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Testing ion exchange resin for quantifying bulk and throughfall deposition of macro- and micro-elements in forests

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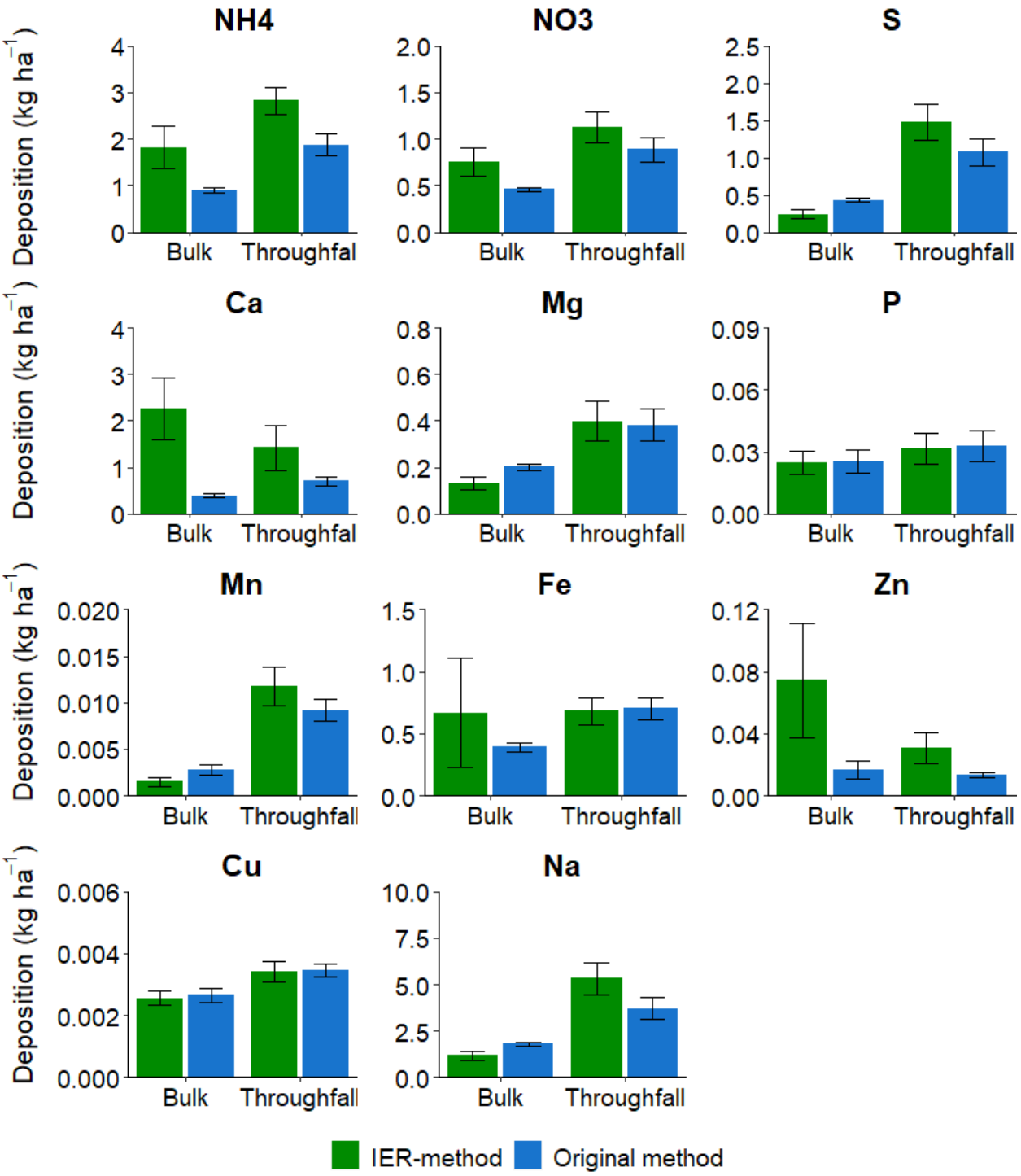

Figure S1: Deposition estimates of the IER-method (kg ha^{-1}) and the original water-method (kg ha^{-1}) in for the bulk deposition and the throughfall for a 10-week measurement period.

