2012 Vegetation and Soil Analyses from Warner Park

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Summary

This report contains the results of chemical analyses of plant and soil samples from Warner Park sampled in June and July, 2012, before and after the Rhythm and Booms fireworks event. Sixteen plant leaf samples and surface soils were collected at three sites and analyzed for chemical elements. Most of the plant species showed elevated concentrations of elements associated with pyrotechnics 23 days following the Rhythm and Booms event. Perchlorate, in spite of small samples sizes, increased the most, followed by Ba, Sr and Mg, all important compounds in pyrotechnics. The launch pad showed the highest number of element increases after the event, followed by the viewing area site, and then the island south of the launch pad, although the differences were minor. Foliage of woody plants increased in pyrotechnics associated elements more than herbaceous species. The most correlated elements across species and sites were those that co-occur in pyrotechnics: Ba, K, Mg, Sr, chloride and perchlorate. Maximum concentrations of Al, Ba, Co, Fe, Mg, S, and some of the perchlorate values were considered either at critical levels or nearing toxicity levels for plants.

Introduction

The Madison Committee on the Environment received funding in 2012 to conduct a study of fireworks residues in plants, soils, sediments and water in Warner Park before and after the June 30th Rhythm and Booms fireworks event. The committee received $25,000 from the City of Madison and $4000 from Wild Warner for a total of $29,000 for the study. It is known from the scientific literature that trace elements of barium, strontium, magnesium as well as perchlorate and other elements have been found in these organisms and media following fireworks events. These elements and others are found in the chemicals that cause the various colors in fireworks (http://chemistry.about.com/od/fireworkspyrotechnics/a/fireworkcolors.htm). The purpose of this study was to determine if traces of fireworks chemicals existed in these organisms and soil at Warner Park.

Methods

Plants and soils in Warner Park were collected on June 22 and July 23, 2012 by J. Bennett, J. Carrier, A. Weir, B. Bemis and T. Nelson. The June samples were taken before the fireworks event, and the July samples were taken after the first large rainfall event following the fireworks. On both dates samples were taken from the fireworks launch mound (Site 1), the island directly south of the launch mound (Site 2), and the spectator areas east of the launch mound (Site 3)(**map needed**). Only leaves of the plant species were sampled, generally at breast height. Soils were sampled from the top layer. All samples were bulked. No replicates were taken as this was a pilot study.

Sixteen plant species were sampled:

- Alfalfa (*Medicago sativa*)
- Arrowwood (*Viburnum acerifolium*)
- **Black willow** (*Salix nigra*)
- Box elder (*Acer negundo*)
- Buckthorn (*Rhamnus carthatica*)
- **Cat tail** (*Typha latifolia*)
- **Cottonwood** (*Populus deltoids*)
- Creeping Charlie (*Glechoma hederacea*)
- Dandelion (*Taraxacum officinale*)
- Dogbane (*Apocynum androsaemifolium*)
- Duckweed (*Lemna minor*)
- Honeysuckle (*Lonicera tartarica*)
- Plantain (*Plantago major*)
- **Smartweed** (*Polygonum lapathifolium*)
- **Vervain** (*Verbena hastata*)
- Water lily (*Nymphaea odorata*)

The five species in bold font were collected on both dates at all three sites. Alfalfa was only sampled in June as no specimens could be located in July. The leaves were oven dried for 48 hours and stored until chemical analyses. After grinding, the 67 leaf and 9 soil samples were acid extracted and analyzed at the UW Soil and Plant Analysis Laboratory by means of ICP/OES, ICP/MS, and ion chromatography (Ellington & Evans 2000) for aluminum (Al), barium (Ba), cobalt (Co), chromium (Cr), iron (Fe), potassium (K), magnesium (Mg), sulfur (S), strontium (Sr), chloride, and perchlorate. These elements and ions were selected because of their known occurrences in fireworks and pyrotechnic emissions (Barman et al 2009; Li et al 2013; Munster et al 2009; Steinhauser et al 2008). Included with the plant and soil samples were spikes of Standard Reference Material 1575, tomato leaves from the National Bureau of Standards to perform data quality assurance results. Recoveries ranged from 59% to 140% and averaged 98%, with aluminum being low and barium being high due to the extraction methods. 62 of the 67 plant samples had no measurable chromium and this element will not be presented in this report. All remaining chemicals had acceptable measurable amounts, resulting in 688 data points (Appendix 1). No statistical analyses of the data have been performed because of the lack of within site replication, the small number of samples, and possible confounding of variables by interacting factors (e.g. site x sampling date).

Results

A complete tabulation of all the data is presented in Appendix 1, followed by a summary in Appendix 2, that was presented at the January 28th COE meeting.

The results are presented in five sections providing data to answer the following questions:

- Were there differences in concentrations before and after the fireworks?
- Were there differences in concentrations among the three sites?
- Were there differences in concentrations among species?
- Were there correlations among the elements that mean anything?
- How high were the concentrations?

Each section contains 10 tables presenting element data by sampling date and the other variable of interest for each question. Rows of data that are in bold font are those showing an increase in concentrations on the July sampling date compared to the June date. Soil data are presented in each table as well.

Recoveries of certified elements from the SRM ranged from 59% (Al) to 140%(Ba) and averaged 98%. The low and high recoveries mentioned were due to the acid extraction method used by SPAL differing from the one used by the certifying organization.

Differences in concentrations before and after the fireworks event

These tables show the concentrations of each element and compound for each plant species and soil on the two sampling dates, averaged across sites. The sample sizes for each average therefore range from one to three.

