Atmospheric Pollutants and Trace Gases

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

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ABSTRACT

Conventional throughfall collection methods are labor intensive and analytically expensive to implement at broad scales. This study was conducted to test an alternative approach requiring infrequent sample collection and a greatly reduced number of chemical analyses. The major objective of the study was to determine the feasibility of using ion exchange resin (IER) to measure N deposition in throughfall with field deployment periods of 3 to 12 mo. Nitrogen deposition measurements in bulk throughfall collected under pine (*Pinus* sp.) canopies and in forest clearings were compared between co-located conventional throughfall solution collectors and IER throughfall collectors using mixed bed IER columns. Deposition data were collected for 1 yr at a high deposition site (Camp Paivika, CP) and a relatively low one (Barton Flats, BF) in the San Bernardino Mountains in southern California: Annual throughfall deposition values (kg ha^{-1} of NH_4–N + NO_3–N) under large ponderosa pine trees (*Pinus ponderosa* Laws.) were 145.8 and 143.9 at CP and 17.0 and 15.0 at BF according to the IER and conventional methods, respectively. Analogous values for bulk deposition in forest clearings were 15.6 and 12.3 at CP and 4.0 and 3.3 at BF. It was concluded that the IER collectors can be used for routine monitoring of deposition in throughfall and bulk deposition, provided that field blanks are used to account for background levels of N in the IER columns, which at times are slightly elevated, possibly from slow release of amine groups from the anion exchange resin during field exposures.

Because of the widespread and largely detrimental aspects of elevated atmospheric N deposition, quantification of ecosystem N inputs from air pollution is needed. Quantification of deposition inputs fosters greater understanding of cause and effect relationships between pollutants and ecosystem responses and is critical for identifying terrestrial and aquatic resources most at risk from N enrichment and acidification effects. Measuring total N deposition to forests or other ecosystems is a challenge due to the technical difficulties and expense associated with measuring atmospheric concentrations and deposition fluxes for the array of dry-deposited gaseous and particulate forms of N, in addition to wet deposition and fog or cloudwater deposition of N. Determining the deposition of these many compounds to complex recipient ecosystem surfaces under dynamic meteorological conditions is a daunting task on the local scale and particularly impractical and cost prohibitive over extensive landscapes. As a result, total N deposition estimates to ecosystems are generally highly uncertain or nonexistent.

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

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

Throughfall is an attractive alternative method for estimating atmospheric deposition to forests and other ecosystems (Thimonier, 1998). Deposition of N in throughfall is the hydrologic flux of N from the canopy to the forest floor. Throughfall measurements of N deposition

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Abbreviations: BF, Barton Flats; CP, Camp Paivika; IER, ion exchange resin; SBM, San Bernardino Mountains, California, USA.

generally underestimate total N deposition to the forest because the canopy retains a portion of the N it intercepts and deposition to understory vegetation and direct deposition to the ground surface usually are not measured. Nonetheless, throughfall collection and analysis seems to have greater potential than other methods for widespread monitoring of atmospheric deposition to forests and other ecosystems. This conclusion is substantiated by the Pan European intensive monitoring program of the European Union International Cooperative Program (ICP-Forests): it has chosen to monitor throughfall for large scale N deposition monitoring. Throughfall is currently being measured in 488 plots (Bleeker et al., 2003). Throughfall is often the method of choice because of the impracticality of other methods of monitoring dry deposition at the scale needed for characterizing atmospheric deposition over large forested landscapes. However, traditional throughfall methods are labor intensive and analytically expensive to implement at broad scales—because of the need to frequently collect and analyze a large number of replicate samples (generally on a precipitation-event basis).

