TITLE: Assessing the risk of nitrogen deposition to natural resources in the Four Corners area

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PROJECT SUMMARY:
Nitrogen (N) deposition in the western U.S. is on the rise and is already dramatically affecting terrestrial ecosystems. For example, N deposition has repeatedly been shown to lower air and water quality, increase greenhouse gas emissions, alter plant community composition, and significantly modify fire regimes. Accordingly, the effects of N deposition represent one of our largest environmental challenges and make difficult the National Park Service's (NPS) important mission to "preserve the scenery and the natural and historic objects and the wildlife… unimpaired for the enjoyment of future generations". Due to increased population growth and energy development (e.g., natural gas wells), the Four Corners region has become a notable 'hotspot' for N deposition. However, our understanding of how increased N deposition will affect these unique ecosystems, as well as how much deposition is actually occurring, remains notably poor. Here we used a multi-disciplinary approach to gathering information in an effort to help NPS safeguard the Four Corners national parks, both now and into the future. We applied modeling, field, and laboratory techniques to clarify current N deposition gradients and to help elucidate the ecosystem consequences of N deposition to the national parks of the Four Corners area. Our results suggest that NOx deposition does indeed represent a significant source of N to Mesa Verde National Park and, as expected, N deposition significantly affects coupled biogeochemical cycling (N, carbon, and phosphorus) of these landscapes. We also found some surprising results. For example, perhaps due to the low nutrient availability in these (and other) dryland ecosystems, although most other research suggests that adding N reduces N fixation rates, N additions did not consistently reduce natural N inputs via biological N_2 fixation at our dryland sites. While the timeline of this pilot project is too brief to elucidate all the potential insight from the approach utilized here (e.g., we have fertilization plots to explore how N deposition affects *Bromus tectorum* invasion that will surely yield provoking results), we plan to continue this exciting line of questioning and expect further insight to be forthcoming.

INTRODUCTION

Humans have approximately doubled the input of available nitrogen (N) to the Earth's land surface and numerous papers have documented the significant effects of this change on ecosystem properties. For example, increased N deposition has been shown to decrease air and water quality, increase greenhouse gas emissions and exotic plant invasion, and to potentially alter natural fire regimes (e.g., Aber et al. 1989, Townsend et al. 2003, Galloway et al. 2008, Zavaleta et al. 2009). Thus, we know that N deposition can have dramatic effects on important aspects of terrestrial ecosystem function. However, not all ecosystems respond in the same way to N deposition and we have a notably incomplete understanding of how increased N deposition will affect ecosystems in the Four Corners region of the United States (U.S.). Dryland communities such as those found in the Four Corners may be particularly sensitive to changes in N deposition due to a combination of climate (with organisms inactive for much of the year due to water limitation), shallow and/or poorly developed soils, low standing stocks of N, and relatively low rates of ecosystem processes (e.g., primary productivity) that could constrain N uptake and the N retention capacity of the ecosystem (e.g., Fig. 1). Nevertheless, due to increases in population growth, energy development, as well as the presence of two outdated coal-fired power plants, the Four Corners region has become a 'hotspot' for N deposition (NPS Air Quality in National Parks Report, Fenn et al. 2003). A lack of understanding regarding how increased N deposition will affect the unique systems found within the Southwest hinders the ability of the National Park Service (NPS) to protect the organisms and landscapes of the Four Corners national parks, and requires research efforts that integrate modeling, field, and laboratory approaches. The overarching framework of this pilot study was to initiate research that would ultimately provide the information necessary to incorporate N deposition into effective NPS management strategies for the Four Corners national parks.

PROJECT OBJECTIVES

The goals of this research were to (1) elucidate patterns of N deposition in the Four Corners region and (2) assess the ecosystem consequences of increased deposition, concentrating on exotic plant invasion, changes to natural fire regime, and coupled biogeochemical cycles. Toward that end, we developed a multi-faceted approach that focused on the following four topics:

1. ***NOx deposition in Mesa Verde National Park and the surrounding region***

Hypothesis: Summertime dry deposition of NOx represents a significant input of N into Mesa Verde National Park and the surrounding region

Nitrogen can be deposited into ecosystems in a variety of forms making N deposition rates difficult to quantify (Fenn et al. 2003). In addition, different forms of N are likely to have assorted ecosystem consequences, as different N molecules (e.g., NH_4^+, NO_3^-) behave very differently within terrestrial ecosystems (Vitousek et al. 2002). Here we set out to investigate the nature of sources of airborne N into Mesa Verde National Park. Indeed, the proximity of major NOx stationary sources to Mesa Verde is a primary impetus for this study and the scope of the issue is easily apparent when looking at satellite derived NO_2 column amounts over the western U.S. (Fig. 2; taken from Kim 2009). In this figure, the collective emissions from the Four Corners and San Juan generating stations produce a regional plume that appears comparable to

those produced by mid-sized urban areas such as Las Vegas, Nevada. With such a massive set of point sources within a few tens of kilometers from Mesa Verde – a Class I air shed under the Clean Air Act – it is important to have a full understanding of the impact of all sources of power plant pollution on the park and its ecosystems.

The transport and deposition of mercury from these power plants to Mesa Verde has been studied extensively (e.g., Wright & Nydeck 2010) and this research indicates that mercury transport to Mesa Verde has the greatest impact on precipitation chemistry (and hence deposition) during the summer, particularly from late June through the end of September. This is the time when many storms arrive at Mesa Verde out of the south, passing over the Four Corners and San Juan power plants along the way. Climatologically, this is part of the pattern known as the North American Monsoon (e.g., Adams & Comrie 1997), in which summer continental heating, low-level moisture from the Gulf of California and mid-tropospheric moisture from the Gulf of Mexico combine to produce an increased frequency of thunderstorms. At Mesa Verde, precipitation typically reaches a minimum in June and then peaks in July as the monsoon sets in.[1] Wind roses for the Mesa Verde monitoring site indicate that flow from the due south or southeast is most common in the summer, with northerly flow predominant in all seasons, and a pronounced diurnal pattern favoring northerly flow at night.[2]

In the case of mercury, it is probably sufficient to consider power plants in the transport analysis. In recent years, however, the N emissions from the power plants near Farmington, New Mexico have been augmented by extensive development of natural gas and coal-bed methane deposits in the entire San Juan basin. Table 1 shows estimates for emissions of NOx ($NO + NO_2$) from all stationary sources in the San Juan basin. In total, the estimated emissions in the basin are ~96,385 tons/year, approximately the equivalent of NOx emissions from all sources in the metropolitan Phoenix area[3]. While emissions from the two power plants have decreased, these decreases are being offset by the increases due to the dramatic growth of oil and gas operations. Thus, there is a large potential for NOx deposition in Mesa Verde to be notably high.

Monitoring of N deposition at Mesa Verde happens through several national networks that operate co-located monitoring sites on Chapin Mesa. These include:

- The IMPROVE (Interagency Monitoring of Protected Visual Environments) Network, which monitors speciated particulate matter through filter sampling on a three-day continuous schedule.
- CASTNET (Clean Air Status and Trends Network) and the National Deposition Network, which monitor air quality trends and pollutant deposition in areas remote from urban areas.
- National Atmospheric Deposition Program/National Trends Network, measures precipitation chemistry and tracks trends of acid generating pollutants.

Combined wet/dry deposition data for the years 2001-2010 indicate that the average total N deposition is 2.46 kg N/ha/yr, with no apparent trend over that decade. Of that, 37% was due to dry deposition (33% of the total was dry deposition of HNO_3).[4]

The intention of this study was to expand the understanding of the contribution of all sources to the total N deposition at Mesa Verde, and to better understand the meteorological

[1] http://www.wrcc.dri.edu/cgi-bin/cliMAIN.pl?co5531
[2] http://www.coha.dri.edu/web/state_analysis/Colorado/MesaVerdeNP_metsfcwind.html
[3] http://www.epa.gov/cgi-bin/broker?polchoice=NOX&_debug=0&_service=data&_program=dataprog.national_1.sas
[4] http://www.epa.gov/castnet/javaweb/site_pages/MEV405.html

conditions that control this process. A particular focus was on the possible role that gas-phase dry deposition of NO_2 might play, as that parameter is not monitored as part of CASTNET. Since the atmospheric lifetime of NO_2 varies from one to twelve hours before it is oxidized to HNO_3 depending on conditions, it is normally sufficient to measure HNO_3 to capture the gas-phase deposition potential. However, in the case of Mesa Verde, the CASTNET monitoring site is 56 and 45 air kilometers north of the Four Corners and San Juan power plants, respectively, and approximately 45 km from the edge of the high concentration of oil and gas wells in the San Juan basin. With an average wind speed of 28 km/hr at Mesa Verde[5], that puts the monitoring site within two hours of transport time to both power plants under typical conditions. Under these circumstances, it is possible that dry deposition of NO_2 can contribute significantly to the overall deposition inventory. For example, modeling done in Phoenix indicates that dry deposition of NO_2 can contribute on the order of 10-25% of total N deposition within several hours of transport time downwind of the source (Fenn et al. 2003). Here we set out to quantify NOx deposition in Mesa Verde National Park to compare to existing data for dry and wet N deposition, as well as to use back-trajectory modeling to study the transport patterns during key times of meteorological transition during the photosynthetically-active summer period.

2. ***Fire chronosequence at Mesa Verde National Park***

Overarching Hypothesis: We will observe patterns in nutrient fertility (N and P) across fire chronosequences and within sites (e.g., higher nutrients beneath plant canopies) that will elucidate links between N deposition, ecosystem recovery after fire, biogeochemistry, and invasion by exotic plant species.

Hypotheses: a) There will be an increase in soil fertility under plant canopies relative to intercanopy suggestive of "islands or patches" of fertility.

b) Nitrogen and P availabilities will pulse immediately after fire and will decline over time, eventually segregating into pockets of higher and lower fertility within the old-growth piñon-juniper woodlands.

c) High levels of N and P will increase the susceptibility of soils to invasive grasses and forbs.

Research from other ecosystems has shown important links between N deposition, fire, and soil nutrient availability, and here we explored such linkages in our Four Corners ecosystems. First, it has been suggested that increasing nutrient inputs (*e.g.*, via N deposition) would result in an increase in annual exotic grass invasion and this would, in turn, increase the frequency of fire. Besides this question, we also set out to explore how nutrient availability varies with time since fire in order to create a deeper understanding of how nutrient availability, N deposition, exotic plant invasion and fire are linked in Mesa Verde National Park. In a previous study, members of our research team investigated patterns of weed (primarily *Carduus nutans* [muskthistle] and *Cirsium arvense* [Canada thistle]) distribution in Mesa Verde National Park to identify the plant communities most vulnerable to post-fire weed invasion, and we created a spatially explicit "weed-risk" model to predict the most vulnerable sites (Floyd et al. 2006). This previous study

[5] http://www.usa.com/mesa-verde-national-park-co-weather.htm

demonstrated that, at the scale of the entire park, mature piñon-juniper woodlands growing on two particular soil types were most vulnerable to post-fire weed invasion. The study also revealed that mountain shrublands on all soils were the least vulnerable to invasion because these communities are dominated by native species capable of rapid and vigorous re-sprouting after fire. At a finer-scale, greater richness of native species was correlated with greater numbers of non-native species, indicating that habitats with high native biodiversity are at the greatest risk of weed invasion. In unburned areas, muskthistle density increased with increased soil N, phosphorus (P), and salinity. At the time of this prior work, *Bromus tectorum* was not a prevalent invader to southern Colorado.

Yet, *Bromus tectorum* (cheatgrass) has now become much more common in Mesa Verde National Park and is an invasive weed of particular concern because of its well-known propensity to promote frequent and extensive burning (e.g., Mack 1981, Billings 1990, Whisenant 1990, D'Antonio & Vitousek 1992, Brooks et al. 2004, Link & Hill 2005, Link et al. 2006). This non-native annual grass has become increasingly prevalent in the Mesa Verde region during the past decade, especially in disturbed areas. For example, we observed relatively little cheatgrass after the 1989 fire in Mesa Verde National Park, but cheatgrass quickly dominated portions of the 2000, 2002, and more recent fires. Due to positive correlations between nutrient fertility and invasion by cheatgrass in other ecosystems (e.g., Bashkin et al. 2003), here we hypothesized that higher soil fertility (measured in soil N and P pools) would relate to cheatgrass abundance. Thus, processes that increased fertility would, in effect, increase the potential for cheatgrass invasion. This relationship would be directly applicable to considerations of N deposition and its potential to increase soil N availability and cheatgrass invasion. Given the centuries-long prehistoric fire cycles in piñon-juniper woodlands of this region (Floyd et al. 2004; Scott Anderson, report to NPS), the presence and N-enhancement of cheatgrass, an unprecedented fine fuel, becomes all the more alarming. We explored how fire, time since fire, and plant distribution related to patterns of soil nutrient availability.

3. ***Nitrogen deposition plots in Arches and Mesa Verde National Parks***

> *Hypothesis: Increased N deposition will result in increased invasion by the exotic annual grass* Bromus tectorum *(cheatgrass), and will also affect native plant chemistry, biological soil crusts, and multiple aspects of biogeochemical cycling (e.g., available P pools, microbial biomass C and N).*

As a first step, we set out to determine if there were regional gradients in N deposition that could help us assess how increased inputs of anthropogenically-derived N would affect National Park ecosystems in the Four Corners area. Unfortunately, we were unable to locate any such gradient due to the fact that too many variables varied along potential N deposition gradients (e.g., soil type, plant community, land use history) and that quantifying total N inputs across space and time in the Four Corners region is difficult to do with enough certainty to feel confident in N gradient identification. This emphasized the importance of the proposed fertilization experiment in helping to elucidate how changes to N deposition rates would affect native plant communities, ecosystem invasibility by exotic plants, biological soil crusts, and biogeochemical cycles. Fertilization experiments have been used to explore the effects of N deposition across a range of ecosystems (e.g., Bobbink et al. 2010, Pardo et al. 2011) and offer an opportunity to investigate both the direct and indirect effects of N deposition because the addition of N is occurring within

the same ecosystem and in an experimentally controlled manner. To take advantage of this approach we created a series of fertilization plots in Mesa Verde and Arches national parks.

In Mesa Verde, we constructed fertilization plots in paired burned and unburned sites. Because fire is relatively common at Mesa Verde and because changes to the fire regime are a concern for a variety of stakeholders (including the NPS), in Mesa Verde we focused on exploring the interactions between fire, N deposition, cheatgrass invasion and biogeochemical cycling. In Arches national park, fire is uncommon and instead of focusing on interactions with fire, we used a textural gradient to determine how soil texture, N deposition, cheatgrass invasion, and biogeochemistry are connected. Previous research has suggested that cheatgrass may invade more readily on finer textured soils (Belnap & Phillips 2001), and a hypothesis has been proposed that the finer texture soils allow for higher soil nutrient concentrations and thus increased invasion. At Arches, we employed multiple levels of N deposition (ranging from 0 to 8 kg N/ha/yr) in an attempt to determine a potential N deposition threshold (Fig. 3). We expected that N deposition amounts below this threshold would result in little to no alterations to the ecosystems and to *Bromus tectorum* germination, while deposition amounts above this threshold would result in significant changes to ecosystem structure and/or function.

4. ***Nitrogen fixation, phosphatase activity and nitrogen deposition***

Hypothesis: Increases in N deposition will result in reductions in N_2 fixation rates and thus the total amount of N moving into ecosystems from the atmosphere will be smaller than would be predicted if N_2 fixation did not change. In addition, additions of N will increase phosphatase activity.

Biological N_2 fixation is a process where N_2 is 'fixed' by particular organisms into biologically available forms (NH_4^+; Reed et al. 2011). In dryland ecosystems, N_2 fixation can occur both through plants that maintain symbiotic relationships with bacteria (e.g., legumes), as well as within biological soil crusts (biocrusts). In fact, in many drylands, these biocrusts are the largest fixer of N_2 (Belnap & Lange 2003). Assessments of N inputs into ecosystems in the Four Corners are on the magnitude of 2-4 kg N/ha/yr, and biological N_2 fixation can easily reach and exceed these levels (Belnap 1996). However, a variety of research has suggested that biological N_2 fixation will commonly decline when inputs of N occur to the system: biological N_2 fixation is an energetically expensive process and thus N_2-fixing organisms can preferentially take N from their environment (e.g., as NO_3^- or NH_4^+) and cease fixing N_2 (Reed et al. 2011). If N_2 fixation rates do indeed go down with increased N deposition, then the total amount of N coming into the ecosystem (anthropogenic-N + N_2 fixation-N) would likely be significantly less than if N_2 fixation rates remain the same. That said, although the total N in this system could remain the same if increased N deposition caused an analogous decrease in N fixation, the forms of N (e.g., organic N vs. NO_3^- vs. NH_4^+) in the system may still be significantly altered. This is important, as studies have suggested that the form of N can be just as important in affecting ecosystem processes as the amount of N (Austin et al. 2006). Nevertheless, understanding if and under what circumstances N_2 fixation will respond to N deposition inputs is critical for understanding how increasing anthropogenic N inputs will affect terrestrial ecosystems.

