Testing Ion Exchange Resin for quantifying bulk and throughfall deposition of macro and micro-elements on forests

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Abstract. Atmospheric deposition is a major nutrient influx in ecosystems and high anthropogenic deposition may disrupt ecosystem functioning. Quantification of the deposition flux is required to understand the impact of such anthropogenic pollution. However, current methods to measure nutrient deposition are costly, labor intensive and potentially inaccurate.

Ion Exchange Resin (IER) appears a promising cost-and labor-effective method. The IER-method is potentially suited for deposition measurements on coarse time scales and for areas with little rainfall and/or low elemental concentrations. The accuracy of the IER-method is, however, hardly classified beyond nitrogen. We tested the IER-method for bulk deposition and throughfall measurements of macro and micro-elements, assessing resin adsorption capacity, recovery efficiency, and field behavior.

We show that IER is able to adsorb 100% of Ca, Cu, Fe, K, Mg, Mn, P, S, Zn and NO_3 and >96% of P and Na. Loading the resin beyond the capacity resulted mainly in losses of Na, P, NH_4 while losses of Ca, Cu, Fe, Mg, Mn and Zn were hardly detected. Heat (40°C), drought and frost (-15°C) reduced the adsorption of P by 25%. Recovery was close to 100% for NH_4 and NO_3 using KCl (1 or 2M) while high (83-93%) recoveries of Ca, Cu, Fe, K, Mg, Mn and S were found using HCl as an extractant (2-4M). We found good agreement between the conventional and the IER-method for field conditions.

Overall, IER is a powerful tool for the measurement of atmospheric deposition of a broad range of elements as the measurements showed high accuracy. The IER-method has therefore the potential to expand current monitoring networks and increase the number of sampling sites.

1   Introduction

Atmospheric deposition is a major nutrient influx in many ecosystems and therefore crucial for ecosystem functioning (Van Langenhove et al., 2020). However, due to anthropogenic pollution, atmospheric deposition can potentially disrupt ecosystem

nutrient balances, leading to exceedance of critical deposition thresholds of for example nitrogen which can in turn degrade ecosystem functioning (Rabalais, 2002; de Vries et al., 2011). Such degradation of ecosystems involves accelerated soil acidification and reduced availability of critical soil nutrients, such as base cations, which has detrimental impacts on biodiversity and water quality (Houdijk et al., 1993; Johansson et al., 2001; Stevens et al., 2004; Bowman et al., 2008; Horswill
35   et al., 2008; Solberg et al., 2009; de Vries et al., 2014; Lu et al., 2014). Atmospheric deposition is therefore of major importance to many ecosystems and monitoring deposition is necessary for policy, management, and conservation.

Measurements of atmospheric deposition are, however, costly and labor intensive. Direct measurements of dry deposition (i.e. input of elements as airborne particles) and wet-only deposition (i.e. input of elements via precipitation) (Lovett and Reiners, 1986; Balestrini et al., 2007) are scarce and current technology limits widespread measurements. For forests, the common
40   method to assess total deposition (i.e., wet and dry deposition combined) is the collection of precipitation below forests, called throughfall, in collection devices of various shapes and sizes, while accounting for canopy exchange (Draaijers et al., 1996; Thimonier, 1998), which is based on the additional measurement of precipitation outside the forest, known as bulk deposition. The combined measurement of nutrient inputs in precipitation below and outside forests, further called in this paper the bulk deposition method, is readopted in many monitoring networks (i.e. ICP forest network (Bleeker et al., 2003; de Vries et al.,
45   2003; De Vries et al., 2007), the DONAIRE network (Pey et al., 2020) and the nationwide monitoring network in China (Xu et al., 2019)). However, the use of bulk deposition measurements requires frequent (up to weekly) sampling as ammonium in the collected rainwater may relative rapidly be transformed to nitrate by nitrification, with the speed being dependent on local weather conditions (Nicholas Clarke and König, 2016). The high sampling frequency and the high cost of traveling and laboratory analysis, limits the spatial and temporal scales at which this method can be applied. The alternative is larger
50   sampling intervals but this may cause inaccurate assessment of the input, especially of ammonium versus nitrate. An adequate assessment of both N compounds is especially crucial in regions where the allocation of N sources is highly sensitive (ammonium being caused by NH3 emissions from agriculture and nitrate from NOx emissions by traffic and industry). Better alternatives are needed to measure deposition efficiently in the field, improve the reliability of the measurements, reduce sampling effort and costs, and thus allow for more effective large-scale deposition monitoring programs.

55   The Ion Exchange Resin method (IER) was previously developed to measure bulk deposition at large spatial and temporal scales, but use of the method is yet limited to remote areas (Brumbaugh et al., 2016) the monitoring network of California (Fenn et al., 2018) or case studies (Clow et al., 2015; Garcia-Gomez et al., 2016; Hoffman et al., 2019). Wide-spread application of the IER-method is promising as the method allows to measure the accumulated deposition over long time periods (up to a year), which strongly reduces both the sampling effort in the field and the number of lab analysis, leading to major
60   cost savings (Fenn and Poth, 2004; Kohler et al., 2012). Furthermore, the method is more reliable for nitrogen as the resin inhibits mineralization, nitrification and denitrification as affected by local weather conditions (Fenn and Poth, 2004; Kohler et al., 2012). Finally, the IER-method is able to measure the deposition in areas with low rainfall or low elemental concentrations, avoiding problems with detection limit and minimal sample size required in the bulk deposition method (Kohler et al., 2012). Because of these advantages, the IER-method is already more commonly used in other research fields

65   ranging from analysis of available nutrients in soil water fluxes to purification of waste-water (Sibbesen, 1977; Binkley and Matson, 1983; Crabtree and Kirkby, 1985; Rengaraj et al., 2001; Verbych et al., 2005; Risch et al., 2020).

The IER-method is most commonly used for NH_4 and NO_3 measurements (Fenn et al., 2002; Fenn and Poth, 2004; Fang et al., 2011; Kohler et al., 2012; Clow et al., 2015; Garcia-Gomez et al., 2016; Hoffman et al., 2019), but few studies reported measurements of other elements (e.g. S, K, Ca, Mg, Na and Cl) (Van Dam et al., 1987; Simkin et al., 2004; Fenn et al., 2018).

70   The applicability of the method to measure a broad range of elements depends on the performance of the resin, measured as the adsorption capacity (percentage of the total element flux bound to the resin) and the recovery efficiency of elements (percentage of the total element flux recovered from the resin) (Garcia-Gomez et al., 2016). Often though the adsorption capacity and recovery efficiencies are not reported (Fenn and Poth, 2004; Boutin et al., 2015; Fenn et al., 2015; Risch et al., 2020). Studies reporting the adsorption capacity (Simkin et al., 2004; Fang et al., 2011; Garcia-Gomez et al., 2016) describe

75   only the adsorption of a limited number of elements under laboratory conditions. Recovery efficiency under laboratory conditions is more often reported, with in general high recovery efficiencies (87-100%) although the recovery of some macro elements (i.e. Ca and Mg) was below 50% (Simkin et al., 2004; Fang et al., 2011; Kohler et al., 2012; Clow et al., 2015; Wieder et al., 2016; Cerón et al., 2017). Despite the promising applicability, the adequacy of the IER-method to derive bulk deposition and throughfall under field conditions is hardly tested. The limited information on adsorption capacity combined with bad

80   recoveries for some elements (i.e., Ca, Mg, Fe and Al) potentially limits the use of the IER-method for bulk deposition measurements.

