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# Deposition and Distribution Factors for the Endocrine Disruptor, 4-Nonylphenol, in the Sierra Nevada Mountains, California, USA

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**Abstract**

4-nonylphenol (4NP), a breakdown product of nonylphenol polyethoxylate, is a potent endocrine disruptor and persistent organic pollutant (POP). Due to physical and chemical properties, 4NP is capable of long range transport as both an aerosol and attached to dust particulates. Since nonylphenol polyethoxylates make up a substantial portion of many pesticides, agricultural regions are often sources of 4NP. Physical barriers such as mountain ranges may alter the distribution of this POP but does not stop the long range transport. The Central Valley of California, USA is an intensely farmed region adjacent to the Sierra Nevada Mountains subjected to onshore prevailing winds from the Pacific Ocean. Previous work revealed that the winter snow pack in the Sierra Nevada showed at least an order of magnitude more 4NP than surface water during summer months. As a result, spring melt water may send high concentrations of 4NP to organisms during critical developmental periods. Physical and geographical characteristics of snow and terrain were assessed to determine which factors affect 4NP accumulation in snow and regions at higher risk of 4NP exposure. Samples were taken from snow, surface water and atmospheric deposition for four consecutive years and analyzed by gas chromatography-mass spectroscopy for 4NP. Snow water and dust particulates in snow were analyzed separately. Additionally, snow chamber simulations were run to assess snow characteristics that would lead to increased 4NP deposition in snow. Wind speed was found to correlate inversely with 4NP deposition. Snowflake size showed a positive correlation with 4NP deposition due to increasing surface area. The amount of dust in snow was poorly correlated with 4NP concentration. A geospatial model was developed for the Eastern Sierra Nevada using ArcGIS software that included wind speed, snowflake size, and topographic shielding. Regions that were predicted to be at high risk for 4NP deposition correlated strongly with empirical data from the field.

**Keywords:** Pollutant distribution; Atmospheric deposition; Physical barrier; Endocrine disruptors

## Introduction

Endocrine disruptors are emerging contaminants of concern, recognized as early as the 1990's. Since then, many industrial and agricultural compounds have been identified as biologically active, specifically targeting the endocrine system. Bisphenol A (BPA) is among the more notorious of the endocrine disrupting compounds (EDCs) for its effects on prenatal and developing organisms, including vertebrates [1,2]. BPA has been nearly ubiquitously detected in human urine samples collected over extended periods of time [3]. As a result, plastics have been developed and marketed that do not contain BPA. 4-nonylphenol (4NP), a lesser known EDC, is also prevalent. Nonylphenol polyethoxylates are nonionic surfactants commonly used as constituents in cleaning agents, paints, plastics, and pesticides [4]. Once nonylphenol polyethoxylate enters the environment, it is anaerobically digested into 4-nonylphenol. About 80% of surfactants currently in use in North America are nonylphenol polyethoxylates [5].

4NP is part of a group of lipophilic compounds that act as endocrine disruptors by mimicking one of the strongest female sex hormones, 17-β-estradiol (Figure 1). Typical steroid hormones like 17-β-estradiol can diffuse directly through a cell's plasma membrane to bind with its receptor protein within the cytoplasm. Hormones then transfer through the nuclear envelope and bind to their respective strand of DNA to initiate protein production and produce a response. In the presence of an endocrine disruptor such as 4NP, this protein production can be activated at atypical periods of time which can lead to adverse effects. These effects are more detrimental during development due to the importance of chemical signals during the early stages of life. It has been determined that aquatic organisms exposed to 4NPs show signs of feminization, birth defects, and higher mortality rates [6,7]. In humans, the effects of 4NP may include an impaired immune system function [8]. 4NP can also bind to non-tumorous human cells at the estrogen receptor site and cause proliferation and/or cell death [9,10]. 4NP has been linked to various forms of hormone dependent cancers such as ovarian and breast cancer [11,12]. There are currently no exposure limits set for human subjects.

4-nonylphenol, the branched isomer that most closely resembles estrogen, has octanol-air partition coefficients ($K_{OA}$) and vapor pressures that make 4NP a good candidate for long range transport (LRT) and accumulation in cooler or high altitude regions. $K_{OA}$ describes the concentration of 4NP in air relative to the concentration in octanol when at equilibrium between the two phases [13]. As shown below in Equation 1, $K_{OA}$ can be estimated from the ratio of $K_{OW,}$ the octanol-water coefficient, and $K_{AW}$, the air-water partition coefficient.

$$K_{OA} = \frac{K_{OW}}{K_{AW}} \quad (1)$$

Only persistent organic compounds with log $K_{OA}$ values between 6.5 and 10 will have significant potential for long-range air transport and deposition [14]. The calculated log $K_{OA}$ for 4NPs is 7.9 suggesting that LRT is likely.

Vapor pressure describes the tendency a liquid or solid has for transforming into a gas. The vapor pressure for 4-nonylphenol is approximately 0.02 Pa, indicating that it will condense near -15°C. Atmospheric temperatures at high altitudes are frequently at or below the condensation point of NP. The more branched isomers of NPs, such as the estrogenic mimic, have lower vapor pressures allowing them

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to condense more easily than their straight chained counterparts [6]. Additionally, the more branched isomers also have a lower $K_{OA}$ which slightly decreases their susceptibility to LRT.

The California landscape hosts geographical features that make it an interesting case study of LRT. The Central Valley is one of the primary producers of agriculture in the United States. Fresno County, California's number one ranked pesticide user, is located between the Pacific Coast and the Sierra Nevada Mountains (see Figure 2) [15]. Onshore winds generated on the Pacific Ocean move across the state from west to east for the majority of the year, potentially carrying pesticide residues such as 4NP into the fragile ecosystems of the Sierra Nevada Mountains to the east. The Sierra Nevada Mountain range bisects the state of California trending in a north-south direction. Figure 2 shows the drainage divide in the Sierra Nevada, with drainages to the left of the ridgeline flowing west and to the right of the ridgeline flowing east. The divide is populated by peaks, some higher than 14,000 feet (>4200 m), which create an impressive physical barrier.

Localized topography and prevailing wind patterns are two major factors in determining where pollutants undergoing LRT are atmospherically deposited [16]. Localized topography can act as a barrier to incoming atmospheric deposition, an idea that has been referred to as directional sheltering. The concept of directional sheltering as it pertains to long-range transport of compounds across the Sierra Nevada Mountain range was introduced in the 2007 study by Davidson and Knapp [17]. They evaluated the amount of sheltering in an alpine canyon based on the direction of the prevailing wind relative to the direction the canyon was facing. Davidson and Knapp proposed that directional sheltering could shield frog populations in lakes from the influences of atmospherically deposited pollutants. This pattern was further investigated by Lyons et al. [18]. Large-scale data that was collected from 2012-2013 was used to link features in the landscape with deposition patterns. For east facing canyons, 4NP concentrations correlated with the slope of the canyon headwall (S), the height of the headwall (h), and the distance from the headwall (d) by the relationship

$$\tau = \frac{S \times h}{d} \quad (2)$$

where τ is referred to as topographical shielding. Several drainages on the east side of the Sierra Nevada crest were sampled for surface water concentrations of 4NP. The Convict Creek drainage is shown as an example of increasing concentrations of 4NP in snow at greater distances from the headwall with less topographical shielding (Figure 3). This trend points to dry deposition or dust-borne 4NP as a significant transport mechanism for 4NP. Given this region's tendency towards drought, more 4NP transport would be expected as conditions become drier.

