

**Sulfur Speciation Analyses of Heated Soils using  
X-ray Absorption Near Edge Structure Spectroscopy**

BY

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M.S., University of Illinois at Chicago, 2012

THESIS

Submitted as partial fulfillment of the requirements  
for the degree of Master of Science in Earth and Environmental Sciences  
in the Graduate College of the  
University of Illinois at Chicago, 2012

Chicago, Illinois

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This thesis is dedicated to Byron, Miranda, Francisco, and Gregoria—my loving family, who provided me with encouragement and support throughout my graduate studies.

## ACKNOWLEDGEMENTS

I would like to thank my thesis committee—Kathryn Nagy, Roy Plotnick, and D’Arcy Meyer-Dombard—for their support, guidance, and advice. I would like to especially thank Kathryn Nagy for her patience, kindness, and for giving me the opportunity to explore environmental science from a new perspective. Thank you also to Alain Manceau from the Centre National de la Recherche Scientifique who led the acquisition of all of the X-ray scans performed on the soil samples; this project could not have been accomplished without him. I would also like to thank Matthew Marcus from the Advanced Light Source for help with the X-ray experiments and for providing the software used for spectral analyses, and Ben Kamark from the University of Colorado Boulder who collected the soil samples and performed the heating experiments used in this study under the guidance of Joseph N. Ryan (CU Boulder) and George R. Aiken (USGS).

I would like to thank the faculty, staff, and students of the Department of Earth and Environmental Sciences at the University of Illinois at Chicago, especially Kim Stallings and Ken Kearney of the Nagy Research Group, Sayaka Araki, and Kristin Woycheese. Your friendship and encouragement were beacons of light through my path in graduate school.

In addition, I acknowledge the National Science Foundation who funded my research and graduate school studies via a Graduate Research Fellowship, an IGERT Training Fellowship and Grant EAR-0952311. I would like to thank Mary Ashley, who headed the LEAP IGERT fellowship program at UIC; the experiences provided by the LEAP IGERT program were memorable and irreplaceable. Many thanks also to the following LEAPers: Kelly Granberg, Janet Backs, Elaine Grehl, and Mike Iverson; and, to Jayashree Prabhu,

### **ACKNOWLEDGEMENTS (continued)**

Priscilla Viana, and Solidea Bonina from the Civil and Materials Engineering Department for your friendship and advice.

Lastly, with warmest affection, I would like to thank my wonderful family.

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## SUMMARY

The determination of sulfur speciation changes in soils that result from wildfires is important for understanding the mobility of soil mercury (Hg), which is most strongly bound to reduced sulfur ligands. The transport of leached sulfate and Hg particulates to water bodies is enhanced after a fire as a result of increased susceptibility of soils to erosion, and could increase the production of toxic methyl mercury. X-ray absorption near-edge structure spectroscopy was used to measure the changes in sulfur speciation of soils collected from near Vallecito Reservoir (Durango, CO), an area affected by the 2002 Missionary Ridge wildfire. A soil sample from a burned area in this region was heated at 225°C for 120 min. Separate aliquots of another soil from an unburned area were heated in a muffle furnace for 120 min at 25, 150, 175, and 225°C, and at 225°C for 15, 30, and 345 min. In general, the fraction of sulfate increased by 71 to 209%, and the sulfoxide, reduced aliphatic sulfur, sulfonate, and sulfone fractions decreased by 80 to 98%, 55 to 91%, 40 to 49%, and 23 to 39%, respectively. The fraction of aromatic sulfur remained relatively unchanged. When changes in only the organic sulfur content were considered, the reduced aromatic sulfur content increased by 35 to 86%, while the sulfonate and sulfone content remained relatively the same at 21 to 25% and 5 to 6%, respectively. Sulfoxide and reduced aliphatic sulfur content decreased by 71 to 96% and 30 to 79%, respectively. The fractions of sulfite and sulfonium content were generally < 2% of the total sulfur. The apparent oxidation of reduced aliphatic sulfur due to heating suggests that mercury originally bound to these functional groups is likely released during a wildfire. Some mercury may persist, however, bound to reduced aromatic or aliphatic sulfur that remain in the soil or to weaker chemical functional groups in soil organic matter or minerals. Mercury(II) may therefore be more readily

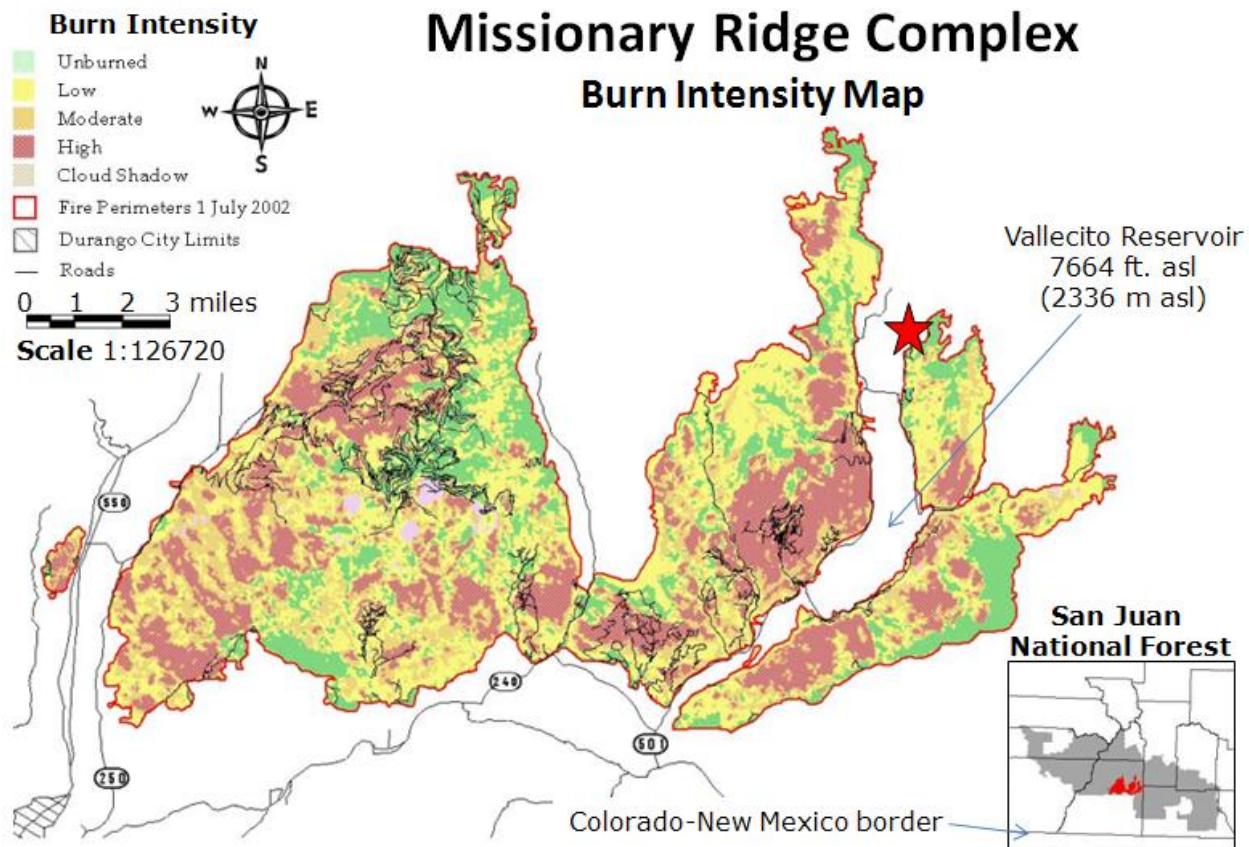
### **SUMMARY (continued)**

mobilized during precipitation events and, in addition to the increase in oxidized sulfur that provides a leachable source of sulfate, may possibly contribute to enhanced methylation in nearby surface waters.

## INTRODUCTION

This study is part of a collaborative project with researchers at the University of Colorado Boulder, the United States Geological Survey (USGS), and the Centre National de la Recherche Scientifique to determine how the Missionary Ridge Wildfire affected Hg mobility near the Vallecito Reservoir (Durango, CO). In June and July of 2002, the Missionary Ridge wildfire burned >70,000 acres (>28,000 ha) of forest in southwestern Colorado [Figure 13; 1]. Portions of the San Juan National Forest were affected, which included stands of mixed conifers (e.g., firs, spruces, pines), oaks, and aspens [1, 2]. The fire also affected the perimeter of the Vallecito Reservoir, which is located in the south-central portion of the San Juan National Forest (Figure 1). Within three months of the fire, rainfall from storms caused considerable surface runoff, flooding, and debris-flow because of a reduction in vegetation cover and the hydrophobicity of soils caused by fire [1, 2]. In 2006, a study on fish collected from the reservoir two years after the fire concluded that a consumption advisory should be placed on two fish species because of high levels of Hg [3]. Nearby coal-fired power plants may have been a major source of Hg to the Vallecito Reservoir area prior to the fire. A study on sediment cores from the Narraguinne Reservoir (located approximately 75 mi west of Vallecito Reservoir) concluded that the most likely source of Hg to the reservoir was atmospheric emissions from coal-fired power plants [4]. The Missionary Ridge Wildfire may have remobilized Hg that otherwise would have remained in the soil. Because Hg binds most strongly to reduced sulfur (S) in soils, an understanding of the forms of soil S before and after the wildfire is critical to comprehending possible changes in Hg input and bioavailability in the reservoir.

**Figure 1.** Map of the Missionary Ridge Complex, which shows the boundaries and burn intensities of the Missionary Ridge wildfire that occurred in June and July of 2002 (based on July 1, 2002 satellite data). The red star (★) approximates the Vallecito Reservoir VR-4 and VR-5 sampling locations. (This map was edited and reproduced with permission from the U.S. Forest Service Department of Agriculture – San Juan National Forest Office. The original map was created by the Missionary Ridge Complex Burned Area Emergency Response (BAER) Team, the U.S. Department of the Interior Bureau of Land Management, the U.S. Geological Survey, and the U.S. Forest Service Department of Agriculture.)



X-ray absorption spectroscopy (XAS) and adsorption studies on organic methyl mercury [5, 6] and inorganic mercury(II) species [7-10] have shown that both types of mercury preferentially bind to reduced organic sulfur moieties in natural organic matter. Soil organic sulfur may range between 70 to 95% of the total sulfur in mineral soil (i.e., A, E, and B horizons) and up to 99% of the total sulfur in organic soil [i.e., O horizons; 11, 12]. In general, the total content of sulfur in soil may range between 0.002 to 3.5%<sub>wt</sub> [13]. The effects of fire and heat on the total sulfur content in foliage, litter, and soil have been studied previously; however, how controlled burning and wildfire affect organic sulfur speciation in the mineral soil has been largely uninvestigated.

In prescribed fires, significant decreases have been observed in the total sulfur content of forest litter [14] and organic O horizons [12, 15]. For example, Binkley et al. [12] observed a 38.3% and 49.6% decrease ( $p < 0.10$ ) in the total sulfur content of the Oe and Oa horizons of a loblolly and longleaf pine forest burned annually and biennially, respectively. However, observed changes in the total sulfur content in mineral soil horizons have been varied [12, 14, 16] or not measured at all [15]. In studies by Ponder et al. [14] and Binkley et al. [12], no significant changes in the total sulfur content in mineral soil horizons were observed after a prescribed fire, while in a study by Castelli et al. [16] increases in the total sulfur content in mineral soil horizons from a shrubland and grassland were observed one year after a prescribed burn. Castelli et al. [16] attributed the observed increase to enhanced microbial mineralization processes in the shrubland and to litter accumulation from the rapid growth of herbaceous vegetation in the grassland after the prescribed fire.

With respect to natural wildfires, Murphy et al. [17] observed a decrease in the total sulfur content in the organic soil horizons after a wildfire event in a mixed coniferous forest,

while Czimczik et al. [18] observed no significant changes in the total sulfur content of the organic soil horizons in a boreal forest following a wildfire. In both studies, sulfur content in the mineral soil horizons was not measured.

In a laboratory study, the total mass of sulfur in forest foliage and litter samples decreased after heating in a muffle furnace at temperatures between 375-575°C, 575-775°C, 775-975°C, and 975-1175°C ( $p \leq 0.05$ ) [19]. Sulfur losses in the forest litter were significant after five minutes of heating over all temperature ranges, however no statistically significant changes were observed when samples were heated further for 30 and 60 min. In other investigations, the amount of sulfate that could be leached from forest litter and soil before and after fires and after laboratory-controlled heat treatments were measured [17, 20-22]. Yet in all of these studies, changes in the relative proportions of reduced sulfur species and in the amounts of reduced sulfur species that were oxidized within the mineral soil by fire and heat have not been investigated.

In previous studies, chemical fractionation approaches were used [11, 23, 24] to determine the relative amounts of inorganic and organic sulfates, inorganic sulfur, and carbon-bonded sulfur in soils [11, 23, 24]. Strehl and Prietzel [25] further refined these techniques to determine the contents of combined organic thiols and disulfides in foliage and organic soil. However, chemical fractionation cannot distinguish the presence of many other specific sulfur groups (e.g., sulfones, sulfoxides, and monosulfides). Also, samples may not be reused after a fractionation analyses because samples are destroyed in the chemical process. Fortunately, non-destructive sulfur X-ray absorption near edge structure (S-XANES) spectroscopy has been gaining more use over the past two decades to probe sulfur speciation in natural organic matter [6, 7, 10, 26-33] and whole soils [34-40]. With S-XANES, detailed

sulfur speciation is possible because the absorption edge energy of the sulfur atom in a molecular configuration correlates with the oxidation state of sulfur [28, 41]. Gaussian functional fits [28] or linear combination fits using the spectra of model compounds [41] have been used to determine the relative amounts of specific sulfur species in a sample.

In this study, we used S-XANES spectroscopy to determine changes in the relative proportions of sulfur species in unheated and heated mineral soil samples from near the Vallecito Reservoir and from laboratory experiments, in which the effects of heating time ( $t = 0, 15, 30, 120, \text{ and } 345$  minutes) and temperature ( $T = 25, 150, 175, \text{ and } 225^{\circ}\text{C}$ ) were evaluated. In addition, the relative amounts of reduced sulfur species, which have the potential to bind to inorganic mercury(II), that were oxidized within the mineral soil were also measured. Our results on the changes in speciation of sulfur in soil will ultimately be combined with data from our collaborators on the organic matter and mercury concentration of the same soils. The combined results will be used to characterize the nature of mercury that may be available for microbial methylation reactions in both the soils and the eroded materials transported to the Vallecito Reservoir.



## MATERIALS AND METHODS

**Forest Soils.** *Sample Collection and Preparation.* Unburned (VR-4) and naturally burned (VR-5) soil samples were collected near the Vallecito Reservoir (Bayfield, CO) during May of 2009 by B. Kamark—a student collaborator studying mercury remobilization during forest fires at the Department of Civil, Environmental, and Architectural Engineering at the University of Colorado Boulder. The red star in Figure 1 indicates the approximate sampling locations. The VR-4 soil samples were from a site that showed no visual or satellite evidence of the Missionary Ridge wildfire, while VR-5 soil samples were collected from a site where the entire heights of 95% of the trees in the area were burned. Samples were obtained from the top seven centimeters of soil at each site and stored in a freezer within 24 and 48 hours of sampling. Soils were then freeze dried, passed through a 25-mesh (710  $\mu\text{m}$ ) sieve, and homogenized with an agate mortar and pestle.

*Heating Experiments.* As part of the Hg remobilization studies, soil heating experiments (Table 1) were also conducted by B. Kamark. For this study, these experiments served to investigate the effects of heat on the evolution of sulfur speciation in forest soils. To examine the effects of heating time, 10 g portions of prepared VR-4 soil were placed in separate eight centimeter diameter crucibles and heated in a muffle furnace at 225°C for 15, 30, 120, or 345 minutes. A 10 g portion of VR-5 soil was also placed in a crucible and heated at 225°C for 120 minutes. To examine the effects of temperature, 10 g portions of prepared VR-4 soil were placed in separate crucibles and heated at 150 or 175°C for 120 minutes. The soil temperatures used were similar to those reported during a prescribed forest fire at soil depths between one and two inches below ground level [42]. All experiments were conducted in triplicate, after which, individual soil samples were combined according to heat treatment.

**Table 1. SUMMARY OF EXPERIMENTAL HEAT CONDITIONS APPLIED TO VR-4 AND VR-5 SOILS.**

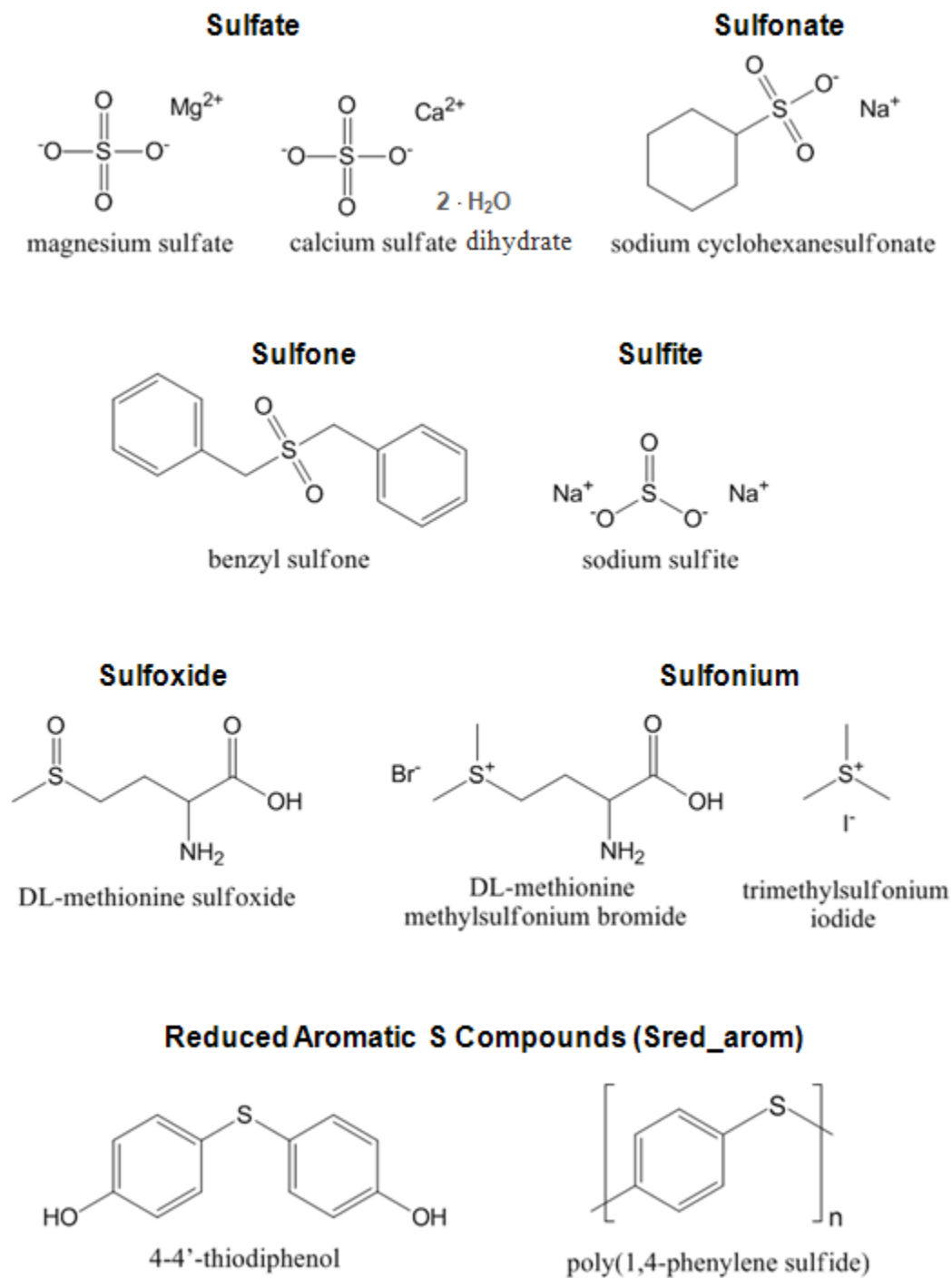
		<b>Sample Name</b>	<b>Temperature (°C)</b>	<b>Time (min)</b>
<i>Time series</i>	VR-4	4U	n/a	n/a
		V4_15	225	15
		V4_30	225	30
		4225	225	120
		V4_345	225	345
	VR-5	5U	n/a	n/a
		5225	225	120
<i>Temperature series</i>	VR-4	4U	n/a	n/a
		4150	150	120
		4175	175	120
		4225	225	120

n/a = not applicable

Control samples consisted of prepared VR-4 and VR-5 soils that remained unheated (labeled in tables and figures as 4U or 5U, to represent VR-4 or VR-5 unheated control samples, respectively). This procedure allowed us to view snapshots of how temperature and heating times affected sulfur speciation in soil under forest fire conditions.

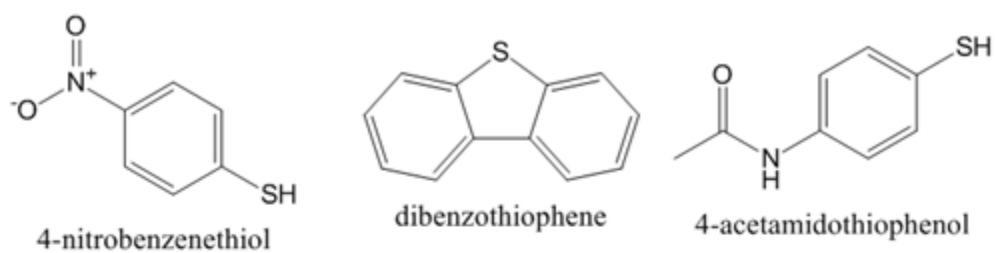
*Total Sulfur and Organic Matter Content.* Total soil sulfur content was measured by Huffman Labs (Golden, CO) and soil organic matter content was estimated by loss on ignition at 550°C [LOI 550; 43] at the United States Geological Survey (Boulder, CO).

**Reference Compounds.** The following S-XANES reference sulfur compounds were obtained from Fisher Scientific and Sigma-Aldrich, and used as received with no further purification: magnesium sulfate, calcium sulfate dihydrate, sodium cyclohexanesulfonate,

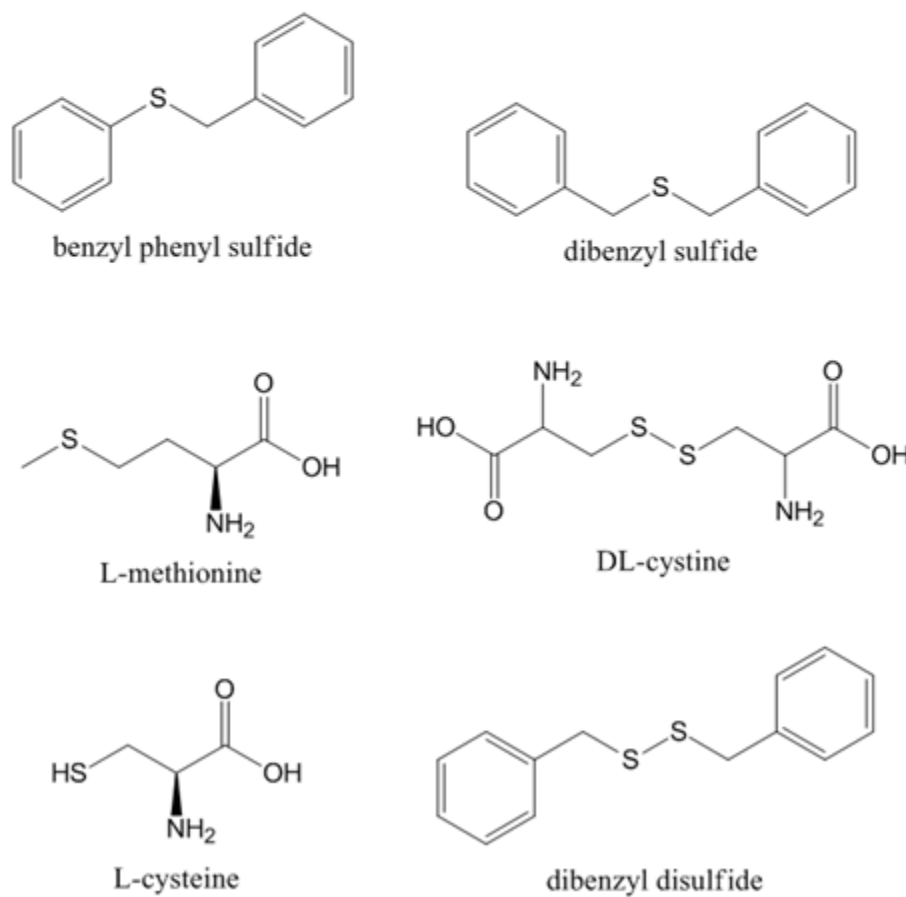


**Figure 2.** Chemical structures of reference sulfur compounds.

### Reduced Aromatic S Compounds (Sred\_arom)



### Reduced Aliphatic S Compounds (Sred\_aliph)



**Figure 2.** Chemical structures of reference sulfur compounds (continued).

benzyl sulfone, sodium sulfite, DL-methionine sulfoxide, DL-methionine methylsulfonium bromide, trimethylsulfonium iodide, 4-4'-thiodiphenol, poly(1,4-phenylene sulfide), 4-nitrobenzenethiol, dibenzothiophene, 4-acetamidothiophenol, benzyl phenyl sulfide, dibenzyl sulfide, L-methionine, DL-cystine, L-cysteine, and dibenzyl disulfide (Figure 2).

An observed form of mercury bound to organic sulfur from a mercury-contaminated floodplain soil near Oak Ridge, TN was also used as a S-XANES reference compound. The structure of this species is similar to that of mercury(II) thought to be coordinated to aromatic organic sulfur moieties, which was observed in the experimental uptake of mercury(II) by peat [10].

**X-ray Absorption Spectroscopy (XAS).** All XAS experiments were conducted under room temperature conditions at beamline 10.3.2 at the Advanced Light Source, Lawrence Berkeley National Laboratory (ALS-LBNL). The top-off current at the ALS was 500 MA.

Micro-X-ray fluorescence ( $\mu$ -XRF) mapping and micro-X-ray Absorption Near-Edge Spectroscopy ( $\mu$ -XANES) at the S-K edge were used to locate and determine the speciation of sulfur in the soils. Fluorescence detection was used to collect the XANES data for the soil samples and the organic sulfur compound that was obtained from near Oak Ridge, TN. A two-crystal Si (111) monochromator was used to focus X-rays into a He-N<sub>2</sub> gas-filled ionization chamber and fluorescence signals were recorded with a seven element Ge detector (Canberra; Meriden, CT). The estimated uncertainty in energy is 0.1 eV [44]. All soil sample measurements were conducted under ambient air conditions.

For reference sulfur compounds, XANES spectra at the S-K edge were collected in transmission mode using total-electron-yield (TEY) detection, which minimizes self-absorption effects that results from the analysis of concentrated and/or thick samples [45].

*Forest soils.* Soil samples were first ground and homogenized using an agate mortar and pestle. Most ground samples were pressed into circular pellets (~5.0 mm diameter and ~0.5 mm thick) and a few (unheated VR-4, unheated VR-5, and VR-4 heated at 225 °C for 120 min) were prepared as thin films by pressing a small amount of ground soil between two pieces of Kapton tape. Pellets and thin-film samples were individually mounted onto sample holders and scanned. Multiple regions of each soil sample were examined (Table 2), and grey-scale and bicolor XRF maps were created for each region. The pixel (or spot) size used for all maps was 7  $\mu\text{m}$  x 7  $\mu\text{m}$  and all maps were adjusted to a common sulfur “white level” for ease of visual comparison. Grey-scale maps were used to select the locations for  $\mu$ -XANES analyses. Bicolor maps were used to detect the presence of sulfur and iron (Fe) so that possible locations of Fe-S minerals (e.g., pyrite) could be identified.

For each soil sample except one (VR-4 soil heated at 225°C for 120 minutes; n = 7) individual XANES spectra at the S-K edge were measured from at least 20 areas where diffuse concentrations of sulfur were detected on the XRF maps. Bright spots on the maps were avoided because these regions were dominated by inorganic mineral sulfates. Sulfur and iron signals from bicolor maps did not correlate well, indicating that there were no obvious Fe-S spots to avoid.

Sample spectra were calibrated to the absorption edge for calcium sulfate dihydrate, whose main white line peak was assigned to the energy position of 2482.74 eV. Scans were obtained between 2420 and 2625 eV (approx. -60 below and +140 eV above the sulfur K-

**Table 2.** XRF SCANNING CONDITIONS USED TO MAP SOIL SAMPLES

	Sample	Incident energy (eV)	Map size (µm x µm)	Dwell time (ms/pixel)	Horiz. slits <sup>a</sup> (µm)	Vert. slits <sup>a</sup> (µm)
VR-4	4U	2481.3	400 x 400 <sup>5</sup> 1500 x 1500 <sup>6</sup>	200 <sup>5</sup> 140 <sup>6</sup>	100 <sup>1</sup> 300 <sup>4</sup> 120 <sup>6</sup>	50
	4150	2481.0	500 x 500 <sup>1</sup> 1000 x 1000 <sup>2</sup>	140	120	50
	4175	2481.0	1000 x 1000 <sup>1</sup> 1500 x 1500 <sup>2</sup>	140	120	50
	V4_15	2481.0	1000 x 1000 <sup>1</sup> 1500 x 1500 <sup>2</sup>	140	120	50
	V4_30	2481.0	1000 x 1000 <sup>1</sup> 1500 x 1500 <sup>2</sup>	140	120	50
	4225	2481.3	600 x 600 <sup>1,3</sup> 400 x 400 <sup>2</sup>	140	100	50
	V4_345	2481.0	1500 x 1500 <sup>1</sup> 1000 x 1000 <sup>2</sup>	140	120	50
VR-5	5U	2481.3 <sup>5</sup> 2482.0 <sup>7</sup>	400 x 400 <sup>1</sup> 400 x 300 <sup>4</sup> 1000 x 1000 <sup>7</sup>	140	100 <sup>5</sup> 120 <sup>7</sup>	50
	5225	2481.0	1000 x 1000 <sup>1</sup> 1500 x 1500 <sup>2</sup>	140	120	50

<sup>a</sup> The horizontal and vertical slit sizes correspond to the aperture dimensions of adjustable slits, which control the size of the impinging beam on the soil sample.

<sup>1</sup> Region 1

<sup>3</sup> Region 3

<sup>5</sup> Regions 1 to 3

<sup>7</sup> Regions 4 and 5

<sup>2</sup> Region 2

<sup>4</sup> Regions 2 and 3

<sup>6</sup> Region 4

edge of calcium sulfate dihydrate). A small step size of 0.2 eV was used between 2460 and 2490 eV to capture spectral details in this region. For all scans, the aperture dimensions of

adjustable slits (cf. footnote, Table 2) were set to a horizontal and vertical width of 300  $\mu\text{m}$  and 50  $\mu\text{m}$ , respectively.

*Reference compounds.* Pure reference sulfur compounds were also ground and homogenized prior to S-XANES analyses. A thin layer of the ground compound was secured onto a metal mount using double-sided electrical tape, which was then placed inside a metal holder that was sparged with helium gas. At least five S-XANES spectra for each reference sulfur compound were obtained. Individual spectra were calibrated relative to the position of a persistent glitch in the  $I_0$  signal, which was likely caused by the setup of electronic equipment at the beamline [46], and then averaged. Aperture dimensions and the energy range of the incident beam were set to the same values as those used for soil samples.

**Spectral Analyses.** The analyses of S-XANES spectra allow for the identification of the presence of a range of sulfur oxidation states. The position of the main white-line peak in a S-XANES spectrum is diagnostic of the oxidation state of sulfur in a sample (Figure 3). The peaks of highly oxidized sulfur functional groups occur at a higher energy than the peaks of reduced sulfur groups. All spectra were analyzed to determine the type and relative amounts of sulfur species in the soil samples. The general procedure was to first normalize the spectra, separate the spectra into groups and subgroups, and then fit the spectra using linear least-squares fitting of reference compounds. The software used in all steps was provided by M. Marcus (ALS-LBNL) and may be downloaded from <http://xraysweb.lbl.gov/uxas/Beamline/Software/Software.htm>.

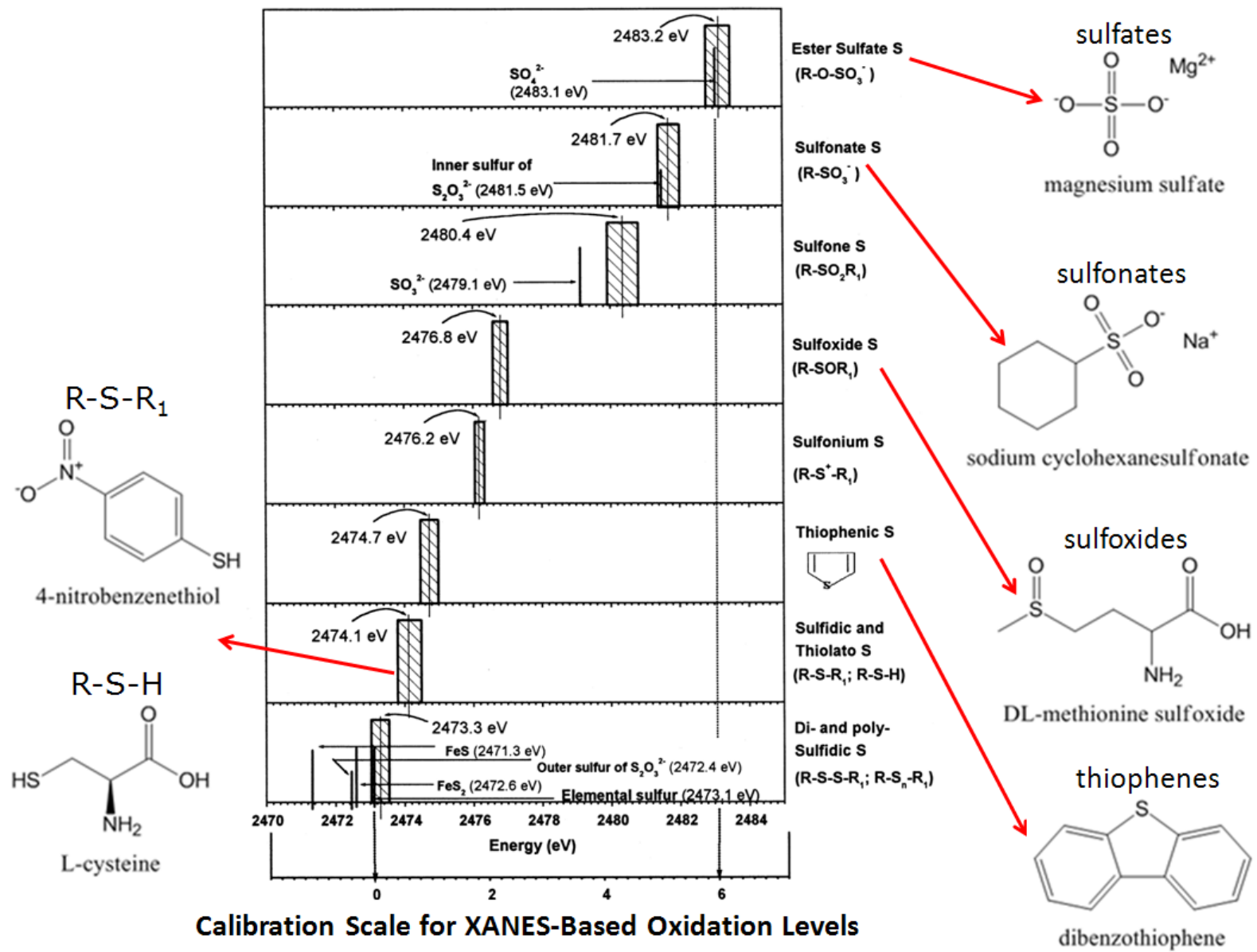
*Normalization.* All individual spectra for both references and samples were normalized as follows. First, a linear background function in the pre-edge region below



**Figure 3.** Variation in the white-line peak position of chemical compounds containing different sulfur functional groups. Hatched blocks represent a range in white-line peak locations for compounds containing the same sulfur functional group. Single-valued lines represent white-line peak locations of inorganic sulfur compounds.

In general, the peaks of highly oxidized sulfur species occur at a higher energy than the peaks of reduced sulfur species. As sulfur oxidation state decreases, the location of the main peak shifts toward lower energies. This is because electrons are easier to excite in sulfur atoms with more populated electron valence shells (i.e., reduced sulfur species). For example, the most oxidized form of sulfur is sulfate, which has an oxidation state of +6, and its white-line peak is positioned around 2483 eV. Sulfonates, which contain sulfur with an oxidation state of +5, has white-line peaks at a lower energy (~2482 eV). The most reduced sulfur species examined in our study are sulfides and thiolates, which have an oxidation state of 0 and -1, respectively, and their white-line peaks occur at around 2471 eV.

The chemical structures shown provide examples of sulfur functional groups investigated in this study (This figure was adapted from Vairavamurthy 1998 [27]; the exact peak positions shown were determined by Vairavamurthy).



~2470 eV was subtracted. Then, the region between ~2510 and 2540 eV was fit with a linear function to normalize the post-edge region to one.

*Spectral groups and subgroups.* Groups and subgroups of spectra for each soil sample were formed to assess the heterogeneity of sulfur species and to help characterize trends and changes in sulfur speciation. Groups and subgroups were determined based on similarities in spectral peak positions and peak height ratios.

For each spectrum, four peaks were measured,  $p_1$ ,  $p_2$ ,  $p_{SO_3}$ , and  $p_{SO_4}$  (Figure 4a), and are defined as follows:

$p_1$  = “first” sulfur peak located between 2470.00 and 2475.50 eV (peak may represent the sum of signals from several sulfur species)

$p_2$  = “second” sulfur peak located between 2475.50 and 2479.00 eV (peak may represent the sum of signals from several sulfur species)

$p_{SO_3}$  = sulfonate shoulder on sulfate peak located between 2479.00 and 2482.00 eV

$p_{SO_4}$  = sulfate peak at 2482.74 eV

Because the calcium sulfate dihydrate peak was calibrated to 2482.74 eV, we expected the sulfonate peak to be located at 2481.34 eV. However, for our initial assessment of spectral variation, we assumed a range of positions for the sulfonate peak that was based on the estimated location of an observed shoulder on  $p_{SO_4}$ . The position of this shoulder shifts depending on the ratio of the amounts of sulfonate and sulfate components.

Once peak positions were identified, the corresponding peak heights were measured. Plots comparing peak positions ( $p_1$  vs.  $p_{SO_3}$ ,  $p_2$  vs.  $p_{SO_3}$ , and  $p_1$  vs.  $p_2$ ) and peak height ratios ( $p_1:p_{SO_4}$  vs.  $p_2:p_{SO_4}$ ;  $p_1:p_{SO_4}$  vs.  $p_{SO_3}:p_{SO_4}$ ; and  $p_2:p_{SO_4}$  vs.  $p_{SO_3}:p_{SO_4}$ ) were then used to assign spectra to groups and subgroups. Each point on a plot represents a measurement from a single spectrum. The plots of  $p_2$  vs.  $p_1$  and  $p_2:p_{SO_3}$  vs.  $p_1:p_{SO_3}$  were the most useful in

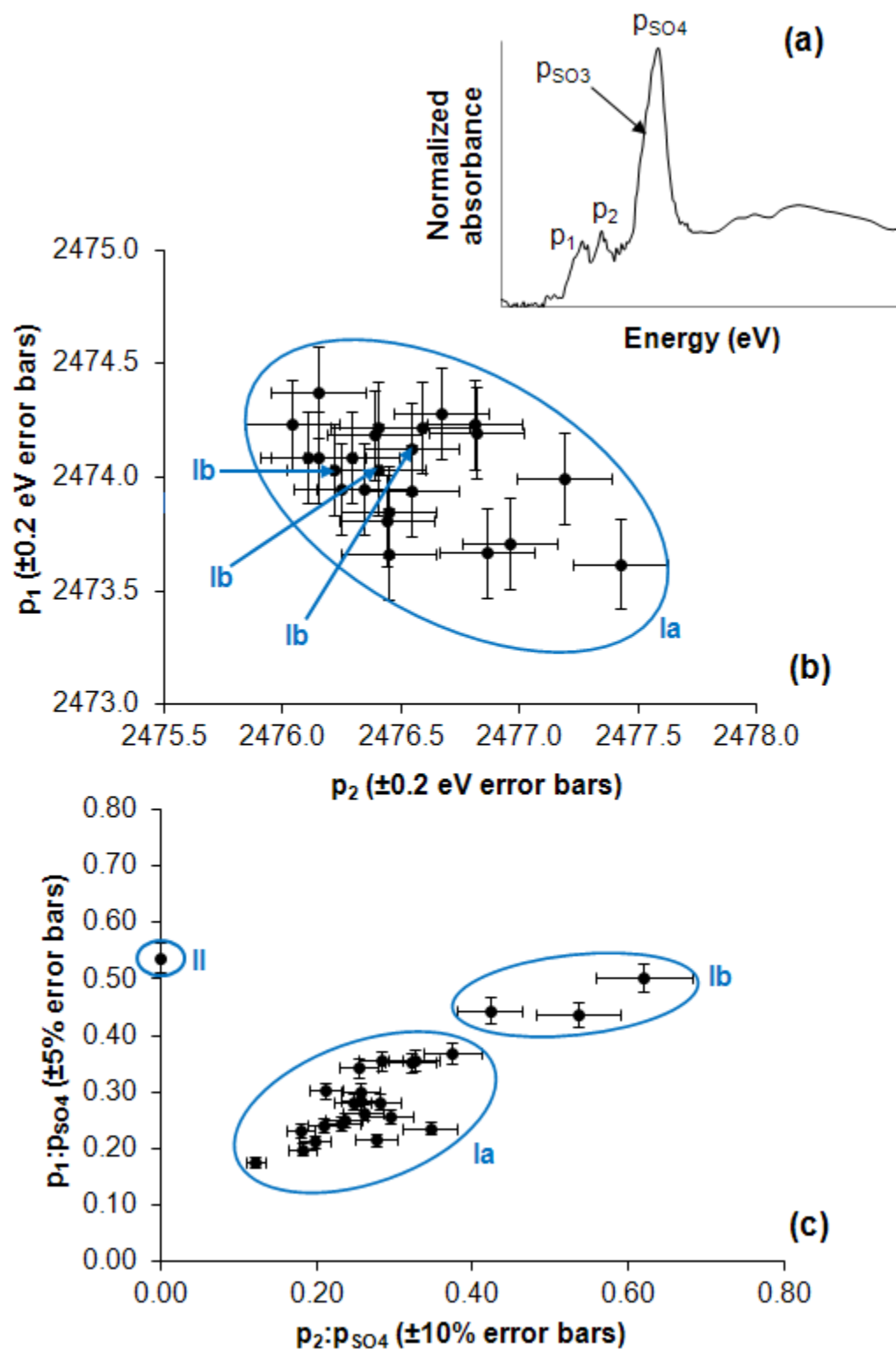
delineating groups and subgroups in the S-XANES spectra of all soil samples (Figures 4b and 4c).

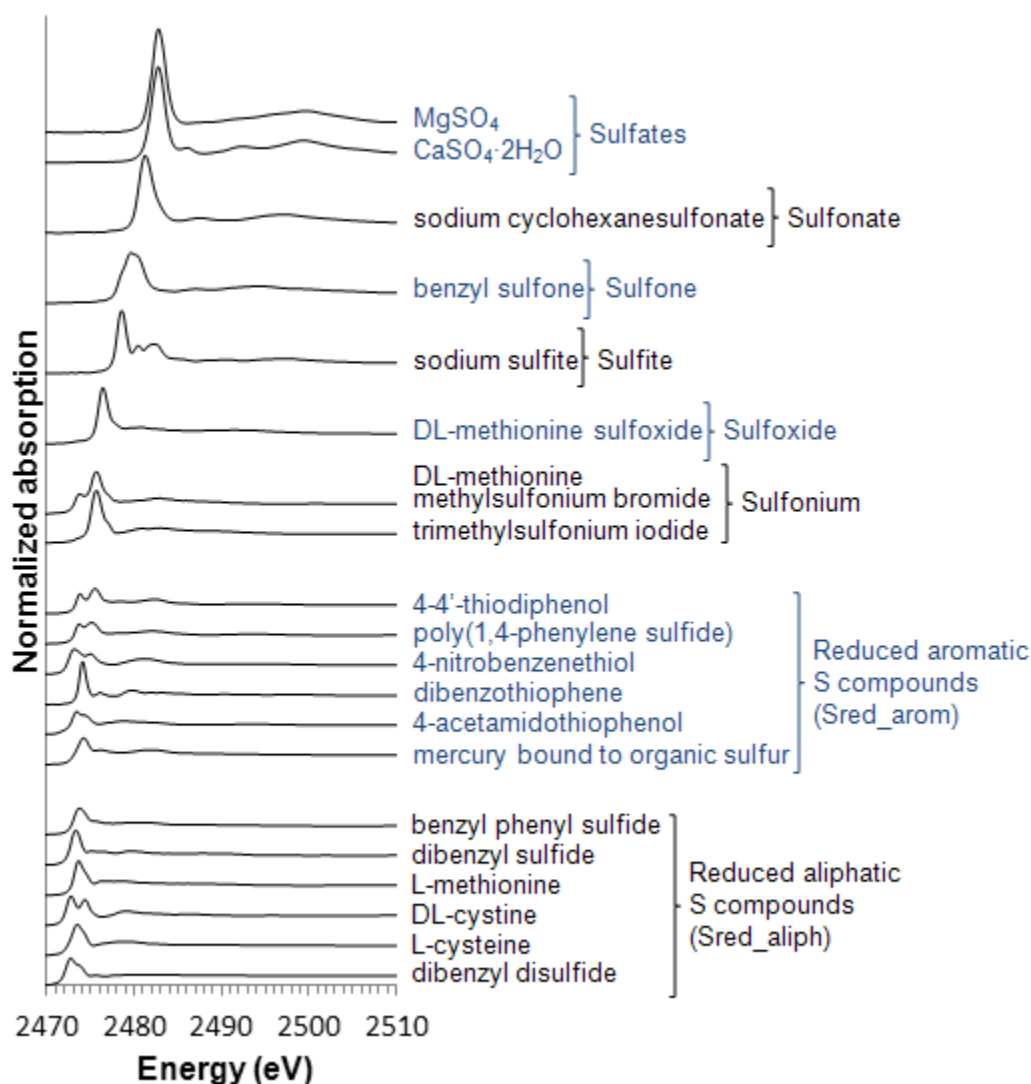
*Linear Least-Squares Fitting.* Linear least-squares fitting was used to determine the types of sulfur present and their relative concentrations in each soil. The program, *Linear fit w overabsorption* [47], was used to fit the spectra of reference sulfur compounds (Figure 5) to the S-XANES spectra of each soil sample. Two energy ranges were examined: a short-energy range (2465 to 2490 eV) and a full-energy range (2465 to 2510 eV). Typically, the short-energy range has been used in previous publications, but the full-energy range captures resonance oscillations of all species (i.e., the extended X-ray absorption fine structure (EXAFS) oscillations beyond the absorption edge).

Two approaches were used to fit all S-XANES spectra over the two energy ranges. In the first approach, all individual spectra within each group and subgroup of a single soil sample were combined and the average,  $+1\sigma$ , and  $-1\sigma$  spectra were calculated. These spectra were then fit to determine the average and  $\pm 1\sigma$  values for each sulfur species. In the second approach, individual spectra were first fit and then the average,  $+1\sigma$ , and  $-1\sigma$  values were calculated for each sulfur species in each group and subgroup.

The steps in the fitting program are as follows. Initially, all sulfur references were included in a calculation. Individual spectra were then systematically removed from a fit in the order of most negative to least negative calculated component value; the program recalculates a fit with the remaining spectra when a single spectrum is removed. After all remaining component fractions became positive, sulfur components that had been excluded were then reintroduced one by one into the list of components. If their calculated fractional values became positive at this step, they were retained. All components with positive

**Figure 4.** Example of plots used to group spectra. Each point on a plot represents a measurement from a single spectrum. (a) Positions of the  $p_1$ ,  $p_2$ ,  $p_{SO_3}$ , and  $p_{SO_4}$  peaks on the S-XANES spectrum of the VR-4 soil burned at 150°C for 120 min. (b) Plot of  $p_2$  vs.  $p_1$  peak positions. The data points for Groups Ia and Ib overlapped because their spectra had similar  $p_1$  and  $p_2$  peak positions. The data point for Group II is absent because its spectrum had no discernible  $p_2$  peak. (c) Plot of  $p_2:p_{SO_4}$  vs.  $p_1:p_{SO_4}$  peak height ratios. Group Ia spectra had smaller  $p_2:p_{SO_4}$  and  $p_1:p_{SO_4}$  peak height ratios than Groups Ib and II spectra, and the Group II spectrum had a  $p_2:p_{SO_4}$  peak height ratio of zero because it had no discernible  $p_2$  peak. An uncertainty of  $\pm 0.20$  eV was assumed for peak positions, while uncertainties of  $\pm 5\%$  and  $\pm 10\%$  were assumed for  $p_1:p_{SO_3}$  and  $p_2:p_{SO_3}$  peak height ratios, respectively.





**Figure 5.** The spectra of reference sulfur compounds, which are grouped and labeled according to the type of sulfur functional group present in its chemical structure. Spectra are also arranged in descending order from most oxidized to least oxidized sulfur moiety.

fractional values were accepted in the final fit, regardless of how small the value. At the end of each fit, the magnesium sulfate and calcium sulfate dihydrate components were summed to provide the sulfate constituent value; DL-methionine methylsulfonium bromide and trimethylsulfonium iodide components were summed to provide the sulfonium constituent value; 4-4'-thiodiphenol, poly(1,4-phenylene sulfide), 4-nitrobenzenethiol,

dibenzothiophene, 4-acetamidothiophenol, and mercury bound to organic sulfur components were summed to provide the reduced S – aromatic compound (Sred\_arom) constituent value; and benzyl phenyl sulfide, dibenzyl sulfide, L-methionine, DL-cystine, L-cysteine, and dibenzyl disulfide components were summed to provide the reduced S – aliphatic compound (Sred\_aliph) constituent value.

*Statistical analyses.* Box plots and histograms were created for each sulfur constituent of each soil sample. The constituent values used were those that were determined using the second fitting approach, where individual spectra were first fit before calculating the average,  $+1\sigma$ , and  $-1\sigma$  of each sulfur component. Because the frequency distribution of each sulfur constituent was generally skewed (see Results), we used the nonparametric Kolmogorov-Smirnov two-sample test [48] to determine if heating temperature and time significantly changed fractional sulfur constituent values. For the Kolmogorov-Smirnov two-sample test, the null hypothesis,  $H_0$ , was that sulfur constituent values were the same across all heat treatments. The alternative hypothesis,  $H_1$ , is that sulfur constituent values were different. We chose a threshold p-value of 0.05 so that if  $p \leq 0.05$ , then there would be a less than 5% chance that the sulfur constituent in a heated sample is not statistically distinct from the unburned soil. All statistical analyses were carried out using MYSTAT (Systat Software, Inc.).



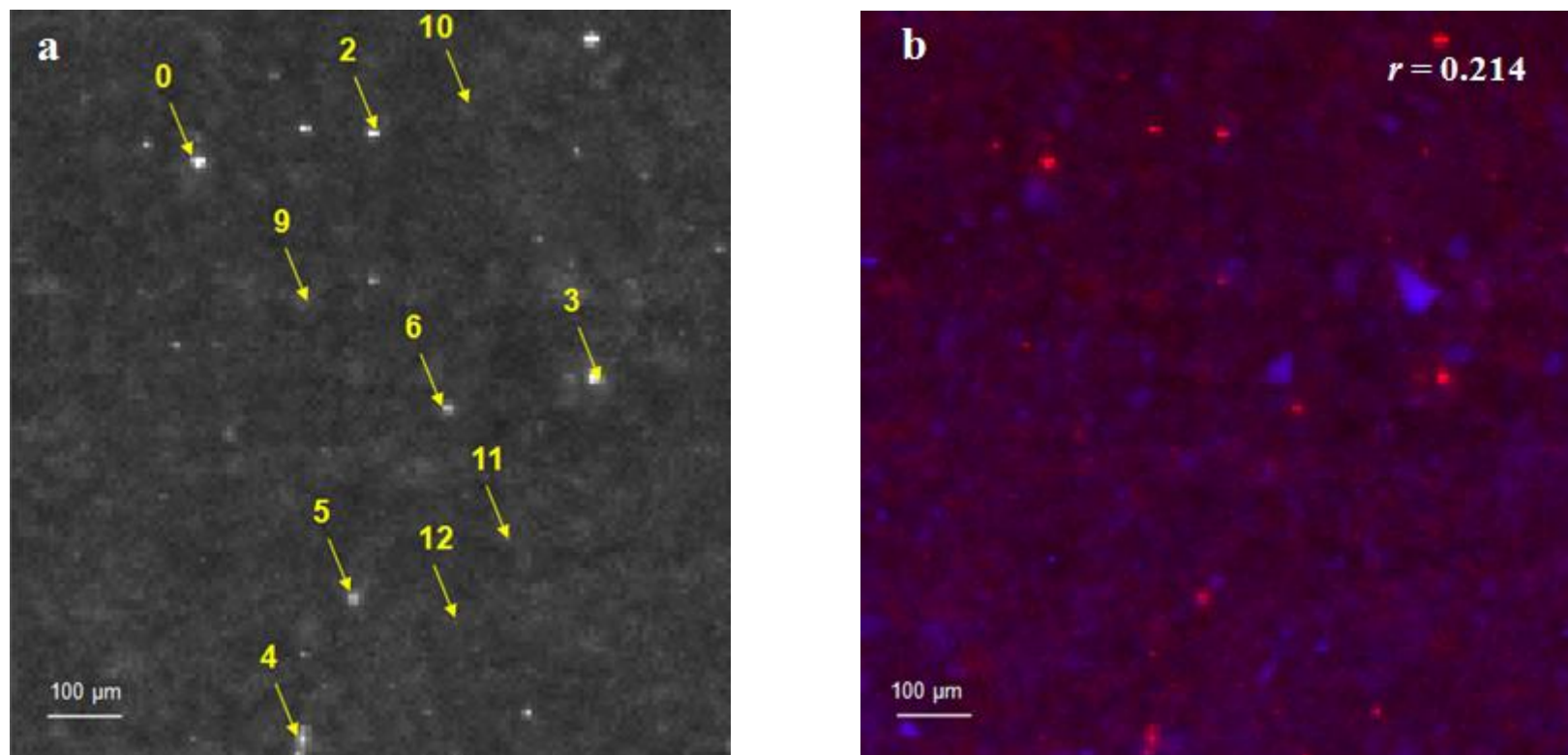
## RESULTS

The  $\mu$ -XRF maps, which are presented first, and demonstrate that the distribution of sulfur in the soils was heterogeneous. This heterogeneity played a role in how we chose our preferred fitting approach, the results of which follow. Finally, the changes in sulfur speciation that occurred during the heating experiments on VR-4 soil (unburned at the field site) are presented, along with a comparison of sulfur speciation in the VR-4 and VR-5 (burned in the Missionary Ridge wildfire) soils.

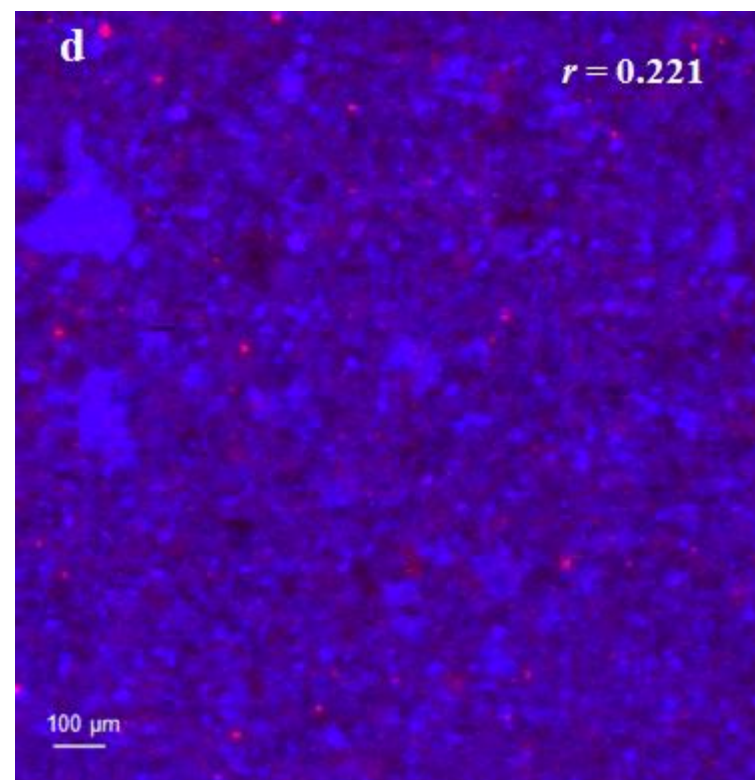
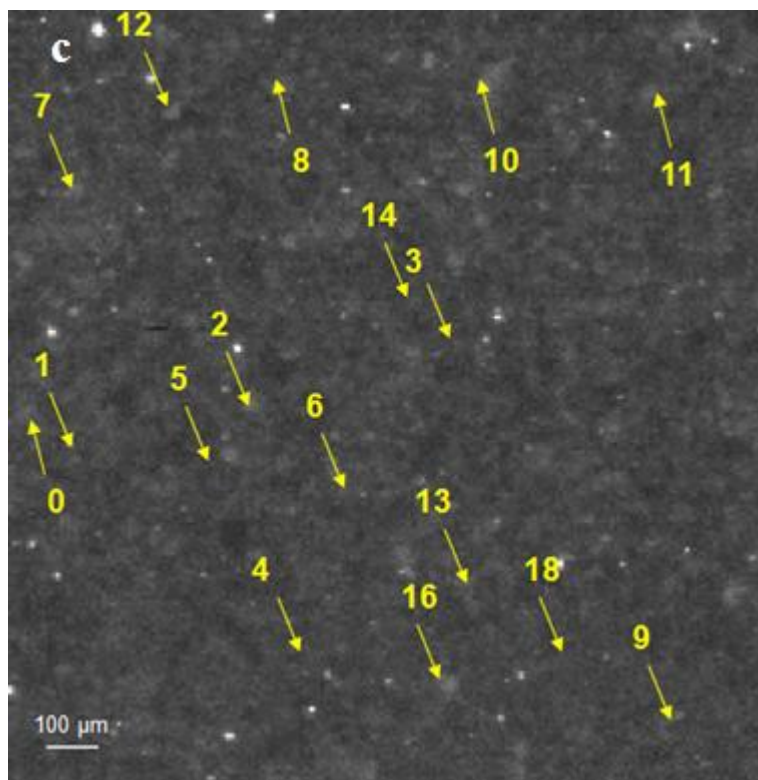
**$\mu$ -XRF Maps.** Although all soils were homogenized prior to XAS analyses,  $\mu$ -XRF maps revealed that the distribution of both sulfur and iron in the soils was heterogeneous (Figures A1-A8; Appendix A). Sulfur concentration varied greatly within each individual soil sample as indicated by regions of diffuse signal in the organic-mineral matrix and bright spots from sulfate minerals (cf., Figures A1a, c, and e; Appendix A). Although areas of high and low iron content were also apparent (cf., Figures 6b and 6d, respectively), iron and sulfur typically were not correlated, as indicated by Pearson correlation values between their XRF signals of  $|r| \leq 0.24$ . These low values also suggest that the amounts of pyrite ( $\text{FeS}_2$ ) and other Fe-sulfides were small.

The numbered arrows in grey-scale maps indicate locations of S-XANES scans. The number of usable spectra (cf., Tables 3 through 8) was usually less than the total number of scans because spectra that were dominated by inorganic sulfates and those marred by electronic glitches were excluded from further analyses.

**Selection of Best Fitting Approach.** *Fits of Averaged vs. Individual Spectra.* Both approaches appeared to fit the S-XANES spectra well at energies below, but not above, 2485 eV (Figures 7 and 8). In general, the fit to an average of multiple spectra from a particular



**Figure 6.** (a) Grey-scale XRF map from Region 1 of the VR-4 soil sample heated at 225°C for 30 minutes. Dark areas correspond to regions of low sulfur, while brighter areas correspond to a continuum of increasing sulfur. Numbered arrows indicate the locations of S-XANES scans. (b) Bicolor XRF map from the same sample. Red and blue areas correspond to sulfur and iron, respectively. The Pearson correlation,  $r$ , between the iron and sulfur signals is displayed. Map sizes: 600 μm x 600 μm.



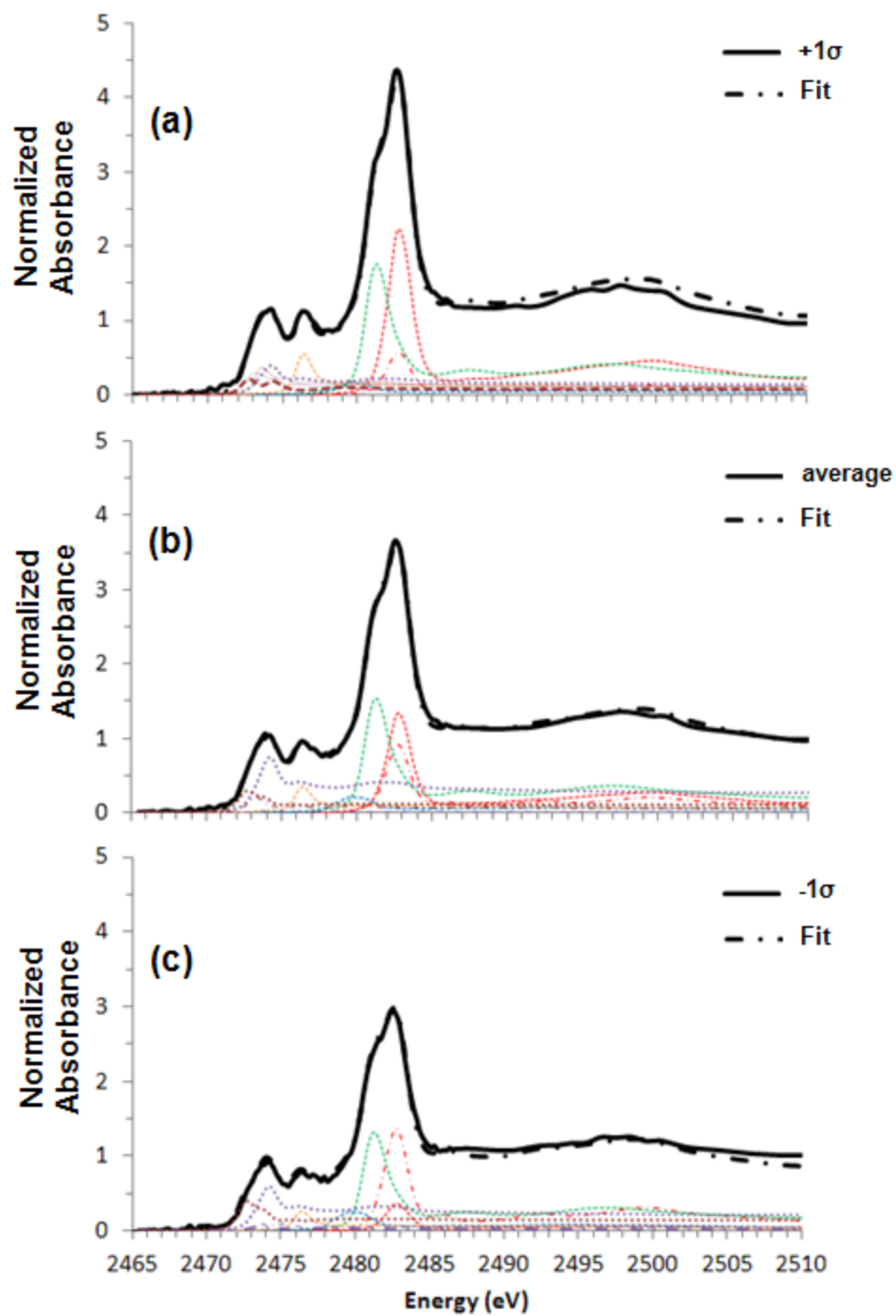
**Figure 6 (continued).** Grey-scale (c) and bicolor (d) XRF maps taken from Region 2 of the VR-4 soil sample heated at 225°C for 30 minutes. Map sizes: 1500 μm x 1500 μm.

