Transport and retention of copper fungicides in vineyards

MARCEL VAN DER PERK, VICTOR JETTEN, ERIK HESKES, MARJA SEGERS & INGRID WIJNTJENS

Department of Physical Geography, Utrecht University, PO Box 80115, 3508 TC Utrecht, The Netherlands

m.vanderperk@geog.uu.nl

Abstract Copper fungicides, for example Bordeaux mixture, are frequently used in vineyards to protect young grapes against mildew. The copper accumulates in the topsoil layer where it is adsorbed to clay minerals and soil organic matter. Part of the copper may be transported across the vineyard by surface runoff and soil erosion, which could then enter the fluvial system. To investigate the transport and retention of copper in vineyards, detailed mapping of both the lateral and vertical spatial distribution of copper in vineyard soils was performed in two vineyards located in the Ouvèze catchment in southeastern France. The vertical distributions of copper concentrations over the soil profile, and the spatial distribution patterns of copper deposition densities enabled us to identify and assess the redistribution mechanisms and transfer rates of sediment-associated copper within the vineyard fields.

Key words copper; deposition; erosion; France; heavy metals; spatial variation; vineyards

INTRODUCTION

Copper (Cu) fungicides, such as Bordeaux mixture (a mixture of lime and copper sulphate), are frequently used in viticulture to protect young grapes against mildew. Most Cu accumulates in the upper layer of the soil (Deluisa *et al.*, 1996), where is binds to soil organic matter and ferric oxides in the clay fraction (Parat *et al.*, 2002). Soil erosion processes may lead to Cu redistribution within the vineyards and Cu export to the fluvial system (Ribolzi *et al.*, 2002). Depending on the downstream physico-chemical conditions, this Cu may lead to, or contribute to, toxicity to aquatic life.

This study aims to quantify long-term copper transport within and from vineyards due to soil erosion and deposition. Detailed mapping of both the vertical and lateral spatial distribution of copper was carried out in two vineyards (Bigaude and Madeleine) located near Malaucène in the Ouvèze catchment in southeastern France. Table 1 lists the main geomorphological features of these vineyards. The subsoil of both vineyards consists of Pliocenic calcareous loamy sands. The loss on ignition content of the topsoil ranges between 1.5% and 3%. The Bigaude vineyard contains 35 vine rows of approximately 60 to 80 years age and the Madeleine vineyard contains 28 vine rows of about 40 years age (Heskes *et al.*, 2003).

SOIL SAMPLING AND ANALYSIS

During summer 2001, soil samples from both vineyards were taken using a stainless steel corer with a diameter of 70 mm. To explore short range variation of Cu concentrations, the topsoil (0–5 cm) in each vineyard was sampled every 10 m along a transect parallel to the

Table 1 Geomorphological features of the vineyards studied.

Feature	Bigaude	Madeleine
Surface area (ha)	0.99	0.39
Maximum width (m)	89	70
Maximum length (m)	120	91
Maximum altitude difference (m)	4.4	4.3
Mean slope (%)	3.2	4.4

vine rows. Each sampling location was subdivided into four sublocations, viz. below the grapevine (about 10 cm from the vine stem), in the rill along the vine row (about 25 cm), in the wheel track (about 60 cm), and in the middle between the vine rows (about 125 cm). In total 48 topsoil samples were collected from the Bigaude vineyard, and 40 topsoil samples from the Madeleine vineyard. To investigate the vertical distribution pattern of Cu, five soil profiles in the Bigaude vineyard and four soil profiles in the Madeleine were sampled along the same transects. Bulk samples were taken at depths of 0–1, 1–5, 5–10, 10–15, 15–20, 20–40 and 40–60 cm.