Average of Al (ppm)	Sampling Date	
Species	**June (before)**	**July (after)**
alfalfa	12.88	
arrowwood	**28.75**	**31.77**
black willow	**11.43**	**12.42**
boxelder	**40.69**	**52.61**
buckthorn	**27.89**	**37.62**
cat tail	12.90	9.91
cottonwood	**7.94**	**16.86**
creeping charlie	**144.41**	**387.42**
dandelion	**31.74**	**54.98**
dogbane	**15.89**	**16.82**
duckweed	**214.18**	**785.69**
honeysuckle	**38.29**	**46.11**
plantain	**40.70**	**400.82**
smartweed	42.61	12.95
soil	7936.11	6191.18
vervain	**14.94**	**47.11**

	June (before)	July (after)
waterlily	35.95	34.74
Grand Average	1173.97	868.75

Average of Ba (ppm)	Sampling Date	
Species	**June (before)**	**July (after)**
alfalfa	25.79	
arrowwood	**125.70**	**136.33**
black willow	**6.10**	**10.56**
boxelder	**23.27**	**41.83**
buckthorn	**47.68**	**61.03**
cat tail	**10.49**	**16.74**
cottonwood	**32.52**	**41.11**
creeping charlie	**79.88**	**91.23**
dandelion	40.30	36.10
dogbane	20.42	19.64
duckweed	160.09	136.08
honeysuckle	**62.44**	**103.27**
plantain	103.73	87.65
smartweed	**106.70**	**157.72**
soil	162.53	115.31
vervain	**35.45**	**92.14**
waterlily	11.16	8.80
Grand Average	**69.51**	**74.49**

Average of Chloride (ppm)	Sampling Date	
Species	**June (before)**	**July (after)**
alfalfa	1562.00	
arrowwood	**656.75**	**745.50**
black willow	**1248.42**	**1313.50**
boxelder	**1286.88**	**1917.00**
buckthorn	**2680.25**	**4396.08**
cat tail	**10312.75**	**14762.08**
cottonwood	360.92	331.33
creeping charlie	4588.38	3266.00
dandelion	16844.75	12984.13
dogbane	5999.50	4881.25
duckweed	**16702.75**	**19782.38**
honeysuckle	**115.38**	**195.25**
plantain	23190.38	10561.25
smartweed	7987.50	7389.92
soil	27.45	21.15
vervain	**2402.17**	**5455.17**
waterlily	**17022.25**	**17501.50**
Grand Average	**5926.10**	**5988.35**

Average of Co	Sampling Date	

(ppm)		
Species	**June (before)**	**July (after)**
alfalfa	0.14	
arrowwood	**0.01**	**0.07**
black willow	0.32	0.22
boxelder	**0.01**	**0.15**
buckthorn	**0.04**	**0.08**
cat tail		0.12
cottonwood	**0.82**	**1.11**
creeping charlie	**0.06**	**0.26**
dandelion	**0.06**	**0.28**
dogbane		0.04
duckweed	**0.68**	**1.00**
honeysuckle	0.09	0.09
plantain	**0.10**	**0.31**
smartweed	0.69	0.34
soil	4.57	3.54
vervain	0.12	0.04
waterlily	**0.06**	**0.07**
Grand Average	1.00	0.72

Average of Fe (ppm)	**Sampling Date**	
Species	**June (before)**	**July (after)**
alfalfa	72.80	
arrowwood	56.77	56.02
black willow	**63.30**	**69.18**
boxelder	**65.75**	**106.05**
buckthorn	81.90	68.81
cat tail	**53.40**	**71.14**
cottonwood	**57.51**	**82.41**
creeping charlie	**177.61**	**441.15**
dandelion	**74.34**	**105.76**
dogbane	57.29	54.64
duckweed	**660.06**	**2148.11**
honeysuckle	**66.17**	**77.73**
plantain	**125.25**	**411.63**
smartweed	125.31	66.09
soil	9711.14	8384.79
vervain	**48.78**	**71.06**
waterlily	171.92	165.09
Grand Average	1348.38	1126.54

Average of K (%)	**Sampling Date**	
Species	**June (before)**	**July (after)**
alfalfa	1.23	
arrowwood	**0.71**	**0.73**
black willow	1.13	0.87
boxelder	1.79	1.02

	June	July
buckthorn	1.88	1.50
cat tail	**1.59**	**1.67**
cottonwood	**1.14**	**1.22**
creeping charlie	**2.15**	**2.34**
dandelion	3.26	3.11
dogbane	1.30	1.05
duckweed	3.07	2.77
honeysuckle	0.91	0.76
plantain	2.10	1.73
smartweed	**1.44**	**1.61**
soil	0.13	0.11
vervain	0.87	0.80
waterlily	1.80	1.75
Grand Average	1.44	1.36

Average of Mg (%)	**Sampling Date**	
Species	**June (before)**	**July (after)**
alfalfa	0.61	
arrowwood	0.59	0.57
black willow	**0.27**	**0.36**
boxelder	**0.33**	**0.43**
buckthorn	**0.29**	**0.30**
cat tail	**0.14**	**0.20**
cottonwood	0.48	0.44
creeping charlie	0.58	0.56
dandelion	**0.51**	**0.59**
dogbane	0.85	0.60
duckweed	**0.41**	**0.48**
honeysuckle	**0.67**	**0.72**
plantain	**0.42**	**0.43**
smartweed	**0.61**	**0.63**
soil	**1.47**	**1.68**
vervain	**0.38**	**0.66**
waterlily	0.23	0.21
Grand Average	**0.57**	**0.60**

Average of Perchlorate (ppm)	**Sampling Date**	
Species	**June (before)**	**July (after)**
alfalfa		
arrowwood		
black willow		10.37
boxelder		16.46
buckthorn	8.72	
cat tail	25.42	
cottonwood	3.67	
creeping charlie		

Species	June (before)	July (after)
dandelion		
dogbane		
duckweed	52.59	
honeysuckle		
plantain		41.52
smartweed		83.19
soil	12.41	
vervain		70.06
waterlily		
Grand Average	**20.56**	**44.32**

Average of S (%)	Sampling Date	
Species	**June (before)**	**July (after)**
alfalfa	0.53	
arrowwood	**0.14**	**0.17**
black willow	**0.31**	**0.32**
boxelder	0.18	0.18
buckthorn	0.15	0.14
cat tail	**0.23**	**0.28**
cottonwood	**0.76**	**0.95**
creeping charlie	0.32	0.30
dandelion	**0.37**	**0.43**
dogbane	0.82	0.41
duckweed	0.49	0.38
honeysuckle	**0.19**	**0.22**
plantain	0.50	0.35
smartweed	0.27	0.25
soil	0.09	0.08
vervain	**0.31**	**0.45**
waterlily	0.28	0.22
Grand Average	0.32	0.32

