Reviewer 2

Overview

This work provides insights into using ion exchange resins for precipitation sampling, both in a controlled laboratory setting and field studies. This is interesting and relevant work, as IER are under used and could provide a cheaper more robust alternative for precipitation sampling in a wide variety of environments. The introduction emphasizes the importance of this work well. The laboratory studies highlight the feasibility of this approach for a wide variety of analytes under several conditions that mimic the environment, as well as determine an efficient method for extracting analytes from the resin. The field studies show the application of this technique in practice. However, the field studies do have a limited sample size, which could impact their reliability. I recommend this manuscript for publication in Atmospheric Measurement Techniques, following major revisions. Overall, the statistical analysis of the data is unclear and requires clarity so that readers can be confident in the use of IER for sampling. While the statistical analysis is the major point of concern, please refer to my specific comments below.

We thank the reviewer for the positive evaluation and suggestions for improving the provided statistics: we modified the applied statistics according comments of this reviewer (see below), and others. See for details our replies below.

Specific Comments

Lines 138-142: I think this info regarding stock solutions and concentrations tested for each nutrient would be easier to read as table. Furthermore, ensure that all chemicals have numbers subscripted.

> The subscripts have been adjusted to meet the correct standards. The molecular formula of $Cu(NO_3)2.3H_2O$ has been changed to $Cu(NO_3)2.3H_2O$, and the molecular formula of $Zn(NO_3)2.6H_2O$ has been changed to $Zn(NO_3)2.6H_2O$. Given the density of information in these lines, we agree with the reviewer that presenting the content in a table will enhance readability. The table replacing lines 138-142 is shown below.

Stock solution		Туре	Total	Ca	Cu	Cl	Fe	K	Mg	Mn	Na	PO_4	SO_4	Zn NH ₄	NO_3
Code	Mol		$mL L^{-1}$							um	ol				
Na ₂ SO ₄	0.5	Macro	0.90								450		450		
NaCl	1	Macro	1.40			1400					1400)			
KNO ₃	1	Macro	0.18					180)						180
KH ₂ PO ₄	1	Macro	0.02					20				20			
NH ₄ NO ₃	1	Macro	1.82											1820	1820

Table 1: The throughfall flux used to test the adsorption capacity and recovery efficiency of the ion exchange resin. We used stock solutions with known molarity to make the macro and the micro solution used to drip through the resin. The total volume of the used stock solution (in ml L^{-1}) and the concentration in umol per element are given.

NH ₄ Cl	1	Macro	2.18			2180									2180	
MgSO ₄	1	Macro	0.3						300				300			
CaCl ₂	0.5	Macro	0.8	400		400										
FeCl ₂	0.1	Micro	6.0			600	600									
$Cu(NO_3)_2 \cdot 3H_2O$	0.275	Micro	0.036		9.9											9.9
$Zn(NO_3)_2 \cdot 6H_2O$	0.267	Micro	0.075											20		20
MnSO ₄ ·H ₂ O	0.01	Micro	15.0							150			150			
		•	total	400	9.9	4580	600	200	300	150	1850	20	900	20	4000	2030

2.2 Laboratory Tests: were blanks (water with no nutrients in solution) analyzed for both the adsorption capacity and recovery efficiency test? These should be described somewhere within this section.

