SHORT COMMUNICATIONS

Pesticide Applications of Copper on Perennial Crops in California, 1993 to 1998

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Abstract

Inorganic copper is used as a broad-spectrum fungicide and bacteriocide on a variety of agricultural crops. After application, the copper residue typically accumulates in the upper 15 cm of soil. Data from the California Pesticide Use Reports were used to estimate the augmentation of copper in the soil that resulted from pesticide applications for the six years from 1993 to 1998 on 12 crops that are grown without rotation. The estimated mean mg Cu kg^{-1} soil added to the upper 15 cm during the six years was the following: walnut (*Juglans regia* L.), 28; peach [*Prunus persica* (L.) Batsch var. *persica*], 22; nectarine [*Prunus persica* (L.) Batsch var. *nucipersica* (Suckow) C.K. Schneid], 19; cherry (*Pseudolmedia oxyphyllaria* Donn. Sm.), 18; rice (*Oryza sativa* L.), 16; apricot (*Prunus armeniaca* L.), 11; orange [*Citrus sinensis* (L.) Osbeck] and plum (*Prunus domestica* L. subsp. *domestica*), 9; lemon [*Citrus limon* (L.) Burm. f.] and almond [*Prunus dulcis* (Mill.) D.A. Webb], 6; pear (*Pyrus communis* L.), 4; and grape (*Vitis vinifera* L.), 3. In addition, for the first five of these crops, we estimated the area that was treated with each level of kg Cu ha^{-1}. For example, for walnut orchards, we estimated that 12 500 ha, or 17% of the planted area, was treated with a quantity of Cu that would increase the total concentration of Cu in the upper 15 cm of soil by at least 50 mg Cu kg^{-1} soil. A comparison of the amount of Cu per unit planted area that was applied in the first and second half of the study indicated that the intensity of copper use is either relatively constant or increasing, depending on the crop. The findings are discussed in relation to the potential effect of continued long-term use of Cu pesticides on soil sustainability.

ALTHOUGH copper is required as a micronutrient, it is a broad-spectrum biocide at higher concentrations (Fleming and Trevors, 1989). Formulations of inorganic Cu, most commonly as copper hydroxide and copper sulfate, are used as agricultural pesticides to control fungi, bacteria, and in some instances, invertebrates and algae. After application on plants in the field, the Cu residue typically accumulates in the upper 15 cm of soil, bound to the organic matter and fine clay fraction (Kabata-Pendias and Pendias, 1992; Flores-Vélez et al., 1996). In the USA, the Cu content of agricultural surface soil ranged from 0.3 to 495 mg Cu kg^{-1} (HNO_3–extractable) with a geometric mean 18 mg Cu kg^{-1} (Holmgren et al., 1992); higher values reflect agricultural inputs. In other reports, soils with repeated pesticide applications have had concentrations as high as 110 mg Cu kg^{-1} (HNO_3–extractable) (Frank et al., 1976), 130 mg Cu kg^{-1} ($HClO_4$ + HF + HNO_3–extractable) (Magalhães et al., 1985), 323 mg Cu kg^{-1} (HF-extractable) (Flores-Vélez et al., 1996), 534 mg Cu kg^{-1} (EDTA-extractable) (Dickinson et al., 1988), 605 mg Cu kg^{-1} (0.1 *M* HCl-extractable) (Aoyama and Nagumo, 1996), and 1500 mg Cu kg^{-1} (Hirst et al., 1961; Tiller and Merry, 1981). Concentrations that are reported as toxic vary; critical factors include the organism, whether acute or chronic toxicity was determined, the extraction method, and soil characteristics such as pH and organic matter and clay content. Bacteria, fungi, and mollusks are generally the most sensitive to Cu compared with flowering plants and vertebrate animals (Domsch, 1989; Giller et al., 1998). Solutions containing 1 mg Cu L^{-1} are toxic to fungal spores. The mycorrhizal fungus *Glomus mosseae* colonized fewer onion (*Allium cepa* L.) roots in soil amended with 15 mg Cu kg^{-1} (Gildon and Tinker, 1983) and *G. intraradices* colonized fewer citrus roots in soil amended with 34 mg Cu kg^{-1} (Graham et al., 1986). Soil respiration was reduced in soil amended with 50 mg Cu kg^{-1} (Chang and Broadbent, 1981). Concentrations of 80 to 110 mg Cu kg^{-1} in orchard and other soils resulted in a decline in earthworm populations (Edwards and Bohlen, 1996; Martin, 1986; Paoletti et al., 1995). Particularly in sandy acidic soil, 100 to 150 mg total Cu kg^{-1} (Alva et al., 1993; Reuther and Smith, 1953; Tiller and Merry, 1981) or 20 mg kg^{-1} of either diethylenetriamine pentaacetic (DTPA)- or 0.1 *M* HCl-extractable Cu (Walsh et al., 1972) decreased productivity of Cu-sensitive crops. Despite the potential negative effects to soil flora and fauna, in the USA, Cu pesticide labels do not indicate that beneficial microflora and fauna are adversely affected by soil-borne copper and that persistent use of copper in fields has the potential to diminish the sustained productivity of the soil. The only environmental caution on U.S. Cu pesticide labels regards toxicity to fish and aquatic organisms, and phytotoxicity to Cu-sensitive cultivars.

