The use of copper as plant protection product contributes to environmental contamination and resulting impacts on terrestrial and aquatic biodiversity and ecosystem functions

Stéphane Pesce, Laure Mamy, Wilfried Sanchez, Joan Artigas, Annette Bérard, Stéphane Betoulle, Arnaud Chaumot, Marie-Agnès Coutellec, Olivier Crouzet, Juliette Faburé, et al.

Environmental Science and Pollution Research

https://doi.org/10.1007/s11356-024-32145-z

Accepted on 18 January 2024 in the special issue *« Key Learnings from A Collective Scientific Assessment on the Effects of Plant Protection Products on Biodiversity and Ecosystem Services Along the Land to Sea Continuum »*

The use of copper as plant protection product contributes to environmental contamination and resulting impacts on terrestrial and aquatic biodiversity and ecosystem functions

Author names and affiliations:

Stéphane Pesce* – INRAE, UR RiverLy, 69625 Villeurbanne, France
Laure Mamy – Université Paris-Saclay, INRAE, AgroParisTech, UMR ECOSYS, 91120 Palaiseau, France
Wilfried Sanchez – Ifremer, Direction Scientifique, 34200 Sète, France
Joan Artigas – Université Clermont Auvergne, CNRS, Laboratoire Microorganismes: Génome et Environnement (LMGE), 63000 Clermont-Ferrand, France
Annette Bérard – INRAE, Avignon Université, UMR EMMAH, F-84000, Avignon, France
Stéphane Betoulle - Université de Reims Champagne-Ardenne, Normandie Université, ULH, INERIS, SEBIO, UMR-I 02, 51100 Reims, France
Arnaud Chaumot – INRAE, UR RiverLy, 69625 Villeurbanne, France
Marie-Agnès Coutellec – DECOD (Ecosystem Dynamics and Sustainability), INRAE, Institut Agro–Agrocampus Ouest, IFREMER, Rennes, France
Olivier Crouzet – OFB, Direction Recherche Et Appui Scientifique, Service Santé-Agri, 78610 Auffargis, France
Juliette Faburé – Université Paris-Saclay, INRAE, AgroParisTech, UMR EcoSys, 91120 Palaiseau, France
Mickael Hedde – INRAE, UMR Eco&Sols, 34060 Montpellier, France
Christophe Leboulanger – MARBEC, Univ Montpellier, CNRS, Ifremer, IRD, Sète, France
Christelle Margoum – INRAE, UR RiverLy, 69625 Villeurbanne, France
Fabrice Martin-Laurent – Agroécologie, Institut Agro, INRAE, Université Bourgogne-Franche-Comté, 21110 Dijon, France
Soizic Morin – INRAE, UR EABX, 33612 Cestas Cedex, France
Christian Mougin – Université Paris-Saclay, INRAE, AgroParisTech, UMR EcoSys, 91120 Palaiseau, France
Dominique Munaron – MARBEC, Univ Montpellier, CNRS, Ifremer, IRD, Sète, France.
Sylvie Nélieu – Université Paris-Saclay, INRAE, AgroParisTech, UMR ECOSYS, 91120 Palaiseau, France
Céline Pelosi – INRAE, Avignon Université, UMR EMMAH, 84000 Avignon, France
Sophie Leenhardt – INRAE, Directorate for Collective Scientific Assessment, Foresight and Advanced Studies, 75338 PARIS, France

* Corresponding author: stephane.pesce@inrae.fr

Keywords:

fungicide, soil, water, sediments, microbial communities, invertebrates, trace metal, collective scientific assessment

Declarations:

Ethics approval and consent to participate: Not applicable

Consent for publication: Not applicable

Availability of data and materials: Not applicable

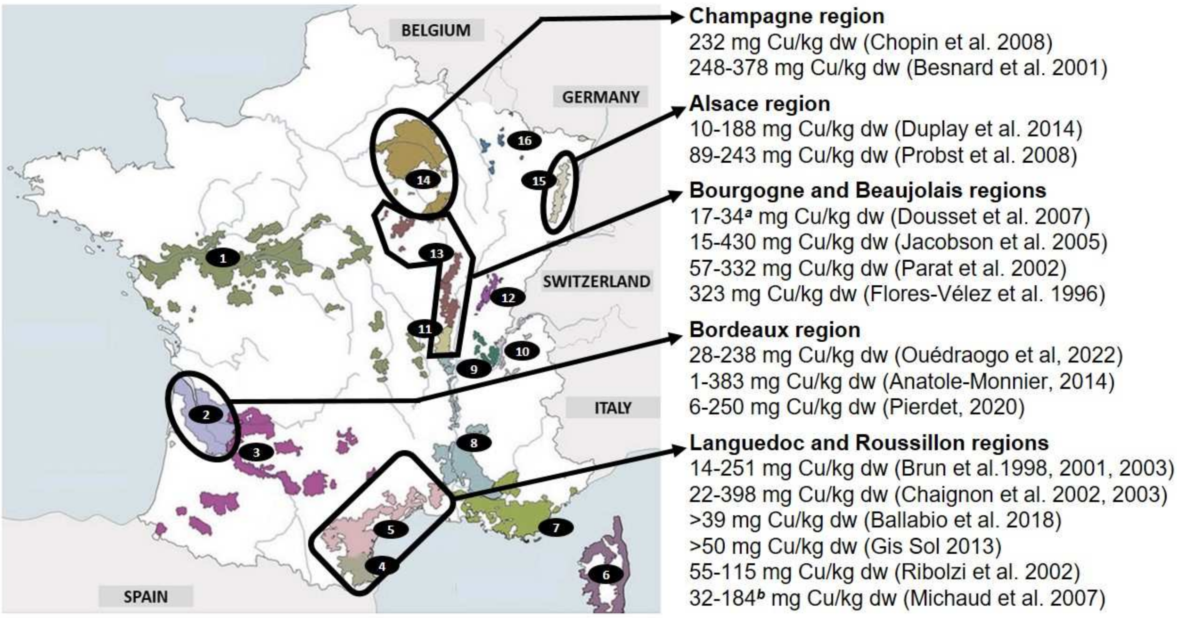
Competing interests: The authors declare that they have no competing interests.

Funding: This collective scientific assessment received financial support from the French Office for Biodiversity (OFB) through the national ECOPHYTO plan.
Author contributions: SP, LM, WS, JA, AB, SB, AC, MAC, OC, JF, MH, CL, CM1, FML, SM, CM2, DM, SN, CP, and SL performed the scientific collective assessment based on an analysis of more than 4500 scientific articles. SP drafted the first version of the manuscript based on this original contribution. SP, LM, WS, JA, AB, SB, AC, MAC, OC, JF, MH, CL, CM1, FML, SM, CM2, DM, SN, CP, and SL contributed to subsequent revisions to the manuscript and approved the final submitted version.

Abstract:
Copper-based plant protection products (PPPs) are widely used in both conventional and organic farming, and to a lesser extent for non-agricultural maintenance of gardens, greenspaces, and infrastructures. The use of copper PPPs adds to environmental contamination by this trace element. This paper aims to review the contribution of these PPPs to the contamination of soils and waters by copper in the context of France (which can be extrapolated to most of the European countries), and the resulting impacts on terrestrial and aquatic biodiversity, as well as on ecosystem functions. It was produced in the framework of a collective scientific assessment on the impacts of PPPs on biodiversity and ecosystem services in France. Current science shows that copper, which persists in soils, can partially transfer to adjacent aquatic environments (surface water and sediment) and ultimately to the marine environment. This widespread contamination impacts biodiversity and ecosystem functions, chiefly through its effects on phototrophic and heterotrophic microbial communities, and terrestrial and aquatic invertebrates. Its effects on other biological groups and biotic interactions remain relatively under-documented.

Introduction
Copper is an essential mineral nutrient that is vital to the health of all living organisms (including humans) at trace concentrations, yet it also holds a special place in farming where it has been used as a pesticide since the nineteenth century. Professor Alexis Millardet accidently discovered the "Bordeaux mixture" in 1880 (Johnson 1935), and since then, copper-based plant protection products (PPPs) have been widely used in both conventional and organic farming (and in more niche use for non-agricultural maintenance of gardens, greenspaces, and infrastructures) to combat a variety of fungal, bacterial, and oomycete diseases, mainly on wine grapes, fruit crops, and vegetable crops (Andrivon et al. 2018; Tamm et al. 2022). According to Andrivon et al. (2018), copper is mainly used in France as a PPP against grape downy mildew (vineyards occupied 782,700 ha of agricultural land in France in 2016), apple scab (apple orchards occupied 36,500 ha of land in France in 2016), and potato late blight (around 200,000 ha of potatoes are planted in France each year). Copper use as PPP in organic grape production in France can reach average values of 5 kg Cu/ha/year in years marked by intense downy mildew pressure. These values may also vary between regions, with less than 2 kg Cu/ha/year in the Alsace region to more than 6 kg Cu/ha/year in the Champagne and Languedoc-Roussillon regions (Andrivon et al. 2018) (Fig. 1). Other examples include organic olive and tomato production, where despite these crops being far less widely grown in France, the estimated quantity of copper used in 2018 reached about 5.0 and 5.5 kg/ha/year, respectively (Katsoulas et al. 2020). Over the 2010–2019 period, the quantities of copper-based PPPs sold in France held relatively steady, with total sales at 1500–2000 t copper/year, mainly as copper sulfate and, to a lesser extent, copper hydroxide (Andrivon et al. 2018). In 2018, the EU passed a re-approval procedure that reduced the maximum dose of copper-based formulations used in both conventional and organic farming systems from 6 down to 4 kg/ha/year, averaged over a rolling 7-year period (i.e., a maximum of 28 kg/ha over a period of 7 years; Regulation (EU) 1018/1981 2018).

***Fig. 1**: Main wine-growing regions of France highlighted by colored areas (1: Loire; 2: Bordeaux; 3: Southwest; 4: Roussillon; 5: Languedoc; 6: Corsica; 7: Provence; 8: Rhone; 9: Bugey; 10: Savoy; 11: Beaujolais; 12: Jura; 13: Burgundy; 14: Champagne; 15: Alsace; 16: Lorraine) and non-exhaustive illustration of surface vineyard soil copper concentrations reported for seven of them (adapted and completed from Komárek et al. 2010)*



a. Concentrations measured in newly-planted vineyards ; b. Localized contamination reaching 1030 mg Cu/kg dw (occasional spills of Cu)

Several studies have highlighted widespread contamination of environmental compartments by copper through agricultural uses (Rabiet et al. 2015; Iñigo et al. 2020; Komárek et al. 2010; Tamm et al. 2022). However, PPPs are not the only source of copper in the environment. First, as a natural element in the Earth's crust, copper exists naturally and natively in all the environmental compartments, including soil, surface water, and sediment, with strong geographical variations according to geochemical background (Reimann and Garrett 2005). In France, such geological background has been estimated to result in 3 to 100 mg/kg of copper in uncontaminated soils (Andrivon et al. 2018). Furthermore, copper is also approved as a biocide for various applications, including as a disinfectant and an algicide (not intended for direct application to humans or animals), and as an antifoulant (PPDB, Pesticide Properties DataBase 2023). A further agricultural source of copper is fertilization with organic waste, particularly pig slurry (Panagos et al. 2018). These multiple sources and vectors pose challenges for assessing the role of copper-based PPP use in environmental contamination, the resulting impacts on biodiversity in terrestrial, freshwater and marine ecosystems, and the consequences on ecosystem functions.

This article aims to set out the main conclusions about the contribution of copper-based PPPs to the environmental copper contamination in the context of France (which can be extrapolated to most of the European countries) and the resulting impacts on terrestrial and aquatic biodiversity, as well as on ecosystem functions. This work is based on a collective scientific assessment performed from 2020 to 2022 by a panel of 46 scientific experts to analyze the science on impacts of PPPs (including but not limited to copper) on biodiversity and ecosystem services (Pesce et al. 2023). Collective scientific assessment, which differs from meta-analysis or systematic review, is intended to inform public policy and foster public debate (Pesce et al. 2021).