The adsorption capacity and the recovery efficiency can be influenced by environmental field conditions like drought, frost or high temperatures (Qian and Schoenau, 2002; Bayar et al., 2012). However, there is hardly any study testing the influence of environmental field conditions on both the adsorption capacity and the recovery efficiency of the resin. Furthermore, most

85   tests refer to bulk deposition, whereas atmospheric deposition on forest is also measured as throughfall underneath vegetation canopies. Dissolved organic substances are higher in throughfall than in bulk deposition for which the adsorption capacity of the resin is lower (Langlois et al., 2003). Overall, recovery rates from resin exposed to environmental field conditions appear to be lower, urging the need for better evaluation of IER performance under field conditions (Krupa and Legge, 2000; Brumbaugh et al., 2016). Therefore, new tests are necessary to evaluate the effect of environmental conditions and organically-

90   rich throughfall on the elemental recovery from the resin.

The recovery efficiency can be optimized by the use of different extraction methods. An often used extraction method is 2M KCl for nitrogen extraction (Fenn et al., 2002; Garcia-Gomez et al., 2016; Hoffman et al., 2019), but also combinations of either KI, HNO_3, NaCl, H_2SO_4 and HCl were used (Van Dam et al., 1991; Kohler et al., 2012; Brumbaugh et al., 2016; Fenn et al., 2018). The KCl extraction method and the KI extraction method do not allow measurements of K deposition and are, as

95   high dissolved salt solutions, problematic for measurements using inductively coupled plasma-atomic emission spectrometers (ICP-AES) (Hislop and Hornbeck, 2002; Brumbaugh et al., 2016). New tests are therefore needed to increase the recovery efficiency allowing to measure a broad range of elements including all macronutrients and micronutrients.

In this study we aim to test the capacity of IER as a method to quantify atmospheric deposition for a broad range of macro- and micro-elements, comparing results under laboratory and field conditions and in the latter case comparing bulk deposition and throughfall. We first tested the method under controlled laboratory conditions to indicate efficient resin volumes and to assess adsorption capacities and recovery efficiencies. Next, the behavior of the IER-method was tested under field conditions covering a gradient from closed forests to open areas to account for the effect of dissolved organic substances on the performance of the resin columns. From this, we provide different methodological protocols with accuracies for detecting different macro- and micro elements under field conditions, including forests.

2   Methods

2.1   Preparation of the resin columns

We prepared 45 resin columns for the laboratory tests of elemental adsorption and recovery, followed by the preparation of 30 columns for the field test of the IER-method. First, the resin columns were cleaned using 0.2M HCl and demineralized water. Then, the cleaned and dried resin columns were washed three times with demineralized water in the laboratory prior to filling the column with IER. To fill the columns, a plug of clean polyester fiber was placed inside the resin column and pushed to the bottom. A cleaned cap was screwed loosely at the bottom of the resin column, stabilizing the polyester plug. The resin column was placed vertically above a container to collect the reagents. The ion exchange resin (Amberlite IRN 150, a 1:1 mixture of H^+ and OH^-) was washed with 8L demineralized water in batches of 500g of resin to remove small particles within the resin and to remove the resins smell which could attract animals. All liquids were drained from the resin using a vacuum pump, and for each resin column 9.8g of resin was weighted out and poured in the resin column using a pipette with demineralized water. When excess water had passed through, a second plug of polyester fiber was placed on top of the resin and both sides of the column were screwed tightly with cleaned caps. A schematic overview of these steps is in figure 1.
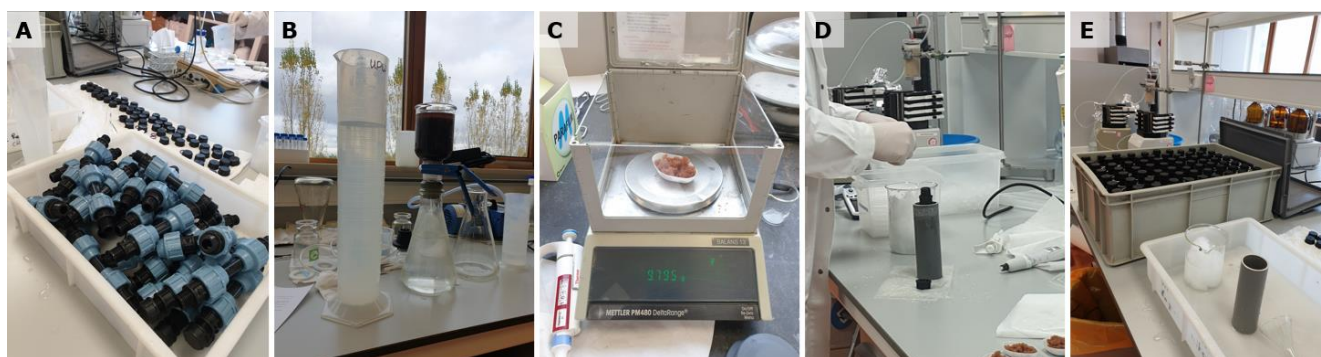
Figure 1: Preparation of the resin columns. A: Cleaned resin columns prior to filling with IER. B: cleaning of the Amberlite IRN-150 exchange resin using a vacuum pump. C: Weighing the resin prior to filling the resin column. D: Resin column stabilized in a holder during filling with resin. E: Overview of filled resin columns with the resin column stabilizer and the polyester plugs shown in the front.

2.2 Laboratory tests

The adsorption capacity and recovery efficiency of the IER (Amberlite IRN 150 H$^+$ and OH$^-$ form) was tested at the Soil Chemistry Laboratory (CBLB), Wageningen University. First, based on existing deposition data (RIVM, 2015), we estimated the bulk deposition amounts (kg ha^{-1}) for different elements, and then used those to determine the needed molarity of the solution that was used to test the adsorption capacity of the resin. Both the adsorption capacity and recovery efficiency were subsequently tested for annual maximum bulk deposition rates across the Netherlands of the following elements: PO_4^{2-}, SO_4^{2-}, $N-NO_2^- + N-NO_3^-$, $N-NH_4^+$, Ca^{2+}, Mg^{2+}, K^+, Na^+, Fe^{2+}, Mn^{2+}, Cu^{2+} and Zn^{2+}.

To estimate the maximum bulk deposition values, the monthly measurements of existing bulk deposition data of representative stations (umol l^{-1}) (RIVM, 2015), were summed to seasonal concentrations for the funnel surface and the stations were selected with the highest seasonal deposition, occurring during summer, for both macro- and micronutrients, based on the total molarity of the rainwater. Thereafter, the deposition of the summer was multiplied by 2, which is an average correction factor to convert bulk deposition to throughfall (Table S1). The concentration of this throughfall flux, multiplied by 4 (assumed that the summer values are representative of the entire year, which is a precautionary approach), was dissolved in a 1 L solution separately for macro and micronutrients using stock solutions of Na_2SO_4, NaCl, KNO_3, KH_2PO_4, NH_4NO_3, NH_4Cl, $MgSO_4$, $CaCl_2$ for the macronutrient solution and using stock solutions of $FeCl_2$, $Cu(NO_3)2.3H_2O$, $Zn(NO_3)2.6H_2O$ and $MnSO_4.H20$ for the micronutrient solution. The solution used to test the adsorption and recovery capacity of the resin consisted of 400 µmol Ca, 10 µmol Cu, 2500 µmol Cl, 400 µmol Fe, 200 µmol K, 300 µmol Mg, 150 µmol Mn, 2300 µmol Na, 20 µmol PO$_4$, 750 µmol SO$_4$, 20 µmol Zn, 4000 µmol NH$_4$ and 2000 µmol NO$_3$.

