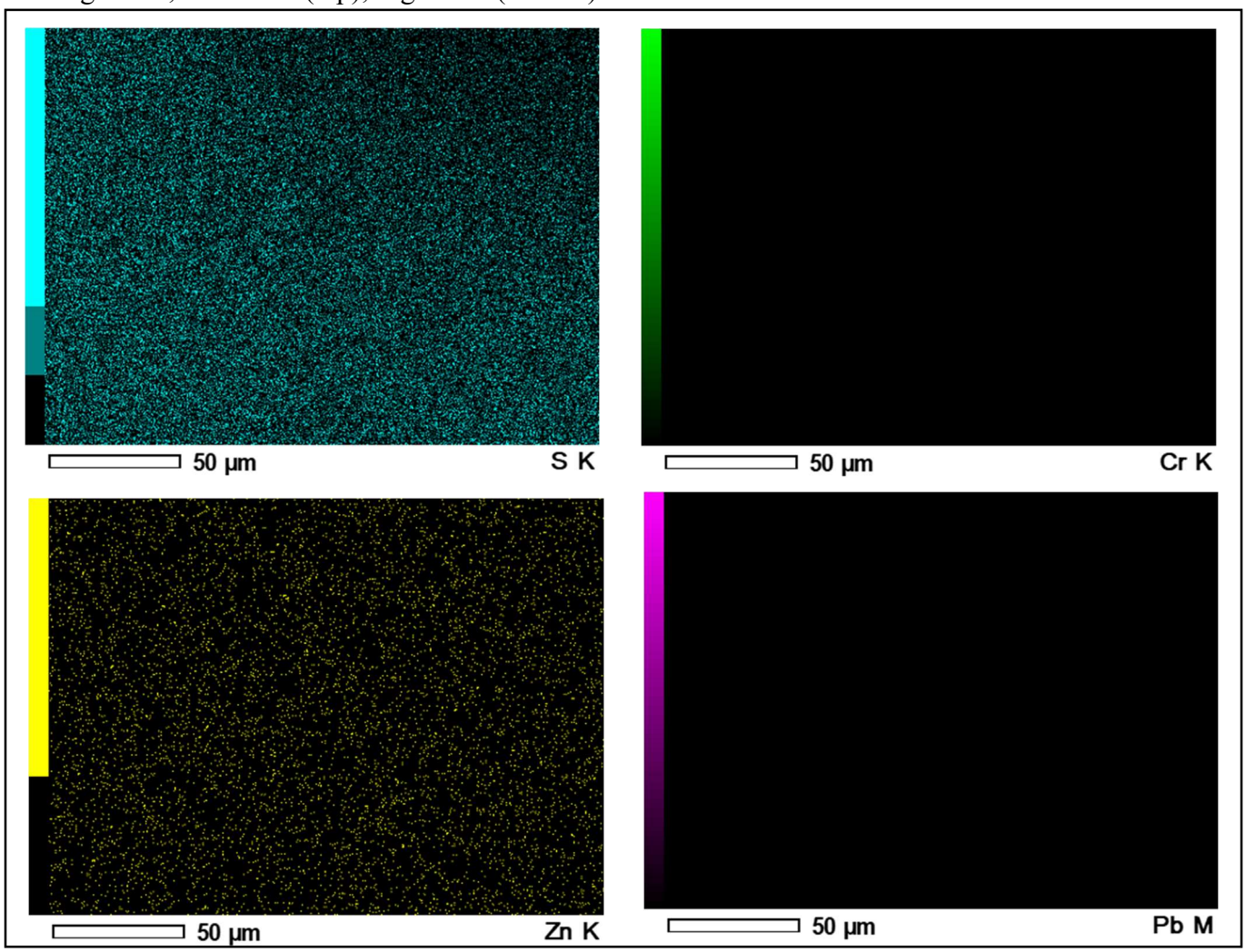
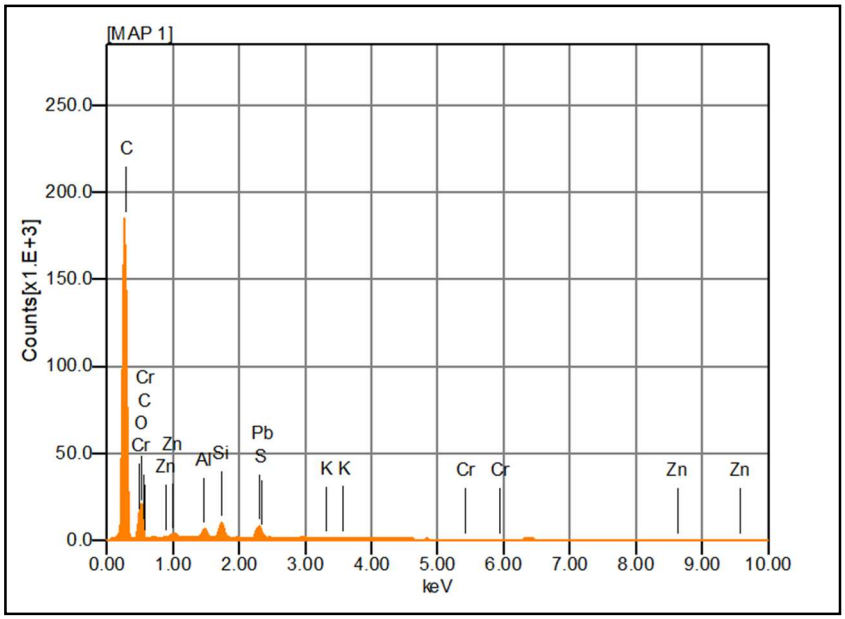


