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A REVIEW OF AGRIBUSINESS COPPER USE EFFECTS ON ENVIRONMENT

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Abstract

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Pest control is a critical factor in most commercial orchards and vineyards. There is a demand from growers for increased efficiency of spraying, i.e. improving efficiency of deposition, reducing drift and increasing sprayer output. However, incorrect and uncontrolled use of plant protection products can cause an economic damage due to inadequate yields and quality, wild life damage with undesired effects on non-target species and environment damage because of a direct pollution. Various modern studies in a field of plant protection products are directed to the development of methods used to determine the deposit of plant protection products in order to reduce their direct environmental impact. Evaluations of various spray equipments and application parameters in a plant protection often involve quantitative methods for assessment of spray coverage, deposit and drift. Copper and its compounds have a long year and wide-ranging employment in agriculture. In a review paper a role of cooper in a plant protection and as a spray tracer is outlined, specially related to its long year accumulation in soil and consequently its effects on environment.

Key words: Farm management, plant protection, copper, environment

Introduction

Plant protection is one of the fundamental measures in modern agriculture production and is important for quality and sufficient yields of cultivated plants. The aim of plant protection measures is to keep the infection of plants on a level which does not cause an economic damage. If we do not spray as it is recommended for integrated pest (and disease) management (IPM) or in the worst case, if we do not spray at all, a total damage on the plants may appear.

Downy mildew is for example one of the most damaging diseases of grapevines. It is caused by the fungus *Plasmopara viticola* (Berk & Curt.) Berl. & de Toni. Downy mildew spores are omnipresent. Consequently, preventive fungicides, preferably those which are very persistent, have to be used regularly.

Various plants and their varieties can exhibit fairly different susceptibilities to downy mildew. A good fungicide spray program is extremely important to protect grapevine against downy mildew. It can be effectively controlled by properly timed and effective fungicides. In order to control *Plasmopara viticola*, fungicides with three types

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of activity can be used: contact (not transported within the plant), locally systemic (penetrating into the plant and transported within the treated organ) and systemic (transported to other parts of the plant). It is a good plant protection practice to apply contact fungicide sprays preventively, and to use locally systemic or systemic fungicides (with a curative effect) when climatic conditions are especially favourable for the development of downy mildew and the risk of infection is great. In any case, it is advised always to use locally systemic (azoxystrobin, cymoxanil, dimethomorph) and systemic compounds (benalaxyl, fosetil-Al, metalaxyl) in combination with a contact fungicide (captan, folpet, copper hydroxide, copper oxychloride, mancozeb, metiram, propineb).

Quantity and timing of applications are critical and the efficiency of chemical control greatly depends on the quality of application techniques. An adequate level or mean amount of plant protection product per area unit needs to be deposited in all zones of the treated plants. The sprayer should uniformly deposit material on the canopy, with a minimum of off-target loss. So, it is very important to choose the right sprayer for a particular use, the right nozzle size, the right number of nozzles, a suitable pressure and ground speed as well as the right volume rate. If the operational parameters of the sprayer are correctly set, the maximum relative amount of spray emitted from the sprayer will be deposited on treated plants. Additionally, the minimum still acceptable level of deposit will be achieved in the most inaccessible parts, usually the undersides of the leaves in the centre of the canopy. So it becomes evident that the determination of spray deposit and spray coverage is far from being only an academic issue.

Deposit of Plant Protection Products

Protection of foliage and developing bunches of cultivated plants from attack of various pests and especially fungal pathogens, is essential for the production of adequate yields of good-quality. Correct application of any plant protection product, usually as spray, is a fundamental necessity for the crop, and is often specified in detail by advisory services concerned with the maintenance of the highest quality of the product. For protection against some of the most important diseases, a programme of fungicide sprays serves as a rule in most circumstances as stated by the European and Mediterranean Plant Protection Organisation (EPPO, 2002). Use of biological control agents has little place in the protection of plants, mainly because the most important pests are fungi.

