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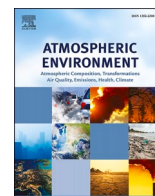


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## Construction of copper, iron and manganese anthropogenic emission inventories for Europe

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### HIGHLIGHTS

- We developed a new Cu emission inventory for Europe.
- We created European emission inventories for Fe and Mn.
- Abrasion sources dominate anthropogenic emissions for Cu and Fe.
- The Cu inventory is reliable.
- Strong negative biases appear for Fe and Mn inventories.

### ABSTRACT

Trace metal elements in atmospheric particulate matter (PM) have significant adverse health effects. However, emissions of some metals, such as copper (Cu), are not yet consistently reported to the EMEP program by European countries under the Convention on Long-range Transboundary Air Pollution (CLRTAP), as their reporting is only encouraged but not mandatory. Other unregulated metals such as iron (Fe) and manganese (Mn), are not considered at all. In this study, we improved the current European Cu inventory by correcting and adjusting existing data and completing the inventory through gap-filling. In addition, we developed the first European anthropogenic inventories for Fe and Mn, considering key anthropogenic sources such as brake wear, road abrasion, engine lubricant combustion, fuel combustion, waste incineration and rail wear. These emissions were geographically distributed based on the spatialization of PM<sub>10</sub> emissions proposed in the reference inventories. For Cu, our new inventory shows that the heterogeneity of emissions between different countries is greatly reduced; for Fe and Mn, the inventory confirms the importance of abrasion processes in the rail and road traffic sectors, as well as that of combustion processes. To evaluate the emission inventory, the Fe/Cu and Mn/Cu ratios in the emissions were directly compared to ambient measurements. The results indicate an underestimation of Fe and Mn emissions compared to Cu, potentially due to the omission of certain emission sources, such as industrial activities or resuspension by traffic, or to contributions from natural sources such as desert mineral dust. We also compared our inventory with existing national and global inventories. This comparison suggests an underestimation of emissions from industrial activities in our inventory but also a potential misrepresentation of road traffic (or railway) sources in other inventories. Further work, including simulations using a chemistry and transport model, and comparison with extended concentration data, is needed to better assess and improve the accuracy of these inventories.

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## 1. Introduction

Ambient air pollution has a proven impact on human health, resulting in adverse health effects and increased mortality (Lelieveld et al., 2015; Shiraiwa et al., 2017; West et al., 2016). The excess mortality caused by PM<sub>2.5</sub> (particles having an aerodynamic diameter less than 2.5 µm) pollution in the EU Member States was estimated to be 253,000 premature deaths in 2021, including 20,100 in France (European Environment Agency, 2023). Among air pollutants, PM comprises a wide range of different compounds, emitted into the atmosphere by various anthropogenic activities and natural sources, and formed by a variety of physicochemical processes. It is the major contributor to the mortality of air pollutants in Europe, ahead of NO<sub>2</sub> and O<sub>3</sub> (European Environment Agency, 2023).

The World Health Organization (WHO) has established specific guidelines values that are commonly defined in terms of PM<sub>10</sub> (particles having an aerodynamic diameter less than 10 µm) or PM<sub>2.5</sub> mass concentrations. This implicitly assumes that all particles of the same mass are equally toxic. However, numerous studies show that the toxicity of PM varies significantly according to its chemical composition and therefore with emission sources and physicochemical transformations (Fussell et al., 2022; Gerlofs-Nijland et al., 2019; Park et al., 2018; Weichenthal et al., 2021). In particular, the metal content in PM, including Cu, Fe and Mn, has been shown to be associated with adverse health effects such as cardiovascular and respiratory diseases (Chen et al., 2022; Maciejczyk et al., 2021; Vithanage et al., 2022). The review of Gonet and Maher (2019) shows that Fe-bearing nanoparticles, are linked with health problems and neurodegenerative diseases.

