

Reviewer 3

I would like to congratulate the authors for a very thorough work. A multitude of variables have been taken into account and the experimental and field design are excellent. It is a very necessary work from the point of view of forest monitoring, since the use of methodologies based on ion exchange resins is not widespread despite being used for decades already, and it could be because of the scarcity of methodological approaches such as the one here it is presented.

- We would like to thank the reviewer for the kind words. We fully agree with the reviewer's opinion that the ion exchange resin method has the potential to become a widely adopted technique if thoroughly tested under various conditions, such as different climatic regions, sampler types, field durations, and more. When we initiated the testing of this method, we recognized the scarcity of studies on how to test the resin and assess its reliability. This gap in research motivated us to write this manuscript, aiming to address these issues comprehensively.

I would like to recommend the publication of this manuscript, but not before suggesting some minor changes and raising some questions:

Line 108: First, the resin columns were cleaned using 0.2M HCl and demineralized water - Please add some few words to fully explain the cleaning method. Demineralized water was used for cleaning or for rinsing (as stated in the next sentence)?

- We used 0.2M HCl to clean the empty resin columns, removing weakly attached chemicals from the materials. These chemicals have the potential to transfer from the column walls to the resin beads during subsequent use, introducing contaminants into both laboratory and field tests. Since we utilized newly constructed resin columns, there was no need to address residuals from previous measurement sets. However, we recommend washing the columns again post-use. We added the reason why we cleaned the resin columns to the manuscript.
- After cleaning the empty resin columns with the 0.2M HCl solution, we ensured the removal of any remaining HCl. The reason why we cleaned the columns was added to the revised manuscript. Residuals of this fluid can be adsorbed by the resin, thus reducing its capacity for both field and lab tests. Although this reduction in exchange capacity due to residual absorption is likely minimal, we aimed to prevent unnecessary pollution. Therefore, we rinsed the resin columns three times with demineralized water, following standard laboratory cleaning procedures. Upon the third rinse with demineralized water, we sampled the columns for chemical analysis of HCl concentration, which was found to be below the detection limit. This confirmed that the columns were thoroughly cleaned. We omitted this additional verification from the manuscript for readability.
- We added the reason why we washed the empty columns with 0.2M HCl (to remove weakly attached chemicals from the column walls) and the reason why we rinsed the empty columns with demineralized water (to ensure the removal of any remaining HCl) to the manuscript text.

Line 136: Thereafter, the deposition of the summer was multiplied by 2, which is an average correction factor to convert bulk deposition to throughfall (Table S1). - It is unclear how 2 is an average of what it is shown in Table S1. Moreover, Table S1 presents factors to convert bulk to total deposition, but in the text it is stated that the factor is used to convert to throughfall deposition values.

- This is indeed unclear. We have now changed the header of table S1 to “Ratios factor of throughfall (mostly also including stemflow, SF) to bulk deposition reported in literature.
- In the manuscript text, we added a note that the factor of 2 is primarily based on the tracer Na. The other elements showed high variation in their throughfall to bulk deposition ratios, but generally, a factor of 2 is applicable for most elements. The revised Table S1 now shows the throughfall to bulk deposition data, replacing the original table.

Line 151: Three loaded resin columns were thereafter flushed with demineralized water to test the stability of the adsorption. - Which three resin columns?

- These were three of the columns that were loaded up to 70% of the resin’s capacity. These columns were not used in the further lab testing, so no extraction test was performed on these columns. To clarify this, the sentence in the manuscript is changed to ‘Three resin columns loaded up to 70% of the resin’s exchange capacity were thereafter flushed with demineralized water to test the stability of the adsorption.’

Line 152: Both the samples of the leachate and the demineralized water used to wash the loaded columns, were analyzed for N-NH₄, and N-NO₂ + N-NO₃ content using a Segmented Flow Analyzer (SFA type 4000, Skalar Analytical B.V., the Netherlands), and the content of Ca, Cu, Fe, Mg, Mn, Na, total-P, S and Zn using the ICP-AES (Thermo-Scientific iCAP 6500 DUO, USA). - This sentence should be moved to end of the next paragraph, adding the extracted solution to the list of samples analysed.

- The sentence was relocated to the end of the preceding paragraph, with additional details included regarding the analysis of the extracted solution. Here's the refined version:
- "The samples of the leachate of the micro- and microfluid to load the columns, of the demineralized water to wash the loaded columns, and the samples of the extraction of the elements from the columns were analyzed. Specifically, N-NH₄ and N-NO₂ + N-NO₃ content were determined using a Segmented Flow Analyzer (SFA type 4000, Skalar Analytical B.V., the Netherlands), while the content of Ca, Cu, Fe, Mg, Mn, Na, total-P, S, and Zn was analyzed using the ICP-AES (Thermo-Scientific iCAP 6500 DUO, USA)."
- By integrating this information into the next paragraph, the original sentence at line 152 was removed.

Table S2: Please consider changing macro- and microfluid by "macro- and micro elements".

- We have updated the terminology in Table S2 from 'macro- and microfluid' to 'macro- and micro solution', which we believe more accurately represents the entire solution containing these elements, not just the elements themselves. We trust this adjustment aligns with your expectations and is suitable for the manuscript.