Average of Sr (ppm)	Sampling Date	
Species	**June (before)**	**July (after)**
alfalfa	30.17	
arrowwood	**27.95**	**28.77**
black willow	**9.08**	**11.96**
boxelder	**15.55**	**23.18**
buckthorn	**29.67**	**36.00**
cat tail	**6.11**	**9.12**
cottonwood	**23.68**	**26.18**
creeping charlie	**22.07**	**23.03**
dandelion	26.87	25.00
dogbane	11.73	10.34
duckweed	**27.94**	**38.04**
honeysuckle	**31.68**	**41.36**
plantain	36.52	31.92
smartweed	34.52	29.96

soil	33.35	27.17
vervain	**11.91**	**23.87**
waterlily	**4.18**	**5.06**
Grand Average	**23.38**	**25.11**

Differences in concentrations among the three sites

These tables show the concentrations of each element and compound for each site of the three sampling sites, averaged across plant species. The sample sizes for each are 16 or less depending on site.

Average of Al (ppm)	Sampling Date	
Site	June (before)	July (after)
1	1835.23	1241.53
2	688.72	301.20
3	1001.01	1078.35
Grand Average	1173.97	868.75

Average of Ba (ppm)	Sampling Date	
Site	June (before)	July (after)
1	**67.09**	**73.45**
2	66.05	54.51
3	**74.73**	**92.44**
Grand Average	**69.51**	**74.49**

Average of Chloride (ppm)	Sampling Date	
Site	June (before)	July (after)
1	**4223.86**	**4434.97**
2	**5204.60**	**7979.66**
3	8125.19	5502.04
Grand Average	**5926.10**	**5988.35**

Average of Co (ppm)	Sampling Date	
Site	June (before)	July (after)
1	1.29	0.98
2	0.95	0.43
3	0.77	0.77
Grand Average	1.00	0.72

Average of Fe (ppm)	Sampling Date	
Site	June (before)	July (after)
1	1855.55	1511.80
2	1028.49	532.17

| 3 | | 1151.63 | 1333.29 |
| Grand Average | | 1348.38 | 1126.54 |

Average of K (%)	Sampling Date		
Site	June (before)		July (after)
1		**1.20**	**1.29**
2		1.43	1.31
3		1.65	1.46
Grand Average		1.44	1.36

Average of Mg (%)	Sampling Date		
Site	June (before)		July (after)
1		**0.68**	**0.79**
2		0.50	0.50
3		**0.53**	**0.54**
Grand Average		**0.57**	**0.60**

Average of Perchlorate (ppm)	Sampling Date		
Site	June (before)		July (after)
1		3.67	
2		**10.57**	**54.54**
3		39.00	28.99
Grand Average		**20.56**	**44.32**

Average of S (%)	Sampling Date		
Site	June (before)		July (after)
1		**0.32**	**0.33**
2		0.35	0.31
3		**0.30**	**0.33**
Grand Average		0.32	0.32

Average of Sr (ppm)	Sampling Date		
Site	June (before)		July (after)
1		26.85	26.55
2		**18.19**	**22.54**
3		24.61	26.20
Grand Average		**23.38**	**25.11**

Differences among species types and soils

These tables show the concentrations of each element and compound for each of two types of plant species and soil on the two sampling dates, averaged across sites. The sample sizes for each average therefore range from nine to 21.

Average of Al (ppm)	Sampling Date	
Types	June (before)	July (after)
herbaceous	**58.39**	**217.91**
woody	**24.05**	**32.11**
soil	7936.11	6191.18

Average of Ba (ppm)	Sampling Date	
Types	June (before)	July (after)
herbaceous	**66.19**	**80.55**
woody	**39.10**	**54.62**
soil	162.53	115.31

Average of Chloride (ppm)	Sampling Date	
Types	June (before)	July (after)
herbaceous	**10349.10**	**10441.67**
woody	**1049.98**	**1649.48**
soil	27.45	21.15

Average of Co (ppm)	Sampling Date	
Types	June (before)	July (after)
herbaceous	0.33	0.32
woody	**0.30**	**0.34**
soil	4.57	3.54

Average of Fe ppm	Sampling Date	
Row Labels	June (before)	July (after)
herbaceous	**151.63**	**371.47**
woody	**65.14**	**77.49**
soil	9711.14	8384.79

Average of K (%)	Sampling Date	
Types	June (before)	July (after)
herbaceous	1.84	1.84
woody	1.28	1.07
soil	0.13	0.11

Average of Mg (%)	Sampling Date	
Types	June (before)	July (after)
herbaceous	0.45	0.49
woody	0.42	0.44
soil	1.47	1.68

Average of Perchlorate (ppm)	Sampling Date	
Types	June (before)	July (after)
herbaceous	39.00	64.92
woody	6.19	13.42
soil	12.41	

Average of S (%)	Sampling Date	
Types	June (before)	July (after)
herbaceous	0.36	0.34
woody	0.34	0.37
soil	0.09	0.08

Average of Sr	Sampling Date	
Row Labels	June (before)	July (after)
herbaceous	22.14	23.17
woody	21.54	27.16
soil	33.35	27.17

Correlations among elements (plants only)