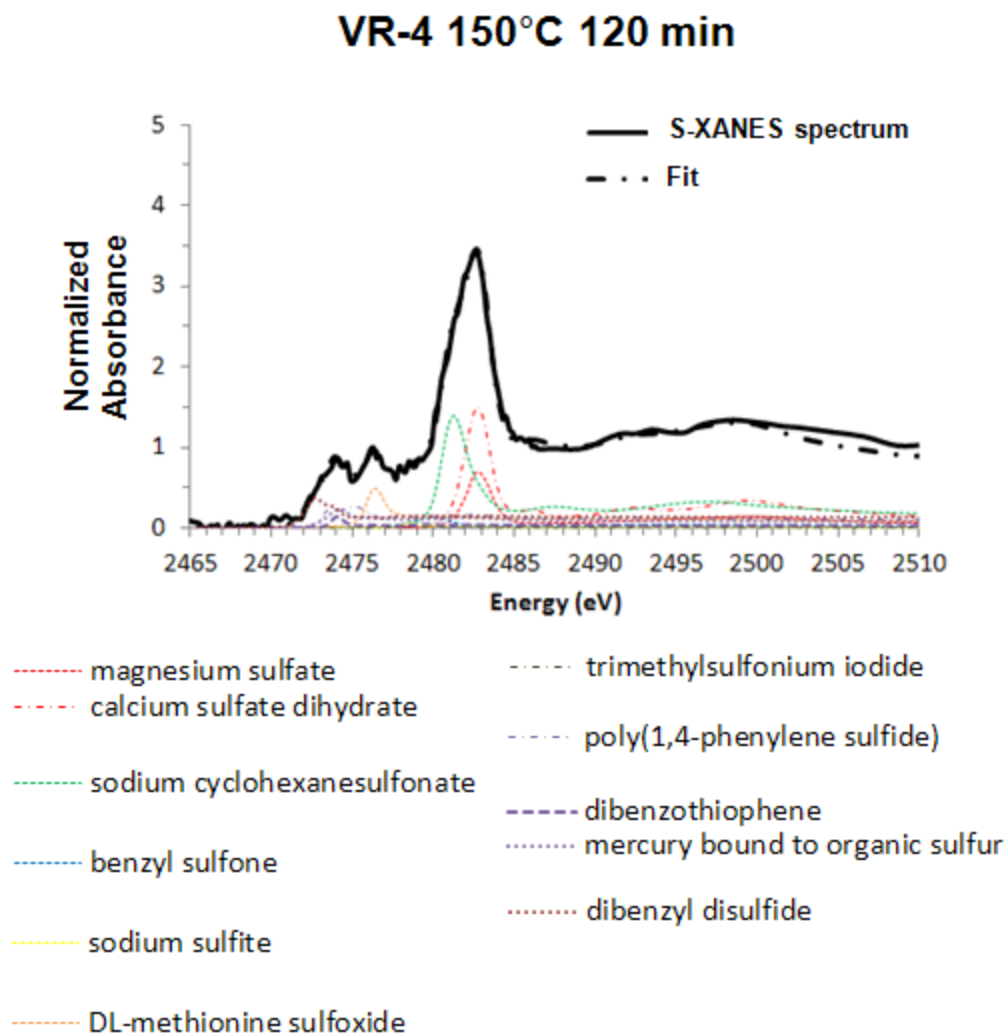
**Figure 7.** Linear combination fit of reference sulfur compounds to the (a)  $+1\sigma$ , (b) average, and (c)  $-1\sigma$  spectra of the VR-4 soil sample heated at  $150^{\circ}\text{C}$  for 120 min.

Legend:

----- magnesium sulfate	- - - - - dibenzyl sulfide
- - - - - calcium sulfate dihydrate	..... L-methionine
----- sodium cyclohexanesulfonate	- - - - - DL-cystine
----- benzyl sulfone	..... dibenzyl disulfide
----- DL-methionine sulfoxide	
- - - - - poly(1,4-phenylene sulfide)	
..... 4-nitrobenzenethiol	
- - - - - 4-acetamidothiophenol	
..... mercury bound to organic sulfur	

## VR-4 150°C 120 min





**Figure 8.** Linear combination fit of reference sulfur compounds to an individual spectrum of the VR-4 soil sample heated at 150°C for 120 min.

soil sample appeared to be precise at all energies, whereas the fitted curve overestimated the  $+1\sigma$  spectrum and underestimated the  $-1\sigma$  spectrum at  $\geq 2485$  eV (Figures 7a and 7c, respectively). For comparison, the calculated fit of an individual spectrum from the same soil sample was also underestimated at  $\geq 2485$  eV (Figure 8). Other fits of individual spectra (not shown) either over- or underestimated the data over the same energy range. Only the fit to the average spectrum of combined spectra (Figure 7b) appears to be precise.

The two approaches also yielded differing fit-determined sulfur species (Figures 7 and 8). However, the fractional amounts of each sulfur constituent were comparable usually to within 15% (Tables 3-8). Larger differences in the fractional amounts of reduced aliphatic sulfur compounds were observed in the following samples: VR-5 unheated (samples were not subjected to laboratory heat treatments, though they had been previously burned by the Missionary Ridge wildfire), VR-4 heated at 175°C for 120 minutes, and VR-4 heated at 225°C for 15 minutes. These were three of four data sets whose spectra could be separated into spectral groups and subgroups (see below). The larger differences typically occurred for sulfur constituents comprising  $\leq 5\%$  of the total sulfur content (e.g., sulfite and sulfonium).

Combining all individual spectra within spectral groups and subgroups (see below) of a single soil sample was performed initially to obtain an average spectrum with an improved signal-to-noise ratio. This approach also generated associated average  $\pm 1\sigma$  spectra, which were fit to obtain the  $\pm 1\sigma$  values for each fractional sulfur species. However, the equal weight assigned to all spectra in the averaging step did not accurately represent the true distribution of sulfur species in the soil. Heterogeneity in the types and distribution of sulfur may have caused exaggerated shapes in the  $\pm 1\sigma$  spectra and a lack of true representative distribution may be the reason why the standard deviations of the sulfur constituents often shared the same sign or were unequal (Tables 3 to 8). If each sulfur species were more homogeneously distributed or if a greater number of individual spectra were measured, the averaging approach would be more accurate. Thus, the best results were obtained using the second approach, in which fitting of individual spectra was followed by calculating the average and  $\pm 1\sigma$  values of each sulfur constituent. The resulting distribution of some sulfur species calculated for each sample was typically skewed (Appendix B).

**Table 3. SHORT SPECTRUM FITTING RESULTS OF VR-4 TIME SERIES DATA\***

	<b>Sulfate</b>		<b>Sulfonate</b>		<b>Sulfone</b>		<b>Sulfite</b>	
	Combined	Individual	Combined	Individual	Combined	Individual	Combined	Individual
VR-4 4U (n = 20)	18.24	18.33	18.80	18.87	5.07	4.89	0.00	0.05
T = 25°C, t = n/a	(+7.58/-5.36)	(±9.00)	(+3.23/-1.12)	(±4.32)	(-1.59/+1.67)	(±1.70)		(±0.11)
V4_15 (n = 27)	25.30	25.63	19.49	19.65	3.35	3.24 <sup>a</sup>	0.00	0.27
T = 225°C, t = 15 min	(+4.87/-3.60)	(±9.20)	(+3.32/-2.42)	(±5.03)	(-0.14/+0.64)	(±2.32)		(±0.72)
Ia (n = 20)	29.18	29.65	19.48	19.60	3.07	2.87	0.00	0.33
Ib (n = 2)	17.06	16.94	32.70	32.44	4.45	4.86	0.12	0.39
Ic (n = 5)	13.06	13.02	14.57	14.70	4.00	4.08	0.00	0.00
V4_30 (n = 25)	35.95	36.50 <sup>a</sup>	15.89	15.92 <sup>a</sup>	3.91	3.86	0.00	0.13
T = 225°C, t = 30 min	(+4.57/-3.76)	(±10.44)	(+1.45/-1.35)	(±3.55)	(+0.74/-0.41)	(±1.97)		(±0.38)
4225 (n = 7)	48.74	48.73 <sup>a</sup>	11.08	11.18 <sup>a</sup>	3.26	3.24 <sup>a</sup>	0.00	0.07
T = 225°C, t = 120 min	(+6.95/-3.89)	(±3.80)	(+0.86/-0.65)	(±2.61)	(-0.44/+0.67)	(±1.29)	(+0.00/+0.20)	(±0.19)
V4_345 (n = 23)	56.90	56.96 <sup>a</sup>	9.63	9.73 <sup>a</sup>	4.31	4.04 <sup>a</sup>	0.00	0.24
T = 225°C, t = 345 min	(+11.91/-4.88)	(±9.41)	(+0.86/-0.05)	(±3.85)	(+1.76/-1.24)	(±2.59)	(+0.00/+0.11)	(±0.59)

\*Average, +1 $\sigma$ , and -1 $\sigma$  values shown in **black** are the result of calculated fits of “Combined” spectra. Values shown in **blue** are the result of calculated fits of “Individual” spectra, where average, +1 $\sigma$ , and -1 $\sigma$  values were calculated subsequent to individual fits. In both cases, averages are displayed with the  $\pm 1\sigma$  values shown in parentheses below.

<sup>a</sup>p  $\leq$  0.05; the average was significantly different between this and the unheated sample



**Table 3. SHORT SPECTRUM FITTING RESULTS OF VR-4 TIME SERIES DATA (continued)\***

	<b>Sulfoxide</b>		<b>Sulfonium</b>		<b>S<sub>red</sub> aromatic</b>		<b>S<sub>red</sub> aliphatic</b>	
	Combined	Individual	Combined	Individual	Combined	Individual	Combined	Individual
VR-4 4U (n = 20)	7.28	7.93	0.00	0.19	30.44	30.72	20.17	19.02
T = 25°C, t = n/a	(+4.27/-1.27)	(±3.46)	(+0.00/+0.26)	(±0.70)	(-1.57/-0.86)	(±7.67)	(+5.63/-2.52)	(±7.66)
V4_15 (n = 27)	6.63	6.94	0.00	0.41	38.60	33.54	6.63	10.32 <sup>a</sup>
T = 225°C, t = 15 min	(+2.47/-1.75)	(±3.08)		(±1.32)	(+3.57/-9.25)	(±9.93)	(+0.82/+5.65)	(±5.98)
Ia (n = 20)	5.69	6.00	0.00	0.54	35.54	30.30	7.05	10.70
Ib (n = 2)	8.61	7.97	0.00	0.00	31.38	32.08	5.69	5.32
Ic (n = 5)	10.04	10.28	0.00	0.03	50.90	47.09	7.43	10.79
V4_30 (n = 25)	3.51	3.60 <sup>a</sup>	0.00	0.24	35.35	31.58	5.38	8.16 <sup>a</sup>
T = 225°C, t = 30 min	(+0.18/+0.03)	(±1.41)		(±0.53)	(+6.67/-10.17)	(±10.70)	(-1.64/+5.07)	(±4.65)
4225 (n = 7)	0.07	0.49 <sup>a</sup>	0.00	0.14	30.93	30.38	5.93	5.77 <sup>a</sup>
T = 225°C, t = 120 min	(-0.07/+0.02)	(±0.90)	(+0.00/+1.23)	(±0.35)	(+5.79/-4.27)	(±5.89)	(-0.04/+0.52)	(±2.60)
V4_345 (n = 23)	0.12	0.27 <sup>a</sup>	0.00	0.57	28.33	25.83 <sup>a</sup>	0.71	2.37 <sup>a</sup>
T = 225°C, t = 345 min	(-0.12/+0.45)	(±0.41)	(+0.00/+0.26)	(±1.15)	(+6.94/-3.58)	(±8.34)	(-0.71/+0.77)	(±2.24)

\*Average, +1 $\sigma$ , and -1 $\sigma$  values shown in **black** are the result of calculated fits of “Combined” spectra. Values shown in **blue** are the result of calculated fits of “Individual” spectra, where average, +1 $\sigma$ , and -1 $\sigma$  values were calculated subsequent to individual fits. In both cases, averages are displayed with the  $\pm 1\sigma$  values shown in parentheses below.

<sup>a</sup>p  $\leq$  0.05; the average was significantly different between this and the unheated sample

**Table 4.** FULL SPECTRUM FITTING RESULTS OF VR-4 TIME SERIES DATA\*

	Sulfate		Sulfonate		Sulfone		Sulfite	
	Combined	Individual	Combined	Individual	Combined	Individual	Combined	Individual
VR-4 4U (n = 20)	18.41	18.53	19.25	19.30	4.77	4.59	0.00	0.18
T = 25°C, t = n/a	(+6.73/-5.32)	(±8.93)	(+3.53/-1.75)	(±4.51)	(-1.67/+2.16)	(±1.62)		(±0.35)
V4_15 (n = 27)	25.61	25.73	19.92	19.95	3.28	3.08 <sup>a</sup>	0.00	0.43
T = 225°C, t = 15 min	(+4.29/-3.84)	(±9.14)	(+2.73/-2.83)	(±5.23)	(-0.36/+0.81)	(±2.34)	(+0.54/+0.00)	(±0.81)
Ia (n = 20)	29.52	29.73	19.86	19.86	2.95	2.68	0.05	0.44
Ib (n = 2)	17.18	17.11	33.30	33.25	4.32	4.43	1.36	1.28
Ic (n = 5)	13.23	13.17	14.87	14.99	4.10	4.13	0.00	0.05
V4_30 (n = 25)	36.41	36.58 <sup>a</sup>	16.17	16.14 <sup>a</sup>	3.93	3.66	0.00	0.34
T = 225°C, t = 30 min	(+3.69/-4.33)	(±10.19)	(+1.29/-1.49)	(±3.62)	(+0.47/-0.43)	(±2.05)		(±0.70)
4225 (n = 7)	48.78	48.57 <sup>a</sup>	11.47	11.53 <sup>a</sup>	2.94	2.82 <sup>a</sup>	0.00	0.21
T = 225°C, t = 120 min	(+5.78/-4.48)	(±3.78)	(+0.79/-0.61)	(±2.81)	(-0.71/+0.55)	(±1.12)	(+0.00/+0.45)	(±0.49)
V4_345 (n = 23)	57.40	57.22 <sup>a</sup>	9.96	10.06 <sup>a</sup>	4.08	3.66 <sup>a</sup>	0.00	0.38
T = 225°C, t = 345 min	(+10.44/-5.69)	(±9.51)	(+1.14/-0.13)	(±3.89)	(+1.12/-1.19)	(±2.56)	(+0.00/+0.20)	(±0.68)

\*Average, +1 $\sigma$ , and -1 $\sigma$  values shown in **black** are the result of calculated fits of “Combined” spectra. Values shown in **blue** are the result of calculated fits of “Individual” spectra, where average, +1 $\sigma$ , and -1 $\sigma$  values were calculated subsequent to individual fits. In both cases, averages are displayed with the  $\pm 1\sigma$  values shown in parentheses below.

<sup>a</sup>p  $\leq$  0.05; the average was significantly different between this and the unheated sample

**Table 4.** FULL SPECTRUM FITTING RESULTS OF VR-4 TIME SERIES DATA (continued)\*

	Sulfoxide		Sulfonium		S <sub>red</sub> aromatic		S <sub>red</sub> aliphatic	
	Combined	Individual	Combined	Individual	Combined	Individual	Combined	Individual
VR-4 4U (n = 20) T = 25°C, t = n/a	7.65 (+4.30/-1.46)	8.35 (±3.46)	0.00	0.30 (±0.78)	28.75 (-8.25/+2.19)	26.79 (±7.41)	21.17 (+9.94/-3.43)	21.96 (±8.29)
V4_15 (n = 27) T = 225°C, t = 15 min	6.93 (+2.07/-1.97)	7.05 (±3.19)	0.00	0.58 (±1.81)	33.06 (+0.51/-3.02)	31.07 (±10.41)	11.21 (+1.76/+1.29)	12.11 <sup>a</sup> (±7.25)
Ia (n = 20)	5.96	6.05	0.00	0.75	31.42	28.69	10.24	11.79
Ib (n = 2)	8.10	7.97	0.00	0.29	27.60	27.07	8.13	8.60
Ic (n = 5)	10.30	10.70	0.00	0.00	45.07	42.19	12.43	14.77
V4_30 (n = 25) T = 225°C, t = 30 min	3.67 (+0.04/-0.04)	3.73 <sup>a</sup> (±1.34)	0.00	0.46 (±1.11)	31.44 (+6.55/-5.24)	30.85 <sup>a</sup> (±10.41)	8.38 (-2.55/+1.86)	8.23 <sup>a</sup> (±4.51)
4225 (n = 7) T = 225°C, t = 120 min	0.00 (+0.00/+0.29)	0.44 <sup>a</sup> (±0.91)	0.77 (-0.77/+0.22)	0.34 (±0.63)	31.38 (+8.93/-4.64)	31.63 (±6.22)	4.65 (-4.26/+1.90)	4.46 <sup>a</sup> (±3.20)
V4_345 (n = 23) T = 225°C, t = 345 min	0.00 (+0.00/+0.69)	0.17 <sup>a</sup> (±0.38)	1.15 (+0.06/-1.15)	1.11 <sup>a</sup> (±1.59)	27.41 (+4.46/-2.23)	25.36 (±8.68)	0.00 (+0.00/+1.73)	2.05 <sup>a</sup> (±2.29)

\*Average, +1 $\sigma$ , and -1 $\sigma$  values shown in **black** are the result of calculated fits of “Combined” spectra. Values shown in **blue** are the result of calculated fits of “Individual” spectra, where average, +1 $\sigma$ , and -1 $\sigma$  values were calculated subsequent to individual fits. In both cases, averages are displayed with the  $\pm 1\sigma$  values shown in parentheses below.

<sup>a</sup>p  $\leq$  0.05; the average was significantly different between this and the unheated sample

**Table 5. SHORT SPECTRUM FITTING RESULTS OF VR-4 TEMPERATURE SERIES DATA\***

	<b>Sulfate</b>		<b>Sulfonate</b>		<b>Sulfone</b>		<b>Sulfite</b>	
	Combined	Individual	Combined	Individual	Combined	Individual	Combined	Individual
VR-4 4U (n = 20)	18.24	18.33	18.80	18.87	5.07	4.89	0.00	0.05
T = 25°C, t = n/a	(+7.58/-5.36)	(±9.00)	(+3.23/-1.12)	(±4.32)	(-1.59/+1.67)	(±1.70)		(±0.11)
4150 (n = 25)	22.96	23.03 <sup>a</sup>	20.19	20.33	4.38	4.30	0.00	0.19
T = 150°C, t = 120 min	(+4.87/-5.15)	(±7.11)	(+2.32/-2.99)	(±3.33)	(-0.91/+0.66)	(±2.50)		(±0.45)
Ia (n = 21)	25.42	25.35	20.06	20.22	4.28	4.17	0.00	0.23
Ib (n = 3)	10.88	11.00	19.90	19.85	5.90	5.78	0.00	0.00
II (n = 1)	10.41	10.41	24.25	24.25	2.65	2.65	0.00	0.00
4175 (n = 26)	24.52	24.70	17.12	17.40	3.40	3.49	0.00	0.10
T = 175°C, t = 120 min	(+10.25/-6.34)	(±11.85)	(+2.29/+0.47)	(±4.32)	(-2.55/+2.70)	(±1.59)		(±0.22)
Ia (n = 14)	23.26	23.50	19.49	19.73	3.62	3.73	0.00	0.12
Ib (n = 1)	7.26	7.26	6.64	6.64	6.00	6.00	0.00	0.00
Ic (n = 3)	12.38	12.42	13.90	13.98	2.70	2.85	0.00	0.00
II (n = 7)	37.94	37.90	16.85	17.01	3.29	3.35	0.00	0.15
III (n = 1)	3.42	3.42	8.52	8.52	0.52	0.52	0.00	0.00
4225 (n = 7)	48.74	48.73 <sup>a</sup>	11.08	11.18 <sup>a</sup>	3.26	3.24 <sup>a</sup>	0.00	0.07
T = 225°C, t = 120 min	(+6.95/-3.89)	(±3.80)	(+0.86/-0.65)	(±2.61)	(-0.44/+0.67)	(±1.29)	(+0.00/+0.20)	(±0.19)

\*Average, +1 $\sigma$ , and -1 $\sigma$  values shown in **black** are the result of calculated fits of “Combined” spectra. Values shown in **blue** are the result of calculated fits of “Individual” spectra, where average, +1 $\sigma$ , and -1 $\sigma$  values were calculated subsequent to individual fits. In both cases, averages are displayed with the  $\pm 1\sigma$  values shown in parentheses below.

<sup>a</sup>p  $\leq$  0.05; the average was significantly different between this and the unheated sample

**Table 5.** SHORT SPECTRUM FITTING RESULTS OF VR-4 TEMPERATURE SERIES DATA (continued)\*

	<b>Sulfoxide</b>		<b>Sulfonium</b>		<b>S<sub>red</sub> aromatic</b>		<b>S<sub>red</sub> aliphatic</b>	
	Combined	Individual	Combined	Individual	Combined	Individual	Combined	Individual
VR-4 4U (n = 20)	7.28	7.93	0.00	0.19	30.44	30.72	20.17	19.02
T = 25°C, t = n/a	(+4.27/-1.27)	(±3.46)	(+0.00/+0.26)	(±0.70)	(-1.57/-0.86)	(±7.67)	(+5.63/-2.52)	(±7.66)
4150 (n = 25)	6.46	6.63	0.00	0.97	30.12	28.49	15.88	16.05
T = 150°C, t = 120 min	(+2.48/-1.97)	(±3.28)	(+0.00/+0.16)	(±1.83)	(+5.26/-3.48)	(±7.66)	(-3.04/-0.95)	(±5.86)
Ia (n = 21)	5.83	5.94	0.00	1.15	28.53	27.43	15.88	15.51
Ib (n = 3)	12.65	12.62	0.00	0.00	35.59	35.74	15.07	15.00
II (n = 1)	3.25	3.25	0.00	0.00	28.91	28.91	30.52	30.52
4175 (n = 26)	5.45	6.09 <sup>a</sup>	0.00	0.07	39.75	34.75	9.76	13.40 <sup>a</sup>
T = 175°C, t = 120 min	(+4.07/-0.01)	(±3.00)		(±0.21)	(+7.16/-9.72)	(±12.10)	(+5.25/-0.08)	(±11.65)
Ia (n = 14)	6.55	6.91	0.00	0.02	40.26	35.10	6.83	10.89
Ib (n = 1)	5.32	5.32	0.37	0.37	73.30	73.30	1.10	1.10
Ic (n = 3)	8.44	8.74	0.00	0.00	42.31	40.95	20.27	21.06
II (n = 7)	3.99	4.29	0.00	0.15	29.09	26.84	8.85	10.30
III (n = 1)	0.00	0.00	0.00	0.00	28.02	28.02	59.52	59.52
4225 (n = 7)	0.07	0.49 <sup>a</sup>	0.00	0.14	30.93	30.38	5.93	5.77 <sup>a</sup>
T = 225°C, t = 120 min	(-0.07/+0.02)	(±0.90)	(+0.00/+1.23)	(±0.35)	(+5.79/-4.27)	(±5.89)	(-0.04/+0.52)	(±2.60)

\*Average, +1 $\sigma$ , and -1 $\sigma$  values shown in **black** are the result of calculated fits of “Combined” spectra. Values shown in **blue** are the result of calculated fits of “Individual” spectra, where average, +1 $\sigma$ , and -1 $\sigma$  values were calculated subsequent to individual fits. In both cases, averages are displayed with the  $\pm 1\sigma$  values shown in parentheses below.

<sup>a</sup>p  $\leq$  0.05; the average was significantly different between this and the unheated sample

**Table 6.** FULL SPECTRUM FITTING RESULTS OF VR-4 TEMPERATURE SERIES DATA\*

	Sulfate		Sulfonate		Sulfone		Sulfite	
	Combined	Individual	Combined	Individual	Combined	Individual	Combined	Individual
VR-4 4U (n = 20)	18.41	18.53	19.25	19.30	4.77	4.59	0.00	0.18
T = 25°C, t = n/a	(+6.73/-5.32)	(±8.93)	(+3.53/-1.75)	(±4.51)	(-1.67/+2.16)	(±1.62)		(±0.35)
4150 (n = 25)	22.99	23.08 <sup>a</sup>	20.36	20.58	4.30	4.18	0.00	0.23
T = 150°C, t = 120 min	(+4.63/-5.09)	(±7.14)	(+2.53/-3.19)	(±3.56)	(-1.09/+0.82)	(±2.44)		(±0.45)
Ia (n = 21)	25.41	25.37	20.24	20.44	4.13	4.01	0.00	0.28
Ib (n = 3)	11.01	11.10	20.11	20.02	6.03	5.83	0.00	0.00
II (n = 1)	10.94	10.94	25.24	25.24	2.68	2.68	0.00	0.00
4175 (n = 26)	25.17	24.94	17.67	17.75	3.57	3.34	0.04	0.33
T = 175°C, t = 120 min	(+8.74/-6.86)	(±11.89)	(+1.77/-0.11)	(±4.36)	(-2.89/+2.70)	(±1.69)	(+0.92/-0.04)	(±0.50)
Ia (n = 14)	23.89	23.74	20.12	20.11	3.82	3.66	0.00	0.30
Ib (n = 1)	7.26	7.26	6.74	6.74	5.94	5.94	0.00	0.00
Ic (n = 3)	12.79	12.72	14.58	14.46	2.84	2.77	0.00	0.25
II (n = 7)	38.46	38.14	17.20	17.31	2.99	2.98	0.50	0.50
III (n = 1)	3.72	3.72	8.75	8.75	0.58	0.58	0.00	0.00
4225 (n = 7)	48.78	48.57 <sup>a</sup>	11.47	11.53 <sup>a</sup>	2.94	2.82 <sup>a</sup>	0.00	0.21
T = 225°C, t = 120 min	(+5.78/-4.48)	(±3.78)	(+0.79/-0.61)	(±2.81)	(-0.71/+0.55)	(±1.12)	(+0.00/+0.45)	(±0.49)

\*Average, +1 $\sigma$ , and -1 $\sigma$  values shown in **black** are the result of calculated fits of “Combined” spectra. Values shown in **blue** are the result of calculated fits of “Individual” spectra, where average, +1 $\sigma$ , and -1 $\sigma$  values were calculated subsequent to individual fits. In both cases, averages are displayed with the  $\pm 1\sigma$  values shown in parentheses below.

<sup>a</sup>p  $\leq$  0.05; the average was significantly different between this and the unheated sample

**Table 6.** FULL SPECTRUM FITTING RESULTS OF VR-4 TEMPERATURE SERIES DATA (continued)\*

	<b>Sulfoxide</b>		<b>Sulfonium</b>		<b>S<sub>red</sub> aromatic</b>		<b>S<sub>red</sub> aliphatic</b>	
	Combined	Individual	Combined	Individual	Combined	Individual	Combined	Individual
VR-4 4U (n = 20)	7.65	8.35	0.00	0.30	28.75	26.79	21.17	21.96
T = 25°C, t = n/a	(+4.30/-1.46)	(±3.46)		(±0.78)	(-8.25/+2.19)	(±7.41)	(+9.94/-3.43)	(±8.29)
4150 (n = 25)	6.40	7.03	0.00	0.73	29.09	26.44	16.85	17.73
T = 150°C, t = 120 min	(+3.49/-1.72)	(±3.39)		(±1.53)	(-2.96/-0.48)	(±7.90)	(+0.95/-2.38)	(±7.07)
Ia (n = 21)	5.79	6.33	0.07	0.87	28.37	25.91	15.99	16.79
Ib (n = 3)	12.93	12.88	0.00	0.00	32.44	34.29	17.49	15.87
II (n = 1)	4.08	4.08	0.00	0.00	14.07	14.07	42.99	42.99
4175 (n = 26)	5.90	6.24	0.00	0.17	29.08	30.29	18.57	16.94 <sup>a</sup>
T = 175°C, t = 120 min	(+2.42/-0.32)	(±3.19)		(±0.37)	(+0.38/+2.53)	(±12.03)	(+9.12/-9.05)	(±13.76)
Ia (n = 14)	7.28	7.11	0.00	0.06	30.00	30.33	14.88	14.69
Ib (n = 1)	5.26	5.26	0.88	0.88	73.23	73.23	0.68	0.68
Ic (n = 3)	8.98	9.25	0.00	0.00	28.06	31.29	32.76	29.27
II (n = 7)	3.97	4.23	0.00	0.39	25.15	25.41	11.73	11.04
III (n = 1)	0.00	0.00	0.00	0.00	18.00	18.00	68.96	68.96
4225 (n = 7)	0.00	0.44 <sup>a</sup>	0.77	0.34	31.38	31.63	4.65	4.46 <sup>a</sup>
T = 225°C, t = 120 min	(+0.00/+0.29)	(±0.91)	(-0.77/+0.22)	(±0.63)	(+8.93/-4.64)	(±6.22)	(-4.26/+1.90)	(±3.20)

\*Average, +1 $\sigma$ , and -1 $\sigma$  values shown in **black** are the result of calculated fits of “Combined” spectra. Values shown in **blue** are the result of calculated fits of “Individual” spectra, where average, +1 $\sigma$ , and -1 $\sigma$  values were calculated subsequent to individual fits. In both cases, averages are displayed with the  $\pm 1\sigma$  values shown in parentheses below.

<sup>a</sup>p  $\leq$  0.05; the average was significantly different between this and the unheated sample

**Table 7.** SHORT SPECTRUM FITTING RESULTS OF VR-5 TEMPERATURE SERIES DATA\*

		<b>Sulfate</b>		<b>Sulfonate</b>		<b>Sulfone</b>		<b>Sulfite</b>	
		Combined	Individual	Combined	Individual	Combined	Individual	Combined	Individual
VR-5	5U (n = 26)	31.50	31.59	16.16	16.32	3.70	3.64	0.00	0.26
	T = 25°C, t = n/a	(+10.64/-12.12)	(±16.88)	(+0.47/-0.62)	(±6.57)	(-0.21/-0.41)	(±2.37)	(+0.00/+1.02)	(±0.64)
	Ia (n = 16)	25.94	25.99	19.95	20.04	4.17	4.07	0.00	0.15
	Ib (n = 2)	9.16	9.22	15.59	15.81	2.86	2.93	0.00	0.00
	IIa (n = 4)	64.95	64.86	6.24	6.16	2.59	2.49	0.00	0.22
	IIb (n = 4)	31.16	31.90	11.33	11.88	3.24	3.46	0.93	0.86
	5225 (n = 24)	54.08	53.83 <sup>a</sup>	7.97	8.29 <sup>a</sup>	3.54	2.91	0.00	0.84
T = 225°C, t = 120 min		(+9.97/-10.26)	(±7.81)	(+0.76/-0.88)	(±3.80)	(-0.97/+0.86)	(±2.11)		(±1.34)
		<b>Sulfoxide</b>		<b>Sulfonium</b>		<b>S<sub>red</sub> aromatic</b>		<b>S<sub>red</sub> aliphatic</b>	
VR-5	5U (n = 26)	4.32	4.40	0.00	0.64	32.58	30.00	11.75	13.15
	T = 25°C, t = n/a	(+2.61/-2.21)	(±3.25)	(+0.00/+1.63)	(±1.22)	(-2.94/-10.67)	(±10.47)	(+8.37/-1.36)	(±7.60)
	Ia (n = 16)	4.46	4.63	0.00	0.60	31.58	31.38	13.90	13.14
	Ib (n = 2)	11.63	11.72	0.00	0.36	51.61	47.27	9.14	12.69
	IIa (n = 4)	2.98	2.76	0.00	0.44	18.41	17.49	4.83	5.58
	IIb (n = 4)	1.35	1.48	0.00	1.11	33.46	28.36	18.54	20.95
	5225 (n = 24)	0.00	0.82 <sup>a</sup>	0.00	0.56	28.58	26.21	5.83	6.54 <sup>a</sup>
T = 225°C, t = 120 min		(+0.00/+0.37)	(±1.06)		(±1.34)	(+5.46/-6.09)	(±9.02)	(-1.37/+1.39)	(±4.23)

\*Average, +1 $\sigma$ , and -1 $\sigma$  values shown in **black** are the result of calculated fits of “Combined” spectra. Values shown in **blue** are the result of calculated fits of “Individual” spectra, where average, +1 $\sigma$ , and -1 $\sigma$  values were calculated subsequent to individual fits. In both cases, averages are displayed with the  $\pm 1\sigma$  values shown in parentheses below.

<sup>a</sup>p  $\leq$  0.05; the average was significantly different between this and the unheated sample



**Table 8.** FULL SPECTRUM FITTING RESULTS OF VR-5 TEMPERATURE SERIES DATA\*

		<b>Sulfate</b>		<b>Sulfonate</b>		<b>Sulfone</b>		<b>Sulfite</b>	
		Combined	Individual	Combined	Individual	Combined	Individual	Combined	Individual
VR-5	5U (n = 26)	31.41	31.54	16.31	16.61	3.59	3.44	0.00	0.35
	T = 25°C, t = n/a	(+9.89/-11.64)	(±16.91)	(+1.24/-0.64)	(±6.70)	(-0.69/+0.50)	(±2.44)	(+0.00/+0.32)	(±0.61)
	Ia (n = 16)	25.93	26.03	20.09	20.34	4.08	3.82	0.00	0.24
	Ib (n = 2)	9.44	9.42	16.39	16.36	3.09	3.06	0.00	0.00
	IIa (n = 4)	65.38	65.05	6.48	6.44	2.31	2.17	0.26	0.49
	IIb (n = 4)	30.57	31.10	11.47	11.96	3.29	3.39	0.30	0.80
	5225 (n = 24)	54.08	53.86 <sup>a</sup>	8.24	8.48 <sup>a</sup>	3.13	2.65	0.28	0.94
T = 225°C, t = 120 min		(+9.02/-10.39)	(±8.18)	(+0.61/-1.04)	(±3.74)	(-1.73/+1.28)	(±2.07)	(+0.88/-0.28)	(±1.38)
		<b>Sulfoxide</b>		<b>Sulfonium</b>		<b>S<sub>red</sub> aromatic</b>		<b>S<sub>red</sub> aliphatic</b>	
VR-5	5U (n = 26)	4.27	4.91	0.00	0.42	32.19	27.54	12.23	15.20
	T = 25°C, t = n/a	(+2.36/-0.40)	(±3.47)	(+1.59/+0.00)	(±0.79)	(-9.79/-9.24)	(±9.93)	(+10.42/+0.76)	(±8.51)
	Ia (n = 16)	4.48	5.26	0.00	0.22	31.79	29.07	13.63	15.00
	Ib (n = 2)	12.47	12.35	1.14	1.00	37.58	37.77	19.89	20.04
	IIa (n = 4)	2.82	2.56	0.83	1.02	15.98	15.58	5.95	6.69
	IIb (n = 4)	1.82	2.12	0.00	0.34	38.02	28.23	14.54	22.06
	5225 (n = 24)	0.00	0.82 <sup>a</sup>	0.00	0.56	28.24	26.21	6.03	6.54 <sup>a</sup>
T = 225°C, t = 120 min		(+0.00/+0.36)	(±1.06)		(±1.34)	(+7.76/-5.47)	(±9.02)	(-5.56/+1.87)	(±4.23)

\*Average, +1 $\sigma$ , and -1 $\sigma$  values shown in **black** are the result of calculated fits of “Combined” spectra. Values shown in **blue** are the result of calculated fits of “Individual” spectra, where average, +1 $\sigma$ , and -1 $\sigma$  values were calculated subsequent to individual fits. In both cases, averages are displayed with the  $\pm 1\sigma$  values shown in parentheses below.

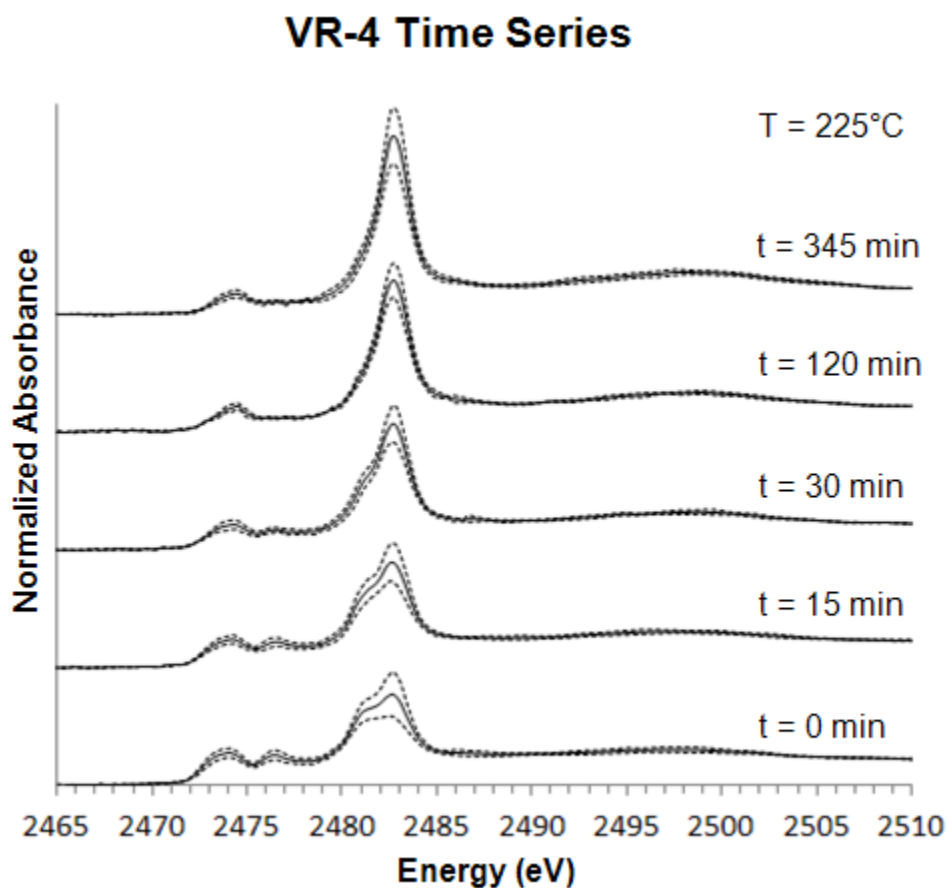
<sup>a</sup>p  $\leq$  0.05; the average was significantly different between this and the unheated sample

*Fits Using Short- vs. Full-Energy Range Spectra.* The relative amounts of each sulfur constituent calculated from short-energy (2465-2490 eV) and full-energy (2465-2510 eV) range spectra were similar. Like the comparison between fits of averaged and of individual spectra, most differences were again generally within 15% (Tables 3 to 8). One exception was the reduced aliphatic sulfur content in VR-4 soil heated at 175°C for 120 minutes, where the difference was 20.9%. Larger differences were again observed in cases where the relative amount of a sulfur constituent consisted of  $\leq 5\%$  of the total sulfur content.

In general, fits to full-energy range spectra showed slightly greater amounts of sulfate, sulfonate, sulfite, sulfoxide, sulfonium, and Sred\_aliphatic content compared to fits that used the short-energy range. Conversely, lower amounts of sulfone and Sred\_aromatic content were estimated in fits to the full-energy range. Despite these slight differences, fits to the full-energy range spectra were preferred because extended X-ray absorption fine structure features in the sulfate spectra are not excluded at this scale (2465 to 2510 eV; Figure 5).

**Changes in Sulfur Speciation upon Heating.** In general, the relative amount of sulfates (the most oxidized form of sulfur) in the soils increased with increasing temperature and duration of heating. The relative amounts of other oxidized sulfur constituents, as well as reduced aliphatic sulfur, which is an important Hg binding agent, decreased as relative amounts of reduced aromatic sulfur content in the soils remained mostly constant.

*VR-4 Time Series.* The shape of the S-XANES spectra for the VR-4 soil displays the general features of changes in the sulfur speciation (Figure 9). The height of the p<sub>1</sub> (2470.0 to 2475.5 eV) and p<sub>2</sub> (2475.5 to 2479.0 eV) peaks, which represent the reduced aliphatic and aromatic sulfur peaks (p<sub>1</sub> peak) and the sulfoxide and sulfonium peaks (p<sub>2</sub> peak), both decreased with increased duration of heating. After 30 minutes, the height and shape of the p<sub>1</sub>



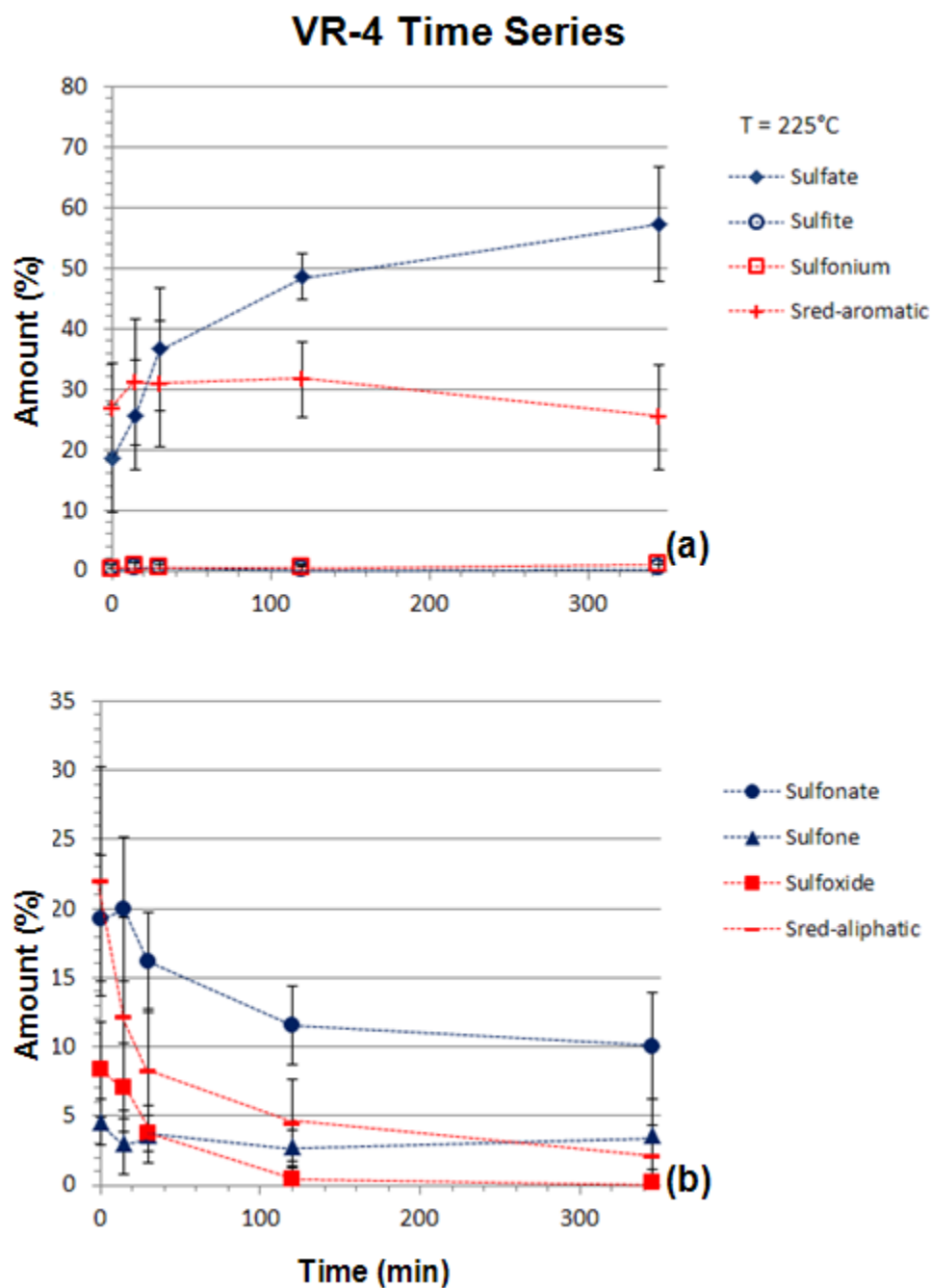
**Figure 9.** Average (—) and  $\pm 1\sigma$  (--) S-XANES spectra of VR-4 soil samples heated at 225°C for various times.

peak no longer appeared to change, while the  $p_2$  peak could no longer be distinguished. The  $p_{SO_3}$  sulfonate shoulder (2479.0 to 2482.0 eV), which spans the range of where the sulfonate, sulfone, and sulfite peaks are located, became less pronounced with longer heating time. Also, similar to the  $p_2$  peak, the  $p_{SO_3}$  sulfonate shoulder disappeared after 30 minutes. In contrast, the height of the  $p_{SO_4}$  sulfate peak (2482.74 eV) regularly increased and became more distinct with increased heat.

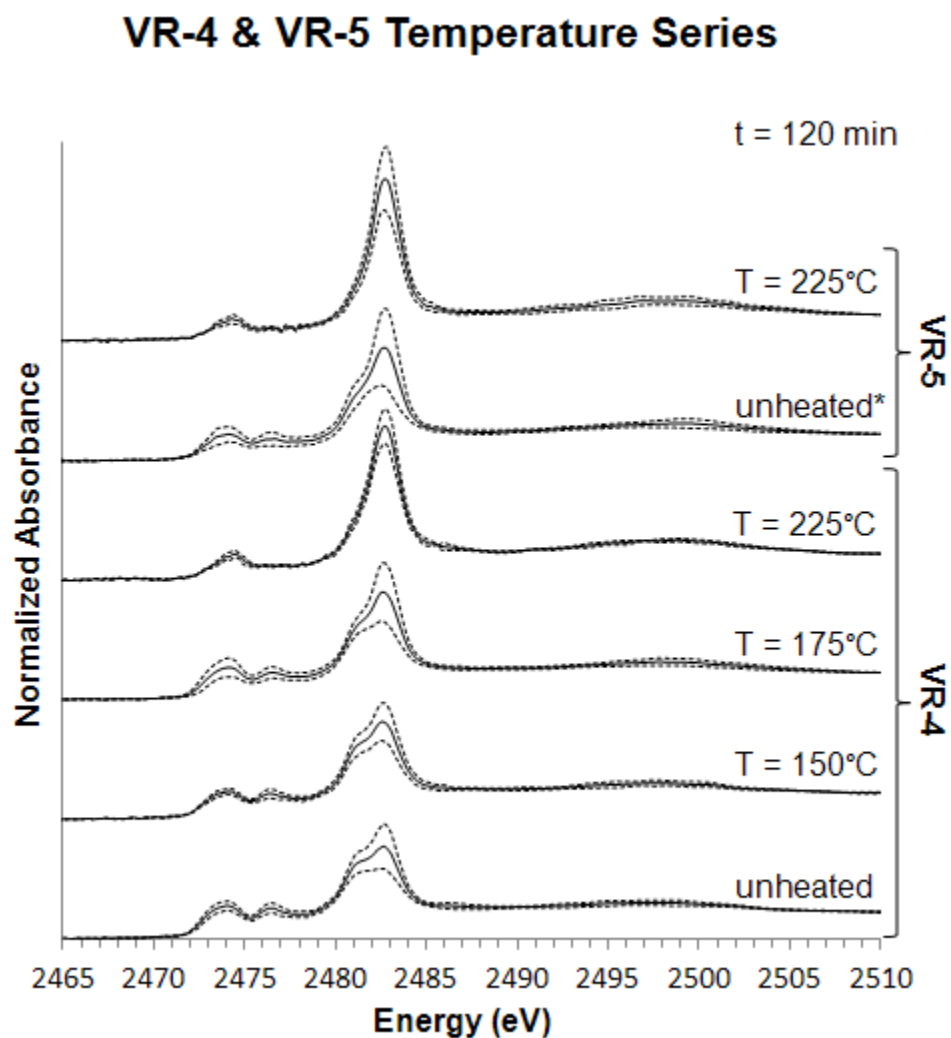
As temperature was maintained at 225°C, the fractional amount of sulfate in VR-4 soil increased over the entire 345 min heating period (Table 4; Figure 10). This increase was statistically significant ( $p \leq 0.05$ ) between 30 and 345 min of applied heat. The amounts of other oxidized sulfur constituents decreased over time. Sulfonate and sulfoxide content decreased ( $p \leq 0.05$ ) after 30 min. Sulfone content decreased ( $p \leq 0.05$ ) within 15 minutes, remained similar to the unheated sample from 15 to 30 minutes, and then decreased ( $p \leq 0.05$ ) again between 120 and 345 min. The reduced aliphatic sulfur content, which include Hg-binding thiol groups, decreased ( $p \leq 0.05$ ) over the entire 345 min heating period. On the other hand, despite an increase ( $p \leq 0.05$ ) at 30 min, the reduced aromatic sulfur content was not statistically different from the unheated sample at  $t = 15, 120$ , and 345 min. Furthermore, no significant changes in sulfite content occurred, whereas sulfonium content increased ( $p \leq 0.05$ ) at 345 min. However, the fractional amounts of both sulfite and sulfonium constituents, were generally  $< 1\%$  of the total sulfur, suggesting that an accurate evaluation of these two compounds may not be possible.

*VR-4 Temperature Series.* The S-XANES spectra of the VR-4 soil showed an abrupt change towards greater sulfate content and decreased reduced sulfur content when the heating temperature was increased from 175° to 225°C (Figure 11). This was apparent at 225°C where only the  $p_1$  and  $p_{SO_4}$  peaks in the spectra were distinct. At lower temperatures, the shape of the S-XANES spectra was similar to that of the unheated control.

Fit-calculated fractional amounts quantitatively showed that oxidized sulfate in VR-4 soil increased as soils were heated for 120 min with increasing temperature. These changes were significant ( $p \leq 0.05$ ) at 150°C and 225°C (Table 6, Figure 12). The amounts of other oxidized sulfur constituents—sulfonate, sulfone, and sulfoxide—remained relatively constant

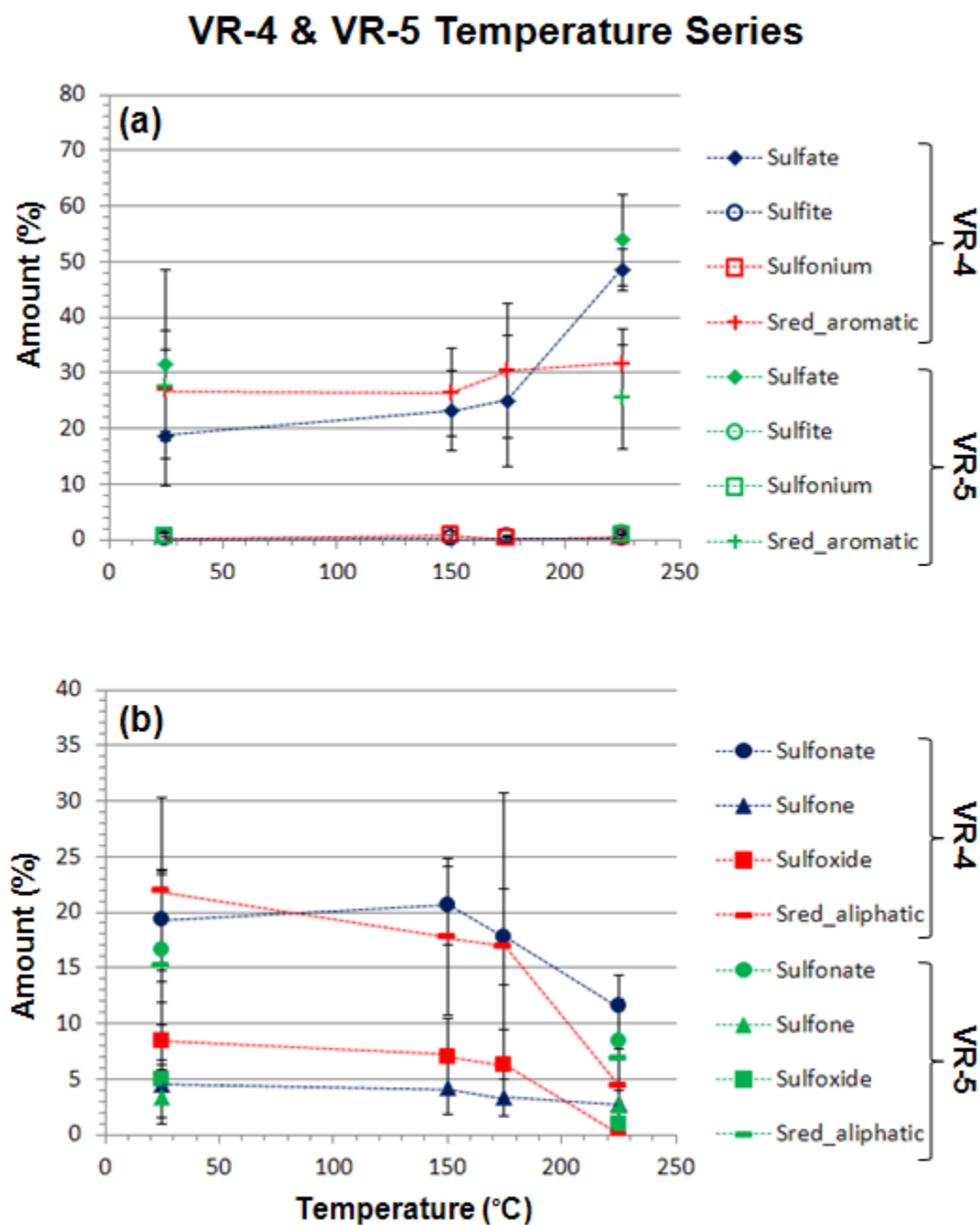


**Figure 10.** Sulfur speciation changes in VR-4 soil samples heated at 225°C as a function of time. (a) Trends in sulfate, sulfite, sulfonium, and Sred\_aromatic content. (b) Trends in sulfonate, sulfone, sulfoxide, and Sred\_aliphatic content. Sulfur speciation was calculated using the second fitting approach on full-energy range (2465 to 2510 eV) spectra. Error bars represent  $\pm 1\sigma$  values.



**Figure 11.** Average (—) and  $\pm 1\sigma$  (--) S-XANES spectra of VR-4 and VR-5 soil samples heated for 120 min at various temperatures.

\*VR-5 unheated samples were not subjected to laboratory heat treatments, though they had been previously burned by the Missionary Ridge wildfire.



**Figure 12.** Sulfur speciation changes in VR-4 and VR-5 soil samples heated for 120 min as a function of temperature. (a) Trends in sulfate, sulfite, sulfonium, and Sred\_aromatic content. (b) Trends in sulfonate, sulfone, sulfoxide, and Sred\_aliphatic content. Sulfur speciation was calculated using the second fitting approach on full-energy range (2465 to 2510 eV) spectra. Error bars represent  $\pm 1\sigma$  values.

at 150 and 175°C, then decreased ( $p \leq 0.05$ ) at 225°C. For the reduced aliphatic sulfur content, a constant decrease was observed over the entire temperature range with decreases being statistically significant ( $p \leq 0.05$ ) at 175°C and 225°C. For the reduced aromatic sulfur content, the fractional amount remained relatively constant at 175°C and 225°C, which is similar to what was observed in the time series experiments. Again, there were no statistically significant changes in the sulfite or sulfonium content, which together comprised  $< 1\%$  of the total sulfur.

*VR-5 Soils.* Similar to the VR-4 soil, the height of the  $p_{SO_4}$  peak in the VR-5 S-XANES spectra heated at 225°C for 120 min increased and its shape became more distinct (Figure 11). Also, the shape of the  $p_2$  peak and  $p_{SO_3}$  shoulder became indistinguishable in the spectra and the  $p_1$  peak appeared relatively unchanged.

The S-XANES spectra of the naturally burned VR-5 control soil was most similar to the VR-4 soil heated at 175°C for 120 min. The fractional amounts of the major sulfur constituents typically differed within 10% (Table 8). The only exception was sulfate, which was 20% greater in the VR-5 than in the VR-4 soil. Larger differences were observed in the minor sulfoxide and sulfonium constituents, which each comprised  $< 5\%$  of the total sulfur content.

Between the VR-5 and VR-4 soils, comparable changes were observed when both samples were heated at 225°C for 120 min (Table 8, Figure 11). The fractional sulfate content increased ( $p \leq 0.05$ ) while the sulfonate and sulfoxide contents decreased ( $p \leq 0.05$ ). As seen previously in the VR-4 soils, the fractional reduced aliphatic sulfur content also decreased ( $p \leq 0.05$ ) and there was again no significant change in the fractional reduced



**Table 9. SULFUR AND ORGANIC MATTER IN VR-4 AND VR-5 SOILS**

	<b>Sample Name</b>	<b>Temperature (°C)</b>	<b>Sulfur Content (mg/kg)</b>	<b>Sulfur Content Retained (%)</b>	<b>Organic Matter (%<sub>wt</sub>)</b>	<b>Organic Matter Retained (%)</b>	<b>Mass Sulfur/ Mass Organic Matter (%<sub>wt</sub>)</b>
VR-4	4U	unheated	800	n/a	23.6	n/a	0.34
	4225	225	700	87.5	18.6	78.8	0.31
VR-5	5U	unheated*	500	n/a	16.1	n/a	0.38
	5225	225	400	80.0	12.9	80.1	0.31

n/a = not applicable

\*VR-5 unheated samples were not subjected to laboratory heat treatments, though they had been previously burned by the Missionary Ridge wildfire.

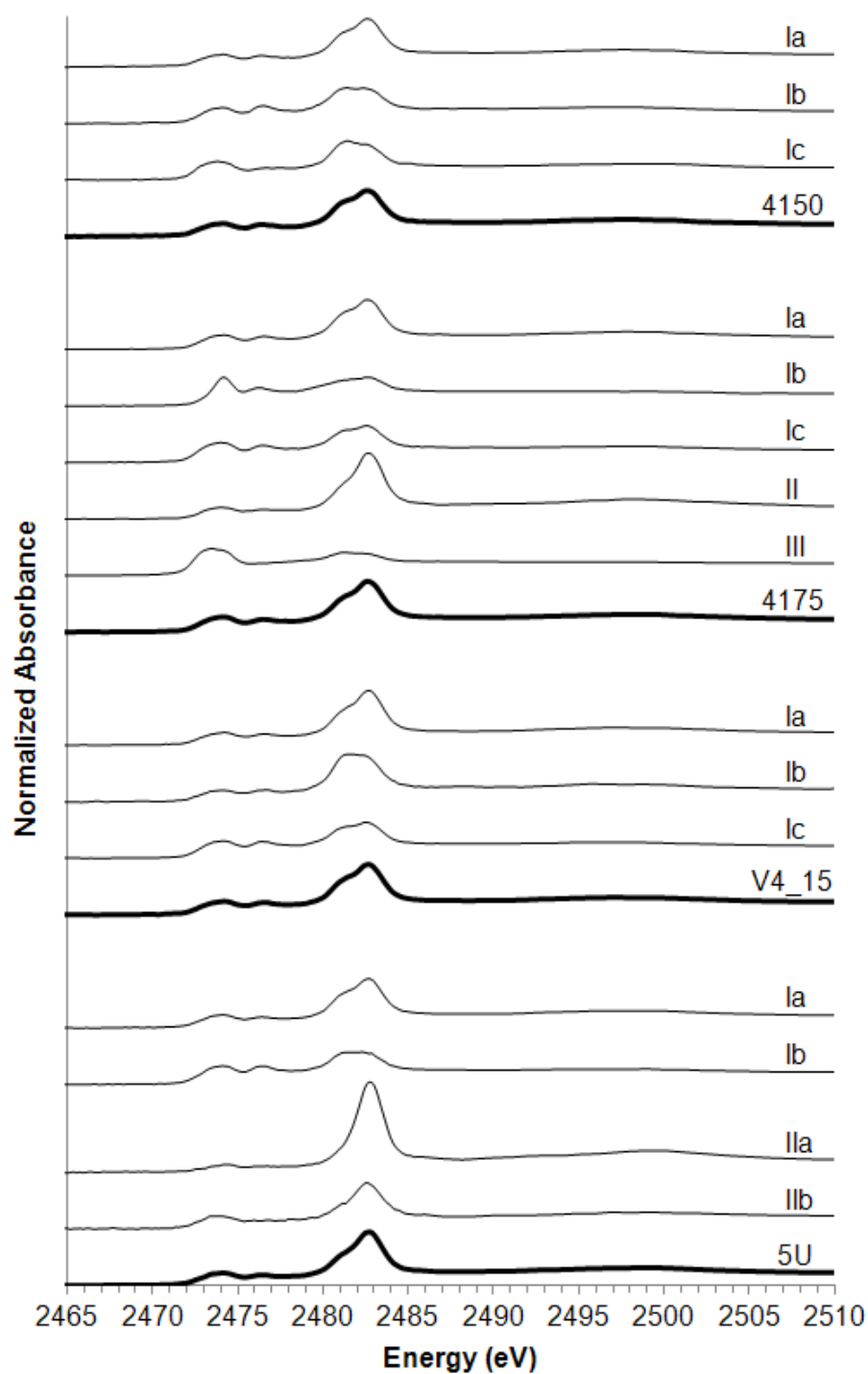
aromatic sulfur content. The sulfone, sulfite, and sulfonium content also remained relatively unchanged, though the fractional amounts of each was generally < 5% of the total sulfur.

*VR-4 and VR-5 Soil Comparison.* The unheated VR-4 soil, which was not affected by the Missionary Ridge wildfire, had approximately 40% more sulfur and 30% more organic matter than the VR-5 soil both before and after heating at 225°C for 120 min (Table 9). Yet, the ratio of total sulfur to total organic matter was similar in the two soils and remained fairly constant at approximately 0.35 before and after the heat treatment.

*Groups and Subgroups.* The spectra of only four soil samples could be separated into spectral groups and subgroups: VR-4 soil heated at 150°C for 120 min, VR-4 soil heated at 175°C for 120 min, VR-4 soil heated at 225°C for 15 min, and VR-5 soil unheated (Figure 13). The average spectra (in bold, Figure 13) of these four soils looked similar, although the VR-5 spectrum had a slightly more pronounced  $p_{SO_4}$  peak.

As previously mentioned in the observations for the time and temperature series, there was little significant ( $p \leq 0.05$ ) change in the fractional content of all sulfur constituents in the VR-4 soils heated at 150°C for 120 min, at 175°C for 120 min, and at 225°C for 15 min, when compared to the unheated VR-4 soil (Tables 4 and 6). The spectra of the VR-4 unheated soil, however, could not be separated into groups and subgroups. Thus, the spectra of the groups and subgroups show how sulfur pools were evolving at the early stages of heating. As time progressed ( $t \geq 30$  min) and as temperature increased to 225°C, the distribution of sulfur species in the soils became more similar.

Also, as previously mentioned, the S-XANES spectra and the fractional amounts of sulfur species in the unheated (but, naturally burned) VR-5 control soil and the VR-4 soil heated at 175°C for 120 min were similar (Figure 11, Tables 6 and 8). In addition, the spectra of their spectral groups and subgroups were also generally similar except for Groups Ib and III in the VR-4 soil, which had a large reduced aromatic and aliphatic sulfur content and for Group IIa in the VR-5 soil, which had a large sulfate content.



**Figure 13.** The overall average S-XANES spectra (in bold) and the average spectra of groups and subgroups identified in certain soil samples: VR-4 soils heated at 150°C for 120 min (4150), 175°C for 120 min (4175), 225°C for 15 min (V4\_15), and of the naturally burned VR-5 control soil (5U).

## DISCUSSION

Increasing both the temperature and duration of heating resulted in an increase in the fractional amount of sulfate ( $S^{+VI}$ ), the most oxidized form of sulfur, and a decrease in more reduced forms of sulfur in the VR-4 and VR-5 soils. Sulfonate ( $S^{+V}$ ), sulfone ( $S^{+IV}$ ), sulfoxide ( $S^{+II}$ ), and Sred\_aliphatic ( $S^{0,-I}$ ) content decreased, while the amounts of sulfite ( $S^{+IV}$ ), sulfonium ( $S^{+I}$ ), and Sred\_aromatic ( $S^{0,-I}$ ) content remained relatively unchanged. The combined sulfite and sulfonium content was generally  $< 5\%$  of the total sulfur, which precludes determination of absolute changes in these species. Thus, most of the sulfur species that remained in the soil likely oxidized to sulfates ( $S^{+VI}$ ). Reduced aliphatic sulfur compounds may have been oxidized and reduced aromatic sulfur compounds, which include an organic form of sulfur bound to mercury, appears to be recalcitrant.

**Changes in Spectral Grouping.** The decrease in reduced aliphatic sulfur, conservation of reduced aromatic sulfur, and increase in oxidized sulfate content are qualitatively recognized from changes in the VR-4 and VR-5 S-XANES spectra (Figures 9 and 11). All peaks ( $p_1$ ,  $p_2$ ,  $p_{SO_3}$ , and  $p_{SO_4}$ ) were present in the spectra of unheated controls, but only the  $p_1$  and  $p_{SO_4}$  peaks remained after exposure to maximum heating conditions (i.e., 345 min at 225°C for VR-4 samples and 120 min at 225°C for VR-5 samples). The VR-4 spectra of soils heated at lower temperatures for 2 h (150°C for 120 min, 175°C for 120 min) and at a higher temperature for a shorter time (225°C for 15 min) could be separated into groups and subgroups (Figure 13). Heating at 225°C for longer time periods caused the spectral groups and subgroups to disappear, indicating that changes in soil sulfur speciation were reaching a steady or final state under these conditions.

