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Quantifying atmospheric N deposition in dryland ecosystems: A test of the Integrated Total Nitrogen Input (ITNI) method

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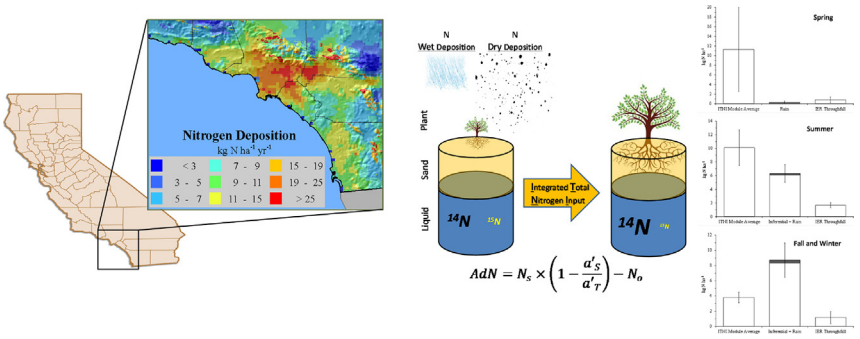
HIGHLIGHTS

- The ITNI method captures all N deposition forms and processes in arid regions.
- ITNI plant biomass production is positively correlated to uptake of atmospheric N.
- Throughfall collectors underestimate N deposition in coastal sage scrub ecosystems.
- The inferential and ITNI methods produce similar rates of annual N deposition.
- Further research is needed on the impacts of watering on N deposition rates.

GRAPHICAL ABSTRACT



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ABSTRACT

Estimating nitrogen (N) deposition to terrestrial ecosystems is complicated by the multiple forms and routes of N loading from the atmosphere. We used the integrated total nitrogen input (ITNI) method, which is based on the principle of isotope dilution within a plant-liquid-sand system, to quantify N inputs to coastal sage scrub ecosystems in Riverside, California. Using the ITNI method, we measured atmospheric N deposition of 29.3 kg N ha^{-1} yr^{-1} over a range of aboveground plant biomass of 228 to 424 g m^{-2}. From 85 to 96% of the atmospheric N inputs were taken up by plants in the ITNI modules with most of the assimilation mediated by, and stored in, aboveground biomass. Parallel measurements using conventional approaches yielded deposition rates of 25.2 kg N ha^{-1} yr^{-1} when using the inferential method and 4.8 kg N ha^{-1} yr^{-1} using throughfall collectors. The relatively low throughfall estimates were attributed to canopy retention of inorganic N, low rainfall, and to the fact that the throughfall flux data did not include organic N and stomatal uptake of N gases. Also, during dry periods, frequent watering of ITNI modules may have increased stomatal conductance and led to overestimates of N deposition. Across published studies that used the ITNI method, areal N deposition rates varied by ~40-fold, were positively correlated with plant biomass and 90% of the variability in measured deposition rates can be explained by plant biomass production. The ITNI method offers a holistic approach to measuring atmospheric N deposition in arid ecosystems, although more study is needed to understand how watering rates effect N deposition measurements.

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1. Introduction

Human activity has altered nitrogen cycling in ecosystems with a range of deleterious effects including acidification and eutrophication of lakes and streams, N-saturation, contamination of groundwater with nitrate (NO_3^-), increased emissions of greenhouse gases including N_2O and changes in ecosystem structure and biodiversity (Galloway et al., 2008; Bobbink et al., 2010; Meunier et al., 2016). Understanding and mitigating the effects of atmospheric N deposition requires accurate measurements of N deposition rates and are especially important when establishing critical loads of N deposition for different ecosystem types (Sutton et al., 2014). Inorganic and organic N can be deposited from the atmosphere in wet, particulate and gaseous forms making it challenging to accurately quantify all N inputs across a region (Fenn et al., 2009). During early attempts to measure atmospheric N deposition, bulk collectors were used to capture all forms of atmospheric fallout, but it was recognized early on that contaminants such as insects and bird droppings along with biological activity within the samples themselves, made the chemistry of bulk deposition measurements difficult to interpret (Galloway and Likens, 1976). Later research highlighted the role of vegetation in N deposition processes including canopy interception of solutes in precipitation and dry deposition, and the exchange of gaseous N forms between the atmosphere and plant canopies (Fenn and Bytnerowicz, 1993; Hanson and Lindberg, 1991).

Wet N deposition is relatively simple to collect using an automated rain collector (Lamb and Bowersox, 2000), but, in arid or semi-arid regions, deposition of particulates and gases are typically the dominant route for atmospheric N deposition (Fenn et al., 2010) and its measurement is more challenging. Current methods of measuring dry deposition include the use of passive samplers to determine atmospheric concentrations of N-bearing compounds and coupling this data with empirical models that estimate the rate at which these compounds deposit to surfaces (Zhang et al., 2003); this approach is often referred to as the inferential method (Bytnerowicz et al., 2015). Other approaches involve installing rain collectors below plant canopies to quantify throughfall (direct precipitation + dry-deposited compounds washed from canopy surfaces – canopy uptake). To reduce the frequency of throughfall collection, ion-exchange resins (IER) collectors can be used which adsorb inorganic N ions from throughfall solutions over long exposure periods (e.g., 6 months; Fenn and Poth, 2004). In selecting the best technique to measure N deposition, researchers must understand the assumptions and uncertainties inherent to each technique. Importantly, it is often necessary to employ multiple measurement techniques simultaneously to quantify all N forms and pathways of deposition, with each method contributing error to the total deposition estimate and raising the complexity and cost of monitoring programs.

The integrated total nitrogen input method (henceforth ITNI method) offers the potential for a holistic estimate of N deposition which would be especially advantageous in regions where particulate deposition and gaseous uptake by plants are important pathways for N deposition (Bytnerowicz and Fenn, 1996). The ITNI method uses a plant-liquid-sand (PLS) system consisting of a living plant, liquid reservoir, and sand substrate (Böhme et al., 2003; He et al., 2010; Mehlert et al., 1995; Russow and Böhme, 2005). The PLS system is isotopically enriched with ^{15}N, but is open to the atmosphere, collecting all forms of atmospheric inorganic- and organic-N that deposit to the surfaces of the sand and plant. The N deposition measured includes both wet (including fog) and dry forms; the latter including particulates and gaseous deposition, including stomatal uptake of gaseous N. The rate of N deposition to the PLS system can be determined by the amount of isotope dilution occurring during exposure to the atmosphere which contains N with much lower concentrations of ^{15}N compared to the isotopically-enriched PLS system. The rate of N deposition can be computed once the module is harvested and all PLS components are analyzed for their N content and N isotope composition.

The ITNI method has been previously used in agricultural systems to measure atmospheric N inputs to vegetable and cereal plant species (Böhme et al., 2003; He et al., 2007; He et al., 2010; Russow and Böhme, 2005; Weigel et al., 2000). More recently, the ITNI method was used to measure N deposition and assess the nitrogen saturation status of peat bogs in Germany (Hurkuck et al., 2015). In this study, we deployed ITNI modules in a semiarid region in southern California from March 2013 through March 2014. During the deployments, we also measured wet and dry inorganic N loading via wet deposition collector, throughfall collectors, and the inferential method. Our main objective was to evaluate the ITNI method using non-agricultural plants in a semiarid region where dry deposition and gaseous plant uptake are dominant routes for N inputs. Secondly, overlapping deployment of additional N deposition collectors allowed us to compare N deposition measurements among a range of methods and to assess their biases and uncertainties. Finally, we summarized observations from previous ITNI studies to investigate the comparability of deposition estimates made using different plant species.

2. Material and methods

2.1. Study sites

All atmospheric deposition measurements were made near the United States Department of Agriculture, Forest Service Pacific Southwest Research Station (PSW RS) in Riverside, California. This site was selected due to the availability of ongoing atmospheric deposition measurements and supporting weather data from a nearby climate station operated by the California Irrigation Management Information System (CIMIS station no. 44). Riverside has a semiarid climate with hot, dry summers and cool, moderately wet winters. During the study, daily maximum and minimum air temperatures ranged between 10 and 40 °C and 0–25 °C, respectively (Fig. S1).