To improve the assessment of this toxicity, many studies focus on the oxidative potential (OP) of aerosols, an indicator that aims to mimic one of the main biological processes associated with air pollution exposure. It assesses their ability to oxidize other molecules when dissolved in lung epithelial fluid, generating reactive oxygen species (ROS), namely radical species such as OH<sup>•</sup>, and O<sub>2</sub><sup>-•</sup>, and their precursors, such as H<sub>2</sub>O<sub>2</sub>. There are different methods to measure OP, each with different sensitivities to the different molecules present in aerosols (Gao et al., 2020). Some studies show a correlation between transition metals, notably Cu, Fe and Mn, and specific assays for OP measurement (Gao et al., 2020; Shahpoury et al., 2021; Shiraiwa et al., 2017). These transition metals are known to catalyze redox reactions promoting ROS generation (Deguillaume et al., 2005; See et al., 2007). A lung chemistry model developed in a series of papers strongly links the presence of Fe, Cu and Mn in lung fluid to the generation of oxidizing species that can induce inflammation (Fang et al., 2019; Lakey et al., 2016; Lelieveld et al., 2021; Wei et al., 2022).

According to observations at urban sites (Fang et al., 2017), Cu, Fe and Mn are mainly present in the coarse PM mode (diameter from 2.5 to 10 µm). For these three metals, some atmospheric emission sources are already well identified. Vehicle brake abrasion is a significant source of Cu, accounting for about 50 % of Cu emissions in Europe (Gietl et al., 2010; Grigoratos and Martini, 2015; Hulskotte et al., 2007); Fe and Mn are also significantly emitted to the atmosphere by vehicle-related abrasion processes (Birmili et al., 2006; Gonet and Maher, 2019). These three metals are therefore strongly associated with road transport (Charron et al., 2019). Combustion of fuels and biomass is also a source of Fe in the atmosphere, often considered in global inventories (Wang et al., 2015). Fe can also be emitted through road surface wear emissions, as well as railway abrasion emissions (Gonet and Maher, 2019). According to Karagulian et al. (2015), the industrial sector remains a significant source of PM<sub>10</sub> in Europe, particularly in Western Europe, with a contribution estimated to 22 % on a yearly basis for a period between 1990 and 2014. It should be noted that in this later study, the industrial sector includes emissions from industrial processes, industrial combustion, and energy production. For France, Citepa (2025) indicates also that 17 % or 22 % of PM<sub>10</sub> emissions could be attributed to industrial activities (processes and combustion) and construction for year

2010 and 2023. Several studies have shown that, for PM<sub>10</sub>, Fe, Mn and, to a lesser extent, Cu can represent a significant fraction of the PM from this sector (Alleman et al., 2010). Based on a PMF analysis in France, Weber et al. (2000) also demonstrate that industrial sources can be significant emitters of these metals, particularly Mn and Fe, but with very high variability, likely due to different emission processes, and generally for localised areas, as only a few sites include this industrial factor.

In addition to these anthropogenic sources, these metals, notably Fe and to some extent Mn and to a lesser extent Cu, are co-emitted with dust in arid areas, with a mass ratio in dust of 10–310 ppm for Cu, 310–910 ppm for Mn and 20,000 to 52,000 ppm for Fe (Calzolari et al., 2015; Moreno et al., 2006). These three metals are also present in urban road dust and can be resuspended by traffic (Amato et al., 2016; Casotti Rienda and Alves, 2021).

Spatialized inventories for these three metals have been developed for the USA (Reff et al., 2009), East Asia (Kajino et al., 2020), and worldwide (Ito and Miyakawa, 2023; Wang et al., 2015). However, at the European level, there are no spatialized inventories for the ensemble of these metals. Currently, the available information such as total emissions by European country remains limited to Cu. This is probably due to the fact that, unlike mercury (Hg), lead (Pb), cadmium (Cd), arsenic (As) and nickel (Ni), these three metals are not regulated by the European legislation on ambient air, leading to a limited interest in the development of such inventories by Member States, despite their possible large impact on human health.

