Copper mobilization affected by weather conditions in a stormwater detention system receiving runoff waters from vineyard soils (Champagne, France)

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1. Introduction

New legislations such as the EU-Water Framework Directive (WFD) require from Member States to take measures against relevant pollutants entering surface waters (Gregoire et al., 2008). Copper, a priority substance on the EU-Water Framework Directive list, is widely used to protect grapevines against fungus diseases. Many vineyards being located on steep slopes, large amounts of Cu could be discharged in downstream systems by runoff water. The efficiency of stormwater detention basins to retain copper in a vineyard catchment was estimated. Suspended solids, dissolved (Cu\text{diss}) and total Cu (Cu\text{tot}) concentrations were monitored in runoff water, upstream, into and downstream from a detention pond. Mean Cu\text{tot} concentrations in entering water was 53.6 mg/L whereas it never exceeded 2.4 mg/L in seepage. Cu\text{tot} concentrations in basin water (> 100 mg/L in 24% of the samples) exceeded LC50 values for several aquatic animals. Copper was principally sequestered by reduced compounds in the basin sediments (2/3 of Cu\text{tot}). Metal sequestration was reversible since sediment resuspension resulted in Cu remobilization. Wind velocity controlled resuspension, explained 70% of Cu\text{diss} variability and could help predicting Cu mobilization.

Keywords: Copper, Detention pond, Partitioning, Oxidation, Resuspension

Copper concentrations with values commonly ranging from 100 up to 1500 mg/kg (Chaignon et al., 2003; Chopin et al., 2008; Fernández-Calviño et al., 2008; Mirlean et al., 2007; Vavoulidou et al., 2006). In runoff water, Cu appears to be predominantly transported by suspended matter (Velleux et al., 2006; Leblanc and Schroeder, 2008). This results from Cu high affinity for clay minerals, organic matter, Fe- and Mn-oxides (Hoang et al., 2008; Sipos et al., 2008). In vineyard, the bare soil located between crop rows can easily be eroded and transported by water runoff. Numerous vineyards are planted on steep slopes (mean slope: 10–14% in the Champagne region, Ballif, 1994). Theses slopes favor runoff and erosion during storms (Wainwright, 1996; Kosmas et al., 1997; Besnard et al., 2001). Thus, soil being extremely susceptible to erosion (up to 8 ton/ha/year) could result in large quantities of Cu being introduced into downstream water systems (Ballif, 1994).

In many countries, dry stormwater detention basins have been built for flood control and retention of contaminant-rich particles (Youssef et al., 1994; Ribolzi et al., 2002). In particular, suspended solids removals in basins result from a combination of physical, chemical and biological processes (Scholes et al., 1998; Cheng et al., 2002) and can generally be as high as 60–90% (USEPA, 1985). However, removals can be much lower and depend mainly on the...
residence time of water and the level of sediment accumulation within the basin (Chavan et al., 2008).

To keep stormwater basins fully functional, sediments have to be removed from basins every 10–25 years (MOEE, 1994; Youssef et al., 1994). Subsequently, the sediments can be spread on agricultural fields. Dredging of Cu-enriched sediments from retention basins and spreading them onto agricultural soils induce changes in physical and chemical conditions potentially modifying Cu bioavailability (Bramley and Rimmer, 1988; Bedell et al., 2006). In this context, this study intends:

1. to assess the efficiency of a stormwater basin to retain copper;
2. to identify the conditions responsible for copper remobilization that can further induce surface- and groundwater contamination.

2. Material and methods

2.1. Study area

The studied stormwater detention system is located in an agricultural catchment in the heart of the Champagne vineyard area (Marne, NE France; Fig. 1). The surface of the catchment area represents 3.8 km² mainly covered by vineyards (34%) and forest (34%). The Champagne region has a suboceanic climate with continental influences (Ballif, 1994). Each year, in July and August, approximately 8 kg/ha of copper are sprayed on the vineyards to fight mildew. The average slope in vineyards is 11% and average annual rainfall is 596 mm during the 1999–2008 period (recorded at the local weather station). The retention system aims at controlling soil erosion in the Champagne region.