The average spectra and the spectra of groups and subgroups were generally similar for the unheated VR-5 control and the VR-4 soil sample heated at 175°C for 120 min (Figures 11 and 13). The only differences were in the VR-5 Group IIa spectrum, which had a relatively strong sulfate signal compared to other spectra, and in the VR-4 Groups Ib and III spectra, which had strong reduced aliphatic and aromatic sulfur signals. The general similarity between the averaged spectra of the two soil samples may be related to the previous exposure of VR-5 soil to the Missionary Ridge wildfire. If S-XANES measurements had been performed on VR-5 soils that were collected shortly after the fire, then perhaps its spectra would have appeared more similar to the spectra of the VR-4 soil heated at 175°C for 120 min. However, since soils were collected seven years after the wildfire, spectra of the VR-5 unheated control likely reflect how sulfur species transformed as soils recovered.

**Formation of Sulfates.** For both the VR-4 and VR-5 soils, the fractional amount of sulfate increased ( $p \leq 0.05$ ) with increasing temperature and duration of heating. In contrast, Binkley et al. [12] observed no statistical difference between the sulfate content of recently burned and unburned mineral soil from a loblolly and longleaf pine forest (Francis Marion and Sumter National Forest; Huger, SC). In their study, soils that had been subjected to annual, perennial, triennial, and quadrennial prescribed burns for thirty years had experienced a fire one year, two years, three years, and one year before sampling, respectively. Interestingly, although generally not statistically significant, Binkley et al. (1992) observed a trend of increasing sulfate content in the 0-0.1 m depth soil horizon as the interval between prescribed burns increased from annual to quadrennial. One significant ( $p < 0.10$ ) increase in the 0-0.1 m depth soil horizon was observed where sulfate content increased from 3.3  $\mu\text{g SO}_4^{2-}\text{-S/g}$  soil in the annually burned soil to 7.5  $\mu\text{g SO}_4^{2-}\text{-S/g}$  soil in the quadrennially burned

soil. In the 0.1-0.2 m depth soil horizon, sulfate content also increased from 4.0 to 26.9  $\mu\text{g SO}_4^{2-}\text{-S/g soil}$ , although the statistical significance of this change was not noted. These results, along with ours, suggest that fire induces sulfate formation in soils, but that these sulfates may be leached from the soil surface and then redeposited at shallow depth during precipitation events. The increase in sulfate content coincident with the increase in interval between prescribed burns in the Binkley et al. (1992) study also suggests that time is a factor.

As sulfate is leached from soils, there is a potential for sulfate concentrations to increase in waterways near burn locations. Loupe et al. [22] observed an increase in the sulfate loading from 19.40 to 129.76  $\text{mg SO}_4^{2-} \text{ y}^{-1}$  in the surface runoff from a mixed coniferous forest (Tahoe City, CA) that was exposed to a prescribed burn. Similarly, Murphy et al. [3] observed a decrease ( $p = 0.01$ ) in the soil-water-extractable sulfate concentration in the A, B1t, and B2t mineral soil horizons in a Jeffrey pine forest (Tahoe National Forest; Truckee, CA) following a prescribed fire that may be attributed to sulfate leaching following the fire event. Furthermore, Chorover et al. [49] observed a large increase in the sulfate concentration of a nearby creek and of soil solution in burned plots following a prescribed fire in a mixed coniferous forest (Giant Forest; Sequoia National Park, CA). The change in sulfate concentration was greatest in the soil solution of sequoia-dominated sites after the first year. Average sulfate concentration in the soil solution of the A mineral horizon increased from  $8.95 \times 10^{-3}$  to 1.22 mM and increases were also observed in forest floor leachate and in the soil solution of the AC mineral horizon. The authors suggested that sulfate increases were linked to the amount of litter burned and the topographical and physical features of the burned sites. By the third year following the prescribed burn, they observed a decrease in sulfate concentrations that appeared to recede to pre-burn conditions.

Stephens et al. [50] also observed an increase in the sulfate concentration (from  $2.14 \times 10^{-3}$  to  $2.74 \times 10^{-2}$  mM  $\text{SO}_4^{2-}$ ;  $p \leq 0.05$ ) of ephemeral creeks following a prescribed fire in a mixed coniferous forest (Sugar Pine Point State Park; Lake Tahoe, CA). In contrast, in a study on the effects of prescribed burns on ground- and stream water quality in a loblolly-pine dominated forest (Santee Experimental Forest; Charleston, SC), Richter et al. [20] observed no statistically significant change in the sulfate concentration of a nearby stream that could be attributed to prescribed fires. Richter et al. suggested that this was because of the low ash content of burned pine litter and because ash particulates and leachates were filtered through unburned soil horizons and unburned buffer zones prior to reaching groundwater and the stream.

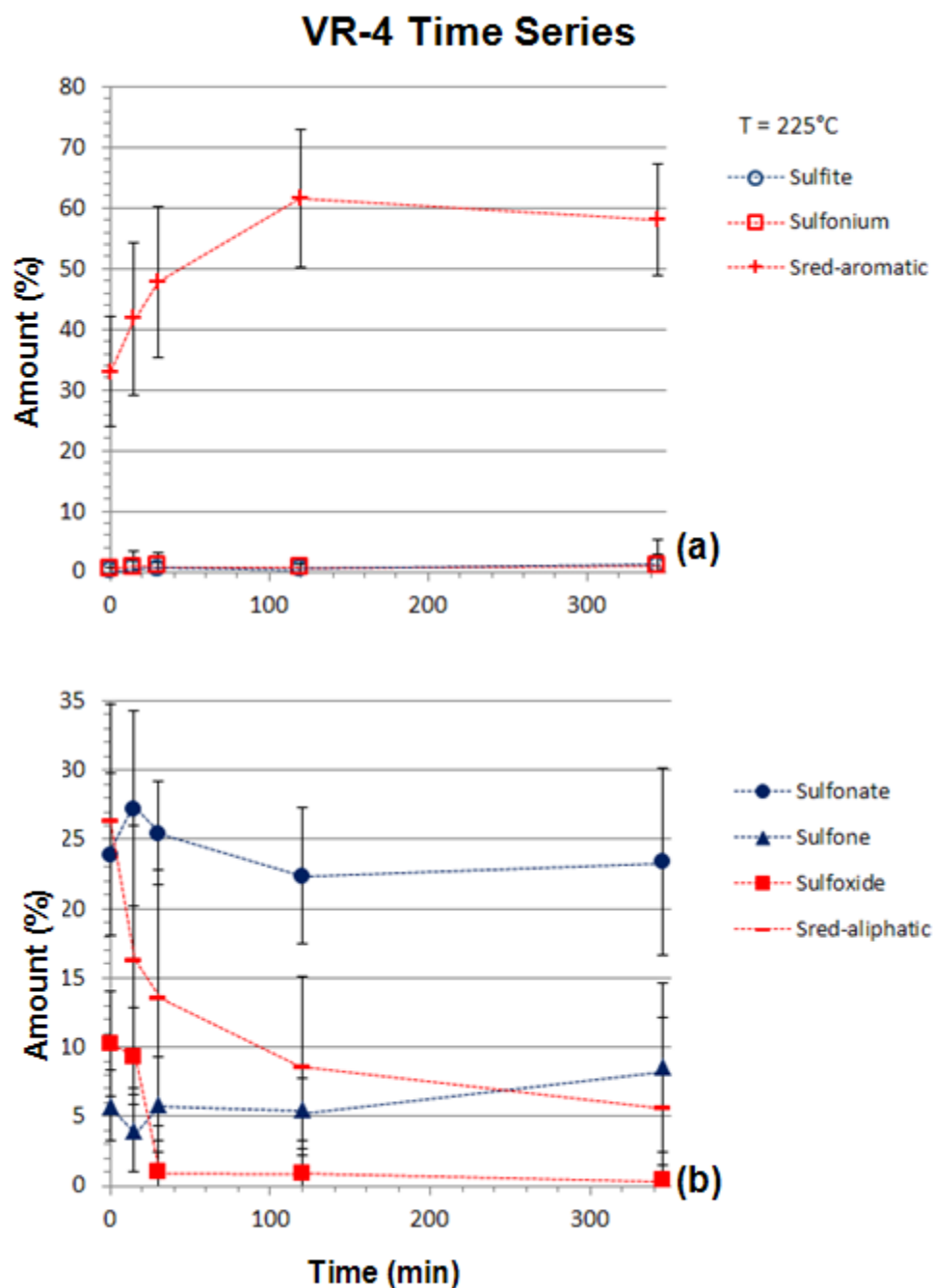
The transport of sulfate to waterways is important, especially when waterways like the Vallecito Reservoir are contaminated with mercury [3]. This is because under anoxic conditions (e.g., benthic zone of a lake), inorganic mercury(II) species may transform into the more toxic methylated organic mercury species via the activity of sulfate-reducing bacteria [51]. In our study, the likelihood that soil sulfates that formed during the Missionary Ridge wildfire were transported to the Vallecito Reservoir may therefore depend on the proximity of fire-affected soils to the reservoir, the amount of forest floor burned, and the topographical and physical features of fire-affected areas.

**Changes in the Reduced Aromatic and Aliphatic Sulfur Content.** In the VR-4 time series, an initial apparent increase and subsequent gradual decline in the reduced aromatic sulfur content was observed as the duration of heating was increased. The fractional amount of Sred\_aromatic sulfur increased ( $p \leq 0.05$ ) from 26.79 to 30.85% after heating at 225°C for 30 minutes (cf., Table 4), however the Sred\_aromatic sulfur content at longer

times was not statistically different from the unburned sample. These changes in the fractional amount of reduced aromatic sulfur are less rapid than both the increase in sulfate content and decrease in content of the more reduced sulfur constituents, particularly reduced aliphatic sulfur compounds (cf., Table 4 and Figure 10). To help elucidate these changes, the time series data were replotted to focus solely on changes in the organic sulfur content [35; Figure 14]; the fractional amounts of inorganic sulfate were excluded from the total amount of sulfur because mineral sulfates are the major form of inorganic sulfur in soils.

In the revised VR-4 time series plot (Figure 14), the reduced aromatic sulfur content increased from 33.03 to 61.54% in the first 120 min then decreased slightly to 58.09% upon further heating to 345 min. Meanwhile, the reduced aliphatic sulfur content decreased from 26.41 to 5.59% over the entire 345 min heating period. Kelemen et al. [35] observed a similar increase in the aromatic sulfur content and decrease in the aliphatic sulfur content of several peat samples that were heated for varying lengths of time (5 min to 7 d) and at various temperatures (175 to 400°C). When natural lignite and coal were compared to heated peat samples, the authors also observed a similar increase in the aromatic sulfur content and decrease in the aliphatic sulfur content that depended on the degree of coalification (i.e., length of time and temperature of heat exposure) experienced by the samples. Kelemen et al. suggested that the fractional amount of aromatic sulfur increased with increasing level of peat pyrolysis via loss of aliphatic sulfides, disulfides, organic sulfites, and via the emission of sulfur dioxide. Furthermore, sulfites may have formed from the oxidation of pure-compound mercaptans and disulfides [35], which may partially account for the decrease in Sred\_aliphatic content observed in VR-4 soils. These transformations may have likely





**Figure 14.** Sulfur speciation changes of organic sulfur constituents in VR-4 soil samples heated at 225°C as a function of time. (a) Trends in sulfite, sulfonium, and Sred\_aromatic content. (b) Trends in sulfonate, sulfone, sulfoxide, and Sred\_aliphatic content. Sulfur speciation was calculated using the second fitting approach on full-energy range (2465 to 2510 eV) spectra. Error bars represent  $\pm 1\sigma$  values.

occurred in our soil samples and may account for the constant decrease in reduced aliphatic sulfur and increase in sulfate content over the 345 min heating period.

Similar to the results of Kelemen et al. [35], heat caused an increase in the aromatic carbon content of forest floor samples from a Siberian Scots pine forest that experienced a natural fire [52]. A decrease in the oxygen-containing alkyl content and increases in the oxygen-free alkyl, carboxyl, and carbonyl carbon contents were observed in burned forest floor samples. Almendros et al. [53] also observed a decrease in the content of aliphatic carbon and a parallel increase in the content of aromatic carbon in soil humic acid that was subjected to heating in a furnace at 350°C for 120 s. In addition, the carbonyl signal in the humic acid remained prominent during the heating process. Almendros et al. [11] proposed that changes in carbon were caused by the decarboxylation and dehydration/condensation of oxygen-containing alkyl structures during heating.

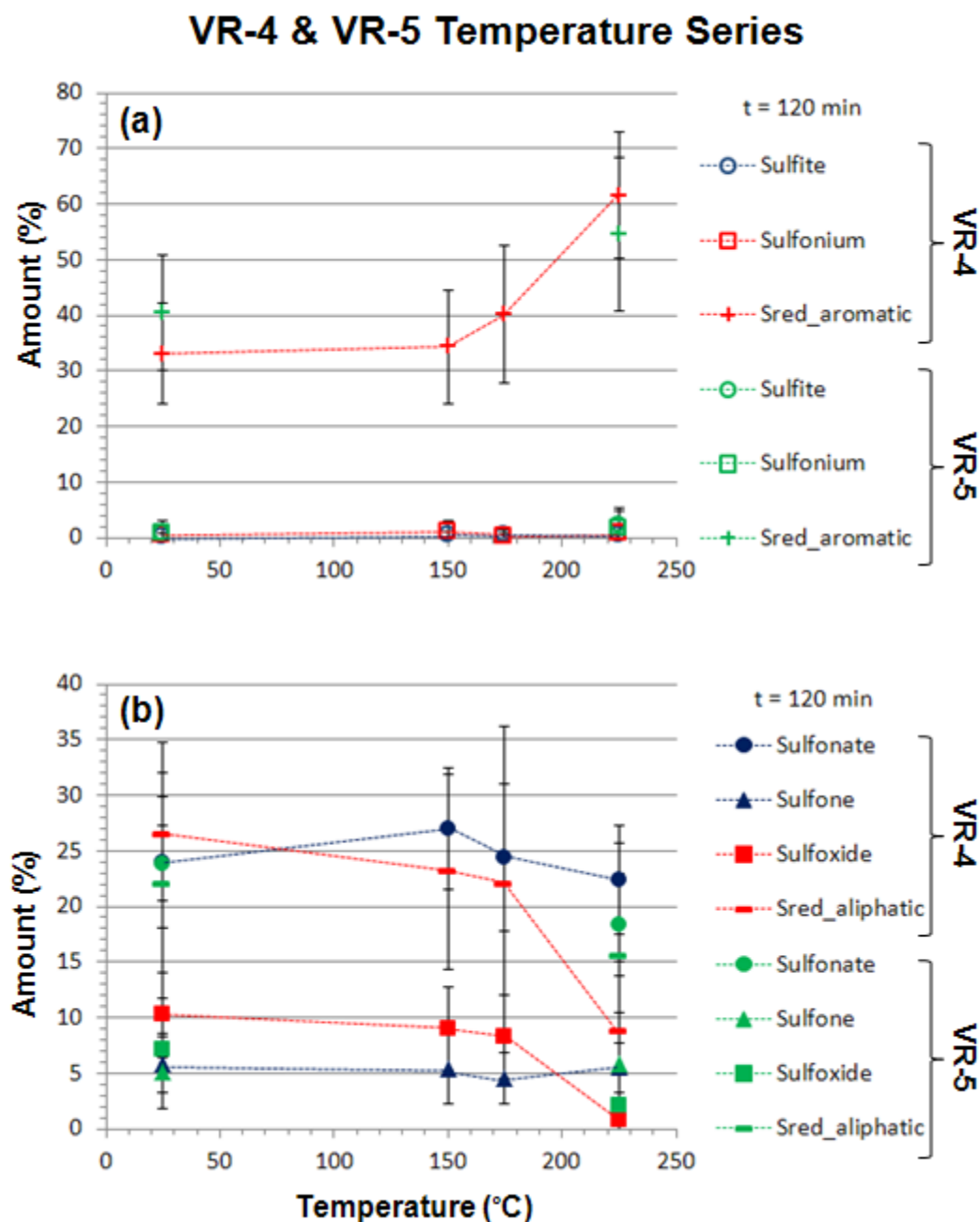
In the original VR-4 temperature series plots (Figure 12), which took all sulfur constituents into consideration, changes in the fractional amounts of each constituent were most apparent at 225°C. The Sred\_aliphatic content decreased at 175°C from 21.96 to 16.94%. However, the Sred\_aromatic sulfur content in heated samples did not significantly differ from the unburned control regardless of temperature (Table 6, Figure 12). Although we did not measure gaseous sulfur emissions, sulfur dioxide adsorbed to aerosol particles may have oxidized to form sulfites that may subsequently oxidized to sulfates [54].

Also, in contrast to the constant decrease in Sred\_aliphatic content observed in the time series (Table 4, Figure 10), there was no statistical difference in the Sred\_aliphatic content between the unburned control and the soil heated to 150°C for 120 min (Table 6, Figure 12). Krein and Aizenshtat [55], who heated synthesized aliphatic polysulfides to

160°C, observed the transformation of polysulfides into (aliphatic) cyclic mono- and polysulfides. Thus, similar to their findings, aliphatic polysulfides that may have been present in our soils could have transformed into cyclic mono- and polysulfides, which would result in no apparent change in the fractional Sred\_aliphatic sulfur content, as we observed.

As the temperature in our experiments was increased from 150°C to 175 and 225°C, the fractional Sred\_aliphatic content in VR-4 soils decreased ( $p \leq 0.05$ ) while the Sred\_aromatic content remained relatively unchanged. It is possible that Sred\_aromatic compounds might form with both time (e.g., as in the VR-4 times series discussed above) and temperature, but that its formation rate is slower than the transformation of Sred\_aliphatic compounds to sulfates. Thus, the overall sulfur transformation rate in our soils is likely controlled by temperature-induced oxidation to sulfate of more reduced sulfur compounds.

In order to observe these changes in the Sred\_aromatic and Sred\_aliphatic content in our VR-4 and VR-5 temperature series, we again examined only the organic sulfur constituents in the soils (Figure 15). In this case, the Sred\_aromatic sulfur content continually increased and the Sred\_aliphatic content decreased, especially as temperature increased from 175 to 225°C. Although our experimental setup did not allow us to identify the formation of specific sulfur compounds, we hypothesize that at these temperatures, possible aliphatic cross-linked macromolecular polysulfides in the soil may have transformed into aromatic isoprenoid thiophenes and heterocyclic sulfur compounds [55, 56]. This may explain the continual increase in Sred\_aromatic sulfur content and decrease in the Sred\_aliphatic content when only organic sulfur constituents were considered. Alternatively, Sred\_aliphatic compounds, such as Hg-binding thiols, may have transformed into Hg-bound Sred\_aromatic species that are similar to the S-XANES reference we used of an observed mercury-bound



**Figure 15.** Sulfur speciation changes of organic sulfur constituents in VR-4 and VR-5 soil samples heated for 120 min as a function of temperature. (a) Trends in sulfite, sulfonium and Sred\_aromatic content. (b) Trends in sulfonate, sulfone, sulfoxide, and Sred\_aliphatic content. Sulfur speciation was calculated using the second fitting approach on full-energy range (2465 to 2510 eV) spectra. Error bars represent  $\pm 1\sigma$  values.

organic sulfur species, which was obtained from a mercury-contaminated floodplain soil near Oak Ridge, TN.

**Changes in the Content of Other Sulfur Constituents.** When only organic sulfur constituents were considered, the fractional sulfoxide content decreased both with time and temperature, with the largest changes observed at 225°C (Figures 14 and 15). However, the sulfonate and sulfone content fluctuated around 23-25% and 5-6%, respectively. Since the oxidation of pure-compound sulfides have been observed to produce sulfoxides and sulfones [57], perhaps a portion of Sred\_aliphatic sulfides in our soils oxidized to sulfoxides, which may have then quickly oxidized further to sulfones or other products. Because the fractional amount of sulfonate and sulfone was more or less unchanged, perhaps there is a higher energy barrier to oxidizing sulfonates and sulfones than sulfoxides. In the environment, microbe-facilitated redox transformations are also known to transform sulfonates, sulfones, and sulfoxides [58-63], however further studies are needed to determine if there are any effects of natural fire on changing the amounts of these sulfur compounds in the soil.

**Comparison of Changes in the VR-4 and VR-5 Total Sulfur and Organic Matter Content.** Before heating, the unburned VR-4 control had 60% more total sulfur and 47% more organic matter (by dry mass) than the unheated VR-5 control sample, which had been previously exposed to the Missionary Ridge Wildfire (cf., Table 9). After heating for 120 minutes at 225°C, the sulfur content in both the VR-4 and VR-5 soils decreased, but the VR-4 soil had 75% more total sulfur and 44% more organic matter than the VR-5 soil sample. Furthermore, the fractional amounts of sulfate and Sred\_aromatic sulfur constituents were less and the fractional amount of Sred\_aliphatic constituent was greater in the VR-4 unheated soil compared to the unheated VR-5 control (cf., Tables 6 and 8). After heating, the sulfate

and Sred\_aliphatic content were less and the Sred\_aromatic content was greater in the VR-4 soil than in the VR-5 soil sample. Thus, the VR-4 soil retained more sulfur and organic matter and resulted in more Sred\_aromatic sulfur content after heating than the VR-5 soil. This suggests that sulfur and organic matter may be more labile in soils that have been previously exposed to fire.

In a fire, pyrolysis may induce the formation and release of organic flammable gases (e.g., methane, formaldehyde, ethanol) and cause temperatures to elevate to 300-600°C, stimulating the flaming combustion of fuels [e.g., woody debris; 64]. Sulfur dioxide ( $\text{SO}_2$ ;  $\text{S}^{+IV}$ ) is the major type of gaseous sulfur species emitted from fuels during combustion [64-66]. Smaller amounts of carbonyl sulfide ( $\text{S}^{-II}$ ), dimethyl sulfide ( $\text{S}^{-2}$ ), and dimethyl disulfide ( $\text{S}^{-1}$ ) may also be formed [67-69], although carbonyl sulfide emission is more prevalent at lower temperatures [e.g., fuel pyrolysis and smoldering combustion; 70]. The conditions in our experiments were relatively low in temperature (25-225°C) and did not involve an open flame, which is most similar to pyrolysis settings. Thus, sulfur lost during heating was most likely emitted as carbonyl sulfide, though dimethyl sulfide and dimethyl disulfide may have also been emitted. In addition to the decrease in the total sulfur content, the emission of these aliphatic sulfur compounds likely contributed to the systematic decrease in fractional Sred\_aliphatic sulfur content observed during our heat treatments. Furthermore, sulfoxide constituents may have been transformed and released as sulfur dioxide.

## CONCLUSIONS

In this study, we used S-XANES spectroscopy to measure changes in the relative proportions of sulfur species in mineral soil that were affected by heat from a wildfire and/or from laboratory heating experiments. The results of our S-XANES analyses showed that soil sulfur was oxidized with heat. In general, the fractional amount of sulfate increased by 71 to 209%, and the sulfoxide, reduced aliphatic sulfur, sulfonate, and sulfone content decreased by 80 to 98%, 55 to 91%, 40 to 49%, and 23 to 39%, respectively. These changes were observed with increasing heating time and temperature regardless of whether or not soil had been burned in the wildfire. When changes in only the organic sulfur content were considered, the reduced aromatic sulfur content increased by 35 to 86%, while the sulfonate and sulfone content remained relatively the same at 21 to 25% and 5 to 6%, respectively. The sulfoxide and reduced aliphatic sulfur content decreased by 71 to 96% and 30 to 79%, respectively, and the fractional amounts of sulfite and sulfonium content in soils were generally < 2% of the total sulfur.

The rate of change of the increase in fractional sulfate content appeared to be fastest, followed by changes in the reduced aliphatic sulfur, reduced aromatic sulfur, and sulfoxide contents. With respect to heating conditions used in our experiments, our results likely reflect the soil sulfur changes that might occur when soils are exposed to smoldering heat from a wildfire or prescribed burn. Since reduced aliphatic sulfur moieties are important ligands that bind strongly to mercury, then oxidation of sulfur due to fire potentially reduces the capacity of soils to bind mercury. In addition, the observed increase in the fractional soil sulfate content may pose an added hazard if affected soils are located near water bodies such as the Vallecito Reservoir (Durango, CO). Increased sulfate leaching into the reservoir could

accelerate the formation of methyl mercury at the sediment-water interface via microbially-induced reactions in which sulfate is reduced to sulfide. However, some mercury may remain bound to reduced aromatic or aliphatic sulfur, although the significance of this in terms of understanding mercury mobility in a watershed requires further study. Also, the rate of change of sulfur speciation in recovering soils after a fire still needs to be examined. An investigation of the role of sulfur speciation changes resulting from wildfire on the mercury-retaining capacity of fire-affected soils is ongoing.

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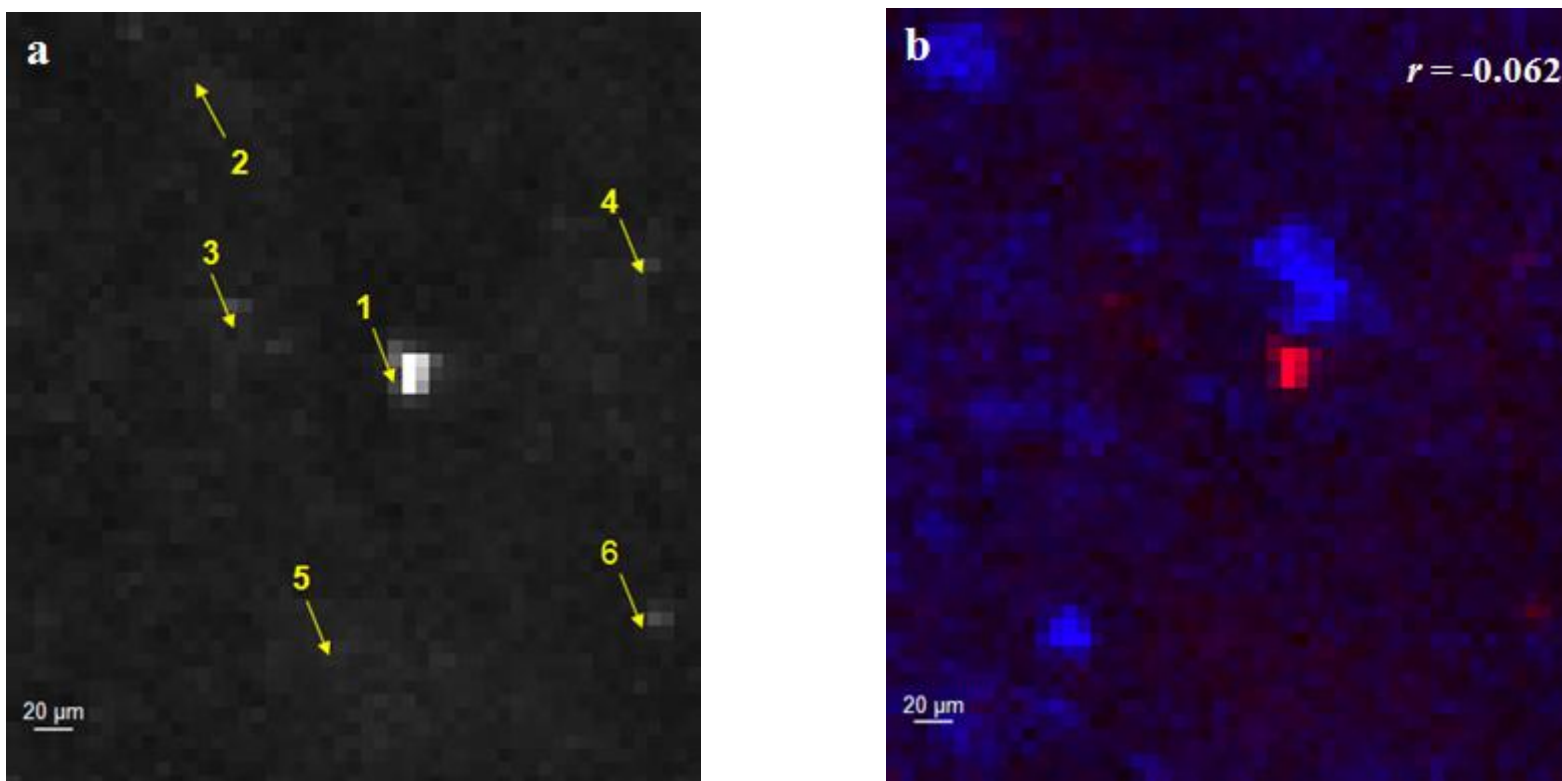
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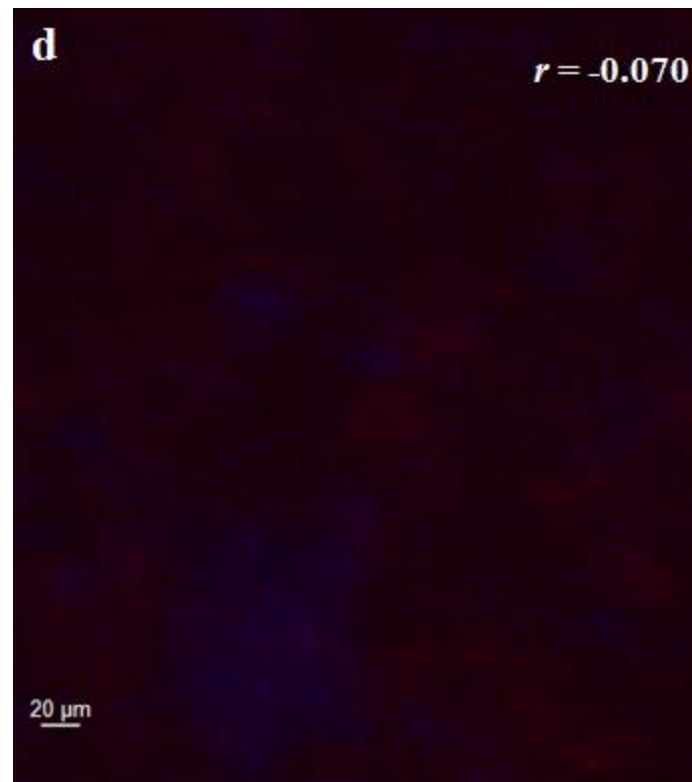
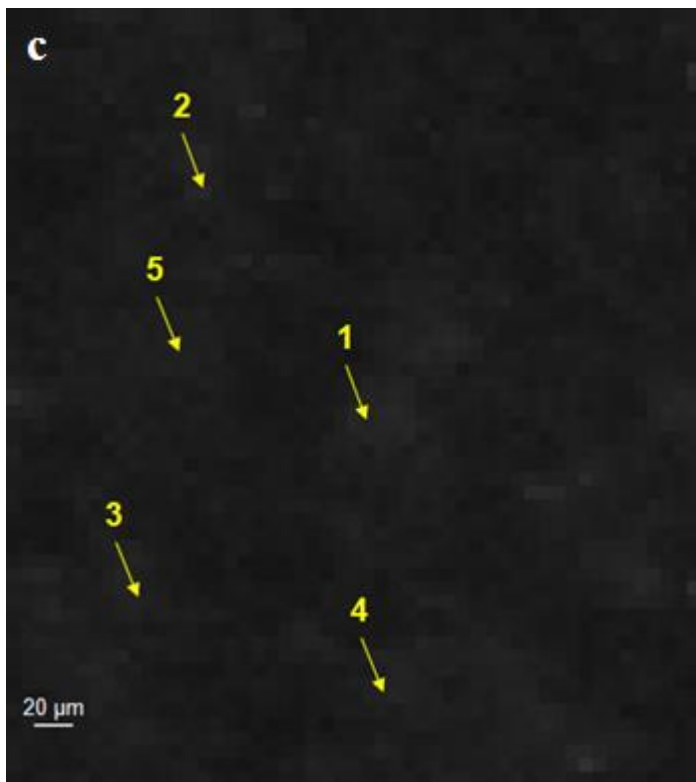
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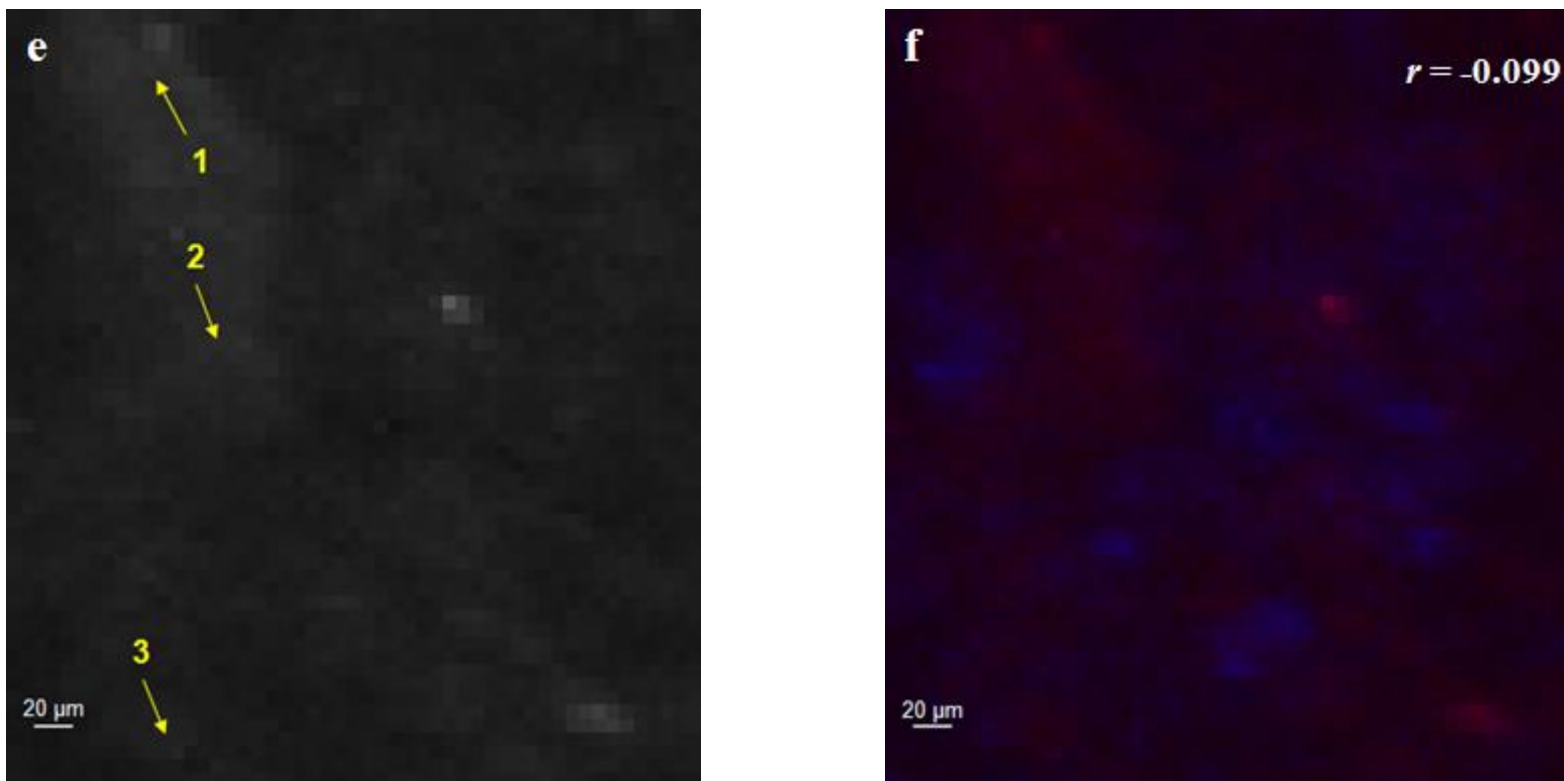
**Appendix A.** The XRF maps of all heated and unheated soils.



**Figure A1.** (a) Grey-scale XRF map from Region 1 of the VR-4 unheated soil sample. Dark areas correspond to regions of low sulfur, while brighter areas correspond to a continuum of increasing sulfur. Numbered arrows indicate the locations of S-XANES scans. (b) Bicolor XRF map from the same sample. Red and blue areas correspond to sulfur and iron, respectively. The Pearson correlation,  $r$ , between the iron and sulfur signals is displayed. Map sizes: 400  $\mu\text{m}$  x 400  $\mu\text{m}$ . (NOTE: A thin film sample was used, not a soil pellet.)

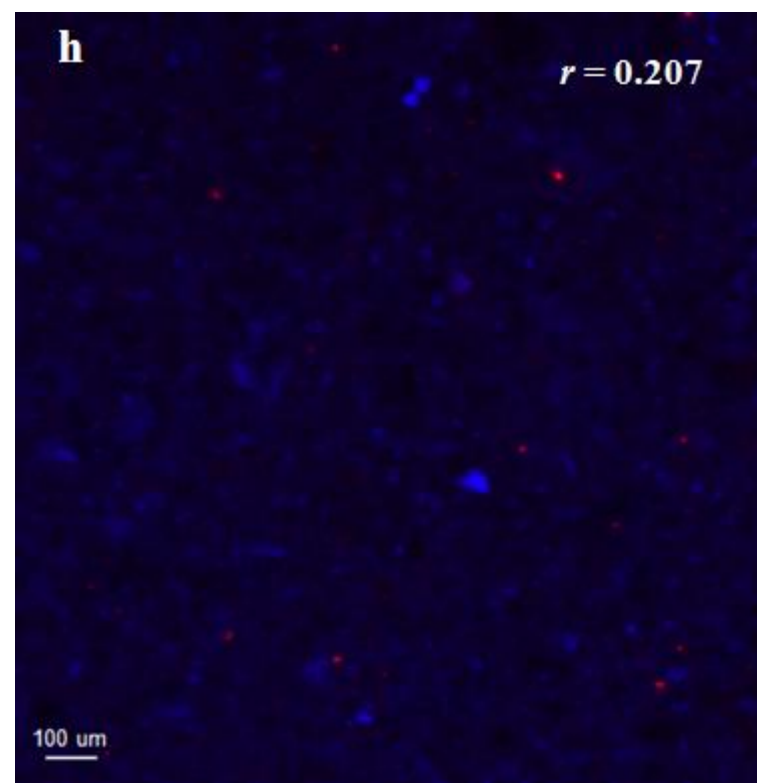
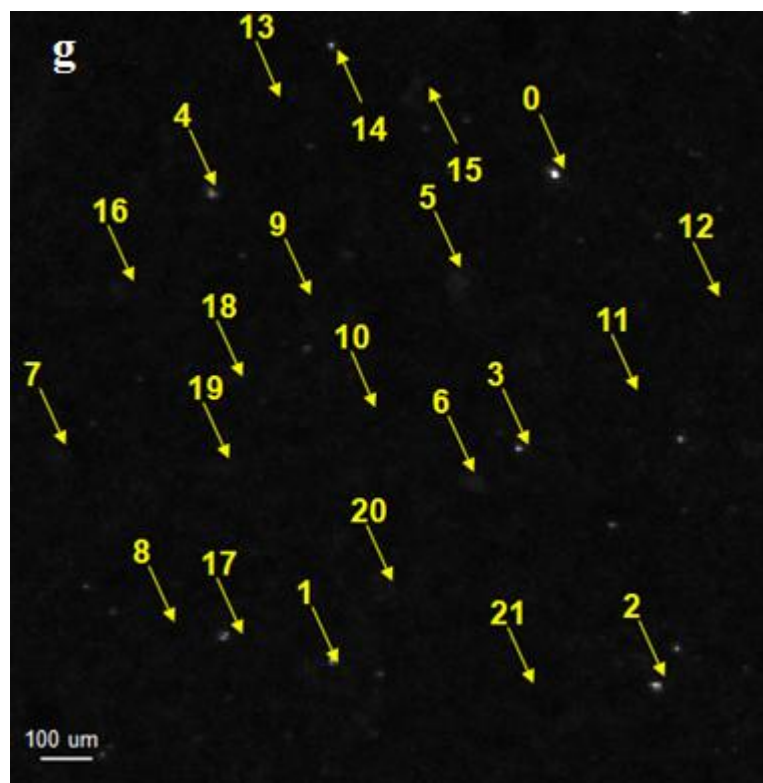


**Figure A1 (continued).** Grey-scaled (c) and bicolor (d) XRF maps taken from Region 2 of the VR-4 unheated soil sample. Map sizes: 400 μm x 400 μm. (NOTE: A thin film sample was used, not a soil pellet.)

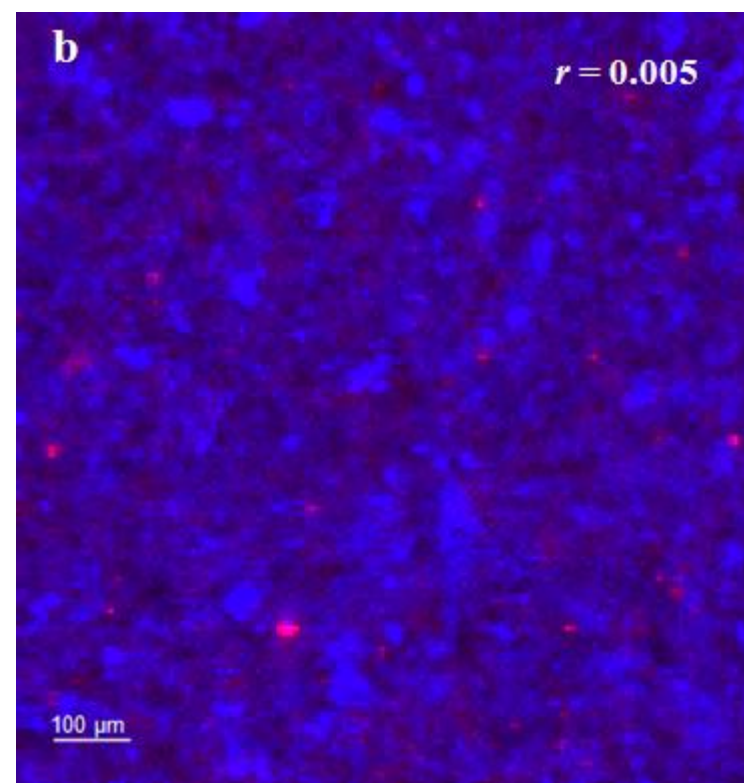
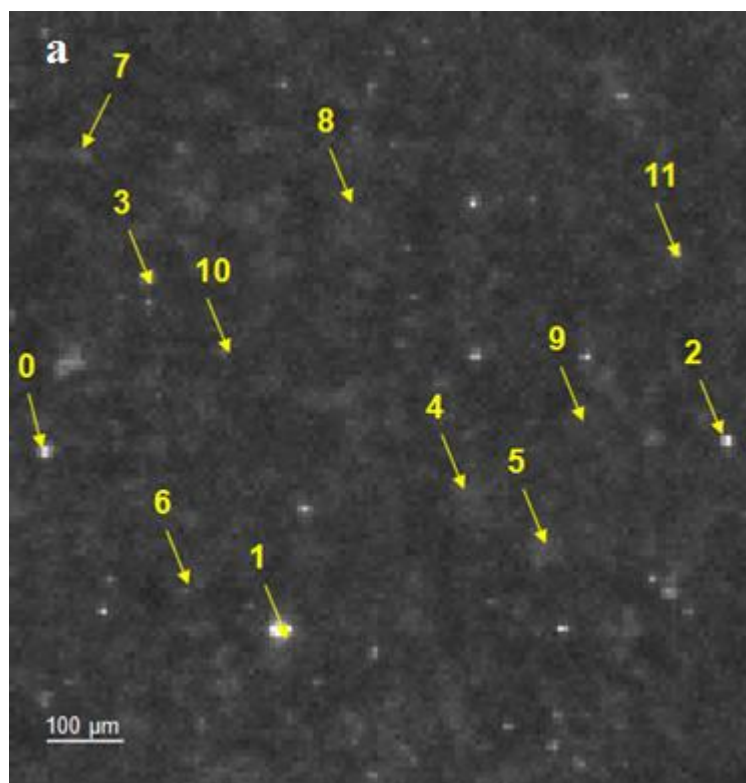


**Figure A1 (continued).** Grey-scaled (e) and bicolor (f) XRF maps taken from Region 3 of the VR-4 unheated soil sample. Map sizes: 400 μm x 400 μm. (NOTE: A thin film sample was used, not a soil pellet.)

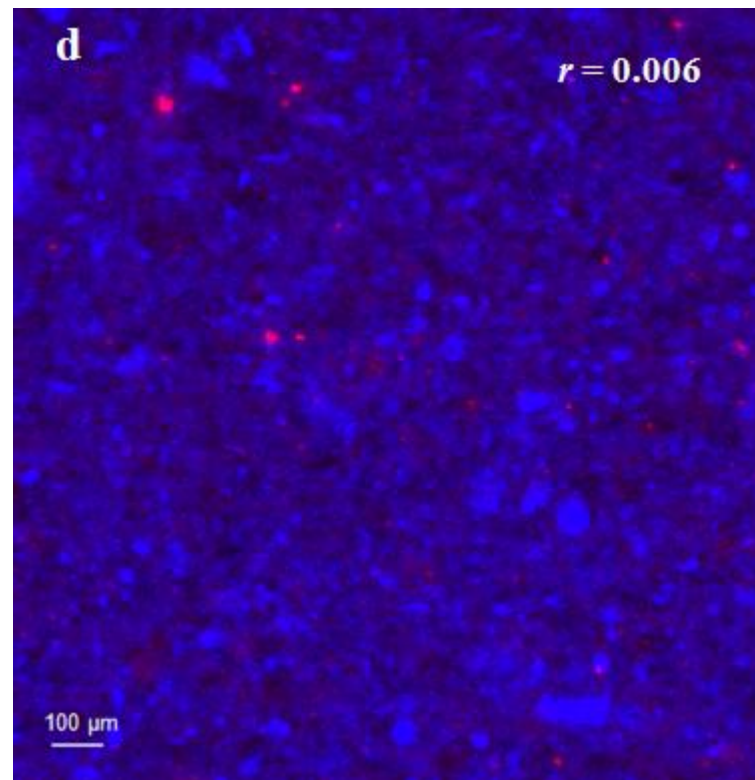
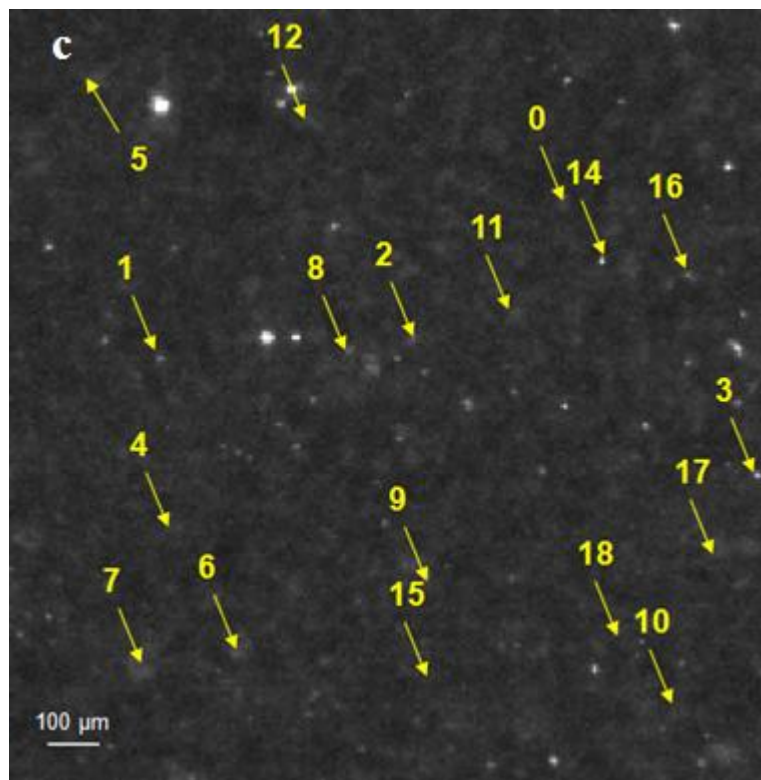




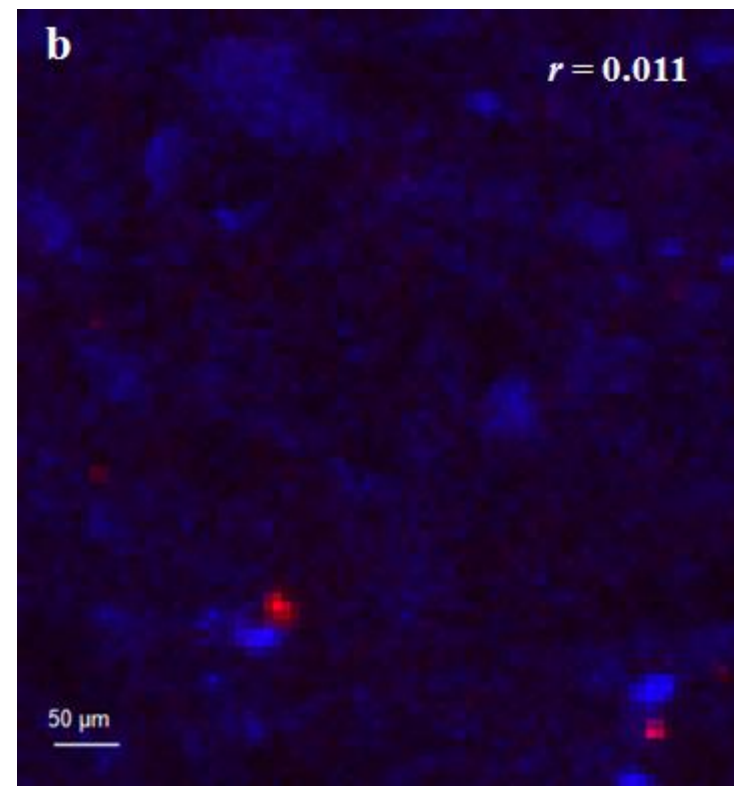
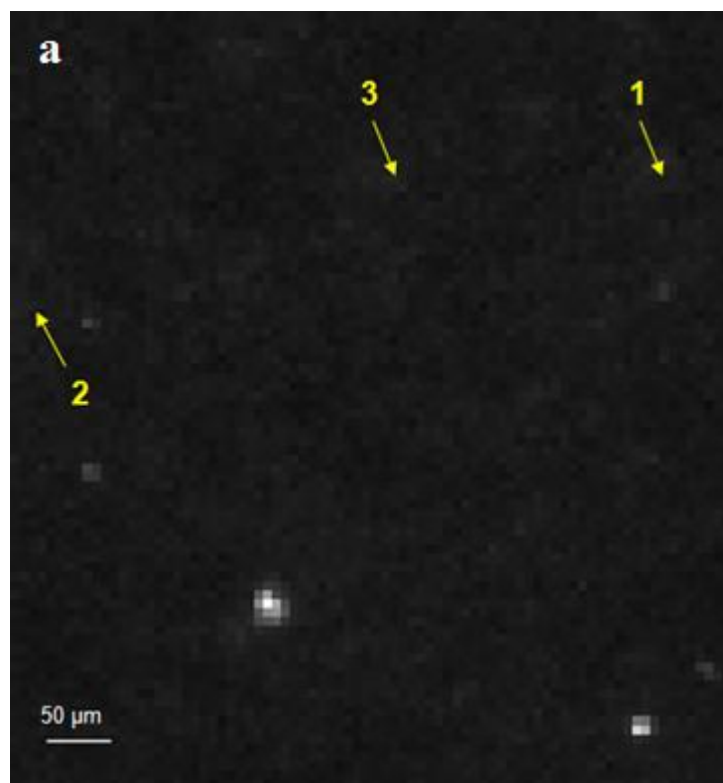
**Figure A1 (continued).** Grey-scaled (g) and bicolor (h) XRF maps taken from Region 4 of the VR-4 unheated soil sample. Map sizes: 1500  $\mu\text{m}$  x 1500  $\mu\text{m}$ .



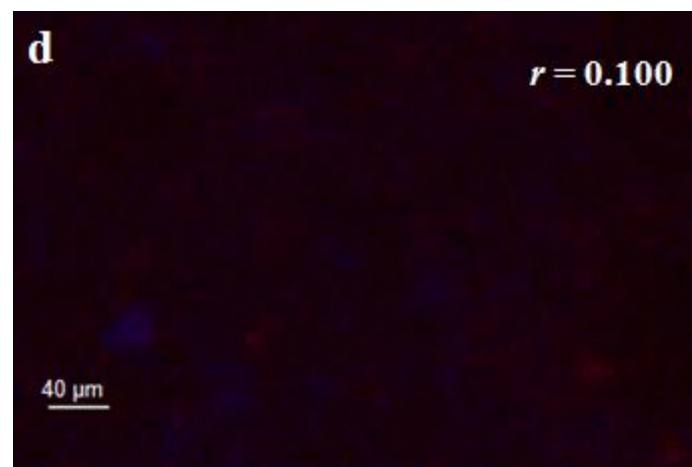
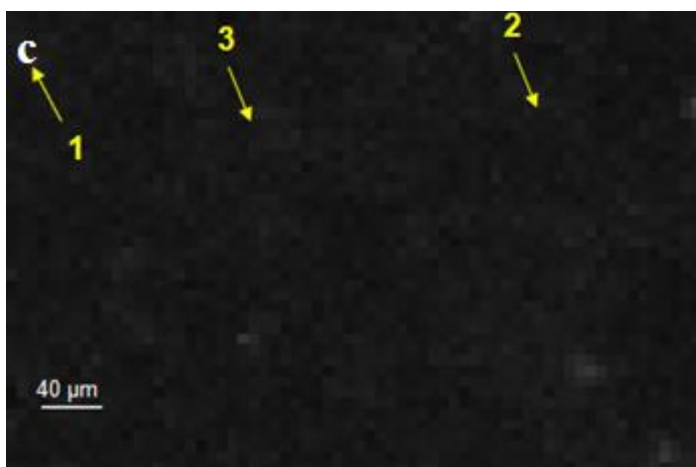
**Figure A2.** Grey-scaled (a) and bicolor (b) XRF maps taken from Region 1 of the VR-4 soil sample heated at 225°C for 15 minutes. Map sizes: 1000  $\mu\text{m}$  x 1000  $\mu\text{m}$ .



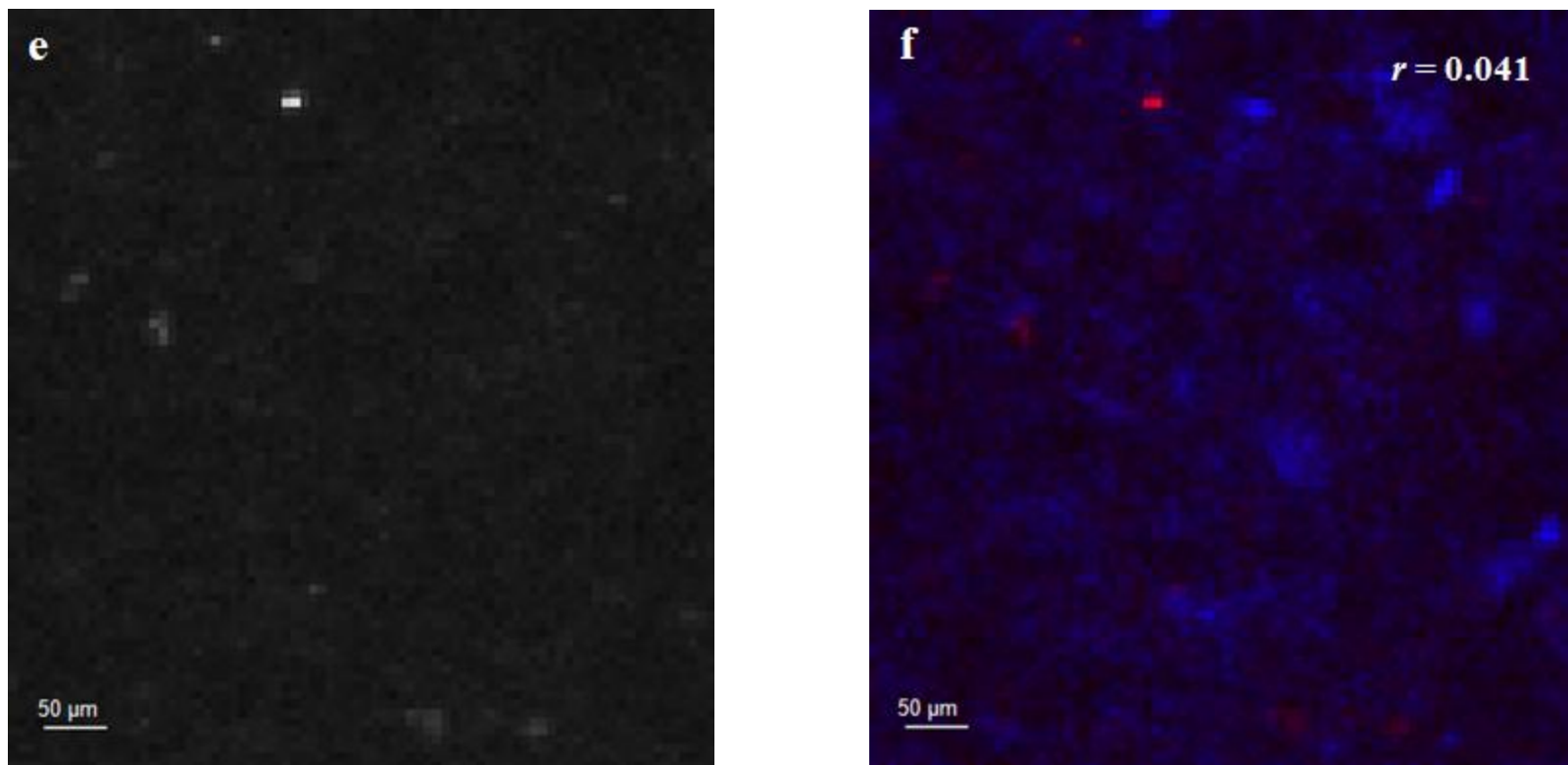
**Figure A2 (continued).** Grey-scaled (c) and bicolor (d) XRF maps taken from Region 2 of the VR-4 soil sample heated at 225°C for 15 minutes. Map sizes: 1500 μm x 1500 μm.



**Figure A3.** Grey-scaled (a) and bicolor (b) XRF maps taken from Region 1 of the VR-4 soil sample heated at 225°C for 120 minutes. Map sizes: 600 μm x 600 μm. (NOTE: A thin film sample was used, not a soil pellet.)

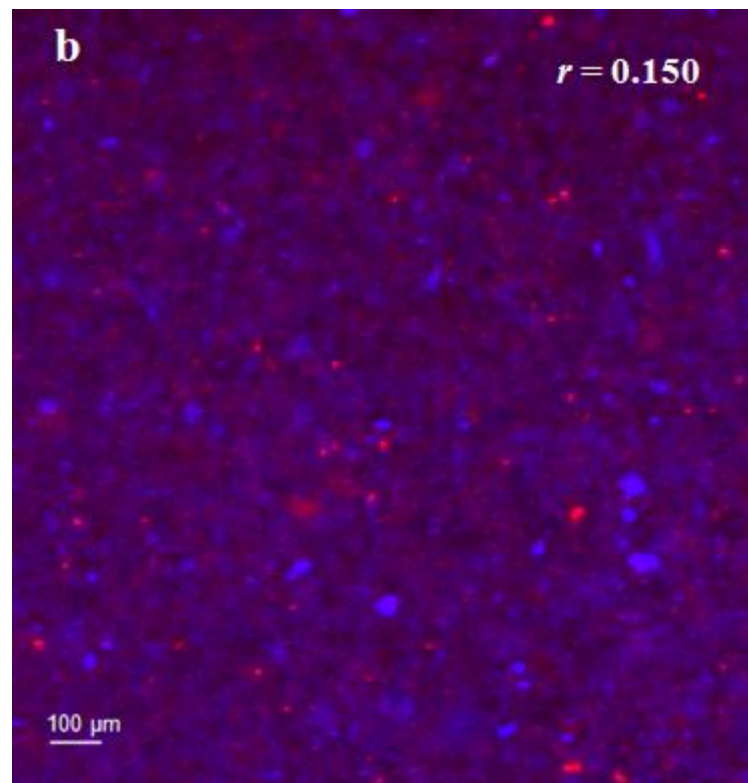
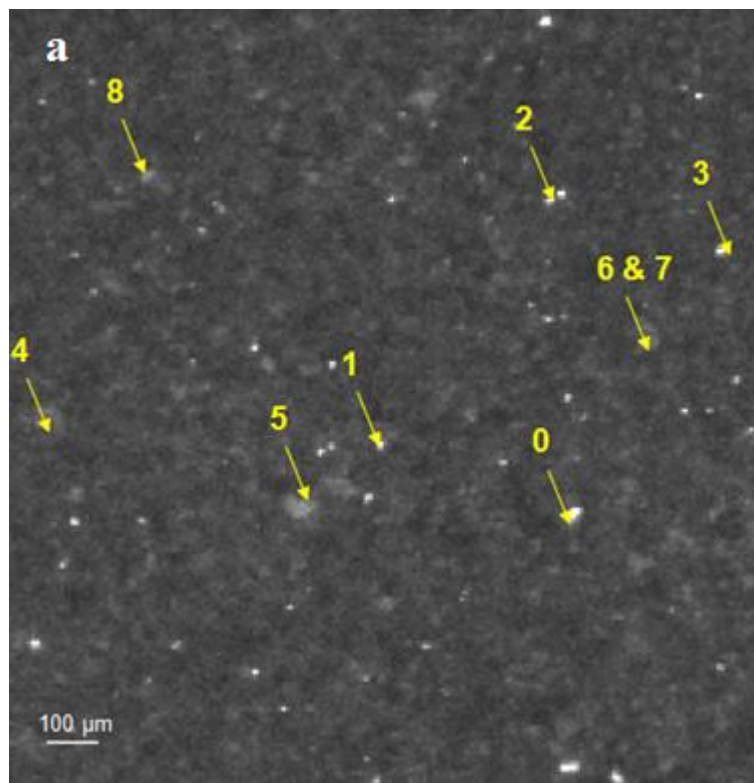


**Figure A3 (continued).** Grey-scaled (c) and bicolor (d) XRF maps taken from Region 2 of the VR-4 soil sample heated at 225°C for 120 minutes. Map sizes: 500 μm x 300 μm. (NOTE: A thin film sample was used, not a soil pellet.)

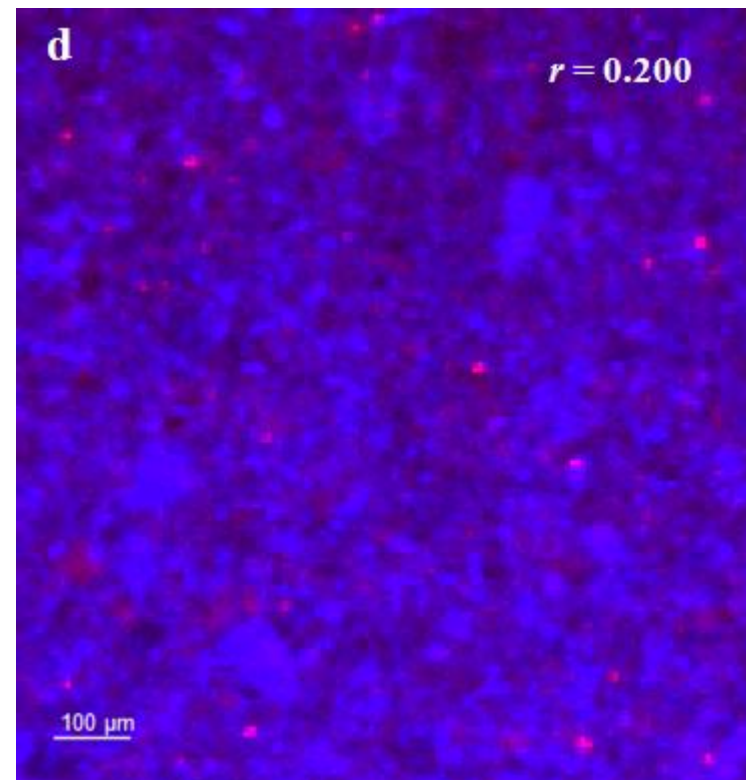
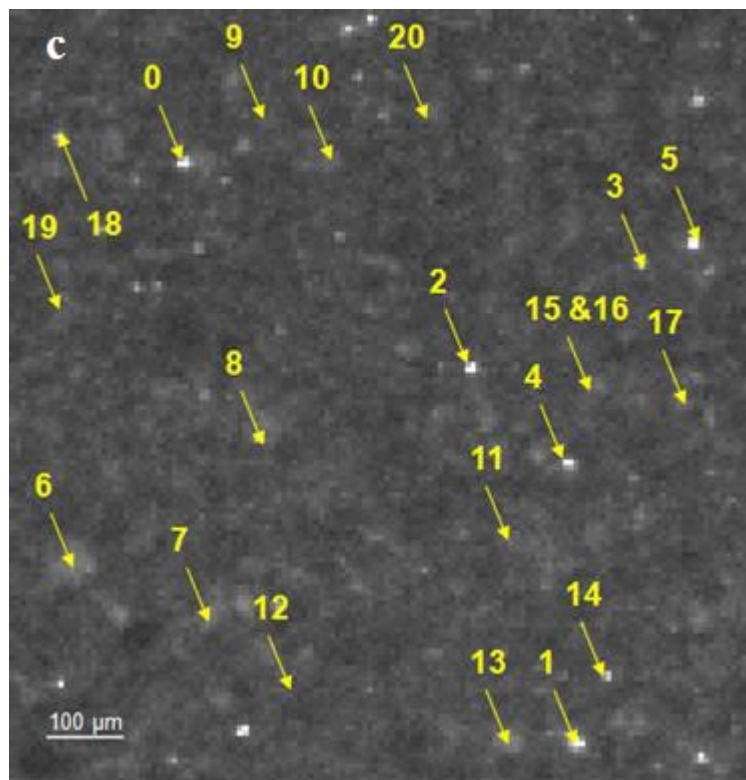


**Figure A3 (continued).** Grey-scaled (e) and bicolor (f) XRF maps taken from Region 3 of the VR-4 soil sample heated at 225°C for 120 minutes. Map sizes: 600 μm x 600 μm. (NOTE: A thin film sample was used, not a soil pellet.)



