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**Appendix D**

1     **Monitoring Nitrogen Deposition in Throughfall Using Ion Exchange Resin Columns: A**  
2                             **Field Test in the San Bernardino Mountains**

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17    **Abbreviations:** IER, ion exchange resin; CP, Camp Paivika; BF, Barton Flats; SBM, San  
18    Bernardino Mountains.

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## ABSTRACT

1  
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 in bulk throughfall collected under pine canopies and in forest clearings  
8 were compared as measured with co-located conventional throughfall solution collectors and  
9 IER throughfall collectors using mixed bed IER columns. Deposition data were collected for one  
10 year at a high (Camp Paivika, CP) and relatively low (Barton Flats, BF) deposition site in the  
11 San Bernardino Mountains in southern California. Annual throughfall deposition values ( $\text{kg ha}^{-1}$   
12 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 17.0 and  
13 15.0 at BF according to the IER and conventional methods, respectively. Analogous values for  
14 bulk deposition in forest clearings were 15.6 and 12.3 at CP and 4.0 and 3.3 at BF. It was  
15 concluded that the IER collectors can be used for routine monitoring of deposition in throughfall  
16 and bulk deposition, provided that field blanks are used to account for background levels of N in  
17 the IER columns which at times are slightly elevated, possibly from slow release of amine  
18 groups from the anion exchange resin during field exposures.

## INTRODUCTION

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21 Because of the widespread and largely detrimental aspects of elevated atmospheric N deposition,  
22 quantification of ecosystem N inputs from air pollution are 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 challenging task due to the technical difficulties and expense associated with  
3 measuring atmospheric concentrations and deposition fluxes for the array of dry-deposited  
4 gaseous and particulate forms of N, in addition to wet deposition and fog or cloudwater  
5 deposition of N. Determining the deposition of these many compounds to complex recipient  
6 ecosystem surfaces under dynamic meteorological conditions is a daunting task on the local scale  
7 and particularly impractical and cost prohibitive over extensive landscapes. As a result, total N  
8 deposition 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 and dry deposition, wet deposition is  
14 the smallest component of total deposition inputs, particularly in ecosystems with high leaf area  
15 index values, where plant canopies serve as efficient scavengers of air pollutants in wet and dry  
16 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. Passive monitors for obtaining average  
20 concentrations of gaseous pollutants is now recognized as a vital methodology for measuring  
21 gaseous pollutant exposure in forests and other areas without electric power and where the cost  
22 of maintaining multiple active monitors is prohibitive (Bytnerowicz et al., 2002; Krupa and  
23 Legge, 2000). However, total N deposition fluxes cannot be determined solely from gaseous

1 pollutant concentrations; considerable meteorological data, pollutant deposition velocity values,  
2 and information on plant community characteristics are also required (Baumgardner et 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 of canopy retention of a portion  
7 of the N intercepted by the canopy and because deposition to understory vegetation and direct  
8 deposition to the ground surface are usually not measured. Nonetheless, throughfall collection  
9 and analysis seems to have greater potential than other methods for widespread monitoring of  
10 atmospheric deposition to forests and other ecosystems. This conclusion is substantiated by the  
11 Pan European intensive monitoring program of the European Union International Cooperative  
12 Programme (ICP-Forests), which has chosen to monitor throughfall for large scale N deposition  
13 monitoring; throughfall is currently being measured in 488 plots (Bleeker et al., 2003).

14 Throughfall is often the method of choice because of the impracticality of other methods of  
15 monitoring dry deposition at the scale needed for characterizing atmospheric deposition over  
16 large forested landscapes. However, traditional throughfall methods are labor intensive and  
17 analytically expensive to implement at broad scales----because of the need to frequently collect  
18 and analyze a large number of replicate 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; Kjønnaas, 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 easily extracted 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 (Kjønnaas, 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 In this study, N deposition in throughfall and precipitation was measured for one year with  
14 conventional throughfall solution collectors and co-located IER column collectors at a high and  
15 relatively low pollution site in the SBM. The primary objective of the study was to evaluate how  
16 well IER throughfall collectors function under field conditions and to determine how long the  
17 IER 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).