The soils are classified as mollic Leptosol (FAO-WRB, 2006), commonly known as Rendzinas or Rendosols (INRA, 1995), and were developed on Mesozoic chalk. They show alkaline pH (7.9 ± 0.1), high organic carbon (3.1 ± 0.4%; NF ISO 14235), high CaCO₃ content (15.8 ± 3.4%; NF ISO 10693), and high copper concentrations (278 ± 35 mg/kg; Marin et al., 2008). Soils are clayey silt loam. Local average water hardness is 250 mg/L as CaCO₃ and pH is 7.8.

The water detention system is composed of two successive unplanted stormwater retention basins with a surface area of 4000 and 7000 m², respectively (Fig. 1). Because of frequent submersion, vegetation (graminious and herbaceous) was scarce in the first basin whereas the entire surface of the second basin was colonized. The basins are surrounded with a 1.6 m high clayey earth embankment.

Input to the system results from runoff from the surrounding vineyard soils. Runoff waters are discharged into the first basin through pipes 1 and 2 (60 and 80 cm Ø, respectively; Fig. 1). Water is exported from the first basin into the second one by discharge ducts 3 and 4 (30 cm Ø pipes) and a 4 m wide spillway (location 5; Fig. 1). Water accumulates in the southeast corner of the second basin due to the bottom slope. Since their construction 16 years earlier and until the end of the study period, no water was ever discharged from Basin 2 to the Vesle River by overflow. Water outputs from the second basin are limited to evaporation and seepage.

2.2. Meteorological data

Daily maximal wind velocities and daily rainfalls were recorded at a weather station (Cimel Enerco 407) located on the catchment area at 2 m above ground level. Wind velocities was measured continuously and integrated over daily periods using Cimel AN 155A sensor. Rainfalls were measured using Cimel PL1881 sensor and recorded daily. Evaporation in ponds (Ep) was estimated as evaporation measured in an evaporation pan (1200 mm Ø; 250 mm height; located 10 cm above the maximal basin level) multiplied by a corrective factor (F). Previous studies on evaporation in ponds estimated corrective factors of 0.7 (Hounam, 1973) and 0.8 (Boyd, 1985) using similar evaporation pans (US Weather Bureau Class A evaporation Pan). Therefore, in this study, a corrective factor of 0.75 was applied.

2.3. Flow rate measurement and sample collection

2.3.1. Input- and output-waters

During the whole study period (from March 11th to June 6th 2002), water flows were measured continuously at sampling locations 1 to 4 using MADOSOLO stations (s/n 2303 data logger with type 26 pressure sensor usable in the 0–500 mbar range) and were estimated by gauging at sampling location 5 when overflow from the first basin occurred. Waters were sampled using 0.5 L polyethylene flasks, automatically every 90 min at locations 1 to 4 using Sigma 9000 automatic samplers and manually at location 5 with the same frequency and the same flasks. Flasks were combined by four before analyzes. Over the whole sampling period, 43 water samples at the inlets...
(locations 1 and 2) and 28 at the outlets (locations 3 to 5) were analyzed for suspended solid (SS) and copper (total and dissolved) concentrations. Samples were kept at 4°C and processed within 24 h. All vessels were soaked in 2 M HNO3 for 48 h and rinsed three times with denized water prior to sample processing.

2.3.2. Waters in Basin 1
Over the whole study period, 25 samples of water were collected in the first basin. Water was pumped from the tank twice a week using a polyethylene pipe connected to the deepest part of the basin (location 6), at 5 cm above bottom sediments.

2.3.3. Seepage
In order to collect infiltrated water, three piezometers were installed at locations a, b and c (Fig. 1). The piezometers were made of PVC tube (8 cm Ø, 90 cm long), perforated (1 mm Ø holes) all around the tube at 45 cm depth. Every week, piezometers were emptied dry and water was pumped and collected for analysis the following day.