Beyond changes to N cycling, a tight coupling between N and P cycling has been observed in other ecosystems (e.g., Marklein & Houlton 2012), and thus additions of N via N deposition have the potential to directly affect P cycling. But what are the mechanisms that

connect N and P cycling? Some research has shown direct links between increased N availability and increased phosphatase activity. Phosphatase enzymes cleave the bonds that tie P to organic matter, and thus liberate P to become part of the available P pool. Enzymes such as phosphatase are N-rich, and a variety of studies have suggested that increasing N availability allows for increased production of phosphatase (for review see Marklein & Houlton 2012). In other words, increasing N availability can result in an increase in P availability. Understanding these linkages is important because changes to P availability can also affect dryland ecosystems; for example, increased P availability in some grasslands has been shown to positively correlate with *Bromus tectorum* abundance (Bashkin et al. 2003) and to drive the loss of rare plant species (Wassen et al. 2005). Here we set out to explore how manipulating N inputs affected N_2 fixation rates and soil phosphatase activity for the lichen (*Collema tenax*) collected in Mesa Verde National Park and near Arches National Park.

METHODS

1. *NOx deposition in Mesa Verde National Park and the surrounding region*

Monitoring of NO_x was conducted in a trailer installed at the CASTNET/NADP/IMPROVE monitoring site at Mesa Verde (latitude 37.1979 degrees, longitude -108.491 degrees, elevation 2162 m a.s.l.). During the spring and summer of 2012, a Monitor Labs Model 8840 NOx monitor was used. Analog signal data from the instrument was input to a Picolog ADC-16 analog-to-digital converter, which was then recorded on a laptop computer using Picolog software. Data were averaged and recorded at one minute intervals. Calibration of the instrument was achieved using a 30 ppmv NO standard mixed with "zero air" provided by Air Liquide. Mixing of gases was accomplished using Teledyne Hastings mass flow meters. Additionally, a permeation tube containing a slowly leaking solution of dissolved NO_2 was held at constant temperature in a calibration device. The mass of the permeation tube was measured using a microbalance and the emission rate was calculated and used to determine concentrations at various dilution flow rates. Flow rates in the permeation calibration source were calibrated using bubble flow meters. Full calibration of the instrument was conducted every 4-8 weeks (depending on availability of personnel) with weekly calibration checks conducted using the permeation tube source. Additional NOx data were retrieved from two nearby monitoring sites. The Southern Ute tribe operates a NOx monitor near Bondad, Colorado, 57 km ESE of the Mesa Verde monitoring site. Data for this site were retrieved from the EPA AQS system. The San Juan Substation monitoring site is operated by the State of New Mexico and is 47 km due south of the Mesa Verde monitoring site. Air quality data for this site was retrieved via the Internet.[6]

Lagrangian back trajectories for the Mesa Verde monitoring site were calculated using the Hysplit model (Draxler & Rolph, 2003), which can be run from the NOAA website.[7] Trajectories were run using EDAS 40 km gridded meteorological data, with the model set to calculate vertical velocities from an initial elevation of 100 m above ground level. Trajectory runs were 48 hours in length, and were initiated every 6 hours for the month of June, 2012. Hysplit text output files were imported to Excel where unique identifiers were created for each trajectory. These files were imported to ArcGIS for plotting the trajectory paths and trajectories were initially imported into GIS as point files. These were converted to line files for display and

[6] http://air.nmenv.state.nm.us/getParameters.php?stationNo=1
[7] http://ready.arl.noaa.gov/HYSPLIT.php

analysis. Line features of individual trajectories were used to determine which trajectories (and how many) passed over the N hotspots (power plant buffer and a density surface of operational gas wells). Point locations along these lines provided dates that air masses passed over N hotspots and reached MEVE.

Possible N emission hotspots were identified and mapped as follows.

- *Power plants*: The locations of the Four Corners and San Juan Generating Stations were identified. A 10 km buffer was created in the GIS and this was used as the source location hotspot for N from electrical generation.

- *Gas and Oil Wells*: An ArcGIS shape file was obtained from the USGS.[8] This documents the oil and gas well locations within the UCRB (upper Colorado River Basin) as of 2007 (a little dated, but are the best available). Only currently active wells were selected from this dataset. Using the active well sites, a density surface was generated in ArcGIS within a 300 km zone surrounding Mesa Verde National Park. The areas of highest well density (1 – 6 wells per sq. km) were identified and mapped. These areas served as the N hotspots for gas and oil well production.

The back-trajectories that intersected the N hotspots were identified. Using these features, the points along each trajectory were selected that were nearest to the target location within the park to provide dates when the atmospheric N would most likely have reached the park. Also, those trajectory points that intersected the N hotspots were also selected to identify the dates that the air masses may have intercepted increased levels of N. Separate but similar analyses were conducted for each hotspot (power plants vs. wells) as the character of the emissions differ (point source vs. dispersed and higher altitude vs. ground level).

2. ***Fire chronosequence at Mesa Verde National Park***

Site descriptions: Data were collected from two distinct chronosequences to determine changes in soil nutrient status over ecosystem recovery from fire and to correlate soil nutrient properties with diversity and abundance of native and invasive plants. First, data were collected from sites that span a long-term (>200 yr old) chronosequence, with sites in old-growth stands and in places where fire occurred in 1800, 1989, 1996, 2000, 2002, 2003 and 2005 (Fig. 4). These sites were sampled in 2010 and 2011. Second, to further explore patterns observed in the long-term chronosequence, soils were collected along a fire chronosequence of fires that occurred in 1934, 1972, 1989 and 2000. These sites occur in one geographic area of Mesa Verde National Park where 4 fires and comparable unburned woodlands were found on similar soils (Fig. 5). This sampling took place in 2012.

Sampling: For the longer-term chronosequence, in 2010 and 2011 we selected sites to determine how soil nutrient cycling changes over time since fire, as well as how soil nutrient concentrations correlate with the diversity and abundance of native and non-native plants. Soil sampling was done opportunistically in conjunction with an on-going study of post-fire succession on Mesa Verde and samples were taken across the National Park and Ute Mountain Ute tribal lands (Fig.

[8] http://water.usgs.gov/GIS/dsdl/SIR2010_5064_UCRB_OGDBshapefile.zip

4). For the second chronosequence of sites on similar soils, we collected 6 replicate soil samples from under plants (beneath canopy) and in adjacent intercanopy spaces on Wetherill Mesa in the western portion of Mesa Verde National Park on September 12, 2012 (Fig. 5). Collections were made in the 1934 fire, the 1972 fire, the 1989 fire, and the 2000 fires.

Plant abundance and diversity: Sample locations in Mesa Verde National Park and UMU Tribal Lands were selected using a stratified random approach. Using ArcGIS, we identified fire history polygons (either from historic UMU and MEVE fire outlines or from previous determinations by Floyd et al. 2000 and 2004), and generated random samples in each fire category. Two 10 m by 10 m releve plots were established at each end of 100 m transects and the cover/abundance of each plant species was recorded using the Braun-Blanquet scale (Mueller-Dombois and Ellenburg 2002). Using a 0.25-m^2 point-frame sampling quadrat repeated six times at 20 m increments, alternating along sides of the 100 m transect, we measured the relative cover of all shrubs, graminoids, and forbs.

Soil nutrient analyses:

Soil samples for the 2010-2011 chronosequence were analyzed for available ammonium (NH_4^+) and nitrate (NO_3^-) using 2N KCl extracts (Reed et al. 2008), available P using anion exchange resin (Lajtha et al. 1999), gravimetric soil moisture, texture by hydrometer (Sheldrick & Wang 1993), and soil pH in deionized water (2:1 water/soil). The soil pH, moisture, available P concentrations, and texture were determined at the Prescott College Soils Lab. Nitrate and ammonium concentrations were analyzed by the Soil and Plant Analysis Lab at Brigham Young University in Provo, UT.

For the second chronosequence, which was sampled in 2012, soils were analyzed for inorganic N (Reed et al. 2008), available P, total carbon (C), total organic C, total inorganic C, total N, extractable organic C and N, and microbial biomass C and N using methods found in Section 3 below. Analyses were carried out at the USGS Biogeochemistry Lab in Moab, Utah.

3. ***Nitrogen deposition plots in Arches and Mesa Verde National Parks***

Sites, fertilization plots, and sampling—Mesa Verde: Fertilization plots were placed at the southern end of Mesa Verde National Park (Fig. 6). Half the study area is characterized by dense, old growth woodland comprised of piñon pine (*Pinus edulis)* and Utah juniper (*Juniperus osteosperma)*. The understory is dominated by shrubs, composed of bitterbrush (*Purshia tridentata*), mountain mahogany (*Cercocarpus montanus*), and big sagebrush (*Artemisia tridentata*). Muttongrass (*Poa fendleriana*), and Indian Ricegrass (*Achnatherum hymenoides*) are common native grasses, and banana yucca (*Yucca baccata*), low penstemon (*Penstemon linearoides*), and numerous other native forbs make up the understory (Floyd 2003). Biologic soil crusts are also present and are generally in patches between canopies in the woodland. Non-native, invasive, grasses or forbs are essentially absent from undisturbed portions of the community.

The 2002 Long Mesa fire characterized the second half of the study area. This fire was a large, stand-replacing event, as is natural for this vegetation community (Floyd *et al.* 2004). Ten years after the fire, the landscape is still peppered with standing snags. Ground cover is denser and more diverse in this area than in the unburned site. The common native forbs include toadflax (*Commandra umbellata*), penstemon (*Penstemon linarioides* ssp. *coloradoensis*),

smallflower tansyaster (*Machaeranthera parviflora*), scarlet globemallow (*Sphaeralcea coccinea*). Non-native forbs include nodding thistle (*Carduus nutans ssp. macrolepis)* and, less commonly, Russian thistle (*Salsola australis*). Native, perennial grasses in this entity include squirreltail (*Elymus elymoides)*, muttongrass (*Poa fendleriana*), and Indian ricegrass (*Achnatherum hymenoides).* The non-native annual, cheatgrass (*Bromus tectorum),* is abundant in the burned area. Biological soil crusts are becoming initiated.

At each of three locations we paired a burned area with an unburned counterpart. We selected these three locations on the south end of the park from an array of randomly generated points in GIS. From these we navigated to points accessible from main roads and where burned and unburned comparable sites were available in close proximity (Table 2). We used a GPS unit to mark the approximate center of each point and established plots within 1 ha on similar aspect and slope arranged approximately as in Figures 6 and 7. At each of the paired locations we established ten paired plots. In late April 2011, we placed each square meter plot in an area of canopy interspace that lacked vegetation with its pair in close proximity (no more than approximately two meters away). We established a total of 60 plot pairs in the six burned and unburned locations (Figs. 6 and 7).

When we established the plots in April 2011, we treated half of each pair with an application rate equivalent to 10 kg N/ha/yr using dissolved NH_4NO_3 (ammonium nitrate). This amount is estimated to be approximately twice the background level of nitrogen deposition in the Mesa Verde area, although deposition rates may be in actuality higher (see the results in Section 1). Though this amount is likely not enough to evoke a dramatic response from invasives in a single growing season, we regarded the amount a realistic quantity for an anthropogenic source. Over all plots, we applied the fertilizer solution evenly with a hand-pump backpack sprayer. The other half of the pair was treated as a control and sprayed with the same volume of deionized water. All plots received the same treatment again the last week of June 2011, at an application rate of 10 kg N/ha/yr as ammonium nitrate for a total of 20 kg N/ha/yr.

Sites, fertilization plots, and sampling—Arches: In 2010, we selected three sites within the Salt Valley Wash area of Arches National Park (Fig. 8) that vary significantly in soil texture (Table 3). At each of the three sites we established twenty 1.5 x 1.5 m plots (data and sample collection only occur within the center 1 x 1 m square, allowing for a border to reduce any edge effects) and randomly assigned them to one of four treatments (0, 2, 5, or 8 kg N/ha/yr; n = 5 for each treatment). Each plot has an *Achnatherum hymenoides* at its center. There are a total of 60 plots in Arches National Park. In August of 2011, we planted one quarter of each plot with *Bromus tectorum* seeds (seeds were acquired locally and seed viability tests showed high seed viability with ~100% germination success). This planting was meant to minimize the variability in germination that could result from natural variation in *Bromus tectorum* seedbanks and thus allowed us to more directly assess the effects of N deposition on cheatgrass germination. We then fertilized each plot with ½ of its selected annual deposition rate and collected a variety of plant and soil data (described below). In February of 2012 and August of 2012 we repeated the data collection and fertilization, except plant community and biological soil crusts assessments are only collected once per year (in August). We plan to continue fertilizing and collecting data for as long as we are able to support the work.

Plant community assessments—Mesa Verde:

In June 2011 (concurrent with the second fertilization treatment) and again in late September 2011 and July 2012 we recorded the number of total plant individuals per species as a measure of abundance and diversity. We also attempted to record the number of planted *Bromus tectorum* germinants in subplots (only minimal germination occurred and the seedlings died before the data collection took place). In September 2011, we clipped the above ground biomass of each individual within the plots. We combined all individuals within a species. After drying each sample at 70°C for 24 hours, we recorded the dry weight of each species by plot as a measure of above-ground biomass.

Plant community and biological soil crust assessments—Arches:
We used a 100 point frame (10 cm between points) that is built to stand above the plant canopy to assess the plant and biological soil crust community composition. The reader used a long thin pointer and at each of the 100 points recorded all of the components that 'hit' that pointer (e.g., live and dead plant tissue recorded by species, leaf litter recorded by size class, and biological soil crust recorded by developmental class (e.g., bare ground, light crust). In the quadrat of the plot where cheatgrass was planted, we also counted the number of cheatgrass individuals that germinated.

Soil nutrient analyses:

- *'Available' N*: Inorganic N (NO_3^- + NH_4^+) concentrations were determined for fresh soils extracted using the 2N KCl extraction procedures outlined in Reed and others (2008; based on Robertson et al. 1999). Briefly, solutions are shaken in KCl, filtered to remove all solids, and concentrations are assessed colorimetrically.

- *'Available' P'*: In Mesa Verde, available P was assessed using anion exchange resin (Lajtha et al. 1999). In Arches, available P concentrations were determined using the method described by Olsen and others (1954). Briefly, each soil sample is extracted in 0.5M $NaHCO_3$ (adjusted to a pH of 8.5), filtered, and P concentrations are determined using an ascorbic acid molybdate colorimetric analysis (Kuo 1996).

- *Extractable total organic carbon (TOC) and total dissolved N (TDN)*: Assessments occurred as described in Reed and others (2011). Briefly, fresh soils were extracted with 0.5M K_2SO_4, filtered, and TOC and TDN concentrations were determined using a TOC-Vcpn/TN-1 analyzer.

- *Microbial biomass C and N*: The chloroform fumigation method was used to assess microbial biomass C and N (Brookes et al. 1985, Vance et al. 1987) and as described in Reed and others (2011). Briefly, for each soil, TOC and TDN concentrations were determined as described immediately above. A second subsample of the same fresh soil was placed into a vacuum desiccation chamber and the headspace filled with chloroform. Samples are left in this headspace in the dark for ~5 d and are then extracted with 0.5M K_2SO_4 as described above. Unfumigated C and N values were subtracted from post-fumigation values to determine microbial biomass C and N concentrations. The proportionality constant Kc = 0.45 was used to correct microbial C concentrations (Vance et al. 1987) and the constant Kn = 0.54 was used for microbial biomass N concentrations (Brookes et al. 1984).

- *Soil total C and N*: Soil samples were sieved to 4 mm, oven-dried, ground to a fine powder, and oven-dried again at 105°C for 48 h. Samples were then wrapped in tins and analyzed for total soil C and N using an elemental analyzer (Reed et al. 2008). Many of the soils in the Four Corners region contain significant amounts of inorganic C, thus we also quantified inorganic C using a modified pressure calcimetry method (Sherrod et al. 2002). We calculated organic C concentrations as total C concentrations with the inorganic C subtracted.

- *Foliar total C and N*: All foliage was oven-dried, ground to a fine powder) and oven-dried again at 70°C for 48 h. Samples were then wrapped in tins and analyzed for total C and N using an elemental analyzer.

4. ***Nitrogen fixation, phosphatase activity and nitrogen deposition***

Soil collection: Using 1" diameter clear acrylic tubes, we collected 55 *Collema tenax* samples each from Mesa Verde National Park and from a site near Arches National Park that had well-developed biocrusts and brought the samples back to the greenhouse in Moab, UT for incubation. Samples were given three days of ample moisture and sunlight prior to the beginning of the experiment.

Fertilization: Each sample was randomly assigned one of 11 fertilization treatments, with 5 replicates for each treatment from each site (for a total of 110 samples). Treatments were control (deionized water), N0.5; N1; N2.5; N5; N10; P2; N1P2; N2.5P2; N5P2; and rain. The N and P represent fertilization with N and/or P, respectively. The number following the letter signifies the amount of N or P the sample received. For example, N5 signifies a *C. tenax* that received the equivalent of 5 kg N/ha/yr for that time period (since the incubations only lasted 1 week, the samples received only 1 week's worth of that annual input). A sample receiving the treatment N2.5P2 would receive the equivalent of 2.5 kg N/ha/yr and 2 kg P/ha/yr. Fertilization with N occurred as dissolved NH_4NO_3 and P was added as dissolved KH_2PO_4. The 'rain' treated samples received natural rainfall instead of deionized water.

