Supporting Information

Detection of Carbon Nanotubes in Indoor Workplaces Using Elemental Impurities

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SEM and TEM Analyses

Electron microscopy provides morphological and chemical information about the carbon nanotube (CNT) material used in this study, which supports the concept of using residual catalysts and other metal impurities as CNT tracers for workplace monitoring. Test samples of CNT dispersed in 99% ethanol were placed on 300 mesh copper grip coated with holey carbon film, then dried for 12 hr under vacuum (10^{-8} torr) generated by a turbo pump (Varian V-81M Turbo Station). Diameter and cell wall thickness of aerosolized and parent SWCNT samples were measured using a JEM-2100F Transmission Electron Microscope (TEM; JEOL Industry) at high resolution (± 0.2 nm) and length was measured using a JSM-7500F Scanning Electron Microscope (SEM; JEOL Industry). Transmission electron diffraction (TED) mode was used for image analysis. Backscatter electron (BSE) mode was used to locate elements heavier than carbon (metal impurities) in the amorphous carbon component of the agglomerates and x-ray energy dispersive spectrometry (EDS) was used to identify these heavier elements (>1%).

Table S - 1 Physical characterization of three single-wall carbon nanotube materials (Aldrich, NRC Test and NRC SWCNT-1 SRM) using TEM to determine diameter and wall width and SEM to determine length (n= number of measurements). Bundles of Aldrich SWCNT ranged from 5 to 10 nm in diameter and were well-formed, typically containing from 3 to 20 individual nanotubes. The NRC SWCNT-1 bundles were well formed, ranging from 1.4 to 45 nm in diameter. The NRC Test bundles were smaller in diameter (< 3nm), shorter, and contained a higher proportion of amorphous material (relative to nanotubes) compared to the Aldrich SWCNT and NRC-SWCNT-1. All nanostructure measurements were normally distributed (both Kolmogorov-Smirnov and Shapiro-Wilk normality tests $p > .2$).

Aldrich SWCNT	**Diameter (nm)**	**Wall Width (nm)**	**Length SEM (μm)**
	n=27	**n=27**	**n=31**
Mean	1.7 (sd 0.2)	0.4 (sd 0.1)	2.13 (sd 1.08)
Median	1.8	0.4	2.15
Range	1.3 – 2.0	0.3 – 0.5	0.32 – 4.70
NRC Test SWCNT	**Diameter (nm)**	**Wall Width (nm)**	**Length SEM (μm)**
	n=32	**n=32**	**n=31**
Mean	1.6 (sd 0.2)	0.3 (sd 0.1)	0.93 (sd 0.88)
Median	1.6	0.3	0.68
Range	1.0 – 2.0	0.2 – 0.5	0.07 – 5.2
NRC SWCNT-1 SRM	**Diameter (nm)**	**Wall Width (nm)**	**Length SEM (μm)**
	n=54	**n=54**	**n=77**
Mean	1.5 (sd 0.2)	0.4 (sd 0.1)	3.49 (sd 2.5)
Median	1.5	0.4	2.75
Range	1.2 – 2.1	0.2 – 0.6	0.25 – 9.42