Figure 14, continued (top); Figure 15 (bottom)



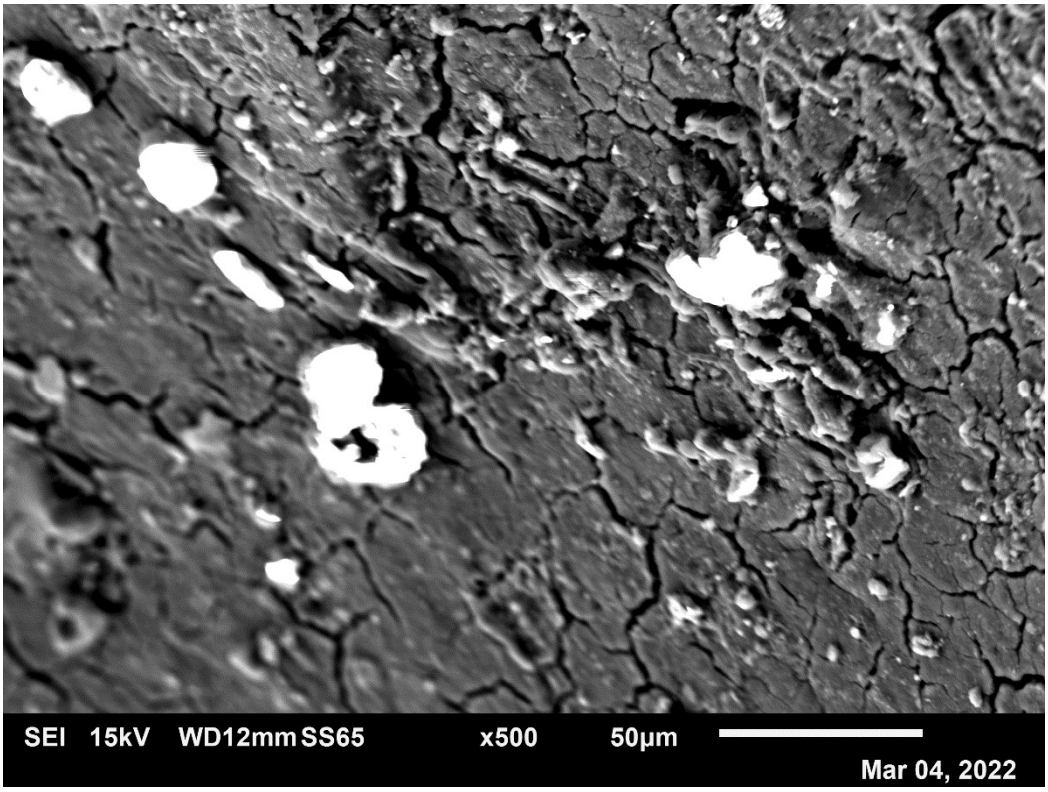


Qualitative Analysis of Specimen 3- Brockport State College's Crumb Rubber Pellets:

