

Evidence of Enhanced Atmospheric Ammoniacal Nitrogen in Hells Canyon National Recreation Area: Implications for Natural and Cultural Resources

Linda H. Geiser and Anne R. Ingersoll

U.S. Forest Service, Pacific Northwest Air Resource Management Program, Corvallis, OR

Andrzej Bytnerowicz

U.S. Forest Service, Pacific Southwest Research Station, Riverside, CA

Scott A. Copeland

Cooperative Institute for Research in the Atmosphere, Lander, WY

ABSTRACT

Agriculture releases copious fertilizing pollutants to air sheds and waterways of the northwestern United States. To evaluate threats to natural resources and historic rock paintings in remote Hells Canyon, Oregon and Idaho, deposition of ammonia (NH_3), nitrogen oxides (NO_x), sulfur dioxide (SO_2), and hydrogen sulfide (H_2S) at five stations along 60 km of the Snake River valley floor were passively sampled from July 2002 through June 2003, and ozone data and particulate chemistry were obtained from the Interagency Monitoring of Protected Visual Environments (IMPROVE) station at Hells Canyon. NH_3 concentrations were high; biweekly averages peaked at 5–19 ppb in spring and summer and the nutrient-laden Snake River is a likely source. Fine particulate ammonium nitrate (NH_4NO_3) averaged $2.6 \mu\text{g}/\text{m}^3$ during the 20% of worst visibility days with winter drainage of air masses from the Snake River Basin and possibly long distance transport from southern California. Other pollutants were within background ranges. NH_3 is corrosive to clay-based pictographs; nitrogen deposition can alter natural biotic communities and terrestrial ecosystem processes at levels reported here.

INTRODUCTION

Hells Canyon National Recreation Area (HCNRA), encompassing 71 mi of the Snake River along the Oregon and Washington border (Figure 1), contains one of the best-preserved collections of riverine archaeology in North America.¹ Over 200 pictographs and carved petroglyphs ranging in age from 200 to 7100 yr are recorded in the

IMPLICATIONS

Ammoniacal nitrogen from regional agriculture may threaten natural and cultural resources in Hells Canyon National Recreation Area; volatilized NH_3 from the Snake River and winter atmospheric transport of NH_4NO_3 from the Snake River Basin and southern California are the most probable sources.

United States' official list of cultural resources worthy of protection against damage, disturbance, or collection under the National Heritage Protection Act of 1966—the National Register of Historic Places. Historic peoples painted smooth, vertical to concave, basalt rock faces that were protected from rain using bright red, white, and blue clay pigments mixed with natural binders that formed durable bonds to rock minerals; petroglyphs were carved on boulders exposed to the elements.¹

During the mid-1990s, U.S. Forest Service career archaeologists expressed concern that pictographs in HCNRA along the Snake River had deteriorated in recent decades.² Because air pollutants can dissolve rock and clay minerals³ and enhance the growth of biological weathering agents of culturally modified stone,^{4,5} they postulated that air pollution in the Snake River corridor could be a cause of rock art weathering in Hells Canyon.

In 2000, agency biologists conducted a 1-wk lichen study of the Snake River valley, its primary tributaries, and the adjacent Imnaha watershed, all within HCNRA.⁶ The extensive colonies of nitrophytic bark lichens and high nitrogen concentrations in thalli of saxicolous lichens indicated that deposition of nitrogen-containing pollutants was high throughout the study area but especially high on the Snake River valley floor where most of the pictographs are located. Higher bark pH at moist sites with higher lichen cover pointed to an ammoniacal as opposed to acidic deposition source. Sulfur concentrations in lichen thalli were comparable to background ranges at all sites, except the valley floor, where they were intermediate to and not different from regional sites with enhanced sulfur deposition and clean sites.

Geiser et al.⁶ concluded that despite HCNRA's remote location, deposition of nitrogen- (and possibly sulfur-) containing pollutants was enhanced relative to other remote sites in the northwestern United States. In this study we use direct measurements of ambient concentrations of criteria pollutants and analysis of existing monitoring data from the Interagency Monitoring of Protected Visual Environments (IMPROVE) station 20 km south of the HCNRA boundary to evaluate the degree and sources of

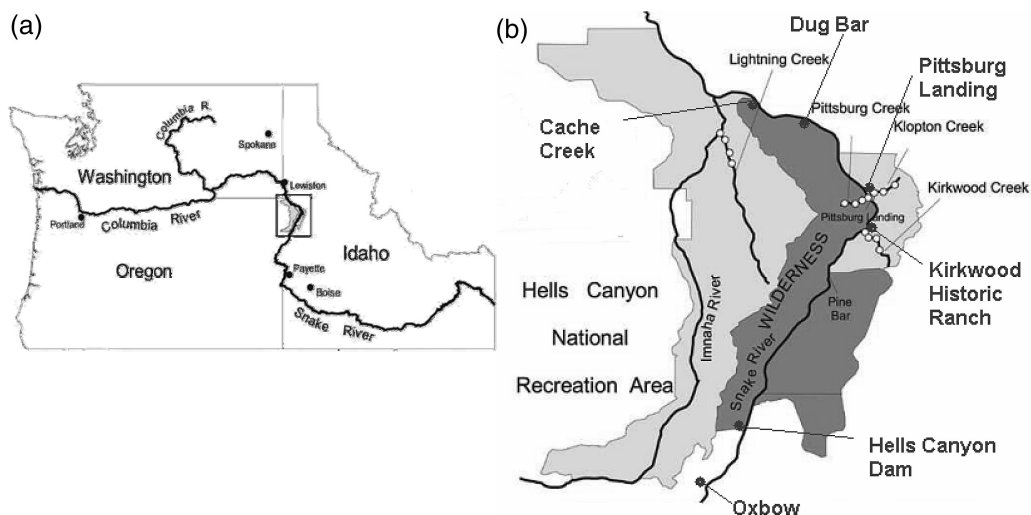


Figure 1. Study area maps. (a) Inset of HCNRA in Oregon and Idaho. (b) Close-up of the recreation area (light gray), wilderness (dark gray), and location of passive sampling stations (filled black circles), previous lichen monitoring locations (small white circles), and IMPROVE site with ozone monitor (dot at Oxbow). Thick black lines indicate waterways. All passive sampling stations were within the Wild & Scenic River boundaries for the Snake River, which extend 0.4 km from the riverbanks. Wild & Scenic River status provides additional federal protection for historic artifacts.

the threat. The study was limited to the Snake River valley floor within the boundaries of the designated Wild and Scenic portions of the Snake River, where the threat was perceived to be greatest.

From July 2002 through June 2003, we monitored ambient ammonia (NH_3), nitrogen oxides (NO_x), sulfur dioxide (SO_2), and hydrogen sulfide (H_2S) using passive samplers, and ozone using an active monitor. We also obtained biweekly ammonium nitrate (NH_4NO_3) and ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$) concentrations in fine particulates from the Hells Canyon IMPROVE station at Oxbow for 2000–2004. To aid our analysis, we obtained water chemistry, temperature, and flow-rate data for the Snake River at the entry point to HCNRA and additional meteorological data from the Pittsburg Landing Remote Access Weather Station near the valley floor in HCNRA. Our objectives were to (1) measure levels of nitrogen- and sulfur-containing pollutants that could volatilize from the Snake River or be transported into HCNRA from other local or regional atmospheric sources; (2) identify which pollutants, if any, could adversely affect HCNRA cultural or natural resources at observed levels; and (3) identify the most likely sources and peak transport times of these pollutants. Our working hypothesis was that agricultural nitrogen from regional sources is enhancing deposition of nitrogen-based air pollutants in Hells Canyon, threatening cultural and natural resources.