N_2 fixation assessment: Samples were assessed for N_2 fixation rate using the acetylene reduction assay as developed by Belnap (1996) and described in Reed and others (2008). Briefly, samples are incubated in a 10% v/v acetylene headspace for 4 hr. After the incubation time, headspace is subsampled and assessed for ethylene concentrations (nitrogenase – the enzyme complex responsible for fixing N_2 – will preferentially reduce acetylene to ethylene). Thus, higher rates of acetylene reduction relate to higher rates of N_2 fixation.

Phosphatase activity: After being assessed for N_2 fixation rate, samples were analyzed for phosphatase activity using the method described by German and others (2011). We took care to use all of the controls and required. Briefly, soil samples are homogenized in a buffer that represents their native pH and are combined with the fluorescent dye-conjugated 4-methylumbelliferyl-phosphate (4-MUB phosphate). Calculations of activity are described in detail in German and others (2011).

RESULTS

1. *NOx deposition in Mesa Verde National Park and the surrounding region*

Take home message: NOx likely represents a significant input of N to Mesa Verde National Park and fluxes may be larger than N inputs as HNO_3, at least during particular seasons. While the nearby power plants are probably the source of the dirtiest air at Mesa Verde, oil and gas operations in the San Juan Basin are likely contributing significantly to anthropogenic N deposition.

During the duration of the monitoring project and in subsequent data analysis, it was clear that a suite of analytical, environmental, and operational problems damaged the quality of the NOx data collected. The Monitor Labs 8840 NOx instrument is an older device that was not as stable or reliable as good QA protocols would dictate. For example, there was an artifact in the data that was determined in May 2012 to be due to a light leak in the photomultiplier tube. While steps were taken to attempt to fix this light leak, it was never completely resolved, and this artifact clearly contaminates all daytime data collected during the experiment. Additionally, the remote site and difficult environmental conditions led to substantial periods of operational downtime. For example, a severe lightning storm in July 2012 caused the computer hard drive to fail. During the same storm, water splashed into the instrument inlet, filling the instrument gas plumbing with water. With a wide range of temperatures in the instrument trailer, operational failures seemed to be more common than expected, including the failure of two vacuum pumps. Given those challenges, the data were examined carefully to see what periods of interest had usable monitoring results. Since NO_2 deposition is primarily believed to happen through stomatal uptake, it is primarily of importance during the time of active photosynthesis. For this reason, we focused on June 2012 data. This was also the time when the transition to the monsoon period begins, with the possibility of more frequent south or southeasterly flow.

Figure 9 shows NOx concentrations averaged over the two hours after midnight for each day of June 2012. This period was chosen after examining the data for obvious artifacts and this period was one where the instrument appeared stable, thus we trust the data. Given that the monitoring conditions were relatively constant each night during this period, this offered the best opportunity to measure true variability in NOx, as opposed to the troublesome data artifacts described above. The concentrations of NOx in June were relatively high compared to typical measurements in rural areas of the western U.S, and there was significant day-to-day variation, with concentrations varying from 0 to 170 ppbv. Most of this NOx was measured in the form of NO, as one would expect for emissions at night, where there is no photochemistry to push the catalytic cycles that lead to the creation of oxidants such as ozone and hydroxyl radicals. The NO_2 to NO ratio varied from 0 to 0.59, with an average of 0.14. NOx concentrations appeared, overall, to increase towards the end of the month.

These results were compared to NOx monitors at the San Juan substation and in Bondad, Colorado, for the same period. Concentrations in Bondad were considerably lower, despite the close proximity of the site to numerous oil and gas wells in the northern San Juan basin (the monitoring site is in a valley location below the wells and apparently doesn't experience much transport during the summer months). The Bondad monitoring location is somewhat further from any power plant sources; 60 km versus 46 km for the Mesa Verde site. The San Juan Substation monitoring site, in contrast, regularly sees NOx concentrations between 100 and 200 ppbv. There

was no obvious correlation with the Mesa Verde data, but this is unsurprising, given the very different geographic situations of the two monitoring sites.

The Mesa Verde NOx data were also compared to other monitoring data at the site. For example, HNO_3 concentrations and deposition fluxes were retrieved from the CASTNET database. One would expect HNO_3 and NOx to be correlated, as HNO_3 is derived from the oxidation of NO_2. Figure 10 shows the calculated HNO_3 deposition flux from April through August 2012. In it is an apparent trend towards higher deposition rates during the month of June. Closer examination reveals correspondence of some key features of the two time series, including a small peak in the first week of June, followed by a brief drop-off, and then leading to the highest values at the end of June (Fig. 10).

This apparent transition from cleaner conditions in the early summer to dirtier conditions as the monsoon develops corresponds well to the transport pattern identified in the mercury deposition study described above (Wright & Nydeck 2010). In order to better understand this important transition, back trajectories from the Mesa Verde site during June 2012 were examined for likely interactions with the two major stationary source types. Figure 11 shows all the trajectories that crossed over the 10 km buffer zone established around the Four Corners and San Juan power plants. This included 15 of the 120 trajectories that were modeled. One aspect that is notable in the trajectory runs is that a number of these transport paths cross over the emission zone coming from southwesterly or even northwesterly trajectories and then loop back to Mesa Verde. This is perhaps an important meteorological mechanism for transport to Mesa Verde even during the southwesterly flow common in late spring. However, given the small scale of these atmospheric motions it is likely that the trajectory model is working at its limit to accurately represent this behavior, as it is right at the scale of the gridded meteorological data (40 km) used as model input.

Figure 12 shows the same analysis repeated for the oil and gas wells of the San Juan basin. The contoured surface represents the density of wells; each trajectory during June crossing the boundary of the 1 well per square km threshold was tagged and identified for further analysis. This included 52 of the 120 trajectories. Despite the location of the basin to the southeast of Mesa Verde, the majority of the tagged trajectories had their origin in the southwest.

The results of the trajectory analysis were categorized by the number of trajectories in each day that were tagged as crossing a NOx source region (Fig. 13). Comparing this to Figure 9, there appears to be reasonable correspondence between the measured NOx concentrations and the source of the trajectories. For example, the low concentrations in the second week of June correspond to the lack of tagged trajectories. The first week of June was dominated by transport from the oil and gas wells. The last week of June saw the most frequent trajectories arriving from the power plants.

While this analysis doesn't allow for the definitive attribution of NOx arriving at Mesa Verde to the different sources, it does appear that both categories of sources are impacting Mesa Verde. Given the overall trend towards higher concentrations and more frequent transport from the power plants, however, it appears that the influence of the two power plants is likely the stronger of the two. While regional oil and gas wells emit as much NOx as the power plants, those emissions are spread across an area of approximately 4000 sq. km. The power plants are emitting at a much higher elevation above the ground (75 and 90 m in the case of the Four Corners plant). This protects nearby areas from exposure to high concentrations, but actually enhances the chances that a coherent plume will be transported to nearby higher-elevation areas such as Mesa Verde.

One of the primary purposes of this study was to determine if dry deposition of NOx species that are not measured in CASTNET was potentially significant to the overall N deposition budget at Mesa Verde. Because of its low reactivity and very short atmospheric lifetime, dry deposition of NO is usually ignored. Deposition of NO_2 is considered more significant, but is also slower than the easily adsorbed HNO_3. Zhang and others (2003) provided a useful review of techniques for calculating dry deposition fluxes and a catalog of deposition velocities for different surface types and chemical species. The deposition velocity for HNO_3 is primarily dependent on the atmospheric variables that control the rate of diffusion to the ground; once at a solid surface, it is rapidly taken up. For dry deposition of NO_2 to occur requires the gas to enter a stomatal space in a photosynthesizing plant (e.g., Flechard et al. 2011). This obviously depends greatly upon the plant community and the season.

For this study, the weekly dry deposition velocity for HNO_3 calculated using the Multilayer Model (MLM) was scaled according to the dry deposition velocities for a thorn shrub plant type (0.8 cm/s for NO_2 versus 3.7 cm/s for HNO_3; Zhang et al. 2003). This ratio of 1 to 4.625 is well within the range described in the literature (typically 1 – 10 cm/s; e.g., Flechard et al. 2011). When scaled appropriately, the adjusted deposition velocity for NO_2 was used to calculate weekly deposition fluxes using the measured NO_2 concentrations (Fig. 14). Except for the last week of June, the calculated flux of NO_2 was higher than that of HNO_3. Even if the lowest literature value for NO_2 deposition velocity was used, NO_2 fluxes would have been calculated as at or above those for HNO_3 for most of the month.

While there is considerable disagreement about NO_2 deposition velocities in the literature, it is generally agreed by both theoretical and empirical studies that above a compensation level of about 0.5 ppbv, NO_2 deposition can be significant during the growing season, and the majority of the measurements in June were above this threshold. While the lack of a complete NOx time series prevents more definitive conclusions, this is highly suggestive that NO_2 dry deposition at Mesa Verde is a significant contributor to the N budget during the summer, perhaps rivaling or exceeding that of HNO_3, which is identified in current analyses as providing 1/3 of the total N to the site annually. Given the seasonal limitations to NO_2 deposition, this likely would put the contribution of NO_2 in the 10-25% range that was identified above as expected for receptor sites within a few hours transport time of the N source.

2. ***Fire chronosequence at Mesa Verde National Park***

Take home message: A broad pattern in the availability of key nutrients was revealed in our study: Fire induces a pulse of soil P and nitrate, which gradually tends to decline over the subsequent century. After many hundreds of years, old-growth forests segregate nutrients into high-fertility islands under tree canopies, and low-fertility areas in the canopy inter-spaces. Available P is high in the high-fertility islands, but nitrate remains low. That both P and nitrate are elevated in the years following burns suggests an important window of vulnerability to invasive weeds.

Canopy vs. inter-canopy comparison: We hoped that comparing soils from canopy vs. intercanopy (interspace) habitats would allow us to better understand the challenges inherent in comparing recent burns, which have minimal canopy cover, to old-growth sites, which have distinct mature canopies. Further, by separating and comparing soils from interspaces with those from beneath plant canopies, we could explore the idea that "islands of fertility" in the post burn

sites might be favored sites for invasive weeds following fires (Schlesinger et al. 1996). One outlier pair was removed from the statistical analysis. In the remaining 11 pairs, there were significantly greater extractable NO_3^- and P concentrations in the 'beneath canopy' soils relative to 'intercanopy soils', and conductivity was twice as high in canopy soils relative to interspace soils (Fig. 15) (t=2.6, p=0.017 for NO_3^-; and t=2.5, p=0.02 for P; and t=2.6, p=0.014 for conductivity). Differences in mean NH_4^+ values between canopy and interspace soils were not significant. These findings support our hypothesis that canopy areas are more fertile than adjacent intercanopy spaces and might therefore become favored sites for the invasion of non-native species after fire.

Nutrient trends across the fire long-term chronosequence: Analysis of variance (ANOVA) statistical assessments suggested there were no significant differences in the mean NH_4^+ or NO_3^- concentrations, nor in conductivity across the long-term fire chronosequence; however, there was a significant difference in P concentrations (Fig. 16; F=1.94,p=0.05). The most recent fire (2005) had the largest soil available P concentrations. Although fire can result in large losses of N from ecosystems (Raison et al. 1985), as long as ash is not blown away, increases in P availability are not uncommon following fire (Eisele et al. 1989). Thus, fire may result in a pulse of P to the ecosystems, and this increase in available P pools can subsequently become smaller over time as plants and microbes immobilize P into their biomass (i.e., as the plant community regrows after fire). However, strong conclusions from this longer-term chronosequence are made difficult by the fact that the fires were scattered throughout the Mesa Verde cuesta, and thus occurred on several different soil types. Accordingly, variables other than time-since-fire may have influenced the available P levels.

To further elucidate these potential patterns, we used ANOVA to assess the fire chronosequence soils collected on Wetherill Mesa. We first tested for differences in the mean values of each dependent variable in the four stages of fires chronosequence (2000, 1989, 1972, 1934 and old-growth/unburned for many centuries). We found a significant difference in total soil N (%) levels (F=3.245, p=0.019), with the greatest value in the old growth and similar, lower values among the recent fires. We also found a significant difference in total organic C (%) concentrations (F=3.8, p=0.008), with the greatest value in the old growth soils and similar, lower values among the recent fires. Interestingly, the C:N ratio of soil was also significantly different among the four burn categories (F=4.2, p=0.005); the greatest C:N occurs in the old-growth, while more recent fires have lower values. Extractable organic C and total dissolved N values were similar across the fire chronosequence, but there was a significant difference in the C:N ratio of these extractable components (F=.6, p=0.001), with the highest values in the old-growth soil.

We were especially interested in P levels in this fire chronosequence, given the data noted above in 2010/2011 data. For this 2012 dataset, there was significantly greater available P in old-growth soils relative to the soils that had more recently experience fire (Fig. 17; F=13.98, p<0.001). To further tease out soil trends that might be attributed to time-since-fire and to investigate possible canopy effects, we focused our statistical analyses *only* on the burns. There was a significant difference in P with canopy (F=30.4, p<0.001) and recent fire date (F=4.1, p=0.014) but no significant interaction (i.e., P levels in each fire responded in a similar way to canopy position). As with the earlier data (Fig. 16), the highest soil available P concentrations were found in the most recent fire and the lowest in the oldest fire (Fig. 18).

This pattern is intriguing and suggests that fire offers a significant P pulse into these dryland ecosystems. While it could also be hypothesized that available P would build over time so that older burns would have higher values relative to newer burns, our data show the opposite trend and support the idea that there may be a net P release with fire. Further, the data suggest that this available P pool then becomes smaller over the course of recovery (perhaps due to uptake of P by regrowing organisms). However, by the time the ecosystem reaches old-growth status, available P pools have climbed again, and reach their highest levels (Fig. 17). Taken together, these data suggest interesting pattern in soil available P pools over the course of recovery and there are some data linking P availability to cheatgrass invasion. However, pool data cannot elucidate the processes that lead to these trends. In particular, soil development (i.e., pedogenesis), pH, and variations in other P pools (e.g., organic P) could all play a role in regulating P cycling and would help explain the patterns we observed in available P. While P is likely to be important to recovery and likely to be linked to fluxes in soil available N (which is more difficult to assess due to N's mobility) more work is clearly needed to help explore these results.

In particular, explorations of how plant cover is related would be particularly interesting. If we consider plant uptake and the fact that available P is a pool created from multiple gross fluxes that involve extraction and inputs, the cover and type of vegetation may be critical. The oldest (1934) fire supports dense stands of perennial sprouting shrubs *Amelanchier utahensis, Quercus gambelii, Fendlera rupicola* and the actinorhizal *Purshia tridentata*. These perennials resprout vigorously immediately following fire and may be responsible for depleting pools of available P. The 1989 fire also supports these species, but they are less dense and have fewer years to accumulate biomass. In contrast, the 1972 burn has far fewer perennial species and supports more open low shrubs such as *Penstemon linearoides, Lupinus* species and perennial grasses *Poa fendleriana* and *Stipa hymenoides*, while the 2000 fire is a grassland today dominated by *Agopyron* species, *Poa fendleriana*, and *Elymus elymoides*. The potential of these vegetation types to extract available P as well as to add P through decomposition can be highly variable and may in part explain some of the trends noted in Figure 17. Soil NO_3^- concentrations were significantly different when mean values were compared across the fire chronosequence with one way ANOVA ($F=3.8$, $p=0.008$), with the highest values in the most recent fire and a steady decline with greater time-since-fire (Fig. 19). This trend shows consistently in intercanopy spaces only.

<u>*Invasive species trends in 2010 and 2011*</u>: There was a significant difference in the cover of cheatgrass ($F=2.1$, $p=0.03$) when compared across the fire chronosequence; old-growth stands (e.g., 1400) rarely support any invasive species, while there is considerable variability in the cover of cheatgrass in the fires (Fig. 20). The "1800s" fires are currently grazed on Ute Tribal Land. The 2002 fire occurred on the heavily visited Chapin Mesa in Mesa Verde National Park. These disturbances might in part account for spikes in cheatgrass seen in Figure 20. Also, annual precipitation was low during the study and these moisture levels resulted in little germination of *Bromus tectorum* and *Carduus nutans*. Germination is dependent on winter precipitation in this region. The precipitation was much greater in the 2009/2010 winter months (22.3 cm rainfall and 182 cm snow) than the 2010/2011 winter months (10.0 cm rainfall and 40.2 cm snow). When searching for correlations among natives and invasive plant diversity or abundance with soil properties, we focus on 2010 trends in this report. In 2010, there was a significant positive correlation of the cover (%) of *Bromus tectorum* with soil NO_3^- ($r=0.34$, $p=0.002$) and

conductivity, a measure of salinity (r=0.298, p=0.004) but not with NH_4^+ or available P. There were so few invasive forbs in our samples in 2010 that no analysis was undertaken.

