# Emissions Approaches and Uncertainties - Crop



# Uncertainties in the Current Knowledge of Atmospheric Trace Gases Associated with Cropping Systems in the U.S.

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#### Abstract

Emissions of C- and N-derived trace gases from agriculture-related activities have a significant influence on the nation's air quality. Approximately 80 different crop species are grown in the US in widely differing geographic areas and climatic conditions. Other crop growth regulating factors consist of differences in soil types, moisture availability, nutrients and management practices. The crops grown include both C3 and C4 species, and a multitude of cultivars. Although the majority of cultivated acreage in the US is planted with only about ten major crop species, uncertainties associated with trace gas emissions arise from: (1) limited data availability and consequently inaccurate estimates due to the large temporal and spatial variability in trace gas (principally CO<sub>2</sub>, CH<sub>4</sub>, NH<sub>3</sub> and N<sub>2</sub>O) composition and amounts released from agricultural activities, (2) characteristics of pollutant emissions from animal feed-lots (including emissions from dairy animals) and their geographic distribution and (3) our limited understanding of semi-volatile organic compounds (SVOCs) associated with agriculture. SVOCs range in their composition from relatively simple acids to complex organo-chlorines and pesticides. These compounds exist in both particle (solid and liquid) and gas phases, with a highly variable rate of transition from one phase to the other, as governed by their chemical structure, receptor characteristics and by environmental factors.

While emission issues are of concern, so is atmospheric wet and dry deposition of N, mineral nutrients and organic compounds to cropping systems that can, in turn, have feedback effects on trace gas emissions. There are many gaps in our understanding of these processes. At present, a number of research groups are investigating agriculture-related emissions of trace gases (primarily CO<sub>2</sub>, CH<sub>4</sub>, NH<sub>3</sub> and N<sub>2</sub>O). However, there are advantages and limitations associated with the various methodologies used for quantifying emissions and deposition (e.g., flux measurements, use of continuous monitoring versus passive sampling of the air, sample collection and chemical analyses). There is also a frequent lack of sufficient number of monitoring sites (sample size) to satisfy the requirements of spatial mapping of the measured variable with confidence. Other considerations include: (1) the effects of increasing concentrations of atmospheric O<sub>3</sub> and  $CO_2$  on crop production, and the potential changes in management practices of cropping systems, (2) the changing use of N fertilizers in agriculture and consequent alterations in atmospheric  $NO_x$ ,  $N_2O$  and  $NH_3$ emissions and deposition, and (3) changing air temperature effects on crop production and also its impacts on trace gas emissions, particularly molecules other than CO<sub>2</sub>. Overall, studies are needed at various scales with better-coordinated approaches to sufficiently quantify temporal and spatial trends in trace gas emissions and deposition and their relationships to agricultural practices in the US, in a changing global climate.



# Nitrous Oxide Emissions in the Northern Great Plains as Influenced by Cropping Systems and N Fertility

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#### Abstract

Nitrous oxide is a powerful greenhouse gas and contributes to degradation of ozone in the atmosphere. Although agriculture has been identified by the Intergovernmental Panel on Climate Change (IPCC) as the major anthropogenic source of N<sub>2</sub>O emissions, field measurements of N<sub>2</sub>O are limited for agricultural systems, particularly in the semi-arid Northern Great Plains (NGP) region. This study was undertaken to learn more about N<sub>2</sub>O seasonal emission patterns and levels from two-year cropping systems adapted for the Northern Great Plains, and to determine if the IPCC methodology for estimating fertilizer N induced N<sub>2</sub>O losses is accurate for this region. Three no-till (NT) cropping systems (fallow-wheat, wheat-wheat, pea-wheat), one conventional till (CT) system (fallow-wheat) with varying N fertility regimes and one perennial grass system (no fertilizer N applied) were sampled throughout the year using static chambers. Emission losses ranged from 169 to 1115 g N<sub>2</sub>O-N ha<sup>-1</sup> for the sampling period (22-March 2004 to 2-Feb 2006). Losses were greatest from the wheat-wheat rotations because of additional N fertilizer inputs. Inclusion of a legume in the rotation did not elevate emissions beyond that observed in wheat-fallow systems. Tillage did not greatly impact losses of N<sub>2</sub>O for the wheat-fallow systems (NT vs. CT). Emissions were episodic in nature though overall N<sub>2</sub>O emission activity was greatest during two distinct periods. The first period (10-wk) occurs immediately after application of N. The second period occurs during the winter when soil water-filled pore space exceeded 90%. These periods collectively accounted for 69 to 94% of total emissions. Fertilizer induced emissions of N<sub>2</sub>O ranged from 0.08 to 0.13% of applied N in 2004, to 0.51% of applied N in 2005. These emission rates are considerably below the IPCC 1.25% default value, and indicate that IPCC methodology greatly overestimates emissions for the Northern Great Plains.

#### Introduction

In recent years there has been an increased concern about the build-up of  $CO_2$  and trace greenhouse gases in the atmosphere. Nitrous oxide is one trace gas that has drawn particular attention because it is a potent greenhouse gas that is estimated to have a global warming potential 270 times that of  $CO_2$  (Duxbury et al., 1993). In addition, it has been implicated in the destruction of the ozone layer. Nitrous oxide is emitted from both anthropogenic and natural sources. Although global estimates of N<sub>2</sub>O emissions are quite variable, agriculture has been identified by the Intergovernmental Panel on Climate Change (IPCC) as the major (77%) contributor (Kroeze et al., 1999) to anthropogenic emissions.