This graph shows a group of 2-way plots pairing each element with each other. The data are points and an ellipse is drawn around the points showing how they vary together. Ellipses that are highly slanted and narrow indicate high correlations. Highly correlated variables (across all plant samples, sites and sampling dates) are indicated with red arrows.
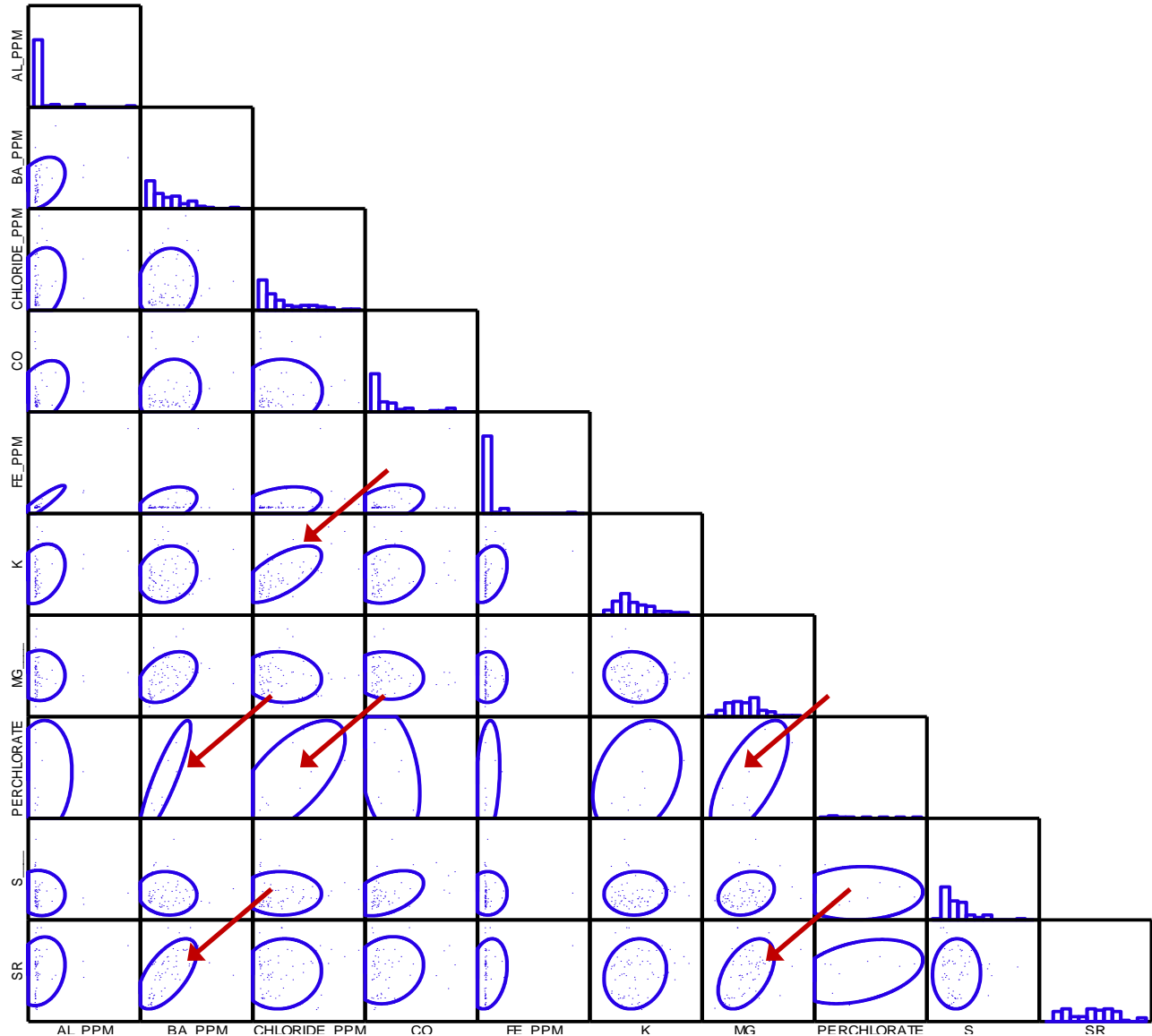
How high were the concentrations?

These tables show the highest concentrations (max) of each element by species and sampling dates. The sample sizes for these values are one.

Max of Al (ppm)	Sampling Dates	
Species	**June (before)**	**July (after)**
alfalfa	12.88	
arrowwood	**28.75**	**31.77**
black willow	13.90	13.91
boxelder	**40.69**	**52.71**
buckthorn	41.85	40.61

cat tail	17.87	9.91
cottonwood	**9.93**	**21.80**
creeping charlie	**261.03**	**729.19**
dandelion	**38.71**	**57.57**
dogbane	**15.89**	**16.82**
duckweed	**313.98**	**1386.77**
honeysuckle	**50.72**	**69.34**
plantain	**67.49**	**722.08**
smartweed	100.05	13.99
soil	13355.79	9788.93
vervain	**16.95**	**80.72**
waterlily	35.95	34.74

Max of Ba (ppm)	Sampling Dates	
Species	**June (before)**	**July (after)**
alfalfa	25.79	
arrowwood	**125.70**	**136.33**
black willow	**7.72**	**15.01**
boxelder	**38.46**	**45.27**
buckthorn	**50.82**	**78.62**
cat tail	**13.36**	**23.06**
cottonwood	**61.47**	**80.01**
creeping charlie	**84.82**	**127.19**
dandelion	47.00	48.19
dogbane	20.42	19.64
duckweed	256.87	152.59
honeysuckle	**64.27**	**110.06**
plantain	115.67	88.07
smartweed	**136.30**	**185.44**
soil	217.41	166.67
vervain	**44.39**	**97.97**
waterlily	11.16	8.80

Max of Chloride (ppm)	Sampling Dates	
Species	**June (before)**	**July (after)**
alfalfa	1562.00	
arrowwood	**656.75**	**745.50**
black willow	**1597.50**	**2147.75**
boxelder	**1402.25**	**2857.75**
buckthorn	**2698.00**	**6798.25**
cat tail	**12105.50**	**18406.75**
cottonwood	**426.00**	**479.25**
creeping charlie	6496.50	4047.00
dandelion	20590.00	15850.75
dogbane	5999.50	4881.25
duckweed	25347.00	21424.25
honeysuckle	**159.75**	**248.50**
plantain	29518.25	15407.00
smartweed	**9709.25**	**13152.75**

soil	63.90	30.18
vervain	**3354.75**	**9975.50**
waterlily	**17022.25**	**17501.50**

Max of Co (ppm)	Sampling Dates	
Species	**June (before)**	**July (after)**
alfalfa	0.14	
arrowwood	**0.01**	**0.07**
black willow	0.46	0.27
boxelder	**0.01**	**0.15**
buckthorn	**0.04**	**0.12**
cat tail	**0.00**	**0.12**
cottonwood	**1.52**	**1.65**
creeping charlie	**0.06**	**0.35**
dandelion	**0.06**	**0.28**
dogbane	**0.00**	**0.04**
duckweed	**0.77**	**1.54**
honeysuckle	0.14	0.15
plantain	**0.11**	**0.54**
smartweed	1.44	0.41
soil	6.68	5.29
vervain	0.13	0.06
waterlily	0.06	0.07