The ITNI modules and a wet deposition collector were installed side-by-side and exposed to the atmosphere within an open area at the PSW RS; the installations met site-selection criteria developed by the National Atmospheric Deposition Program (NADP; Bigelow et al., 2001). For the inferential method, passive samplers for gaseous inorganic N species were installed 50 m northwest of the ITNI modules. Throughfall collectors were installed at "Coyote Hill", 1-kilometer northeast of the PSW RS. This site contains a mosaic of mature stands of coastal sage scrub (CSS) vegetation, and invasive annual and perennial species. Throughfall measurements were made under *Eriogonum fasciculatum* and *Hirschfeldia incana* plants.

2.2. Integrated total nitrogen input method

Details of the construction, isotopic labelling, and operation of the ITNI modules are summarized in the Supplementary materials. Briefly, the ITNI method utilized a plant, liquid reservoir, and soil substrate module that was isotopically enriched with ^{15}N-labelled Hoagland solution (a plant growth media adapted from Parker and Norvell, 1999). The initial NO_3^- concentration in the solution was 18 mM N-KNO_3 with an isotopic composition of 1.01 atom % ^{15}N (Fig. 1). For comparison, ambient atmospheric N deposition in Riverside, California, has an isotopic composition of ca. 0.366 ± 0.002 atom % ^{15}N (Bell et al., 2014). The soil reservoir was comprised of N-free, #16 silver (silica) sand (see Supplementary materials for further details). The individual ITNI modules were designed so that the plant grew in the sand reservoir, which was stacked on top of the liquid reservoir (Fig. 1). An airlift system, powered by a small air compressor (equipped with a charcoal filter), periodically moved nutrient solution from the liquid reservoir up through a tubing ring that distributed the solution to the sand surface (Fig. 1). Excess liquid in the sand reservoir drained directly back into the liquid reservoir.

While the sand media lacks many of the characteristics of natural soils including organic matter and associated microbial communities it

Fig. 1. Example of an ITNI module. The upper dark brown insert contains the quartz sand substrate in which the plants are grown. The brown water ring distributes water to the plants from the lower tan-colored reservoir when air is pumped from the small clear plastic tubing into the white plastic riser (i.e., an air-lift). The blue plastic tubing is used to measure the water level in the lower reservoir and to add deionized water to the module when necessary. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

is unlikely that deposition rates measured were seriously biased. Importantly, chaparral plants have been demonstrated to be superior competitors for atmospheric nitrogen during the plant growing season (Homyak et al., 2014), and since, in contrast to plants, soil microbes have no ability to directly remove NH_3, oxidized (NO, NO_2) and organic N gases from the atmosphere, the absence of soil microbes in the ITNI modules did not appreciably limit total nitrogen uptake. Furthermore, using natural soils would severely reduce the sensitivity of the ITNI method to detect N deposition since the amount of atmospheric N deposition would be very small relative to the initial amount of N in the modules.

ITNI modules were assembled in a climate-controlled greenhouse to prevent premature exposure to ambient N deposition. Germinated seeds were sown into the sand reservoir and the 9-liter liquid reservoir filled with ^{15}N-labelled Hoagland solution. The liquid reservoirs were wrapped in aluminum foil to discourage algal growth. Three different plant species were used in three field deployments: i) *Eriogonum fasciculatum* (California Buckwheat), a common species in the California coastal sage scrub community; ii) *Bromus rubens* (Red Brome) a common invasive annual grass species native to southern Europe; and iii) *Hirschfeldia incana* (Summer Mustard) an invasive perennial herb common to southern California. Red Brome was used in Deployment 1 (Table 1) and the modules were moved into the field immediately after sowing the seeds because this species has a relatively short lifecycle. During Deployment 2, both California Buckwheat and Summer Mustard were used, while only Summer Mustard was used in Deployment 3. During Deployment 2 and Deployment 3, the modules were kept in the greenhouse for 1 to 2 weeks after sowing to allow the plant seedlings to grow into viable young plants before moving them into the field. Air temperatures were higher at the start of Deployment 2 and Deployment 3 than at the start of Deployment 1 (Fig. S1) and would have stunted or killed very small seedlings, so greenhouse rearing prior to deployment was necessary. Fencing was used to discourage herbivores from grazing on the plants growing in the ITNI modules during field deployment.

Ambient exposure of ITNI modules occurred during the following periods: Deployment 1: March 8, 2013 to May 20, 2013 (74 days); Deployment 2: May 28, 2013 to August 12, 2013 (77 days); and Deployment 3: November 15, 2013 to March 24, 2014 (130 days; Table 1). Gaps in the deployments occurred because of delays related to seed germination and plant growth rates. Inferential measurements of gaseous N species were made during Deployment 2 and Deployment 3 on almost identical schedules but were not made during Deployment 1. As part of an independent N deposition monitoring project, the IER collectors were deployed on a different schedule than the ITNI modules and inferential measurements, but their deployment overlapped sufficiently enough that useful comparisons could be made. The automated rain collector was operated continuously throughout Deployments 1 through 3 and sampled on an event basis.

After field deployment, all isotopically-labelled components in the ITNI modules were destructively harvested and analyzed for dry mass, N content and ^{15}N abundance. The N content and N isotope abundance of all plant samples were determined at the Facility for Isotope Ratio Mass Spectrometry (FIRMS) at the University of California, Riverside using a Thermo Delta-V isotope ratio mass spectrometer interfaced with a Costech ECS 4010 elemental analyzer and zero-blank autosampler. A mass-weighted average of the above and below ground

Table 1
Schedule of N deposition measurements made during the study. No inferential measurements were made during Deployment 1. The rain collector was operated continuously between March 1, 2013 through March 24, 2014. Also indicated are the species of plants used in the ITNI deployments.

	ITNI deployment	Ion exchange deployment	Inferential deployment
Deployment 1[a] (Spring)	3/8/2013 to 5/20/2013 (74 days[a])	11/11/2012 to 6/6/2013 (208 days)	–
Deployment 2[b,c] (Summer)	5/28/2013 to 8/12/2013 (77 days[b,c])	6/6/2013 to 11/18/2013 (166 days)	5/28/2013 to 8/12/2013 (77 days)
Deployment 3[b] (Autumn and Winter)	11/15/2013 to 3/24/2014 (130 days[b])	11/18/2013 to 6/6/2014 (201 days)	11/15/2013 to 3/24/2014 (130 days)

[a] *Bromus rubens* (invasive species).
[b] *Hirschfeldia incana* (invasive species).
[c] *Eriogonum fasciculatum* (native species).

tissues isotopic composition was calculated to represent total ^{15}N abundance for the entire plant.

At harvest, the volume of the liquid reservoir was measured, and a subsample was collected for determination of N content and ^{15}N abundance; this liquid potentially contained N in the form of NO_3^-, NH_4^+, dissolved organic N and particulate N. Liquid samples for the measurement of $NO_3^- + NO_2^-$ and NH_4^+ were filtered through a 0.4 μm polycarbonate membrane filter and analyzed on a SEAL AQ2 discrete analyzer. Unfiltered samples were collected for total nitrogen (TN), and digested in persulfate oxidizing reagent and analyzed on an AQ2 discrete analyzer (Valderrama, 1981). The nutrient analyses demonstrated that NH_4^+ and NO_2^- were below detection (detection limits: $NH_4^+ = 0.5$ μmol L^{-1}; $NO_2^- = 0.2$ μmol L^{-1}) in all deployments. Furthermore, the sum of dissolved organic N plus particulate N (computed as the difference between total N (TN) and NO_3^-) was 1.3% of TN during Deployment 1, 0.4% during Deployment 2, and 0.6% during Deployments 3, demonstrating that almost all of the N in solution was NO_3^-. The dual isotopic composition of the NO_3^- ($\delta^{15}N$ and $\delta^{18}O$) was then measured on the mass spectrometer using the microbial denitrifier method (Coplen et al., 2012) and calibrated using the isotopic standards described above.

The sand matrix was homogenized by hand and duplicate, 5-gram subsamples were collected and extracted with 2 M KCl (Maynard et al., 2007) and stored frozen until analyzed. Nitrate and NH_4^+ concentrations were determined on the AQ2 discrete analyzer; NH_4^+ concentrations were below detection. The ^{15}N abundance of NO_3^- was determined using the microbial denitrifier method with modifications recommended by Bell and Sickman (2014) to account for background N contamination in the KCl extractant.