METHODS

Study Area

HCNRA is located on the Oregon-Idaho border in the U.S. Pacific Northwest (Figure 1). The recreation area is bisected by the Snake River, a designated Wild and Scenic River. HCNRA is remote from major population centers and portions are designated Class I Wilderness. Topography is rugged and steep; elevation on the Snake River valley floor within HCNRA ranges from 625 to 270 m, the valley walls rise to 1800 m on the Idaho side. On the

valley floor, summers are hot and dry; winters are mild and bring most of the annual precipitation. Mean annual precipitation varies from 25 cm on the valley floor to more than 125 cm in the surrounding mountains.⁷ Mean maximum July and minimum January temperatures on the valley floor at the remote automated weather station at Brownlee Dam from 1966–2005 were 34.8 °C and –3.9 °C, respectively.⁸

The steep walls of the Snake River canyon are sparsely covered by perennial grasses, sagebrush and other drought-tolerant plants, and are deeply notched by tributaries. The valley floor and the tributaries support denser, species-rich, riparian vegetation, and provide water, food, shelter, and passageways for animals. The net-leaved hackberry (*Celtis laevigata* var. *reticulata*) is the dominant tree on the valley floor and moisture retained in these stands is associated with a high cover of nitrophytic lichens.⁶ Most of the historic art is within 100 m of the river, the remainder is on cliffs and boulders up to 0.5 km upslope.

Study Design

To measure ambient air pollutants, we established five passive monitoring stations, more or less evenly spaced, along 60 km of the Snake River valley floor in Oregon and Idaho, from the southern to northern boundaries of HCNRA (Figure 1, Table 1). Each station consisted of a polyvinyl chloride post secured to the ground over a length of rebar with three Ogawa passive air samplers (Ogawa & Co.), one each under separate shelters for NO_x /nitrogen monoxide (NO), nitrogen dioxide (NO_2)/ SO_2 , and NH_3 , fastened to the post at a height of 2.1 m above ground and two H_2S samplers (Maxxam Analytics, Inc.) fastened to the post under a single shelter at 1.8 m (Figure 2). Shelters were inverted, opaque plastic cups that protected samplers from rain, wind, dust, birds, and other disturbances. Passive sampling occurred from July 1, 2002 to June 20, 2003.

Table 1. Monitoring station locations and target pollutants.

Monitoring Station	Coordinates (dd)	Elevation(m)	Pollutants Monitored	Distance from River Bank (m)	River Mile
HECA	116.8395 °W 44.9932 °N	625	Ozone, NH ₄ NO ₃ , (NH ₄) ₂ SO ₄	624	267
Hells Canyon Dam	116.6963 °W 45.2561 °N	457	NH ₃ , O ₃ , NO _x , NO, SO ₂ , H ₂ S	32	247
Kirkwood Creek	116.49917 °W 45.5681 °N	332	NH ₃ , O ₃ , NO _x , NO, SO ₂ , H ₂ S	16	220
Pittsburg Landing	116.469 °W 45.6271 °N	380	NH ₃ , O ₃ , NO _x , NO, SO ₂ , H ₂ S	227	215
Dug Bar	116.6870 °W 45.8054 °N	323	NH ₃ , O ₃ , NO _x , NO, SO ₂ , H ₂ S	64	196
Cache Creek	116.9034 °W 45.9816 °N	270	NH ₃ , O ₃ , NO _x , NO, SO ₂ , H ₂ S	32	177

Notes: See methods section for sampling intervals and protocols. dd = decimal degrees.

Our sixth station was the IMPROVE visibility monitor (HECA1) in the village of Oxbow (Figure 1), 20 km south of HCNRA and the closest accessible source of continuous electrical power. From this station we obtained 2001 through 2003 NH₄NO₃ and (NH₄)₂SO₄ concentrations in fine particulate matter (<2.5 μm; PM_{2.5}), air mass back trajectories, and July through September 2002 average hourly ambient ozone concentrations from a portable ozone monitor (Model No. 202, 2B Technologies, Inc.) (see Data Collection).



Figure 2. The passive sampling station at Kirkwood Ranch. The large inverted cup shelters the Maxxam samplers; small cups shelter the Ogawa samplers.

Data Collection

NO_x, NO₂, SO₂, and NH₃. Each Ogawa sampler held two collection pads onto which the target pollutant was passively collected, providing two replicate samples per pollutant per monitoring station. Collection pads were replaced with clean, unexposed pads every 2 weeks, except November–April when, because of wintertime accessibility limitations, the collection pads were exchanged every 4 weeks. After each replacement, the exposed collection pads were stored in airtight vials and frozen for later analysis. Sampler components, pollutant extraction procedures, and calculations of ambient concentrations used by the analytical laboratory (U.S. Department of Agriculture Forest Service [USDA], Pacific Southwest Research Station, Riverside, CA) are described in detail in reference 9. SO₂ was analyzed only from June to September. Independent field tests with co-located active continuous monitors have shown that Ogawa passive samplers provide reliable, comparable estimates under the exposure times and concentrations for which we used them in HCNRA.^{10–12}

H₂S. Each of the two Maxxam samplers held a single silver-nitrate-coated collection pad, providing two replicate samples of H₂S per monitoring station. Samplers were replaced every 4 weeks from July to January. Exposed samplers were placed in airtight containers and shipped to Maxxam Analytics for extraction and analysis by fluorometry. Fluorimetric results were combined with average relative humidity, temperature, and wind speed data from the Pittsburg Landing and Snake River Remote Automated Weather Stations (RAWS) to calculate the final concentration of H₂S as described by Tang.¹³ Field tests with co-located active continuous active filter pack H₂S monitors have shown that Maxxam passive samplers yielded an accuracy of greater than 85%.¹⁴

Ozone. The ozone monitor was housed in the HECA1 IMPROVE shed, and air inlet tubes were fastened to the roof of the shed and operated according to the manual specifications.¹⁵ The instrument draws 1 L of air sample per minute and uses a photodiode to measure ultraviolet (UV) absorption at 254 nm (the absorption maximum of ozone) across a 15-cm long absorption cell; a low-pressure mercury lamp is the light source. Ozone concentrations are calculated every 10 sec by comparison of the air sample UV absorption (*I*) to that of a scrubbed sample (*I*₀) according to the Beer–Lambert law:

$$O_3(\text{ppbv}) = 1/\alpha l \times \ln(I_0/I) \quad (1)$$

where σ , the extinction coefficient, is $308 \text{ atm}^{-1} \cdot \text{cm}^{-1}$ and l , the path length, is 15 cm. Hourly means were recorded continuously from July 1 through September 15. In principle the instrument requires no calibration because it is an absolute measurement but slight nonlinearity in the photodiode response is calibrated at the factory. Data were downloaded biweekly at which time the zero reading (scrubbed air only) was checked and reset if necessary to maintain a zero between -3 and 7 ppb.

NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$. IMPROVE is a national network of instrumented visibility monitoring stations. The samplers collect 24-hr speciated $\text{PM}_{2.5}$ and nonspeciated coarse particulate matter ($<10 \mu\text{m}$; PM_{10}) samples every third day. Module B captures $\text{PM}_{2.5}$ on a 37 mm Nylasorb filter mounted behind a nitric acid denuder. Exposed filters are analyzed by ion chromatography for nitrate (NO_3^-), nitrite (NO_2^-), chloride (Cl^-), and sulfate (SO_4^{2-}) ions at Crocker Nuclear Laboratory at the University of California–Davis. Calculations of NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ concentrations in $\text{PM}_{2.5}$ assume that all NO_3^- and SO_4^{2-} have been balanced by ammonium ions. The uncertainties in individual measurements of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 at Hells Canyon average approximately 5 and 15%, respectively. Details of IMPROVE sampling and analysis protocols are described by Sisler et al.¹⁶ HECA1 has operated since September 2000.