Our objective was to determine if the amounts of inorganic Cu applied as pesticides in California on perennial crops are sufficient to question whether continued use may ultimately reduce soil function. Here, we show the intensity of use of inorganic Cu in California on the major perennial crops and on rice, which is generally replanted without a rotation. The potential effect of continued Cu applications on soil sustainability is discussed.

Materials and Methods

Data were retrieved as individual applicator records from the California Department of Pesticide Regulation (DPR) (Department of Pesticide Regulation, 2000; Epstein et al.,

Department of Plant Pathology, Univ. of California, Davis, CA 95616-8680. Received 7 July 2000. *Corresponding author (lepstein@ucdavis.edu).

Published in J. Environ. Qual. 30:1844–1847 (2001).

2001). Although the DPR has a process for quality control, a small percentage of the Pesticide Use Report (PUR) records contain errors (Department of Pesticide Regulation, 2000; Epstein et al., 2001). Consequently, records were cleaned as follows. For the PUR, each planting is divided into geographic sections, each with a typical area of 259 ha. Any record with planted area greater than 518 ha is in error and was discarded. For sites for which several values of the planted area were reported, the median was used. Because each record contains application information for a single day, when the area treated exceeded the planted area for any day, the record is in error and the area treated was set to the planted area. The effect of gross errors in the amount of active ingredient was mitigated in the following way. First, the 5th and 95th percentiles of the application rates for each active ingredient, for each crop, for each county were determined. Then the application rate of Cu of any single record whose application rate exceeded the county's 95th percentile was reduced to make the application rate equal to the application rate of the 95th percentile. Values below the 5th percentile were adjusted similarly.

We analyzed perennial crops that had more than 650 reported applications of inorganic Cu in 1998. Although rice is an annual crop, it was included because rice fields are generally planted exclusively to rice without rotation to another crop.