In this article we describe comparisons between conventional throughfall deposition measurements and a modified throughfall collection technique using ion exchange resin (IER) columns. The ion exchange resin, usually deployed in resin bags, have often been used for nutrient cycling studies (Binkley and Hart, 1989; Brooks et al., 1996; Qian and Schoenau, 2002; Skogley and Dobermann, 1996; Susfalk and Johnson, 2002), although less frequently for atmospheric deposition measurements (Köchy and Wilson, 2001; Kjønaas, 1999a; Simkin et al., 2004; Van Dam et al., 1991). We chose the resin column design with the expectation that this would be a highly efficient technique for ion capture from throughfall or precipitation samples as the flow is directed through the IER column, enhancing contact of the solutions with the resin. Other advantages of the IER column design used in this study are that the resins are not in contact with the soil or forest floor and that the resins can be extracted easily in the laboratory from the same columns used during the field exposure. Extraction of inorganic N ions from IER columns with KCl is an exchange or equilibrium reaction and is most efficiently done with the extractant solution percolated through the resin column, as opposed to batch extractions (Kjønaas, 1999b). Crabtree and Kirkby (1985) used an IER column design to measure soil water solute flux, Susfalk and Johnson (2002) used an IER layer sandwiched between sand layers within a PVC tube to measure solute fluxes in snowmelt and soil solution, and others have measured ionic deposition in throughfall with IER columns (Garten, 1992; Simkin et al., 2004).

Nitrogen deposition in throughfall and precipitation was measured for 1 yr with conventional throughfall solution collectors and co-located IER column collectors at a high and relatively low pollution site in the San Bernardino Mountains (SBM). The primary objective of the study was to evaluate how well IER throughfall collectors function under field conditions and to determine how long the IER collectors can be employed in the field, with the hope that these collectors can be used to measure N deposition in throughfall without the need for frequent sample collection. A preliminary report of a portion of this work has been published (Fenn et al., 2002).

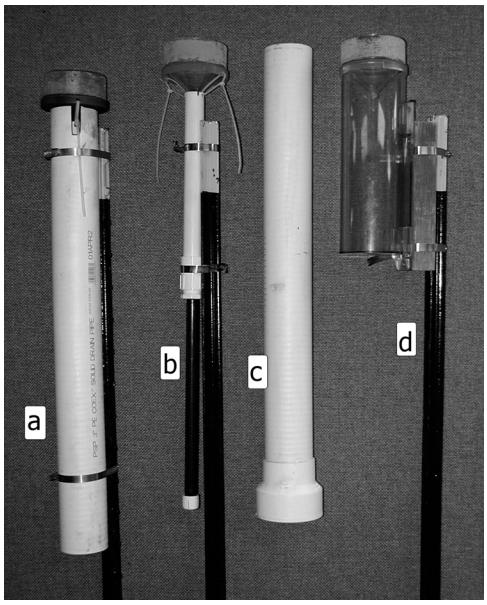

Fig. 1. Photograph of throughfall/precipitation collectors used in this study: (a) Ion exchange resin (IER) column collector with a protective tube installed around the IER column to reduce heating from solar radiation; (b) IER collector with the solar shield tube removed, showing the IER column at the 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.

MATERIALS AND METHODS

Sampler Design

Standard cylindrical rain gauges with a funnel opening (10 cm i.d.; Glaubig and Gomez, 1994) were used for conventional sampling of throughfall and precipitation. In spring and summer a fine mesh screen was placed in the funnel opening to keep out debris. In winter, snow tubes (7.4 cm i.d. by 0.8 m) were installed in the collector openings to allow for snow collection within the tubes (Fig. 1). The same funnel tops and snow tubes were used to collect throughfall or precipitation with the IER collectors (Fig. 1). The rain collector funnel was connected to the IER column (a 1.27 cm by 35.6 cm polyvinyl chloride [PVC] tube) with PVC fittings and tubing. A double-walled white plastic tube (7.1 cm i.d.) was placed around the IER column to protect it from direct solar radiation.

The resin used for the IER collectors is a mixed bed polystyrene anion and cation exchange resin (Amberlite MB150 Rohm and Haas, Philadelphia, PA; mention of trade names or products is for information only and does not imply endorsement by the USDA). The cation exchange resin is highly basic with an hydroxy ionogenic group and H^+ as counterion. The anion exchange resin is highly acidic with a quaternary amine ionogenic group with OH^- as counterion. Sixty mL of resin, with a total ion exchange capacity of 33 $cmol_c$, was added to PVC columns and rinsed with distilled water. This volume of resin is sufficient to collect N equivalent to a field deposition flux of 416 kg N ha^{-1} (assuming equal amounts as NO_3^- and NH_4^+) plus counterbalancing anions and cations. This is ap-

Table 1. Comparison of N deposition fluxes (kg N ha^{-1} yr^{-1}) measured with ion exchange resin (IER) collectors† and conventional liquid collectors at Camp Paivika (CP) and Barton Flats (BF).