The use of copper as a plant protection product contributes to the contamination of soil and aquatic environments

Contamination of soil ecosystems

Only a fraction of copper found in soil is (bio)available. This fraction is classically evaluated by mild extraction techniques using various salts or complexing agents such as CaCl2 or EDTA (Brun et al. 1998, 2001; Chaignon et al. 2003). Furthermore, there is evidence that Cu(EDTA) and Cu(CaCl2) concentrations could make indicators of a potential risk for soil organisms (Michaud et al. 2007; Komárek et al. 2010; Sereni et al. 2023). Copper concentrations in French soils were accurately mapped by the French Soil Quality Monitoring Network ('Réseau de Mesures de la Qualité des Sols' (RMQS) in French; Gis Sol 2013) via a first sampling campaign (2002–2009), based on a systematic 16 × 16 km grid covering the entire French mainland. The campaign evidenced strong variability in copper concentrations according to soil type, ranging from less than 1 mg/kg in sandy soil to more than 100 mg/kg in other types. However, differentiating between natural Cu and anthropic-origin Cu remains an as-yet-unresolved challenge. Attempts using the 65Cu isotope or 65Cu/63Cu ratio were not systematically successful (El Azzi et al. 2013; Babcsányi et al. 2016; Blotevogel et al. 2018). However, the Cu concentration extracted by EDTA has been demonstrated to correlate with intensity of copper treatment in vineyards (El Hadri et al. 2012) or, more generally to an anthropic origin (Saby et al. 2009). Soil surveys have shown that vineyard and orchard soils generally present the highest levels of contamination by copper (Saby et al. 2009; El Hadri et al. 2012; Ballabio et al. 2018; Panagos et al. 2018). Ballabio et al. (2018) reported a pan-EU average copper concentration of about 49 mg/kg in vineyard topsoils, and France had the highest national average concentration (91 mg/kg). A review by Komárek et al. (2010) concluded that intensive use of copper-based fungicides is a major source of contamination of vineyard soils (Fig. 1). Total copper concentrations in vineyard soils often exceed 200 mg/kg and can occasionally reach 1000 mg/kg (Flores-Vélez et al. 1996; Michaud et al. 2007). However, vineyard-soil copper contamination is highly dependent on climate, which modulates the likelihood of downy mildew growth (and thus the need to use copper-based fungicides). For example, the soils of French Mediterranean vineyards contain lower levels of copper than those of the Champagne wine region that is located in the colder and rainier north-eastern region of France (Brun et al. 1998; Besnard et al. 2001) (Fig. 1).

However, and as mentioned above, vineyard practices are not the only source of copper in the environment. The RMQS database made it possible to define the main sources of copper in French soils according to its use on different types of crops or other uses and to regional characteristics (Saby et al. 2009; 2011; El Hadri et al. 2012). For instance, while vineyard practices are probably the main source of copper in soils in the French regions with a strong wine industry (e.g., Nouvelle Aquitaine, Occitanie and Grand-Est regions), this is not the case in Brittany, where soil contamination by copper is largely driven by the use of pig manure as a soil amendment. Furthermore, in some regions, such as Massif Central one (central France), the main source of copper in soils may be a geological origin (Saby et al. 2011). At European scale, studies have reported high copper concentrations in olive-grove and fruit-orchard soils, especially when the climate is humid and therefore when antifungal treatments are frequently required (Ballabio et al. 2018).

There has been little research into the effects of the non-agricultural use of copper as a PPP on soil contamination. Joimel et al. (2021) recently measured copper concentrations in topsoil samples from a set of 104 urban vegetable gardens at 26 allotment sites selected in three French cities (i.e., Nancy, Nantes, and Marseille), and showed that copper concentrations were higher in gardens treated with "Bordeaux mixture" (78 mg/kg on average) compared to untreated soils (49 mg/kg). A study by Zhong et al. (2022) suggests continued use of "Bordeaux mixture" under the same conditions in these areas would lead to a > 180% increase in copper concentration in the allotment garden soils after a century. Copper is generally largely immobilized in soil. Soils with high contents of Fe-(hydr)oxides or humic substances, such as humic acid and fulvic acid, possibly have the greatest copper retention capacity (see Komárek et al. 2010; and references therein). However, copper can transfer from soils to aquatic systems, especially from acidic soils (as an acidic pH facilitates copper export through particulate transport), tilled soils, and soils affected by intensive erosion. Copper transfer through infiltration is also greater in sandy soils than in clay soils (Komárek et al. 2010). Several types of organisms can also influence the fate of copper in soils (Komárek et al. 2010; Mackie et al. 2012). Some plants able to absorb copper in its reduced form via their root system transfer it to the upper part of the plant where copper can accumulate (Mackie et al. 2012; Mir et al. 2021). However, recent studies have reported that some perennial plants can exude copper from their root system, and thus release copper into the soil (Cesco et al. 2021). The complexity of rhizosphere dynamics means that soil management under perennial crops requires a deeper understanding of the soil–plant system and its dynamics, and the role of in-soil microorganisms, some of which can increase Cu solubility (Lin et al. 2022). Invertebrate organisms, such as earthworms, can also influence the fate of copper in soil by sequestering it in their tissues (Mackie et al. 2012; Zeb et al. 2020) or through bioturbation processes (Van Zwieten et al. 2004).

Contamination of aquatic ecosystems

Copper concentrations in French freshwater ecosystems range from a few µg/L to tens of µg/L in surface waters, and from tens to hundreds of mg/kg in sediments. Like for soils, the bulk of scientific articles dealing with freshwater contamination by copper due to its specific use as a PPP have focused on streams and rivers located in vineyard areas. El Azzi et al. (2013) studied the isotopic composition of copper in rivers located in southern France and estimated that more than 75% of the total copper concentration measured in surface sediments and suspended particulate matters came from anthropogenic sources. This finding is consistent with Perk and Jetten (2006) who demonstrated that vineyard soil erosion is a major source of copper pollution in aquatic environments in Mediterranean vineyard regions. The quantity of copper exported by soil erosion from the two vineyard plots studied averaged 0.74 kg/ha/year and 1.02 kg/ha/year, respectively, and the highest value observed came from the steeper-sloped plot (Perk and Jetten 2006). Their data was corroborated by the recently performed mapping of potential copper transfers from vineyard soils to water at Europe-wide scale (Droz et al. 2021). The alternating cycle of rainy periods and drought periods (as in the Mediterranean Region and/or in case of climate extreme events) induces a higher risk of transfer, especially if the organic matter content of the soil is low and the slope is steep. In the Beaujolais vineyard region (central-eastern France), Rabiet et al. (2015) estimated that up to 70% of copper export from a vineyard watershed to its receiving stream took place in the dissolved phase in base flow conditions, whereas during intense rainfall events, copper transfer to the stream was predominantly driven by the particulate fraction (74%–80%; Rabiet et al. 2015). Consequently, more than 90% of copper export over the course of the study occurred within a very short period of time (less than 17% of the period studied; Rabiet et al. 2015). This observation supports the general idea that copper transfers from vineyard soils to adjacent rivers increase with larger rainfall events and soil erosion (Babcsányi et al. 2016; Meite et al. 2018; Imfeld et al. 2020).

In the marine environment, copper has been detected in coastal surface waters, sediments and biota (e.g., Fey et al. 2019; Ong et al. 2021). The highest sedimentary copper content measured on the French coastline was at the Cortiou station at the sea outfall of treated wastewaters from the Marseille urban area (943.7 mg/kg dw; Mauffret et al. 2018). However, this high copper concentration in a natural coastal environment is probably mainly caused by biocidal uses of copper. Among these uses, anti-fouling paints used to control biofouling on ships contribute significantly to harbor sediment contamination, with surface sediment concentrations in ten French harbors ranging from 10 to 170 mg/kg dw (CEREMA 2020; Mauffret et al. 2018), with the highest concentration observed in the largest European marina at Port Camargue (maximum: 1961 mg/kg dw in the upper 10-cm-layer surface sediment; Briant et al. 2022). The Port Camargue sediment cores showed higher copper concentrations in the upper layers (0–10 cm) than below (10–40 cm). Studying copper contamination in the muddy plug of the Gironde estuary, Petit et al. (2013) showed that the isotope fractionation method was able to help discriminate inputs related to the use of copper as a PPP (i.e., agricultural fungicide) from inputs originating from wastewater treatment plant discharges from the city of Bordeaux and from natural sources. However, this kind of approach is still in its early stages, and further development is needed to better characterize sources of copper contamination in marine environments or to use stable copper isotopes as effective tracers of the antifouling paints in marine environments (Araujo et al. 2019, 2021, 2022). Regarding the biota, copper accumulation has been reported in more than 40 different marine species, including primary producers (such as seagrass and phytoplankton; Chouvelon et al. 2019; Lewis and Devereux 2009), invertebrates (such as echinoderms, crustaceans, and mollusks; Metian et al. 2010, Breitwieser et al. 2020), fish (Oliveira Ribeiro et al. 2005; Burgeot et al. 2017; Chouvelon et al. 2019; Dron et al. 2019), and mammals (Frodello and Marchand 2001). For instance, a maximum average copper concentration of 59 µg/g dw was reported by Chouvelon et al. (2019) in 6–60 µm size plankton collected in spring and summer 2010 in the East part of the Gulf of Lions in the French Mediterranean Sea. Copper concentrations reached 22 µg/g dw in roots and rhizomes of Posidonia oceanica sampled in French and Italian Mediterranean Sea (Lewis and Devereux 2009). Breitwieser et al. (2020) reported copper concentrations up to 353 µg/g dw in the shellfish's digestive glands of the scallop Mimachlamys varia sampled in the La Rochelle marina (French Atlantic coast). Copper concentrations up to 1097 µg/g dw were also measured in the hepatopancreas of a pooled sample of the Pacific blue shrimp Litopenaeus stylirostris, collected in the aquaculture farm of Saint- Vincent, SW New Caledonia (Metian et al. 2010). Finally, copper concentrations reached about 72 µg/g dw in eel liver in the Camargue nature reserve (Anguilla Anguilla from the Vaccarès lagoon; Oliveira Ribeiro et al. 2005) and about 46 µg/g dw in five toothed whale species of the Mediterranean Sea (Frodello and Marchand 2001).

The use of copper as a plant protection product contributes to ecotoxicological effects on terrestrial and aquatic biodiversity

Levels of knowledge on the effects of copper on biodiversity vary widely among different types of organisms. Indeed, most of the published studies concern microorganisms and invertebrates in terrestrial and aquatic environments.

Effects on terrestrial biodiversity

The analysis of the corpus considered in the collective scientific assessment identified only a few studies assessing the direct unintended effects of copper-based PPPs on higher plants. Simonin et al. (2018) found no effect of treatments with copper-based PPPs in nanoparticle form (30 mg/m2 Kocide formulation containing 26.5% copper as the hydroxide salt) on non-target plant species. Nonetheless, several studies have observed effects of copper on plants through the response of root symbiotic microorganisms. Sharaff and Archana (2015) showed negative effects of copper (CuSO4 at above 250 mg/kg soil) on the rhizobacterial diversity of mung beans (Vigna radiata). Conversely, Bary et al. (2005) studied soils taken from golf courses regularly exposed to synthetic and mineral fungicides (including copper, at concentrations between 1 and 9 mg/kg) and showed that neither copper nor synthetic fungicides affected the establishment of the annual bluegrass Poa annua root colonization by endomycorrhizal fungi. More recently, Zhang et al. (2022a) showed by high-throughput sequencing that fungal diversity increases under long-term moderate contamination of soil by copper (50 mg/kg) but decreases under far higher contamination levels than those observed in soils treated by copper-based PPPs (1600 and 3200 mg/kg). The relative abundance of arbuscular mycorrhizal fungi increased under the moderate contamination level, leading to an improvement of plant nutrient absorption, but decreased at the highest levels. There was a significant positive correlation between fungal species richness and plant (maize and wheat) dry weights (Zhang et al. 2022a).