To calculate the total planted area, for each year, the hectares planted in all of the sites were summed. Intensity of Cu use is the mass of Cu applied per unit planted area. To document changes in Cu use during the study period and to minimize annual fluctuations, for each 3-yr period, the average mass of Cu was divided by the average planted area, and the percentage change was determined. To determine whether the observed increases in Cu use might be due to replacement of other pesticidal compounds, we determined the following. For each crop in which Cu use increased (shown in Table 1), and in which there were alternatives to Cu, we examined the total cumulative area treated with the Cu alternatives divided by the planted area. We also determined the total area treated with Cu divided by the planted area. Cu alternatives on the selected crops were as follows: for grapes, azoxystrobin [methyl (*E*)-2-2-6-(2-cyanophenoxy)pyrimidin-4-yloxy-phenyl-3-methoxyacrylate], benomyl [methyl 1-(butylcarbamoyl)benzimidazol-2-ylcarbamate], captan (*N*-trichloromethylthio-4-cyclohexene-1,2-dicarboximide), dicloran (2,6-dichloro-4-nitroaniline), iprodione [3-(3,5-dichlorophenyl)-*N*-(1-methylethyl)-2,4-dioxo-1-imidazolidinecarboxamide], fenarimol [α-(2-chlorophenyl)-α-(4-chlorophe nyl)-5-pyrimidine-methanol], mancozeb (coordination product of zinc ion, manganese ethylene bisdithiocarbamate), maneb (manganese ethylenebisdithiocarbamate), mefenoxam [*N*-(2,6-dimethylphenyl)-*N*-(methoxyacetyl)-*D*-alanine methylester], myclobutanil [α-butyl-α-(4-chlorophenyl)-1*H*-1,2,4-triazole-1-propanenitrile], tebuconazole [α-[2-(4-chlorophenyl)-ethyl]-α-(1,1-dimethylethyl)-1*H*-1,2,4-triazole-1-ethanol], triadimefon [1-(4-chlorophenoxy)-3,3-dimethyl-1-(1*H*-1,2,4-triazol-1-yl)-2-butanone], triflumizole [(*E*)-4-chloro-α,α,α-trifluoro*N*-(1-imidazol-1-yl-2-propoxyethlidene)-*o*-toluidine], and ziram [zinc bis(dimethyldithiocarbamate)]; also as a separate tally for grapes, sulfur and lime sulfur; for lemon and orange, azinophos-methyl [*O*,*O*-dimethyl *S*-[4-oxo-1,2,3-benzotriazin-3(4*H*)-yl)methyl] phosphorodithioate], fosetyl-Al [aluminum tris (*O*-ethyl phosphonate)], mefenoxam [*N*-[2,4-dimethyl-5-[[(trifluoromethyl)sulfonyl]amino] phenyl]acetamide], metalaxyl [*N*,(2,6-dimethylphenyl)-*N*-(methoxyacetyl)-*DL*-alanine methyl ester], and metaldehyde (2,4,6,8-tetramethyl-1,3,5,7-tetroxocane); for peach, azoxystrobin, chlorothalonil (tetrachloroisophthalonitrile), and ziram; for pear, fosetyl-Al, oxytetracycline, and streptomycin (streptomycin sesquisulfate); and for rice, carbaryl (1-naphthyl methylcarbamate) and methyl parathion [*O*,*O*-dimethyl *O*-(4-nitrophenyl) phosphorothioate]. For cherry and plum trees, there were no alternatives to Cu as a dormant treatment for bacterial canker.

Probability values are not presented because we analyzed every reported application, rather than a sample of agricultural pesticide use. Consequently, there are no sampling errors. However, because there is some percentage of nonreporting, the true figures of Cu use are higher than those reported here.

Results and Discussion

Table 1 shows the average intensity of Cu use on selected "permanent" crops for the 6-yr period from 1993 to 1998, in order from most intense to least intense. Based on the 6-yr study, the intensity of Cu use in California appears to be either relatively constant or increasing, depending upon the crop (Table 1). Of the 12 crops, the largest percentage increase in intensity of Cu use was in vineyards, in which there was a 70% increase in the kg Cu km^{-2} planted; both the percentage of growers who applied Cu in vineyards, and the percentage of the planted area that was treated with Cu increased (data not shown). In addition to an increased intensity of Cu use in vineyards, between the first and the second half of the study, the planted area with vineyards increased 10%. Overall in the USA, use of copper hydroxide in agricultural production increased approxi-

Table 1. Cumulative pesticide applications of inorganic copper for the 6-yr period from 1993 to 1998 in California on the twelve "permanent" crops with the largest number of records of applications.

