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Assessment of diffuse contamination of agricultural soil by copper in Aquitaine region by using French national databases

Hind El Hadri [a,b,*], Philippe Chéry [b], Stéphanie Jalabert [b], Alexandre Lee [b], Martine Potin-Gautier [a], Gaëtane Lespes [a]

[a] Université de Pau et des Pays de l'Adour/CNRS, LCABIE UMR5254, IPREM 2 avenue Pierre Angot 64053 PAU Cedex 09, France
[b] Bordeaux Science Agro, 1 cours du Général De Gaulle, 33175 Gradignan, France

HIGHLIGHTS

► National databases to assess the link between copper in soils and wine-growing areas.
► A statistical approach has established a significant exponential-based model.
► 50 mg kg^{-1} of Cu_{EDTA} in topsoils is reached when 81% of UAA is covered by vines.

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ABSTRACT

A long-term application of copper-based fungicides to fight against downy mildew has led to soil contamination by copper particularly in Aquitaine region where viticulture is important. This work aims to statistically validate the origin of diffuse contamination of Aquitaine agricultural soils and show that contamination is closely related to wine-growing in this region. For this purpose, several national databases have been used. From the French National Soil Monitoring Network (Réseau de Mesures de la Qualité des sols RMQS) data, an Exploratory Data Analysis (EDA) was performed to bring out the copper contamination. The French test soil database (Base de Données des Analyses de Terre BDAT) and the national census of agriculture (Recensement Général Agricole RGA) have been crossed. A statistical approach has been used to determine the relationship between the median concentration of copper extracted by Ethylene Diamine Tetra-acetic Acid (EDTA) referred to as CuEDTA in cultivated topsoils of the Aquitaine region and the ratio between winegrowing area (Svine) and the Used Agricultural Area (UAA) expressed as the form Svine/UAA. The results revealed a strongly significant exponential correlation between these two variables. They allow concluding that at cantonal scale, when vines cover more than 80% of the UAA, an overexposure of soils to the diffuse contamination by copper can occur.

1. Introduction

In 1878, a parasite (*Plasmopara viticola*) was introduced into the southwest of France and colonized all European vineyards. This fungus, called downy mildew, attacks the above-ground parts of the vine, initially the leaves, causing necrosis (Agrios, 2005). To fight against it, copper-based fungicides have been applied extensively in wine-growing areas. Bordeaux mixture has been the most commonly used product on vines since its discovery by Millardet at the end of the 19th century (Ayres, 2004). It is a mixture of copper sulphate ($CuSO_4$, $5H_2O$) and lime ($Ca(OH)_2$) (Ayres, 2004). A current EU regulation (Regulation CE 889/2008) sets the amount of copper applied to 6 kg ha^{-1} $year^{-1}$. By derogation, this limit could be exceeded to accommodate a five year average. It is especially important in organic viticulture due to the fact that copper based fungicides (Bordeaux mixture, oxychloride, copper hydroxide, etc.) are the main fungicide allowed (Jonis, 2009). Other types of fungicides can be used in organic viticulture such as mineral oils, potassium permanganate or sulphur (EC No 889/2008). However Cu based fungicides are the most efficient and the most used in organic and classic viticulture.

The systematic treatment by Bordeaux mixture has led to copper contamination of vineyard soils. Due to the strong immobilisation of this element by the soil constituents, especially organic matter, Fe and/or Mn-(hydr)oxides, the highest copper concentrations are found in the upper layers of the soil profile (Komárek et al., 2008; Pietrzak and McPhail, 2004). Brun et al. (1998) have shown that copper mainly

* Corresponding author at: Université de Pau et des Pays de l'Adour/CNRS, LCABIE UMR5254, IPREM 2 avenue Pierre Angot 64053 PAU Cedex 09, France. Tel.: +33 559407762; fax: +33 559407674.
E-mail addresses: hind.el-hadri@etud.univ-pau.fr (H. El Hadri), p-chery@agro-bordeaux.fr (P. Chéry), s-jalabert@agro-bordeaux.fr (S. Jalabert), a-lee@agro-bordeaux.fr (A. Lee), martine.potin@univ-pau.fr (M. Potin-Gautier), gaetane.lespes@univ-pau.fr (G. Lespes).