The provided chemical analyses are shown in the forms of secondary and backscatter micrographs, as well as spot analyses, spectral maps, and elemental maps that were created in EDS mode. Figure 16 is a secondary micrograph of the crumb rubber that was collected from Brockport State College's athletic field. Figure 17 is a backscatter micrograph of the crumb rubber pellets that were collected from Brockport State College's athletic field. Both figures 16 and 17 were taken at 500x magnification. Figure 18 contains the data from the point analyses that were performed in EDS mode. Figure 19 shows an elemental mapping created by energy-dispersive X-ray analysis. Figure 20 is the elemental spectra that was generated from the specimen.

None of the point analyses taken from Brockport State College's crumb rubber specimen indicate the presence of any lead (Figure 18). There is also no peak for lead included in the spectra for this particular specimen (Figure 18, Figure 20). No lead x-rays were detected when the elemental mapping was performed (Figure 19). From a qualitative standpoint, this data shows us that there is no lead in this particular sample of crumb rubber pellets collected from Brockport State College's artificial turf field.

Figure 16 (top); Figure 17 (bottom)



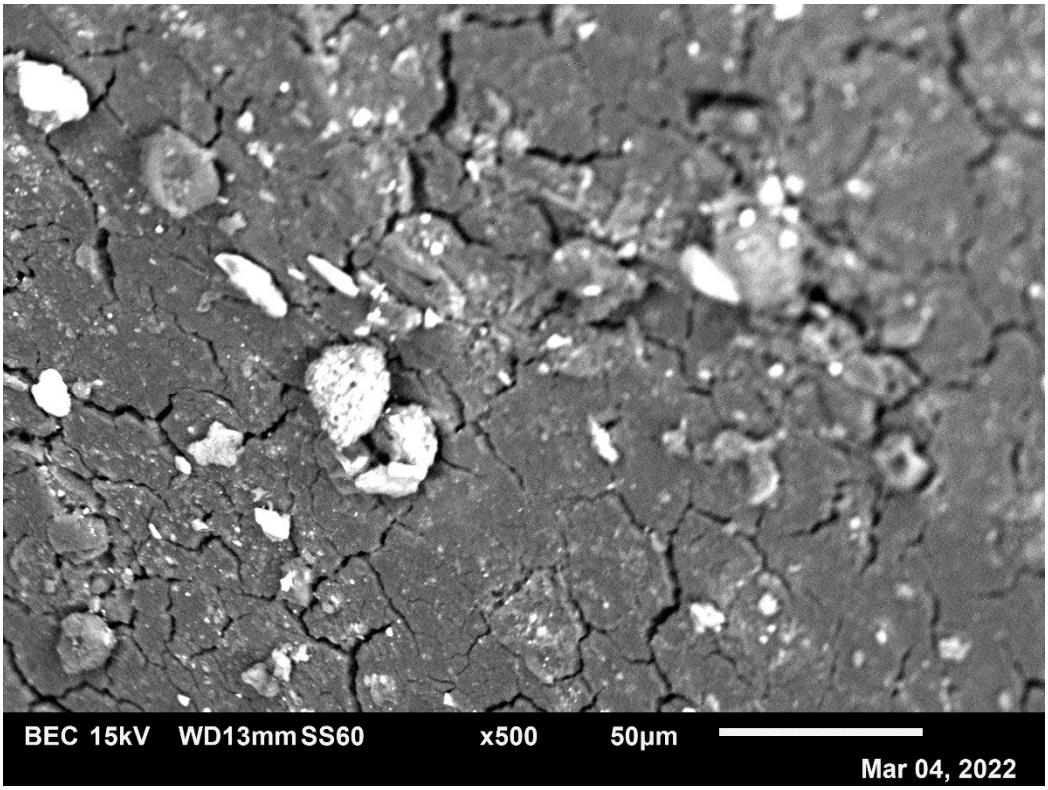
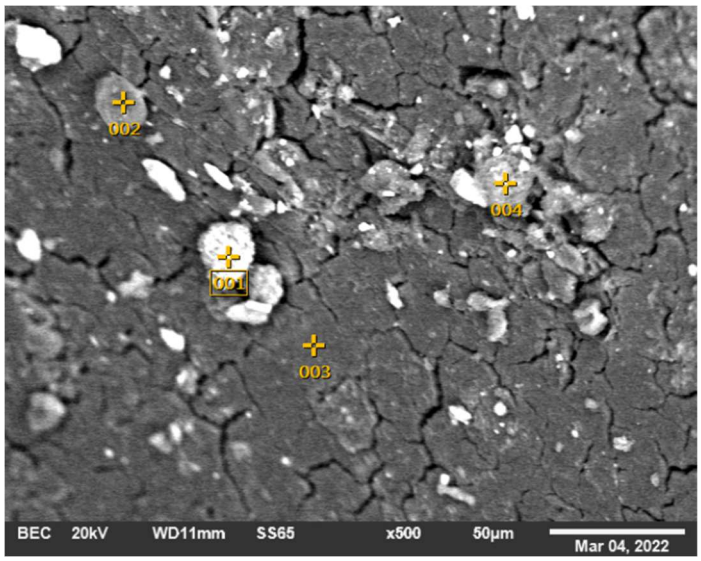
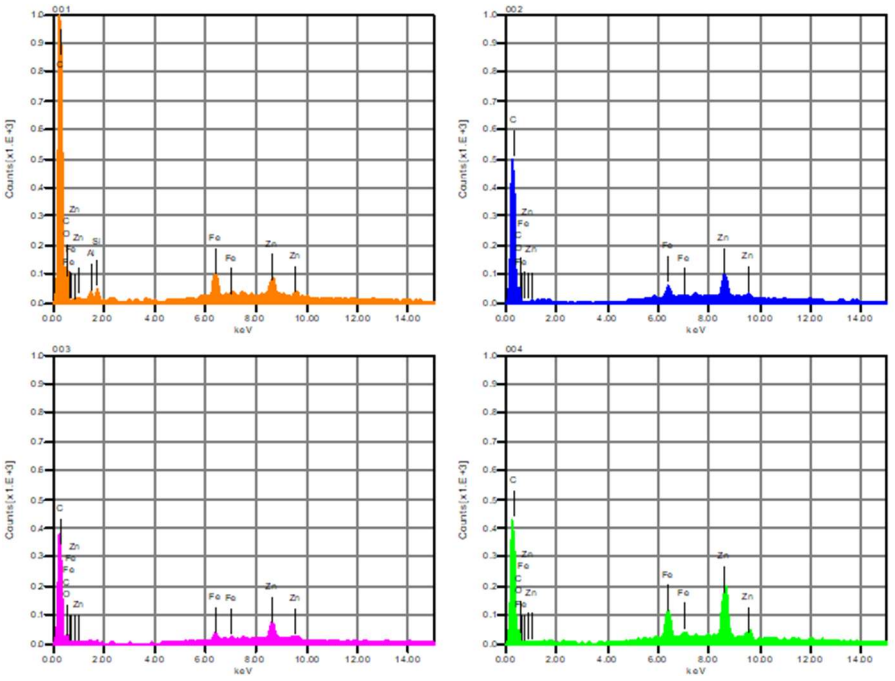