Snow pack was also sampled in this region for 4NP during the winters of 2012 and 2013. It was found that the concentration of 4NP in snow could be as high an order of magnitude more than in surface water [18]. Snow pack represents an integration of precipitation and associated contaminant over a period of time, possibly many months. A high concentration in snow pack, however, could potentially cause high surface water concentrations in spring snow melt, or a 4NP "pulse", during a time when many organisms are in sensitive developmental stages. During the course of the spring melt, dust tends to stay in place in the snow pack and become more concentrated while the snow water seeps into the ground or streams [19]. This has some implications about the mobility of 4NP after it is deposited. Dust-borne deposition in the winter would have a more localized effect in spring, while the aerosolized 4NP found in the snow water would travel downstream.

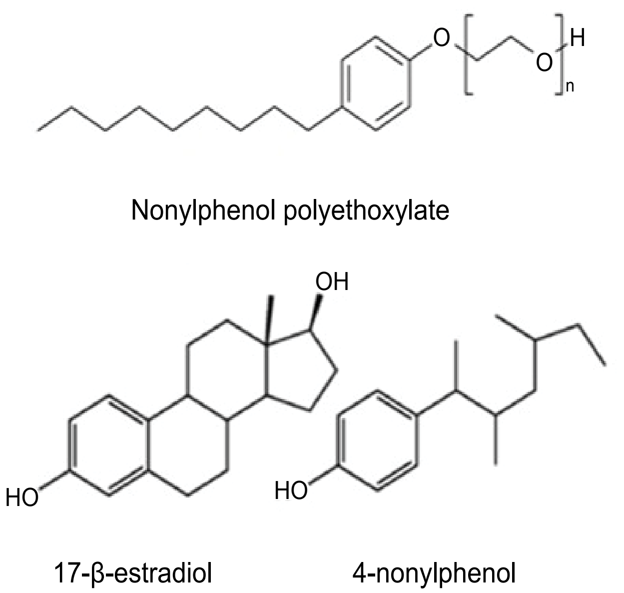


**Figure 1:** The structures of nonylphenol polyethoxylates (NPE), the female hormone 17-β-estradiol and the estrogen mimic, 4-nonylphenol.

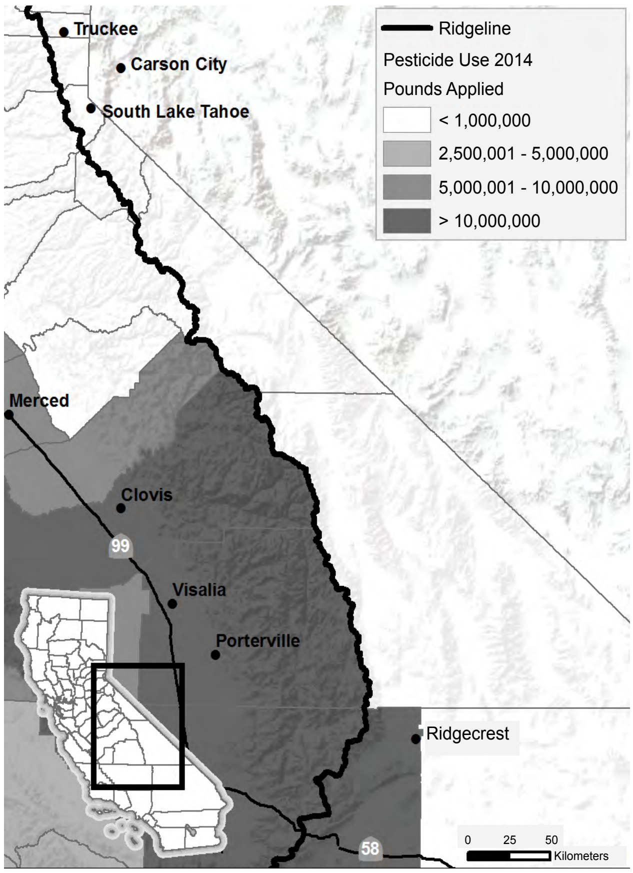


**Figure 2:** Pesticide use ranked according to county in Central California. The dark line represents the Sierra crest ridgeline separating eastern and western flowing drainages. (Map coordinates=-120.62, 39.46;-116.24, 34.96 NAD1927 UTM Zone 11 N).

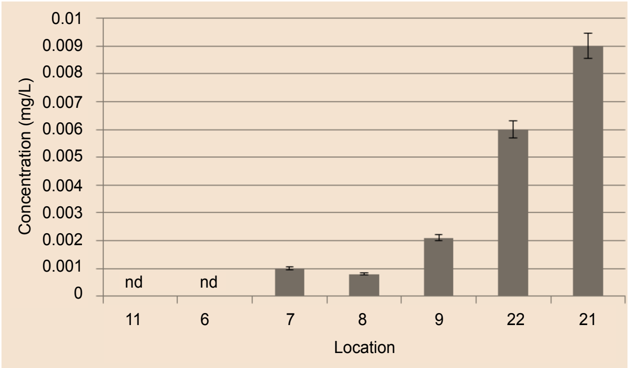


**Figure 3:** Concentration (mg/L) of nonylphenol in water along Convict Creek and in Convict Lake during the spring and summer of 2014. Locations listed on Table 1, in order of highest to lowest elevation. (n=6 per location, error bars represent CI95%) Figure adapted from Lyons et al.

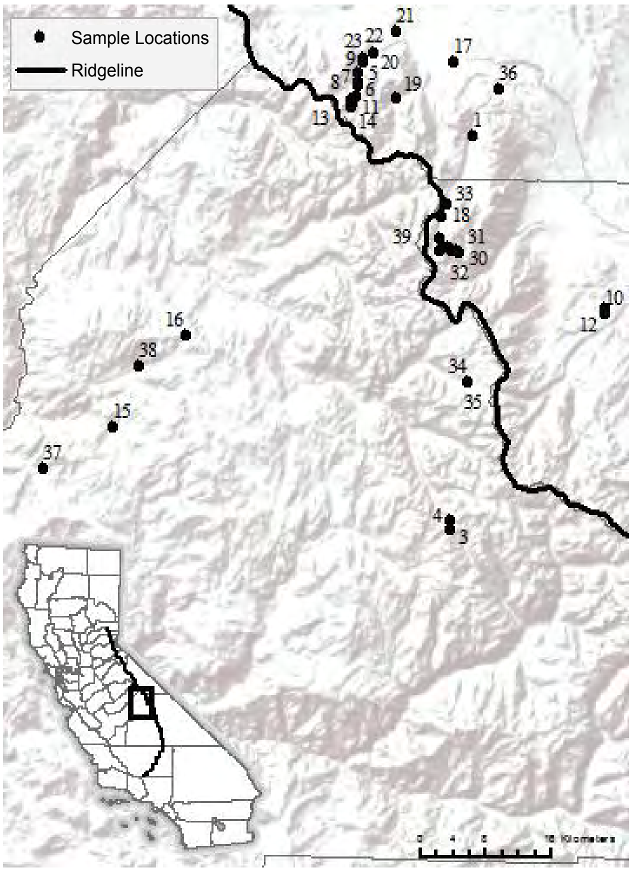


**Figure 4:** Sampling site locations and abbreviations for 2012-2016 for the Sierra Nevada (Map coordinates=-120.62, 39.46;-116.24, 34.96 NAD1927 UTM Zone 11 N).

