ELSEVIER

Environmental Pollution 117 (2002) 261–271

ENVIRONMENTAL POLLUTION

www.elsevier.com/locate/envpol

Speciation and origin of particulate copper in runoff water from a Mediterranean vineyard catchment

O. Ribolzi[a,1], V. Valles[a], L. Gomez[b], M. Voltz[c,*]

[a] *Unité de Science du Sol INRA, BP 91 Domaine Saint-Paul, 84143 Montfavet Cedex, France*
[b] *Unité d'Agronomie INRA, BP 91 Domaine Saint-Paul, 84143 Montfavet Cedex, France*
[c] *UMR Sol et Environnement INRA/ENSA, 2 Place P. Viala, 34060 Montpellier Cedex 01, France*

Received 3 March 2001; accepted 10 August 2001

"Capsule": *Results indicate that in vineyard catchments covered mainly by stony red soils the risk of surface water contamination by copper will be greatest.*

Abstract

Fungicide treatments have led to large copper contents of the topsoils of most vineyards. This paper examines the contamination of surface waters by copper in a Mediterranean wine-growing catchment. Its aims were to characterise the forms of copper associated with suspended matter during a heavy autumn storm event and to identify which soils contribute the most to the copper exports. A mixing model involving three reservoirs, corresponding to three soil-landscape units (plateau, terraces and footslope-depression system) and two tracers (reducible iron content and dolomite/calcite ratio) was used to estimate the contribution of each reservoir to erosion during a storm flow. The average copper concentration of the suspended matter was 245 mg kg^{-1}, of which 1% was exchangeable, 4% acid-soluble, 10% oxidizable, 23% reducible and 63% residual. The soils of the plateau of the catchment (chromic luvisols and haplic calcisols—FAO soil classification) were the source of 42% of copper exports but represented only 27% of the total catchment area.

Keywords: Suspended matter; Storm flow; Erosion; Tracer; Heavy metal pollution

1. Introduction

Copper has been used to protect vines against fungus disease since the end of the eighteenth century (Lafforgue, 1928). Even today, a high proportion of fungicides are in the form of copper compounds. It is known that such inputs tend to accumulate in the surface layers of the soil, and in turn the topsoils of most vineyards contain large amounts of copper (Flores Velez, 1996). However, copper is only partially trapped in the surface horizons since many vineyards are subject to water erosion phenomena (Vogt et al., 1986; Litzler et al., 1988). These can wash the copper to downstream crops or ecosystems. Depending on the speciation of copper in runoff water, the downstream physico-chemical conditions (organic complexants, pH, ionic strength, etc.) are likely to favour its solubilisation (Serpaud et al., 1994; Dawson and Macklin, 1998), and thereby its toxicity. It is therefore of interest to characterise the speciation of copper transported by runoff water leaving areas with highly contaminated soils. This is especially the case in south France which presents the largest vineyard area in the world and a Mediterranean rainfall regime leading to intense surface runoff and erosion processes (Gomer, 1994; Albaladejo et al., 1995). Besides, it must be pointed out that copper seems to be predominantly transported by suspended matter in runoff water (e.g. Gilbin et al., 2000; Xue et al., 2000), which can be related to the affinity of copper for sorption on some components of suspended sediments like organic matter, clay minerals and hydrous metal oxydes (Flemming and Trevors, 1989). In this context, this study intends to:

1. characterise the amounts and forms of copper transported by suspended matter during storm

* Corresponding author. Tel.: +33-4-99-61-23-40; fax: +33-4-67-63-26-14.

E-mail address: voltz@ensam.inra.fr (M. Voltz).

[1] Present address: IRD (ex-ORSTOM) 01 BP 182, Ouagadougou 01, Burkina Faso.

0269-7491/02/$ - see front matter
PII: S0269-7491(01)00274-3

flow in a catchment that is representative of the soils and the agricultural practices of the Mediterranean wine-growing region; and
2. identify which soils contribute the most to the particulate copper load of runoff water.

Total copper content is an inadequate variable to use to characterise the behavioural differences of copper in soil, suspended matter or sediment. Copper in soil is known to be distributed among several solid fractions with different physico-chemical properties (Darmendrail, 1987). Five fractions are usually considered: (1) the soluble exchangeable fraction, often low (Emmerich et al., 1982; Shuman, 1986; Saha et al., 1991; Keller and Vedy, 1994); (2) the acid-soluble fraction, usually high in carbonated soils (Misra and Tiwari, 1966; Cavallaro and McBride, 1984); (3) the reducible fraction, associated with iron and manganese oxides and oxyhydroxides if the organic matter content is low (Kuo et al., 1983; Singh et al., 1988); (4) the oxidizable fraction, preponderant in soils with a high organic matter content (Emmerich et al., 1982; Saha et al., 1991); and (5) the residual fraction, which can be higher than the sum of the other four fractions (Emmerich et al., 1982; Kuo et al., 1983).

The five fractions can be determined analytically using chemical or physical methods (X-ray diffractometry, electron microscopy, NMR, etc.). Physical methods give very good results when applied to reference materials, but were shown to be much less precise when applied to raw heterogeneous soils (Flores Velez, 1996). Chemical methods are used more frequently and make it possible to isolate and extract the metals of the different soil constituents by means of extractants. Most extractants, however, are non-specific and also extract elements from the untargeted soil constituents (Nirel and Morel, 1990; Ure, 1996). As a result, the solid phase speciation obtained differs from speciation in the strict sense of the term, since it is rather an "operational" speciation dependent on the extraction method used. This type of approach can nevertheless be very useful in environmental studies (Dawson and Macklin, 1998). It can be used to estimate the risk of trace elements being released when exposed to changes in physico-chemical conditions.

In this study, the chemical extractions proposed by Tessier et al. (1979) were applied to suspended matter samples collected during a heavy autumn storm flow on a small catchment in the wine-growing plain of the Hérault River (Languedoc-Roussillon, France). A mixing model involving three reservoirs, corresponding to the main soil units, and two chemical tracers (reducible iron and dolomite/calcite ratio) was used to identify the spatial origin of the suspended matter and the copper collected at the outlet. This method is widely used to recognize the major water pathways and contributing areas to runoff in catchments (e.g. Pinder and Jones, 1969; Christophersen et al., 1990; Eshelman et al., 1993; Ribolzi et al., 2000).