Table S1: Ratios of throughfall (mostly also including stemflow, SF) to bulk deposition reported in literature, where throughfall consists of wet deposition and dry deposition corrected for canopy uptake while bulk deposition consists of the wet deposition including a small fraction of dry deposition.

Species	Na	NH_4	NO_3	K	Mg	SO_4	PO_4	Ca	Mn	Zn	Cu	Country	SF	Source
Beech	1.1	0.84	1.6	8.6	3.3	1.6	2.3	2.1	21			Germany	Yes	(Talkner et al., 2010)
Beech	2.3	1.7	1.6	38	4.5	4.7		3.5				Belgium	Yes	(Adriaenssens et al., 2012)
Beech	1.2	1.3	1.7	10	3.5	1.6		2.6				Czech Republic	Yes	(Růžek et al., 2019)
Beech	1.2	0.82	1.2	6.2	1.9	1.2	1.7	1.8	6.9	1.1	2.1	Poland	Yes	(Kowalska et al., 2016)
Douglas fir	2.3	1.8	42	8.0	6.0	3.3	0.6	5.3				France	Yes	(Marques et al., 1997)
Douglas fir	2.3	3.3	2.1	14	2.9	3.6	3.5	3.6				Netherlands	Yes	(Draaijers et al., 1997)
Spruce										2.1	0.64			(Bergkvist et al., 1989)
Scots pine	2.0	1.1	1.0	11	3.4	1.5	5.6	1.6	21	1.1	1.3	Poland	No	(Kowalska et al., 2016)
Scots pine	2.5	3.8	3.4	4.4	1.1	1.8		2.1				Poland	No	(Kozłowski et al., 2020)
Corsican pine	1.5	3.9	3.1	3.8	1.9			1.4				Belgium	No	(De Schrijver et al., 2004)
Average														
Beech	1.5	1.2	1.5	16	3.3	2.3	2.0	2.5	14	1.1	2.1			
Douglas fir	2.3	2.6	22	11	4.5	3.5	2.1	4.5			0.6			
Scots pine	2.0	2.9	2.5	6.4	2.1	1.7	5.6	1.7	21	1.1	1.3			

N.B. The bulk throughfall deposition of SO_4^{2-} was assumed to be not influenced by canopy exchange as the stomatal uptake of SO_2 is balanced by foliar leaching of SO_4^{2-} (Draaijers and Erisman, 1995). However, Staelens et al. (2007) estimated that canopy leaching contributed 7% to the combined bulk throughfall and stemflow of SO_4^{2-} which was in line with the findings of Potter et al. (1991). Canopy exchange of Al and Cu are neglectable as both elements in deposition is found in a colloidal fraction and almost entirely complexed by DOC (Gandois et al., 2010). The free metal ion forms of Zn (on average 30%) do interact with the canopy however concentration is only slightly increased or decreased (Gandois et al., 2010).

Table S2: Overview of the columns (n = 45) prepared for the different laboratory tests.

Pre-treatment	Loading	n	Used for adsorption tests	Used for extraction tests
Heat	1 * macro- and micro solution	3	Yes	Yes
Drought	1 * macro- and micro solution	3	Yes	Yes
Frost	1 * macro- and micro solution	3	Yes	Yes
None	1 * macro- and micro solution	30	Yes, 3 columns	Yes
None	2 * macro- and micro solution	3	Yes	No
None	3 * macro- and micro solution	3	Yes	No

Table S3: ANOVA F and P values for HCl extraction of different molarities, pre-treatments (DW or FW) and different extraction types (Drip or Shake-Drip). The post-hoc tests for the interactions are in table S6-S9.

