Assessment of trace metal backgrounds for National Trends Network collectors at site WI93 (Madison, WI)

National Atmospheric Deposition Program

Wisconsin State Laboratory of Hygiene
UNIVERSITY OF WISCONSIN–MADISON

Meagan Ankney[1], Christa Dahman-Zaborske[1], Ella Osby[2], Nichole Miller[2], Sarah Benish[2], Kirsten Widmayer[1]

Background

Since 1978, the NADP's National Trends Network has monitored precipitation chemistry across the United States, analyzing samples for eight major ions and acidity[1]. This vast network also has the potential to be used to monitor trace metals in precipitation that are of concern to human and environmental health, both to evaluate long-term trends and in response to acute threats (e.g., wildfires, industrial accidents).

Aims

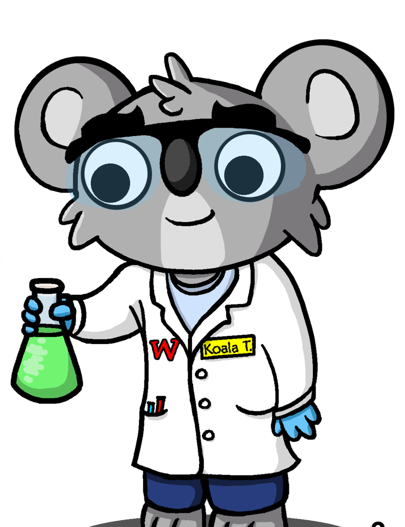
This study is the first step in determining which elements can be meaningfully detected in NTN samples using an exposure study to estimate a network limit of detection based upon blank background. We evaluated the following factors:

- **Use of N-CON vs. Aerochem collector**
- **Effect of filtration**
- **Detectability in precipitation samples over blanks**
- **Interlaboratory comparison of precipitation analyses**

Methods

A total of six field blanks plus one precipitation sample were collected weekly in duplicate from October to November 2025 at NTN site WI93 in Madison, Wisconsin. For the blanks, two aliquots consisting of one liter of ultrapure water were deployed each week in closed collectors and retrieved after seven days of continuous exposure to the sampler interior, one from each collector type (N-CON and Aerochem). No special precautions were taken to limit systemic exposure to metals during the deployment, collection, transportation, or filtering processes outside of standard NTN procedures. Filtered and unfiltered aliquots were collected into acid-washed 50 mL polypropylene containers and acidified to 2% v/v ultrapure nitric acid.

Samples were analyzed for a suite of 55 elements using a Thermo Element XR SF-ICP-MS located in the Trace Element Clean Laboratory (TECL) in the Wisconsin State Laboratory of Hygiene and the laboratory's standard operating procedure based upon EPA Method 200.8. An initial limit of detection (LOD) was calculated for both the unfiltered and filtered blanks using the mean plus three times the standard deviation according to guidelines laid out in 40 CFR Appendix B to Part 136[1]. This limit of detection was then used to determine which elements are detectable in the precipitation samples. For interlaboratory comparison purposes, an additional set of 20 precipitation samples from various NTN collection sites were obtained from NADP and acidified to 2% v/v ultrapure nitric acid in autosampler vials prior to analysis and analyzed as described above.



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Results

TABLE 1. LIMITS OF DETECTION* FOR UNFILTERED AND FILTERED NTN WI93 BLANKS

Element	*Unfiltered*	*Filtered*	*Element*	*Unfiltered*	*Filtered*	*Element*	*Unfiltered*	*Filtered*
Li	0.029	0.030	**Zn**	0.294	1.05	**Ce**	0.0010	0.0037
Be	0.021	0.018	**As**	0.002	0.002	**Pr**	0.0002	0.0002
B	0.059	0.062	**Br**	0.367	0.402	**Nd**	0.0006	0.0004
Na	2.43	5.82	**Se**	0.721	0.665	**Sm**	0.0003	0.0013
Mg	2.21	1.80	**Rb**	0.003	0.003	**Eu**	0.0004	0.0014
Al	1.50	1.17	**Sr**	0.039	0.030	**Dy**	0.0001	0.0005
P	0.699	0.787	**Y**	0.001	0.001	**Ho**	0.0001	0.0003
S	2.52	2.89	**Zr**	0.001	0.001	**Yb**	0.0002	0.0003
Si	10.9	11.5	**Nb**	0.002	0.006	**Lu**	0.0001	0.0001
Ca	5.80	8.54	**Mo**	0.0015	0.0031	**Hf**	0.0006	0.0005
Sc	0.001	0.001	**Ru**	0.0004	0.0004	**Ta**	0.0018	0.0010
Ti	0.030	0.023	**Rh**	0.0009	0.0004	**W**	0.0017	0.0017
V	0.005	0.005	**Pd**	0.0011	0.0007	**Pt**	0.0030	0.0029
K	1.67	2.07	**Ag**	0.0036	0.0046	**Hg**	0.0045	0.0039
Cr	0.003	0.046	**Cd**	0.0028	0.0015	**Tl**	0.0002	0.0003
Mn	0.041	0.006	**Sn**	0.0061	0.0104	**Pb**	0.0182	0.0012
Fe	0.429	0.130	**Sb**	0.0010	0.0014	**Th**	0.0015	0.0009
Co	0.003	0.002	**Cs**	0.0018	0.0016	**U**	0.0001	0.0001
Ni	0.114	0.100	**Ba**	0.1118	0.0812			
Cu	0.052	0.108	**La**	0.0006	0.0011			