The adsorption capacity (i.e., percentage of total elemental influx adsorbed by the resin) was tested using 18 of the 45 resin columns for laboratory tests. Out of these 18 columns, 9 columns were used to mimic heat, drought, and frost conditions and 9 columns were used to test the columns capacity (Table S2). Heat, drought, and frost conditions were mimicked using 3 columns for each treatment which consisted of heating to 40°C, drying at 20°C to a constant weight and freezing at -19°C for 72 hours, respectively, followed by drip-wise loading with the macro- and micro solution. The resins capacity was simulated by dripping the macro- and the micro solutions through the resin columns using the normal concentration (3 columns and for the heat, drought and frost conditions), the double concentration (3 columns) and the triple concentration (3 columns), loading the columns up to respectively 70%, 140% and 210% of their capacity. Samples of the leachate were taken when all the solution was drained from the resin (after approximately 4 hours). Three loaded resin columns were thereafter flushed with demineralized water to test the stability of the adsorption. Both the samples of the leachate and the demineralized water used to wash the loaded columns, were analyzed for N-NH$_4$, and N-NO$_2$ + N-NO$_3$ 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).

The recovery efficiency (i.e., percentage of total elemental flux recovered from the resin) was tested using 39 out of the 45 resin columns for laboratory tests, re-using 12 columns from the adsorption capacity test. Only the columns loaded with the double and triple concentration of the macro- and micro solutions were excluded (Table S2). All unloaded columns were, similar to the previously loaded columns, drip-wise loaded with the macro- and micro solutions. Recovery efficiency was

160 tested using a 2M KCl extraction for NH_4 and NO_3 based on previous reported high recovery rates (Fenn et al., 2002; Fenn and Poth, 2004; Fang et al., 2011; Kohler et al., 2012; Clow et al., 2015; Hoffman et al., 2019) and multiple molarities of HCl (ranging from 1 to 4M) for the other elements (Ca, Mg, K, Fe, Mn, Zn, Cu, Na, and S) since previous studies reported that low recovery efficiencies might be related to the molarity of the extraction solution used (Fenn et al., 2018). For both the KCl and HCl extractions, we varied the extraction volume, the extraction type, and the extraction method (Table 1).

165 Extraction volumes used were respectively 50 mL, 100 mL and 150 mL and extraction type was either single column extraction or batch extraction. Using the single column extraction type, the extractant was applied on the entire column while in batch extraction the resin was divided into smaller samples. These subsamples of the resin were either fresh (i.e., solution drained resin) or dried at 28 ˚C to a constant weight (Table 1). Drying of the resin facilitates subsampling and the calculation of the deposition flux. The extraction method was either drip, in which the extractant was slowly dripped over the resin, or a shake-

170 drip combination in which the resin was shaken in 50mL of the extractant for 1 hour and the remaining extractant was dripped over the resin.

Table 1: Overview of the test for effective extraction of the ion exchanger. The KCl extraction was used for the extraction of NH_4 and NO_3 while the HCl extraction is used for the extraction of Ca, Mg, K, Fe, Mn, Zn, Cu, Na, and S. The single column extraction included the entire loaded column (9.8g of resin) while for batch extraction a subsample (avg. 2.5g dried resin) was used which was

175 **extracted either fresh (i.e., solution drained) or dried.**

	Extraction fluid		Type	Resin	Samples	Method
	M	*mL*				
KCl	2	50	Single column	Fresh	3	Drip
	2	100	Single column	Fresh	3	Drip
	2	50	Batch	Fresh	2	Drip
	2	50	Batch	Dried	2	Drip
	2	50	Batch	Dried	2	Drip
HCl	1	50	Single column	Fresh	3	Drip
	1	100	Single column	Fresh	3	Drip
	2	100	Batch	Fresh	2	Drip
	2	100	Batch	Dried	2	Drip
	2	100	Batch	Fresh	2	Shake & drip
	2	100	Batch	Dried	2	Shake & drip
	4, 2 & 1	150	Batch	Fresh	2	Drip

4, 2 & 1	150	Batch	Dried	2	Drip
1 & 2	100	Batch	Fresh	1	Drip
1 & 2	100	Batch	Dried	1	Drip
2.5	100	Batch	Dried	2	Shake & drip
3	100	Batch	Dried	2	Shake & drip
3.5	100	Batch	Dried	2	Shake & drip
4	100	Batch	Dried	1	Shake & drip

2.3   Field tests

To evaluate the accuracy of the IER-method to quantify bulk deposition and throughfall, a field study was caried out in the
Netherlands (GPS 52.015745, 5.759924) in which we collected paired observations of bulk deposition and throughfall using
water samples (referred to as the water-method) and the IER-method. The chosen field site consisted of a mature stand of
European beech (*Fagus sylvatica*) which has been harvested at different intensities in February 2019, which resulted in four
¼-ha plots within the same stand: an unharvested control (~0% canopy openness), a high-thinning (~25% canopy openness),
a shelterwood (~75% canopy openness) and a clearcut (100% canopy openness) (Vos et al., 2023a; Vos et al., 2023b). The
different harvest intensities allow to test the method for quantifying bulk deposition and throughfall including the effect of
organic substances on the performance of the IER-method. The forest stand has a temperate maritime climate with a mean
annual temperature of 10.4°C and a mean annual rainfall of 805mm (KNMI, 2022). An overview of the study site
characteristics and the placement of the paired samples are in table 2.

Table 2: Characterization of the study site and placement of the paired samplers in open gaps (bulk deposition) and underneath the forest canopy (throughfall).

Treatment	Canopy cover	Number of trees	Paired samplers	
	%	trees ha-1	Bulk deposition	Throughfall
Control	94	245	6	1
High-thinning	72	180	5	2
Shelterwood	16	32	2	5
Clearcut	0	0	0	7

In each forest harvest treatment plot, 7 pairs of collectors were installed resulting in 28 common deposition collectors and 28
IER deposition collectors. These 7 collectors per plot had a collection surface >2000cm^2 above which the reliability of the
measurement is significantly increased (Bleeker et al., 2003). The collectors consisted of a polyethylene funnel mounted to a