Current IPCC methodology assumes 1.25% (referred to as the IPCC "default value") of all N inputs from commercial fertilizer, animal manure, decomposition of plant residues, and biological N fixation is lost directly as N<sub>2</sub>O. This default value is applied uniformly to all regions, even though climates and production practices may differ. Given that N<sub>2</sub>O emissions are known to be affected by a multitude of environmental factors (e.g. precipitation, temperature, soil physical properties, and soil N and C pools) and management practices (e.g. cropping sequences, tillage, N fertilization rates) it seems likely there will be strong regional biases in the fraction of applied N lost as N<sub>2</sub>O. Current research in the semiarid Canadian prairies indicates that IPCC methodology may greatly overestimate actual N<sub>2</sub>O emissions (Lemke and McConkey, 2000; Lemke et al. 2003) from commercial fertilizer and biological N fixation (Rochette and Janzen, 2005). Comparatively little information exists on N<sub>2</sub>O emissions from neighboring regions in the United States, and it is not known whether the current IPCC methodology (IPCC, 1997) accurately applies to this region.

This study was undertaken to learn more about emission levels of  $N_2O$  from several cropping systems adapted for the semi-arid Northern Great Plains of the United States. It is part of a larger, ongoing study

that examines the impact of best management practices (BMP), including no-till and continuous cropping, on C sequestration. The work being done on N<sub>2</sub>O is being integrated with the studies on C sequestration to provide a more complete analysis of the effect of BMP in our region on greenhouse gases balances. The objective of this presentation will be to i) illustrate seasonal patterns of N<sub>2</sub>O emissions and periods of peak losses in several cropping systems; 2) estimate total season losses of N<sub>2</sub>O and fertilizer induced losses of N<sub>2</sub>O under these cropping systems; and 3) contrast field-measured losses of N<sub>2</sub>O against predicted N<sub>2</sub>O losses using IPCC methodology.

#### Methods

Nitrous oxide emission data reported here were collected from a long term cropping system being conducted at the Montana State University- Post Research Farm near Bozeman. The soil at the study site is classified as an Amsterdam silt loam (fine-silty, mixed, superactive, frigid Typic Haplustolls) with 8% sand, 65% silt, 27% clay, pH 8, and 2% organic matter in the surface 30-cm. The study consists of nine cropping systems (only 4 cropping systems will be mentioned here) main-plots (24.4 x 7.4 m) replicated four times in a random complete block design (Table 1). The site was managed as a single-phase cropping system study with only one phase of the rotation occurring in any one season. Treatments were divided into sub-plots representing moderate N, and high N fertility, plus an unfertilized 0 N control. Fertilizer N. in addition to starter N applications, was applied only during phases of the rotation where wheat was grown. The moderate and high N fertility rates were determined from spring soil samples to a 60-cm depth in 2004 and 2005. The fertilizer N rates were adjusted to provide 100 and 200 kg ha<sup>-1</sup> available N (soil  $NO_3-N$  + fertilizer N), respectively. Soil  $NO_3-N$  levels were determined in all sub-plots during the spring using established procedures (Mulvaney, 1996). During the 2004 season, fertilizer N was surface broadcast applied as urea to the winter wheat sub-plots on 13-April. Seeding of winter wheat occurred in September of the previous year (2003). In 2005, fertilizer N was band applied as urea to spring wheat at seeding (14-April). In 2006, winter wheat was seeded 30-September, 2005 and fertilizer N was band applied as urea. In all cases direct-seeding equipment with disc-openers for minimal disturbance was used to seed plot areas. Conventional tillage was performed in Treatment 1 with discs and cultivators equipped with sweeps.

Trt #	Cropping Sequence (2004-2005)			
1	winter wheat – fallow (conventional tillage)			
2	winter wheat – fallow (no-till)			
3	winter wheat – spring wheat (no-till) ¶			
4	winter wheat - spring pea (grain)(no-till)			
5	perennial grass and alfalfa to mimic CRP			
I winter wheat	gooded in the Sentember 2005			

¶ winter wheat – seeded in the September, 2005

Gas sampling was conducted using vented chamber techniques (Hutchinson and Mosier, 1981). The chambers were made of plexi-glass with insulated tops. Chambers covered 1000 cm<sup>2</sup> of soil surface and were placed between crop rows. Gas sample collection followed the accepted protocols of Lemke et al. (1998). Samples were collected from the head space during the early to mid-afternoon (13:00-15:00 h). Air-temperatures inside the chambers and below the soil surface (2.5 cm-depth) were recorded continuously with Onset (Onset Computer Corporation, Bourne, MA) temperature sensors and dataloggers. Soil cores (0-10 cm) were collected at all sampling events to determine volumetric water content and water-filled pore space. Gas samples from the headspace were collected with a 25 mL syringe and then transferred to pre-evacuated 13 ml exetainers. The concentration of N<sub>2</sub>O in the exetainer was determined using a gas chromatograph equipped with a  $^{63}$ NI electron capture detector. Nitrous oxide flux was estimated from the concentration change in the chamber headspace over a 60 min. collection period as described by Nyborg et al. (1997). Briefly, changes in concentration over time were assumed to be linear and were calculated by subtracting the time-zero (or background) concentration from the final concentration. Time-zero concentrations were calculated using the approach of Anthony et al. (1995). A

series of ambient air samples was collected at each sampling event. The mean of these samples was used as the time-zero concentration.