Site/deposition form	IER 4 × 3 mo	IER 4 × 3 mo SE‡	IER 12 mo	IER 12 mo SE	Conventional collector	Conventional collector SE
BF open NH_4^+	1.79	0.12	2.06	0.22	1.14	0.08
BF open NO_3^-	2.23	0.01	1.98	0.08	2.19	0.08
BF total inorganic N	4.02		4.04		3.33	
BF throughfall NH_4^+	7.57	0.78	7.87	0.61	5.56	0.58
BF throughfall NO_3^-	10.19	0.80	9.13	0.29	9.48	0.14
BF total inorganic N	17.76		17.00		15.04	
CP open NH_4^+	7.29	0.97	8.33	2.87	5.49	1.06
CP open NO_3^-	6.67	1.16	7.26	2.20	6.80	1.12
CP total inorganic N	13.96		15.59		12.29	
CP throughfall NH_4^+	59.87	6.35	69.20	10.12	64.32	9.90
CP throughfall NO_3^-	77.59	8.18	76.62	10.13	79.57	10.41
CP total inorganic N	137.46		145.82		143.89	

† Data are shown for IER collectors as the sum of four consecutive 3-mo exposures (new tubes installed every 3 mo; 4 × 3 mo) and for IER collectors left in the field for 12 consecutive months. Twenty collectors of each type and for each exposure period were used at each study site (four collectors/tree; five replicate trees).

‡ SE represents the standard error of the mean.

proximately three times greater than the amount of N deposition measured in 12 mo under large pine trees at Camp Paivika (Table 1), which is by far the highest N deposition scenario. Polyester floss was inserted at the bottom (as a support platform) and top (as a filter) of the resin columns. The bottom end of the IER column was closed using a standard PVC cap with an X cut into it to allow for drainage.

Field Sampling

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

Resin Column Extraction and Chemical Analyses

Background levels of NO_3^- and 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 200-mL extractions with 2 *M* KCl. Considering the surface area of the throughfall collectors without snow tubes attached, the amount of N extracted from unexposed resin columns was equivalent to a background deposition of 0.032 kg NO_3–N ha^{-1} and 0.049 kg NH_4–N ha^{-1}. Background N in the resin, although minimal, was subtracted from the deposition data to determine actual throughfall N deposition. Multiple extractions of field-exposed columns revealed that typically 91 to 94% of the NO_3^- and was extracted in the first 200-mL extraction, compared with 98 to 99% in the case of NH_4^+. Laboratory tests with IER columns preloaded with a simulated throughfall solution, which was equivalent to a deposition rate of 70 kg NO_3–N ha^{-1} and 36 kg NH_4–N ha^{-1}, showed virtually complete (98–104%) ion recovery in the first 200 mL KCl extraction (Fenn et al., 2002).

At the end of the field sampling period, the resin columns were unscrewed from the funnel assembly, capped off, and returned to the laboratory. The columns were prerinsed with 100 mL of distilled water and extracted by percolating 200 mL of 2 *M* KCl solution through each one. Initially, the columns were extracted three times. However, because the amount of N removed in the third extraction was insignificant (on average 0.07% of the NO_3^- and 0.1% of the NH_4^+ extracted), we discontinued the third extraction. All bulk throughfall, bulk precipitation, and resin extract samples were analyzed for NH_4^+ and NO_3^- with a TRAACS 800 Autoanalyzer (Tarrytown, NY).

RESULTS

Bulk Deposition in Precipitation: Ion Exchange Resin vs. Conventional Collectors

At both sites NH_4^+ 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 and fourth quarterly periods at CP was 0.45 kg NH_4–N ha^{-1} greater in the IER collectors than in the conventional solution collectors (Fig. 2a). At BF bulk deposition of NH_4^+ was 0.25 and 0.45 kg NH_4–N ha^{-1} higher in the IER collectors during these same periods (Fig. 2b). The discrepancy in bulk deposition of NH_4^+ between the two collector types at BF and CP generally increased during the 12 mo of the study, except for the 9-mo exposure at CP, for which the discrepancy was reversed (i.e., in the 9-mo exposure, deposition to the con-