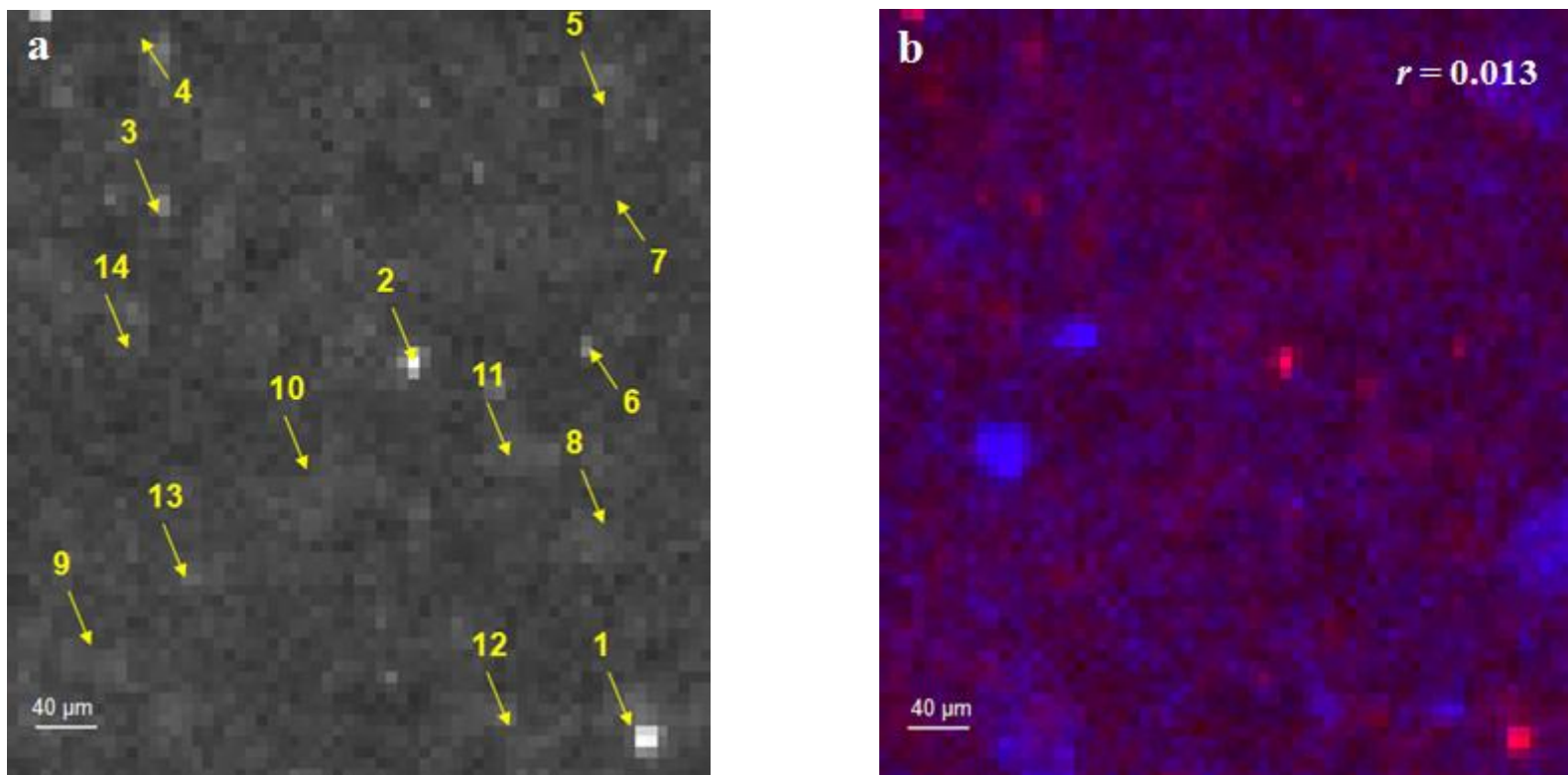


**Figure A4.** Grey-scaled (a) and bicolor (b) XRF maps taken from Region 1 of the VR-4 soil sample heated at 225°C for 345 minutes. Map sizes: 1500 μm x 1500 μm.

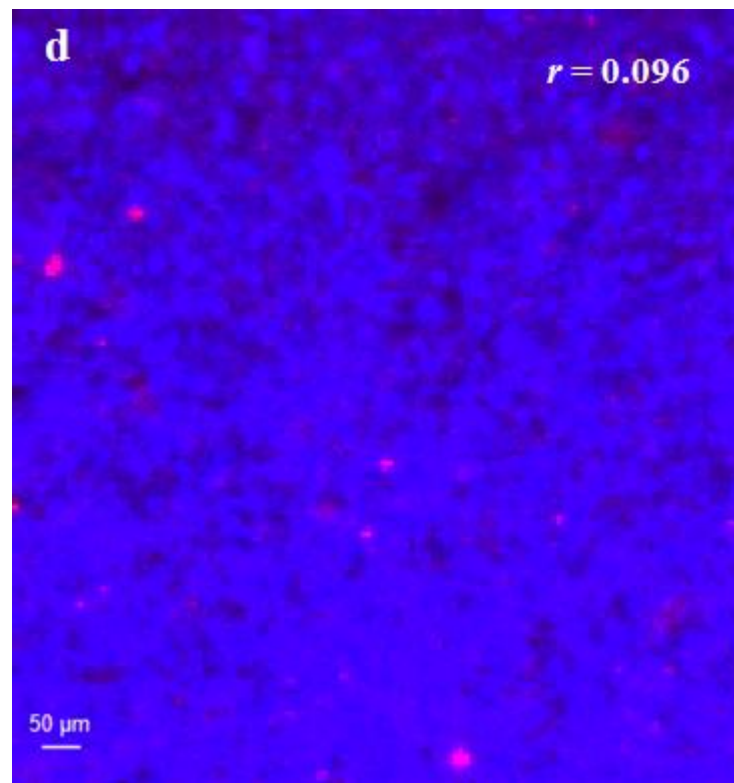
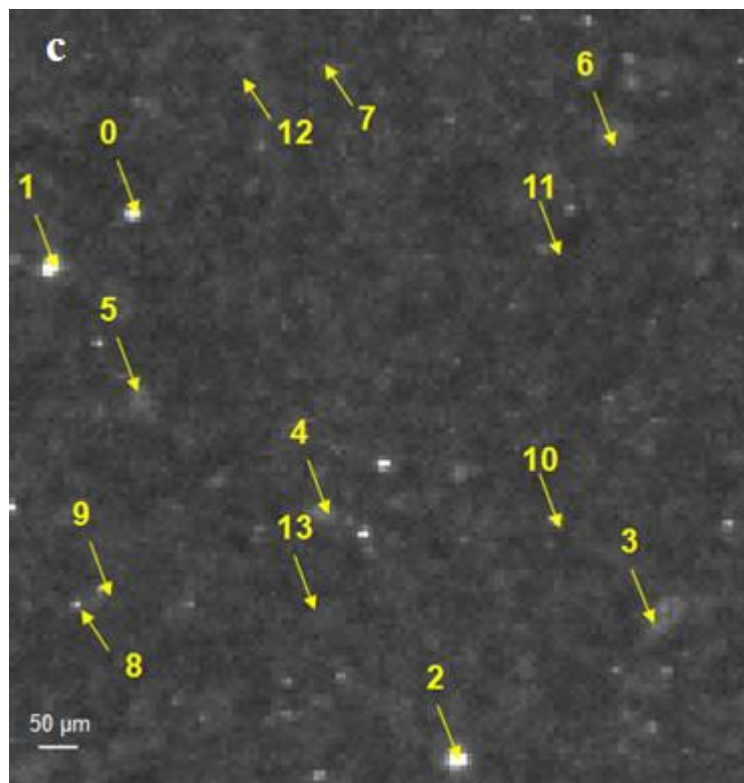


**Figure A4 (continued).** Grey-scaled (c) and bicolor (d) XRF maps taken from Region 2 of the VR-4 soil sample heated at 225°C for 345 minutes. Map sizes: 1000 µm x 1000 µm.

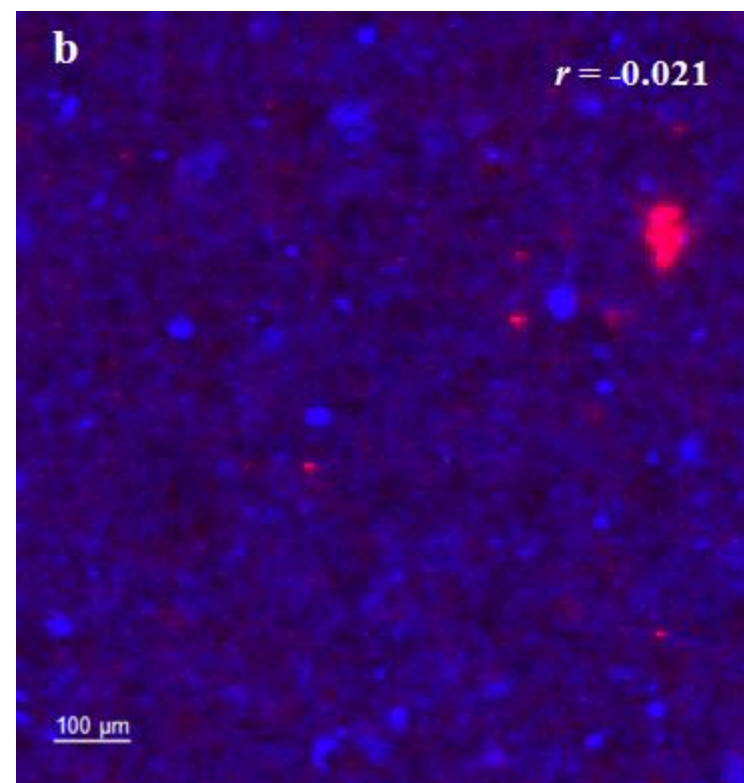
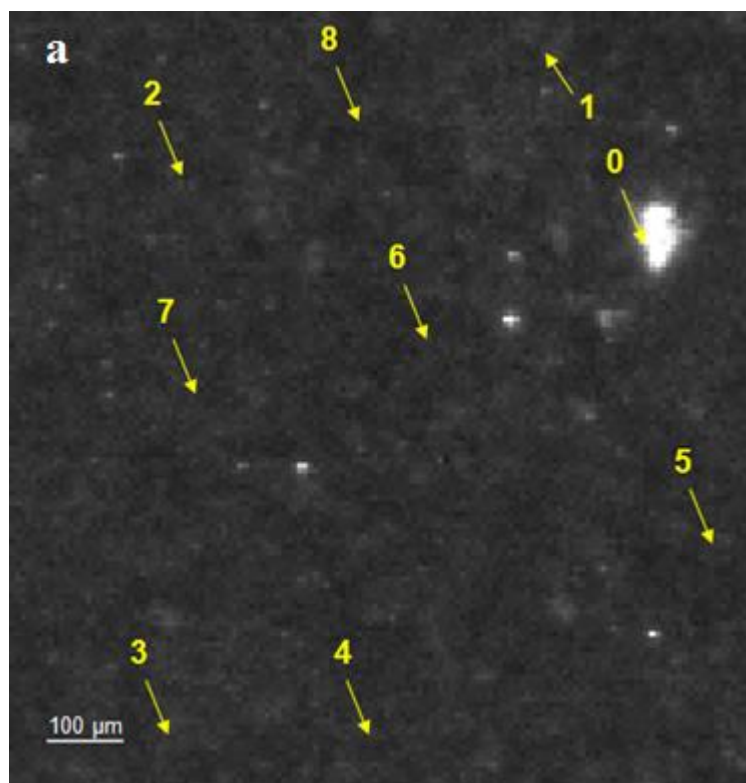




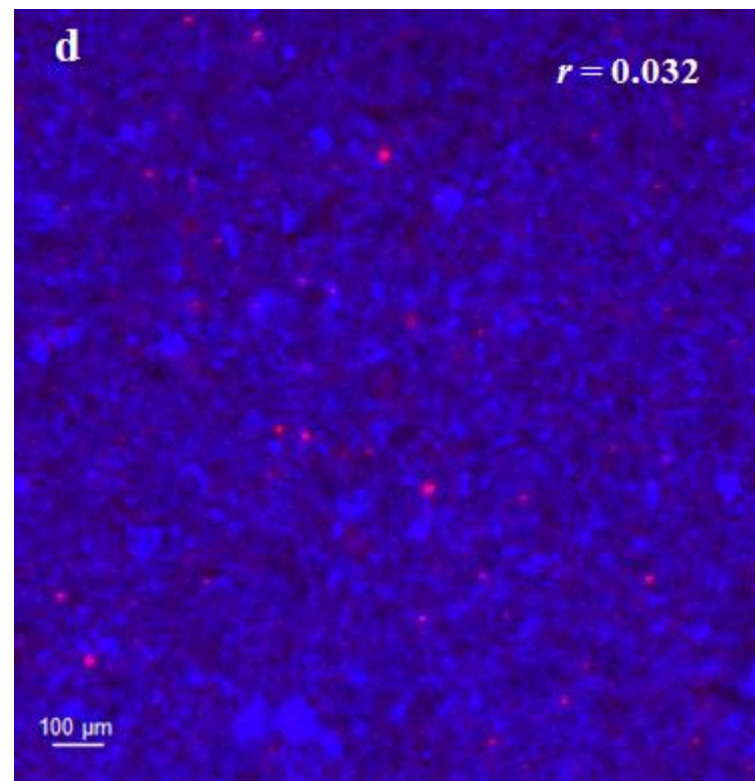
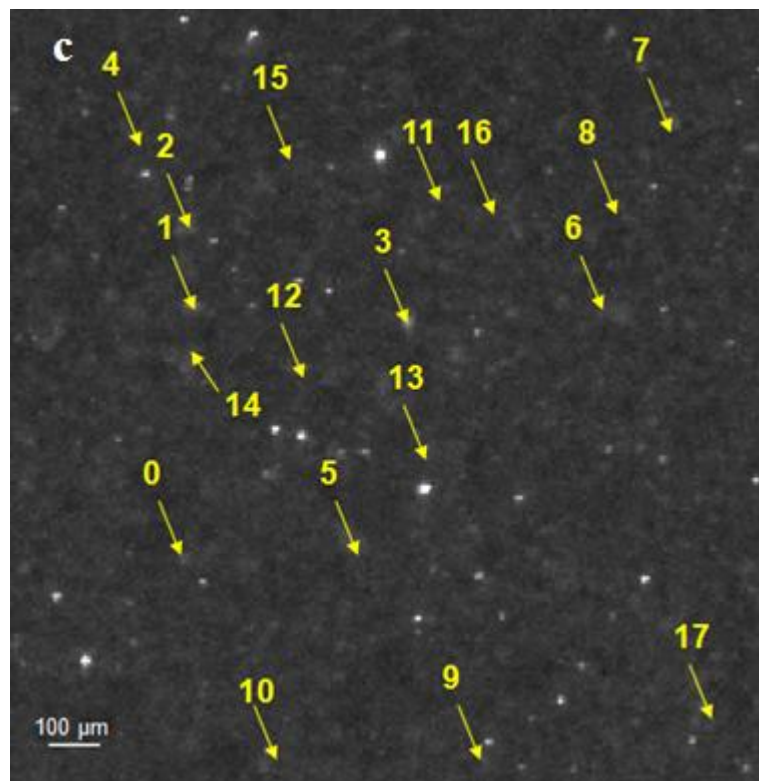
**Figure A5.** Grey-scaled (a) and bicolor (b) XRF maps taken from Region 1 of the VR-4 soil sample heated at 150°C for 120 minutes. Map sizes: 500 µm x 500 µm.



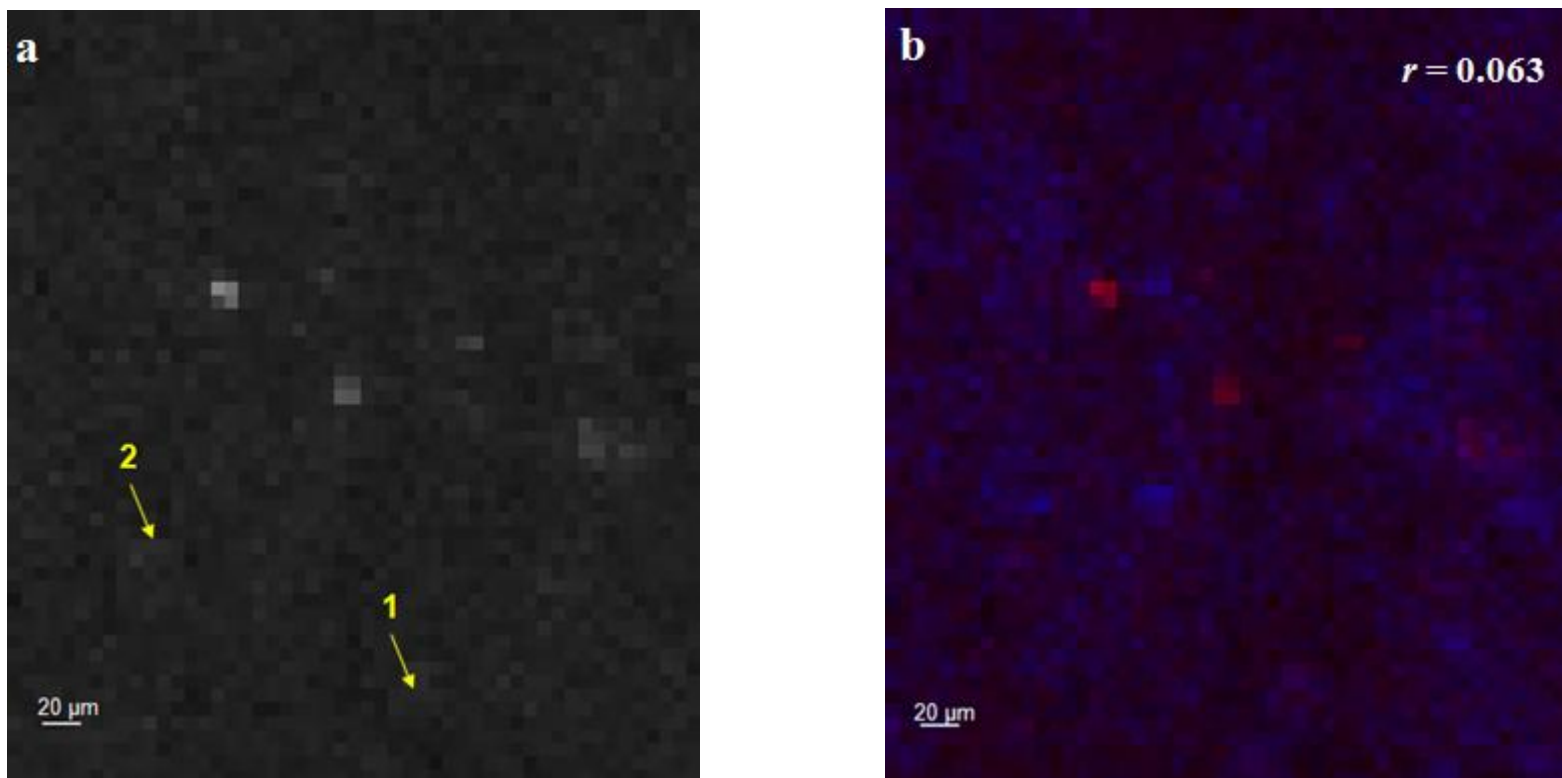
**Figure A5 (continued).** Grey-scaled (c) and bicolor (d) XRF maps taken from Region 2 of the VR-4 soil sample heated at 150°C for 120 minutes. Map sizes: 1000 µm x 1000 µm.



**Figure A6.** Grey-scaled (a) and bicolor (b) XRF maps taken from Region 1 of the VR-4 soil sample heated at 175°C for 120 minutes. Map sizes: 1000 µm x 1000 µm.



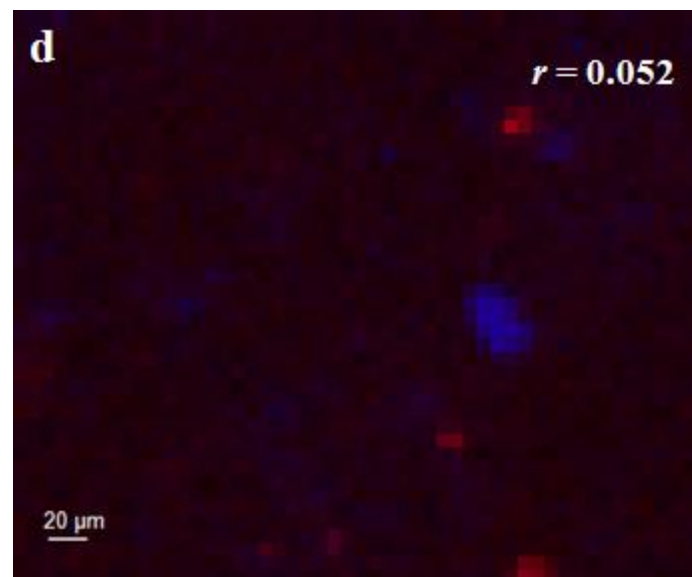
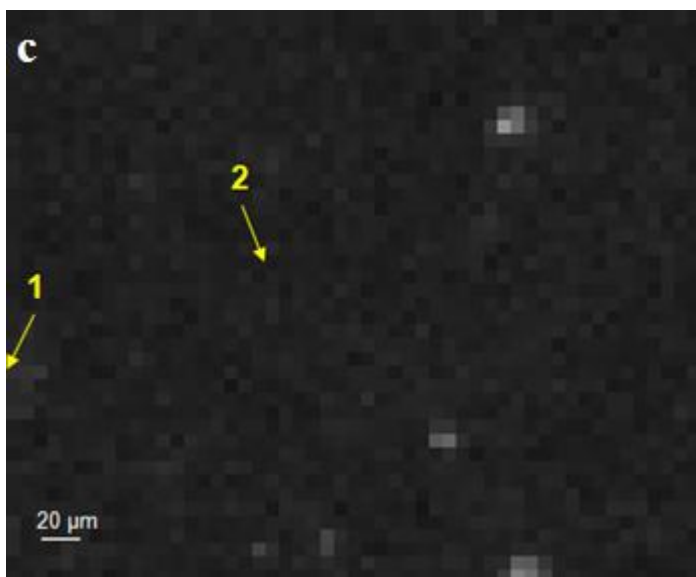
**Figure A6 (continued).** Grey-scaled (c) and bicolor (d) XRF maps taken from Region 2 of the VR-4 soil sample heated at 175°C for 120 minutes. Map sizes: 1500 µm x 1500 µm.



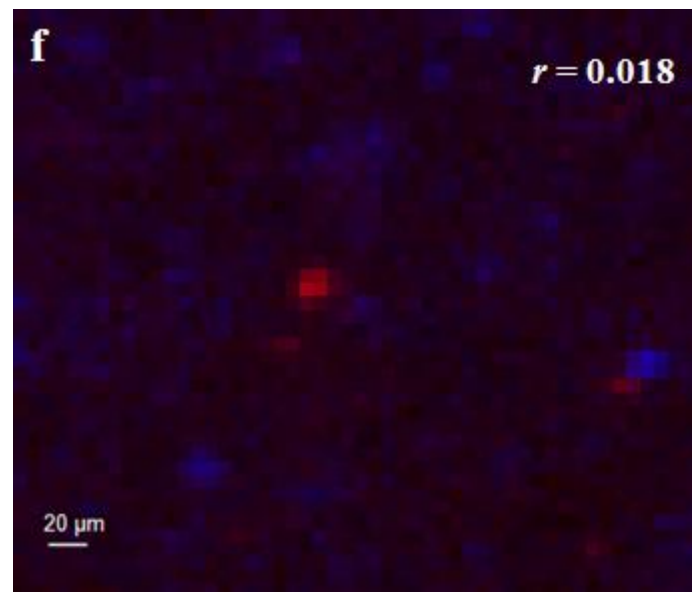
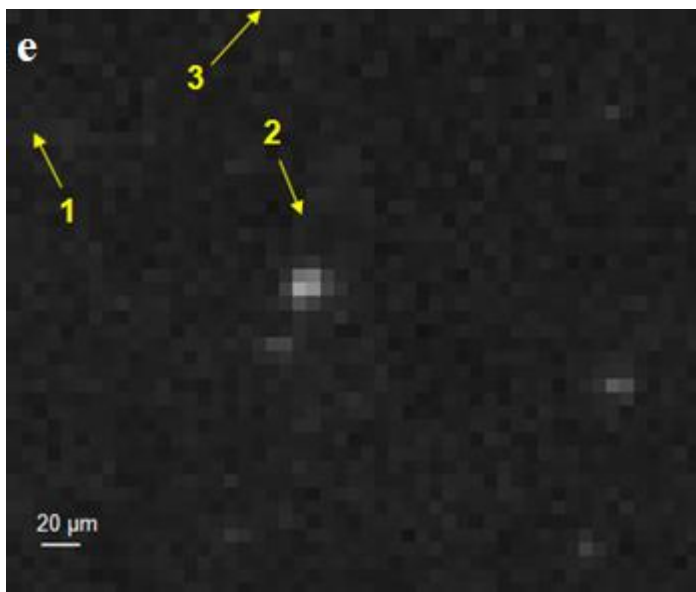
**Figure A7.** Grey-scaled (a) and bicolor (b) XRF maps taken from Region 1 of the VR-5 unheated\* soil sample. Map sizes: 400 μm x 400 μm. (NOTE: A thin film sample was used, not a soil pellet.)

\*VR-5 unheated samples were not subjected to laboratory heat treatments, though they had been previously burned by the Missionary Ridge wildfire.

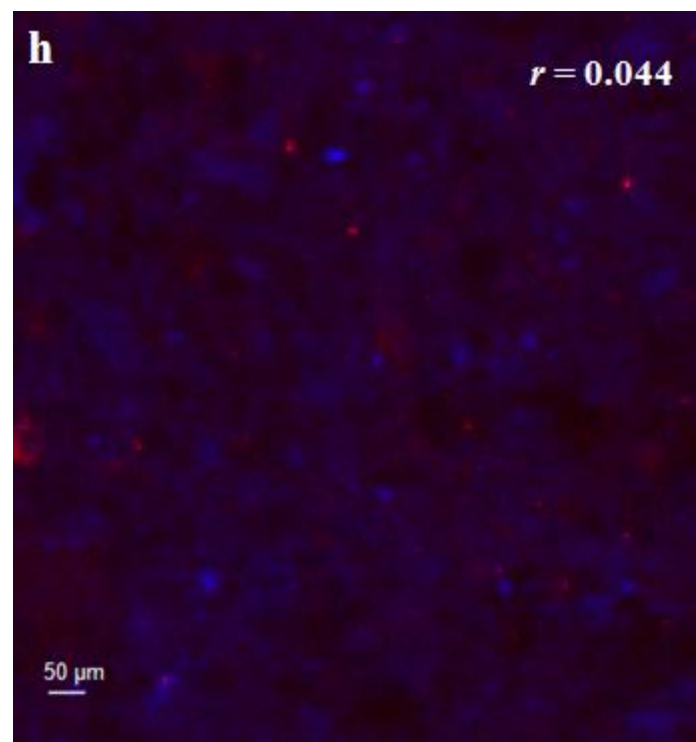
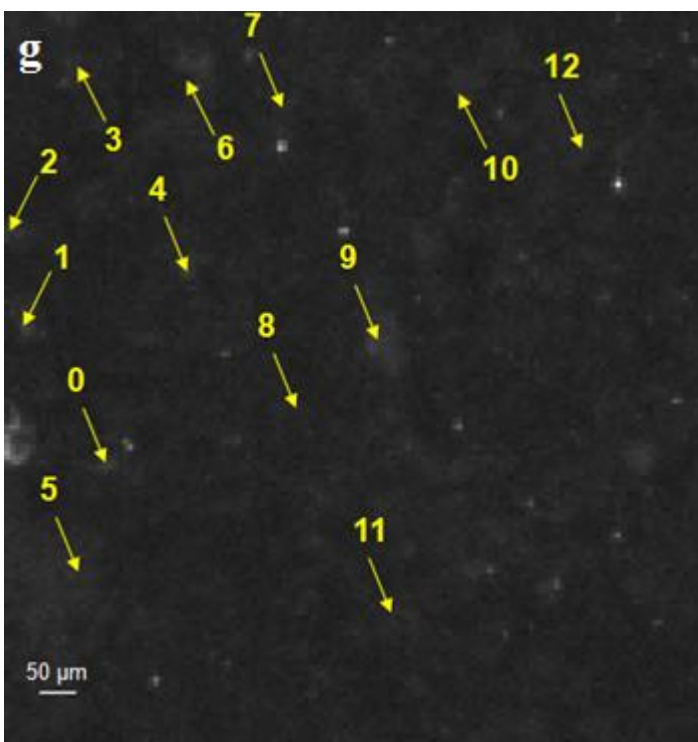




**Figure A7 (continued).** Grey-scaled (c) and bicolor (d) XRF maps taken from Region 2 of the VR-5 unheated soil sample. Map sizes: 400 μm x 300 μm. (NOTE: A thin film sample was used, not a soil pellet.)

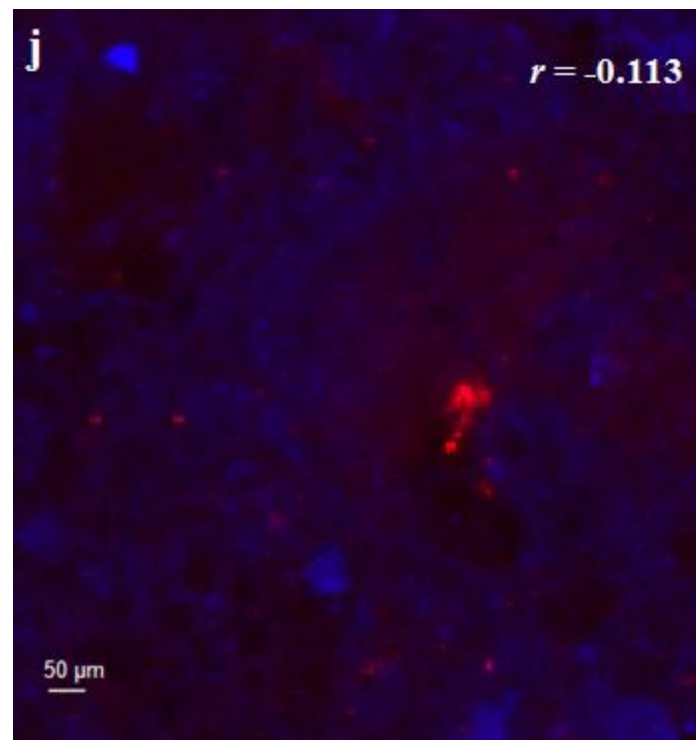
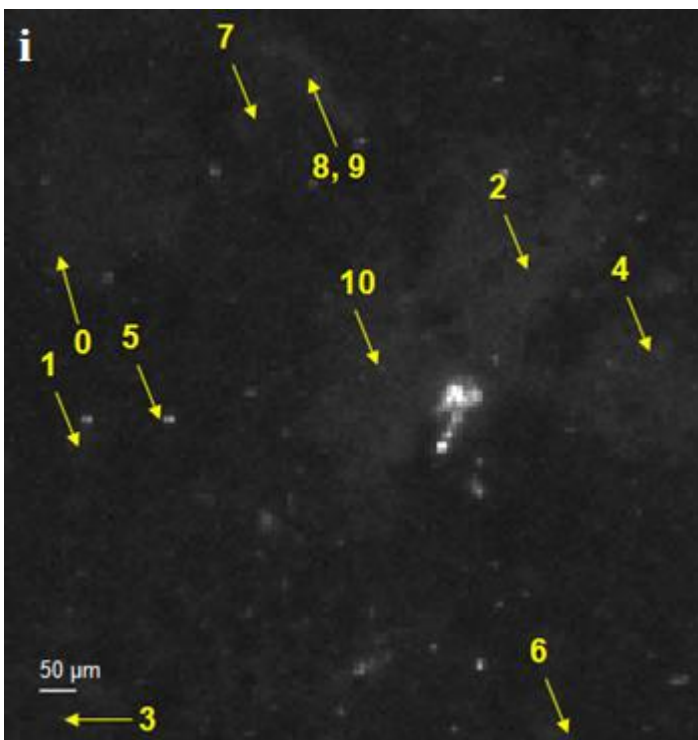


**Figure A7 (continued).** Grey-scaled (e) and bicolor (f) XRF maps taken from Region 3 of the VR-5 unheated soil sample. Map sizes: 400 μm x 300 μm. (NOTE: A thin film sample was used, not a soil pellet.)

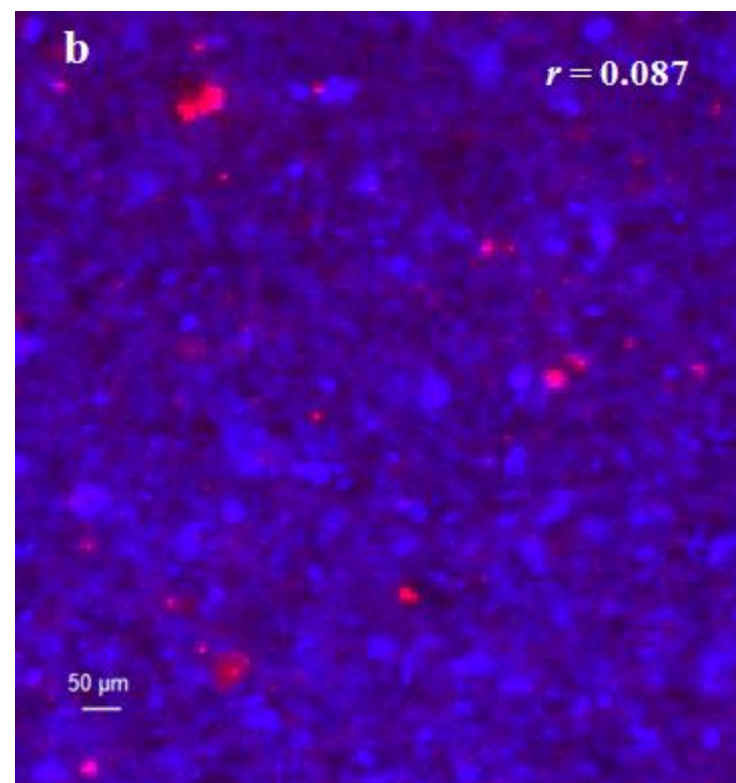
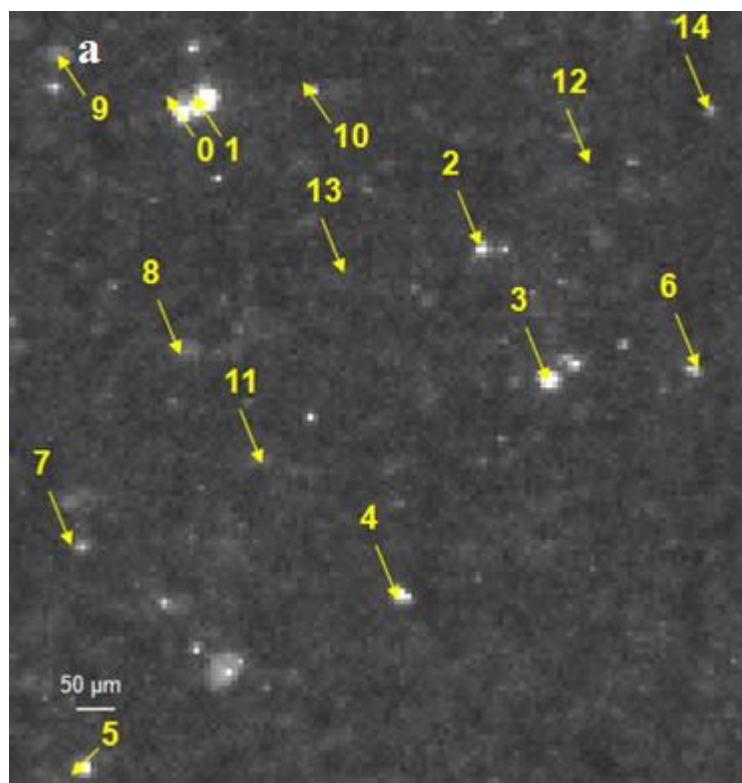


**Figure A7 (continued).** Grey-scaled (g) and bicolor (h) XRF maps taken from Region 4 of the VR-5 unheated soil sample. Map sizes: 1000 μm x 1000 μm.



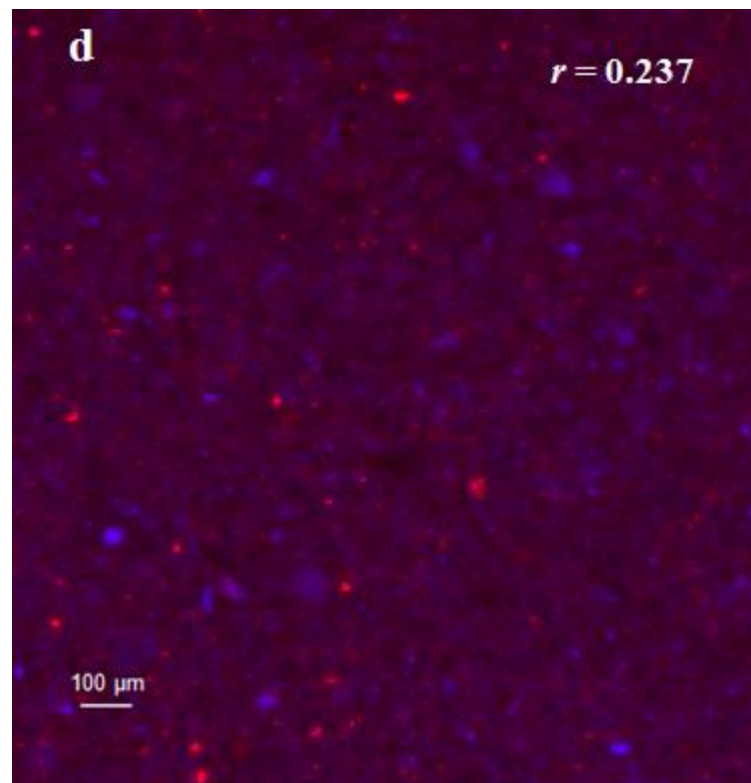
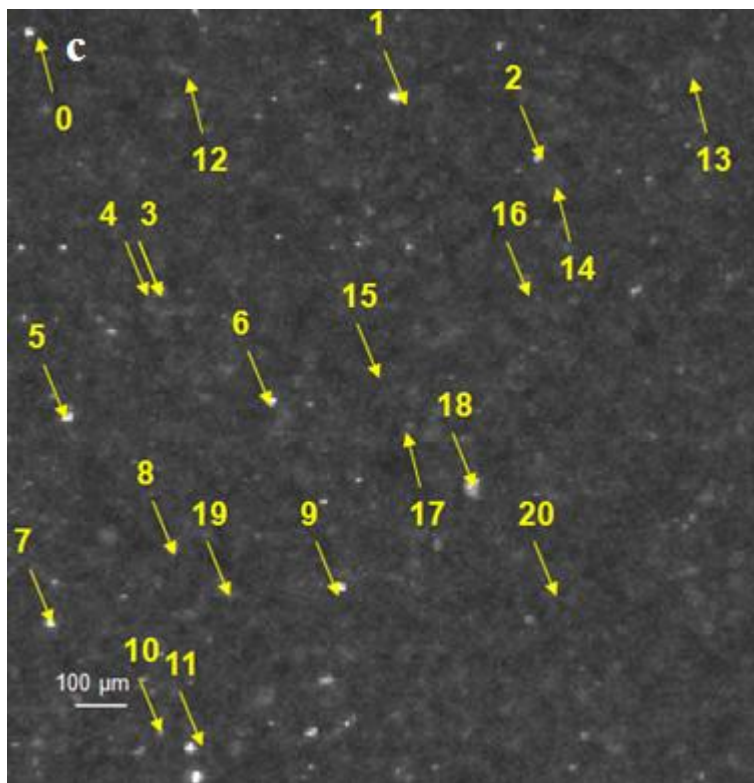


**Figure A7 (continued).** Grey-scaled (i) and bicolor (j) XRF maps taken from Region 5 of the VR-5 unheated soil sample. Map sizes: 1000 µm x 1000 µm.



**Figure A8.** Grey-scaled (a) and bicolor (b) XRF maps taken from Region 1 of the VR-5 soil sample heated\* at 225°C for 120 minutes. Map sizes: 1000 μm x 1000 μm.

\*VR-5 heated samples had been previously burned by the Missionary Ridge wildfire and were subjected to further heat treatment in the laboratory.



**Figure A8 (continued).** Grey-scaled (c) and bicolor (d) XRF maps taken from Region 2 of the VR-5 soil sample heated at 225°C for 120 minutes. Map sizes: 1500 μm x 1500 μm.

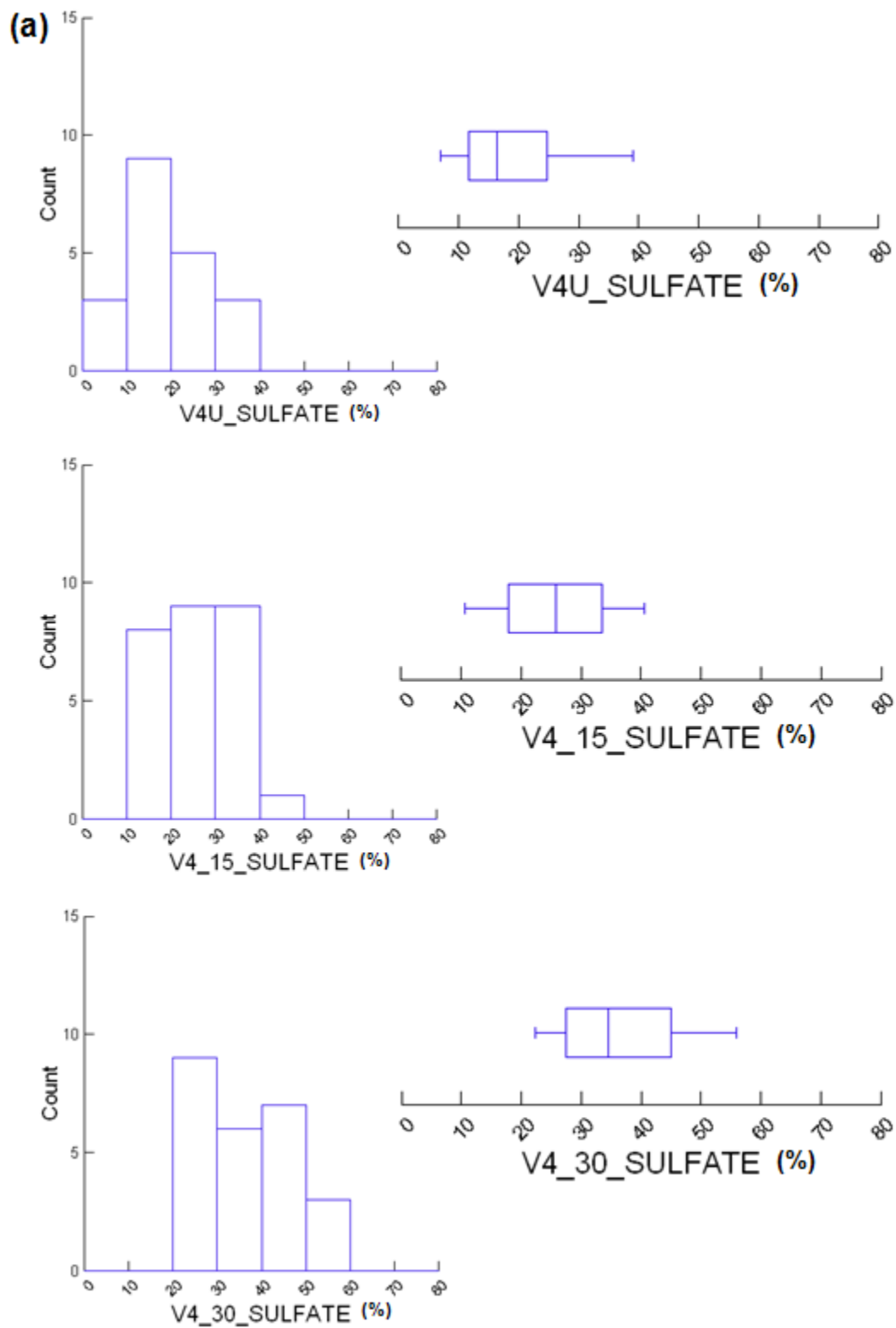
**Appendix B.** Histograms and boxplots of all soil sulfur constituents of the VR-4 time, VR-4 temperature, and VR-5 temperature series.

**Figure B1.** Histograms and box plots of the (a) sulfate, (b) sulfonate, (c) sulfone, (d) sulfite, (e) sulfoxide, (f) sulfonium, (g) reduced aromatic sulfur (Sred\_arom), and (h) reduced aliphatic sulfur (Sred\_aliph) constituents in soil from the VR-4 Time Series. The time series consists of unheated soil (V4U\*) and soils heated at 225°C for 15 min (V4\_15), 30 min (V4\_30), 120 min (V4225\*), and 345 min (V4\_345). The fractional amounts of each sulfur constituent were determined using full-energy range (2465 to 2510 eV) spectra and the second fitting approach.

Histograms and box plots were used to determine the form (e.g., Gaussian-normal, uniform, exponential, etc.) of the frequency distribution of each sulfur constituent. The form shows which mathematical transformations may be appropriate to apply to data so that frequency distributions become Gaussian-normal. If data can be transformed to a Gaussian-normal distribution, then a parametric test may be used for further statistical analyses. If not, then a nonparametric test is used. Since most of our data were skewed, we chose to perform nonparametric Kolmogorov-Smirnov two-sample tests in subsequent statistical analyses.

\*NOTE: Because the MYSTAT program requires that the first character of a variable name be a letter, the labels “V4U” and “V4225” do not match the previously assigned names for the VR-4 unheated soil sample and the VR-4 sample heated at 225°C for 120 min, respectively (c.f., Table 1).

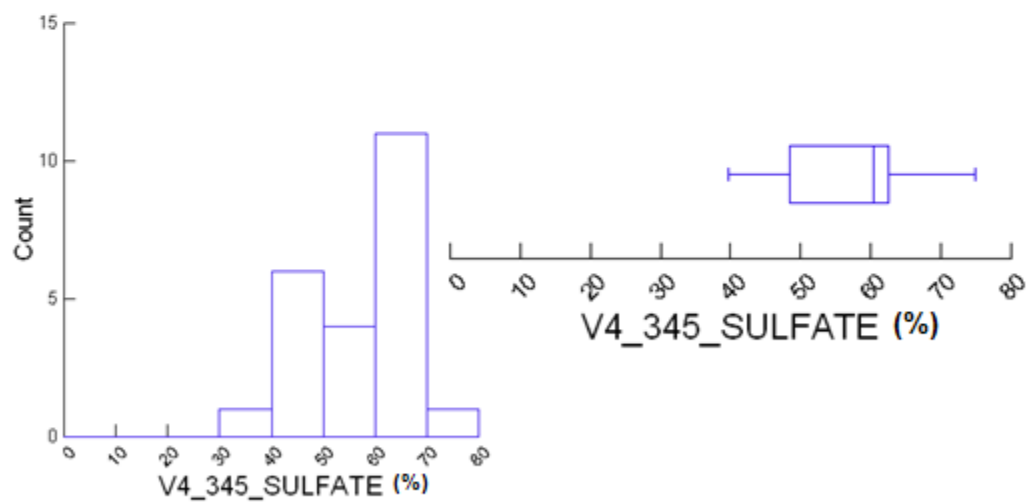
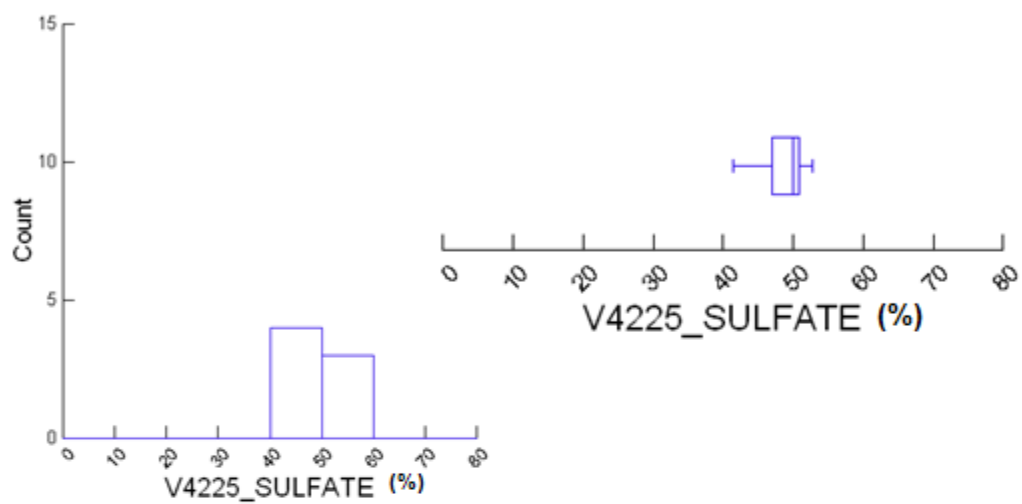
## APPENDIX B (continued)



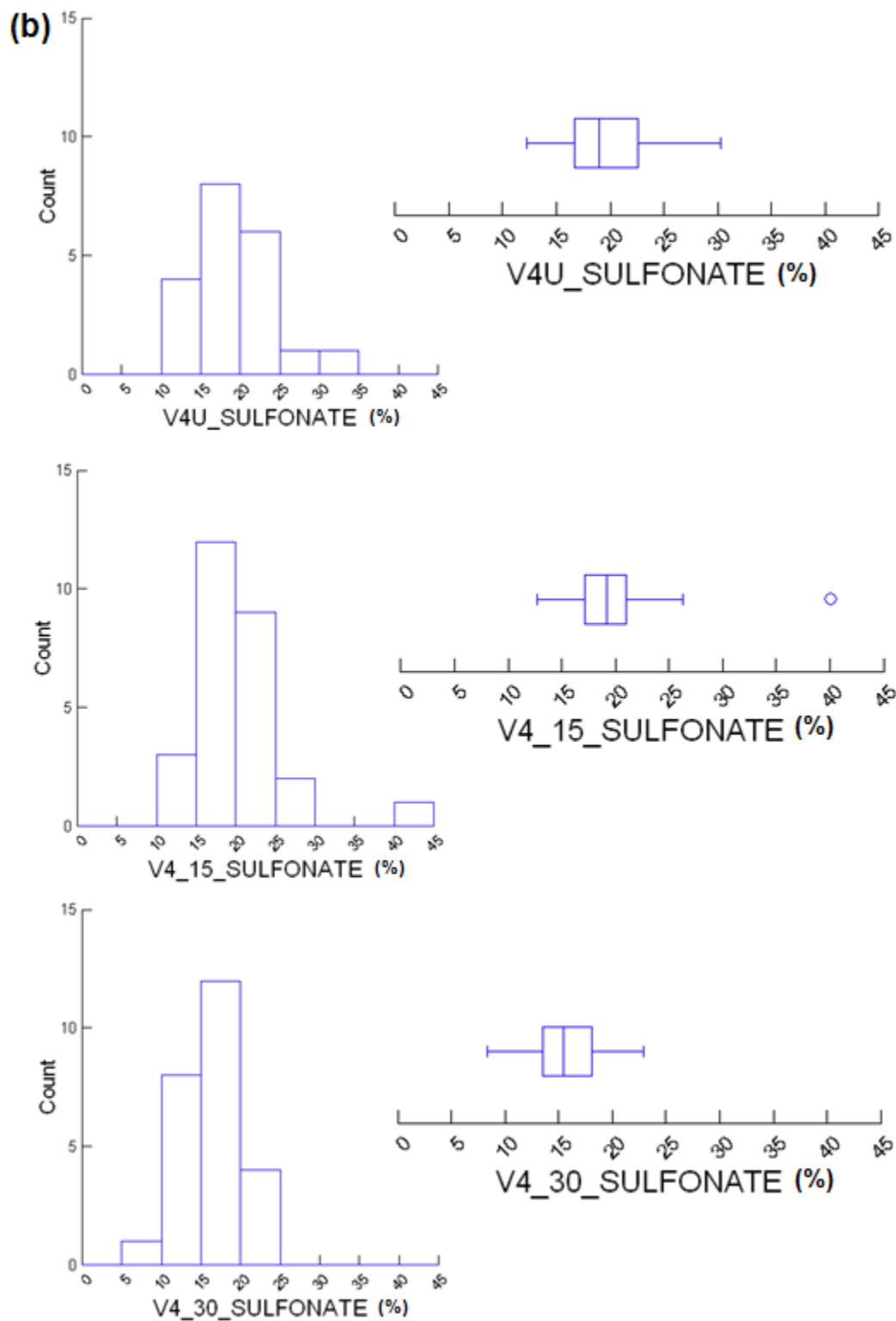
## APPENDIX B (continued)

## APPENDIX B (continued)

(a) (continued)



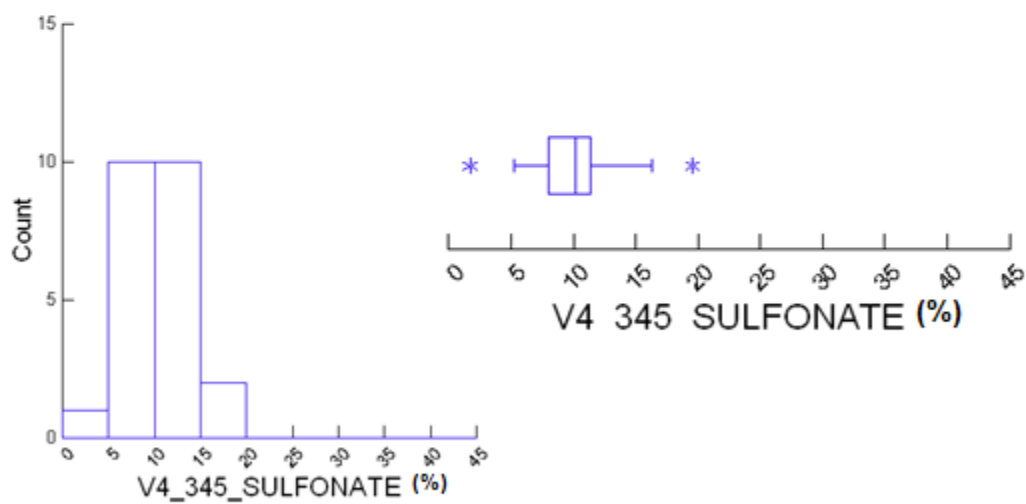
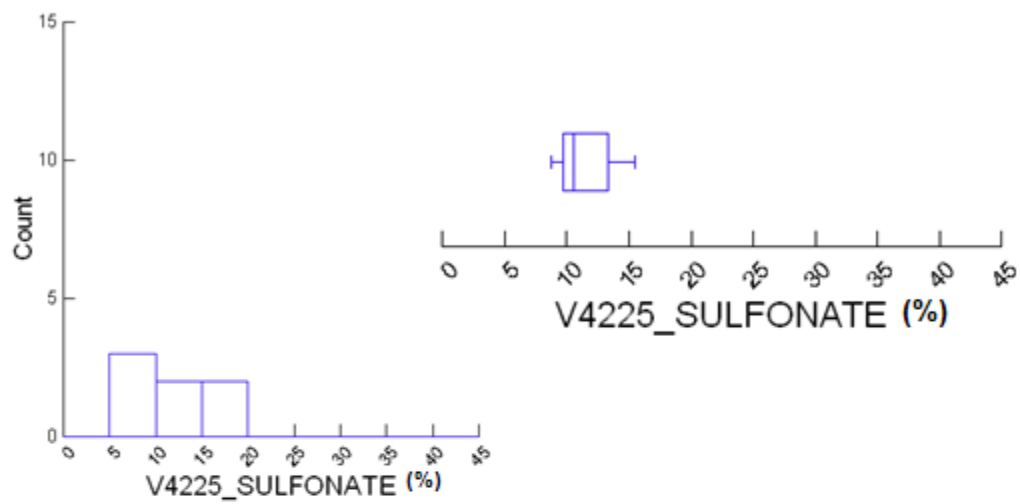
## APPENDIX B (continued)



## APPENDIX B (continued)

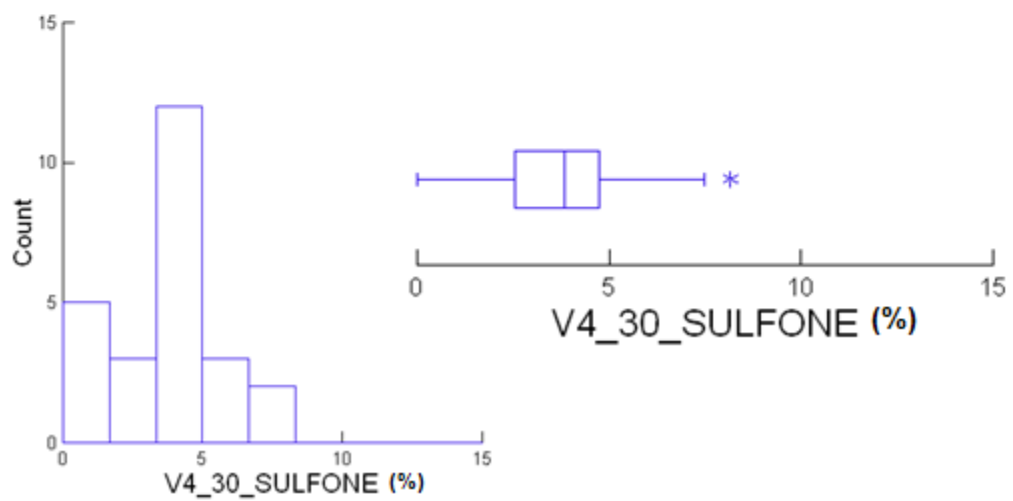
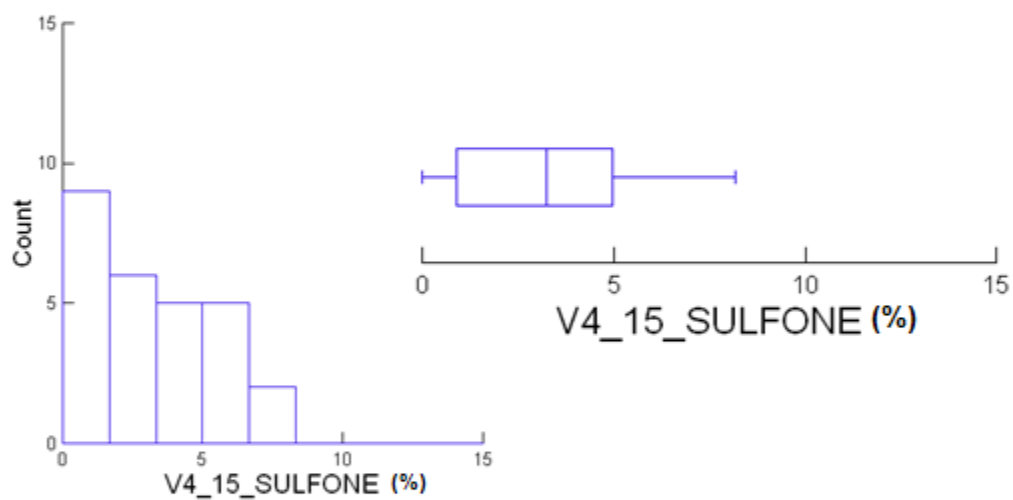
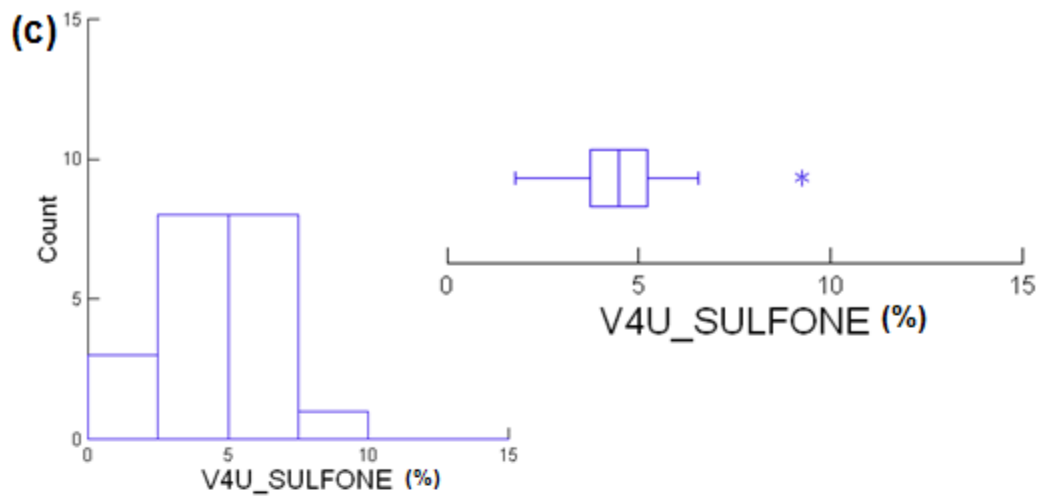
## APPENDIX B (continued)

(b) (continued)



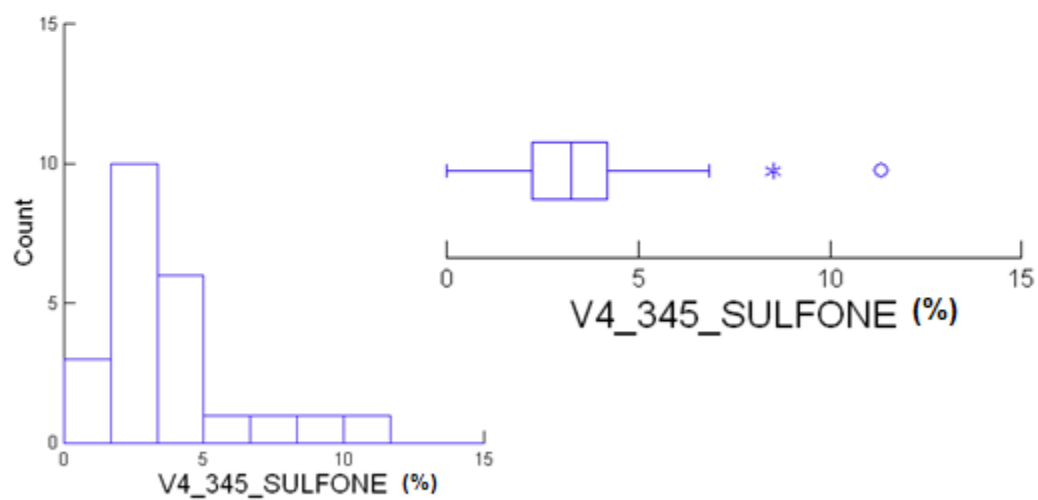
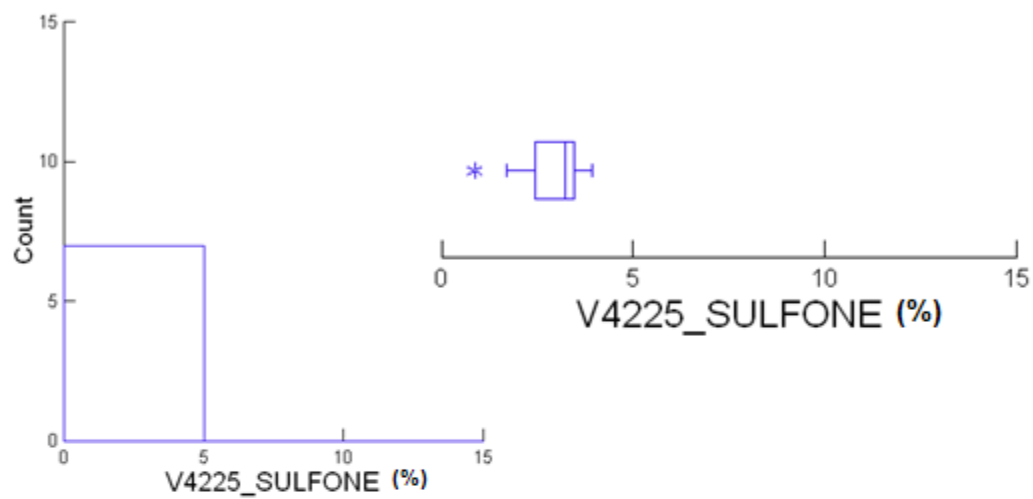