The user-designed queries featured at the Visibility Information Exchange Web System (VIEWS; <http://vista.cira.colostate.edu/views>) allowed us to retrieve 24-hr NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ concentrations for the 20% of best and worst visibility days; all days for HECA1; all other Oregon, Washington, and Idaho IMPROVE stations from 2001 to 2003; and to create on-the-fly contour maps and timeline bar charts of that data. We also retrieved back trajectory data from VIEWS to correlate air mass source regions with days of peak NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ concentrations. The back trajectories were calculated daily using the Atmospheric Transport and Diffusion (ATAD) model for IMPROVE stations from regional meteorological stations.¹⁷ Trajectories were calculated by interpolating winds and temperature from stations within 250 km through a single transport layer between 300 m above ground and the lowest level of a critical inversion, defined by potential lapse rate; terrain effects were not considered.

Emissions. Year 2001 county NH_3 , NO_x , and SO_2 emissions for the western United States were obtained from the U.S. Environmental Protection Agency (EPA) Office of Air Quality Planning and Standards National Emissions Inventory to help identify primary source regions relevant to HCNRA. See EPA's website for details regarding emissions inventory calculations (<http://www.epa.gov/oar/oaqps>).

Data Analyses

Replicate-averaged passive sampling data and ozone daily minimums, maximums, and means were plotted over time to visualize seasonal patterns, station-to-station variability, and the duration and intensity of peak episodes.

All values were compared with previously reported ranges for urban and remote sites.

Dunnnett's test, a specialized multiple comparison test to compare a single control group to all other groups,¹⁸ was used to assess significant differences between mean NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ concentrations on the 20% of worst visibility days at HECA1 compared with all other Oregon, Idaho, and Washington IMPROVE stations.

To identify source regions, IMPROVE data at HECA1 were first sorted by NH_4NO_3 concentration and the highest 20% of NH_4NO_3 days were used to represent peak impacts. Then, the ATAD back trajectory data from the atmospheric transport and dispersion model were superimposed on a 50-km grid. Trajectory endpoints in each grid cell corresponding to all sample days and to sample days with the highest 20% of measured NO_3^- were counted. Each trajectory is followed for 96 hr; a point is laid down every 3 hr yielding 32 endpoints per trajectory. There are four trajectories arriving at HECA1 per sample day, or 128 endpoints. Only trajectories corresponding to days when NO_3^- was measured were used, but over 3 yr, 2001–2003, the endpoints provided substantial statistical power. Two kinds of maps were produced: endpoint density and conditional probabilities. The endpoint density map shows the average number of endpoints in each cell on high NO_3^- days at HECA1. The conditional probabilities map shows the odds that a trajectory that passed through one of the 50-km grid squares was a high NO_3^- day. It is calculated by dividing the number of high NO_3^- endpoints by the total number of endpoints in each grid square.

RESULTS

NH_3

NH_3 concentrations peaked in spring and summer (Figure 3), with the highest 2-week averages peaking between 5 and 19 ppb at Hells Canyon Dam, Kirkwood Creek, Pittsburg Landing, and Cache Creek (Figure 4) between mid-March and early September. From October through February, NH_3 concentrations were 5 ppb or less at all stations. Mean standard deviation for replicate readings was 0.39 ppb. Not all stations experienced peaks simultaneously, indicating that variable conditions at individual sites contributed to NH_3 formation. For example, seasonal changes in river flow rates could differentially affect water temperature and the exposure of algae-covered rocks depending on riverbed depth and topography. Relative to other remote locations in the western United States, the peak NH_3 values at all stations were high. Bytnerowicz and Fenn¹⁰ reported 24-hr ranges for NH_3 at remote sites in California between 0.2 and 3.6 ppb. Krupa's review¹⁹ lists annual mean ranges for remote sites from 0.05 to 2 ppb, and for agricultural areas and feedlots from 2 to 84 ppb. Mean annual background NH_3 concentrations in a 2-yr Alberta study were 0.37 ppb.²⁰

NO_x

Unlike NH_3 , other gas concentrations were within expected background ranges throughout the year. NO peaks in HCNRA occurred in spring and summer (Figure 3). The highest values (up to 8.5 ppb) occurred simultaneously at all sites in May (Figure 4); fall and winter values averaged

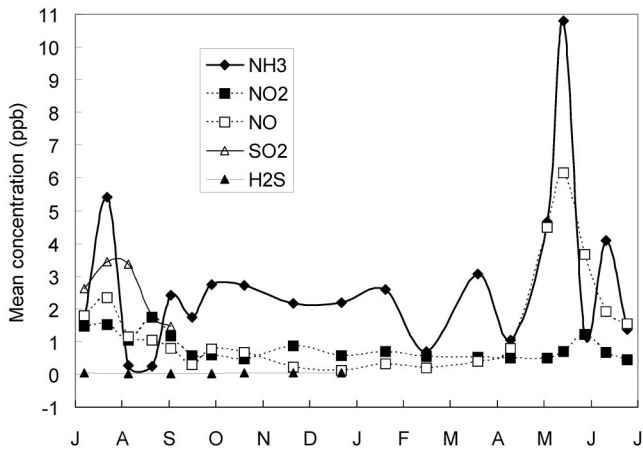


Figure 3. Mean ambient concentrations of nitrogen- and sulfur-containing gases from five monitoring stations along the Snake River in HCNRA from July 1, 2002 through June 30, 2003.

less than 1 ppm. NO₂ peaked later in summer, between July and early September, at 2 ppb and averaged 0.5 ppb for the remainder of the year except for one anomalous high value of 4 ppb at Hells Canyon Dam in June. The 24-hr background ranges in California are 1.5–15 ppb for NO and 3.6–18 ppb for NO₂.¹⁰ Mean standard deviations for replicate readings of NO and NO₂ were 0.14 and 0.06 ppb, respectively.

The NO peaks in May indicate fresh combustion emissions affecting all stations. May is the peak month for prescribed fire treatments in eastern Oregon and western Idaho, and smoke from these treatments would be a feasible explanation of the NO peaks (and potentially NH₃ also if ammonium phosphate or (NH₄)₂SO₄ were used as flame retardants^{21,22}). However, records for wildland and prescribed fire for the surrounding public lands (Wallowa Whitman, Payette, and Nez Perce) indicate that there were no wildland fires in May of 2003 and that prescribed fires in the area were either very small (<100 acres) and only a few days in duration or too far away to account for