The aim of this study is to develop an anthropogenic emission inventory of these three metals at the European scale, focusing specifically on the PM<sub>10</sub> fraction of aerosols. This inventory will provide an estimate of the metal fluxes associated with anthropogenic sources. Natural sources (desert mineral dust, volcanic eruptions, forest fires, vegetation, etc.) are not explicitly represented, as they are generally considered by parameterizations or dedicated modules in chemistry-transport models (CTM). The same applies to resuspension by traffic. This work is a first step towards the simulation of these metals in CTM, which should make it possible to better assess the relative impact of various emission sources, with a metric such as OP that includes toxicity. Ultimately, this will contribute to the development of tools to support policy decisions on emission control strategies.

## 2. Methodology

### 2.1. General strategy

In Europe, the EMEP's Centre on Emission Inventories and Projections (CEIP) program aims to compile **emission data inventories reported** by European countries, and to **develop and share spatialized emission datasets for modeling purposes**. Each Member State must report its own total emissions each year, and its spatialized emissions every four years, for several pollutants and each activity sector. EMEP then uses an internal method described in an annual report (<https://www.ceip.at/ceip-reports>), using data from the Copernicus Atmospheric Modelling System (CAMS), the Emission Database for Global Atmospheric Research (EDGAR) or from other databases, to correct some discrepancies between the reported data, to fill in missing information and to spatialize emissions for missing years. Many documents providing technical guidance for emissions reporting are published and updated annually by EMEP, whether for spatialization or for assessing emissions in specific sectors. All the reports are publicly available on the CEIP website ([www.ceip.at](http://www.ceip.at)). The reported pollutants include those regulated by the Directive (EU) 2024/2881 of the European Parliament, such as particulate matter (PM<sub>2.5</sub> and PM<sub>10</sub>) or specific metals (As, Cd, Ni, Pb), as well as other non-regulated pollutants, such as Cu. However, to our knowledge, no Fe or Mn inventories have been reported to the CEIP, and no gridded annual or even national-scale emissions are available. An exception is the Mn emissions data for the United Kingdom

in the National Atmospheric Emissions Inventory (NAEI, [Goddard et al., 2019](#)).

In this study, we build an inventory for Fe and Mn, using Cu as a reference inventory. Fe and Mn emissions are then derived from Cu emissions, using the information available in the literature on Fe/Cu and Mn/Cu ratios for the different emission sources. The fact that some activity sectors do not have co-emissions between these different metals is a limitation of our approach, but this probably concerns second-order sources. It should be noted that we could also have used ratios between Fe, Mn and PM<sub>10</sub> instead of Cu to estimate emissions by activity sectors. This is probably an interesting approach to test in the future. In addition, special attention was also paid to the Cu emissions already reported, in order to evaluate the techniques used to estimate them and to proceed to some harmonization between estimates for different countries.

The nomenclature used by EMEP for emission inventories is the GNFR one (Gridded Nomenclature For Reporting), which defines seventeen macro-sectors. Each sector is then subdivided into a larger number of NFR (Nomenclature For Reporting) sectors. However, some NFR sectors are already aggregates of several emissions, the nature of which may be different: for example, the NFR 1A3c represents railway emissions, which are actually the sum of abrasion from brakes, wheels, rails, catenary, as well as combustion of fuel for traction. Thus, some NFRs have here been divided into several categories, to which we refer as sub-NFRs. Some examples of the nesting of GNFR, NFR and sub-NFR used in this work are presented in [Table 1](#). The different GNFR sectors and their descriptions are shown in [Table S1](#).

With the available data, the inventories for European countries indicated in [Table S2](#) can be built from 1990 to 2017 (2017 being the last year with information on UK mileage). However, the emission factors used in this work are the most recent possible, which may lead to inconsistencies for the oldest years of the inventory. Addressing these inconsistencies is beyond the scope of this work. To simplify the presentation of the results, we have shown those for the year 2013, since this is the year for which we could collect the most atmospheric measurements for Cu, Fe and Mn, which will be later used for comparison with the emission estimates.