The results from the isotopic and elemental analyses were incorporated into the following equation from Russow et al. (2001):

$$AdN = N_s \quad \left(1 - \frac{a\prime_S}{a\prime_T}\right) - N_o \tag{1}$$

where AdN is atmospherically-derived nitrogen input to the module (in milligrams (mg)); a'$_s$ is the mass-weighted *excess* ^{15}N abundance of the PLS system at the end of the field deployment (i.e., $a' = a$ - 0.366; 0.366 is the ^{15}N abundance in the atmospheric N_2 baseline); a'$_T$ is the excess ^{15}N abundance (i.e., $a' = a$ - 0.366) of the original tracer added to the PLS system; N_o is the original N mass (mg) in the plant seed or seedling; and N_s is the total mass of N in the PLS system (mg). When computing a'$_s$ we weighted the excess ^{15}N abundances of the individual system components (aboveground plant tissues, belowground plant tissues, sand, and liquid) by their N mass.

During Deployment 1, we included two types of experimental controls to observe how the isotope tracer behaved in the absence of plants: i) plantless modules which were spiked with isotopically enriched Hoagland solution ("Hoagland Control") and ii) plantless modules that were spiked with only ^{15}N tracer ("N-Only Control"). We specifically wanted to test whether there was any loss of N from the liquid reservoir that could not be accounted for by plant uptake, (e.g., denitrification and microbial N immobilization).

2.3. Scaling of ITNI measurements to the landscape

There are three main methods used for scaling ITNI measurements from the module level to the landscape (Russow and Böhme, 2005): The Area, Plant Number, and Biomass Methods. The Area Method uses the area of the ITNI modules, where flux units of mg N module^{-1}, are divided by the area of module in m^2 to yield areal units of mg N m^{-2} (and then further converted to units of kg N ha^{-1}). For the Area Method to be valid, the surface conditions of the ITNI module should be like that in the simulated ecosystem (e.g., the relative proportions of leaf area and bare soil surface should be similar). The Plant Number Method multiplies the deposition rate derived from the Area Method by the ratio of plant density in the field (plants m^{-2}) to plant density in the ITNI module and is most appropriate for agricultural systems. The Biomass Method multiplies the deposition rate derived from the Area Method by the ratio of plant biomass in the field (grams dry weight) to plant biomass in the module and is an appropriate method for scaling ITNI deposition in agricultural and natural ecosystems.

In our study, the mean total plant biomass (dry weight) of modules ranged from 269 to 564 g m^{-2} with aboveground biomass ranging from 228 to 424 g m^{-2} (Table 2). Since we sought to estimate N deposition rates to coastal sage scrub (CSS), we reviewed ecological studies of CSS and found three that reported aboveground biomass for species found in Riverside. Gray (1981) reported plant biomass (dry weight) of 925 g m^{-2} for stands of CSS containing *Artemisia californica* and *Salvia mellifera*. Vourlitis et al. (2009) reported biomass of these same species over a four-year period and their aboveground biomass varied from about 250 to 650 g m^{-2}. Finally, Rundel (2007) reported 919 g m^{-2} for *A. californica*, 888 g m^{-2} for *S. mellifera*, and 246 g m^{-2} for *Encelia californica*.

Since these literature values apply only to plant canopy, they do not account for bare ground in the CSS landscape. In Riversidean CSS, plant cover ranges from about 40% in dry years to about 60% in wet years (Edith Allen, personal communication, March 16, 2018). Values from Vourlitis et al. (2009) are based on Diegan CSS which have stand cover of about 80% (Edith Allen, personal communication, March 16, 2018). After correcting for plant cover, the landscape-level, plant biomass for *A. californica- and S. mellifera*-dominated CSS probably ranges from 200 to 700 g m^{-2} and for landscapes dominated by *E. californica*, plant biomass may be as low as 100 to 150 g m^{-2}. This range of plant density, 100–700 g m^{-2} fully brackets the range of plant biomass produced in our ITNI modules. Thus, our ITNI modules represent realistic simulations of typical CSS ecosystems in terms of plant species, land surface characteristics and aboveground plant biomass, and therefore did not require correction using the Biomass Method. Instead, we elected to use the Area Method for scaling of AdN rates from the modules (mg N module^{-1}) to areal units of kg N ha^{-1}.

2.4. Conventional deposition methods

Methods for collection of wet deposition, throughfall and the inferential method are summarized below, and details are presented in the Supplementary materials.

Rain was collected in an ADS 00-120 wet deposition sampler manufactured by N-Con Systems and is the same model used by the US National Atmospheric Deposition Program (NADP; Supplementary materials Fig. S2). Most samples were processed within 24 h of the end of precipitation event. The sample volume was converted into rainfall depth using the area of the bucket opening and rainfall depths measured at the nearby CIMIS station were used to validate rain depths obtained from the bucket volumes.

The IER collectors in this study are part of long-term, atmospheric deposition collections made by the USFS and were deployed on a 5 to 7-month schedule. Ion exchange resin collectors were comprised of a PVC tube filled with Amberlite IRN 150 mixed-bed ion exchange resin (Fenn et al., 2018a). After exposure, the resin in the IERs was extracted with 1 M potassium iodide (KI; Fenn et al., 2013). Ammonium was measured colorimetrically and NO_3^- was measured by ion chromatography (Fenn and Poth, 2004).

The inferential method estimates deposition rates of chemical compounds from atmospheric concentration measurements and deposition velocities and represents dry deposition of a variety of N-containing species, including NH_3, HNO_3 and NO_2 (Lovett, 1994; Schmitt et al., 2005). For total N deposition, wet deposition is added to deposition measured by the inferential method. In our study, concentrations of gaseous N compounds were measured using passive samplers (Ogawa, 2014) and combined with compound-specific deposition velocities to yield N deposition rates (Bytnerowicz et al., 2005). The deposition velocities considered settling surfaces, wind speed, relative humidity,

Table 2
Average (±standard deviation) biomass and isotopic composition of nitrogen pools in subcomponents of the ITNI modules, at harvest, during the three deployments (the number of replicate modules is shown in column 1). Different letters (a through c), where shown, denote ITNI components with statistically different ($p = 0.05$) isotopic composition within a single deployment. Different letters (x through z), where shown, denote statistically significant ($p = 0.10$) differences in above ground dry weight across deployments. Also presented is the average distribution of N mass within the ITNI modules, the average N recovery in the modules (±standard deviation) and the average (±standard deviation) N deposition amount computed by the ITNI method for each deployment. The experimental controls were modules without plants that were spiked with ^{15}N tracer with and without Hoagland nutrients.

	Plant biomass				Sand reservoir atom % ^{15}N	Liquid reservoir atom % ^{15}N	Partitioning of AdN (Plant:Sand: Liquid)	N deposition mg N module^{-1}
	Above ground dry weight (g m^{-2} ± SD)	Below ground dry weight (g m^{-2} ± SD)	Above ground atom % ^{15}N	Below ground atom % ^{15}N				
Deployment 1 (*B. rubens*; n = 5)	228 (81) x	164 (55) x	0.78 (0.11) a	0.72 (0.10) a	0.64 (0.12) b	0.38 (0.01) c	85%: 14%: 0.9%	59.7 (46.0)
Deployment 1 Hoagland Control (n = 5)	–	–	–	–	0.77 (0.11) a	0.80 (0.15) a	–: 20%: 80%	–
Deployment 1 N-Only Control (n = 5)	–	–	–	–	0.64 (0.06) a	0.49 (0.07) b	–: 20%: 80%	–
Deployment 2 (*H. incana*; n = 6)	339 (44) y	42 (13) y	0.87 (0.04) a	0.93 (0.01) a	0.68 (0.01) b	0.64 (0.18) b	96%: 3.6%: 0.2%	61.4 (15.3)
Deployment 2 (*E. fasciculatum*; n = 6)	424 (24) z	140 (47) x	0.90 (0.02) a	0.91 (0.02) ab	0.75 (0.07) b	0.80 (0.17) b	94%: 5.9%: 0.1%	45.4 (7.94)
Deployment 3 (*H. incana*; n = 8)	196 (78) x	74 (10) y	0.89 (0.03) a	0.94 (0.01) a	0.59 (0.19) b	0.53 (0.16) b	89%: 9.1%: 2.4%	20.1 (3.70)

and other climatic variables. Weather data from the nearby CIMIS station were used to determine appropriate surface conditions. Deposition velocities for these surface conditions were based on land use category 11 (deciduous shrubs) from Zhang et al., 2003 and Leiming Zhang, personal communication, March 11, 2015 (Table S1).