#### **Results and Discussion**

#### Precipitation

Annual precipitation amounts at the study site were close to the long-term averages for the two years. The distribution of precipitation by month followed the long-term norms during 2004 (Figure 1). Weather in 2005 was characterized by above normal precipitation in April, Oct., Nov. and Dec, and below normal precipitation in May.



Figure 1. Precipitation amounts and patterns at the study site, Bozeman, MT

#### **Emission Profiles**

Gas sampling was initiated in late-March 2004 and has continued through the present. Nitrous oxide emission profiles for this measured sampling period (March 2004-February 2006) are summarized by Figures 2-5 for the four cropping systems. In general, the greatest emission activity occurs over two distinct periods. The first period follows application of fertilizer N, or urea and lasts approximately 10 weeks for spring application events. During this period, emission activity is elevated above ambient levels and peaks approximately two to three weeks following the fertilization event. For fertilizer urea applied in the fall (i.e. 30-Sept, 2005) elevated emission activity lasted well into the early winter months. The second period occurs during the winter or at winter thaw events. Overall, emission activity was enhanced by N fertilization. Tillage (CT vs. NT) did not greatly impact emissions for wheat-fallow systems except during the winter thaw (2-wk period) and immediately following tillage events in the summer (< 1 week/tillage event). Cropping intensity affected emissions only to the extent that fertilizer N was applied. Wheat-pea rotations produced lower emissions (P < 0.05) than wheat-wheat in 2005, as peas were not fertilized with N in the second year of the rotation. Inclusion of legumes in rotation did not result in elevated emissions (P > 0.05) compared to fallow systems either during the growing season, or following harvest.

Elevated  $N_2O$  emission activity following N fertilization was believed to result primarily from nitrification of fertilizer N. Soil moisture contents at the field site were typically below 70% water-filled pore space, and outside the water content range where denitrification processes predominate. In addition,  $N_2O$  emission activity following application of urea and KNO<sub>3</sub> were compared at this field site in a related study. The results demonstrated that  $N_2O$  emission activity was relatively low following application of KNO<sub>3</sub> in contrast to urea (data not presented). During the winter denitrification processes may be occurring in addition to nitrification as soil water-filled pore space was >90% during thawing events. This occurred in late February to early March in 2005, and during the winter of 2005-2006. The importance of winter emissions may have been enhanced by application of N fertilizer in the fall.

#### Estimated N<sub>2</sub>O Losses

Estimated losses of  $N_2O$  for the examined cropping systems were generally modest in scale, ranging from 169 to 1115 g N ha<sup>-1</sup> for the 22 month sampling period. Nitrous oxide emissions significantly exceeded those observed from the perennial grass system (or CRP) for only the fertilized wheat-wheat system (Table 2). The fertilized wheat-wheat exhibited the highest emission losses due to additional N inputs needed over the full cropping sequence. The two primary periods of  $N_2O$  emissions, i.e. post-N application and winter, accounted for 69 to 94% of total emissions over the 22 month sampling period. Winter emissions for unfertilized plots ranged from 30 to 42% of total sequence emissions. While winter emissions for fertilized treatments accounted for 48 to 61% of total sequence emissions. Winter emissions during the winter, where soils remain unfrozen, highlights the importance of fall fertilization in determining N<sub>2</sub>O losses from cropping systems. Overall, our results suggest that new crop management strategies for the Northern Great Plains, such as no-till and inclusion of legumes in cropping systems, are secondary in importance to N fertilizer management practices such as N fertilization rate, timing (fall vs. spring) and methods of application (band vs. broadcast).



Figure 2. Nitrous oxide emission profiles over a winter wheat – fallow (CT) rotation at two levels of N fertility (low=no fertilizer, high = 200 kg ha<sup>-1</sup> available N). Arrows indicate date of fertilizer N application. Bozeman, MT. Mean of four reps.



Figure 3. Nitrous oxide emission profiles over a winter wheat – fallow (no-till) rotation at two levels of N fertility (low=no fertilizer, high = 200 kg ha<sup>-1</sup> available N). Arrows indicate date of fertilizer N application. Bozeman, MT. Mean of four reps.



Figure 4. Nitrous oxide emission profiles over a winter wheat – spring wheat (no-till) rotation at two levels of N fertility (low=no fertilizer N; high = 200 kg ha<sup>-1</sup> available N). Arrows indicate date of fertilizer N application. Bozeman, MT. Mean of four reps.



Figure 5. Nitrous oxide emission profiles over a winter wheat – spring pea (no-till) rotation at two levels of N fertility (low=no fertilizer N high = 200 kg ha<sup>-1</sup> available N). Arrows indicate date of fertilizer N application. Bozeman, MT. Mean of four reps.

Trt#	Cropping system	N level	Emission levels			
		application events over 22 months)	10 wks post N application	Winter	Total	
			g N <sub>2</sub> O-N ha <sup>-1</sup> (% of total)			
1	w. wheat-fallow (CT)	low (0)	62 (38.5)	64 (30.6)	169	
1	w. wheat-fallow (CT)	high (2)	127 (26.3)	327 (60.6)	518	
2	w. wheat-fallow (no till)	low(0)	62 (31.1)	134 (42.2)	250	
2	w. wheat-fallow (no till	high (2)	120 (29.6)	225 (53.5)	414	
3	w. wheat-s. wheat (no till)	low (0)	92 (43.2)	107 (40.6)	235	
3	w. wheat-s. wheat (no till)	high (3)	428 (46.4)	633 (47.6)	1115	
4	w. wheat – s. pea (no till)	low (0)	88 (39.1)	68 (29.7)	225	
4	w. wheat – s. pea (no till)	high (2)	140 (28.7)	271 (55.4)	487	
5	perennial grass or CRP	low (0)	77 (35.2)	87 (37.2)	227	
	LSD (0.05)		60	310	325	

Table 2. Estimated losses of  $N_2O$  during the 10-week period following N fertilization (% season total) and full season (22-March, 2004 to 2-February, 2006).