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## MATERIALS and METHODS

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### 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. A fine mesh screen was

1 placed in the funnel opening in spring and summer 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<sup>1</sup> Rohm and Haas, Philadelphia, PA). The cation exchange resin is  
10 highly basic with an hydroxy ionogenic group and H<sup>+</sup> as counterion. The anion exchange resin  
11 is highly acidic with a quaternary amine ionogenic group with OH<sup>-</sup> as counterion. Sixty mls of  
12 resin (0.55 meq ml<sup>-1</sup> capacity), with a total ion exchange capacity of 33 meq, was added to PVC  
13 columns and rinsed with distilled water. This volume of resin is sufficient to collect N equivalent  
14 to a field deposition flux of 416 kg N ha<sup>-1</sup> (assuming equal amounts as NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>) plus  
15 counterbalancing anions and cations. This is approximately three times greater than the amount  
16 of N deposition measured in twelve months under large pine trees at Camp Paivika (Table 1),  
17 which is by far the highest N deposition scenario. Polyester floss was inserted at the bottom (as a  
18 support platform) and top (as a filter) of the resin columns. The bottom end of the IER column  
19 was capped off with a standard PVC cap cut in an X pattern at the bottom to allow for drainage.

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## Field Sampling

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<sup>1</sup> Mention of trade names or products is for information only and does not imply endorsement by the U.S. Department of Agriculture.

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 to the 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 the 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 at a height of 1.7 m above ground level. The co-located IER  
12 and conventional solution collectors were placed 0.1-0.5 m apart in the field. In addition, co-  
13 located ion exchange and conventional collectors were placed in four canopy-free open areas at  
14 each site (n=4 for each exposure time). Bulk throughfall and precipitation solutions from the  
15 conventional samplers were collected on a precipitation-event basis, while the IER columns were  
16 collected every three months (four months in one instance). Additional IER columns were left in  
17 place for 6, 9 and 12 months to test the reliability of the resin collectors with longer exposure  
18 times. For comparisons of deposition measured by the two collector types, 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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### **Resin Column Extraction and Chemical Analyses**

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

1 200-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 the column.  
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).

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## RESULTS

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### **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) showed a trend of  
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  $0.45 \text{ kg NH}_4\text{-N ha}^{-1}$  greater in the IER collectors  
2 compared to the conventional solution collectors (Fig. 2a). At BF bulk deposition of  $\text{NH}_4^+$  was  
3  $0.25$  and  $0.45 \text{ kg NH}_4\text{-N ha}^{-1}$  higher in the IER collectors during these same periods (Fig. 2b).  
4 The discrepancy in bulk deposition of  $\text{NH}_4^+$  between the two collector types at BF and CP  
5 generally increased over the twelve months of the study, except for the 9-month exposure at CP,  
6 for which the discrepancy was reversed (i.e., in the 9-month exposure, deposition to the  
7 conventional collector was higher than the IER; Fig. 2a). After 12 months  $\text{NH}_4\text{-N}$  deposition was  
8  $0.93$  and  $2.83 \text{ kg ha}^{-1}$  greater in the IER collectors than in the conventional collectors at BF and  
9 CP, respectively (Fig. 3).

10 During the two winter exposure periods at CP, bulk deposition of  $\text{NH}_4^+$  was highly similar in  
11 one case and  $1.11 \text{ kg ha}^{-1}$  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  $\text{kg ha}^{-1}$  higher in the conventional collector in the second winter exposure (Fig. 2b).

14 Bulk deposition of  $\text{NO}_3^-$  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  $\text{NO}_3\text{-N}$  deposition was  $0.67 \text{ kg ha}^{-1}$  higher in the IER collectors during the fourth quarterly  
17 exposure period and  $3.15 \text{ kg ha}^{-1}$  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  
20 heterogeneity in canopy cover. After nine months,  $\text{NH}_4^+$  deposition at CP was also higher in the  
21 conventional collectors (by  $1.08 \text{ kg N ha}^{-1}$ ) than in the IER collectors (Figs. 2a and 4a).

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

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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 twelve 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 collectors and  
10 values were equivalent between the two collector types after 6 months of monitoring (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 the conventional collectors.

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

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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 twelve months and annual deposition fluxes measured in the  
19 conventional solution collectors (Table 1; Fig. 4). Similar findings were observed in comparisons  
20 of  $\text{NO}_3^-$  deposition in the conventional collectors and that 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 nine-months at CP and BF are an anomaly, possibly  
5 due to an unknown error in the field or in the laboratory for these collectors, or variation in  
6 canopy cover, as mentioned previously.