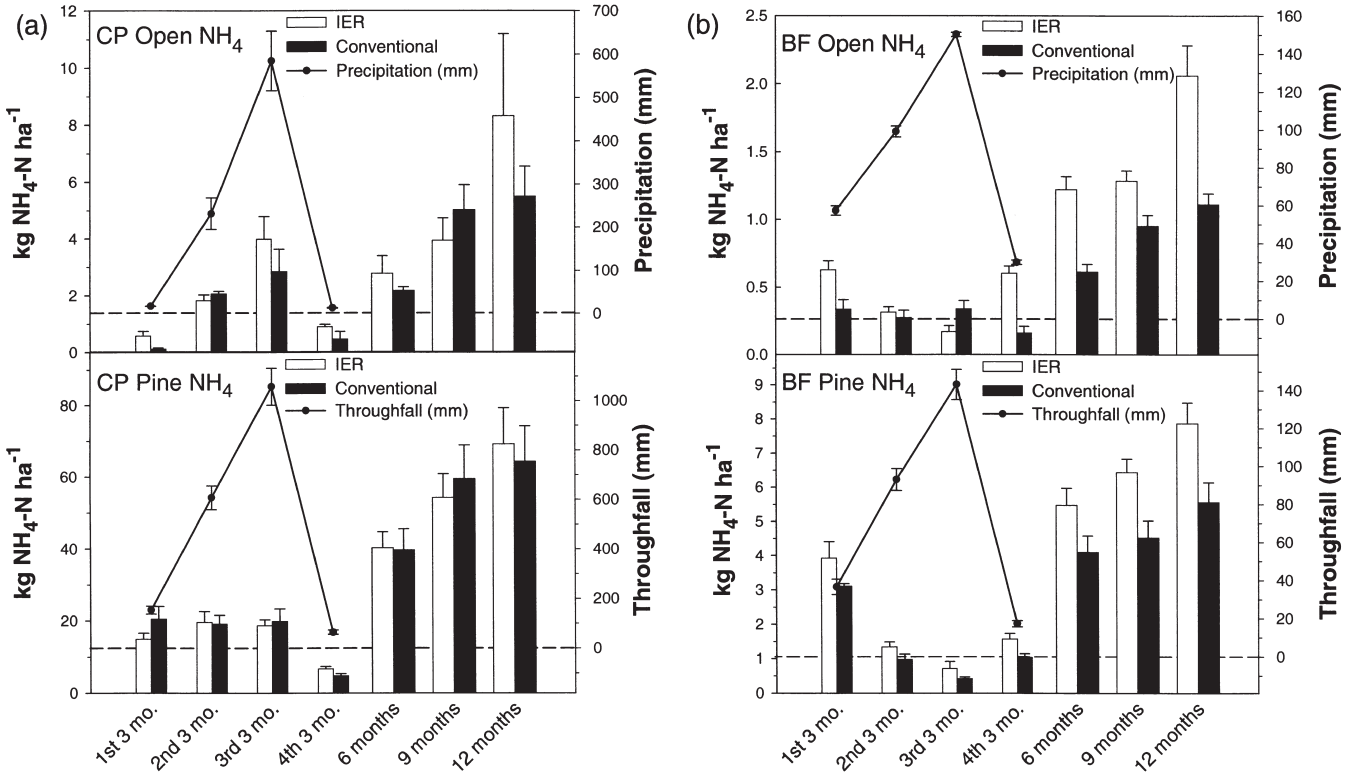

Fig. 2. Comparison of deposition of NH_4–N to ion exchange resin collectors (open bars) and conventional solution collectors (black bars) in open areas and under mature ponderosa pine trees at (a) Camp Paivika and (b) Barton Flats. The first four pairs of histogram bars represent four consecutive 3-mo exposures. The last three pairs of histogram bars are for the 6-, 9- and 12-mo 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.

ventional collector was higher than to the IER; Fig. 2a). After 12 mo NH_4–N deposition was 0.93 and 2.83 kg ha^{-1} greater in the IER collectors than in the conventional collectors at BF and CP, respectively (Fig. 3).

During the two winter exposure periods at CP, bulk deposition of NH_4^+ was highly similar in one case and 1.11 kg ha^{-1} higher in the IER collector in another case (Fig. 2a). At BF bulk deposition was highly similar among the two collector types in the first winter exposure and 0.17 kg ha^{-1} higher in the conventional collector in the second winter exposure (Fig. 2b).

