

# Dry Deposition of Aerosol Nitrogen and Organic Carbon in the CAP Area

## Background and Motivation

In the Central Arizona – Phoenix (CAP) area, high emissions of nitrogen and organic carbon species cause an increase in atmospheric aerosol formation. These aerosols are eventually removed from the atmosphere by wet or dry deposition, with dry deposition often accounting for more than half of the total. Deposited materials augment the available pools of nitrogen and carbon for soil ecosystems, possibly altering nutrient cycling in urban and near-urban deserts where plant and soil systems may respond differently to external inputs.

## Inferential Flux Estimates

The inferential method can be used to estimate aerosol dry deposition fluxes from measured gas and aerosol concentrations and modeled deposition velocities

$$F = -v_d C$$

The deposition velocity is estimated using a simple parameterization of experimental meteorological measurements to determine atmospheric transport characteristics (Slinn, 1982; Zhang et al., 2001).

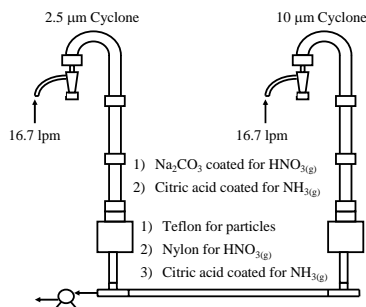
$$v_d = v_g + \frac{1}{(R_a + R_b)}$$

where  $v_g$  = gravitational settling velocity (function of particle size)

$R_a$  = aerodynamic resistance to deposition (function of atmospheric conditions and terrain)

$R_b$  = surface resistance to deposition (function of terrain, particle size and atmospheric conditions)

Filter and denuder bank samplers are used to measure the concentration of gas (ammonia and nitric acid) and particle phase nitrogen (ammonium-nitrate) without introducing sampling artifacts known in filter collection methods (Hering and Cass, 1999). The sampler consists of two sampling trains to estimate concentrations of particulate matter smaller than 2.5  $\mu\text{m}$  ( $\text{PM}_{2.5}$ ), particulate matter smaller than 10  $\mu\text{m}$  ( $\text{PM}_{10}$ ), and gas phase acids and bases. Each sampling train has a cyclone separator to remove particles larger than the designed cut point. These are followed by annular denuders to remove gas phase materials entering the sampler which could lead to overestimation of aerosol pollutant concentrations. Filter packs with Teflon filters are used to collect particle phase materials. Two backup filters are used to collect gas phase ammonia and nitric acid that can dissociate from ammonium-nitrate particles collected on the first filter and cause underestimation of the particle phase pollutant concentrations.



Schematic diagram of the filter and denuder bank sampler.

## Experimental

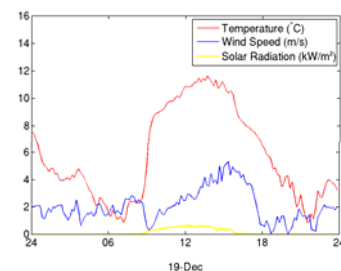
As part of the Organic Carbon and Nitrogen Deposition (CNDep) project, fifteen sites were selected for plant growth and total relative nitrogen deposition measurements. The sites are evenly divided along the dominant air-flow gradient through the CAP area: upwind, core, and downwind of Phoenix. Sites from each type were chosen for additional measurements, including meteorological monitoring and filter & denuder sample collection to estimate deposition using the inferential method. These sites are located at the White Tanks Regional Park (WTM), Desert Botanical Garden (DBG), and Lost Dutchman State Park (LDP).



Location of three sites along the air-flow gradient through the CAP area. Meteorological and aerosol concentration data are collected to estimate gas and particle deposition fluxes. (Image © Google Earth)

## Results and Discussion

Meteorological data, including temperature, wind speed, wind direction, solar radiation, relative humidity, and precipitation, have been measured and recorded at the Lost Dutchman State Park since May 2005. This data provides information about atmospheric conditions that drive air-surface exchange of pollutants which can be used to predict dry deposition fluxes.



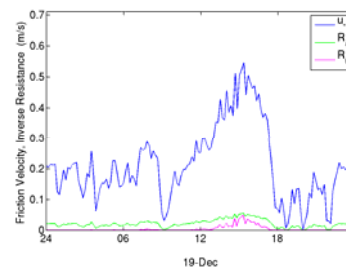
Example meteorological data from the Lost Dutchman State Park site on 19 December 2006. Temperature, wind speed, and incoming solar radiation can be used to estimate the turbulent state of the atmosphere in order to predict dry deposition of gases and aerosols.