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remains in the first 30 cm of contaminated soils. Usually, total Cu ranges from 1 to about 50 mg kg^{-1} in arable soils (Adriano, 2001; Besnard et al., 2001; Brun et al., 1998) whereas in wine-growing areas Cu contents can exceed 100 mg kg^{-1} and reach 1500 mg kg^{-1} (Besnard et al., 2001; Flores-Velez et al., 1996). However, despite its strong immobilisation by soil constituents, copper contained in topsoils is susceptible to lateral water erosion and migration through the soil profile (Devez, 2004; Fernández-Calviño et al., 2008; Komárek et al., 2010). Consequently, it presents a risk for water quality and aquatic organisms (Komárek et al., 2010; Zyadah and Abdel-Baky, 2000).

The high copper concentrations in soils can affect plant growth and soil quality by interfering with microbially mediated processes (Fernández-Calviño et al., 2010; Flemming and Trevors, 1989; Nagajyoti et al., 2010). It could decrease diversity, density and activity of microorganisms due to the toxicity of the free ionic form (Cu^{2+}) (Borkow and Gabbay, 2005; Lejon et al., 2010; Ranjard et al., 2008).

At the European Union (EU) and national levels only threshold values related to the application of sewage sludge in agricultural soils have been defined. In the EU, warning and critical limits set total copper contents in soils at 50 and 140 mg kg^{-1}, respectively (Council directive 86/278/EEC, 1986). The French norm (JournalOfficiel, 1998) requires a limit value at 100 mg kg^{-1}. A non-official threshold was also established by wine-growers and soil analysis laboratories according to the toxicity observed on the young vines above this threshold. It was fixed at 50 mg of copper extracted by EDTA (Cu_{EDTA}) kg^{-1} minimum according to the soil nature and can be considered as an accepted limit (Baize et al., 2006).

Copper contamination in soils can be evaluated in different ways. For instance, total concentration of the element can be considered. However, many studies indicate that the assessment of the available copper concentration is more appropriate for the prediction of fraction of soil metal that can be taken up by biological organisms and for environmental risk assessment (Brun et al., 1998; Chaignon et al., 2003; Wu et al., 2010). Different chemical extractants can be used to assess the availability of copper in soil: salt solutions (CH_3COONH_4, $CaCl_2$, $Ca(NO_3)_2$, etc.), chelating agents (Ethylene Diamine Tetra-acetic Acid, EDTA; Diethylene Triamine Penta-acetic Acid, DTPA), diluted acids or water (Brun et al., 1998; Chaignon et al., 2003). Extraction using EDTA is generally the common soil testing procedure for assessing the “available” copper in soil, estimated by the concentration Cu_{EDTA} in the extract (Chaignon et al., 2003; Baize et al., 2006). However, this method overestimates exchangeable copper. Thus, in addition to exchangeable copper, EDTA extracts both the organically bound copper and copper linked by iron and manganese oxides (Baize et al., 2006; Chaignon et al., 2003; Feng et al., 2005). Nevertheless, Cu_{EDTA} is currently considered as an accepted estimation of the copper that can be potentially taken up by biological organisms (Brun et al., 2001; Komárek et al., 2010; Michaud et al., 2007).