Crop	Total Cu applied	Planted area	Mean Cu	Change in the kg Cu ha^{-1} from 1993–1995 to 1996–1998	Estimated mean Cu addition†
	Mg	10^3 ha	kg Cu ha^{-1}	%	mg Cu kg^{-1} soil
Walnut	4090	75	54	−10	28
Peach	1400	32	43	+8	22
Nectarine	600	16	38	−13	19
Cherry	250	7	34	+45	18
Rice	6440	204	32	+15	16
Apricot	180	8	21	−10	11
Orange	1560	85	18	+23	9
Plum	280	16	17	+24	9
Lemon	300	27	11	+47	6
Almond	2360	205	11	−15	6
Pear	80	10	7	+17	4
Grape	1870	335	6	+71	3

† This assumes that all pesticidal applications of Cu are reported in the California Pesticide Use Reports and that all of the Cu was incorporated into the upper 15 cm of a soil with a bulk density of 1.3 g cm^{-3}.

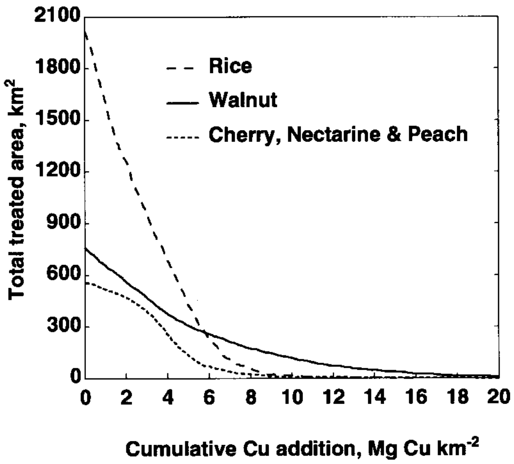

Fig. 1. The cumulative distribution from right to left of the total area treated with the indicated megagrams of copper to each square kilometer for the 6-yr period from 1993 to 1998. Data were calculated on a per-section basis, and the data for the following number of geographic sections are illustrated: rice, 1414; walnuts, 1889; and either cherry, nectarine, and/or peach, 1900.

mately sevenfold from an estimated 700 Mg in 1987 to 5200 Mg in 1997 (Aspelin and Grube, 1999). Because Cu has lower mammalian toxicity than most synthetic pesticides, we used the Pesticide Use Reports to determine if there was evidence that growers had replaced synthetic pesticides with Cu. However, for those crops in which there was an increase in intensity of Cu use, there was no evidence from the Pesticide Use Reports that there was a reduction in use of other fungicides.

Because there is no unequivocal threshold of Cu toxicity in soil, we present the data in Fig. 1 so that the reader can determine the amount of area that has received the indicated amount of Cu over the 6-yr period. We illustrate with an example. Assuming that the Cu in an aerial application is ultimately deposited on the soil and retained in the upper 15-cm depth, and assuming a bulk density of soil of 1.3 g cm^{-3}, an orchard that was treated with a total of 9.75 Mg Cu km^{-2} would have an expected addition of 50 mg Cu kg^{-1} soil dry weight in the upper 15 cm. For walnut orchards, a value of 9.75 Mg Cu km^{-2} on the horizontal axis in Fig. 1 corresponds to a value of 125 km^2 on the vertical axis. Thus, 125 km^2 of walnut orchards were treated with a total of 9.75 Mg Cu or more. As shown in Table 1, there are 750 km^2 of walnut orchards. Thus, 17% of the orchard area was treated with a minimum of 9.75 Mg Cu km^{-2}. However, many walnut orchards in California are managed with minimum or no tillage, and for these farms, the actual Cu concentrations could be twice as high in the upper 7.5 cm. In the USA, pesticide labels for perennial crops typically recommend repeated applications of 1 to 9 kg Cu ha^{-1}, depending upon the crop and the target pathogen. Assuming a bulk density in soil of 1.3 g cm^{-3} and total Cu deposition and retention in the upper 15 cm, a single application of 9 kg Cu ha^{-1} would ultimately result in an increase of 4.6 mg Cu kg^{-1} soil (dry weight). We note that this concentration would be lower if there was movement of Cu off-site due to spray drift, removal of plant material with adsorbed or absorbed Cu, soil erosion, or leaching from the soil. However, in these agricultural systems, very little biomass is removed from the site. Moreover, a preliminary survey of Cu in walnut orchards in Sutter County, California indicated that orchards that had been treated with bacteriocidal applications of inorganic copper had from 73 to 272 mg total Cu kg^{-1} in the upper 15 cm of soil (data not shown). These values support the contention that pesticidal applications of Cu are largely retained in the topsoil. In a Cu budget for a 24-yr-old coffee (*Coffea arabica* L.) plantation that was routinely sprayed with inorganic Cu fungicides, 95 and 4% of the applied Cu was accounted for in the soil and litter, respectively (Dickinson and Lepp, 1985). After Cu sprays were ceased for a 2-yr period, the concentration of Cu in the soil in the upper 20 cm in a coffee plantation remained unchanged (Dickinson et al., 1988). Total soil Cu was positively correlated with stand age and negatively correlated with soil depth (Lepp et al., 1984; Dickinson et al., 1988). Similar data have been documented for other agricultural systems. Pesticidal applications of Cu were primarily recovered from the top 2 and 2.5 cm of soil in vineyards (Flores-Vélez et al., 1996) and tomato (*Lycopersicon esculentum* Mill.) fields (Gallagher et al., 2001), respectively.