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### 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 144-146  $\text{kg ha}^{-1}$  at CP and 15-17  $\text{kg ha}^{-1}$  at  
11 BF. By comparison, bulk deposition in open areas ranged from 12-16  $\text{kg ha}^{-1}$  at CP and 3-4  $\text{kg}$   
12  $\text{ha}^{-1}$  at BF (Table 1). These data summarizing annual deposition loadings demonstrate how  
13 comparable the two collector types performed overall, and they also indicate that annual N inputs  
14 in the western San Bernardino Mountains are extremely high under large trees, particularly in  
15 years with extensive fog exposure (Table 1; Figs. 2 and 4). Nitrogen deposition at BF was lower  
16 than at CP because of lower pollution exposure and also because fog frequency and fog density  
17 are consistently lower at BF (Fenn et al., 2000). Total annual throughfall and precipitation  
18 volumes were 290 and 337 mm at BF compared to 1882 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. Kjønnaas (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 compared to 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  $2.84 \text{ kg N ha}^{-1} \text{ yr}^{-1}$  percent higher in the IER collectors compared to the conventional collectors (Fig. 2; Table 1). Garten (1992; using IER columns) and Kjønnaas (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) didn't 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  $\text{NH}_4^+$ . Kjønåas (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. Kjønåas (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 (Kjønåas, 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 insure 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 is 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 could also 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.,  $\text{N}_2\text{O}$ ,  $\text{NO}$  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 throughfall sample collection in the field and when the samples were stored in a freezer  
9 (typically 1-3 days), especially considering that the  $\text{NH}_4^+$  discrepancy also occurred in the open  
10 precipitation collectors, that are not expected to be colonized by a nitrifier community of  
11 organisms. The  $\text{NH}_4^+$  discrepancy in open areas at CP and BF was generally greatest during the  
12 first and fourth exposure periods when temperatures were higher (except at CP where the  
13 discrepancy in the third period was also high). Higher temperatures could favor any of the  
14 potential processes causing the discrepancy: volatilization, release of amine groups from the  
15 resin, or nitrification. Collectors placed in canopy-free areas in the field were exposed to higher  
16 levels of solar radiation and heating. Nonetheless, comparisons of the  $\text{NH}_4^+$  discrepancy between  
17 collector types in open areas with the discrepancy between collector types under large pine  
18 canopies indicate that the discrepancy was often greater in throughfall collectors placed under  
19 pine trees. At BF, the discrepancy between the two collector types was consistently greater under  
20 pine trees than in open areas, while at CP the level of discrepancy between the collector types  
21 under pine 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 more accurately estimated based on the discrepancy in the precipitation collectors placed

1 in canopy-free or open areas. The average of the 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 of  
3 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 not for bulk deposition  
5 at the two sites or for throughfall deposition at BF.

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

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

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

1 summer-dry climate results in long dry periods when atmospheric pollutants accumulate on plant  
2 canopies. Infrequent low-volume rain events under these conditions can represent a  
3 proportionally significant deposition flux that is important to quantify (Fenn and Bytnerowicz,  
4 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 should also 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 in the field to ensure the resin is functioning properly and  
10 to ascertain what the true ionic background levels are for the resin after field exposure. At the  
11 end of the monitoring period when IER columns are brought back to the laboratory for extraction  
12 and analysis, the unexposed control tubes are simultaneously extracted to determine ionic  
13 background levels of field-exposed resin columns. This background value is then used to blank-  
14 correct data from the IER columns used for deposition measurements (Kjønaas, 1999b).

15 Alternatively, if release of amine groups from anion-exchange resin is found to be a problem  
16 with a batch of resin, the cation exchange and anion exchange resin collectors can be  
17 implemented separately. In this case, any release of amine groups from the anion exchange resin  
18 columns would not affect extractable  $\text{NH}_4^+$  levels from the separate cation exchange resin  
19 samples. However, employing separate anion and cation columns doubles the number of  
20 collectors needed and also means that cations and anions will not be collected from the identical  
21 microsites and will be extracted and analyzed from separate IER columns, introducing greater  
22 variability and cost.

23

## CONCLUSIONS

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

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).