To explore the spatial distribution of Cu inventories in both vineyards, bulk samples were collected up to a depth of 30–60 cm below the soil surface using a stratified random sampling scheme (Heskes *et al.*, 2003). Thirty-five bulk samples were collected from the Bigaude vineyard and 30 bulk samples from the Madeleine vineyard. In addition, 12 bulk samples were collected along the transect in the Bigaude vineyard and 10 bulk samples along the transect in the Madeleine vineyard. The sampling depth depended on topographical position and was based on a pilot field study on the vertical distribution in soil using a field Cu test (Merck© Photometric Copper Test Kit Cat. no. 1.14767.0001). This pilot study showed that a sampling depth of 30 cm at the top of the slopes, increasing to 60 cm in the downslope direction, is sufficient to sample the majority of Cu present in the soil profile. To minimize the effect of short range spatial variation, at each sampling location three subsamples were collected at an interval of about 0.3 m perpendicular to the vine rows, and were bulked manually to one composite sample in a plastic bucket in the field. The bulk sample was weighed to determine soil bulk density. After homogenization, an aliquot of about 600 g was taken from the bulked sample to reduce sample weight. In the laboratory, these portions of the samples were dried and weighed. The Cu content was determined by decomposing about 0.5 g of sample with 2 mol l^{-2} HNO_3 in a microwave oven. The Cu concentration in the extract was measured by inductively coupled plasma atomic emission spectrometry (ICP-AES).

SHORT-RANGE VARIATION

Figure 1 shows the Cu concentrations in the topsoil along the transects in the Bigaude and Madeleine vineyards at the various sublocations perpendicular to the vine row. In the Bigaude vineyard, the Cu concentrations increase generally from approximately 100 mg kg^{-1} at the top of the slope to nearly 250 mg kg^{-1} at the foot of the slope. In the Madeleine vineyard, a similar trend can be observed, but the concentration levels are lower (approximately 40 mg kg^{-1} and 150 mg kg^{-1}, respectively). The Cu concentrations in the rill,

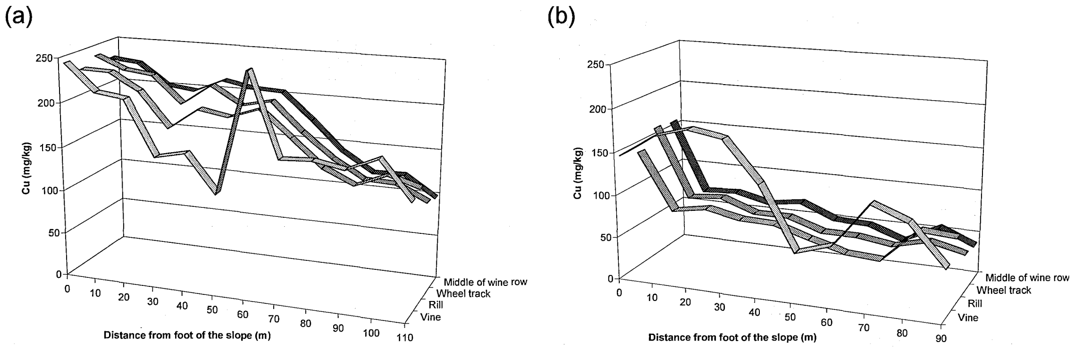

Fig. 1 Short range variation of Cu concentrations in the topsoil along a transect in: (a) the Bigaude vineyard, and (b) the Madeleine vineyard.

wheel track, and the middle of the wine row follow are almost equal along the transects in both vineyards. However, the Cu concentrations in the topsoil below the grapevines show much more variation. In the Madeleine vineyard, the Cu concentrations below the vines are generally larger than farther away from the vines.

VERTICAL VARIATION

The vertical Cu distribution patterns of the upper and lower profile along the transects in the Bigaude and Madeleine vineyards are shown in Fig. 2. These vertical distributions show that the majority of Cu is concentrated in the top 20 cm of the soil profile. In the Bigaude vineyard, the Cu concentrations below the 20 cm are close to the background concentrations of about 6.8 mg kg^{-1} (average Cu concentration of the deepest samples). In the Madeleine vineyard, the vertical distribution is more variable. Only in the upper vineyard profiles do the Cu concentrations decrease close to the background concentration (minimum concentration = 5.9 mg kg^{-1}). The Cu concentrations at 40 and 60 cm depth in the two lower soil profiles remain elevated. Figure 2 also shows that in both vineyards, the Cu concentrations in the topsoil exhibit an increasing trend from the top to the foot of the slope.

