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Sources of copper into the European aquatic environment

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Abstract

Chemical contamination from point source discharges in developed (resource-rich) countries has been widely regulated and studied for decades; however, diffuse sources are largely unregulated and widespread. In the European Union (EU), large dischargers report releases of some chemicals, yet little is known of total emissions (point and diffuse) and their relative significance. We estimated copper loadings from all significant sources including industry, sewage treatment plants, surface runoff (from traffic, architecture, and atmospheric deposition), septic tanks, agriculture, mariculture, marine transport (antifoulant leaching), and natural processes. A combination of European datasets, literature, and industry data were used to generate export coefficients. These were then multiplied by activity rates to derive loads. A total of approximately 8 kt of copper per annum (ktpa) is estimated to enter freshwaters in the EU, and another 3.5 ktpa enters transitional and coastal waters. The main inputs to freshwater are natural processes (3.7 ktpa), agriculture (1.8 ktpa), and runoff (1.8 ktpa). Agricultural emissions are dominated by copper-based plant protection products and farmyard manure. Urban runoff is influenced by copper use in architecture and by vehicle brake linings. Antifoulant leaching from boats (3.2 ktpa) dominates saline water loads of copper. It is noteworthy that most of the emissions originate in a limited number of copper uses where environmental exposure and pathways exist, compared with the bulk of copper use within electrical and electronic equipment and infrastructure that has no environmental pathway during its use. A sensitivity analysis indicated significant uncertainty in data from abandoned mines and urban runoff load estimates. This study provided for the first time a methodology and comprehensive metal load apportionment to European aquatic systems, identifying data gaps and uncertainties, which may be refined over time. Source apportionments using this methodology can inform more cost-effective environmental risk assessment and management. *Integr Environ Assess Manag* 2022;00:1–17. © 2022 The Authors. *Integrated Environmental Assessment and Management* published by Wiley Periodicals LLC on behalf of Society of Environmental Toxicology & Chemistry (SETAC).

KEYWORDS: Apportionment; copper; diffuse; Europe; source; water

INTRODUCTION

Apportioning point and diffuse source emissions of chemicals has been identified as an issue across the globe, because reliable source apportionments critically underpin qualitative environmental risk assessment and management (Damania, 2019; OECD, 2017). Under the Water Framework Directive (WFD; European Union [EU], 2000) European Union Member States are required to report annual emissions, discharges, and losses of priority substances at the spatial scale of the River Basin District and on the loads discharged to the aquatic environment. This provides information on the success of measures to reduce emissions, meet environmental targets, and indicate whether further efforts may be needed to deliver good chemical status of surface waters. Such emission inventories can be generated only if sufficient data exist for major sources of chemicals to water. Results from the Second River Basin Management Plan (RBMP) cycle indicate difficulties associated with the consistency, completeness, and quality of reported emission data (Giakoumis & Voulvoulis, 2018). The first inventory was incomparable between Member States (MS), one reason being a lack of reliable emission factors and apportionment. Although there are statutory obligations to report point source emission data for chemicals of interest, that is not currently the case for diffuse sources, although they may be voluntarily reported to the European Union (EU).

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To date, there has been no attempt to quantify the loads of chemicals from a comprehensive list of diffuse as well as point sources to the aquatic environments of the entire EU at the same time on a tons-per-annum (tpa) basis. Source apportionment exercises that include diffuse sources have been undertaken for limited individual countries such as the UK (Comber et al., 2013), the Netherlands (Van den Roovaart & van Duijnhoven, 2020), and certain river basins in Germany (Hüffmeyer et al., 2009). The research presented here describes the methodology developed and provides estimates generated for quantifying the main sources of chemicals to the aquatic environment of European countries, using copper as an example.

Copper is a ubiquitous, multiuse, transition metal, with a mean crustal abundance of $60\,mg\,kg^{-1}$ (CRC, 2017). Its specific properties mean copper and copper alloys are used for a wide array of purposes including electric vehicles and charging infrastructure, sustainable energy sources such as wind and solar, electric networks and power distribution, heating and cooling of buildings, water distribution, telecommunications, industrial equipment, motors, and architecture. In addition, several copper compounds are used in biocidal products such as antifoulants, plant protection products, food supplements, and cosmetics. The widely distributed occurrence of copper minerals, and its ubiquity within society, means that copper can be detected within all environmental compartments either through natural sources, anthropogenic releases, or both. Within the EU, copper is designated as a specific pollutant under the WFD (EU, 2000). Reliable source apportionment data can help assess if strategies to minimize copper releases are expected to be cost-effective.

The aim of this research was to develop a methodology for identifying and quantifying the sources of chemicals to the aquatic environment at the continental scale, using copper as an example. The methodology allows for continuous improvement. To reduce uncertainty, the source apportionment can be refined as further data become available. To stimulate such refinements, uncertainties are highlighted where loads have been assigned to sources based on limited datasets. Source apportionments using this method can critically underpin environmental assessment of chemicals at a continental scale.

METHOD

Source apportionments are best conducted by consulting a wide variety of information sources. In addition to retrieving data from the open scientific literature, we obtained data from emission repositories as well as from published and unpublished reports held by stakeholders in national authorities, consultancies, researchers, and industry. More specifically, we used the following information sources to map the known sources of copper into the aquatic environment, to categorize them, and to calculate loads.

- European and other international risk assessment reports (e.g., vRAR, 2008);
- Supplied industry sector data;
- European datasets (Eurostat/European Pollutant Release and Transfer Register [E-PRTR]);
- Individual country datasets (per capita water use, drinking water quality, etc.);
- National authority reports;
- National authority emission inventories;
- Consultant reports (e.g., Deltares; WCA, 2021);
- MS contacts via authors;
- Open literature and published reports.

For the source categories quantified below, specific data sources have been cited. Wherever possible, post-2010 published data were used. Individual country datasets, national and international registry data, and national authority and consultant reports (in general available to the public) were important sources for assessing both inter- and intracountry variabilities. For France and the UK, extensive datasets were available for sources and the fate of copper in sewage treatment works (sewage treatment plants [STPs]), with French data also available for contaminant loads to agricultural soils, drinking water quality, and mining at a national scale.

Open literature sources were also used where available to support other datasets or to provide read-across as part of the gap-filling process. The data collection was focused on EU member states or countries reporting to the E-PRTR (2017); this was to ensure that most data, where possible, were derived based on European emissions and usages. However, data from outside the EU-27 were not disregarded if they filled data gaps or were used to support other data, particularly data generated from the UK Chemical Investigation Programme (e.g., Comber et al., 2014). Based on the sources and the uses of copper included in the aforementioned datasets, the relevant sources of copper to the aquatic environment were listed and grouped to obtain 12 overarching categories. Each of these categories may have direct emission to freshwater, direct emissions to marine water, and emission to water via soil.

Diffuse emissions are calculated by multiplying an activity rate (AR), for instance, the number of inhabitants or buildings, by an emission factor (EF), expressed as an emission per unit of the AR.

$$\text{Emission} = \text{Activity rate (AR)} \times \text{Emission factor (EF)}$$

Table 1 provides a summary of the methods and data sources used for the emission calculations for each source.

DIRECT INPUTS OF COPPER TO WATER

Sewage treatment plants

Domestic copper loads to STP. A detailed dataset is available for individual European country's household water use and per capita volumes of water used for bathing, dishwashing, laundry cleaning, toilet flushing, and "other," which included activities such as hand washing, drinking, car