2. Materials and methods

2.1. Study site

The study area was a catchment located in the French Mediterranean region, in the Hérault river basin about 60 km west of Montpellier (43°30′ N, 3°19′ E). Its 91 ha have for many decades been occupied almost exclusively by vineyards. The landscape consists of three main morphopedological units (Fig. 1):

1. The plateau (24.8 ha), which rises to an altitude of 120 m, consists of two major soil types: (1) stony red soils which are acid at a few locations (chromic luvisols, FAO, 1989), but mostly with secondary carbonates (haplic calcisols, FAO, 1989); and (2) stony brown calcareous soils (haplic calcisols, FAO, 1989). The red soils, which cover the major part of the plateau, are characterised by the presence of crystallised (goethite) or amorphous manganese and iron oxides (Bouzigues et al., 1997). All soils of the plateau are subject to temporary waterlogging phases, caused by the temporary rise of permanent groundwater fluctuating between 1 m and 5 m according to the period of the year.
2. The slopes (30.3 ha) are re-profiled into small terraces and consist of calcareous clay soils low in organic matter content (loamy calcaric regosols, FAO 1989) and affected by the appearance of springs at certain times of the year. On steep slopes the parent material, composed in particular of calcite and dolomite, is exposed.
3. The footslope-depression system (35.6 ha) consists of calcareous soils with poorly differentiated profiles and a loamy texture (loamy calcaric cambisols, FAO 1989) on the gently sloping colluvial footslope, and with a medium- to fine texture with hydromorphic features (gleyic cambisols, FAO 1989) in the depression, where shallow groundwater persists over many months.

The climate is subhumid Mediterranean, with a prolonged dry season and an average annual rainfall of 650 mm. Annual potential evapotranspiration is mostly close to 1000 mm. The summer is dry with rare storms that can cause sporadic flows at the catchment outlet. With the autumn resumption of rain, recharge of the groundwater maintains continuous base flow until spring. Intense surface runoff (Ribolzi et al., 1996, 2000) is responsible for the transport of suspended matter.

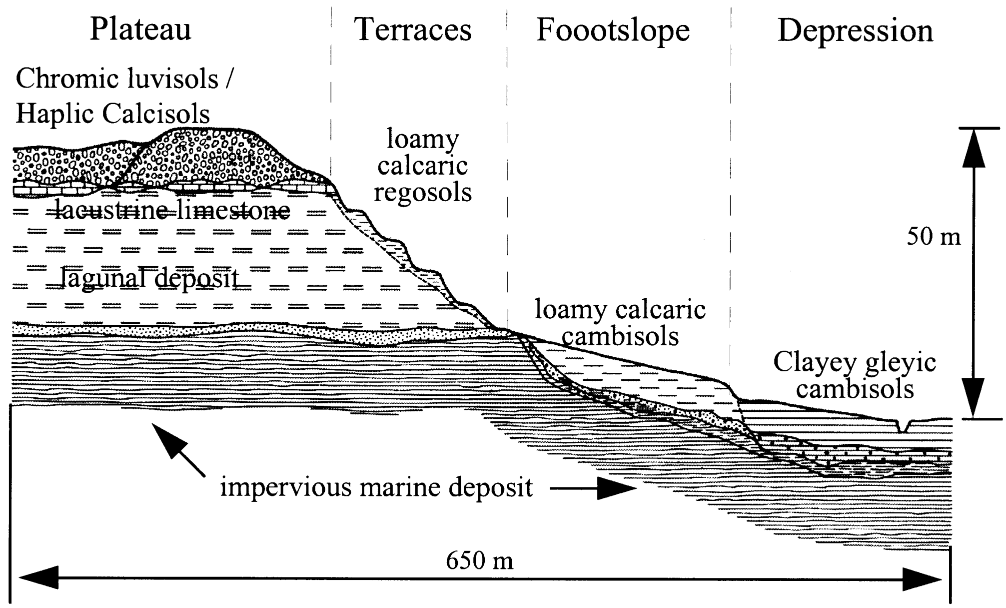

Fig. 1. East–west section of the Roujan catchment.

Table 1
Major mineralogical characteristics of the suspended matter collected in the different morphopedological units[a]

Morphological unit	Carbonates		Oxides		Silicates			
	D/Q	Ca/Q	G/Q	F/Q	S/Q	M/Q	K/Q	Cl/Q
Plateau	t	+	+ +	+ +	+	+	+	+
Terraces	+ + +	+ +	t	t	+ +	+ +	+ +	+ + +
Footslope-depression	+	+	+	–	+ +	+ +	+ +	+ +

[a] The semi-quantitative results of this table were deduced from the abundance of the minerals relative to quartz: + + +, very well represented; + +, well represented; +, moderately to poorly represented; t, traces; –, absence. Q, quartz; D, dolomite; Ca, calcite; F, feldspar; G, goethite; S, smectite; M, mica; K, kaolinite; Cl, chlorite.

2.2. Hydro-meteorological devices

The hydro-meteorological equipment of the Roujan catchment has been described in detail by Voltz et al. (1997). The rainfall measurements presented in this study were taken using a rainfall recorder (model 91, SERPE-TESM, Rennes, France) with tipping buckets (the buckets tipping after 0.5 mm of rain). Discharge at the outlet was measured by an automatic recording station, consisting of a venturi flume, a pressure sensor (model CCl, SERPE-TESM, Rennes, France) and a data logger (model ChloeD, SERPE-TESM, Rennes, France).

2.3. Suspended matter samples and analyses

2.3.1. Samples and mineralogical analyses

The suspended matter was collected using water samples taken manually at the catchment outlet and in the surface runoff during the storm flow event of 4 and 5 November 1994 (Fig. 2). The surface runoff samples came from the plateau, the terraces and the footslope-depression system.

Fifty water samples were taken at the outlet between the start and end of the storm flow event, and 10 samples out of the 50 were selected for determining the mineralogical and chemical characteristics of the suspended matter. It should be noted that the instantaneous variability of the suspended matter content for this storm flow event in the flume section showed a coefficient of variation of the order of 5% during the highest solid flows. Because of this small spatial variation, we were able to limit sampling to a single sample taken from the middle of the flume section.

All water samples were microfiltered using a 0.45-μm filter. The suspended matter content was then determined by weighing after oven-drying the microfiltrates (48 h at 105 °C). The colour of the suspended matter was evaluated on the dry samples using the Munsell code.

The mineralogical composition of the suspended matter and the soil was determined by X-ray diffraction after crushing the total fraction in an agate mortar (Table 1).