3. Results

3.1. Wet deposition

Measurable rainfall occurred on 13 days during the ITNI deployments (Fig. S3) with individual events ranging in depth from 1.27 mm (July 11, 2013) to 38.1 mm (November 21, 2013). The sum of NO_3^- and NH_4^+ concentrations varied with season and volume of rainfall with the highest concentrations occurring in small storms during the summer (12 to 35 mg N L^{-1}) and the lowest concentrations observed during the fall, winter and spring (1 to 12 mg N L^{-1}). Nitrate and NH_4^+ concentrations were highly correlated in rainfall ($R^2 = 0.95$) with NH_4^+ exceeding NO_3^- by about 50% (Fig. S4).

3.2. Throughfall

Ion exchange resin, throughfall collectors were deployed three times for periods of 165 to 215 days (Table 3). The amount of inorganic N deposition measured was relatively similar among the deployments ranging from 1.8 to 3.1 kg ha^{-1} (Table 3). Collectors deployed during the summer and autumn had the highest N deposition. During all IER deployments, deposition of N-NH_4^+ was greater than N-NO_3^- with an average mass ratio of 1.8 (range 1.5 to 2.2).

3.3. Dry deposition

For Deployment 2, the average duration of passive sampler exposure was 15.2 days with most of the period being rain-free with only 2 rain days and 0.5 rain nights (Table 4). During Deployment 3, the average exposure period was 16.3 days and, other than 4 rain days, 2.5 rain nights, and 1.5 dew nights, dry weather dominated. Nitric acid had the lowest concentration of the measured N species across Deployments 2 and 3 (deployment-weighted mean concentrations were 7.6 μg m^{-3} and 2.0 μg m^{-3}, respectively). The most abundant N species was NO_2 (deployment-weighted mean = 20.1 μg m^{-3} and 39.6 μg m^{-3}, respectively for Deployment 2 and 3). Nitrogen deposition estimated from the inferential method was 5.9 kg ha^{-1} and 8.4 kg ha^{-1} during Deployments 2 and 3, respectively.

3.4. Integrated total nitrogen input

The mean and standard deviation of module-level N deposition measured during ITNI Deployment 1 was 59.7 ± 46.0 mg N module^{-1} (Table 2). The relatively high variability in atmospherically derived N (AdN) in Deployment 1 can be explained by rabbit herbivory in some of the modules during the first half of the deployment (more extensive fencing was used in the second half of Deployment 1 and for all subsequent deployments). Total aboveground biomass varied by 35% (±

Table 3
Summary of throughfall N deposition measured by ion exchange resin collectors. During each deployment, there were 24 replicate throughfall collectors installed below coastal sage scrub plant canopies.

	Date installed	Date removed	DIN (kg N ha^{-1})	NH_4^+ (kg N ha^{-1})	NO_3^- (kg N ha^{-1})	Ratio: NH_4:NO_3
Deployment 1	11/2/2012	6/6/2013	2.36	1.59	0.76	2.1
Deployment 2	6/6/2013	11/18/2013	3.58	2.15	1.44	1.5
Deployment 3	11/18/2013	6/6/2014	1.79	1.24	0.55	2.2
∑ All deployments			7.73	4.98	2.75	
Annual deposition			4.85	3.13	1.73	

Table 4
Dates of passive sampler deployments/retrievals for inferential N deposition measurements. Also shown are the breakdowns on surface conditions during the deployments and the average concentration of key gaseous nitrogen compounds.

	Passive sampler deployment	Passive sampler retrieval	Elapsed time (24 h days)	Dry days	Dry nights	Rain days	Rain nights	Dew nights	NO_2 μg/m^3	HNO_3 μg/m^3	NH_3 μg/m^3
Deployment 2	5/28/2013	6/12/2013	15.1	7.5	7.5	0.0	0.0	0.0	16.6	3.4	9.9
	6/12/2013	6/25/2013	13.2	6.6	6.6	0.0	0.0	0.0	16.2	3.3	9.6
	6/25/2013	7/9/2013	14.1	6.0	7.0	1.0	0.0	0.0	24.2	12.9	10.9
	7/9/2013	7/31/2013	21.7	7.8	9.8	3.0	1.0	0.0	22.5	14.2	9.9
	7/31/2013	8/12/2013	12.1	6.0	6.0	0.0	0.0	0.0	19.4	4.0	8.0
Deployment 3	11/15/2013	12/2/2013	16.7	5.4	6.4	3.0	1.0	1.0	33.8	2.1	4.6
	12/2/2013	12/16/2013	14.0	6.0	7.0	1.0	0.0	0.0	40.0	2.1	4.5
	12/16/2013	12/30/2013	14.1	6.0	6.0	1.0	0.0	1.0	44.4	2.6	5.4
	12/30/2013	1/13/2014	14.0	7.0	7.0	0.0	0.0	0.0	60.0	1.9	9.4
	1/13/2014	1/28/2014	14.9	7.5	7.5	0.0	0.0	0.0	46.1	1.7	5.6
	1/28/2014	2/11/2014	14.0	6.0	6.0	1.0	1.0	0.0	32.9	1.1	8.2
	2/11/2014	2/24/2014	13.0	6.5	6.5	0.0	0.0	0.0	51.5	2.4	11.8
	2/24/2014	3/24/2014	28.1	12.0	10.0	2.0	3.0	1.0	24.8	1.9	4.2

standard deviation) during Deployment 1 which was almost 3× the average biomass variability from Deployments 2 and 3 (13%).

Deployment 2 produced deposition of 61.4 ± 15.3 mg N module^{-1} for modules containing *Hirschfeldia incana* and 45.4 ± 7.94 mg N module^{-1} for modules containing *Eriogonum fasciculatum*. Based on a *t*-test, N deposition in *H. incana* modules was significantly higher than in *E. fasciculatum* modules ($p = 0.048$) During Deployment 3, deposition was 20.1 ± 3.70 mg N module^{-1}. Summing across all three deployments (including the average for invasive and native plants in Deployment 2) produced deposition of 133.2 mg N module^{-1} for the 281 days of the ITNI deployments between March 8, 2013 and March 24, 2014.

3.5. Nitrogen dynamics of ITNI modules

Measurements of the mass of N in the ITNI modules allowed us to quantify the partitioning of N within the ITNI modules and compute the overall recovery of N and ^{15}N tracer in the experiments. At the start of our experiment, each module contained ~250 mg of N and about 2.5 mg of ^{15}N, which was almost entirely supplied by the ^{15}N-enriched Hoagland solution—the original seeds contained <0.5 mg or 0.02% of starting N mass and the N content of the sand added to the modules was below detection (detection limit: 0.02 wt%). At the end of our experiment, plants stored 85–96% of total N in the modules. Aboveground plant biomass was 3–8 times greater than belowground biomass in Deployments 2 and 3, but only 40% greater than belowground biomass in Deployment 1, likely owing to herbivory in some of the modules. Plants were also the main repository of the ^{15}N tracer spike; plant biomass was most enriched in ^{15}N (0.72 to 0.94 atom %) relative to the sand (0.59 to 0.64 atom %) and liquid reservoirs (0.38 to 0.80 atom %; Table 2). The sand reservoir contained 3.6 to 14% of the total N in the ITNI modules and was the second highest repository of ^{15}N tracer. At the end of the deployments, very little N remained in the liquid reservoirs of ITNI modules with plants (0.1 to 2.4%).

In contrast to the ITNI modules containing plants, most of the total N in the control modules was held in the liquid reservoirs (80%) with similar ^{15}N concentrations in both the sand and liquid reservoirs (Table 2). In both controls, the N contained in the liquid reservoir consisted of NO_3^- and dissolved and particulate organic N. In the Hoagland Controls about 26% of the total N in the liquid was organic N compared to 47% in N-Only controls. Organic N was also detected in the liquid reservoirs of plant-containing ITNI modules in all three deployments, but the absolute mass was small relative to the content of N in above- and belowground plant biomass (Table 2).