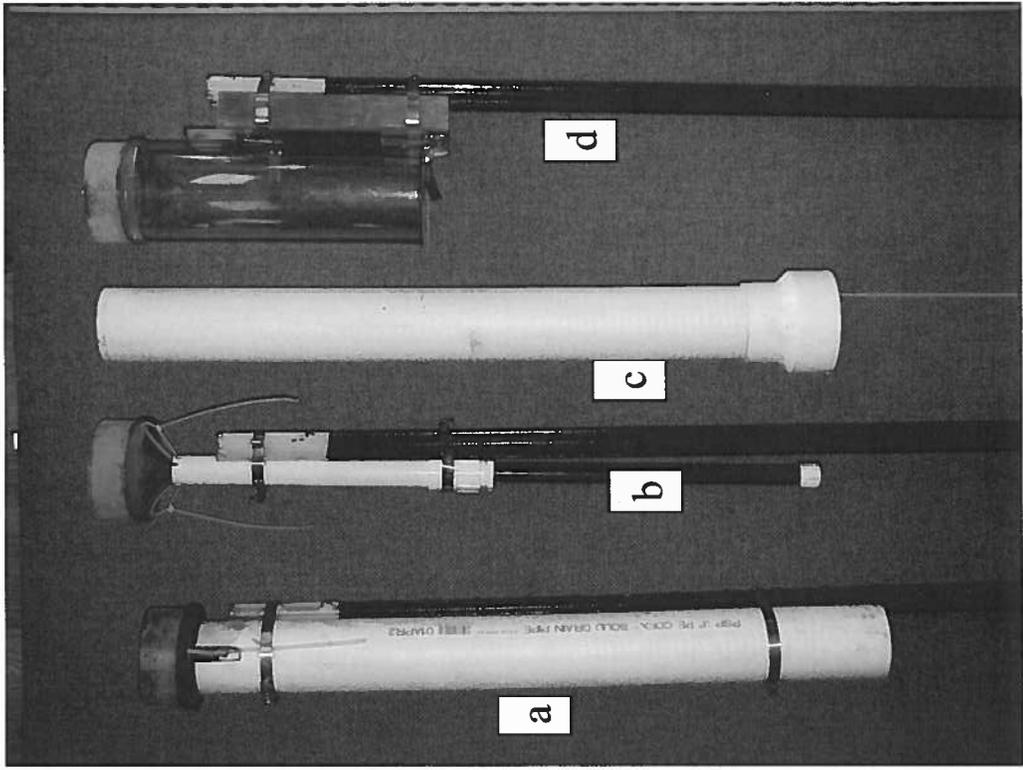
	IER 4 x 3 months	IER 4 x 3 months s.e. <sup>‡</sup>	IER 12 months	IER 12 months s.e.	Conventional collector	Conventional collector s.e.
BF open $\text{NH}_4^+$	1.79	0.12	2.06	0.22	1.14	0.08
BF open $\text{NO}_3^-$	2.23	0.01	1.98	0.08	2.19	0.08
BF total inorganic N	<b>4.02</b>		<b>4.04</b>		<b>3.33</b>	
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>	

5  
 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).

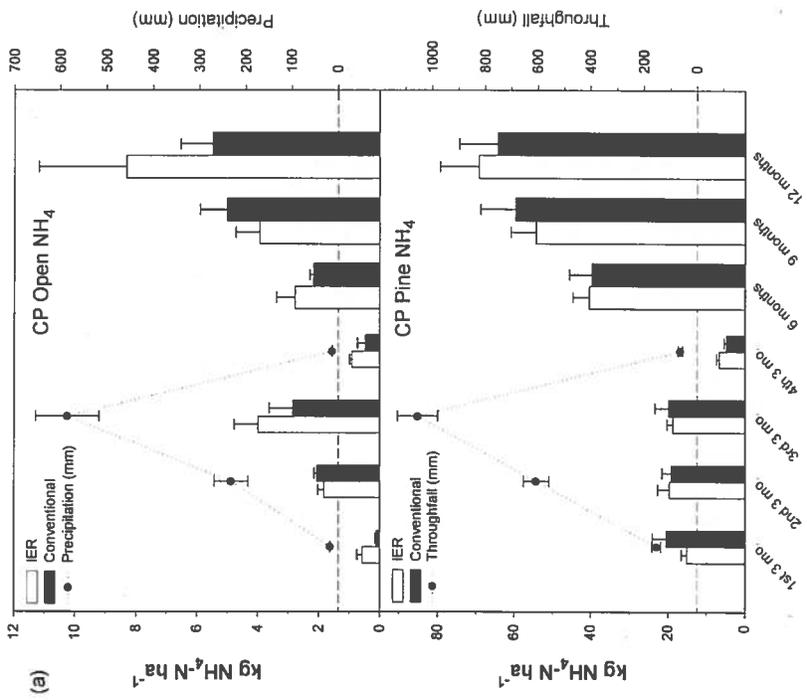
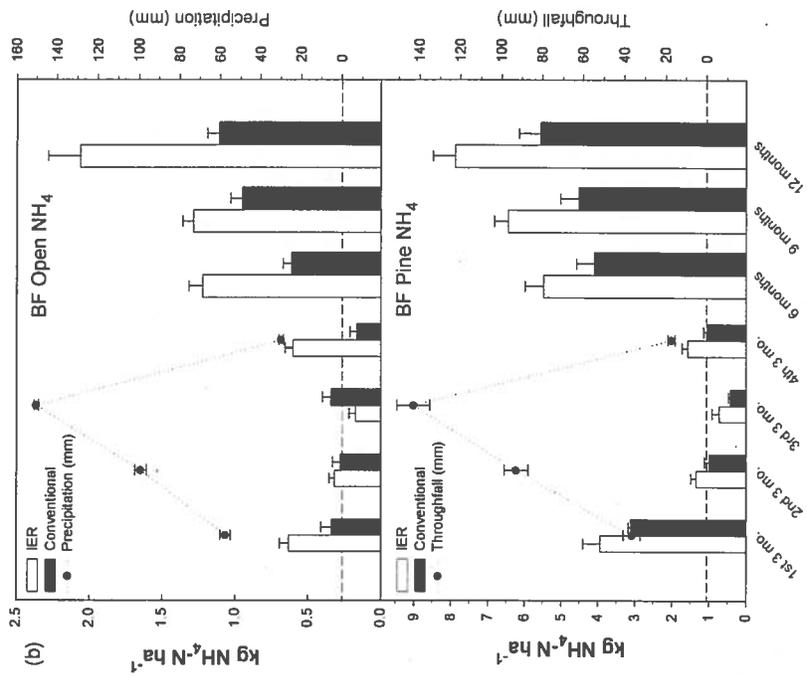
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11 <sup>‡</sup>S.E. represents the standard error of the mean.