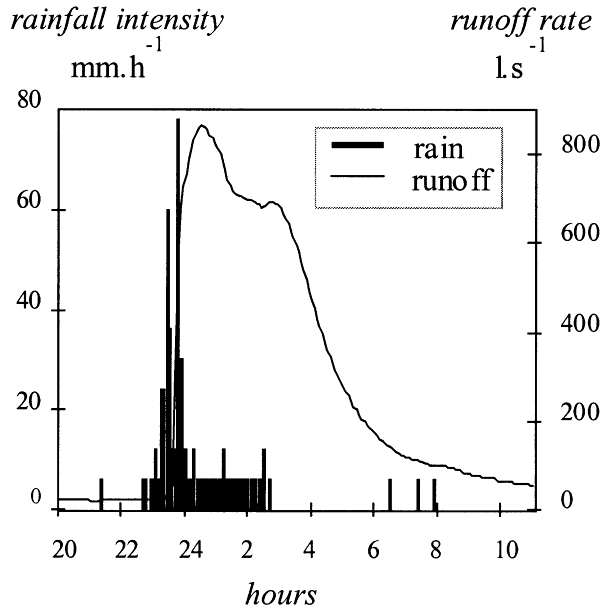

Fig. 2. Catchment runoff and rainfall distribution, as computed over 5 mn time steps, during the storm event of 4 and 5 November 1994.

The relative abundance of each mineral was then estimated by comparing the area of its first order peak to the area of the first order peak of a reference mineral. Quartz was selected as the reference mineral for comparison and mineralogical characterisation of the different spatial units because of its abundance throughout the catchment. However, calcite rather than quartz was used as reference mineral when monitoring dolomite over time at the catchment outlet since it has a rhombohedral crystalline system like dolomite.

2.3.2. Chemical extractions and measurements of copper and iron

There are a large number of protocols for sequential chemical extractions, with different domains of validity (Bermond, 1989). So that we could compare our own results with previous ones from published works, we opted for the frequently used protocol of Tessier et al. (1979).

This method considers five "operational" solid fractions: (1) exchangeable; (2) acid-soluble (associated with the carbonates); (3) reducible (associated with crystallised and amorphous iron and manganese); (4) oxidizable (associated with the organic matter); and (5) residual (incorporated in the crystalline structure of the minerals). The extractants used for these different fractions are listed in Table 2.

The reducible iron content was also determined by this method in order to estimate the iron content associated with the amorphous and crystallised iron oxides in the suspended matter. After extraction, the total copper concentration was measured by atomic absorption spectrometry (Perkin-Elmer, 2100).

Table 2
Chemical extractants advocated by the Tessier et al. (1979) method for the determination of operational fractions of copper in soil or sediment

Operational fraction	Extractant[a]
Soluble exchangeable	$MgCl_2$ 1M at pH 7
Acid-soluble	NaOAc 1M at pH 5
Reducible	$NH_2OH.HCl$ 0.4M in 25% (v/v) HOAc at 96 °C
Oxidizable	HNO_3 0.02 M in 30% H_2O_2 at pH 2 at 85 °C then NH_4OAc 3.2M in 20% HNO_3
Residual	Concentrated $HClO_4$, HF and HCl

[a] NaOAc, sodium acetate; HOAc, acetic acid

2.4. Soil samples and analyses

To characterise copper and iron status in the different soils of the catchment, samples were taken from four pedological profiles that were representative of the different morphopedological situations (Fig. 1): the plateau (profile P32), the small terraces (profile P6), the footslope (profile P5) and the depression (profile P18). The sites were selected using the 1:5000 soil map for the Roujan catchment (Andrieux et al., 1993), which is based on an observation of 56 soil profiles and nearly 500 auger samples.

The physicochemical analyses, presented in Table 3, and the measurements of total copper contents in soil (Fig. 3) were made on samples taken from the horizons of the observed soil profiles to about 2 m depth.

2.5. Mixing model description

To estimate the specific contribution of the plateau, the terraced slopes and the footslope-depression system, to the suspended matter flux at the catchment outlet we used a mixing model involving three reservoirs and two tracers. The two tracers selected for the separation were the reducible iron content and the dolomite/calcite ratio. They were selected because there were great differences in the catchment soils with respect to these two criteria (Table 4). In order to take into account both the processes of granulometric sorting and the spatial variability of the soil, the mineralogical signatures of the reservoirs were estimated using the suspended matter collected within each morphopedological unit. This led to the following system of three mixing equations:

$$\begin{aligned} F_{\text{outlet}} &= F_{\text{plateau}} + F_{\text{terraces}} + F_{\text{footslope-depression}} \\ D/C_{\text{outlet}} F_{\text{outlet}} &= D/C_{\text{plateau}} F_{\text{plateau}} + D/C_{\text{terraces}} \\ &\quad + D/C_{\text{footslope-depression}} F_{\text{footslope-depression}} \\ \text{RI}_{\text{outlet}} F_{\text{outlet}} &= \text{RI}_{\text{plateau}} F_{\text{plateau}} + \text{RI}_{\text{terraces}} F_{\text{terraces}} \\ &\quad + \text{RI}_{\text{footslope-depression}} F_{\text{footslope-depression}} \end{aligned} \tag{1}$$

where F_{plateau}, F_{terraces}, $F_{\text{footslope-depression}}$ and F_{outlet} represent the instantaneous flows of suspended matter

Table 3
Selected physical and chemical properties of four soil profiles located along a transect (Fig. 1) through the plateau (P32), the small terraces (P6), the footslope (P5) and the depression (P18) (after Andrieux et al., 1993)[a]

Profile	Soil type	Depth (cm)	C	L	S	OM	pHwater	CEC
			g kg^{-1}					Mmol$_c$ kg^{-1}
P32	Haplic calcisol	0–50	312	218	470	12.9	8.5	169
		50–80	295	298	407	nd	8.6	139
		80–120	121	175	704	nd	8.8	64
P6	Loamy calcaric regosol	0–20	179	431	390	10.2	8.5	84
		20–40	156	509	335	nd	8.5	80
		60–65	111	501	388	nd	8.9	61
		70–75	175	688	137	nd	8.7	90
P5	Loamy calcaric cambisol	0–35	165	306	529	7.7	8.5	83
		35–95	113	445	566	nd	8.7	54
		95–200	55	119	826	nd	8.9	36
P18	Gleyic cambisol	0–45	289	453	258	13.5	8.5	167
		45–75	236	357	407	nd	8.6	115
		75–105	262	373	365	nd	8.5	128
		105–125	337	384	279	nd	8.5	174

[a] C, clay <2 μm; L, loam 2–50 μm; S, sand 50–2000 μm; OM, organic matter; pHwater, pH measured in the water; CEC, cationic exchange capacity; nd, not determined.