4. Discussion

We used the ITNI method, which is based on the principle of isotope dilution in a plant-liquid-sand system, to measure N deposition in coastal sage scrub ecosystems. Ours is the third application of the ITNI method in non-agricultural systems and the first to employ the technique in an aridland ecosystem. Below, we compare ITNI against measurements of wet deposition, throughfall and dry deposition made with conventional methods and discuss the relative uncertainties, strengths, and weaknesses of these measurement techniques. We then discuss factors affecting the incorporation of atmospheric N into plant biomass and the recovery of ^{15}N tracer. Lastly, we combine our ITNI measurements with those reported from other studies to develop a framework for comparing N deposition estimates across studies that use different plant species and experimental procedures.

4.1. ITNI vs. conventional methods

During Deployment 1 (March to May 2013) we compared N deposition estimates made by a rain collector (wet deposition of inorganic N only), throughfall collectors (assumed to collect wet and dry deposition of inorganic N washed through and from the canopy, minus canopy-retained inorganic N) and ITNI (organic & inorganic wet, particulate deposition, gaseous deposition and fog deposition) (Fig. 2). Wet deposition of inorganic N during Deployment 1 was 0.31 kg N ha^{-1} or only 2.8% of the N deposition measured by the ITNI method, implying that during the spring and early summer of 2013, particulate deposition both (inorganic and organic) and stomatal uptake comprised >95% of atmospherically deposited N in Riverside CSS ecosystems.

The throughfall collectors also underestimated N deposition relative to ITNI during Deployment 1. While the IER deployments overlapped the entire period of ITNI operation, comparisons between the methods required temporal scaling of the IER data. Scaling the IER throughfall deposition measured over 215 days to the 74-day ITNI deployment (DIN deposition from Table 3 multiplied by 74/215), yields throughfall of about 0.81 kg N ha^{-1}, which was far below the amount recorded by the ITNI method (11.3 kg N ha^{-1}). Throughfall measured over the entire 215-day IER deployment, 2.4 kg N ha^{-1}, was still less than a quarter of the ITNI deposition measured over 74 days.

Some of the discrepancy between ITNI and throughfall estimates during Deployment 1 may be explained by the fact that rainfall occurred on only 2 dates during the final three months of the IER deployment (March 8 to June 6; total rainfall depth = 6.3 mm), therefore there was little wet deposition of N and little washoff of dry-deposited N

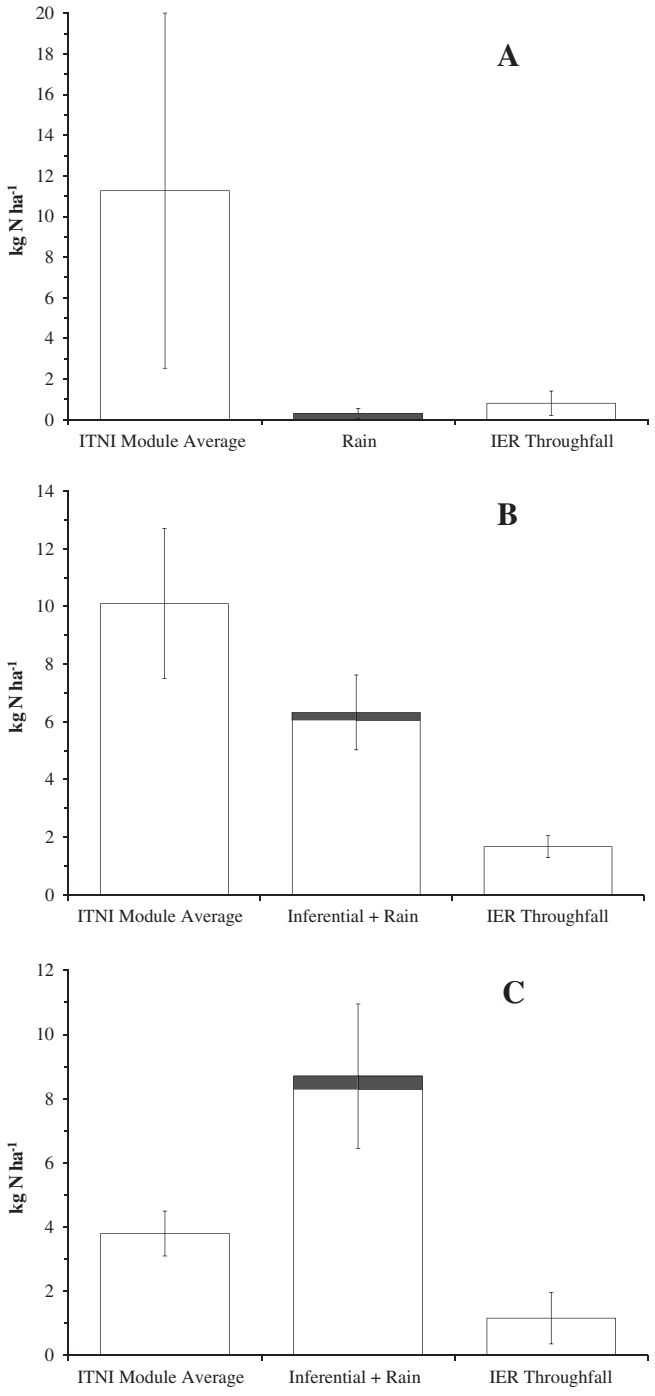

Fig. 2. Comparison among the methods used for assessing rates of atmospheric N deposition in ITNI Deployments 1–3. The black shaded region indicates the contribution of N deposition from rain alone - no inferential measurements were made during Deployment 1. Error bars indicate the total uncertainty of the N deposition estimates. Values for the IER collectors were scaled to match the deployment length for the ITNI modules.

from vegetation. In contrast, dry deposition of N onto the ITNI modules can be directly assimilated by plant foliage (Sparks, 2009) and dry deposition onto the ITNI sand surface would be washed into the sand during daily watering where it could be taken up by plant roots. In addition, daytime air temperatures during the spring of 2013 ranged from 15 to 30 °C, suggesting that the plants in the ITNI module were actively transpiring water, which provided opportunities for direct uptake of gaseous forms of N via plant stomata (Chaparro-Suarez et al., 2011; Sparks et al., 2003; Sparks, 2009); direct uptake of gaseous N is not measured in throughfall solutions.

During Deployment 2, mean ITNI deposition for *H. incana* modules was 11.6 ± 2.9 kg N ha^{-1} and 8.6 ± 1.5 kg N ha^{-1} in *E. fasciculatum* modules; the average for both plant species was 10.1 ± 2.6 kg N ha^{-1} (Fig. 2). Adding dry deposition from inferential measurements with wet N deposition yielded 6.35 ± 1.3 kg N ha^{-1} which is about 55% of ITNI deposition. Downscaling of the throughfall measurements (i.e., DIN deposition in Table 3 multiplied by 77/165) produced N deposition of 1.46 kg N ha^{-1}, which is <15% of ITNI N deposition, implying plants accounted for about 85% of atmospherically derived N in the ITNI modules. The summer of 2013 had only one significant rainfall event on July 20, 2013, with 7.3 mm of precipitation, providing little opportunity for washing dry deposition into the throughfall collectors.

During Deployment 3, the ITNI modules measured 3.8 kg N ha^{-1} (Fig. 2). During this period, the inferential method yielded deposition of 8.3 kg N ha^{-1} and rainfall contributed 0.40 kg N ha^{-1} for a total of 8.70 kg N ha^{-1}. Downscaling of the IER measurements (deposition from Table 3 multiplied by 130/200) yielded 1.16 kg N ha^{-1} for throughfall N deposition.

To estimate annual N deposition using the ITNI method we multiplied the sum of deposition for the three deployments, 22.9 kg N ha^{-1}, by 365/285 to yield an annual deposition rate of 29.3 kg N ha^{-1} yr^{-1} for aboveground plant biomass in the range of 228 to 424 g m^{-2}. This computation is an average daily N deposition rate scaled to an entire year. To estimate the equivalent annual deposition using the inferential + rain method we took the total N deposition from rainfall between March 8, 2013 to March 7, 2014 and added to it upscaled inferential deposition (14.3 kg N ha^{-1} multiplied by 365/207) which yielded annual deposition of 25.2 kg N ha^{-1} yr^{-1}. To compute annual throughfall deposition we summed the deposition measured between 12/2/2012 and 6/6/2014 (582 days) and multiplied this by 365/582 which yielded 4.85 kg N ha^{-1} yr^{-1} (Table 3).