WITHIN-FIELD SPATIAL VARIATION

General

The Cu concentration values (mg kg^{-1}) of the bulk samples were converted into Cu inventories (kg m^{-2}) using soil bulk density and sampling depth. To obtain the anthropogenic Cu enrichment in the soil profile, the Cu inventories were corrected for the local background Cu concentrations mentioned above. Table 2 presents the basic statistics of anthropogenic Cu enrichment in the Bigaude and Madeleine vineyards subdivided into stratified random samples and the transect samples. These statistics show that the soil of the Bigaude vineyard contains more Cu than the soil of the Madeleine vineyard. The distributions of the Cu inventories are positively skewed.

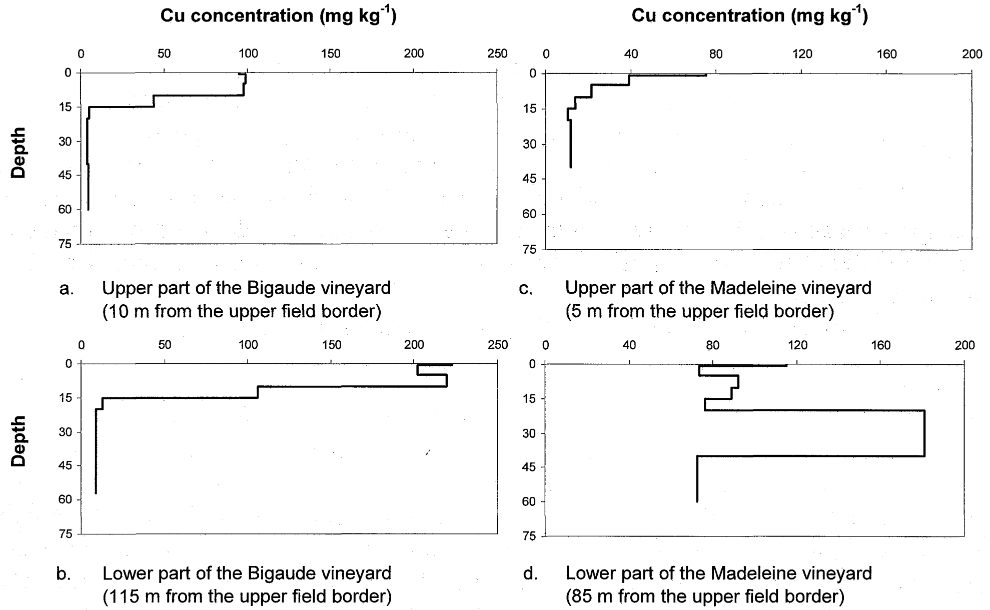

Fig. 2 Short range variation of Cu concentrations in the topsoil along a transect in: (a) the Bigaude vineyard, and (b) the Madeleine vineyard.

Table 2 Statistics of Cu inventories in the vineyard soils.

	Bigaude Stratified random	Transect	Total	Madeleine Stratified random	Transect	Total
N	35	12	47	30	10	40
Mean (kg m^{-2})	0.0369	0.0558	0.0418	0.0302	0.0344	0.0313
Median (kg m^{-2})	0.0322	0.0502	0.0332	0.0198	0.0223	0.0200
St. dev. (kg m^{-2})	0.0167	0.0314	0.0226	0.0266	0.0320	0.0277
Skewness	2.70	1.82	2.49	2.09	1.49	1.83

Relationship between Cu inventories and soil erosion

The relationship between soil erosion and Cu inventories in vineyard soil was explored using a straightforward GIS-based sediment budget index model based on a rill erosion model described by Govers *et al.* (1993). The basic map for analysis of erosion and deposition patterns was comprised of a 1 m × 1 m resolution digital elevation model (DEM) from which the necessary input for the sediment budget index model was derived.