Table 1: Please consider changing here (and in the rest of the manuscript) extraction fluid by "extraction solution".

- We have changed the phrase "extraction fluid" to "extraction solution" throughout the manuscript, as per your suggestion.

Table 2: The columns of Paired samples (Bulk deposition and Throughfall) seem to be switched.

- You are correct. I have switched the column names so that the correct names are now above the appropriate columns.

Line 169: The extraction method was either drip, in which the extractant was slowly dripped over the resin, or a shake drip combination in which the resin was shaken in 50 mL of the extractant for 1 hour and the remaining extractant was dripped over the resin. - For the shake-drip method, how the resin was shaken? was the resin put into the column again after shaken it in a plate? Please, clarify.

- The resin was shaken using a GLF 3015 platform shaker at a speed of 120 movements per minute. To facilitate the shaking process, half of the extraction fluid was added to a clean 50 ml centrifuge tube (item No 210261, Greiner bio-one) with a blue screw cap to prevent sample loss. After shaking, the resin was returned to the original column, and the extractant in which the resin was shaken was allowed to drain from the resin and captured. This involved allowing the shaken extraction solution to drip out of the resin. Subsequently, the remaining half of the extraction fluid was allowed to drip over the resin. These details have been added to the manuscript for clarification.

Line 226: the resin columns were collected on January 14th, 2020, dried together with lab blanks to a constant weight at 28°C and subsamples were taken for 2M KCl extraction followed by N-NH₄ and NNO₂ + N-NO₃ content analysis using a Segmented Flow Analyzer (SFA 4000, Skalar Analytical B.V., the Netherlands) and for 3.5M HCl extraction followed by Ca, Cu, Fe, Mg, Mn, Na, P, S and Zn content analysis using the ICP-AES. - Why this methodology (drying and concentration of extraction solution) was selected for the field comparison? Also, what volume of extraction solution was used?

- We chose to dry the resin because we needed at least three samples per resin column: one for KCl extraction to measure nitrogen components, one for HCl extraction to measure other elements, and one as a spare in case of processing errors or contamination. When necessary, we used these spare samples to ensure the best data quality. Splitting the sample into three parts without drying would be problematic due to the varying wetness both within and between samples, which could lead to significant uncertainties.
- We choose to dry before extraction in the lab instead of after extraction to control the amount of resin compared to the amount of the extractant. This standardization needed the dry resin, which was tested and shown that drying the resin improved the extraction efficiency. During the extraction of the field samples, we used a volume of 100 mL, which was tested and validated in the laboratory.
- We selected 2M KCl and 3.5M HCl for extraction because these methods provided reliable results using the shake method. For KCl we used the 2M extractant as the effect of 1M on dry samples was not yet tested and we choose for shake-drip as this method was faster. For the HCl extraction, while other molarities appeared

to yield higher recovery efficiencies, each had its own pitfalls. For instance, the drip extraction on dried resin using 2M HCl generally resulted in a high overall recovery efficiency (94%, Table 3), but the recovery of phosphorus (P) was only 40%, making it unsuitable for P extraction. The shake-drip extraction method with 2M HCl showed values above 100%, indicating possible contamination and rendering this extractant unreliable, as the recovery percentages could not be accurate. We chose the 3.5M HCl extractant because it offered relatively high P recovery and overall reasonable recovery of other elements. In situations where P extraction is not needed, other methods may perform better, such as the 2M dry weight drip or the 4-2-1M dry weight drip method. To avoid unclarities in the manuscript, we added this information in line 230.

Line 265: The adsorption capacity was not influenced by the flushing of the resin with demineralized water. - I believe that this result corresponds to the text named before as “stability of absorption”. It is not well explained in the methodology section and some more words to clarify the implications of the results could be added here or in the discussion.

- Yes, that is correct. To clarify why we tested this stability, we added a phrase to the methods section: “This stability needed to be tested to check if the ion exchange resin would release nutrients when exposed to (very) wet conditions.” Furthermore, we revised the sentence in question to: “The adsorption capacity was not influenced by the flushing of the resin with demineralized water, indicating that the elements, once adsorbed, are not released through an excess of water such as heavy precipitation.” Finally, in the discussion, we revised the sentence: “We show that IER is also able to adsorb above 99% for a range of other elements including the base cations and some micronutrients” to: “We show that IER is also able to adsorb above 99% for a range of other elements, including the base cations and some micronutrients, and that the adsorbed elements are not released in response to an excess of water such as heavy precipitation,” indicating the implications of this test.

Line 272: Elemental adsorption within the resins exchange capacity was thus close to 100% for all elements except P which was underestimated under extreme conditions. - Please, consider adding to the sentence the following (or a similar one) particularization: “under the different simulated environmental condition”.

- In response to your comment, we revised the sentence to: "Elemental adsorption within the resin's exchange capacity was thus close to 100% for all elements when the resin was used within its capacity, except for P, which was underestimated under the different simulated environmental conditions." This adjustment moves away from the term "extreme conditions" and accurately reflects the specific laboratory conditions that were tested.