Many fruit and vine growers are trying to apply chemicals in the most efficient and cost effective manner and wherever possible they are moving to integrated pest (and disease) management (IPM) strategies, where the use of pesticide is generally minimised and monitored by a board of experts. Many are also changing the wasteful high-volume spraying for more efficient and cheaper low-volume spraying. Efficient concentrate spraying also reduces off-target environmental contamination (Furness et al., 1998). Because of high costs and time consuming work the biological experiments are often applied only for the final verification of technical assessments of spraying techniques. The measurements of the spray deposit and those of the coverage give either absolute or relative data about the spray distribution within the crop canopy (Holownicki et al., 2002). A high correlation between the deposit and the sprayer characteristics has been verified (De Moor et al., 2000a; De Moor et al., 2000b; Salyani and Fox, 1994). The data about the deposit of pesticides on treated plants, (their dependence on the way of application, on spray volume, on timing of the application, on choice of spray formulation, on type of equipment, on calibration of equipment, on weather and on other conditions) are of great importance (Pergher and Gubiani, 1997; Praat et al., 1996; Hoffmann and Salyani, 1994). For this reason, the spray deposit is often measured by the means of several quantitative methods and expressed as amount of spray per area unit (Cross et al., 1997; Salyani and Fox, 1994). These methods usually use tracers which can be easily analysed (Holownicki et al., 2002).

Copper in Environment and Agriculture

Copper Fungicides

Only a small percent of world copper production is used in agriculture (app. 6 % reported by Lander and Lindestrom, 1999), which effect directly the environment and it represents one of the important sources of dissipation of in-use copper to the soil and the whole environment (Graedel et al., 2002).

Joseph (1999) did quote that copper and its compounds have an extensive employment in agriculture where the first recorded use was in 1761, when it was discovered that seed grains soaked in a weak solution of copper sulphate solution inhibited seed borne fungi. The greatest breakthrough for copper salts undoubtedly came in the 1880s when the French scientist Millardet, while looking for a cure for downy mildew disease (*Plasmopara viticola*) of vines noticed that those vines that have been daubed with a paste of copper sulphate and lime in water in order to make the grapes unattractive to passers-by, appeared freer of downy mildew. This chance observation led to experiments and in 1885 Millardet announced that he found a cure for dreaded mildew. The mixture becomes known as Bordeaux mixture and since then it has been intensive used not only against downy mildew disease, but also against the whole host of fungus diseases of plants. Copper sulphate is not the only copper fungicide. Other copper fungicides which are important against over 300 diseases on almost 50 food crops are copper hydroxide (copper (II) hydroxide ($Cu(OH)_2$)), copper oxide (copper(I) oxide (Cu_2O)) copper sulphate (copper(II) sulphate(VI) ($CuSO_4$)), copper oxychloride (dicopper chloride trihydroxide ($Cu_2Cl(OH)_3$)), and others (Richardson, 1997). Copper has also the inhibitory effects on mites, bacterium, nematodes, etc. (Rusjan et al., 2006).

In spite of good efficacy against pests the copper is still heavy metal which is accumulated on grapes and in soil. The repeated use of copper fungicides since the end of the 19th century to control vine downy mildew, caused by the plant pathogenic fungus *Plasmopara viticola*, has been responsible for the heavy increase of total copper content in the upper layers of vineyard soils (Brun et al., 2003). Repeated spraying with copper fungicides in vineyards lead to serious copper enrichment in soils, but copper toxicity is very rare. High concentrations of copper ions can disrupt the uptake and translocation of iron and copper toxicity induces symptoms resembling those of iron deficiency (Bergman, 1992). Because of the frequent and wide use of copper it becomes serious pollutant.

Copper Accumulation in Soil

Copper is naturally present in soil in content from 2 to 60 mg kg^{-1}, while arable land usually presents amounts of copper between 5 and 30 mg kg^{-1}. In many vine and hop growing areas copper concentrations between 200 and 500 mg kg^{-1} have been found (Macek et al., 1976a; Macek et al., 1976b; Brun, 2003), sometimes even up to 1500 mg kg^{-1} in the topsoil (Chaignon et al., 2003). The world soil has an average concentration of 30 mg kg^{-1} (Adriano, 1986).

It is known that copper tends to accumulate in surface layers of the soil and consequently the topsoil of most vineyards contain large amounts of copper. Furthermore, the major parts of vineyards are located on steep slopes and this leads to extensive soil-erosion processes. All these can wash the copper to downstream crops or ecosystems and copper is disseminated in the environment by run-off.

It was estimated (Besnard et al., 2001) that 1.7 mg soil/ha/year were removed by erosion in Champagne vineyards between 1985 and 1994, corresponding to the removal of an 8 mm thick soil layer during this period. Organic amendments are efficient to limit soil erosion and to increase

Table 1
Average value of copper (mg kg^{-1}) in vineyard soil in the Bizeljsko region

Soil depth / Age	up to 20 cm	20 to 40 cm	40 to 60 cm
vineyard (> 20 years old)	72	46.6	14.5
vineyard (<20 years old)	17.5	12.3	8.4
forests	0.8	0.9	1

soil fertility.