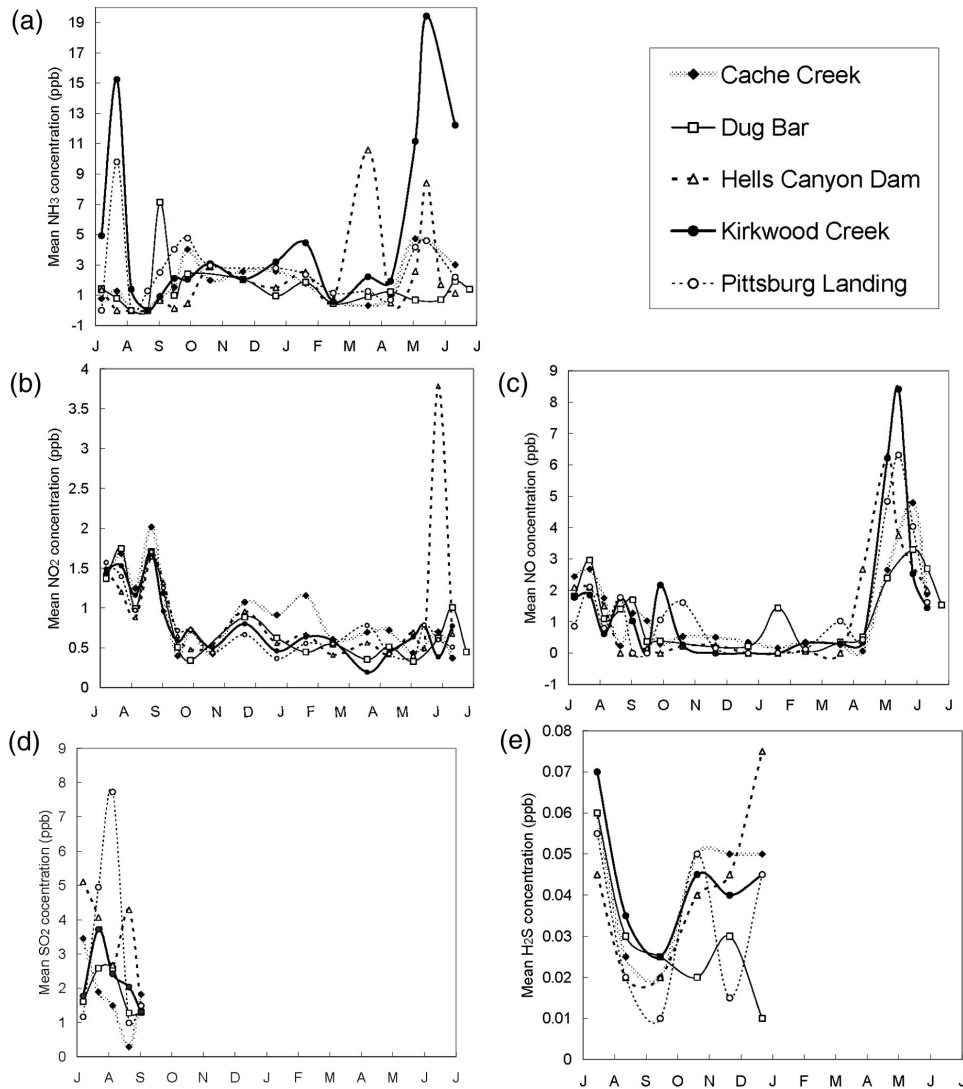


Figure 4. Concentrations of gaseous pollutants (ppb) at five monitoring sites along the Snake River in HCNRA: (a) NH₃, (b) NO₂, (c) NO, (d) SO₂, and (e) H₂S. Values are averages of two replicates for 2- to 4-week exposure periods from July 1, 2002 to June 30, 2003, marked at the midpoint of the exposure period.

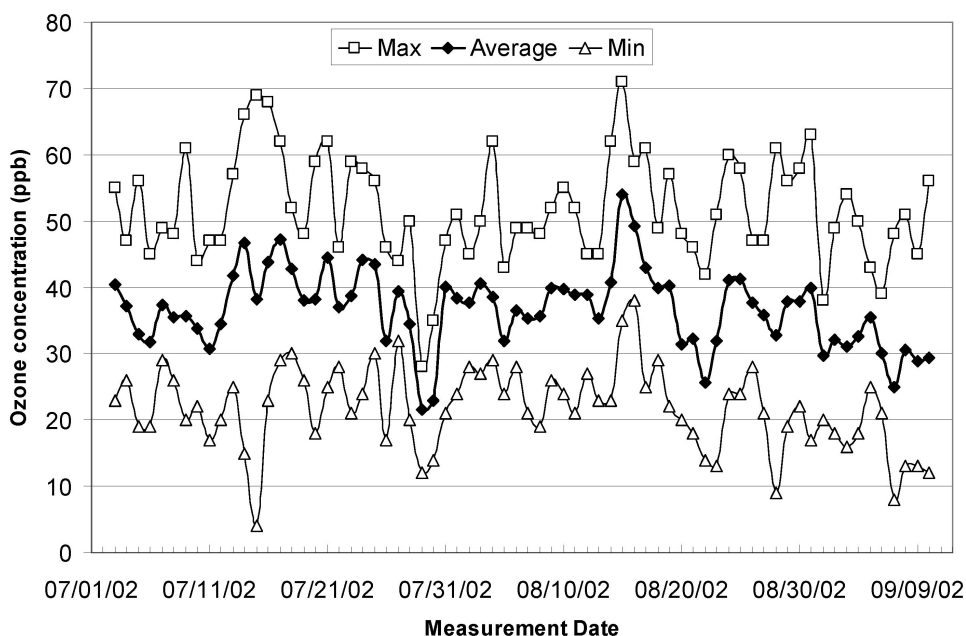


Figure 5. Daily average, minimum, and maximum summer ozone concentrations at Oxbow, OR, in 2003.

a fresh NO emissions signal. Additionally, flame retardants are not used by any of these forests in prescribed burn activities. One explanation for the NO peak in May 2003 is construction activity at Hells Canyon Dam when heavy equipment was brought on-site to repair the access road; perhaps the NO₂ peak there resulted from the month-long repair work. Another possibility is that the NO was from smoke emitted by agricultural burning to the south of Hells Canyon in Oregon or Idaho. Both explanations are consistent with the chronological order of the NO peaks from furthest south (Hells Canyon Dam) to furthest north (Dug Bar and Cache Creek). A third possibility is that fresh NO results from boat traffic on the Snake River within HCNRA; peak season is May through September which seems to coincide in general with highest NO levels along the river. Access points are Pittsburg Landing, Dug Bar, and Hells Canyon Dam. In any case, levels of NO and NO₂ along the valley floor, at least during low wildfire years such as 2002–2003, do not seem high enough to be of concern.

SO₂ and H₂S

SO₂ was low throughout the limited summer study period (<4 ppb). All H₂S concentrations were low (<75 ppt). Mean standard deviations for replicate readings of SO₂ and H₂S were 1.10 ppb and 4 ppt, respectively. Background H₂S concentrations may be approximately 65 ppt for coastal regions, 35–60 ppt for forests, 450–840 ppt for wetlands, and approximately 365 ppt for urban areas.²³

Ozone

Mean daily ozone concentration over the summer study period, July 1–September 15, were low to moderate at 40 ppb (range for daily means 25–55 ppb); the mean daily maximum was 55 ppb (range 42–71 ppb); and the mean daily minimum was 20 ppb (range 4–38 ppb) (Figure 5). The highest hourly means for ozone (71 and 69 ppb)

occurred on July 15 and August 15. Although mean concentrations in the cooler Cascade ranges are lower, 19–35 ppb,²⁴ the level observed at HECA1 were much lower than areas in California where ozone injury has been documented (means of 60–80 ppb with peaks of 200–350 ppb).²⁵

NH₄NO₃ and (NH₄)₂SO₄

In contrast to late spring and summer peaks for NH₃ and NO_x, NH₄NO₃ associated with PM_{2.5} peaked in November through March; values on the 6 days with highest concentrations were 3.3–6.4 μg/m³ (Figure 6). Concentrations from April to October were very low, generally less than 0.05 μg/m³. When the worst 20% of days are compared with the worst 20% of days in the western United States (Figure 7a) it is apparent that HECA is a hotspot for NH₄NO₃ in the western United States. In contrast, (NH₄)₂SO₄ concentrations showed little seasonal pattern (Figure 6) and even on worst days were comparable to other remote locations in the western United States (Figure 7b); peak daily concentrations were 1.8 and 1.65 μg/m³ in April and November, respectively.

