



1 **ABSTRACT**

2 Conventional throughfall collection methods are labor intensive and analytically expensive to  
3 implement at broad scales. This study was conducted to test an alternative approach requiring  
4 infrequent sample collection and a greatly reduced number of chemical analyses. The major  
5 objective of the study was to determine the feasibility of using ion exchange resin (IER) to  
6 measure N deposition in throughfall with field deployment periods of three to twelve months.  
7 Nitrogen deposition measurements in bulk throughfall collected under pine canopies and in  
8 forest clearings were compared between co-located conventional throughfall solution collectors  
9 and IER throughfall collectors using mixed bed IER columns. Deposition data were collected for  
10 one year at a high deposition site (Camp Paivika, CP) and a relatively low one (Barton Flats, BF)  
11 in the San Bernardino Mountains in southern California: Annual throughfall deposition values  
12 ( $\text{kg ha}^{-1}$  of  $\text{NH}_4\text{-N} + \text{NO}_3\text{-N}$ ) under large ponderosa pine trees were 145.8 and 143.9 at CP and  
13 17.0 and 15.0 at BF according to the IER and conventional methods, respectively. Analogous  
14 values for bulk deposition in forest clearings were 15.6 and 12.3 at CP and 4.0 and 3.3 at BF. It  
15 was concluded that the IER collectors can be used for routine monitoring of deposition in  
16 throughfall and bulk deposition, provided that field blanks are used to account for background  
17 levels of N in the IER columns, which at times are slightly elevated, possibly from slow release  
18 of amine groups from the anion exchange resin during field exposures.

19  
20 **INTRODUCTION**

21 Because of the widespread and largely detrimental aspects of elevated atmospheric N deposition,  
22 quantification of ecosystem N inputs from air pollution is needed. Quantification of deposition  
23 inputs fosters greater understanding of cause/effect relationships between pollutants and  
24 ecosystem responses and is critical for identifying terrestrial and aquatic resources most at risk

1 from N enrichment and acidification effects. Measuring total N deposition to forests or other  
2 ecosystems is a challenge due to the technical difficulties and expense associated with measuring  
3 atmospheric concentrations and deposition fluxes for the array of dry-deposited gaseous and  
4 particulate forms of N, in addition to wet deposition and fog or cloudwater deposition of N.  
5 Determining the deposition of these many compounds to complex recipient ecosystem surfaces  
6 under dynamic meteorological conditions is a daunting task on the local scale and particularly  
7 impractical and cost prohibitive over extensive landscapes. As a result, total N deposition  
8 estimates to ecosystems are generally highly uncertain or nonexistent.

9 Where N deposition data are available, a variety of approaches, such as the inferential  
10 method, simulation modeling, and throughfall (Lovett, 1994) have been used to determine N  
11 deposition or some components of total N deposition. Deposition fluxes in precipitation (wet  
12 deposition) are frequently monitored because this is the least complex and most reproducible  
13 component to measure. However, in areas of significant fog or dry deposition (or both), wet  
14 deposition is the smallest component of total deposition inputs, particularly in ecosystems with  
15 high leaf area index values, where plant canopies serve as efficient scavengers of air pollutants in  
16 wet and dry forms (Fenn et al., 2003).

17 Because it is generally not feasible to monitor atmospheric concentrations and deposition of  
18 the suite of important atmospheric pollutants over an extensive number of sites, alternative  
19 approaches are needed to estimate N deposition inputs. The use of passive monitors for obtaining  
20 average concentrations of gaseous pollutants is now recognized as a vital methodology for  
21 measuring gaseous pollutant exposure in forests and other areas without electric power and  
22 where the cost of maintaining multiple active monitors is prohibitive (Bytnerowicz et al., 2002;  
23 Krupa and Legge, 2000). However, total N deposition fluxes cannot be determined solely from  
24 gaseous pollutant concentrations; considerable meteorological data, pollutant deposition velocity

1 values, and information on plant community characteristics also are required (Baumgardner et  
2 al., 2002).

3 Throughfall is an attractive alternative method for estimating atmospheric deposition to  
4 forests and other ecosystems (Thimonier, 1998). Deposition of N in throughfall is the hydrologic  
5 flux of N from the canopy to the forest floor. Throughfall measurements of N deposition  
6 generally underestimate total N deposition to the forest because the canopy retains a portion of  
7 the N it intercepts and deposition to understory vegetation and direct deposition to the ground  
8 surface usually are not measured. Nonetheless, throughfall collection and analysis seems to have  
9 greater potential than other methods for widespread monitoring of atmospheric deposition to  
10 forests and other ecosystems. This conclusion is substantiated by the Pan European intensive  
11 monitoring program of the European Union International Cooperative Programme (ICP-Forests):  
12 it has chosen to monitor throughfall for large scale N deposition monitoring. Throughfall is  
13 currently being measured in 488 plots (Bleeker et al., 2003). Throughfall is often the method of  
14 choice because of the impracticality of other methods of monitoring dry deposition at the scale  
15 needed for characterizing atmospheric deposition over large forested landscapes. However,  
16 traditional throughfall methods are labor intensive and analytically expensive to implement at  
17 broad scales—because of the need to frequently collect and analyze a large number of replicate  
18 samples (generally on a precipitation-event basis).

19 In this paper, we describe comparisons between conventional throughfall deposition  
20 measurements and a modified throughfall collection technique using ion exchange resin (IER)  
21 columns. IER, usually deployed in resin bags, have often been used for nutrient cycling studies  
22 (Binkley and Hart, 1989; Brooks et al., 1996; Qian and Schoenau, 2002; Skogley and  
23 Dobermann, 1996; Susfalk and Johnson, 2002), although less frequently for atmospheric  
24 deposition measurements (Köchy and Wilson, 2001; Kjonaas, 1999a; Simkin et al., 2004; Van

1 Dam et al., 1991). We chose the resin column design with the expectation that this would be a  
2 highly efficient technique for ion capture from throughfall or precipitation samples as the flow is  
3 directed through the IER column, enhancing contact of the solutions with the resin. Other  
4 advantages of the IER column design used in this study are that the resins are not in contact with  
5 the soil or forest floor and that the resins can be extracted easily in the laboratory from the same  
6 columns used during the field exposure. Extraction of inorganic N ions from IER columns with  
7 KCl is an exchange or equilibrium reaction and is most efficiently done with the extractant  
8 solution percolated through the resin column, as opposed to batch extractions (Kjønaas, 1999b).  
9 Crabtree and Kirkby (1985) used an IER column design to measure soilwater solute flux, Susfalk  
10 and Johnson (2002) used an IER layer sandwiched between sand layers within a PVC tube to  
11 measure solute fluxes in snowmelt and soil solution, and others have measured ionic deposition  
12 in throughfall with IER columns (Garten, 1992; Simkin et al., 2004).