TABLE 1 Summary of information sources for the source apportionment

Source	Emission factor Literature data	Comments		Activity rate Data source
Sewage treatment plants (STP)				
Total domestic wastewater	Concentration (μg L^{-1})		×	Eurostat water statistics (Eurostat, 2017) (m m^3 day^{-1})
Plumbing	Industry: Cu plumbing use (%)	EU MS corrected to UK Cu use, itself corrected for age of house and hardness	×	Eurostat water statistics for internal domestic water usage (Eurostat, 2018) (L cap^{-1} day^{-1})
Domestic activity (bathing, clothes, and dishwashing)	Concentration (μg L^{-1})	Over and above plumbing and mains input (UK data)	×	Eurostat water statistics for internal domestic water usage (Eurostat, 2018) (L cap^{-1} day^{-1})
Potable tap water supply	Concentration (μg L^{-1})		×	Eurostat water statistics (Eurostat, 2018) (m m^3 day^{-1})
Urine	Concentration (μg L^{-1})		×	Literature (L $capita^{-1}$ day^{-1})
Feces	Concentration (mg kg^{-1})		×	Literature (g $capita^{-1}$ day^{-1})
Industry to STP	E-PRTR (kg $year^{-1}$)	With main subcategories		
Services	Concentration (μg L^{-1})	UK data only	×	Eurostat water statistics (Eurostat, 2018) (m m^3 day^{-1})
Runoff (total)	Event mean concentration for road/roof runoff (μg L^{-1})		×	Eurostat settlement area (Eurostat, 2018) (km^2) × 22% impermeable area × % to sewer
Runoff (transport—oil, exhaust, tire, brake, road)	Concentration (μg km^{-1} or m^{-1})		×	Eurostat transport data (Eurostat, 2018) (m vehicle km $year^{-1}$) for lorry, bus, car, motorbike
Atmospheric deposition	Concentration (EMEP) (μg L^{-1}) × rainfall (mm $year^{-1}$)		×	Eurostat settlement area (Eurostat, 2018) (km^2) × 22% impermeable area × % to sewer
Construction materials (architectural copper)	Cu loss m^{-2} of roof Assumes a mean pitch of 68°	Assumes 50% of tonnage for roofs. Release from gutter and drainpipes assumed negligible	×	Industry: Cu stock (tons)
STP influent	Concentration (μg L^{-1})		×	Eurostat wastewater statistics (Eurostat, 2018) (m m^3 day^{-1})
STP effluent	Concentration (μg L^{-1})		×	Eurostat wastewater statistics (Eurostat, 2018) (m m^3 day^{-1})
Domestic unsewered				
Septic tanks	Concentration (μg L^{-1})	Corrected for removal, drainage, slope, soil permeability, distance to water (all default)	×	Eurostat wastewater statistics (Eurostat, 2018) (m m^3 day^{-1})

(*Continued*)

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TABLE 1 (*Continued*)

Source	Emission factor Literature data	Comments		Activity rate Data source
Agriculture				
Animal manure	Concentration (mg kg^{-1}) for cattle, pigs, poultry, sheep, goats	Manure production (kg animal day^{-1}) × Cu content ((mg kg^{-1})—90% assumed returned to land	×	Eurostat farm animal statistics (Eurostat, 2018) (million animals)
Inorganic fertilizer	Concentration (mg kg^{-1}) as impurity in inorganic fertilizer		×	Eurostat P fertilizer usage (Eurostat, 2017) (t $year^{-1}$)
Biosolids (sludge)	Concentration (mg kg^{-1})		×	Eurostat sludge data (Eurostat, 2017) (t $year^{-1}$)
Pesticides	Industry (t $year^{-1}$)			
Atmospheric deposition	Concentration (EMEP) (μg L^{-1} × rainfall (mm $year^{-1}$)		×	Eurostat area (Eurostat, 2018) (km^2)
Anthropogenic soil additions to water	Summed agricultural sources	Literature 9% loss for FYM, inorganic fertilizer, biosolids, atmospheric deposition and pesticides; 1.08% for pesticides in vineyards	×	Calculated within individual agricultural sources
Natural processes to water				
Soil loss	FOREGS background metal concentration (mg kg^{-1})	Corrected for soil transmission factor to water	×	Eurostat agricultural + forestry area (Eurostat, Eurostat,) (km^2) × Eurostat Soil loss (t ha^{-1} $year^{-1}$)
Direct atmospheric deposition onto water	Concentration (EMEP) (μg L^{-1}) × rainfall (mm $year^{-1}$)		×	Eurostat inland water data (Eurostat, 2018) (km^2)
Other sources to freshwater				
Disused mines	Load (kg day^{-1}) for UK + Germany	Mean kg day^{-1} km^{-2} of favorable Cu area	×	EGDI Promine database—favorability for copper area
Industry inputs to freshwater	E-PRTR (kg $year^{-1}$)			
Sources to marine waters				
Transport—commercial antifoulant use	Industry total use (kg $year^{-1}$)			
Transport—leisure antifoulant use	Industry (μg cm^{-1} $year^{-1}$) loss from painted hulls of average length	Corrected for 270 days in water	×	Literature on boat ownership per capita
Aquaculture	E-PRTR (2017) (kg $year^{-1}$) + SEPA and Norway			

Abbreviations: EMEP, European Monitoring and Evaluation Programme; E-PRTR, Eurostat/European Pollutant Release and Transfer Register; EU MS, European Union Member States; FOREGS, Forum of European Geological Surveys; FYM, farmyard manure; SEPA, Scottish Environment Protection Agency.

washing, garden watering, and so forth (Eurostat, 2021). This formed the basis of an AR, which could be multiplied by an EF associated with the specific sources. We identified plumbing, mains supply, urine, and feces as relevant domestic sources of copper to STP.

Plumbing is an important source of copper, particularly in countries where it is the predominant material used in sanitary, hot and cold water systems. The quantity of copper leached is a product of the quantity used, its age, water temperature, and pH and hardness and/or alkalinity (NDWAC, 2015). Hard water can be more aggressive to copper plumbing than softer water (Comber et al., 2011). However, the release will also be controlled by pH if the mains supply is not circumneutral. Hot water copper concentrations were available for different house ages (Comber & Gunn, 1996), and so an average concentration could be derived based on the age of the UK housing stock (Supporting Information: Table S1). Furthermore, a correlation could be generated between copper plumbing concentrations and water hardness for mains supply. This relationship could then be used to adjust hot and cold water plumbing concentrations for any given European country based on the country's average hardness (Supporting Information: Table S2) and proportion of each type of water used within domestic households (Supporting Information: Table S3). These loads could then be adjusted for proportions of copper present in plumbing for any given country (Supporting Information: Table S4).

To quantify the contribution of copper from the mains supply water, volumes of water used within households were multiplied by the mean copper concentration in the cold mains supply reported for 29 countries for fully flushed mains supply water (Flem et al., 2015; Supporting Information: Table S5). This generates copper loads to sewers from mains supply, which is considered a background load. Feces and urine copper loads were based on reported per capita values (Supporting Information: Table S6). Copper is also present in dirt particles, absorbed to skin and an impurity in some domestic and personal care products. The albeit very limited data for copper additions to wastewater from dishwashing, clothes washing, and bathing activity-related copper sources (Comber & Gunn, 1996) were multiplied by the volumes of water used to generate a daily activity per capita load (Supporting Information: Table S7). These were combined with plumbing inputs to derive a load for domestic water use. Country-specific loads for domestic sources were therefore calculated by summing the loads from the domestic water supply, water use, feces, and urine (Supporting Information: Table S7), which could be compared with loads generated by multiplying reported domestic wastewater copper concentrations (Supporting Information: Table S6) by total domestic wastewater volume reported via Eurostat (2021) for each European country.

Industrial sources to STPs. Industrial sources of copper to STPs were obtained from the E-PRTR (European Environment Agency [EEA], 2020) using the most recent (2017) datasets for STPs (with a design flow greater than 10 000 $m^3 \, day^{-1}$). However, only emissions greater than 50 kg $year^{-1}$ must be reported (EC, 2006), which may lead to an underestimate of loads from this source, although they may also be captured under the services sector (as detailed below).

Services discharge to STPs. A significant volume of wastewater is generated from "services" associated with urban activities typically found in industrial estates and town centers, where water is used mainly for similar purposes to households (EC, 2006). Wastewater volumes from service industries available for European countries (Eurostat, 2021) were multiplied by concentrations reported from two UK studies (Comber et al., 2014; Rule et al., 2006; Supporting Information: Table S8). A derived mean concentration for total copper (67.3 $\mu g \, L^{-1}$) was multiplied by the volume of wastewater generated from services in each country to derive a load.

Storm event runoff to STPs and surface water. There are no estimates of surface water flows provided by Eurostat databases. Consequently, the following approach was adopted (Comber et al., 2013):

$$\begin{aligned}\text{Volume of runoff to STP} = {} & \text{mean rainfall} \times \text{urban area} \\ & \times \%\ \text{impermeable urban area} \\ & \times \%\ \text{runoff to sewer}\end{aligned}$$

Mean annual rainfall data are easily accessible from the EEA on a per-country basis (2019 data). Urban settlement areas per country are also available from Eurostat (2015). A default value for impermeable urban areas of 22% was used for this apportionment based on UK data (Comber et al., 2013). The percentage of runoff entering the combined sewer system has been estimated at 50% for the UK and was used as a default where no other data were available. Some literature data were available for Denmark, Finland, Norway, and Sweden, where combined sewers are less prevalent (Sola et al., 2018).

Loads for urban runoff to STP were derived using two methods: (1) using a mean of reported urban runoff copper concentrations multiplied by a total volume of surface water flow entering STPs as described above, and (2) using a more detailed breakdown of loads contributing to urban runoff. The following relevant sources of copper to runoff were identified: architecture contributions, atmospheric deposition, rail transport (overhead power lines), road, tire and brake wear, exhaust emissions, and oil loss (Figure 1). A detailed explanation of the methodology and results is provided in Supporting Information: S2.1.

