An assessment of the challenge presented by copper in the UK natural environment

A joint analysis by the Hazardous Substances Advisory Committee (HSAC) and the Expert Committee on Pesticides (ECP)

Andrew Johnson, Dave Spurgeon, Peter Matthiessen, Mike Depledge, Mick Whelan, Rod Blackshaw, Tom Hutchinson.

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Executive Summary

Copper is a natural component of the earth's crust, rivers and oceans. However, its many desirable properties mean that copper is mined, smelted and used in a range of industrial and domestic applications. It also has applications in agriculture including use as a fungicide. Although a certain level of copper is vital as a micronutrient for many species, in excess it is toxic to aquatic and terrestrial wildlife. Environmental monitoring data show that levels in UK rivers have declined since the 1980s, possibly due to reductions in emissions from industry and the transport sector. However, it is still at levels of some concern and it remains as one of the highest ranked toxic metals in our rivers. Unlike rivers, there is less evidence for a decline in soils and indeed it may be increasing in some circumstances. Because of the presence of natural chemicals in the environment capable of binding freely available copper in less-toxic forms , assessing environmental risks is not straightforward. Fortunately, scientifically derived biotic ligand models can help predict the freely available copper and hence real world environmental risks. From the data available, the relative risks to wildlife from current copper levels in aquatic, marine and terrestrial ecosystems are high. This would suggest that applications which lead to additional emission, such as in fungicides, should not be encouraged.

Disclaimer: This report has been produced by members of Defra's HSAC and ECP committees. It does not claim to be either an exhaustive or authoritative review. However, the information presented should be adequate as an introduction to the UK situation with regards to copper in the environment.

Overview of copper in the environment and its sources

Copper is a trace element essential for all living organisms (Roussel et al., 2007). It is required in small amounts (5-20 µg/g) by all known living species because of its role in a number of significant biochemical processes. Copper is associated with several important enzymes, including cytochrome C, mixed function oxidases and superoxide dismutase. Copper is also an essential element in the respiratory systems of many invertebrates (it is needed for the formation of haemoglobin and in the metal co-factors in haemocyanin, the oxygen-transporting pigments in arthropods and molluscs).. Because copper is an essential micronutrient or trace element, many aquatic organisms have developed strategies for regulating internal copper. This is based on the presence of a series of copper chaperones and trafficking enzymes (Sakar, 1999), storage by general metal and specific metallothioneins and a number of small chelation molecules (Dallinger et al., 2020). This capacity for copper handling and storage, however, has its limits (Bossuyt and Janssen, 2004). When this homeostatic capacity is exceeded, cellular excess of free copper can lead to toxicity.

Copper is one of the most widely used metals to meet a range of current societal needs, as it has been throughout much of history. Copper has had many and varied uses in modern society including coins, jewellery, aquaculture screens, air conditioners, automobile parts, roofing, plumbing and heating systems (https://copperalliance.org). Annual global consumption is reported as currently 28 million tonnes (https://copperalliance.org), placing copper as one of the most widely extracted, processed and used of the commercially significant metals. Releases of copper to the environment can occur at different steps from extraction to use and disposal. Locally, mining can be a source of elevated concentrations of copper in the environment (Hirst et al., 2002). Further contamination can occur when the ore is processed by smelting and the resulting copper used for fabrication (Dudka and Adriano, 1997).

Copper is emitted into the air from both natural and anthropogenic sources and can be transported from one environmental compartment to another via transport processes including atmospheric resuspension, deposition, run-off, leaching and sedimentation. Historical global atmospheric anthropogenic and natural emissions of copper have been estimated to be 35×10^6 and 28×10^6 kg/year, respectively (Nriagu, 1989) and global demand for copper is rising (Schipper et al., 2018). Atmospheric deposition (e.g. industrial release) can influence concentrations of copper in soil. A UK soil pollutant survey reported 67% higher copper concentration (28.8 mg/kg) in soils in areas close to industrial sites compared to rural sites unaffected by industry (Panagos et al., 2018). In addition to industrial release, particles can also be released into the atmosphere from the wear of automobile brakes which can contain copper (Sinha et al., 2020). In Europe, it is estimated that copper emission due to brake wear could be around 2.4×10^6 kg/ year affecting both soil and surface water (Hulskotte et al., 2007).

Sources of copper entering the rural landscape include the application of sewage sludge to land (Charlton et al., 2016), farmyard manure from the use of copper in some animal feeds (Nicholson et al., 1999) and in some medicines (McBride and Spiers, 2001), as well as copper in plant protection products (Karimi et al., 2021). The toxic and persistent properties of copper have promoted its use as an algaecide, bactericide, fungicide, herbicide, and molluscicide, (EFSA, 2018; Roussel et al., 2007). Because copper has a high affinity to natural organic matter, these interactions can have a strong effect on the fate and transport of copper in soils and surface waters. Once present in soils, copper binding to the soil solid phase can limit copper leaching. Indeed, these strong interactions mean that copper added to soil may be retained for centuries to millennia (Lofts et al., 2013), indicating the potential for the long-term accumulation in soil as a result of historic excess copper addition.

Use of copper in the agri-food sector

Copper has a number of applications in the agri-food sector that can result in soil and water exposure. It is given as a feed amendment to piglets to support foetal growth and early post-natal development. The absorption of dietary copper in pigs is incomplete and even when absorbed, the added fraction can be readily excreted. As a result, a significant amount of feed copper can be lost in pig manures that can reach land either directly in outdoor rearing situations or indirectly through the spreading of pig manures (or digestate if manure is used in anaerobic digestors) to land.

Other organic amendment added to soil (e.g. sewage sludge, composts) can also contain elevated concentrations of copper. Where the soil has a copper deficiency, copper may be added as a trace element fertiliser. This circumstance is more usually encountered in highly weathered tropical soils; in temporate regions there are few cases where deliberate addition of copper as a potential micronutrient is needed. The potential for the presence of a range of metals, including copper, at elevated concentrations in sewage sludge has been known for many decades. Management to reduce the loading of metals to sewage sludge have been in routine practice and generally concentrations of metals that are routinely measured in sludge have been falling. However, despite some reductions, trace metals in sewage sludge, which is added to approximately 1% of the UK's total arable land area, remains an important route through which copper reaches the terrestrial environment (Davis and Rudd, 1999) .

There is a long-history of the use of copper for plant protection. This use has drawn on the broad spectrum biocidal properties of copper and copper-containing minerals. Traditionally, copper has been used as a fungicide for the treatment of a number of notable fungal pathogen diseases, especially relating to soft fruit crops. A well know example is 'Bordeaux mixture' which has been a traditional treatment for the protection of grapes (and other crops) from infestations of downy mildew, powdery mildew and other fungi. Bordeaux mixture is a combination of copper (II) sulphate ($CuSO_4$) and quicklime (CaO). It is sprayed on plants primarily as a preventive treatment, hence, its use is primarily prophylactic, leading to the potential for repeat application from year to year.

The common application of Bordeaux mixture for treatment of fungal pathogens associated with plantation crops such as grapes and other soft fruits over multiple years has resulted in the accumulation of copper in soils in these areas (Karimi et al., 2021). Copper concentrations in soil resulting from repeated use of Bordeaux mixture have been shown to reach harmful levels which can result in the elimination of sensitive soil faunal groups, including earthworms, and to changes to soil microbial community structure and function. Hayes et al. (2019) developed a data integration and meta-analysis approach based on the use of "logic chains" to review the overall evidence linking copper fungicide use to changes in soil communities and ultimately to impacts on ecosystem processes and service provision. The available evidence indicated that there was high confidence that direct impacts of copper, accumulated as a result of fungicidal use, occurred on functional diversity of fungi, earthworm abundance and rhizobacterial populations in vineyard settings. Although the strength of the science linking these changes to processes was variable, evidence based links could be made.