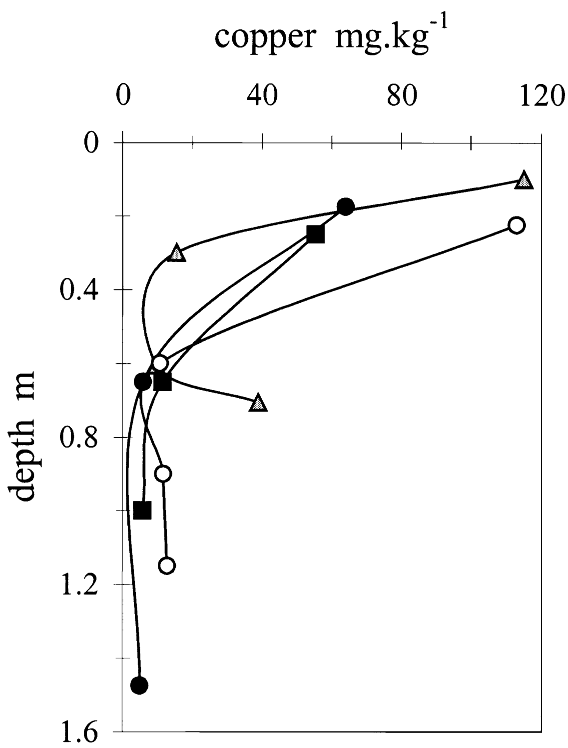

Fig. 3. Examples of the vertical distribution of total copper content in the soils of the plateau (■, profile P32), the terraces (▷, profile P6), the footslope (●, profile P5), and the depression (○, profile P18) (after Andrieux et al., 1993).

from the plateau, the terraces, the footslope-depression system and at the outlet, respectively. Likewise, D/C_{plateau}, D/C_{terraces}, $D/C_{\text{footslope-depression}}$ and D/C_{outlet} symbolize the dolomite/calcite ratios measured on the plateau, the terraces, the footslope-depression system and at the outlet. RI_{plateau}, RI_{terraces}, $RI_{\text{footslope-depression}}$ and RI_{outlet} represent the reducible iron contents measured on the plateau, the terraces, the footslope-depression system and at the outlet.

3. Results

3.1. Characterisation of the spatial units

3.1.1. Mineralogical characteristics of the soil and the suspended matter

The morphopedological units of the catchment had some mineralogical characteristics in common and a few specific characteristics (Andrieux et al., 1993). Quartz was abundant in all pedological units of the catchment. Calcite was also common to all units, with the exception of the small spots of acid red soils of the plateau, which represent less than 3% of the total catchment area. As indicated in Section 2.1, amorphous and crystallised oxides of iron were found mainly in the soils of the plateau, although amorphous form of iron was also observed in the footslope-depression system but in a smaller quantity (Bouzigues et al., 1997). Dolomite originated from the dolomitic limestone layers of the parent material, it was well represented on the terraces.

The major minerals identified in the suspended matter of surface runoff were: quartz, feldspars, mica, kaolinite, chlorite and smectite for the silicates; calcite and dolomite for the carbonates; goethite for crystallised oxides (Table 1). Thus, the mineralogical characteristics

Table 4
Mineralogical characteristics of the suspended matter extracted from the surface runoff water on the three main morphopedological units

Location of sampled water	Reducible iron content (mg kg^{-1})	Dolomite/calcite ratio
Plateau	6148	0.000001[a]
Terraces	3525	0.20
Footslope-depression	2673	0.015

[a] Estimated value to calculate the separation of the suspended solids graph.

of soils reappeared in the suspended matter of the surface runoff. The suspended matter collected on the plateau had a reddish-yellow coloration (HUE 7.5YR 6/6$\pm$1 chroma) and a high reducible iron content (Table 4), resulting from the presence of the iron oxides. As far as the terraces were concerned, they were characterised by a significantly higher dolomite/calcite ratio than for the rest of the catchment (Table 4) and a brownish-yellow coloration (HUE 10YR 6/6$\pm$1 chroma). Dolomite was also found in the colluvia of the footslope and the depression, but in smaller quantities than on the terraces.

3.1.2. Copper content of the soil and the suspended matter

The copper content profiles showed an accumulation in the topsoil for all morphopedological units (Fig. 3). The concentrations observed in the 15–25 cm deep soil layer were 55 mg kg^{-1} on the plateau, 115 mg kg^{-1} on the terraces, 64 mg kg^{-1} on the footslope and 113 mg kg^{-1} in the depression. This surface accumulation can be explained by the nature of the soil, the majority of which was calcareous with a pH of over 8 (Table 3), favouring trapping of the copper already at the surface (Flores Velez, 1996).

The total copper content of the suspended matter (Table 5) was two to four times higher than the total copper contents measured in the 15–25 cm soil layer. This difference is related to the fact that the suspended matter comes from the preferential mobilisation of fine particles in the first few centimeters of the soil, which is the richest part of the soil profile. In effect, a recent sampling of the 0–2 cm surface layers of several soils of the catchment showed an average copper content of 175 mg kg^{-1} (Chaignon et al., 2001) which is close to the copper contents of the suspended matter. Table 5 indicates the respective contents of the different forms of copper for the suspended matter samples collected in the surface runoff water. The residual copper fraction, i.e. the one firmly bound to the minerals because it is incorporated in the crystalline structure, was dominant over the whole catchment. It represented 58% of the total copper on the plateau, 54% on the terraces, and 65% in the depression. Either the reducible or the oxidizable fraction came in second place, depending on the unit. The reducible fraction was higher on the plateau and the terraces, where it represented 26 and 28%, respectively, of the total fraction, as against 11% in the depression. This difference was associated with the presence of oxides on the plateau and the terraces, particularly on the edge of the plateau. The oxides represented a privileged fraction for trapping metals like copper, and this result confirmed the observations of Domingues et al. (1989). The oxidizable fraction was 19% in the depression, as against 7% on the terraces and the plateau. The minority fractions are the exchangeable and the acid-soluble fractions.

3.2. Temporal variations at the catchment outlet

3.2.1. Description of the "downpour-storm flow" event

The studied event took place on 4 November 1994 after the autumn resumption of rain (Fig. 2). Before it rained, the soil was almost saturated with water and the groundwater was less than a meter deep from the surface. The storm flow resulted from a cloudburst of about 43 mm with a maximum intensity, calculated at 5-min time steps, of 78 mm h^{-1}. The downpour was followed by continuous rain of 8 mm h^{-1} of average intensity. Specific peak flow at the catchment outlet, 944 l s^{-1} km^{-2}, occurred with a response time of about 1 h. Intense surface runoff was observed on the cultivated plots, the roads and the paths.

3.2.2. Suspended matter content and mineralogy

Changes in suspended matter content as a function of flow rate at the outlet showed a strong hysteresis between the rise and fall of the water (Fig. 4). The peak of suspended matter content in water flow preceded the water discharge peak by about 0.5 h. The hysteresis effect had already been observed on small cultivated Mediterranean catchments by Gomer (1994). Tu and Graf (1993) explain this phenomenon by the greater shearing forces (higher rates of friction at the bottom) when the hydrograph rises. Another possible explanation might be the initial mobilisation of the non-cohesive particles available at the soil surface at the start of the storm flow.