The long term research reports from Slovenia point out that the amount of copper in soil changes a lot because of the geographical structure. The major amounts of copper are especially in agricultural and industrial regions where the amount of copper in soil exceeds 50 mg kg^{-1}.

Macek et al. (1976a) found that Slovenian vineyard soils contained in average 71.82 mg kg^{-1} of copper (between 23 and 265 mg kg^{-1}). The monitoring was made in all 3 Slovenian vineyard regions. Big differences in contents of copper in vineyard soil between all three regions were found:

- Podravje region - contained 82.36 mg kg^{-1} of copper, from 34 to 142 mg kg^{-1}.
- Posavje region - contained 99.9 mg kg^{-1} of copper, from 35 to 265 mg kg^{-1}.
- Primorje region - contained 52.06 mg kg^{-1} of copper, from 23 to 147 mg kg^{-1}.

Stritar and Pavlovic (1988) found the following amounts of copper in vineyard soil in the Posavje region - Bizeljsko (Table 1):

Another research (Rusjan et al., 2006) showed that the content of copper in vineyard soil is the following:

- Primorje region - Goriska Brda contained 75.83 mg kg^{-1} of copper, from 57 to 99 mg kg^{-1}, where the content of copper significantly increases with the age of the vineyard (Table 2).

The comparison of analyses of Macek et al. (1976a) and those of Rusjan et al. (2006) of copper in vineyard soil shows that the pollution with copper in vineyard soil increased for 23.77 mg kg^{-1} during thirty years.

Besides, the contamination of soil in vineyard regions, the contamination of soil in Slovenian hop growing regions where copper fungicides were widely in use, was studied. The results of monitoring (Macek et al., 1976b) in the Savinja valley on hop fields where the copper fungicides were used for 50 years showed the following copper concentrations:

- hop soil - 30.3 mg kg^{-1}, from 5.6 to 80 mg kg^{-1},
- grasslands sampled near the hop fields - 14.7 mg kg^{-1}, from 4.5 to 44.8 mg kg^{-1}.

The results of monitoring (Macek et al., 1976b) in other Slovenian hop growing areas where the copper fungicides were used for 20 years showed the following copper concentrations:

- hop soil - 21.4 mg kg^{-1}, from 4.5 to 108 mg kg^{-1},
- grasslands near sampled hop fields - 9.5 mg kg^{-1}, from 3.5 to 62.6 mg kg^{-1}.

The average copper concentrations in vineyards are above the limit value (the limit value for Slovenia is 60 mg of copper per kg of dry matter (Directive, 1996)) in all vineyard regions. So, it can be concluded that soil pollution with copper is generally present in areas where vine production exists for many years. The main source of this pollutant in all vineyard regions is intensive viticulture practice, especially the use of copper fungicides.

The main problem is that copper is one of the least mobile of the trace elements. Applied

Table 2
Average value of copper (mg kg^{-1}) in vineyard soil in the Goriska Brda

Soil depth / Age	up to 20 cm	20 to 40 cm	40 to 60 cm
vineyard (> 20 years old)	99	88	86
vineyard (<20 years old)	73	67	72
forests	51	51	52

or deposited copper persists in soil because it is strongly fixed by organic matter, oxides of iron, aluminium and manganese, and clay minerals (Adriano, 1986).

Copper Bioavailability to Different Plants

The solubility, mobility and availability of copper to plants depend largely on the pH of the soil. Copper availability is drastically reduced at a soil pH above 7, it is most readily available below pH 6 and especially at pH below 5 (Adriano, 1986).

From an environmental point of view, one of the major issues is to quantify the bioavailability and toxicity of copper accumulated in vineyards to a range of living organisms including cultivated plants. Copper accumulated in soils can be responsible for phytotoxicity above the threshold, which depends on both: plant species and soil properties. The phytotoxicity of copper is mainly observed in acidic soils, and is most likely to occur at pH <6 in soils exhibiting low cation exchange capacity (Brun et al., 2003).

As copper remains concentrated mostly in the upper layers of the soil (0 to 15 cm), plants with the bulk of their roots in the top soil are affected directly by high soil copper concentrations. Most of these plants are ruderals. Weedy or ruderal species are adopted to survive in disturbed environments and are characterized by short life cycles, high rates of dry matter production, and early reproduction (Brun et al., 2003).