13 N deposition in throughfall and precipitation was measured for one year with conventional  
14 throughfall solution collectors and co-located IER column collectors at a high and relatively low  
15 pollution site in the SBM. The primary objective of the study was to evaluate how well IER  
16 throughfall collectors function under field conditions and to determine how long the IER  
17 collectors can be employed in the field, with the hope that these collectors can be used to  
18 measure N deposition in throughfall without the need for frequent sample collection. A  
19 preliminary report of a portion of this work has been published (Fenn et al., 2002).

20

21

## **MATERIALS and METHODS**

22

### **Sampler Design**

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Standard cylindrical rain gauges with a funnel opening (10 cm i.d.; Glaubig and Gomez, 1994)

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were used for conventional sampling of throughfall and precipitation. In spring and summer a

1 fine mesh screen was placed in the funnel opening to keep out debris. In winter, snow tubes (7.4  
2 cm i.d. x 0.8 m) were installed in the collector openings to allow for snow collection within the  
3 tubes (Fig. 1). The same funnel tops and snow tubes were used to collect throughfall or  
4 precipitation with the IER collectors (Fig. 1). The rain collector funnel was connected to the IER  
5 column (a 1.27 cm x 35.6 cm polyvinyl chloride [PVC] tube) with PVC fittings and tubing. A  
6 double-walled white plastic tube (7.1 cm i.d.) was placed around the IER column to protect it  
7 from direct solar radiation.

8 The resin used for the IER collectors is a mixed bed polystyrene anion and cation exchange  
9 resin (Amberlite™ MB150 Rohm and Haas, Philadelphia, PA; mention of trade names or  
10 products is for information only and does not imply endorsement by the U.S. Department of  
11 Agriculture.). The cation exchange resin is highly basic with an hydroxy ionogenic group and  
12 H<sup>+</sup> as counterion. The anion exchange resin is highly acidic with a quaternary amine ionogenic  
13 group with OH<sup>-</sup> as counterion. Sixty mls of resin (0.55 meq ml<sup>-1</sup> capacity), with a total ion  
14 exchange capacity of 33 meq, was added to PVC columns and rinsed with distilled water. This  
15 volume of resin is sufficient to collect N equivalent to a field deposition flux of 416 kg N ha<sup>-1</sup>  
16 (assuming equal amounts as NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>) plus counterbalancing anions and cations. This is  
17 approximately three times greater than the amount of N deposition measured in 12 months under  
18 large pine trees at Camp Paivika (Table 1), which is by far the highest N deposition scenario.  
19 Polyester floss was inserted at the bottom (as a support platform) and top (as a filter) of the resin  
20 columns. The bottom end of the IER column was closed using a standard PVC cap with an X cut  
21 into it to allow for drainage.

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23

### Field Sampling

1 Throughfall collectors were installed at two mixed conifer forest sites in the San Bernardino  
2 Mountains (SBM) in southern California, located within the South Coast (Los Angeles) Air  
3 Basin. Camp Paivika (CP) is located on the western end of the SBM, and Barton Flats (BF) is 45  
4 km east of CP (Fenn et al., 2000). At each site, one pair of co-located IER collectors and  
5 conventional throughfall collectors (the liquid sample is collected) were placed under the north,  
6 east, south and west quadrants of five typical dominant or co-dominant pine trees. Collectors  
7 were placed at the midpoint between the bole and outer edge of the canopy. These were  
8 ponderosa pine (*Pinus ponderosa* Laws.) trees at CP and the closely related Jeffrey pine (*P.*  
9 *jeffreyi* Grev. & Balf.) trees at BF. At each site n=20 for each exposure time. Due to the semiarid  
10 climate of these forests, the canopies do not have significant epiphytic communities. Collectors  
11 were attached to metal fence posts 1.7 m above ground level. The co-located IER and  
12 conventional solution collectors were placed 0.1-0.5 m apart in the field. In addition, co-located  
13 ion exchange and conventional collectors were placed in four canopy-free open areas at each site  
14 (n=4 for each exposure time). Bulk throughfall and precipitation solutions from the conventional  
15 samplers were collected on a precipitation-event basis, while the IER columns were collected  
16 every three months (four months in one instance). Additional IER columns were left in place for  
17 6, 9, and 12 months to test the reliability of the resin collectors with longer exposure times. For  
18 comparisons of deposition measured by the two collector types, the amount of N deposition  
19 collected in the individual precipitation events by the solution collectors was summed over the  
20 same time period in which the IER collectors were exposed in the field.

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22

### **Resin Column Extraction and Chemical Analyses**

23 Background levels of  $\text{NO}_3^-$  and  $\text{NH}_4^+$  in resin columns unexposed to atmospheric deposition and  
24 stored at room temperature were determined by extracting ions from the resin columns; with

1 three 200-ml extractions with 2 N KCl. Considering the surface area of the throughfall collectors  
2 without snow tubes attached, the amount of N extracted from unexposed resin columns was  
3 equivalent to a background deposition of 0.032 kg NO<sub>3</sub>-N ha<sup>-1</sup> and 0.049 kg NH<sub>4</sub>-N ha<sup>-1</sup>.  
4 Background N in the resin, although minimal, was subtracted from the deposition data to  
5 determine actual throughfall N deposition. Multiple extractions of field-exposed columns  
6 revealed that typically 91-94% of the NO<sub>3</sub><sup>-</sup> was extracted in the first 200-ml extraction,  
7 compared to 98-99% in the case of NH<sub>4</sub><sup>+</sup>. Laboratory tests with IER columns preloaded with a  
8 simulated throughfall solution, which was equivalent to a deposition rate of 70 kg NO<sub>3</sub>-N ha<sup>-1</sup>  
9 and 36 kg NH<sub>4</sub>-N ha<sup>-1</sup>, showed virtually complete (98-104%) ion recovery in the first 200 ml  
10 KCl extraction (Fenn et al., 2002).