- Yes, we had three different types of blanks including a blank for adsorption capacity, a blank for the recovery efficiency test in the laboratory and a blank for the possible field contaminations. Further details on these blanks are given below:
 - Blank for adsorption capacity: during the laboratory tests, we tested the quality of the demineralized water that was used to flush the resin. This water was used to flush 500 grams of resin which we did prior to filling the resin tubes with this resin (lines 112-114). We took the sample from the first two liters which we used to flush this resin, in this sample there was no contamination as elemental concentrations in this sample could not be detected or was more than 10 times lower than the detection limit. As there could not be any element be detected in this blank sample, we are confident that the elements in the leachate of the adsorption test (see row "70% loading" in the revised table 4) are a result of the lower affinity of the resin to adsorb these elements (Na, P and NH₄). We added in the manuscript (lines 163 in the revised version) the following sentence to indicate the existence of this blank: "Furthermore, demineralized water used to clean the resin was taken as a blank sample for the adsorption test".
 - Blanks for recovery efficiency test in the laboratory: these blanks consisted of pure resin that was treated exactly the same way as the resin used for the extraction tests. We included these blanks to remove noise due to sample contamination in the laboratory which might have been caused by the drying process, the extraction of the resin itself or by the measurement of the chemical content of the sample. We added in the manuscript (lines 165-167 in the revised version) the following sentence to indicate the existence of these blanks: "Besides these 36 loaded columns, 2 blanks were included to distinguish between the recovery efficiency of the loaded solution and background contamination out of the resin or contamination caused sample contamination in the laboratory".
 - Field blanks: these blanks were placed in the field both in sun exposed place (representative for the bulk deposition samples) and in a shadowed place (representative for the throughfall samples). These blanks stayed in the field for the same time as the field-test samples and were extracted with the extractant. The field blanks were subject to the lab protocol meaning that these field blanks were extracted with 2M KCl

and with 3.5M HCl following the protocol developed in the lab. These blanks are mentioned in the manuscript both for the field placement (lines 291-292 in the revised version) as well as the laboratory extraction (lines 302-306 of the revised version).

Line 237: Going back to my previous comment, you mention field and lab blanks here. Be sure to include information on how both were prepared in section 2.2.

The general description of the preparation of the columns is in section 2.1. Blank columns were created using the same protocol. To explicitly include this, we added the phrase "(including the blanks)" in line 112 of the revised manuscript. Furthermore, in section 2.2., we now explicitly describe the sampling of the leachate of the washed resin as a blank for the adsorption test (line 182 of the revised manuscript) and the sampling of the blanks used for the recovery efficiency tests (lines 196-198 of the revised manuscript). The field blanks were already described in the manuscript in section 2.3.

Line 265: I am assuming you highlighting data in the "leachate" row of Fig.3, however I think it would be useful to explicitly direct the reader to that portion of the figure.

Your assumption is correct. For clarification, we changed the name "leachate" to 70% loading, and we added the phrase "when loaded up to 70% of the resins exchange capacity" in line 265. We now direct the reader to the relevant part of that table.

Figure 3: Do these represent average values across several trails? Finding a way to include standard deviations for this data, if so. This might help support your claim that certain nutrients had decreased capacity when loading was increased. Were t-tests done (or any statistical analysis) to support that these values are indeed different from each other?

- Yes, the data represent average values. The number of samples for each test is provided in lines 143-155 of the manuscript. To address the confusion around the figure, we replaced it with a table that includes information on the standard error of the mean. For all the tests presented in Table 4, we used a sample size of 3 samples per test. We have now specifically included the sample size in the table header.
- In response to your feedback, we conducted a generalized test per treatment group, as individual element-specific tests were impractical due to consistently low sample sizes and standard errors, resulting in essentially constant data that lacks statistical evaluability. For elements where mean adsorption was less than 100%, we used the Wilcoxon signed rank test to assess the hypothesis of adsorption equality to 100%. Excluding the values equal to 100% was necessary to deal with ties.

Lines 289-290: This sentence is really confusing and I was having a difficult time connecting it to the data presented in Table 3.

We simplified the sentence from "Recovery efficiency of Ca, Cu, Fe, K, Mg, Mn, Na, P, S and Zn following HCl extraction was high (>90%) for Ca, K, Na and Mn, slightly lower (>80%) for Mg, S, Cu and Fe, relatively low for P (40-91%) and very low (6-25%) for Zn (Table 4)" to "The average recovery efficiency following HCl extraction was high (>90%) for Ca, K, Na and Mn, slightly lower (>80%) for Mg, S, Cu and Fe, relatively low for P (40-91%) and very low (6-25%) for Zn (Table 4)". We also rewrote the next sentences for readability.

Line 292: What does 4-2-1M indicate? This needs more description.