## 2.2. Spatialization

Although there are no gridded Cu data on the EMEP website, many other pollutants are spatialized according to GNFR sectors. In addition, [Fang et al. \(2017\)](#) and [Harrison et al. \(2021\)](#) have shown that in urban environments where vehicle wear emissions dominate, Cu, Fe and Mn are mainly found in the PM<sub>2.5-10</sub> (particles 2.5–10 μm in diameter) fraction of the aerosol. This does not rule out that these metals may also be present in PM<sub>2.5</sub>, particularly when combustion-related emissions are significant. In this work, the EMEP spatial distribution of PM<sub>10</sub> emissions was used to spatially distribute Cu emissions over Europe in order to avoid inconsistencies between PM<sub>10</sub> and PM<sub>2.5</sub>, the difference of which in some cases give negative values. This is due to reporting errors in the

**Table 1**  
List of some used GNFR, NFR and sub-NFR link.

GNFR	NFR	Sub-NFR
E_Solvent	2G	Engine lubricant Unspecified sub-NFRs
	Other NFRs	-
F_RoadTransport	1A3bvi	Brake abrasion Tyre abrasion
	Other NFRs	-
I_Offroad	1A3c	Brake abrasion Catenaries abrasion Rail and wheel abrasion Unspecified sub-NFRs
	Other NFRs	-
	Other NFRs	-

data submitted to EMEP. Thus, for each GNFR sector and for each country, we calculated an emission ratio R which is the ratio of Cu and PM<sub>10</sub> emissions (Equation (1)). These ratios were then applied to the spatialized PM<sub>10</sub> data to obtain a spatialized Cu inventory, according to equation (2). The same methodology was used for Fe and Mn emissions.

$$R_{(Cu,GNFR,country)} = \frac{Cu_{(GNFR,country)}}{PM10_{(GNFR,country)}} \quad (6)$$

Equation (1): Cu/PM<sub>10</sub> emission ratio for spatialization of Cu emissions

$$Cu_{(GNFR,country,x,y)} = R_{(Cu,GNFR,country)} \times PM10_{(GNFR,country,x,y)} \quad (7)$$

Equation (2): Calculation of spatialized Cu emissions from PM<sub>10</sub> emission reports and spatialized PM<sub>10</sub> data.

## 2.3. Evaluation by measurements

To assess the accuracy of the inventories produced, we first collected several datasets of Cu, Fe and Mn measurements from two open databases: UK-AIR ([uk-air.defra.gov.uk](#)) and EBAS ([ebas.nilu.no](#)). Other data were also gathered from the IDAEA (Instituto de Diagnóstico Ambiental y Estudios del Agua), the CARA program (detailed in [Favez et al., 2021](#)), and the air quality monitoring network of the Atmo Auvergne-Rhône-Alpes ([www.atmo-auvergnerhonealpes.fr](#)). In the end, our database contains 48 stations with a total of 2824 Cu measurements, 2360 Fe measurements and 2822 Mn measurements for the year 2013. From the 48 sites, 25 of are classified as "rural background", 17 as "urban background" and 6 as "urban traffic" depending mainly on population density (rural, urban) and the distance to the emission sources (background vs. traffic). The frequency of measurements varies, some being daily, others weekly or monthly. All these metals are measured in the PM<sub>10</sub> fraction of the aerosol. Station locations are shown in [Fig. 1](#).

In the absence of direct measurements of emission rates, we used Fe/Cu and Mn/Cu concentration ratios, by type of station to first assess the relevance of the inventories. We assumed that metals within PM<sub>10</sub> are usually quite stable once emitted, compared to organic matter at least. It should be noted, however, that these comparisons must be made with caution, as the effects of source mixing can complicate the analysis of results for measurements made far from sources. Thus, the ratios present in background environments can be different from the ratios present near emission sources. This is the case, for example, for the road traffic source, as shown later in the study. This comparison of measurements and emission ratios can guide the analysis of Fe and Mn inventories, to indicate whether the mass of Fe and Mn in the inventory seems correct in relation to the mass of Cu. This also assumes that the Cu inventory is fairly reliable at least compared to Fe and Mn inventories; an assumption supported by the fact that a Cu inventory already exists and that precise information is available for the various sectors of activity for France and even Germany. It should be noted that the spatial distribution of the stations is unbalanced, with many in the UK, which may be a source of bias in our results.