Most of the knowledge about copper effects on soil microbial communities (reviewed by Giller et al. 2009) is based on microcosm experiments using different copper-based fungicides used alone or in combination with other synthetic PPPs (fungicides and herbicides). Vazquez-Blanco et al. (2020) compared the impact of copper salts (copper sulfate and copper nitrate) and four commercial copper fungicides on microorganisms by exposing soil collected from a two-year-old vineyard to five concentrations ranging from 127 to 2033 mg/kg for 91 days. The highest concentrations of copper salts (> 500 mg Cu/kg) substantially decreased soil pH (a loss of 1–2 pH units depending on copper concentration applied) as well as bacterial and fungal growth basal soil respiration, without recovery over the duration of the experiment. In contrast, the application of commercial Cu-based products did not affect soil pH or basal respiration of soil microflora (Vazquez-Blanco et al. 2020). However, early during exposure, commercial Cu-based products significantly decreased bacterial growth regardless of the dose applied, but bacterial growth then showed recovery 2 to 3 months after soil treatment (Vazquez-Blanco et al. 2020). Keiblinger et al. (2018) studied two different agricultural soils (an acidic sandy loam and an alkaline silt loam, respectively) treated with a commercially available copper-based fungicide at five concentrations (from 50 to 5000 mg Cu/kg) and evidenced a clear negative dose–response relationship between copper concentrations and both soil microbial biomass carbon and soil fungal biomass (estimated from soil ergosterol concentration). The half-maximal effective concentration (EC50) of EDTA-extractable copper in soil ranged between 76 and 142 mg/kg for microbial biomass carbon, and between 9 and 94 mg/kg for fungal biomass depending on sampling timepoint (4 or 15 weeks) and soil type. Microbial respiration was also reduced in a similar range of copper concentrations, but only in the acidic soil (Keiblinger et al. 2018). The influence of soil characteristics on both the fate and effects of copper on soil microbial communities was also demonstrated by Ranjard et al. (2006). Moreover, Keiblinger et al. (2018) observed a copper-induced change in fungal community composition in vineyard soils. The composition and structure of microbial communities can also be modified by the development of copper-resistant microbial populations following prolonged exposure in soil repeatedly treated by copper (Lamichhane et al. 2018 and references therein). Such modifications can lead to increased community tolerance to copper toxicity, in line with the concept of pollution-induced community tolerance (PICT, first introduced by Blanck et al. 1988). For instance, PICT processes were reported in different soils historically treated with copper using short-term toxicity tests on substrate-induced microbial respiration (Wakelin et al. 2014), on thymidine and leucine incorporation (Díaz-Raviña et al. 2007), and on potential nitrification rate (Mertens et al. 2010). Copper-polluted soils are also frequently contaminated by other PPPs, but the effects of these combined exposures on soil microbial communities are still under-researched. In planted soil microcosms, Parada et al. (2019) showed that the combined application of copper nanoparticles and the herbicide atrazine could lead to a 60% decrease in bacterial abundance compared to atrazine alone.

There are very few ecotoxicological studies addressing the effects of contaminants on terrestrial microalgae and cyanobacteria. However, Kuzyakhmetov (1998) demonstrated that copper used at agronomic doses has effects on the diversity of soil microalgae and cyanobacteria, which can explain,

at least partially, the particularly low levels of algal and cyanobacterial diversity and biomass in wine-growing soils compared to other types of agroecosystems (Zancan et al. 2006). Concerning lichens, copper accumulation measurements, and physiological response assessment (mainly related to photosynthesis) have been studied as indicators of aerial pollution (Garty et al. 2000).
The scientific literature also evidences effects of copper on soil invertebrates, including earthworms (Paoletti et al. 1998; Komárek et al. 2010; Mackie et al. 2012; Amossé et al. 2020). These extremely useful soil organisms are particularly sensitive to copper, and many studies have shown their copper-induced harm manifests at different levels of biological organization (Uwizeyimana et al. 2017; Bart et al. 2017). Several studies have reported negative effects of copper on earthworm populations, and even population eradication at copper concentrations above 200–250 mg/kg in sandy agricultural soils (Klok et al. 1997; Ma 2005; Klok 2007). Other studies have reported lower copper-toxicity thresholds for earthworms, based on laboratory experiments (e.g., Zhou et al. 2013, with weight loss and reduced cocoon production at 50 mg/kg copper nitrate) or field exposures (e.g., van Rhee 1967, with eradication at concentrations > 80 mg/kg). Ma (2005) proposed using critical body residue values as thresholds of copper toxicity (in the range of a few mg/kg to a tens of mg/kg body weight for adult Lumbricus rubellus and Aporrectodea caliginosa earthworms) based on ecotoxicological effects on mortality, fecundity and field recolonization rate. Nematodes can also be impacted by copper, as shown in soil microcosms (Martinez et al. 2016; Chauvin et al. 2020). On nematodes, copper can impair population fitness, change interspecific interactions (Martinez et al. 2016), and modify community and taxonomic richness (Chauvin et al. 2020). This is also the case for the smaller Oligochaetes, i.e., Enchytraeidae. Indeed, Maraldo et al. (2006) reported a reduced diversity of enchytraeids in copper-polluted soils, with substantial changes in population density and species composition at concentrations higher than 300 mg Cu/kg dry soil. By contrast, Amossé et al. (2018) did not observe any effects on enchytraeid populations in plots contaminated with up to ten times the recommended rate of the fungicide formulation Cuprafor Micro® composed of 500 g/kg copper oxychloride. Based on two studies performed under laboratory conditions with natural soils (Bogomolov et al. 1996; Bart et al. 2017), Karimi et al. (2021a) concluded that earthworm biomass was reduced by 15% after application of 200 kg Cu/ha/year, microbial activity decreased by 30% in soils receiving copper at application higher than 400 kg/ha/year, and collembola and enchytraeid reproduction declined by 50% after application of 400 and 1895 kg Cu/ha/year, respectively. In contrast, nematode abundances were not affected by copper concentrations up to 3200 kg/ha/year.

Effects on aquatic biodiversity

There is an extensive literature on the effects of copper on the biodiversity of phototrophic and heterotrophic aquatic microbial communities. Most of this literature reports ecotoxicological effects of environmental copper concentrations. Concentrations in the range of just a few tens of µg/L (e.g., 10–30 µg/L) have been shown to significantly reduce the biomass of freshwater periphytic communities within just a few weeks (Serra and Guasch 2009; Lambert et al. 2012; 2016; Pesce et al. 2018), although this is not always the case (Tlili et al. 2010). Chronic exposure to copper generally favors green algae to the detriment of diatoms (Serra and Guasch 2009; Lambert et al. 2016), whereas cyanobacteria seem indifferent or even tolerant (Massieux et al. 2004; Serra et al. 2009). Copper effects on freshwater diatom communities include changes in specific diversity (Serra et al. 2009; Lavoie et al. 2012; Morin et al. 2017), with a selection of copper-tolerant species from the genera Achnanthidium (Lavoie et al. 2012; Morin et al. 2017) and Nitzschia (Pesce et al. 2018). Teratologic impacts were also observed, with a significant increase in the proportion of deformed frustules with increasing exposure to copper (Lavoie et al. 2012; Morin et al. 2012a). Diatom adaptation to copper can occur at the species level: Roubeix et al. (2012) observed higher tolerance to copper in a strain of the diatom Encyonema neomesianum isolated downstream of a copper-contaminated river, compared to the strain collected upstream. Several studies have also focused on marine phototrophic microbial communities, but most of them tested much higher copper concentrations than those found in marine environments, which strongly limits the possibility of extrapolating the results to realistic exposure contexts and linking them directly to the impacts induced by copper used as a PPP. However, toxicity thresholds close to or at the upper limit of environmental concentrations have been reported. For example, De la Broise and Palenik (2007) observed changes in natural phytoplankton communities exposed to copper at 2.5 µg/L in in situ mesocosms. These effects mainly consisted in a drastic drop in the abundance of cyanobacteria in the genus Synechococcus while the abundance of photosynthetic picoeukaryotes increased (De la Broise and Palenik 2007). Changes in the structure and diversity of marine phytoplankton communities following chronic exposure to copper can result in increased copper tolerance, as shown by Biswas and Bandyopadhyay (2017). This is again coherent with the concept of PICT, which has been mainly applied to freshwater ecosystems in studies on environmental effects of copper. Indeed, several studies have reported an increase in tolerance of freshwater phototrophic microbial communities to copper toxicity following chronic copper exposure (Tlili et al. 2010; Lambert et al. 2012; Larras et al. 2016; Pesce et al. 2018).

This increase in copper tolerance in response to chronic copper exposure was also reported, in combination with changes in community structure and diversity, in heterotrophic microbial communities from periphyton (Tlili et al. 2010; Pesce et al. 2018) and sediment (Mahamoud-Ahmed et al. 2020). Environmentally realistic exposure to copper (45–55 mg/kg) can thus drive drastic shifts in the structure of bacterial communities in river sediments from as early as 7 days of exposure (Mahamoud-Ahmed et al. 2018), due to a significant decrease in bacterial diversity (Mahamoud-Ahmed et al. 2020). Carley et al. (2020) also showed a significant effect of copper nanoparticles (as copper hydroxide) on bacterial community diversity as well as protozoan and fungal community structure in a wetland sediment.

The acquisition of copper tolerance by (heterotrophic and autotrophic) microbial communities has been widely reported, but recovery of these copper-impacted communities is less clear. For example, Larras et al. (2016) showed a recovery of phytoplankton communities in Lake Geneva after 10 years of reduced copper contamination. In contrast, Dorigo et al. (2010) did not observe complete recovery in a 9-week periphyton transplantation experiment in a river. Besides the exposure level (i.e., duration and concentration) and the duration of the recovery period, the architecture of microbial communities environment (e.g., extracellular polymeric substances organic matrix of periphytic assemblages; Serra and Guasch 2009) is an important factor in community responses to copper. In addition, the connectivity between pristine and previously exposed communities (e.g., between upstream non-contaminated and downstream contaminated sections along the river continuum) is also a key driver of the recovery of phototrophic communities after copper contamination, due to the role of immigration in microbial recolonization processes (Lambert et al. 2012; Morin et al. 2012b).

Despite the existence of various studies on the toxicity of copper to invertebrates, including experimental assessment and prediction (e.g., Biotic Ligand Model; De Schamphelaere et al. 2006; Beaudouin and Péry 2013), and on detoxification mechanisms (e.g., metallothioneins, Palacios et al. 2011; reviewed in Calvo et al. 2017), less investigation has been focused on the specific effects of copper-based PPPs on macroorganisms in contaminated aquatic ecosystems. De Caralt et al. (2020) revealed that although adult biomass, height, and photosynthetic yield of the marine macroalgae Carpodesmia crinita remain almost unaffected in long-term copper laboratory exposures, low Cu levels of 30 µg/L completely suppress adult fertility. In addition, all the assays have a strong and negative impact on the survival and growth of recruits, suggesting that the long-term viability of C. crinita may be severely compromised. In invertebrates, a mesocosm experiment showed that vorticella can proliferate under copper contamination, whereas other planktonic taxa, such as rotifers, cladocerans, and copepods, proved to show a dose-dependent pattern of sensitivity to copper exposure (Joachim et al. 2017). Some aquatic invertebrate populations can adapt to cope with copper toxicity following chronic or acute exposure. For instance, the freshwater snail Lymnaea stagnalis showed genetic variation in response to copper (Cote et al. 2015). A study using the PICT concept was applied to nematodes and showed higher copper tolerance of nematode communities from a Cu-contaminated estuary compared to those from an adjacent less-contaminated estuary (Millward and Grant 2000). Furthermore, the diversity of nematodes was lower in the contaminated estuary than in the less-contaminated estuary. Moreover, genotype diversity can promote the persistence of certain populations in the event of severe copper stress, as demonstrated by Loria et al. (2022) with Daphnia populations. Buffet et al. (2013) described several effects of two forms of copper (CuO nanoparticles - NPs- and soluble salt CuNO3) on two marine endobenthic species (Scrobicularia plana and Hediste diversicolor), during outdoor mesocosms experiments. Bioaccumulation of CuO NPs was observed in both species. Copper uptake was higher in worms exposed to CuO NPs vs soluble copper, whereas in clams the opposite was observed, suggesting that copper accumulation rate was specie- and its form-dependent. After 14 days of exposure, the activity of the worm H. diversicolor was reduced (i.e., the burrowing/undulation frequency and head movements/feeding significantly decreased). Slower burrowing by endofauna could make it more vulnerable to predators in environments impacted by CuO NPs. The authors described also genotoxic effects on worms exposed to copper (Buffet et al. 2013). Embryotoxic and genotoxic effects of copper were similarly described for the oyster Crassostrea gigas larvae from copper concentrations of 10 µg/L and 1 µg/L, respectively (Sussarellu et al. 2018). Akcha et al (2022) recently showed that trophic transfer of copper from contaminated phytoplankton to oyster spats decreased the condition index in Crassostrea gigas spat in concomitance with a change in the microalgal fatty acid profile and enhanced oyster energy demand. These effects, while not directly letal to shellfish larvae, tend to weaken them through genotoxicity or in terms of energy reserves, possibly making them less viable to become mature individuals.