## Acknowledgements

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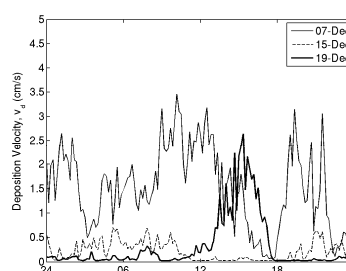
## Results and Discussion

Data collected from the weather stations is then used to predict the parameters necessary to estimate aerosol deposition. The friction velocity,  $u_*$ , is the magnitude of the vertical transport of horizontal momentum and is estimated from its relationship to the measured wind speed. The aerodynamic resistance,  $R_a$ , is the resistance to transport by turbulence above the surface and can be calculated from the friction velocity and measured incoming solar radiation. The surface resistance,  $R_b$ , is the resistance of the layer of air very near the deposition surface and can be calculated from the friction velocity, temperature, and aerosol physical properties.



Example calculated deposition parameters from 19 December 2006. The friction velocity is calculated from the measured wind speed, the aerodynamic resistance and surface resistance are then estimated from the friction velocity, temperature, incoming solar radiation, and aerosol physical properties.

Deposition velocities were estimated for  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  using the parameters calculated from the meteorological data and the Slinn model.  $\text{PM}_{10}$  values are higher because of their larger settling velocity and  $\text{PM}_{2.5}$  aerosols are mostly transported by atmospheric turbulence.



Example calculated  $\text{PM}_{2.5}$  deposition velocities for three days of meteorological measurements at the Lost Dutchman State Park site.  $\text{PM}_{10}$  deposition velocities (not shown) were also calculated and are slightly higher due to higher settling velocities.

## References

- Slinn, W.G.N., 1982. Predictions for Particle Deposition to Vegetative Canopies, *Atmos. Environ.*, 16, 1785-1794.
- Hering, S. and Cass, G., 1999. The magnitude of bias in the measurement of  $\text{PM}_{2.5}$  arising from volatilization of particulate nitrate from Teflon filters, *J. Air Waste Manage.*, 49, 725-735.
- Zhang, L., Gong, S., Padro, J., and Barrie, L., 2001. A Size-Segregated Particle Dry Deposition Scheme for an Atmospheric Aerosol Module. *Atmos. Environ.*, 35, 549-560.

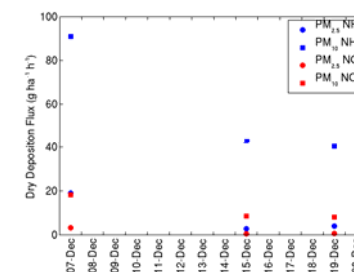
## Results and Discussion

Filter and denuder samples collected at the Lost Dutchman site were analyzed for ammonium and nitrate after aqueous extraction. High concentrations of ammonia and ammonium-nitrate aerosols are typical of the CAP area in winter time.

### Typical concentrations of ammonium and nitrate from gas and particle phase pollution.

		Concentration ( $\mu\text{g}/\text{m}^3$ )
$\text{PM}_{2.5}$	$\text{NH}_4^+$	35
	$\text{NO}_3^-$	6.0
$\text{PM}_{10}$	$\text{NH}_4^+$	60
	$\text{NO}_3^-$	12
Gas Phase	$\text{NH}_3$	9.5
	$\text{HNO}_3$	7.5

Dry deposition fluxes were then calculated from the filter & denuder measurements and deposition velocities parameterized from co-located meteorological observations. As expected, the high concentrations of ammonia and ammonium-nitrate aerosols lead to higher dry deposition fluxes. The estimated mean  $\text{PM}_{10}$  deposition velocity on 07 December was significantly higher due to increased atmospheric turbulence, resulting in higher deposition fluxes.



Dry deposition fluxes calculated from measured concentrations and modeled deposition velocities at the Lost Dutchman State Park.

## Conclusions

Meteorological observations at the Lost Dutchman State Park were used to estimate the deposition velocities of  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  from parameterizations of atmospheric transport variables and models which also incorporate terrain characteristics and aerosol physical properties (Slinn, 1982). Filter & denuder samplers were used to collect aerosol ammonium-nitrate, ammonia gas, and nitric acid gas during December 2006. Dry deposition flux estimates calculated from the inferential method vary with atmospheric conditions and future measurements at the other CNDep sites are expected to vary due to air flow and concentration gradients across the CAP area. Dry deposition estimates along with plant and soil measurements from the CNDep sites along the upwind, core, and downwind gradient can be used to evaluate hypotheses about ecosystem response to anthropogenic inputs in the CAP area.

## Future Work

- Measure pollutant concentrations at upwind and core monitoring sites.
- Estimate dissolved organic carbon fluxes from filter samples.
- Compare inferential flux estimates to ion-exchange collectors deployed at 15 CNDep sites.