A late spring rain storm may actually have a larger pulse of 4NP than snow melt if the accumulation is primarily in the residual dust.

The goals of the most recent studies of 4NP deposition focus on the distribution of 4NP and physical and geographical parameters that would cause its accumulation in snow. Wind speed, snowflake size, the amount of dust within the snow pack, topographical shielding, and snow depth were all investigated. Several of these factors were combined to determine areas most at risk for 4NP deposition and disruption of life cycles in organisms.

## Methods

### Sampling methods/locations

Locations for sampling were chosen using ArcGIS programs to identify canyons, headwalls, slope, elevation and wind direction. Sample sites were selected to show a representation of conditions in the Sierra Nevada on both the eastern and western slopes. Figure 4 is map of sampling sites giving sample location and abbreviation. Table 1 shows the site abbreviation, GPS coordinates and type of samples taken along with the seasons and years the location was sampled.

Snow, surface water and atmospheric deposition samples were collected in this study. Nitrile gloves were worn at all times when samples were being collected to prevent contamination from personal hygiene products. One liter water grab samples were taken from the surface of the water and from a depth of 3 m. Grab samples were collected in separate 1 L borosilicate glass bottles, wrapped in aluminum foil to prevent photolysis and placed in a cooler for transport. Compounds were extracted from lake water on site using brass Passive *In situ* Concentrator and Extraction Samplers (PISCES). PISCES were filled with approximately 250 mL of hexane (Sigma Aldrich). PISCES were left in place over a two week period at depths of 1 and 3 meters [20].

Snow samples were taken at a depth of 1 meter from fashioned side walls of snow patches. To collect these samples the snow patch was first split and separated with a clean shovel rinsed with cool hexane. This creates a freshly exposed vertical wall in the snow patch to which a snow corer could then be inserted horizontally at a depth of 1 m for sample collection. Four snow cores were taken from each drift and collected into one wide mouth 1 L glass bottle. The bottle was also wrapped in aluminum foil to prevent photolysis.

A Pasco Xplorer GLX-PS-2002 field data collection system with interchangeable probes was used to collect physical atmospheric conditions at each sampling site, specifically temperature, wind speed and direction. Deposition samplers consisted of a wide mouth funnel (d=22.86 cm) with a coarse screened aperture. The funnel was attached to a 5 L glass collection vessel. Samplers were placed in areas free of overhead interference. Deposition samplers were left out for four week sampling periods. The volume of wet deposition collected in each sampler was measured on site with a graduated cylinder before being transferred to an opaque glass jar for transport.

### Laboratory snow chamber

The snow chamber was used to simulate environmental conditions in the laboratory. All pieces of equipment were metal, Teflon™, or glass parts to prevent the analyte from partitioning to the equipment. Artificial snow particles were kept at a consistent -4°C. 4NP was introduced into the chamber in an aerosol created by passing 4NP solution through a nebulizer (Figure 5). Air flow was provided by a compressed air source and monitored using a Pitot tube.

Snow was sieved to a consistent diameter for snow chamber trials. Aerosolized 4NP was introduced to the chamber at a wind speed of 1 m/s. For a snow pack of a 0.25 $m^2$ surface area and depth of 0.25 m, a total mass of 4.0 g of 4NP was introduced via nebulizer. Concentrations of 4NP in the snow water were analyzed after melting.

### Analytical methods

| Number | Site name | Latitude | Longitude | Season (year) | Type of Sample |
|---|---|---|---|---|---|
| 1 | Big Meadow | 37.50928 | -118.7141 | Summer (2015) | Deposition |
| 2 | Dade Lake | 37.3852 | -118.75638 | Summer (2015) | Deposition |
| 3 | Dale Lake-3w | 37.09026 | -118.736 | Summer (2015) | Deposition |
| 4 | Dale Lake-4w | 37.09936 | -118.73429 | Summer (2015) | Deposition |
| 5 | Convict Creek-1 | 37.5591 | -118.87271 | Spring (2012)<br>Spring (2014) | Water<br>Water |
| 6 | Convict Creek-2 | 37.54750 | -118.87417 | Winter (2012-2013)<br>Summer (2013)<br>Spring (2014) | Water, Grab, Snow (Wet and dry)<br>Grab, Deposition<br>Deposition |
| 7 | Convict Creek-3 | 37.56308 | -118.87332 | Spring (2012)<br>Summer (2012)<br>Winter (2012-2013)<br>Spring (2013)<br>Summer (2013)<br>Winter (2013-2014)<br>Spring (2014)<br>Winter (2015-2016) | Grab<br>Grab<br>Water, Grab, Snow (Wet and dry)<br>Grab<br>Grab, Deposition<br>Snow (wet and dry)<br>Deposition<br>Snow (wet and dry) |
| 8 | Convict Creek-4 | 37.57240 | -118.87375 | Sumer (2012)<br>Winter (2012-2013)<br>Summer (2013)<br>Winter (2013-2014)<br>Spring (2014)<br>Winter (2015-2016) | Grab<br>Water, Grab, Snow (Wet and dry)<br>Grab, Deposition<br>Grab, Snow (wet and dry)<br>Deposition<br>Snow(wet and dry) |
| 9 | Convict Creek-5 | 37.58498 | -118.8654 | Summer (2012)<br>Winter (2012-2013)<br>Summer (2013)<br>Winter (2013-2014)<br>Spring (2014) | Grab<br>Water, Grab, Snow (Wet and dry)<br>Grab, Deposition<br>Grab<br>Deposition |
| 10 | Lake Dorothy-E1 | 37.32217 | -118.52738 | Spring (2013) | Grab |
| 11 | Lake Dororthy-E1m | 37.541000 | -118.880000 | Summer (2013) | Grab |
| 12 | Lake Dorothy-N1 | 37.32795 | -118.52881 | Spring (2013) | Grab |
| 13 | Lake Dorothy-N1m | 37.545000 | -118.882000 | Summer (2013) | Grab |
| 14 | Lake Dorothy-S | 37.536330 | -118.881548 | Spring (2013)<br>Spring (2014)<br>Summer (2013) | Snow (wet and dry), Grab<br>Snow (wet and dry)<br>Grab |
| 15 | Huntington Lake | 37.192113 | -119.200335 | Winter (2015-2016) | Snow (wet and dry) |
| 16 | Kaiser Pass | 37.291390 | -119.102580 | Winter (2015-2016) | Snow (wet and dry) |
| 17 | Lake Crowley-S | 37.58600 | -118.74200 | Spring (2012)<br>Spring (2013)<br>Winter (2013-2014)<br>Spring (2014) | Grab<br>Grab<br>Snow (wet and dry)<br>Snow (wet and dry) |
| 18 | Little Lakes Valley | 37.42273 | -118.75413 | Spring (2014)<br>Winter (2013-2014) | Snow (wet and dry)<br>Snow (wet and dry) |
| 19 | McGee Creek | 37.547456 | -118.819382 | Winter (2015-2016) | Snow (wet and dry) |
| 20 | Convict Lake-E | 37.584976 | -118.865404 | Spring (2013) | Water |
| 21 | Lower Convict Creek | 37.618616 | -118.822654 | Winter (2012-2013)<br>Winter (2013-2014) | Atmosphereic<br>Atmosphereic |
| 22 | Convict Lake-N1 | 37.595 | -118.853 | Spring (2012)<br>Summer (2012)<br>Winter (2012-2013)<br>Summer (2013) | Grab, Water<br>Grab<br>Grab, Water<br>Grab |
| 23 | Convict Lake-W | 37.588117 | -118.865433 | Winter (2012-2013)<br>Winter(2013-2014)<br>Summer (2013) | Atmosphereic<br>Atmosphereic<br>Grab |
| 24 | Morgan Lake drainage | 37.38694 | -118.73944 | Summer (2013)<br>Summer (2013) | Grab<br>Deposition |
| 25 | Upper Morgan Lake-E | 37.38806 | -118.74306 | Summer (2013) | Grab |
| 26 | Upper Morgan Lake-N | 37.38913 | -118.74421 | Summer (2013) | Grab |
| 27 | Upper Morgan Lake-W | 37.390170 | -118.749040 | Summer (2013) | Deposition, Grab |
| 28 | Upper Morgan Lake drainage | 37.38464 | -118.72893 | Summer (2013) | Deposition |
| 29 | Morgan Creek | 37.384640 | -118.728930 | Summer (2013) | Deposition |
| 30 | Lower Morgan Lake-E | 37.38472 | -118.72972 | Summer (2013) | Grab, water |
| 31 | Lower Morgan Lake-N | 37.38667 | -118.73278 | Summer (2013) | Grab |
| 32 | Lower Morgan Lake-W | 37.38600 | -118.73600 | Summer (2013) | Grab, Water |
| 33 | Mosquito Flats | 37.435 | -118.74723 | Summer (2015) | Deposition |
| 34 | Paiute Pass-1w | 37.24643 | -118.71417 | Summer (2015) | Deposition |