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**Fig. 1**



**Fig. 2**

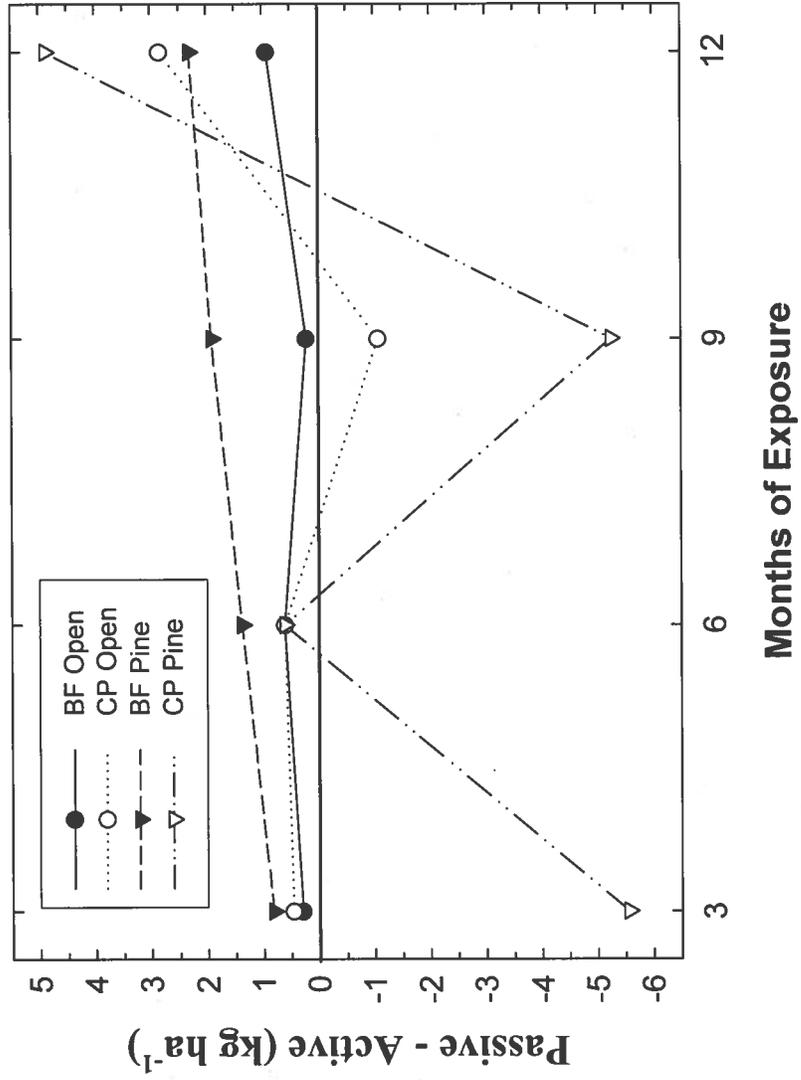