11 At the end of the field sampling period, the resin columns were unscrewed from the funnel  
12 assembly, capped off, and returned to the laboratory. The columns were pre-rinsed with 100 ml  
13 of distilled water and extracted by percolating 200 ml of 2 N KCl solution through each one.  
14 Initially, the columns were extracted three times. However, because the amount of N removed in  
15 the third extraction was insignificant (on average 0.07% of the NO<sub>3</sub><sup>-</sup> and 0.1% of the NH<sub>4</sub><sup>+</sup>  
16 extracted), we discontinued the third extraction. All bulk throughfall, bulk precipitation, and  
17 resin extract samples were analyzed for NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> with a TRAACS 800 Autoanalyzer  
18 (Tarrytown, NY).

19

20

## RESULTS

21

### **Bulk Deposition in Precipitation: IER vs. Conventional Collectors**

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At both sites NH<sub>4</sub><sup>+</sup> deposition in the bulk deposition collectors (open areas) trended toward higher values in the IER collectors, particularly in the first and fourth quarterly exposures. These are the exposures that occurred during summer and early fall. Ammonium deposition in the first

1 and fourth quarterly periods at CP was 0.45 kg NH<sub>4</sub>-N ha<sup>-1</sup> greater in the IER collectors than in  
2 the conventional solution collectors (Fig. 2a). At BF bulk deposition of NH<sub>4</sub><sup>+</sup> was 0.25 and 0.45  
3 kg NH<sub>4</sub>-N ha<sup>-1</sup> higher in the IER collectors during these same periods (Fig. 2b). The discrepancy  
4 in bulk deposition of NH<sub>4</sub><sup>+</sup> between the two collector types at BF and CP generally increased  
5 over the 12 months of the study, except for the 9-month exposure at CP, for which the  
6 discrepancy was reversed (i.e., in the 9-month exposure, deposition to the conventional collector  
7 was higher than to the IER; Fig. 2a). After 12 months NH<sub>4</sub>-N deposition was 0.93 and 2.83 kg  
8 ha<sup>-1</sup> greater in the IER collectors than in the conventional collectors at BF and CP, respectively  
9 (Fig. 3).

10 During the two winter exposure periods at CP, bulk deposition of NH<sub>4</sub><sup>+</sup> was highly similar in  
11 one case and 1.11 kg ha<sup>-1</sup> higher in the IER collector in another case (Fig. 2a). At BF bulk  
12 deposition was highly similar among the two collector types in the first winter exposure and 0.17  
13 kg ha<sup>-1</sup> higher in the conventional collector in the second winter exposure (Fig. 2b).

14 Bulk deposition of NO<sub>3</sub><sup>-</sup> in precipitation was nearly always highly similar between the two  
15 collector types at both BF and CP (Fig. 4). The only exceptions to this pattern were at CP where  
16 NO<sub>3</sub>-N deposition was 0.67 kg ha<sup>-1</sup> higher in the IER collectors during the fourth quarterly  
17 exposure period and 3.15 kg ha<sup>-1</sup> higher in the conventional collectors for the collectors exposed  
18 for nine months (Fig. 4a). The latter instance seems to be an anomaly, possibly due to a  
19 systematic error or because of inherent variation in throughfall fluxes as a result of heterogeneity  
20 in canopy cover. After nine months, NH<sub>4</sub><sup>+</sup> deposition at CP was also higher in the conventional  
21 collectors (by 1.08 kg N ha<sup>-1</sup>) than in the IER collectors (Figs. 2a and 3).

22

### **Bulk Throughfall: IER vs. Conventional Collectors**

1  
2 No consistent differences between the conventional and IER collectors were observed in  
3 deposition of  $\text{NO}_3^-$  in throughfall at CP and BF (Fig. 4) or of  $\text{NH}_4^+$  at CP (Fig. 2a). However,  
4 deposition of  $\text{NH}_4\text{-N}$  in throughfall at BF was 0.82-2.31  $\text{kg ha}^{-1}$  higher in the IER collectors than  
5 the conventional collectors after 3, 6, 9, and 12 months of monitoring (Fig. 2b). The discrepancy  
6 in bulk deposition of  $\text{NH}_4^+$  in throughfall between the two collector types at BF increased  
7 steadily over the 12 months of the study (Fig. 3). At CP however, no consistent pattern of  
8 differences in throughfall deposition between the two collector types was observed. After 3 and 9  
9 months of monitoring,  $\text{NH}_4\text{-N}$  deposition was 5.25-5.56  $\text{kg ha}^{-1}$  lower in the IER; after 6 months  
10 of monitoring, collectors and values were equivalent between the two collector types (Fig. 3).  
11 After 12 months of sampling, the average value for throughfall deposition of  $\text{NH}_4\text{-N}$  in the IER  
12 samplers at CP was 4.88  $\text{kg ha}^{-1}$  greater than in the conventional collectors.