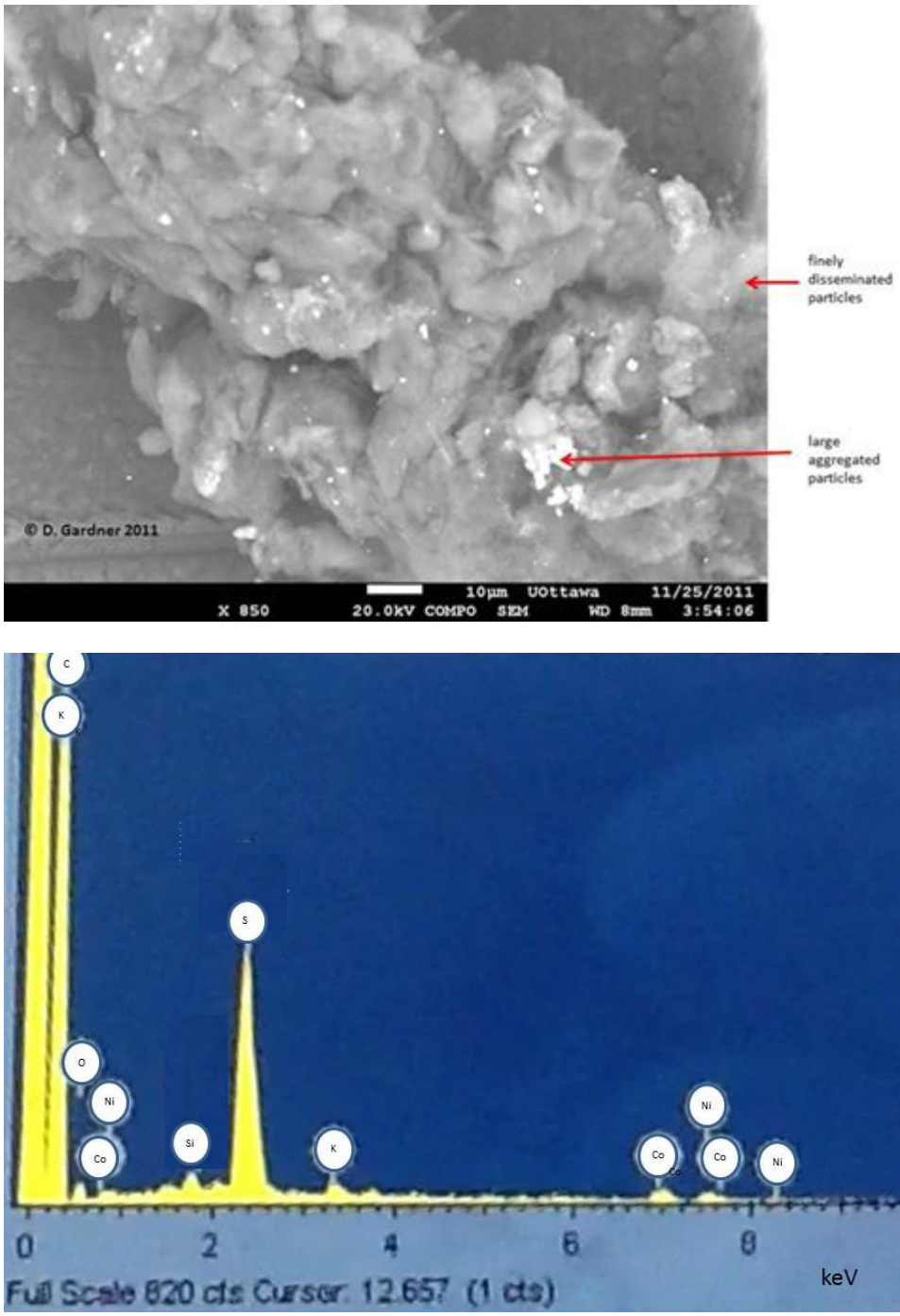

Figure S - 1 Photomicrograph of NRC SWCNT-1 SRM (upper) using SEM in backscatter mode. Metal impurities (in this case Co and Ni) appear as bright spots (red arrows) on the BSE micrograph. Co and Ni identified in sample EDS spectrum (lower) from NRC SWCNT-1. NRC Certificate of Analysis indicates that the purity of NRC SWCNT-1 is 67 % carbon nanotubes with the remaining mass fraction (approximately 33%) consisting of amorphous carbon, graphitic nanoparticles, and residual catalyst impurities.