Besides direct toxic effects, copper can indirectly impact aquatic invertebrates through trophic interactions with photosynthetic microorganisms, as shown by Mensens et al. (2018) who observed that copepods fed with diatoms exposed to 500 µg/L copper had a 50% lower essential fatty acid content compared to copepods fed with non-exposed diatoms. Although this type of study is rare, the few results available illustrate the potential impacts of copper on the quality of trophic resources and energy transfers in aquatic biota.

Knowledge on the effects of copper on aquatic populations from higher trophic levels is also difficult to connect to the specific context of copper used as a PPP, and it mainly concerns biochemical or molecular responses in individual fish species. Copper is an essential element that is involved in various physiological functions, particularly for biochemical processes related to energy and oxidative metabolism (Grosell 2011). Accidental acute exposures may therefore have significant toxicological impacts on higher-trophic-level organisms. For example, Maes et al. (2016) showed that a 7-day exposure of juvenile roach (Rutilus rutilus) to copper at 10, 50, and 100 µg/L led to disturbances in their cell energy metabolism (e.g., a decrease in ATP concentrations and an increase in AMP concentrations), which was associated with an increase in anaerobic metabolism. Like other PPPs, copper is known to induce oxidative stress in aquatic vertebrates by modulating the activities of antioxidant enzymes such as Cu/Zn superoxide dismutase (Grosell 2011). In this context, copper induces oxidative stress in the liver and lymphoid anterior kidney of common carp (Cyprinus carpio L.; Dautremepuits et al. 2004; Zhang et al. 2022b). Juvenile carp exposed to 0.2 mg/mL of copper for 30 days also showed disturbances in gut microbiota richness (Zhang et al. 2022b).

We currently have no data available on the effects of copper PPPs on aquatic vertebrate biodiversity. Indeed, most of the experimental strategies used to date are not adapted to the context of natural populations exposed to variable copper concentrations in space and time. Moreover, in natural environments, aquatic vertebrates may be able to detect and escape copper contamination (Islam et al. 2019). It is therefore very difficult at this point to firmly rule on whether contamination of hydrosystems by copper-based PPPs does or does not damage aquatic vertebrate populations. However, some authors have been able to extrapolate consequences at fish-populations scale from data acquired in laboratory experiments. For example, the growth rate of Chinook salmon (Oncorhynchus tshawytscha) juveniles submitted to chronic exposure at low copper concentrations (i.e., a few µg/L) was reduced by about 7%, that could be enough to cause significantly reduced survival (from 23 to 52%) in a natural environment (Mebane and Arthaud 2010). In contrast, a lab-bred population of three-spined sticklebacks (Gasterosteus aculeatus) chronically exposed to a high but realistic copper concentrations (75 µg/L) for 18 months in an outdoor mesocosm showed significantly higher body length and abundances (due to higher reproduction rates) compared to the non-exposed populations (Roussel et al. 2007).This finding may be due to indirect ecological parameters (food and habitat availability, lower predation pressure on eggs and juveniles) that need to be taken into account to improve ecotoxicological risk assessments on copper for aquatic vertebrate populations (Roussel et al. 2007).

Copper effects on terrestrial and aquatic biodiversity have consequences on ecosystem functions

Ecosystem functions potentially directly and/or indirectly impacted by PPPs were classified into 12 categories by the scientific experts involved in the collective scientific assessment (Pesce et al. 2023). The literature corpus mobilized by these experts documented that environmental contamination due to the use of copper as a PPP generates risks and/or effects for at least 7 of these 12 categories.

Consequences on the regulation of gaseous exchanges

In aquatic environments, copper contamination can reduce oxygen production through its impact on photosynthesis in phototrophic communities. For example, a significant reduction in the photosynthetic activity of aquatic microbial communities has been demonstrated at copper concentrations of a few tens to a few hundred µg/L (e.g., Massieux et al. 2004; Tlili et al. 2010; Oukarroum et al. 2012; Lambert et al. 2016). This impact is sometimes transient, suggesting a possible resilience of the microbial communities (Barranguet et al. 2003). Environmental copper concentrations can also impair respiration and denitrification processes involving heterotrophic microorganisms, as shown by Mahamoud-Ahmed et al. (2018) in river sediments. Based on a meta-analysis, Karimi et al. (2021a, b) estimated that microbial respiration was reduced by 50% in soils experiencing several years of copper applications at 200 kg/ha/year. They suggested that applying the dose recommended by the European Commission (i.e., 4 kg/ha/year; Regulation (EU) 2018/1981 2018) would not substantially alter the biological quality of vineyard soils. However, this conclusion was challenged by Imfeld et al. (2021) who argued that it is necessary to take into account local variables encountered in vineyards, such as the level of previous copper contamination in soils or soil pH which has a major influence on the in-soil speciation of copper and its ecotoxicity with respect to organisms living in the soil. In their response to Imfeld et al. (2021), Karimi et al. (2021b) agreed that the ecotoxicological risk of copper used as a PPP depends on both the dose applied, the amount of copper already present in the soil, and on soil physical–chemical parameters, such as pH and organic matter content that influence copper bioavailability in the soil. They confirmed that the application of copper at the authorized annual dose of 4 kg/ha would have no impact on soil quality in the short-term, but they also flagged the fact that we do not have enough scientific information to document the long-term effect of repeated applications of copper at the European Commission-authorized dose in vineyards, thus echoing the concern raised by Imfeld et al. (2021).

Consequences on the dissipation of contaminants

Several studies have reported copper retention through accumulation in aquatic biota. For example, Bonnineau et al. (2021) reviewed the literature on trace element and organic contaminants in aquatic biofilms and showed that adsorption of copper (and other trace elements) in the biofilm matrix was fairly fast and well correlated with exposure concentrations in surface waters. Based on the dataset analyzed, they suggested that a saturation of cellular binding sites may occur at high exposure concentrations to mixtures of contaminants, resulting in competitive sorption (thus removal) of the contaminants (including copper).

Other competitive mechanisms have been described in soil microorganisms. High copper concentrations can limit the adsorption of organic PPPs to soil, thus making them more bioavailable or more mobile, and thus potentially more accessible to microorganisms capable of degrading them. Such a hypothesis was supported by Abiven et al. (2006) who studied the influence of copper on sorption of the herbicide terbumeton (and its transformation products) onto soils, and by Pérez Guaita et al. (2011) who studied adsorption via complexation of flumequine, a quinolone antibiotic, but not by Jacobson et al. (2005) studying the herbicide diuron. Demanou et al. (2006) showed that copper oxide applied at 128 mg/kg did not modify the microbial activity responsible for mineralization of the fungicide mefenoxam applied at 4 mg/kg.

Consequences on production and inputs of organic matter

The literature shows that environmental concentrations of copper can negatively impact primary production and sometimes highlights a tight link with photosynthesis inhibition. However, although this could therefore have repercussions on the production of organic matter, the quantitative impact of copper (or other PPPs) on this type of function is hardly ever discussed. Mensens et al. (2018) showed an ecotoxic impact of copper on the transfer of organic matter and energy to higher trophic levels in a marine environment after exposure of phytoplankton to high copper concentrations (200 and 500 µg/L).

Consequences on nutrient regulation

Several studies have reported that environmental concentrations of copper can either inhibit or stimulate, in either a transient or a prolonged manner, various different microbial processes involved in the biogeochemical cycles of carbon, nitrogen and phosphorus, thus potentially disrupting the regulation of nutrient cycles in terrestrial and aquatic ecosystems. Wang et al. (2009) investigated the effects of long-term application of Cu-based fungicides on apple orchards soils and showed that soil copper contamination could explain a large part of the total variance of microbial biomass and activities, with possible consequences on microbial-mediated ecological processes such as nutrient cycling. In a vineyard context, Wightwick et al. (2013a) observed that phosphomonoesterase, urease, arylsulfatase, and phenol oxidase enzyme activities were lower in copper-treated vineyard soils (n = 10, copper concentrations ranging from 19 to 162 mg/kg) than in non-treated reference soils (n = 10). In general, the measured enzyme activities (i.e., phosphomonoesterase, urease, and arylsulfatase) were lower in the treated soils than in the reference soils. However, a negative relationship between copper concentration and enzyme activity was only found for phosphomonoesterase activity, and soil physical–chemical properties (i.e., organic carbon, pH) were the greatest determinants of soil enzyme activities (Wightwick et al. 2013a). Wightwick et al. (2013b) went on to perform a microcosm study but did not observe any significant impact of copper hydroxide (up to 156 mg/kg) on soil phosphomonoesterase and urease activities. Similarly, in the microcosm study by Demanou et al. (2006), the combined application of copper oxide (128 mg/kg) and the fungicide mefenoxam (4 mg/kg) on soils did not affect most of the measured enzyme activities (cellobiohydrolase, xylosidase, aminopeptidase, and phosphatase), but the treatment led to an in increase in chitinase and laccase activities, whereas β-glucosidase activity was increased at 24 days after treatment but returned to its initial state at 2 months after treatment. In aquatic environments, Lambert et al. (2012) and Mahamoud-Ahmed et al. (2018) observed that environmental concentrations of copper (about 20 µg/L and 40 mg/kg sediment, respectively) significantly inhibited the β-glucosidase activity of periphytic and sediment microbial communities, respectively. In addition, Mahamoud-Ahmed et al. (2018) also reported a significant decrease in leucine amino-peptidase and phosphatase activities in sediment chronically exposed to copper.

Copper contamination can also negatively impact the decomposition of particulate organic matter in both terrestrial and aquatic ecosystems. A review by Schoffer et al. (2020) found that the accumulation of copper in orchard soil due to repeated application of copper-based fungicides can generate a decrease in microbial litter decomposition. In addition, it has been suggested that high copper concentrations would explain a significant accumulation of particulate organic matter in vineyard soils due to a decrease in decomposition rates, thus modifying the distribution of organic carbon among the particle-size fractions (Parat et al. 2002).

The negative impact of environmental concentrations of copper (40 mg/kg) on the decomposition of particulate organic matter in river surface sediments was also shown experimentally by Pesce et al. (2020), and an in situ study conducted by Fernandez et al. (2015) in 17 stream sites in a German vineyard area. These works showed that both leaf litter decomposition rates by invertebrates and gammarid feeding rates were negatively correlated with sediment copper concentrations.

Consequences on soil (and sediment) structure formation and maintenance

There is some work showing the effects of copper on soil structure, through a decrease in bioturbation activities of the copper-contaminated soil by invertebrates (Van Zwieten et al. 2004), which may lead to an increase in soil bulk density (Eijsackers et al. 2005; Bunemann et al. 2006). Furthermore, there is evidence that other biological communities, such as microorganisms known to act on erosion limitation through soil and sediment structure (e.g., Crouzet et al. 2019; Gerbersdorf et al. 2020), are sensitive to copper. However, no study to our knowledge has focused on the effects of copper on microorganism-driven soil and sediment maintenance.

Consequences on the dispersion of propagules

Duarte et al. (2008) assessed the ecotoxicological effect of copper and zinc mixtures at concentrations (several mg/L) far higher than those measured in contaminated aquatic ecosystems and reported a significant decrease in sporulation rates of aquatic hyphomycetes colonizing decaying leaves. However, Roussel et al. (2008) tested more environmentally realistic copper concentrations (5 to 75 µg/L) and did not observe any effects on fungal sporulation in copper-contaminated freshwater mesocosms.

Consequences on the provision and maintenance of biodiversity and biotic interactions

Effects of copper-based PPPs on terrestrial and aquatic biodiversity are described in the section "The use of copper as a plant protection product contributes to ecotoxicological effects on terrestrial and aquatic biodiversity." For some of these effects, the literature sometimes informs on causes or consequences that are associated with biotic interactions, such as symbiotic plant–microorganism relationships at root-systems level (Sharaff and Archana 2015), lytic induction of cyanobacterial phages (Lee et al. 2006), or indirect effects through trophic links (Barranguet et al. 2003; Mensens et al. 2018). For instance, Mensens et al. (2018) demonstrated that copper exposure resulted in a decrease in the quantity of lipids in phytoplankton, thus impacting the quality of the diet of copepods feeding on it. In addition, Soares et al. (2017) suggested that copper can affect biotic interactions involved in biological control by inhibiting the vegetative growth and sporulation (but not germination) of Beauveria bassiana, an entomopathogenic fungus used to control crop pests. These interactions were affected regardless of whether the fungus was inoculated before or after the application of copper as a fungicide. However, the findings of this work need to be confirmed before they can be generalized to the natural environment.