## APPENDIX B (continued)

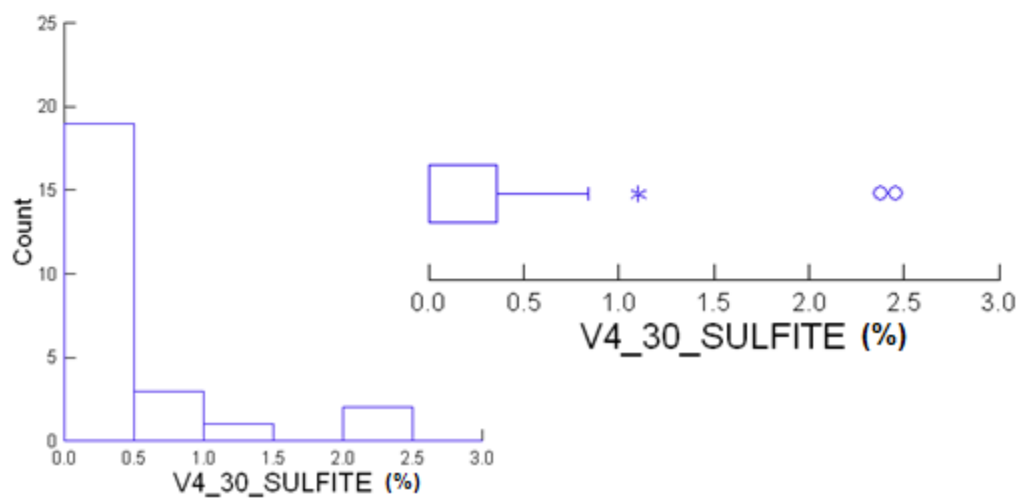
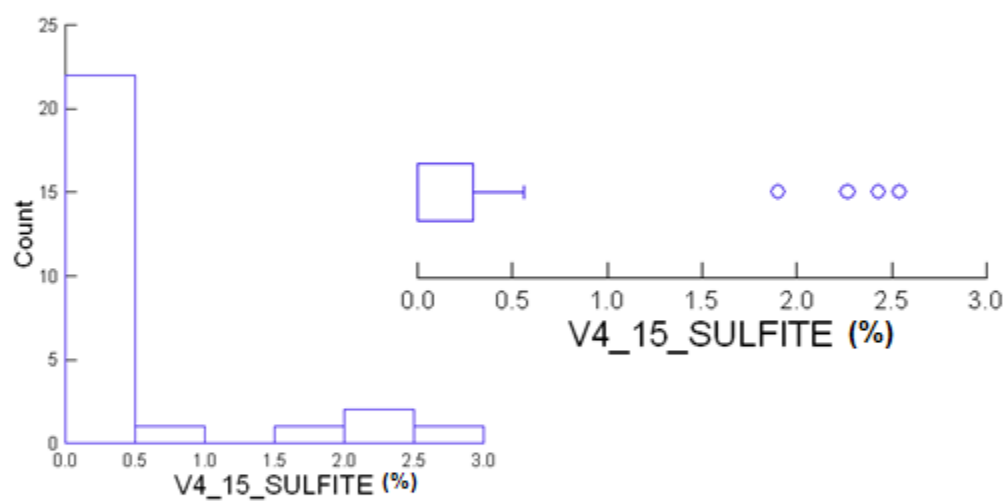
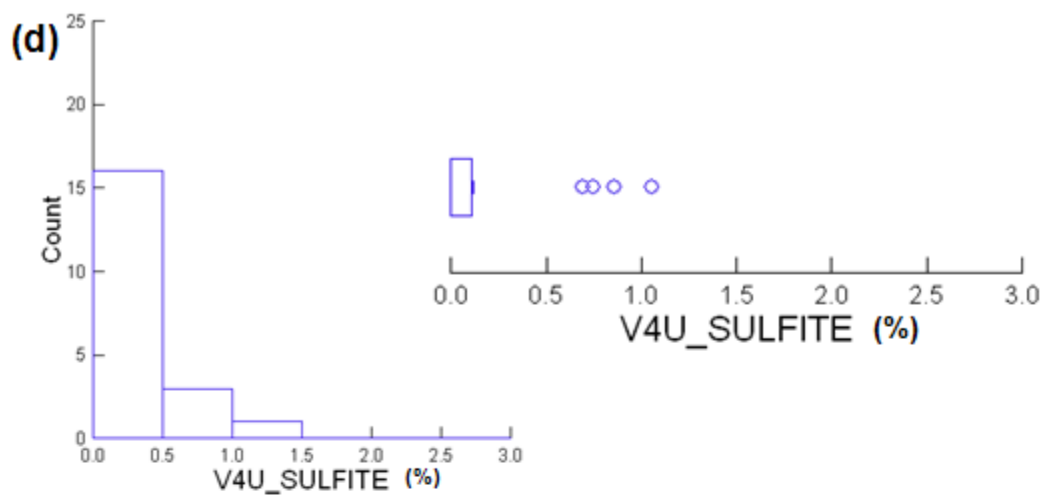


## APPENDIX B (continued)

(c) (continued)

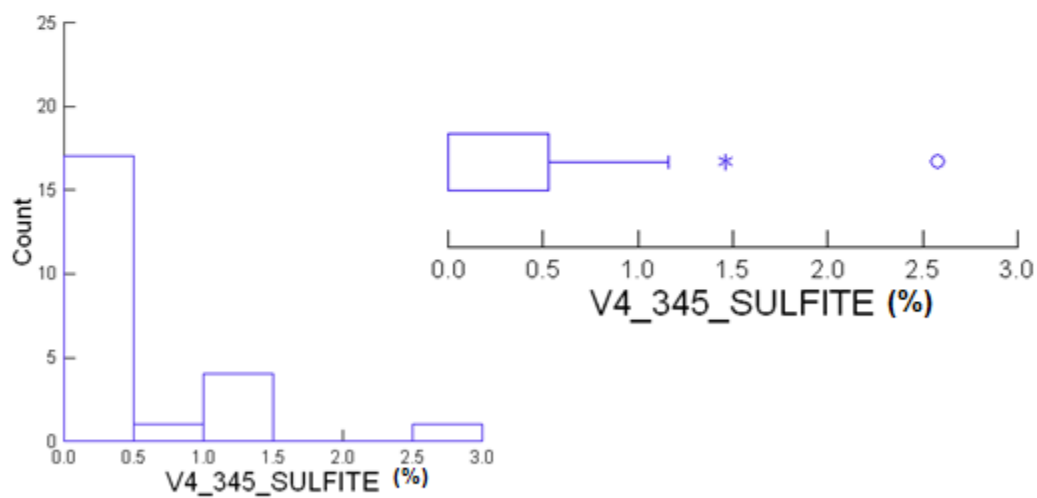
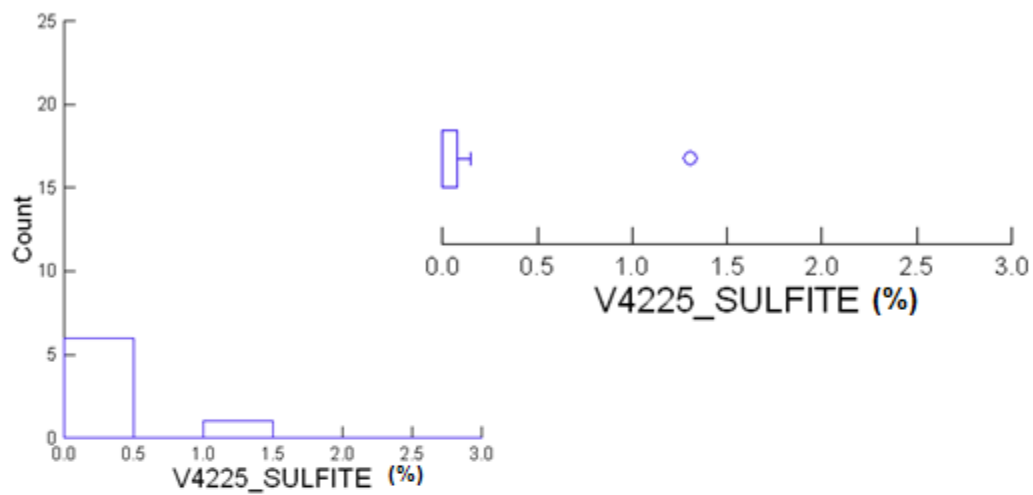


## APPENDIX B (continued)

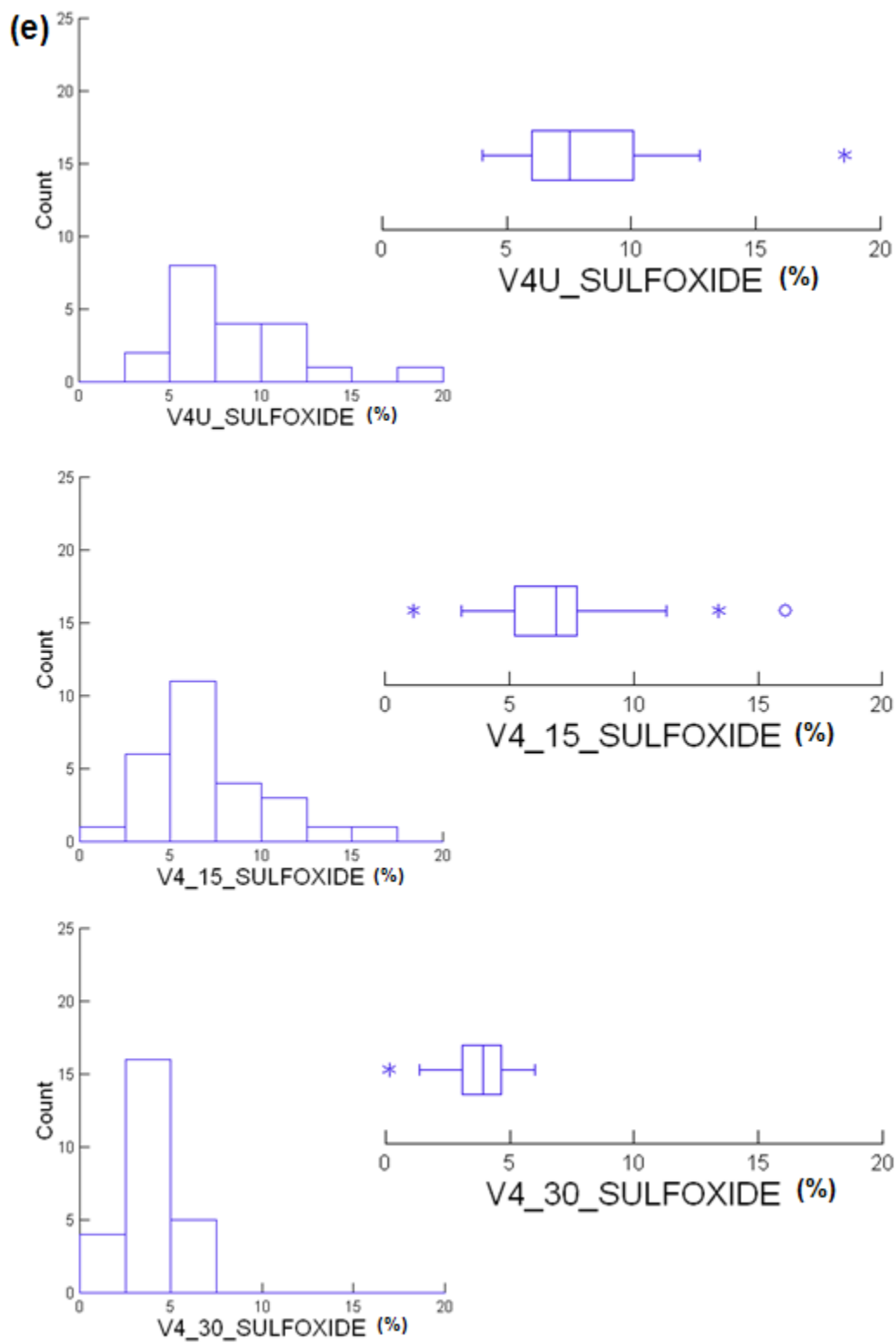


## APPENDIX B (continued)

(d) (continued)



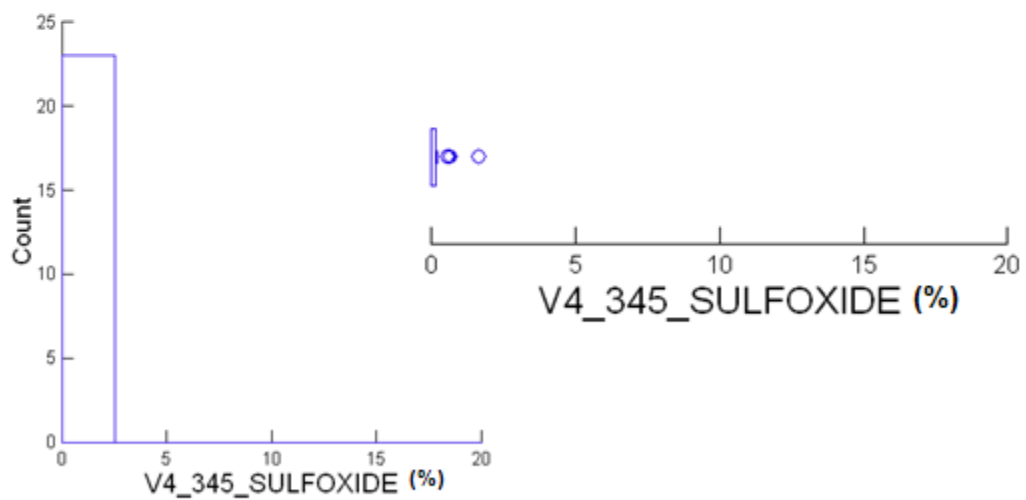
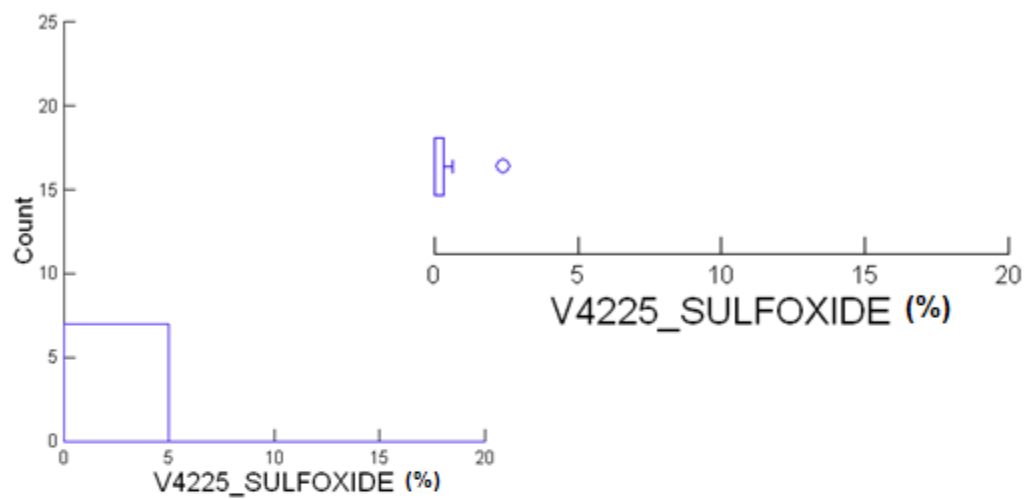
## APPENDIX B (continued)



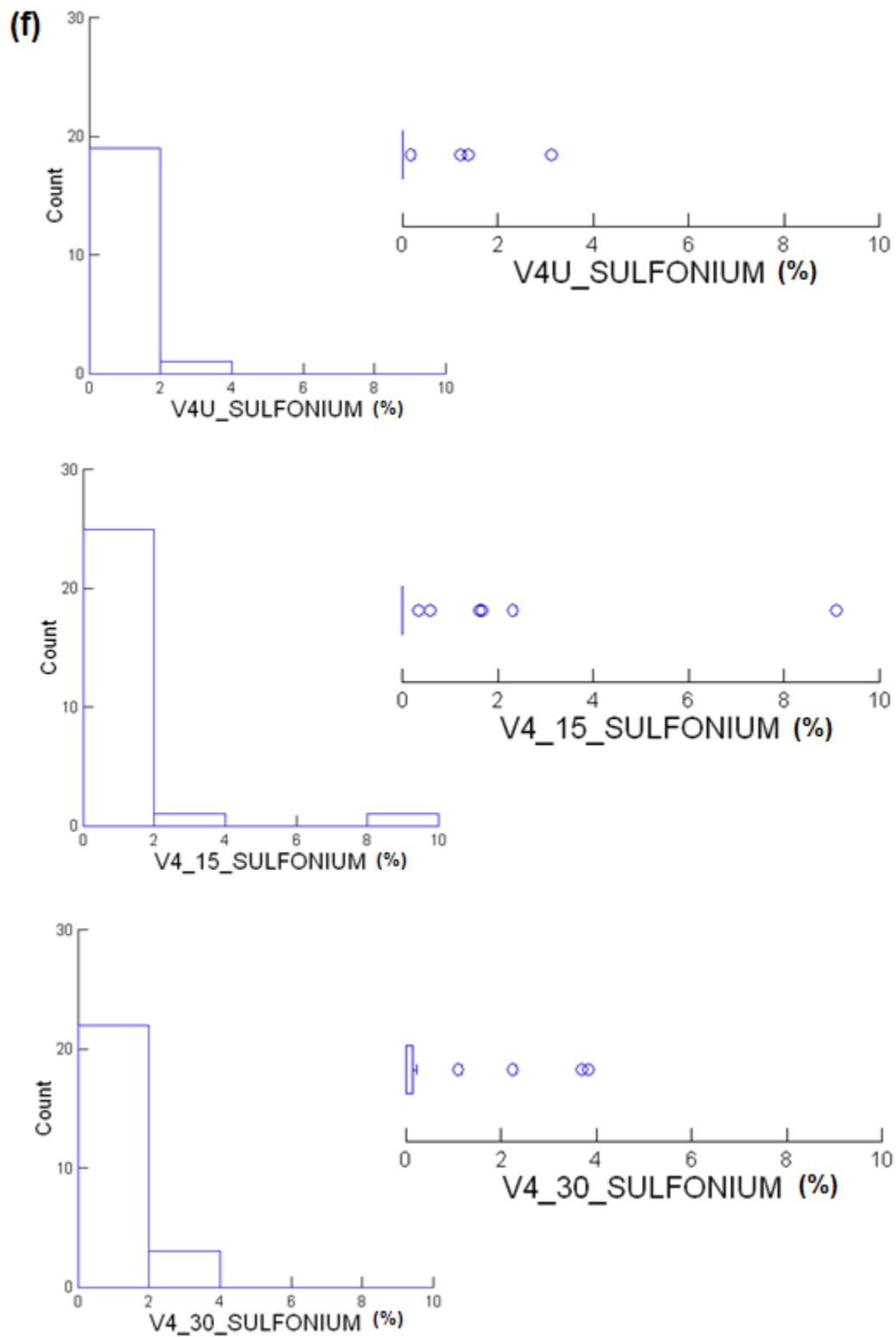
## APPENDIX B (continued)

## APPENDIX B (continued)

(e) (continued)

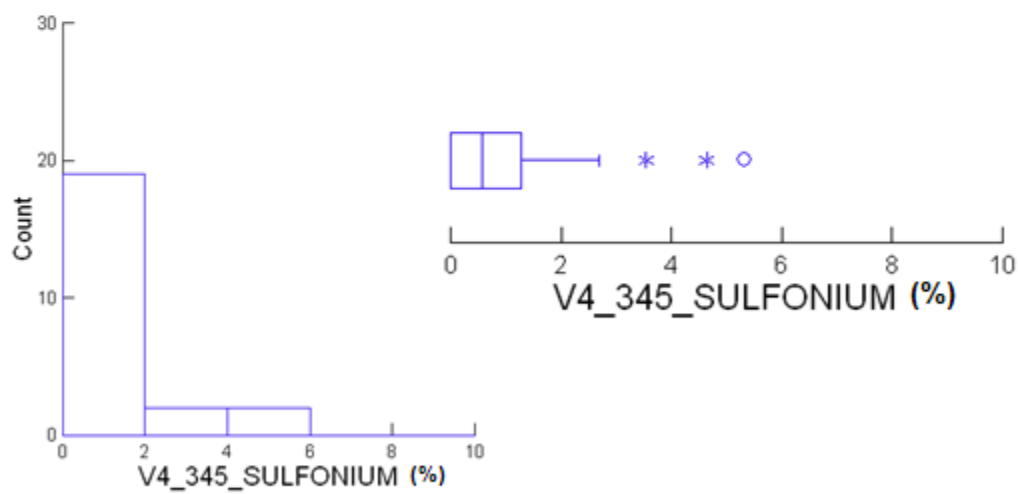
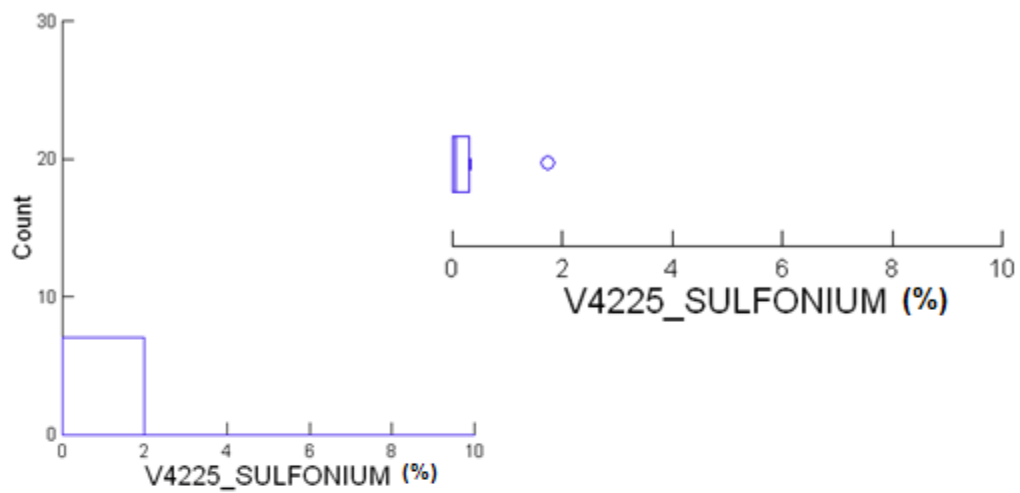


## APPENDIX B (continued)



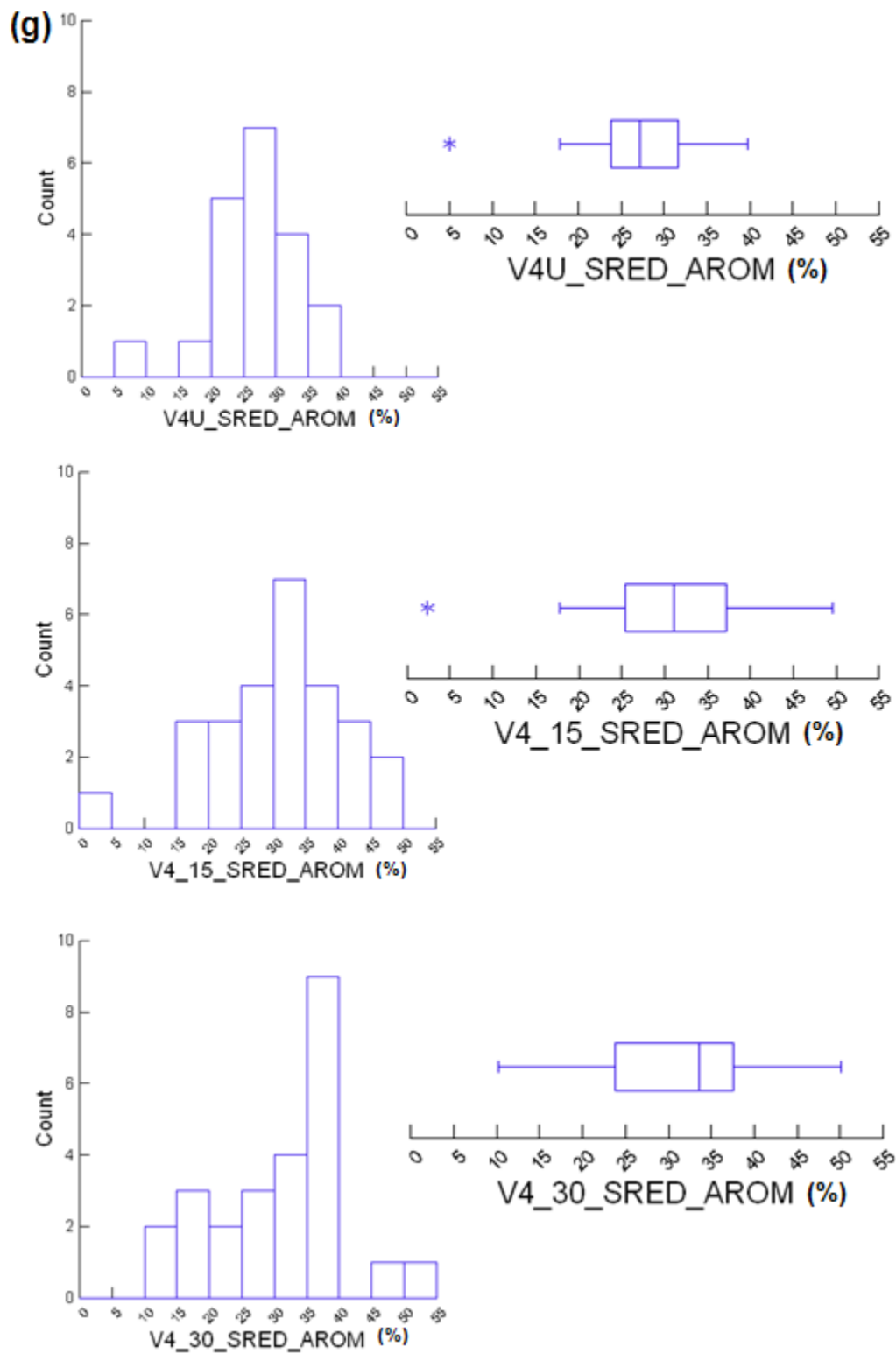
## APPENDIX B (continued)

(f) (continued)



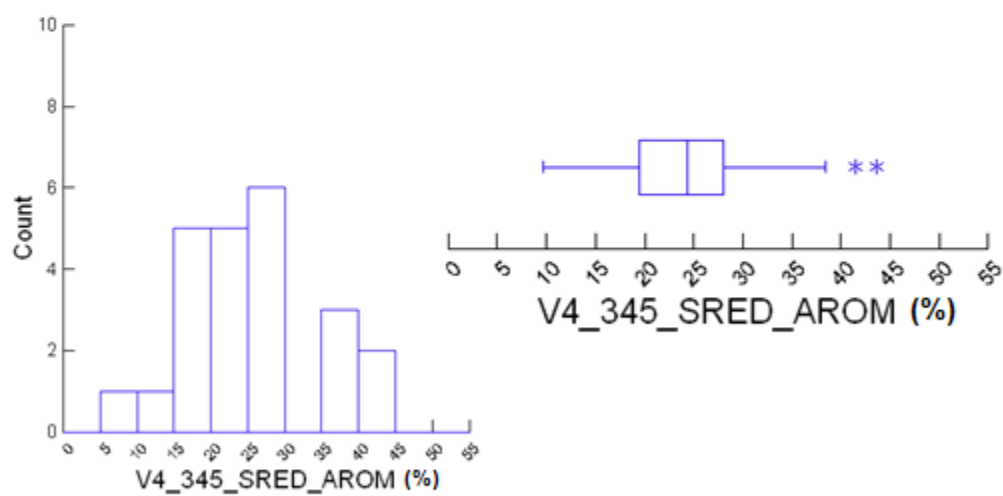
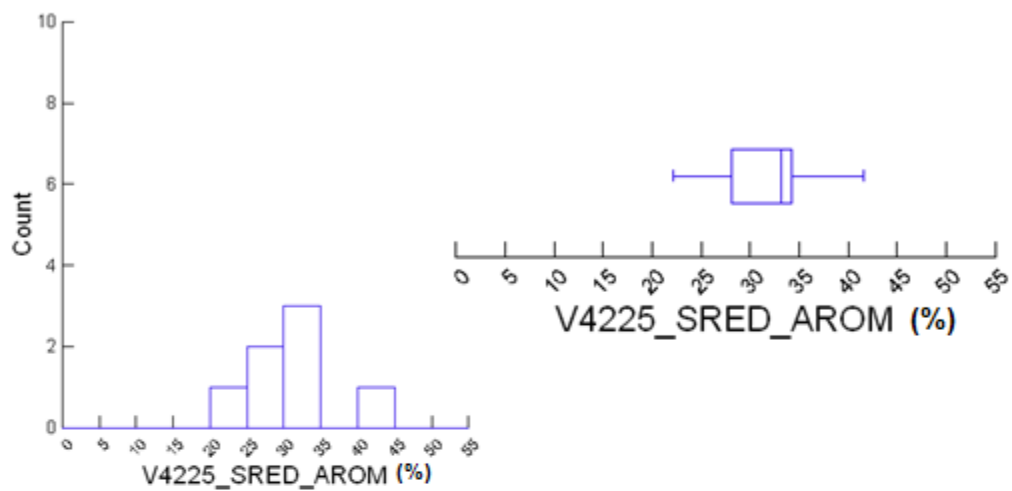


## APPENDIX B (continued)

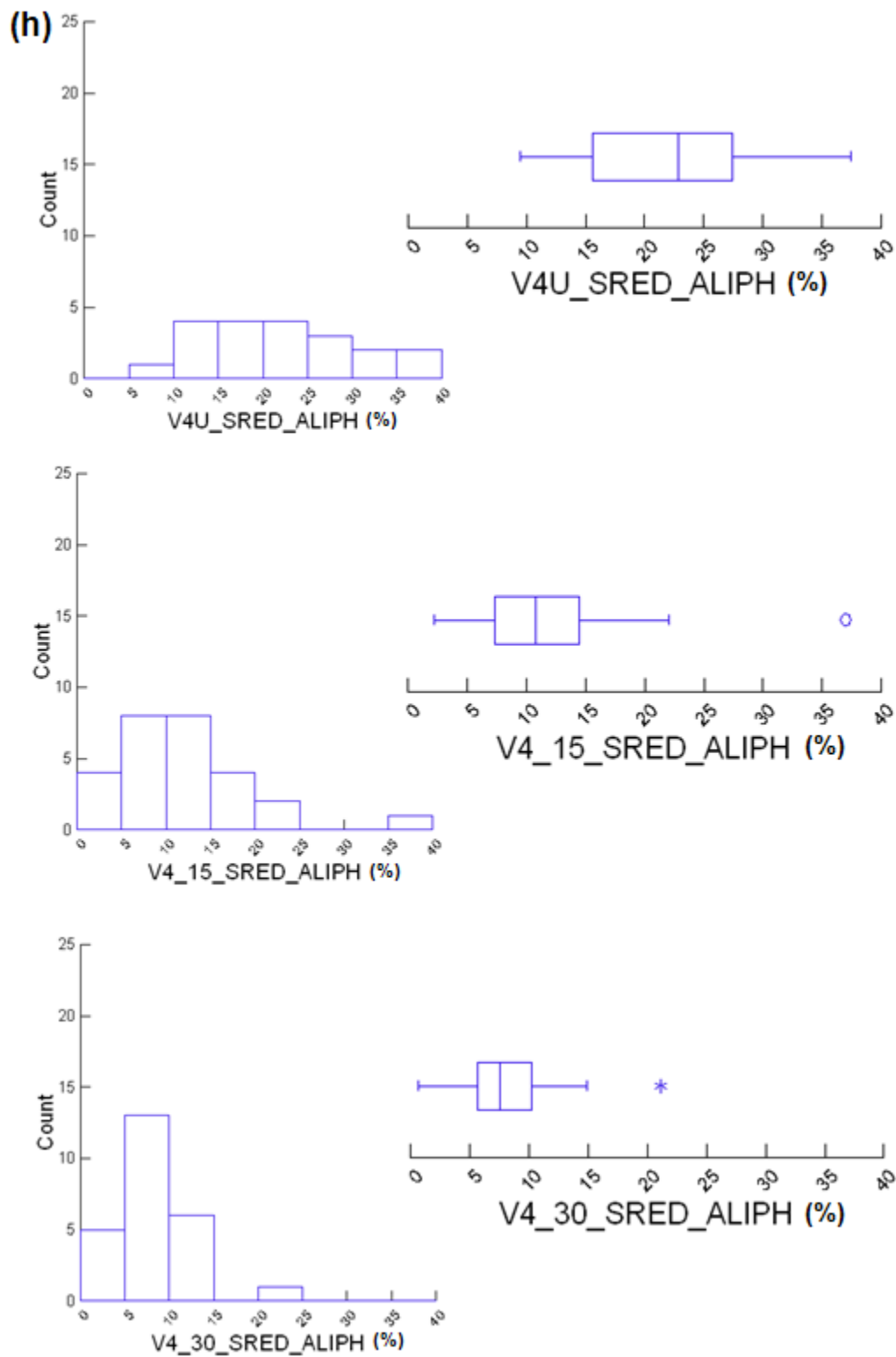


## APPENDIX B (continued)

(g) (continued)

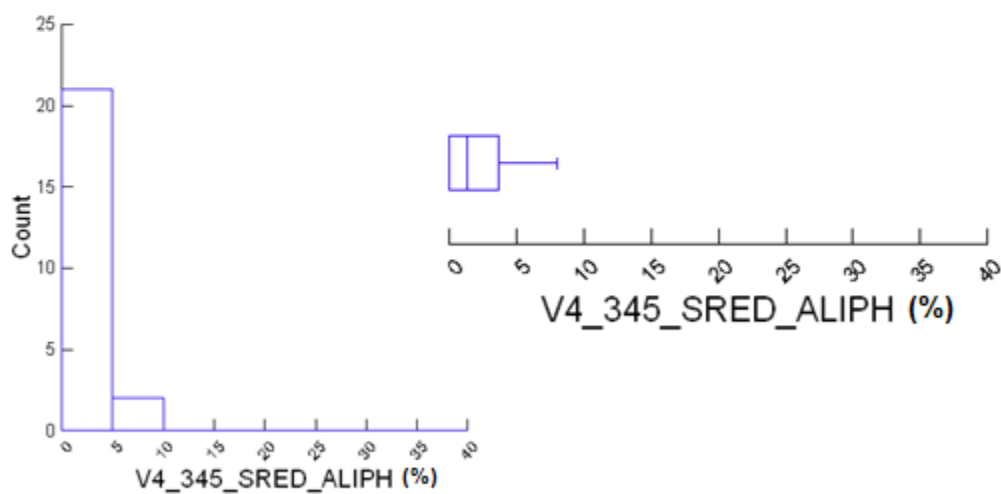
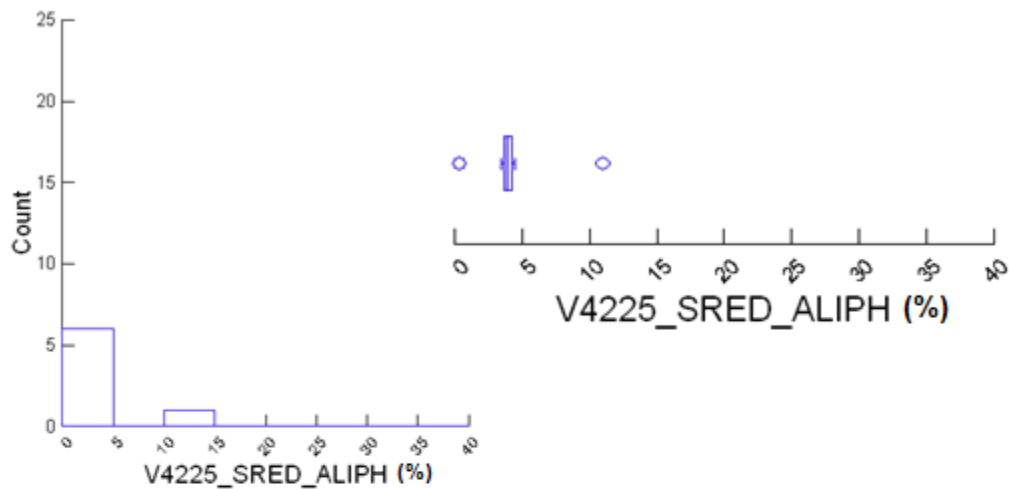


## APPENDIX B (continued)



## APPENDIX B (continued)

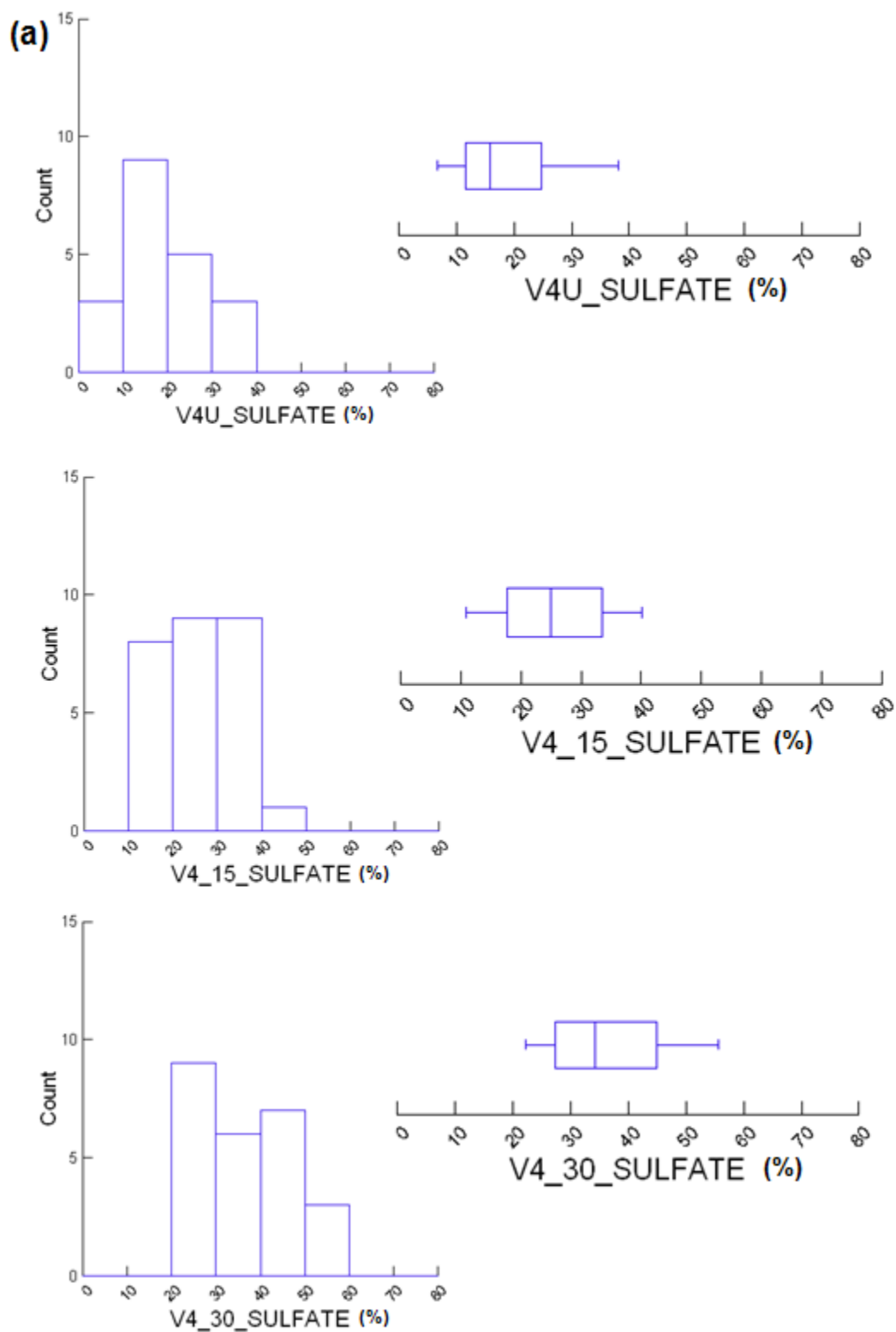
(h) (continued)



**APPENDIX B (continued)**

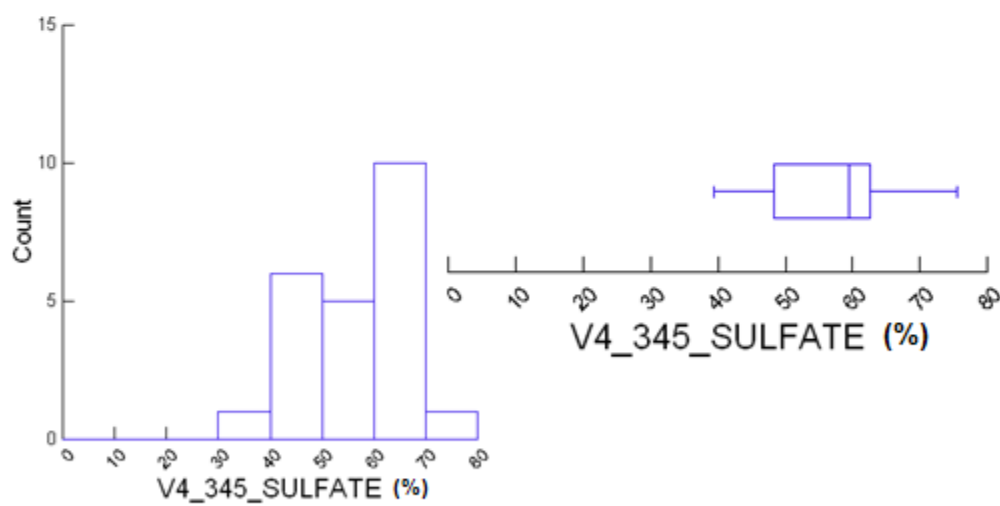
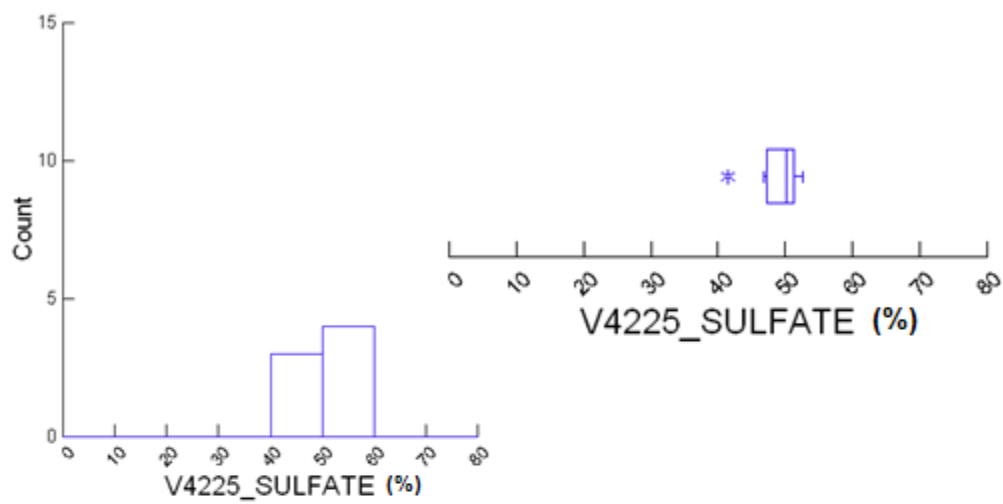
**Figure B2.** Histograms and box plots of the (a) sulfate, (b) sulfonate, (c) sulfone, (d) sulfite, (e) sulfoxide, (f) sulfonium, (g) reduced aromatic sulfur (Sred\_arom), and (h) reduced aliphatic sulfur (Sred\_aliph) constituents in soil from the VR-4 Time Series. The fractional amounts of each sulfur constituent were determined using short-energy range (2465 to 2490 eV) spectra and the second fitting approach.

## APPENDIX B (continued)

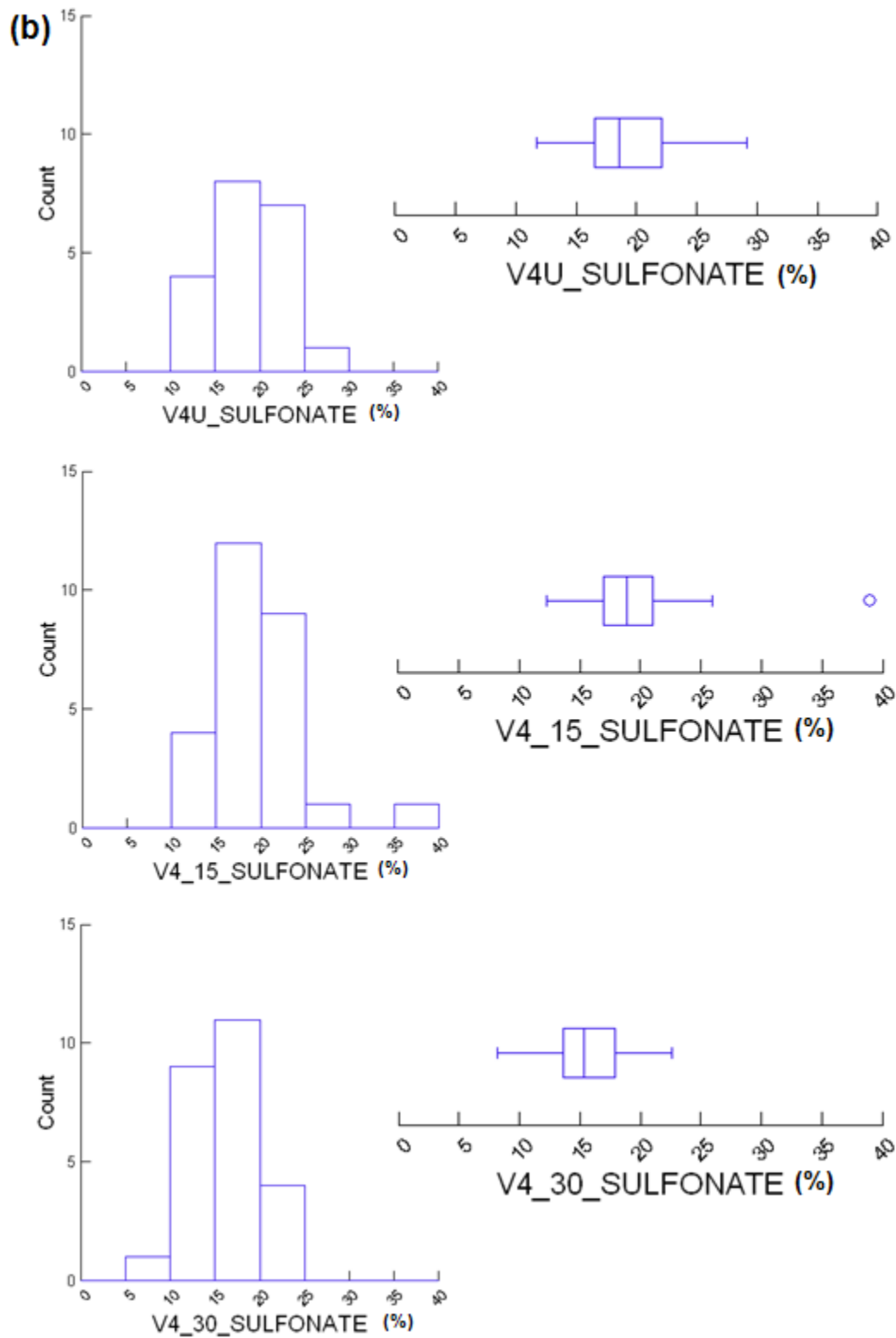


## APPENDIX B (continued)

(a) (continued)



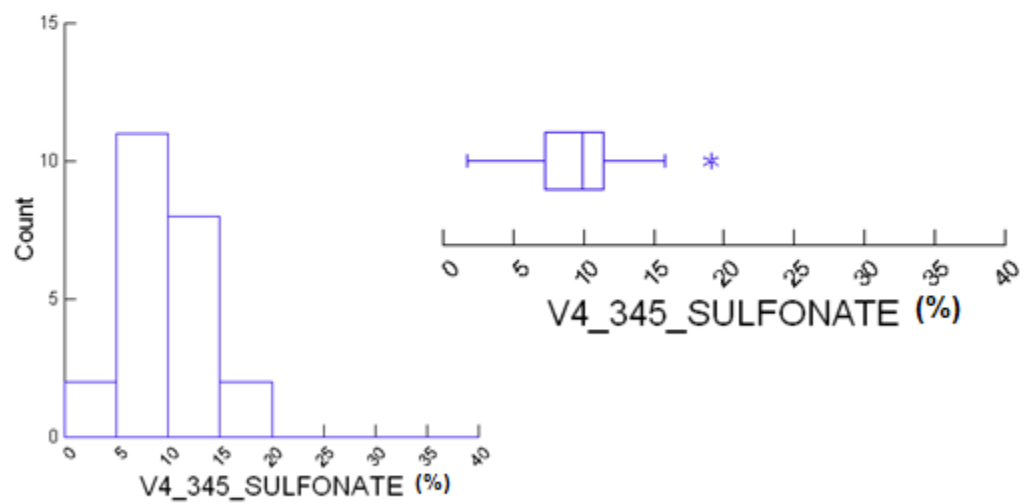
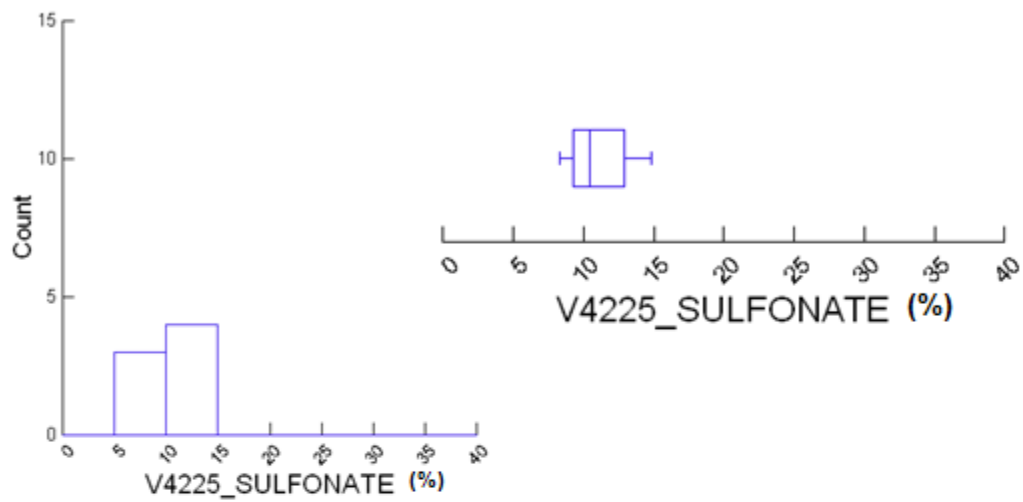
## APPENDIX B (continued)

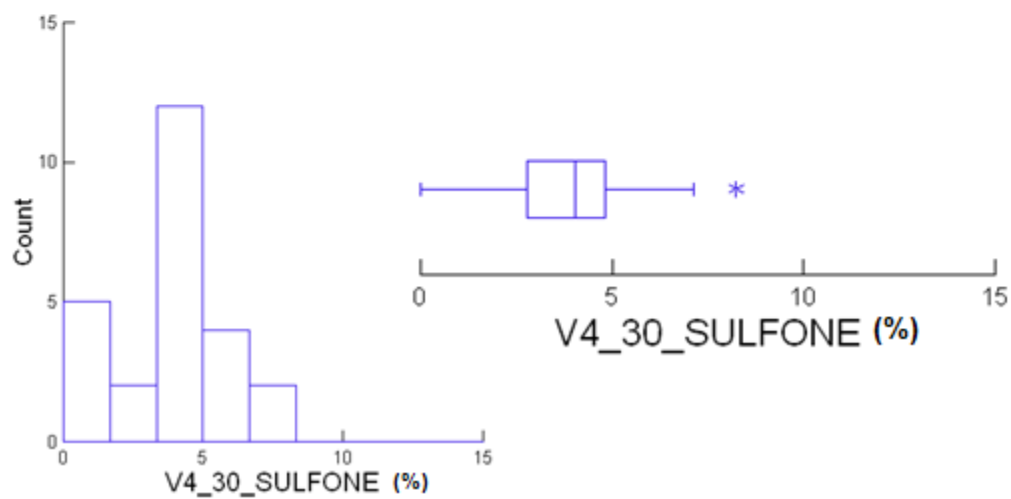
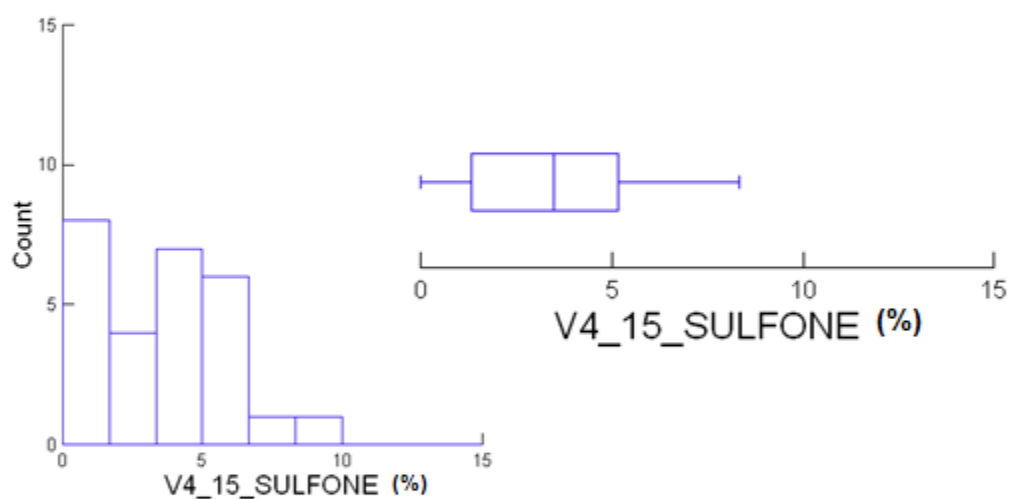
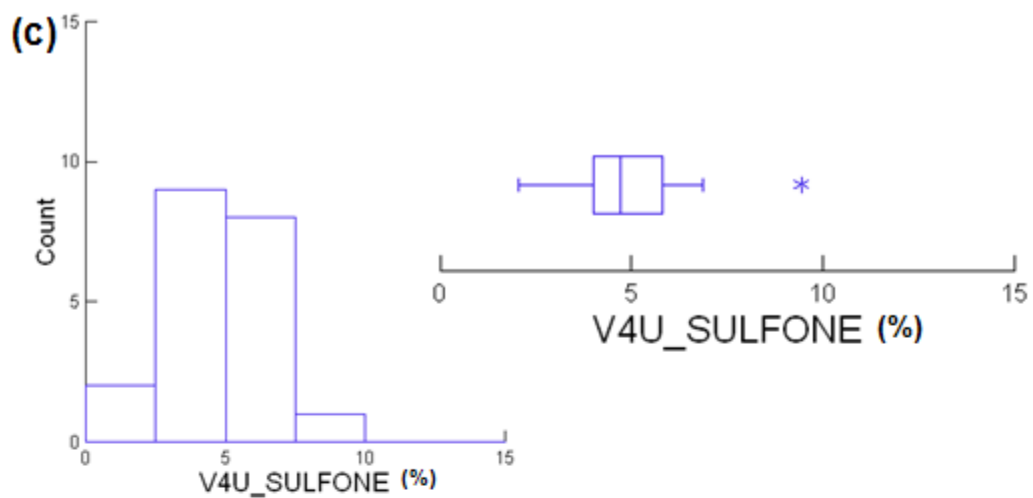




## APPENDIX B (continued)

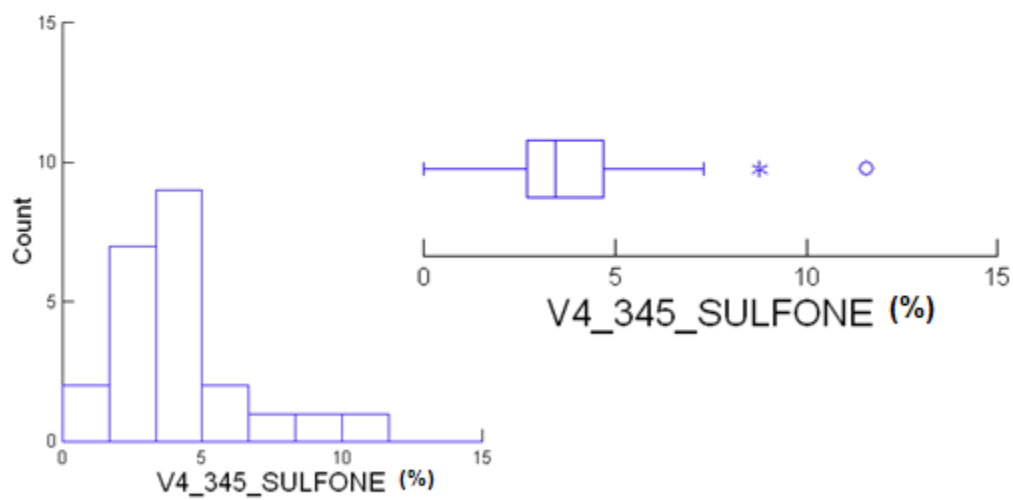
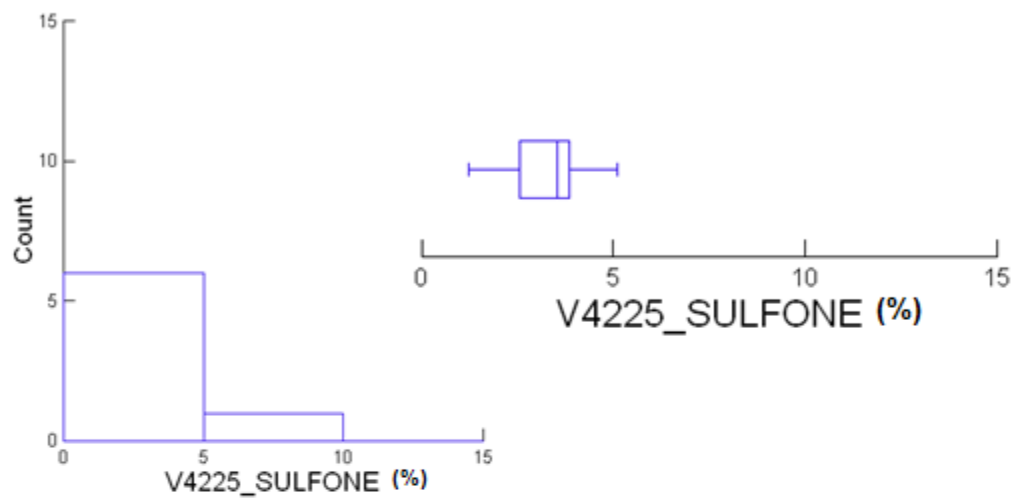
(b) (continued)



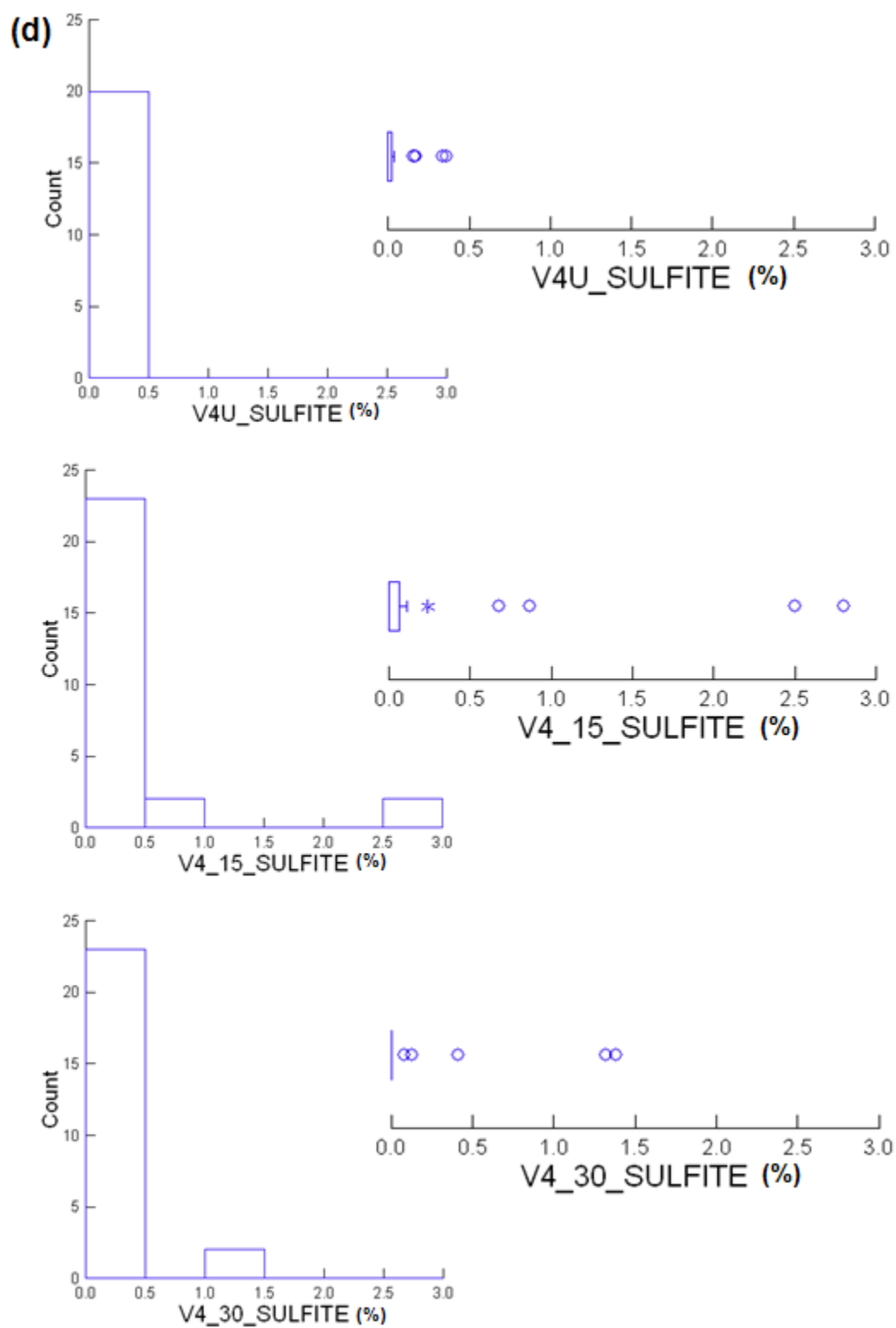


## APPENDIX B (continued)

(c) (continued)

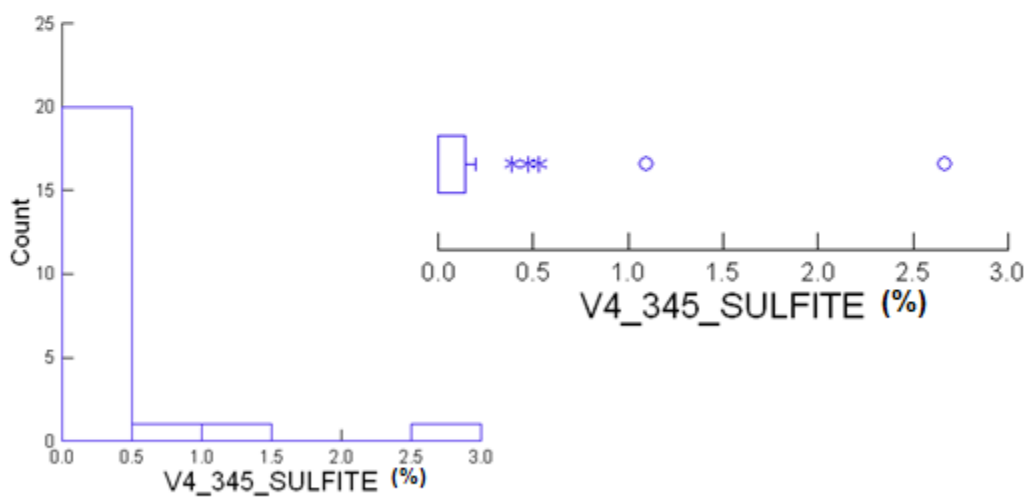
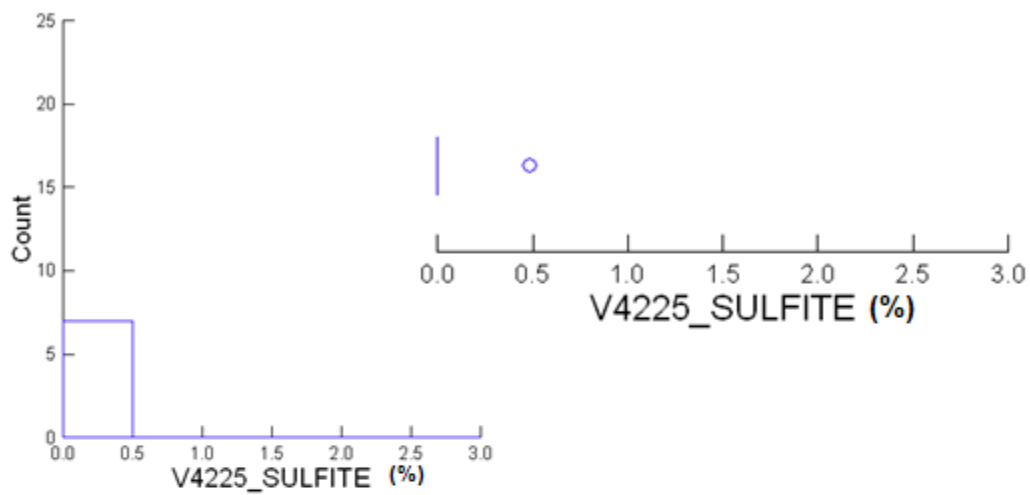