Dunnnett's test provided good evidence (α = 0.05) that mean NH₄NO₃ concentrations on the worst 20% of visibility days were higher than those of all other Oregon, Washington, and Idaho IMPROVE sites except for the two monitors in the Columbia River Gorge and the Seattle urban monitor (Table 2). In contrast, even on the worst visibility days, HECA1 mean (NH₄)₂SO₄ concentrations were not significantly different than the 10 cleanest monitors (Table 3).

Back trajectory data showed that grid cells with the highest number of endpoints on high NO₃⁻ days at HECA are concentrated in the upper Snake River Basin of Idaho to the southeast, and in the lower Snake River Basin of southeast Washington and northwest Oregon (Figure 8a). The conditional probability map (Figure 8b) shows that

Hells Canyon 2000-2003

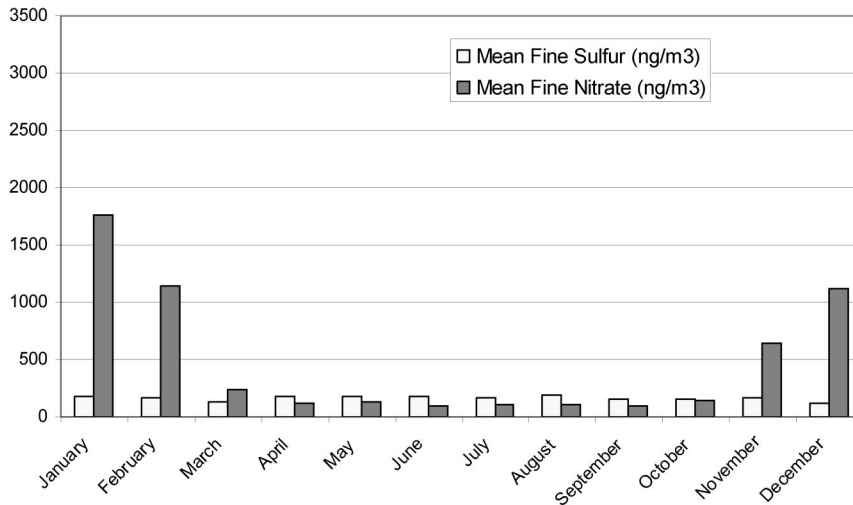


Figure 6. Mean 2002–2003 NH_4NO_3 and $(\text{NH}_4)_2\text{SO}_4$ concentrations in $\text{PM}_{2.5}$ at HECA the IMPROVE site. $(\text{NH}_4)_2\text{SO}_4$ concentrations are similar year round but NH_4NO_3 concentrations dip in summer months, presumably because high temperatures decrease its stability in the atmosphere.

air masses arriving from the south and southeast have the highest likelihood of being high NH_4NO_3 days. These maps are consistent with fall and winter transport from the Snake River Basin and possibly as far away as southern California, the San Francisco Bay area, and the Salt Lake City basin. The two trajectory maps are superimposed on county NH_3 and NO_x emissions from the EPA Office of Air Quality Planning and Standards. The co-occurrence of high conditional probability and high endpoint density grid cells in the agricultural heartlands of the Snake River Basin and southern California support the hypothesis

that agricultural nitrogen and (to a lesser extent) urban nitrogen are contributing to air pollution in Hells Canyon.

Uncertainties in trajectory models increase with distance and pollutants disperse during transport. However, the trajectory maps show that the prevailing transport patterns during “ NO_3^- season” do allow for transport of NO_x from the huge (factor of 10–50 larger than southwest Idaho) NO_x sources in California. Because of prevailing winds, massive NO_x sources, and transport times of approximately 50 hr (500 mi/10 mph), it is reasonable to assume that some of the NO_x will still be present after 2

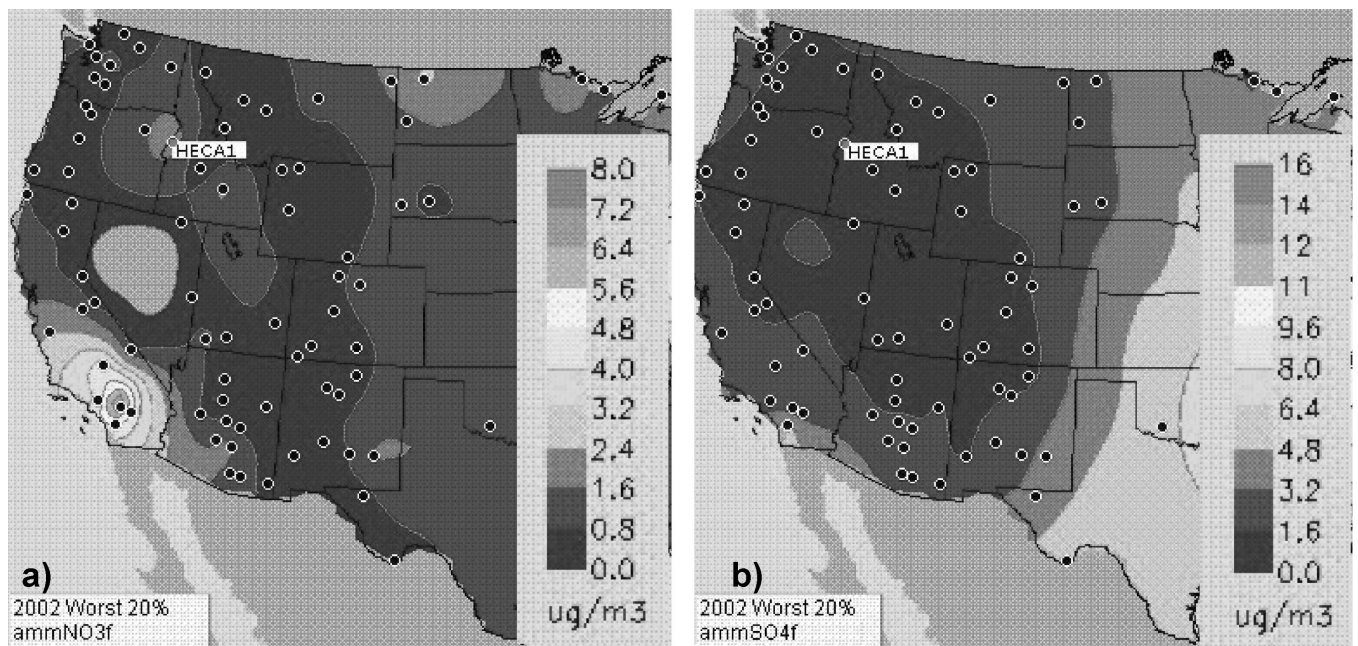


Figure 7. 2002 (a) NH_4NO_3 and (b) $(\text{NH}_4)_2\text{SO}_4$ concentrations in $\text{PM}_{2.5}$ on the 20% of days with the worst visibility measured by the IMPROVE network in the western United States. HECA is a regional hotspot for NH_4NO_3 but not $(\text{NH}_4)_2\text{SO}_4$. Note, all measurements $>3.2 \mu\text{g} \cdot \text{m}^{-3}$ NH_4NO_3 and $4.75 \mu\text{g} \cdot \text{m}^{-3}$ $(\text{NH}_4)_2\text{SO}_4$ are in southern California, and $(\text{NH}_4)_2\text{SO}_4$ only, the eastern Great Plains states. Data were unavailable for much of Nevada.