For Europe, databases are available providing country-by-country data for total number of kilometers of roads broken down into type of road as defined by the EU: motorway (primary roads), state (maintained by the state), provincial (maintained by regional authorities), and communal (local roads maintained by local authorities) roads. Furthermore,

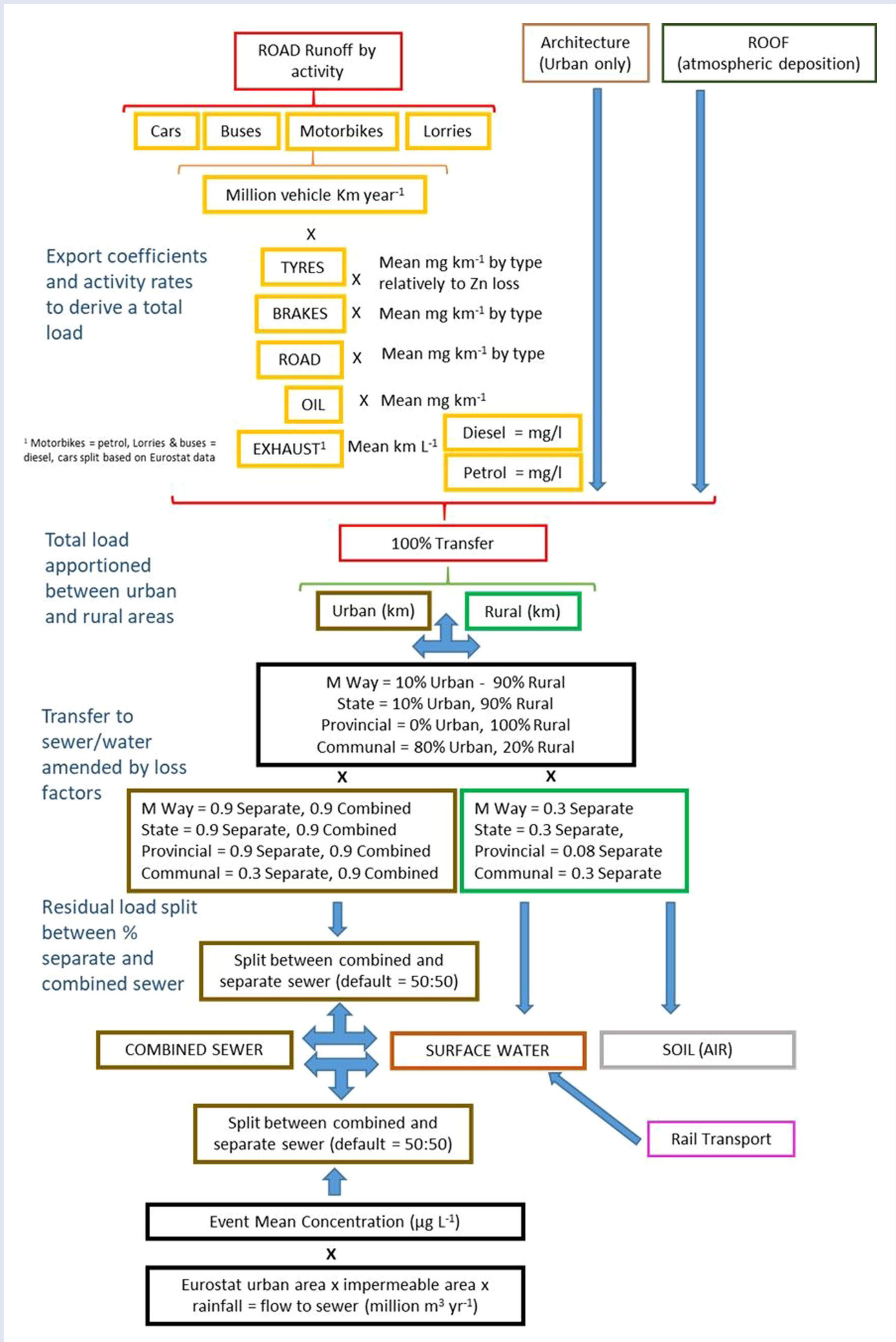

FIGURE 1 Schematic for calculating urban runoff loads

distance data reported as million vehicle kilometers are also broken down into vehicle type (cars, motorcycles, commercial vehicles, and buses) as well as a split between length of roads within and outside built-up areas. This therefore provided the opportunity to split urban and highway runoff loads of copper for vehicular traffic (Eurostat, 2020a, 2020b, 2020c). To generate a load, these values must be multiplied by an EF. Reported data for mg vehicle km^{-1} loss of metal for road, tire, and brake abrasion multiplied by the km driven by vehicle type per country were considered the most reliable method and adopted here (ESI S2.2; Figure 2). Literature data for copper content in brake pads (Supporting Information: Tables S9 and S10), tires (Supporting Information: Table S11), road surfaces (Supporting Information: Table S12), and fuel and oils (Supporting Information: Tables S13 and S14) were multiplied by vehicle km $year^{-1}$ to derive loads.

Significant amounts of copper and copper alloys are used in roofs, facades, gutters, and downpipes, particularly in countries such as Germany, Switzerland, Italy, and Austria. Market data (ECI, 2020) for these uses suggest an annual European market of approximately 60 000 t of copper in 1980, increasing to 200 000 t in 2000, and thereafter decreasing to 40 000 t currently (Supporting Information: Table S15). Assuming a linear relationship over time, a total stock for the EU27 can be estimated as 5.86 million t. Furthermore, a breakdown in use across Europe was provided for 2002 (Supporting Information: Table S16; ECI, 2020). Utilizing average thickness and density, a surface area can be derived that can be converted into a load using reported release rates that consider roof pitch, rainwater pH, and SOx concentration (Hedberg et al., 2014). Architectural copper was assumed to be used only within the urban environment and that there was no retention before entering the sewer system (Figure 1). Although a detailed analysis would be of great interest for local situations, for example, countries or regions with significant architectural copper use, it is beyond the scope of this pan-EU study.

To quantify the loadings from atmospheric deposition, 16 European countries reported copper concentrations in rainfall under the EMEP Co-operative Programme for Monitoring and Evaluation of the Long-range Transmission of Air Pollutants in Europe (Aas & Bohlin-Nizzetto, 2017; Supporting Information: Table S17). Observed rainfall concentrations integrate all emissions of copper to air, natural and anthropogenic. A load per country could therefore be derived based on annual rainfall multiplied by copper concentration in deposition multiplied by road length multiplied by standard widths for the four types of roads.

Transfer from surface water runoff to the aquatic environment

Using an event mean concentration, it is simple to derive a load to sewers based on flow estimates split between combined and separate sewer systems. For emissions based on road and vehicle type, however, a further split of the apportioned loads is required because not all of a country's road system lies in urban environments, and vehicles do not