resin column, which was filled with resin for the IER-method but left empty for the water-method, and a PVC hose connecting the resin column to a polypropylene water reservoir (Fig. 2A). The funnel had a surface of 288cm^2 (including half the rim, Fig. 2B) and the resin column (volume of 15.7ml) had an inner diameter and length of respectively 12.4 and 130mm. Both the funnel and the resin column were chemically resistant and not susceptible to damage through UV-light or low temperatures. Wire couplings, in which a mesh with the size of 2mm was mounted, were used to connect the resin column to the funnel and to a hose-tail (Fig. 2C, Fig. 2D). Prior to field installation, the funnel and the resin column including the wire couplings were cleaned from chemicals loosely bound to the surface by submerging into a 0.2M HCl solution for three hours, followed by a 15-hour immersion in demineralized water which was continuously refreshed. Afterwards, the compartments were allowed to dry in a clean room and stored in clean plastic bags.
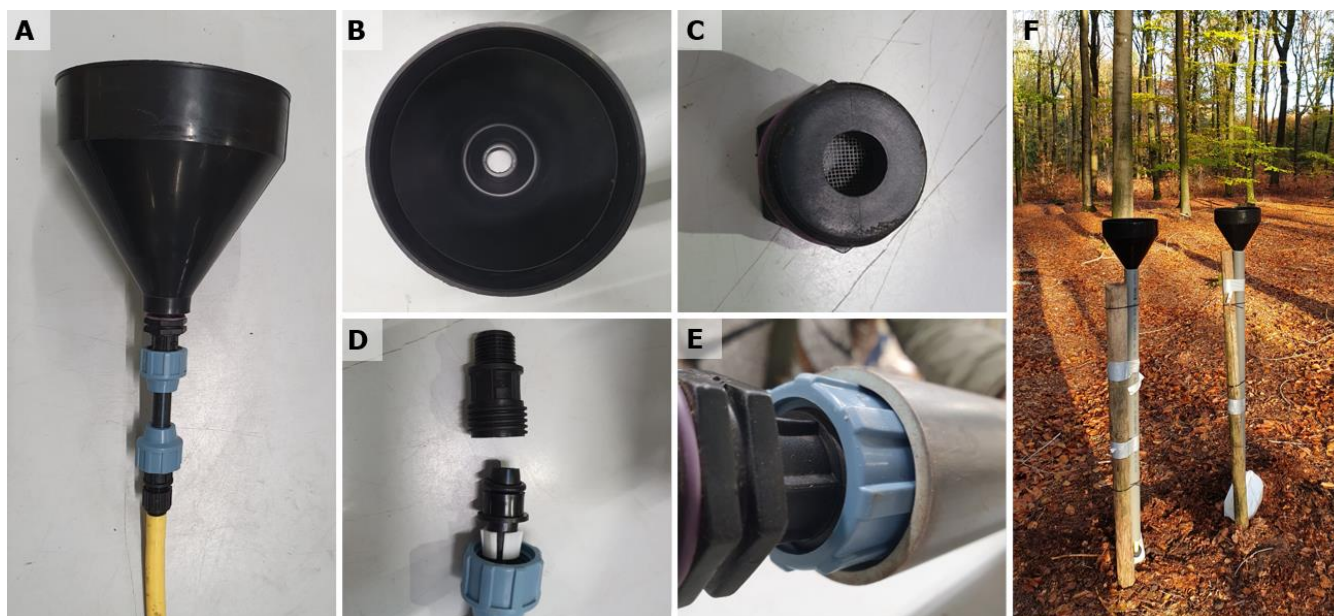
Figure 2: Construction of the deposition samplers. A: the connected sampler ready for use in the field. B: the used funnel with a collection surface of 288cm^2. C: The wire coupling between the funnel and the resin column containing a mesh to prevent larger objects entering the resin column. D: Overview of the resin column with the wire couplings. E: the resin column fitted tightly into the PVC tube which allowed easy installation of the resin columns in the field.

Field placement of the collectors was based on a digital elevation map of the canopy cover, assessed by drone-based photogrammetry (camera FC220). This digital elevation map was converted to a canopy cover map using 'reclassify' in ArcMap (version 10.6.1) in which all datapoints above 10m were assigned to be covered by canopy. Each plot was, thereafter, divided into an equal sized, seven block grid and the locations of the collectors were determined in each of these blocks using random points reflecting the canopy cover (%). Samplers were installed in the field using those random points on November 6th, 2019, by placing the clean, connected sampler in the holder (PVC-tube) and connecting the sample to the partly buried

reservoir (Fig. 2F). The PVC tube was placed vertically so that the funnel, which was placed on top of the PVC tube, was aligned horizontal. The wire couplings of the resin column and the funnel fitted tightly into this PVC tube (Fig. 2E). Closed field blanks were installed simultaneously with the collectors, with one field blank in the clearcut (sun-exposed) and one field
220 blank in the control (shade). Collectors and field blanks were operational for 10 weeks. Funnel contamination (leaf litter and bird droppings) was recorded, and contaminated funnels were cleaned weekly. For the water-method, the leachate was collected every week and send to the laboratory. In the laboratory, the sample volume was recorded and sample pH was measured followed by the contents of Al, Ca, Cu, Fe, K, Mg, Mn, Na, P, S and Zn using ICP-AES (Thermo-Scientific iCAP 6500 DUO, USA) and the contents of $N-NH_4$, $N-NO_3+N-NO_2$, and inorganic carbon (IC) and total carbon (TC) using a
225 Segmented Flow Analyzer (SFA 4000, Skalar Analytical B.V., the Netherlands) within 24h of sampling. The volume of the leachate of the IER collectors was collected monthly, 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 $N-NH_4$ and $N-NO_2 + N-NO_3$ 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 (Thermo-
230 Scientific iCAP 6500 DUO, USA). As a result of contaminations by bird feces, only 18 out of the 28 paired collectors were used for the comparison. Uncontaminated paired collectors were evenly distributed over the canopy openness treatments.

2.4   Calculations and statistical analysis

The concentrations of the resin columns used within the laboratory and field test were corrected for the subsampling in case
235 of batch extraction, corrected for field- and lab blanks and corrected for sample dilution prior to chemical analysis. To correct for subsampling, the concentration of the subsample was multiplied to the concentration of the entire column based on the weights of the subsample and the entire column respectively. Concentrations of the field and lab blanks were subtracted from the concentrations of the entire column to correct for field and lab contamination. For the samplers in the forest gaps the sunlight exposed field blank was used, for the samplers underneath the forest canopy, the shadow field blank was used.
240 Subsequently, the concentrations of the resin columns used within the field test were converted to the amounts per ha^{-1} for the entire measurement period. Thereafter, the deposition in kg ha^{-1} was calculated based on the funnels surface. For the water-method, the precipitation in L ha^{-1} was calculated based on the water volume per funnel (mL). Then the measured weekly concentrations were converted to kg L^{-1} and multiplied with the precipitation (L ha^{-1}). Finally, for both methods, the samples were checked for bird droppings based on the P content, and samples with a P influx (in kg ha^{-1}) larger than the mean plus the
245 2 times the standard deviation were removed.

For the laboratory test, we calculated the adsorption capacity and the recovery efficiency. The adsorption capacity (i.e., percentage of total elemental influx adsorbed by the resin) was calculated as:

$$Adsorption\ capacity = \left(1 - \left(\frac{A_{out}}{A_{in}}\right)\right) * 100$$

In which A_{in} is the total amount of macro and micronutrients in the solution (in µmol) applied to the resin and A_{out} is the amount

250   in the leachate (in µmol). The recovery efficiency (i.e., percentage of total elemental flux recovered from the resin) was calculated as:

$$Recovery\ efficiency = \frac{A_{ex}}{A_{in}} * 100$$

In which A_{ex} is the amount of macro and micronutrients in the leachate applied extract (in µmol) which was poured over the loaded resin.