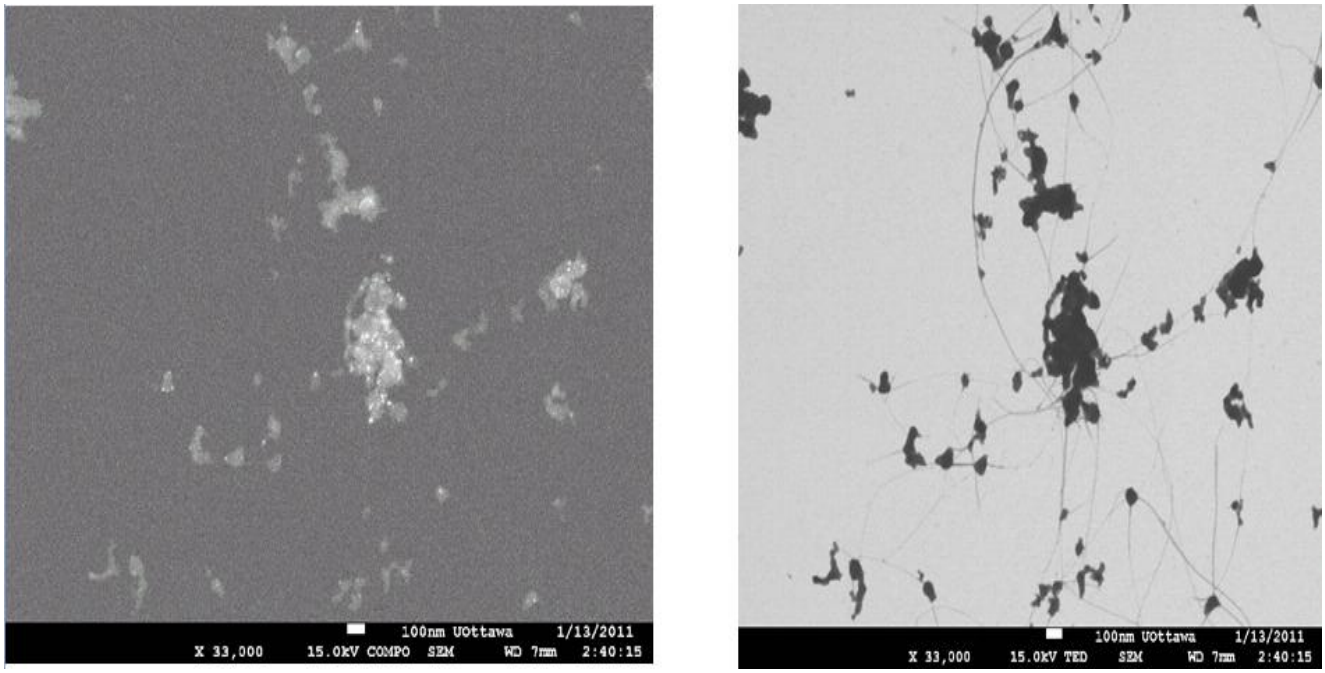

Figure S - 2 CNT Test (NRC) as backscatter image (left) and TED image (right) at the same location on the grid. Illuminated areas of amorphous carbon (left) indicate the presence of heavier elements (catalyst metals Ni, Co and Y).

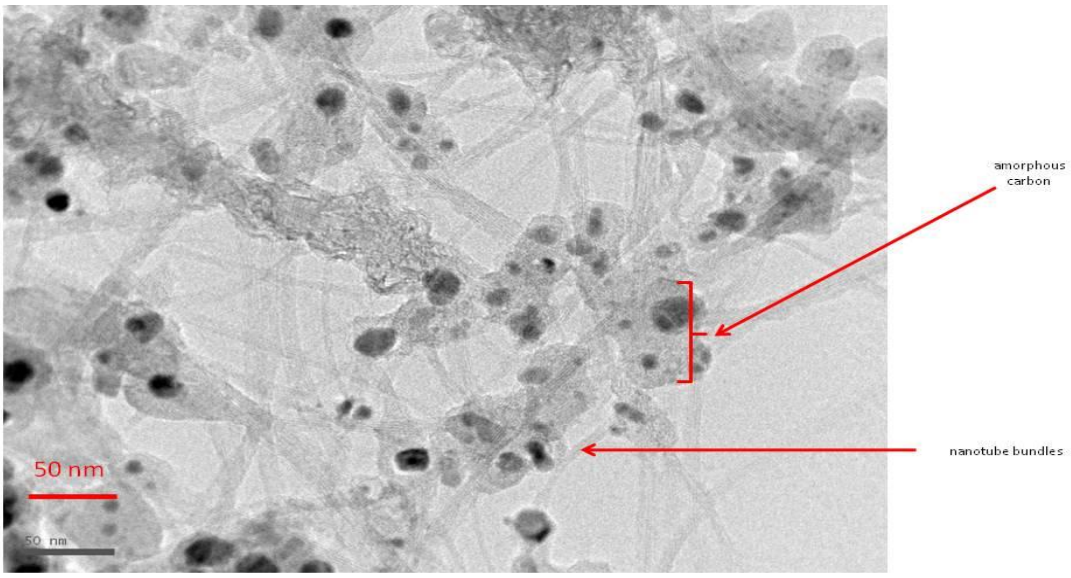

Figure S - 3 TEM image of Aldrich SWCNT showing amorphous carbon with radiating nanotube bundles. Dark material in amorphous carbon is likely residual metal catalyst. According to information provided by Sigma-Aldrich, this material contains 40-60 wt% carbon content and 30-35% metal content.

