Analytical Method for the Dithiocarbamate Fungicides Ziram and Mancozeb in Air: Preliminary Field Results

James E. Woodrow and James N. Seiber*

Center for Environmental Sciences and Engineering and Department of Environmental and Resource Sciences, University of Nevada, Reno, Nevada 89557

Donald Fitzell

California Air Resources Board, Sacramento, California 95812

Airborne particulate residues that resulted from commercial applications of the dithiocarbamate fungicides ziram and mancozeb were trapped on glass fiber filters at 14–16 L/min for up to 24 h. Hydrochloric acid hydrolysis, with stannous chloride reduction, was used to convert these residues to carbon disulfide, which was partitioned into isooctane for assay using sulfur-mode flame photometric gas chromatography. Limits of detection were about 0.3 μg (ziram) and 0.5 μg (mancozeb) per filter, which were equivalent to about 14–23 ng/m^3 (24 h). Samples of these fungicides were collected during and following their applications and of mancozeb only in one ambient field situation. Measurable residues were detected up to 3 days after application within 18 m of the treated fields. Concentration ranges in the field for detectable residues were 15–2300 ng/m^3 (ziram) and 48–1600 ng/m^3 (mancozeb).

Keywords: *Fungicides; ziram; mancozeb; air sampling*

INTRODUCTION

The dithiocarbamate fungicides have wide usage on nut and fruit trees and on vegetable and other field crops as protective agents against plant diseases. Two common agents, ziram and mancozeb, are zinc and manganese dithiocarbamates that are practically insoluble in water and have negligible vapor pressures. Consequently, movement from the target site should occur only as a result of drift of compound particulates during application and wind erosion of deposited particulate residues.

There is concern over the potential impact ziram and mancozeb usage may have on human health. While acute toxicity for these compounds is low [LD$_{50}$ = 1400 (ziram)–11 200 (mancozeb) mg/kg oral and 6000 (ziram)–15 000 (mancozeb) mg/kg dermal; TLV (for both) (time weighted average) = 1 mg/m^3, based on thiram (ACGIH, 1991)], there is some concern over chronic exposure to these fungicides since they are suspected carcinogens. Furthermore, mancozeb is a source of ethylenethiourea (ETU), which is also a suspected carcinogen, as well as a mutagen and teratogen. Information that describes potential human exposure to the presence of these dithiocarbamates in air resulting from agricultural usage is lacking. In part, this is because of the lack of a method for determining their air residues at anticipated ambient levels. This method, and resulting analytical information, is needed to form a basis for human exposure risk assessment. Such an assessment is required for these fungicides, and many other pesticides, as a consequence of the Toxic Air Contaminant Act of California, incorporated in state law in Health and Safety Code Section 39650 and Food and Agricultural Code Section 14021 (Seiber, 1995).

In this paper, we describe the development and validation of a method for the assay of ziram and mancozeb residues trapped on glass fiber filters (GFFs) from air during application and from ambient air in an agricultural region of fungicide use. We also discuss the selection of suitable solvents for these fungicides and their stability on GFFs during air sampling and cold (−15 to −20 °C) storage.

MATERIALS AND METHODS

Fungicides. Crystalline ziram (dimethyldithiocarbamic acid zinc salt; 96.0%) and mancozeb [ethylenebis(dithiocarbamic acid) manganese (20%)/zinc (2.5%) salt; 74.0%] were obtained from Chem Service (West Chester, PA) and AXACT (Amityville, NY), respectively. **CAUTION: Both fungicides are suspected carcinogens and should be handled with care.** Standards for analysis were prepared by dissolving ziram in acetone and mancozeb in 0.1 M EDTA (tetrasodium salt).

Ziram Samples (March 27–31, 1994). Five air sampling stations were set up around an almond orchard of about 22 ha located in Butte County, CA. One station was located about 18 m from the eastern side, two collocated samplers about 18 m from the southern perimeter, one about 9 m from the northern perimeter, and one about 14 m from the western side (Figure 1A). The application required about 4 h to complete and was done by two air-blast sprayers. Ziram 76 (76% active ingredient; FMC Corp.) was applied at a rate of 6.7 kg/ha and Topsin (thiophanate, a systemic carbamate fungicide; 1.2 kg/ha), Nu-Film-P (a spreader/sticker; 0.3 kg/ha), and a fertilizer (12 kg/ha) were also included.