Figure 18



Volt : 20.00 kV
Mag. : x 500
Date : 2022/03/04
Pixel : 640 x 480



Acquisition Condition
Instrument : 6010LA
Volt : 20.00 kV
Current : ---
Process Time : T1
Live time : 30.00 sec.
Real Time : 30.11 sec.
DeadTime : 1.00 %
Count Rate : 1129.00 CPS

	Fe	O	C	Al	Si	Zn
001	5.80	11.58	71.38	0.39	0.46	10.40
002	3.88	7.65	67.49			20.98
003	3.04	7.42	68.15			21.39
004	6.82	4.27	57.36			31.54
Average	4.89	7.73	66.09	0.39	0.46	21.08
Deviation	1.73	2.99	6.06	0.00	0.00	8.64

Figure 19

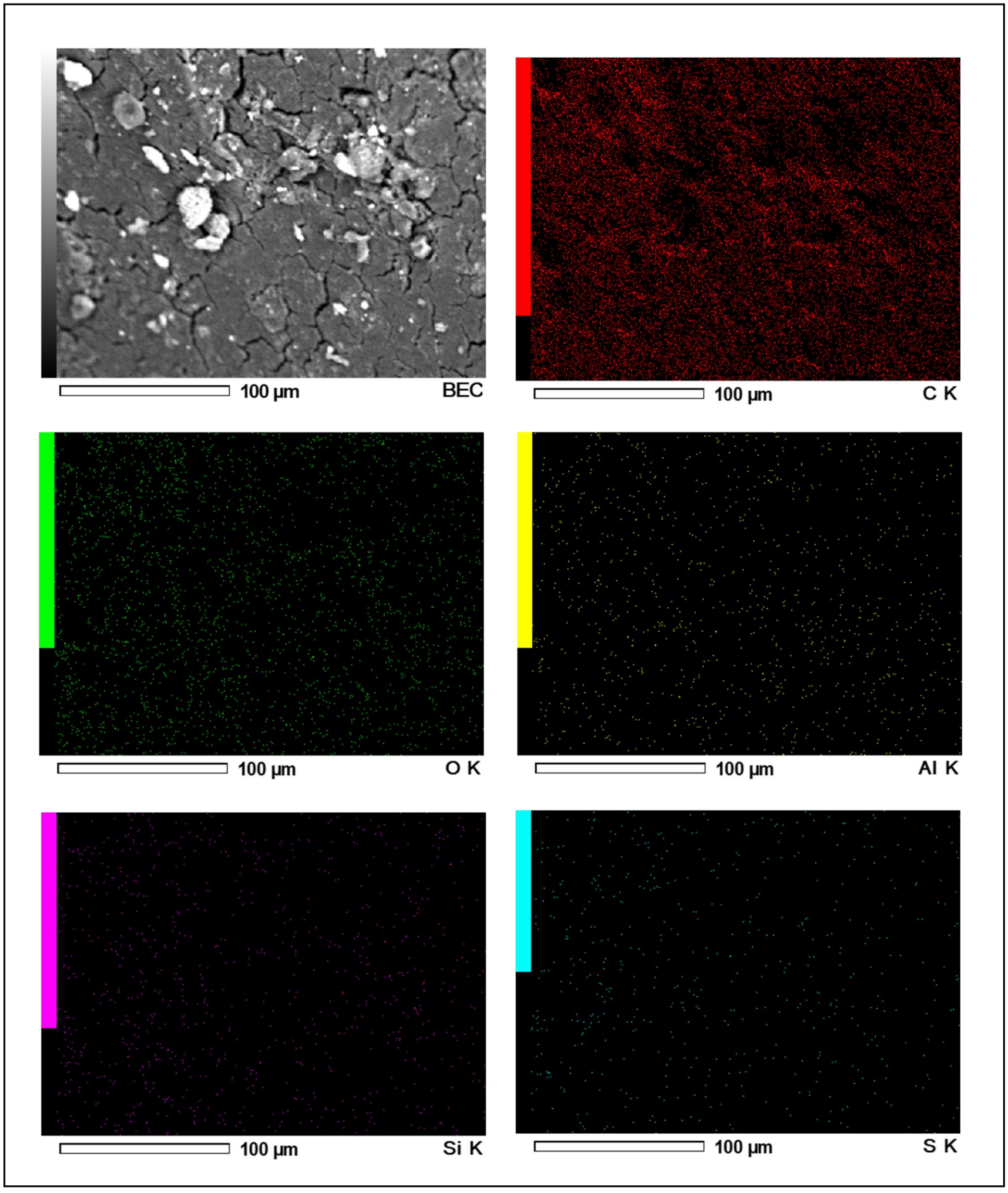
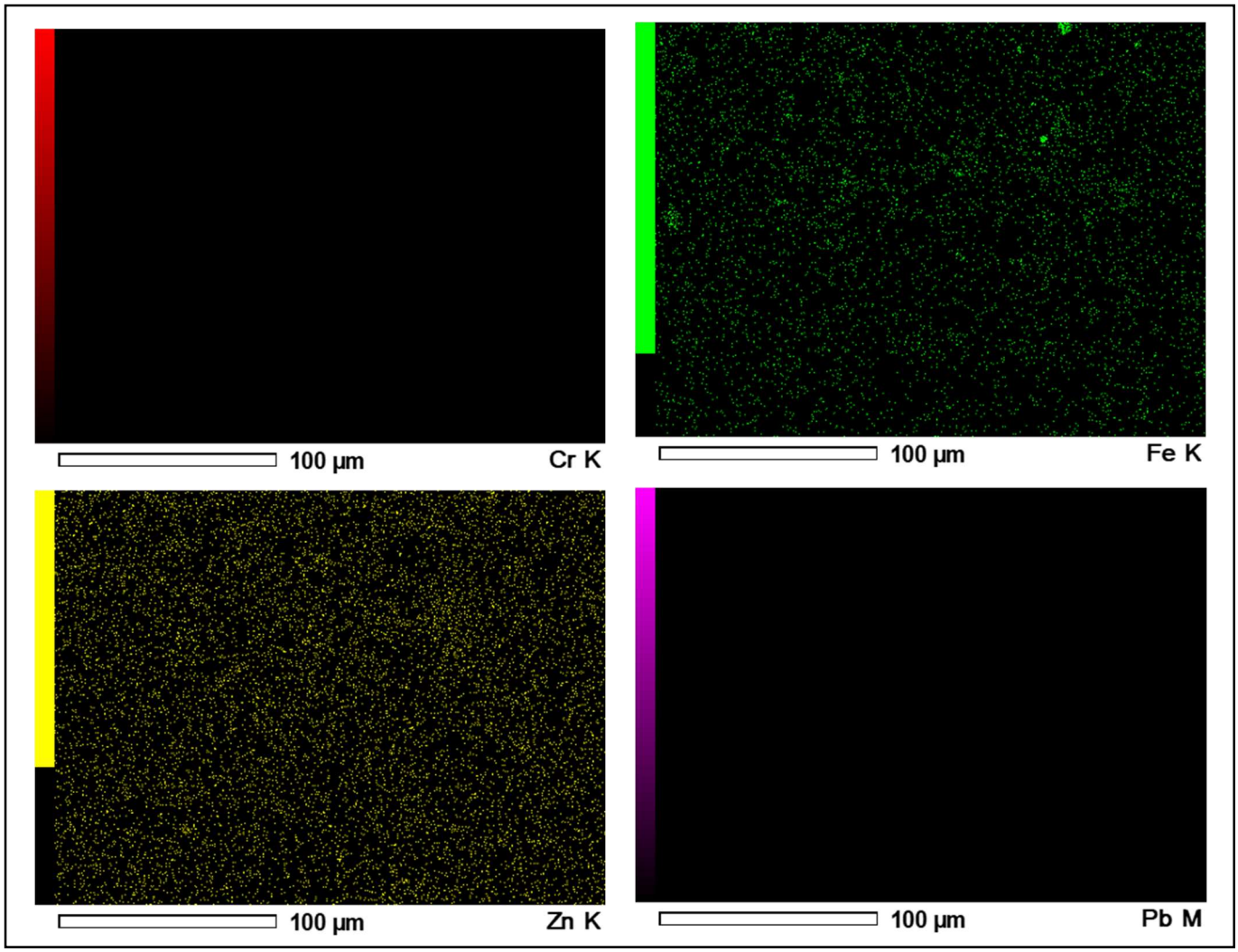
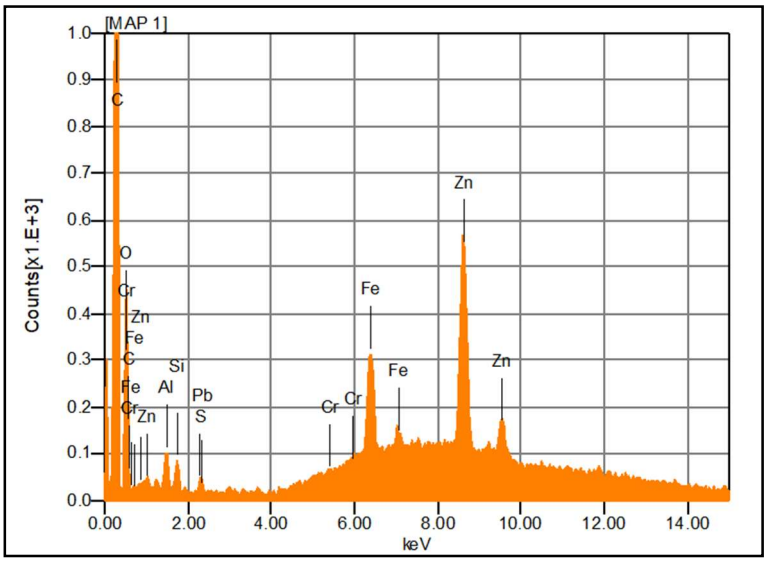