#### Fertilizer Induced Emissions

We calculated the fraction of fertilizer N lost as  $N_2O$  in 2004 and 2005 based on our estimates of total losses observed from 13-April 2004 to 13-April 2005, and 14-April 2005 to 2-Februrary, 2006, respectively. Nitrous oxide losses from treatments not receiving fertilizer N were considered background levels. These levels were subtracted from estimated  $N_2O$  losses for the high N treatments, yielding "fertilizer induced" losses. These losses were expressed as a percentage of the total N applied and the results are presented in Table 3. Our results indicate that for all cropping systems, fertilizer N induced emissions in 2004 were well below the IPCC default value of 1.25%. Losses ranged from 0.09 to 0.13% of fertilizer N, or more than one order of magnitude lower than the IPCC default value. In 2005, fertilizer N was only applied to the continuous wheat system (Trt 3). Estimated fertilizer induced losses of  $N_2O$  (i.e. 0.50%) were much greater during this season but still below the IPCC default value. These results suggest that IPCC default methodology will greatly overestimate  $N_2O$  emissions for the semi-arid Northern Great Plains region.

For the continuous wheat systems, the large difference in fertilizer induced losses of  $N_2O$  between the two years may have been the result of two factors. First, differences in fertilizer N placement strategies may have impacted  $N_2O$  emissions. Fertilizer N was applied to spring wheat at seeding in a subsurface band (2005), while fertilizer N was surface broadcast applied to winter wheat in 2004. Though direct comparisons between band and surface applications of fertilizer N in the field are limited, laboratory studies by Tenuta and Beachamp (2000) found relatively high concentrations of urea placed in small volumes of soils increased the fraction of N lost as  $N_2O$ . The second factor that may have impacted losses is the level of competition between plants and microbes for  $NH_4$  derived from fertilizer N. Although, microbes have traditionally been viewed as superior competitor for this N (Rosswall, 1982), it is curious that fertilizer N applied to an actively growing winter wheat crop in the spring (i.e. 2004) resulted in substantially lower emission peaks than when N was applied to wheat at seeding (2005, both spring and fall).

Trt	Cropping system	2004†		2005:	÷
		g ha <sup>-1</sup>	%	g ha <sup>-1</sup>	%
1	w. wheat-fallow (CT)	88	0.13	-	-
2	w. wheat-fallow (no till)	70	0.08	-	-
3	w. wheat-s. wheat (no till)	97	0.11	333	0.51
4	w. wheat-s. pea (no till)	124	0.09	-	-

† 2004 period = 14-April, 2004 to 14-April, 2005

<sup>‡</sup> 2005 period = 15-April, 2005 to 30-Sept, 2005. Fertilizer N was not applied to fallow and peas in 2005.

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# **Aerosol Emissions from Field Planting Operations**

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#### Abstract

Dust plumes generated by agricultural field preparation and planting operations were measured remotely via aerosol lidar and sampled with a variety of aerosol point samplers in order to generate plume space and time dynamics, quantify aerosol concentrations and determine the chemical composition of generated dust. Particle number and mass distributions measured from two cotton operations (disking, harvesting) in a flood irrigated field in New Mexico indicate approximately 45-50% of the measured mass was  $PM_{2.5}$  and 85-95% was  $PM_{10}$ . Plume dynamics and local wind condition interactions were quantified and visualizations from the lidar measurements are shown.

#### Introduction

Agriculture is under increased scrutiny as a source of airborne particulate matter and the relative lack of research documenting the emissions of fine ( $PM_{2.5}$ ) and coarse ( $PM_{10}$ ) particulate matter from agricultural operations leads to uncertainty in agriculture's contributions. Previous studies that quantified agricultural emissions represent a very limited number of sites, a low number of replicate samples, and few early studies quantified  $PM_{10}$ . Instead, total suspended particulate (TSP) matter or industrial workplace respirable dust ( $PM_4$ ) was measured. The application of lidar remote sensing techniques to PM emission factor measurements is relatively new (Holmén et al., 1998, 2000a,b). Lidar techniques help overcome one of the major limitations of point sampling methods; namely, the uncertainty in determining the dust plume height over which to integrate modeled PM concentrations. Previous field investigations resulted in a framework for categorizing vertical  $PM_{10}$  profiles and an emission factor quality rating system (Holmén et al., 2000a,b). To our knowledge, no previous studies have quantified the particle size distributions and plume dynamics of agriculturally-derived field preparation and harvesting operations.

The overall objectives of this research are to use the joint capabilities of the lidar and point samplers to quantify emission factors from different agricultural operations. In this paper, the point sampler particle size distribution and lidar spatial statistics data for fugitive dust emitted during two cotton operations – disking and harvesting – are used to further refine the sampling and data analysis methodologies for agricultural  $PM_{2.5}$  emissions estimation.