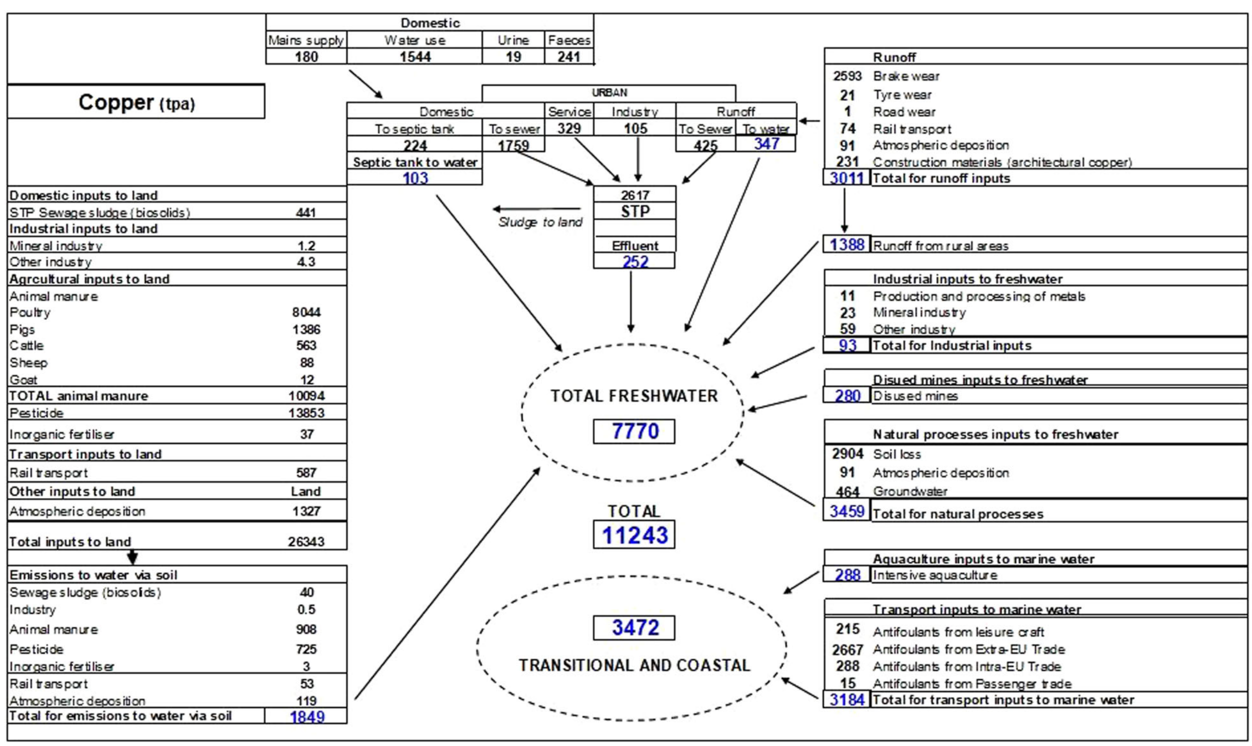

FIGURE 2 Schematic of copper loads to surface waters of the EU27

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drive solely in urban environments (Figure 1). Furthermore, in many urban settings, depending on road type, runoff may pass through sustainable urban drainage systems (SuDs) before entering surface waters. These systems are associated predominantly with suburban and highway runoff, where space is available to construct them in new developments. A literature review indicated an average of 70% Cu removal in SuDS (Supporting Information: Table S18), which was used to amend the loads of copper entering the aquatic environment via runoff. Copper runoff loads were multiplied by the transmission factor based on road type within urban and rural settings, as well as an assumed proportion of road length by type within urban and rural areas (Figure 2; Supporting Information: Tables S19 and S20).

Sewage treatment plant influent

Influent STP loads could be calculated by summing the loads from domestic, industry, services, and runoff as calculated above. An alternative was to multiply the Eurostat flows to STP for each country by a mean reported copper STP influent concentration (52.8 μg L^{-1}; Supporting Information: Table S21) based on 10 reports from across Europe and the world. It was then possible to compare the outputs from each calculation method.

Sewage treatment plant effluents

Sewage treatment plant effluent loads were derived either by taking measured or summed influent loads and subtracting loads of copper removed via removal efficiencies at each stage of the possible treatment process, that is, primary, secondary, and tertiary treatment (41%, 73%, and 82%, respectively; Supporting Information: Table S21), based on available treatment technology data reported by countries under the Urban Wastewater Treatment Directive (EEA, 2017). Removal rate data were predominantly for secondary treatment and so could have introduced a bias into the calculated STP discharged loads. Effluent loads were also calculated by simply multiplying reported effluent copper concentrations by the available flow of wastewater from member state STPs (EEA, 2017).

Rail transport

Electrified rail systems produce friction and spark erosion of the current collectors (pantographs) and the overhead contact lines, which results in emissions of copper from trains, trams, and metros. Emission data from rail traffic is reported in the Dutch and Norwegian national registries (Norwegian Environment Agency, 2020; RIVM, 2020). Data are reported for both soil and direct to surface water for the Dutch data and only for soil for the Norwegian data. The Dutch reported values expressed in grams of emission per unit of energy consumption (RIVM, 2016). The average emission direct to water was 1087 kg $year^{-1}$ in the Netherlands between 2015 and 2017, and 1000 to approximately 1700 kg $year^{-1}$ to soil for Norway and the Netherlands, respectively. To extrapolate this on a European scale, the average copper emission per kilometer of rail for Norway and Netherlands was applied to all other European countries with rail networks. Although data for only two countries are being used to extrapolate to the EU, wear of overhead rail lines would be expected to be relatively constant for all electrified rail systems, wherever they are.

Industrial inputs direct to water

Production and processing of metals. The industrial inputs category covers two major industrial sectors included in the E-PRTR: production and processing of metals (e.g., metal smelting, refining, and fabrication) and the mineral industry (e.g., mining and quarrying). Other industries are grouped in a third sector known as "other industries." Annual loads extracted from the E-PRTR on a three-year average were used within this apportionment exercise, supplemented with information reported in the national registers of the Netherlands (RIVM, 2020), Scotland (Scottish Environment Protection Agency [SEPA], 2020), Spain (Ministerio para la Transición Ecológica y el Reto Demográfico, 2020), and Sweden (Swedish Environmental Protection Agency, 2020), which was preferentially used where available, particularly where lower reporting thresholds are applied.

Mineral industry

The emissions from this sector include several (sub-) activities as detailed in Supporting Information: Table S22 averaged over three years. The Swedish Register (Swedish Environmental Protection Agency, 2020) provided supplemental data with a lower reporting threshold (20 kg $year^{-1}$ to water reporting threshold) leading to loads of 67 kg $year^{-1}$, compared with 71 kg $year^{-1}$ from the national register (2017–2019). Read-across of these data to other countries, where data do not exist, was not used to complete data gaps, because the sites were typically large and would therefore have reported to the E-PRTR if they existed for other countries.

Other industries

"Other industries" encompassed a large range of chemicals (EEA, 2020) including energy, chemicals, paper, and animal production, all reported and abstracted from the E-PRTR. Data were further supplemented with national pollutant registers for Netherlands, Scotland, Spain, and Norway, which often reported lower threshold loads, thus providing more complete estimates of load. Where relevant, data gaps were filled using average EFs multiplied by relevant activity rates.

Disused mine inputs

Metal inputs from abandoned mines are likely to be a significant source of copper for countries historically rich in copper-bearing mineralogy; these include Scandinavia, Spain, France, and the Alpine regions (Comber & Casse, 2008). Although loads from working mines are reported via the E-PRTR, loads from disused and/or abandoned mines go largely unrecorded, and these legacy sources are left largely to the regulatory authorities to address, both from point source drainage and diffuse sources from old spoil heaps, ancient smelting, and processing works. Data from only two sources were available, reporting loads from abandoned mines in the UK and Germany (Environment Agency, 2008; Fuchs et al., 2010). Data were estimated only from point source drainage pipe discharges rather than wider leaching from old workings, contaminated land, and so forth, and so these values are likely to be an underestimate by at least a factor of 2 (Turner, 2011). United Kingdom and German data reported loads to water of 107 and 38 kg day^{-1}, respectively. When considering read-across, the likelihood of copper mining having previously occurred will be a function of the underlying geology. The presence of current mining activity would also potentially suggest the locations of historical mining. Maps of likely mineralization are available (EGDI, 2020; Supporting Information: Figure S2). Consequently, areas of likely mineralization were estimated for each country as a percentage and converted to an area based on the total area of the country (km^2). Accordingly, for the UK and Germany, a kg day^{-1} km^{-2} can be calculated by dividing the reported load to water by the mineralization area, which was then applied to all other countries with mineralized areas (Supporting Information: Table S23). The assumption that copper mining is a function of the underlying geology may not hold in some more sparsely populated countries. For example, Finland has a larger area of likely copper mineralization than Germany, but it has only approximately 32 abandoned mines (SYKE, 2018), compared with more than 100 in Germany (Fuchs et al., 2010). Therefore, the copper emissions from abandoned mines, which we derived for sparsely populated countries, may be overestimated. Overall, there is considerable uncertainty associated with these values; therefore, they can only be considered as a first estimate-load to water to compare with other loads.

Natural processes

Soil loss. Copper is a naturally occurring element in soil, and background concentration data for individual countries are available (FOREGS, 2020), with mean reported levels (for 2–117 sites within each country) provided in Supporting Information: Table S24. Soil loss data are also available (Eurostat, 2016), including total soil loss data selected for agricultural and forestry areas (t ha^{-1} $year^{-1}$). Runoff from storm events therefore carries mineralogical copper found in the soil into adjacent water courses. Background copper losses via soil erosion entering water can therefore be calculated by multiplying the soil loss by the background copper concentration. However, not all soil lost from land will enter rivers; roads, verges, and ditches will intercept a significant proportion. Borrelli et al. (2018) estimated soil transfer from land to water for individual European countries, calculating a mean loss of 15% (ranging from 4.1% for the Netherlands to 23% for Italy). By multiplying the soil loss copper load by this percentage, a load to water can be generated (Supporting Information: Table S25).

Atmospheric deposition

Copper enters the atmosphere via sources including road and rail transport emissions, industry, as well as natural sources such as volcanism and wildfires. Atmospheric deposition can therefore include both wet (dissolved metal) and dry (particulate metal) deposition, which are integrated based on measurement of copper in rainwater. As described above (Aas & Bohlin-Nizzetto, 2017) rainfall copper concentrations are available for individual European countries. Given that agricultural area data are also available (Eurostat, 2017), atmospheric deposition of copper to soil was derived by the concentration for each country by the annual rainfall by the total agricultural area (Supporting Information: Table S26).