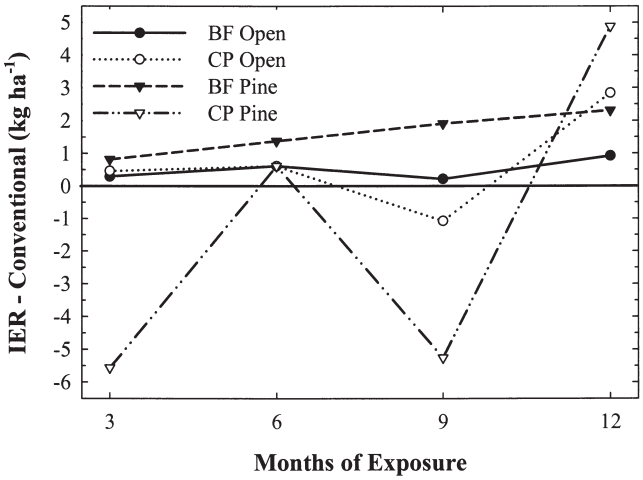

Fig. 3. Discrepancy in NH_4–N deposition (IER minus conventional) in open areas and under pine canopies between the IER collectors and the conventional throughfall solution collectors at Barton Flats (BF) and Camp Paivika (CP).

Bulk deposition of NO_3^- in precipitation was nearly always highly similar between the two collector types at both BF and CP (Fig. 4). The only exceptions to this pattern were at CP where NO_3–N deposition was 0.67 kg ha^{-1} higher in the IER collectors during the fourth quarterly exposure period and 3.15 kg ha^{-1} higher in the conventional collectors for the collectors exposed for 9 mo (Fig. 4a). The latter instance seems to be an anomaly, possibly due to a systematic error or because of inherent variation in throughfall fluxes as a result of heterogeneity in canopy cover. After 9 mo, NH_4^+ deposition at CP was also higher in the conventional collectors (by 1.08 kg N ha^{-1}) than in the IER collectors (Fig. 2a and 3).

Bulk Throughfall: Ion Exchange Resin vs. Conventional Collectors

No consistent differences between the conventional and IER collectors were observed in deposition of NO_3^- in throughfall at CP and BF (Fig. 4) or of NH_4^+ at CP (Fig. 2a). However, deposition of NH_4–N in throughfall at BF was 0.82 to 2.31 kg ha^{-1} higher in the IER collectors than the conventional collectors after 3, 6, 9, and 12 mo of monitoring (Fig. 2b). The discrepancy in bulk