## APPENDIX B (continued)

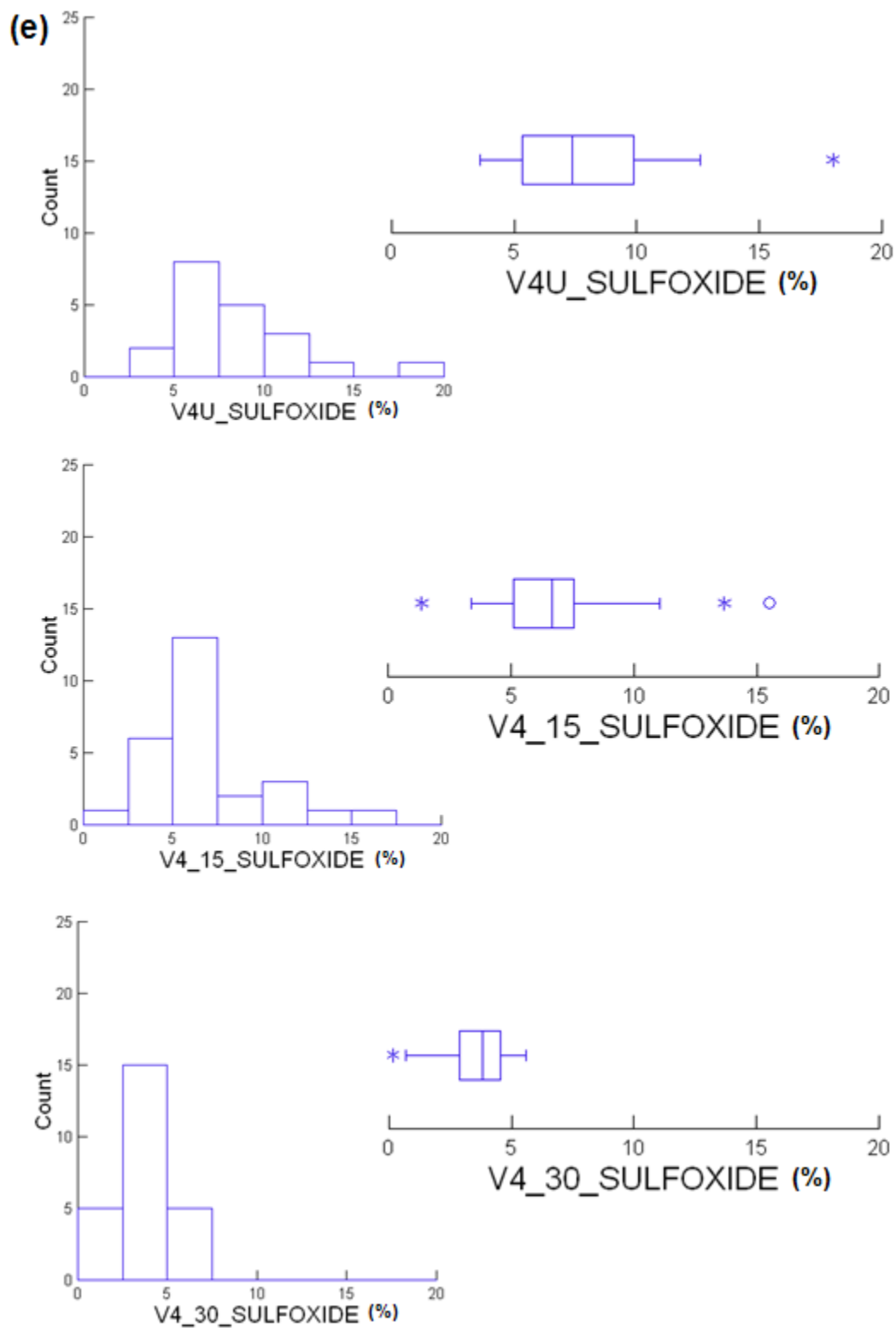


## APPENDIX B (continued)

(d) (continued)

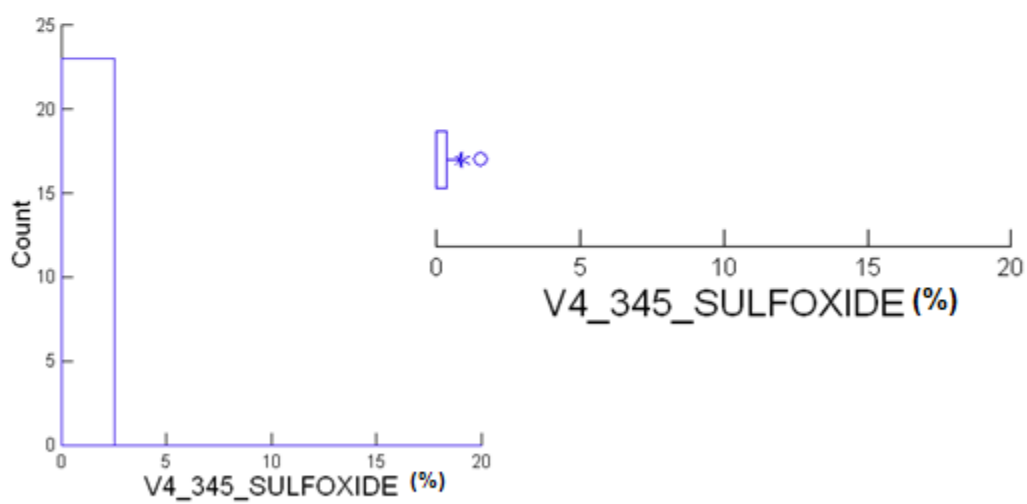
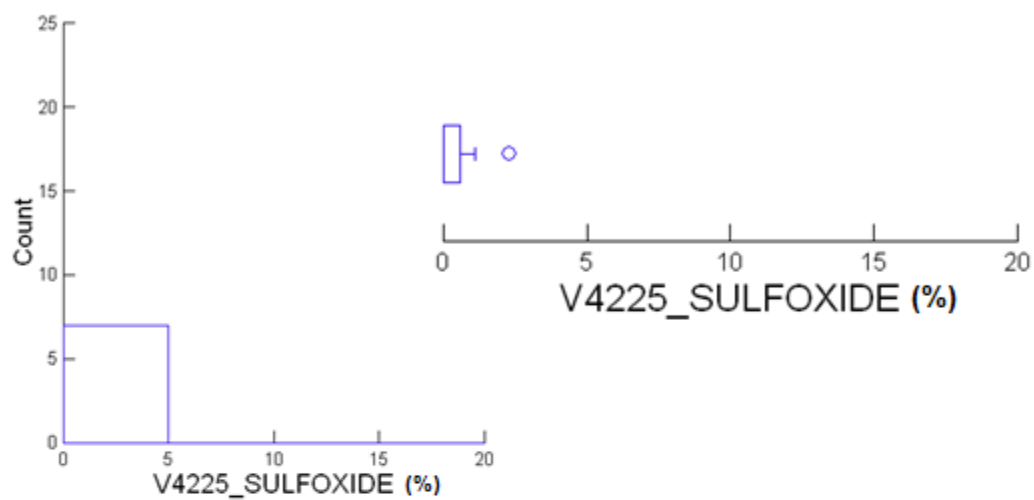


## APPENDIX B (continued)

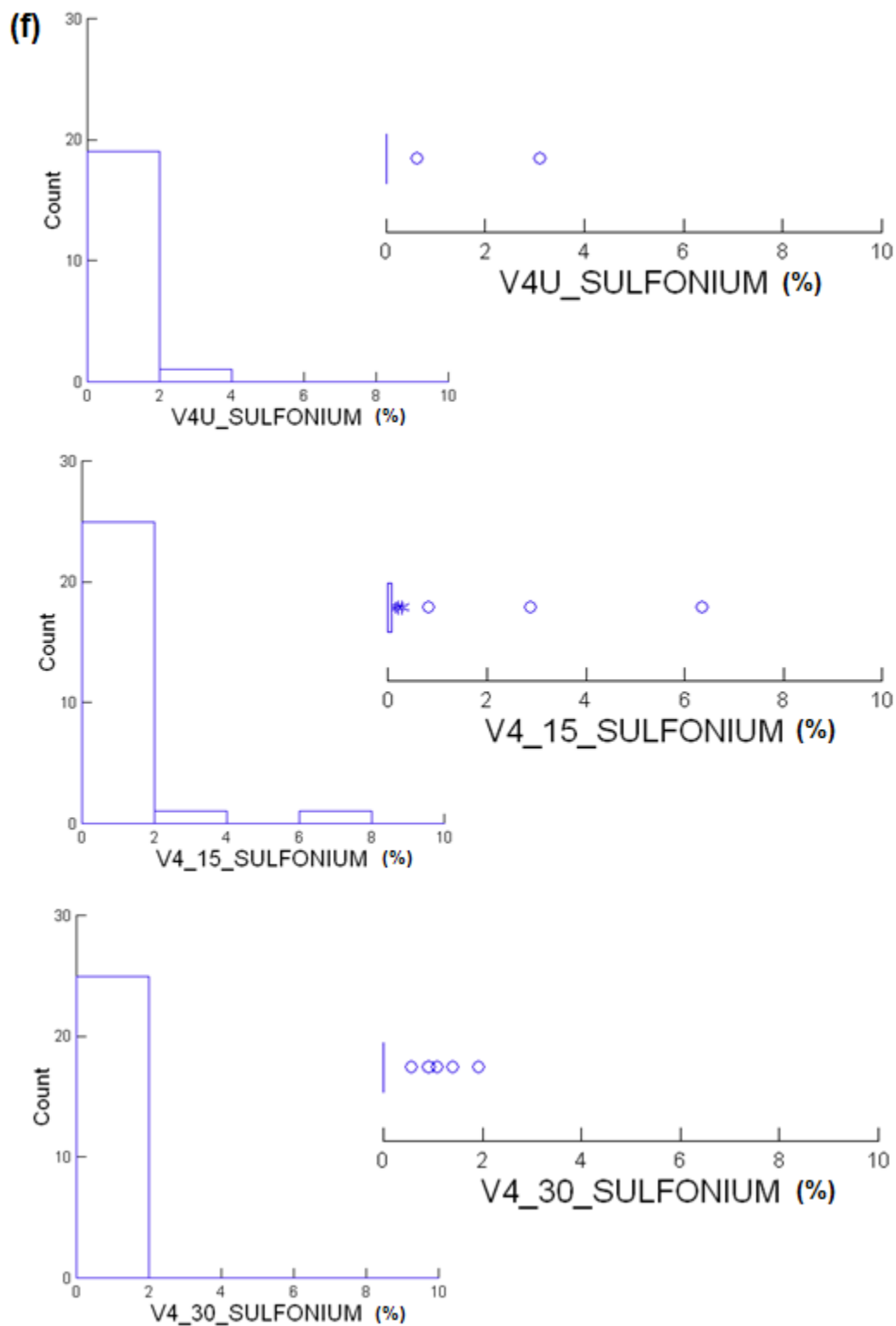


## APPENDIX B (continued)

(e) (continued)



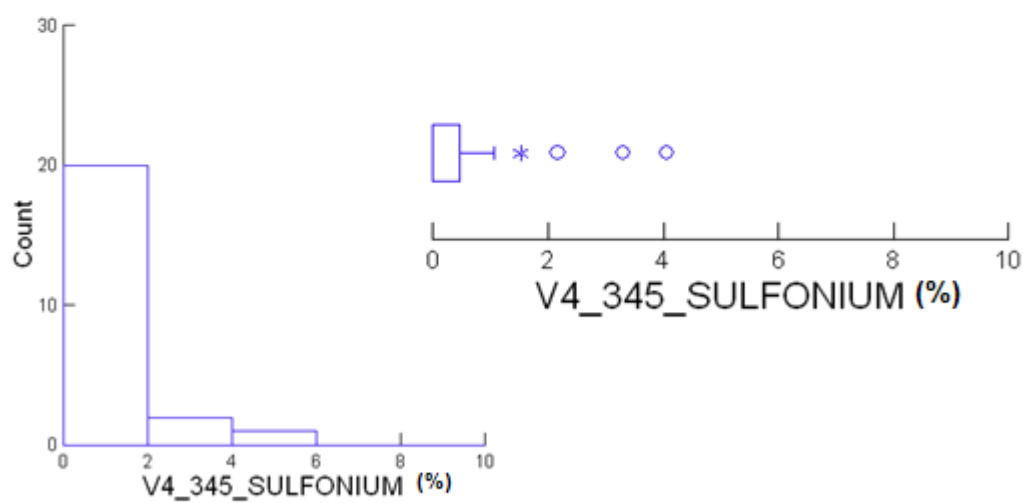
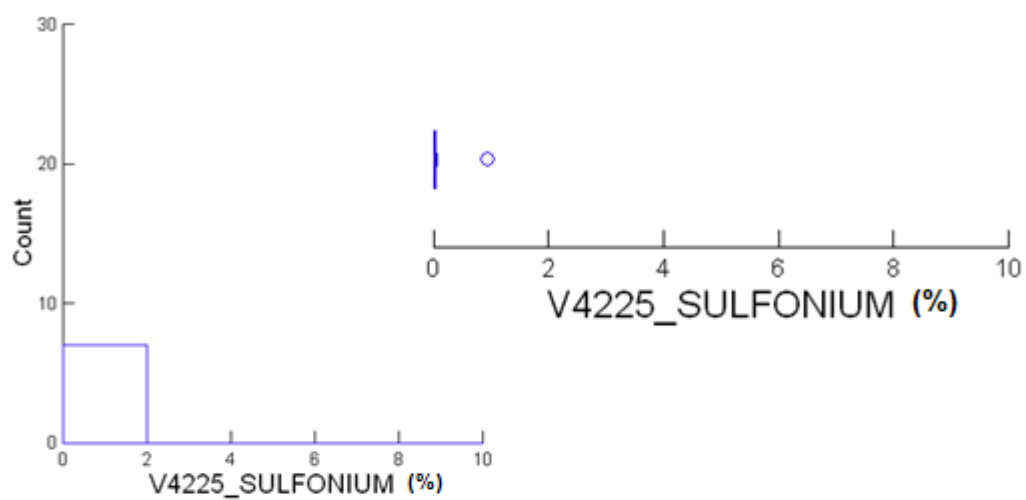
## APPENDIX B (continued)





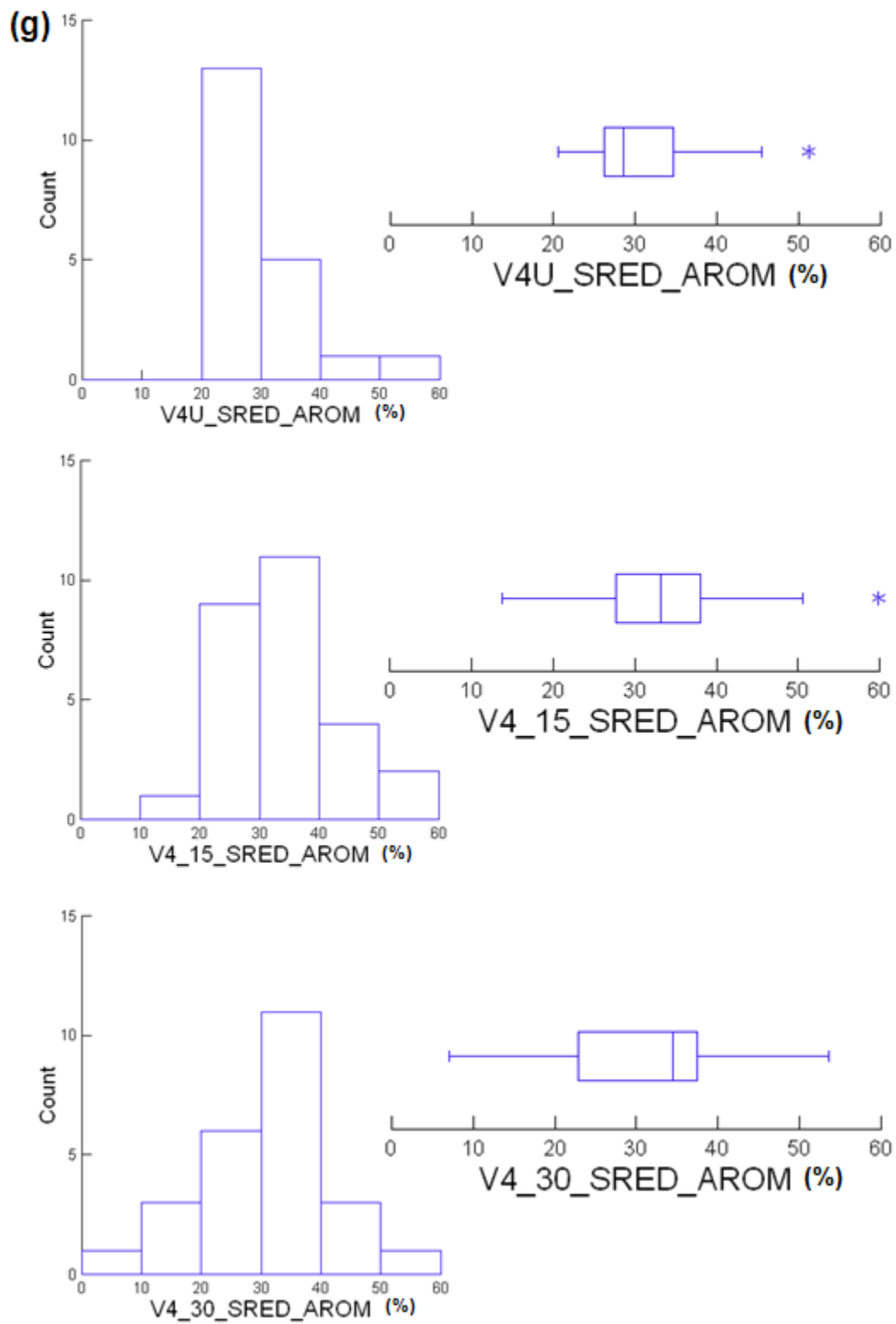
## APPENDIX B (continued)

(f) (continued)



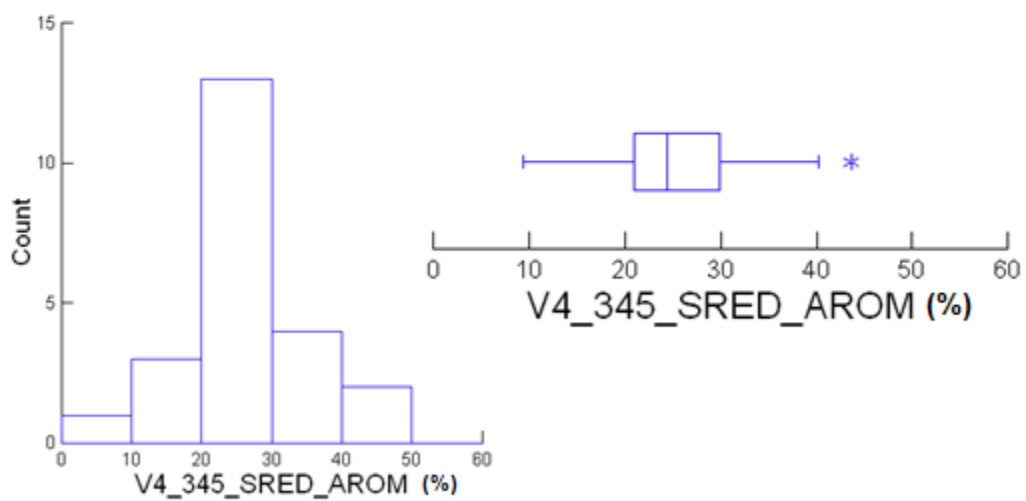
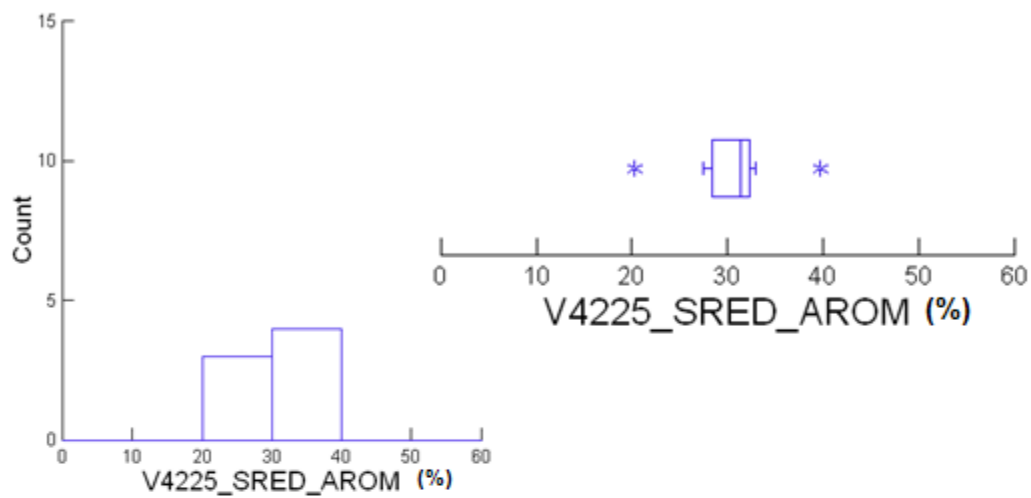
)

## APPENDIX B (continued)

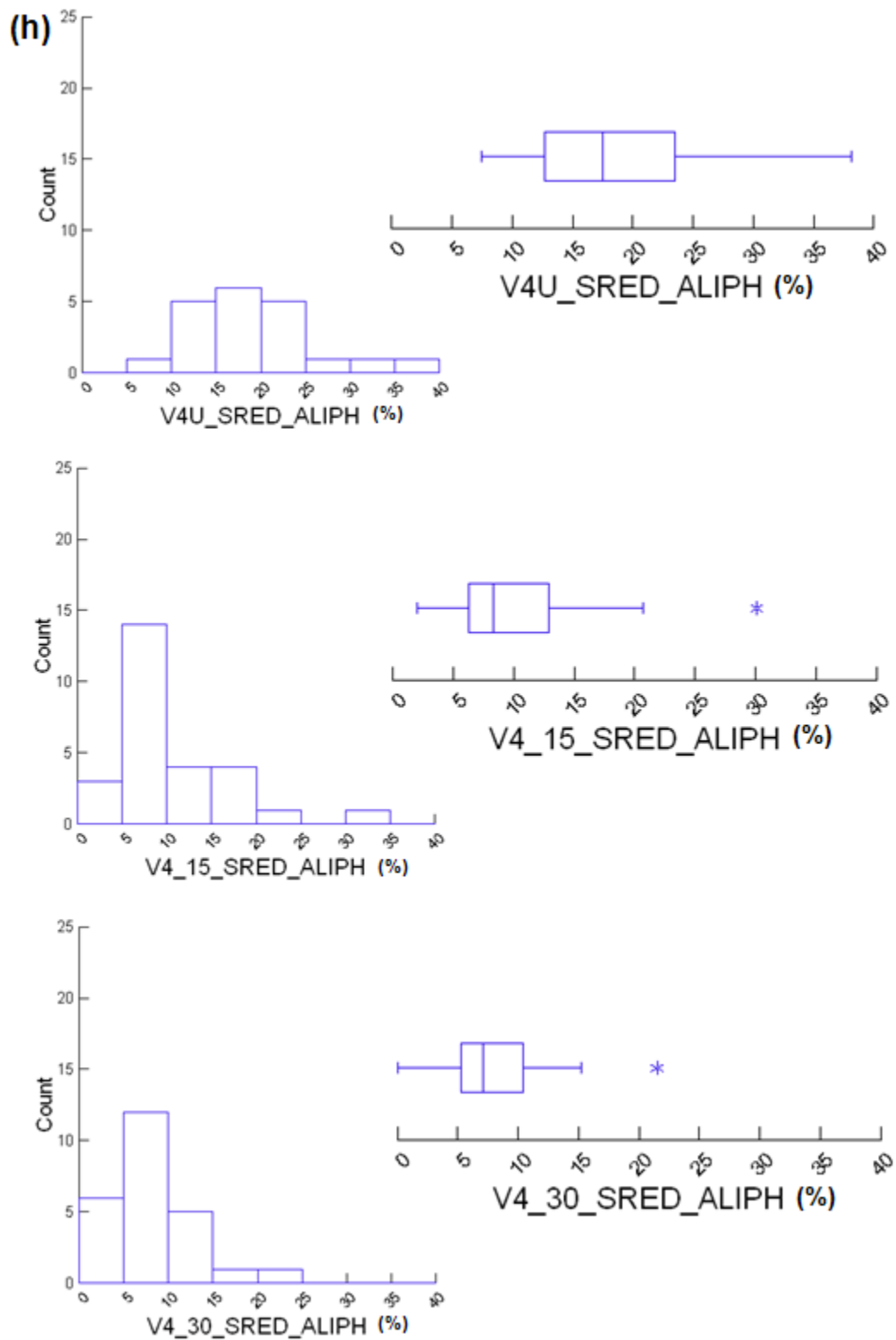


## APPENDIX B (continued)

(g) (continued)

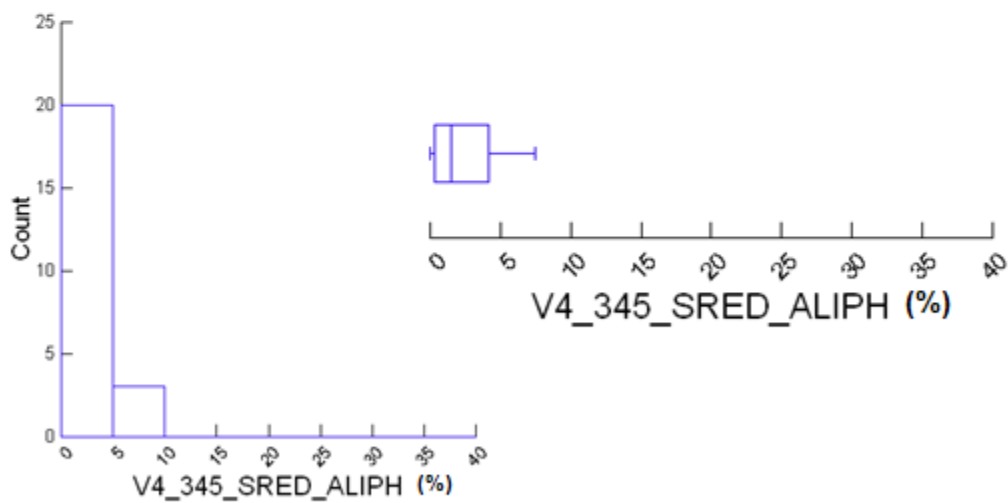
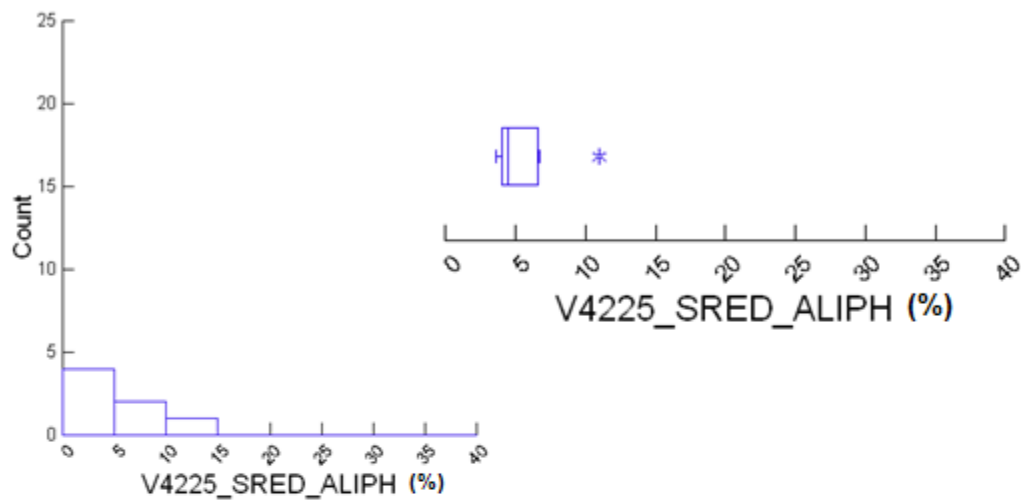


## APPENDIX B (continued)



## APPENDIX B (continued)

(h) (continued)



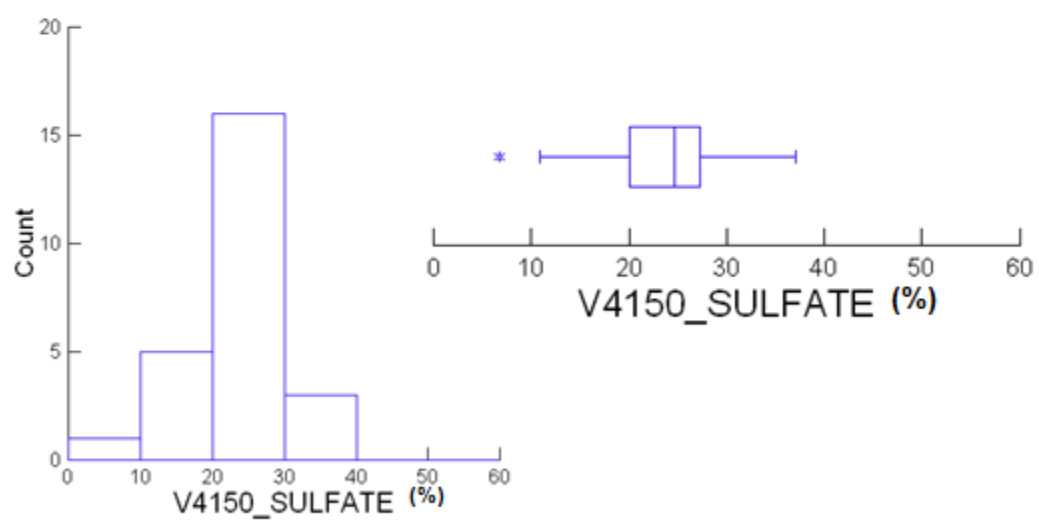
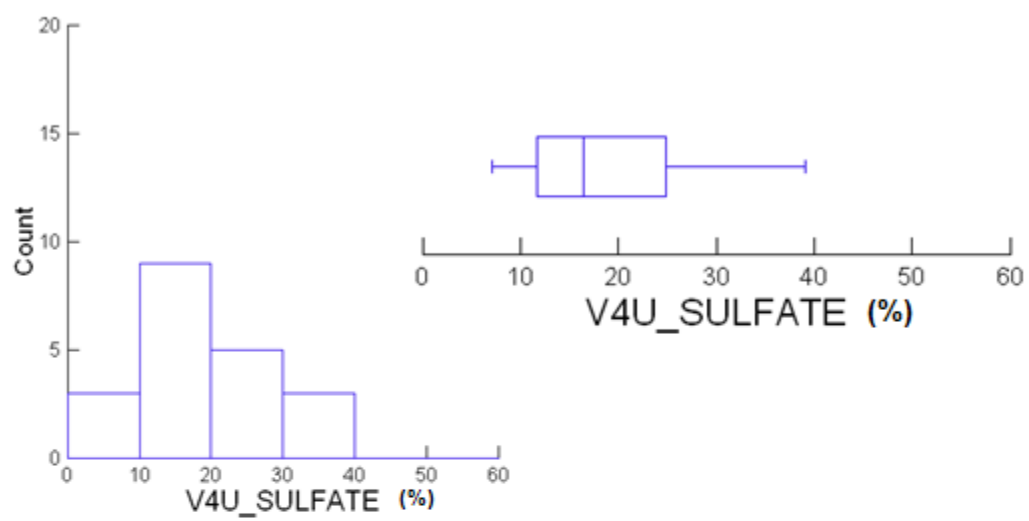
**APPENDIX B (continued)**

**Figure B3.** Histograms and box plots of the (a) sulfate, (b) sulfonate, (c) sulfone, (d) sulfite, (e) sulfoxide, (f) sulfonium, (g) reduced aromatic sulfur (Sred\_arom), and (h) reduced aliphatic sulfur (Sred\_aliph) constituents in soil from the VR-4 Temperature Series. The temperature series consists of unheated soil (V4U\*) and soils heated for 120 min at 150°C (V4150\*), 175°C (V4175\*), and 225°C (V4225\*). The fractional amounts of each sulfur constituent were determined using full-energy range (2465 to 2510 eV) spectra and the second fitting approach.

\*NOTE: Because the MYSTAT program requires that the first character of a variable name be a letter, the labels “V4U,” “V4150,” “V4175,” and “V4225” do not match the previously assigned sample names (c.f., Table 1).

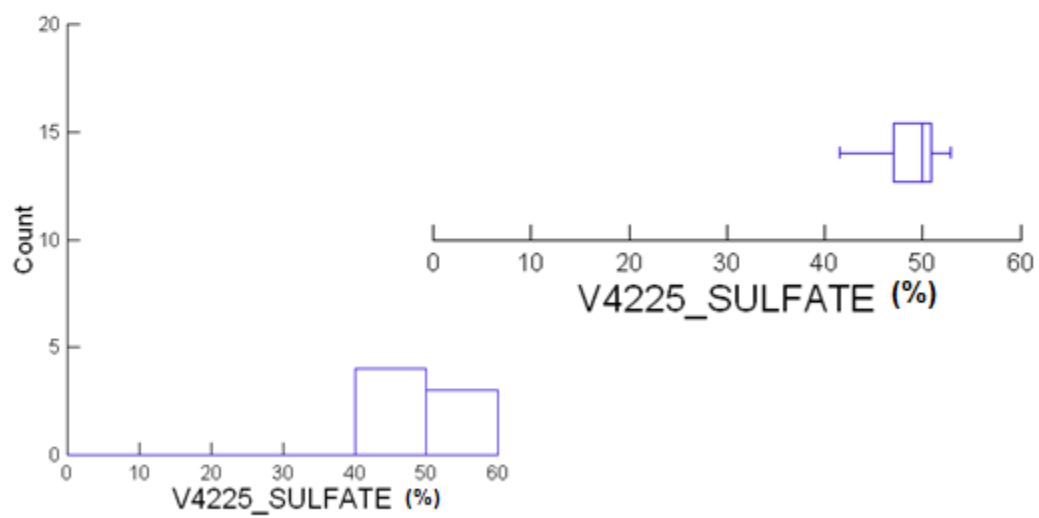
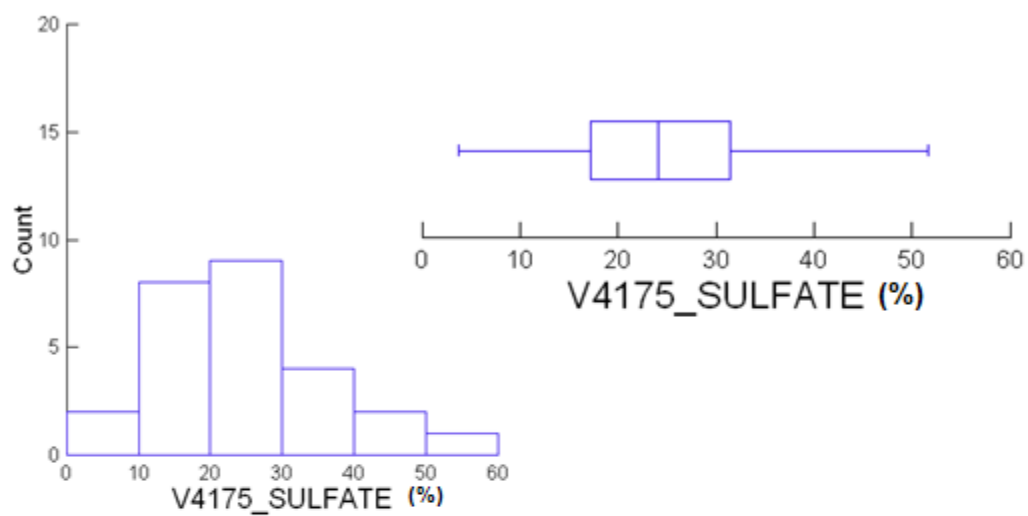
## APPENDIX B (continued)

(a)



## APPENDIX B (continued)

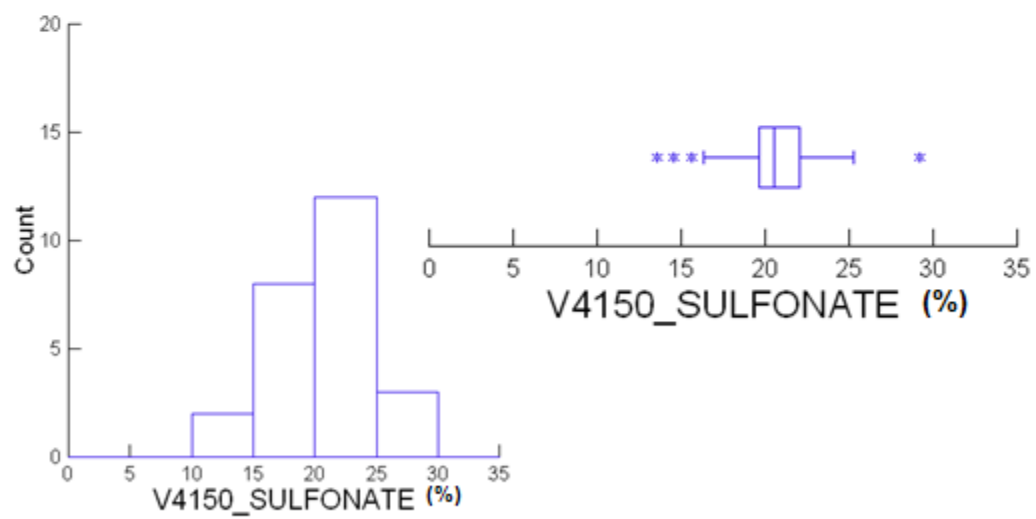
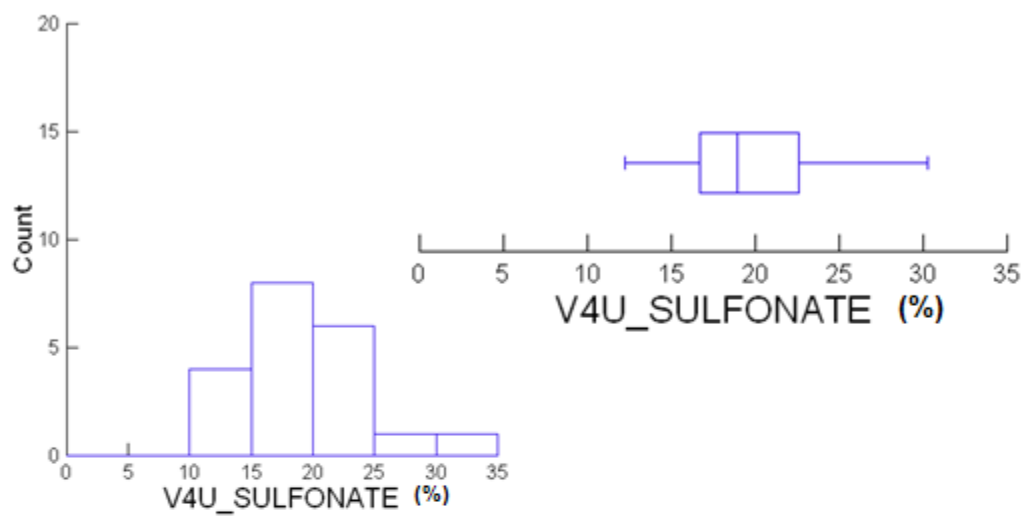
(a) (continued)





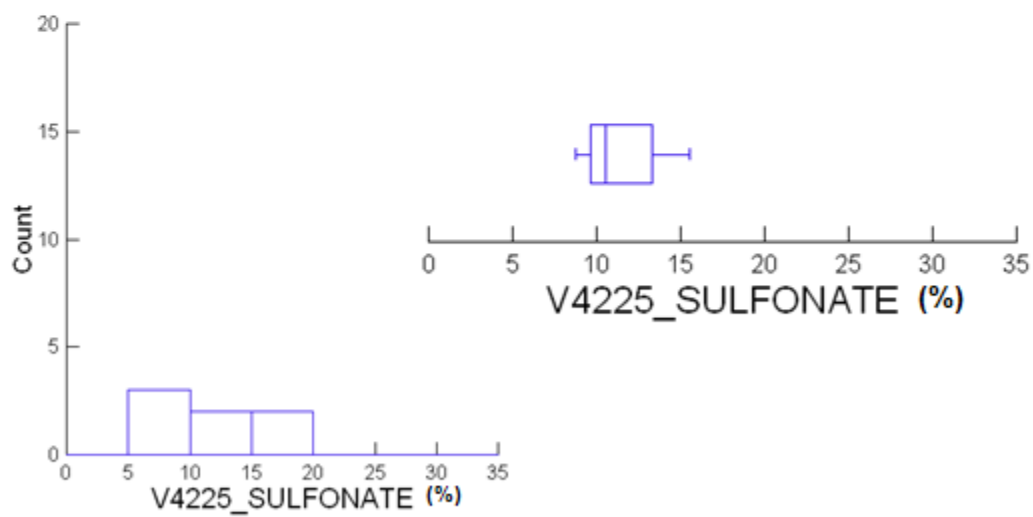
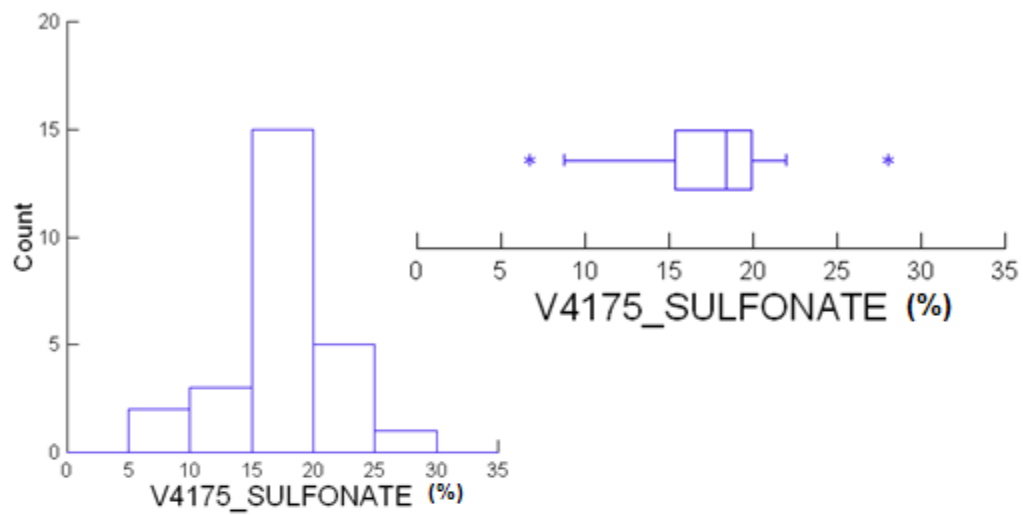
## APPENDIX B (continued)

(b)



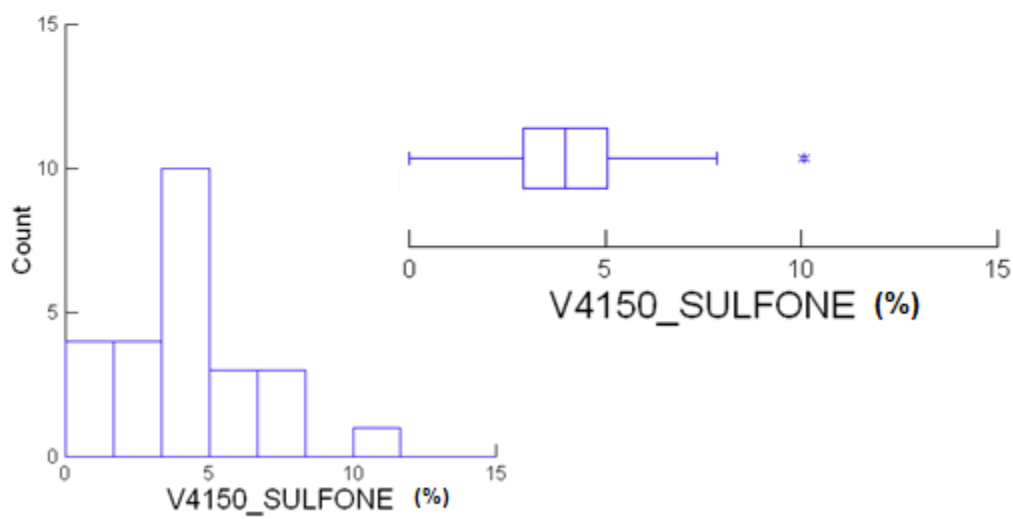
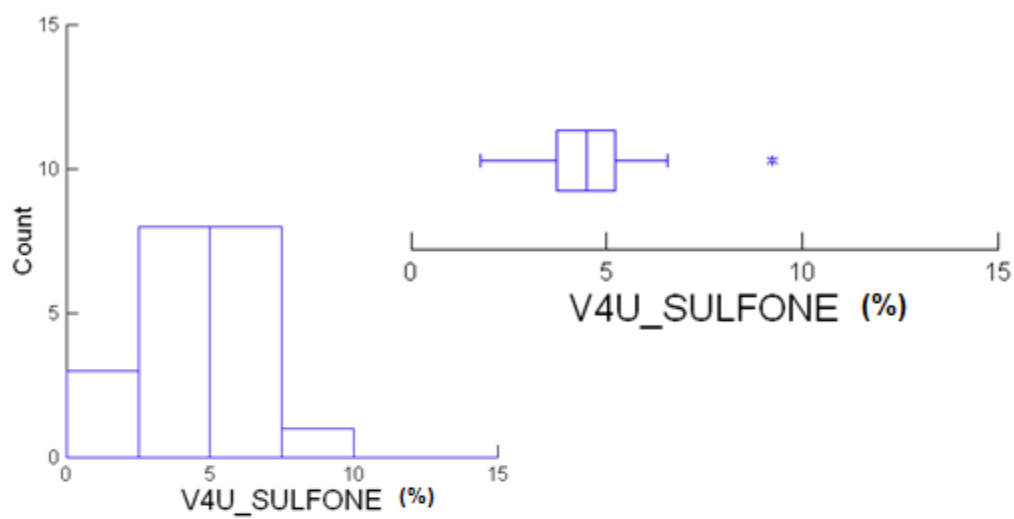
## APPENDIX B (continued)

(b) (continued)



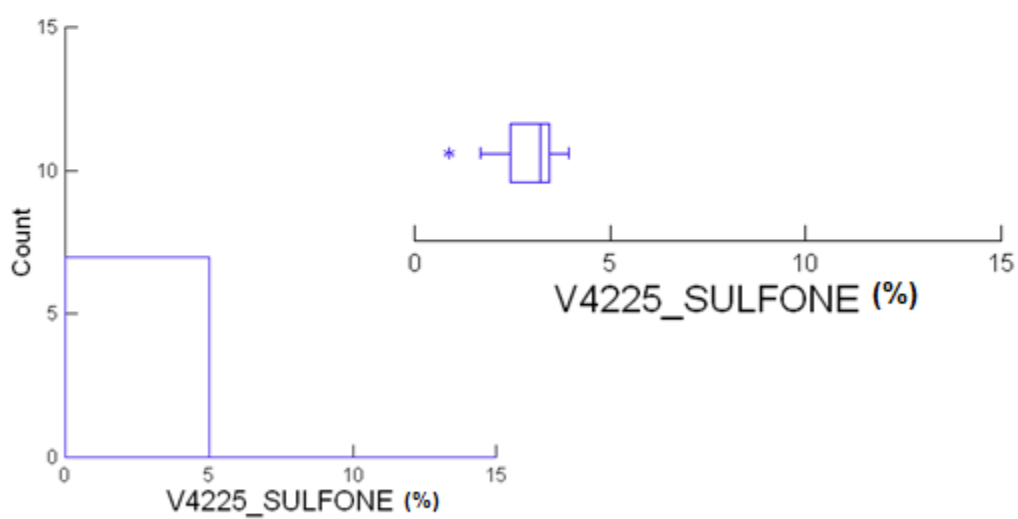
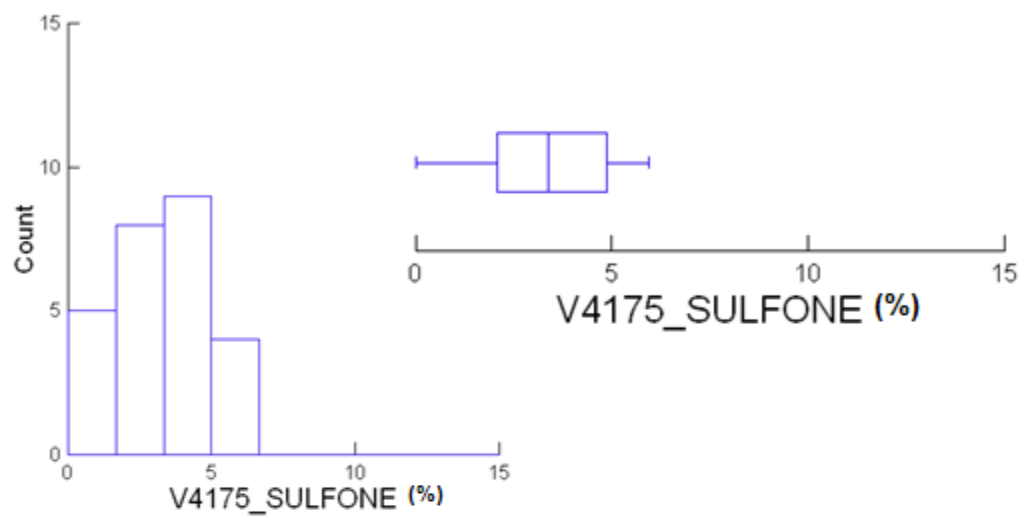
## APPENDIX B (continued)

(c)



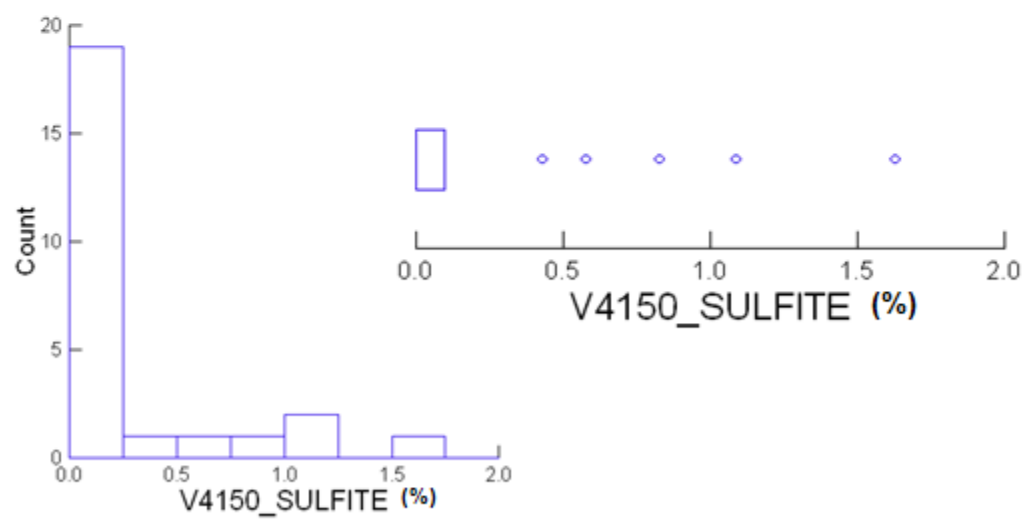
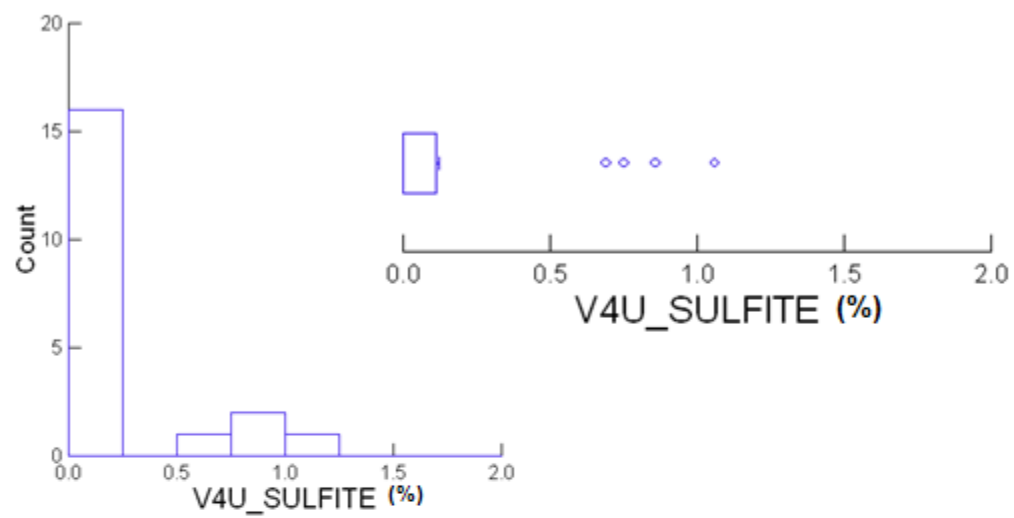
## APPENDIX B (continued)

(c) (continued)



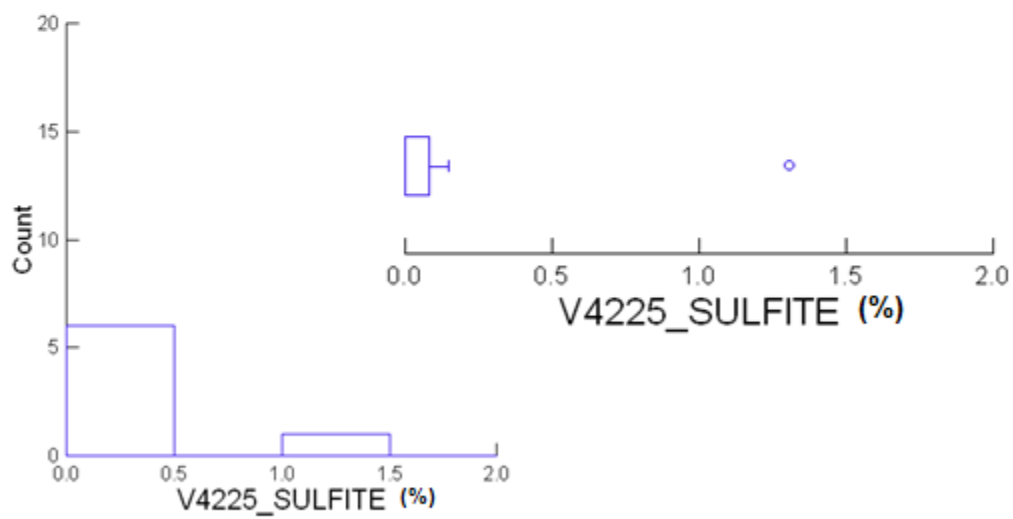
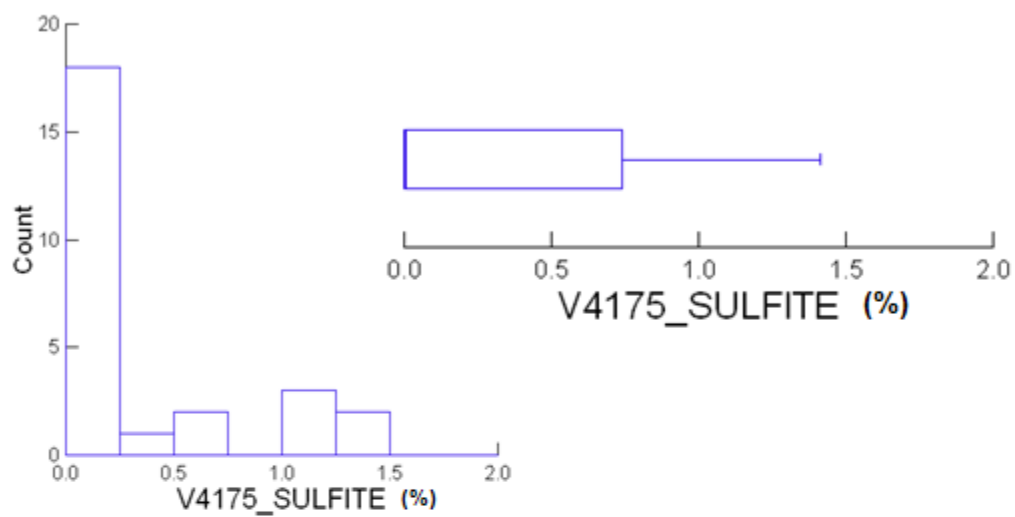
## APPENDIX B (continued)

(d)



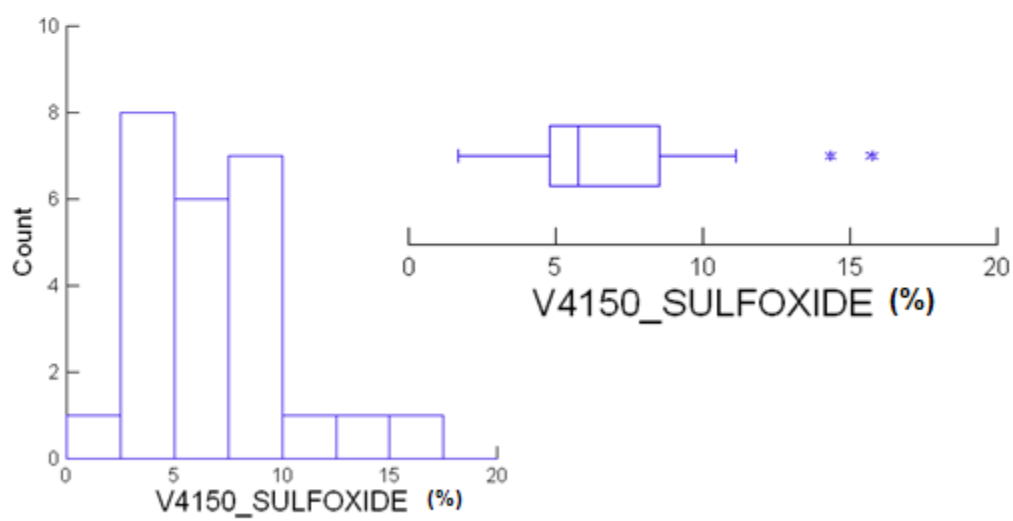
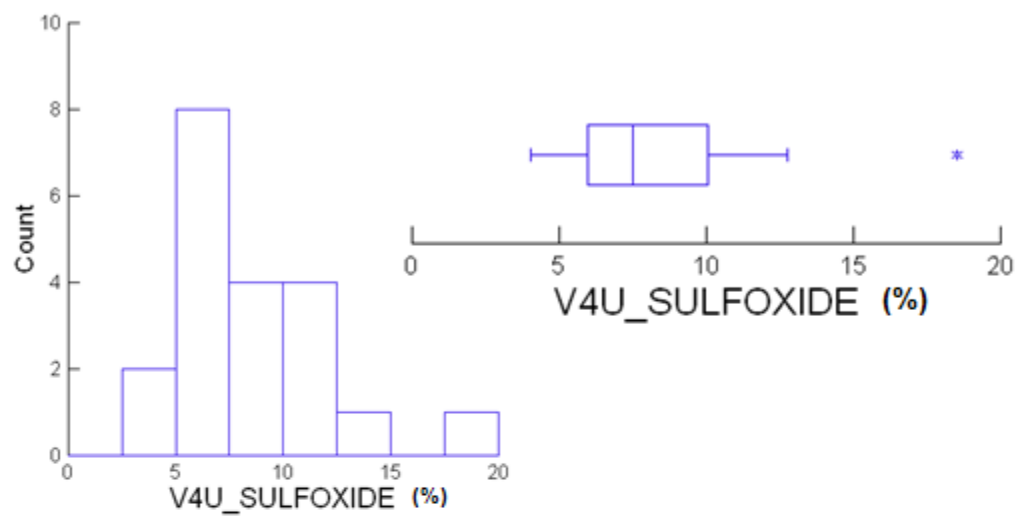
## APPENDIX B (continued)

(d) (continued)



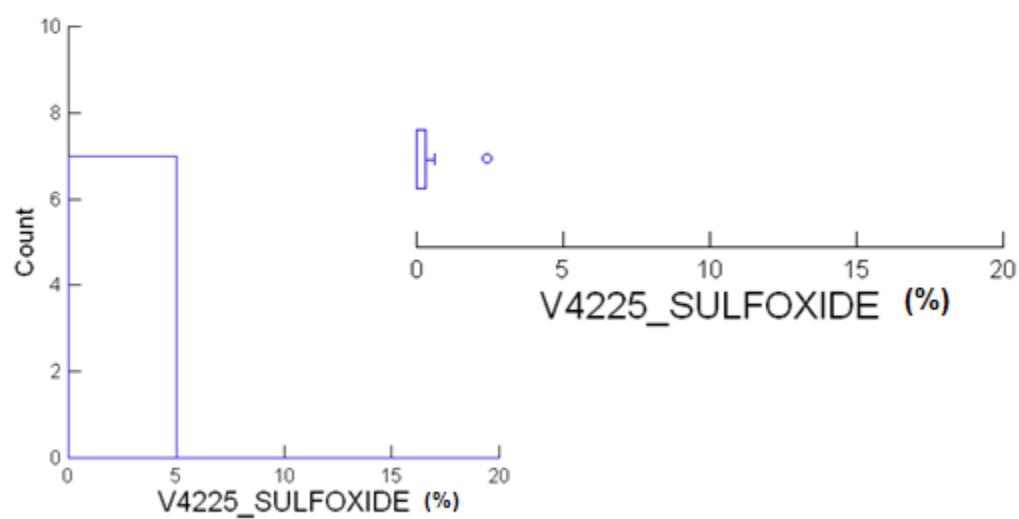
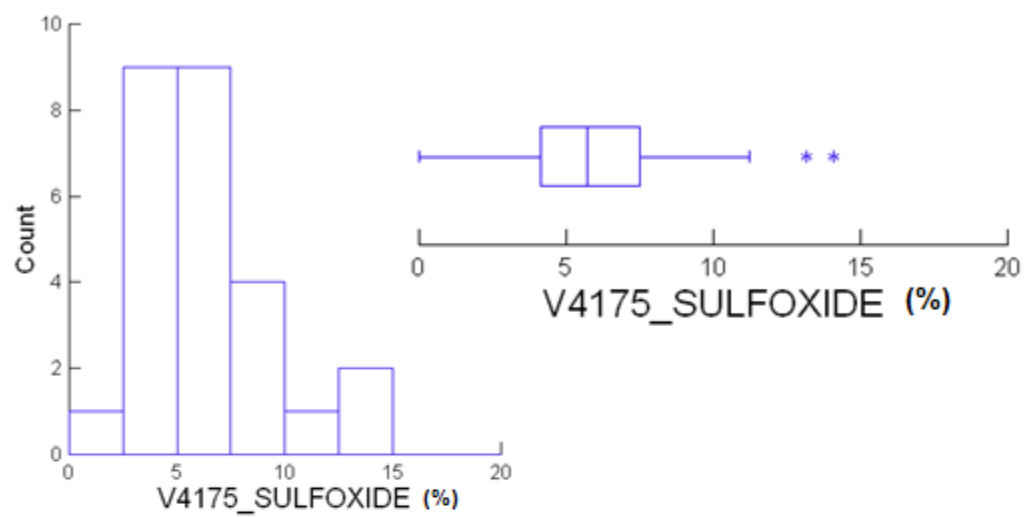
## APPENDIX B (continued)

(e)