It is likely that plant canopy N retention of NH_4^+ and NO_3^- contributed to the relatively large discrepancy between IER throughfall and ITNI annual N deposition. Throughfall deposition fluxes measured in the greater Los Angeles Air Basin under chaparral vegetation, and more particularly in CSS stands, resulted in annual throughfall N fluxes that were much lower than expected based on the dry-deposition N loading common to this region (Fenn et al., 2018b). In another recent study in a semiarid environment, Avila et al. (2017) found that around 60% of the NH_4^+ and 40% of the NO_3^- deposited was retained by the canopy. Assuming similar canopy inorganic N retention in our CSS plants, we estimate that the rate of inorganic N deposition at Coyote Hill could be about 12 kg ha^{-1} yr^{-1}. Besides plant canopy retention, the IER values do not account for organic nitrogen in throughfall. At the nearby Converse Flat research site, operated by the USFS, about 25–30% of atmospheric N deposition is contributed by organic nitrogen (M. Fenn, unpublished data), further increasing the putative deposition rate at Coyote Hill to about 15 kg N ha^{-1} yr^{-1}. Plant canopies also absorb organic N, but this process is poorly studied and difficult to quantify but, would be captured by the ITNI method (Sparks et al., 2008). Lastly, N deposition in stemflow was not measured by the IER collectors and the importance of that flux in CSS vegetation has not been studied.

An important implication of the discrepancy between throughfall and ITNI deposition is that it demonstrates that aboveground plant biomass plays a dominant role in N exchange between the atmosphere and CSS ecosystems. The greatest drawback of using throughfall to measure N deposition is the unknown proportion of N deposited to the canopy that is retained in the canopy and not measured during throughfall collection (Hansen et al., 2013; Lovett and Lindberg, 1993). This limits our ability to estimate total N deposition from throughfall flux data (Fenn et al., 2018a). Canopy retention mechanisms remain poorly understood as are the rates and mechanisms of canopy assimilation of reactive atmospheric N (Harrison et al., 2000; Sparks, 2009). If we assume that the IER throughfall measurements approximate the net amount of N

deposition passing through or being washed from the plant canopy, then the difference between ITNI deposition and IER throughfall would provide a first approximation of the relative N assimilation rates between aboveground and belowground components of CSS ecosystems. We computed the difference between ITNI and IER throughfall measurements for each deployment after increasing the throughfall measurements by 30% to account for unmeasured organic nitrogen ($[ITNI - (IER_{Throughfall} \times 1.3)] / ITNI$ = fraction of N deposition acquired by aboveground uptake). From these calculations we estimate that about 90%, 81% and 60% of ITNI N deposition occurred via uptake by aboveground plant canopy during Deployments 1 through 3; on an annual basis approximately 78% of N deposition occurred via canopy N assimilation.

The similarity between annualized rates of N deposition from inferential + rain and ITNI measurements is partly a result of compensating errors, i.e., ITNI deposition was greater than inferential deposition in the summer and less than inferential deposition in the winter. Earlier ITNI studies were conducted in agricultural settings where both the ITNI plants and field crops received regular watering. Under these conditions, plant physiology and N assimilation were likely similar between the experimental plants and crops, so it was straightforward to transfer deposition values to the field scale. In contrast, native plants in semiarid regions experience drought stress (Fig. S5), possibly making them less able to assimilate atmospheric N deposition and grow than ITNI plants. Prior research has shown that stomatal conductance is positively related to leaf uptake of organic and oxidized forms of N (Sparks et al., 2003; Chaparro-Suarez et al., 2011).Thus, it is possible that the plants grown during ITNI Deployments 1 and 2 (spring and summer) had higher N assimilation rates than native plants growing in the field because of regular watering. This watering effect may also help explain differences between inferential and ITNI method estimates of N deposition. However, the potential bias caused by watering is somewhat mitigated by the low water holding capacity of the sand media in which the plants grew and the fact that biomass production in the ITNI modules, 17 to 67 g m^{-2} $month^{-1}$, was similar to biomass production in native stands of CSS, 10 to 90 g m^{-2} $month^{-1}$ (Vourlitis et al., 2009). Future studies should attempt to better understand the physiological artifacts introduced by regular irrigation of dryland plants and their effects on N deposition measurements.

Higher ITNI N deposition in the summer was offset by lower deposition in the winter when plants began to senesce and go to seed, reducing stomatal uptake which was assumed to occur at a constant rate in the inferential method, independent of plant phenology. Because we applied the maximal summer deposition velocities from Zhang et al. (2003 and 2015 personal communication) to the winter inferential measurements, it is likely that we overestimated winter N deposition with the inferential method (although it is difficult to develop a well-supported seasonal correction factor for the deposition velocities based simply on leaf area index). In any region with strong seasonality of temperature and rainfall, it may be desirable to use more than one plant species to maintain strong growth rates during ITNI deployments (Hurkuck et al., 2015; He et al., 2010).

4.2. Nitrogen dynamics of the ITNI system

There was a consistent pattern of N allocation in the PLS system across all three of the ITNI deployments (Table 2). Plants represented the largest pool of N at the end of the deployments followed, in order of mass, by the sand matrix and then the liquid reservoir (Table 2). Our findings are consistent with most previous ITNI experiments, where plant biomass stored most of the measured atmospheric N deposition (AdN; Table 5). Very little N was present in the liquid reservoirs of plant-containing modules since N inputs were assimilated by plants, presumably suppressing microbial biomass and the production of organic N in the sand matrix and liquid reservoir. While plant roots and soil microbes strongly compete for soil N, plant tissues are relatively long-lived and therefore plant uptake acts, essentially, as a unidirectional flow of N (Kuzyakov and Xu, 2013).

Table 5
Summary of results from previous ITNI experiments.

Citation	Setting/region	Plants used	Number of replicate modules per species	Deployment duration	N partitioning: % AdN in Plant	^{15}N recovery	ITNI N deposition rate (g/ha/day)	Alternative methods employed	N deposition measured by alternative methods
Weigel et al., 2000	Farmland/Germany	Grain and vegetable crops	Not reported	83–221 days	Not reported	80–99%	107–377	N-balance	50 kg/ha/yr
Russow et al., 2001	Farmland/Germany	Grain and vegetable crops	4	84–221 days	Not reported	80–90%	108 (ryegrass) 241 (barley) 378 (corn) 158 (cabbage)	Bulk deposition	36.5 kg/ha/yr
Böhme et al., 2003	Farmland/Germany	Grain and vegetable crops	4	59 to 191 days	45–83%	Not reported	129 to 362	Not reported	Not reported
Bohlmann et al., 2005	Wetland/Germany	Hairy reed grass	3	475 days	10%	Not reported	82	Bulk deposition	27–47 kg/ha/yr
Russow and Böhme, 2005	Farmland/Germany	Grain and vegetable crops	Not reported	59–188 days	Not reported	Not reported	117–474	Not reported	Not reported
He et al., 2007	Farmland/China	Maize and Ryegrass	3	112 days	56% maize 63% ryegrass	Not Reported	744 (maize) 434 (ryegrass)	Crop uptake method	83 kg/ha/yr
Hurkuck et al., 2015	Peatland/Germany	Ryegrass and Sedge	5 to 8	86 to 156 days	55–68% (ryegrass) <15% (sedge)	46 to 91% (ryegrass) 18–79% (sedge)	66 to 150 (ryegrass) 96 to 138 (sedge)	Various	14 kg/ha/yr (throughfall) 28 kg/ha/yr (inferential)
This study	Coastal Sage Scrub/California	Mustard, Brome, California Buckwheet	5 to 8	74–130 days	85–96%	42% (D-1 brome) 85% (D-2 mustard) 73% (D-2 buckwheat) 25% (D-3 mustard)	153 (D-1 brome) 151 (D-2 mustard) 112 (D-2 buckwheat) 29 (D-3 mustard)	Ion Exchange Resins Inferential +Rain	4.8 kg/ha/yr (throughfall) 25.4 kg/ha/yr (inferential+rain)

Table 6
Average (±standard deviation) of N recovery in ITNI modules containing plants and two types of controls.