### **Effect of Time of Exposure on Performance of IER Columns**

13  
14  
15 Nitrate deposition values were not significantly different between IER columns left in the field  
16 for twelve months compared to the sum of deposition values of IER columns of the four  
17 successive quarterly periods (Table 1). Likewise,  $\text{NO}_3^-$  deposition was equivalent between the  
18 IER collectors exposed for 12 months and annual deposition fluxes measured in the conventional  
19 solution collectors (Table 1; Fig. 4). Similar findings were observed in comparisons of  $\text{NO}_3^-$   
20 deposition in the conventional collectors and to deposition measured with the IER collectors  
21 exposed for 3, 6, and 9 months. These comparisons indicate that the IER collectors function well  
22 with exposure times as long as a year, even in areas with unusually high N deposition such as  
23 CP. The sole exceptions to these general conclusions were the low  $\text{NO}_3^-$  deposition levels  
24 measured in the open-area IER collectors exposed for 9 months at CP and to a lesser degree at

1 BF. The cause of these low readings is unknown. However, the IER deposition values for the  
2 sum of the first three quarterly open-area exposures at CP and BF were similar to deposition  
3 values in the conventional collectors. These findings suggest that the unusually low values for  
4 the IER collectors exposed in open areas for 9 months at CP and BF are an anomaly, possibly  
5 due to an unknown error in the field or in the laboratory, or variation in canopy cover, as  
6 mentioned previously.

7

### 8 **Nitrogen Deposition Based on Two Methods at CP and BF**

9 Total inorganic N deposition ( $\text{NO}_3\text{-N} + \text{NH}_4\text{-N}$ ) under large pine canopies with the two types of  
10 collectors over the twelve months of exposure was  $144\text{-}146 \text{ kg ha}^{-1}$  at CP and  $15\text{-}17 \text{ kg ha}^{-1}$  at  
11 BF. By comparison, bulk deposition in open areas ranged from  $12\text{-}16 \text{ kg ha}^{-1}$  at CP and  $3\text{-}4 \text{ kg}$   
12  $\text{ha}^{-1}$  at BF (Table 1). These data summarizing annual deposition loadings demonstrate how  
13 comparable the two collector types performed overall. They also indicate that annual N inputs in  
14 the western San Bernardino Mountains are extremely high under large trees, particularly in years  
15 with extensive fog exposure (Table 1; Figs. 2 and 4). Nitrogen deposition at BF was lower than  
16 at CP because of lower pollution exposure and also because fog frequency and fog density are  
17 consistently lower at BF (Fenn et al., 2000). Total annual throughfall and precipitation volumes  
18 were 290 mm and 337 mm at BF compared to 1882 mm and 846 mm at CP. The ratio of annual  
19 throughfall volume to precipitation volume was 0.86 and 2.22 at BF and CP. The higher ratio of  
20 throughfall to precipitation volume at CP is a result of the greater fog occurrence at CP as  
21 demonstrated in a previous study (Fenn et al., 2000).

22

## DISCUSSION

### Comparison of N Deposition Fluxes with IER and Conventional Throughfall Collectors

The overall results of this study demonstrate that the IER collectors performed well under field conditions and that in most instances the IER columns gave results similar to the conventional collectors even after field exposure times as long as 12 months (Table 1). This is particularly true for throughfall measurements at CP where deposition values were highly similar with both sampling methods and at all times of exposure. Kjønås (1999a) reported that IER bags placed on the forest floor for throughfall deposition measurements functioned equally well during two-month and six-month exposures; the latter being the longest exposure times used in the study. Deposition measurements for  $\text{NO}_3\text{-N}$  in bulk throughfall and bulk precipitation with the two collector types were highly similar at CP and BF with few exceptions (Fig. 4). However at BF, annual  $\text{NH}_4^+$  deposition in throughfall was  $2.31 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  higher in the IER collectors than in the conventional collectors. Similarly, annual  $\text{NH}_4^+$  deposition in bulk precipitation at BF and CP was  $0.92 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  and  $2.84 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  higher in the IER collectors than in the conventional collectors (Fig. 2; Table 1). Garten (1992; using IER columns) and Kjønås (1999a; using IER bags) also reported that measurements of atmospheric deposition of  $\text{NH}_4^+$  were higher when using IER collectors compared to conventional solution collectors. However, measurements of  $\text{NO}_3^-$  deposition were similar with both collector types in both studies. Although Simkin et al. (2004) did not measure  $\text{NH}_4^+$  deposition, they found that IER columns worked well for measuring anion deposition (sulfate, nitrate, and chloride). Their report focused mainly on IER collector design and laboratory analytical methods, with only short-term field testing (three 4-6 week bulk deposition collections).

### Possible Sources of $\text{NH}_4^+$ Discrepancy Between Collector Types

1 Further tests are needed to determine the cause of the discrepancy in  $\text{NH}_4^+$  deposition rates  
2 between the IER and conventional collectors. The most likely factor contributing to this  
3 discrepancy would seem to be the release of quaternary amine compounds from the anion  
4 exchange resin polymer, resulting in higher background  $\text{NH}_4^+$  levels when extracting the resin.  
5 Since most commercial anion exchange resin beads employ either trimethylamine (Type I resins)  
6 or dimethyl- $\beta$ -hydroxyethylamine (Type II resins) groups (Skogley and Dobermann, 1996) there  
7 is a concern that under prolonged use or severe conditions, amine groups could be released, thus  
8 contaminating the samples with  $\text{NH}_4^+$ . Kjønnaas (1999b) found that freeze-thaw cycles did not  
9 affect resin stability or function, but that resin drying could affect ion adsorption or ion release to  
10 a slight degree. Kjønnaas (1999b) also reported evidence of  $\text{NH}_4^+$  release from dried Amberlite  
11 MB1 mixed bed resin over long time periods, although differences between moist and dried resin  
12 were not statistically significant. For other similar resin types there was no evidence of  $\text{NH}_4^+$   
13 release (Kjønnaas, 1999b). Mamo et al. (2004) exposed mixed bed IER to repeated freeze-thaw  
14 and wet-dry cycles and found that resin bead integrity was not affected and that the IER retained  
15 virtually 100% of the adsorbed nitrate and ammonium even after the most severe freeze-thaw  
16 and wet-dry treatments. We suggest that any IER to be used in long-term environmental  
17 monitoring programs should be tested for reliability under appropriate environmental extremes to  
18 ensure that the IER are quantitatively capturing ions of interest and releasing them during the  
19 extraction procedure.