Effects of copper on biodiversity and ecosystem functions are modulated by various environmental factors

The ecotoxicological effects of copper are primarily driven by its environmental bioavailability in both terrestrial and aquatic ecosystems. Therefore, all the environmental parameters that can modify the bioavailability of copper are likely to modulate its effects, including both physical factors, such as pH, temperature and light, and chemical factors, such as (dissolved) organic matter and nutrients. For example, the bioavailability and toxicity of copper in soil and aquatic environments vary according to its complexation capacity, which is dictated by pH (among other factors; Barranguet et al. 2000; Le Jeune et al. 2007; Levy et al. 2009; Komárek et al. 2010; Sereni et al. 2023). Increasing temperatures were also shown to decrease copper bioavailability to freshwater biofilms (Lambert et al. 2016). For the same reasons, the binding capacity of organic matter in soils, which limits microbial community exposure to copper in PICT bioassays, may lead to an overestimation of copper-induced tolerance (Campillo-Cora et al. 2023). Cheloni et al. (2014) showed that the copper tolerance of biofilm communities decreased with increasing light intensity during colonization. Besides influencing copper exposure through bioaccumulation in microbial assemblages, these factors also modify the composition of microbial communities, which could also play a role in modulating their sensitivity to copper (Morin et al. 2017; Pesce et al. 2018).

In surface water, the ligand complexation capacity can also be modulated by the concentrations of dissolved organic matter (Grosell et al. 2002), and nutrients such as nitrates or phosphates (Serra et al. 2010; Tlili et al. 2010). Therefore, in agricultural watersheds, the toxic impact of copper may be partially masked by concomitant fertilizer inputs. Guasch et al. (2004) experimentally demonstrated that periphyton in oligotrophic streams were more sensitive to copper than periphyton in more eutrophic environments. Given the many environmental parameters that influence copper toxicity, but also the intrinsic properties of microbial communities which evolve over time through species succession, Navarro et al. (2002) and Larras et al. (2016) logically observed seasonal differences in the copper sensitivity of phototrophic communities (river periphytic biofilms) and microalgal communities (lake phytoplankton).

Although less studied, prey–predator relationships are also likely to modulate the effects of copper on aquatic microbial communities by impacting top-down control, as illustrated for example by Barranguet et al. (2003) and Le Jeune et al. (2007). However, cascading effects associated with copper trophic exposure has been poorly studied, and the indirect effects of copper on food webs have not yet been documented in either terrestrial or aquatic ecosystems.

Conclusions

The widespread use of copper-based formulations as a plant protection product in both conventional and organic agriculture as well as for non-agricultural uses, together with its natural native sources and its wider use as a biocide, makes copper an ubiquitous contaminant in the different environmental compartments, where it tends to accumulate over time. Copper that persists in soils can be partially transferred to adjacent aquatic environments (in surface water and sediment) and, ultimately, to the marine environment. The results presented here clearly highlight that this contamination, which is mainly reported in vineyard areas, impacts biodiversity and ecosystem functions, in particular through effects on phototrophic and heterotrophic microbial communities, and on terrestrial and aquatic invertebrates. There is still a shortage of knowledge on the effects of copper on other biological groups and biotic interactions, despite the fact that copper is still in massive use worldwide.

Acknowledgments

The authors thank all the experts involved in the above-mentioned collective scientific assessment (CSA) and the French Ministries for Ecology, Agriculture and Research who commissioned this CSA.

References

Abiven D, Boudesocque S, Guillon E, Couderchet M, Dumonceau J, Aplincourt M (2006) Sorption of the herbicide terbumeton and its metabolites onto soils. Influence of copper(II). Environ Chem 3:53–60. https://doi.org/10.1071/en05060

Akcha F, Coquillé N, Sussarellu R, et al. (2022) Trophic transfer of copper decreases the condition index in Crassostrea gigas spat in concomitance with a change in the microalgal fatty acid profile and enhanced oyster energy demand. Total Sci Environ 824: 153841. https://doi.org/10.1016/j.scitotenv.2022.153841

Amossé J, Bart S, Brulle F. et al. (2020) A two years field experiment to assess the impact of two fungicides on earthworm communities and their recovery. Ecotox Environ Saf 203:11. http://dx.doi.org/10.1016/j.ecoenv.2020.110979

Amossé J, Bart S, Pery ARR, Pelosi, C (2018) Short-term effects of two fungicides on enchytraeid and earthworm communities under field conditions. Ecotoxicology 27:300–312. http://dx.doi.org/10.1007/s10646-018-1895-7

Anatole-Monnier L (2014) Effets de la contamination cuprique des sols viticoles sur la sensibilité de la vigne à un cortège de bioagresseurs. Thèse de doctorat, université de Bordeaux. https://tel.archives-ouvertes.fr/tel-01198938/file/MONNIER_LAETITIA_2014.pdf ; Accessed 10 January 2024)

Andrivon D, Bardin M, Bertrand C, et al. (2018) Can organic agriculture cope without copper for disease control? Synthesis of the collective scientific assessment report, INRA (France), 64 p. (https://www.inrae.fr/sites/default/files/pdf/can-organic-agriculture-cope-without-copper-for-disease-control-synthesis-of-the-collective-scientific-assessment-report-1.pdf ; Accessed on 3 January 2024)

Araujo DF, Knoery J, Briant N, et al. (2021) Metal stable isotopes in transplanted oysters as a new tool for monitoring anthropogenic metal bioaccumulation in marine environments: The case for copper. Environ Pollut 290:10. https://doi.org/10.1016/j.envpol.2021.118012

Araujo DF, Knoery J, Briant N, Vigier N, Ponzevera E (2022) “Non-traditional” stable isotopes applied to the study of trace metal contaminants in anthropized marine environments. Mar Pollut Bull 175:113398. https://doi.org/10.1016/j.marpolbul.2022.113398

Araujo DF, Ponzevera E, Briant N, et al. (2019) Copper, zinc and lead isotope signatures of sediments from a Mediterranean coastal bay impacted by naval activities and urban sources. Appl Geochem 111:104440. https://doi.org/10.1016/j.apgeochem.2019.104440

Babcsányi I, Chabaux F, Granet M, Meite F, Payraudeau S, Duplay J, Imfeld G (2016) Copper in soil fractions and runoff in a vineyard catchment: insights from copper stable isotopes. Sci Total Environ 557–558:154–162, https://doi.org/10.1016/j.scitotenv.2016.03.037

Ballabio C, Panagos P, Lugato E et al. (2018) Copper distribution in European topsoils: An assessment based on LUCAS soil survey. Sci Total Environ 636:282–298. https://doi.org/10.1016/j.scitotenv.2018.04.268

Barranguet C, Charantoni E, Plans M, Admiraal W (2000) Short-term response of monospecific and natural algal biofilms to copper exposure. Eur J Phycol 35:397–406. http://dx.doi.org/10.1017/s0967026200002924

Barranguet C, van den Ende FP, Rutgers M et al. (2003) Copper-induced modifications of the trophic relations in riverine algal-bacterial biofilms. Environ Toxicol Chem 22:1340–1349. http://dx.doi.org/10.1002/etc.5620220622

Bart S, Laurent C, Péry ARR, Mougin C, Pelosi C (2017) Differences in sensitivity between earthworms and enchytraeids exposed to two commercial fungicides. Ecotox Environ Saf 140:177–184. http://doi.org/10.1016/j.ecoenv.2017.02.052

Bary F, Gange AC, Crane M, Hagley KJ (2005) Fungicide levels and arbuscular mycorrhizal fungi in golf putting greens. J Appl Ecol 42:171–180. http://dx.doi.org/10.1111/j.1365-2664.2004.00989.x

Beaudouin R, Péry ARR (2013) Comparison of species sensitivity distributions based on population or individual endpoints. Environ Toxicol Chem 32:1173–1177. https://doi.org/10.1002/etc.2148

Besnard E, Chenu C, Robert M (2001) Influence of organic amendments on copper distribution among particle-size and density fractions in Champagne vineyard soils. Environ Pollut 112:329–337. https://doi.org/10.1016/s0269-7491(00)00151-2
Biswas H, Bandyopadhyay D (2017) Physiological responses of coastal phytoplankton (Visakhapatnam, SW Bay of Bengal, India) to experimental copper addition. Mar Environ Res 131:19–31. http://dx.doi.org/10.1016/j.marenvres.2017.09.008n
Blanck H, Wängberg SA, Molander S (1988) Pollution-induced community tolerance—a new ecotoxicological tool. In: Cairns J and Pratt JR (Eds.), Functional Testing of Aquatic Biota for Estimating Hazards of Chemicals. 1988; ASTM STP 988, Philadelphia, pp. 219–230.
Blotevogel S, Oliva P, Sobanska S, et al. (2018). The fate of Cu pesticides in vineyard soils: A case study using delta Cu-65 isotope ratios and EPR analysis. Chem Geol 477:35–46. http://dx.doi.org/10.1016/j.chemgeo.2017.11.032
Bogomolov DM, Chen SK, Parmelee RW, Subler S, Edwards C (1996) An ecosystem approach to soil toxicity testing: a study of copper contamination in laboratory soil microcosms. Appl Soil Ecol 4:95–105. https://doi.org/10.1016/0929-1393(96)00112-6
Bonnineau C, Artigas J, Chaumet B, et al. (2021) Role of biofilms in contaminant bioaccumulation and trophic transfer in aquatic ecosystems: Current state of knowledge and future challenges. Rev Environ Contam Toxicol 253:115–153. https://doi.org/10.1007/398_2019_39
Breitwieser M, Barbarin M, Plumejeaud-Perreau C, et al. (2020) Biomonitoring of Mimachiamys varia transplanted to areas impacted by human activities (La Rochelle Marina, France). Chemosphere 243:10. https://doi.org/10.1016/j.chemosphere.2019.125199
Briant N, Freydier R, Araujo DF, Delpoux S, Elbaz-Poulichet F (2022). Cu isotope records of Cu-based antifouling paints in sediment core profiles from the largest European Marina, The Port Camargue. Sci Total Environ 849:157885. https://doi.org/10.1016/j.scitotenv.2022.157885
Brun LA, Maillet J, Richarte J, Herrmann P, Remy JC (1998) Relationships between extractable copper, soil properties and copper uptake by wild plants in vineyard soils. Environ Pollut 102:151–161. https://doi.org/10.1016/s0269-7491(98)00120-1
Brun LA, Maillet J, Hinsinger P, Pepin M (2001) Evaluation of copper availability to plants in copper-contaminated vineyard soils. Environ Pollut 111:293–302. https://doi.org/10.1016/s0269-7491(00)00067-1
Brun LA, Le Corff J, Maillet J (2003) Effects of elevated soil copper on phenology, growth and reproduction of five ruderal plant species. Environ Pollut 122:361-368. https://doi.org/10.1016/S0269-7491(02)00312-3
Buffet P-E, Richard M, Caupos F, et al. (2013) A mesocosm study of fate and effects of CuO Nanoparticles on endobenthic species (Scrobicularia plana, Hediste diversicolor). Environ Sci Technol 47:1620–1628. http://dx.doi.org/10.1021/es303513r
Bunemann EK, Schwenke GD, Van Zwieten L (2006) Impact of agricultural inputs on soil organisms - a review. Austr J Soil Res 44:379–406. http://dx.doi.org/10.1071/sr05125
Burgeot T, Akcha F, Menard D, et al. (2017) Integrated monitoring of chemicals and their effects on four sentinel species, Limanda limanda, Platichthys flesus, Nucella lapillus and Mytilus sp. in Seine Bay: A key step towards applying biological effects to monitoring. Mar Environ Res 124:92–105. https://doi.org/10.1016/j.marenvres.2016.10.009
Calvo J, Jung H, Meloni G (2017) Copper metallothioneins. IUBMB Life 69:236–245. https://doi.org/10.1002/iub.1618
Campillo-Cora C, Gonzalez-Feijoo R, Arias-Estevez M, Fernandez-Calvino D (2023) Dissolved organic matter as a confounding factor in the determination of pollution-induced community tolerance (PICT) of bacterial communities to heavy metals using the leucine incorporation method. Geoderma 430:116335. https://doi.org/10.1016/j.geoderma.2023.116335
Carley LN, Panchagavi R, Song X, et al. (2020) Long-Term Effects of Copper Nanopesticides on Soil and Sediment Community Diversity in Two Outdoor Mesocosm Experiments. Environ Sci Technol 54: 8878–8889. http://dx.doi.org/10.1021/acs.est.0c00510
CEREMA, 2020. Enquête dragage 2017. Enquête nationale sur les dragages des ports maritimes. Rapport Collection: données. ISBN: 978-2-37180-483-8
Cesco S, Pii Y, Borruso L, et al. (2021) A smart and sustainable future for viticulture is rooted in soil: how to face Cu toxicity. Appl Sci 11:907. https://doi.org/10.3390/app11030907
Chaignon V, Di Malta D, Hinsinger P (2002) Fe-deficiency increases Cu acquisition by wheat cropped in a Cu-contaminated vineyard soil. New Phytologist 154:121-130. https://doi.org/10.1046/j.1469-8137.2002.00349.x
Chaignon V, Sanchez-Neira I, Herrmann P, Jaillard B, Hinsinger P (2003). Copper bioavailability and extractability as related to chemical properties of contaminated soils from a vine-growing area. Environ Pollut 123:229–238. http://dx.doi.org/10.1016/s0269-7491(02)00374-3