Aside from historic applications in fruit and vineyards, copper-based fungicides have a niche application for the treatment of organic crops and are certified as compliant with organic farming principles (Katsoulas et al., 2020). Although the land area involved is comparatively small, there is the potential for repeat applications and build-up of copper in soils over time since metals such as copper do not biodegrade and are persistent in the environment. Recently, new nanomaterial copper formulations have been developed, which could play a role in agricultural systems. These have not yet been used or approved in the UK and they have thus far been used in biocidal applications such as timber treatment and as biocidal paints and coatings (e.g. antifouling), although antifungal applications have been proposed. However, research to assess their efficacy for plant protection product applications is already underway (Pariona et al., 2019).

Copper hazard data for soil and water organisms

Soil organisms

Given the long residence times of copper as a contaminant in soil environments, there are widespread concerns about the potential for copper amendments to accumulate in soils and affect biologically mediated soil processes such as carbon sequestrations and nutrient cycling. Key functional groups of the soil biota are known to be sensitive to copper. Previous work has linked the presence of copper in soils to changes in the structure and function of earthworm and fungal communities and, thereby, to the delivery of terrestrial ecosystem services (Hayes et al., 2018). To develop an approach for assessing the large-scale risk of copper exposure, Lofts et al. (2004) collected toxicity information for copper to a range of different terrestrial species, including invertebrates, plants and microbes. A comparative analysis between these different taxa indicated that invertebrates were significantly more sensitive than plants and microbial processes to copper exposure. A large proportion of the invertebrate endpoints in this taxonomic database for copper (seven of eight EC_{10} values and four of nine NOEC values) were from tests on Oligochaetes (earthworms and enchytraeids). A number of species from these taxa have been shown to be sensitive to copper and this has been given as the reason for the reduced abundance and diversity of earthworms in copper-treated vineyard soils (Eijsackers et al., 2005). Copper is also an effective molluscicide, indicating that slug and snail species may be affected by copper exposure affecting both pest species and also other members of this class.

As well as earthworms, the soil microbial community, such as fungi and bacteria, have also been identified as being potentially sensitive to copper exposure. Numerous studies have addressed the effects of copper exposure on the structural and functional characteristics of soil fungal communities. Application of metagenomics has identified the physiological mechanisms through which copper may impact the functional characteristics of these organisms. Common effects seen for copper relate to impacts on different aspects of energy metabolism and respiration, indicating that elevated copper exposure may affect rates of organic matter cycling. The high frequency of antibiotic resistance genes detected in the metagenomic studies indicates that copper may also be a stimulant for antimicrobial resistance, including through mechanisms of horizontal gene transfer (Zhang et al., 2019). Our knowledge of the environmental chemistry and prevalence of copper in different media is usually sufficient for performing robust risk assessments, although there are still some data gaps for some organisms such as bees, birds and mammals (EFSA, 2018). Research support by industry, funded through a programme run and maintained by the European Copper Institute, has already compiled this information and used it to provide extensive additional data for risk assessments being conducted for copper and copper substances under REACH. Such information is transferrable to assessments of agricultural applications, although some specific issues around formulation, fate and hazard would also need to be included.

Freshwater and Marine Organisms

A recent review looking at hazardous chemicals in British rivers (Johnson et al., 2017) found that on the topic of copper AND toxicity there were 36,666 papers and on Copper AND fish AND toxicity: 1,904 papers. This large volume of literature indicates that copper is one of the best studied of all the potential contaminants of surface waters, with perhaps only macronutrients being more widely studied. Metals present in surface water may occur in many different chemical forms, including free ions and as inorganic and organic complexes, as well as a fraction associated with organic and inorganic colloidal materials. This chemical speciation of metals influences their potential bioavailability and hence, uptake and toxicological effects in aquatic organisms. The most bioavailable and, therefore, most toxic form of copper is the cupric ion (Cu^{2+}) which primarily drives toxicity to freshwater organisms (Wood et al., 2012). Hence, changes in water chemistry that favour ionic speciation can result in an increase in toxicity relative to other water chemistries.

Examples of this toxicity in freshwater water include the zebrafish (*Brachydanio rerio*) affected by copper at 0.63 µg/L (LOEC) (Dave and Xiu, 1991), rainbow trout *(Oncorhynchus mykiss)* affected by copper at concentrations above 2.8 µg/L (Hansen et al., 2002) and the common shrimp (*Gammarus pulex*) affected by copper concentrations of 14.6 -18.2 µg/L (Maund et al., 1992). The results of a recent review on the range of concentrations which cause aquatic toxicity (Johnson et al., 2017) are shown in

Table 1. Species sensitivity distributions (SSD) carried out for copper indicate that invertebrates tend to be the most sensitive organisms (Adam et al., 2015; Brix et al., 2001).

Reported mechanisms of toxicity include acting as an osmoregulatory toxicant – by decreasing sodium influx, e.g. Roussel et al., (2007) for fish. This latter mechanism of action is the basis for the widely used biotic ligand models, which use chemical speciation modelling and ionic competition theory to predict the potential binding of copper ions to a biotic ligand linked to toxicity (Santore et al., 2001). In the biotic ligand model developed from work in fish, Na^+/K^+-ATPases that act as ionic pumps in cell membranes (especially of the gill) have been identified as a critical site. Another commonly identified mechanism of copper effect is through reducing the amount of metabolic energy available for growth, reproduction and maintenance. Reasons for this are unclear, but may be linked to the role of copper in the electron transport chain or an increase in oxidative stress through Fenton chemistry resulting in wider mitochondrial damage, e.g. in freshwater crustaceans (Maund et al., 1992). Environmental risk assessments have also been conducted for marine and estuarine ecosystems, reflecting the widespread use of copper as an ingredient in antifouling paints for shipping and netting in aquaculture (Hall & Anderson, 1999).

Table 1 Range of copper concentrations where toxic effects on aquatic have been reported. The data were largely retrieved from the USEPA ECOTOX site (Johnson et al., 2017).

Type of data	Number of data/data sets	Lowest recorded effect (µg/L)	10^{th} percentile effect level (µg/L)	Median effect level (µg/L)	Max. (µg/L)
Ecotoxicity	107	0.63	5.9	53.3	9,210

Risk assessments for copper

Terrestrial environmental risk assessments

Unlike many organic chemicals, copper is not biotransformed and is naturally persistent. Hence, additions to soils can only be lost through the relatively slow processes of leaching and (where relevant) cropping. Hence, addition of copper to land, whether occurring directly during outdoor livestock rearing on copper augmented diets, through copper use in pesticides, or indirectly from manure, digestate or sludge spreading, has the potential to increase soil copper concentrations. In a re-survey of soils, 9 years after initial sampling, the Countryside Survey (2007) identified an increase in soil copper concentrations that was especially marked in improved grassland habitats that were used for the rearing of livestock (Fig. 11). This survey also identified that there were indications of an increase in soil copper loading in other habitats (e.g. heathlands and bog). This suggests that atmospheric deposition may underlie some of the changes to soil concentrations identified by this survey. That said, the specific challenges of repeat measurements over time using different methods and instrumentation, mean that any indications of changes in soil copper need to be interpreted with care.