| | | | | | |
|---|---|---|---|---|---|
| 35 | Paiute Pass-2w | 37.2476 | -118.71415 | Summer (2015) | Deposition |
| 36 | Ranger Station 4E | 37.55978 | -118.67842 | Summer (2015) | Deposition |
| 37 | Shaver Lake | 37.145748 | -119.295026 | Winter (2015-2016) | Snow (wet and dry) |
| 38 | Snow Park-Kaiser Pass | 37.256612 | -119.167250 | Winter (2015-2016) | Snow (wet and dry) |
| 39 | Upper Little Lakes Valley | 37.39893 | -118.75628 | Winter (2013-2014) | Snow (wet and dry) |

**Table 1:** Sampling sites and dates, GPS points and type of samples used during the study.

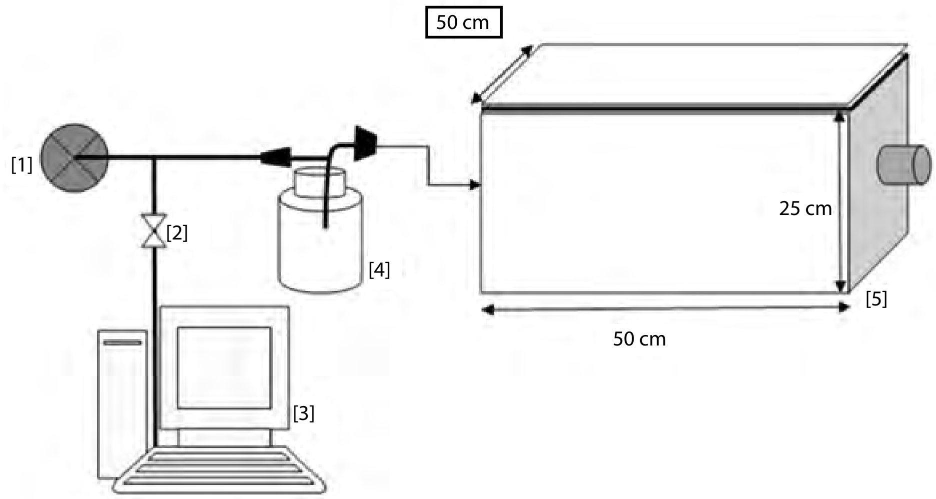


**Figure 5:** Snow chamber schematic: [1] compressed air supply [2] Pitot tube [3] monitor for Pitot tube [4] 50 mL glass nebulizer with 4NP solution [5] gasket sealed metal chamber with exhaust port (port diameter=1 cm).

Each sample was vacuum filtered through a Milli-poreTM filtering apparatus with a pre-weighed 55 mm diameter Whatman-Schleicher and Schuell methyl cellulose filter paper with a pore size of 0.45 µm. The filters were pre-dried at 110°C to remove excess moisture and left to sit for 24 h before being weighed again. Water, dust and snow samples were extracted in triplicates using 100 mL of hexane. All samples were then condensed from 300 mL to 10 mL on an Organomation Associates, Inc. Kuderna-Danish apparatus. Samples were then blown over with nitrogen gas to concentrate them down to a final volume of 1 mL.

Samples were analyzed via gas chromatography-mass spectroscopy. All samples were run on a Varian 431-GC and a Varian 220-MS with an ion trap mass analyzer by the following method: Using a splitless injection, the injector temperature was set at 250°C with a helium carrier gas flow of 1 mL/min on a 30 m × 0.25 mm DB-1MS column (Agilent). The column temperature began at 50°C and was held constant for the first 3.5 min of the run. The temperature was then ramped at a rate of 10°C/min up to a maximum of 275°C where the temperature was held constant for five minutes for a total run time of 36 min. All isomers of nonylphenol under this method had a retention time between 18 and 19 min. The mass detection range was set from m/z 50 to 600. The characteristic fragments of 4NP, created by electron ionization, were seen at mass to charge ratios of 107, 121, 135, and 149. As described by Wheeler et al., the simultaneous presence of these mass charges indicated the presence of the estrogenic isomer of NP, shown in Figure 1 [21]. The area under these characteristic peaks was integrated using the integration produced by the software. Samples were taken in duplicate and analyzed in triplicate. Hexane blanks were run every tenth sample. Five point calibration curves were constructed and assessed by evaluating regression model fit ($R^2$), calculating the percent error at each concentration level [22]. The average $R^2$ value was 0.995. An internal standard was used for all sample analysis. A stock solution of 4.00 µg/mL 1,4-dichlorobenzene in hexane was used as an internal standard (IS) for all sample analyses. Each 1.00-mL sample extract was spiked with 10.0-uL of IS stock resulting in a final concentration of 40.0 µg/mL of the IS. The internal standard eluted at 8.3 minutes [23].