Table 2. Dunnet's comparison tests of mean NH_4NO_3 concentrations in $\text{PM}_{2.5}$ during the 20% of days with the worst visibility at Hells Canyon (HECA) to other IMPROVE stations in Oregon, Washington, and Idaho from 1998 to 2006.

IMPROVE Site Code	Site Location	Latitude	Longitude	Years of Data	NH_4NO_3 Mean $\mu\text{g}/\text{m}^3$	SD	Dunnet's Test
PUSO	Seattle, WA	47.57	-122.31	6	1.045	0.340	↑
CORI	Columbia River, WA	45.66	-121.00	9	1.038	0.385	↑
COGO	Columbia Gorge, WA	45.57	-122.21	7	0.866	0.205	↑
HECA	HCNRA, OR	44.97	-116.84	6	0.586	0.208	=
CRMO	Craters of the Moon NP, ID	43.46	-113.56	7	0.568	0.167	=
SPOK	Spokane Reservation, WA	47.90	-117.86	4	0.455	0.104	=
STAR	Starkey Experimental Forest, OR	45.22	-118.51	7	0.426	0.120	=
SNPA	Snoqualmie Pass, WA	47.42	-121.43	8	0.385	0.060	=
OLYM	Olympic NP, WA	48.01	-122.97	5	0.353	0.044	=
MOHO	Mount Hood W, OR	45.29	-121.78	7	0.227	0.027	↓
MORA	Mount Rainier NP, WA	46.76	-122.12	9	0.189	0.033	↓
KALM	Kalmiopsis W, OR	42.55	-124.06	7	0.187	0.023	↓
PASA	Pasayten W, WA	48.39	-119.93	6	0.159	0.028	↓
NOCA	North Cascades NP, WA	48.73	-121.06	7	0.127	0.017	↓
WHPA	White Pass, WA	46.62	-121.39	7	0.126	0.011	↓
THSI	Three Sisters W, OR	44.29	-122.04	9	0.121	0.015	↓
CRLA	Crater Lake NP, OR	42.90	-122.14	9	0.113	0.053	↓
SAWT	Sawtooth W, ID	44.17	-114.93	7	0.082	0.018	↓

Notes: Only stations in the Columbia River Gorge (COGO and CORI) and Seattle (PUSO) had concentrations comparable to (=) or higher than (↑) HECA; levels at other stations were significantly lower (↓) than HECA ($\alpha = 0.05$). SD = standard deviation.

days. If California is a source of NO_x , much of the conversion to NH_4NO_3 may happen after the plume gets to the intensive agricultural areas of eastern Oregon and southwest Idaho. IMPROVE NO_3^- data from Jarbidge Wilderness in Nevada, which would be in line with the predicted NO_x plume, does not show massive NO_3^- hits during the NO_3^- season. In contrast, there are obvious NO_3^- spikes at Craters of the Moon National Park (south

central Idaho) and Starkey Experimental Forest and Range (east central Oregon).

DISCUSSION

Natural and Anthropogenic Sources Of Nitrogen-Containing Pollutants

NH_3 is naturally emitted from soils, wildlife wastes, and decaying vegetation during mineralization of organic matter by microbes.²⁶ NH_3 and its reaction product, ammonium, are emitted at low altitude and are mainly deposited in close proximity to the source.^{27,28} The steep slopes and rugged topography of Hells Canyon concentrate vegetation, animal populations, and nutrients along riparian corridors, and moist soils could be expected to support active microbial decomposition.

Large forest or range fires can produce significant amounts of NO_x .²⁹ Natural fire frequency in HCNRA is relatively high, but because of fire suppression policies, and unlike other parts of the Snake River plain where cheatgrass invasions have greatly increased fire frequency,³⁰ NO_x emissions in the past 50 yr from wildfire are probably lower or not different than historic rates³¹ and therefore not likely to be the cause of recent degradation of archeological sites.

Anthropogenic nitrogen-containing atmospheric pollutants are dominated by NO_x and NH_3 . NO_x are produced during combustion, and major anthropogenic sources of NO_x are emissions from combustion of fossil fuels by motor vehicles, electric utilities, and industrial boilers. Annual NO_x emissions from anthropogenic sources in Idaho and Oregon were stable at 80,000 and 200,000 t, respectively, from 1975–1985—the lowest state-wide emissions of the 11 western states.²⁹ Annual emissions of NO_x in southeastern Washington, northeast Oregon, and the Snake River Basin of Idaho (Ada, Adams,

Table 3. Dunnet's comparison tests ($\alpha = 0.05$) of mean $(\text{NH}_4)_2\text{SO}_4$ concentrations in $\text{PM}_{2.5}$ during the 20% of days with the worst visibility at IMPROVE stations in Oregon, Washington, and Idaho from 1998 to 2006.

Site Code	$(\text{NH}_4)_2\text{SO}_4$ Mean	SD	Dunnet's Test
PUSO	1.938	0.101	↑
COGO	1.467	0.243	↑
CORI	1.289	0.146	↑
MORA	1.029	0.196	↑
OLYM	0.978	0.015	↑
SNPA	0.919	0.196	↑
SPOK	0.835	0.110	=
NOCA	0.803	0.084	=
KALM	0.730	0.068	=
HECA	0.673	0.076	=
STAR	0.665	0.071	=
THSI	0.639	0.063	=
CRMO	0.618	0.062	=
MOHO	0.615	0.064	=
WHPA	0.523	0.078	=
PASA	0.517	0.046	=
SAWT	0.481	0.061	↓
CRLA	0.440	0.053	↓

Notes: $(\text{NH}_4)_2\text{SO}_4$ concentrations at Hells Canyon were comparable to other remote sites. See Table 2 for site locations and notation descriptions.