Mancozeb Samples (May 3–7, 1993). Four air sampling stations were set up around the three sides of the east half (approximately 16 ha) of a 32 ha potato field located in Kern County, CA. Two collocated samplers were placed about 18 m south of the field, one was placed about 18 m north of the field, and one was placed about 18 m from the east side of the field (Figure 1B). The field was treated at a rate of 2.2 kg/ha with M-45 (80% mancozeb; Rohm and Haas) by aircraft and required about 15 min to complete.

Ambient air monitoring was performed only for mancozeb (April 20–May 7, 1993). Four sampling sites were established in areas of expected mancozeb usage in Kern County, CA, near Bakersfield, and they were operated during periods of anticipated application. A fifth "roving" station was moved among the sampling sites to obtain duplicate collocated samples to be used to evaluate the precision of the data. After about a week, one of the fixed stations was moved into Bakersfield to assess possible exposure in a major urban area.

Air Sampling for Ziram and Mancozeb

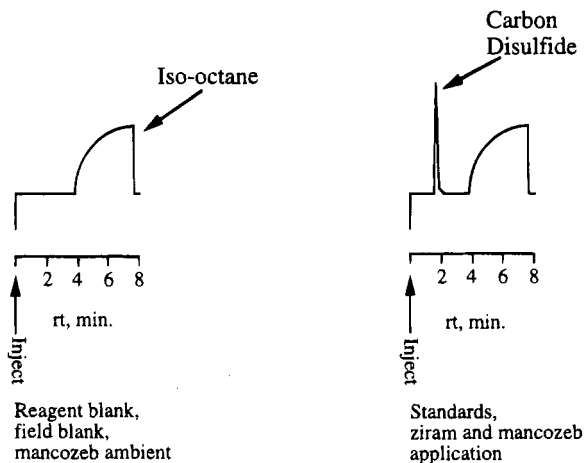*J. Agric. Food Chem.,* Vol. 43, No. 6, 1995 **1525**
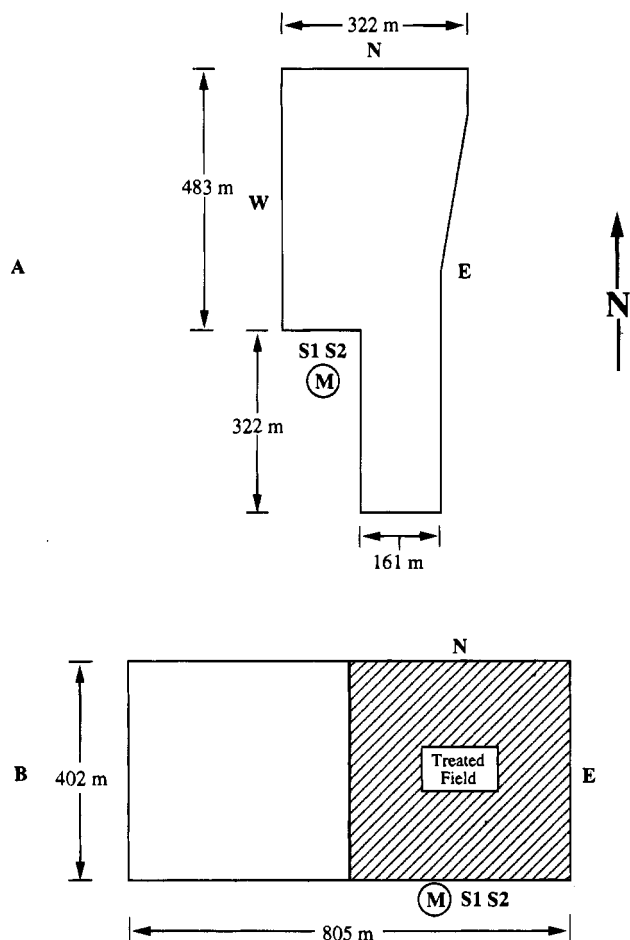
Figure 1. Ziram (A, 22 ha) and mancozeb (B, 16 ha) application monitoring sites. N, S1, S2, E, and W are sampling stations, and M is the meteorology station.

Figure 2. Gas chromatograms of carbon disulfide derived from ziram and mancozeb fungicide field samples, including standards and blanks.

Air Sampling. For both fungicides, residues in air were trapped on 47 mm diameter glass fiber filters (GF/A, >90% efficiency for <0.5 μm diameter particulates; Fisher, Fair Lawn, NJ) at air sampling rates of about 14−16 L/min using 12 VDC Teflon membrane pumps (Thomas, Santa Clara, CA). The filters were mounted in Teflon holders (inlet: 3.6 cm diameter × 3.8 cm; Savillex Corp., Minnetonka, MN) and operated 1.5 m above the ground with sampler inlets facing the ground. Sampling periods ranged from 2 h (1.7−1.9 m^3) to 24 h (20.2−23.0 m^3) for the application sampling situations; all ambient sampling was done for 24 h.