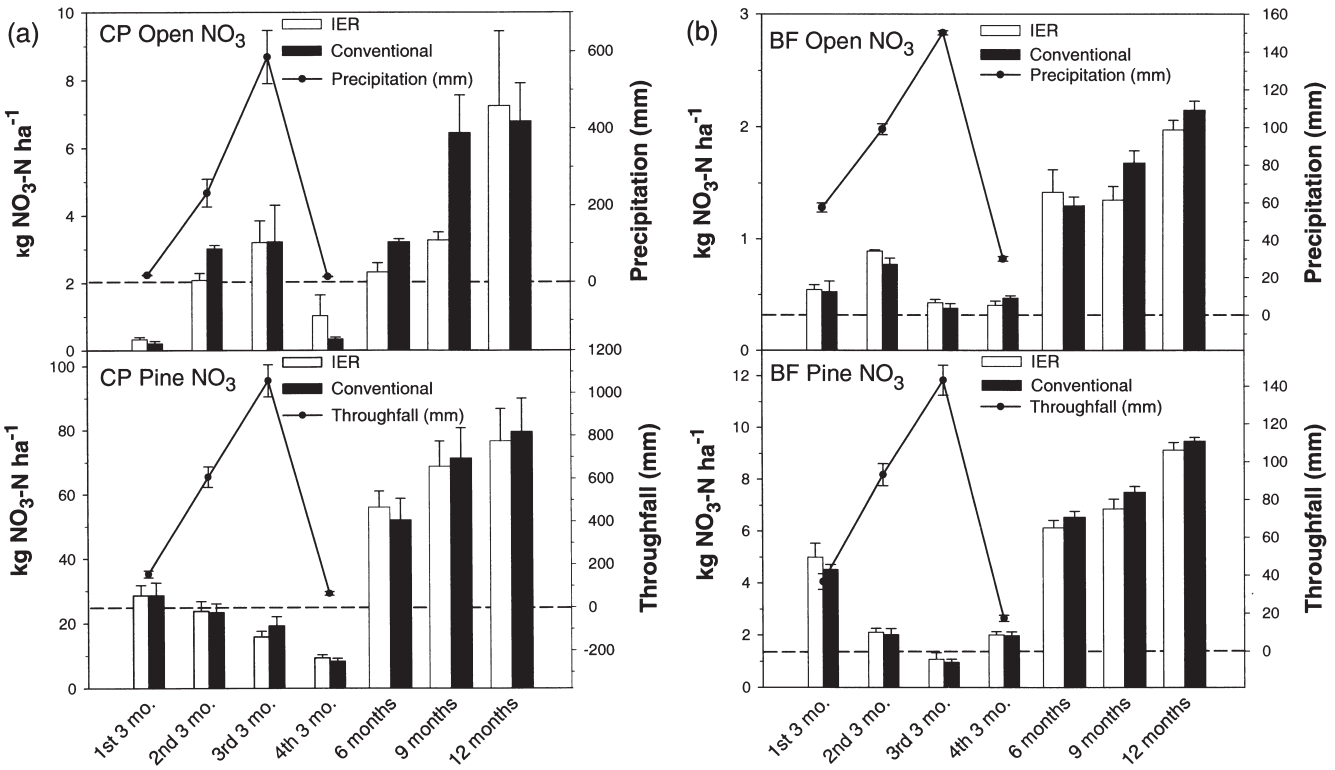

Fig. 4. Comparison of deposition of NO_3–N to conventional throughfall solution collectors and ion exchange resin collectors in open areas and under mature ponderosa pine trees at (a) Camp Paivika and (b) Barton Flats. See caption to Fig. 2 for a description of the histogram bars.

deposition of NH_4^+ in throughfall between the two collector types at BF increased steadily during the 12 mo of the study (Fig. 3). At CP, however, no consistent pattern of differences in throughfall deposition between the two collector types was observed. After 3 and 9 mo of monitoring, NH_4–N deposition was 5.25 to 5.56 kg ha^{-1} lower in the IER; after 6 mo of monitoring, collectors and values were equivalent between the two collector types (Fig. 3). After 12 mo of sampling, the average value for throughfall deposition of NH_4–N in the IER samplers at CP was 4.88 kg ha^{-1} greater than in the conventional collectors.

Effect of Time of Exposure on Performance of IER Columns

Nitrate deposition values were not significantly different between IER columns left in the field for 12 mo compared with the sum of deposition values of IER columns of the four successive quarterly periods (Table 1). Likewise, NO_3^- deposition was equivalent between the IER collectors exposed for 12 mo and annual deposition fluxes measured in the conventional solution collectors (Table 1; Fig. 4). Similar findings were observed in comparisons of NO_3^- deposition in the conventional collectors and to deposition measured with the IER collectors exposed for 3, 6, and 9 mo. These comparisons indicate that the IER collectors function well with exposure times as long as 1 yr, even in areas with unusually high N deposition such as CP. The sole exceptions to these general conclusions were the low NO_3^- deposition levels measured in the open-area IER collectors exposed for 9 mo at CP and to a lesser degree at BF. The cause of these low readings is unknown. However, the IER deposition values for the sum of the first three quarterly open-area exposures at CP and BF were similar to deposition values in the conventional collectors. These findings suggest that the unusually low values for the IER collectors exposed in open areas for 9 mo at CP and BF are an anomaly, possibly due to an unknown error in the field or in the laboratory, or variation in canopy cover, as mentioned previously.