Chauvin C, Trambolho M, Hedde M, Makowski D, Cérémonie H, Jimenez A, Villenave C (2020) Soil nematodes as indicators of heavy metal pollution: A meta-analysis. Open J Soil Sci 10:579–601. http://dx.doi.org/10.4236/ojss.2020.1012028

Cheloni G, Cosio C, Slaveykova VI (2014) Antagonistic and synergistic effects of light irradiation on the effects of copper on Chlamydomonas reinhardtii. Aquat Toxicol 155:275–282. http://dx.doi.org/10.1016/j.aquatox.2014.07.010

Chopin EIB, Marin B, Mkoungafoko R, et al. (2008) Factors affecting distribution and mobility of trace elements (Cu, Pb, Zn) in a perennial grapevine (Vitis vinifera L.) in the Champagne region of France. Environ Pollut 156:1092–1098. https://doi.org/10.1016/j.envpol.2008.04.015

Chouvelon T, Strady E, Harmelin-Vivien M et al (2019) Patterns of trace metal bioaccumulation and trophic transfer in a phytoplankton-zooplankton-small pelagic fish marine food web. Mar Pollut Bull 146:1013–1030. https://doi.org/10.1016/j.marpolbul.2019.07.047

Cote J, Bouetard A, Pronost Y et al (2015) Genetic variation of Lymnaea stagnalis tolerance to copper: A test of selection hypotheses and its relevance for ecological risk assessment. Environ Pollut 205:209–217. http://dx.doi.org/10.1016/j.envpol.2015.05.040

Crouzet O, Consentino L, Petraud JP et al. (2019) Soil photosynthetic microbial communities mediate aggregate stability: Influence of cropping systems and herbicide use in an agricultural soil. Front Microbiol 10:15. https://doi.org/10.3389/fmicb.2019.01319

Dautremepuits C, Paris-Palacios S, Betoulle S, Vernet G (2004) Modulation in hepatic and head kidney parameters of carp (Cyprinus carpio L.) induced by copper and chitosan. Comp Biochem Physiol C Toxicol Pharmacol 137:325–333. http://dx.doi.org/10.1016/j.cca.2004.03.005

De Caralt S, Verdura J, Vergés A, Ballesteros E, Cebrian E (2020) Differential effects of pollution on adult and recruits of a canopy-forming alga: implications for population viability under low pollutant levels. Sci Rep 10:1–11. https://doi.org/10.1038/s41598-020-73990-5

De la Broise D, Palenik B (2007) Immersed in situ microcosms: A tool for the assessment of pollution impact on phytoplankton. J Exp Mar Biol Ecol 341:274–281. https://doi.org/10.1016/j.jembe.2006.10.045

De Schamphelaere KAC, Heijerick DG, Janssen CR (2006) Cross-phylum comparison of a chronic biotic ligand model to predict chronic toxicity of copper to a freshwater rotifer, Brachionus calyciflorus (Pallas). Ecotox Environl Saf 63:189–195. https://doi.org/10.1016/j.ecoenv.2005.07.012

Demanou J, Sharma S, Dorfler U, et al. (2006) Structural and functional diversity of soil microbial communities as a result of combined applications of copper and mefenoxam. Soil Biol Biochem 38:2381–2389. http://dx.doi.org/10.1016/j.soilbio.2006.03.007

Díaz-Raviña M, Calvo de Anta R, Bååth E (2007) Tolerance (PICT) of the bacterial communities to copper in vineyards soils from Spain. J Environ Qual. 36:1760–1764. http://dx.doi.org/10.2134/jeq2006.0476

Dorigo U, Bérard A, Rimet F, Bouchez A, Montuelle B (2010) In situ assessment of periphyton recovery in a river contaminated by pesticides. Aquatic Toxicol. 98:396–406. https://doi.org/10.1016/j.aquatox.2010.03.011

Dousset S, Jacobson AR, Dessogne JB, Guichard N, Baveye PC, Andreux F (2007) Facilitated transport of diuron and glyphosate in high copper vineyard soils. Environ Sci Technol 41:8056–8061. https://doi.org/10.1021/es071664c

Dron J, Revenko G, Chamaret P, Chaspoul F, Wafo E, Harmelin-Vivien M (2019) Contaminant signatures and stable isotope values qualify European conger (Conger conger) as a pertinent bioindicator to identify marine contaminant sources and pathways. Ecol Indic 107:105562–105562. https://doi.org/10.1016/j.ecolind.2019.105562

Droz B, Payraudeau S, Martin JAR, et al. (2021) Copper content and export in European vineyard soils influenced by climate and soil properties. Environ Sci Technol 55:7327–7334. https://doi.org/10.1021/acs.est.0c02093

Duarte S, Pascoal C, Alves A, Correia A, Cassio F (2008) Copper and zinc mixtures induce shifts in microbial communities and reduce leaf litter decomposition in streams. Freshwat Biol 53:91–101. http://dx.doi.org/10.1111/j.1365-2427.2007.01869.x

Duplay J, Semhi K, Errais E, Imfeld G, Babcsanyi I, Perrone T (2014). Copper, zinc, lead and cadmium bioavailability and retention in vineyard soils (Rouffach, France): The impact of cultural practices. Geoderma, 230–231:318–328. https://doi.org/10.1016/j.geoderma.2014.04.022

Eijsackers H, Beneke P, Maboeta M, Louw JPE, Reinecke AJ (2005) The implications of copper fungicide usage in vineyards for earthworm activity and resulting sustainable soil quality. Ecotox Environ Saf 62:99–111. http://dx.doi.org/10.1016/j.ecoenv.2005.02.017

El Azzi D, Viers J, Guiresse M, et al. (2013) Origin and fate of copper in a small Mediterranean vineyard catchment: New insights from combined chemical extraction and delta Cu–65 isotopic composition. Sci Total Environ 463:91–101. https://doi.org/10.1016/j.scitotenv.2013.05.058

El Hadri H, Chery P, Jalabert S, Lee A, Potin-Gautier M, Lespes G (2012) Assessment of diffuse contamination of agricultural soil by copper in Aquitaine region by using French national databases. Sci Total Environ 441:239–247. https://doi.org/10.1016/j.scitotenv.2012.09.070

Fernandez D, Voss K, Bundschuh M, Zubrod JP, Schafer RB (2015) Effects of fungicides on decomposer communities and litter decomposition in vineyard streams. Sci Total Environ 533:40–48. http://dx.doi.org/10.1016/j.scitotenv.2015.06.090

Fey P, Bustamante P, Bosserelle P, et al. (2019) Does trophic level drive organic and metallic contamination in coral reef organisms? Sci Total Environ 667:208–221. https://doi.org/10.1016/j.scitotenv.2019.02.311

Flores-Vélez LM, Ducaroir J, Jaunet AM, Robert M (1996) Study of the distribution of copper in an acid sandy vineyard soil by three different methods. Eur J Soil Sci 47:523–532. https://doi.org/10.1111/j.1365-2389.1996.tb01852.x

Frodello JP, Marchand B (2001) Cadmium, copper, lead, and zinc in five toothed whale species of the Mediterranean Sea. Inter J Toxicol 20:339–343. https://doi.org/10.1080/109158101753333613

Garty J, Weissman L, Tamir O, et al. (2000) Comparison of five physiological parameters to assess the vitality of the lichen Ramalina lacera exposed to air pollution. Physiol Plant 109:410–418. https://doi.org/10.1034/j.1399-3054.2000.100407.x

Gerbersdorf SU, Koca K, de Beer D, et al. (2020) Exploring flow-biofilm-sediment interactions: Assessment of current status and future challenges. Water Res 185:18. https://doi.org/10.1016/j.watres.2020.116182

Giller KE, Witter E, McGrath SP (2009) Heavy metals and soil microbes. Soil Biochem 41:2031–2037. https://doi.org/10.1016/j.soilbio.2009.04.026

Gis Sol. 2013. The state of the soils in France. A synthesis / Groupement d'intérêt scientifique sur les sols, France, 24p. https://www.gissol.fr/rapports/synthesis_HD.pdf ; Accessed 3 January 2024)

Grosell M, Nielsen C, Bianchini A (2002) Sodium turnover rate determines sensitivity to acute copper and silver exposure in freshwater animals. Comp Biochem Physiol C Toxicol Pharmacol 133:287–303. http://dx.doi.org/10.1016/s1532-0456(02)00085-6

Grosell M (2011) Copper. Fish Physiol 31:53–133. https://doi.org/10.1016/S1546-5098(11)31002-3

Guasch H, Navarro E, Serra A, Sabater S (2004) Phosphate limitation influences the sensitivity to copper in periphytic algae. Freshwat Biol 49:463–473. http://dx.doi.org/10.1111/j.1365-2427.2004.01196.x

Imfeld G, Meite F, Wiegert C, Guyot B, Masbou J, Payraudeau S (2020) Do rainfall characteristics affect the export of copper, zinc and synthetic pesticides in surface runoff from headwater catchments? Sci Total Environ 741:140437. https://doi.org/10.1016/j.scitotenv.2020.140437

Imfeld G, Duplay J, Payraudeau S (2021) Comment on 'Ecotoxicity of copper input and accumulation for soil biodiversity in vineyards' by Karimi et al. (2021). Environ Chem Lett 19:3525–3527. http://dx.doi.org/10.1007/s10311-021-01259-y

Iñigo V, Marín A, Andrades M, Jiménez-Ballesta R (2020) Evaluation of the copper and zinc contents of soils in the vineyards of La Rioja (Spain). Environments 7:55. https://doi.org/10.3390/environments7080055

Islam MA, Blasco J, Araújo CVM (2019). Spatial avoidance, inhibition of recolonization and population isolation in zebrafish (Danio rerio) caused by copper exposure under a non-forced approach. Sci Total Environ 653:504–511. https://doi.org/10.1016/j.scitotenv.2018.10.375

Jacobson AR, Dousset S, Guichard N, Baveye P, Andreux F (2005) Diuron mobility through vineyard soils contaminated with copper. Environ Pollut 138:250–259. https://doi.org/10.1016/j.envpol.2005.04.004

Joachim S, Roussel H, Bonzom JM, et al. (2017) A long-term copper exposure in a freshwater ecosystem using lotic mesocosms: invertebrate community responses. Environ Toxicol Chem 36:2698–2714. http://dx.doi.org/10.1002/etc.3822

Joimel S, Cortet J, Consales JN, Branchu P, Haudin CS, Morel JL, Schwartz C (2021) Contribution of chemical inputs on the trace elements concentrations of surface soils in urban allotment gardens. J Soil Sed 21:328–337. https://doi.org/10.1007/s11368-020-02784-z

Johnson GF (1935) The early history of copper fungicides. Agric Hist 9:67–79

Karimi B, Masson V, Guilland C, et al. (2021a) Ecotoxicity of copper input and accumulation for soil biodiversity in vineyards. Environ Chem Lett 19:2013–2030. http://dx.doi.org/10.1007/s10311-020-01155-x

Karimi B, Maron PA, Ranjard L (2021b) Reply to the comment by Imfeld et al. on 'Ecotoxicity of copper input and accumulation for soil biodiversity in vineyards' by Karimi et al. (2021). Environ Chem Lett 19:3529–3530. https://doi.org/10.1007/s10311-021-01260-5

Katsoulas N, Løes AK, Andrivon D et al (2020) Current use of copper, mineral oils and sulphur for plant protection in organic horticultural crops across 10 European countries. Org Agr 10:159–171. https://doi.org/10.1007/s13165-020-00330-2