After sampling, the filters were sealed in screw-cap glass jars and transported over dry ice to the laboratory, where they were immediately stored at −15 to −20 °C. Clean filters were spiked with standards of the fungicides (1−3 μg of ziram and 6−9 μg of mancozeb), and the spiked samples were placed in the same freezer along with the field samples.

Analysis. The glass fiber filters containing fungicide residues were folded twice and placed in 22 mL glass headspace vials (Perkin-Elmer, Norwalk, CT); 2 mL of isooctane (Fisher) and 5−10 mL of a mixture of concentrated HCl (37%; Fisher) and 3% (w/v) SnCl$_2$ (Aldrich Chemical Co., Milwaukee, WI) were added to each vial, and the vials were sealed with crimped caps containing Teflon-lined silicone rubber septa (Perkin-Elmer). The vials were then placed in an oven heated to 80 °C and after an hour were removed and allowed to cool to room temperature; during cooling and just prior to removal of the caps, the vials were shaken to help partition the carbon disulfide (CS$_2$) into the isooctane layer. After the caps were removed, the isooctane layer was pipetted into screw-cap-sealed 4 mL vials, 2 mL of distilled water was added, and the vials were sealed and shaken vigorously to wash the isooctane.

Residues of CS$_2$ in 4 μL injections of isooctane were chromatographed using a Hewlett-Packard 5890 Series II gas

chromatograph equipped with a 30 m × 0.53 mm (i.d.) DB-1 megabore fused silica column (J&W Scientific, Folsom, CA) and a flame photometric detector (FPD) in the sulfur mode (394 nm filter). The carrier gas (helium) flow was set at about 4.5−5.0 mL/min, and the column, injection port, and detector temperatures, respectively, were set at 45, 120, and 230 °C. Carbon disulfide retention time typically fell in the range 1.8−2.3 min, as determined by injections of pure CS$_2$ (Aldrich) dissolved in isooctane; isooctane eluted as a misshapen peak beginning about 4 min after injection. Residues were determined by comparing instrument responses with those of standard injections. Carbon disulfide standards for quantitation were prepared by spiking a series of clean glass fiber filters with various amounts of the fungicides dissolved in suitable solvents and treating the spiked filters using the procedure described for the preparation of the field samples for analysis. Typical chromatograms are shown in Figure 2.

RESULTS AND DISCUSSION

To analyze the dithiocarbamates using gas chromatography, it was necessary to reproducibly convert ziram and mancozeb into a volatile component that could be used to represent the mass of material trapped from air. A commonly used method involves converting the fungicide residues to CS$_2$ under hot mineral acid reflux, with subsequent conversion of the evolved CS$_2$ to a colored complex for spectrophotometric determination (Lowen and Pease, 1964; Keppel, 1971; Mumma et al., 1985). Acid hydrolysis is essentially the reverse of the synthesis of dithiocarbamate fungicides, in which CS$_2$ undergoes a nucleophilic attack at the carbon atom by secondary amines in alkaline medium and in the presence of metal cations to form the fungicide complex. The above analytical approach, however, is time-consuming and tedious and therefore not practical for those situations that require rapid turnaround from sampling to results. Alternative methods, which do not use CS$_2$ derivatization, also involve hot acid treatment of fungicide residues, but the CS$_2$ evolved from the reaction mixture is analyzed directly as the gas or is immediately trapped in an organic solvent (e.g., hexane, isooctane) and analyzed directly (MAFF, 1981; Maini and Boni, 1986). In this case, dithiocarbamate fungicides are treated with concentrated hydrochloric acid (HCl) containing a small amount of stannous chloride (SnCl$_2$) (Keppel, 1971) to promote conversion to CS$_2$. This conversion is aided in part by the formation of the mildly reducing trichloro species from divalent tin in concen-

**1526** *J. Agric. Food Chem.,* Vol. 43, No. 6, 1995

Woodrow et al.

trated chloride. The reducing agent probably helps to more efficiently free the dithiocarbamate ligand from the complexing metal center for increased CS_2 yield from acid hydrolysis of the ligand.