20 Volatilization losses of  $\text{NH}_3$  from the solutions in the conventional collectors are another  
21 possible source of discrepancy between the two collector types. Either of these two processes  
22 (release of amine groups or volatilization) would lead to higher deposition estimates in the IER  
23 collectors compared to the conventional collectors. However, it is necessary to know which  
24 process or to what extent both processes may be occurring before it can be determined which

1 collector type is more accurate. Nitrification of  $\text{NH}_4^+$  in the liquid samples also could account for  
2 the discrepancy, but we did not find corresponding increases in nitrate in the liquid samples  
3 compared to the IER collectors as would have been expected with this mechanism, assuming  
4 complete nitrification. Incomplete nitrification could also account for the discrepancy, and would  
5 result in gaseous losses of N from the solutions as the  $\text{NH}_4^+$  is oxidized to nitrogenous trace gas  
6 forms (e.g.,  $\text{N}_2\text{O}$ , NO or  $\text{NO}_2$ ). However, it seems unlikely that nitrification activity in  
7 throughfall solutions would be quantitatively significant in the short interval of time between  
8 collection of throughfall samples in the field and storage of samples in a freezer (typically 1-3  
9 days), especially considering that the  $\text{NH}_4^+$  discrepancy also occurred in the open precipitation  
10 collectors, that were not expected to be colonized by a nitrifier community of organisms. The  
11  $\text{NH}_4^+$  discrepancy in open areas at CP and BF was generally greatest during the first and fourth  
12 exposure periods when temperatures were higher (except at CP where the discrepancy in the  
13 third period was also high). Higher temperatures could favor any of the potential processes  
14 causing the discrepancy: volatilization, release of amine groups from the resin, or nitrification.  
15 Collectors placed in canopy-free areas in the field were exposed to higher levels of solar  
16 radiation and heating. Nonetheless, comparisons of the  $\text{NH}_4^+$  discrepancy between collector  
17 types in open areas with the discrepancy between collector types under large pine canopies  
18 indicate that the discrepancy was often greater in throughfall collectors placed under pine trees.  
19 At BF, the discrepancy between the two collector types was consistently greater under pine trees  
20 than in open areas, while at CP the level of discrepancy between the collector types under pine  
21 versus open areas was variable over the course of the study (Fig. 3).

22 Because of the much greater variability in throughfall fluxes of N as a result of canopy  
23 interactions with atmospheric N, we assume that the discrepancy between the two collector types  
24 can be estimated more accurately when based on the discrepancy in the precipitation collectors

1 placed in canopy-free or open areas. The average discrepancy between collector types in open  
2 areas at the two sites is  $1.88 \text{ kg NH}_4\text{-N ha}^{-1} \text{ yr}^{-1}$ . We, therefore, suggest this as the best estimate  
3 of how much the IER collectors overestimated deposition of  $\text{NH}_4\text{-N}$  in this study. For throughfall  
4 under pine trees at CP, this discrepancy is within the margin of error, but a discrepancy of  $1.88$   
5  $\text{kg NH}_4\text{-N ha}^{-1} \text{ yr}^{-1}$  is greater than the margin of error for bulk deposition at the two sites or for  
6 throughfall deposition at BF.

7

### 8 **Considerations for the Use of IER Deposition Collectors**

9 The greatest advantage of ion-exchange resin throughfall collectors is the opportunity they afford  
10 to quantify atmospheric deposition inputs over a much greater geographic and temporal scale  
11 than otherwise feasible. With conventional collectors, sample volumes must be accurately  
12 measured, usually on a precipitation-event basis, to calculate deposition fluxes. With IER  
13 collectors, precipitation or throughfall volumes aren't needed to calculate deposition loads  
14 because deposited ions from multiple precipitation events are captured on the resin independent  
15 of precipitation amount. However, if volume information is needed it can be obtained easily by  
16 capturing the leachate from the resin columns (Garten, 1992).

17 Low sample volumes in bulk deposition or throughfall solution collectors inherently lead to  
18 uncertainty in deposition estimates. With only trace amounts of precipitation, the conventional  
19 solution collectors typically do not collect enough sample for analysis, although the ionic  
20 concentration of the sample is likely to be unusually high during dry periods. If there is minimal  
21 volume for collection and analysis, a significant proportion of the sample will be left as residue  
22 in the collector after it is decanted. The ion exchange collectors, on the other hand, will retain  
23 whatever ions are transported by gravitational flow from the funnel collector to the resin column,  
24 even in low volumes. These may seem like trivial issues, but in areas with prolonged dry periods

1 such as in the San Bernardino Mountains or the Sierra Nevada, the summer-dry climate results in  
2 long dry periods when atmospheric pollutants accumulate on plant canopies. Under these  
3 conditions, infrequent low-volume rain events can represent a proportionally significant  
4 deposition flux that is important to quantify (Fenn and Bytnerowicz, 1997; Fenn et al., 2000).

5 Control, blank IER columns that are not exposed to atmospheric deposition should be  
6 deployed in at least a subset of the monitoring sites to determine IER background ammonium  
7 and nitrate levels after exposure to field conditions. However, a true control blank also should be  
8 exposed to the same wetting/drying cycles as the treatment collectors. Wet-dry and freeze-thaw  
9 cycles could be mimicked in the lab, or wet-dry cycles could be applied in the field to ensure the  
10 resin is functioning properly and to ascertain what the true ionic background levels are for the  
11 resin after field exposure. At the end of the monitoring period when IER columns are brought  
12 back to the laboratory for extraction and analysis, the unexposed control tubes should be  
13 simultaneously extracted to determine ionic background levels of field-exposed resin columns.  
14 This background value is then used to blank-correct data from the IER columns used for  
15 deposition measurements (Kjønaas, 1999b). Alternatively, if release of amine groups from  
16 anion-exchange resin is found to be a problem with a batch of resin, the cation exchange and  
17 anion exchange resin collectors can be implemented separately. In this case, any release of amine  
18 groups from the anion exchange resin columns would not affect extractable  $\text{NH}_4^+$  levels from the  
19 separate cation exchange resin samples. However, employing separate anion and cation columns  
20 doubles the number of collectors needed and also means that cations and anions will not be  
21 collected from the identical microsites; they will be extracted and analyzed from separate IER  
22 columns, introducing greater variability and cost.