	DF	F-value	P-value
Element	9	660	< 0.0001
Pre-treatment	1	120	< 0.0001
Molarity	6	17	< 0.0001
Extraction type	1	4.3	0.040
Element * Pre-treatment	9	52	< 0.0001
Element * Molarity	54	9.8	< 0.0001
Element * Extraction type	9	2.5	0.012
Pre-treatment * Extraction type	1	15	0.0002

Table S4: Intercept and slope (± s.e) and the significances of the linear models comparing the elemental contents of the deposition (both throughfall and bulk deposition) between the IER-method and the common method.

Element	Intercept	Slope
NH_4	0.062 ± 0.21 $^{n.s.}$	1.5 ± 0.14 ***
NO_3	0.081 ± 0.18 $^{n.s.}$	1.1 ± 0.30 **
S	-0.83 ± 0.20 ***	2.5 ± 0.31 ***
P	0.0053 ± 0.0078 $^{n.s.}$	0.43 ± 0.17 *
K	0.043 ± 0.13 $^{n.s.}$	1.6 ± 0.069 ***
Ca	0.014 ± 1.4 $^{n.s.}$	3.2 ± 2.6 $^{n.s.}$
Mg	-0.30 ± 0.099 **	2.1 ± 0.40 ***
Mn	-0.0031 ± 0.0012 *	1.6 ± 0.15 ***
Cu	0.0022 ± 0.00085 *	0.18 ± 0.27 $^{n.s.}$
Fe	-0.15 ± 0.35 $^{n.s.}$	1.1 ± 0.69 $^{n.s.}$
Zn	-0.014 ± 0.057 $^{n.s.}$	4.3 ± 5.0 $^{n.s.}$
Na	-4.7 ± 1.1 ***	3.2 ± 0.45 ***

*** < 0.001; ** 0.01 >< 0.001; * 0.05 <> 0.01; n.s. is not significant

Table S5: Elemental concentrations under detection limit (%) after 10-week long field sampling of the atmospheric bulk (throughfall) deposition in the Netherlands. Elemental concentrations were often under detection limit for the original method (Org), especially for the treatments (TM) shelterwood (SW) and clearcut (CC) and less often for the treatments control (CO) and high thinning (HT). For the Ion Exchange resin method (IER) values were less often under detection limit.

TM	Method	Ca	Cu	Fe	K	Mg	Mn	Na	P	S	Zn	NH4	NO3
CO	Org	83	100	100	0	0	50	0	100	0	83	0	0
HT	Org	100	100	100	0	0	100	0	100	0	100	0	0
SW	Org	100	100	100	50	17	100	0	100	0	100	0	0
CC	Org	100	100	100	100	33	100	0	100	0	83	0	0
CO	IER	0	0	20	0	0	0	0	40	0	0	0	0
HD	IER	0	0	40	0	0	0	0	20	0	0	0	0
SK	IER	0	0	17	0	0	0	0	0	0	17	0	0
KK	IER	0	0	0	0	0	0	0	60	0	20	0	0

Table S6: Post-hoc test results of the interaction between the element and the pre-treatment of the resin (DW is dry weight and FW is fresh weight). The mean ± s.e. of each extraction type is given and the p-value of the Tukey post-hoc test.

Extraction type	Ca	Cu	Fe	K	Mg	Mn	Na	P	S	Zn
Dry weight	110 ± 6.1	88 ± 3.2	88 ± 4.7	98 ± 2.4	91 ± 3.2	95 ± 3.9	98 ± 2.6	71 ± 6.4	87 ± 3.8	14 ± 3.0
Fresh weight	57 ± 8.7	81 ± 3.2	72 ± 5.5	90 ± 3.6	70 ± 4.4	91 ± 3.3	92 ± 2.9	59 ± 4.9	94 ± 1.5	21 ± 4.4
p-value	*< 0.001*	*0.34*	*0.56*	*1.0*	*0.13*	*0.19*	*0.67*	*1.0*	*1.0*	*1.0*

Table S7: Post-hoc test results of the interaction between the element and the molarity of the extractant. The mean ± s.e. of each extraction type is given. Significant differences between groups ($p < 0.05$) based on the Tukey post-hoc test are marked with small letters.