We also tested if varying molarities from the extraction fluid would result in a more effective extraction of the resin. The 4-2-1 M means that we first extracted the resin with an 4M HCl extractant of 50mL, followed by a extraction with a 3M HCl extractant of 50mL followed by an extraction with 1M HCl of 50mL. We added the description in the manuscript in lines 201-203 of the revised version: "In one test, we combined multiple molarities of HCl, resulting in an extraction sequence of 50 mL of 4M HCl, followed by 50 mL of 2M HCl, and finally an extraction with 50 mL of 1M HCl (Table 2)". Furthermore, we added an extra explanation to the header of table 2.

Table 3: Is there a way to incorporate the statistics presented in Table S3 into this main table?

We chose to add the statistics shown in Table S3 to the newly added Tables S6-S8 for better readability. The post-hoc test of each interaction results in different groups, making it challenging to include the complete statistics correctly and interpretably in Table 3 (now Table 5 in the revised manuscript). Even including the general ANOVA results (presented in Table S3) in Table 3 (Table 5 in the revised manuscript) is challenging and, in our opinion, would not enhance readability.

Table 3: What does the column labeled "Mol" represent? I'm seeing here the dashed values again (ex: 1-2). This needs some clarity. In addition, is the Avg column necessary? This accounts for some poor recoveries for some species and artificially makes the method look reasonable. I think this will allow readers to justify using a less than optimal extraction technique.

- Mol was used as an abbreviation of the molarities. We added this abbreviation to the table header.
- In the revised version of the manuscript, we choose to remove the test showing 1-2M extraction (which actually meant that we first extracted the sample with 50 mL 1M HCl followed by 50 mL of 2M HCl) because we lacked replication. Fur the 4-2-1 M test we added the descriptions as explained in the response to your previous comment.
- The columns providing the arithmetic averages are indeed not necessary, but we believe they give a good overview of the overall performance of the different extractions, guiding the reader toward the extraction method that might be best for their own research. Furthermore, the average recoveries of the elements across different tests indicate how easily each element can be extracted from the ion exchange resin. For example, if researchers are interested in using the IER method for Zn, this information directly warns them that Zn extraction from the resin is problematic.

Figure 4: Do the percentages indicate canopy cover? Please provide that detail in the figure caption.

Yes, these percentages indeed reflected the canopy cover. However, in response to the comment, we decided to move away from the artificial groups based on canopy cover and instead used the funnel positions in the statistics and in the figure. In the new Figure 4 of the revised manuscript, we refer to throughfall and bulk deposition, avoiding the confusion caused by the canopy cover percentages.

Table 5: Either ensure that the variations in the intercept and slope are on the same line or create a separate row title for these values. It's challenging to read.

> We added a separate row title, namely s.e., in front of every row containing the standard errors of the mean.

Line 324: Why was an ANOVA done of the comparison of IER method to water-method if there were only two categories? If I'm missing additional categories, then this needs emphasized.

Solution of the treatment plot where the samples were placed as a categorical variable. This variable included the treatments control (high canopy cover) till clearcut (no canopy cover). For details on these categories see table 2. However, upon reflection, we realized our main focus was comparing the waterbased deposition method with the ion exchange resin method in forest gaps (bulk deposition) and beneath the canopy (throughfall). In line with this, we revised the field study statistics to exclude the treatments (control, high-thinning, shelterwood, and clearcut), focusing instead on the funnel's position (throughfall or bulk deposition). We ran linear models for all elements with the funnel position as a random structure. These models were constructed as $yij=\beta 0+\beta 1xij+uj+\epsilon ij$, where *y* is the result using the IER method, *x* is the result using the original method, *u* represents the random structure, and ϵ the residuals. The random structure was included only if it improved model performance by $\Delta 2$, following Zuur et al. (2009). None of the models showed improved performance with the funnel position as a random variable. The results are visualized in the revised Figure 4. Line 324 and other lines were we referred to the canopy cover, or canopy openness plots were revisited and rewritten.

Line 325: What were the treatments analyzed using the Tukey's test? The lines surrounding this sentence could use additional clarification so the reader understands what is being compared.

In this version, we excluded the canopy openness treatments because they were not our primary focus. Line 325, which addressed the canopy openness treatments in the original manuscript, has been removed. Instead, results are added comparing the relationship between the IER-method and the original water method for bulk deposition and throughfall samples.