255   Recovery efficiencies of lab extractions differing in molarity, resin pre-treatment and extraction type and the effect of element and canopy openness on field recovery were tested using ANOVA type I error for unbalanced data following construction of a generalized least squares model. Heterogeneity between groups was overcome using the varIdent weighting from the R package "*nlme*". Tukey's post-hoc (HSD) test was performed following ANOVA using the R package "*emmeans*" to test for differences between groups. Goodness of fit between the original and the IER-method of the field test were tested using linear

260   models corrected for outliers in the data. Remaining outliers were removed from the linear models when the Cook's distance was larger than 4/n in which n is the number of observations.

3   Results

3.1   Adsorption capacity

The adsorption capacity of the resin (i.e., % of elemental flux bound to the resin) under controlled laboratory conditions was

265   100% for all nutrients, with only Na and P being slightly lower (96-97%) (Fig. 3). The adsorption capacity was not influenced by the flushing of the resin with demineralized water.

Overloading the resin up to 150% of the cation bed capacity resulted in decreased adsorption of Na>NH$_4$>K and a maximum loading of the cation bed of 115%. Overload of the anion bed up to 160% decreased the adsorption of P>NO$_3$. Increasing the elemental flux over the resin up to 230% of the cation bed capacity and 240% of the anion bed capacity resulted in lower

270   adsorption of almost all elements except Ca and Zn (Fig. 3). Lab-controlled environmental conditions mimicking heat, drought and frost reduced the adsorption capacity of Na and P, and heat and drought slightly lowered the adsorption capacity of NH$_4$. Elemental adsorption within the resins exchange capacity was thus close to 100% for all elements except P which was underestimated under extreme conditions.

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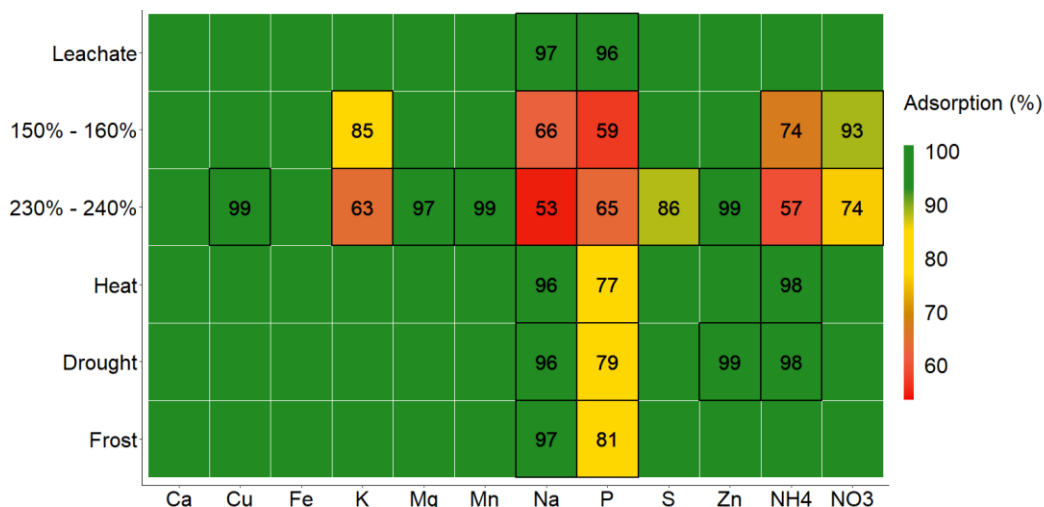
Figure 3: Overview of the adsorption capacity of the resin following different tests. Tests included the loading of the resin with known concentrations within the resins capacity (leachate), loading the resin beyond the resins capacity (150% - 160% of respectively cation and anion bed and 230% - 240% of respectively the cation and anion bed), and resin pre-treatments including warmth, drought, and frost. For adsorption capacities ≤99% numbers of the adsorption capacity are given. Cells without numbers represent adsorption capacities of >99%.

3.2   Recovery efficiency

The recovery efficiency of NH_4 and NO_3 under laboratory conditions (i.e., % of the elements that can be extracted from the resin) was generally high (mostly 90-100%) with recovery depending on the molarity of the extraction (Table 3). The recovery efficiency of NH_4 and NO_3 was weakly but significantly higher with 1M KCl as an extractant compared to 2M KCl (Anova, F-value: 4.4, P-value: 0.048, Df: 22). We did not find differences between fresh or dry resin, or between drip or shake-drip treatments using KCl extractions.

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 3). Because extraction of Zn was unreliable, this element is not further included in average recovery numbers. The average recovery efficiency was highest (90-100%) following either 2M HCl extraction or 4-2-1M HCl extraction. Recovery efficiency was significantly higher following an extraction on dried resin (avg. recovery 88%) compared to fresh resin (avg. recovery 80%), and recovery efficiency was slightly higher following a shake-drip treatment (avg. recovery 87%) compared to drip only treatment (avg. recovery 84%) (table S3). We found an interaction effect between elements and pre-treatment, elements and molarity and elements and extraction type, indicating that different elements responded differently to the different treatments. Overall, highest average recoveries using HCl were found for the 2M dry weight shake and drip treatment, resulting in an average recovery of 100% whereas lowest average recoveries (72%) were found for the 1M fresh weight drip treatment (Table 3).

300   **Table 3: Recovery efficiency of Ca, Cu, Fe, K, Mg, Mn, Na, P, S and Zn following HCl extractions and of NH$_4$ and NO$_3$ following KCl extractions. Recovery efficiencies are expressed as a % of the total elemental content poured over the resin. The efficiencies of the recovery were tested using extractions with different molarities, based on fresh (FW) or dried (DW) resin and based on drip or shake-drip treatments. The number of samples (n) for each extraction combination, the average recovery per extraction combination (Avg) and the average recovery for each element (Avg element) is given. Recovery percentages per element close to 100 are indicated**
305   **in bold. Differences in recovery efficiencies between elements is indicated with small capital letters based on the average element recovery, test statistics are given in Table S3.**

Mol	Resin	Method	n	Ca	Cu	Fe	K	Mg	Mn	Na	P	S	Zn	Avg*	NH$_4$	NO$_3$
1	FW	Drip	6	30	80	56	88	59	91	97	59	92	17	72	**100**	**98**
2	DW	Drip	2	130	94	99	**100**	98	**100**	93	40	91	21	94	97	94
2	DW	Shake-Drip	2	130	**100**	110	110	**100**	110	**100**	65	**100**	7.6	100	94	89
2	FW	Drip	2	85	81	88	86	84	91	82	43	96	25	82	80	95
2	FW	Shake-Drip	2	82	80	87	87	81	88	84	69	93	5.4	83		
1-2	DW	Drip	1	110	87	85	90	86	90	91	57	88	21	87		
1-2	FW	Drip	1	82	77	77	80	77	81	80	60	93	42	79		
2.5	DW	Shake-Drip	2	86	78	72	**100**	85	81	**100**	91	78	6.1	86		
3	DW	Shake-Drip	2	82	71	67	98	77	77	99	84	70	6.1	81		
3.5	DW	Shake-Drip	2	99	89	80	88	93	96	84	83	83	11	88		
4	DW	Shake-Drip	1	86	66	69	92	80	80	93	76	73	8.1	79		
4-2-1	DW	Drip	2	**100**	92	99	93	88	**100**	89	49	96	31	90		
4-2-1	FW	Drip	2	86	85	90	**100**	80	92	82	49	97	**44**	85		
		Avg element		91[d]	83[bc]	83[c]	93[ab]	84[c]	91[b]	90[a]	63[e]	88[b]	19[f]			

*Average without Zn as this element was unreliable using our extraction method.