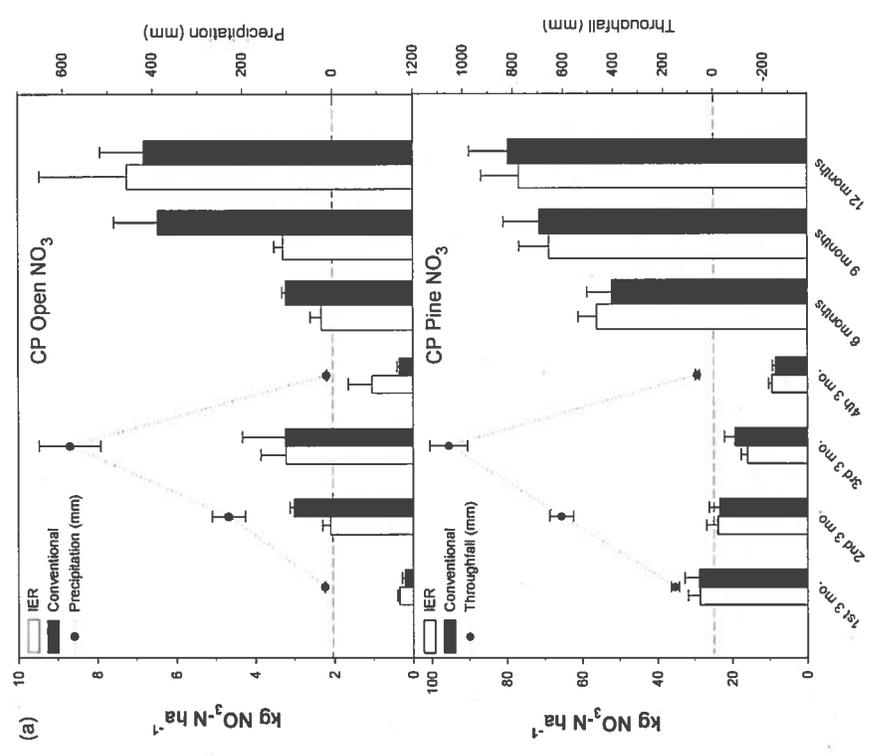
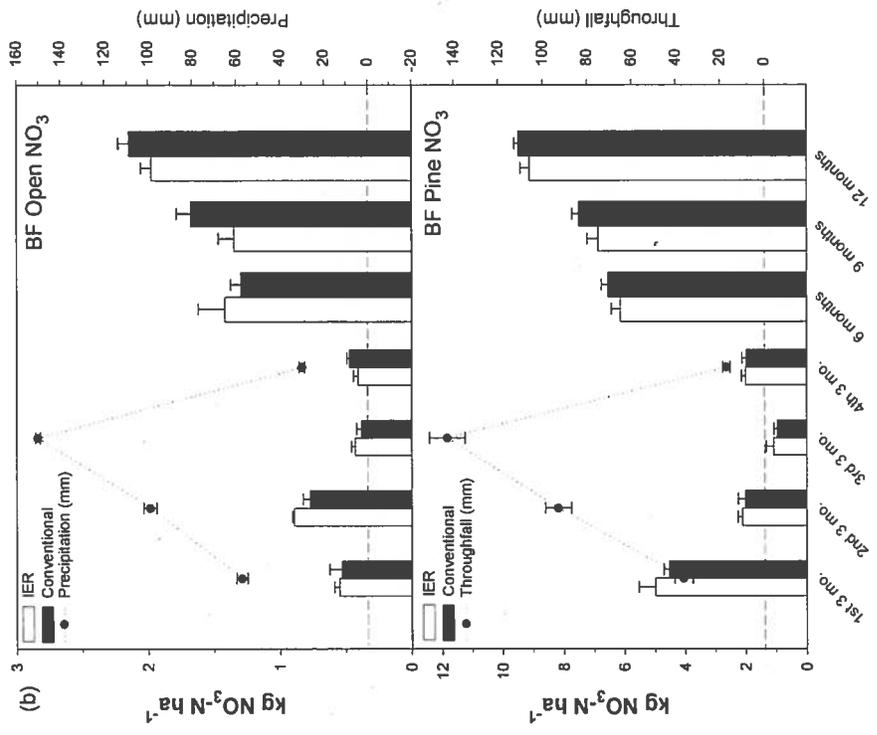


Fig. 3



**Fig. 4**