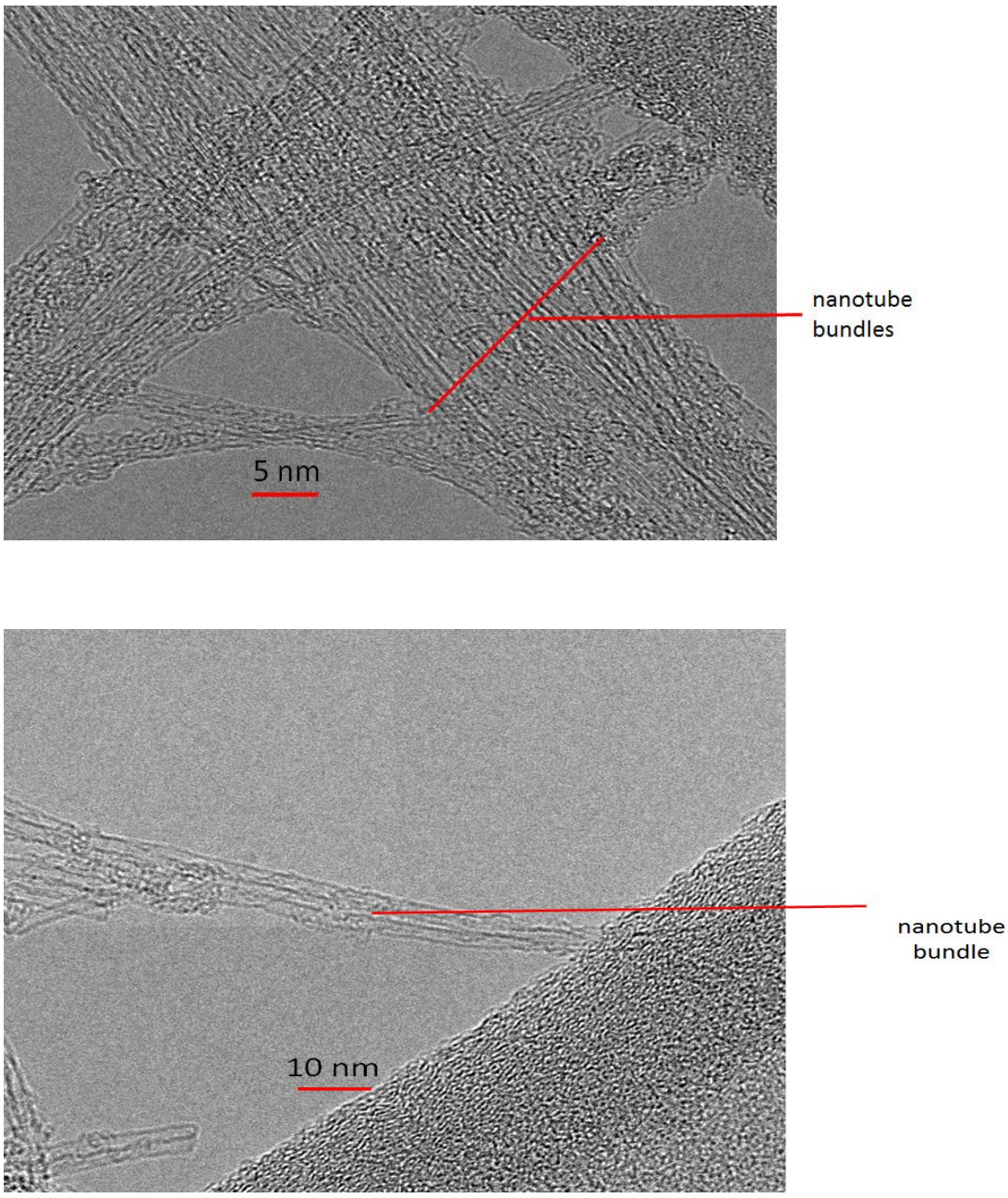

Figure S - 4 High resolution TEM images of NRC SWCNT-1 (upper) and CNT Test (lower). The NRC SWCNT-1 nanotube bundles are well formed and uniform, compared to the CNT Test bundles which were narrower, broken and less flexible. The CNT Test bundles were observed to contain numerous irregularities in the wall structure of individual nanotubes.

