



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

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Copper in stormwater basin is efficiently retained but can be released during windy events or after dredging.

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ABSTRACT

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_{diss}) and total Cu (Cu_{tot}) concentrations were monitored in runoff water, upstream, into and downstream from a detention pond. Mean Cu_{tot} concentrations in entering water was 53.6 $\mu\text{g/L}$ whereas it never exceeded 2.4 $\mu\text{g/L}$ in seepage. Cu_{tot} concentrations in basin water (>100 $\mu\text{g/L}$ in 24% of the samples) exceeded LC_{50} values for several aquatic animals. Copper was principally sequestered by reduced compounds in the basin sediments (2/3 of Cu_{tot}). Metal sequestration was reversible since sediment resuspension resulted in Cu remobilization. Wind velocity controlled resuspension, explained 70% of Cu_{diss} variability and could help predicting Cu mobilization.

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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 is one of the metals included on the WFD list of priority substances. Since the end of the 19th century, Cu-based fungicide treatments (i.e. Bordeaux mixture $\text{Ca}(\text{OH})_2 + \text{CuSO}_4$) have been widely applied to vineyards in order to prevent and treat fungus diseases, such as vine downy mildew (Lafforgue, 1928). Nowadays, over 6000 tons of Cu are spread annually in French agriculture as metal-based pesticides and metal-containing organic amendments and such compounds tend to accumulate in surface soils (Ranjard et al., 2008). Consequently, most vineyard topsoils exhibit elevated

Cu 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). These 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 solid 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

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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 ($3.1 \pm 0.4\%$; NF ISO 14235), high CaCO₃ content ($15.8 \pm 3.4\%$; 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 (gramineous 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

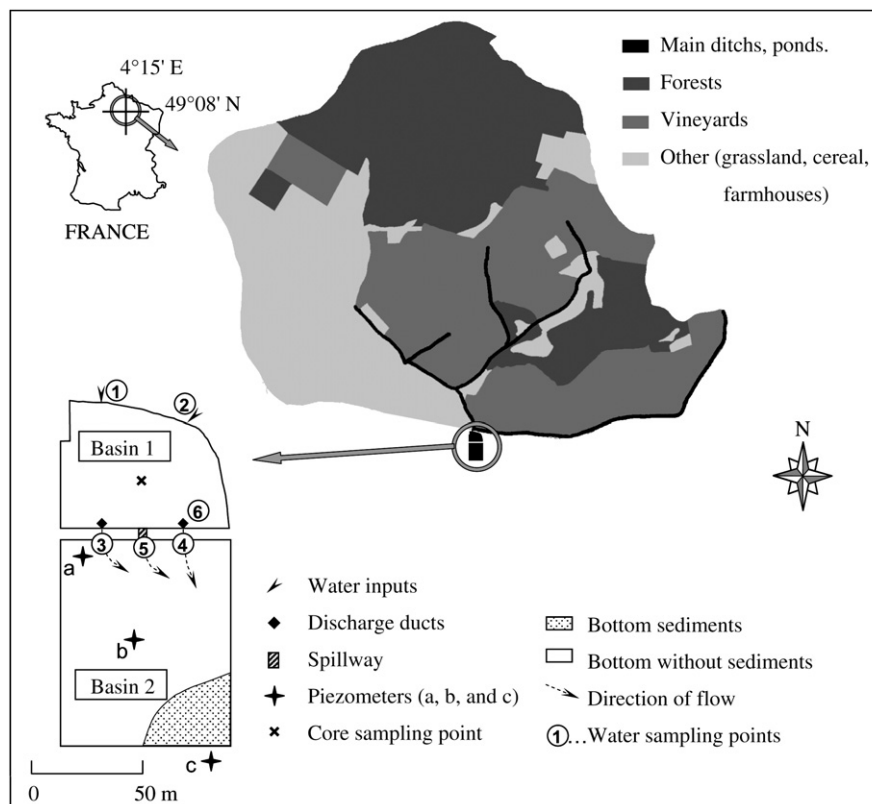


Fig. 1. Location of (a) the study area; (b) catchment showing vineyards and main ditches; (c) Basin 1 and 2 showing water inputs, outputs, and flow direction; and (d) sampling points.

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