Molarity	Ca	Cu	Fe	K	Mg	Mn	Na	P	S	Zn
1	30 ±	80 ±	56 ±	88 ±	59 ±	91 ±	99 ±	62 ±	92 ±	17 ±
	5.2 ^{a}	6.3 ^{a}	4.2 ^{a}	1.1 ^{a}	4.5 ^{a}	6.5 ^{a}	3.0 ^{a}	6.5 ^{a}	2.2 ^{a}	3.6 ^{a}
2	110 ±	89 ±	96 ±	95 ±	92 ±	98 ±	93 ±	56 ±	96 ±	15 ±
	9.2 ^{c}	3.7 ^{a}	3.3 ^{c}	4.0 ^{a}	4.8 ^{a}	3.9 ^{a}	3.8 ^{a}	7.3 ^{a}	2.3 ^{a}	3.9 ^{a}
2.5	86 ±	78 ±	72 ±	100 ±	85 ±	81 ±	110 ±	95 ±	78 ±	6.1 ±
	1.2 ^{ab}	0.65 ^{a}	0.6 ^{ab}	3.1 ^{a}	4.5 ^{a}	0.2 ^{a}	1.3 ^{a}	0.7 ^{a}	11 ^{a}	0.4 ^{a}
3	82 ±	71 ±	67 ±	98 ±	77 ±	77 ±	100 ±	87 ±	70 ±	6.1 ±
	5.6 ^{ab}	6.3 ^{a}	8.9 ^{ab}	6.9 ^{a}	9.1 ^{a}	7.8 ^{a}	2.8 ^{a}	1.5 ^{a}	1.2 ^{a}	0.6 ^{a}
3.5	99 ±	89 ±	80 ±	88 ±	93 ±	96 ±	86 ±	87 ±	84 ±	11 ±
	0.0 ^{ab}	0.45 ^{a}	1.9 ^{abc}	8.1 ^{a}	1.9 ^{a}	2.4 ^{a}	5.2 ^{a}	4.1 ^{a}	6.9 ^{a}	2.6 ^{a}
4 – 2 – 1	94 ±	89 ±	95 ±	99 ±	84 ±	97 ±	88 ±	51 ±	97 ±	38 ±
	6.3 ^{bc}	3.4 ^{a}	3.1 ^{bc}	10 ^{a}	3.3 ^{a}	3.6 ^{a}	3.7 ^{a}	3.3 ^{a}	2.0 ^{a}	6.1 ^{a}

Table S8: Post-hoc test results of the interaction between the element and the extraction type (either drip or the shake-drip method). The mean ± s.e. of each extraction type is given and the p-value of the Tukey post-hoc test.

Extraction type	Ca	Cu	Fe	K	Mg	Mn	Na	P	S	Zn
Drip	73 ± 9.4	84 ± 2.7	78 ± 5.0	92 ± 2.9	76 ± 4.2	93 ± 2.8	93 ± 2.2	54 ± 3.4	94 ± 1.2	25 ± 3.2
Shake-drip	96 ± 6.9	84 ± 3.8	83 ± 4.9	96 ± 3.4	88 ± 4.1	90 ± 4.4	97 ± 3.4	82 ± 5.0	85 ± 4.3	7.2 ± 0.78
p-value	*1.0*	*1.0*	*1.0*	*1.0*	*1.0*	*1.0*	*1.0*	*0.035*	*1.0*	*0.40*

Table S9: Post-hoc test results of the interaction between the pre-treatment of the resin (DW is dry weight and FW is fresh weight) and the extraction type (either drip or the shake-drip method). Significant differences between groups ($p < 0.05$) based on the Tukey post-hoc test are marked with small letters.

Pre-treatment	Extraction type	Recovery efficiency (%)
DW	Drip	84^{c}
DW	Shake-drip	81^{b}
FW	Drip	72^{ac}
FW	Shake-drip	76^{a}