Comparison of Preliminary and Follow-up Surveys

Figure S-5 shows surface loadings (ng/cm^2) of five metals determined using Ghost Wipe samples in three locations of the CNT manufacturing facility for the preliminary mapping (Al-1, Fe-1, Co-1, Ni-1 and Mo-1; from Figure 2 in the paper), and for the follow-up sampling (Al-2, Fe-2, Co-2, Ni-2 and Mo-2). Locations are given in Table 1 in the paper. Sample digestion for the preliminary wipe samples used a simple nitric-HF acid mixture and ultrasonic bath procedure described by Niu et al. (2013) whereas the HBMW method (using nitric acid) described by Avramescu et al. (2015) was used for the follow-up samples. In Figure B-1 averages of 5 samples per location (floor and unused shelf surfaces) are shown for the preliminary survey, and averages of 2 samples per location (one floor and one unused shelf) are shown for the follow-up survey. Preliminary mapping was conducted during downtime, and the follow-up sampling was conducted about one month later during production. Despite differences in sampling surfaces, digestion method, and timing (in-between production versus during production), results from the two surveys are comparable demonstrating the reliability and reproducibility of active surface wipes for the purpose of this study.

References

Avramescu, M. L.; Rasmussen, P. E.; Chénier M. Digestion methods to determine metal impurities in wipe samples of carbon nanotubes. Proceedings of the 30th Annual International Conference on Soils, Sediments, Water, and Energy, 2014 October 20-23, Amherst, Massachusetts. AEHS Foundation, 2015, 20, 21-29.

Niu J, Rasmussen P E, and Chénier M. 2013. Ultrasonic dissolution for ICP-MS determination of trace elements in lightly loaded airborne PM filters. Int. J. Envron. Anal. Chem. 93 (6): 661-678.

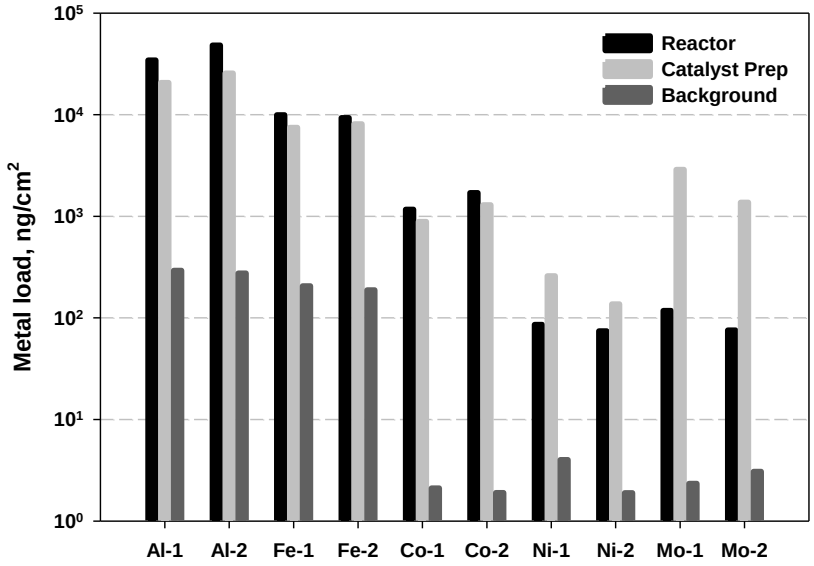

Figure S - 5 Comparison of surface loadings (ng/cm^2) in the preliminary mapping (Me-1) and follow-up survey (Me-2).

ICP-MS Quality Control Information

Table S - 2 Reagent Blanks and Calculation of LOD and LOQ. Procedural reagent blanks (mean, SD) are shown separately for quartz filter batch (n=6) and Ghost Wipe batch (n=5). LOD = 3 X SD and LOQ = 10 X SD.