**LOD = Average blank + 3*StDev*

TABLE 2. WI93 PRECIPITATION SAMPLES

Element	*Unfiltered*	±	*Filtered*	±
Be	0.010	0.001	0.005	0.001
P	0.455	0.137	0.239	0.059
S	132	36.3	133	36.5
Ti	0.029	0.011	0.020	0.007
Cr	0.011	0.004	0.027	0.010
Mn	0.086	0.022	0.052	0.008
Fe	1.00	0.271	0.420	0.073
Co	0.001	0.001	0.001	0.001
Ni	0.109	0.021	0.094	0.019
Cu	0.098	0.020	0.216	0.036
Zn	1.231	0.236	1.507	0.287
As	0.040	0.016	0.050	0.019
Br	1.89	0.240	1.85	0.162
Se	0.310	0.086	0.332	0.092
Cd	0.0052	0.0014	0.0051	0.0022
Sb	0.0521	0.0098	0.0510	0.0096
Hg	0.0039	0.0047	0.0034	0.0045
Tl	0.0005	0.0001	0.0005	0.0001
Pb	0.0267	0.0039	0.0138	0.0021
Th	0.0007	0.0001	0.0005	0.0001
U	0.0004	0.0002	0.0003	0.0001

Notes for Table 1. This table presents a summary of the limits of detection for a set of unfiltered (n=11-12) and filtered (n=12) blanks. Values are reported in ug/L (ppb). Each set is a combination of samples collected from both the N-CON and Aerochem collectors. Colors indicate elements of interest, where blue = reported by NTN[2] and orange = Hazardous Air Pollutant (HAP)[3].

Notes for Table 2. This table presents selected elements measured in precipitation samples collected at the WI93 N-CON and Aerochem collectors. Each value is an average of the two collectors. Values are reported in ug/L (ppb). Colors indicate elements of interest as noted in the notes for Table 1. The gray font indicates where the samples are less than the LOD listed in Table 1.

Key Results & Observations

1. There were no statistically significant differences observed between the two collector types (N-CON and Aerochem).
2. Despite exposure to outdoor and indoor environments outside of the clean laboratory during collection and filtration of the samples, average blanks are remarkably low relative to values measured in blank 2% v/v ultrapure nitric acid mixed within the clean lab.
3. Filtration had minor effects on some key elements. For example, Cr and Cu were consistently higher in filtered aliquots, including in the precipitation samples. Pb, on the other hand, was consistently higher in the unfiltered aliquots of both the blanks and precipitation samples.
4. Due to the low blanks, detection of many trace metals of concern to human and environmental health are possible at the ppb or ppt level, and were detectable in the WI93 precipitation samples.
5. Analyses of 20 additional precipitation samples from other NTN sites in the TECL were generally in good agreement with the results measured and reported by NADP, suggesting retroactive analysis of samples for trace metals is a viable option. Large discrepancies were noted for all of the samples for P and for two of the samples for S. Data is available by scanning the QR code.

Conclusions & Future Work

Overall, our results suggest that the NTN network is a promising, largely untapped, resource for tracking trends in and/or acute threats from hazardous trace metals that can be incorporated into precipitation. Future work will seek to further verify these results. This could include tests such as the deployment of spiked, artificial precipitation samples at WI93 to validate recoveries of elements of interest, as well as conducting a blank study at another NTN collection site.

Acknowledgements and Institutions

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Selected References: 1. eCFR Title 40: https://www.ecfr.gov/current/title-40/chapter-I/subchapter-D/part-136/appendix-Appendix%20B%20to%20Part%20136; 2. NADP NTN website: https://nadp.slh.wisc.edu/networks/national-trends-network/; 3. CAA112(b) HAP - Hazardous Air Pollutants: https://cdxapps.epa.gov/oms-substance-registry-services/substance-list-details/165

1. Wisconsin State Laboratory of Hygiene, Environmental Health Division, Madison, WI
   Direct correspondence to the Trace Element Clean Laboratory at WSLH: TECLinfo@slh.wisc.edu
2. National Atmospheric Deposition Program, Wisconsin State Laboratory of Hygiene, Madison, WI
3. Lab Koala-T by Bryce Johnson