Although there are several potential sources of soil-borne Cu, pesticides are typically the largest input (Tiller and Merry, 1981); according to our analysis, approximately 3.8×10^3 Mg of Cu were used as pesticide in California in 1997. Although copper also can be added to soil as a fertilizer for soils low in Cu, and as a contaminant in fertilizers, these inputs are comparatively low in California. The concentrations of Cu in sewage sludge and manure are highly variable (USEPA, 1999). Sludge containing either industrial waste (Chang et al., 1989) and swine manure or poultry manure can be high in Cu. The USEPA 503 regulations allow an annual maximum addition of 75 kg Cu ha^{-1} or a cumulative maximum addition of 1500 kg Cu ha^{-1}. California's Title 22 limits water-soluble copper to 25 mg L^{-1}. Based on the U.S. sludge standards, McGrath et al. (1994) estimated that USA agricultural soils could have a maximum input of 750 mg total Cu kg^{-1} soil, a concentration that is above the lethal dose for some microorganisms that are crucial for soil function (Kabata-Pendias and Pendias, 1992; Tyler, 1975; Chaudri et al., 2000) and for many crops (Walsh et al., 1972; McBride, 1995). In contrast, in the European Community, soils treated with sewage sludge are limited by law to a maximum soil concentration of 50 to 140 mg total Cu kg^{-1}, depending upon the country (McGrath et al., 1994; Matthews, 1996). There is scientific debate on whether even these lower concentrations are sufficient to ensure soil sustainability (Giller et al., 1998), or whether the European limits are overly protective (Smith, 1997). Indeed, the more lax USEPA 503 standards for Cu in sludge are supported by literature (USEPA, 1992), although McBride (1995) has argued that the standards are overly based on corn (*Zea mays* L.), a relatively copper-insensitive crop.

Copper has been used as a fungicide since the 1800s and is considered by farmers and pest management advisors in the USA to be safe and relatively inexpensive.

Indeed, compared with the amount of Cu applied, there are relatively few reports of adverse agricultural consequences of repeated Cu use (e.g., Aoyama and Nagumo, 1996; Graham et al., 1986; Hirst et al., 1961; Reuther and Smith, 1953; Tiller and Merry, 1981; Walsh et al., 1972). Nonetheless, for efficacy, Cu must be applied prophylactically. Thus, given its relatively low cost and perception as a "soft" product, it is often used as insurance against a potential infection event. Although there is concern among pest management personnel about emerging resistance of some pathogens to Cu, and vigilance about avoiding applications at time periods when contact phytotoxicity may occur, there is little acknowledgement of a potential long-term threat to soil sustainability by annual use of Cu, particularly with multiple applications per season with the standard application rates for tree crops.

Acknowledgments

We thank R. Meyer, T. Winsome, and D. Cooksey for helpful discussions, and R. Meyer and S. McGrath for reviewing the manuscript. This study was supported in part by a grant from the University of California Statewide Integrated Pest Management Program.

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