Max of Fe (ppm)	Sampling Dates	
Species	**June (before)**	**July (after)**
alfalfa	72.80	
arrowwood	56.77	56.02
black willow	93.46	79.56
boxelder	**78.94**	**118.91**
buckthorn	97.58	81.63
cat tail	**61.22**	**77.04**
cottonwood	**91.01**	**147.41**
creeping charlie	**286.21**	**801.10**
dandelion	**76.22**	**106.83**
dogbane	57.29	54.64
duckweed	**869.95**	**3514.84**
honeysuckle	**77.38**	**94.46**
plantain	**204.16**	**720.63**
smartweed	247.52	69.99
soil	14484.37	12778.76
vervain	**53.11**	**80.68**
waterlily	171.92	165.09

Max of K (%)	Sampling Dates	
Species	**June (before)**	**July (after)**
alfalfa	1.23	
arrowwood	0.71	0.73

black willow	1.44	1.10
boxelder	2.04	1.10
buckthorn	2.03	1.68
cat tail	1.92	1.70
cottonwood	1.56	1.33
creeping charlie	**2.27**	**2.46**
dandelion	3.67	3.11
dogbane	1.30	1.05
duckweed	3.47	2.93
honeysuckle	0.98	0.76
plantain	2.38	1.83
smartweed	**2.09**	**2.13**
soil	0.19	0.17
vervain	1.11	1.02
waterlily	1.80	1.75

Max of Mg (%)	Sampling Dates	
Species	**June (before)**	**July (after)**
alfalfa	0.61	
arrowwood	0.59	0.57
black willow	**0.30**	**0.43**
boxelder	**0.38**	**0.46**
buckthorn	**0.30**	**0.35**
cat tail	**0.19**	**0.22**
cottonwood	0.59	0.56
creeping charlie	0.60	0.72
dandelion	0.51	0.65
dogbane	0.85	0.60
duckweed	0.45	0.52
honeysuckle	0.72	0.73
plantain	0.49	0.48
smartweed	1.09	0.67
soil	**2.67**	**2.74**
vervain	**0.56**	**0.99**
waterlily	0.23	0.21

Max of Perchlorate (ppm)	Sampling Dates	
Species	**June (before)**	**July (after)**
alfalfa		
arrowwood		
black willow		10.37
boxelder		16.46
buckthorn	8.72	
cat tail	25.42	
cottonwood	3.67	
creeping charlie		
dandelion		
dogbane		

duckweed	52.59	
honeysuckle		
plantain		41.52
smartweed		83.19
soil	12.41	
vervain		70.06
waterlily		

| Max of S (%) | Sampling Dates | |
Species	June (before)	July (after)
alfalfa	0.53	
arrowwood	**0.14**	**0.17**
black willow	**0.36**	**0.39**
boxelder	0.22	0.20
buckthorn	0.16	0.17
cat tail	**0.24**	**0.30**
cottonwood	**0.83**	**1.25**
creeping charlie	**0.40**	**0.42**
dandelion	**0.42**	**0.47**
dogbane	0.82	0.41
duckweed	0.54	0.40
honeysuckle	0.23	0.24
plantain	0.56	0.41
smartweed	0.42	0.30
soil	0.21	0.10
vervain	**0.33**	**0.51**
waterlily	0.28	0.22

| Max of Sr (ppm) | Sampling Dates | |
Species	June (before)	July (after)
alfalfa	30.17	
arrowwood	**27.95**	**28.77**
black willow	**10.39**	**13.04**
boxelder	**20.46**	**23.75**
buckthorn	**30.61**	**48.79**
cat tail	**6.99**	**12.02**
cottonwood	29.04	28.52
creeping charlie	**23.32**	**24.37**
dandelion	**29.30**	**29.56**
dogbane	11.73	10.34
duckweed	**33.07**	**39.01**
honeysuckle	**32.79**	**46.14**
plantain	36.59	33.34
smartweed	48.92	31.15
soil	42.43	36.12
vervain	**14.16**	**27.76**
waterlily	**4.18**	**5.06**

Maximum of Al (ppm)	Sampling Date	
Type	**June (before)**	**July (after)**
herbaceous	**313.98**	**1386.77**
woody	**50.72**	**69.34**
Grand Maximum	**313.98**	**1386.77**

Maximum of Ba (ppm)	Sampling Date	
Type	**June (before)**	**July (after)**
herbaceous	256.87	185.44
woody	**125.70**	**136.33**
Grand Maximum	256.87	185.44

Maximum of Chloride (ppm)	Sampling Date	
Type	**June (before)**	**July (after)**
herbaceous	29518.25	21424.25
woody	**2698.00**	**6798.25**
Grand Maximum	29518.25	21424.25

Maximum of Fe (ppm)	Sampling Date	
Type	**June (before)**	**July (after)**
herbaceous	**869.95**	**3514.84**
woody	**97.58**	**147.41**
Grand Maximum	**869.95**	**3514.84**

Maximum of K (%)	Sampling Date	
Type	**June (before)**	**July (after)**
herbaceous	3.67	3.11
woody	2.04	1.68
Grand Maximum	3.67	3.11

Maximum of Mg (%)	Sampling Date	
Type	**June (before)**	**July (after)**
herbaceous	1.09	0.99
woody	0.72	0.73
Grand Maximum	1.09	0.99

Maximum of Perchlorate (ppm)	Sampling Date	
Type	**June (before)**	**July (after)**
herbaceous	**52.59**	**83.19**
woody	**8.72**	**16.46**
Grand Maximum	**52.59**	**83.19**

Maximum of S	Sampling Date

(%)		
Type	**June (before)**	**July (after)**
herbaceous	0.82	0.51
woody	**0.83**	**1.25**
Grand Maximum	**0.83**	**1.25**

Maximum of Sr (ppm)	**Sampling Date**	
Type	**June (before)**	**July (after)**
herbaceous	48.92	39.01
woody	**32.79**	**48.79**
Grand Maximum	48.92	48.79

Discussion

When discussing results I refer to 15 plant species with changes from June to July because alfalfa is excluded.