Variations were also noted in the colour and mineralogical composition of the suspended matter during storm flow. The suspended matter sampled when the water rose was brownish-yellow in colour (HUE 10YR 6/6) and had a high dolomite/calcite ratio. The ratio reached its maximum a few minutes before the peak of suspended matter (Fig. 5). These characteristics of suspended matter during the hydrograph rise were similar to those of the suspended matter sampled in surface runoff water from the terraces and, to a lesser extent, to those from the footslope-depression system (Table 4). They indicate that the suspended matter came from the

Table 5
Copper solid phase speciation in the samples of suspended matter taken from the surface runoff water of the three morphopedological units

Fraction	Particulate copper content					
	Plateau		Terraces		Footslope-depression	
	mg kg^{-1}	%	mg kg^{-1}	%	mg kg^{-1}	%
Soluble exchangeable	6±2	3	9±3	4	4±1	2
Acid-soluble	14±1	6	17±2	7	9±1	3
Reducible	60±5	26	72±6	28	28±2	11
Oxidizable	16±2	7	18±3	7	50±7	19
Residual	131±8	58	137±9	54	171±11	65
Total	227	100	253	100	262	100

The analytical uncertainty corresponds to that estimated by Tessier et al. (1979).

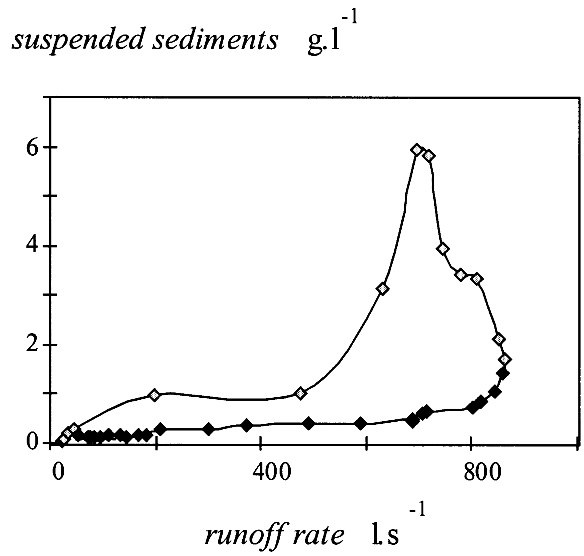

Fig. 4. Changes in suspended sediment contents as a function of runoff rate during the rise (◇) and fall (◆) of the 4 and 5 November 1994 storm event.

slopes and the areas close to the outlet. In contrast, the samples collected as the suspended matter content in storm flow fell had a small dolomite/calcite ratio, and a reducible iron content that rose to 4000 g kg^{-1} (Fig. 5). Their colour gradually changed to reddish-yellow (HUE 7.5YR 6/6). These latter characteristics are close to those of the suspended matter leaving the plateau, which gives evidence of a delayed contribution from the unit, which is furthest from the outlet. Consequently, the observed hysteresis phenomenon in suspended matter content is also due to the temporal variation of the relative contributions to flow of the different geomorphological compartments of the catchment.

3.2.3. Separation of the suspended matter discharge

The separation of the suspended matter discharge as estimated by using the mixing model is shown in Fig. 6. Four temporal stages can be distinguished: (1) A relatively short first stage, lasting about 10 min, during which the plateau, terraces and footslope-depression system contributed 50, 25 and 25%, respectively. This first stage corresponded to the mobilisation of sediment deposited in the ditches during previous storm flows. It concerned a negligible amount of sediment over the duration of the event (around 1% of the total sediment losses). (2) A second stage, of about 15 min, during which the contribution of the terraces was markedly dominant (up to 95% of the instantaneous discharge) and coincided with the peak of the suspended matter content in runoff water. This result points out the role of erosion on the slopes in the hysteresis of the flow rate–suspended matter concentration relationship (Fig. 4). (3) Then, for 20 min, only the plateau and the footslope-depression system participated, in proportions of 50% each. It will be noted that although the footslope-depression system was near the outlet, its maximum contribution occurred after that of the terraces, which were further away. This can be associated with the intense surface runoff on the terraces and the effectiveness of the ditch network, which collected the flows at the field outlets and took them to the catchment outlet. (4) Finally the contribution of the footslope-depression system declined in favour of that of the plateau. The contribution of the plateau was delayed and spread over a long period of time because of its distance and its spatial extent.

Over the period during which the contribution of each compartment was estimated, namely between 23:39 and 00:37, the total erosion amounts from the plateau, the terraces and the footslope-depression system were 267, 138 and 113 kg ha^{-1}, respectively. Thus, although the plateau represented only 27% of the total catchment area, it contributed over 45% of off-site exports of solid matter during the monitoring period. The terraces and the footslope-depression system contributed 28 and 27%, respectively.

3.2.4. Forms and spatial origin of the copper of the suspended matter

In this part, the quantities of copper coming from the different compartments and their distribution among

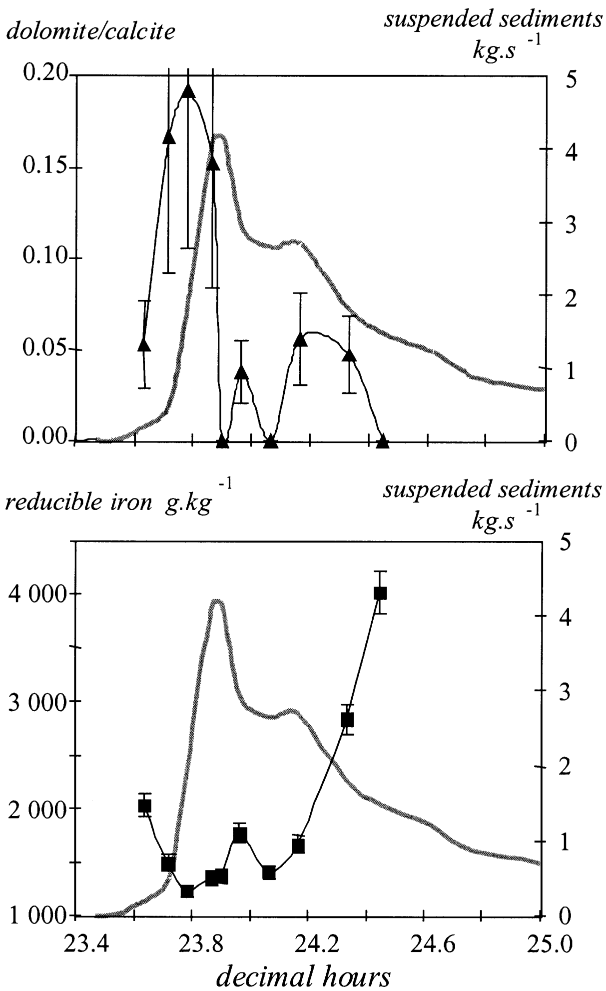

Fig. 5. Temporal changes in suspended sediment contents (▬), in dolomite/calcite ratio (—▲—) and in reducible iron content (—■—) of the catchment runoff water during the 4 and 5 November 1994 storm flow. The vertical bars represent the standard deviations.