Groundwater contribution

On a European scale, groundwater contributions are difficult to calculate due to wide variations in geology both between and within countries. The average groundwater concentration of copper in the EU can be estimated to be 1.3 μg L^{-1}, according to the data presented in Geochemistry of European Bottled Water (Reimann & Birke, 2010). Annually, 811 km^3 of groundwater flows into rivers in continental Europe (Chernogaeva, 1970). However, the surface area of the EU is only 44% of Europe; therefore, based on this, the estimate can be corrected to 357 km^3 $year^{-1}$ (or 357×10^{12} L $year^{-1}$) for the EU. By combining these two estimates, a copper load of 464 t $year^{-1}$ from groundwater for the EU can be calculated. Although this is a simplistic assumption and does not apportion loads by EU country, it provides an indication of scale of emission, which may be either considered insignificant or worthy of further research to reduce uncertainty, which is an objective of such a source apportionment exercise.

Aquaculture inputs to marine waters (mariculture)

Sources of copper within aquaculture are derived from use as a biocide via impregnation of nets or painting of cages to prevent fouling, use in feed additives for treating disease and parasites, as well as controlling blue-green algae. Data on the use of copper in intensive aquaculture are available from numerous sources. The most recent data from the E-PRTR (EEA, 2020) were sourced (data for only Malta, Norway, and the UK are reported in the E-PRTR). Further data were also identified for Norway (Norwegian Environment Agency, 2020) and Scotland (SEPA, 2020), which report average emissions of 706 667 and 64 148 kg $year^{-1}$. These additional data were deemed to be more representative of the sectors in these countries due to the lower reporting thresholds in these registries. Fish farming is not exclusive to these three countries in Europe; therefore, a read-across strategy was devised to fulfill the data gaps. Eurostat reports data for the total quantity of fish production, crustaceans, mollusks, and other aquatic organisms

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from aquaculture ("fish farming") in Europe (Eurostat, 2020a, 2020b, 2020c). Therefore, the average copper emission, in kg, for each ton of farmed fish (or other aquatic organisms) was calculated based on reported data, and this was used to estimate the Cu emission for each country.

Transport inputs to marine waters

Copper is a major constituent in antifoulant biocides used on marine vessels and structures (Boxall et al., 2000), with loads reported from a variety of maritime sources, Safinah (2010) reporting EU27 loads of copper for leisure, passenger, and intra-EU and extra-EU trade (Supporting Information: Table S27). Emissions from leisure vessels (assumed to be used in national waters) were broken down based on an estimated 622 000 leisure craft in the EU27 using antifoulants (Safinah, 2010), with application assumed to be annually. Using a release rate of $6\,\mu g\,cm^{-1}\,day^{-1}$ and assuming 270 days a year generates a load of $262\,t\,year^{-1}$ (Safinah, 2010). This total load was apportioned based on data for the number of leisure craft within European countries (Supporting Information: Table S28), with data gaps filled by using average boat per capita data. For commercial vessels, data are available for the percentage of national, intra-EU, extra-EU, and "unknown" for several EU27 countries with significant ports. This percentage was converted into tons via direct calculation, with "unknown" percentages, where reported, split between intra-EU and extra-EU and passengers based on their relative proportions. The total copper leached was then attributed to the different categories per country ("passenger" vessels were assumed to be national tonnage). No estimates could be generated for antifoulant use on maritime structures owing to a lack of data.

INDIRECT INPUTS OF COPPER TO WATERS

This section discusses copper inputs to soil, as well as the subsequent transfer from the soil to the freshwater compartment.

Industrial inputs to land

The industrial inputs to land cover emissions from three main activities, application of sewage sludge to land, the mineral industry, and other industries. The emissions detailed here are the emissions to land from each activity, which can enter the aquatic environment indirectly.

Copper in sewage sludge

Sewage sludge is recycled to land in several European countries at varying rates (~80% of all sludge produced for the UK to zero for the Netherlands) under the control of the EU Sewage Sludge Directive (EC, 1986), meaning concentration data and volumes returned to land are reported, which can be multiplied together to generate a load. Where copper concentrations were not reported but the load of sludge concentrations were, the mean copper concentration was applied to derive a load (Supporting Information: Table S29).

Mineral industry and other industries

The activities covered by these industries correspond to the same activities of the direct emissions for these sector names. The data were collected from the same sources and treated following the same methodology as detailed above for the mineral industry and other industries.

Agricultural inputs to land

Plant protection product use. Data have been supplied by ECI on the use of copper-based plant protection products (pesticides) for several countries for 2018 (Supporting Information: Table S30; ECI, 2020). To fill in the gaps, arable hectares for 2018 including vineyards, fruit, potatoes, and cereals were extracted (Eurostat, 2018) for all EU27 countries, and the "Rest of Europe" fungicide copper load was apportioned according to the ratio of crop use type for the individual country (ha) to the total for Europe.

Copper in NPK inorganic fertilizer

Unlike nitrate fertilizers, mineral phosphate fertilizers contain relevant copper impurities. Two thorough studies (Azzi et al., 2016) report data for copper in a variety of inorganic fertilizers, giving a mean of $33\,mg\,Cu\,kg^{-1}$ for 233 fertilizers. This concentration was simply multiplied by Eurostat data for European country phosphate fertilizer use (Eurostat, 2020a) to generate a load.

Copper in farmyard manure

It has been reported that 90% of all animal manure is used as a fertilizer (Koninger et al., 2021). Data were first collected on the concentration of copper in farmyard manure (FYM; Supporting Information: Table S31). Combining this concentration with the average manure production per day (Lorimer et al., 2004) made it possible to calculate the mean amount of copper excreted per head of each category of animal. Eurostat databases (Eurostat, 2018) provided data of heads of farm animals per country and the number slaughtered per year for poultry. Poultry slaughtered per country were divided by their mean weight (2.5 kg) to generate a total number of birds. After these data were collated, it was a simple matter of multiplying the amount of copper excreted per day by the number of animals to derive a load, all of which is assumed to be returned to agricultural land (Supporting Information: Table S32).

Atmospheric deposition of copper onto agricultural soil

Rainfall copper data are provided in Supporting Information: Table S36 (Aas & Bohlin-Nizzetto, 2017) as used for direct atmospheric loads to water and deposition onto urban areas. Atmospheric deposition of copper to soil was determined by multiplying this concentration for each country by the annual rainfall by the total agricultural area available via the Eurostat databases (Eurostat, 2020a; Supporting Information: Table S33).

Transport inputs to land

As with direct emission to water from rail transport, emission data to soil is reported in the Dutch and Norwegian national registries (Norwegian Environment Agency, 2020; RIVM, 2020), reporting loads based on electricity consumption multiplied by an EF expressed in grams of emission per unit of energy consumption (RIVM, 2016). The average emission to soil was estimated to be 1000 and 1700 kg $year^{-1}$ for Norway and the Netherlands, respectively. This emission rate was applied on a pro rata basis to all the other countries in Europe with known rail networks.

Loads that have not been considered

Owing to a lack of available data, copper loads from any feed additives have not been considered but will be included in the reported data for animal FYM. In rare cases, copper can be sprayed onto land as fertilizer, to supplement natural areas where the soil is deficient in this essential nutrient. The lack of data for location, frequency, and application rates made it impossible to derive a load.

Total loads of copper lost from agricultural soils to water

A proportion of copper entering agricultural soil will leach into groundwater, be taken up by crops, or will be bound to particulates and enter the mineral phases. Sadovnikova et al. (1998) reported a mean of 9% loss to water (median = 10.8%, $n = 13$, 95% confidence interval = 2.95%) for a variety of soil types. Monteiro et al. (2010) reported an average 6.2% loss to water (median = 4.67%, $n = 10$, confidence interval = 3.1%) for a similar range of soil types. A mean of all data provides a leaching percentage of 9% per year (median = 8.8%, $n = 23$, 95% confidence interval = 2.3%), which was applied to the calculated loads of copper to soil for all sources except vineyards. This approach may overestimate the transfer from soil to water, as it does not consider for example retention of copper in soils caused by aging reactions (Ma et al., 2006; Smolders et al., 2012). More detailed information was available for vineyards and was used for such soils: the estimated copper lost from vineyards is 1% (Babcsányi et al., 2016) and 1.16% (Droz et al., 2021); therefore, a mean of 1.078% loss was applied to the export of copper from vineyard soil to water.

RESULTS AND DISCUSSION

The above methodology was applied to calculate loads of copper to water based on EU27 emissions (Figure 2).