23

1 **CONCLUSIONS**

2 The bulk precipitation/throughfall collectors described in this study are based on adsorption of  
3  $\text{NO}_3^-$  and  $\text{NH}_4^+$  ions onto a mixed bed ion exchange resin (IER) column. This inexpensive  
4 collector is highly efficient at collecting N deposition in throughfall or precipitation at a fraction  
5 of the labor and analysis costs of conventional throughfall solution collectors. Results of this  
6 study, indicate that these IER collectors give good results with deployment times as long as a  
7 year---the longest exposure time that was tested. However, field IER blanks should be placed in  
8 the field to determine true background levels of ions in the resin at the end of the monitoring  
9 period. This is particularly important for  $\text{NH}_4^+$  because background levels may increase slightly  
10 over time, possibly due to a slow release of quaternary amine groups from the anion exchange  
11 resin beads. In summary, this study demonstrates the usefulness and practicality of monitoring  
12 ionic deposition in precipitation and throughfall using IER columns. This same method also can  
13 be used to measure ionic deposition in stemflow or in other hydrologic fluxes by directing the  
14 hydrologic flow through an IER column.

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## Figure Captions

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Fig. 1. Photograph of throughfall/precipitation collectors used in this study: (a) Ion exchange resin (IER) column collector with a protective tube installed around the IER column to reduce heating from solar radiation; (b) IER collector with the solar shield tube removed, showing the IER column at the bottom of the collector assembly; (c) Tube that is attached to the funnel collector opening in winter to capture snow; (d) Conventional type rain gauge collector used to collect bulk precipitation or throughfall solutions.

Fig. 2. Comparison of deposition of  $\text{NH}_4\text{-N}$  to ion exchange resin collectors (open bars) and conventional solution collectors (black bars) in open areas and under mature ponderosa pine trees at Camp Paivika (a) and Barton Flats (b). The first four pairs of histogram bars represent four consecutive three-month exposures. The last three pairs of histogram bars are for the 6-, 9- and 12-month exposures. In each case, the IER collectors were continuously exposed in the field for the indicated time periods. The data for the conventional solution collectors are the sum of deposition in the throughfall or precipitation solutions collected in the conventional collectors for the indicated time periods. The horizontal dashed line traversing each figure represents the zero baseline for precipitation or throughfall volume.

Fig. 3. Discrepancy in  $\text{NH}_4\text{-N}$  deposition (IER minus conventional) in open areas and under pine canopies between the IER collectors and the conventional throughfall solution collectors at Barton Flats (BF) and Camp Paivika (CP).

1 Fig. 4. Comparison of deposition of  $\text{NO}_3\text{-N}$  to conventional throughfall solution collectors and  
2 ion exchange resin collectors in open areas and under mature ponderosa pine trees at Camp  
3 Paivika (a) and Barton Flats (b). See caption to Fig. 2 for a description of the histogram bars.  
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1 Table 1. Comparison of nitrogen deposition fluxes ( $\text{kg N ha}^{-1} \text{ yr}^{-1}$ ) measured with ion exchange  
 2 resin (IER) collectors<sup>†</sup> and conventional liquid collectors at Camp Paivika (CP) and Barton Flats  
 3 (BF).

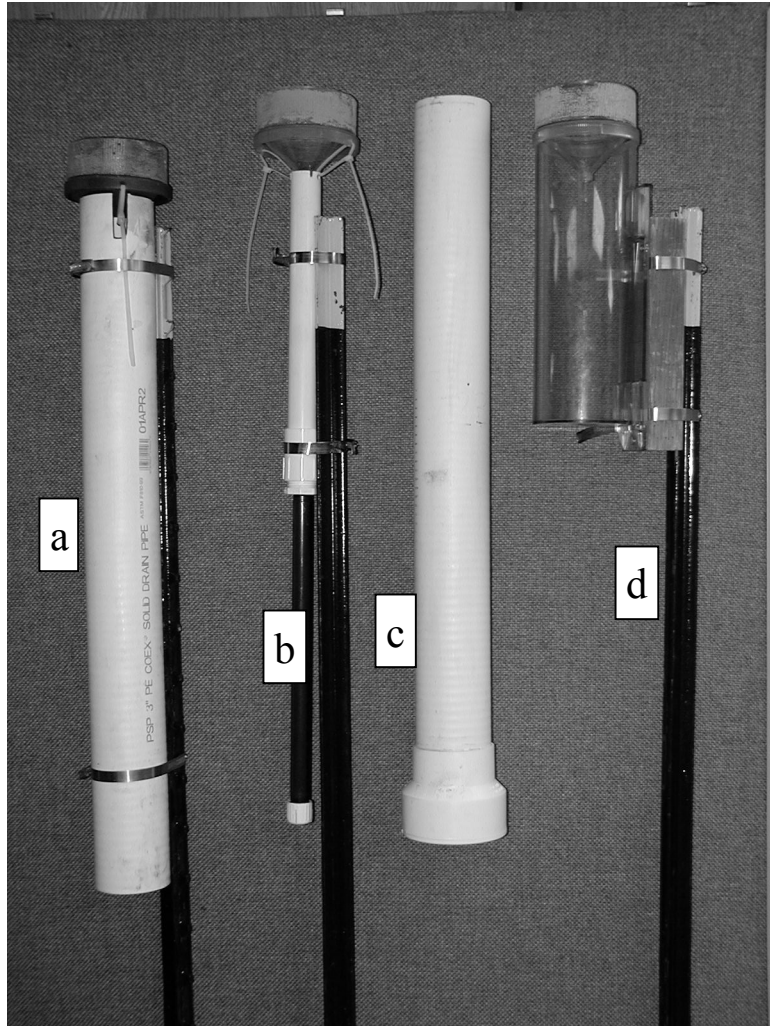
	IER 4 x 3 months	IER 4 x 3 months s.e. <sup>‡</sup>	IER 12 months	IER 12 months s.e.	Conventional collector	Conventional collector s.e.
BF open $\text{NH}_4^+$	1.79	0.12	2.06	0.22	1.14	0.08
BF open $\text{NO}_3^-$	2.23	0.01	1.98	0.08	2.19	0.08
BF total inorganic N	<b>4.02</b>		<b>4.04</b>		<b>3.33</b>	
BF throughfall $\text{NH}_4^+$	7.57	0.78	7.87	0.61	5.56	0.58
BF throughfall $\text{NO}_3^-$	10.19	0.80	9.13	0.29	9.48	0.14
BF total inorganic N	<b>17.76</b>		<b>17.00</b>		<b>15.04</b>	
CP open $\text{NH}_4^+$	7.29	0.97	8.33	2.87	5.49	1.06
CP open $\text{NO}_3^-$	6.67	1.16	7.26	2.20	6.80	1.12
CP total inorganic N	<b>13.96</b>		<b>15.59</b>		<b>12.29</b>	
CP throughfall $\text{NH}_4^+$	59.87	6.35	69.20	10.12	64.32	9.90
CP throughfall $\text{NO}_3^-$	77.59	8.18	76.62	10.13	79.57	10.41
CP total inorganic N	<b>137.46</b>		<b>145.82</b>		<b>143.89</b>	