Keiblinger KM, Schneider M, Gorfer M, et al. (2018) Assessment of Cu applications in two contrasting soils—effects on soil microbial activity and the fungal community structure. Ecotoxicology 27:217–233. https://doi.org/10.1007/s10646-017-1888-y

Klok C (2007) Effects of earthworm density on growth, development, and reproduction in Lumbricus rubellus (Hoffm.) and possible consequences for the intrinsic rate of population increase. Soil Biol Biochem 39:2401–2407. https://doi.org/10.1016/j.soilbio.2007.04.016
Klok C, De Roos A, Marinissen JCY, Baveco HM, Ma WC (1997) Assessing the effects of abiotic environmental stress on population growth in Lumbricus rubellus (Lumbricidae, Oligochaeta). Soil Biol Biochem 29:287–293. https://doi.org/10.1016/S0038-0717(96)00050-8
Komárek M, Cadkova E, Chrastny V, Bordas F, Bollinger JC (2010) Contamination of vineyard soils with fungicides: A review of environmental and toxicological aspects. Environ Int 36:138–151. https://doi.org/10.1016/j.envint.2009.10.005
Kuzyakhmetov GG (1998) Algological evaluation of the toxicity of copper compounds in gray forest soil and leached chernozem. Eura Soil Sci 31:877–882.
Lambert AS, Dabrin A, Morin S, et al. (2016) Temperature modulates phototrophic periphyton response to chronic copper exposure. Environ Pollut 208:821–829. http://dx.doi.org/10.1016/j.envpol.2015.11.004
Lambert AS, Morin S, Artigas J, et al. (2012) Structural and functional recovery of microbial biofilms after a decrease in copper exposure: Influence of the presence of pristine communities. Aquat Toxicol 109:118–126. http://dx.doi.org/10.1016/j.aquatox.2011.12.006
Lamichhane JR, Osdaghi E, Behlau F, Kohl J, Jones JB, Aubertot JN (2018) Thirteen decades of antimicrobial copper compounds applied in agriculture. A review. Agron Sustain Dev 38:18. http://dx.doi.org/10.1007/s13593-018-0503-9
Larras F, Rimet F, Gregorio V, et al. (2016) Pollution-induced community tolerance (PICT) as a tool for monitoring Lake Geneva long-term in situ ecotoxic restoration from herbicide contamination. Environ Sci Pollut Res 23:4301–4311. http://dx.doi.org/10.1007/s11356-015-5302-0
Lavoie I, Lavoie M, Fortin C (2012) A mine of information: Benthic algal communities as biomonitors of metal contamination from abandoned tailings. Sci Total Environ 425:231–241. http://dx.doi.org/10.1016/j.scitotenv.2012.02.057
Lee LH, Lui D, Platner PJ et al (2006) Induction of temperate cyanophage AS-1 by heavy metal – copper. BMC Microbiol 6:17. https://doi.org/10.1186/1471-2180-6-17
Le Jeune AH, Charpin M, Sargos D, et al. (2007) Planktonic microbial community responses to added copper. Aquat Toxicol 83:223–237. http://dx.doi.org/10.1016/j.aquatox.2007.04.007
Levy JL, Stauber JL, Wakelin SA, Jolley DF (2009) The effect of bacteria on the sensitivity of microalgae to copper in laboratory bioassays. Chemosphere 74:1266–1274. http://dx.doi.org/10.1016/j.chemosphere.2008.10.049
Lewis MA, Devereux R (2009) Non nutrient anthropogenic chemicals in seagrass ecosystems: fate and effects. Environ Toxicol Chem 28:644–661. https://doi.org/10.1897/08-201.1
Lin Y, Zhang Y, Liang X, et al. (2022) Assessment of rhizosphere bacterial diversity and composition in a metal hyperaccumulator (Boehmeria nivea) and a nonaccumulator (Artemisia annua) in an antimony mine. J Appl Microbiol 132:3432–3443. https://doi.org/10.1111/jam.15486
Loria A, Cristescu ME, Gonzalez A (2022) Genotype diversity promotes the persistence of Daphnia populations exposed to severe copper stress. J Evol Biol 35:265–277. http://dx.doi.org/10.1111/jeb.13979
Ma WCW (2005) Critical body residues (CBRs) for ecotoxicological soil quality assessment: copper in earthworms. Soil Biol Biochem 37:561–568. http://dx.doi.org/10.1016/j.soilbio.2004.09.002
Mackie KA, Muller T, Kandeler E (2012) Remediation of copper in vineyards - A mini review. Environ Pollut 167:16–26. http://dx.doi.org/10.1016/j.envpol.2012.03.023
Maes V, Betoulle S, Jaffal A, et al. (2016). Juvenile roach (Rutilus rutilus) increase their anaerobic metabolism in response to copper exposure in laboratory conditions. Ecotoxicology 25:900–913. http://dx.doi.org/10.1007/s10646-016-1648-4
Mahamoud-Ahmed A, Lyautey E, Bonnineau C, Dabrin A, Pesce S (2018) Environmental concentrations of copper, alone or in mixture with arsenic, can impact river sediment microbial community structure and functions. Front Microbiol 9:13. http://dx.doi.org/10.3389/fmicb.2018.01852
Mahamoud-Ahmed A, Tardy V, Bonnineau C, Billard P, Pesce S, Lyautey E (2020) Changes in sediment microbial diversity following chronic copper-exposure induce community copper-tolerance without increasing sensitivity to arsenic. J Hazard Mat 391:12. http://dx.doi.org/10.1016/j.jhazmat.2020.122197
Maraldo K, Christensen B, Strandberg B, Holmstrup M (2006) Effects of copper on enchytraeids in the field under differing soil moisture regimes. Environ Toxicol Chem 25:604–612. http://dx.doi.org/10.1897/05-076r.1
Martinez JG, Paran GP, Rizon R, De Meester N, Moens T (2016) Copper effects on soil nematodes and their possible impact on leaf litter decomposition: A microcosm approach. Eur J Soil Biol 73:1–7. http://dx.doi.org/10.1016/j.ejsobi.2015.12.004

Massieux B, Boivin MEY, van den Ende FP, et al. (2004) Analysis of structural and physiological profiles to assess the effects of Cu on biofilm microbial communities. Appl Environ Microbiol 70:4512–4521. http://dx.doi.org/10.1128/aem.70.8.4512-4521.2004

Mauffret A, Chiffoleau JF, Burgeot T, Wessel N, Brun M (2018) Evaluation du Descripteur 8 "Contaminants dans le Milieu" en France Métropolitaine. Rapport Scientifique pour l'évaluation 2018 au titre de la DCSMM Rapport Ifremer RBE-BE / ODE-VIGIES, 280 p. (https://archimer.ifremer.fr/doc/00461/57294/59374.pdf ; accessed 3 January 2024)

Mebane CA, Arthaud DL (2010). Extrapolating growth reductions in fish to changes in population extinction risks: Copper and chinook salmon. Hum Ecoll Risk Assess 16:1026–1065. https://doi.org/10.1080/10807039.2010.512243

Meite F, Alvarez-Zaldívar P, Crochet A, Wiegert C, Payraudeau S, Imfeld G (2018) Impact of rainfall patterns and frequency on the export of pesticides and heavy-metals from agricultural soils. Sci Total Environ 616–617:500–509, https://doi.org/10.1016/j.scitotenv.2017.10.297

Mensens C, De Laender F, Janssen CR, Rivera FC, Sabbe K, De Troch M (2018) Selective and context-dependent effects of chemical stress across trophic levels at the basis of marine food webs. Ecol Appl 28:1342–1353. http://dx.doi.org/10.1002/eap.1737

Mertens J, Wakelin SA, Broos K, McLaughlin MJ, Smolders E (2010) Extent of copper tolerance and consequences for functional stability of the ammonia-oxidizing community in long-term copper-contaminated soils. Environ Toxicol Chem 29:27–37. https://doi.org/10.1002/etc.16

Metian M, Hédouin L, Eltayeb MM, Lacoue-Labarthe T, Teyssié J-L, Mugnier C, Bustamante P, Warnau M (2010) Metal and metalloid bioaccumulation in the Pacific blue shrimp Litopenaeus stylirostris (Stimpson) from New Caledonia: Laboratory and field studies. Mar Pollut Bull 61:576-584. https://doi.org/10.1016/j.marpolbul.2010.06.035

Michaud AM, Bravin MN, Galleguillos M, Hinsinger P (2007) Copper uptake and phytotoxicity as assessed in situ for durum wheat (Triticum turgidum durum L.) cultivated in Cu-contaminated, former vineyard soils. Plant Soil 298:99–111. https://doi.org/10.1007/s11104-007-9343-0

Millward RN, Grant A (2000) Pollution-induced tolerance to copper of nematode communities in the severely contaminated Restronguet creek and adjacent estuaries, Cornwall, United Kingdom. Environ Toxicol Chem 19:454–461. https://doi.org/10.1002/etc.5620190227

Mir AR, Pichtel J, Hayat S (2021) Copper: uptake, toxicity and tolerance in plants and management of Cu-contaminated soil. Biometals 34: 37–759. http://dx.doi.org/10.1007/s10534-021-00306-z

Morin S, Pesce S, Kim-Tiam S, Libert X, Coquery M, Mazzella N (2012a) Use of polar organic chemical integrative samplers to assess the effects of chronic pesticide exposure on biofilms. Ecotoxicology 21(5):1570–1580. http://dx.doi.org/10.1007/s10646-012-0910-7

Morin S, Lambert AS, Artigas J, Coquery M, Pesce S (2012b) Diatom immigration drives biofilm recovery after chronic copper exposure. Freshwat Biol 57:1658–1666. https://doi.org/10.1111/j.1365-2427.2012.02827.x

Morin S, Lambert AS, Rodriguez EP, Dabrin A, Coquery M, Pesce S (2017) Changes in copper toxicity towards diatom communities with experimental warming. J Hazard Mat 334:223–232. http://dx.doi.org/10.1016/j.jhazmat.2017.04.016

Navarro E, Guasch H, Sabater S (2002) Use of microbenthic algal communities in ecotoxicological tests for the assessment of water quality: the Ter river case study. J Appl Phycol 14:41–48. http://dx.doi.org/10.1023/a:1015242301451

Oliveira Ribeiro CA, Vollaire Y, Sanchez-Chardi A, Roche H (2005) Bioaccumulation and the effects of organochlorine pesticides, PAH and heavy metals in the Eel (Anguilla anguilla) at the Camargue Nature Reserve, France. Aquat Toxicol 74:53-69. https://doi.org/10.1016/j.aquatox.2005.04.008

Ong MC, Pan HJ, Shazili NAM, Menier D, Dupont V, Révillon S, Connell A (2021) Heavy metals concentration in sediments of South Brittany waters, France: An ecological risk assessment approach. Open J Mar Sci 11:55–68. https://doi.org/10.4236/ojms.2021.111004

Ouedraogo F, Cornu JY, Janot N, Nguyen C, Sourzac M, Parlanti E, Denaix L (2022). Do DOM optical parameters improve the prediction of copper availability in vineyard soils? Environ Sci Pollut Res 29:29268-29284. https://doi.org/10.1007/s11356-021-16361-5

Oukarroum A, Perreault F, Popovic R (2012) Interactive effects of temperature and copper on photosystem II photochemistry in Chlorella vulgaris. J Photochem Photobiol B Biol 110:9–14. http://dx.doi.org/10.1016/j.jphotobiol.2012.02.003

Palacios Ò, Pagani A, Pérez-Rafael S et al (2011) Shaping mechanisms of metal specificity in a family of metazoan metallothioneins: evolutionary differentiation of mollusc metallothioneins. BMC Biology 9:4. https://doi.org/10.1186/1741-7007-9-4

Panagos P, Ballabio C, Lugato E, et al. (2018). Potential sources of anthropogenic copper inputs to European agricultural soils. Sustainability 10:2380. https://doi.org/10.3390/su10072380

Paoletti MG, Sommaggio D, Favretto MR, Petruzzelli G, Pezzarossa B, Barbafieri M (1998) Earthworms as useful bioindicators of agroecosystem sustainability in orchards and vineyards with different inputs. Appl Soil Ecol 10:137–150. http://dx.doi.org/10.1016/s0929-1393(98)00036-5