3.3   Performance under field conditions

310   There was a positive significant linear relationship between the deposition estimates of the water-method and the IER-method for all elements except for Ca, Zn and Fe (Table 5, Fig. 4). Absence of a relation for Ca, Zn and Fe was not related to the correction for contamination in blanks and for the lab-recovery (Table 5).
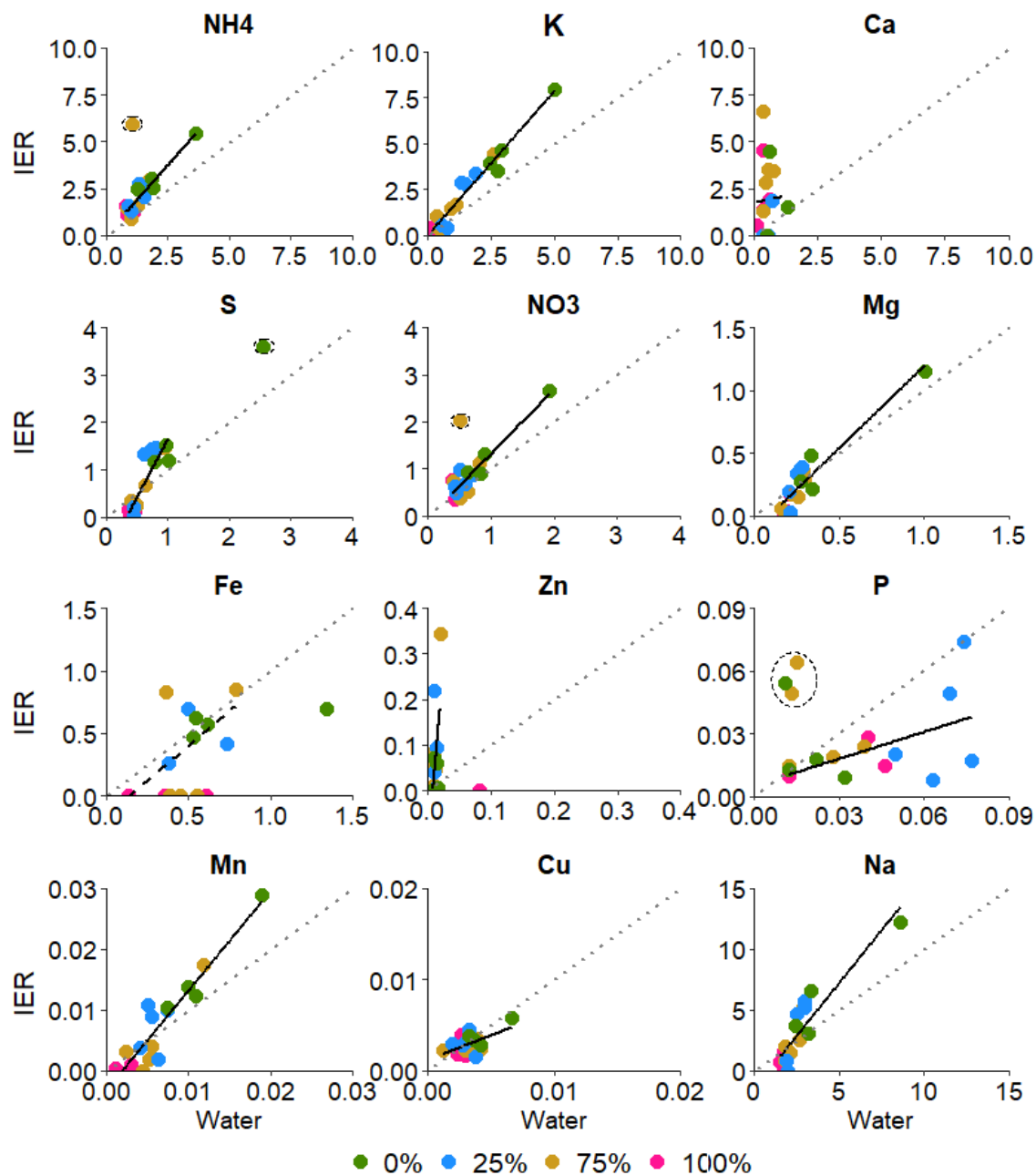
Figure 4: Relationship between the deposition estimates of the IER-method (kg ha⁻¹) and of the water-method (kg ha⁻¹) for the 10-week measurement period. Significant relationships are depicted with a solid black line, non-significant relationships with the dashed black line. The 1:1 line is shown as the dotted grey line.

Table 5: Regression coefficients and R^2 of models for the relation between IER columns and ORG columns including correction for blank and lab recovery (n = 18). Differences between corrected, blank corrected and recovery corrected is related to the corrections for contaminations (blank corrected) and for the recovery of the elements (recovery corrected). The corrected shows the data which is corrected for both the contamination and the recovery. The R^2-adj. of the model with the best fit is highlighted in bold.

		NH$_4$	NO$_3$	S	P	K	Ca	Mg	Mn	Cu	Fe	Zn	Na
Corrected	Intercept	0.062 ± 0.21	-0.051 ± 0.098	-0.83 ± 0.20***	0.0053 ± 0.0078	0.051 ± 0.15	1.1 ± 0.97	-0.11 ± 0.042*	-0.0031 ± 0.0012*	0.0012 ± 0.00066	0.0020 ± 0.0061	-0.13 ± 0.086	-1.5 ± 0.63*
	Slope	1.5 ± 0.14***	1.4 ± 0.13***	2.5 ± 0.31***	0.43 ± 0.17*	1.6 ± 0.077***	1.1 ± 1.6	1.3 ± 0.13***	1.6 ± 0.15***	0.54 ± 0.19*	0.015 ± 0.010	16 ± 6.9*	1.7 ± 0.20***
	R²-adj	**0.88**	0.87	**0.80**	**0.27**	**0.96**	-0.036	**0.86**	**0.87**	**0.29**	0.069	**0.21**	**0.82**
Blank cor.	Intercept	0.11 ± 0.18	-0.02 ± 0.077	-1.39 ± 0.50*	-2.6 ± 0.32**[1]	0.38 ± 0.36	2.0 ± 2.6	-0.26 ± 0.12*	-0.0049 ± 0.0031	0.0040 ± 0.0015*	0.0067 ± 0.013	0.030 ± 0.025	-8.0 ± 2.6**
	Slope	1.1 ± 0.12***	1.1 ± 0.11***	5.2 ± 0.8***	-3.8 ± 8.0[1]	4.0 ± 0.20***	4.5 ± 4.4	3.6 ± 0.36***	4.3 ± 0.43***	1.2 ± 0.46*	0.036 ± 0.022	4.4 ± 2.1*	6.6 ± 1.2***
	R²-adj	0.82	0.84	0.70	-0.043[1]	**0.96**	**0.0028**	0.84	0.84	0.25	**0.081**	0.16	0.64
Recov. Cor.	Intercept	0.15 ± 0.22	8.9 10^{-5} ± 0.095	0.070 ± 0.17	0.0053 ± 0.0078	0.051 ± 0.15	2.8 ± 1.2*	0.13 ± 0.039**	0.00087 ± 0.0011	0.0012 ± 0.00066	0.020 ± 0.0061**	-0.085 ± 0.094	-0.43 ± 1.0
	Slope	1.5 ± 0.14***	1.4 ± 0.13***	1.6 ± 0.26***	0.43 ± 0.17*	1.6 ± 0.077***	1.6 ± 2.1	1.2 ± 0.12***	1.3 ± 0.15***	0.54 ± 0.19*	-0.0025 ± 0.010	15 ± 7.6	1.9 ± 0.43***
	R²-adj	**0.88**	**0.88**	0.71	**0.27**	**0.96**	-0.024	0.85	0.83	0.29	-0.063	0.16	0.54