Native species trends in 2010: There was a significant correlation of the cover of native forbs with available P (r=0.518, p<0.001). However, no relationship between native grasses and the tested nutrients could be detected.

3. ***Nitrogen deposition plots in Arches and Mesa Verde National Parks***

Take home message: We are continuing this manipulative experiment and, due to regional drought, *Bromus tectorum* was rare in Mesa Verde and did not germinate in any of the Arches National Park plots. However, initial data suggest that fertilization did affect diversity and abundance of other species and that fertilization is beginning to affect coupled biogeochemical cycles for certain soils.

Mesa Verde—For 2011 data, we ran a series of paired t-tests on burned and unburned areas separately, testing for differences in diversity and abundance in fertilized and control pairs. In June, 2011, diversity of plants was not influenced by fertilization in unburned plots, but was increased significantly from 2.8 to 3.6 plant species per 1 m^2 plots in fertilized burned plots (T=2.04, p=0.05). There was a greater abundance of all plants (native and invasive combined) in fertilized plots in both burned and unburned treatments (Table 4). So, while diversity responds to fertilization only if burned, fertilization increases the abundance of plants in burned and unburned habitats. For invasive species, in general the effects of fertilization treatment are far less clear than the influence of fire in supporting invasive plants, and we observed far more cheatgrass in burned plots (F=35.6, p<0.001). There were no significant differences in mean cheatgrass abundance in paired samples t-tests comparing fertilized with unfertilized plots in burned or unburned plots. In two-way ANOVAs, cheatgrass abundance did not respond to the fertilization treatments in either burned or unburned (interactive term F=0.48, p>0.05). There simply was not sufficient rainfall to support cheatgrass germination and growth during 2011 or 2012. Biomass was significantly greater in burned areas than unburned areas, but it did not respond to the fertilization treatment in either burned or unburned plots.

Precipitation was negligible in May and June, 2012, and few forbs were present in the piñon-juniper zones. Thus, the invasive species cheatgrass and muskthistle were notably absent from all plots, as were many of the native annual species one would expect to see in these areas. Given the extreme drought conditions, our data collected in 2012 are likely relatively unusual. We ran a series of paired t-tests on burned and unburned areas separately, testing for differences in diversity and abundance in fertilized and controls. No statistical differences were noted in unburned areas. However, in stark contrast to 2011, in the burned plots, we found significantly greater diversity of plant species in the untreated plots relative to the fertilized plots. We intend to continue monitoring these plots in 2013.

The potential mechanisms by which N fertilization may induce greater success by weeds are likely to occur at the germination and growth stages. Germination of several important agricultural weeds has been shown to respond positively to increases in soil nitrate (Mohler 2001). In the data collected thus far from Mesa Verde, there is no evidence that this mechanism is important during drought years. Some weeds show marked responses in growth to increased N availability (Brookes 2003). The increase in productivity can result in appropriation of other

limiting resources (non-N nutrients, light, water) and subsequent suppression of other species. Thus weed growth responses to N fertilization can result in lower overall diversity. The data from Mesa Verde to date suggest this mechanism may be important, however, no biomass data were taken in June of 2011, or July of 2012, which is when lower diversity in the fertilized plots was measured. Taken together, the data suggest interesting links between climate and the consequences of N deposition, such that the interactions may help determine effects on native and exotic plants from year to year. We hope to continue to explore this relationship by continuing to fertilize and monitor the fertilization plots, as they represent an exciting scientific resource.

Arches—The Arches plots center around a single *Achnatherum hymenoides* with interspace surrounding on all sides. To observe a change in diversity we would need to see an increase or reduction in the number of species present, which for this plot design would occur mostly via changes in the annual plant community. Due to the lack of rainfall in 2011 and 2012, we observed no annuals in any of the plots, not even any cheatgrass germination in the quadrat of the plot where cheatgrass seeds were planted. As for Mesa Verde, we need a longer timeline that includes more 'normal' precipitation in order to elucidate how increased N is affecting the native and exotic plant communities. However, as long as we can maintain plot treatment and data collection, the dry period was an exciting event because it will allow us to tease apart how climate and N deposition interact to regulate exotic species abundance and diversity in both Mesa Verde and Arches National Parks.

While exploration of N deposition effects on exotic plant invasion was made difficult by the drought, we were able to begin investigating how the N manipulations affected aspects of N cycling, as well as other biogeochemical cycles. In particular, we focused on assessments of different pools of N ('available' N, extractable organic N, total soil N, microbial biomass N), pools of C (extractable organic C, total C, microbial biomass C), and P (available P using the Olsen extraction [Olsen et al. 1954]). First, we noticed that our gradients in texture did indeed related to gradients in fertility, as the finer-texture soils had significantly greater available N and P relative to the coarser soils (Fig. 21). However, we did not find significant effects of N fertilization on the C and N pools we measured. Soils in the Arches fertilization plots are sampled once per year and the sampling occurs just before fertilization. Thus, the soils have had 6 months of 'rest' from fertilization at the time of sampling (because fertilization occurs twice per year). What our data suggest is that, at least for the year and a half of fertilization that has occurred to date, the effects of N addition do not remain observable in C and N cycles six months after fertilization. For example, we don't see significant differences among the fertilization plots in available N, microbial biomass C or N, nor in extractable organic C and N concentrations. This is hopeful information, because it suggests that in the face of relatively low N deposition occurring very infrequently, the ecosystem can release added N during periods without N additions and the C and N pools are not remaining effected. If this pattern and the inputs of N continued, this of course would have implications for downstream communities if the N left the system via leaching and for air quality and global change concerns if the N left as a gas. However, it would also suggest that these terrestrial communities are below an N deposition threshold with the amounts being added and with the pulse-driven addition style (i.e., not adding N continuously). That said, it is very important to remember that, while N deposition can vary seasonally and even day-to-day, it is not likely that the inputs will occur only every 6 months. In

addition, the effects of N inputs to C and N cycles may be additive and we may need a longer time monitoring the fertilization plots to see changes.

In addition, we are indeed beginning to see signs of interactions between N deposition and P cycling, such that the coarser-textured soils did have larger available P pools in the plots receiving 5 and 8 kg N/ha/yr relative to those receiving 0 and 2 kg N/ha/yr (Fig. 22; $p<0.05$). Changes to P availability have the ability to alter ecosystem structure and function (e.g., Wassen et al. 2005) and these data suggest that N deposition may affect P cycling quite rapidly and thus N inputs could indirectly affect processes such as exotic plant invasion through changes to P. In addition, because N fertilization only affected one of the three soil textures, the coupled biogeochemical effects of N deposition could vary among soils in drylands. Also, the responses to N deposition are likely to build over time and these coarser-textured soils may be the early indicators of change we will see in other soils as fertilization continues.

4. ***Nitrogen fixation, phosphatase activity and nitrogen deposition***

Take home message: Based on a number of studies in other ecosystems, we expected N_2 fixation rates to decrease with increasing N deposition; however, a laboratory incubation of biological soil crusts from the Four Corners region suggests that N_2 fixation does not consistently decline with increasing anthropogenic N inputs, but instead may even increase in some instances. These data suggest that overall N inputs into the ecosystems (anthropogenic N inputs + N_2 fixation inputs) may be greater than expected. We found no significant effects of N inputs on phosphatase activity of soils, likely due to the fact that phosphatase activity was highly variable.

Nitrogen fixation rates behaved as expected in Mesa Verde National Park, with increasing N inputs resulting in reduced N_2 fixation, and with P additions resulting in N_2 fixation stimulation (Fig. 23). This implies that N_2 fixation could indeed down-regulate in response to increased anthropogenic N inputs, which would be beneficial from an N balance perspective. However, N fixation for samples collected near Arches actually increased N_2 fixation rates at higher levels of N inputs, a result that was quite unexpected (Fig. 23). There are two hypotheses we've considered to explain this result. First, it has been shown in laboratory settings that at extremely low levels of N, N availability can actually limit N_2 fixation. The N_2-fixing organisms do not have enough N to produce the nitrogenase enzyme, nor to produce protease enzymes that would allow them to break down proteins in order to supply N for building nitrogenase (Reed et al. 2011). This has never been observed in the field and, although N concentrations are extremely low at the site near Arches National Park, it might be too far a stretch to think concentrations are so low that they could limit nitrogenase production. An alternative explanation is that N is so low that, even with the amounts of N added, N remains limiting to biological activity and so N_2 fixation remains a successful approach to acquiring N. If the additions of N are resulting in an increase in the growth and activity of organisms it could also mean an increase in N_2-fixing organisms as well, and thus N_2 fixation rates could actually increase due to an increase in N_2-fixers (as opposed to a stimulation of rates with the same N_2-fixer abundance). Because the N deposition observed and predicted for the Four Corners region is much lower than in other parts of the world (e.g., the northeastern U.S. and Europe) and because N is so low in these ecosystems (e.g., Fig. 1) it could be that N deposition at some sites will actually stimulate N fixation rates up to some threshold of deposition. This would mean that N inputs related to N deposition could actually be *more* than expected from assessments of deposition alone. It's quite

interesting that this result was seen at the site near Arches, where N pools are relatively lower, and not observed at Mesa Verde, where N pools are relatively higher. For example, the available inorganic N concentrations in interspaces at the Wetherill Mesa sites in Mesa Verde were more than ten times greater than the average inorganic N at the fertilization plot sites at Arches and this difference was the result of NO3- concentrations being much higher at Mesa Verde. However, these assessments represent 'snapshots' of N at just one timepoint and inorganic N concentrations at both sites are quite low relative to other biomes. We hope to repeat this experiment at a variety of sites in the Four Corners region to further elucidate the results and implications.

We were also interested in how alterations to N cycling could affect the cycling of P and thus we assessed phosphatase activity in the same samples where N fixation rates were assessed. While there were some significant effects of the treatments, no patterns emerged and thus no overarching theory was discernable (Fig. 24). For example, while we predicted that additions of N would stimulate phosphatase activity (as has been observed elsewhere; Reed et al. 2011), this effect was not consistently observed (Fig. 24). Thus, while the data support the idea that there are important relationships between N and P cycling, they do not help clarify the nature of these relationships. We plan to repeat these assessments in a larger effort (spanning more sites), as well as explore enzyme activities in the fertilization plots.

ONGOING AND FUTURE ACTIVITIES

This pilot study has led to a number of exciting research projects and, indeed, many of the results stemming from this work will take longer to develop. In particular, we plan to continue the fertilization plot experiment, as well as to repeat the N_2 fixation incubation experiment across a larger scale. Finally, we are collaborating with Dr. Nancy Johnson and her NPS-ARD funded group to continue the data collation and literature review that will lead to an updated dataset regarding N deposition in the Four Corners region.

CONCLUSIONS

Nitrogen deposition has a strong potential to significantly affect the structure and function of ecosystems in the Four Corners region and, in particular, to significantly affect exotic plant invasion, soil nutrient availability, and future fire regimes. Perhaps due to the low standing stocks of N (e.g., Fig. 1), Four Corners ecosystems may be particularly sensitive to relatively subtle inputs of anthropogenic N, and the responses may not follow patterns expected from other biomes (e.g., Fig. 23). In addition, our data strongly suggest that, at some locations in the Four Corners, NOx deposition may represent an important and abundant source of N to ecosystems. Nevertheless, while the data presented here are compelling, more time is needed to bring together the multi-faceted components of the research. We plan to continue this important work with the ultimate goal of providing information that augments the National Park Service's capacity to successfully manage these unique landscapes in the face of global change.

DISCLAIMER

Any use of trade names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

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Figure 1. Comparison of total soil N pools (%; 0-10 cm depth) from a temperate forest in Connecticut, a tropical wet forest on the Osa Peninsula in Costa Rica, and a dryland soil from Arches National Park. Data show the large variability in total soil N pools and highlight that N deposition in the Four Corners region is occurring on soils with relatively low soil N concentrations.

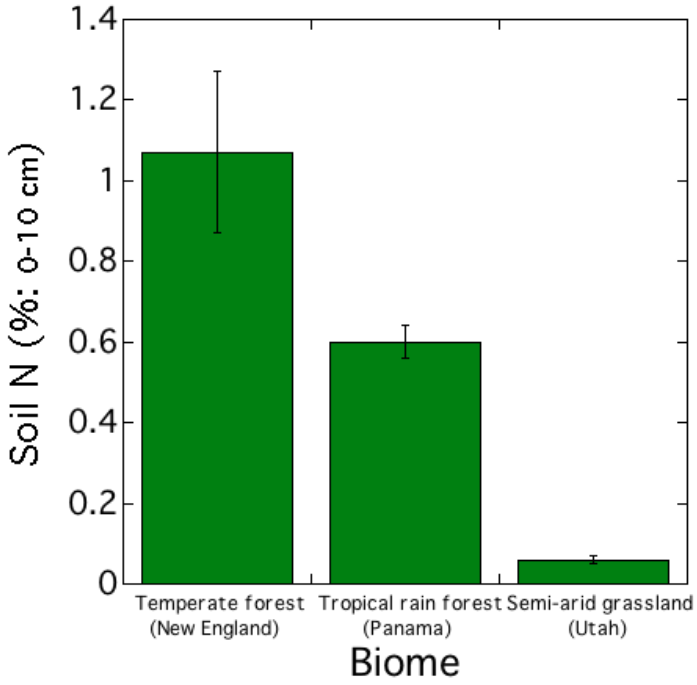

Figure 2. Satellite derived NO_2 integrated vertical column, with likely stationary sources identified (based on Kim 2009).

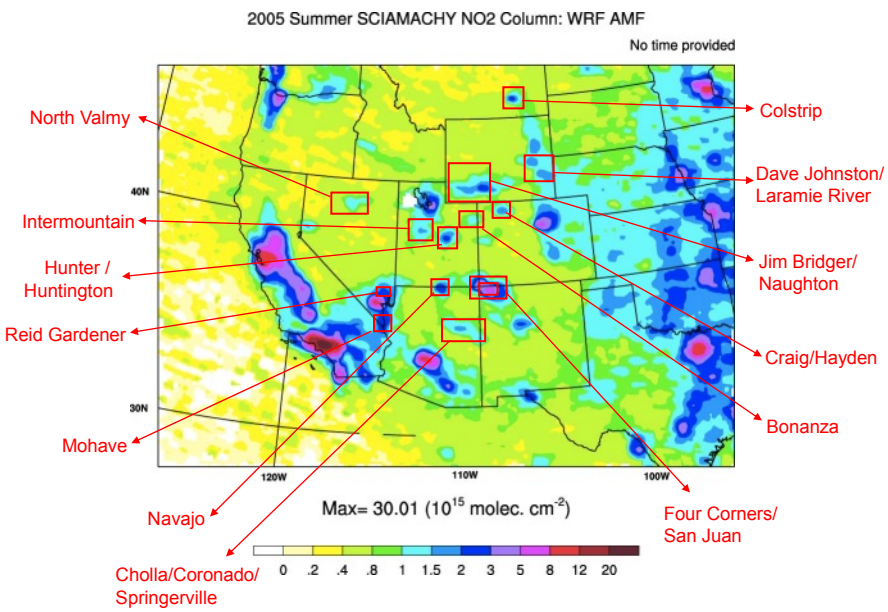

Figure 3. Conceptual model of a N deposition threshold to *Bromus tectorum* invasion. The idea behind the conceptual model is that, as system N status increases (e.g., via increased N deposition rates), the response of the ecosystem will vary based on how much N has been added and the system's ability to cycle or remove that N. At lower levels of N deposition one might not see large increases in *B. tectorum* invasion, perhaps because native plants can utilize the N or because N losses from the ecosystem can maintain relatively low N pools. However, as N continues to increase, the system may cross a threshold (depicted by the dashed vertical line) and after crossing this threshold, invasion may increase dramatically with any subsequent additions of N. At some point the ecosystem would become saturated, and at that time increases in N may not result in further invasion.

