

## CHARACTERIZATION OF POLYETHYLENE BAG LINERS IN ACIDIC DEPOSITION SAMPLING

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The New York State Department of Environmental Conservation (NYSDEC) has operated a statewide acid deposition monitoring network since the mid-1980s. The NYSDEC network has collected wet deposition in rural, suburban, and urban locations throughout the state. It also performs the analysis for cations (Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, and Ca<sup>2+</sup>) and anions (F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>2</sub><sup>-</sup>, Br<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and PO<sub>4</sub><sup>3-</sup>) on a weekly basis. This network complements the efforts of the federally-sponsored nationwide National Atmospheric Deposition Program (NADP) network, which began operation in the 1970s and largely focuses on rural areas. Both networks collect and report quality-assured acid deposition data year round, though operational procedures are different.

Unlike the National Atmospheric Deposition Program (NADP), wet deposition samples from the NYSDEC sites are collected in buckets that are lined with polyethylene bags. In the past, concerns have been raised about whether or not these bucket liners introduced contamination. Even though data from the NYSDEC/NADP co-located site at Whiteface Mountain showed good correlation, we felt that this QA study should proceed. Starting in November 2006, as part of the overall network quality assurance plan, the NYSDEC initiated a detailed study to see whether or not the use of these bags introduced contamination in the collection of wet deposition samples. Environment Canada (EC) also uses polyethylene bags in it's Acid Deposition program and provided NYSDEC with 12 bags for comparison. This report summarizes the findings of this study.

## STUDY DETAILS

The goal of this study was to examine if any artifact signal was observed after placing de-ionized (DI) water in NYSDEC bucket liners. The liners in the study were selected somewhat randomly, that is, four bags were taken from near the top of the shipping box and four bags were taken from near the bottom. This was repeated for all of the boxes that were in storage, yielding 30 bags, 100 ml of DI water were added to each bag. The bags were twisted, shaken and sealed and allowed to stand over a period of four days. The water was then analyzed in the same way as actual rain samples. A 10 ml aliquot of water was removed from each bag and filtered. Four ml were used first to wash the filter, then 3 ml were placed into a vial for analysis. Each sample was analyzed for cations and anions using a Dionex Ion Chromatograph. Similar steps were taken in analyzing and characterizing the 12 bags obtained from EC. To create a sample which was more representative of an actual deposition sample and to ensure that the addition of DI water did not introduce any artifact signal, a large amount of a mid-level standard was prepared. Ten of the original 30 bags which had DI water added, had a mid-level cation standard added. The same standard was added to 30 new bags and both sets of bags were analyzed. Similarly, another 10 of the original had the mid-level anion standard added; this same standard was added to 30 new bags. The goal of this exercise was to see if adding DI water had an appreciable effect on a "representative" acid deposition sample.

Table 1. Control/Manufacturing limits for EC liners and NADP buckets

Ion	Environment Canada limits, ionic ppb	NADP limits, ionic ppb
Na <sup>+</sup>	10	7
NH <sub>4</sub> <sup>+</sup>	6	20
K <sup>+</sup>	10	6
$Mg^{2+}$	5	3
Ca <sup>2+</sup>	10	9
F-	N/A	N/A
Cl-	15	6
NO <sub>2</sub> -	N/A	N/A
Br-	N/A	N/A
SO <sub>4</sub> <sup>2-</sup>	15	20
NO <sub>3</sub> -	15	18
PO <sub>4</sub> <sup>3-</sup>	N/A	10

Environment Canada also collects wet deposition samples using similar polyethylene bags. Above are manufacturing limits which EC & NADP define as "clean bags".