Differences in concentrations before and after the fireworks event

Twelve of the fifteen plant species had increased levels of Al with plantain having the largest increase of about 100%. For Mg, 11 species increased, and for Ba, Fe and Sr, 10 species increased, 9 increased in chloride and Co, 7 increased in S, and 5 increased in K. The grand average across all species increased most for perchlorate at 109%, followed by Sr at 9%, Ba at 6%, Mg at 5% and chloride at 1%. All other grand averages of the elements decreased.

No species increased in all 10 elements, but cat tail increased in 9, arrowwood and black willow in 7, and creeping charlie in 6. Soil decreased in all elements except Mg, where there was a small increase, probably due to different sampling methods.

Differences in concentrations among the three sites

Site 1, the launch pad, had 5 increases in elements between June and July, followed 4 for Site 3, and 3 for Site 2. The largest increase was for perchlorate at Site 2, which increased almost 400%.

Differences among species types and soils

Differences among species were self-evident in the previous tables, so it was decided to group them by life form, i.e. woody vs. herbaceous. Herbaceous species increased concentrations of elements in July compared to June for Al, Ba, chloride, Fe, and perchlorate, with a small increase in Mg. Woody plants increased in Al, Ba, chloride, Co, Fe, perchlorate, S and Sr, with a small increase in Mg. While woody plants increased in more elements than herbaceous plants, they also increased

the largest amount in perchlorate at 116% compared to 67% for herbaceous species. For Ba, woody plants increased 41% compared to 22% for herbaceous species.

Correlations among elements (plants only)

The most correlated elements across all plant species were K and chloride, Ba and Mg, Ba and Sr, and Ba, chloride and Mg with perchlorate. This indicates they vary together, and may be due to coming from the same sources.

How high were the concentrations?

The highest concentrations of each element in relation to the sampling dates were as follows:

Al: 1387 ppm in July in duckweed
Ba: 185 pm in July in smartweed
Chloride: 18407 ppm in July in cat tail
Co: 1.65 ppm in July in cottonwood
Fe: 3515 pm in July in duckweed
K: 3.67% in June in dandelion
Mg: 1.09% in June in smartweed
Perchlorate: 83 ppm in July in smartweed
S: 1.25% in July in cottonwood
Sr: 49 ppm in July in buckthorn and June in smartweed

In general the maxima occurred in July for Al, Fe, perchlorate and S. Although herbaceous species had higher perchlorate maxima than woody species, woody species outnumbered herbaceous species in number of maxima.

Comparisons to known levels and toxicity

This discussion compares the maximum values above with tabulated average values for plants, toxicity levels in plants (if known), and with those for a "reference plant" which is considered a normal set of values of plants in general (Whitehead 2000; Pais and Jones 1997). Maxima that are near toxicity levels or critical levels are highlighted. Critical levels are those that may approach toxicity levels for plants. There are no Environmental Protection Agency criteria for element concentrations in plant materials.

Al. The maximum value is almost 7 times higher than the average level of 200 ppm, and 17 times higher than the 80 ppm level for the reference plant. Levels above 500 ppm are considered very high.

Ba. The highest concentration (above) is more than 10 times higher than that of the average plant (15 ppm) and higher than the standard reference plant value of 40 ppm. However, some species of plants do concentrate Ba in high amounts, but it is unknown if smartweed is a Ba accumulator. The maximum value is close to the moderate toxicity level for some plant species.

Chloride.   Chloride levels in plants are highly variable, ranging from 20 ppm to seveal percent concentrations. The maximum value of 18% is certainly at the high end of this range.

Co. The highest concentration is 10 times higher than that of the reference plant but is not at a toxicity level.

Fe. The maximum values above are 23 times higher than the reference plant level of 150 ppm, and at least 10 times higher than the 20-100 ppm range for most plant species. The critical level for most plants is 50 ppm.

K.   The maximum value in dandelion is just barely over the usual range of K in plants of 1-3.5% so it would not be considered excessive or toxic.

Mg.   The maximum value in smartweed is 10 times higher than the usual range of 0.1 – 0.3% in plants is exceeds the critical levels for herbage plants.

Perchlorate.   The perchlorate levels in the plant samples in this study exceed those of some species in the literature and are less than others. They exceed the 5 – 300 ppb levels in tamarisk (Urbansky et al 2000), 10 ppb in tobacco (Sundberg et al 2008), and the 2 ppm levels in tree species (Smith et al 2004). But they are less than higher levels in tobacco (Smith et al 2004; Sundberg et al 2003; Ellington et al 2001), and cucumber and lettuce (Yu et al 2004). It is possible the two high values of 70 & 83 ppm in duckweed and smartweed in July at Site 2 could be considered possible warning levels for those species. Duckweed is an aquatic species and smartweed grows right next to the water on banks, so both may have been exposed to water-born perchlorate.

S.   The maximum value in cottonwood is 10 times higher than the normal range for plants of 0.15-0.6%. Critical levels of S in plants range from 0.1 – 0.3%.

Sr. The maximum values are within the normal range of 3-3000 ppm and agrees with the 50 ppm for the reference plant. No toxicity levels are known for Sr in plants. Concentrations of this element vary widely in plants.

Conclusions

Most of the plant species showed elevated concentrations of elements associated with pyrotechnics 23 days following the Rhythm and Booms event. Perchlorate, in spite of small samples sizes, increased the most, followed by Ba, Sr and Mg, all important compounds in pyrotechnics. The launch pad showed the highest number of element increases after the event, followed by the viewing area site, and then the island south of the launch pad, although the differences were minor. Foliage of woody plants increased in pyrotechnics associated elements more than herbaceous species. The most correlated elements across species and sites were those that co-occur in pyrotechnics: Ba, K, Mg, Sr, chloride and perchlorate. Maximum concentrations of Al, Ba, Co, Fe, Mg, S, and some of the perchlorate values were considered either at critical levels or nearing toxicity levels for plants.