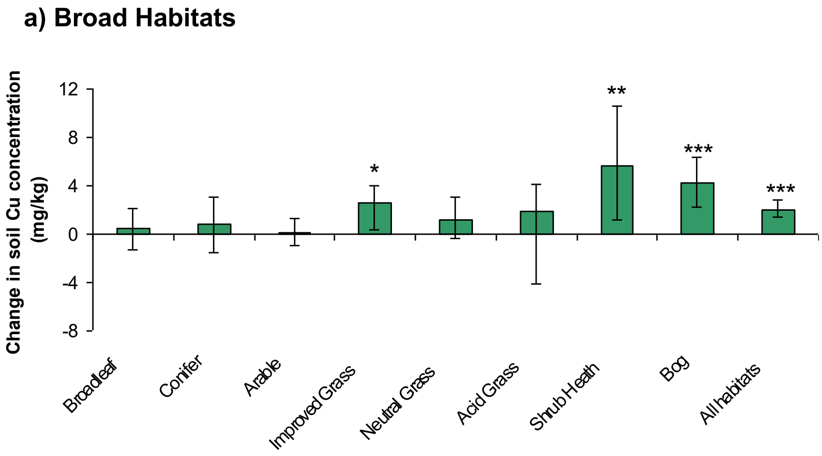

Fig. 1 Changes from 1998 to 2007 in measured Cu concentration in soils (0-15 cm depth) within categorised Broad Habitats across Great Britain. Bars indicate standard error, * p < 0.05, ** p < 0.01, *** p < 0.001.

Information on the range of soil copper concentrations present across major broad habitats, coupled with collected information on soil pH and % loss on ignition (LOI: an indicator of organic matter content) can be used in association with a biotic ligand model (Steenbergen et al., 2005; Thakali et al., 2006a; Thakali et al., 2006b), with regression (Steenbergen et al., 2005) and combined species sensitivity models (Lofts et al., 2005; Lofts et al., 2004) to provide a risk assessment. To conduct a soil risk assessment for copper, Spurgeon et al. (2008) employed the approach of Lofts et al. (2004), which was based on the biotic ligand concept, to calculate site-specific environmental quality criteria (aka "critical limits") for copper that could be used for assessing the extent of risk. Measured soil metal concentrations were then adjusted for site pH and %LOI and divided by this site-specific critical limit to calculate a ratio that could be used as a measure of risk.

Such a risk assessment is essentially precautionary (conservative) because it assumes all the copper in soil is potentially reactive. In reality, it is likely that an important proportion of copper would be refractory (trapped or in non-reactive complexes, Fig. 2). This means that there is a high likelihood that actual effects in field soils may be lower than those suggested by a critical limit assessment. The difference in toxicity between long-term polluted field soils and spiked soils has been allowed for in EU risk assessment by dividing the predicted environmental concentration by a factor of three to correct for the aging aspects in field soil (Bodar et al., 2005). For this reason, interpretation of potential risk associated with metal measurements should focus on exceedance by a factor greater than three. That said, the presence of a bound copper fraction with limited bioavailability may not be wholly relevant to cases of agrichemical copper application (as a fungicide or biocide) since the copper in these formulations is often wholly in a chemically active form.

At the individual site level, measured copper concentrations in soils were compared with site-specific critical limits for copper in the Countryside Survey (2007). The measured soil copper: critical limit ratios indicated exceedance of the critical limit at 40% of sites (Spurgeon et al., 2008). Of these sites, 75% (i.e. 30% of all sites) exceeded the critical limit by at least a factor of three. This relatively high level of exceedance of sites, supports the need to reduce, as far as reasonably possible, additional inputs of copper to soil. Since current levels of copper in many soils may already be affecting sensitive soil fauna, microbial taxa and functions, the scope for the further addition of copper via agricultural applications seems limited.

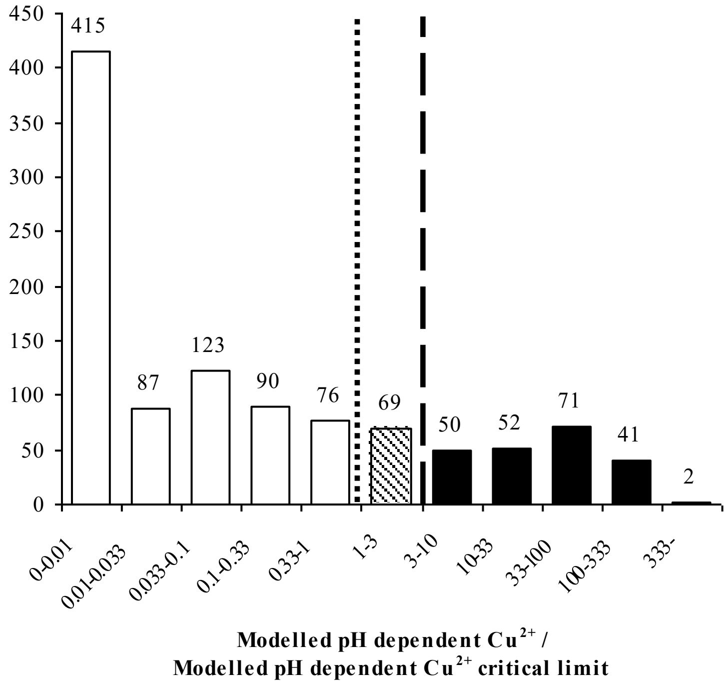

Fig. 2 Histogram of the ratio of measured total soil copper concentration against the modelled site-specific critical limit concentration calculated using the approach of Lofts et al. (2004); white bars indicate ratios less than one, hatched bars ratios of 1-3 and black bars indicate ratios greater than 3 (dashed line); numbers above bar indicate samples in each category.

Freshwater environmental risk assessments

England benefits from an extensive water quality monitoring network, run by the Environment Agency which is digitised in WIMS. Previously, this was collected for all regions of the UK from 1991 by the NRA, but this was then devolved to SNIFFER in NI, SEPA in Scotland and, more recently, NRW in Wales. The WIMS dataset can be interrogated to show common English river concentrations (Table 2).

Table 2 Range of copper concentrations found in British Rivers in 2010-2012 (Johnson et al., 2017).

Type of data	Number of data/data sets	Min. (µg/L)	Median (µg/L)	Max. (µg/L)	Origin and period
English & Welsh river measurements	89,604	0.1	1.66	5,320	WIMS (EA) 2010-2012

We can compare these river measurements with levels reported as causing some level of toxicity (

Table 1). There is some overlap between the two (Fig. 3). However, most of the time the concentrations are below those that might be expected to cause effects (Fig. 4). Without taking bioavailability into account, it can be seen that 1.3% of measurements exceed the lower 10th percentile ecotoxicity level (5.9 µg/L). In other words, about 1% of river locations/occasions have copper at levels which could be causing harm to some aquatic wildlife. However, levels of bioavailable copper will generally be lower in rivers with above neutral pH, chelating organic carbon (e.g. high dissolved organic carbon), $CaCO_3$ or hardness present, which reduces risk (Tipping et al., 2016).

There is the potential for copper to bind to bed-sediments and, hence, bioaccumulate to levels which might be harmful to benthic organisms. Similarly, bed-sediment copper could re-partition into the water column. However, the different sorption mechanisms mentioned above would often reduce bioavailability and lower the risk of toxic impacts on benthic organisms.