## Data acquisition and processing

**Pesticide use:** Total pounds of pesticide active ingredients reported in each county and rank during 2013 and 2014. California Department of Pesticide Regulation, CDPR. Pesticide Use Report; 2014 [24]. The report table provided was compiled into a spreadsheet and joined to the county polygons to geographically represent the distribution of pesticide use per county in 2013 and 2014.

**Temperature:** 30 year (1981-2010) normal mean temperature data (200 meter grid) was downloaded from PRISM Climate Group Northwest Alliance for Computational Science and Engineering (NACSE), based at Oregon State University for December, January, February and March [25]. Using ArcGIS Spatial Analyst, we generated an average 30-year normal mean temperature for our winter study season (December through March). These mean temperature cell values were then re-scaled from 1-10 (low-high risk) with an exponential transformation using ArcGIS's Rescale by Function tool.

**Topographical shielding:** A topographical shielding area grid was generated by creating a point feature class attributed with high, medium, and low shielding values assigned using Equation 2. Using ArcGIS, we then interpolated a raster surface from the points using the Inverse Distance Weighted technique using the ridgeline as an input barrier [26]. The interpolated surface was then re-scaled from 1 to 10 with an exponential transformation using ArcGIS's Rescale by

Function tool. 4NP and topographical shielding was found to have an exponential function in earlier work.

**Ridgeline:** Linear boundaries of the hydrologic unit 'Regions' (level 1 watersheds) from the USGS National Hydrography Dataset (NHD) were used to represent ridgelines [27]. These boundaries were used as barrier for the surface interpolation of the mountain shield areas.

**Wind:** Estimates of *annual average wind resource* provided by the National Renewable Energy Laboratory (NREL) were used to represent the wind factor of the model [28]. This dataset assigns 'wind power classes' based on readings from hubs at 50-meters above surface. While the source wind speed data is not freely available, the NREL provides information regarding how to estimate wind speed based on the assigned 'wind power class'. State-level polygon shapefiles for California and Nevada were merged and converted to raster dataset with a cell size of 200 m. According to the metadata, the source datasets were maintained as rasters with a resolution of 200 m, so no spatial resolution was lost in this conversion. The raster values were re-scaled linearly from 1 to 10 using ArcGIS's Rescale by Function tool.

**Aggregate risk:** An aggregate risk surface was generated using weighted summation and applying equal weights to the 3 factors (33%).

## Results

Sierra Nevada snow pack has been tested for the presence of 4NP from 2012-2016. The dust particulate concentrations and snow water concentrations were considered separately but show similar patterns of concentration moving from west to east away from the Central Valley. The winter average concentration for all years studied was 1.9 (± 1.39) µg/kg taking both west and dry deposition into account; for the east side of the Sierra crest the average was 0.569 (± 0.41) µg/kg. Distribution patterns on the eastern slopes show the highest concentrations appearing at the lower elevations and the lowest concentrations or no 4NP near the Sierra crest. The distribution patterns of 4NP concentrations on the western slopes showed a decrease approaching the Sierra crest (Figure 6). There are several explanations for this trend on the west side of the Sierra. The adiabatic cooling of clouds often drive precipitation as higher elevations push clouds higher. This foments rain out of aerosols on the lower slopes, thus showing increased concentrations at lower elevations.

The east side distribution patterns were discussed in Lyons et al. as a function of windblown dust deposition. The shielding effect of steep headwalls and lee eddy currents in wind prevent even deposition across east-facing canyons in the Sierra; however, other topographically related features affect 4NP distribution as well.

At higher elevations, snowflake size and wind speed may have an effect on the deposition of 4NP. To determine this, the snow chamber was used to examine the effect of increased wind speed and snowflake diameter on deposition. Comparing six different snow diameters from 0.1 to 2 mm showed that the larger diameter snow retained more aerosolized 4NP (Figure 7a). However, after a diameter of 1 mm, the effect became nonlinear. The adsorption isotherm follows the Langmuir model, which would indicate that surface adsorption is primarily responsible for retention of 4NP (Figure 7b). A plot of 1/concentration ($ppm^{-1}$) versus 1/diameter ($mm^{-1}$) is linear with an $R^2$ value of 0.986, demonstrating a Langmuir type relationship. Snow presents a large surface area due to its complex crystal patterns; binding sites on the surface of snowflakes becomes limited by the lower surface area to diameter ratio in larger size snowflakes [29]. This model assumes that a monolayer of 4NP defines the maximum allowable adsorption on snow.

Studies have shown that larger snow particles tend to form at higher temperatures [30]. Snowflakes increase in size as temperatures warm due to dendritic growth and aggregation. Maximum snowflake sizes are at temperatures that are slightly warmer than 0°C. Since lower temperatures are frequently associated with higher elevations, the expectation would be to see greater accumulation of 4NP in the snow pack at lower elevations. Empirical data supports this as Figure 6 would indicate.

The effects of wind speed were also considered. Using the snow chamber with a constant snowflake size of 0.5 mm, 4NP was introduced into the chamber at variable wind speeds from 1 m/s to 25 m/s. Increased wind speeds were related to a decrease in 4NP deposition (Figure 8). This is as expected since deposition velocity is inversely related to wind speeds [31]. Orographic uplift and subsequent air mass cooling create a pressure imbalance towards mountain ridgelines and generates high winds [32]. High winds and lower deposition rates correspond with earlier findings that less 4NP is deposited near the ridgeline of the Sierra Nevada crest [18]. Earlier research also suggests that the ridgeline and head wall of a mountain crest create a lee eddy current that prevents deposition directly behind the head wall. This additional information suggests that topographical shielding plays a role in conjunction with wind speeds at higher elevations.

Earlier work identifies dust as a transport vehicle for 4NP from the Central Valley into the Sierra Nevada. It was originally postulated that the dust concentrations within the snow may serve as a proxy for 4NP concentration. However, this is not necessarily the case. The mass of particles in the snow pack was not directly related to the concentration of 4NP within the snow. 4NP concentration was plotted against particulate concentration within snow to yield a correlation coefficient of 0.512. The low correlation coefficient indicates other sources of dust, not a singular source of dust blown in from the Central Valley. To test this theory, two adjacent snow plots measuring 1 $m^2$ were staked out and measured for initial dust concentration. One plot was covered for two weeks in duration. After two weeks with no additional snowfall, dust particulate content was measured in both plots. Dust increased in the uncovered plot by 35% of the original mass while the uncovered plot showed a 5% increase due to snow melt. So while dust-borne 4NP is clearly a contributor to the total 4NP load in a region, other factors must be considered as well.