Deposit Tracers

A tracer is a substance used to mark the course of a process. This substance may be the active substance in a plant protection product mixture or a chemical selected to mimic the plant protection product. If we are interested only in determining the initial sites of spray deposition, it is reasonable to presuppose that non-plant protection products will suffice, but if it is desirable to follow the subsequent fate of spray deposits then measurement of the active substance of plant protection product, either by radiolabelling or by chemical analysis, is necessary (Cooke and Hislop, 1993).

A comparison of spray equipment and application parameters often involves a quantitative method for assessment of spray coverage, deposit and drift. Some methods provide more reliable results than others. However, none of the existing techniques is suitable for all applications. Therefore, the problems and limitations associated with each technique must be well understood and an appropriate methodology should be selected for a particular application (Salyani and Fox, 1994).

A selection of the most appropriate tracer is based on several criteria, the relative importance of which depends on the particular experiment being undertaken and desirable tracer properties. In practice, the tracers most commonly used belong to the following groups: visible dyes, food colorants, fluorescent compounds and metal tracers.

The utility of multiple tracers was enhanced when Cross et al. (1997b) demonstrated the feasibility of combining three visible dyes to measure spray deposits on apple trees. They showed that tartrazine, erythrosine and Green S could be measured in admixture following sequential spray application. Relative concentrations of up to 20:1 of different tracers in an aqueous sample extract could be analysed. Nevertheless, visible dyes have two disadvantages, the first one is the problem of poor recovery, and the second one that of their spectra exhibiting relatively broad absorbance bands.

Copper as a Deposit Tracer

Historically, tracing sprays via active substances preceded the use of exotic additives. In the simplest and oldest technique an aqueous mixture of quicklime and copper sulphate was applied to grape vines to discourage pilfering (Cooke and Hislop, 1993). The deposits were clearly visible, and thus the sites at which the liquid had been retained were traced. The copper-lime mixture turned out to be an excellent fungicide (known as Bordeaux mixture) and before long the active copper substance was being measured quantitatively and qualitatively by simple colorimetric procedures. In this example, initial copper deposits and subsequent residues can be measured with reasonable ease. However, most modern plant protection products do not lend themselves to such procedures and alternative techniques using dyes have evolved to determine the initial deposition sites of sprays. These have the advantage that potentially noxious plant protection products need not be included in the spray liquid. They do not require specialist analytical skills or sophisticated equipment and are thus quick and cheap to perform (Cooke and Hislop, 1993).

Copper as a deposit tracer was widely used by many authors on various crops to compare different tracers (Whitney et al., 1989; Hoffmann and Salyani, 1996), different determination techniques (Salyani and Whitney, 1988; Kac, 1993), or to avoid the problems associated with fluorescent dye degradation (Salyani et al., 1988; Salyani and McCoy, 1989; Salyani and Whitney, 1990; Salyani, 2000). But the earliest examples of the used of copper as spray tracers was observed (Large et al., 1946; Williams and Morgan, 1954; Cooke et al., 1976; Herrington et al., 1981; Cooke and Hislop, 1993).

Spray Drift as a Plant Protection Negative Effect

Environmental contamination due to the use of plant protection products in agriculture has been the subject of numerous studies (Pergher et al., 1997; Doruchowski and Holownicki, 2000; Holownicki et al., 2000; Cross et al., 2001a; Cross et al., 2001b; Doruchowski et al., 2002; Walklate et al., 2002; Balsari and Marucco, 2004). One of the aspects most considered is spray drift, which is one of the main paths of plant protection products to non-target organisms. Spray drift is the physical movement of plant protection products through air at the time of application or soon thereafter, to any site other than that intended for application - often referred to as off-target (Ozkan, 2000).

Drift is undesirable for economic, environmental and safety reasons. Efficient applicators do not spend money for plant protection products to watch them drift away from their target fields. Today's chemicals are more potent and require more precise application. Unsatisfactory pest control could result if a significant portion of the chemical is lost in drift. This could require respraying the same field (Ozkan, 2000).

Table 3
Factors affecting pesticide drift and deposition

Sprayer	Application	Target	Weather	Operator
Fan size and type	Nozzle type	Canopy structure	Wind speed	Care
Air velocity and direction	Droplet size (VMD*)	Canopy density	Wind direction	Skill
Air volume	Spray pressure	Variety	Temperature	Attitude
Type	Application rate	Leaf area	Humidity	
	Nozzle orientation	Every row	Evaporation	
	Forward speed	Alternate row	Rainfall	
	Chemical formulation			

*VMD (volume median diameter) is used to characterize the relative droplet size of a spray volume from a nozzle. A VMD of 100 microns means that half of the spray volume will consist of droplets that have a diameter of less than 100 microns and the other half of the spray volume will consist of droplets larger than 100 microns (Casady et al., 1999)

Regardless of how accurately an application is made, the possibility of drift is always present. It is possible to minimize this possibility by selecting the right equipment and using sound judgment when applying pesticides. The judgment can mean the difference between an efficient, economical application and one that results in drift, damaging non-target crops and creating environmental pollution (Ozkan, 2000).