It has been reported that the toxic effect of copper is greatest at pH between 6 and 8 (Stockdale et al., 2010). This range covers the pH range typically found in the majority of temperate rivers, except for upland acid waters that drain peatland areas. The toxicity of copper to the ostracods (*Cypris subglobosa*) increases as pH decreases: pH 8.5 (EC50 = 5.1mg/l) vs pH 5.5 (EC50 = 0.35mg/l). The Environment Agency have provided four UK Standard Protection of Inland Freshwaters levels of copper which are specific for different hardness levels (mg/l $CaCO_3$). These are shown in Table 3. Spatial variations in mean water hardness across Great Britain are shown in Fig. 5. Highest freshwater ecotoxicological risk will occur in areas with high levels of copper (Fig. 4) and low $CaCO_3$ concentrations (soft water). Although the 2010-2012 levels (Fig. 4) are largely below levels of concern (unless in soft water) it is important to recall that compared to other major river water contaminants, copper has a high relative risk leaving little margin for error (Johnson et al., 2017).

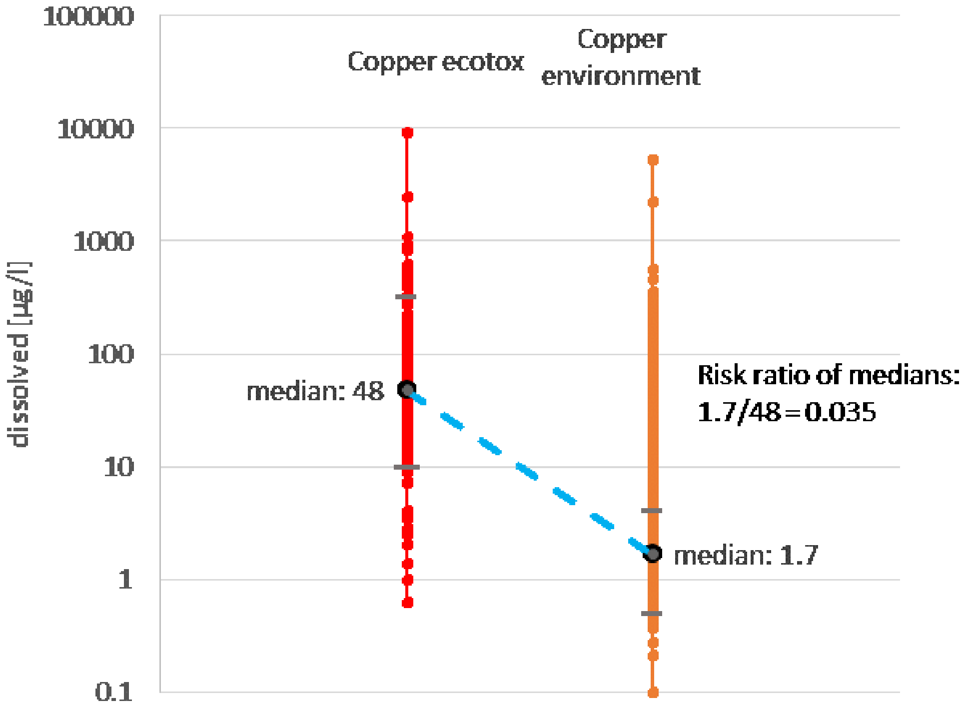

Fig. 3 Comparison of levels at which aquatic ecotoxicity effects are reported (left) and concentrations found in English rivers (right). Median exposure is much lower than median effect level. Note log scale.

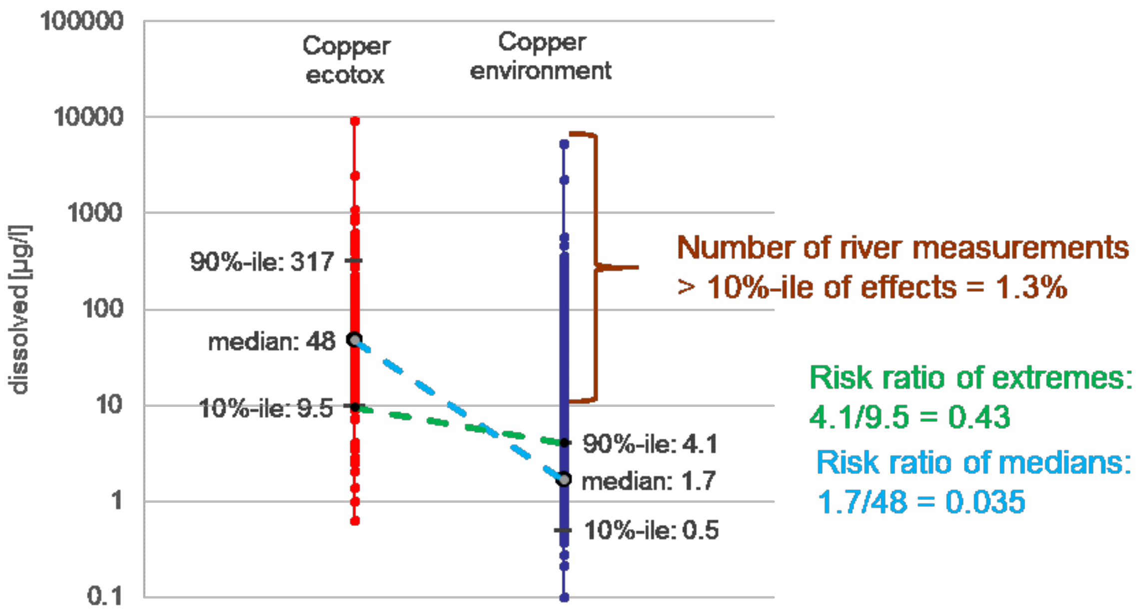

Fig. 4 Comparison of levels at which aquatic ecotoxicity effects are reported (left) and concentrations found in English rivers (right). The 10th, median and 90th percentile levels are shown for both data sets. Just 1.3% of English river concentrations (2010-2012) would exceed the 10th percentile of ecotoxicity effects. Note log scale.

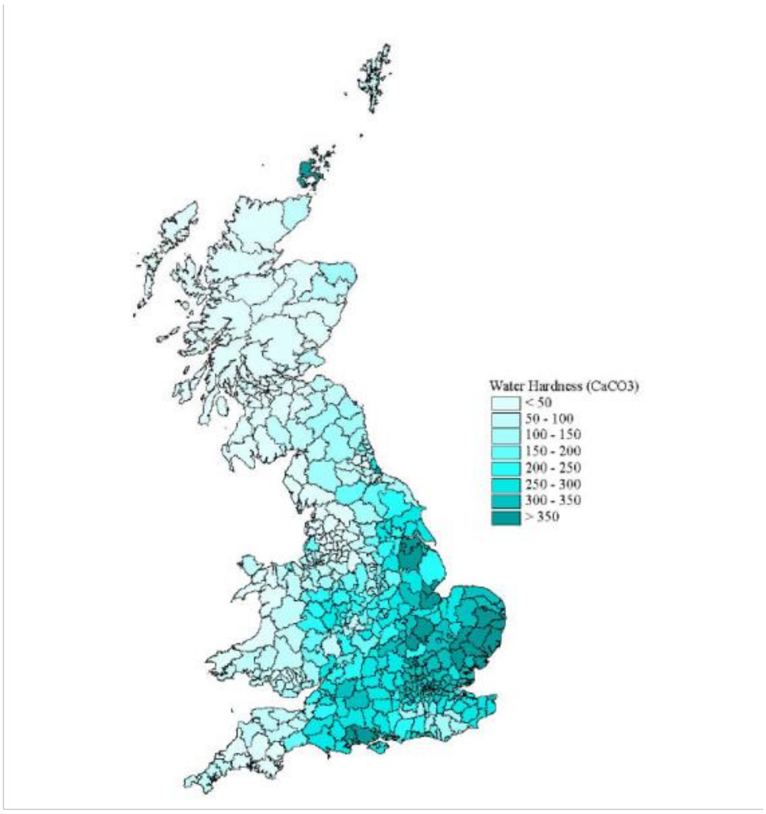

Fig. 5 GB drinking water hardness (mg/l $CaCO_3$). The more calcium carbonate present, the less copper will be bioavailable.