The amount of snow received during the winter has a strong negative correlation with the amount of 4NP in the snow pack. For the four years studied, the average snow water and dry deposition concentrations of 4NP were averaged and evaluated relative to the annual average amount of snow. A correlation coefficient of -0.85 was found between 4NP concentrations and the annual average snow depth (Figure 9). While the amount of pesticide applied to crops is generally consistent from year to year, the amount of precipitation changes drastically during drought years. It is likely that snow accumulation has a diluting effect on the concentration of 4NP present. In 2013 to 2015, California experienced a severe drought where snow pack was at 5% of its typical value in the Sierra Nevada. It is likely that the reduced snow pack acts as a 4NP reservoir for both aerosol and dust forms. This has potentially serious ramifications when spring snow melt occurs. Higher concentrations in snow create a stronger pulse of 4NP in melt water, adversely affecting developing organisms downstream at a critical time in their life cycle. This effect may be especially pronounced in organisms stressed by drought.

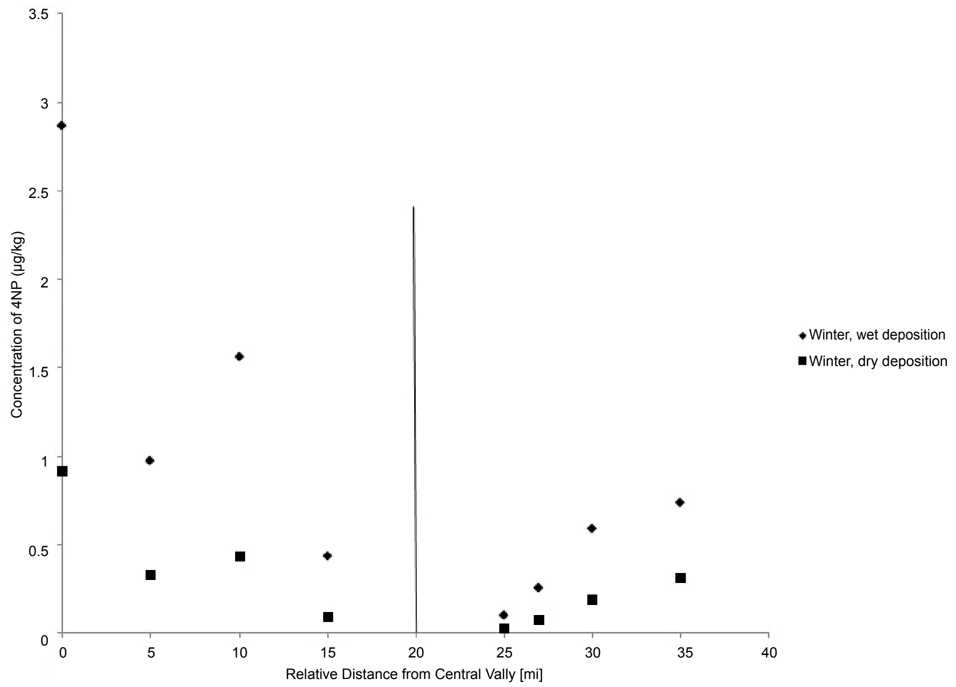


**Figure 6:** The distance from the Central Valley measured in miles and compared with the concentration of 4NP in snow water and dust particulates in snow in µg/kg. The line represents the Sierra Nevada divide into eastern and western facing slopes.

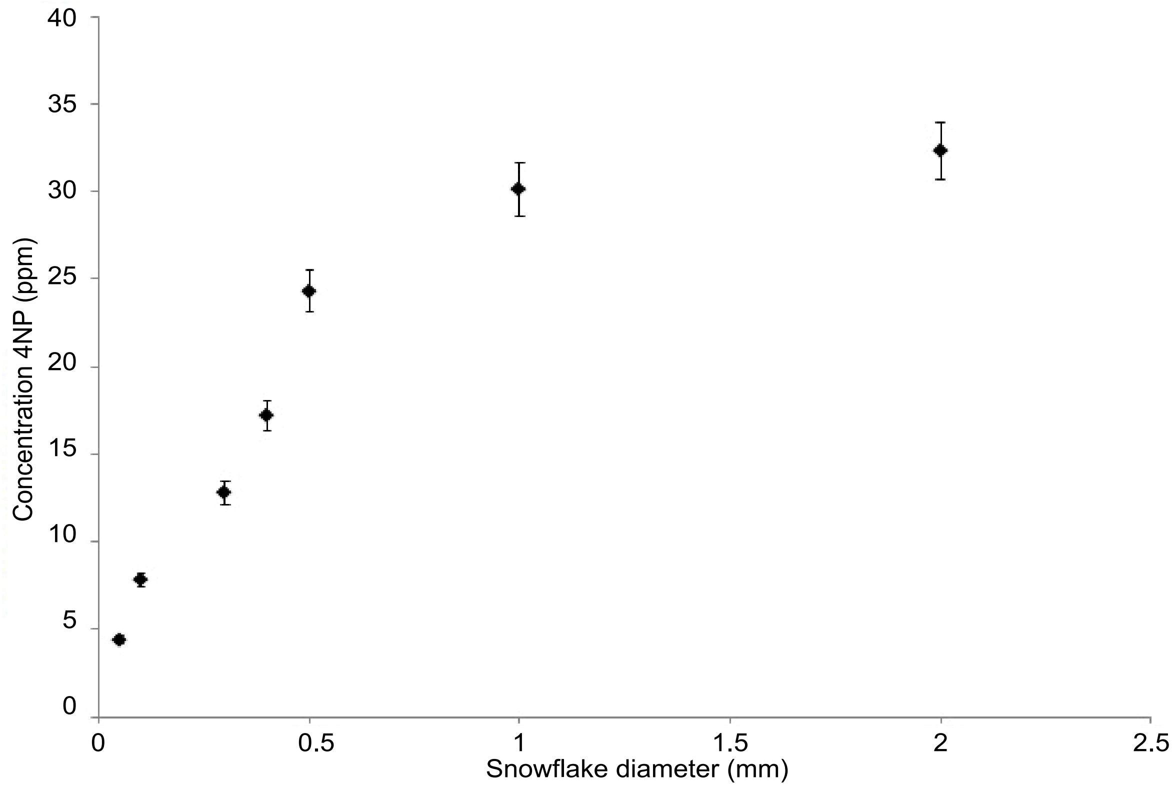


**Figure 7a:** The total concentration of 4NP deposited on snow pack with particles of variable diameter. 4NP was introduced by nebulizer at a rate of 1 m/s.