We made use of this approach, with some modification, to determine ziram and mancozeb trapped on glass fiber filters by sealing the filters in glass headspace vials along with the $HCl/SnCl_2$ mixture and isooctane and heating the contents to promote conversion to CS_2. We used headspace vials instead of screw-cap vials, since the latter would not seal properly and much of the solvent along with the evolved CS_2 escaped. The headspace vials, when sealed with a septum and crimped cap, were gastight and could withstand internal pressures in excess of 700 kPa (actual internal pressures were probably much less than the design limit; however, it is advised, nonetheless, that a headspace vial be used with this method, since the vial cap is designed to release internal pressure before the glass vial would have a chance to rupture). Since CS_2 was contained by the headspace vials, we could minimize the volume of isooctane to aid in lowering the minimum detection limit (MDL). Furthermore, we also reduced the volume of the $HCl/SnCl_2$ mixture from 10 to 5 mL for some of the spiked filters and gained an improved MDL. The clean separation between isooctane and the CS_2 analyte (Figure 2), under the gas chromatographic conditions of this study, also made it possible to achieve a relatively low MDL.

This method lends itself to relatively high sample throughput, which would be limited only by the preparation stage of the analysis and available laboratory resources. In practical terms, two to three dozen samples per set could be prepared at one time by one individual, with three to four sets prepared each day (maximum of over 100 samples per day). Gas chromatographic analysis time for each sample was about 8 min, which meant that for an automated system maximum throughput, after sample preparation, would be about 180 samples in a 24 h period.

Fungicide Solutions and Standard Spikes. A ziram standard was prepared in acetone, with some sonication to promote solubility, and a mancozeb standard was prepared in 0.1 M EDTA (tetrasodium salt) without sonication. Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were also considered as solvents for mancozeb, since these solvents often solubilize recalcitrant materials where other solvents fail. However, the fungicide proved to be unstable in DMF (no CS_2 standards could be prepared from a DMF solution) and DMSO interfered with CS_2 determination. The EDTA solution, on the other hand, appeared to be stable, and CS_2 standards could be readily prepared. Since some breakdown of mancozeb will occur in water (a few percent within 24 h), it is recommended that the CS_2 standards be prepared soon after mancozeb has completely dissolved in the EDTA solution.

Gas Chromatography. To prepare solutions of CS_2 to be used as standards for FPD/GC quantitation, various amounts of fungicide standards were spiked to clean glass fiber filters and the spiked filters were treated with the $HCl/SnCl_2$ mixture to produce CS_2. For ziram, the range of spiking levels was 0.48–17.3 μg, while the range for mancozeb was 0.47–20.5 μg. Response of the FPD/GC was typically nonlinear for the sulfur mode, showing an exponential increase in response with increasing amount injected (Figure 3). The curves were best described by second- and third-order
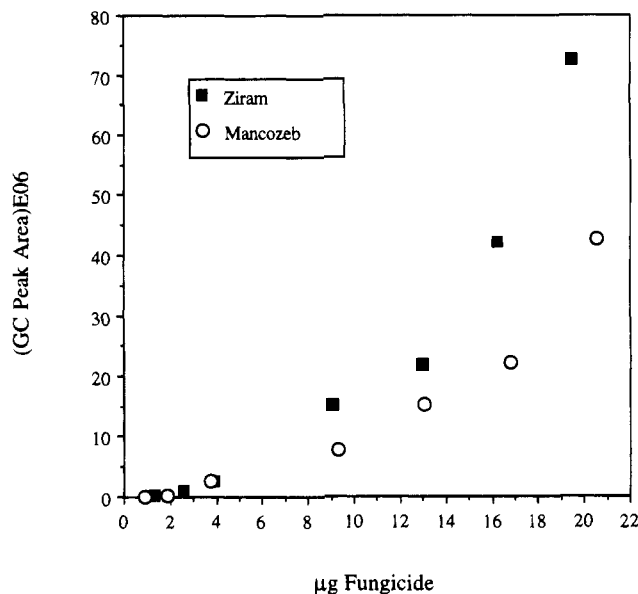
Figure 3. Comparison of ziram- and mancozeb-derived carbon disulfide responses using the flame photometric detector in the sulfur mode.

polynomials. While sulfur-mode FPD/GC is well-known to produce an exponential response curve, a complicating factor with the fungicides that might have affected the shape of the response curve was the dependency of CS_2 evolution on the amount of fungicide in the residue. For example, at the milligram level ziram conversion to CS_2 was >90%, but it was about 75–80% at 20 μg and about 65% at 2–3 μg. To avoid having to factor this varying conversion efficiency into quantitation calculations for the field samples, standard curves were prepared by spiking clean glass fiber filters with standard solutions of the fungicides, and these spikes were prepared for FPD/GC using the same technique as for the GFF field samples.