None of the information sources that were consulted report any copper emissions from several of its most important uses in terms of tonnage, for example, electric networks and power distribution, charging infrastructure, sustainable energy sources such as wind and solar, industrial equipment, and so forth. This resonates with common sense: copper in such uses is not allowed to come into contact with water owing to the risk of short-circuiting, and therefore has no exposure to the environment during its use. Therefore, copper emissions from these sources are likely negligible, owing to a lack of a significant environmental pathway, and they have not been included further in this source apportionment.

It is estimated that approximately 8000 t of copper per annum (tpa) enter the freshwaters of the EU27 countries. Freshwater sources are dominated by natural processes (3459 tpa), mainly loss of mineral copper from soil erosion, a known issue (Panagos & Katsoyiannis, 2019). The other two major sources are leaching of anthropogenic copper inputs from agricultural soil (1848 tpa) and surface water runoff direct to water (1388 tpa). These three sources contribute 86% of the total load (Figure 3). Direct inputs of copper into transitional and coastal waters amount to approximately half the freshwater loads (3849 tpa), mostly from leaching of copper from antifoulant paints, bringing the total load of copper entering EU27 surface waters to 11 620 tpa (Figure 3). Estuaries often act as a sink for sediment-associated elements, and so not all freshwater copper loads would be expected to be transported to the marine environment. It was not possible as part of this exercise to estimate these types of fluxes.

The significant sources of copper making up these loads to all waters are poultry manures (8044 tpa) and plant protection products (13 853 tpa) to agricultural land, brake wear (2593 tpa) in surface water runoff, copper associated with soil loss for agricultural and forestry land (2904 tpa), and antifoulants leaching from large commercial extra-EU trade into saline waters (2667 tpa). Copper associated with wastewater (septic tanks and STP effluent) amount to 355 tpa and reflects improving wastewater treatment and effluent quality as well as diminishing heavy industry in Europe (Marcal et al., 2021).

The copper source apportionment at the country level is shown in Supporting Information: Table S34. The copper loads per country, on a per capita basis, reveal there is significant variation between countries in terms of total loads from 11 g Cu $capita^{-1}$ $year^{-1}$ for Luxembourg to 71 g Cu $capita^{-1}$ $year^{-1}$ for Estonia, but also the split between freshwater and saline water loads (Figure 4). Estonia, for example (and Latvia to a lesser degree), has a high per capita copper emission, dominated by saline copper loads, owing to its Baltic ports. Overall, saline discharges of copper per capita dominate freshwater ones for Belgium, Denmark, Estonia, Finland, Latvia, Lithuania, Malta, the Netherlands, and Sweden, all countries with significant port and seaborne trade.

The copper loads to freshwater range approximately 3.5-fold between countries (between approximately 9 and 33 g Cu $capita^{-1}$ $year^{-1}$). However, there are significant variations in the copper "fingerprints" of different countries' emissions to freshwaters (Supporting Information: Figure S3). For example, soil loss copper loads are particularly significant for Italy and Greece, owing to a combination of greater geogenic background levels and elevated soil loss per hectare, whereas high values for Romania, Slovakia, and Slovenia are more associated with larger soil erosion rates. Transport dominates loads of copper to water in France, Germany, and the Netherlands, associated with the existence of extensive road networks and large urban conurbations with high traffic density. Agricultural losses of copper to water are significant for Italy (plant protection products), Poland and Belgium (poultry

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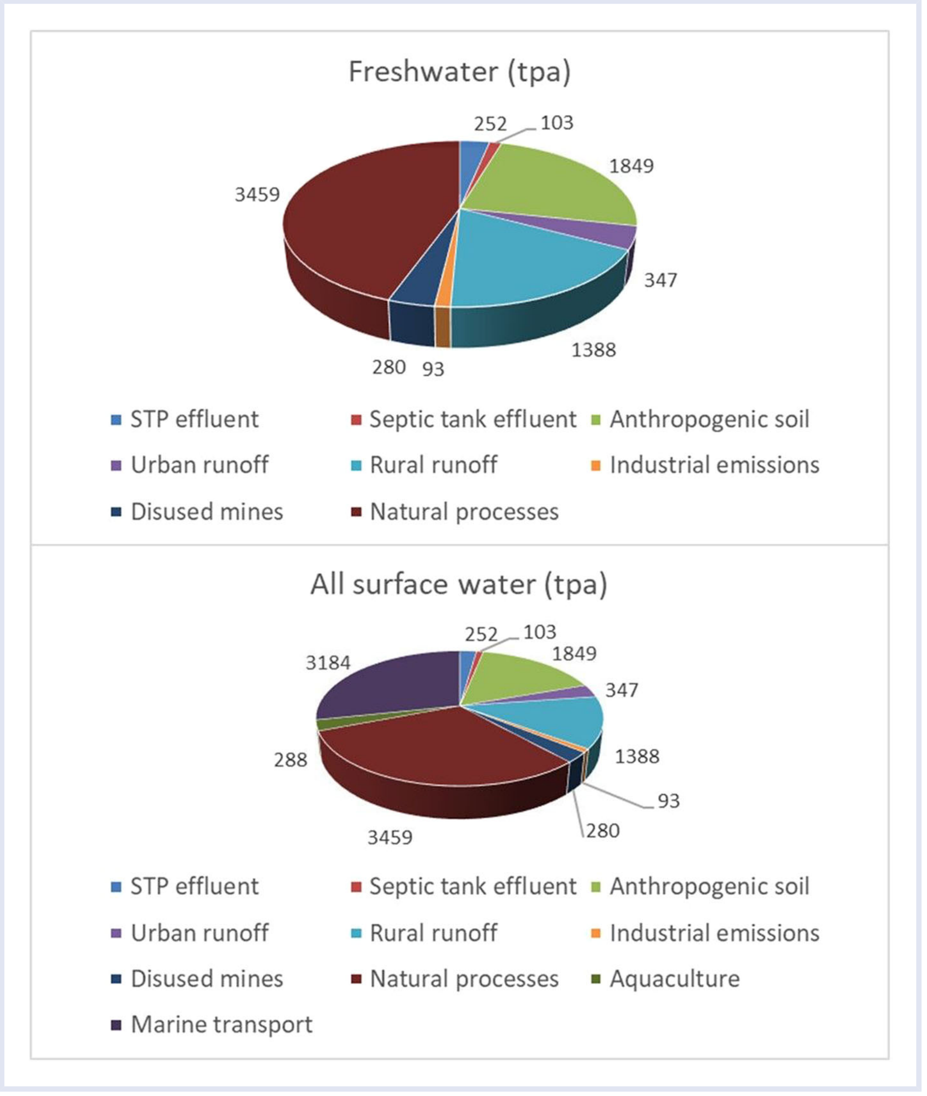

FIGURE 3 Pie charts for total copper loads (tpa) to freshwater and all surface waters of the EU27

manure), and Portugal and Hungary (poultry manure and plant protection products). Italy, France, and Spain account overall for 74% of all plant protection products emitted to surface waters of the EU27, predominantly from viniculture. Abandoned copper mine data are limited, and therefore the conclusions are highly uncertain, but may be significant in Scandinavia, and countries such as Estonia, Czech Republic, Bulgaria, and Cyprus, the latter well known for its current and historical copper mining history (Onuaguluchi & Eren, 2016). Further data are clearly required to better estimate loads. Industrial discharges and wastewater-associated copper emissions are a relatively small and consistent contribution across all member states.

The purpose of this article was to apportion the sources of copper across a large and geographically diverse area, the EU27. It must be emphasized that the assessments at country level have consequently inherited significant uncertainty.

Uncertainties in the datasets were considered as part of the source apportionment exercise. Sufficient data were available to calculate standard deviations for:

(1) copper in brake linings;
(2) anthropogenic copper emissions from variability of predicted copper loss by soil type;
(3) copper loss from soil erosion based on variations in copper in background soils;
(4) concentrations of copper in domestic wastewater;
(5) reported copper levels in STP influent and effluent;
(6) abandoned mining load from variability in UK and German data;
(7) architectural leaching into runoff.