Recommendations

The following are candidate recommendations to be made by the full COE:

- More monitoring needed
- Replication needed, but fewer species
- Control site needed away from Warner Park
- Debris clean up needs to be improved
-

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Appendix 1. Plant and soil chemical data

SPAL No	Date	Site	Species	Al ppm	Ba ppm	Chloride ppm	Co	Cr	Fe ppm	K	Mg (%)	Perchlorate	S (%)	Sr
1	June (before)	1	alfalfa	12.88	25.79	1562.0	0.142	<.001	72.80	1.23	0.61	ND*	0.53	30.17
2	June (before)	1	black willow	<5	5.87	834.3	0.185	<.001	46.55	0.95	0.30	ND	0.32	10.39
4	June (before)	1	cat tail	<5	10.60	11786.0	<.001	<.001	48.20	1.41	0.19	ND	0.20	6.99
5	June (before)	1	cottonwood	9.93	21.74	266.3	0.826	<.001	43.81	1.27	0.49	3.67	0.83	29.04
3	June (before)	1	creeping charlie	27.79	74.94	2680.3	0.061	<.001	69.00	2.27	0.60	ND	0.40	23.32
6	June (before)	1	dandelion	24.77	33.61	13099.5	<.001	<.001	76.22	2.86	0.50	ND	0.42	24.43
7	June (before)	1	honeysuckle	25.86	60.60	71.0	0.135	<.001	54.95	0.84	0.61	ND	0.15	32.79
8	June (before)	1	plantain	13.90	91.80	16862.5	0.098	<.001	46.34	2.38	0.36	ND	0.56	36.45
9	June (before)	1	smartweed	100.05	129.38	6638.5	0.752	<.001	247.52	1.20	0.34	ND	0.15	48.92
10	June (before)	1	vervain	14.96	18.49	1082.8	0.129	<.001	50.01	0.89	0.19	ND	0.33	10.05
11	July (after)	1	black willow	10.93	8.74	994.0	0.197	<.001	69.72	0.89	0.41	ND	0.39	12.31
13	July (after)	1	cat tail	<5	23.06	18406.8	0.117	<.001	68.32	1.66	0.22	ND	0.28	12.02
14	July (after)	1	cottonwood	13.94	16.54	159.8	1.653	<.001	54.61	1.33	0.39	ND	0.72	28.52
12	July (after)	1	creeping charlie	45.66	55.27	4047.0	0.172	<.001	81.20	2.22	0.72	ND	0.42	24.37
15	July (after)	1	dandelion	52.40	24.02	10117.5	0.283	<.001	106.83	3.11	0.53	ND	0.39	20.44
16	July (after)	1	honeysuckle	22.88	96.48	142.0	0.031	<.001	61.00	0.76	0.72	ND	0.20	46.14
17	July (after)	1	plantain	79.56	87.23	5715.5	0.080	<.001	102.64	1.62	0.38	ND	0.41	33.34
18	July (after)	1	smartweed	13.99	185.44	5715.5	0.413	<.001	63.11	1.40	0.57	ND	0.21	29.66
19	July (after)	1	vervain	80.72	91.48	3461.3	<.001	<.001	80.68	1.02	0.46	ND	0.51	23.39
22	June (before)	2	black willow	13.90	7.72	1597.5	0.456	<.001	93.46	1.44	0.25	ND	0.36	10.24
20	June (before)	2	boxelder	<5	8.09	1171.5	0.006	<.001	52.56	2.04	0.28	ND	0.22	10.64
21	June (before)	2	buckthorn	41.85	44.54	2698.0	<.001	<.001	97.58	1.73	0.29	8.72	0.14	28.73
23	June (before)	2	cat tail	17.87	7.50	7046.8	<.001	<.001	50.78	1.43	0.07	ND	0.24	4.82
24	June (before)	2	cottonwood	<5	14.34	426.0	1.523	<.001	37.70	1.56	0.36	ND	0.65	15.61
25	June (before)	2	dogbane	15.89	20.42	5999.5	<.001	<.001	57.29	1.30	0.85	ND	0.82	11.73
26	June (before)	2	duckweed	313.98	256.87	8058.5	0.765	0.316	869.95	2.68	0.38	ND	0.44	22.81
27	June (before)	2	smartweed	29.66	53.22	7188.8	0.339	<.001	77.53	1.32	0.48	ND	0.23	15.90
28	June (before)	2	smartweed	33.75	107.88	8413.5	0.240	<.001	85.24	1.16	1.09	ND	0.28	36.99
29	June (before)	2	vervain	16.95	43.47	2769.0	<.001	<.001	43.23	0.62	0.56	ND	0.30	14.16
30	June (before)	2	waterlily	35.95	11.16	17022.3	0.055	<.001	171.92	1.80	0.23	ND	0.28	4.18
34	July (after)	2	black willow	13.91	15.01	2147.8	0.191	<.001	58.27	0.61	0.43	10.37	0.23	13.04
31	July (after)	2	boxelder	52.71	38.40	2857.8	0.148	<.001	118.91	0.93	0.40	ND	0.20	22.62
32	July (after)	2	buckthorn	40.61	63.35	6798.3	0.012	<.001	60.47	1.30	0.35	ND	0.11	48.79
33	July (after)	2	buckthorn	40.61	41.13	3692.0	0.105	<.001	81.63	1.52	0.26	ND	0.13	21.76
35	July (after)	2	cat tail	<5	12.91	12815.5	<.001	<.001	68.06	1.65	0.20	ND	0.27	7.31
36	July (after)	2	cottonwood	14.83	26.78	479.3	1.283	<.001	45.20	1.19	0.36	ND	0.87	22.62
37	July (after)	2	dogbane	16.82	19.64	4881.3	0.037	<.001	54.64	1.05	0.60	ND	0.41	10.34
38	July (after)	2	duckweed	184.60	119.56	21424.3	0.462	0.329	781.38	2.93	0.43	ND	0.40	37.07
39	July (after)	2	smartweed	11.92	126.35	13152.8	0.271	<.001	69.99	2.13	0.67	83.19	0.30	29.08
40	July (after)	2	vervain	21.89	86.96	9975.5	0.061	<.001	63.68	0.62	0.99	70.06	0.47	27.76
41	July (after)	2	waterlily	34.74	8.80	17501.5	0.074	<.001	165.09	1.75	0.21	ND	0.22	5.06
42	June (before)	3	arrowwood	28.75	125.70	656.8	0.012	<.001	56.77	0.71	0.59	ND	0.14	27.95
45	June (before)	3	black willow	8.96	4.71	1313.5	<.001	<.001	49.89	1.01	0.25	ND	0.24	6.63
43	June (before)	3	boxelder	40.69	38.46	1402.3	0.012	<.001	78.94	1.54	0.38	ND	0.15	20.46
44	June (before)	3	buckthorn	13.93	50.82	2662.5	0.037	<.001	66.22	2.03	0.30	ND	0.16	30.61
47	June (before)	3	cat tail	7.93	13.36	12105.5	<.001	<.001	61.22	1.92	0.17	25.42	0.23	6.51