Line 291: The average recovery efficiency was highest (90-100%) following either 2M HCl extraction or 4-2-1M HCl extraction. - The average here is per element or per extraction combination. Looking at the table it is not clear where this range is extracted from. P is not this range, neither FW method is. It is possible that it refers only to DW method per extraction combination? Please, clarify.

- There were two factors causing the indistinctness in this sentence. First, we forgot to state that this referred to the dried resin and second the use of a range can be misleading here, as we only refer to 3 values shown in

the column Avg in table 3. For clarification we changed the sentence to “The highest average recovery efficiencies were achieved with dried resin using either 2M HCl extraction or 4-2-1M HCl extraction. Specifically, the 2M HCl methods yielded average recovery efficiencies of 94% (drip) and 100% (shake-drip), while the 4-2-1M HCl method on dried resin achieved 90% recovery efficiency.”

Table 5: Please consider adding any error- or bias indicator, such as mean normalized error or/and mean normalized bias. Moreover, the acronym ORG is not explained here and it is missing from the rest of the text.

- We added the explanation of the ORG abbreviation in the header of Table 5. This abbreviation referred to the commonly used method for bulk and throughfall deposition. The first line of the table description is now as follows: “Regression Coefficients (Intercept and Slope \pm s.e.) and R^2 of models for the relation between the IER Method and the commonly used method, including correction for blanks and lab recovery (n = 18)”
- We added the mean absolute error to table 5. This mean absolute error of the regression model was calculated as: $MAE = (1/n) * \sum |y_i - x_i|$, where Y_i indicates that i^{th} observed value, X_i indicates that i^{th} predicted value and N indicates the total number of observations

Line 335: First, the adsorption capacity of the IER when loaded within its capacity was generally high. - Consider clarifying here that the value was 70% of its capacity, as it is done at the beginning of the next paragraph.

- In line with your remark, I have revised the sentence to: " First, the adsorption capacity of the IER, when loaded up to 70% of its capacity as reported by the manufacturer, was generally high".

Line 440: The lower deposition estimates of P can be caused by a better adsorption of inorganic P compared to organic P to the resin. - Have you consider measuring PO₄³⁻ in addition to P? Could it be a further-research objective?

- Yes, we considered measuring PO₄³⁻ in addition to total P, but our attempts to successfully extract PO₄³⁻ were unsuccessful. Following standard lab protocols at the CBLB laboratory, we measured PO₄³⁻ concentration using the Segmented Flow Analyzer (SFA 4000, Skalar Analytical B.V., the Netherlands), the same device used for measuring N-NH₄⁺ and N-NO₃⁻ concentrations. While the device works well with salty solutions, it has issues with acidic solutions, limiting the extractants we could use for measuring PO₄³⁻.
- We tried extracting PO₄³⁻ using 2M KCl, which resulted in an average recovery of only 8% (n = 4). Due to this very low recovery rate, we focused on optimizing total P extraction with HCl, as presented in this paper, and did not pursue further optimization of PO₄³⁻ extraction. Optimizing PO₄³⁻ extraction remains a further-research objective, with several potential extractants still to be tested for better recovery rates.
- We added this to the discussion reflecting on the adsorption of inorganic P and organic P and the knowledge gap due to the problems with PO₄³⁻ extraction.

Line 460: Our results even imply a higher reliability of the IER-method than the water method since uncertainties related to biological reactions and the detection limit for lab measurements could be removed. - I strongly recommend adding a clarification to this sentence, such as “under certain circumstances”. In the field work of the present study, the IER funnels were cleaned weekly (if contaminated), which is something that cannot occur when collectors are only

visited seasonally (or longer). Take into account that IER method is intended also for avoiding frequent visits to field, e.g. in locations with difficult access.

- We added this clarification in the sentence and added two sentences looking into the contamination issue. Our conclusion is now rewritten to: “Our results even imply a higher reliability of the IER-method than the water method under certain circumstances since uncertainties related to biological reactions and the detection limit for lab measurements could be removed. However, possible contamination of the IER collectors due to factors such as bird feces or other animal disturbances is a point of concern, as long field exposure increases the risk of contamination. It is therefore recommended to increase the number of samplers when using the IER method. We conclude that IER is a powerful tool for the monitoring the element input by bulk deposition and throughfall for of a broad range of elements, across a broad range of environmental conditions” . We added the sentences between ‘However’ and ‘using the IER method’.

Finally, a common concern in the use of IER is the pH of the resultant extracted solution. This can pose a problem for the analysis of some elements or their conservation in the sample. Did you perform a pH test in the extracted samples? Do you have any comment on this?

- We did not perform pH tests on the extracted samples in this study. However, we acknowledge that the pH of the resultant extracted solution is a significant consideration in ion exchange resin (IER) applications. To stabilize the samples prior to chemical analysis we diluted the KCl sample 4 times, reducing the molarity to 0.5M. The pH of the HCl extractions were likely highly acidic. A 1M HCl solution has a pH of 0, while the pH of HCl solutions with higher molarities become negative. The extracted elements from the resin will increase this pH but we can assume that the pH was still very acidic.