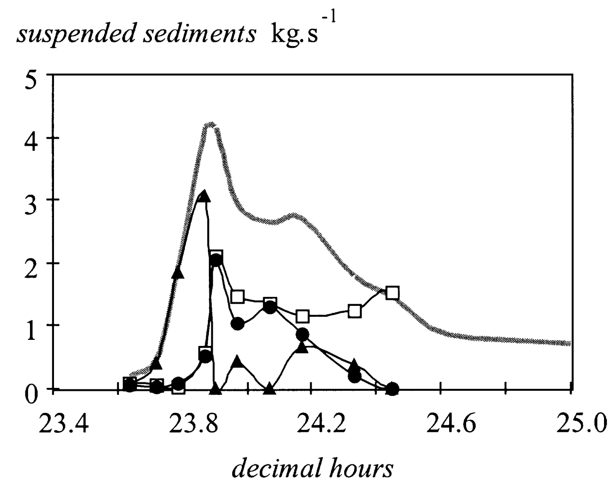

Fig. 6. Estimated contributions to total suspended sediment flow (▬) of flows exiting the plateau (—□—), the terraces (—▲—) and the footslope-depression system (—●—).

the five solid fractions (Table 6) were computed from the estimated contributions of the geomorphological compartments to suspended matter flow at the catchment outlet (cf. Fig. 6) and from the specific copper speciation in the suspended matter exiting each compartment (cf. Table 5). To validate this calculation, we compared the computed losses by runoff of the five copper fraction with those observed at the catchment outlet. Fig. 8 shows a good agreement between the observed and computed quantities.

The contents of exchangeable and acid-soluble copper were low and varied very little during the storm flow (Fig. 8). The values measured at the outlet were of the same order of magnitude as those of the different units (Table 5). This demonstrates the small spatial variability of these two fractions and confirms their secondary role in copper fixation and transport. Over 40% of the copper exported in this form would appear to come from the plateau (Table 6) during the monitoring period, which is consistent with the size of the latter's erosive contribution.

The reducible copper content increased progressively during the storm flow (Fig. 7). This change was closely correlated to that of iron bound to oxides (Fig. 5). The maximum was reached when the suspended matter content fell and coincided with the greatest contribution of suspended matter from the plateau (Fig. 6). These observations show the importance of oxides in copper fixation. Forty-nine percent would appear to be exported from the plateau soil (Table 6), confirming its importance as a source of reducible copper.

Unlike reducible copper, the concentrations of oxidizable copper fell during the storm flow (Fig. 7). The variations occurred in three stages. (1) A first stage corresponded to the highest values. This coincided with resuspension of the sediment deposited in the ditches. It probably involved copper associated with organic matter trapped in the ditches. (2) The oxidizable copper content then fell strongly with the arrival of the suspended matter from the terraces. (3) Finally, it fell gradually. The last samples corresponded to the plateau inputs. They had the lowest values.

The residual copper content also evolved in several stages. A first stage of decline, the minimum of which coincided with the maximum contribution from the terraces. It then increased quite considerably to reach values of between 150 and 200 mg kg^{-1}. This stage coincided with the participation of the downstream system, which had the highest concentration of residual copper. It then fell again to values comparable with those measured on the plateau (Table 5). These observations confirm the concentrations measured in the suspended matter of the surface runoff. They also confirm the importance of the residual fraction, in particular in the footslope-depression system. The variations

Table 6
Runoff losses of the different solid species of copper for the plateau, the terraces and the footslope-depression system during the 4 and 5 November 1994 storm event

Spatial unit	Exchangeable		Acid-soluble		Reducible		Oxidizable		Residual	
	g ha^{-1}	%	g ha^{-1}	%	g ha^{-1}	%	g ha^{-1}	%	g ha^{-1}	%
Plateau	1.6	43	3.7	46	16.0	49	4.3	28	35.0	41
Terraces	1.2	40	2.3	36	9.9	37	2.5	20	18.9	27
Footslope-depression	0.5	17	1.0	18	3.2	14	5.7	53	19.4	32

The values were estimated using a mixing model involving three reservoirs and two tracers (reducible iron content and dolomite/calcite ratio).

in total copper content appear to be governed by variations in the content of residual copper, which constitutes the essential element of particulate copper.

4. Discussion and conclusions

The two objectives that this study was designed to achieve were (1) to identify the amounts and forms of copper transported by suspended matter during storm flow events in the Mediterranean wine-growing region and (2) to assess the specific contributions of the soils of the studied catchment to the forms of particulate copper exported by its stream in a storm flow period. The forms of particulate copper that were considered are the five operational fractions defined by the sequential extraction procedure of Tessier et al. (1979).

The average copper concentration of the suspended matter at the outlet of the Roujan catchment was 245 mg kg^{-1}. It is much larger than the concentrations in particulate copper observed in an other agricultural catchment (Xue et al., 2000) the River Kleine Aa catchment. This can be related to the smaller copper contents of the topsoil and to the less intense rainfalls in this latter catchment as compared to those in the Roujan catchment. Besides it is interesting to notice that the contamination of suspended solids at Roujan is close to that observed in River Aire which receives significant quantities of Cu from sewage treatment works and industrial effluents (Dawson and Macklin, 1998). This indicates that fungicide treatments in vineyards can lead to a large contamination of surface waters by particulate copper during storm events. More generally, it also shows that agriculture, like domestic and industrial effluents, can be a significant source of copper pollution to surface waters.