A relative measure for potential soil erosion was derived using:

$$E_r = L^n S^m \tag{1}$$

where E_r is the relative potential erosion rate per unit area, L is the slope length (m), S is the sine of the slope gradient, and n and m are exponents. The sediment transport capacity (Tr) on a given location in the catchment was considered to be proportional to the potential for erosion (Govers *et al.*, 1993):

$$Tr = g_t E_r \tag{2}$$

where g_t is the transport capacity coefficient. The amount of eroded material per grid cell is transported downstream over the drainage network, as long as it does not exceed the transport capacity. The surplus is deposited. The *accucapacitystate* operator in the PCRaster GIS (PCRaster 2001) was used to obtain the amount of deposited material given the drainage network, the available eroded and transported material from the upstream area, and the transport capacity. The relative sediment budget index D_r is calculated by subtracting the eroded material from the deposited material. A positive value for D_r means deposition and negative value erosion.

The Cu inventory was predicted using the regression equation:

$$Cu = A + B \times D_r + \varepsilon \tag{3}$$

where Cu is the Cu inventory (kg m^{-2}), A and B are regression parameters, and ε is the prediction error with $E(\varepsilon) = 0$. The exponents n and m, the transport capacity coefficient g_t, and the regression parameters A and B were simultaneously estimated for both vineyards by means of least squares fitting using the PEST package (Doherty, 2003), a tool for automatic calibration. The lower and upper parameter bounds for the exponents n and m and coefficient g_t were *a priori* set to the values reported in the literature. The *a priori* and calibrated parameter values are listed in Table 3. Table 3 also lists the R^2 between the predicted and observed Cu inventories.

Figure 3 shows the spatial distribution of the Cu inventories predicted using equation 3. This figure demonstrates that the Cu inventories are relatively small in the upper part of the vineyard and relatively large in the lower part.

Table 3 *A priori* and calibrated parameter values.

Parameter	Initial estimation: Lower limit	Upper limit	Calibrated values: Bigaude	Madeleine
N	0.4	0.8	0.8	0.4
M	1.2	1.5	1.2	1.2
g_t	40	90	41.8	56.6
A	0	0.2	0.0421	0.0343
B	0	0.2	0.025	0.184
R^2			0.319	0.556

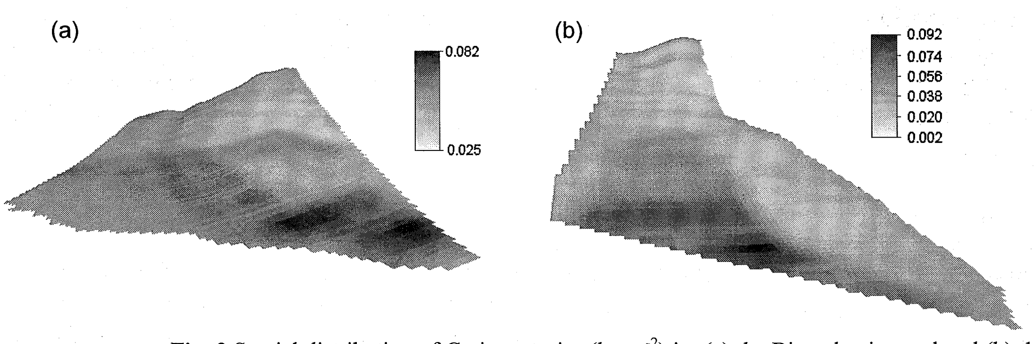

Fig. 3 Spatial distribution of Cu inventories (kg m^{-2}) in: (a) the Bigaude vineyard and (b) the Madeleine vineyard.

ASSESSMENT OF CU TRANSPORT

The vertical distribution of Cu in the soil profiles demonstrates that the Cu is fixed in the upper layer of the soil. This implies that leaching of Cu to deeper horizons is of minor importance. The results from the different sampling campaigns all show that there is a general increasing trend of Cu concentrations in the topsoil and total Cu inventories from the top of the slope to the foot of the slope. These trends suggest that soil erosion and deposition is the principal redistribution mechanism of Cu in the vineyards studied. The soil erosion and deposition processes, as estimated using a straightforward soil redistribution model, account for 32% of the variation in Cu inventories in the Bigaude vineyard and 56% of the variation in Cu inventories in the Madeleine vineyard. The portion of variation that is not explained by soil erosion and distribution may be attributed to spatial differences in the amount of Cu application and accumulation, errors in the model predictions of the relative sediment budget index D_r, and variation due to possible incomplete homogenization of the subsamples.