*** < 0.001; ** 0.01 >< 0.001; * 0.05 <> 0.01; no star is not significant; [1] log transformed values.

The IER data corrected for contamination of blanks and the lab-recovery overall resulted in the highest R^2-adjusted, resulting in a corrected goodness of fit up to 0.96 (K) and between 0.8 to 0.9 for NH_4, NO_3, S, Mg, and Mn (Table 5). Canopy openness treatment significantly influenced the deposition estimates of the IER-method compared to the water-method (ANOVA, F-value: 6.9, P-value < 0.001, Df: 168) although between treatment differences were not significant following Tukey's post-hoc tests (Fig. S1). The IER-method tended to have lower deposition estimates in the 100% canopy openness treatment for Mg, Mn, Na and S, but overall, the IER-method resulted in higher deposition estimates for NH_4, K, S, NO_3, Mg, Mn, and Na compared to the water-method (Fig. 4). For Fe, P, and Cu, for which the water-method yielded higher deposition estimates, all values of the water-method were below detection limit (Table S4).

4   Discussion

4.1   Adsorption capacity

We aimed to test the capacity of IER as a method to quantify atmospheric deposition for a broad range of macro- and micro-elements, comparing results under laboratory and field conditions and in the latter case comparing bulk deposition and throughfall. First, the adsorption capacity of the IER when loaded within its capacity was generally high. High adsorption confirms earlier studies who found no elemental loss of NO_3, NH_4 and SO_4 (Simkin et al., 2004; Sheibley et al., 2012; Sheng et al., 2013) or only slight losses of NH_4 and NO_3 (Fang et al., 2011) and contradicts findings of low resin adsorption (Langlois et al., 2003). We show that IER is also able to adsorb above 99% for a range of other elements including the base cations and some micronutrients. Therefore, IER can be loaded within the 70% of its exchange capacity without risking lower elemental adsorption. However, slightly lower adsorption capacities were found for Na and P. These lower adsorption capacities are caused by the lower cation-exchanger affinity for Na^+ and lower anion-exchanger affinity for HPO_4^{2-} (Skogley and Dobermann, 1996; Park et al., 2014). The lower adsorption capacities when using the resin within its capacity can lead to an underestimation of the total deposition of P by 4%, although other studies report no lower adsorption capacities for P (Tahovská et al., 2016). Despite the possible underestimation of the total deposition, studies using IER report P deposition values within the natural ranges (Decina et al., 2018; Hoffman et al., 2019), indicating that the method usually also works well for P. The lower adsorption capacity of Na, however, can result in lower estimates of the deposition for multiple elements when Na is used as an tracer for canopy exchange processes (Staelens et al., 2008), and the use of Na as a tracer in IER-deposition studies is thus questionable.

To further test the affinity of the resin for the studied elements, the resin was loaded to approximately 160% and 240% of its capacity. Based on the adsorption capacity beyond the resins capacity, we found that the cation bed has an affinity of Ca = Fe > Cu = Mn = Zn > Mg > K > NH_4 > Na which is in line with the previous reported resin affinity (Skogley and Dobermann, 1996). The anion bed has an affinity of S > NO_3 > P which agrees with earlier studies (Skogley and Dobermann, 1996; Park et al., 2014). The resins affinity and the adsorption capacity for different levels of loading beyond the resins capacity is of

importance for resin columns under suspicion of overloading. We did not find lower adsorption of Ca and Fe and only slightly
355   lower adsorption of Cu, Mg, Mn and Zn, indicating that, when columns are slightly overloaded, these estimates are still reliable.
When columns are loaded > 100% of the capacity, the estimates for K, Na, P, S, NH_4 and NO_3 are not reliable. Therefore, in
case of suspicion of ion exchange overload, tests are recommended to check if stoichiometry between any element of Ca, Cu,
Mg, Mn and Zn with K, Na, P, S, NH_4 and NO_3 falls within the stochiometric range of natural deposition estimates. We
strongly recommend to collect the resin columns prior to resin saturation as adsorption of Na and P can further decrease when
360   saturating the resin up to 90 or 100%. The time period that the resin can stay in the field depends on the total atmospheric
deposition and the volume of resin used. For remote areas with low deposition levels and low risk of sample contamination
(e.g. by bird feces) the resin can stay for multiple months up to a year in the field as long as adequate resin volumes are used.
Heat, drought and frost treatments hardly influenced the absorption capacity of most elements, but decreased the P adsorption
capacity and, in case of heat and drought, NH_4 and Zn (the latter only for drought) adsorption. These findings are in line with
365   the adsorption behavior of some other IER types, where drying significantly reduced NH_4 adsorption while frost-thaw cycles
did not (Hart and Binkley, 1984; Kjonaas, 1999). However, in other work extensive dry-wet cycles did not affect the adsorption
of PO_4, NO_3 and NH_4 (Mamo et al., 2004) indicating that the effect of environmental conditions differs per resin type.
Application of the IER-method without an adsorption pre-test of the resin can therefore potentially underestimate NH_4 and P
deposition when used in areas with temperatures above 40°C and can potentially underestimate NH_4, P and Zn deposition in
370   areas with longer drought periods. Despite the effect on some elements, weather circumstances generally seem to have little
effect indicating that the method is suitable under different climatic circumstances, like the boreal zone (Fenn et al., 2015),
temperate zone (Fenn and Poth, 2004; Hoffman et al., 2019) and the tropics (Kohler et al., 2012; Ibrahim et al., 2022). The
robustness of the method under different climatic circumstances implies that it can be used to compare deposition over large
environmental gradients, which is essential to understand regional and global deposition patterns.

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4.2   Recovery efficiency

The recovery efficiency was tested based on differences in molarity, resin pre-treatment and extraction type. Recovery of NH_4
and NO_3 was highest following a 1M KCl extraction based on controlled percolating of the extraction fluid through the resin.
Although highest recovery following a 1M KCl extraction was reported before (Hart and Binkley, 1984), most studies indicate
380   that 2M KCl extractions will lead to higher recovery of both NO_3 and NH_4 (Kjonaas, 1999). However, the 2M KCl recovery
efficiencies of this study were comparable to other studies using 2M KCl as an extractant (Fenn et al., 2002; Sheng et al., 2013;
Tulloss and Cadenasso, 2015). The highest recoveries were obtained by using dried resin and the combined shake-drip
methods.