Reducing spray drift not only improves application efficiency, but also reduces the risk of safety and health-related problems caused by drift. Because it is impossible to eliminate drift altogether, it is recommend always to wear protective clothing when applying pesticides to reduce the exposure of the operator. A respirator is a must, especially if the tractor does not have a cab (Ozkan, 2000).

However, spray drift occurs wherever liquid sprays are applied and depends on many factors which are summarized in Table 3 (Landers and Farooq, 2004).

Therefore it is essential to evaluate basic drift values but also to improve sprayers so that drift can be reduced. Drift reducing sprayers are nowadays available for field crops as well as for vineyards, orchards and hops. Their ability to reduce drift varies from 50 % to more than 90 %. In vineyards the prototype tunnel sprayers are able to reduce drift more than 90 % (Ganzelmeier and Rautmann, 2000).

Balsari and Marucco (2004) results indicate a considerable influence of the canopy characteristics on the amount of drift deposit on the ground in the area adjacent to the vineyard sprayed. The vineyard featured by a narrower spacing and compact vegetation gave lower drift than the vineyard featured by wider spacing and thinner canopy. Higher values of drift were always observed when fine droplets and high air flow rates were used. The use of air inclusion nozzles gave drift reductions up to 37 % of the reference value (conventional hollow cone nozzles).

Results (Landers and Farooq, 2004) of deposition measurements inside the canopy show that the spray coverage decreased with canopy growth. The decrease in coverage of water sensitive cards (water sensitive papers) was shown at each row with increasing canopy density, also the coverage of water sensitive cards decreased with the distance away from the sprayer. The coverage was recorded up to 4th row on 18 June (middle growth stage) while it was only recorded on the first row on 2 and 10 July (full foliage development).

Increasing spray application rate and air output both led to higher losses to the ground and lower deposition on the foliage. Large plant protection product losses and unsatisfactory uniformity of distribution, which have often been reported for conventional axial-fan sprayers fitted with hydraulic nozzles, may reduce the effectiveness of the operation and increase environmental pollution. In vineyards, losses have been recorded that ranged from 64 to 94 %, in the early growth stages of the vines i.e. April to May (Pergher and Gubiani, 1995). During the early growth stages of the vines (May to June) the total losses ranged from 46 to 69 %, and at full foliage development (July to August) from 43 to 67 %. These have been recorded for conventional axial-fan sprayers (Pergher and Gubiani, 1995; Pergher et al., 1997).

Furthermore, Pergher and Gubiani (1995) found out, that losses to the soil ranged from 34.5 to 36.8 % for the lower spray rates (313 to 391 L ha^{-1}), and from 41.3 to 48.9 % for the medium spray rates (648 L ha^{-1} to 782 L ha^{-1}). Losses due to drift outside the experimental plots and deposition on brunches, shoots and poles ranged from 6.5 to 10.5 % for the lower air output (7.0 m^3 s^{-1}), and from 7.8 to 19.8 % for the higher air output (8.6 m^3 s^{-1}), when the commercial, air assisted, axial-fan sprayer with seven hydraulic nozzles per side was used.

Conclusion

The main objective of any application of plant protection product is to ensure optimal status of cultural plants and crop on one hand and minimal ecological damage on the other. For spraying against diseases as downy mildew, which is caused by ubiquitous spores and therefore presents an always threatening infection, preventive fungicides, preferably those which are very persistent have to be used regularly. Consequently the infection pressure on locally non-treated plants grown in generally treated areas is much lower as in areas that have not been exposed to fungicides for a long time.

This review of publications about use of copper in plant protection and its effect on soil and environment contributes to knowledge with intention to reduce incorrect and uncontrolled use of plant protection products and consequently diminish a risk for an economic damage because of inadequate yields and quality, a threat for wild life with undesired effects on non-target species, and a hazard for environment because of a direct pollution. Furthermore, it is an additional project contribution to a formulation of a monitoring agent within the SCADA decision support system related to agribusiness areas with vineyards, orchards and hop fields (Pavlovic et al., 2008).

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