## APPENDIX B (continued)

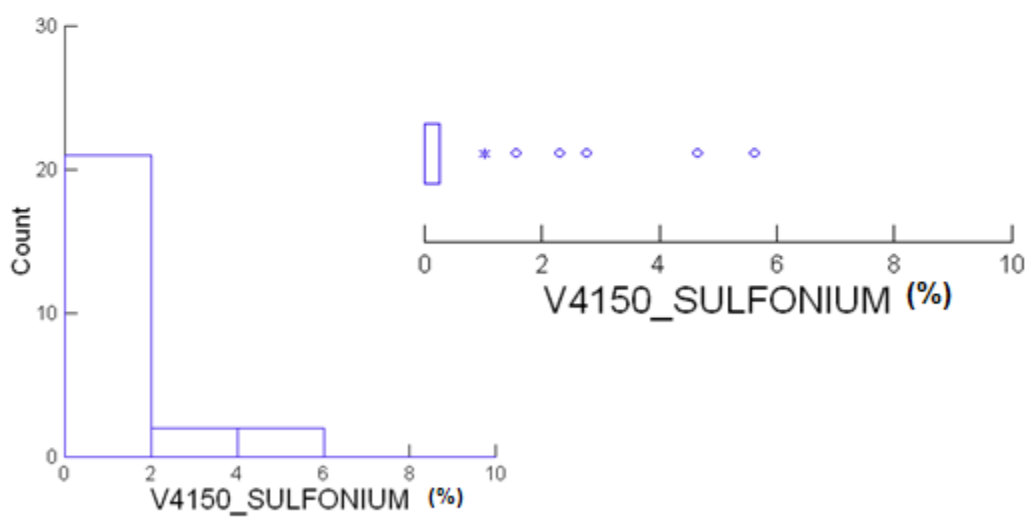
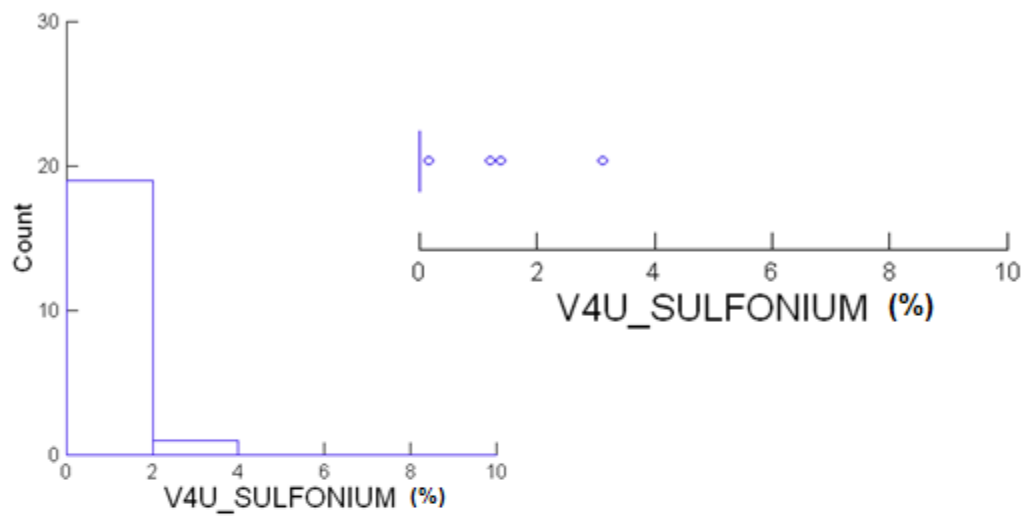
(e) (continued)





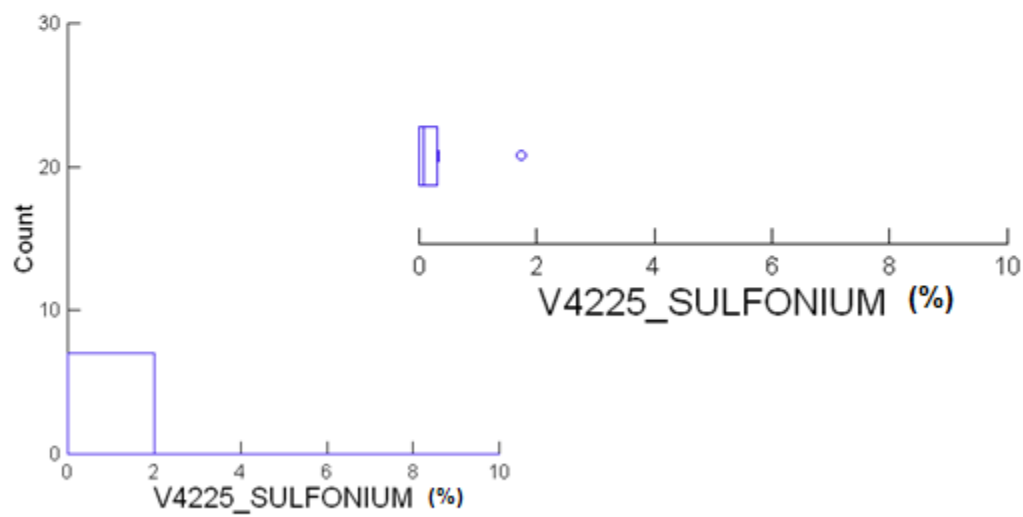
## APPENDIX B (continued)

(f)



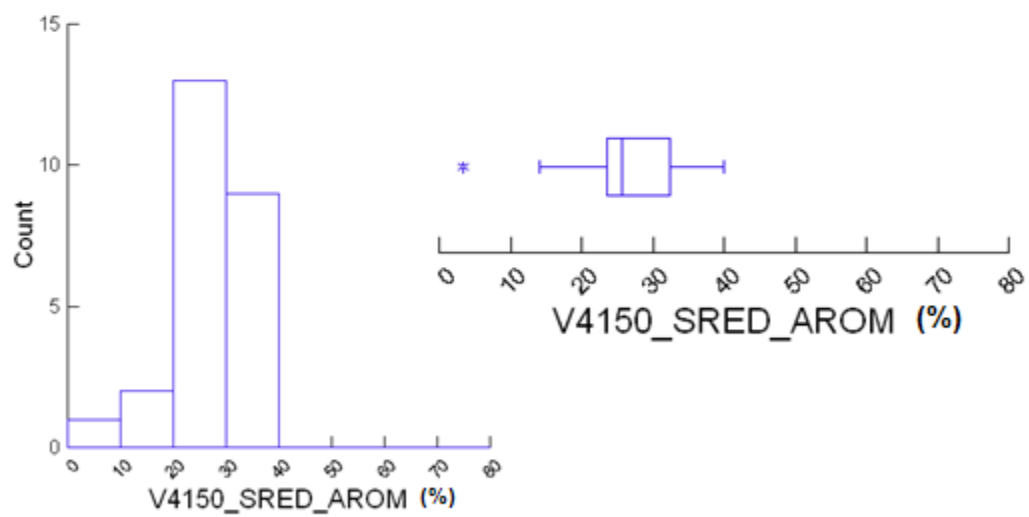
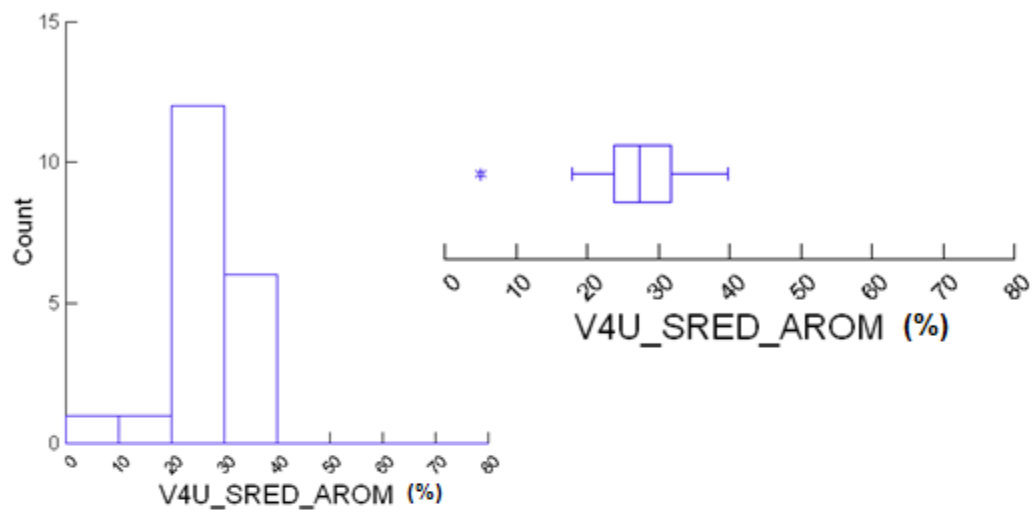
## APPENDIX B (continued)

(f) (continued)



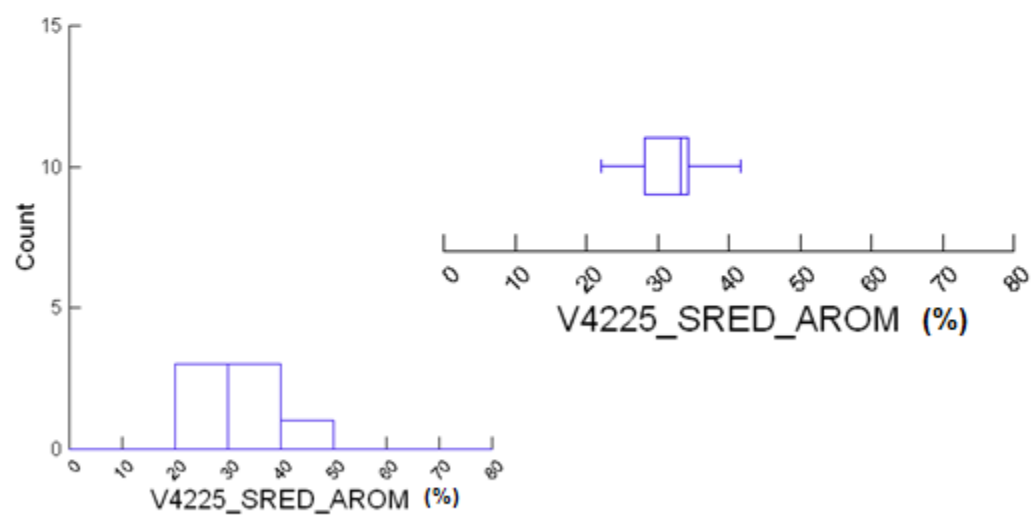
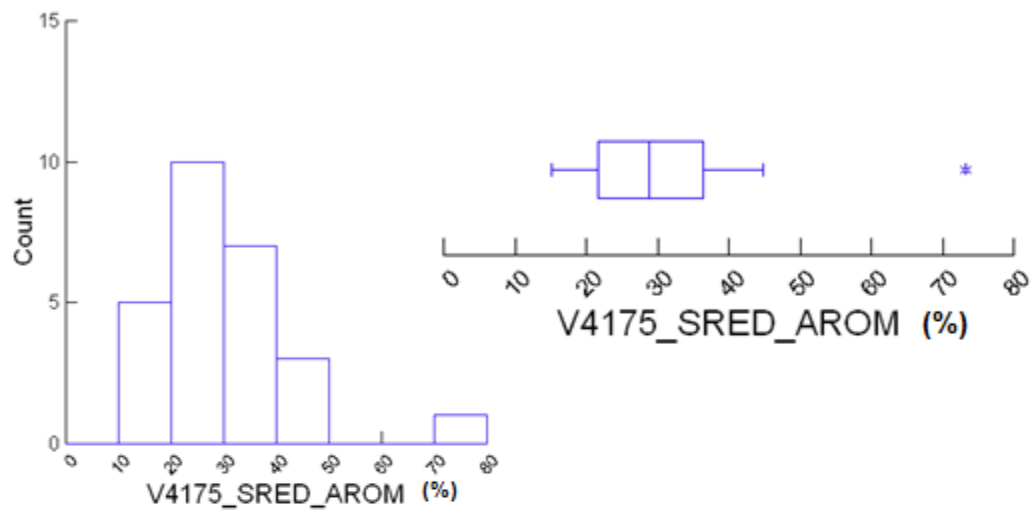
## APPENDIX B (continued)

(g)



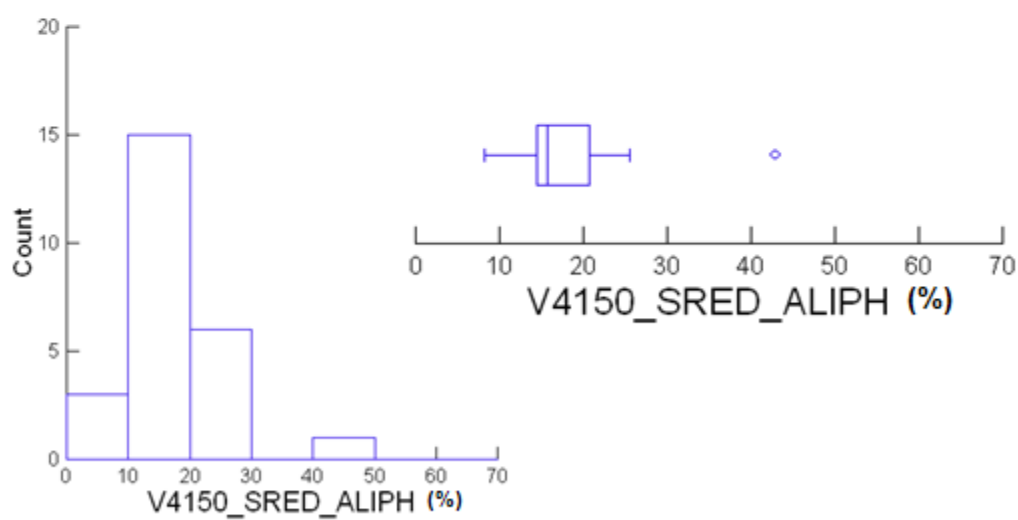
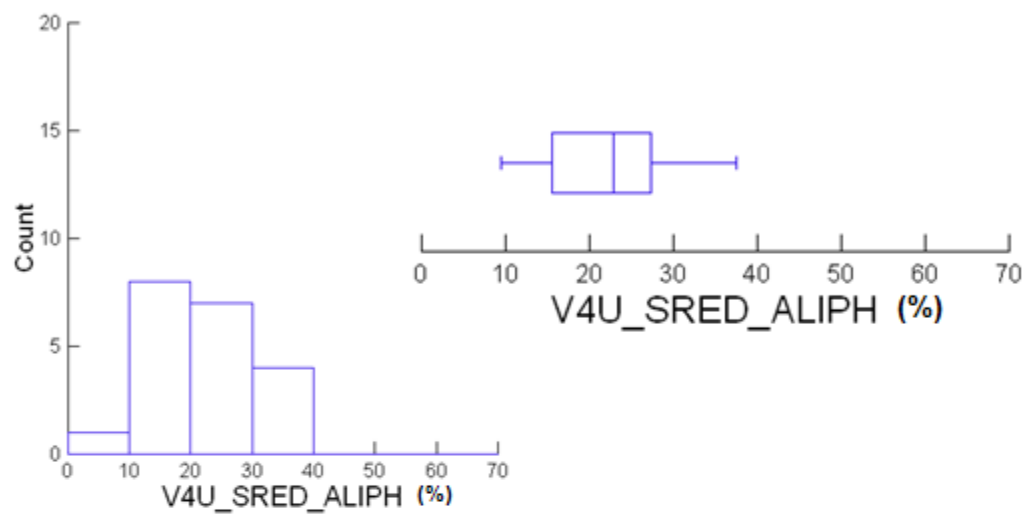
## APPENDIX B (continued)

(g) (continued)



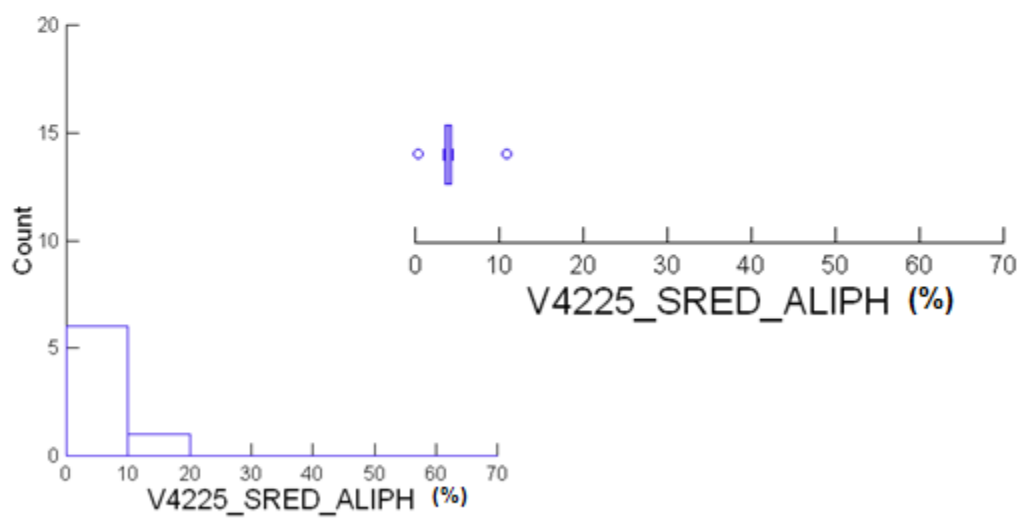
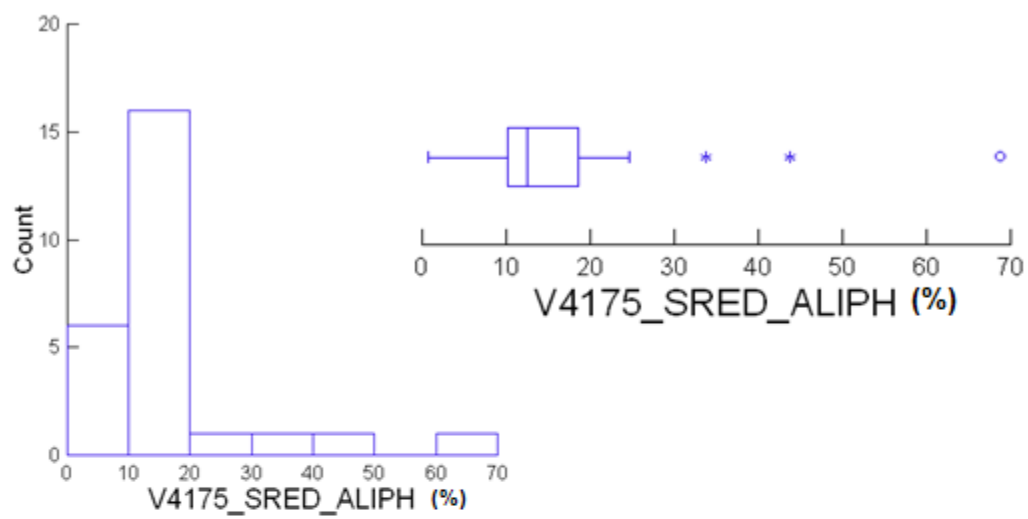
## APPENDIX B (continued)

(h)



## APPENDIX B (continued)

(h) (continued)

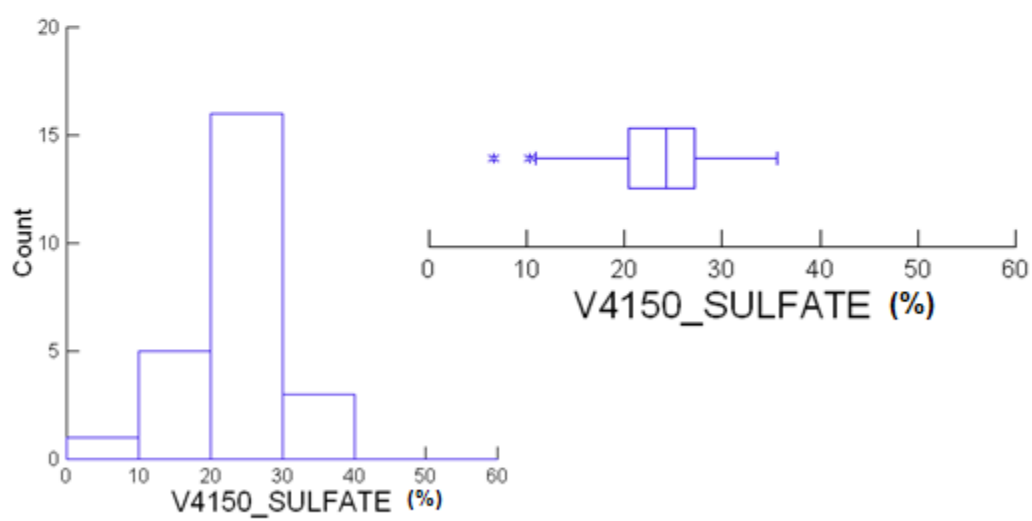
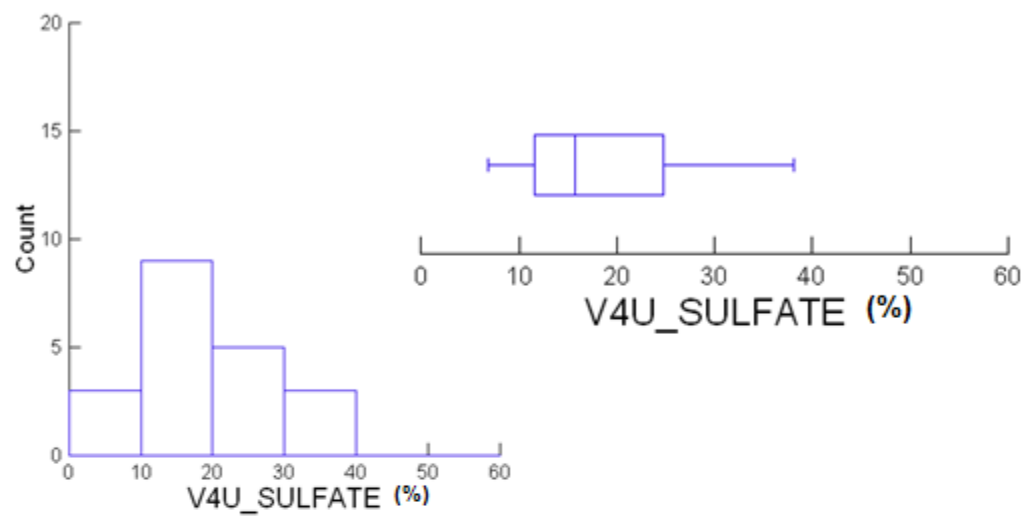


**APPENDIX B (continued)**

**Figure B4.** Histograms and box plots of the (a) sulfate, (b) sulfonate, (c) sulfone, (d) sulfite, (e) sulfoxide, (f) sulfonium, (g) reduced aromatic sulfur (Sred\_arom), and (h) reduced aliphatic sulfur (Sred\_aliph) constituents in soil from the VR-4 Temperature Series. The fractional amounts of each sulfur constituent were determined using short-energy range (2465 to 2490 eV) spectra and the second fitting approach.

## APPENDIX B (continued)

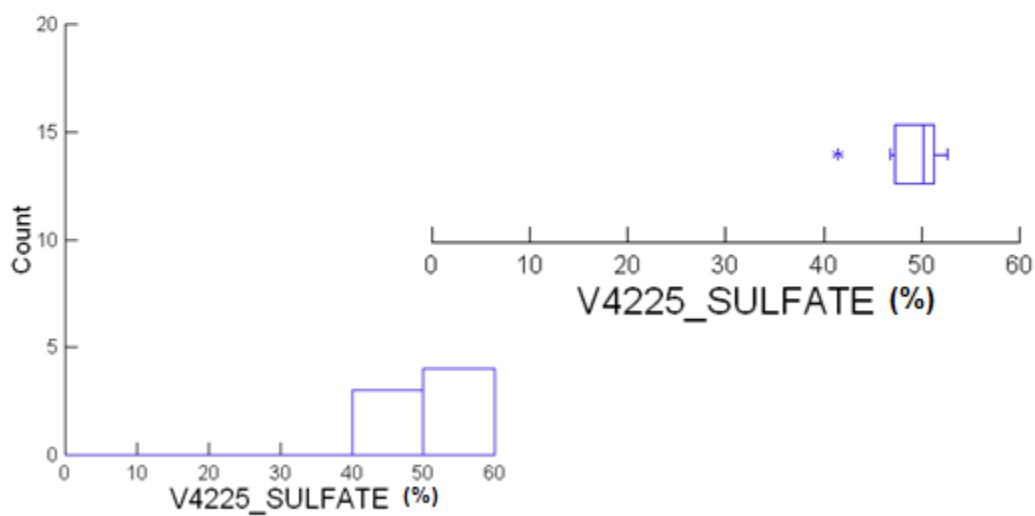
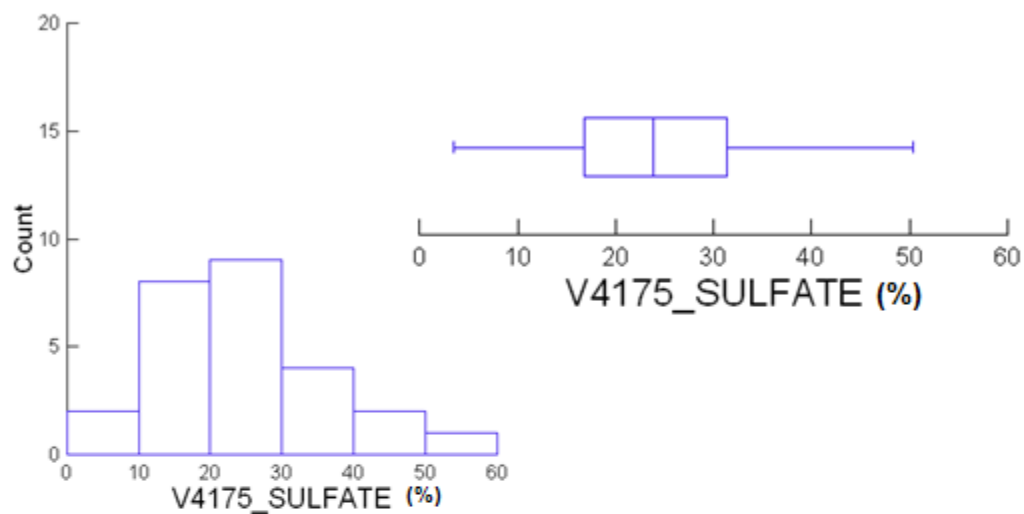
(a)





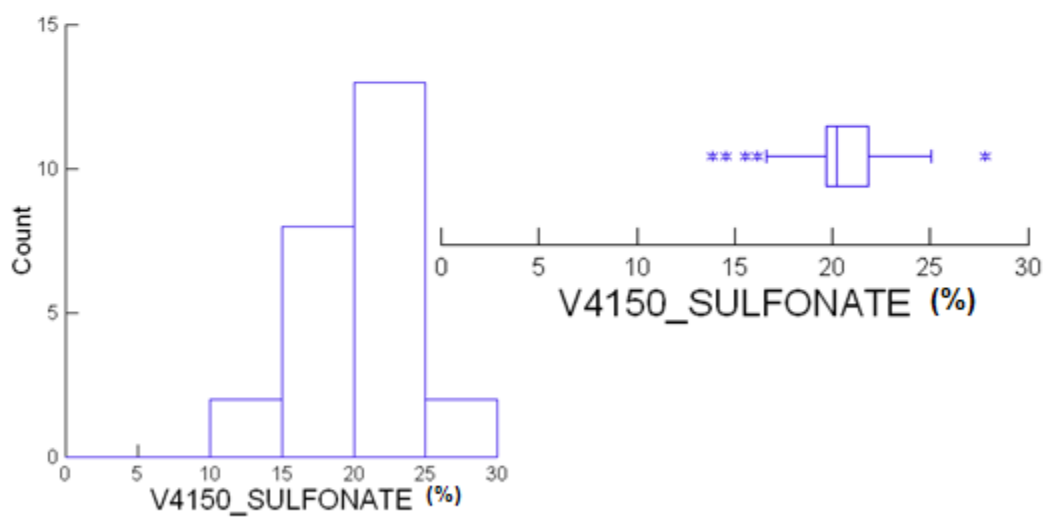
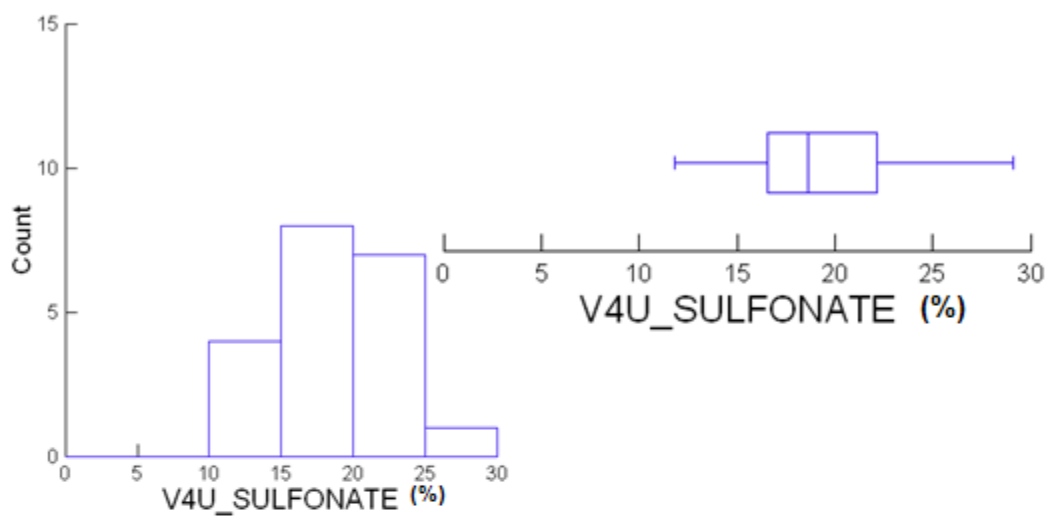
## APPENDIX B (continued)

(a) (continued)



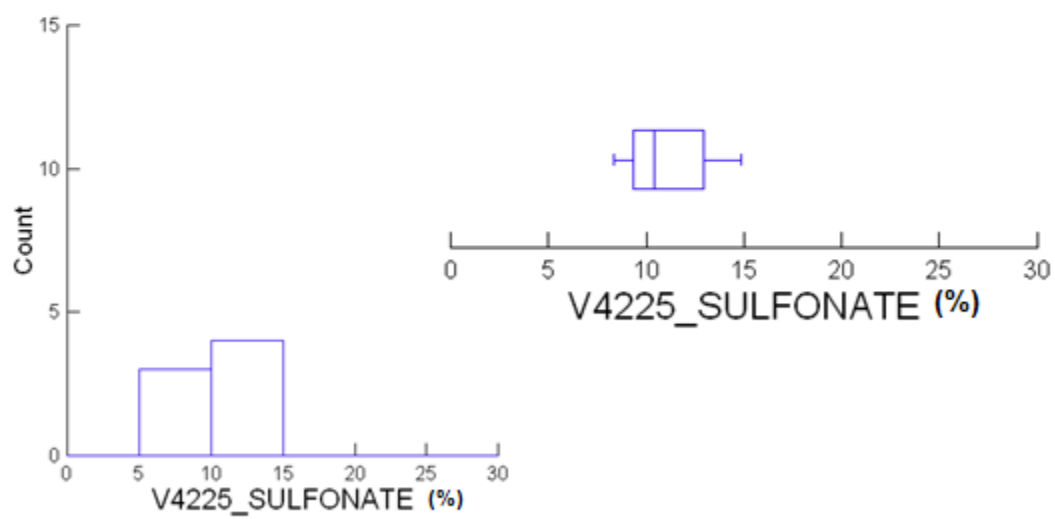
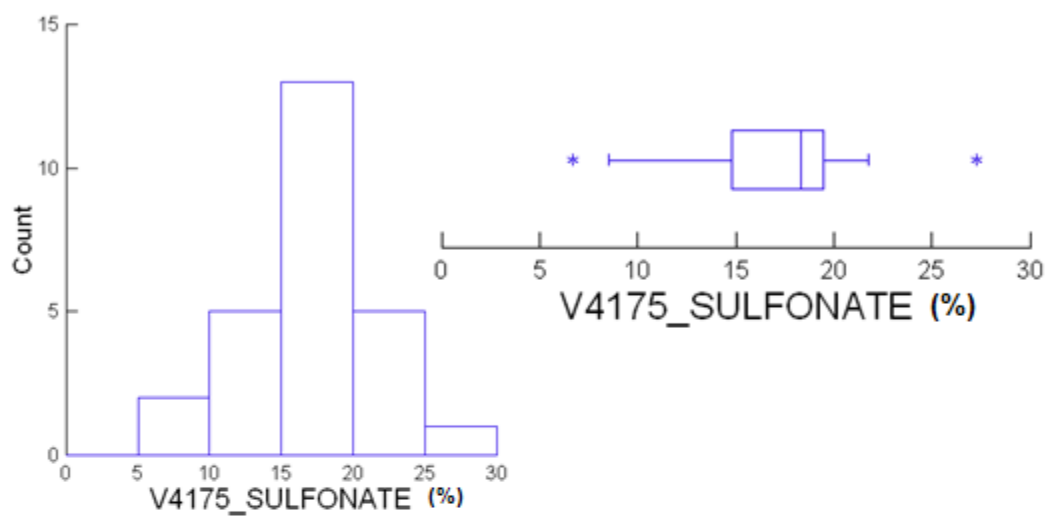
## APPENDIX B (continued)

(b)



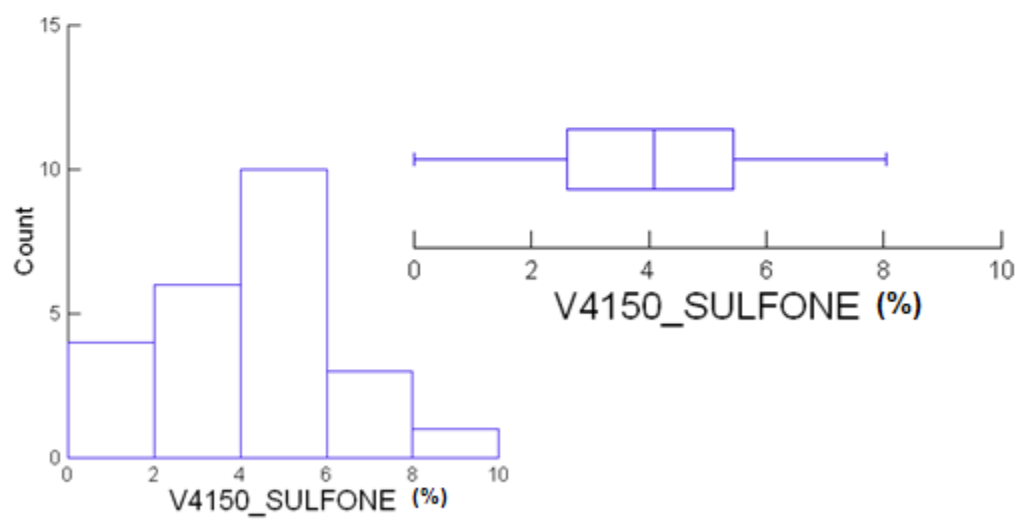
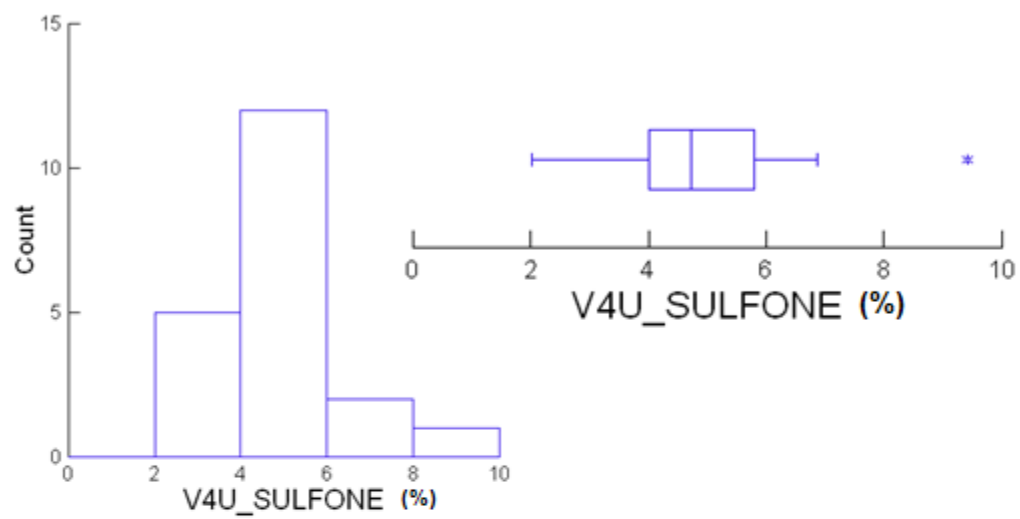
## APPENDIX B (continued)

(b) (continued)



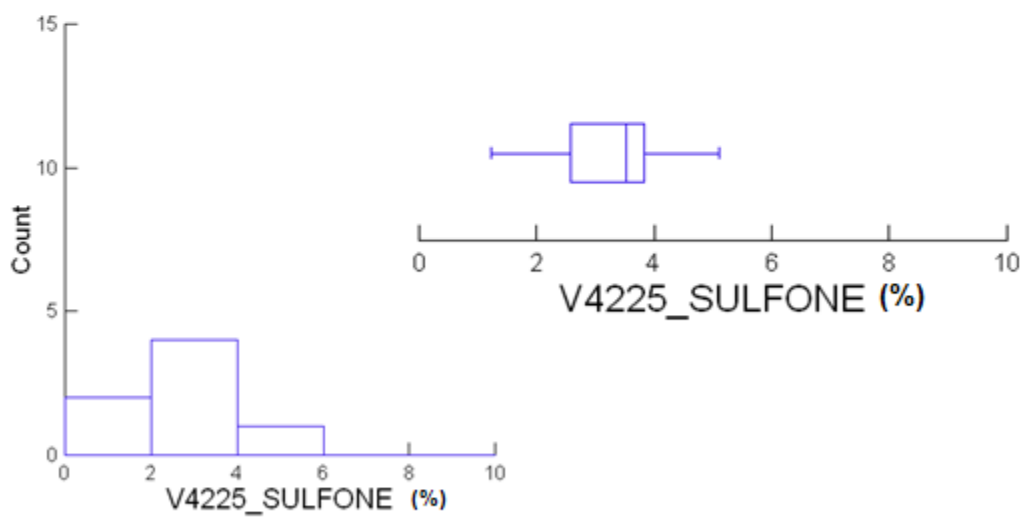
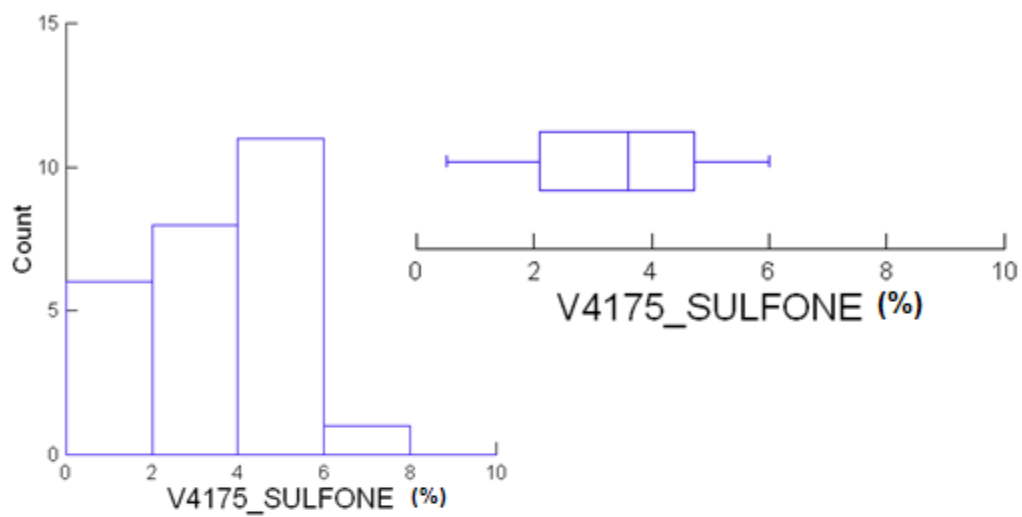
## APPENDIX B (continued)

(c)



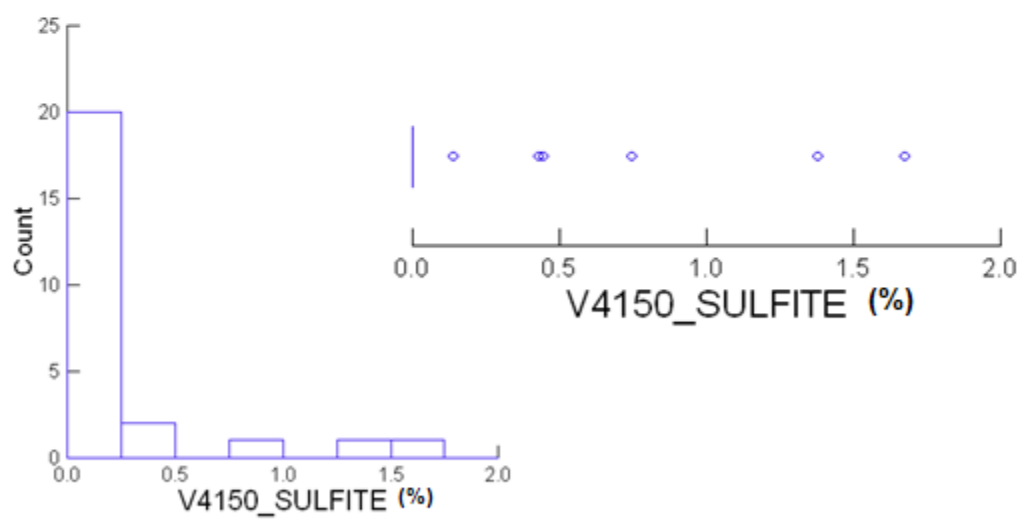
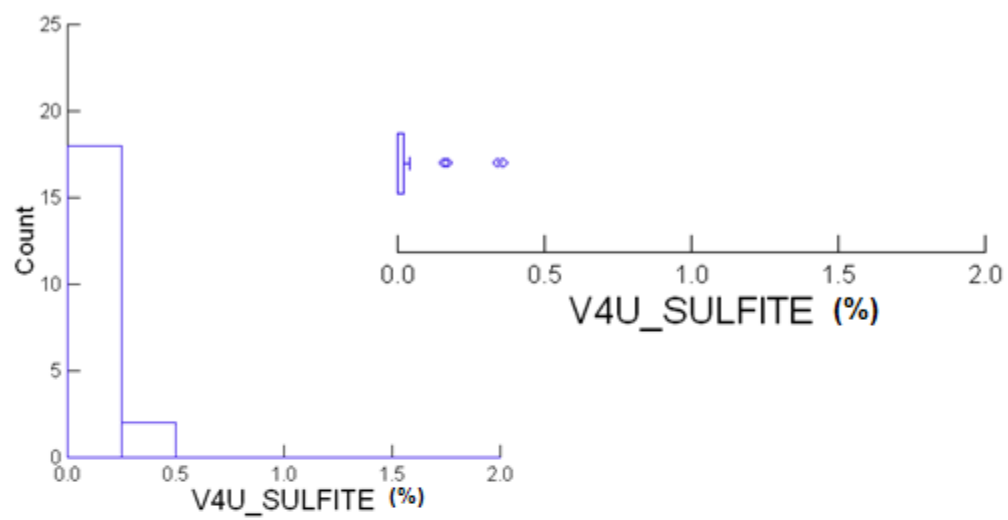
## APPENDIX B (continued)

(c) (continued)



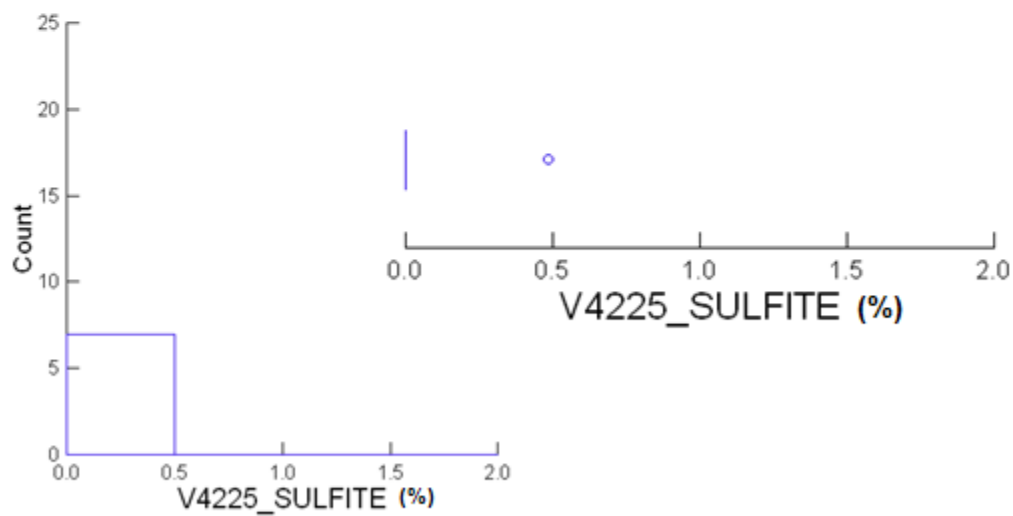
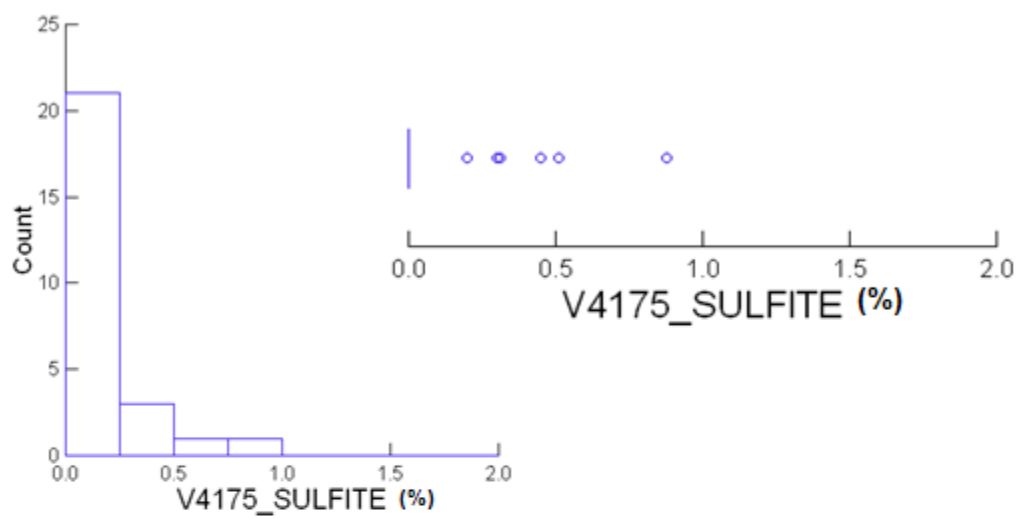
## APPENDIX B (continued)

(d)



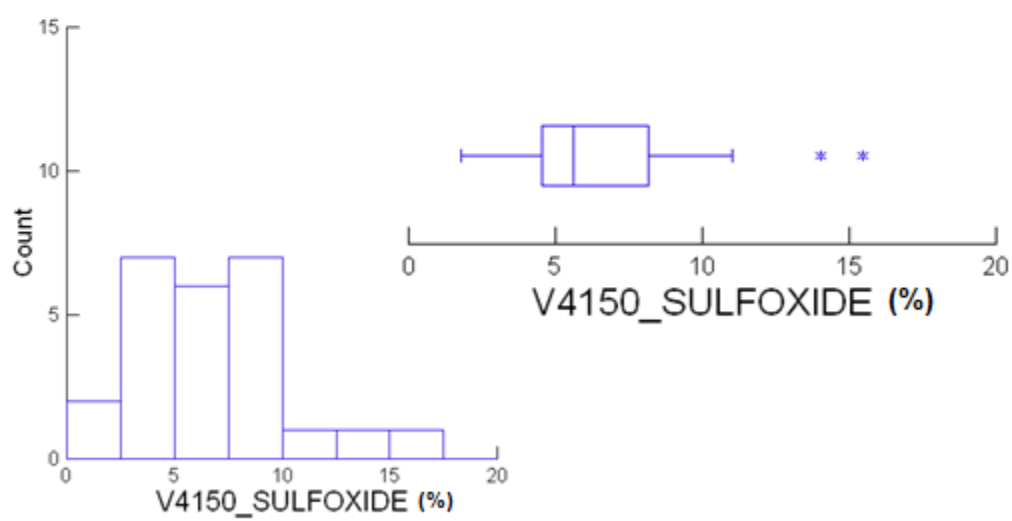
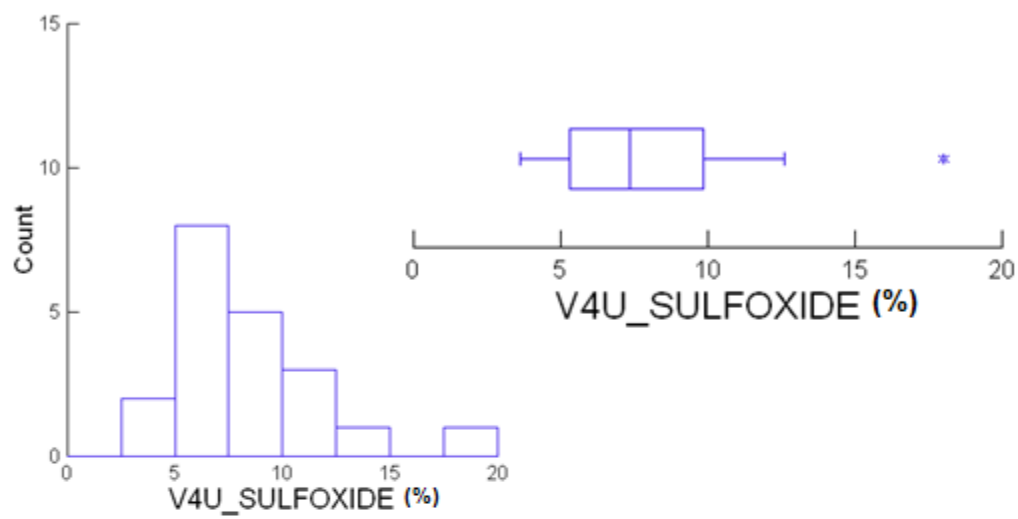
## APPENDIX B (continued)

(d) (continued)



## APPENDIX B (continued)

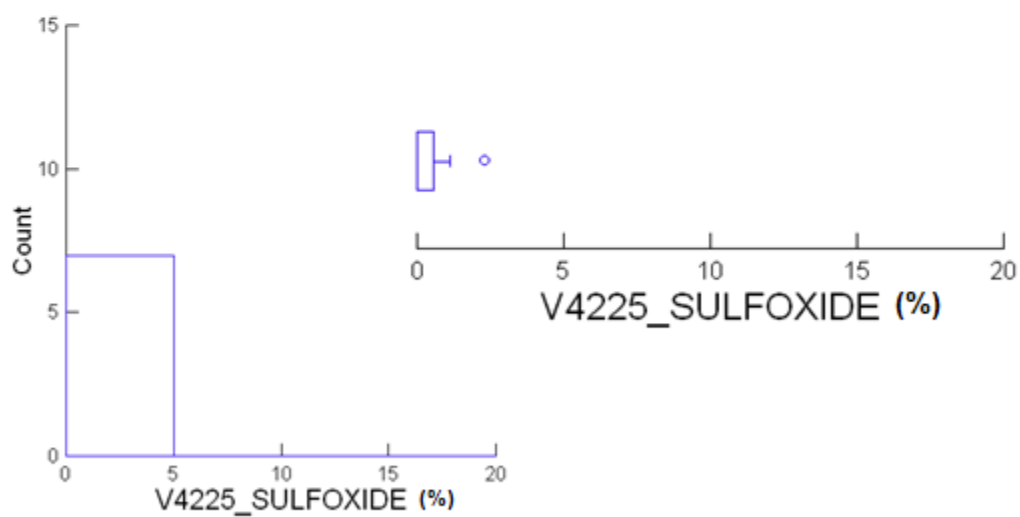
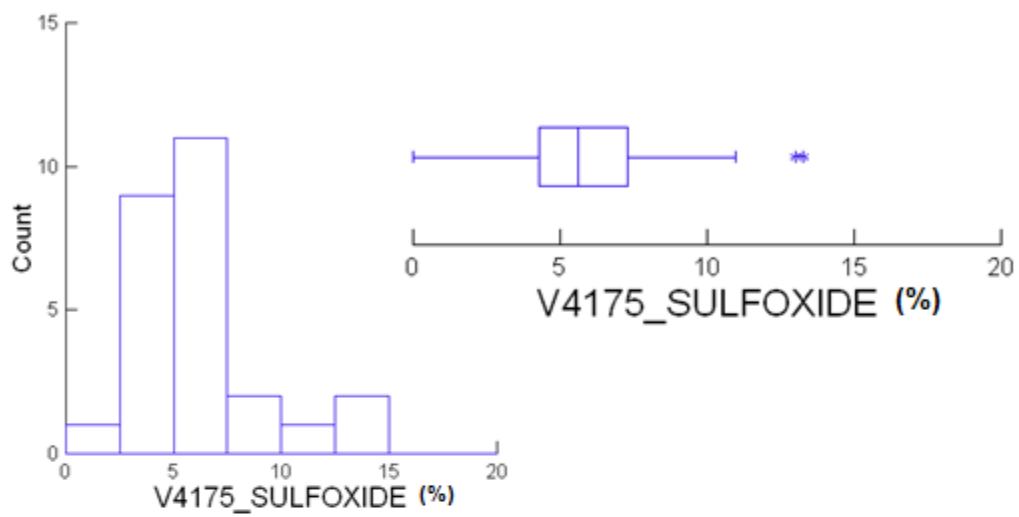
(e)





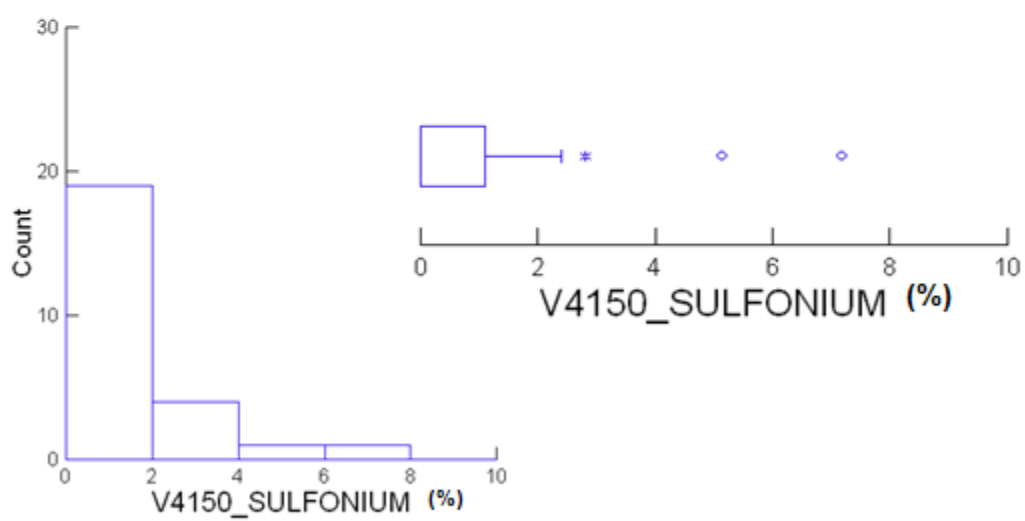
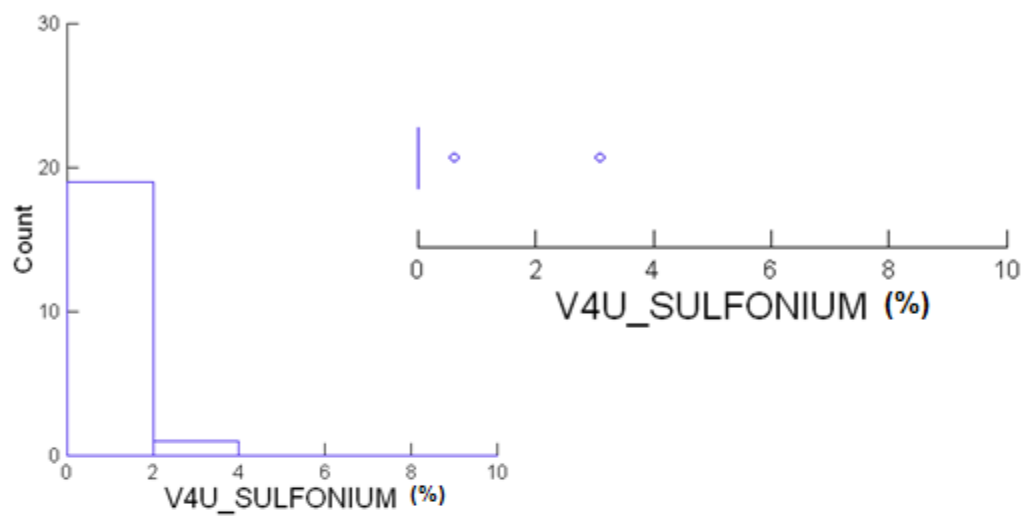
## APPENDIX B (continued)

(e) (continued)



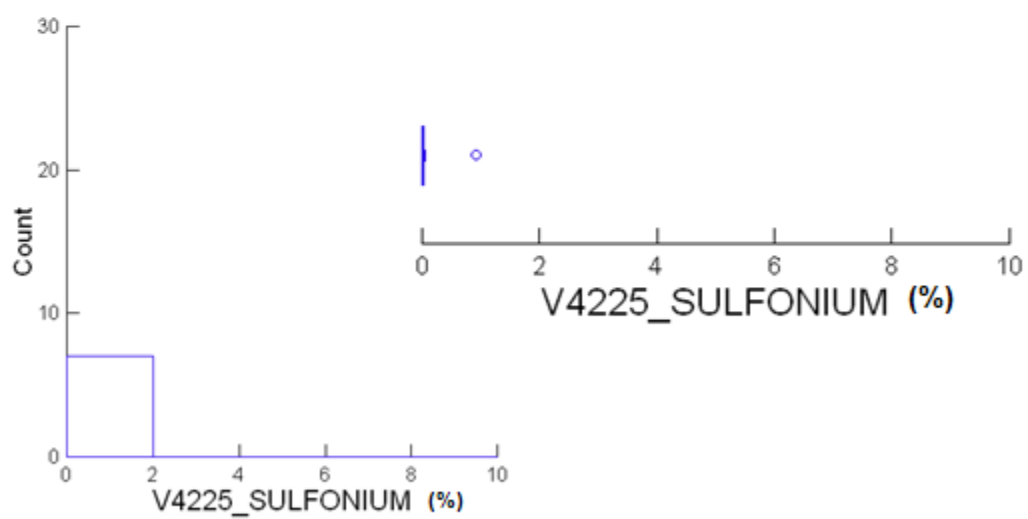
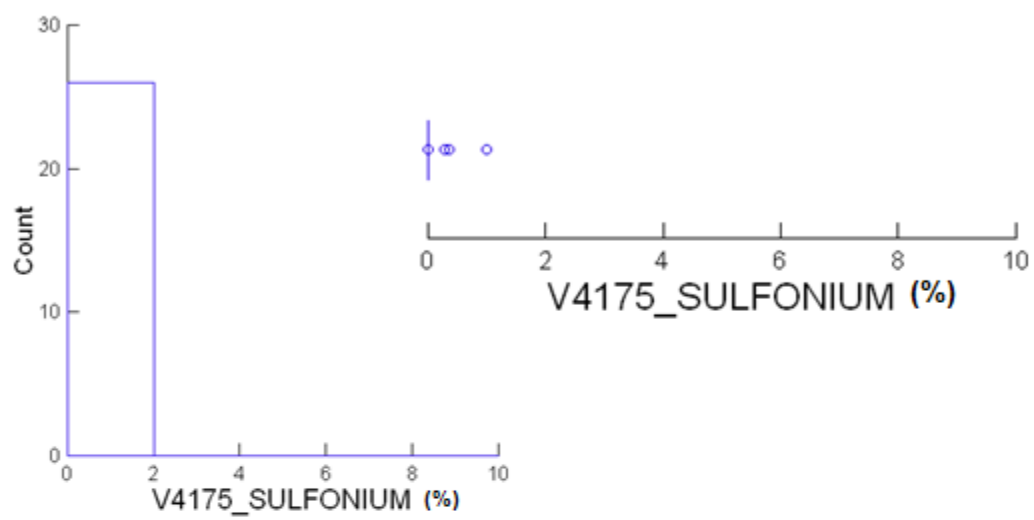
## APPENDIX B (continued)

(f)



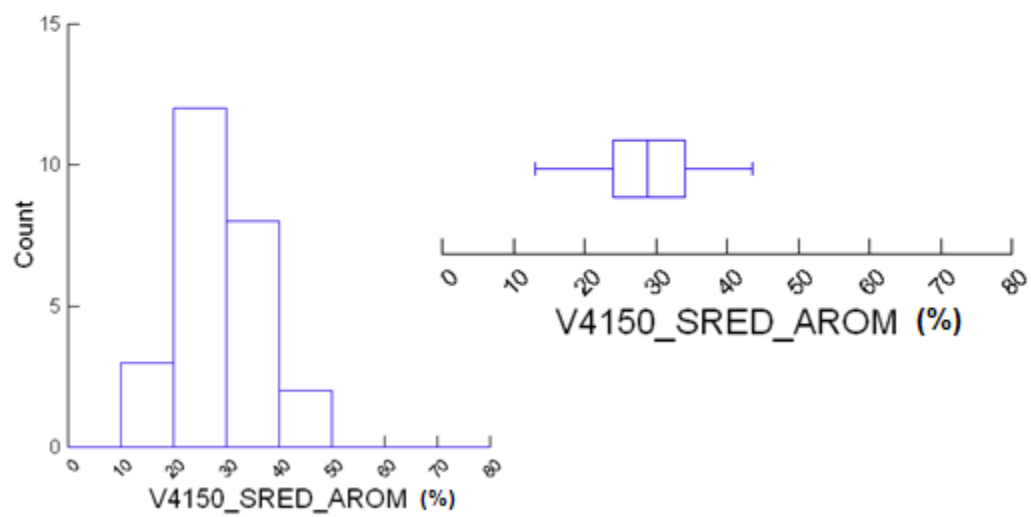
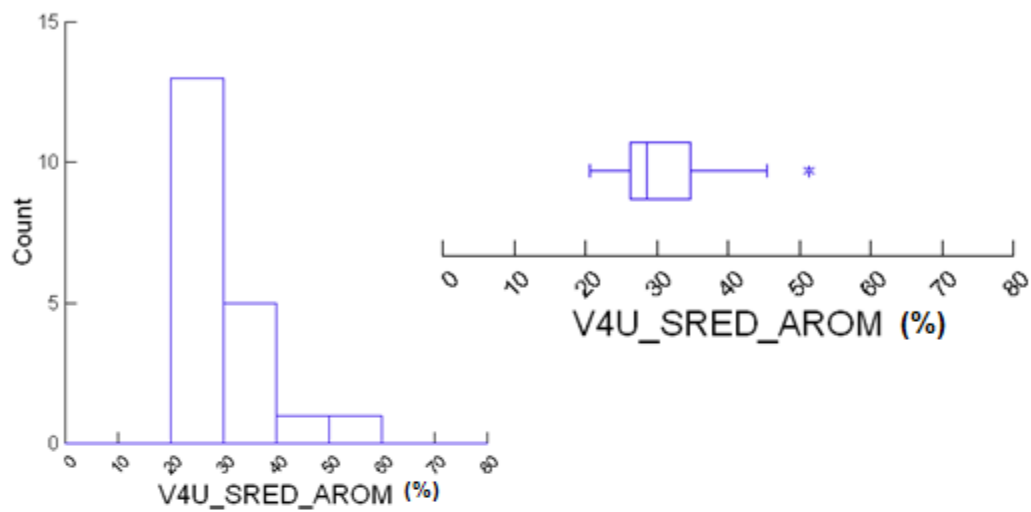
## APPENDIX B (continued)

(f) (continued)