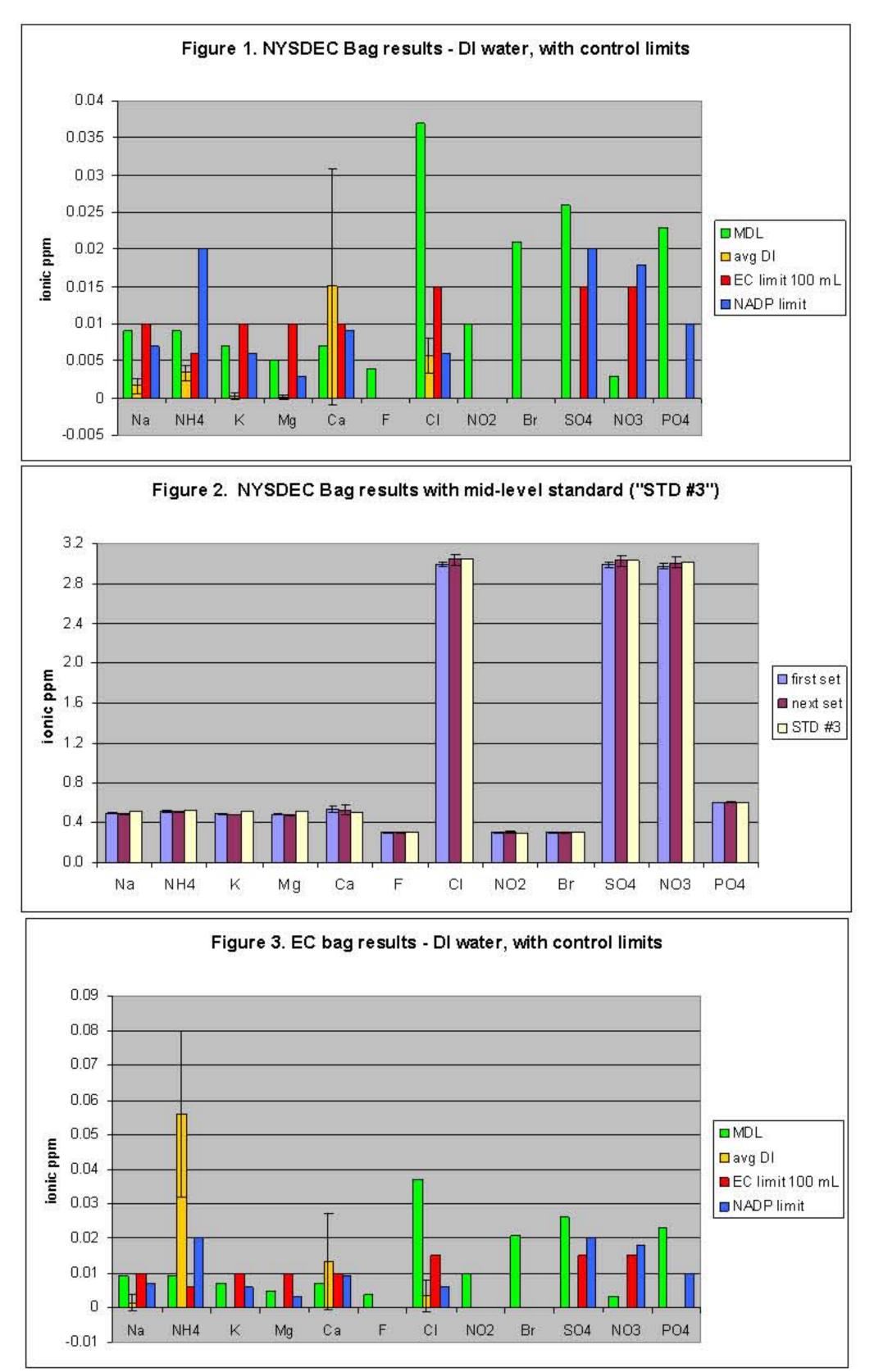


Fig.1 displays the average concentration from the NYSDEC 30 bags w/ DI H<sub>2</sub>O for each cation & anion. For anions only Cl<sup>-</sup> had a detectable signal which on average was 6X < the nominal MDL. For cations, the average Ca<sup>2+</sup> signal was roughly twice the nominal MDL.

Fig. 2 displays results from the mid-level standard analysis. It compares the bags from Fig. 1 with a 2<sup>nd</sup> set of fresh bags. The average difference between the runs was < 2%.

Fig. 3 shows the same information displayed in Fig. 1 for the EC bags. Anion results were essentially the same.  $Ca^{2+}$  was slightly lower and  $NH_4^+$  was substantially higher in the EC bags, > 5x MDL.



## **Summary**

The study has shown that NYSDEC data is valid and unbiased. The polyethylene bucket liners meet both NADP control limits for "clean buckets" and EC manufacture limits for "clean bags" except for Ca<sup>2+</sup>. It should be noted that NYSDEC samples typically are much higher than this potential artifact level of approximately 0.015 ppm.