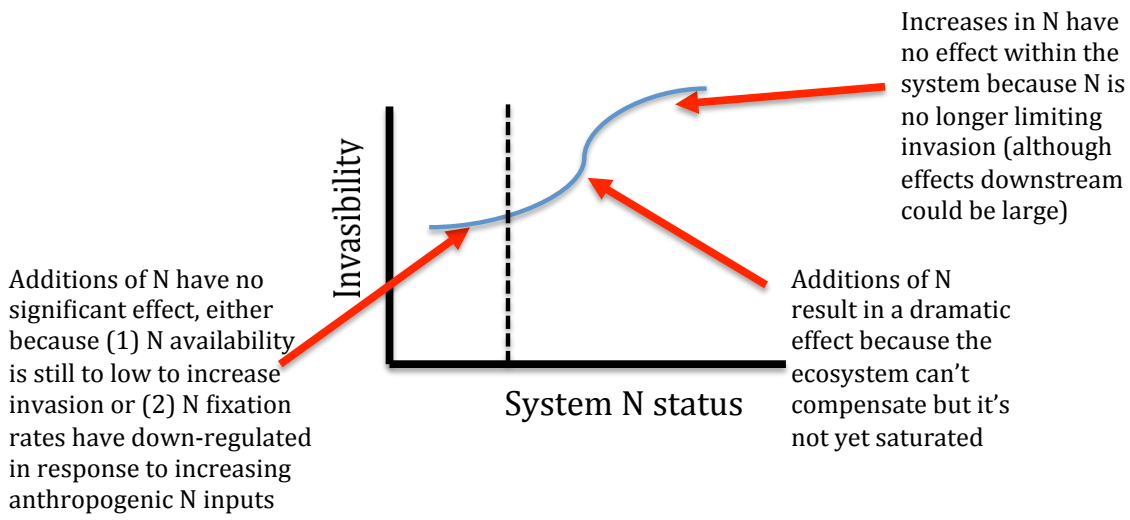

Figure 4. The location of sample points within a study area defined as Mesa Verde National Park and portions of the Ute Mountain Ute Tribal land, southwestern Colorado. The western edge is bounded by the west edge of Eagle Eye Mesa above the east fork of Ute Canyon, and the southern boundary is defined by Grass Canyon. The eastern boundaries are of Mesa Verde National Park (Mancos River) and Ute Mountain Ute Tribal Park.

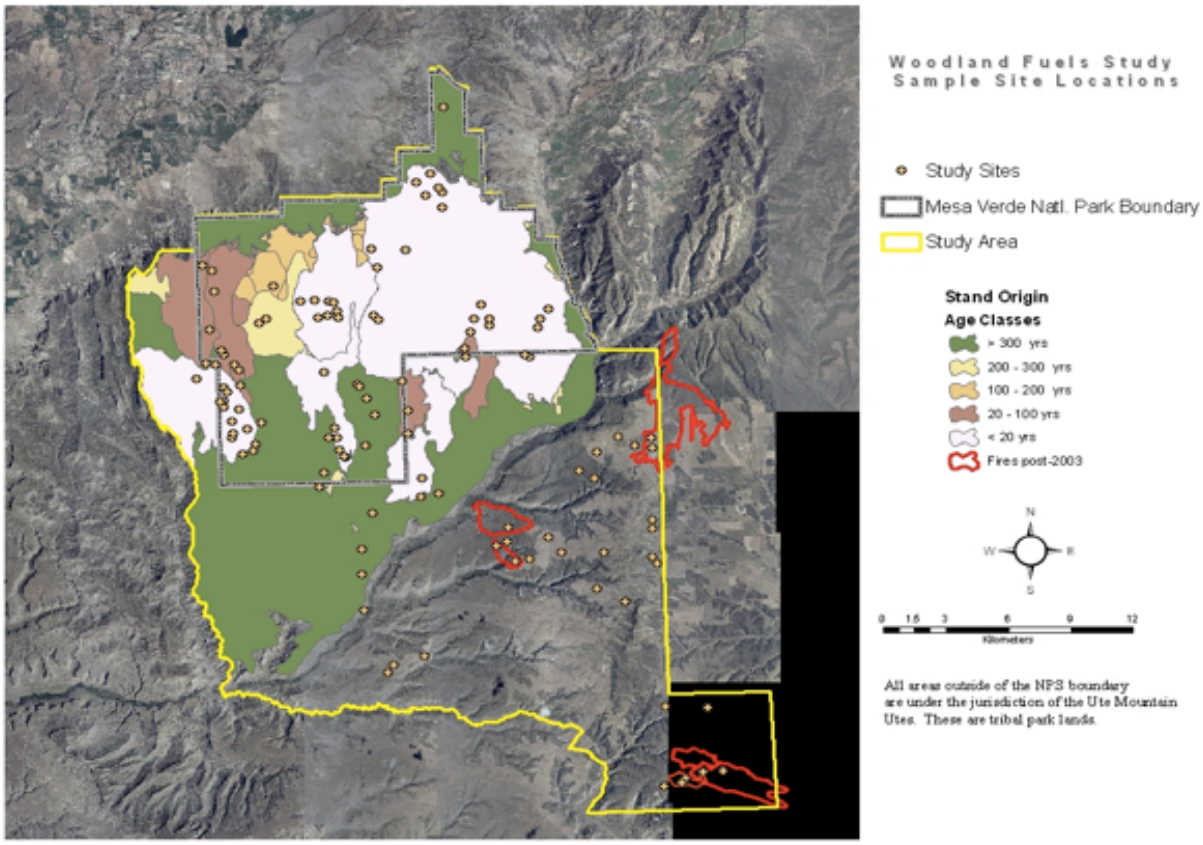

Figure 5. Location of fire chronology sampling points on Wetherill Mesa, Mesa Verde National Park. Western park boundary is shown.

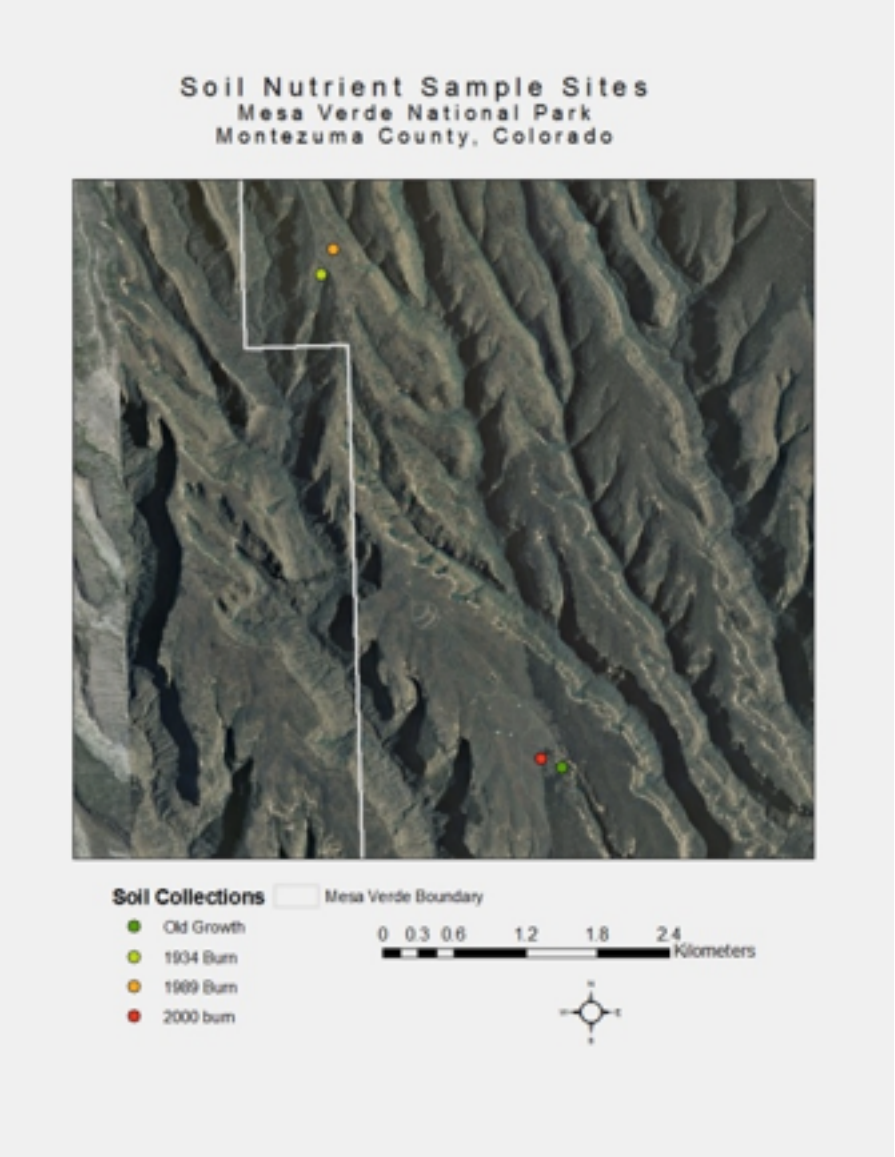

Figure 6. The southern portion of Chapin Mesa, Mesa Verde National Park with locations of fertilization plots.

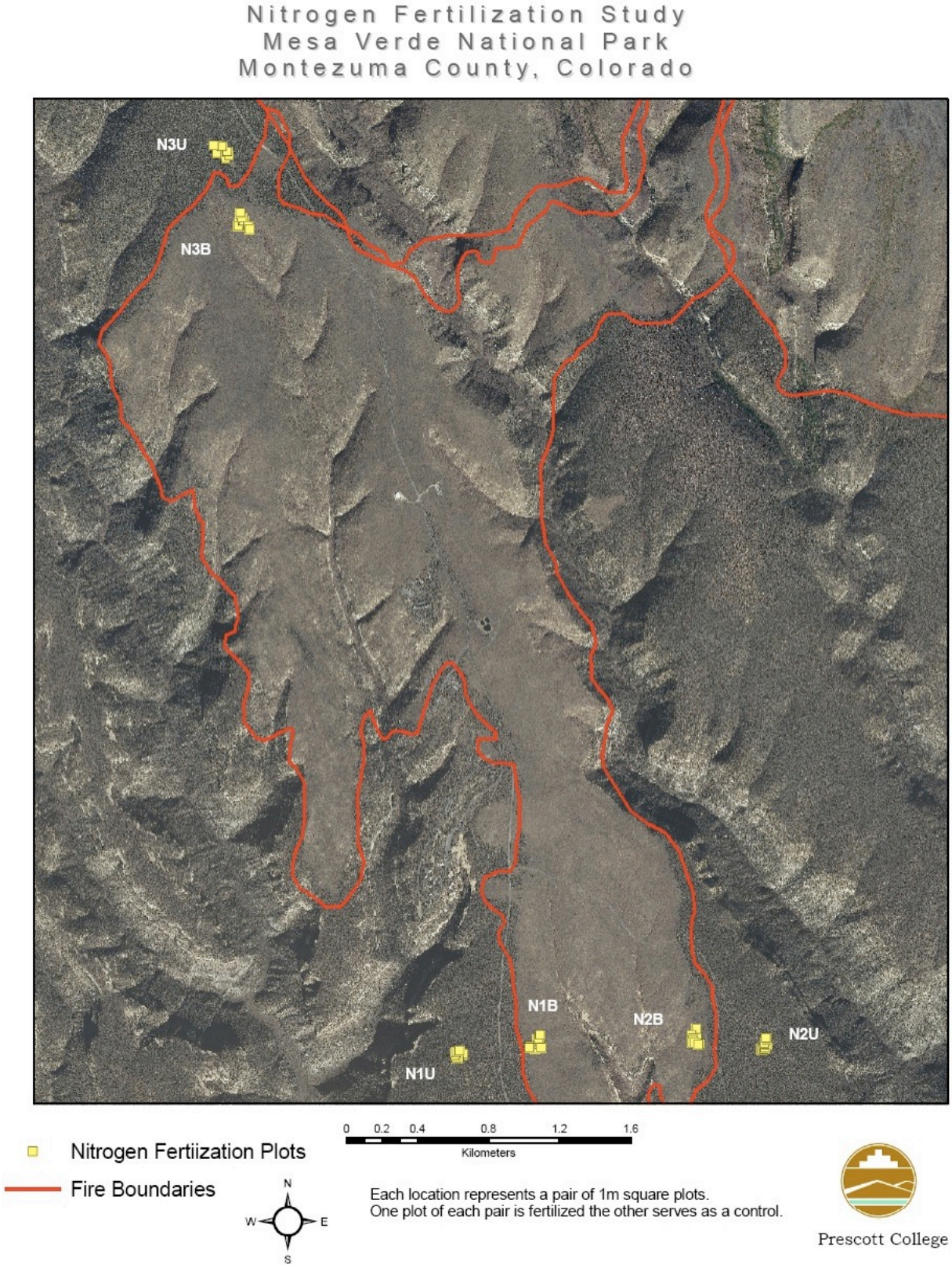

Figure 7. Approximate arrangement of fertilization plots; A=untreated control, B=treated with nitrogen fertilizer.

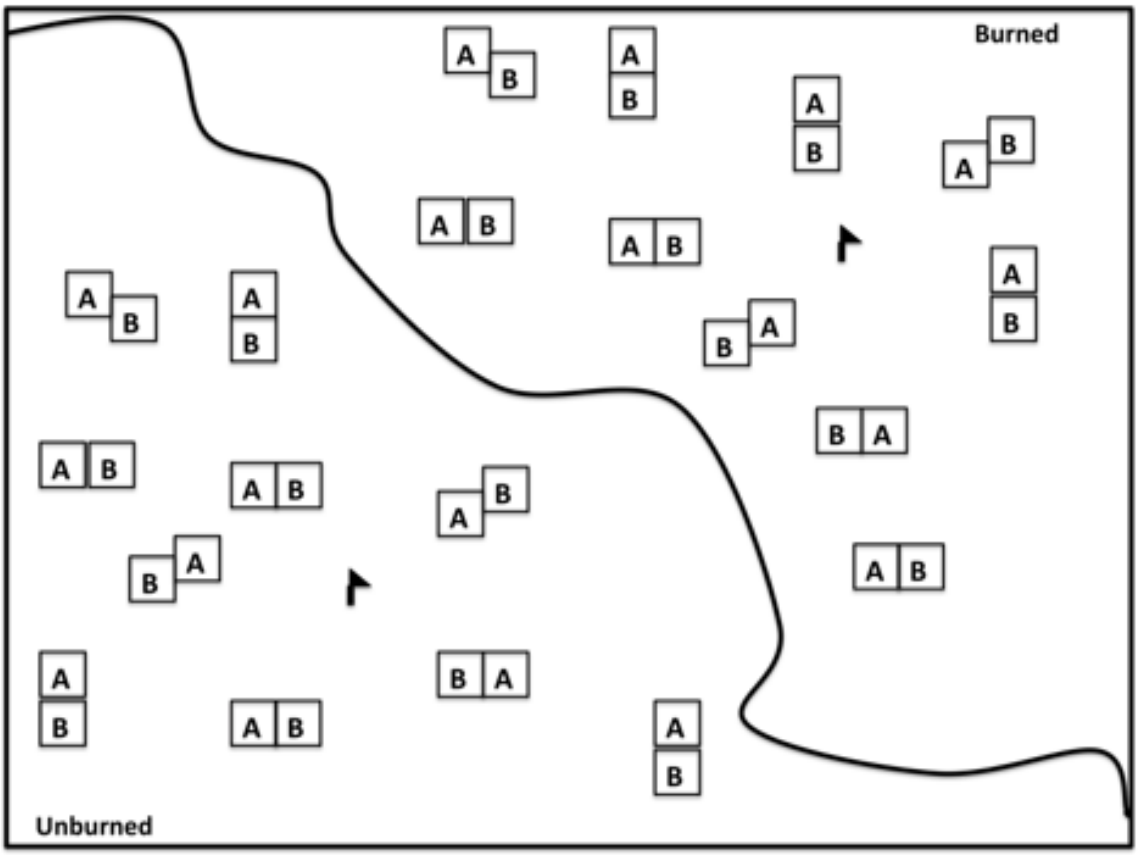

Figure 8. The Salt Valley region of Arches National Park with locations of fertilization plots.

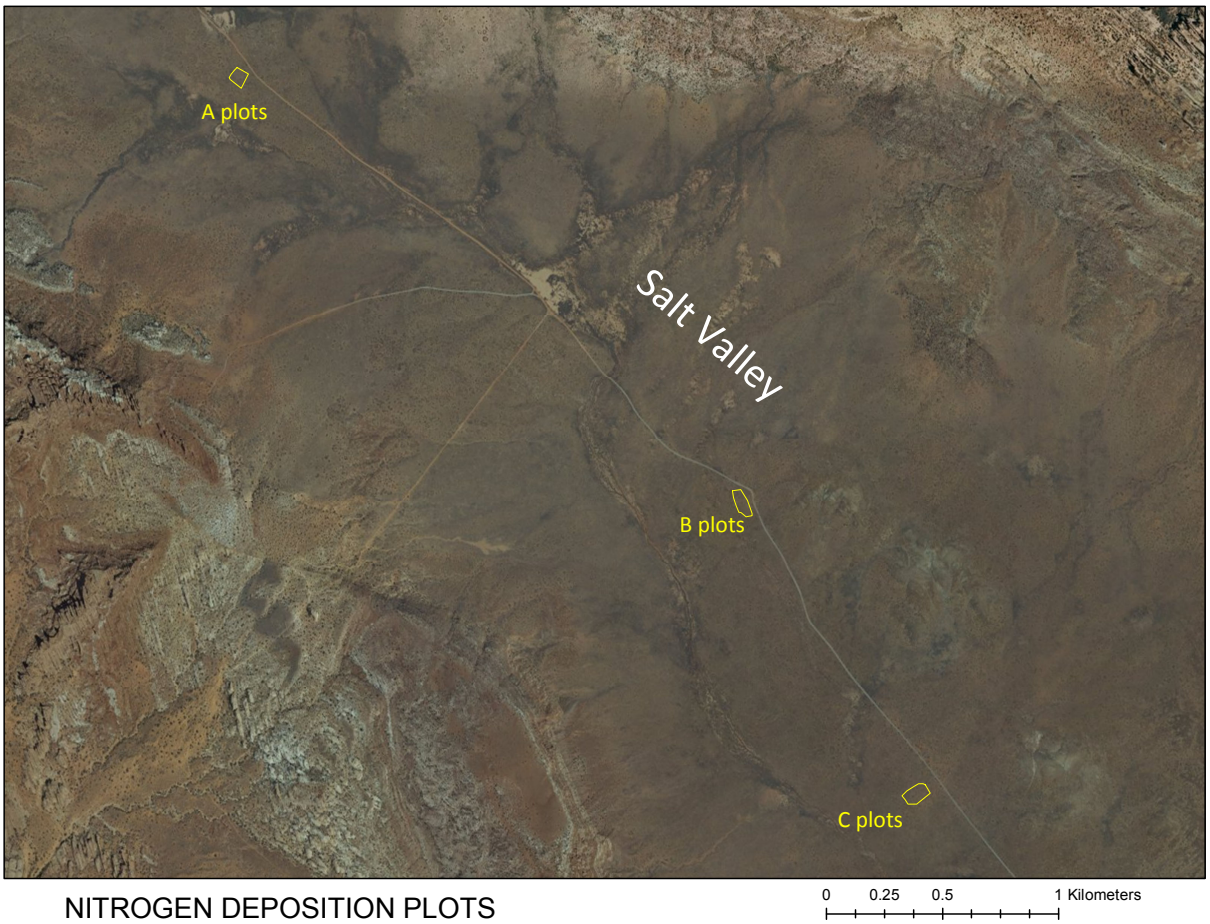

Figure 9. NOx concentrations measured at the Mesa Verde site at night during June 2012. Data are averaged for the 120 one-minute samples taken from midnight to 2 am.