Freezer Stability. Ziram was quantitatively (>95%) recovered from GFFs spiked with acetone solutions and stored at −15 to −20 °C for up to 2 months. However, after only 2 weeks, 15–20% of the mancozeb spikes was recovered for the compound dissolved in EDTA. On the other hand, quantitative (>95%) recovery was achieved for the same storage period by spiking GFFs with methanolic suspensions of mancozeb. Since this compound has a negligible vapor pressure, it was assumed that chelation by EDTA disrupted the integrity of the metal complex so that the ethylenebis-(dithiocarbamate) (EBDC) ligand was allowed to break down and/or dissipate from the dry GFF under freezer conditions.

Air Sampling Stability. Nonchelated, solvent-suspended mancozeb on clean GFFs appeared to be stable under air sampling conditions (15 L/min, 23 °C). Average recovery for about 6 μg after 24 h of air flow was 100.9 ± 5.4%. However, pulling air through clean GFFs spiked with standard ziram in acetone resulted in the apparent disappearance of the fungicide (~16% recovered after 24 h at 15 L/min, 23 °C). Since, like mancozeb, this compound has a negligible vapor pressure, it was assumed that ziram broke down under air sampling conditions and that this was an artifact of ziram being dissolved in acetone solvent. In contrast to the acetone solution, ziram, suspended (not dissolved) in isooctane and spiked to glass fiber filters at 7–10 μg per filter, showed an average recovery of 88.2 ± 19.4% (n = 6) for an air flow of 15 L/min for 24 h. The

Air Sampling for Ziram and Mancozeb

J. Agric. Food Chem., Vol. 43, No. 6, 1995 **1527**

Table 1. Ziram Residues in Air during and after Application to an Almond Orchard in Butte County, CA (March 27–31, 1994)

period	station[a]	wind speed[b]	direction	time,[c] h	concn, μg/m³	period	station[a]	wind speed[b]	direction	time,[c] h	concn, μg/m³
0	W	0.447	SE/NW		<MDL	4	W	0.447	SE/NE/E/S	24.00	<MDL
	S1				<MDL		S1				<MDL
	S2				<MDL		S2				<MDL
	E				<MDL		E				<MDL
	N				<MDL		N				0.0288
1[d]	W	1.34	S/SE/SW/W/NW	4.50	0.146	5	W	0.447	NW/SE/N/S/E/W	34.50	0.0508
	S1				0.400		S1				0.0474
	S2				0.400		S2				–[e]
	E				1.69		E				0.0723
	N				2.26		N				0.0766
2	W	2.68	SSE	8.50	<MDL	6	W	0.447	SE/NE/NW	48.00	0.0371
	S1				<MDL		S1				0.0382
	S2				<MDL		S2				0.0255
	E				<MDL		E				–[e]
	N				0.478		N				0.0312
3	W	1.34	SSE/E	11.50	<MDL	7	W	1.79	S/N	72.00	–[e]
	S1				<MDL		S1				<MDL
	S2				<MDL		S2				–[e]
	E				<MDL		E				<MDL
	N				0.299		N				0.0147

[a] Distance of sampling stations from field: W, 14 m; S1, S2, 18 m; E, 18 m; N, 9 m. [b] Average speed, m/s. [c] Cumulative time (Figure 4). [d] Application. [e] Sampler malfunction.

Table 2. Mancozeb Residues in Air during and after Application to a Potato Field in Kern County, CA (May 3–7, 1993)

period	station[a]	wind speed[b]	direction	time,[c] h	concn, μg/m³	period	station[a]	wind speed[b]	direction	time,[c] h	concn, μg/m³
0	N	2.67	NW		<MDL	4	N	2.22	NW	11.00	<MDL
	S1				<MDL		S1				0.309
	S2				<MDL		S2				0.528
	E				<MDL		E				0.169
1[d]	N	3.56	NW	1.50	<MDL	5	N	0.89	N/S/E/W	23.50	0.0655
	S1				1.33		S1				0.157
	S2				1.81		S2				0.269
	E				0.854		E				<MDL
2	N	3.11	NW		<MDL	6	N	1.33	NW/N/S/E/W	47.50	0.253
	S1				<MDL		S1				0.155
	S2				<MDL		S2				0.176
	E				<MDL		E				0.204
3	N	2.22	NW/W/N/S	7.50	0.292	7	N	3.11	NW/N/W	71.50	<MDL
	S1				0.350		S1				0.102
	S2				<MDL		S2				0.119
	E				0.834		E				0.0478