#### Methods

#### Site and General Cotton Operations

Field measurements were made at two ~ 2.8 ha flood irrigated experimental cotton fields located at the New Mexico State University Leyendecker Plant Science Research Center (lat.  $32.2^{\circ}$  N; Long.  $106.8^{\circ}$  W; elev. 1180 m). Experimental Field 1 was used to measure dust emissions from the field disking on 3/31/05. Field 2 was used to measure the dust emissions from upland 1517 BT cotton harvesting (11/7/05). Both the fields were a mixture of Armijo clay loam and Harkey loam soil types (USDA, 2005). An automated weather station continuously recorded hourly averages of precipitation, solar radiation, wind speed and direction, temperature and relative humidity. A Campbell Scientific three-axis sonic anemometer mounted on a tripod 1.5 meters above the ground measured air temperature (T), virtual air temperature (Tv) and the streamwise (u), cross-stream (v) and vertical (w) wind components at 20 Hz sample rates.

#### **Dust Emissions Measurement Procedures**

Dust emissions were measured simultaneously by point samplers located in the field and also remotely sensed by a LIDAR located 600 m south of the field. Sampling was conducted in replicate for one-way field passes of the implement; sampling began prior to tractor engine start and continued until several minutes after the tractor turned off its engine (when the generated dust plume moved out of the sampling area). The total number of passes sampled for disking and harvesting were 26 and 18. Point samplers were mounted on the 3-point hitch of a second tractor positioned near the center of the field, 2 to 5 rows downwind (4 to 7 meters from the nearest operation row) from the pass path (Figure 1a). After each pass the samplers were relocated to maintain a constant distance from the implement during the various replicate passes.



Figure 1. (a) Cascade impactors and PM samplers mounted on second tractor positioned in the field downwind of the operation; (b) UCONN scanning elastic-backscatter aerosol lidar in the field trailer

#### Point Particulate Matter Instrumentation

Five point PM samplers were used in the field to measure particle number and mass concentrations. An electrical low pressure impactor (ELPI, Dekati LTD., Finland) operating at 30 LPM measured particle number distributions (7 nm – 8  $\mu$ m) in real time with 1-2 second resolution. Samples of particulate matter collected on aluminum foil substrates were also used for chemical analysis. A micro-orifice uniform deposit impactor (MOUDI; Model 110, MSP Corporation, Shoreview, MN) was used to collect time-integrated particle size distribution (56 nm to 18  $\mu$ m in 10 stages) for mass and chemical analysis on 47 mm aluminum foil substrates and a 37 mm Teflon after-filter. A PQ200 sampler (BGI Inc. Waltham, MA) outfitted with the Very Sharp Cut Cyclone was used to collect PM<sub>2.5</sub> at 16.7 LPM on 47 mm Teflon membrane filters. Two GT-640A particulate monitors (Met One Instruments, Inc., Grants Pass, OR) were used to characterize the 1-min real-time mass concentrations of total suspended particles (TSP) and PM<sub>10</sub>. The monitors operate at 4 LPM and the measurements are performed using a forward light scattering detector and a built-in data logger.

#### Lidar Measurements

Dust cloud size, shape and movement were measured remotely via the University of Connecticut portable scanning backscatter elastic lidar (wavelength 1064nm, 125mJ/pulse, 17ns (2.55m) range resolution) (Hiscox et al., 2006). For the disking operation, a series of horizontal scans was designed to sample the entire plume starting at an elevation just above the field and successive scans were collected at increasing elevations. A single lidar sampling sequence, consisting of 5 to 15 different elevation angles, was collected in less than one minute and was repeated 5 to 10 times for each pass depending on the dust's persistence in various meteorological conditions. A similar sequence was used for the harvesting operation, with the addition of a series of vertical scans moving across the field on every fourth pass of the tractor. Each scan was combined in lidar data analysis software to characterize the three dimensional dust plume on this time scale.

#### Results

#### Particle Number and Mass Distributions

The ELPI and MOUDI impactor number- and mass-based size distributions were averaged and compared for the disking and harvesting operations (Figure 2). Both the number and mass-weighted distributions indicate multimodal distributions for both operations. Number distributions displayed two modes for both disking and harvesting: in the ELPI filter stage (7 - 29 nm) and the 1.6 to 2.4 µm diameter stage (Figure 2a). Mass distribution modes were observed in the 320 nm and 5.6 µm diameter MOUDI stages for disking and the 180 nm, 560 nm and 10 µm diameter MOUDI stages for harvesting (Figure 2b). The measured mass emissions were higher for harvesting than for disking for most MOUDI stages. To some extent this reflects the higher observed background signals during harvesting due to activity on nearby fields. Fine particulate matter (PM<sub>2.5</sub>) represented 51 and 45% of the total mass measured by MOUDI for disking and harvesting, respectively.



Figure 2. ELPI (a) and MOUDI (b) particle number and mass distributions for disking and harvesting operations

#### Lidar Detection of Dust Plumes

All lidar returns were combined to give 2-dimensional contour maps of relative density after raw signal background-subtraction and range-correction. Each map was examined visually to identify the dust plume as well as possible interference (dust/spray from offsite fields) that could affect further analysis. Overall, 20 of the 26 disking passes and 10 of the 11 horizontal harvesting passes were classified as valid. To determine dimensional information about the dust plume, an edge value, defined as 20% of the peak return value, was used to isolate the dust plume from the surrounding area. Plume area was quantified and plotted versus height. Plume areas and peak concentration values decreased with height, as expected for a ground-based source. Plume velocity, defined by the movement of the peak concentration values in space over time, indicated detectable plumes within the lidar field of view for at least 10 minutes after some passes. Plume movement was found to correspond with the mean wind direction during each pass. The detectability, plume velocity, size and intensity varied with meteorological conditions. For example as stability increased, the height of the detectable plume decreased. An example of the detectable plume for a single pass of the tractor is shown in Figure 3.