Figure 19, continued (top); Figure 20 (bottom)





5. Conclusions:

According to the data provided from the micrographs and spectra that were collected using the scanning electron microscope, absolutely no lead (Pb) was present in any of the three crumb rubber pellet samples that were collected from Alfred University's, Brockport State College's, and Alfred State College's athletic fields. The quantitative methodology that was developed to test the crumb rubber pellet samples for lead also did not show there to be lead in the Alfred University crumb rubber sample. With this being said, just because the two methods used in this investigation did not show there to be any lead in the crumb rubber samples, does not automatically mean that the possibility of lead in crumb rubber turf pellets can be dismissed. There are a few reasons why individuals in the scientific community should continue to investigate the chemical composition of these crumb rubber pellets.

The methodology used in this study is slightly flawed, as only a handful of the crumb rubber pellets from the millions of pellets on the fields were tested. There is a possibility that other crumb rubber pellets do in fact contain lead. In order to prevent this disparity, future studies done on crumb rubber should work to incorporate a method that allows for more than just a couple crumb rubber pellets to be examined. Investigators could collect multiple crumb rubber samples from all over the field instead of just collecting one crumb rubber sample to avoid this same problem in the future.

Interestingly, although none of the crumb rubber pellets that were investigated contained lead, all three of the samples contained trace amounts of zinc. Zinc is another one of the heavy metals that multiple past investigators have focused on when researching the potential carcinogenic nature of crumb rubber pellets used as infill on artificial turf fields. Zinc products are used on tires during vulcanization, which is a consolidated large-scale process to cross-link

rubber chains, forming a three-dimensional network, which provides mechanical properties, such as elasticity and tensile strength for the tires (Mostoni, 2019) Zinc oxide (ZnO), is a compound that is heavily relied upon within the rubber industry, as it works great when used as a chemical activator during the vulcanization process. Unfortunately, a high amount of ZnO is required during the compounding process, as ZnO is hydrophilic, and rubber is hydrophobic (Mostoni, 2019). Because so much Zn is required during this process, the crumb rubber turf pellets are much more likely to leach zinc into the environment as a result. Although zinc is a natural element and is generally considered to be the least harmful of the heavy metals, it does become toxic to humans above a critical concentration (Mostoni, 2019). Zinc excess may contribute to various health problems, including metabolic diseases, endocrine diseases, neurodegenerative diseases, immune deficiencies, cardiovascular diseases, and cancers (Wang, 2019). It would be beneficial for the scientific community to further investigate the presence of zinc within crumb rubber turf pellets as well and determine if the amounts of zinc within the crumb rubber is at levels that is hazardous for human health.

Artificial turf fields require the crumb rubber infill to be replaced every several years. The decision to continue to fill artificial turf fields with crumb rubber is one that requires much thought for athletic administrators, and field-owners world-wide. Although there is no definitive evidence available that shows there to be hazardous chemicals in crumb rubber that cause cancer, there are definitely an increasing number of studies that have been published that prove there to be known carcinogens in some samples of crumb rubber. It is difficult to just completely abandon artificial turf fields all together, but certain decisions can be made to potentially lower an athlete's risk of playing on these fields. If an athletic director or grounds manager are faced with the choice of whether to order cryogenically ground rubber tires or mechanically ground

rubber tires, they should go with the first option. Mechanically ground tires typically have higher inhalable fractions than cryogenically ground rubber tires. (NTP, 2019). Inhaling the crumb rubber pellets should be avoided, if possible, as more research is required to determine whether these pellets contain carcinogenic substances in amounts high enough to be hazardous to human health. Cork seems to be an effective infill alternative for artificial turf fields. With this being said, cork is a type of plastic, and any plastic infill as well as the crumb rubber both are microplastics. (Armada et al., 2022) Microplastics are considered contaminants of emerging concern since they do not biodegrade and remain in the environment for a long time. (Armada et al., 2022). It may be smart for athletic administrators to start pushing for the use of natural grass fields again. This way, we are not promoting an industry that's main product is harmful to the environment, possibly carcinogenic, and is currently considered to be an emerging contaminant of concern.

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