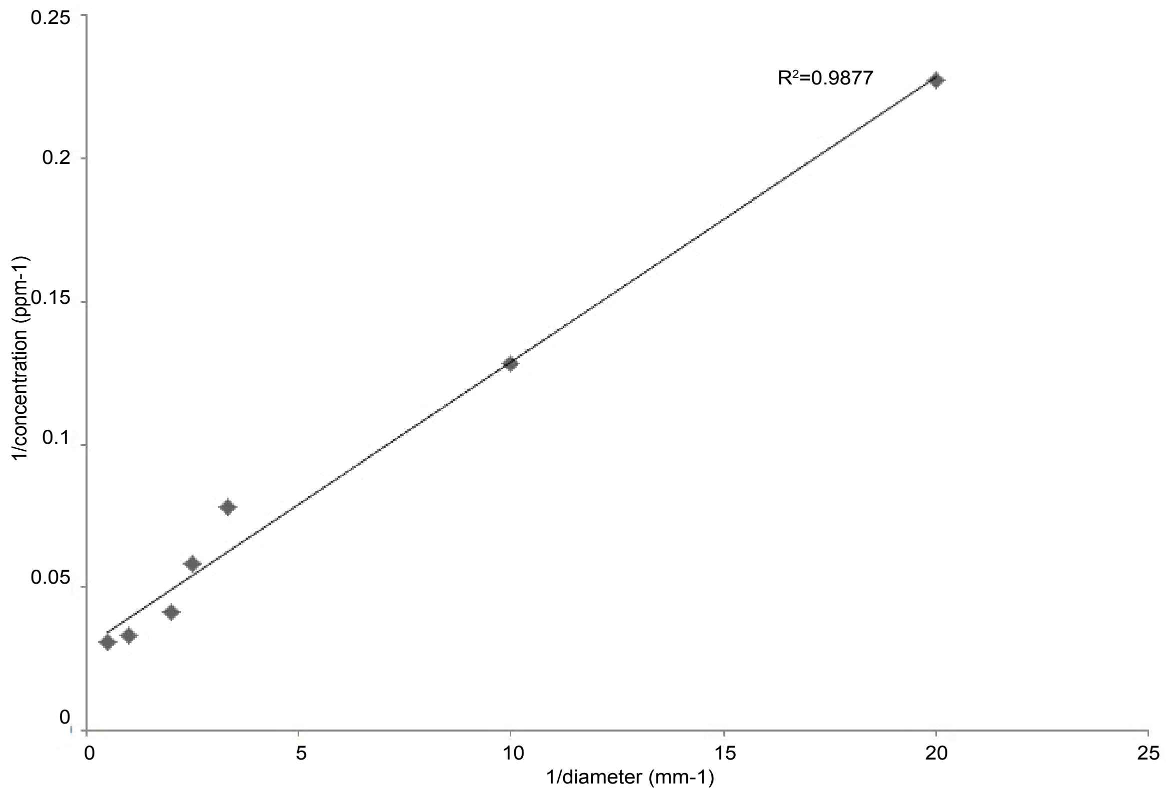


**Figure 7b:** A plot of 1/concentration (ppm$^{-1}$) versus 1/diameter (mm$^{-1}$) yields a linear relationship with an $R^2$ value of 0.987 indicates a reliance on surface site adsorption for 4NP deposition in snow.

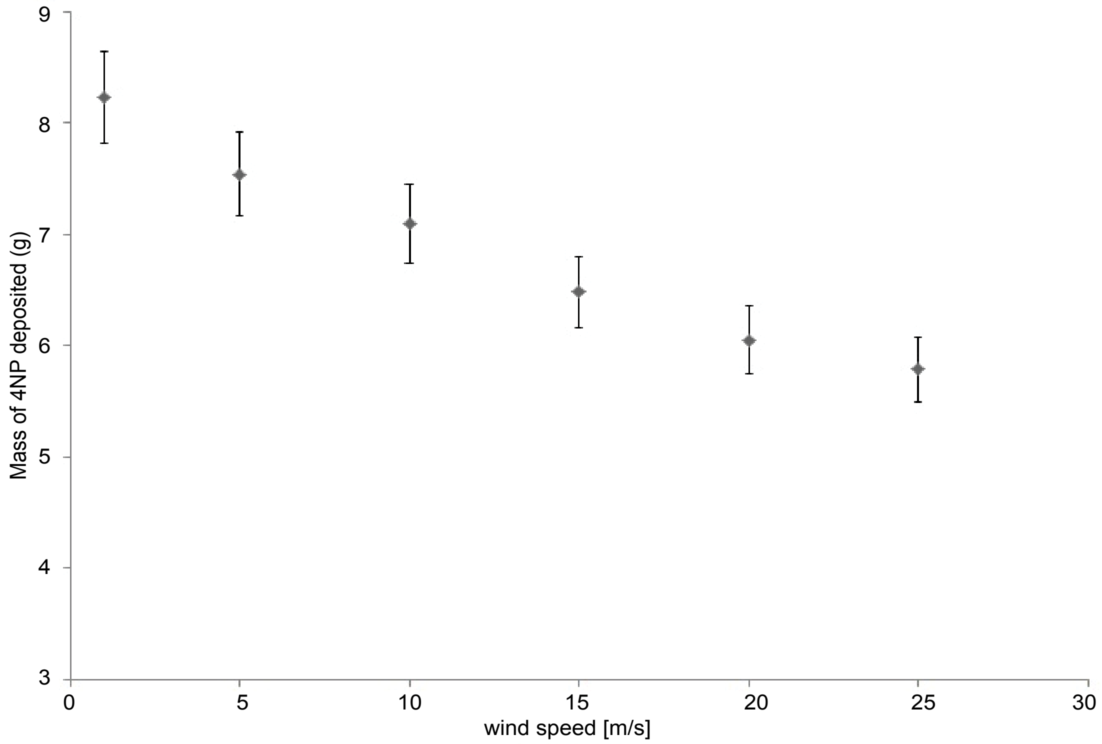


**Figure 8:** Snow chamber results of increasing wind speeds on 4NP aerosol deposition when snowflake size is held constant at 0.5 mm.