	Total N recovery		
	Plant containing modules	Hoagland controls	N-only controls
Deployment 1 (n = 5)	57% (20%)	91% (34%)	82% (4.4%)
Deployment 2 – *H. incana* (n = 6)	94% (19%)	–	–
Deployment 2 - *E. fasciculatum* (n = 6)	96% (6.6%)	–	–
Deployment 3 (n = 8)	46% (11%)	–	–

Total N recovery in individual ITNI modules ranged from 32% to 128%. Average N recovery was lower during Deployments 1 and 3 (57 ± 20% and 46 ± 11%) than during Deployment 2 (94 ± 19% and 96 ± 6.6% for *H. incana* and *E. fasciculatum*) (Table 6). We suspect that herbivory contributed to lower N recovery and greater variation in recovery among the modules in Deployment 1 since the average recovery in the control modules in Deployment 1 was relatively high (82 to 91%). We did note a biological slime on the modules' walls in the control treatment which probably contributed to total N recovery in the controls of <100% (Table 6). Based on the recovery rate in the control modules, it is possible that total N recoveries in the range of 80–90% for plant-containing module can be explained simply by the production of biofilms on container walls. However, additional routes for N loss must have been active during Deployment 3 to explain N recoveries in the 40–60% range. Relatively low plant growth during Deployment 3 may have reduced N retention in plant biomass while facilitating N immobilization in biofilms growing on module surfaces or gaseous N losses. For instance, the magnitude and direction of NH_3 flux between the atmosphere and plant leaves is influenced by several factors including the NH_3 compensation point for individual plant species, ambient NH_3 concentrations in the atmosphere, plant phenology and nutritional status, and air temperature (Farquhar et al., 1980; Mattsson et al., 1998). We hypothesize that conditions were favorable for elevated losses of NH_3 during the first part of Deployment 3 owing to: i) the plants going to seed after anthesis, ii) lower atmospheric partial pressure of NH_3 (Table 4), iii) N-replete conditions from the recent Hoagland solution spike and iv) relatively warm daytime air temperatures (Fig. S1).

ITNI modules may have also lost N through emissions of NO_x, N_2O, and N_2 produced via microbial and abiotic transformations. However, because of the well oxygenated conditions in the ITNI modules, denitrification was unlikely to have occurred in either the sand matrix or liquid reservoir. We base our assumption on the fact that the dual isotope analysis of NO_3^- in the sand and liquid reservoirs exhibited none of the telltale linearity between $\delta^{15}N\text{-}NO_3$ and $\delta^{18}O\text{-}NO_3$ that indicates the kinetic isotope effect of denitrification on residual NO_3^- (Albertin et al., 2012). We also measured NO_x emissions near the middle and end of Deployments 2 and 3 using the methods of Homyak and Sickman (2014) and determined an average flux rate of 1.8 ng NO-N m^2 s^{-1}. Scaling this NO_x flux rate in space and time yields N loss of 0.008 mg N $module^{-1}$ day^{-1} which is only a few percent of total module-level N deposition. Only one published ITNI study included measurements of gaseous N losses (Hurkuck et al., 2015) and it concluded that flux rates of N_2 and N_2O could only explain a small part of N losses from their experimental modules. Thus, in ITNI systems, microbially mediated, gaseous loss of N appears to be a negligible flux.

4.3. ^{15}N tracer recovery

Previous ITNI studies have discussed the impact of tracer recoveries on estimates of atmospheric N deposition (AdN) computed with Eq. (1) (Table 5). Hurkuck et al. (2015) postulated that recoveries <100% indicate that the ITNI method underestimates N deposition rates, but that estimates can be corrected by multiplying the ITNI deposition by 1 over the fractional recovery rate (e.g., multiplication by 1/0.5 for a tracer recovery of 50%). However, it must be recognized that natural processes operating in the ITNI modules return N to the atmosphere and that these processes would be expected to remove ^{15}N tracer. Since the ITNI method measures net deposition of N to individual modules (i.e., N inputs – outputs), <100% recoveries of N caused by N-loss processes occurring in the analogous ecosystem (e.g., denitrification, nitrification, NH_3 emissions from plants) would not seriously bias the ITNI estimates, so long as the N removal rates are similar between ITNI modules and the landscape. If low N recovery results from processes not representative of the landscape, then the ITNI method may underestimate areal N deposition rates. We suspect that the unquantified microbial biofilms in our study, contributed to the uncertainty of ITNI N deposition

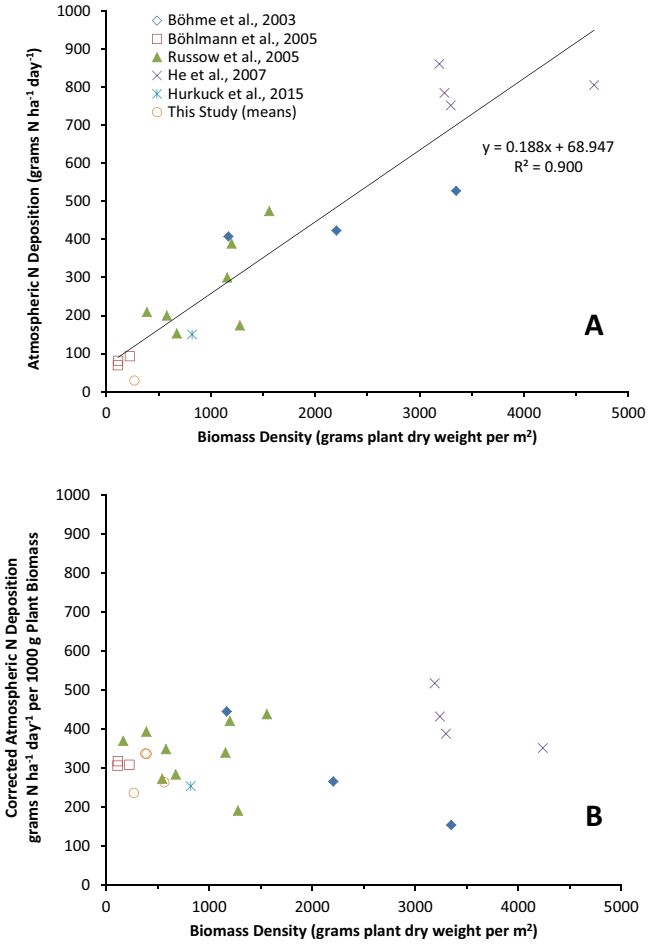

Fig. 3. Relationship between plant biomass production and daily atmospheric deposition rate measured by the ITNI method in previous studies and this study (Panel A). Panel B shows the data from Panel A after the deposition rate was scaled to a biomass level of 1000 g m^{-2} using the regression: Scaled Deposition = Deposition + (((1000-Biomass) × 0.188) + 68.947).

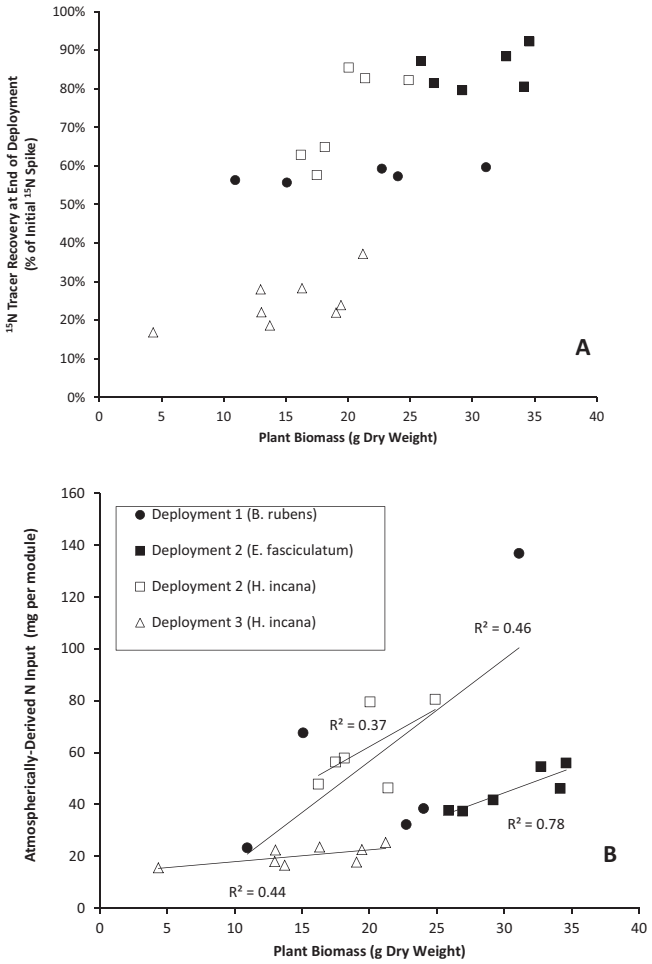

Fig. 4. Relationship between plant biomass and i) ^{15}N recovery (panel A) and ii) atmospherically derived N inputs (AdN from Eq. (1); panel B).