Table 3 Recommended quality standards for copper. WFD is Water Framework Directive. BLM is Biotic Ligand Model.

Reference paper/source	Hardness	Environmental Quality Standards
EC (2011)		1 µg/L, 6 µg/L, 10 µg/L 28 µg/L (based on hardness)
Gardner et al. (2012)		BLM-adjusted dissolved Cu 11 µg/L
Previous legislation: Environment Agency Chemical Standards for the UK The 95th percentile of the concentration of dissolved copper shall not exceed any of the values, if specified, for RE1-RE5, with reference to the hardness of the water.	Water hardness < /= 10 mg $CaCO_3$/l.	5 µg/L
	Water hardness >10 and < /= 50 mg $CaCO_3$/l.	22 µg/L
	Water hardness >50 and < /= 100 mg $CaCO_3$/l	40 µg/L
	Water hardness >100 mg $CaCO_3$/l	112 µg/L
Crane et al. (2007)	UK	8.2 µg/L proposed WFD standard
	Invertebrates	NOEC 4 µg/L
	Fish	NOEC 2.2 µg/L

Marine environmental risk assessments

As a natural element, copper is present in seawater and is often measured in marine sediments and biota. Copper in marine environments can derive from both geogenic and anthropogenic sources (Marcelo-Silva and Christofoletti, 2019). The largest fluxes of anthropogenic copper to the UK marine environment are from historical mining operations in Wales and southwest England. These have produced several "acid mine streams" that flow into major rivers and adjacent coastal water systems. The total flux of copper from freshwater to marine systems in the UK amounts to approximately 2.93×10^5 kg/year, of which 2.17×10^5 kg/year derives from mining (Mayes et al., 2013). Examples of highly contaminated examples of acid mine drainage include Restronguet Creek on the Fal estuary and the Afon Goch Dulas estuary on the Island of Anglesey in North Wales, where fluxes of approximately 1.8×10^4 and 9×10^3 kg/year, respectively, have been measured. A significant source of copper in estuaries derives from copper-based antifouling paints (AFP) on the hulls of ships and boats which can be leached and abraded. This can lead to high levels of contamination. For example, sediments near boat repair facilities can contain up to 40% copper (Turner, 2010). Copper is also used in the aquaculture industry to reduce biofouling of nets on many fish farms. The use of copper-based antifouling paints for shipping and aquaculture are examples where there is a growing use of nanotechnology to formulate more effective copper-based surface coatings.

Good quality research on the presence and effects of copper in UK estuaries has been conducted since the 1970s, and little new has been discovered since the 1990s (Bryan and Langston, 1992; Depledge et al., 1994; Depledge and Rainbow, 1990; Furness and Rainbow, 1990). Taking marine waters first, total dissolved copper levels in oceanic water are generally at or below 0.1 μg/L and are mainly derived from atmospheric deposition (Depledge et al., 1994), but can reach 2.6 μg/L in the North Sea and large estuaries, and up to 176 μg/L at local sites affected by acid mine drainage, such as Restronguet Creek. However, only a portion of the dissolved copper in estuaries is in exchangeable (including free-ion) form, i.e. forms which are potentially bioavailable to cause toxicity. Complexation with suspended solids and dissolved organic matter are important processes that determine the magnitude of these bioavailable forms (Jones and Bolam, 2007). Chemical speciation modelling using tools such as Visual MINTEQ or the Windermere Humic Acid model (WHAM) are available to support the prediction of copper speciation from available water chemistry information. The annual average Environmental Quality Standard (EQS) for seawater set by the EU (see directive 76/464/EEC) is 5 μg/L as dissolved Cu. Although waters in over 20% of sites in UK east coast estuaries, draining largely agricultural catchments, can exceed this value (Matthiessen et al., 1999), very few locations are thought to be experiencing significant impacts on water-column dwellers due to complexation processes which reduce the potential for bioconcentration.

The speciation of copper ions entering salt waters is complex. Copper primarily interacts with carbonate and hydroxide ions, (but other ions also become involved); the ionic charge is associated with uptake and availability both within an organism and within cells. Changes in pH impact the ionic balance and the availability of charged ions and complex copper compounds to which the organisms are exposed. The toxicity risk to estuarine ecology is difficult to predict based on 'clean' laboratory exposure studies. Few laboratory studies reflect the flux of salinity and other factors that drive the speciation of copper, especially in coastal waters; instead laboratory tests are often limited to one exposure condition. It is difficult to know if these exposures are conservative worst case, or relevant for the dynamic situation in the ecosystem. Dissolved organic carbon (DOC) concentration is critical since it can be protective to variable extents. In estuaries, salinity, pH and dissolved oxygen concentrations are all in a constant state of change, as they mix with tides and freshwater flow. Generally DOC is high in estuaries and we see lower direct exposure. Few studies in the literature provide an overview of risks in dynamic systems. There is, thus, an opportunity to move the science forward to fill this gap. Estuaries represent an historic sink for copper from both natural and anthropogenic sources, and these ecosystems represent an environment in which we are least able to predict the long-term risk.

Copper pollution in estuarine sediments remains a serious matter. Although sedimentary copper derived from the water column is largely associated with iron oxides and humic organic compounds, a proportion of it is nevertheless available to deposit feeders, such as some bivalve molluscs and nereid polychaetes (Bryan and Langston, 1992). Bioaccumulation of copper follows the sediment concentration in some species, *e.g.* the polychaete *Nereis (Hediste) diversicolor*, but not in others, *e.g*. the clam (*Scrobicularia plana*) in southwest England (Luoma and Rainbow, 2008). Concentrations above about 200 mg Cu/kg dry wt. are usually harmful to a variety of benthic invertebrates (Millward and Grant, 2000), and these levels do occur in UK estuaries like Restronguet Creek and near some marinas (Boxall et al., 2000). However, in most estuaries, levels of copper in sediment generally lie in the region 7-100 mg/kg dry wt. (Bryan and Langston, 1992). Interestingly, some benthic invertebrates and algae have been able to evolve tolerance to serious copper pollution (Burlinson and Lawrence, 2007; Zhou et al., 2003), and it is a moot point whether this should be considered a form of pollution impact. For example, it is certainly the case that only a restricted number of genotypes within polychaete populations are capable of tolerating elevated copper levels. Consequently genetic diversity is reduced, potentially rendering the population more vulnerable to other threats. High copper levels in some benthic flora and fauna can cause limited bioaccumulation in avian predators such as swans (Molnar, 1983) and redshank (Evans et al., 1987), but there is little evidence that this is causing serious toxic impacts. A recent review of copper and the marine environment revealed that, as in rivers, the load is continuing to decline (UKBI - B5b. Marine pollution | JNCC - Adviser to Government on Nature Conservation).