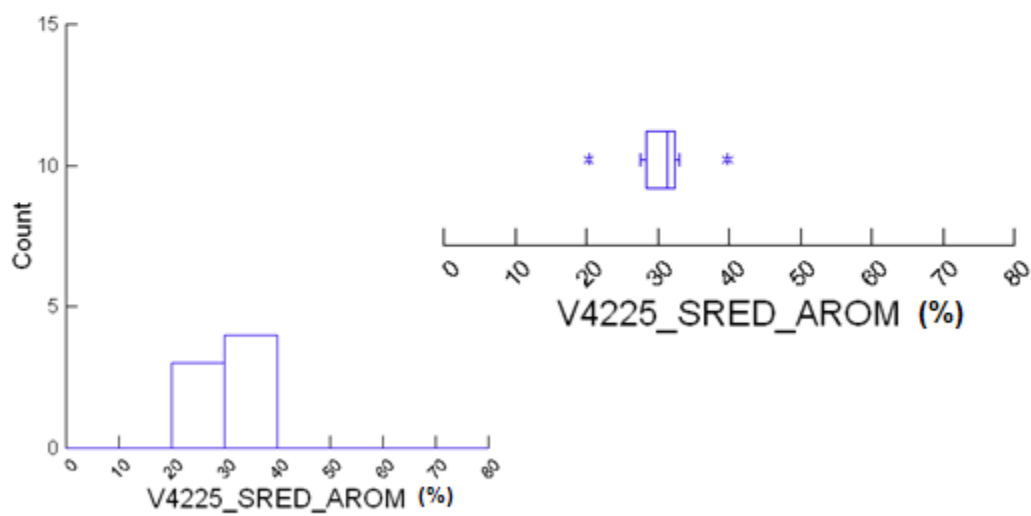
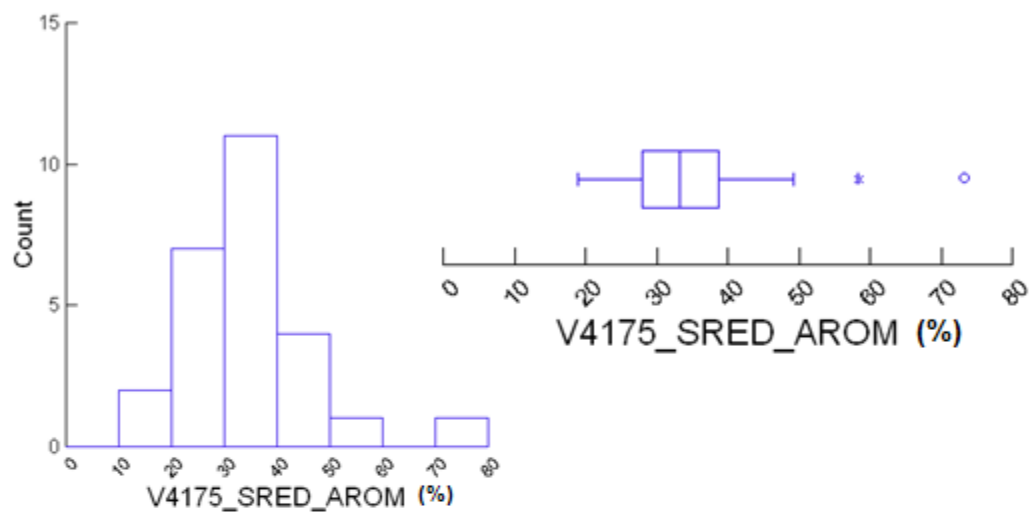
## APPENDIX B (continued)

(g)



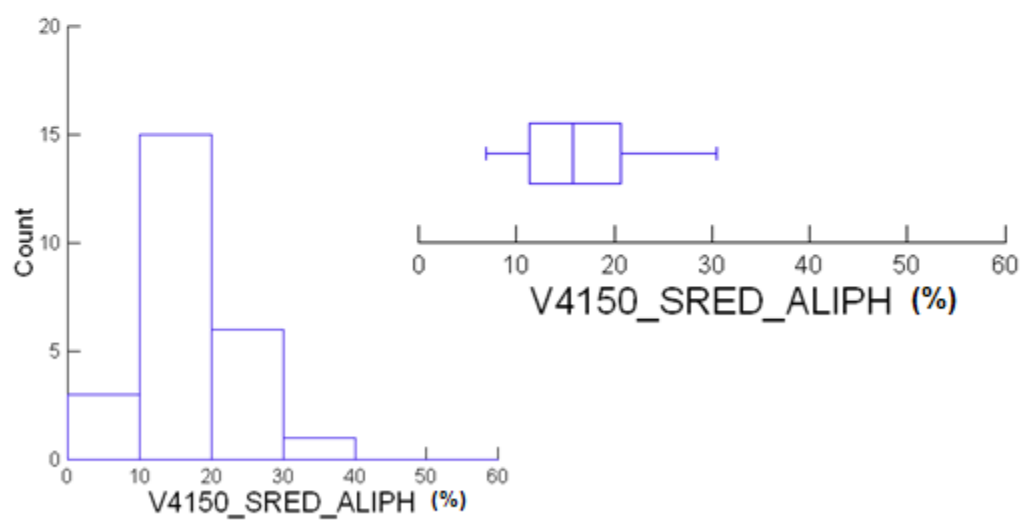
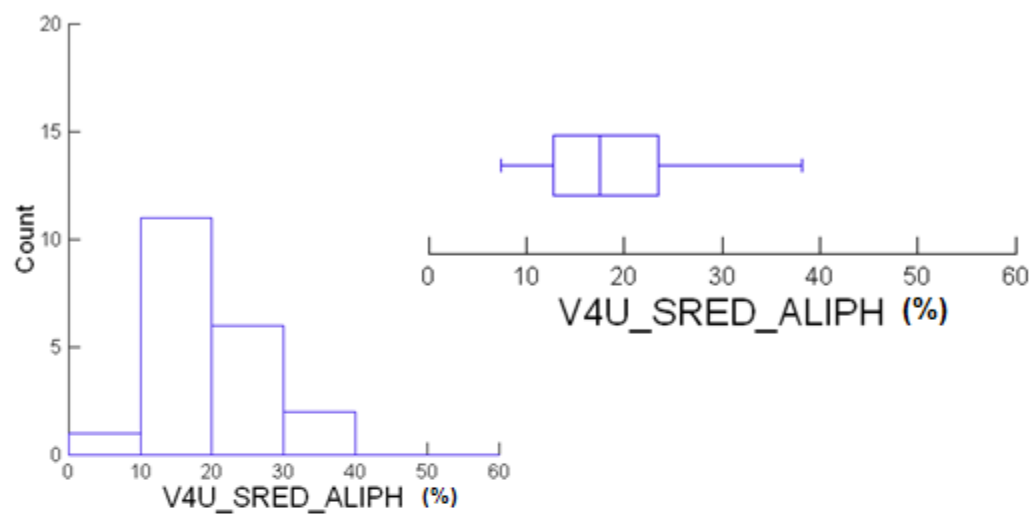
## APPENDIX B (continued)

(g) (continued)



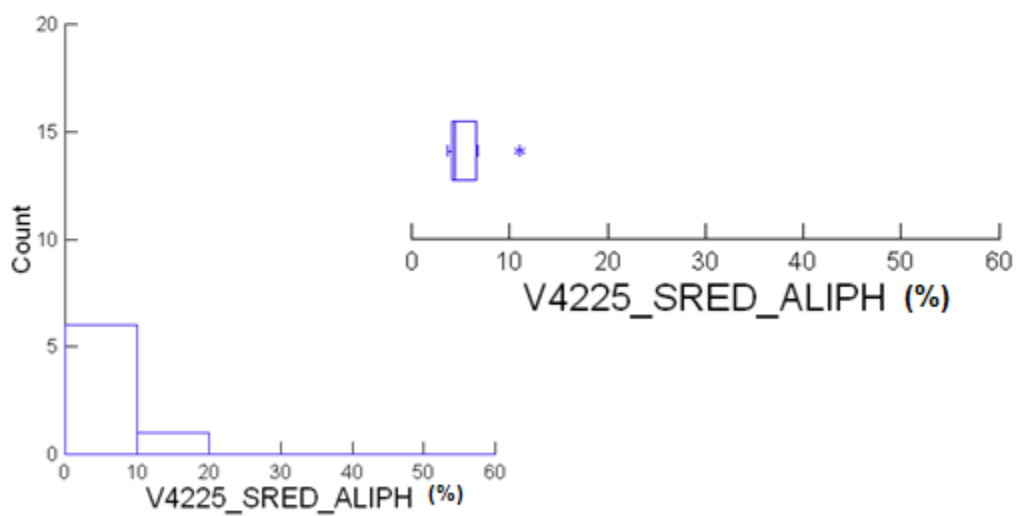
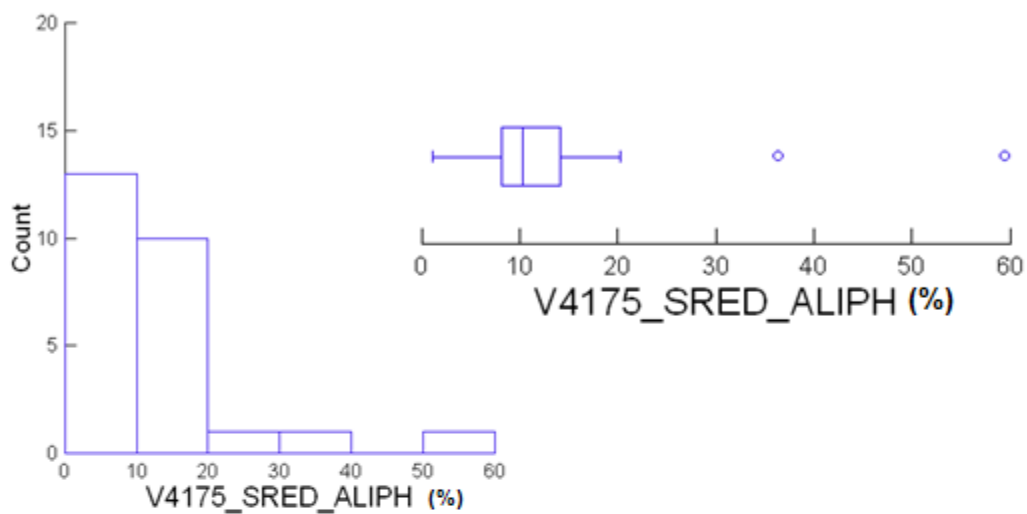
## APPENDIX B (continued)

(h)



## APPENDIX B (continued)

(h) (continued)



**APPENDIX B (continued)**

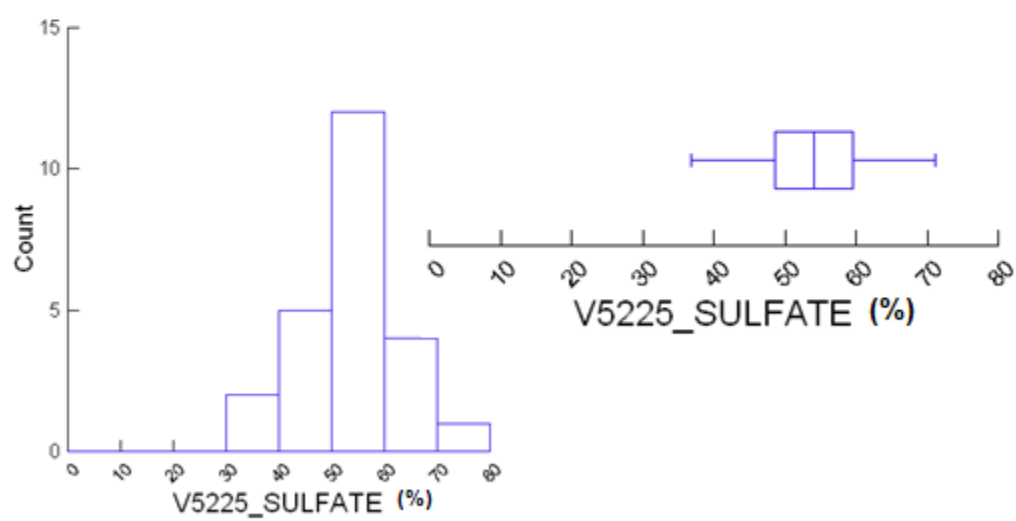
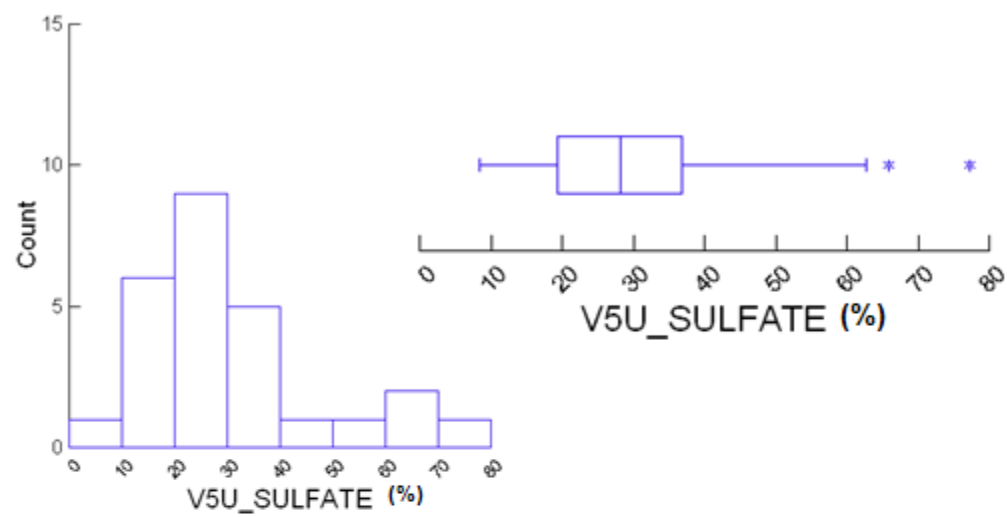
**Figure B5.** Histograms and box plots of the (a) sulfate, (b) sulfonate, (c) sulfone, (d) sulfite, (e) sulfoxide, (f) sulfonium, (g) reduced aromatic sulfur (Sred\_arom), and (h) reduced aliphatic sulfur (Sred\_aliph) constituents in soil from the VR-5 Temperature Series. The temperature consists of unheated soil (V5U\*) and soil heated at 225°C (V5225\*) for 120 min. The fractional amounts of each sulfur constituent were determined using full-energy range (2465 to 2510 eV) spectra and the second fitting approach.

\*NOTE: Because the MYSTAT program requires that the first character of a variable name be a letter, the labels “V5U” and “V5225” do not match previously assigned sample names (c.f., Table 1).



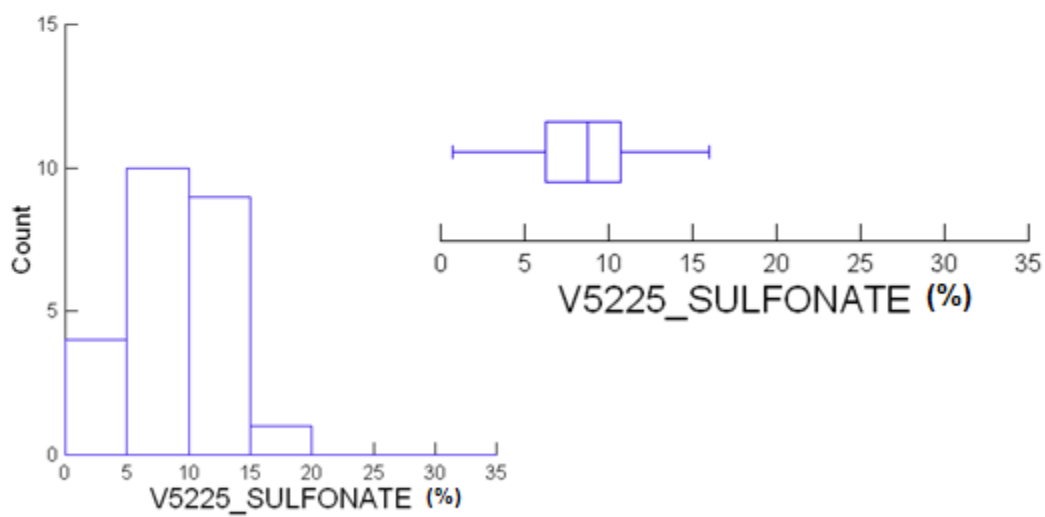
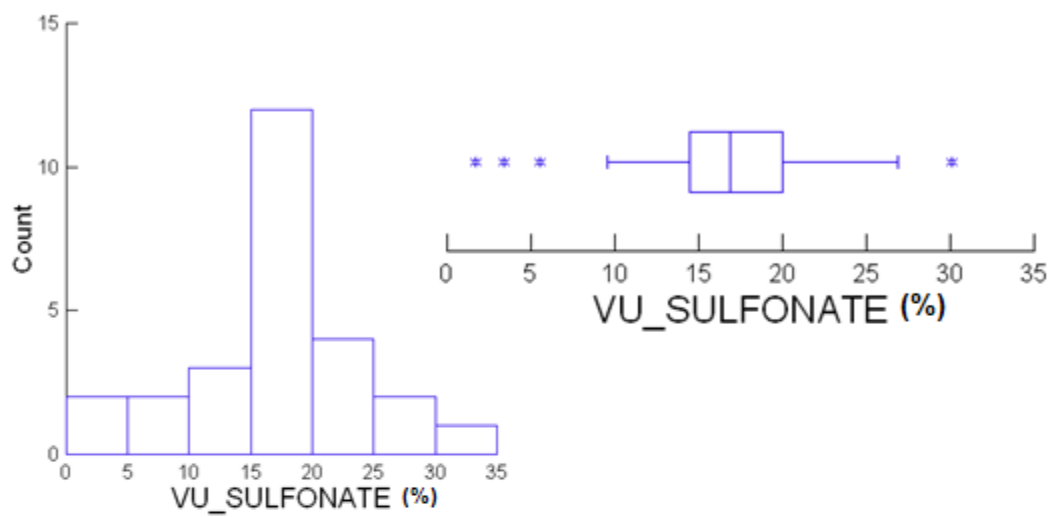
## APPENDIX B (continued)

(a)



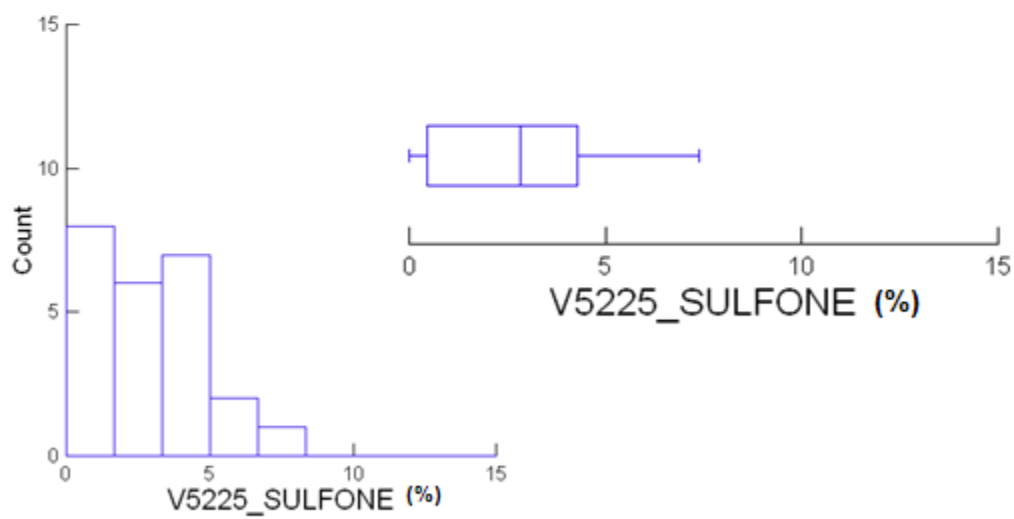
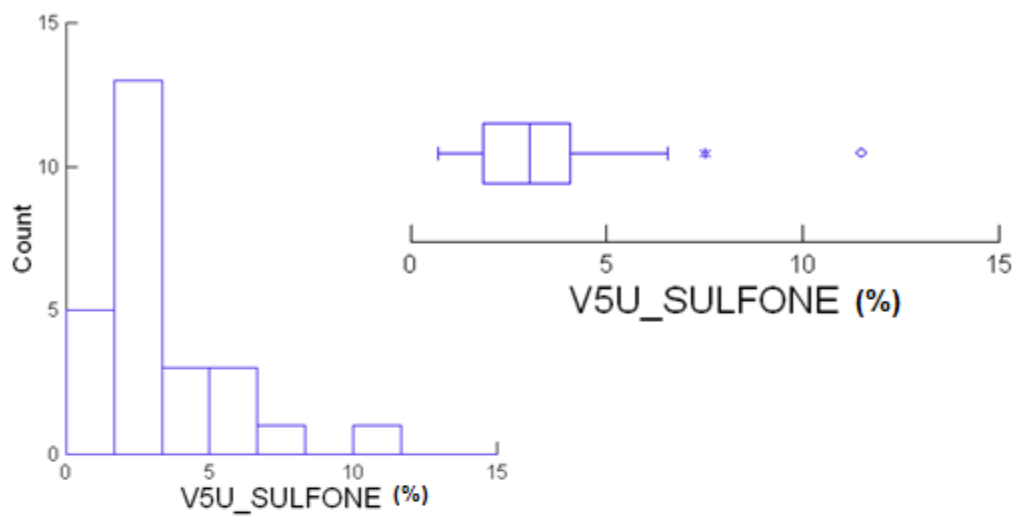
## APPENDIX B (continued)

(b)



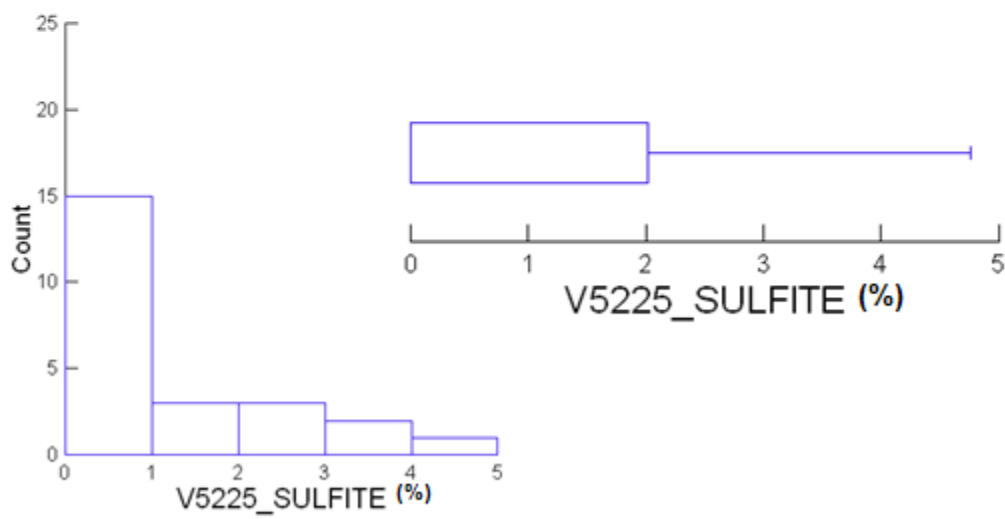
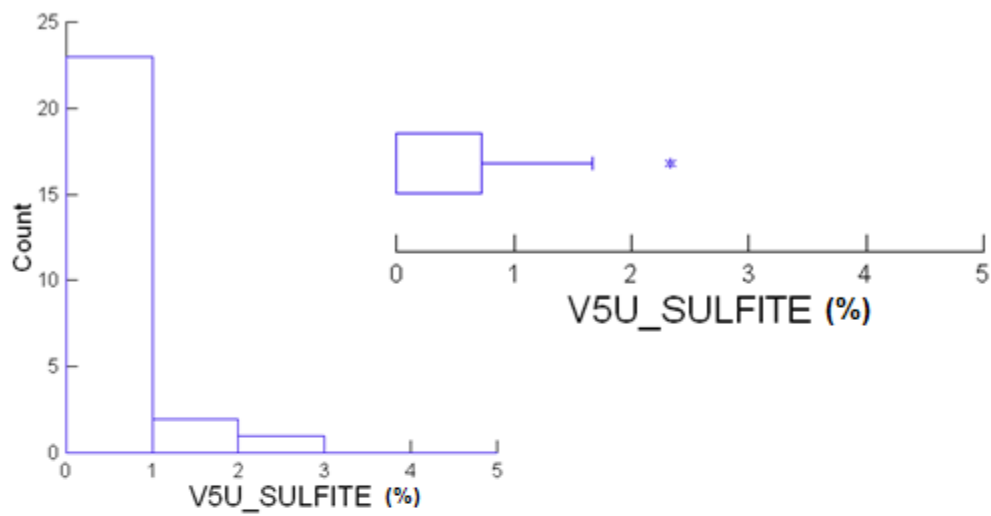
## APPENDIX B (continued)

(c)



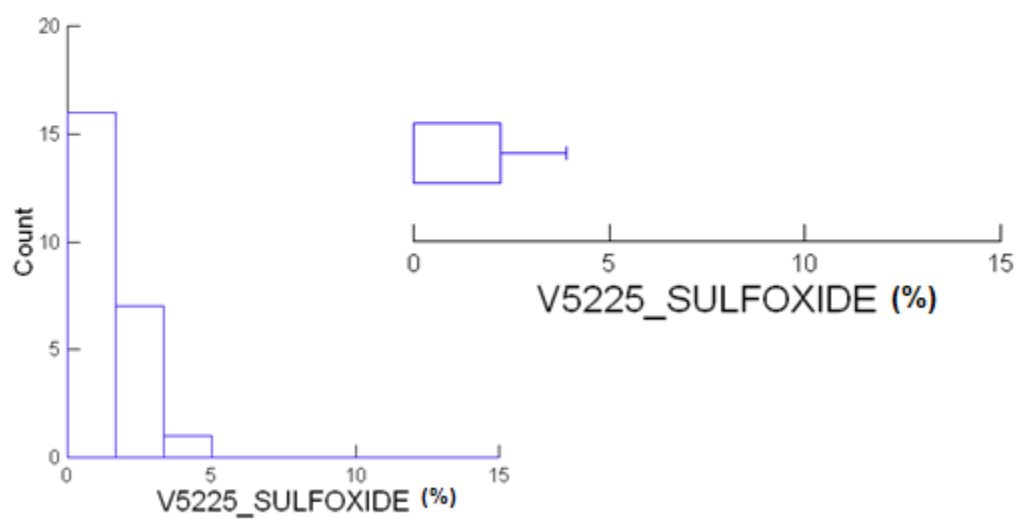
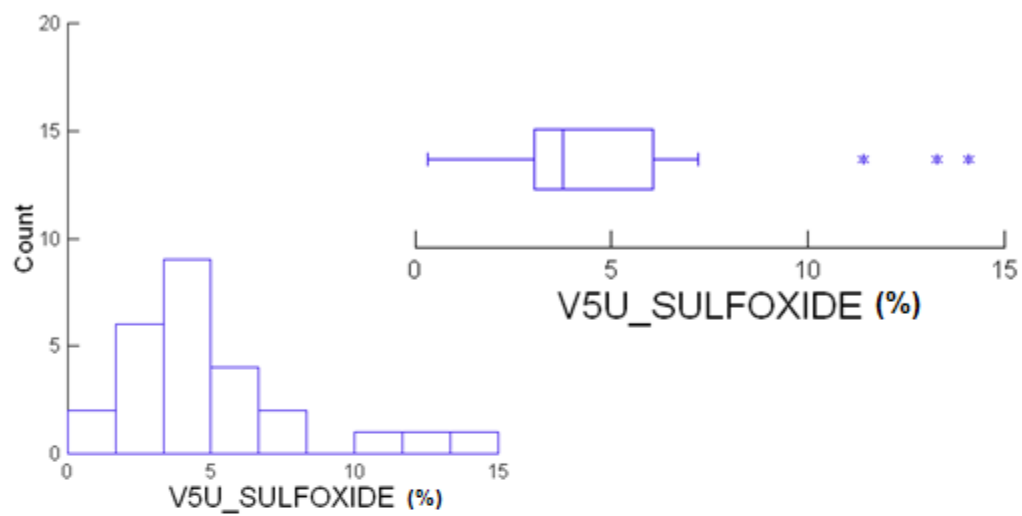
## APPENDIX B (continued)

(d)



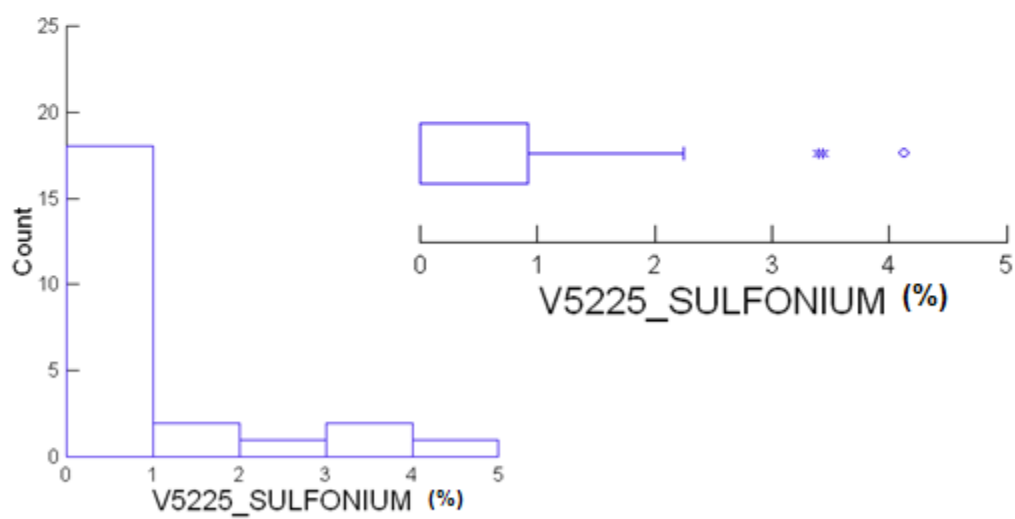
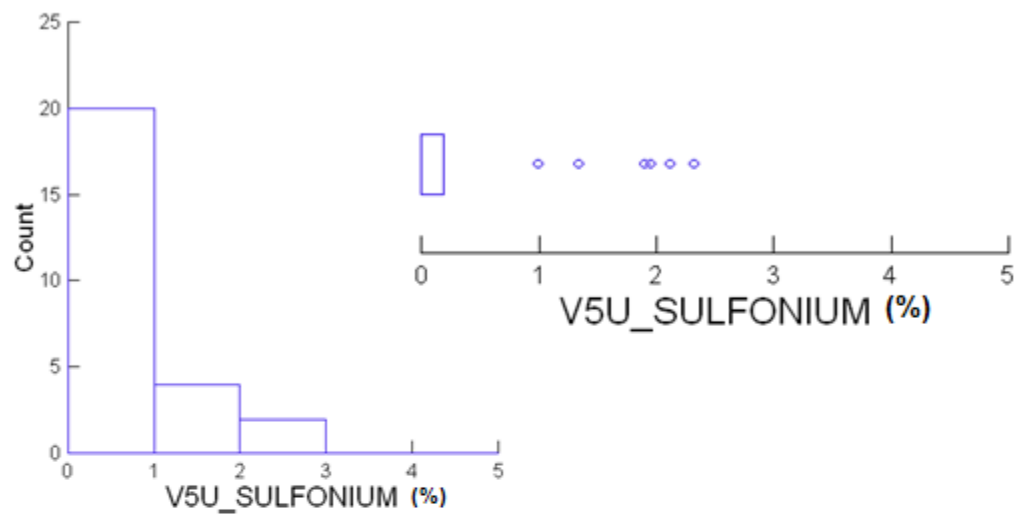
## APPENDIX B (continued)

(e)



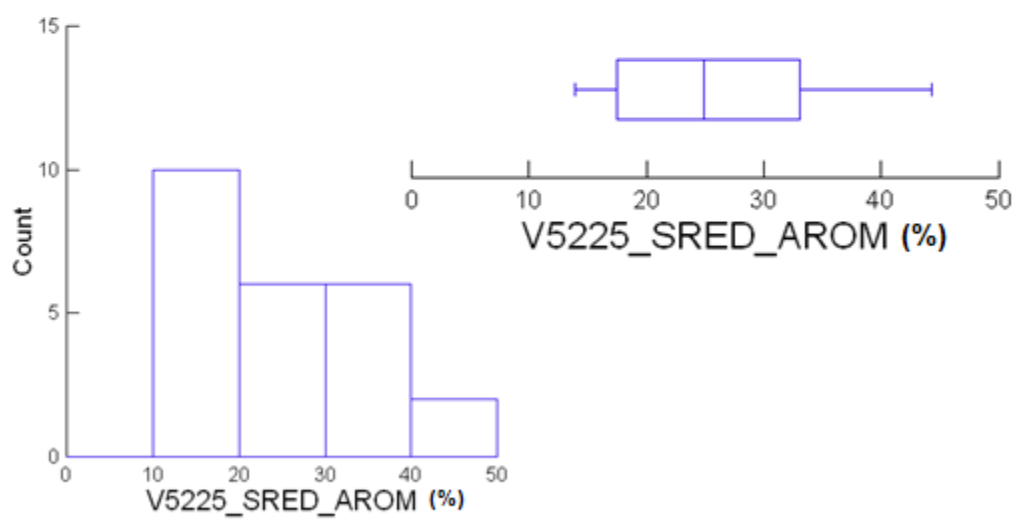
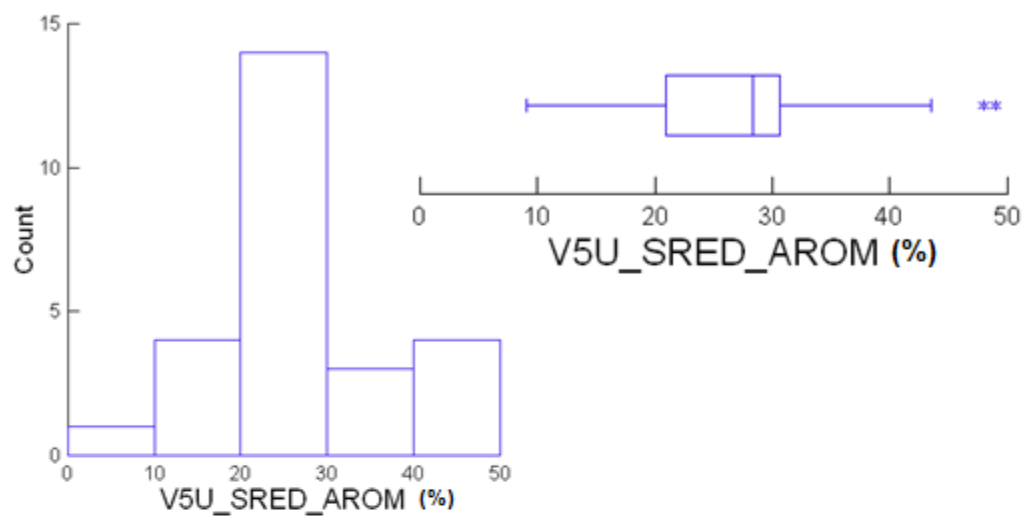
## APPENDIX B (continued)

(f)



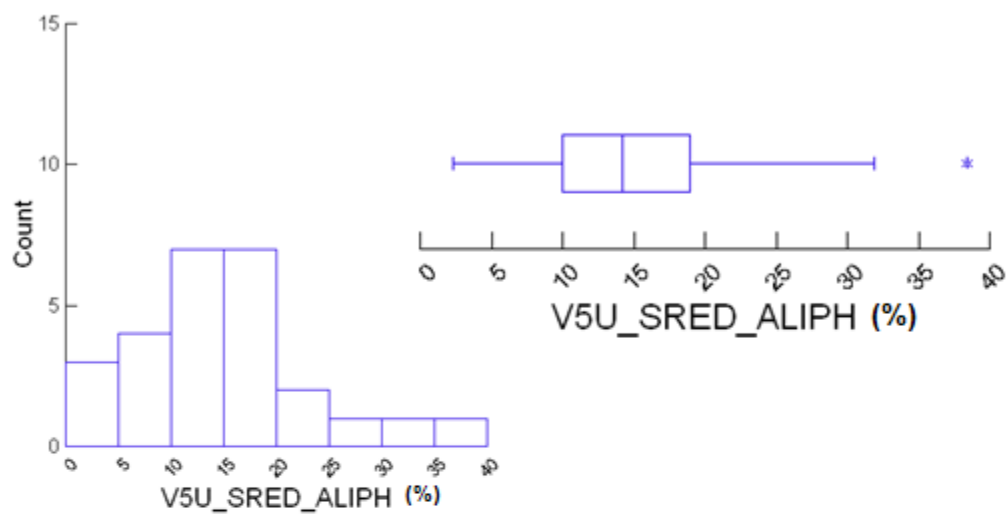
## APPENDIX B (continued)

(g)



## APPENDIX B (continued)

(h)



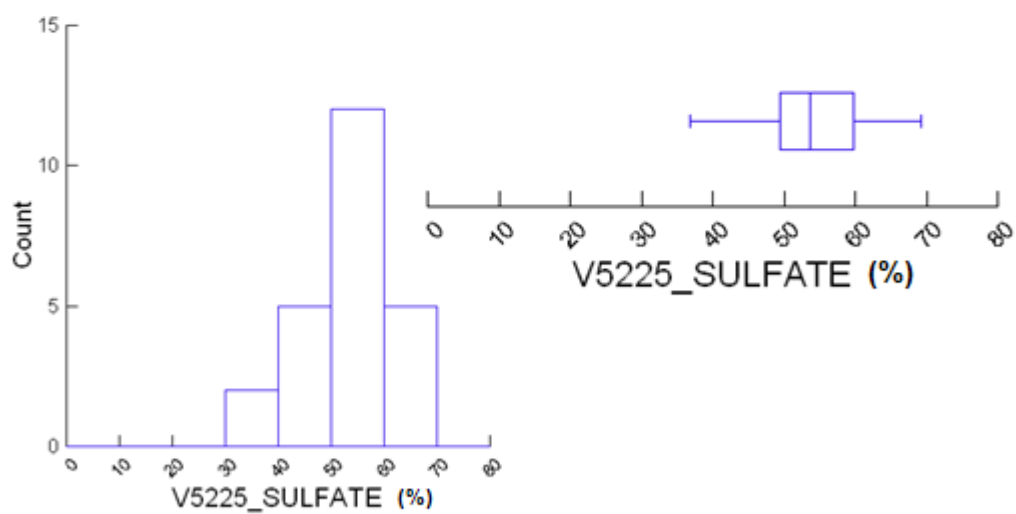
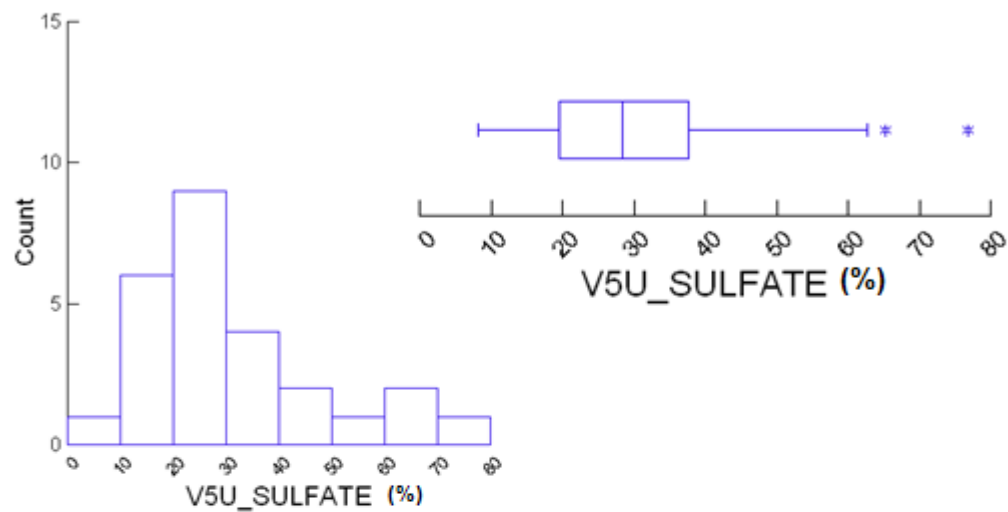


**APPENDIX B (continued)**

**Figure B6.** Histograms and box plots of the (a) sulfate, (b) sulfonate, (c) sulfone, (d) sulfite, (e) sulfoxide, (f) sulfonium, (g) reduced aromatic sulfur (Sred\_arom), and (h) reduced aliphatic sulfur (Sred\_aliph) constituents in soil from the VR-5 Temperature Series. The fractional amounts of each sulfur constituent were determined using short-energy range (2465 to 2490 eV) spectra and the second fitting approach.

## APPENDIX B (continued)

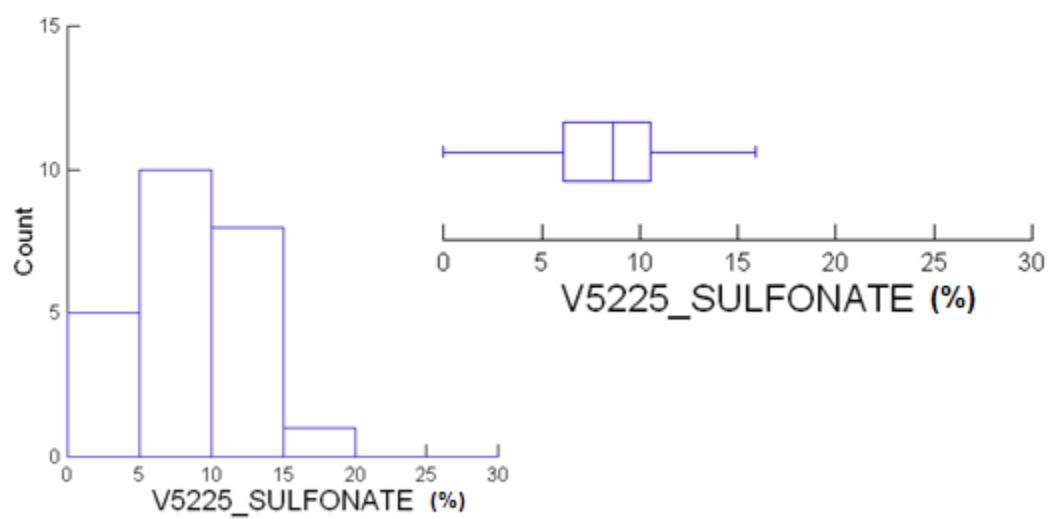
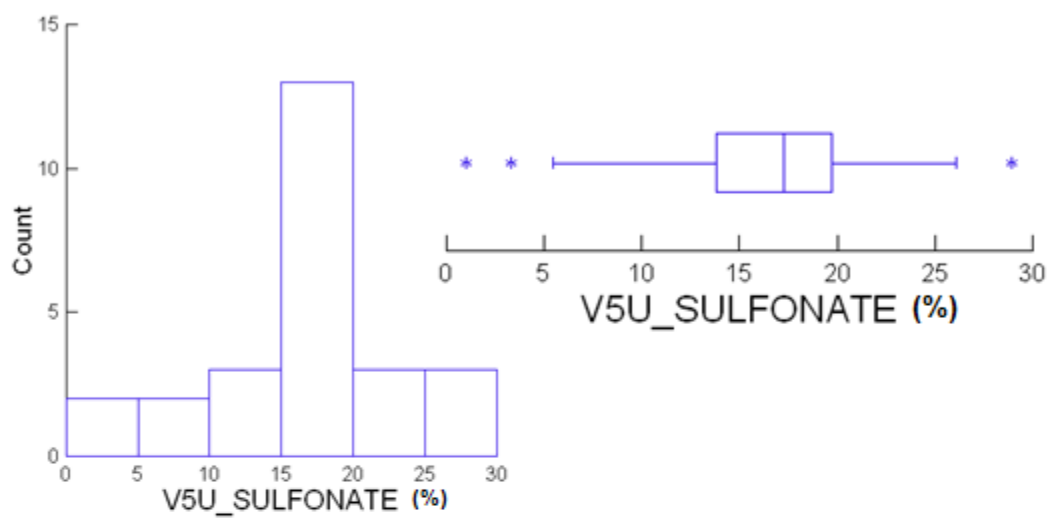
(a)



)

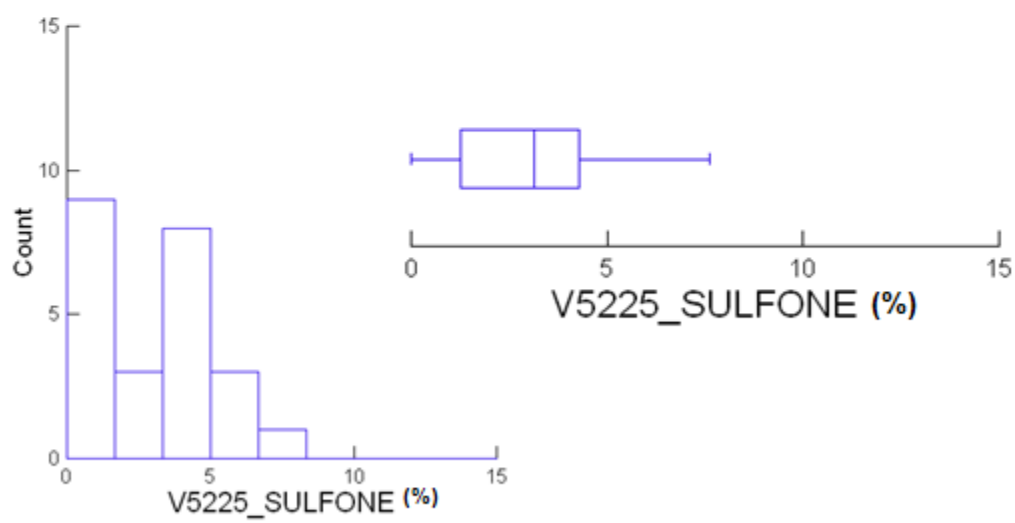
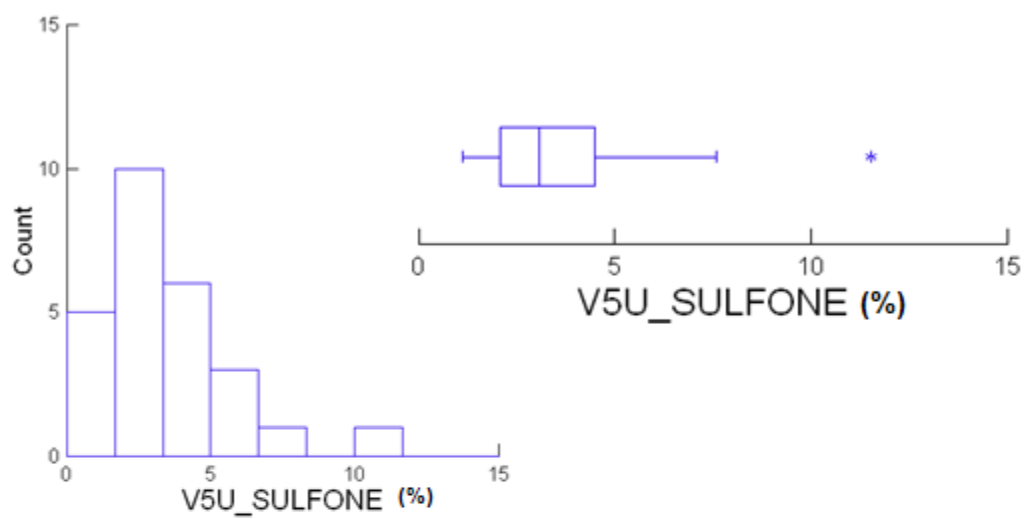
## APPENDIX B (continued)

(b)



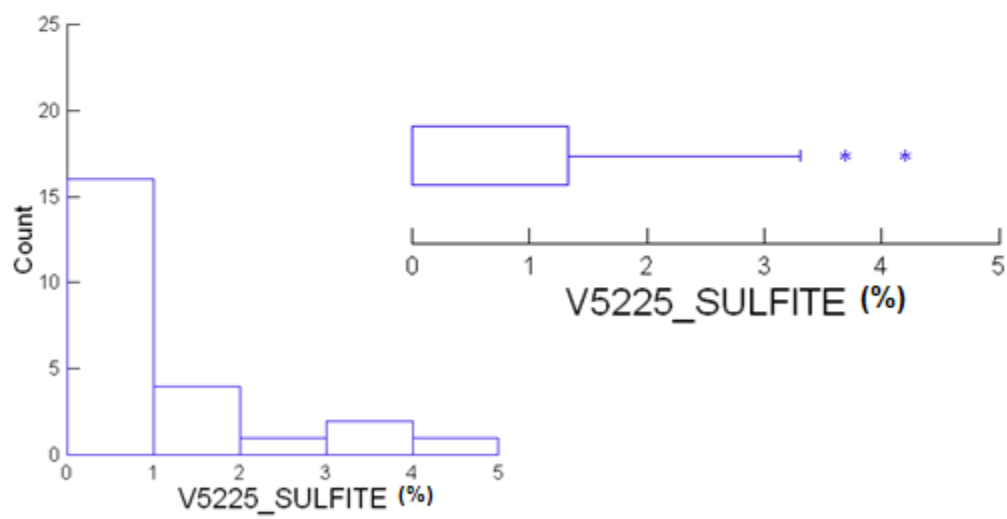
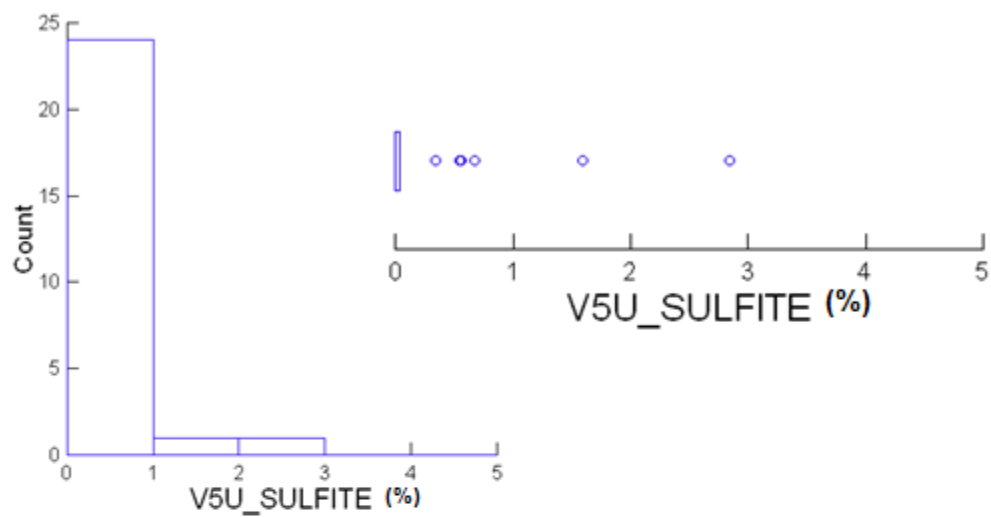
## APPENDIX B (continued)

(c)



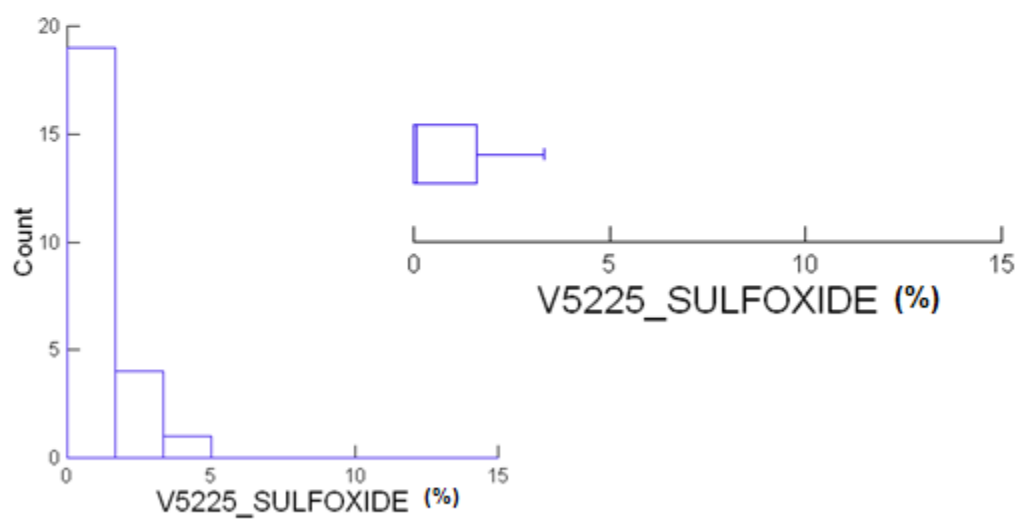
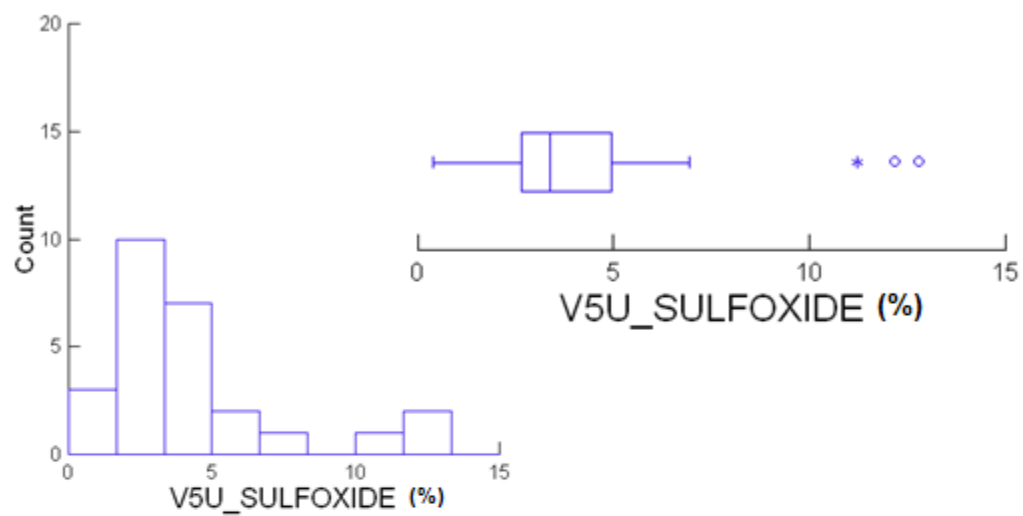
## APPENDIX B (continued)

(d)



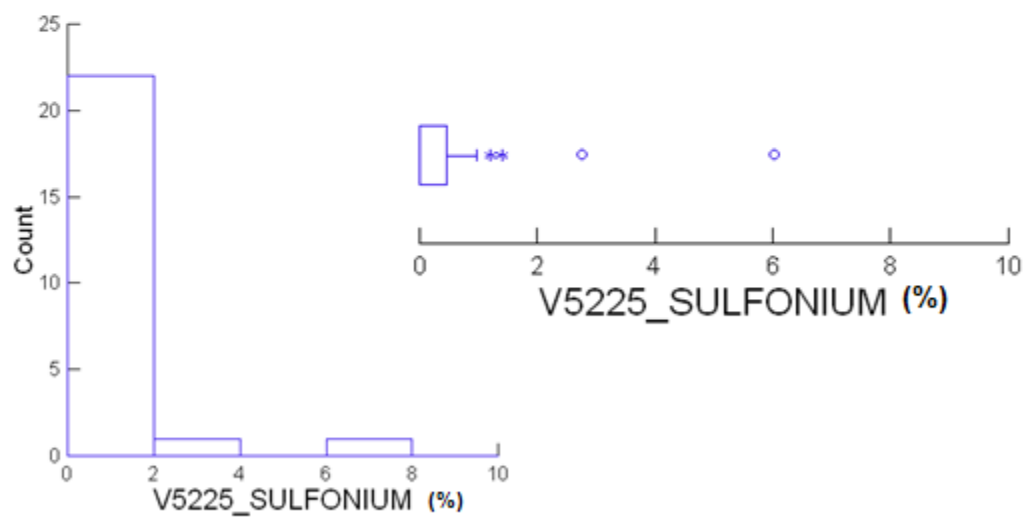
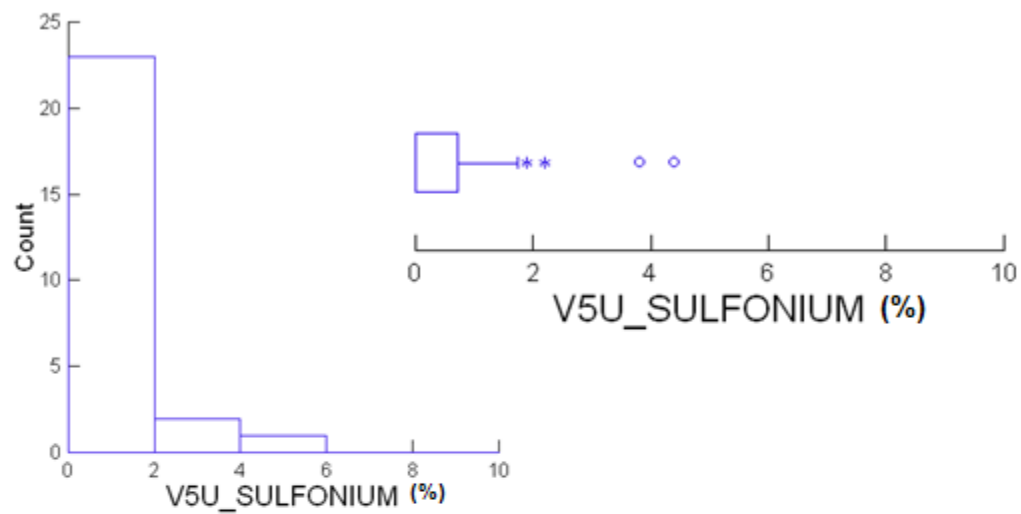
## APPENDIX B (continued)

(e)



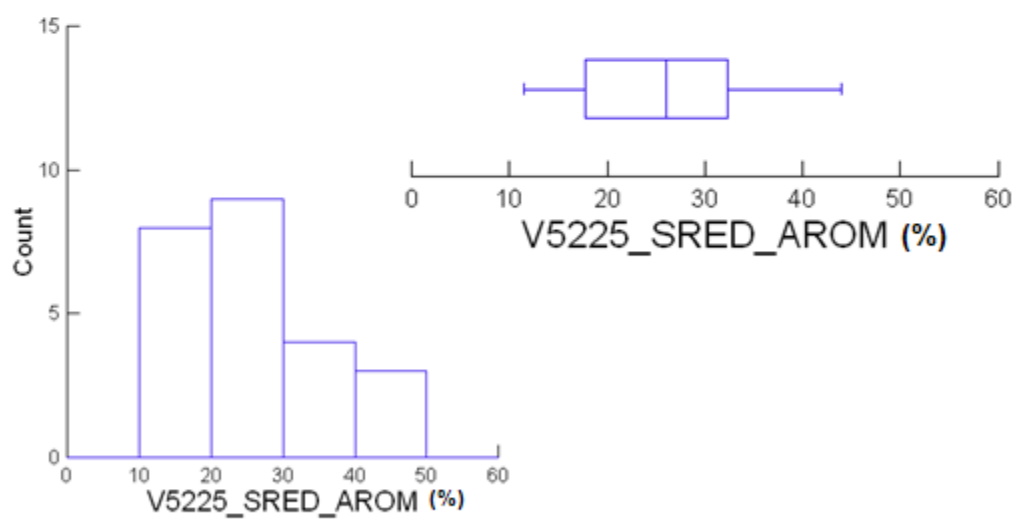
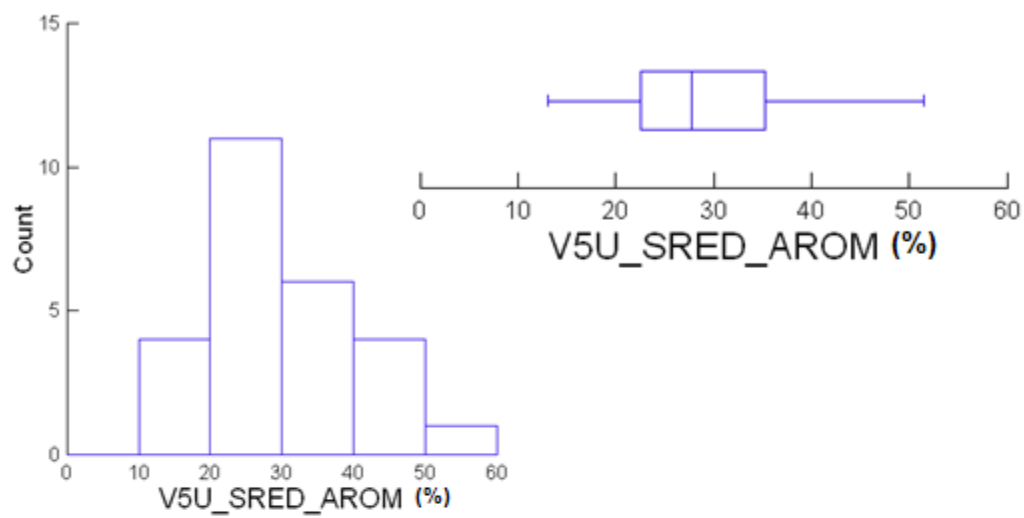
## APPENDIX B (continued)

(f)



## APPENDIX B (continued)

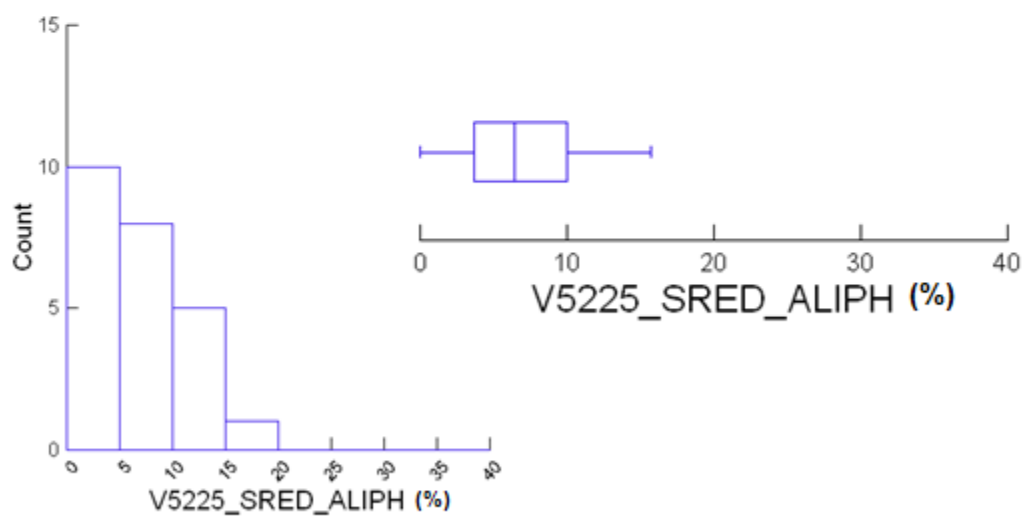
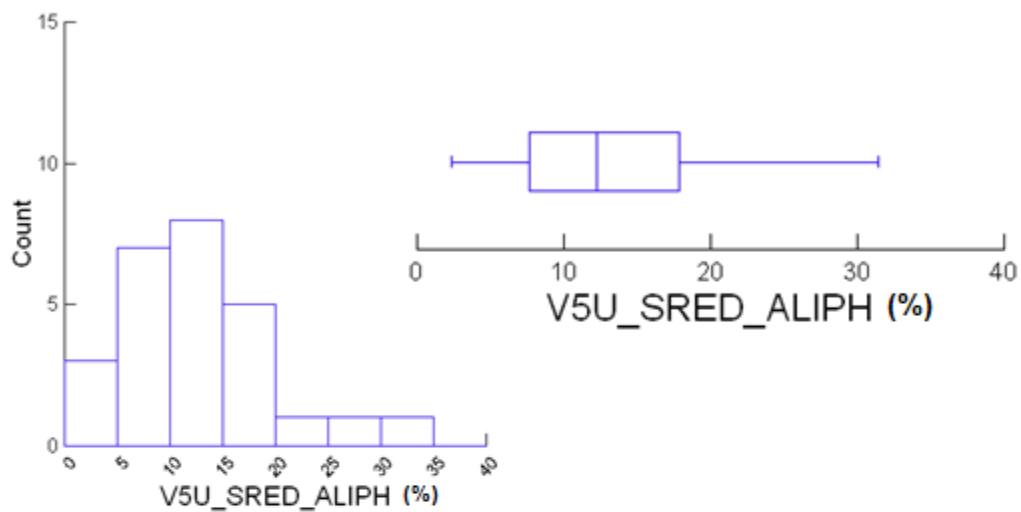
(g)





## APPENDIX B (continued)

(h)



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*Missionary Ridge Complex Burn Intensity Map (circ. 2002)*

From: Pauline E Ellis [plineellis@aol.com](mailto:plineellis@aol.com)  
 To: Genevieve Nano <gvnano@gmail.com>  
 Date: Wed, Jul 18, 2012 at 8:14 PM  
 Subject: Re: Missionary Ridge Fire map

Ms. Nano:

There is a signed letter from the San Juan National Forest confirming your request to use the aforementioned map in a slightly modified format for your thesis. Thank you for confirming!

Best Regards,  
 Pauline E. Ellis  
 Partnership Coordinator  
 San Juan National Forest

*Original Confirmation Request Letter:*

From: Genevieve Nano [gvnano@gmail.com](mailto:gvnano@gmail.com)  
 To: "plineellis@aol.com" <plineellis@aol.com>  
 Date: Wed, Jul 18, 2012 at 7:13 PM  
 Subject: Missionary Ridge Fire map

Pauline Ellis  
 USDA Forest Service  
 San Juan National Forest  
 15 Burnett Court  
 Durango, CO 81301

Dear Pauline,

I would like to confirm your approval for the use of the "Missionary Ridge Complex Burn Intensity Map" (circ. 2002; <http://www.southwestcoloradofires.org/images/bi11x17.jpg>) in my Master's thesis. The map will appear with a few edits to allow it to fit on an 8.5" x 11" sheet and will also include information about my research project's study site.

Thank you for your time. I very much appreciate your help in this matter.

Best regards,  
 Genevieve

**APPENDIX C (continued)**

Vairavamurthy (1998):

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Jul 17, 2012

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