Element	Procedural Blank-Quartz filter Batch (n=6, ppb)				Procedural Blank-Ghost Wipes Batch (n=5, ppb)			
	Blank	SD	LOD	LOQ	Blank	SD	LOD	LOQ
Lithium	0.05	0.07	0.20	0.66	0.02	0.00	0.01	0.02
Boron	1.26	0.14	0.43	1.42	2.02	0.25	0.76	2.54
Aluminum	13.4	4.6	13.8	45.8	31.7	11.3	33.8	112.6
Titanium	1.51	0.83	2.50	8.32	1.39	0.71	2.12	7.06
Vanadium	0.02	0.01	0.02	0.08	0.03	0.01	0.02	0.07
Chromium	0.39	0.27	0.80	2.66	0.29	0.09	0.27	0.90
Manganese	0.51	0.29	0.86	2.87	0.26	0.10	0.30	1.01
Iron	24.8	24.3	72.8	243	18.3	9.9	29.8	99
Cobalt	0.21	0.45	1.34	4.46	0.49	0.68	2.05	6.83
Nickel	0.46	0.20	0.60	1.99	0.19	0.07	0.21	0.69
Copper	1.18	0.29	0.88	2.93	0.71	0.20	0.59	1.97
Zinc	22.0	11.9	35.8	119	14.8	5.7	17.1	57
Arsenic	0.03	0.01	0.02	0.05	0.02	0.00	0.01	0.04
Selenium	0.01	0.02	0.05	0.17	0.02	0.01	0.03	0.10
Rubidium	0.02	0.00	0.01	0.04	0.01	0.00	0.01	0.02
Strontium	1.14	0.07	0.21	0.70	0.65	0.04	0.12	0.38
Molybdenum	0.20	0.37	1.12	3.74	0.58	0.44	1.32	4.38
Cadmium	0.02	0.01	0.03	0.09	0.01	0.00	0.01	0.04
Tin	0.11	0.06	0.17	0.56	-0.17	0.05	0.14	0.45
Antimony	0.47	0.46	1.39	4.64	0.18	0.09	0.27	0.91
Barium	0.51	0.13	0.40	1.35	0.74	0.03	0.09	0.31
Lanthanum	0.01	0.01	0.04	0.15	0.01	0.00	0.01	0.04
Cerium	0.02	0.01	0.03	0.09	0.02	0.00	0.01	0.04
Neodymium	0.01	0.00	0.01	0.05	0.00	0.00	0.00	0.01
Gadolinium	0.00	0.00	0.00	0.01	not measured	not measured	not measured	not measured
Erbium	0.00	0.01	0.02	0.07	0.00	0.00	0.00	0.01
Ytterbium	0.04	0.07	0.20	0.68	0.00	0.01	0.02	0.08
Lead	0.22	0.08	0.23	0.78	0.22	0.07	0.22	0.75
Bismuth	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.01
Uranium	0.00	0.00	0.01	0.02	0.00	0.00	0.00	0.00

Table S - 3 Media blank values (mean, SD) for liquid digests of 2 GhostWipes (2GW) used for passive deposition samples, active wipes (Cut disc GW), and 24 mm quartz fibre filters (QF blanks). Values in red indicate where media blanks are very high due to GW or Quartz matrix.