The forms of particulate copper were in average order of importance: residual (63%), reducible (23%), oxidizable (10%), acid-soluble (4%) and soluble exchangeable (<1%). The order changed only slightly during the storm flow in accordance with the morphopedological origin of the suspended matter. Our results point out that the majority of copper is associated with the residual fraction, which is not very soluble and is therefore not likely to be toxic to organisms. Nevertheless, they

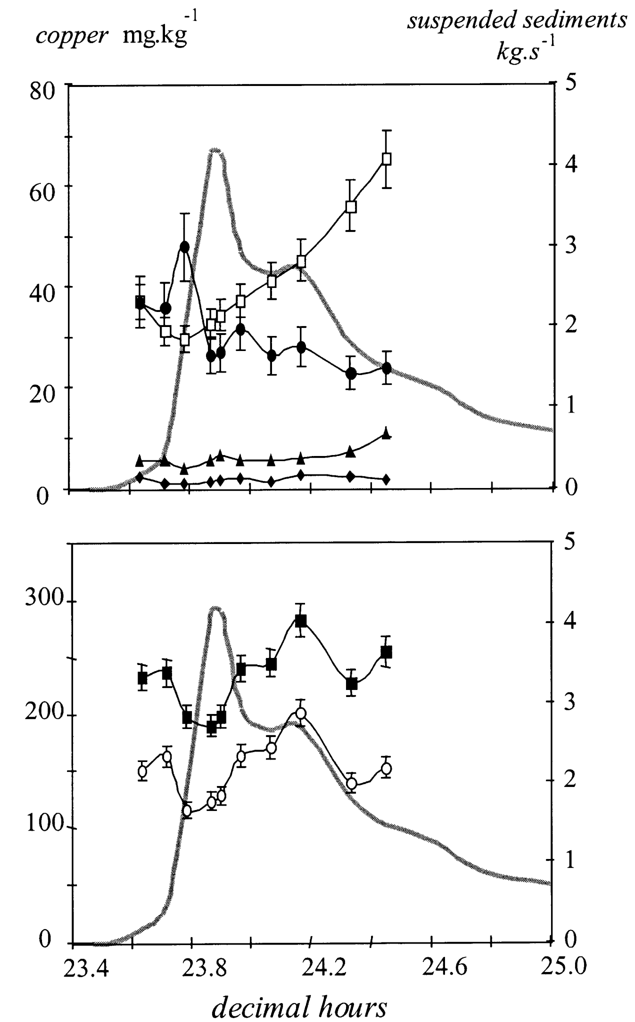

Fig. 7. Temporal variation in suspended sediment content (▬), exchangeable (—◆—), acid-soluble (—▲—), réducible (—□—), oxydizable (—●—), résidual (—○—), total (—■—) copper content of catchment runoff water during the 4 and 5 November 1994 storm event. The vertical bars correspond to the standard deviation.

also underline the importance of the reducible fraction, in other words of the copper associated with the iron and manganese oxides. This may have an environmental impact, since the reducible copper fraction is particularly sensitive to reducing conditions and can therefore be solubilized in the aquatic ecosystems (lagunes), that are downstream of the vineyard area in south France. If

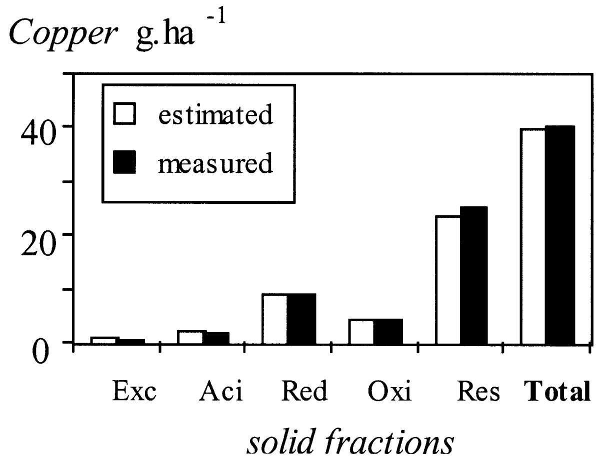

Fig. 8. Comparison of the observed losses in copper fractions (exc, exchangeable; aci, acid-soluble; red, reducible; oxy, oxydizable; res, residual) during the 4 and 5 November 1994 storm event with those estimated by the mixing model [cf. Eq. (1)].

we assume a suspended sediment content of 1 g l^{-1}, the solubilization of the reducible copper fraction would lead on average to a dissolved copper concentration in water of almost 60 μg l^{-1}, which is above the thresholds of toxicity to salmonides, invertebrates and micro-organisms (see review by Flemming and Trevors, 1989).

By using a mixing model involving two tracers (reducible iron and dolomite/calcite ratio) and three reservoirs to separate the graph of suspended solids in the storm flow, we were able to estimate the contribution of each morphopedological unit to runoff losses in particulate copper during the studied storm event. The values for the plateau, the terraces and the footslope-depression system were 60.6, 34.8 and 29.8 g ha^{-1}, respectively. The soils of the plateau appeared to be more sensitive to erosion during the studied storm event: although they represented only 27% of the total catchment area, 42% of the exported copper and 50% of the reducible copper fraction came from this unit. Since the plateau is almost only made of stony red soils which are a major soil type in south France, this suggests that in vineyard catchments covered mainly by stony red soils the risk of surface water contamination by copper will be maximum.

Finally, it must be noticed that a further analysis over a longer monitoring period including several storm events is needed to determine the ranges of variation of the amounts, forms and origin of particulate copper that were observed in this preliminary study.

Acknowledgements

This work was supported by INRA through contract "AIP Valorisation et Protection des Ressources en eau", by the PACA Region and by the Ministry of Environment (contract PNETOX) We thank P. Andrieux and R. Moussa for providing the hydrological and rainfall data, R. Bouzigues for pedological observations, and are grateful to M. Augier for the atomic absorption analyses and to L. Roger for the X-ray diffraction analyses.

References

Andrieux, P., Bouzigues, R., Joseph, C., Voltz, M., Lagacherie, Ph., Bourlet, M., 1993. Le Bassin Versant de Roujan. Caractéristiques Générales du Milieu (Internal Report). Laboratory of Soil Science, National Institute for Agricultural Research, Montpellier.

Albaladejo, J., Ortiz, R., Guillen, F., Alvarez, J., Martinez-Mena, M., Castillo, V., 1995. Erodibility of agricultural soils in the semiarid mediterranean area of Spain. Arid Soil Res. Rehab. 9, 219–226.

Bermond, A., 1989. Localisation des métaux traces dans les sols: limitation des protocoles d'extractions séquentielles. In: Gomez, A. (Ed.), Trends in Trace Elements Bulletin of the FAO Research Network on Trace Elements. INRA-FAO, Versailles, France, pp. 21–28.

Bouzigues, R., Ribolzi, O., Favrot, J.C., Valles, V., 1997. Carbonate redistribution and hydrogeochemical processes in two calcareous soils with groundwater in a Mediterranean environment. Eur. J. Soil Sci. 48, 201–211.

Cavallaro, N., McBride, M.B., 1984. Zinc and copper sorption and fixation by an acid soil clay: effect of dissolution. Soil Sci. Soc. Am. J. 48, 1050–1054.