[a] All sampling stations were 18 m from the field. [b] Average speed, m/s. [c] Cumulative time (Figure 4). [d] Application.

relatively large uncertainty for isooctane was due primarily to the difficulty in obtaining reproducible aliquots from the suspension, since isooctane did not have the polarity to give a relatively stable suspension of the complex (we avoided using methanol, since ziram may have some solubility in this medium). This uncertainty was even more dramatic for hexane, for which average recovery was 109 ± 42% for <0.5 μg spiked to glass fiber filters under the same air flow conditions. Although the uncertainty was high for hexane, again due to a lack of good reproducibility in obtaining aliquots from the suspension, the recovery was essentially quantitative for less than $^{1}/_{10}$ of the amount used for ziram in acetone (5.6 μg). Therefore, as in the case for mancozeb, nonsolvated, but solvent-suspended, ziram should be used to determine recovery from spiked filters under dynamic air sampling conditions. This would best simulate the field situation.

Field Samples. The analytical results (air concentrations) for the ziram and mancozeb field samples taken during application are summarized in Tables 1 and 2. Quantitation was done using eight-point standard curves, with at least two injections per point. The standard curves spanned the range 0.48–17.3 μg of ziram and 0.5–10 μg of mancozeb, and they were described by second- and third-order polynomials, with correlation coefficients (r^2) of 0.99–1.00. From the standard responses of CS_2, resulting from filters spiked with standard ziram and mancozeb, it was possible to read directly the mass of fungicide on each filter. The MDL was about 0.3 μg of ziram (equivalent to about 167 ng/m³ in air, assuming a flow rate of 15 L/min for 2 h, or about 14 ng/m³ in air for a 24 h sampling period at the same flow rate) and 0.5 μg of mancozeb (equivalent to about 278 ng/m³, assuming a flow rate of 15 L/min for 2 h, or about 23 ng/m³ for a 24 h sampling period at the same flow rate). These MDLs were derived from the smallest response that the analytical instrumentation could reliably integrate under the conditions of the study. Furthermore, the higher MDL for mancozeb was due partly to the fact that, mass-for-mass, it gave about half the amount of CS_2 during acid hydrolysis as did ziram (e.g., 6 mg each of ziram and mancozeb gave about 3 and 1.6 mg of CS_2, respectively). All sample and standard chromatograms appeared to be "clean", meaning that only the CS_2 and isooctane peaks were evident (Figure 2). When fungicide levels were less than
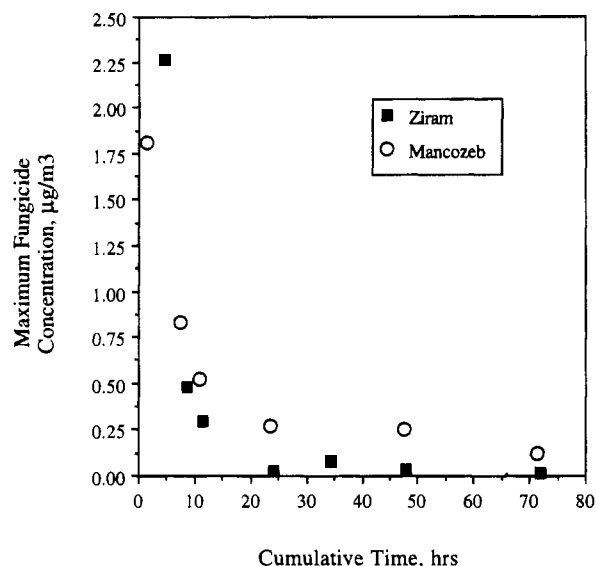
Figure 4. Decline of ziram and mancozeb residues in air postapplication.

the MDLs, the chromatograms were essentially flat lines up to isooctane elution.

While ziram and mancozeb concentrations declined rapidly in air during and after application, measurable residues persisted for the three sampling days (Figure 4). If these data are plotted as Ln(maximum concentration) vs sampling period, extrapolation indicated that the MDL for ziram (~14 ng/m^3) would be reached after about 7 sampling periods (3–4 days), while the MDL for mancozeb (~23 ng/m^3) would be reached after almost 11 sampling periods (7 days), assuming field conditions that prevailed during sampling would persist. These results imply that residues remained suspended and/ or deposited residues were resuspended as a result of wind erosion (wind speed varied between <0.45 and 2.7 m/s during ziram sampling and between 0.9 and 3.5 m/s during mancozeb sampling). Depending on the sizes of these suspended particulates, some of the fungicide residues remaining in air may be respirable, and, if so, would be available for inhalation by workers and residents in a region of use. However, to determine the extent of inhalation exposure, it would be necessary in future field monitoring studies to obtain size-specific data for the suspended particulates, as was done in one of our earlier studies with paraquat dichloride (Seiber and Woodrow, 1981).