In summary, copper is a significant contaminant in some UK estuarine sediments – principally derived from historical mining operations and currently-used antifouling paints. However, overt biological impacts are only seen at a limited number of sites due to natural processes of adsorption and complexation in seawater and sediment. Nevertheless, copper concentrations in many UK estuarine sediments are within a factor of 2-20 of harmful levels, so resilience to increased copper inputs is probably low in some places.

Trends and impacts

Soil environment trends and impacts

A meta-analysis of the literature on copper exposure and effects for soils was conducted by Hayes et al. (2018). This assessed the overall evidence regarding the nature of copper effects, both direct and indirect. The results of this analysis indicated that copper has multiple impacts on soil communities including a negative effect on earthworm abundance, altered microbial activity, reduced diversity, reduced rhizobacterial abundance (leading to reduced N fixation) and reduced plant cover/growth. From these primary impacts, wider impacts of copper in terrestrial ecosystems may include increased agrochemical transport to freshwaters as a result of the effects of the metal on the diversity and function of the soil microbiome, soil erosion due effect on fungal biomass that may affect aggregate stability and exposure to grazing animals.

From the evidence base assembled by Hayes et al. (2018), the effects of copper on individual species, ecological interactions and processes and resulting ecosystem services can be evaluated.

These are illustrated in Fig. 6. Overall, there is high confidence in the initial processes of these links. In particular, there is considerable evidence that direct impacts on functional diversity in fungi, earthworm abundance and rhizobacterial populations can have knock-on effects on nutrient and carbon cycling processes. There is less confidence in the impact of reduced N fixation in native species on plant growth. Nevertheless, the majority of the links shown in Fig. 6 contain individual steps with high or medium strength of supporting science, with very few individual links possessing a low level of supporting science.

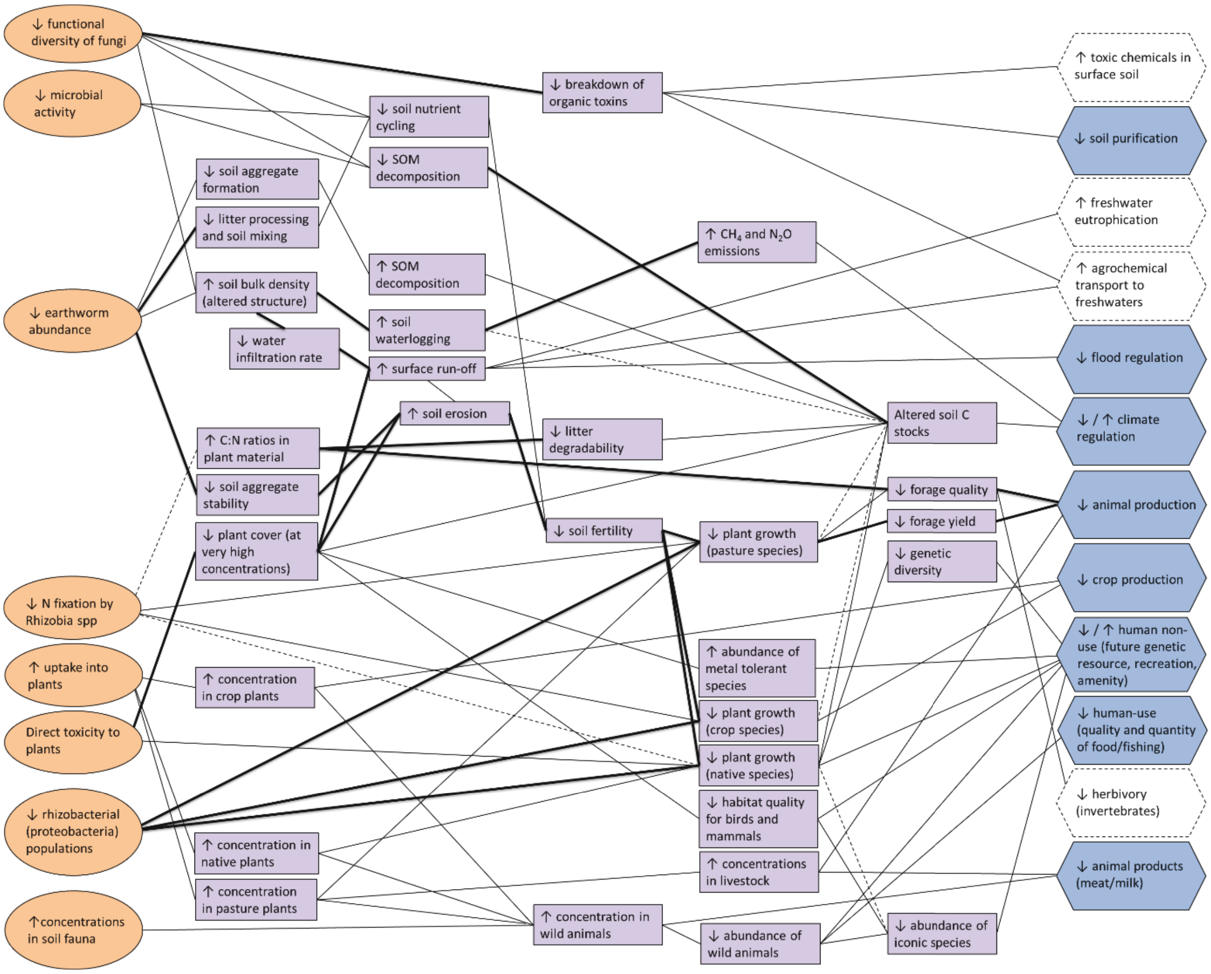

Fig. 6 Schematic network of logic chains for responses of ecosystems to soil metal (copper) pollution, leading to impacts on ecosystem services and products. The relative strength of supporting science for each linkage is indicated by the thickness of the connecting line (-- low strength of science; ─ medium strength of science, ▬ high strength of science). Direct impacts are shown in orange oval boxes, intermediate processes/attributes are shown in purple rectangular boxes, and final ecosystem goods/services are indicated by hexagonal blue boxes. White hexagonal boxes with a dotted edge indicate that further multiple chain impacts occur onwards from this attribute, which have not been considered in the current study.

Trends of measured concentrations of copper in the environment suggest that levels of this metal in terrestrial ecosystems may be increasing (Fig. 1). However, directly comparable analyses for samples taken from the same locations across extended periods of time are not available. Measurements of metals for the UK Heavy Metal Deposition network clearly show that copper deposition to soils and surface waters has decreased from its peak in the post-war period (Ashmore et al., 2008). However, copper has a very high affinity for binding to organic matter which means that, once present in soils, it can be strongly bound and retained. Estimations for the half-life of copper leaching from polluted soils suggests that ~10,000 years may be needed to reduce copper levels significantly. Hence, while deposition and inputs may be relatively low (and declining), the lack of routes for removal suggest that copper in soils can continue to accumulate. Inputs from agricultural sources may add to these loadings locally. Indeed, it is possible that such inputs may lie behind the increase in copper concentration observed across two Countryside Survey measurement campaigns conducted in 1998 and 2007 (Fig. 1). Given that adverse effects of copper on soil systems are indicated and that these have demonstrable links to impacts on important soil functions, it would seem wise to limit copper contamination of soils, wherever possible. Careful assessment of any proposed application of copper directly (e.g. biocidal uses and as supplements) or indirectly (through waste addition) would be needed in a copper stewardship and management strategy.