rates although the direction of the bias is hard to determine. Unaccounted for microbial biomass N would decrease the value of N_s in Eq. (1), resulting in lower AdN, however the isotopic composition of the biofilms could increase or decrease the A_s term leading to lower or higher values of AdN. Future ITNI investigations should attempt to quantify microbial biofilms to improve N recovery rates and reduce uncertainty in N deposition measurements.

Several ITNI studies observed that ^{15}N recovery and the amount of atmospheric N deposition measured in individual modules was positively related to plant biomass production (Table 5 and Fig. 3A). Our results match this pattern with statistically significant, positive relationships between plant biomass production (in gram dry weight) and both ^{15}N recovery and AdN values from Eq. (1) (Fig. 4; note Fig. 4A shows the recovery of ^{15}N only rather than total N recovery). We hypothesize higher plant growth led to greater N sequestration in relatively stable plant biomass and less N allocation to unmeasured pools such as microbial biofilms and gaseous N losses, resulting in greater tracer recovery. Greater plant biomass also increases the surface area of the canopy, enhancing stomatal uptake of N and increasing the collection of dry deposition which can be directly absorbed by the plant canopy or washed into the sand where the N can be assimilated by roots.

The tracer recoveries in Deployment 3 were relatively low (range 17 to 37%) and corresponded to the lowest plant biomass production we observed, suggesting that herbivory and biofilm production alone cannot account for these ^{15}N losses. We suspect that most ^{15}N loss occurred early in Deployment 3 when the concentration of ^{15}N was high in the system. We base this supposition on the fact that average ^{15}N recovery, 25 ± 6.6% was only about half of total N recovery, 46 ± 11% (Table 6), indicating a preferential loss of ^{15}N relative to ^{14}N. As described previously, conditions were favorable for plant NH_3 loss in the early part of Deployment 3 when the system was relatively enriched with ^{15}N; later, ^{14}N from the atmosphere could have partially replenished the total N pool in the modules leading to a proportionally greater recovery of ^{14}N.

4.4. Comparability of ITNI deposition measurements

We reviewed results from publications on N deposition where the ITNI method was used (Table 5). While most of these studies used different C3 and C4 vegetable crops and grains, the experimental conditions were similar in terms of the number of replicate modules and the duration of deployments. Average daily N deposition ranged from <30 to over 700 g N ha^{-1} day^{-1}, with the highest rates measured by He et al. (2007) in maize fields near Beijing, China (Table 5). Scaling these daily rates to a year, we estimate annual N deposition ranged from approximately 10 to 271 kg N ha^{-1} yr^{-1}. China is a global hotpot for N deposition (Jia et al., 2016), with ground-based measurements of inorganic N deposition of over 100 kg ha^{-1} yr^{-1} (Pan et al., 2012). In nearly every study where N deposition rates were also reported from conventional methods (including ours), annual ITNI rates were higher.

Mean daily deposition rates estimated for individual species in the reviewed ITNI literature varied by >40-times. Several of these studies have noted that different plant species produced different estimates of N deposition, with maize often producing the highest rate (He et al., 2007). In our study, we also noted statistically significant differences in N deposition using two different species during Deployment 2. Other factors potentially contributing to variations in deposition rates within and across studies include differences in N concentrations in the growth media, timing of the experiments, and ambient atmospheric concentrations of N species. The wide variability of N deposition rates measured by ITNI, raises the question of whether N deposition is more strongly influenced by plant species or if it is mostly controlled by plant growth rates. For example, the fact that deposition rates measured for *H. incana* in Deployments 2 and 3, 11.6 vs. 3.8 kg ha^{-1} (Table 2), were substantially different, yet ambient concentrations of inorganic N species in the atmosphere were nearly identical (Table 4), may be explained by the greater growth of *H. incana* plants during Deployment 2.

Nearly all previous studies have identified plant biomass as a key variable affecting N deposition rates measured by the ITNI method (Russow and Böhme, 2005). Indeed, if we combine all the published data on N deposition rates and plant biomass production, we observe a strong linear relationship ($r^2 = 0.90$) over a biomass range of almost 5000 g m^{-2} (Fig. 3A). The slope of the regression is statistically significant ($P < 0.01$) and indicates that there is a consistent relationship between biomass production and areal N deposition across at least a dozen plant species and a range of individual studies incorporating different initial fertilization levels, different air quality, and different experimental seasons and duration (Table 5). This linear relationship is not unexpected since in Eq. (1), N mass in the ITNI system is directly proportional to N deposition, and land plants in general exhibit a strong degree of "stoichiometric homeostasis" wherein the ratio of plant biomass to N content is fairly constant (Elser et al., 2010). To test the idea that plant biomass production matters more than plant species in ITNI measurements, we used the regression equation to scale all the individual N deposition rates shown in Fig. 3A to a common biomass mass level using the Biomass Method. In the original data there was a > 40-fold variation in areal N deposition rates. However, after the deposition rates were scaled to a biomass level of 1000 g m^{-2} using the regression: (Biomass Scaled Deposition = Deposition + (((1000-Biomass) × 0.188) + 68.947)), the variation in N deposition rates was reduced to <4-fold (Fig. 3B), showing that plant growth rate is more important than plant species differences in accounting for differences in N deposition across studies. Given the strong influence of plant biomass production on the

ITNI method, we recommend that the Biomass Method be used to estimate landscape-scale deposition when aboveground plant biomass in the ITNI modules and target ecosystem are substantially different.

5. Conclusions and recommendations

We used the integrated total nitrogen input (ITNI) method, and other conventional techniques, to measure N deposition rates over a year-long period in Riverside, California - a semiarid region where dry deposition is the dominant route for atmospheric deposition of N. The N dynamics of the ITNI modules were dominated by assimilation of N in above- and belowground biomass. Nitrogen recovery rates in the experiments were <100% and suggested that losses of N were caused by experimental artifacts (herbivory and biofilm growth on container walls) as well as by natural processes such as NH_3 emission from plant leaves. Annual N deposition estimated using ITNI was 29.3 kg N ha^{-1} yr^{-1} which was similar to the sum of wet and dry deposition, 25.2 kg N ha^{-1} yr^{-1}, estimated from the combination of the inferential method and wet deposition. In contrast, throughfall fluxes of N were unexpectedly low, 4.8 kg N ha^{-1} yr^{-1}, likely because of low precipitation rates and because the throughfall method does not capture stemflow, nor several important pathways for N deposition in southern California, namely, stomatal uptake of gaseous reactive N, and canopy retention of other forms of inorganic N and deposition and absorption of organic N deposition. While we noted shortcomings of the ITNI method in arid environments, most notably, the uncertain effect of frequent watering on plant stomatal conductance and N uptake, intercomparisons among the ITNI method and the inferential and IER throughfall techniques yielded valuable insights on relative N assimilation rates between plant aboveground and belowground biomass and provided independent validation of the models underlying the inferential method.

We and other researchers have noted a strong influence of plant biomass production on the rate of N deposition measured using the ITNI method. When extrapolating deposition from modules to the landscape scale, measurements should be corrected for any significant difference in plant biomass between the individual modules and plant biomass in the landscape. The ITNI method offers a holistic approach to measuring the sum of the multiple forms and pathways of N deposition in dryland and other ecosystems, however methodological challenges, including the effects of watering on stomatal conductance and gaseous N exchange with the atmosphere, must be studied further.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2018.07.320.

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