Figure 3. Sequence of lowest elevation angle lidar images from pass 8 of the tractor (disking operation). Each panel is 1 minute and 13 seconds in duration. The tractor moved from right to left across each image at a distance of 600 meters from the lidar (the horizontal line near the top of each panel approximates tractor path). The tractor pass was completed and the tractor was stopped between the last two images. The structure visible in the last image is the tractor itself. The wind direction for this pass was 319 degrees from north and is indicated by the arrow in the last panel. The lidar aim was approximately 47 degrees off of true north.

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# In Field Assessments of Dust Generation of Harvesting Equipment

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#### Abstract

In tree nut production, the harvesting operation, consisting of removal and separation of the nuts from orchard debris, is recognized as one of the most intensive dust generation activities in crop production. The majority of US nut production, primarily almonds and walnuts, is located in the Central Valley of California, a US EPA non-attainment area for PM in ambient air. Peak levels of ambient particulate concentrations coincide with the peak agricultural harvest season. This project investigated dust generation from tree nut harvesting, specifically the "pick up" operation in which windrowed orchard material is mechanically lifted into a mobile air separation chamber where soil and other debris are removed from the nuts. While long term industrial efforts are addressing redesign of the nut handling machinery, the hypothesis in this project was that operation of existing machinery could be adjusted to reduce dust discharge and that grower-controlled factors such as ground speed and orchard surface preparation could be manipulated to reduce emissions. Particular challenges in investigating in-field processes with significant numbers of variables are the constraints on the number of analytical samples that can be processed and the time delay between sample collection and availability of data. For grower outreach activities and to provide immediate feedback on efficacy of operational changes and to allow simultaneous sampling at multiple sites, rapid, low-cost instrumentation is required. This project used industrial opacity measurement systems mounted in-situ on harvesting equipment and positioned in orchards to determine relative effects of operational changes on potential dust generation. During the 2005 harvest season, the effects of simple operational changes in the harvester equipment, e.g., ground speed, rotational speed of the nut/debris nut separation fan and preparation method for the orchard windrow. Based on air opacity measurements, intensity of dust generation could be reduced by harvesting at lower ground speeds, operating the equipment with lower air velocity and by proper adjustment of windrowing machinery. The immediate availability of data allowed in-field grower education and outreach activities. The monitoring system developed for this on-going study can be used to establish benefits of differences in machine design, harvester operating conditions and orchard management practices. The results from this tool can be used for immediate feedback on potential dust intensity based on soil conditions, soil types, harvester type and harvester operating conditions.



### Concentrations of Current-Use Agricultural Pesticides in the Air, Yakima County, Washington

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#### Abstract

Concentrations of some of the current-use pesticides have been measured in air in many locations throughout the world, but relatively few measurements have been made in irrigated, arid regions. During the 2003 growing season, weekly integrated air concentrations (vapor and particulate phases) of 50 pesticides and selected transformation products were measured at a sampling site in Yakima County in south-central Washington State (about 20 cm/yr of rainfall). The dominant agricultural crops in this area include orchards, corn, alfalfa, and grapes. These are protected by a large number of insecticides, fungicides, and herbicides. The most commonly detected insecticides were carbaryl (100% detection), permethrin (100%), and malathion (57%). Myclobutanil (95%) and metalaxyl (76%) were the most commonly detected fungicides, whereas dacthal (95%), trifluralin (62%), and acetochlor (62%) were the most commonly detected herbicides. Of the 50 target pesticide compounds, 41 of them were detected in the air at least once. No simple relation was observed between pesticide detection frequencies and the application rate in the surrounding area (160 km<sup>2</sup>), their use rank in the surrounding area, their mean air concentrations, or their vapor pressures. All frequently detected compounds were used substantially in 2003 in the surrounding area except for dacthal. Dacthal was used on various crops in parts of south-central Washington and likely was transported through the air to the sampling site. Seasonal variation in the total concentrations for many of the insecticides detected in the air was highest in the spring and late summer, whereas, fungicide and herbicide concentrations were more consistent throughout the growing season. Carbaryl, used extensively in the spring and autumn on orchards in this area, had the highest measured concentrations among the target compounds (280 ng/m<sup>3</sup> in one September air sample).

#### Introduction

As the population grows, there is a greater need for agricultural products. This has led to increased use of pesticides to increase yields. A fraction of the pesticides applied to agricultural fields are transported away from their intended target and can contaminate both water and air. Pesticides enter the atmosphere either through volatilization, wind erosion, or spray drift; pesticides can be removed by wet (rain, snow) and dry (dry fall, vapor partitioning) depositional processes or through photochemical reactions. Atmospheric transport (both short range and long range) has been shown to be an important factor in the transport of pesticides through the hydrologic system (Majewski and Capel, 1995; Shen et al., 2005). There have been a number of local and regional-scale studies that have frequently observed pesticides in the atmosphere (Majewski and Capel, 1995; Majewski et al., 1998; Foreman et al., 2000; Kuang et al., 2003; Peck and Hornbuckle, 2005). There have been very few studies of pesticides in the air in arid regions. This study is the first to report ambient air concentrations of current-use pesticides in Washington. There have been short-term studies of the pesticides 2,4-D, parathion, and methamidophos in the air during and after their application in Washington (Ramaprasad et al., 2004; Reisinger and Robinson, 1976; Batchelor and Walker, 1954) This area provides an interesting environment for studying pesticides in the air, since it is quite arid and is an intensely agricultural area that uses a number of different of insecticides, fungicides, and herbicides on a wide variety of crops.