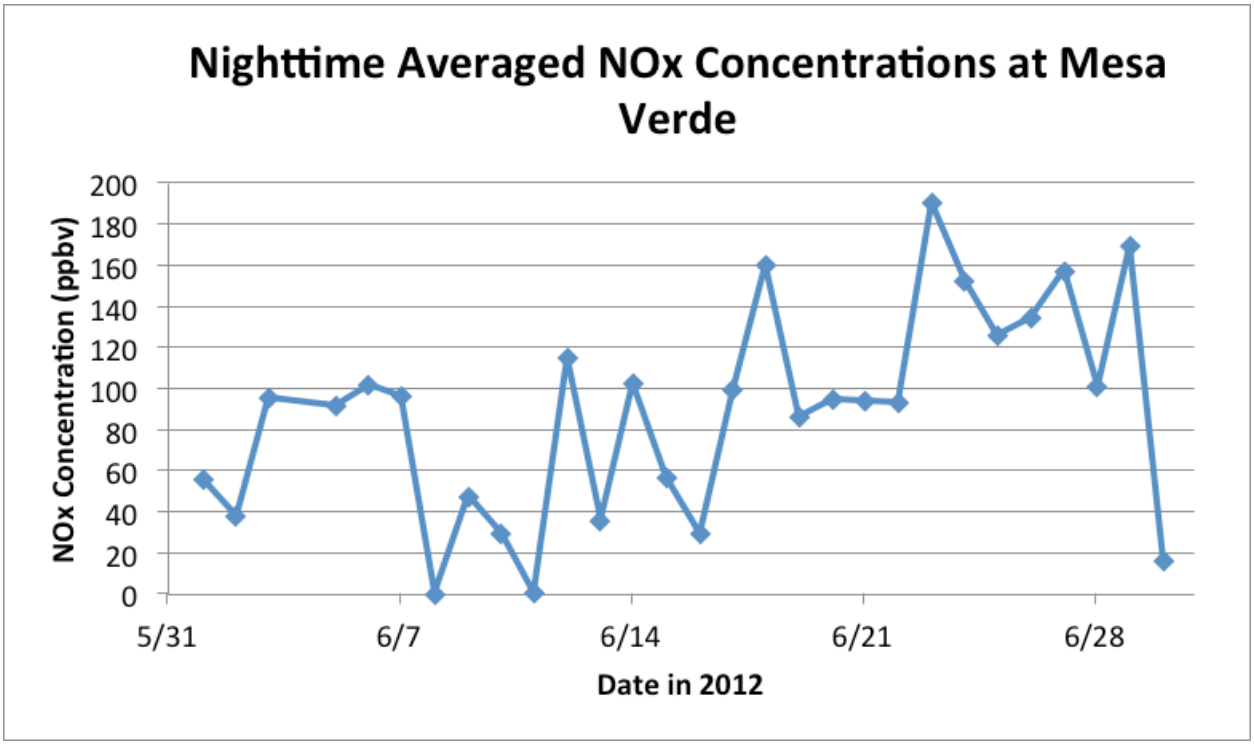

Figure 10. CASTNET HNO_3 dry deposition for late spring and early summer of 2012.

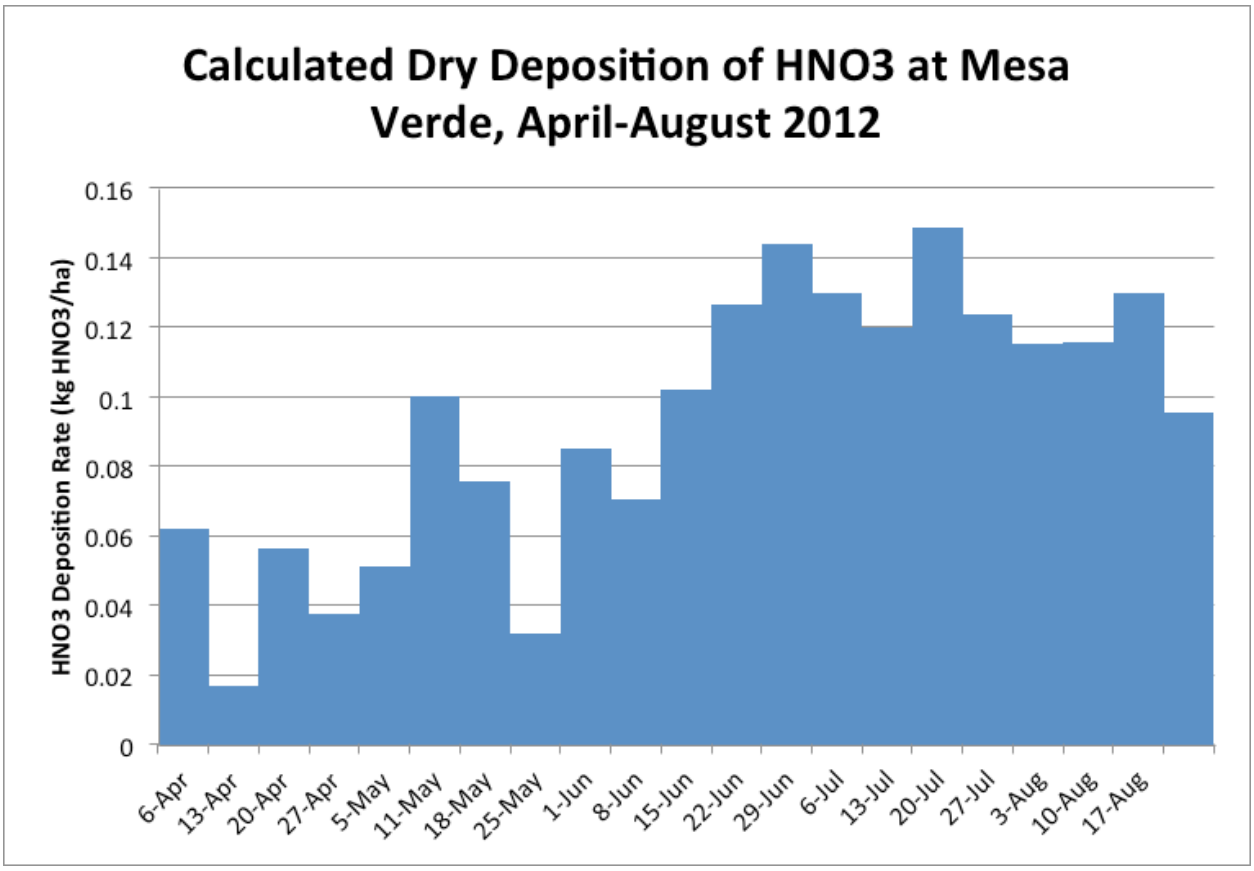

Figure 11. The atmospheric trajectories that intersect power generating stations for June 2012 data.

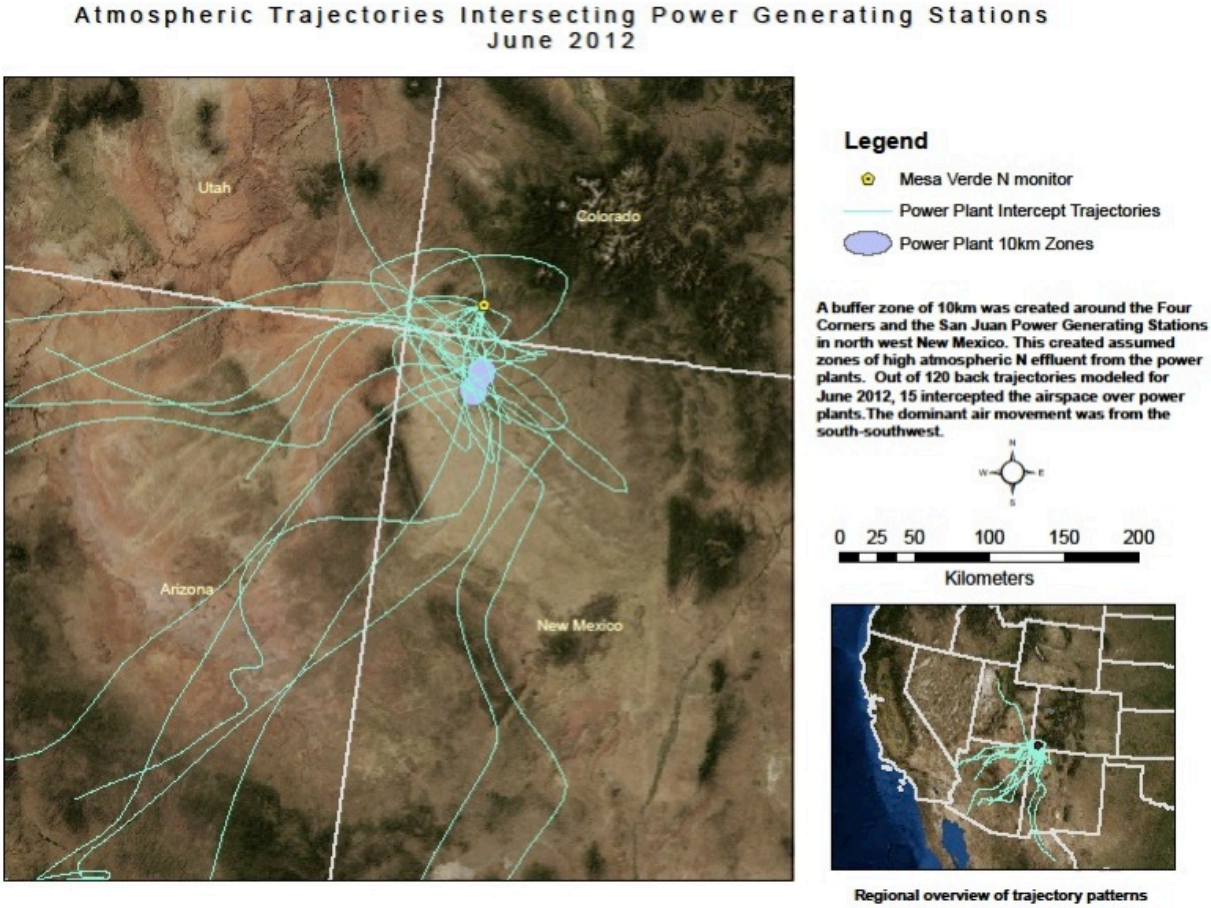

Figure 12. The atmospheric trajectories that intersect high density gas well zones for June 2012 data.

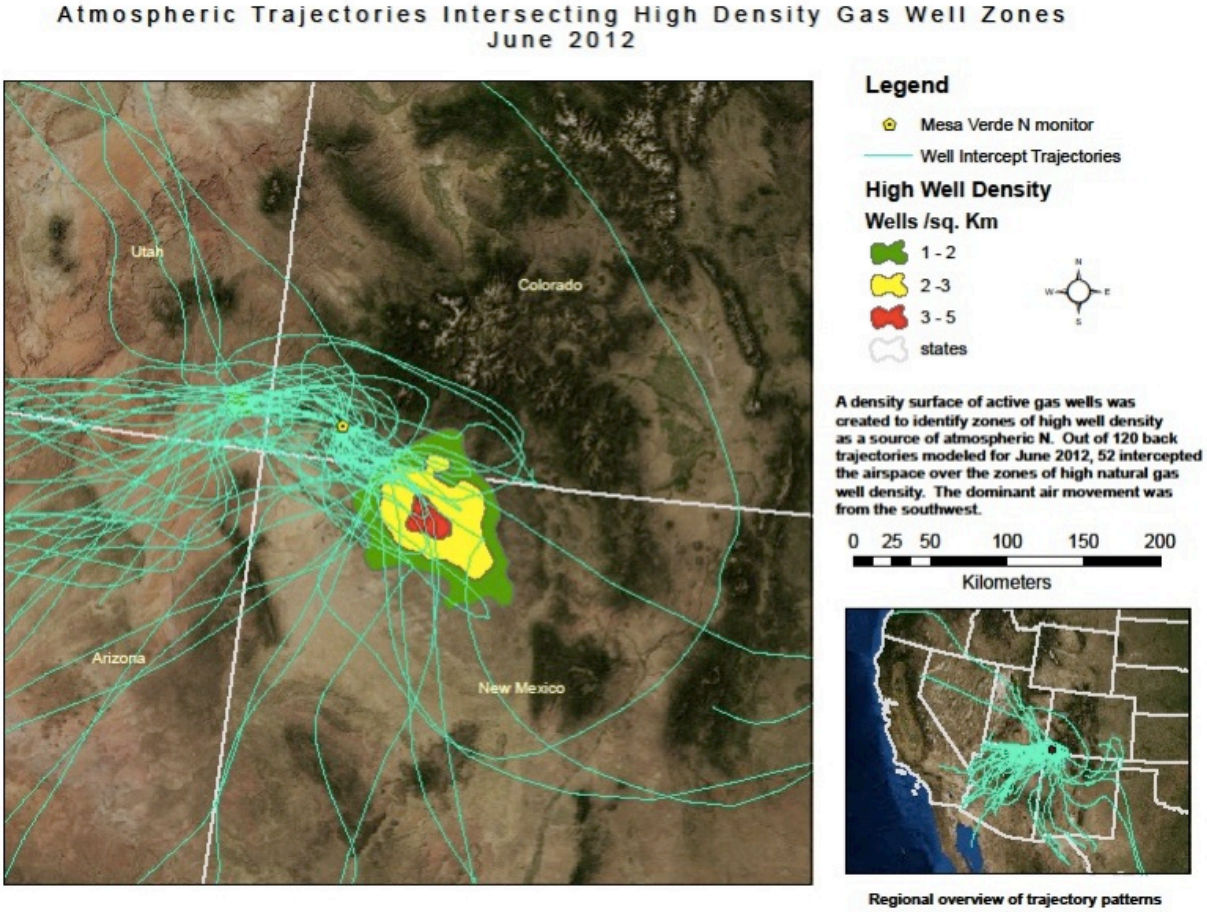

Figure 13. The number of trajectories from Figures 11 and 12 crossing the source regions, by day in June, 2012.