2.3.4. Sediments
A core representing the entire bottom sediment profile (15 cm thick) was collected using a CEMAGREF core sampler (CEMAGREF, 1980) at the centre of the first basin on March 13 (Fig. 1). The core was divided into four sediment layers (0–2, 2–5, 5–10 and 10–15 cm depth, respectively) and dried in an oven at 40°C during 48 h.

2.4. Sample analyses

2.4.1. Water
Suspended solid concentrations were obtained by filtration of 1 L of sampled water with pre-acidified (HNO3) GF/C filters dried at 105°C for a minimum of 24 h following the recommended NFT 90-105 method for water analysis (AFNOR, 1994). Copper concentrations in water were determined using the NFT 90–112 and NFT 90–119 procedures (AFNOR, 1994). Total Cu concentrations (CuTot) in water were obtained from unfiltered water acidified to pH 2 with HNO3, whereas dissolved Cu concentrations (CuDiss) were determined using pre-filtered water subsequently adjusted to pH 2. Analyses were performed using either flame or graphite furnace Atomic Absorption Spectrophotometer (AAS), depending on the concentration levels, as detection limits were estimated at 15 and 0.5 μg/L for flame and graphite furnace, respectively.

2.4.2. Sediments
Sediment samples were digested in 6 mL 69% HNO3 – 2 mL 48% HF – 2 mL 30% H2O2, in a 1:10 (g:mL) ratio, at 140°C for 2.5 h to determine total Cu concentrations according to Sastre et al. (2002).

2.4.2.1. Acid-soluble fraction. A mixture of 1 g of sediment (1 g) and 40 mL of 0.11 M acetic acid was shaken for 16 h at 20°C, then centrifuged at 3600 rpm for 30 min.

2.4.2.2. Reducible fraction. A mixture of fraction 1 residue and 40 mL of 0.5 M hydroxylamine hydrochloride adjusted to pH 2 with nitric acid was shaken for 16 h at 20°C, then centrifuged at 3600 rpm for 30 min.

2.4.2.3. Oxidizable fraction. A mixture of fraction 2 residue and a 10 mL aliquot of 30% H2O2 was digested for 1 h at 85 ± 2°C. After reduction of the volume to approximately 3 mL, a 2nd 10 mL 30% H2O2 aliquot was added. The mixture was heated at 85 ± 2°C for 1 h and the volume was then, reduced to near dryness. After cooling to room temperature, 50 mL 1 M ammonium acetate adjusted to pH 2 with nitric acid was added. The mixture was shaken for 16 h at 20°C, then centrifuged at 3600 rpm for 30 min.

2.4.2.4. Residual fraction. Fraction 3 residue was digested in 69% HNO3 – 48% HF – 30% H2O2 following the procedure described for total concentration determination. After each extraction, the remaining solid was rinsed with denized water and used for the subsequent extractions. All supernatants were filtered prior to analysis and special care was taken to avoid losing sediment material. All the solutions were stored in polyethylene vials at 4°C until analysis and analyzed by AAS. The accuracies of the total and sequential extraction concentrations were evaluated using a Certified Reference Material (CRM 483) and following the strategy described by Marin et al. (1997). The calculated accuracies (5%) indicated good data quality.

2.5. Mass balance calculations
Quantities of SS and Cu carried by water were calculated as the product of the mean concentration (g/L) and mean flow rate (L/h) for two successive samples multiplied by the number of hours separating these two samplings (Banas et al., 2002).

The volume of water discharged in the first basin (VRunoff, expressed in L) was calculated as the sum of runoffs recorded at sampling points 1 and 2.

The volume of direct rainfall on the basins (VRainfall, expressed in L) was estimated as the rainfall measured at the weather station (mm) multiplied by the total surface area of the two basins (m2).

The volume of evaporation (VEvap, expressed in L) was calculated as the product of basin surface area (m2) and evaporation in ponds (Ep, expressed in mm).

The volume of seepage from basins was determined using the following equation:

\[ V_{\text{seep}} = (V_{\text{Rainfall}} + V_{\text{Runoff}}) - (V_{\text{Overf}} + V_{\text{Evap}}) \]

with VOverf corresponding to the volume of water discharged from Basin 2 by overflow (VOverf = 0 in this study as no overflow occurred).