Nitrogen Deposition Based on Two Methods at Camp Paivika and Barton Flats

Total inorganic N deposition (NO_3–N + NH_4–N) under large pine canopies with the two types of collectors during the 12 mo of exposure was 144 to 146 kg ha^{-1} at CP and 15 to 17 kg ha^{-1} at BF. By comparison, bulk deposition in open areas ranged from 12 to 16 kg ha^{-1} at CP and 3 to 4 kg ha^{-1} at BF (Table 1). These data summarizing annual deposition loadings demonstrate how comparable the two collector types performed overall. They also indicate that annual N inputs in the western SBM are extremely high under large trees, particularly in years with extensive fog exposure (Table 1; Fig. 2 and 4). Nitrogen deposition at BF was lower than at CP because of lower pollution exposure and also because fog frequency and fog density are consistently lower at BF (Fenn et al., 2000). Total annual throughfall and precipitation volumes were 290 and 337 mm at BF compared with 1882 and 846 mm at CP. The ratio of annual throughfall volume to precipitation volume was 0.86 and

2.22 at BF and CP. The higher ratio of throughfall to precipitation volume at CP is a result of the greater fog occurrence at CP as demonstrated in a previous study (Fenn et al., 2000).

DISCUSSION

Comparison of Nitrogen Deposition Fluxes with Ion Exchange Resin 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 mo (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. Kjønaas (1999a) reported that IER bags placed on the forest floor for throughfall deposition measurements functioned equally well during 2- and 6-mo exposures, the latter being the longest exposure times used in the study. Deposition measurements for NO_3–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 NH_4^+ deposition in throughfall was 2.31 kg N ha^{-1} yr^{-1} higher in the IER collectors than in the conventional collectors. Similarly, annual NH_4^+ deposition in bulk precipitation at BF and CP was 0.92 and 2.84 kg N ha^{-1} yr^{-1} higher in the IER collectors than in the conventional collectors (Fig. 2; Table 1). Garten (1992; using IER columns) and Kjønaas (1999a; using IER bags) also reported that measurements of atmospheric deposition of NH_4^+ were higher when using IER collectors compared with conventional solution collectors. However, measurements of NO_3^- deposition were similar with both collector types in both studies. Although Simkin et al. (2004) did not measure 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- to 6-wk bulk deposition collections).

Possible Sources of Ammonium Discrepancy between Collector Types

Further tests are needed to determine the cause of the discrepancy in NH_4^+ deposition rates between the IER and conventional collectors. The most likely factor contributing to this discrepancy would seem to be the release of quaternary amine compounds from the anion exchange resin polymer, resulting in higher background NH_4^+ levels when extracting the resin. Since most commercial anion exchange resin beads employ either trimethylamine (Type I resins) or dimethyl-β-hydroxyethylamine (Type II resins) groups (Skogley and Dobermann, 1996), there is a concern that amine groups could be released under prolonged use or severe conditions, thus contaminating the samples with NH_4^+. Kjønaas (1999b) found that freeze–thaw cycles did not affect resin stability or function, but that resin drying could affect ion adsorption or ion release to a slight degree. Kjønaas (1999b) also reported evidence of NH_4^+ release from dried Amberlite MB1 mixed bed resin over long time periods, although differences between moist and dried resin were not statistically significant. For other similar resin types there was no evidence of NH_4^+ release (Kjønaas, 1999b). Mamo et al. (2004) exposed mixed bed IER to repeated freeze–thaw and wet–dry cycles and found that resin bead integrity was not affected and that the IER retained virtually 100% of the adsorbed NO_3^- and NH_4^+, even after the most severe freeze–thaw and wet–dry treatments. We suggest that any IER to be used in long-term environmental monitoring programs should be tested for reliability under appropriate environmental extremes to ensure that the IER are quantitatively capturing ions of interest and releasing them during the extraction procedure.