Parameter A in the regression equation (3) represents the anthropogenic Cu enrichment that would be present in the vineyards if erosion and deposition were absent. Comparison with the mean Cu inventories of the stratified random sampling, which represent the actual Cu enrichment in both vineyards, shows that the actual Cu enrichment is less than the Cu enrichment in the case of no erosion and deposition processes. This implies that there has been a net loss of Cu from the vineyards due to net soil erosion. The time-integrated Cu loss due to soil erosion amounts to 0.0052 kg m^{-2} for the Bigaude vineyard and 0.0041 kg m^{-2} for the Madeleine vineyard. Given the respective ages of both vineyards, 70 years and 40 years, the average net Cu loss rate due to net soil erosion amounts to 0.74 kg ha^{-1} $year^{-1}$ for the Bigaude vineyard and 1.02 kg ha^{-1} $year^{-1}$ for the Madeleine vineyard. Comparison with local Cu application rates is not possible because this information is lacking for the vineyards studied, but the Cu losses found in this study are about one order of magnitude lower than the average Cu input rate reported by Moolenaar & Beltrami (1998) for Italian vineyards (3–16 kg ha^{-1} $year^{-1}$). The greater Cu loss rate from the Madeleine vineyard compared to that from the Bigaude vineyard is probably due to the steeper average slope of the Madeleine vineyard (see Table 1).

CONCLUSIONS

Both the Cu concentrations in the topsoil and Cu inventories in soil in the Bigaude and Madeleine vineyards show a general increasing trend in the downslope direction. The simple soil erosion–deposition model enabled us to estimate the time-integrated Cu losses from the vineyards. Whether the Cu lost is deposited at or near the field borders or transferred into the fluvial system requires further research.

Acknowledgements The authors wish to thank personnel of the Laboratory of Physical Geography for constructing the sampling devices and for carrying out the Cu analyses on the ICP-AES. The authors also thank Mrs P. Scheijen for her contribution to field sampling and laboratory analyses.

REFERENCES

Deluisa, A., Giandon, P., Aichner, M., Bortolami, P., Bruna, L., Lupetti, A., Nardelli, F. & Stringari, G. (1996) Copper pollution in Italian vineyard soils. *Commun. Soil Sci. Plant Anal.* **27**, 1537–1548.

Doherty, J. (2003) *PEST 7.2; Model-independent Parameter Estimation; Manual.* Watermark Numerical Computing, Brisbane, Australia.

Govers, G., Quine, T. A. & Walling, D. E. (1993) The effects of water erosion and tillage movement on hillslope profile development: A comparison of field observations and model results. In: *Farm Land Erosion in Temperate Plains and Hills* (ed. by S. Wicherek), 285–300. Elsevier, Amsterdam, The Netherlands.

Heskes, E., Segers, M. & Wijntjens, I. (2003) Transport of sediment-associated copper on vineyards in the Ouvèze River basin. MSc Thesis, Department of Physical Geography, Utrecht University, The Netherlands.

Moolenaar, S. W. & Beltrami, P. (1998) Heavy metal balances of an Italian soil affected by sewage sludge and Bordeaux mixture applications. *J. Environ. Qual.* **27**, 828–835.

Parat, C., Chaussod, R., Lévêque, J., Dousset, S. & Andreux, F. (2002) The relationship between copper accumulated in vineyard calcareous soils and soil organic matter and iron. *Eur. J. Soil Sci.* **53**, 663–669.

PCRaster (2001) *PCRaster manual*. Department of Physical Geography, Utrecht University, The Netherlands.

Ribolzi, O., Valles, V., Gomez, L. & Voltz, M. (2002) Speciation and origin of particulate copper in runoff water from a Mediterranean vineyard catchment. *Environ. Pollut.* **117**, 261–271.