The maximum quantities of copper loss from basins by seepage (CuSeep) were calculated using the following equation:

\[ Cu_{\text{Seep}} = V_{\text{seep}} \times Cu_{\text{Max}} \]

with CuMax corresponding to the maximum concentration of total copper measured in water collected in piezometers.

2.6. Statistical analyses
Statistical analyses were performed using STATISTICA StatSoft® software (StatSoft, 2002). In order to assess the impact of wind on the resuspension of basin sediments, the best relationships (linear, exponential, and power) between concentrations (SS and copper) in water and daily maximal wind velocity were searched using various time-windows during the seven days prior to water sampling (Banas et al., 2005). In the present study, maximal wind velocity measured on the sampling day was W0 and maximal wind velocity measured during a time lapse of i days preceding the sampling is W0−i. Thus, concentrations measured at t = 0 were correlated with W0−3, W0−2, W0−1, W0, W0+1, W0+2 and W0+3.

2.7. Comparison of Cu concentrations with LC50 values
In the National Criteria Document (USEPA, 1985), all the LC50 values are for total copper in water having a hardness of 50 mg/L as CaCO3. Water hardness in the study area was 250 mg/L as CaCO3. Therefore, to compare Cu concentrations with the reported LC50 values, the LC50 were re-calculated to take into account increased hardness using the following equation (USEPA, 1985):

\[ LC50_{\text{estim}} = e^{-\frac{t}{LC50}} \times \ln(250) \times \ln(50) \]

with LC50estim: LC50 estimated for a hardness of 250 mg/L as CaCO3; LC50: LC50 Values reported in the USEPA document (USEPA, 1985); 0.9422: the pooled slope between hardness and LC50 values for all species in the USEPA database.

3. Results

3.1. Meteorology
During the 88 days of the study period, the rainfall measured at the local weather station was 102.5 mm. A large proportion of rainfall (45.5 mm) occurred between March 18 and 22 (Fig. 2). Rain was then scattered between April 16 and May 27. Daily maximum wind velocity higher than 12 m/s was observed mainly during rainy episodes (March 18–20, April 29; Fig. 2) and exceptionally on dry days (April 6).

3.2. Input- and output-waters
Input volumes of water due to rain falling directly on the two basins (VRainfall) were estimated at 113 m3. Loss of water due to evaporation (VEvap) was estimated at 335 m3. The volume of runoff water (VRunoff) discharged into Basin 1 was estimated at 11 120 m3.
Runoff water was discharged in Basin 1 during three rainy events known as runoff periods (March 18–22, April 26–May 1, May 4–5). The mean and maximal Cu$_{\text{tot}}$ concentration in runoff water were 53.6 and 143.3 µg/L, respectively. During the study period, the mass of Cu$_{\text{tot}}$ discharged into Basin 1 was estimated at 596 g.

Excepted during the first runoff period, no water was discharged from Basin 1 to Basin 2. Mean Cu$_{\text{tot}}$ concentrations recorded in the outlets during this event was 43.5 µg/L. During the whole study period, 3303 kg of SS were discharged from runoff waters (mean SS concentration = 297 mg/L). Basin 1 allowed to retain 26% (2910 m$^3$) of the runoff waters, 45% (1488 kg) of the SS, 40% (239 g) of Cu$_{\text{tot}}$ and 14% (13.8 g) of the Cu$_{\text{diss}}$ (Table 1).

3.3. Suspended solid and Cu concentrations in basin waters

In Basin 1, mean Cu$_{\text{tot}}$ and Cu$_{\text{diss}}$ concentrations were estimated at 56.0 and 19.5 µg/L, respectively. The highest Cu$_{\text{tot}}$ concentration (April, 26) was determined as 120.8 µg/L. No significant differences could be found in total Cu concentrations in sediments with depth (192–203 µg/g; Table 2), indicating that sediment contamination was homogeneous over the entire sediment thickness. Copper was found associated to the oxidizable (2/3 of the total Cu) and residual (1/3 of the total Cu) fractions, with negligible amounts found associated to the acid-soluble and reducible fractions (<1%; Table 2). Copper partitioning remained similar with depth.