Chaignon, V., Sanchez-Neira, I., Jaillard, B., Hinsinger, P., 2001. Relation between copper phytoavailablity and chemical properties of 29 contaminated soils from a vine-growing area. Proceedings of the 6th International Conference on the Biogeochemistry of Trace Elements, 28 July–2 August 2001, Guelph, Ontario, Canada (in press).

Christophersen, N., Neal, C., Hooper, R.P., Vogt, R.D., Andersen, S., 1990. Modelling streamwater chemistry as a mixture of soilwater end-members—a step towards second generation acidification models. J. Hydrol. 116, 307–320.

Darmendrail, D., 1987. Filtration géochimique des métaux lors de leur transfert d'une rivière vers une nappe alluviale—Applications à la nappe des alluvions du Rhône (69) et de la Deule (59). Thèse de Doctorat en Science, Université de Bordeaux III, France.

Dawson, E.J., Macklin, M.G., 1998. Speciation of heavy metals on suspended sediment under high flow conditions in the River Aire, West Yorkshire, UK. Hydrological Processes 12, 1483–1494.

Domingues, H., Vieira E Silva, J.M., Menezes Sequeira, E., 1989. Sequential extraction of heavy metals in soils derived from the main lithological formations of Portugal. In: Gomez, A. (Ed.), Trends in Trace Elements Bulletin of the FAO Research Network on Trace Elements. INRA-FAO, Versailles, France, pp. 51–66.

Emmerich, W.E., Lund, L.J., Page, A.L., Chang, A.C., 1982. Solid phase forms of heavy metals in sewage sludge-treated soils. J. Environ. Qual. 11, 178–181.

Eshleman, K.N., Pollard, J.S., O'Brien, A.K., 1993. Determination of contributing areas for saturation overland flow from chemical hydrograph separations. Water Resour. Res. 29, 3577–3587.

FAO-UNESCO, 1989. Soil Map of the World at 1:5,000,000, 2nd Edition. Food and Agriculture Organization, Rome.

Flemming, C.A., Trevors, J.T., 1989. Copper toxicity and chemistry in the environment: a review. Water, Air and Soil Pollution 44, 143–158.

Flores Velez, L.M., 1996. Essai de spéciation des métaux dans les sols: cas du cuivre dans les vignobles. Thèse de Doctorat en Science, Université de Paris XII, France.

Gilbin, R., Casellas, C., Gomez, E., Balaguer, P., Pardos, M., Wildi, W., 2000. Copper speciation and bioavailability in agricultural watersheds. Proc. 3rd SETAC World Congress, 21–25 May 2000, Brighton, UK.

Gomer, D, 1994. Ecoulement et érosion dans des petits bassins versants à sols marneux sous climat semi-aride méditerranéen. Thèse de Doctorat en Science, Université Technique de Karlsruhe, Allemagne.

Keller, C., Vedy, J.C., 1994. Distribution of copper and cadnium fractions in two forest soils. J. Environ. Qual. 23, 987–999.

Kuo, S., Heilman, P.E., Baker, A.S., 1983. Distribution and forms of Cu, Zn, Cd, Fe and Mn in soils near a copper smelter. Soil Sci. 135, 101–109.

Lafforgue, M., 1928. La Bouillie Bordelaise. 1er Congrés International de la Vigne et du Vin.

Litzler, C., Boidron, R., Lilin, C., 1988. Maîtrise de l'Érosion en Vignoble de Côteau, Aspects Agronomiques. ITVV, INRA, Paris.

Misra, S.G., Tiwari, R.C., 1966. Retention and release of copper and zinc by some Indian soils. Soil Sci. 101, 465–471.

Nirel, P.M.V., Morel, F.M.M., 1990. Pitfalls of sequential extractions. Water Research 24, 1055–1056.

Pinder, G.F., Jones, J.F., 1969. Determination of the ground-water component of peak discharge from the chemistry of total runoff. Water Resour. Res. 5, 438–445.

Ribolzi, O., Valles, V., Bariac, T., 1996. Comparison of hydrograph deconvolutions using residual alkalinity, chloride and oxygen 18 as hydrochemical tracers. Water Resources Research 32, 1051–1059.

Ribolzi, O., Andrieux, P., Valles, V., Bouzigues, R., Bariac, T., Voltz, M., 2000. Contribution of groundwater and overland flows to storm flow generation in a cultivated Mediterranean catchment. Quantification by natural chemical tracing. J. Hydrol. 233, 241–257.

Saha, J.K., Mondal, A.K., Hazra, G.C., Mandal, B., 1991. Depthwise distribution of copper fractions in some ultisols. Soil Sci. 151, 452–458.

Serpaud, B., Al-Shukry, R., Casteignau, M., Matejka, G., 1994. Adsorption des métaux lourds (Cu, Zn, Cd et Pb) par les sédiments superficiels d'un cours d'eau: rôle du pH, de la température et de la composition du sédiment. Revue des Sciences de l'Eau 7, 343–365.

Shuman, L.M., 1986. Effect of liming on the distribution of manganese, copper, iron and zinc among soil fractions. Soil Sci. Soc. Am. J. 50, 1236–1240.

Singh, J.P., Karwasra, S.P.S., Singh, M., 1988. Distribution and forms of copper, iron, manganese and zinc in calcareous soil of India. Soil Sci. 146, 359–366.

Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace metals. Analytical. Chemistry 51, 844–851.

Tu, H., Graf, W.H., 1993. Friction in unsteady open-channel flow over gravel beds. Journal of Hydraulic Research 31, 22–43.

Ure, A.M., 1996. Single extraction schemes for soil analysis and related applications. The Science of the Total Environment 178, 3–10.

Vogt, H., Levy, G., Mettauer, H., 1986. Ablation hydrique en vignoble en conditions d'érosion chronique et exceptionnelle: mécanismes et coûts comparés. Exemple du vignoble de Sigolsheim et Kienzheim, Haut-Rhin, France. Cahier ORSTOM, série Pédologique XXII, 133–137.

Voltz, M., Andrieux, P., Bouzigues, R., Moussa, R., Ribolzi, O., Joseph, C., Trambouze, W., 1997. Main hydrological processes in a farmed catchment of the mediterranean area. In: Viville, D., Littlewood, I. (Eds.), Ecohydrological Processes in Small Basins, 6th ERB Conference Strasbourg, 24–26 Septembre 1996, IHP-V Technical Documents in Hydrology No. 14. UNESCO, Paris, pp. 111–115.

Xue, H., Sigg, L., Gächter, R., 2000. Transport of Cu, Zn and Cd in a small agricultural catchment. Wat. Res. 34 (9), 2558–2568.