While field-specific sampling showed persistent residues in air for both ziram and mancozeb, ambient sampling in a general region where mancozeb was applied did not show any residues above the MDL. Lack of proximity to a treated field was probably the determining factor here, indicating that for particulate matter concentrations in air fall off dramatically with distance from the source. We observed this to be the case in an earlier cotton field study with paraquat dichloride applications, where concentrations of this herbicide salt in air declined from 431 ng/m^3 at 10 m downwind to 27 ng/m^3 at 161 m downwind from one field and from 153 ng/m^3 at 70 m downwind to 49 ng/ m^3 at 216 m downwind from a second field (Seiber and Woodrow, 1981). Using the concentration/distance relationship discussed in this reference and the highest concentration observed for mancozeb application (1.81 μg/m^3 at about 18 m), the MDL (23 ng/m^3) for mancozeb

in air would be reached at about 1400 m downwind of the treated field. A similar calculation for ziram using the highest application concentration observed in the field (2.26 μg/m^3 at about 9 m) indicated that the MDL (14 ng/m^3) would also be reached at about 1400 m downwind of the treated field. So it is obvious that if the dithiocarbamate fungicides pose any kind of a chronic health risk, applicators and field workers or people living very close to treated fields would be the primary groups at risk.

Formulations of EBDC fungicides, such as mancozeb, often contain ETU as an impurity and breakdown product, but typically at levels less than 0.5% (Bontoyan and Looker, 1973; Camoni et al., 1988). However, under warm and moist conditions the ETU content in these formulations can increase by as much as an order of magnitude (Bontoyan and Looker, 1973). Since ETU is a recognized mutagen and teratogen, and is also a suspected carcinogen, the exposure of applicators and field workers to the EBDC fungicides may be a cause for greater concern because of the additional exposure to ETU. For example, in an earlier study, worker exposure to ETU during mancozeb applications ranged from <0.5% to almost 10% of the total mancozeb residue measured (Mumma et al., 1985). However, exposure due to long-range transport of residues is complicated because of the environmental breakdown of ETU in air and on surfaces (Ross and Crosby, 1973; Cruickshank and Jarrow, 1973).

SUMMARY AND CONCLUSIONS

Since the ziram and mancozeb fungicides are metal salt/complexes, they were applied as aqueous suspensions, and their particulate residues in air were sampled by simply trapping them on GFFs. These fungicides appeared to be stable on GFFs, based on 24 h dynamic air sampling tests in the laboratory with filters spiked with solvent suspensions of the compounds. However, ziram solution in acetone broke down under the air sampling conditions of this study. Similarly, mancozeb solution in 0.1 M EDTA also broke down under cold storage, and it is presumed that the same would have happened during the air sampling tests if this mancozeb solution, rather than the methanolic suspension, had been used. These results emphasize the importance of maintaining the integrity of the fungicide metal complexes, by using suspensions rather than solutions, when they are handled under laboratory conditions to best simulate the field situations. The use of ziram and mancozeb solutions to generate standard curves was justified by the improved reproducibility and the fact that filters were contained and analyzed immediately after spiking, so that ligand breakdown or dissipation was unlikely to occur.

Ziram and mancozeb residues in air, down to low nanograms per cubic meter concentrations, were easily determined using an acid hydrolysis method to convert the dithiocarbamate ligands to CS$_2$ for subsequent assay. The low MDLs coupled with clean chromatograms using sulfur-mode FPD/GC make it possible to monitor almost any exposure situation that might be of concern. With refinements to the analytical instrumentation and/or the sample preparation, it should be possible to lower the MDL below the levels achieved in this study. For example, we analyzed only 0.2% of the CS$_2$ derived from the fungicide residues (4 μL injections out of a total volume of 2 mL). However, by sealing the 2 mL samples into headspace vials, heating them to

Air Sampling for Ziram and Mancozeb

J. Agric. Food Chem., Vol. 43, No. 6, 1995 **1529**

promote evaporation, and sampling 0.5−1 mL of the vapor [using either automated headspace techniques or a gastight syringe (MAFF, 1981)], it may be possible to improve CS_2 detection by 1−2 orders of magnitude.