3.4. Seepage

The total volume of seepage discharged from the two basins during the study period was estimated at 10 898 m$^3$. Total Cu concentrations in piezometers exceeded AAS detection limit (0.5 µg/L) for 3 out of the 12 sampling campaigns (March 22, April 12, May 3). Total Cu concentrations in piezometers a, b and c were respectively 2.1, 1.7, and 2.0 µg/L on March 22, 2.4, <0.5, and 1.2 µg/L on April 12, and 1.9, <0.5, and <0.5 µg/L on May 3. The maximum quantity of Cu seeped from the basins during the whole study period (Cu$_{\text{seep}}$) was estimated at 26.2 g (i.e. less than 4.4% of the total Cu mass discharged into Basin 1).

3.5. Copper concentrations and partitioning in detention basin sediments

No significant differences could be found in total Cu concentrations in sediments with depth (192–203 µg/g; Table 2), indicating that sediment contamination was homogeneous over the entire sediment thickness. Copper was found associated to the oxidizable (2/3 of the total Cu) and residual (1/3 of the total Cu) fractions, with negligible amounts found associated to the acid-soluble and reducible fractions (<1%; Table 2). Copper partitioning remained similar with depth.

Table 1

<table>
<thead>
<tr>
<th>Sampling location</th>
<th>Period</th>
<th>n</th>
<th>Water (m$^3$)</th>
<th>SS (kg)</th>
<th>Total Cu (g)</th>
<th>Dissolved Cu (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlets (locations 1, 2)</td>
<td>March 18–24</td>
<td>20</td>
<td>8960</td>
<td>2787</td>
<td>458</td>
<td>179</td>
</tr>
<tr>
<td>Outlets (locations 3, 4, 5)</td>
<td>March 18–24</td>
<td>28</td>
<td>8210</td>
<td>1814</td>
<td>357</td>
<td>222</td>
</tr>
</tbody>
</table>

Fig. 2. (a) Meteorological conditions at the weather station. (b) Suspended solid (SS) and (c) total and dissolved Cu concentrations in Basin 1. Hatchings on the horizontal axis indicate periods during which water was discharged into Basin 1. Vertical arrows indicate sampling campaigns displaying Cu concentrations in seepage water exceeding analytical detection limit.
3.6. Copper concentrations and toxicity to aquatic organisms

Since the toxicity of copper decreases when water hardness increases, LC50 reference values given by the USEPA (1985) were re-calculated (LC50estim.) for a hardness of 250 mg/L following equation (3) for the most sensitive species (D. pulicaria). The USEPA (1985) quoted a Cu acute toxicity for 53 aquatic species. Among these species, the LC50 ranged from 9.3 mg/L for the most sensitive species (D. pulicaria) to 10 240 mg/L for Acrocinus lycorias for a water hardness of 50 mg/L expressed as CaCO3. Our results show that the water entering the detention pond present acute toxicity against D. pulicaria while maximal Cuconcentrations recorded in the inlets were toxic to at least 7 out of the 53 species listed by the USEPA (1985).

Using equation (2), Cu release by infiltration (CuSeep.) from the two basins was estimated to be less than 26.2 g since Cuconcentrations in seepage water never exceeded 2.4 µg/L. As mean Cuconcentration in runoff water was 53.6 mg/L, at least 95% of Cu carried by runoff waters was retained in the stormwater basins. The highest Cu concentrations in seepage waters were observed during the sampling campaigns carried out shortly after windy events (Fig. 2). The high correlation (r² = 0.87) observed in Basin 1 between SS concentrations and wind velocity recorded within one day, highlighted the important and immediate role of the wind on sediment resuspension (equation (4); Fig. 3). This compared well with previous results showing that the increase in SS concentrations in shallow aquatic systems was generally observed between 2 h to 1 day after the increase in wind velocity (Banas et al., 2005). Similarly, the strong relationship between Cuconcentrations and wind velocity recorded during the two days preceding the sampling date could result from significant resuspension of Cu-enriched sediments (equation (5); Fig. 3). Terzakis et al. (2008) described windy and rainy events as the main factors contributing to contaminated sediment resuspension in detention ponds.