The last five sources were all a single value as the means were applied to all countries (Supporting Information: Table S35). There is significant variation in estimates based on the uncertainty in reported values, linked to naturally occurring environmental conditions. Overall, the relative standard deviation (%) was relatively consistent, with only soil erosion varying more than 100% owing to the widely fluctuating background concentrations in countries such as Ireland, Italy, and Spain, reflecting their complex geology (Ballabio

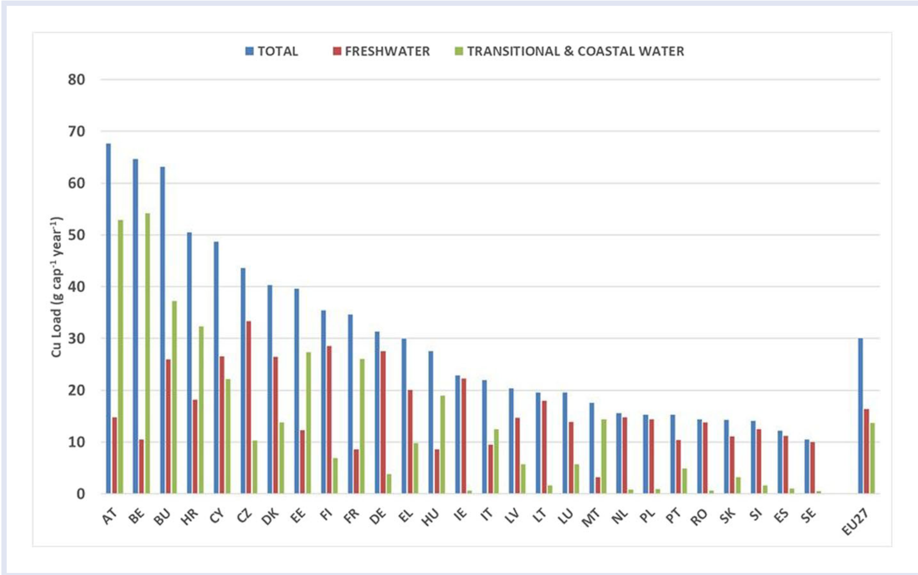

FIGURE 4 Copper loads to surface waters by country (tons copper per annum); AT, Austria; BE, Belgium; BU, Bulgaria; CY, Cyprus; CZ, Czech Republic; DE, Germany; DK, Denmark; EE, Estonia; EL, Greece; ES, Spain; FI, Finland; FR, France; HR, Croatia; HU, Hungary; IE, Ireland; IT, Italy; LT, Lithuania; LU, Luxembourg; LV, Latvia; MT, Malta; NL, the Netherlands; PL, Poland; PT, Portugal; RO, Romania; SE, Sweden; SI, Slovenia; SK, Slovakia; and mean of all EU27

et al., 2019). The assessment suggests that no single source is likely to be more uncertain than any other, although with only two datapoints available for copper loss from abandoned mines, the overall uncertainty is high, although the values for the UK and Germany were relatively consistent.

However, accepting the obvious and expected uncertainty relating to the estimates, for several sources it was possible to generate load estimates by two methodologies, thereby providing a degree of validation. This was undertaken for summed loads in STP influent and effluent by performing a comparison between calculated loads and literature data (Figure 5A,C,D; Van den Roovaart et al., 2013); summed domestic loads of copper to STP compared with those based on measured concentrations multiplied by volumes of wastewater entering STPs (Figure 5B); and runoff loads calculated via event mean concentrations compared with summed loads and volumes of wastewater entering STPs based on calculations generated from this research versus those reported by Eurostat (2021; Figure 5E and F).

As can be seen, near 1:1 relationships are obtained for flows to STPs (Figure 5F), which is crucial in terms of being able to generate consistent and accurate loads when multiplied by concentration data. Good agreement was also obtained for domestic sources (Figure 5B), STP influent (Figure 5A), and effluent (Figure 5C), also with good agreement with a previous source apportionment exercise for STP effluent emissions of copper undertaken by Deltares (Figure 5D; Van den Roovaart et al., 2013). Comparing runoff data revealed a bias toward higher loads generated via observed event mean concentrations (EMC) of copper multiplied by the flows. This is likely to reflect the large number of assumptions and uncertainties associated with estimating loads from several individual surface runoff sources. The key factor is that no allowance for retention of copper SuDs was made using the EMC × flow method, whereas between 10% and 92% retention was assumed using the more detailed methodology (Figure 1).

The final quality assurance exercise was to perform a simple mass balance exercise. Data are available for "internal flow," which is the total volume of river runoff and groundwater generated in natural conditions exclusively by precipitation within the country (Eurostat, 2021). By dividing the total freshwater annual total copper loads from this study by the available water volumes, a simple predicted environmental concentration (PEC) for total copper concentrations can be derived for each country. There are few total copper concentration data reported for European countries because environmental quality standards are based on dissolved concentrations. Consequently, there are dissolved copper concentrations in water that are available, and these data were obtained for 2018 to 2020 from the environmental agency databases of individual countries (more than 103 164 datapoints across 19 EU27 countries) and defined as the measured environmental concentration (MEC). A median was used owing to some very high values biasing the mean and compared with the PECs (Figure 6). The standard deviation for the MEC (often large) of six countries bisected the 1:1 line. For seven countries, the PEC (dissolved) versus MEC (total) was within a factor of 3, a further three were within a factor of 5, and only two countries were more than an order of magnitude different (both 12 times). Spain and Italy had the greatest variance. The MEC was particularly sensitive for Spain owing to mining influences distorting the distribution of concentrations. The fact that the loads of most countries could be translated into water concentrations of the same order of magnitude as those measured suggested that the predicted loads were a reasonable approximation of the reality.

This is a very simple analysis, which does not consider the complex processes that govern the fate of copper after it

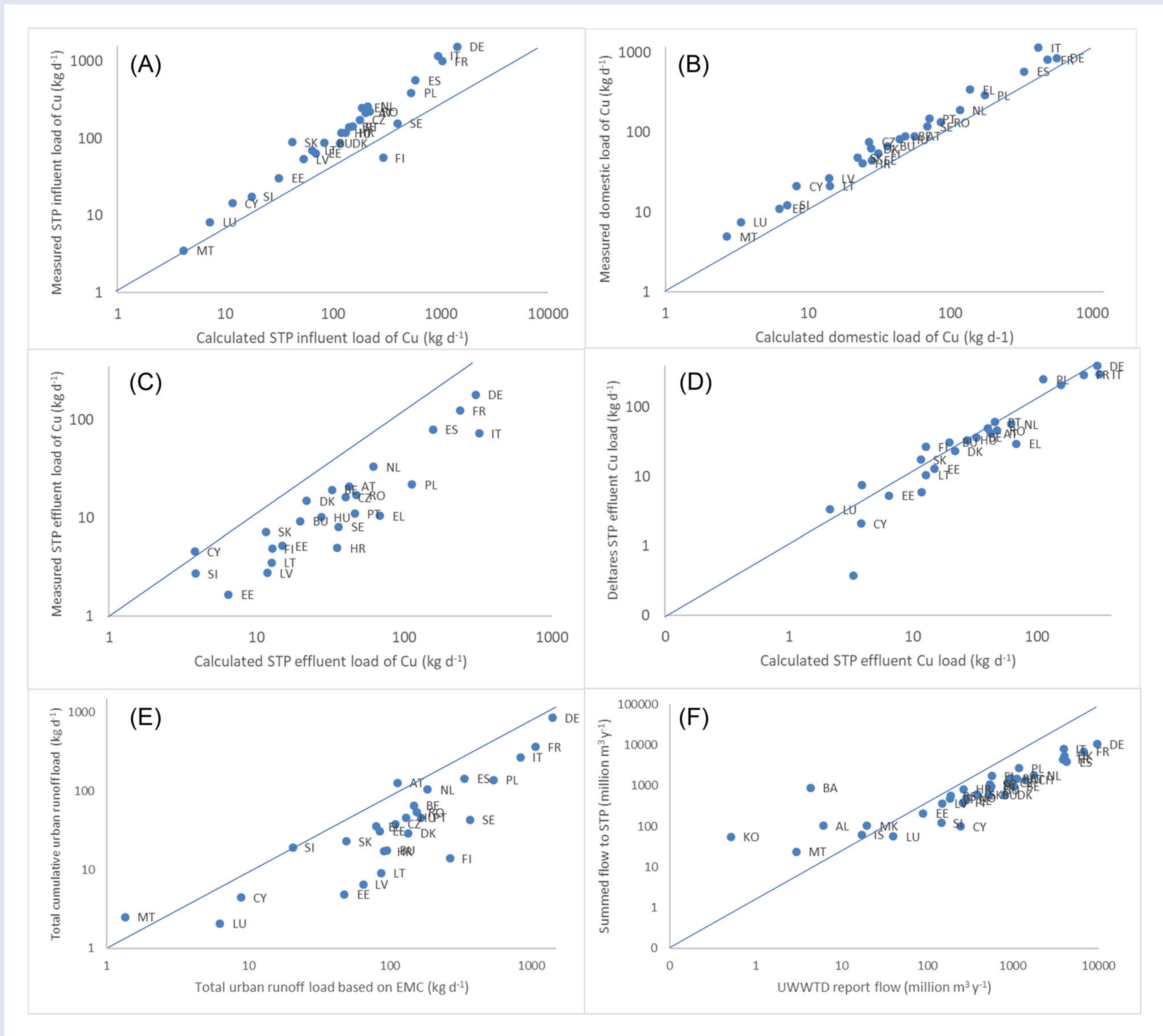

FIGURE 5 Comparison between (A) calculated and measured sewage treatment plant (STP) influent loads; (B) calculated and measured domestic wastewater loads; (C) calculated and measured effluent loads; (D) calculated and reported effluent loads by Deltares (Van den Roovaart et al., 2013), (E) Total urban load based on event mean concentrations versus total cumulative loads from brake, road and tire abrasion, fuel and exhaust emissions, architecture emissions, and atmospheric runoff; and (F) volume of Urban Wastewater Treatment Directive (UWWTD) effluent loads (Eurostat, 2021) versus summed flows from this research

has entered the aquatic environment, for example, complexation, particle binding, settling, resuspension, mineralization, and dissolution (Cervi et al., 2021; Rader et al., 2019). Dissolved copper concentrations reported for the MEC will also obviously be of lower concentrations than the total for the PEC. It is therefore not surprising that the MEC versus PEC does not fully align.