Line 326: I'm not sure how Figure S1 is displaying statistical data.

Figure S1 previously presented the data without highlighting between-group significances, which was an oversight. Following the revised statistical approach mentioned in our previous response, we updated Figure S1 to show the differences between bulk deposition and throughfall. As incorporating these differences did not enhance the linear models for the relationship between the IER samples and the common water samples (as shown in Figure 4 and Table 6 of the revised version), there were no statistical differences to report.

Line 326: Sometimes the authors refer to canopy openness in terms of percentages and other times using words like "clear cut". Using consistent terminology would be useful if these are supposed to represent the same samples.

In the revised version, we excluded the canopy openness treatments because they were not our primary focus. Line 326, which addressed the canopy openness treatments like a clearcut treatment has been removed. Instead, a discussion is added comparing the relationship between the IER-method and the original water method for bulk deposition and throughfall samples.

Line 328: Is these supposed to refer the reader to Figure S4? If not, I'm missing how Fig. 4 connects to your statement.

This statement has been adapted to compare the differences between bulk deposition and throughfall which is now clearly shown in the revised version of figure 4.

Line 335: How was the loading capacity for the resin determined? If obtained from the supplier this might be pertinent information to include in the methods section (either directly in the text or as a supplemental table).

> Yes, the loading (exchange) capacity of the resin was obtained from the manufacturer. We included this information in the method, in section 2.2 (lines 178-179 of the revised manuscript): "The exchange capacity of the resin as reported by the manufacturer was ≥ 0.6 mol L⁻¹ for the anion bed and ≥ 0.7 mol L⁻¹ for the cation bed".

Line 339: How did you determine this 70% if you didn't test below 100%? This statement is confusing.

- We loaded the resin up to 70% of the exchange capacity as reported by the manufacturer (see response to the previous comment). To specify this in this line, we added the text to: "First, the adsorption capacity of the IER, when loaded up to 70% of its capacity as reported by the manufacturer, was generally high".
- We did not make a statement that we didn't test the adsorption capacity of the IER below 100%. We tested this by loading the resin to 70% of it's capacity. However, to avoid this confusion, we changed original figure 3 into a table and replaced the term 'leachate' to '70% loading'.

Section 4.1 Adsorption capacity: In general, how can there still be 100% adsorption if the resin is loaded above its capacity? Is this trying to emphasize that the determined capacity is an underestimation?

- Overloading the cation and/or anion exchange capacity did not result in 100% adsorption capacity for all elements. We observed that only certain elements, which strongly bind to the resin, achieved (nearly) 100% adsorption capacity when the resin was overloaded beyond its exchange capacity. This suggests that the resin has a high affinity for these specific elements. In contrast, other elements, which have lower affinity for the resin, showed lower adsorption capacity under similar conditions. With other words, when the resin is loaded beyond its capacity, it releases loosely attached elements (like K, Na, NH4 and NO3) while still adsorbing more strongly binding elements (like Ca and Fe).
- Furthermore, the capacity reported by the manufacturer was indeed a slight underestimation of the actual exchange capacity. However, we decided not to include these details in the manuscript as they do not add significant value to the main message of this work.

Line 390: Is the highest recovery for each element bolded in Table 3. If may be useful to indicate that and provide an explanation for why values over 100 were not considered.

Not the highest but the value closest to 100%. The purpose of the recovery efficiency tests was to find the extraction that results in the recovery efficiency that was closest to 100%. Ideally this would have been the same as the highest recovery efficiency, however, we clearly had a Ca contamination in some of the samples resulting in recovery efficiencies above 100% which should have been impossible. This was explained in the header of table 3 (table 5 in the revised version): "Recovery percentages per element closest to 100 are indicated in bold".

Line 395: I am not sure how this statement related to the data provided in Table S3. Provide some clarity here.

We changed the reference to the tables S5 and S7. These supplementary tables are added in the revised version of the manuscript and contain the average data and the results of the Tukey's post-hoc tests.

Literature

Zuur, A., Ieno, E.N., Walker, N., Saveliev, A.A., Smith, G.M., 2009. Mixed effects models and extensions in ecology with R. Springer Science & Business Media.