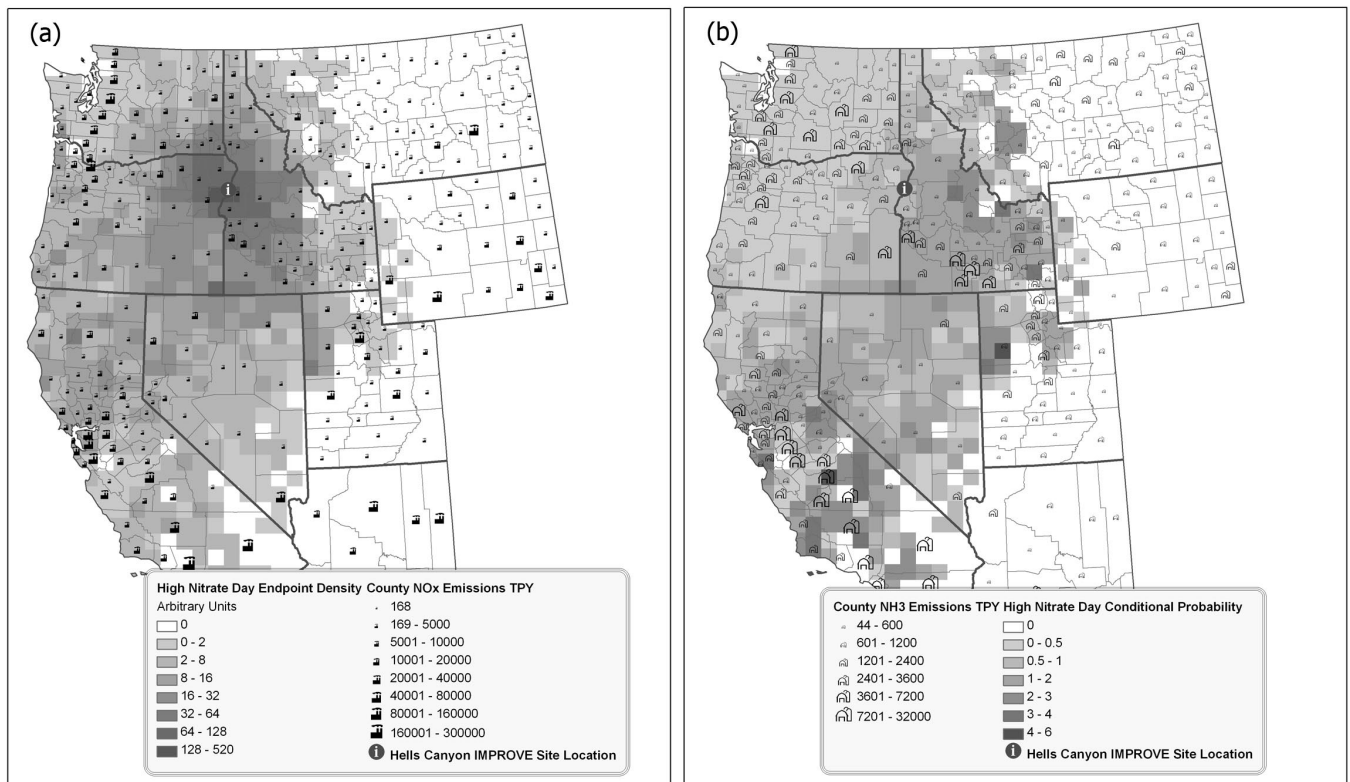


Figure 8. Two views of polluted air mass transport to Hells Canyon on the basis of ADAT back trajectory data from 2000 to 2003. (a) Air masses with the highest NH_4NO_3 concentrations arriving in Hells Canyon pass most recently from the southeast; (i.e., the Snake River Basin of Idaho) and from the northern Snake River Basin from southeast Washington and northwest Oregon. (b) A conditional probability grid for the highest 20% of NH_4NO_3 measurements shows the odds that a trajectory passing through a grid cell was associated with a high NO_3^- date. Air masses arriving from the south and southeast have the highest likelihood of being high NH_4NO_3 days. This is consistent with fall and winter transport from the Snake River Basin of Idaho and possibly as far away as Salt Lake City, UT; southern California; and the San Francisco Bay area. The two trajectory grids are superimposed on county NH_3 and NO_x emissions.

Asotin, Baker, Canyon, Garfield, Gem, Idaho, Lewis, Malheur, Nez Perce, Payette, Wallowa, and Washington counties) rose slowly approximately 0.6%/yr from 1985 to 1998, and totaled 68,700 t in 1998.³² Oregon, Idaho, and Washington NH_3 emissions are highest in the Snake and Columbia River Basins. These geographic areas of high emissions correspond to wind back trajectories for days in Hells Canyon with the worst NH_4NO_3 concentrations in $\text{PM}_{2.5}$. They are also high west of the Cascades in Oregon and Washington but, as we have shown, air masses from these locations are less likely to influence conditions at HCNRA.

Livestock waste from feedlots and agricultural fertilizers account for approximately 80% of NH_3 emissions in the United States.³³ NH_3 emissions have greatly intensified in southeastern Washington, northeast Oregon, and the Snake River Basin of Idaho during the past 50 yr; NH_3 emissions increased from 1990 to 1998 by 4.9%/yr, with total emissions estimated at 43,000 t in 1998.³² Livestock operations (nearly all from cattle) accounted for approximately twice as much ammonium emissions as fertilizer applications. The reaction of nitric acid with NH_3 gas emitted from feedlots and fertilized fields results in the formation of NH_4NO_3 particles. It is possible for NH_4NO_3 transport to deliver nitrogen species to national parks and wildernesses, depending on the pattern of local NH_3 emissions relative to the supply of nitric acid vapor.³⁴ Eilers et

al.³⁵ suggest that the highest concentrations of both NO_3^- and ammonium in precipitation at Craters of the Moon National Monument in Idaho are derived regionally from fertilized fields or feed lots. Movement of regional pollutants into HCNRA via the Snake River valley is favored by the channeling effects of the terrain and wind flow.² Even without accounting for terrain, our back trajectory analyses show that poor air quality days in Hells Canyon are associated with days in which air masses originate in or pass through the upper and lower Snake River Basins. The seasonality of the response can be explained by the greater stability of NH_4NO_3 particles in winter under cooler temperature regimes; the temperature- and humidity-dependent reversibility of the reaction of ammonium with nitric acid to form NH_4NO_3 is well known.^{23,36} Regional transport of ammonium from the Snake River Basin during the summer seems an unlikely explanation of summertime NH_3 peaks at our monitoring stations given that the lichen study demonstrated a rapid drop in NH_3 deposition with distances more than 0.4 km from the river.⁶

Local surface waters are also an important anthropogenic source of nitrogen. The Snake and Boise Rivers, which join upriver from HCNRA, are straddled by three major urban areas (Boise, Twin Falls, and Idaho Falls), many minor urban and industrial areas, and drain Idaho's agricultural heartland. Crop fertilizers, cattle and dairy

production, and fish farming all contribute large quantities of nitrogen and phosphorus to the Snake River. The lakes above Brownslee and Oxbow dams—whose outflow enters Hells Canyon—experience severe algal blooms each summer.³⁷ Chlorophyll a concentrations and phosphate levels do not meet state standards for these water quality indicators nearly 100% of the time³⁷ and hypoxic conditions at the bottom of the lakes behind these dams cause nitrification to cease and NH_3 to accumulate in deep water. No data matching our time frame were available, but in 1997 4.3 million t of ammonium were released from the bottom of Hells Canyon dam into HCNRA, mostly during April and May, and some in late summer and fall.³⁸ This seasonality roughly coincides with the NH_3 gas peaks observed at our passive sampling monitors, which occurred in May, June, and the first half of August. Algal blooms consume large amounts of carbon dioxide (CO_2). This removal of CO_2 (a weak acid) by algae from waterways causes water pH to increase, greatly favoring the conversion rate of dissolved ammonium ions to volatile NH_3 gas.²⁶ The pH of the lower Snake River ranges between 6 and 9.³⁷ Volatilized NH_3 is then easily deposited to nearby vegetation, especially in moist, densely vegetated microsites, lichen-coated rocks, and culturally modified stone near the river. Decomposition of algae leads to reduction of oxygen and the conversion of particulate organic phosphorus to highly available, highly mobile, dissolved orthophosphorus, which is the limiting nutrient for cyanobacterial growth,³⁷ perpetuating high pH and substandard water quality conditions for fish and other aquatic species.