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 6 <sup>†</sup>Data are shown for IER collectors as the sum of four consecutive three-month exposures (new  
 7 tubes installed every three months; 4 x 3 months) and for IER collectors left in the field for 12  
 8 consecutive months. Twenty collectors of each type and for each exposure period were used at  
 9 each study site (4 collectors/tree; 5 replicate trees).

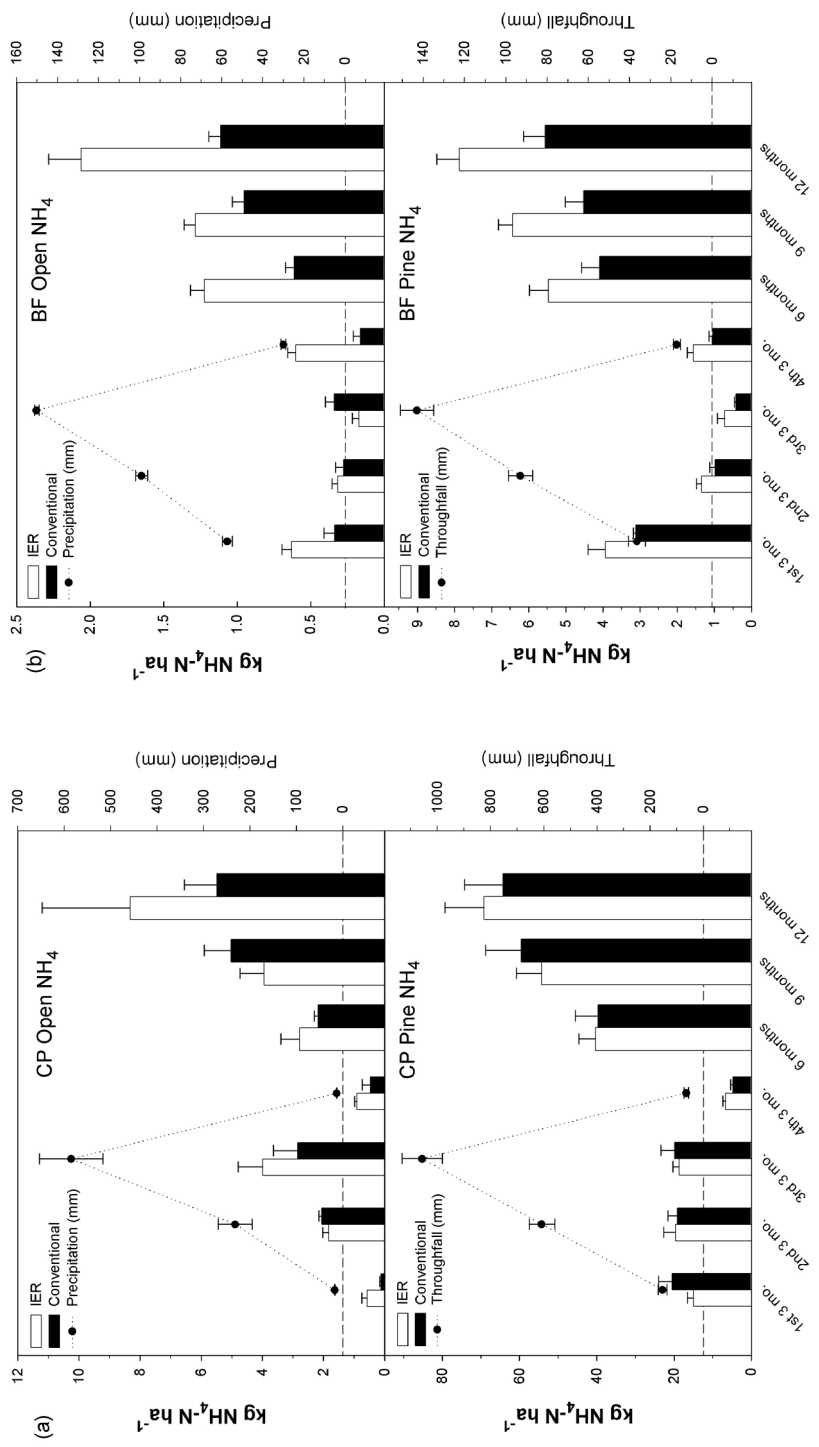
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11 <sup>‡</sup>S.E. represents the standard error of the mean.