Element	2GW Blank n=3, ppb)		*Cut Disc GW blank (n=8, ppb)		QF Blank (n=5, ppb)	
	mean	SD	mean	SD	mean	SD
Lithium	0.98	0.03	0.05	0.01	0.26	0.12
Boron	**87.0**	2.85	4.94	1.01	532	312
Aluminum	**99.9**	6.33	27.9	8.01	649	363
Titanium	5.11	0.38	1.05	0.35	5.16	2.51
Vanadium	1.38	0.08	0.10	0.12	0.06	0.02
Chromium	6.09	0.68	0.53	0.21	3.75	1.20
Manganese	38.7	2.54	0.93	0.57	1.46	0.67
Iron	180	11.3	20.4	8.56	45.9	26.7
Cobalt	0.32	0.12	0.16	0.22	0.35	0.42
Nickel	3.84	1.07	0.35	0.21	1.05	0.57
Copper	169	48.2	5.47	4.84	4.30	4.73
Zinc	4924	1592	106	115	23.1	3.60
Arsenic	3.38	0.67	0.13	0.03	0.06	0.01
Selenium	0.43	0.07	0.03	0.02	0.00	0.02
Rubidium	1.19	0.28	0.04	0.02	0.31	0.15
Strontium	21.0	1.34	1.43	0.24	2.67	0.74
Molybdenum	1.47	0.18	0.39	0.48	1.31	0.49
Cadmium	0.07	0.05	0.02	0.01	0.05	0.08
Tin	0.04	0.04	-0.12	0.15	0.23	0.06
Antimony	2.11	0.65	0.24	0.18	0.61	0.74
Barium	7.50	0.58	1.22	0.30	11.8	7.52
Lanthanum	0.09	0.02	0.03	0.02	0.07	0.04
Cerium	0.27	0.11	0.03	0.02	0.14	0.08
Neodymium	0.07	0.03	0.11	0.10	0.05	0.03
Gadolinium	not measured	not measured	0.03	0.03	0.02	0.01
Erbium	4.53	1.34	0.06	0.09	0.02	0.02
Ytterbium	48.9	14.7	0.71	0.99	0.01	0.01
Lead	2.35	0.18	0.68	0.59	1.10	0.61
Bismuth	0.04	0.04	0.00	0.00	0.09	0.04
Uranium	0.71	0.07	0.02	0.01	0.02	0.01

* Cut disc GW blanks = 9.6 cm2 circular disc of Ghost Wipe for active wipe sampling

Table S - 4 Media blank values (mean, SD) calculated in terms of sampling metrics for 2 GhostWipes (2GW) used for passive deposition samples, active wipes (Cut disc GW), and 24 mm quartz fibre filters (QF blanks). Values in red indicate media blanks which are elevated due to trace contaminants in GW or Quartz matrix.

Element	2GW Blank (n=3, ppb)		*Cut Disc GW blank (n=8, ppb)		QF Blank (n=5, ppb)	
	mean	SD	mean	SD	mean	SD
Lithium	0.00	0.00	0.06	0.01	6.73	3.15
Boron	0.25	0.01	5.73	1.17	13574	7964
Aluminum	0.28	0.02	32.4	9.28	16558	9255
Titanium	0.01	0.00	1.22	0.41	131.7	63.9
Vanadium	0.00	0.00	0.11	0.14	1.56	0.54
Chromium	0.02	0.00	0.61	0.24	95.70	30.52
Manganese	0.11	0.01	1.08	0.66	37.23	17.14
Iron	0.51	0.03	23.6	9.93	1169.3	681.7
Cobalt	0.00	0.00	0.19	0.25	8.90	10.79
Nickel	0.01	0.00	0.41	0.24	26.7	14.6
Copper	0.48	0.14	6.34	5.61	110	121
Zinc	13.9	4.48	123	134	590	91.9
Arsenic	0.01	0.00	0.15	0.03	1.40	0.33
Selenium	0.00	0.00	0.04	0.02	0.02	0.39
Rubidium	0.00	0.00	0.04	0.02	7.85	3.81
Strontium	0.06	0.00	1.66	0.28	68.0	18.8
Molybdenum	0.00	0.00	0.45	0.55	33.5	12.4
Cadmium	0.00	0.00	0.03	0.01	1.34	2.11
Tin	0.00	0.00	-0.14	0.17	5.80	1.41
Antimony	0.01	0.00	0.28	0.21	15.7	18.9
Barium	0.02	0.00	1.41	0.35	301	192
Lanthanum	0.00	0.00	0.03	0.03	1.69	0.91
Cerium	0.00	0.00	0.03	0.03	3.64	2.14
Neodymium	0.00	0.00	0.12	0.12	1.33	0.70
Gadolinium	not measured	not measured	0.03	0.03	0.40	0.24
Erbium	0.01	0.00	0.07	0.10	0.50	0.44
Ytterbium	0.14	0.04	0.82	1.15	0.25	0.14
Lead	0.01	0.00	0.78	0.68	28.0	15.6
Bismuth	0.00	0.00	0.00	0.00	2.23	1.07
Uranium	0.00	0.00	0.02	0.01	0.58	0.30

* Cut disc GW blanks = 9.6 cm2 circular disc of Ghost Wipe for active wipe sampling