Further validation of the predicted loads was done by comparing loads generated in this study with previously reported data. However, there are few studies with which to compare the outputs from this study because loads vary over time. Further validation of the predicted loads was achieved by comparison with previously reported data. However, data were limited and predictions used in other studies were either carried out some time ago, and/or used significantly differing methodologies. The comparison of STP discharges between this study and one performed by Van den Roovaart et al. (2013) as part of a Deltares study is compares favourably (Figure 5D), although the latter study used data more than a decade old. Data are available for three studies regarding loads of copper to agricultural soils, but the Netherlands study was reported in 2003 (Delahaye et al., 2003). A more recent French study (ADEME, 2007) revealed reasonable agreement for total atmospheric deposition between it and this study (250 vs. 266 tpa copper, respectively), NPK Cu inputs (5.5 tpa for this study vs. 9.9 tpa for the French study), and pesticides (1735 tpa for this study vs. 1701 tpa copper for the French study).

Examining older data, the voluntary copper risk assessment report (vRAR, 2008) carried out a detailed assessment of

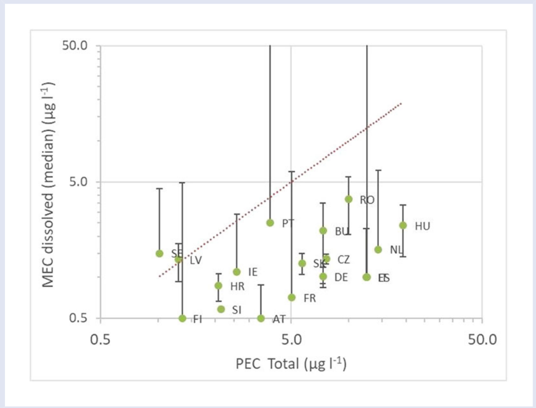

FIGURE 6 Comparison of predicted environmental concentrations (PEC) for total concentration of copper in water versus measured environmental concentrations (MEC) for dissolved copper water concentrations for country-specific rivers (error bars on the MECs are standard deviation)

copper loads entering the European environment (data typically from the early 2000s or earlier). For household copper emissions, 6.5 g capita^{-1} year^{-1} year was established, compared with a value of 8.0 g capita^{-1} year^{-1} for measured loads for this study. The contribution of plumbing based on 1993 data from the Netherlands estimated 52 t of copper to sewer, which compared favorably with 63 t estimated from this study. German estimates for domestic contribution were lower, but this likely reflects the lower rate of use of copper pipework within domestic households (UK = 66% of plumbing as Cu, Germany = 23%, and the Netherlands = 33%). For the Netherlands, the vRAR estimated 166 and 20 tpa (1999 data) entering and leaving STPs, respectively. This study estimated an influent load of 96 tpa for the Netherlands based on observed data and an effluent load of between 12 and 23 tpa depending on how it was calculated (measured or calculated), which is similar to the vRAR loads. Any variations are likely to reflect uncertainty and possibly a combination of increasing domestic and urban runoff loads versus decreasing industrial loads.

For 1999, animal manure to soils of the Netherlands was estimated as 700 t, mineral fertilizer 60 t, and wet and dry deposition 20 t. This study estimates 406, 0.2, and 24 tpa, respectively. The mean concentration of copper in mineral fertilizer used in this study was 33 mg kg^{-1}, in the same range as that reported in the vRAR (0.3–75 mg kg^{-1}). However, the amount of mineral NPK fertilizer used for the Netherlands in the vRAR was reported as 12 314 000 tpa, compared with 2018 Eurostat data of only 6012 tpa, which explains the variations observed, though the reason for the discrepancy is not clear. However, the load of copper from NPK fertilizer use was always smaller than with manures. A comparably greater source of uncertainty is the fact that no information was available to consider loads from the use of copper fertilizer.

The vRAR reports a total load to water from brake wear for the Netherlands of 27 kg day^{-1}, which is lower than this study (50 kg day^{-1}), which was equivalent to 256 t year^{-1} for the EU15 at the time of the vRAR, compared with 964 t year^{-1} for the equivalent EU15 for this study. These differences could reflect an increase in vehicles on the roads over the past two decades. For antifoulant emissions, the vRAR used a leaching rate of 50 µg cm^{-1} day^{-1}, significantly higher than the 6 µg cm^{-1} day^{-1} estimate used in this study (Safinah, 2010). Based on an assumption of 10% of antifoulant paints containing copper (2002 data when TBT was the main antifoulant used) and an average surface area of a vessel being 3555 m^2, the vRAR estimated emissions for the Netherlands of 12.5 and 13 t in 2002 for copper leaching into the Dutch continental shelf and harbors, respectively. This compares with 8.2 tpa estimated for this survey for leisure vessels. As with the other estimates, any discrepancies in predicted loads are a result of different assumptions and more updated data. Overall, it may be concluded that a reasonable comparison exists between previous estimates of copper loads entering the environment and this study, whether on a country or regional basis. Most differences are attributable to variability in the methods used, the age of the data, or assumptions used to generate export coefficients.

This study is the first to conduct an EU-wide source apportionment for a chemical substance from both point and diffuse sources to the environment, using copper as an example. Extensive use of industry data combined with literature studies and European databases has allowed accurate estimates of loads from all the main identified sources of copper. Compared with data available for stocks and flows of copper (Copper Alliance, 2022), it can be seen that there is no correlation between the amount of copper used for certain applications and its emissions to the environment. The dominant source of copper use is in electrical and electronic goods (e.g., electric networks and power distribution, charging infrastructure, sustainable energy sources such as wind and solar, and industrial equipment) which, within their use lifetime, create negligible emissions (Copper Alliance, 2022). Most copper emissions to water originate in a relatively limited number of uses with direct or indirect contact with water.

Significant uncertainty has been identified in estimates of copper from abandoned mines and, although estimated as a relatively small contribution, confidence in the figures is low. Significant uncertainty is also associated with surface water runoff, which has been identified as a major source, but the number of variables used in the methodology, combined with the uncertainty over transmission from surfaces to water mean variability exists depending on the methods and data used. The aim of this exercise was to derive a transparent and rigorous methodology for quantifying loads of copper to the aquatic environment. This served several purposes including identifying the main sources at a continental scale (as well as those of minor importance and therefore require little further investigation), establishing the uncertainty associated with datasets including level of detail, their extent in country-specific data, and whether the data were up to date. However, accepting the uncertainties associated with the data, this continental-scale assessment can be used as an initial screen to identify key copper sources within a country, but refinements will be necessary to consider locally available

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information and the specific situation in each country. The individual country-level assessments should not be considered in isolation because of the uncertainty that is involved. This research has therefore identified areas of further data collection required for reducing uncertainty and has provided a framework for similar source apportionment of other pollutants with extensive point and diffuse sources.

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AUTHOR CONTRIBUTIONS

Sean Comber: Conceptualization; Data curation; Formal analysis; Methodology; Validation; Writing–original draft; Writing–review editing. **Genevieve Deviller:** Data curation; Formal analysis; Investigation. **Iain Wilson:** Data curation; Formal analysis; Investigation; Methodology. **Adam Peters:** Data curation; Formal analysis; Validation; Writing–review editing. **Graham Merrington:** Data curation; Supervision; Validation; Writing–review editing. **Pasquale Borrelli:** Data curation; Formal analysis; Methodology; Validation. **Stijn Baken:** Conceptualization; Funding acquisition; Supervision; Writing–review editing.

DATA AVAILABILITY STATEMENT

Data, associated metadata, and calculation tools are available from corresponding author Sean Comber (sean.comber@plymouth.ac.uk).

SUPPORTING INFORMATION

All of the background data for each specified load.

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