The highest residues that we encountered in the field for both fungicides (1.81−2.26 μg/m^3 during application) were about 2−3 orders of magnitude less than the TLV of about 1 mg/m^3, established to protect workers from acute intoxication (ACGIH, 1991). This means that, taking into consideration the average human male breathing rate of 0.8 m^3/h (CAPCOA, 1993), the maximum inhalation exposure (assuming that all of the airborne residues were respirable and these high levels persisted) would be 12−14 μg/8 h day under the field conditions of this study, compared to a TLV of about 6 mg/8 h day. This, of course, does not take into consideration dermal and oral routes of exposure, but toxicity by these routes is typically low (i.e., 1400−15 000 mg/kg). Therefore, acute toxicity is usually not a problem with these dithiocarbamate fungicides when they are handled properly, and so concern is directed more toward possible subacute and chronic, long-term effects for those persons, such as applicators and field workers, who would be in contact with elevated fungicide residues.

The determination of possible subacute and chronic, long-term effects related to exposure to mancozeb, or other EBDC fungicides, should also include possible effects from exposure to ETU. Although this compound represents only a fraction of the active ingredient in most EBDC formulations, its greater toxicity and its tendency to target certain organs (e.g., thyroid, liver) lend a note of urgency to human health risk assessments of exposure to EBDC fungicides. Therefore, ETU analysis should be included in any mancozeb (or other EBDC fungicide) field study, but this will require development of a suitable sampling/analysis scheme compatible with that for the parent fungicide.

ACKNOWLEDGMENT

LITERATURE CITED

ACGIH. *Documentation of the Threshold Limit Values and Biological Exposure Indices*; American Conference of Governmental Industrial Hygienists: Cincinnati, OH, 1991.

Bontoyan, W. R.; Looker, J. B. Degradation of commercial ethylene bisdithiocarbamate formulations to ethylenethiourea under elevated temperature and humidity. *J. Agric. Food Chem.* **1973**, *21*, 338−341.

Camoni, I.; Di Muccio, A.; Pontecorvo, D.; Citti, P. Survey of ethylenethiourea (ETU) in ethylenebis(dithiocarbamate) (EBDC) fungicides. *Ecotoxicol. Environ. Saf.* **1988**, *16*, 176−179.

CAPCOA. Air Toxics "Hot Spots" Program. *Revised 1992 Risk Assessment Guidelines, Appendix E-1*; California Air Pollution Control Officers Association: Sacramento, CA, 1993.

Cruickshank, P. A.; Jarrow, H. C. Ethylenethiourea degradation. *J. Agric. Food Chem.* **1973**, *21*, 333−335.

Keppel, G. E. Collaborative study of the determination of dithiocarbamate residues by a modified carbon disulfide evolution method. *J. Assoc. Off. Anal. Chem.* **1971**, *54*, 528−532.

Lowen, W. K.; Pease, H. L. Dithiocarbamates. In *Analytical Methods for Pesticides, Plant Growth Regulators, and Food Additives*; Zweig, G., Ed.; Academic Press: New York, 1964; Vol. III, Chapter 7.

MAFF (Ministry of Agriculture, Fisheries and Food). Determination of residues of dithiocarbamate pesticides in foodstuffs by a headspace method. *Analyst* **1981**, *106*, 782−787.

Maini, P.; Boni, R. Gas chromatographic determination of dithiocarbamate fungicides in workroom air. *Bull. Environ. Contam. Toxicol.* **1986**, *37*, 931−937.

Mumma, R. O.; Brandes, G. A.; Gordon, C. F. Exposure of applicators and mixer-loaders during the application of mancozeb by airplanes, airblast sprayers, and compressed-air backpack sprayers. In *Dermal Exposure Related to Pesticide Use: Discussion of Risk Assessment*; Honeycutt, R. C., Zweig, G., Ragsdale, N. N., Eds.; ACS Symposium Series 273; American Chemical Society: Washington, DC, 1985.

Ross, R. D.; Crosby, D. G. Photolysis of ethylenethiourea. *J. Agric. Food Chem.* **1973**, *21*, 335−337.

Seiber, J. N. Toxic air contaminants in urban atmospheres. *Atmos. Environ.* **1995**, in press.

Seiber, J. N.; Woodrow, J. E. Sampling and analysis of airborne residues of paraquat in treated cotton field environments. *Arch. Environ. Contam. Toxicol.* **1981**, *10*, 133−149.