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^2), 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^3 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 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 ± 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 (r^2=0.46) with a trend of increasing 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).

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.

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

[a]: F= fungicide, H = herbicide, I =insecticide, N = nematocide, T = transformation product.
[b]: A = alfalfa, B = beans and peas, C = corn, G = grapes, H = hops, M = mint, O = orchard, N = not reported, P = Pasture and Grass.
[c]: 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.
[d]: 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]: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.
[g]: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^3. In a few samples, concentrations of carbaryl and myclobutanil were substantially higher with maximum concentrations of 280 and 80 ng/m^3, 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 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.

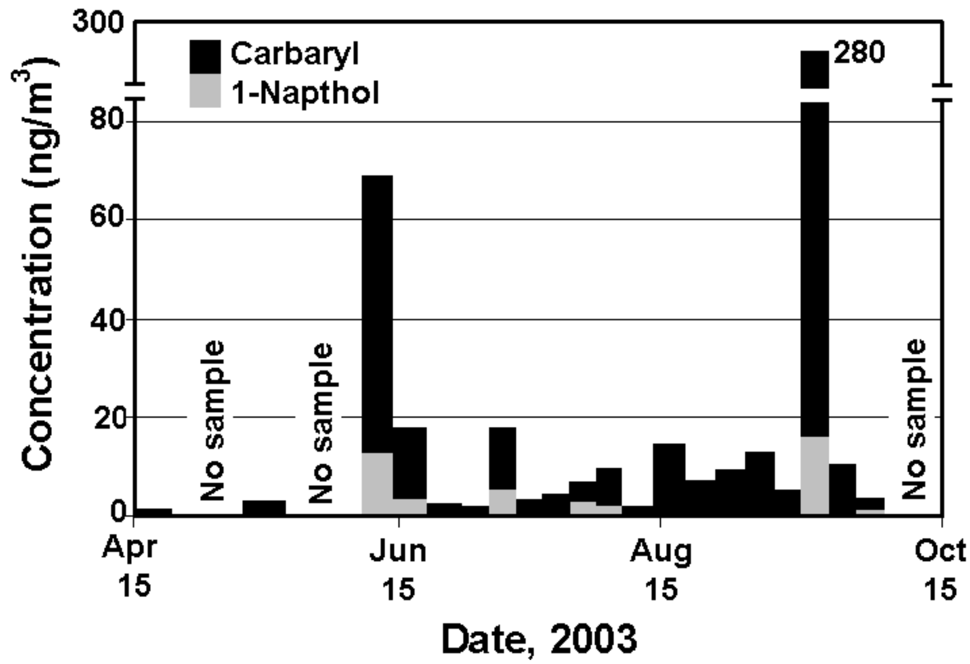

Figure 1. Concentration (vapor plus particulate) of carbaryl and 1-napthol in the air over Granger Drain basin during the 2003 growing season. Carbaryl was detected in every air sample during this period.

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