To assess copper contamination in France, physico-chemical data of soils can be obtained from several sources (Etter et al., 2009): soil analyses collected through the national soil survey and the soil quality monitoring network (RMQS) (Arrouays et al., 2003; Jolivet et al., 2006), or agricultural soil analyses collected in a national database (*Base de Données d'Analyses de Terre* BDAT) (Saby et al., 2004). In addition to these databases, a Census of Agriculture (RGA, *Recensement Général Agricole*) provides the leading source of facts and figures about French agriculture (Agreste, 2009; FAO, 2005). In recent works, soil contamination by trace elements, including copper, was underlined from these soil databases across French territory (Baize et al., 2006; Saby et al., 2009; Bourennane et al., 2010; Saby et al., 2011). Thus, these studies show that copper contamination throughout France has several origins. Viticulture is probably the major source of Cu pollution of soils in Aquitaine, Languedoc–Roussillon and Alsace region, with also pig slurry amendment in Brittany while endogenous copper can be present in Auvergne. The studies were performed from total copper concentrations (Saby et al., 2011) and from EDTA-extracted copper (Cu_{EDTA}) (Baize et al., 2006).

In this context, this study aims at establishing the link between copper contamination and viticulture from national databases and taking stock of the copper contamination in the Aquitaine region where viticulture is essential. To that purpose, two independent databases were used. In a first step, copper contamination in Aquitaine was underlined from RMQS data by an Exploratory Data Analysis. Then, agricultural databases (BDAT and RGA) have been crossed to assess the role of wine-growing on soil pollution by copper. An empirical model based on a non-linear fitting was carried out to measure the relationship between Cu_{EDTA} in the upper horizons of soil and the ratio of vineyard area (S_{vine}) relative to the Used Agricultural Area (UAA) for each canton (local administrative area).

2. Materials and methods

2.1. Study site

The Aquitaine region is the third largest region in metropolitan France, with an area of 41,309 km^2. Located in the southwest of France, it is made up of five departments: Dordogne, Gironde, Landes, Lot-et-Garonne and Pyrénées-Atlantiques (Fig. 1) and divided into 235 cantons. Traditionally, Aquitaine is an agricultural region. It is the leading French region for employment in the farming sector and more particularly in wine-growing (CRA, 2012).

Table 1 shows the different characteristics of interest in wine-growing of each department of the Aquitaine region. The UAA is of the same order of magnitude for the five departments. However, the S_{vine}/UAA indicates that Gironde has the highest percentage of vineyard area, nearly 50%, in comparison with the other departments where it is lower than 5%. This extensive proportion of arable land devoted to viticulture involves a very substantial use of Bordeaux mixture or copper based-fungicides in this area to protect vineyards against mildew.

2.2. Databases

The soil quality monitoring network (RMQS: *Réseau de Mesures de la Qualité des Sols*) is a national survey which consists in monitoring physical and chemical soil parameters and agricultural practices (Arrouays et al., 2003). It is based on a 16 × 16 km systematic grid covering the whole French metropolitan territory (555,000 km^2) and overseas departments (96,642 km^2). Sampling site was selected at the centre of each grid cell. If soil was not available at the centre, sampling was carried out as close as possible to less than 1 km. Only agricultural, forest and grassland soils have been sampled. The sampling was performed on the first 30 cm by considering only the first surface horizon. The Aquitaine region includes 169 monitoring sites on 41,309 km^2 (Fig. 2). In this study, total copper (Cu_{TOT}) content and concentration of Cu extracted by EDTA were used from this selected part of this national database. Cu_{TOT} is obtained by an acid mineralization (HF/$HCLO_3$) according to NF X31-147 (AFNOR, 1996) and detected by ICP-AES (ISO, 2007) and Cu_{EDTA} is determined according to the BCR (Community Bureau of Reference) method (Quevauviller et al., 1998).

The BDAT (*Base de Données d'Analyses de Terre*) is a French soil database which compiles soil analyses from soil-testing laboratories approved by the Ministry of Agriculture (INRA, http://bdat.gissol.fr/geosol/index.php last accessed 14/05/2012). This database provides non-exhaustive physical and chemical characteristics of cultivated soils in France (Schvartz et al., 1997). It only gathers data provided by standardized analytical protocols in the various laboratories so as to obtain homogeneous data. The extraction method by EDTA is normalized by the NF X31-120 standard (AFNOR, 2003), which involves extracting soluble copper in a solution of ammonium acetate at 1.0 mol L^{-1} adjusted at pH 7 in the presence of 0.01 mol L^{-1}