Water environment trends and impacts

Copper concentrations measured by the EA in water column samples from long-term monitoring studies have shown a steady decline since the mid 1980’s, similar to many other metals (Fig. 7). This may reflect a decline in UK heavy industry and changing releases from the transport sector which may lead to reduced environmental emissions. A similar trend is visible in data from the English Midlands (Fig. 8). It is interesting to observe that there has been a copper decline in water in rural areas since the 1985-1989 period as well as at river sites impacted by urban wastewater. A similar decline can be seen in data from individual rivers. An example from the River Ray near Swindon is shown in Fig. 9. This river has a very high contribution of municipal wastewater. These data can be used to tentatively predict annual copper emission to water in the UK. Assuming the population served by the Swindon wastewater treatment works (WwTW) is representative of the UK as a whole, then a copper concentration of 3 µg/L in wastewater and an average wastewater discharge of 200 L/cap/d gives a *per capita* emission of 600 µg/cap/d. This implies that 14.8×10^3 kg/year of copper will be emitted by the UK population (67.8 million) into UK river and marine environments.

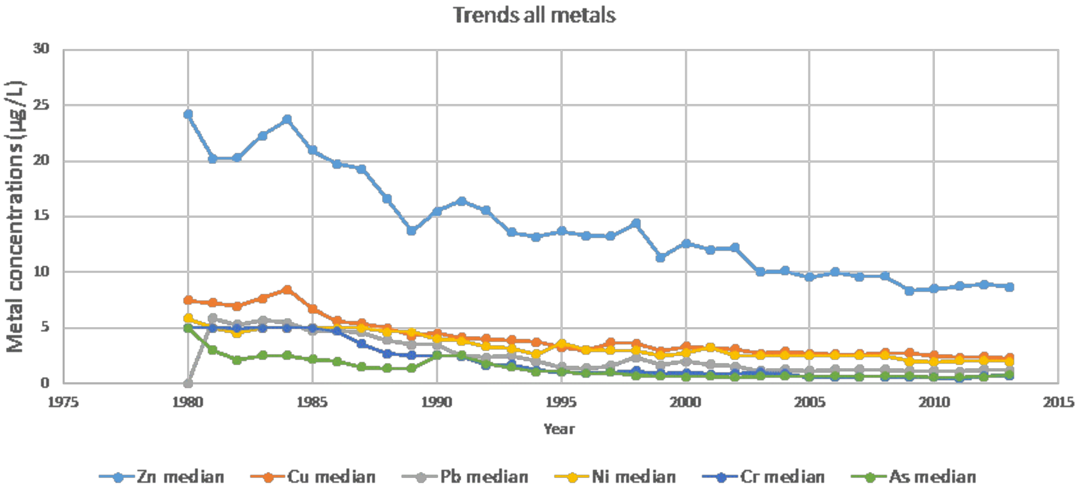

Fig. 7 Trends for several metals in UK rivers measured across 200 sites in the Environment Agency harmonised monitoring network between 1980 and 2013. Historic UK Water Quality Sampling Harmonised Monitoring Scheme Summary Data - data.gov.uk

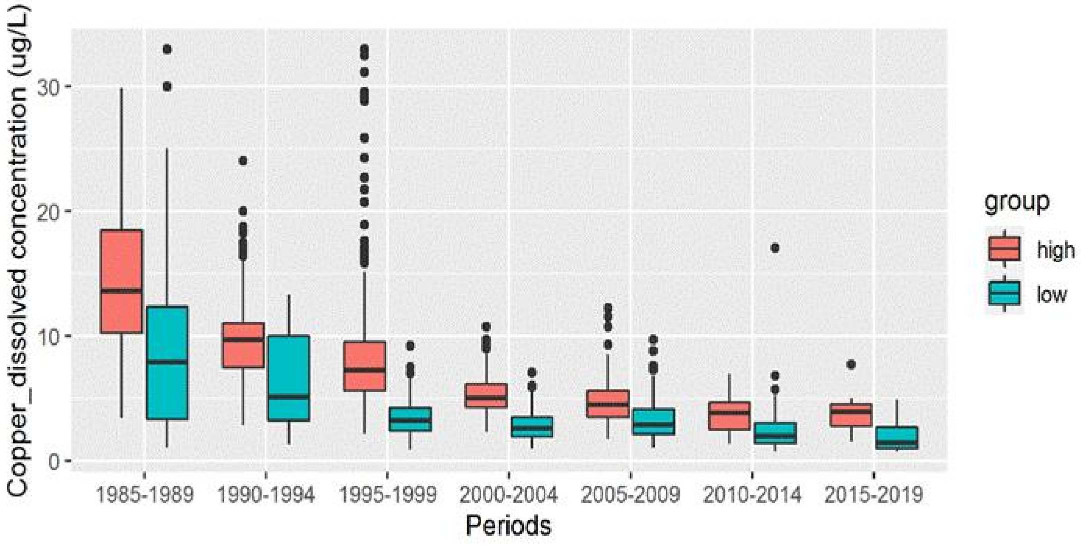

Fig. 8 Examples of changes in copper concentrations at 80 river monitoring sites in the English Midlands since the mid 1980's. The sites were differentiated between those with high wastewater impact (wastewater>25% of mean annual flow) and those with low wastewater impact (wastewater<2.5% of mean annual flow). These can be thought of as urban and rural sites.