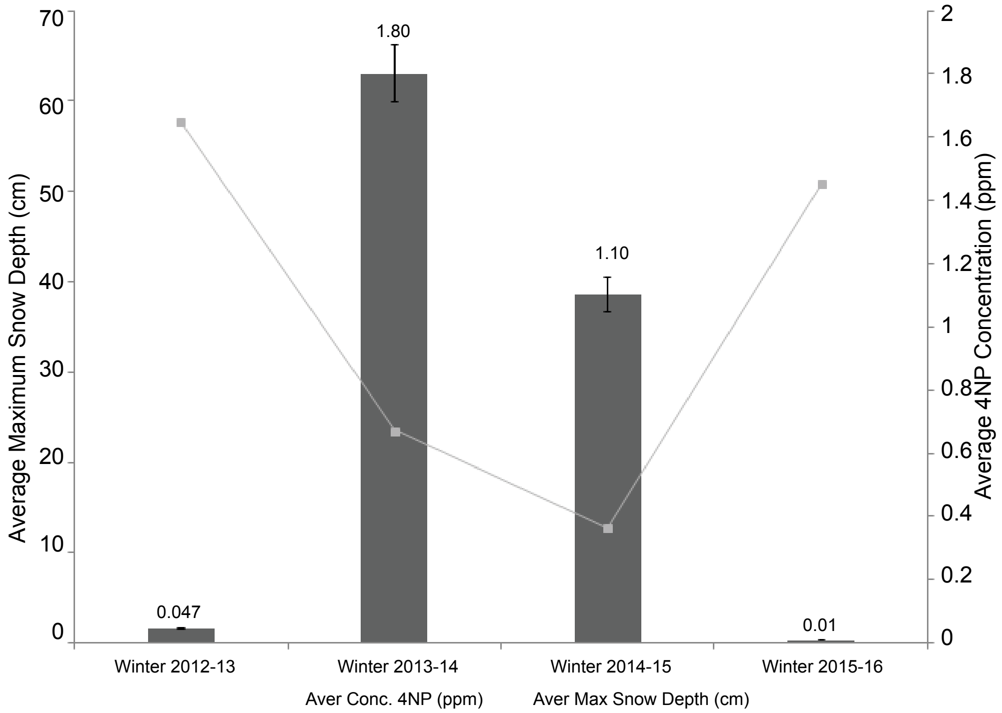


**Figure 9:** Atmospheric deposition samples analyzed by compartment show that summer concentrations of 4NP are compartmentalized differently than winter concentrations. Here the distance from the Central Valley is plotted against concentration of 4NP in µg/kg for dry and wet deposition.

Spatial analysis was performed on the Eastern Sierra Nevada to determine the relative risk of 4NP exposure (Figure 10). Risk was evaluated based on snow particle size, wind speeds, and topographical shielding. A low risk area was considered to have lower temperatures and therefore smaller snow particle sizes, a high degree of topographical shielding, and high wind speeds. High risk areas have less topographical shielding, lower wind speeds, and higher temperatures which create larger snowflakes. By these criteria, low risk regions lie predominantly along the ridgeline on the east side where the Sierra up tilt creates high winds and steep slopes. High risk of exposure exists at greater distances from the ridgeline where topography levels out and wind speeds decrease. The temperature in these regions remains warmer during the winter months, which indicates larger snowflakes are more likely to form, and 4NP accumulation would be favored. Interesting pockets of high risk can be seen locally, for example between Carson City and South Lake Tahoe. These regions are minimally shielded, but remain colder throughout the year relative to warmer desert. They have lower wind speeds, however, which favor more deposition, making them on the balance more likely to accumulate 4NP in snow pack. The geospatial model agrees with the empirical data found thus far, although certainly more sampling could be done in the localized areas of higher risk. Additionally, the model would need to be run in other locations to determine the model's global applicability. Future work would investigate this potential.

## Conclusions

4-nonylphenol is a known endocrine disruptor that makes up 10% or more by volume of many pesticides. The spread of 4NP from the application site is governed by prevailing wind direction, topography and the physical and chemical characteristics of 4NP. It

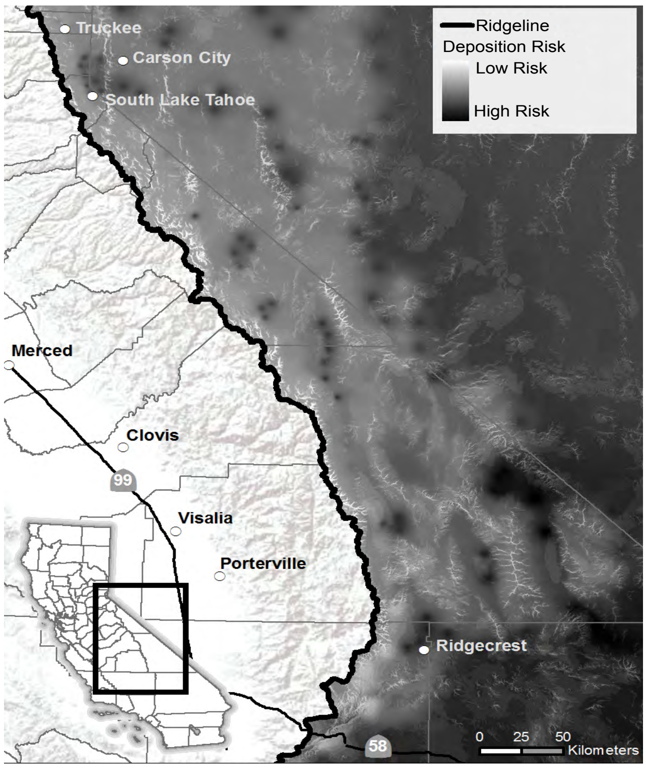


**Figure 10:** The snow depth maximum (cm) per year and the concentration of 4NP in snow water and dry deposition (µg/kg). The resulting inverse correlation coefficient was -0.85. Error bars for 4NP samples show CI 95% for an n-value of 15 per each sampling year.

has been determined that 4NP is capable of long range transport, more specifically crossing physical boundaries such as mountain ranges. The proximity of the agricultural hub of the Central Valley, California, USA to the Sierra Nevada Mountains makes an interesting case study of 4NPs distribution potential and its ability to accumulate in snow packs. Other regions with similar geography such as the Interior Cordilleran located in southcentral British Columbia which lies upwind of the Canadian Rocky Mountains, or the agriculturally rich region of northern Italy and its upwind position relative to the Alps may have similar 4NP deposition patterns that could negatively affect fragile montane ecologies [33]. Snow is in effect a winter reservoir for 4NP. This is concerning since spring snow melt pulses could potentially send bursts of 4NP downstream where organisms are developing. Higher concentrations become more pronounced during drought years when less snow creates more concentrated 4NP in the snow pack, leaving organisms already under stress from drought more susceptible to the effects of 4NP.

Dust serves as a transport vehicle for 4NP over physical boundaries such as the Sierra Nevada as was discussed in previous studies by Lyons et al. However, aerosolized 4NP also factors into total accumulation. Several physical and chemical parameters were considered in this study that would affect both wind-born dust and aerosol distribution. Topographical shielding provides shelter to regions in the Eastern Sierra on a micro scale. Additionally, wind speed correlated inversely with deposition. The size of snowflakes may also have a bearing on whether aerosolized 4NP will adhere to them. Laboratory simulations showed a Langmuir-type isotherm which suggests that surface area regulates potential adsorption to the snowflakes. Since snowflake size is temperature dependent, temperature was used as a proxy for snowflake size in the final analysis of deposition potential.

Spatial analysis of the Eastern Sierra Nevada was performed by overlaying temperature, wind and shielding profiles. The result was a predictive geospatial model for regions that are at high risk for 4NP deposition and accumulation. The model showed less deposition along the Sierra ridgeline and gradually increasing with more distance between the apex of the mountains and the deposition site. The model was especially useful in showing small scale regions that may be subject to several conflicting factors affecting deposition. The distributions shown in the model agreed well with the empirical data collected. Using these methods, a predictive model based on measureable physical features of a region could potentially be used at any location. A similar model for the Western Sierra Nevada would involve determine the controlling factors for deposition on the west side of the mountains. This is currently under investigation.

A predictive model for 4NP is useful for both policy makers and ecologists. As the European Union, the Canadian government, and the United States Environmental Protection Agency consider regulations surrounding the use and application of 4NP, it is helpful to know the areas that most at risk for exposure.

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