#### **Methods**

The Granger Drain basin, a 5.5  $\text{km}^2$  watershed within the Yakima River Basin in Washington, is an agriculturally intense area (Payne et al., 2006). Eighty-seven percent of the watershed area is used for crops and rangeland/pasture. Twenty-eight percent of total area is used for orchards. Corn, alfalfa, and grapes are the next largest crops by land area (22%, 9%, and 8%, respectively). This area receives only about 20 cm/yr

of annual rainfall, mostly in isolated thunderstorms. There are a wide variety of pesticides used in this area to control weeds and insects (Table 1).

Air sampling was conducted from April to September 2003 and again in May 2004 with two samplers. A high-volume air sampler (flow rate of 476 L/min) used one glass-fiber filter to collect particle-associated pesticides followed by two cleaned, polyurethane foam plugs (PUFs) to collect vapor-phase pesticides. A low-volume air sampler (flow rate of 198 L/min), equipped with a pre-weighed glass-fiber filter, collected total suspended particles (TSP). A total of 21 samples were collected. Between sampling and analysis, the PUFs and filters were stored in a freezer. The PUFs and filters for pesticide analysis were individually extracted in a Soxhlet apparatus with a mixture of 70/30 (v/v) hexane/ethyl acetate. The solvent volume was reduced in a Kuderna-Danish apparatus to about 15 mL and then, further reduced to less than 100 µL by a stream of purified nitrogen. The samples were analyzed with a gas chromatograph / mass spectrometer in selective ion monitoring mode. The target chemicals are given in Table 1. All blanks showed no contamination greater than the minimum detection limit. Recoveries of the analytical surrogate, butachlor, were  $60 \pm 38\%$  (N=68). None of the sample data was adjusted according to surrogate recovery. It has been observed that carbaryl degrades to 1-napthol in the detector, but no corrections were made for the concentrations of either compound in these results. After sampling, the pre-weighed, TSP filters were placed in a desiccator to dry until they reached a constant mass and then weighed again on an analytical balanced. Further sampling and analysis details can be found in Ohrt (2005).

#### **Results and Discussion**

Fifty pesticides and pesticide transformation products were targeted in this study (Table 1). All but nine of these compounds were observed at least once during the study. At least 3 of the 50 target chemicals were detected in every air sample including carbaryl and trans-permethrin, which were detected in every sample. Of the 22 target compounds that had been reported used in Granger Drain basin, 20 were detected. The two exceptions, terbufos and fonofos, likely were not detected because they were used in small amounts. The four most commonly detected compounds (two insecticides, carbaryl and trans-permethrin, one fungicide, myclobutanil and one herbicide, dacthal)) were detected in all or all but one of the samples. Pesticide transformation products are not often targeted in environmental air samples, but this study targeted/analyzed for 11 of them. Chlorpyrifos-oxon (from chlorpyrifos) and 1-napthol (from carbaryl) were the two that were most frequently detected. Some fraction of the 1-napthol that was detected in the air could have been produced in the injector port of the gas chromatograph during analysis.

There were essentially no relations between detection frequency and use rank ( $r^2=0.18$ ), mass used ( $r^2=0.10$ ), mean concentration ( $r^2=0.16$ ), and maximum concentration ( $r^2=0.10$ ). Likewise, there were essentially no relations between maximum concentration and use rank ( $r^2=0.13$ ) or mass used ( $r^2=0.31$ ) or between mean concentration and use rank ( $r^2=0.16$ ). The relation between mean concentration and mass used has a high correlation coefficient ( $r^2=0.93$ ), but this relation is largely driven by two data points. This relation disappears when the logarithm of mean concentration is regressed against the logarithm of mass used ( $r^2=0.14$ ). There is a weak relation between the logarithm of detection frequency and the logarithm of mean concentration with increasing detection frequency. There are a number of possible reasons for the observed lack of relations among use, detection frequency, and concentration, such as the environmental conditions that varied throughout the growing season, variable application timing and techniques, and the wide variability in the vapor pressures of the applied pesticides, which affects their degrees of volatilization.

A number of pesticides, such as dacthal, dieldrin, prometon, and tebuthiuron, were frequently detected in the air over Granger Drain basin, but had no reported agricultural use in the watershed during 2003. Dacthal is a herbicide commonly used on vegetables and applied with a conventional ground-rig sprayer at planting time in Washington. Although there is no reported use in Granger Drain basin, there is use outside of the basin in Yakima County and surrounding areas (United States Geological Survey, 2005). The presence of dacthal in the air suggests that it is either transported into the basin from other areas, that the use in the basin is under estimated, or both. The presence of dieldrin is a legacy from the 1960s. It is still frequently detected in surface waters and aquatic biota in this area (Munn and Gruber, 1997). Prometon is widely used for non-agricultural purposes (to control weeds long fence lines and rights-of-way), but has no agricultural use in Washington. It has been widely detected in a variety of environmental matrices in agricultural areas (Capel et al., 1999). Tebuthiuron also is used on rights-of-way in Washington (State of

Washington, 2005), but is not listed as having any agricultural use (United States Geological Survey, 2005).