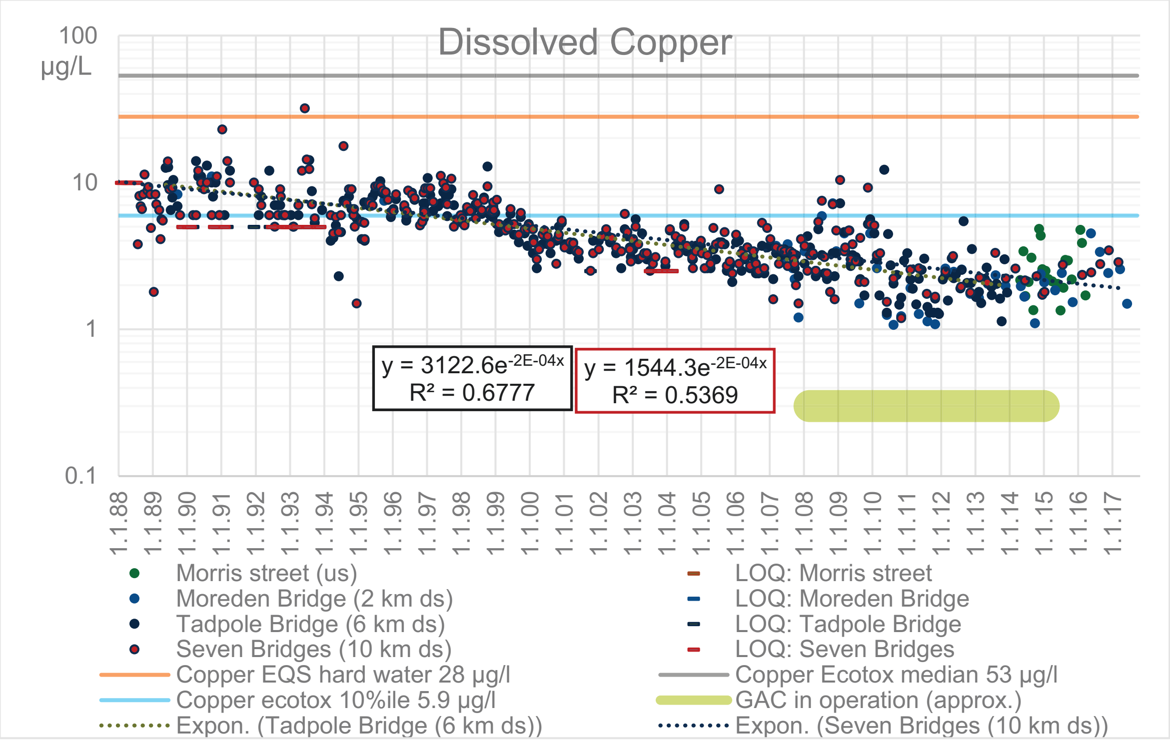

Fig. 9 Copper concentrations in the River Ray downstream of Swindon waste water treatment works (WwTW) over the period 1988 to 2017. This river contains 65-80% treated effluent. Coloured lines show the different EQS levels (Johnson et al., 2019).

Despite this decline in aquatic concentrations, patterns of copper concentrations in fish bodies in English rivers (Fig. 10) from 2007 to 2011, appear to be less clear, albeit based on only few measurements. Copper concentrations measured in the fish (500-1,000 µg/kg) are relatively high compared with data from river water (around 1 µg/L or less) suggesting that bioconcentration or bioaccumulation of copper may be occurring. Reported bioconcentration factors (BCFs) for copper range from 1493 to 1535 (Hoang et al., 2008; McGeer et al., 2003; Shuhaimi-Othman and Pascoe, 2007). These BCFs are higher than those reported for lead (155) and cadmium (366).

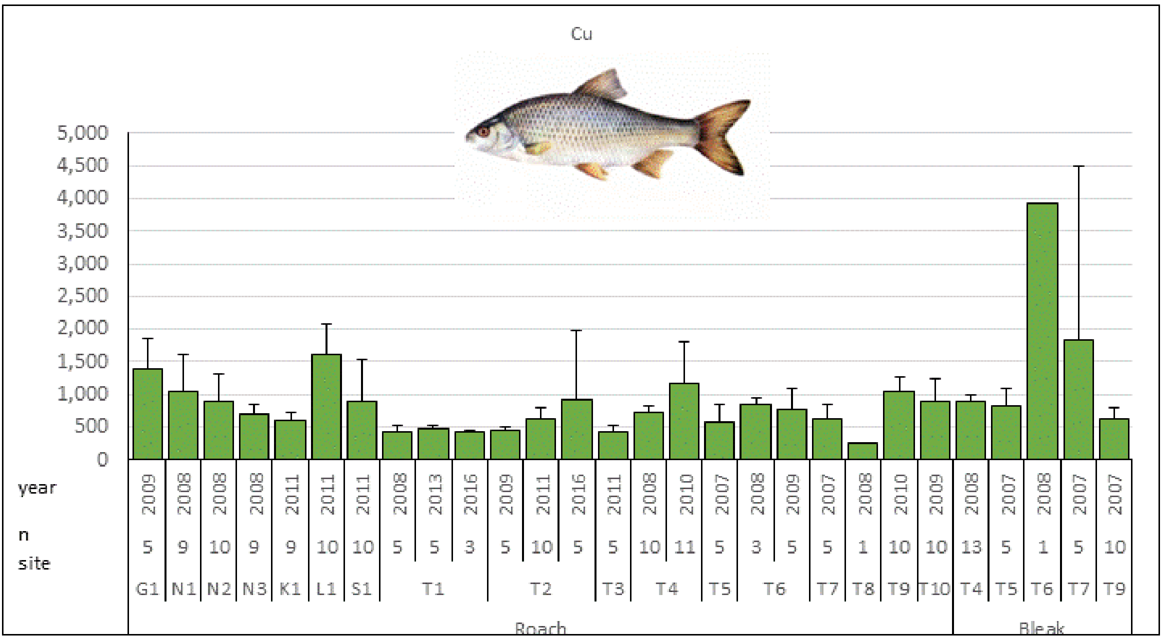

Fig. 10 Examples of copper levels found in individual wild fish (roach and bleak) caught in the Thames and some Anglian rivers.

Conclusions and policy options

Overview

Whilst copper is a natural element and a vital micronutrient, it is persistent in the environment and elevated concentrations are toxic to a wide range of organisms. Based on currently available data, levels appear to be declining in UK rivers but from the evidence we have, this decline is not seen in soils. Copper levels in both rivers and soils are often relatively close to thresholds of toxic effect. This makes additional contamination of the environment with copper highly undesirable.

Water Summary

There is evidence suggesting a decline in the levels of copper in UK Rivers since the 1980s. This may reflect reductions in emissions from heavy industry, although we estimate that approximately 14.8×10^3 kg/year is still being emitted from wastewater. Thus, despite the downward trend, copper remains as one of the highest risk river contaminants in the UK on the basis of the proximity of concentration to toxicity. This does not mean that wildlife in most British rivers is being severely harmed by current levels of copper, as they are largely below effect levels. However, we have little room for manoeuvre if levels were to rise. A relatively high risk for copper has also been identified in the coastal marine environment. Fish body burdens of copper still seem relatively high. It must also be recalled that metals like copper discharged to the aquatic environment can help to stimulate antimicrobial resistance which is also undesirable.

Soil Summary

Copper is naturally present in soils, as well as being added from anthropogenic sources. Copper continues to arrive in soils via atmospheric deposition and it is present in sewage sludge, anaerobic digestate and livestock manure which can all be added to soils, as well as in some pesticides (e.g.

fungicides). Diffuse copper inputs to soils may also arise from industrial sources, abandoned mine workings and transport infrastructure. Evidence from the only national repeat survey of metals in soils suggests that copper levels in most soils are not declining (unlike rivers). Although copper is an essential micronutrient, it is toxic at elevated concentrations. Whilst there is little evidence that copper is a limiting nutrient for crop growth in the UK, there are concerns that levels may be close to or above those expected to cause adverse effects on sensitive species and processes in some soils. Again, the potential for copper to accelerate the development of antimicrobial resistance is an ongoing concern.

Conclusion

Whilst copper concentrations in freshwater appear to be declining this is not the case for soils. Given copper's very widespread toxicity and persistence, there are strong reasons to support a continued restriction of copper applications that could lead to further environmental contamination. A range of synthetic organic fungicides are available to help protect crops. From a scientific position, it is hard to argue that copper is kinder to the environment than a biodegradable synthetic organic fungicide. Although copper-based fungicides are not registered for professional use on most crops, we note that they remain on sale in garden centres for limited use on selected fruit.

If we had to continue using copper for plant protection

Where there are strong reasons for using copper-based products for crop protection involving large quantities and over extensive areas, we would recommend that risk assessments include:

- Using local soil chemistry. Highest risks are often associated with acidic soils.
- Measuring existing soil copper levels to review their proximity to toxic levels;
- Reviewing soil hydrology and drainage to demonstrate that potentially rapid losses to adjacent surface waters (e.g. via soil macropores and artificial field drains) are likely to be minimal;
- Reviewing soil biodiversity pre and post application with a reputable ecological institution.

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