Volatilization losses of NH_3 from the solutions in the conventional collectors are another possible source of discrepancy between the two collector types. Either of these two processes (release of amine groups or volatilization) would lead to higher deposition estimates in the IER collectors compared with the conventional collectors. However, it is necessary to know which process or to what extent both processes may be occurring before it can be determined which collector type is more accurate. Nitrification of NH_4^+ in the liquid samples also could account for the discrepancy, but we did not find corresponding increases in nitrate in the liquid samples compared with the IER collectors as would have been expected with this mechanism, assuming complete nitrification. Incomplete nitrification could also account for the discrepancy, and would result in gaseous losses of N from the solutions as the NH_4^+ is oxidized to nitrogenous trace gas forms (e.g., N_2O, NO, or NO_2). However, it seems unlikely that nitrification activity in throughfall solutions would be quantitatively significant in the short interval of time between collection of throughfall samples in the field and storage of samples in a freezer (typically 1–3 d), especially considering that the NH_4^+ discrepancy also occurred in the open precipitation collectors, that were not expected to be colonized by a nitrifier community of organisms. The NH_4^+ discrepancy in open areas at CP and BF was generally greatest during the first and fourth exposure periods when temperatures were higher (except at CP where the discrepancy in the third period was also high). Higher temperatures could favor any of the potential processes causing the discrepancy: volatilization, release of amine groups from the resin, or nitrification. Collectors placed in canopy-free areas in the field were exposed to higher levels of solar radiation and heating. Nonetheless, comparisons of the NH_4^+ discrepancy between collector types in open areas with the discrepancy between collector types under large pine canopies indicate that the discrepancy was often greater in throughfall collectors placed under pine trees. At BF, the discrepancy between the two collector types was consistently greater under pine trees than in open areas, whereas at CP the level of discrepancy

between the collector types under pine vs. open areas was variable over the course of the study (Fig. 3).

Because of the much greater variability in throughfall fluxes of N as a result of canopy interactions with atmospheric N, we assume that the discrepancy between the two collector types can be estimated more accurately when based on the discrepancy in the precipitation collectors placed in canopy-free or open areas. The average discrepancy between collector types in open areas at the two sites is 1.88 kg NH_4–N ha^{-1} yr^{-1}. We, therefore, suggest this as the best estimate of how much the IER collectors overestimated deposition of NH_4–N in this study. For throughfall under pine trees at CP, this discrepancy is within the margin of error, but a discrepancy of 1.88 kg NH_4–N ha^{-1} yr^{-1} is greater than the margin of error for bulk deposition at the two sites or for throughfall deposition at BF.

Considerations for the Use of Ion Exchange Resin Deposition Collectors

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

Low sample volumes in bulk deposition or throughfall solution collectors inherently lead to uncertainty in deposition estimates. With only trace amounts of precipitation, the conventional solution collectors typically do not collect enough sample for analysis, although the ionic concentration of the sample is likely to be unusually high during dry periods. If there is minimal volume for collection and analysis, a significant proportion of the sample will be left as residue in the collector after it is decanted. The ion exchange collectors, on the other hand, will retain whatever ions are transported by gravitational flow from the funnel collector to the resin column, even in low volumes. These may seem like trivial issues, but in areas with prolonged dry periods such as in the San Bernardino Mountains or the Sierra Nevada, the summer–dry climate results in long dry periods when atmospheric pollutants accumulate on plant canopies. Under these conditions, infrequent low-volume rain events can represent a proportionally significant deposition flux that is important to quantify (Fenn and Bytnerowicz, 1997; Fenn et al., 2000).

Control, blank IER columns that are not exposed to atmospheric deposition should be deployed in at least a subset of the monitoring sites to determine IER background NH_4^+ and NO_3^- levels after exposure to field conditions. However, a true control blank also should be exposed to the same wetting–drying cycles as the treatment collectors. Wet–dry and freeze–thaw cycles could be mimicked in the lab, or wet–dry cycles could be applied in the field to ensure the resin is functioning properly and to ascertain what the true ionic background levels are for the resin after field exposure. At the end of the monitoring period when IER columns are brought back to the laboratory for extraction and analysis, the unexposed control tubes should be simultaneously extracted to determine ionic background levels of field-exposed resin columns. This background value is then used to blank-correct data from the IER columns used for deposition measurements (Kjønaas, 1999b). Alternatively, if release of amine groups from anion exchange resin is found to be a problem with a batch of resin, the cation exchange and anion exchange resin collectors can be implemented separately. In this case, any release of amine groups from the anion exchange resin columns would not affect extractable NH_4^+ levels from the separate cation exchange resin samples. However, employing separate anion and cation columns doubles the number of collectors needed and also means that cations and anions will not be collected from the identical microsites; they will be extracted and analyzed from separate IER columns, introducing greater variability and cost.

CONCLUSIONS

The bulk precipitation/throughfall collectors described in this study are based on adsorption of NO_3^- and NH_4^+ ions onto a mixed bed 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 1 yr—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 particularly important for NH_4^+ because 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 also can 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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