Recovery efficiency following HCl extraction differed between elements and depended on the extraction itself. We choose
385   HCl as an extractant as this extraction fluid allows measurements of a broad range of elements on the ICP-AES and this method
was rarely tested. A limited number of studies used HCl as an IER extractant (Van Dam et al., 1987; Dobermann et al., 1997;

Szillery et al., 2006; Yamashita et al., 2014) but only one study, testing only two elements, reported (high) elemental recoveries (Van Dam et al., 1987). Although H^+ has a relatively low affinity for the cation bed (Skogley and Dobermann, 1996), we expected that increasing molarities would increase recovery efficiency of both the cation and the anion bed. Surprisingly,

390 recovery efficiency was highest using 2M HCl and 4-2-1M HCl, although highest recovery differed between elements (Table 3). Overall, we did find much higher recovery efficiencies for Ca and Mg using HCl extractions compared to KI and H_2SO_4 extractions (Kohler et al., 2012; Wieder et al., 2016), which can be related to a better extraction efficiency of HCl. Absence of higher recoveries using > 3M HCl can be caused by differences in extraction time between treatments (Zarrabi et al., 2014) although the overall differences in recovery efficiencies between extractants were rather small.

395 Recovery efficiency was higher when resin was dried prior to HCl extraction and when using the shake-drip extraction (Table S3). The mechanism behind higher recovery efficiency following pre-extraction drying remains speculative but might be related to a better accessibility of the extract to reach micropores when the resin was dried. Previously, it was argued that pre-loading drying resulted in lower recovery efficiencies because of unavailable micropores due to swelling of the resin after rewetting (Kjonaas, 1999) but this unavailability of micropores was contradicted by Mamo et al. (2004) who found that dry-

400 wet cycles significantly increased the desorption of elements from the resin. Occurrence of dry-wet cycles under field conditions can therefore interfere with the recovery efficiency of elements from the resin which could possibly bias deposition estimates. This effect is, however, likely small as full drying resulted in only 8% more efficient recoveries. The higher recovery following shake-drip treatment can result from longer contact time with the extractant (Zarrabi et al., 2014) while still avoiding the equilibrium reaction which occurs when using the shake treatment only. However, the present paper was not designed to

405 test the effect of extraction time on the recovery efficiency, a complete test of this hypothesis will have to await future experimentation.

Finally, the best extraction to use depends on the elements of interest. When studied elements are limited to the base cations, the 2M HCl extraction provides good recovery efficiencies. However, studies including P and Zn should rather choose for a HCl extract with a higher molarity or choose another extractant. Overall, recovery efficiencies of P and Zn were rather low,

410 which may result from the low initial concentrations (Zarrabi et al., 2014). We did not test for different extraction solutions as there are only limited options for extracting a broad range of macro- and micro-solutions. However, for P and Zn different extraction solutions should be tested to increase the recovery efficiency. Furthermore, using the recovery efficiencies, we found only limited evidence of a release of background levels of elements from the resin. Indications of the release of background levels were present for Ca (up to 130% recovery) and Na (up to 110% recovery). These indications were mainly present in the

415 2M HCl dry weight shake-drip extraction and could possible be caused by lab contaminations. We did not find evidence for high background levels of NO_3 and NH_4, contrary to Langlois et al. (2003) who argued that the IER-method was not suited for monitoring subtle patterns of NO_3 and NH_4 deposition. Together, our findings indicate that both KCl and HCl perform well as an extractant except for P and Zn for which new extraction methods should be tested.

4.3   Performance under field conditions

In general, deposition estimates based on the IER-method were positively related to the deposition estimates of the water-method, however, the IER-method often resulted in higher deposition estimates. Exceptions were Fe and Ca, for which we did not find a relation between the deposition estimates of the IER-method and the water-method. This could indicate pollution related to elevated Ca and Fe leaching from the sample materials. For example, in the sun-exposed field blank we found high Fe pollution causing the Fe deposition levels of all exposed collectors to be 0 (Fig. 4). For the collectors corrected for the shade-exposed field blank, we found good agreement between the deposition estimate of the IER-method (0.68 kg ha^{-1} ± 0.12 s.e.) and the water-method (0.66 kg ha^{-1} ± 0.09 s.e.) with the deposition estimates of both methods within the normal range of throughfall Fe deposition of the winter period (RIVM, 2015). For Zn we found much higher deposition values using the IER-method compared to the water-method in contrast to throughfall which was much higher than bulk deposition estimates multiplied by the throughfall correction factor (Table S1). It could be that the presence of organic particles interfered with the recovery efficiency of Zn, possibly leading to an overestimation of the Zn throughfall.

The higher deposition estimates of the IER-method compared to the water-method for NH_4 and NO_3 can be caused by absence of biochemical reactions which causes losses of these elements in the original samplers (Fenn and Poth, 2004; Kohler et al., 2012). Higher deposition estimates using the IER-method can also be related to the low concentration of elements in the water-method, which were often below detection limit (Table S4). Overall, slightly higher deposition values using IER columns were reported before (Fenn and Poth, 2004; Simkin et al., 2004; Kohler et al., 2012). Because of absence of biochemical reactions and higher reliability of the lab measurements for IER-samples, the IER-method is likely more reliable to quantify both bulk deposition and throughfall compared to the water-method and the generally higher deposition estimates are likely a better representation of the actual atmospheric deposition.

The lower deposition estimates of P can be caused by a better adsorption of inorganic P compared to organic P to the resin (Zarrabi et al., 2014) which potentially reduces the recovery efficiency of P under field-conditions compared to lab-conditions. However, additional field tests are necessary for P to compare the difference between field and laboratory adsorption and recovery efficiencies. For other elements, the comparison of the IER-method and the water-method did not give evidence of lower adsorption or recovery efficiencies under field conditions. Absence of this effect might, however, be related to the winter-period in which the field measurements took place as, for example, pollen were hypothesized to reduce recovery of NH_4, NO_3 and SO_4 from the IER (Brumbaugh et al., 2016). Lower field recovery might therefore, beside the resin type and the extraction method, be related to the amount of organic particles like pollen which was not included in this study.

5   Conclusions

450   We tested the suitability of the IER-method for quantifying bulk deposition and throughfall of macro- and micro nutrients by assessing adsorption capacities and recovery efficiencies under controlled laboratory conditions, followed by an evaluation of the performance of the method under field conditions.

Results showed that (1) the adsorption capacity of the resin under controlled laboratory conditions was close to 100% for all nutrients; (2) Extraction using KCl (1 or 2 M) is effective for nitrogen (NH4 and NO3) with general high recoveries (mostly

455   90-100%) depending on the molarity of the extraction, while extraction using HCl is effective for Ca, K, Na, Mn, Mg, S, Cu and Fe but not for P and Zn for which testing other extraction methods or extraction fluids is recommended; (3) drying the resin prior to extraction and using a shake-drip extraction method increased the recovery efficiencies; (4) the IER-method is useful under a broad range of environmental conditions, since heat (40°C), drought and frost (-15°C) hardly affected the adsorption of nutrients except for P which was reduced up to 25%; and (5) the IER-method performed well under field

460   conditions, resulting in similar but consistent higher deposition estimates compared to the water method.

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. 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.

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Author contributions

Marleen A.E. Vos, conceived the ideas and designed the methodology. Prior to testing the methods, the ins and outs were discussed with W. de Vries and F.J. Sterck. Marleen A.E. Vos tested the Ion Exchange Resin method both in the laboratory and in the field, prepared the samples for chemical analysis which was ultimately performed by the laboratory staff. Statistical

470   analysis was performed by Marleen A.E. Vos. Marleen A.E. Vos led the writing of the manuscript. All authors contributed critically to the drafts and gave final approval for publication.

Data availability statement

No data has been published yet. Data will be made available upon request.

Competing interest

475   The authors have no conflicts of interest to declare that are relevant to the content of this article.

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