On the other hand, the best relationship between Cuconcentrations and wind velocity, explaining 70% of the variability in basin water, was observed when considering a period of five days preceding the sampling date (equation (6); Fig. 3). Wen and Allen (1999) reported a three-day lag between the resuspension of sediments and the observation of a Cu concentration peak in the water column of the “Le An” River. Direct porewater infusion from sediments could partially explain our results but slower processes were likely involved (Petersen et al., 1995; Caetano et al., 2007). According to Waes et al. (2005), metal desorption from suspended particles and re-oxidation of Cu sulfides also participate to the increase in Cuconcentration in the water. Zwolsman et al. (1997; Baeyens et al., 1998). Copper was negligibly associated to the acid-soluble and reducible fractions (<1%) and predominantly found in the oxidizable fraction corresponding to sulfides and/or organic matter (2/3 of the total Cu; Table 2). Under anoxic conditions prevailing in water flooded basins, these oxidizable bonds

### Table 2

<table>
<thead>
<tr>
<th>Depth intervals (cm)</th>
<th>Total Cu concentrations (µg/g)</th>
<th>Acid-soluble phase (%)</th>
<th>Reducible phase (%)</th>
<th>Oxidizable phase (%)</th>
<th>Residual phase (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0–2</td>
<td>203</td>
<td>0.3</td>
<td>0.2</td>
<td>67.6</td>
<td>31.8</td>
</tr>
<tr>
<td>2–5</td>
<td>192</td>
<td>0.4</td>
<td>0.2</td>
<td>68.8</td>
<td>30.6</td>
</tr>
<tr>
<td>5–10</td>
<td>203</td>
<td>0.7</td>
<td>0.2</td>
<td>63.2</td>
<td>35.8</td>
</tr>
<tr>
<td>10–15</td>
<td>202</td>
<td>0.5</td>
<td>0.3</td>
<td>65.0</td>
<td>34.3</td>
</tr>
</tbody>
</table>

Fig. 3. Determination coefficient (r²) of exponential relationships between concentrations of various parameters, and maximal wind velocity recorded during the time period (from sampling day through to seven days) preceding the sampling (samples collected during rainfall and the three following days being excluded).

Fig. 4. Comparison between mean (dashed lines) and maximum (full lines) Cuconcentrations recorded in Basin 1, inlets and outlets, and mean LC50 re-calculated for a hardness of 250 mg/L (LC50estim.) following equation (3) for the most sensitive species (USEPA, 1985).
should be relatively stable (Calmano et al., 1993). However, sediment resuspension may facilitate oxidation processes, which in turn could result in Cu release from sulfides and/or organic materials (Förster et al., 1989; Ciceri et al., 1992; Petersen et al., 1997; Zwolsman et al., 1997). Lors et al. (2004) observed, for several days, large releases of metals from resuspended sediments and assumed that they result from bacterial oxidation of metal sulfides. In our studied stormwater basins, sediment resuspension resulting from windy events combined with biological activities favored by suitable climate conditions (i.e. temperature) could lead to slow oxidation of the oxidizable Cu fraction. Contribution of the different parameters in the oxidation processes remains to be quantified. The resulting solubilized trace elements could further escape the basin through seepage waters.

5. Conclusions

The use of a stormwater basin appeared efficient to limit Cu contamination of downstream aquatic systems by runoff water discharged from vineyards. Indeed, Cu adsorption on organic materials (Fo¨rstner et al., 1989; Ciceri et al., 1992; Petersen et al., 1997; Ciceri et al., 1993) could result in Cu release from sulfides and/or organic material (Calmano, Hong, Fo¨rstner, 1993). Binding and mobilization of heavy metals in contaminated sediments affected by pH and redox potential. Water Science and Technology 28, 223–235.