Parada J, Rubilar O, Sousa DZ, Martinez M, Fernandez-Baldo MA, Tortella GR (2019) Short-term changes in the abundance of nitrifying microorganisms in a soil-plant system simultaneously exposed to copper nanoparticles and atrazine. Sci Total Environ 670:1068–1074. http://dx.doi.org/10.1016/j.scitotenv.2019.03.221

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. https://doi.org/10.1046/j.1365-2389.2002.00478.x

Pérez Guaita D, Sayen S, Boudesocque S, Guillon E (2011) Copper(II) influence on flumequine retention in soils: Macroscopic and molecular investigations. J Colloid Interface Sci 357:453–459. https://doi.org/10.1016/j.jcis.2011.01.097

Pesce S, Campiche S, Casado-Martinez C et al (2020) Towards simple tools to assess functional effects of contaminants on natural microbial and invertebrate sediment communities. Environ Sci Pollut Res 27:6680–6689. http://dx.doi.org/10.1007/s11356-019-07331-z

Pesce S, Lambert AS, Morin S, Foulquier A, Coquery M, Dabrin A (2018) Experimental warming differentially influences the vulnerability of phototrophic and heterotrophic periphytic communities to copper toxicity. Front Microbiol 9:14. http://dx.doi.org/10.3389/fmicb.2018.01424

Pesce S, Mamy L, Achard AL, Le Gall M, Le Perchec S, Réchauchère O, Tibi A, Leenhardt S, Sanchez W (2021) Collective scientific assessment as a relevant tool to inform public debate and policymaking: an illustration about the effects of plant protection products on biodiversity and ecosystem services. Environ Sci Pollut Res 28:38448–38454. https://doi.org/10.1007/s11356-021-14863-w

Pesce S, Mamy L, Sanchez W et al (2023) Main conclusions and perspectives from the collective scientific assessment of the effects of plant protection products on biodiversity and ecosystem services along the land–sea continuum in France and French overseas territories. Environ Sci Pollut Res https://doi.org/10.1007/s11356-023-26952-z

Petit JCJ, Schafer J, Coynel A et al (2013) Anthropogenic sources and biogeochemical reactivity of particulate and dissolved Cu isotopes in the turbidity gradient of the Garonne River (France). Chem Geol 359:125–135. https://doi.org/10.1016/j.chemgeo.2013.09.019

Pierdet M (2020) Évolution spatiale et temporelle de la mobilité des contaminants organiques et inorganiques dans des sols viticoles contrastés. Thèse de doctorat, université de Bordeaux. https://theses.hal.science/tel-03917478v1/file/PIERDET_MANON_2020.pdf ; Accessed 10 January 2024)

PPDB, Pesticide Properties DataBase (2023) Copper sulphate. (http://sitem.herts.ac.uk/aeru/ppdb/en/Reports/178.htm ; accessed 3 January 2024)

Probst B, Schüler C, Joergensen RG (2008) Vineyard soils under organic and conventional management-microbial biomass and activity indices and their relation to soil chemical properties. Biol Fertil Soils 44:443–450. https://doi.org/10.1007/s00374-007-0225-7

Rabiet M, Coquery M, Carluer N, Gahou J, Gouy V (2015) Transfer of metal(loid)s in a small vineyard catchment: contribution of dissolved and particulate fractions in river for contrasted hydrological conditions. Environ Sci Pollut Res 22:19224–19239. https://doi.org/10.1007/s11356-015-5079-1

Ranjard L, Echairi A, Nowak V, Lejon DPH, Nouaïm R (2006) Field and microcosm experiments to evaluate the effects of agricultural Cu treatment on the density and genetic structure of microbial communities in two different soils, FEMS Microbiol Ecol 58:303–315, https://doi.org/10.1111/j.1574-6941.2006.00157.x

Regulation (EU) 2018/1981 (2018). Commission Implementing Regulation (EU) 2018/1981 of 13 December 2018 renewing the approval of the active substances copper compounds, as candidates for substitution, in accordance with Regulation (EC) No 1107/2009 of the European Parliament and of the Council concerning the placing of plant protection products on the market, and amending the Annex to Commission Implementing Regulation (EU) No 540/2011 (Text with EEA relevance). Official Journal of the European Union. (http://data.europa.eu/eli/reg_impl/2018/1981/oj ; accessed 3 January 2024)

Reimann C, Garrett RG (2005) Geochemical background - Concept and reality. Sci Total Environ 350:12–27. https://doi.org/10.1016/j.scitotenv.2005.01.047

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. https://doi.org/10.1016/s0269-7491(01)00274-3

Roubeix V, Pesce S, Mazzella N, Coste M, Delmas F (2012) Variations in periphytic diatom tolerance to agricultural pesticides in a contaminated river: An analysis at different diversity levels. Fresh Environ Bull 21:2090–2094.

Roussel H, Joachim S, Lamothe S, Palluel O, Gauthier L, Bonzom JM (2007). A long-term copper exposure on freshwater ecosystem using lotic mesocosms: Individual and population responses of three-spined

sticklebacks (Gasterosteus aculeatus). Aquat Toxicol 82:272–280. https://doi.org/10.1016/j.aquatox.2007.02.018
Roussel H, Chauvet E, Bonzom JM (2008) Alteration of leaf decomposition in copper-contaminated freshwater mesocosms. Environ Toxicol Chem 27:637–644. http://dx.doi.org/10.1897/07-168.1
Saby NPA, Marchant BP, Lark RM, Jolivet CC, Arrouays D (2011) Robust geostatistical prediction of trace elements across France. Geoderma 162:303–311. https://doi.org/10.1016/j.geoderma.2011.03.001
Saby NPA, Thioulouse J, Jolivet CC, Ratie C, Boulonne L, Bispo A, Arrouays D (2009) Multivariate analysis of the spatial patterns of 8 trace elements using the French soil monitoring network data. Sci Total Environ 407:5644–5652. https://doi.org/10.1016/j.scitotenv.2009.07.002
Schoffer JT, Sauve S, Neaman A, Ginocchio R (2020) Role of leaf litter on the incorporation of copper-containing pesticides into soils under fruit production: a review. J Soil Sci Plant Nut 20:990–1000. http://dx.doi.org/10.1007/s42729-020-00186-1
Sereni L, Guenet B, Lamy I (2023) Mapping risks associated with soil copper contamination using availability and bio-availability proxies at the European scale. Environ Sci Pollut Res 30:19828–19844. http://dx.doi.org/10.1007/s11356-022-23046-0
Serra A, Corcoll N, Guasch H (2009) Copper accumulation and toxicity in fluvial periphyton: The influence of exposure history. Chemosphere 74:633–641. http://dx.doi.org/10.1016/j.chemosphere.2008.10.036
Serra A, Guasch H (2009) Effects of chronic copper exposure on fluvial systems: Linking structural and physiological changes of fluvial biofilms with the in-stream copper retention. Sci Total Environ 407:5274–5282. http://dx.doi.org/10.1016/j.scitotenv.2009.06.008
Serra A, Guasch H, Admiraal W, Van der Geest HG, Van Beusekom SAM (2010) Influence of phosphorus on copper sensitivity of fluvial periphyton: the role of chemical, physiological and community-related factors. Ecotoxicology 19:770–780. http://dx.doi.org/10.1007/s10646-009-0454-7
Sharaff M, Archana G (2015) Assessment of microbial communities in mung bean (Vigna radiata) rhizosphere upon exposure to phytotoxic levels of copper. J Basic Microbiol 55:1299–1307. http://dx.doi.org/10.1002/jobm.201400927
Simonin M, Colman BP, Tang WY, et al. (2018) Plant and microbial responses to repeated Cu(OH)2 nanopesticide exposures under different fertilization levels in an agro-ecosystem. Front Microbiol 9:14. http://dx.doi.org/10.3389/fmicb.2018.01769
Soares FB, Monteiro AC, Barbosa JC, Mochi DA (2017) Population density of Beauveria bassiana in soil under the action of fungicides and native microbial populations. Acta Sci Agron 39:465–474. http://dx.doi.org/10.4025/actasciagron.v39i4.32816
Sussarellu R, Lebreton M, Rouxel J, Akcha F, Rivière G (2018) Copper induces expression and methylation changes of early development genes in Crassostrea gigas embryos. Aquat Toxicol 196:70–78. https://doi.org/10.1016/j.aquatox.2018.01.001
Tamm L, Thuerig B, Apostolov S, et al. (2022) Use of copper-based fungicides in organic agriculture in twelve European countries. Agronomy 12:673. https://doi.org/10.3390/agronomy12030673
Tlili A, Bérard A, Roulier JL, Volat B, Montuelle B (2010) PO43- dependence of the tolerance of autotrophic and heterotrophic biofilm communities to copper and diuron. Aquat Toxicol 98:165–177. http://dx.doi.org/10.1016/j.aquatox.2010.02.008
Uwizeyimana H, Wang M, Chen W, Khan K (2017) The eco-toxic effects of pesticide and heavy metal mixtures towards earthworms in soil. Environ Toxicol Pharmacol 55:20–29. https://doi.org/10.1016/j.etap.2017.08.001
van der Perk M, Jetten VG (2006) The use of a simple sediment budget model to estimate long-term contaminant export from small catchments. Geomorphology 79:3–12. https://doi.org/10.1016/j.geomorph.2005.09.010
Van Zwieten L, Rust J, Kingston T, Merrington G, Morris S (2004) Influence of copper fungicide residues on occurrence of earthworms in avocado orchard soils. Sci Total Environ 329:29–41. http://dx;doi.org/10.1016/j.scitotenv.2004.02.014
Vazquez-Blanco R, Arias-Estevez M, Baath E, Fernandez-Calvino D (2020) Comparison of Cu salts and commercial Cu based fungicides on toxicity towards microorganisms in soil. Environ Pollut 257:8. http://dx.doi.org/10.1016/j.envpol.2019.113585
Wakelin S, Gerard E, Black A et al (2014) Mechanisms of pollution induced community tolerance in a soil microbial community exposed to Cu. Environ Pollut 190:1–9. http://dx.doi.org/10.1016/j.envpol.2014.03.008
Wang QY, Zhou DM, Cang L (2009) Microbial and enzyme properties of apple orchard soil as affected by long-term application of copper fungicide. Soil Biol Biochem 41:1504–1509. http://dx.doi.org/10.1016/j.soilbio.2009.04.010
Wightwick AM, Salzman SA, Reichman SM, Allinson G, Menzies NW (2013a) Effects of copper fungicide residues on the microbial function of vineyard soils. Environ Sci Pollut Res 20:1574–1585. http://dx.doi.org/10.1007/s11356-012-1114-7

Wightwick AM, Reichman SM, Menzies NW, Allinson G (2013b) The effects of copper hydroxide, captan and trifloxystrobin fungicides on soil phosphomonoesterase and urease activity. Wat Air Soil Pollut 224:9. http://dx.doi.org/10.1007/s11270-013-1703-1

Zancan S, Trevisan R, Paoletti MG (2006) Soil algae composition under different agro-ecosystems in North-Eastern Italy. Agri Ecosys Environ 112:1–12. https://doi.org/10.1016/j.agee.2005.06.018

Zeb A, Li S, Wu JN, Lian JP, Liu WT, Sun YB (2020) Insights into the mechanisms underlying the remediation potential of earthworms in contaminated soil: A critical review of research progress and prospects. Sci Total Environ 740:16. http://dx.doi.org/10.1016/j.scitotenv.2020.140145

Zhang XM, Fu GX, Xing SP et al (2022a). Structure and diversity of fungal communities in long-term copper-contaminated agricultural soil. Sci Total Environ 806:13. http://dx.doi.org/10.1016/j.scitotenv.2021.151302

Zhang L, Yang Z, Yang M et al (2022b). Copper-induced oxidative stress, transcriptome changes, intestinal microbiota, and histopathology of common carp (Cyprinus carpio). Ecotox Environ Saf 246:114136. https://doi.org/10.1016/j.ecoenv.2022.114136

Zhong XQ, Joimel S, Schwartz C, Sterckeman T (2022) Assessing the future trends of soil trace metal contents in French urban gardens. Environ Sci Pollut Res 29:3900–3917. https://doi.org/10.1007/s11356-021-15679-4

Cite this article

Pesce, S., Mamy, L., Sanchez, W. et al. The use of copper as plant protection product contributes to environmental contamination and resulting impacts on terrestrial and aquatic biodiversity and ecosystem functions. Environ Sci Pollut Res (2024). https://doi.org/10.1007/s11356-024-32145-z