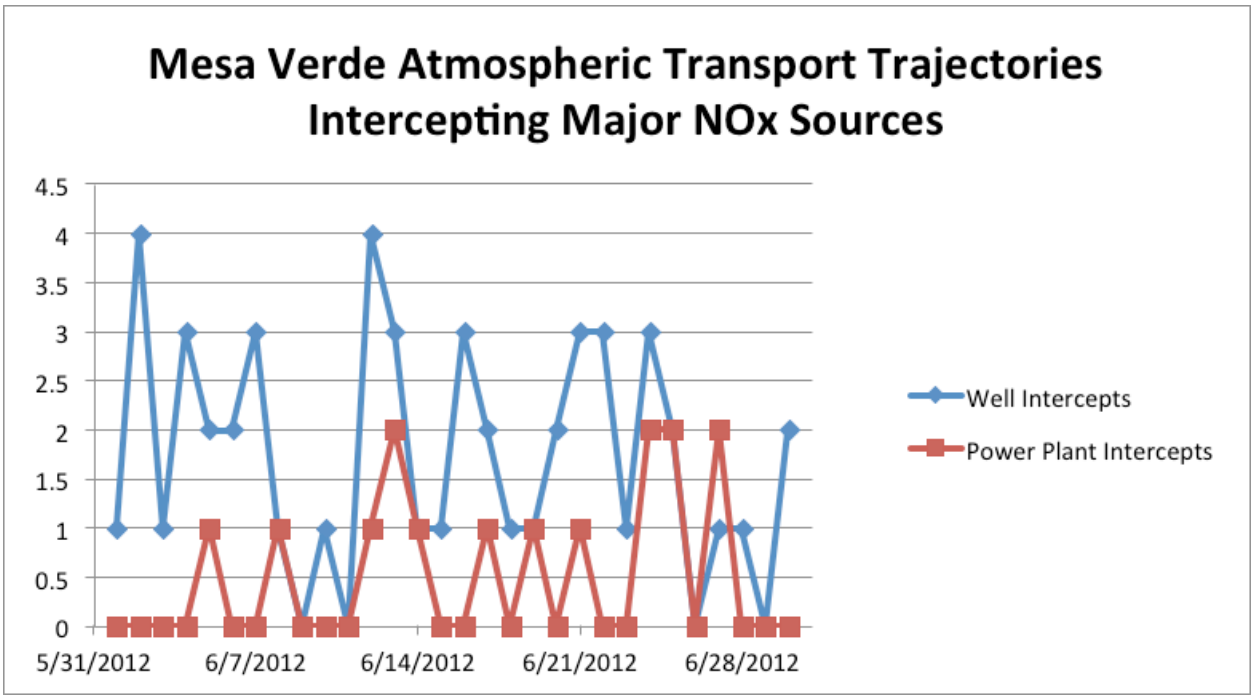

Figure 14. Dry deposition fluxes for NO_2 and HNO_3, calculated as described in the text.

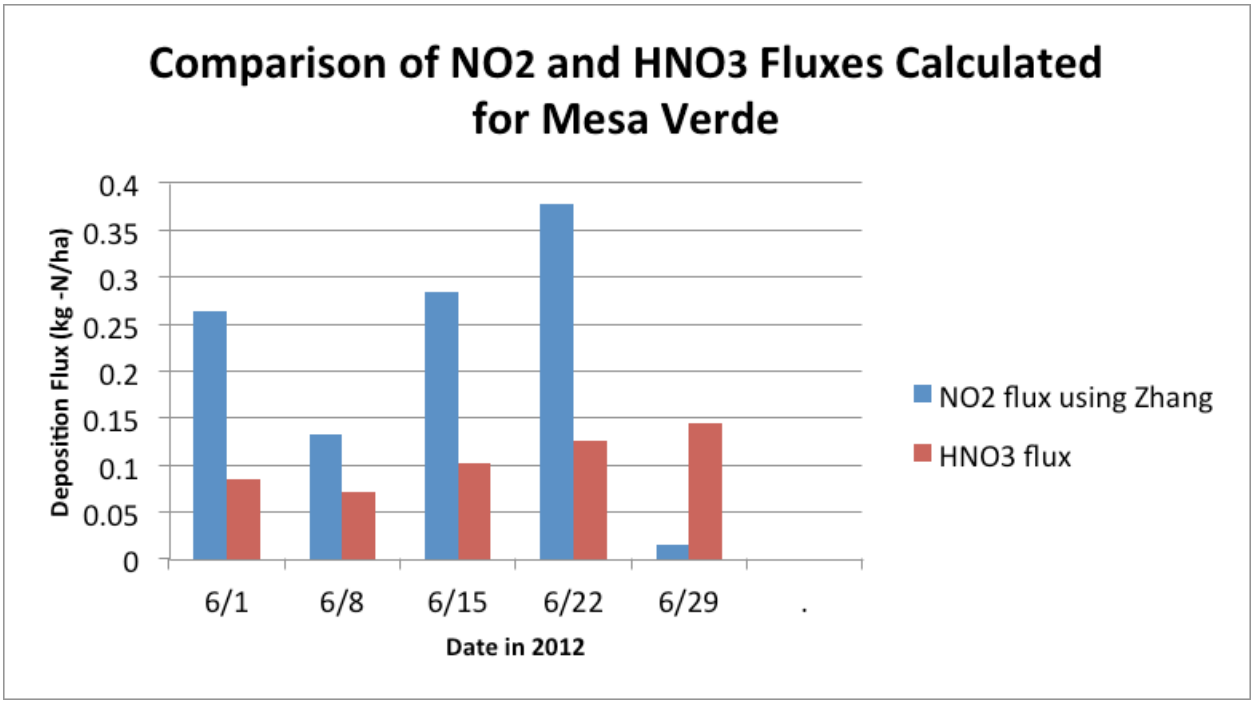

Figure 15. The mean values of ammonium (NH_4^+; µg/g dry soil), nitrate (NO_3^-; µg/g dry soil), P (µg/g dry soil) and conductivity (DS/m, multiplied by a factor of 10 to coincide with axes) are compared in piñon canopy vs. adjacent intercanopy spaces.

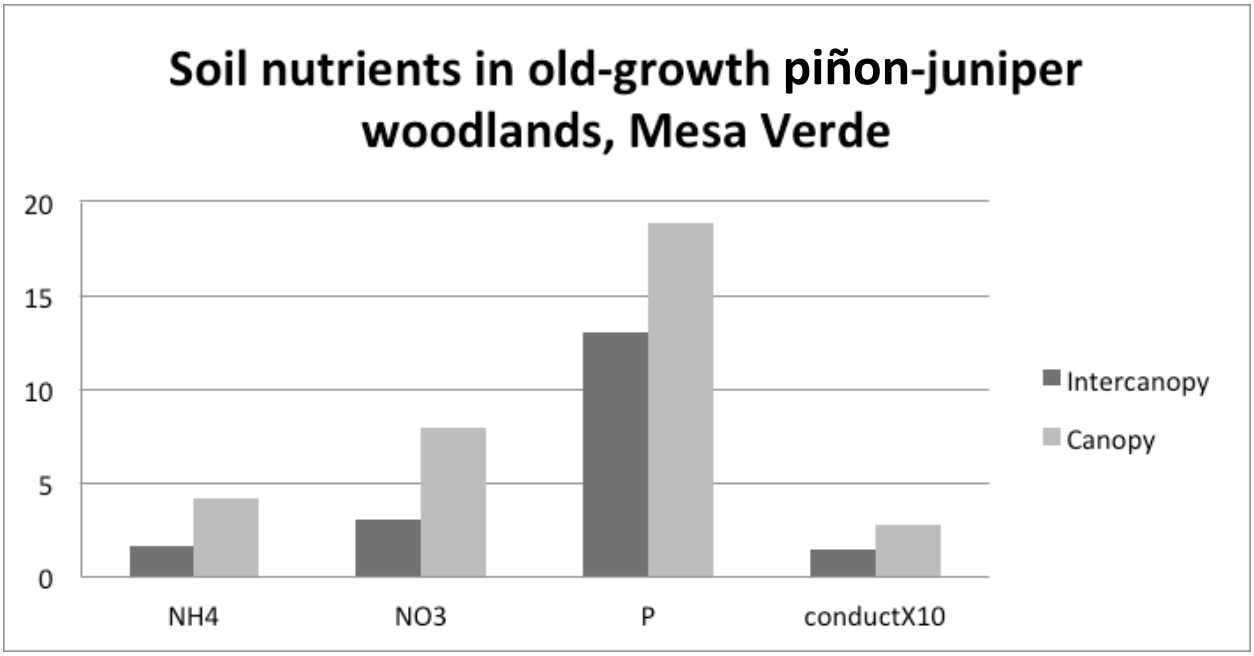

Figure 16. Resin-available P (ug/g dry soil) in stands of different age (time-since-fire) across Mesa Verde. Note 1934, 1972 and 2008 not shown due to low sample size.

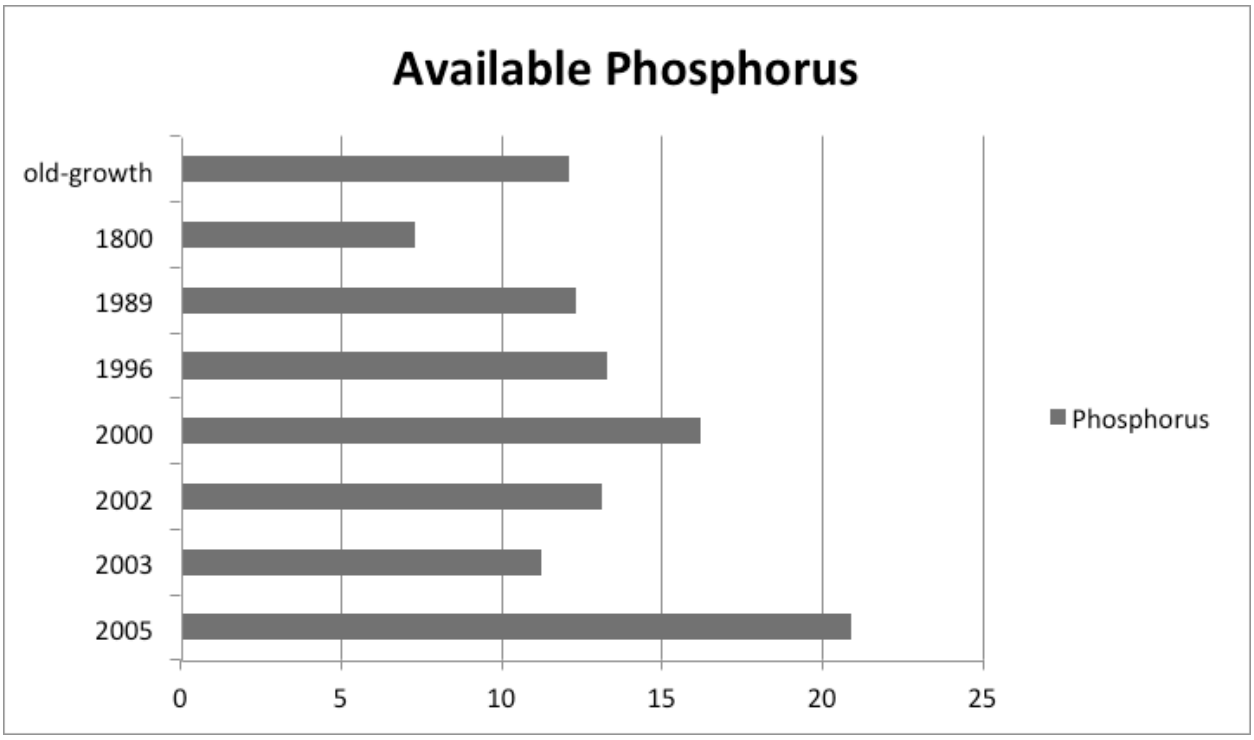

Figure 17. Available P concentrations (µg/g; Olsen extraction [Olsen et al. 1954]) in old-growth soils are significantly greater than nearby burned soils, Mesa Verde National Park.

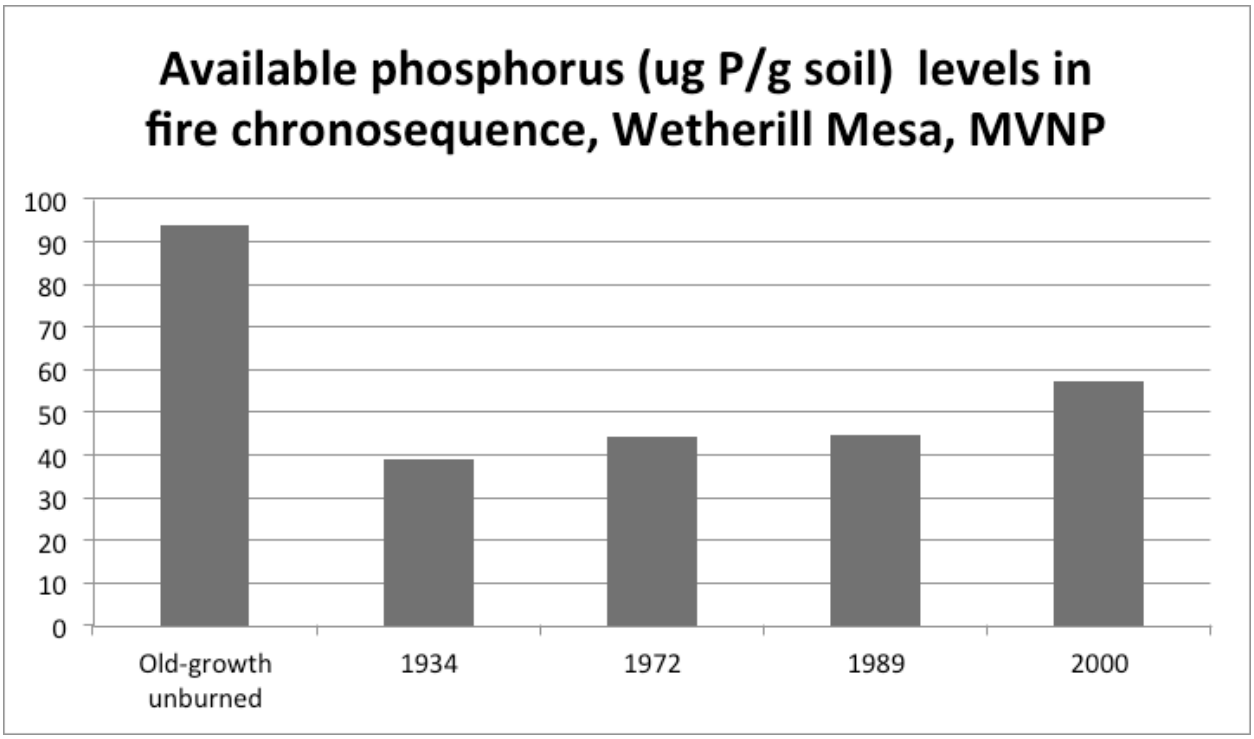

Figure 18. Available P concentrations (µg/g; Olsen extraction; [Olsen et al. 1954]) in canopy and intercanopy soil samples taken in nearby locations on Wetherill Mesa in the 1934, 1972, 1989 and 2000 fires.

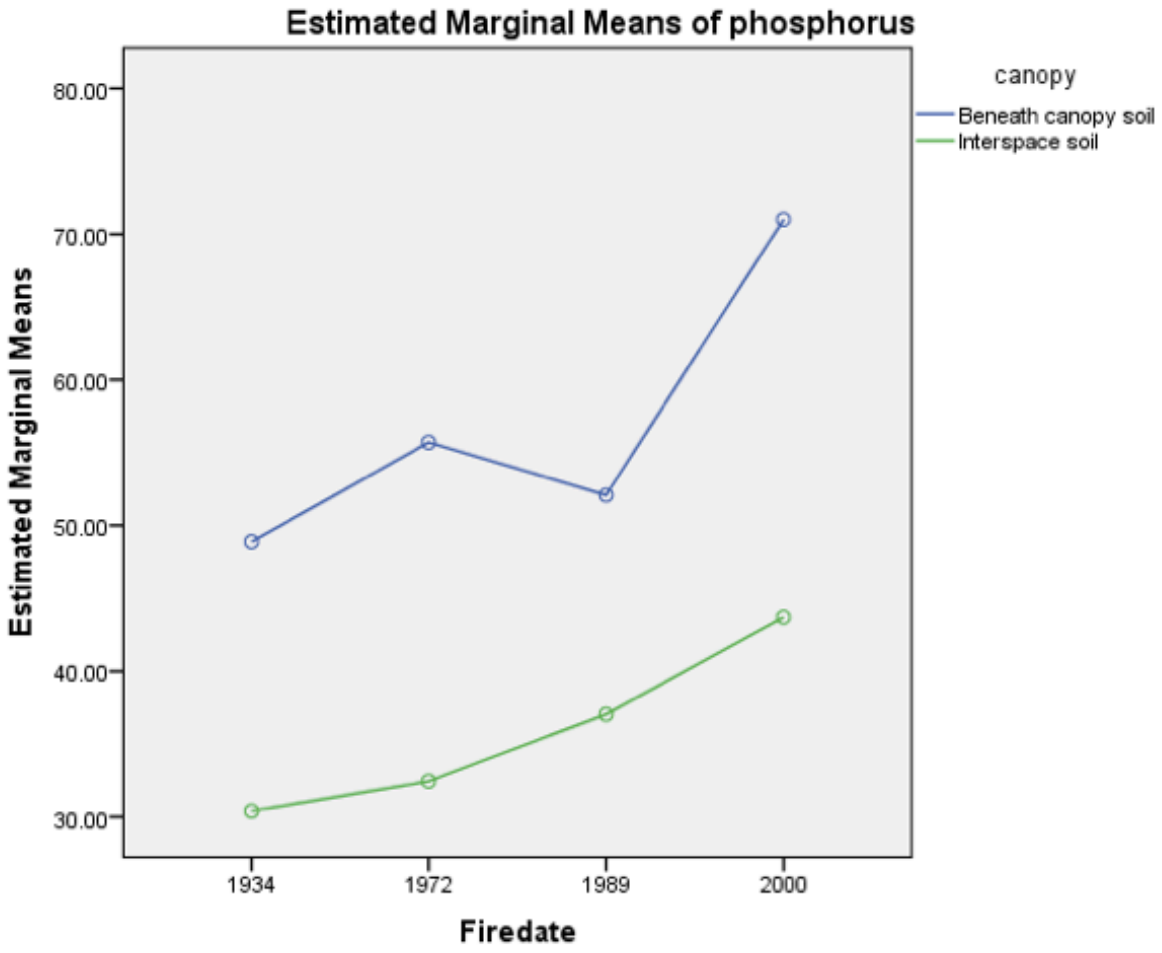

Figure 19. Nitrate (NO_3^-; µg/g dry soil) levels in canopy and intercanopy collected from nearby fires in fire chronosequence, Wetherill Mesa.