48	June (before)	3	cottonwood	5.95	61.47	390.5	0.111	<.001	91.01	0.59	0.59	ND	0.81	26.40
46	June (before)	3	creeping charlie	261.03	84.82	6496.5	0.049	<.001	286.21	2.04	0.55	ND	0.23	20.82
49	June (before)	3	dandelion	38.71	47.00	20590.0	0.055	<.001	72.46	3.67	0.51	ND	0.32	29.30
50	June (before)	3	duckweed	114.37	63.31	25347.0	0.592	<.001	450.17	3.47	0.45	52.59	0.54	33.07
51	June (before)	3	honeysuckle	50.72	64.27	159.8	0.037	<.001	77.38	0.98	0.72	ND	0.23	30.57
52	June (before)	3	plantain	67.49	115.67	29518.3	0.105	<.001	204.16	1.82	0.49	ND	0.43	36.59
53	June (before)	3	smartweed	6.97	136.30	9709.3	1.437	<.001	90.92	2.09	0.53	ND	0.42	36.29
54	June (before)	3	vervain	12.91	44.39	3354.8	0.111	<.001	53.11	1.11	0.40	ND	0.29	11.50
55	July (after)	3	arrowwood	31.77	136.33	745.5	0.067	<.001	56.02	0.73	0.57	ND	0.17	28.77
58	July (after)	3	black willow	<5	7.93	798.8	0.271	<.001	79.56	1.10	0.23	ND	0.32	10.55
56	July (after)	3	boxelder	52.50	45.27	976.3	0.142	<.001	93.18	1.10	0.46	16.46	0.17	23.75
57	July (after)	3	buckthorn	31.64	78.62	2698.0	0.117	<.001	64.34	1.68	0.28	ND	0.17	37.46
60	July (after)	3	cat tail	9.91	14.26	13064.0	<.001	<.001	77.04	1.70	0.18	ND	0.30	8.03
61	July (after)	3	cottonwood	21.80	80.01	355.0	0.407	<.001	147.41	1.12	0.56	ND	1.25	27.40
59	July (after)	3	creeping charlie	729.19	127.19	2485.0	0.351	0.417	801.10	2.46	0.40	ND	0.18	21.69
62	July (after)	3	dandelion	57.57	48.19	15850.8	<.001	<.001	104.70	3.10	0.65	ND	0.47	29.56
63	July (after)	3	duckweed	1386.77	152.59	18140.5	1.542	3.634	3514.84	2.60	0.52	ND	0.37	39.01
64	July (after)	3	honeysuckle	69.34	110.06	248.5	0.154	<.001	94.46	0.76	0.73	ND	0.24	36.59
65	July (after)	3	plantain	722.08	88.07	15407.0	0.543	0.312	720.63	1.83	0.48	41.52	0.29	30.49
66	July (after)	3	smartweed	<5	161.38	3301.5	0.345	<.001	65.16	1.29	0.64	ND	0.24	31.15
67	July (after)	3	vervain	38.71	97.97	2928.8	0.018	<.001	68.81	0.75	0.53	ND	0.38	20.48
68	June (before)	1	soil	9800.85	179.14	11.2	5.26	17.67	10018.99	0.18	1.12	ND	0.09	33.99
69	June (before)	1	soil	7691.11	188.92	7.1	4.60	13.50	8810.89	0.12	0.91	ND	0.09	37.18
70	June (before)	1	soil	2465.39	31.25	8.9	2.04	4.97	4536.81	0.05	2.67	ND	0.02	25.32
71	June (before)	2	soil	6367.41	217.41	63.9	4.26	11.06	10704.66	0.12	1.12	12.41	0.21	42.43
72	June (before)	3	soil	13355.79	195.94	46.2	6.68	25.88	14484.37	0.19	1.52	ND	0.05	27.82
73	July (after)	1	soil	3069.11	53.05	7.1	2.16	7.51	5844.23	0.06	2.74	ND	0.05	25.75
74	July (after)	1	soil	9026.15	166.67	18.3	4.68	15.99	10097.43	0.15	1.55	ND	0.10	36.12
75	July (after)	2	soil	2880.54	95.23	30.2	2.04	4.68	4818.75	0.06	1.12	ND	0.10	24.99
76	July (after)	3	soil	9788.93	146.31	29.0	5.29	20.07	12778.76	0.17	1.32	ND	0.06	21.83

Appendix 2. January 22, 2013 data summary

COE 2012 Warner Park Vegetation and Soil Residue Study

James P. Bennett

January 22, 2013

Factors

1. 2 Dates of sampling: June 22 (before R&B) and July 23 (after), 2012
2. 3 Sites: launch mound (1), island south of mound (2), spectator area east of mound (3)
3. 16 Plant species: bulk leaf samples, 5 species of which were at all sites and dates
4. 2 Plant types: herbaceous and woody
5. 1 Soil sample at each site and date

Results

1. 67 plant samples analyzed
2. 9 soil samples analyzed
3. 11 tissue and soil concentrations:

    Al: 8 BDL values
    Ba: 0 BDL values
    Chloride: 0 BDL values
    Co: 12 BDL values
    Cr: 62 BDL values
    Fe: 0 BDL values
    K: 0 BDL values
    Mg: 0 BDL values
    S: 0 BDL values
    Sr: 0 BDL values
    Perchlorate: 66 BDL values

Total number of data points = 688

Discussion

Questions for COE to discuss:

1. Are there differences in concentrations before and after the fireworks?
2. Are there differences in concentrations among the 3 sites?
3. Are there differences among species in concentrations?
4. Are there correlations among the elements that mean anything?
5. How high are the concentrations?