Natural and Anthropogenic Sulfur Sources

Natural local sources of sulfur compounds include soil microorganisms and vegetation. These natural emissions are in the form of reduced sulfur compounds such as H_2S , dimethyl sulfide, and particle SO_4^{2-} .²⁹ Anthropogenic sulfur compounds are emitted into the atmosphere during combustion of fossil fuels such as coal, smelting of ores, manufacturing of steel, and refining of petroleum. Between 1985 and 1998³² the total annual SO_2 emissions from the 20 counties surrounding HCNRA ranged between 10,500 and 13,000 t; increasing approximately 0.6%/yr. $(\text{NH}_4)_2\text{SO}_4$ particulates are also easily transported, and data from visibility monitoring sites show that $(\text{NH}_4)_2\text{SO}_4$ particulates account for approximately 20–50% of the $\text{PM}_{2.5}$ mass in the west.³⁵ Apparently HCNRA is not downwind of these regional sources or the emissions disperse before reaching HCNRA, because $(\text{NH}_4)_2\text{SO}_4$ concentrations measured by IMPROVE at HECA1 were comparable to low values observed elsewhere in the region.⁶

Threats to Natural Resources

Excess nitrogen has myriad effects on natural terrestrial ecosystems including promotion of weedy species and shifts in natural terrestrial vegetation communities, soil nitrogen saturation, changes in soil pH and chemistry that reduce availability of nutrients or increase the availability of toxic metals, depression of soil microbiota including mycorrhizae, increased susceptibility of plants to pathogens, and increased fire frequency.^{19,39} Some of

these effects may be occurring in HCNRA and further assessment is warranted. Geiser et al.⁶ report nitrophyte-dominated lichen communities, a high incidence of lichen parasitism, and higher cover and number of weedy species at sites closest to the Snake River where the greatest nitrogen deposition was indicated.

Threats to Cultural Stone

The sources of air pollutants and threats they may pose to petroglyphs and pictographs in HCNRA are summarized in Table 4. NH_3 is a highly corrosive gas that binds to rock minerals, especially moist clays, and is a cause of chemical weathering.²⁶ Because rocks in HCNRA were painted with local clay pigments,¹ it seems plausible that in sufficient quantities over time, NH_3 itself could degrade the painting either through direct oxidation of clay pigments or by damaging silica coatings or other thin, mineral rinds that protect the pictographs and petroglyphs. NH_3 and other nitrogen and sulfur-containing pollutants can also stimulate the growth of natural rock-dwelling algae, cyanobacteria, and sulfur-, nitrogen- and NO_2^- -oxidizing chemotrophic bacteria, which in turn can weather cultural stone through the release of nitric and sulfuric acids or through the physical swelling and shrinking of microbial biomass with changing moisture availability.^{4,5} Finally, we note that visitor use to HCNRA has increased dramatically in the past 25 yr, and that many pictographs and petroglyphs are in accessible locations. In a literature review of cultural stone weathering around the world, Pope et al.⁴⁰ pointed to human impact as the greatest cause of deterioration and this sentiment is echoed by regional archeologists who have studied petroglyphs and pictographs of the western United States.^{1,41} It is possible that much of the degradation at well known, more accessible HCNRA sites is because of physical contact by visitors; however, physical contact cannot explain the evenness of fading observed at less accessible, rarely visited sites.

CONCLUSIONS

We found that ozone, SO_2 , H_2S , and NO_x concentrations in ambient air, and $(\text{NH}_4)_2\text{SO}_4$ in $\text{PM}_{2.5}$ along the Snake River valley floor of HCNRA were within background ranges expected for remote areas in the western United States. In contrast, ambient concentrations of gaseous NH_3 and NH_4NO_3 in $\text{PM}_{2.5}$ were seasonally enhanced. NH_3 emissions and nutrient input to waterways have increased significantly over the past 20–40 yr in counties upwind of HCNRA because of intensification of agriculture. Eutrophication of the Snake River is a likely source of volatilized anthropogenic NH_3 , which peaks in spring and summer close to the river banks. Regional atmospheric transport, especially from the Snake River Basin in winter, is the primary source of NH_4NO_3 input, which an earlier study showed to be elevated throughout HCNRA. We conclude that ammoniacal nitrogen in HCNRA is well above background ranges for the western United States and may pose a threat to the integrity of natural and cultural resources in HCNRA, especially along the valley floor. Balancing the needs of a geometrically increasing human population with the protection of the natural and cultural resources that support human needs is a growing

Table 4. Evaluation of potential threats to pictographs and petroglyphs in HCNRA.

Threat	Source	Increasing in Past 50 Yr?	Likely Factor in Accelerated Deterioration of Cultural Stone?
NO _x	Regional: anthropogenic	Yes, but slowly.	No. Ambient concentrations are low to moderate year round.
NO _x	Local: forest and range fire	No, comparable in 2002–2003 to historic levels.	Not at present, but fire frequency is expected to increase with global climate change.
NO _x and NH ₃	Local: mineralization and denitrification of organic matter	No. Wildlife use is high but not likely to be increasing. No difference in nitrogen availability between sites with or without permitted grazing.	No. May contribute to high background nitrogen availability, but not likely to be different than historical levels.
NH ₃	Regional: anthropogenic	Yes, rapidly.	No. NH ₃ has a high deposition velocity that would dampen long distance transport; does not account for significantly higher availability of nitrogen along river banks.
NH ₃	Local: Snake River	Yes. Phosphorous and nitrogen loading of the Snake River has increased dramatically because of intensification of agriculture, concentrated animal feeding, industry, urbanization, and fish farming.	Yes. Volatilized NH ₃ has a high deposition rate; consistent with indications of higher nitrogen availability along the Snake River compared with tributaries and Imnaha River Basin. Seasonally high NH ₃ levels in water released from Hells Canyon Dam correspond with seasonal atmospheric NH ₃ peaks on the valley floor—volatilization driven by eutrophication, sediment scouring, low pH (see Discussion).
SO ₂	Regional: anthropogenic	No.	No. Emissions are low. PM _{2.5} low year round. Deposition along tributaries is low.
SO ₂	Local: Snake River	Unknown, but overall nutrient-loading of the river has increased.	Maybe. Sulfur deposition to lichen surfaces is higher along the valley floor than elsewhere. H ₂ S is low. NH ₃ may be scouring sulfate from the air, causing higher deposition along Snake River banks.
PM _{2.5} , NH ₄ NO ₃	Regional	Unknown	Yes. Winter concentrations in particulates are high relative to other remote western sites and originate in parts of the region with high NH ₃ emissions.
PM _{2.5} (NH ₄) ₂ SO ₄	Regional	Unknown	No. Concentrations in particulates are within ranges observed for other remote western sites even on worst days.
Ozone	Regional and local	Unknown	Maybe. Concentrations were within ranges expected for remote western sites. Summer peaks were <70 ppb.
Physical abrasion	Local: human contact	Yes, rapidly because of better access and jet boats.	Yes, but would not explain evenness of fading or the deterioration of less accessible sites known to few visitors.

challenge. Regionally, enforcement of the new bi-state Total Maximum Daily Loads,³⁷ the federal Regional Haze Rule, and other legislation to reduce emissions and runoff of agricultural pollutants can all be expected to ameliorate environmental impacts. Within HCNRA, long-term monitoring of water quality and the condition of selected paintings can be used to evaluate success of pollution reduction strategies; visitor education can reduce unintentional damage.

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About the Authors

Linda H. Geiser is an ecologist and, at the time of this research, Anne R. Ingersoll was an air resource specialist for the U.S. Forest Service Pacific Northwest Region Air Resources Management Program, encompassing Oregon and Washington national forests. Andrzej Bytnerowicz is a plant physiologist with the U.S. Forest Service Pacific Southwest Research Station at the Riverside Fire Laboratory. Scott A. Copeland is a data analyst for the Cooperative Institute for Research in the Atmosphere. Please address correspondence to: Linda Geiser, U.S. Forest Service/Pacific Northwest Air Program, P.O. Box 1148, Corvallis, OR 97339-1148; phone: +1-541-231-9452; fax: +1-541-750-7234; e-mail: lgeiser@fs.fed.us.