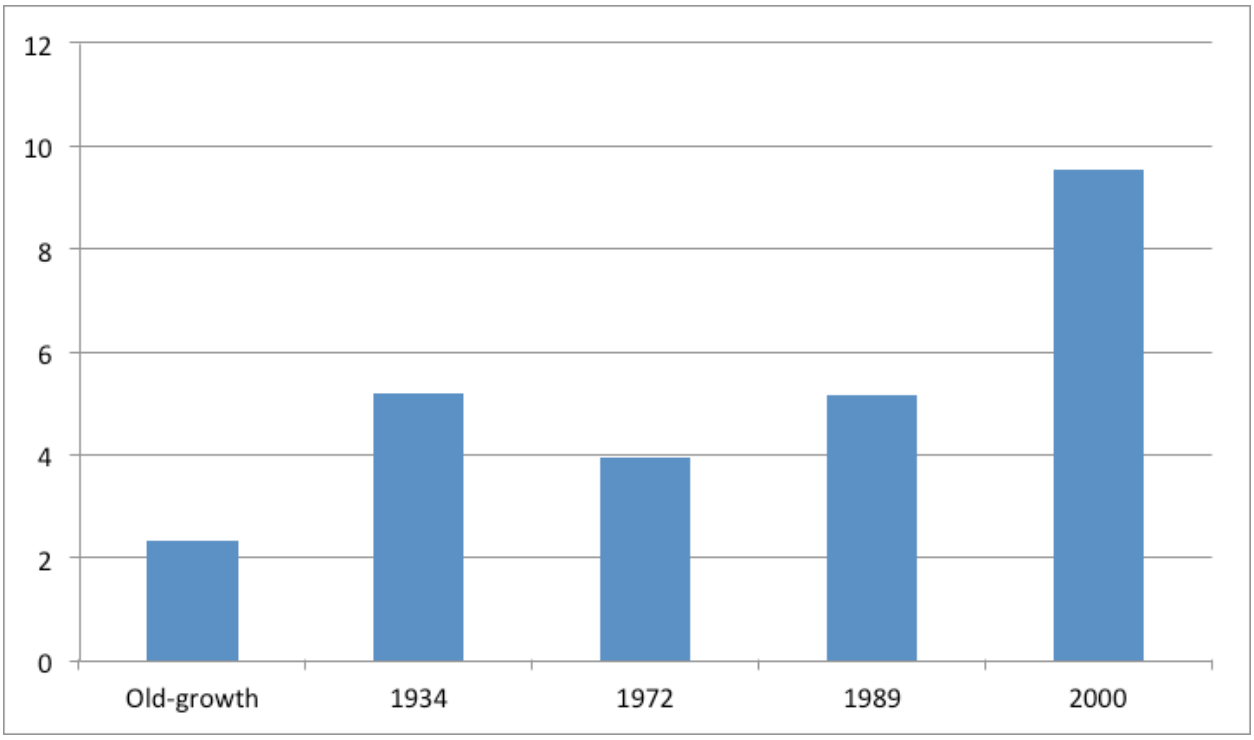

Figure 20. The cover of *Bromus tectorum* in Mesa Verde. Old Growth stands (1400) lack cheatgrass entirely while it was present to varying degree in each sampled fire.

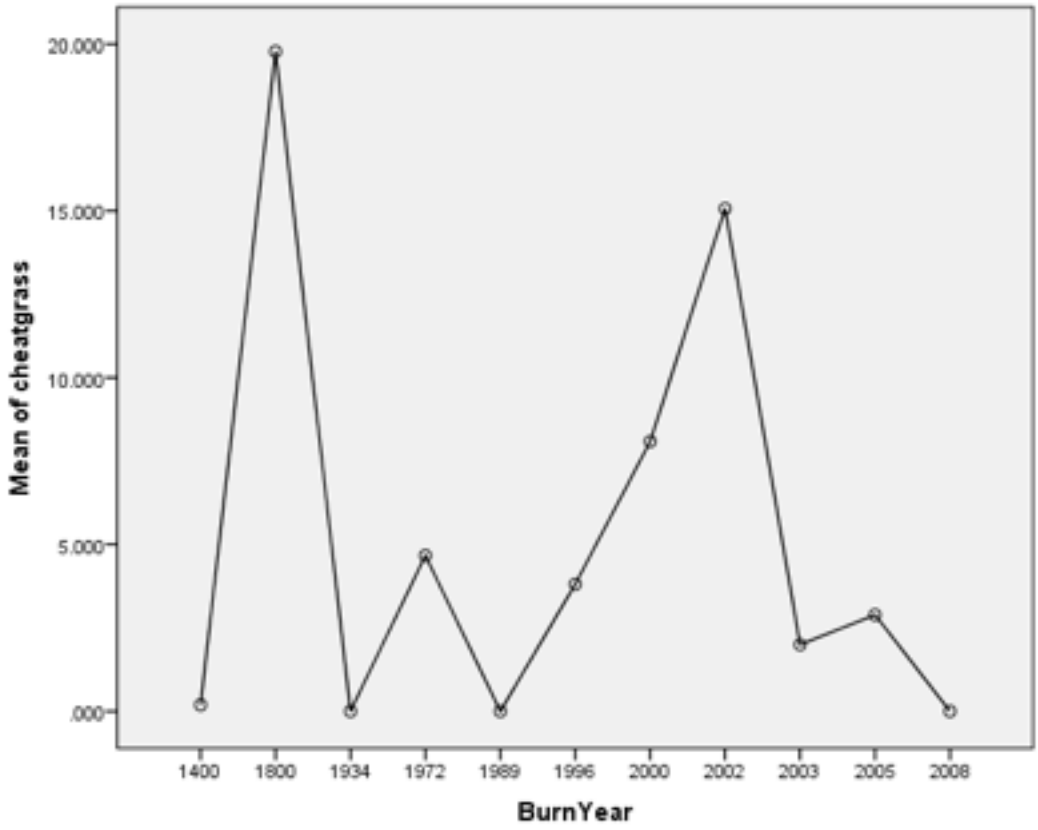

Figure 21. Available soil N (NH_4^++NO_3^-; µg/g) and P (µg/g) pools at the Arches National Park sites. Soils were collected from control (0 kg N/ha/yr) plots.

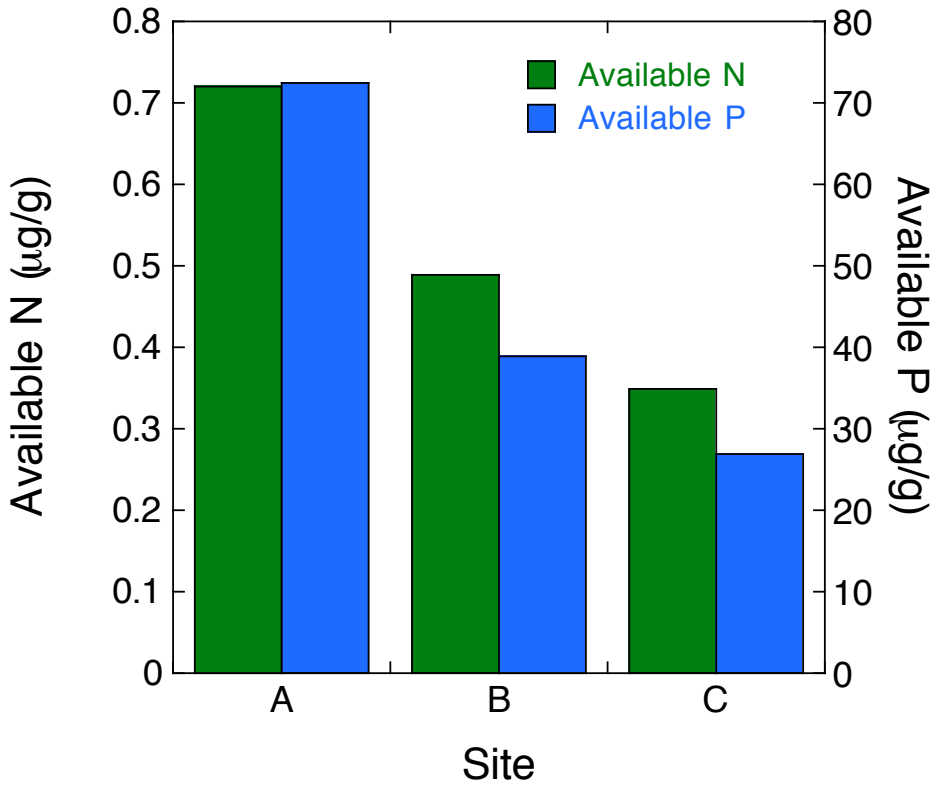

Figure 22. Available P (μg/g) data from the coarsest texture plot showing that available P concentrations increased at the higher level of N fertilization. When N addition data were grouped into those receiving low (0 and 2 kg N/ha/yr plots) and high (5 and 8 kg N/ha/yr plots) fertilization, ANOVA showed that plots receiving higher N fertilization had significantly higher available P.

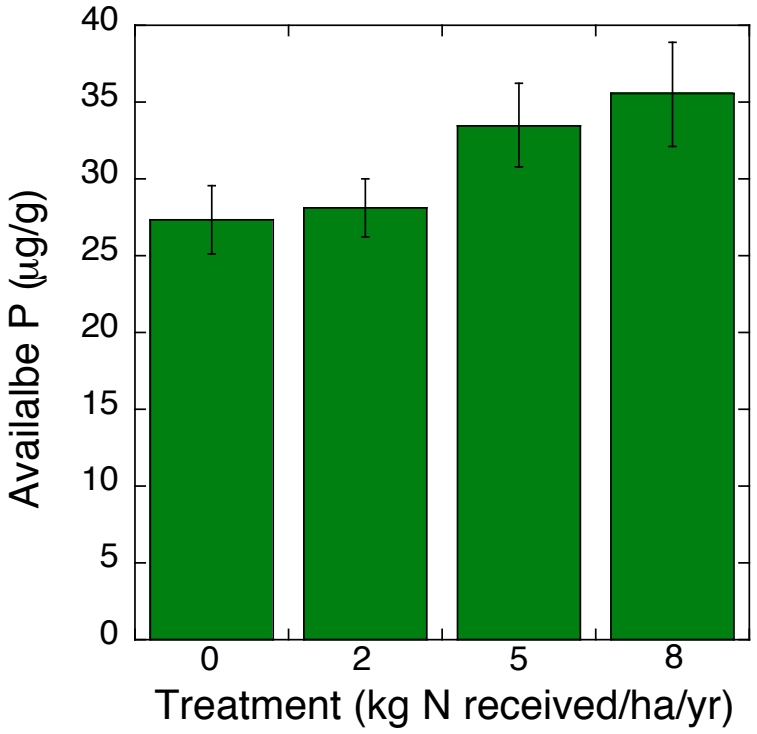

Figure 23. Acetylene reduction rates for *Collema tenax* collected from Mesa Verde and from near Arches National Park. Data suggest that additions of N reduce N_2 fixation rates in Mesa Verde but increase rates at the site near Arches National Park. Additions of P consistently stimulate N_2 fixation rates.

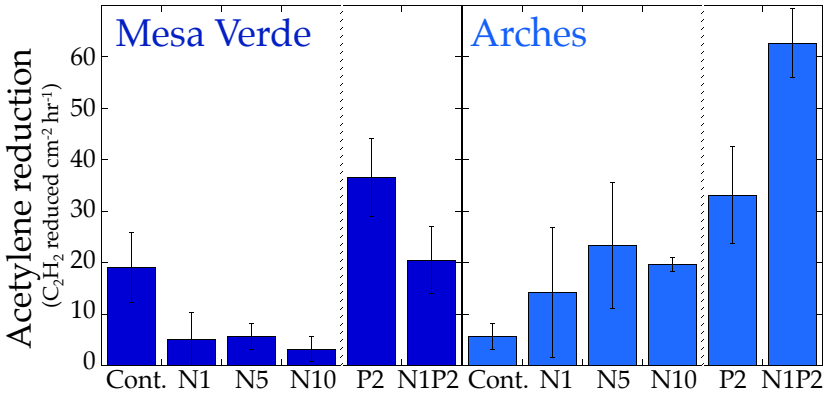

Figure 24. Phosphatase activity for *Collema tenax* collected from Mesa Verde and from near Arches National Park. Data suggest that additions of N and P can have effects on phosphatase activity but overarching patterns in those effects remain difficult to interpret. Asterisks represent phosphatase activities that were significantly different ($p < 0.05$) from control phosphatase activities.

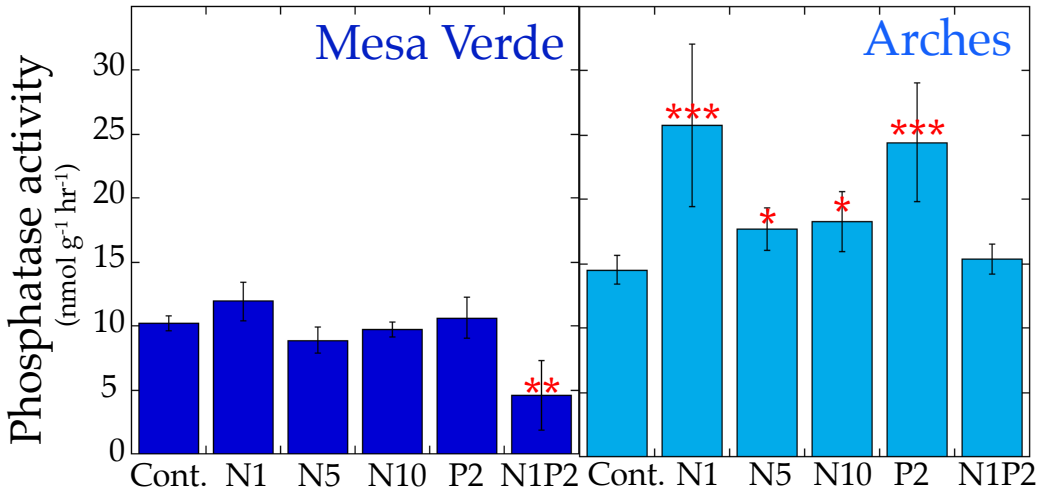

Table 1: Stationary sources of 2012 NOx emission data in the San Juan basin, New Mexico and Colorado.

Source	NOx Emissions (tons/year)
Oil and Gas Production, North San Juan Basin (in Colorado)	4195[9]
Oil and Gas Production , South San Juan Basin (in New Mexico)	43,050[10]
San Juan Generating Station	34,500[11]
Four Corners Power plant	14,640[12]

[9] http://www.wrapair.org/forums/ogwg/PhaseIII_Inventory.html
[10] ibid
[11] http://www.epa.gov/airmarkets/images/ARPCAIRCoal11vs12q12.pdf, est. based on Q1 and Q2 2012 emissions
[12] ibid

Table 2. GPS locations of the center of each Mesa Verde fertilization plot study area.

Plot	**Burn type**	**Easting**	**Northing**
1B	Burned	723497.35	4117387.44
1U	Unburned	722990.22	4117263.35
2B	Burned	724231.07	4117371.25
2U	Unburned	724722.02	4117338.88
3B	Burned	721820.11	4121950.84
3U	Unburned	721683.11	4122340.53

Table 3. Average soil texture components for the three fertilization plot sites in Arches National Park. Sites vary significantly in soil texture ($p<0.05$) with A sites representing the finer texture soils and C sites the coarsest texture.

Site	Depth (cm)	Sand (%)	Silt (%)	Clay (%)
A	0-5	74.00	22.16	3.84
A	5-13	74.72	15.44	9.84
A	13-35	72.72	17.44	9.84
A	35-70	72.00	18.16	9.84
A	70-95+	68.00	16.16	15.84
B	0-5	86.00	8.16	5.84
B	5-20	84.00	8.16	7.84
B	20-40	86.00	8.16	5.84
B	40-80	89.80	7.08	3.12
B	80-90+	85.80	7.08	7.12
C	0-5	87.80	7.08	5.12
C	5 - 40	89.44	7.44	3.12
C	40-70	89.80	7.08	3.12
C	70-100	83.44	11.44	5.12

Table 4. The effect of N fertilization on plant abundance, June 2011, Mesa Verde.

Treatment Status	Fertilized treatment	Abundance	
Unburned	Control	8.6 +10.3	T=2.1, p=0.04
	Fertilized	13.5 + 18.4	
Burned	Control	31.6 + 33.9	T=1.9, p=0.06
	Fertilized	44.8 + 42.4	