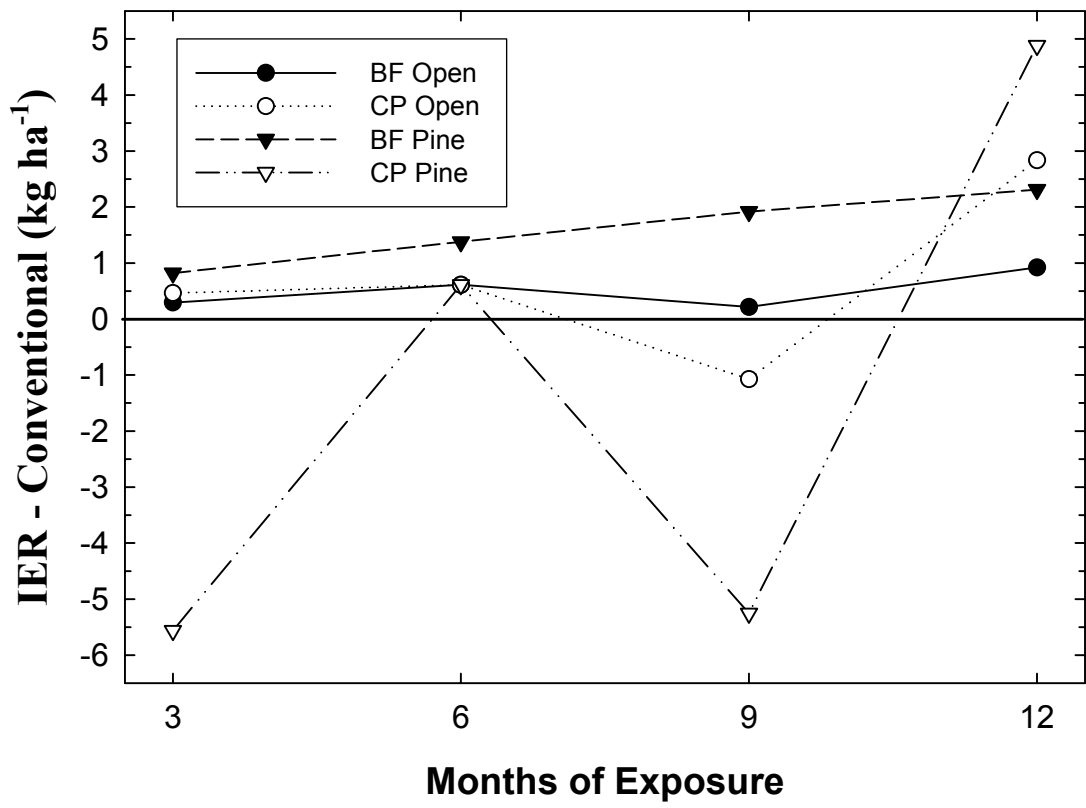
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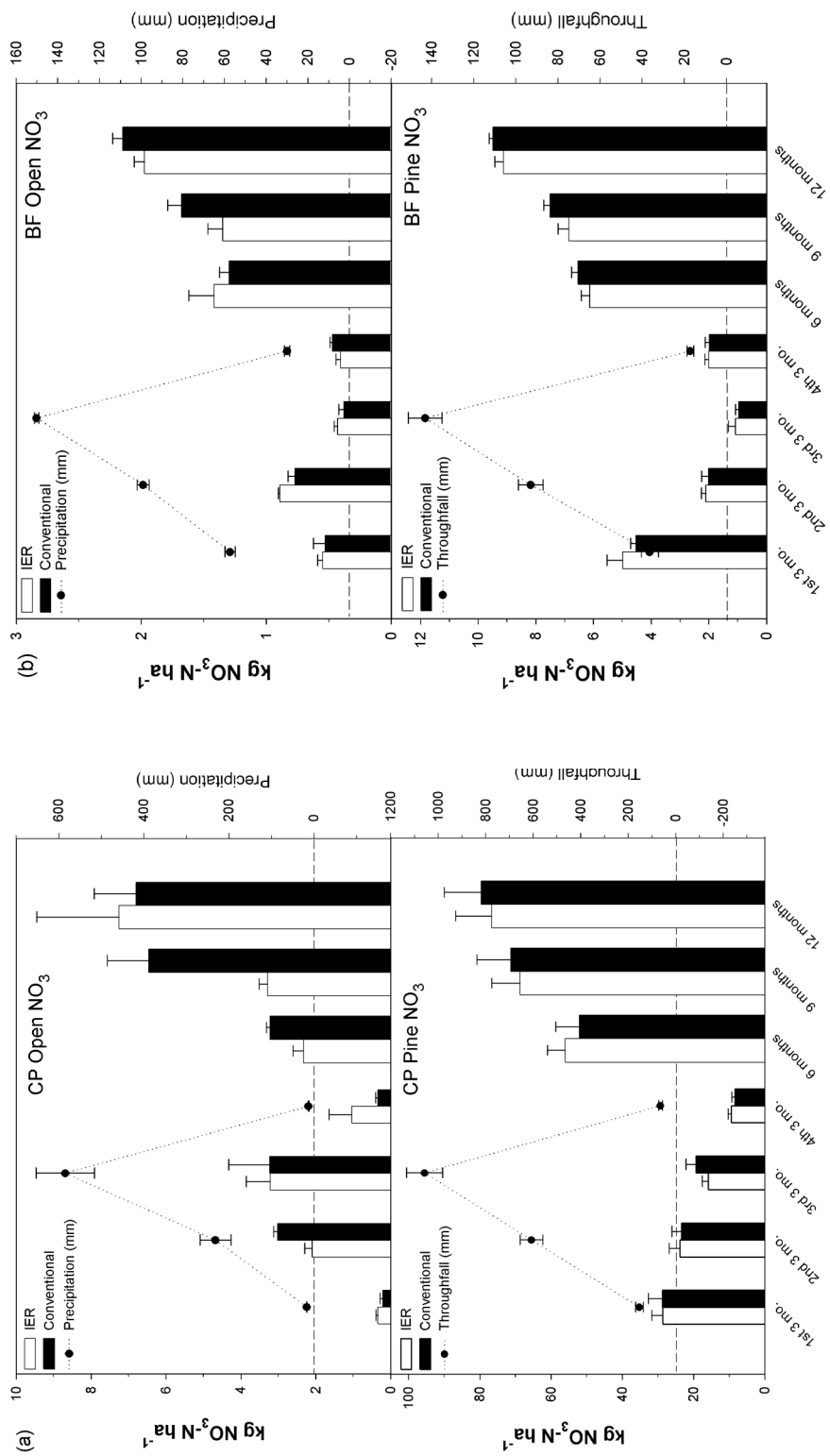
**Fig. 1**



**Fig. 2**



**Fig. 3**



**Fig. 4**