					Air Concentration		
Compound (Purpose) <sup>a</sup>	Target Crop <sup>b</sup>	Mass Used (Mg) <sup>c</sup>	Use Rank <sup>c</sup>	Detection Frequency (%) <sup>d</sup>	Mean <u>+</u> SD (ng/m <sup>3</sup> ) <sup>d</sup>	Maximum (ng/m <sup>3</sup> )	
Target chemicals that were detected in greater than 50% of the samples							
Carbaryl (I)	A,G,O	21	3	100	22 <u>+</u> 60	280	
Trans-permethrin (I)	A,C	0.70	14	100	1.7 <u>+</u> 1.3	4.3	
Dacthal (H)	Ν	0	N/A <sup>e</sup>	95	0.27 <u>+</u> 0.51	2.3	
Myclobutanil (F)	G,H,O	2.6	7	95	6.6 <u>+</u> 17	80	
Cis-permethrin (I)	A,C	0.70	14	90	0.15 <u>+</u> 0.18	0.75	
Chlorpyrifos-oxon (T)			<sup>f</sup>	86	4.9 <u>+</u> 5.3	21	
Metalaxyl (F)	H,O	0.057	23	76	0.85 <u>+</u> .072	2.5	
Acetochlor (H)	С	1.1	11	62	0.55 <u>+</u> 1.0	4.5	
Trifluralin (H)	A,B,G,H,M	0.14	20	62	0.14 <u>+</u> 0.22	0.86	
Malathion (I)	A,H,O,P	11	4	57	0.71 <u>+</u> 0.96	3.0	
Alachlor (H)	B,C	2.6	6	52	0.33 <u>+</u> 0.62	2.64	

# Table 1. Use, detection frequency, and total concentration of the target chemicals in air in the Granger Drain basin, May – September 2003 and May 2004.

Target chemicals that were detected, but in less than 50% of the samples

Atrazine (H), Chlorpyrifos (I), Deethylatrizine (T), Diazinon (I), Diazinon-oxon (T), Dicrotophos (I), Dieldrin (I), Dimethoate (I), Ethion (I), Fenamiphos (N), Fenamiphos sulfone (T), Fipronil (I), Hexazinone (H), Isofenphos (I), Iprodione (F), Malathion-oxon (T), Methidathion (I), Methyl parathion (I), Methyl parathion-oxon (T), Metolachlor (H), Metribuzin (H), Pendimethalin (H), Phorate (I), Prometon (H), Prometryn (H), Simazine (H), Tebuthiuron (H), 1-Naphthol (T), 4-Chloro-2-methylphenol (T), 2,6-Diethylaniline (T)

#### Target chemicals that were not detected in any of the samples

Benfluralin (H), Dichlorvos (I), Fonofos (I), Pronamide (H), Phorate-oxon (T), Terbufos (I), Terbuthylazine (H), 2-Ethyl-6-methylaniline (T), 3,4-Dichloroaniline (T)

<sup>a</sup>: F= fungicide, H = herbicide, I =insecticide, N = nematocide, T = transformation product.

<sup>b</sup>: A = alfalfa, B = beans and peas, C = corn, G = grapes, H = hops, M = mint, O = orchard,

N = not reported, P = Pasture and Grass.

<sup>c</sup>: From Payne et al. (2006). Not all pesticides that were used in Granger Drain basin were included as targets in this study, so there are missing numbers in the use rank list.

<sup>d</sup>: Calculated based on 21 samples. Air concentrations less than the detection limit were assumed to be equal to zero for the mean concentration calculation.

 $e^{e}$ :N/A = Not applicable, since there is no reported use in Granger Drain basin in 2003.

f: --- = Not applicable, use rank is related to parent pesticide.

<sup>g</sup>:N/L = This compound is not listed in the databases used by Payne et al. (2006).

Concentrations of the pesticides detected in the air in this study generally are in the same range that have been observed for these same compounds in other agricultural environments (Peck and Hornbuckle, 2005; Kuang, et al., 2003; Majewski et al., 1998; Foreman et al., 2000; Majewski and Capel, 1995) with mean concentrations in the range of 0.01 to 20 ng/m<sup>3</sup>. In a few samples, concentrations of carbaryl and myclobutanil were substantially higher with maximum concentrations of 280 and 80 ng/m<sup>3</sup>, respectively. There has not been any previously reported concentration of these pesticides in air in Washington.

The temporal air concentrations of carbaryl and its transformation product, 1-napthol, are shown in Figure 1. Most of the time, carbaryl was detected at small concentrations, but during periods of application, the concentration substantially increased. Carbaryl, used mostly in orchards throughout the spring and summer, is applied through a variety of methods including by sprinklers or aerially. Generally, 1-naphthol was

detected only when the air concentration of carbaryl was  $>6 \text{ ng/m}^3$ . The other frequently detected pesticides had similar temporal concentration patterns with generally low concentrations most of the time and one or two weeks of elevated concentrations during their application periods. Periods of elevated concentration occurred in the early and late summer for carbaryl and permethrin, spring for chlorpyrifos and trifluralin, early summer for dacthal, myclobutanil, and acetochlor and late summer for metalaxyl.



Figure 1. Concentration (vapor plus particulate) of carbaryl and 1-napthol in the air over Granger Drain basin during the 2003 growing season. Carbaryl was detected in every air sample during this period.

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