## 3. Cu inventory

### 3.1. Existing emission inventories

The Cu emission inventory, available via EMEP/CEIP, consists of annual reports from all EMEP Member States and other partner countries, listed in [Table S2](#). Emissions by country and by sector for 2013, expressed in GNFR format, are presented in [Fig. 2 \(a\)](#) for a set of 10 European countries (emissions from other European Community countries are shown in [Fig. S3](#)).

For each country represented in [Fig. 2 \(a\)](#), the main source of Cu is the GNFR sector F\_RoadTransport (48 %–95 % of total Cu emissions), representing road transport emissions from exhaust gases, fuel

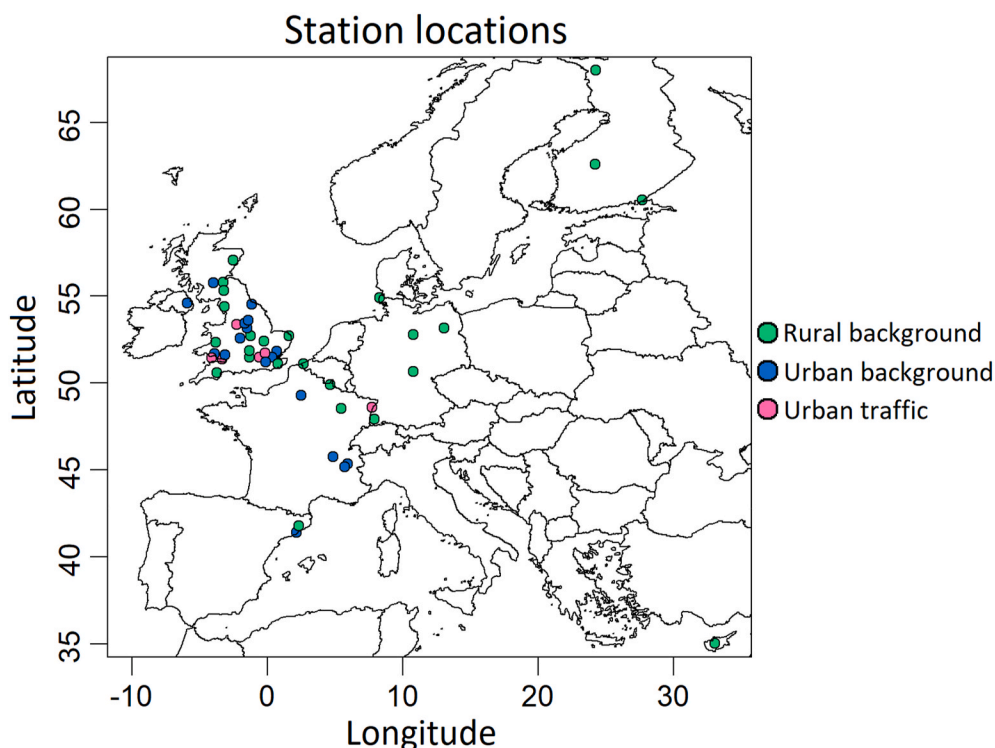


Fig. 1. Positions of the 48 measurement stations of the database for Cu, Fe and Mn concentrations. Colors indicate the typology of the stations. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

evaporation, brake wear, tyres and road surfaces; most of the Cu emitted from these sources comes from brake/tyre wear (56 %–99.9 % of sector F\_RoadTransport), represented in sector 1A3bvi of the NFR, for each country.

These inventories show some differences between countries. France and Germany have 21 % and 16 %, respectively, of their Cu emissions coming from the I\_Offroad sector, which itself comes mainly from 1A3c NFR (99.7 % and 99.4 %, respectively, of I Offroad), which represents

emissions from the railways. However, other countries have negligible emissions from the same I\_Offroad sector (between 5.5 % and 0.03 % of total emissions). Another example is the E\_Solvents sector, which is very important for the UK, France and Germany (respectively 45 %, 22 % and 9.5 % of total Cu emissions), whereas it is negligible for Denmark, Spain or Italy (less than 5 % of total emissions). All the E\_Solvents emissions come from NFR 2G, representing the "use of other solvents", and more specifically the non-energy combustion of lubricants in a four-stroke

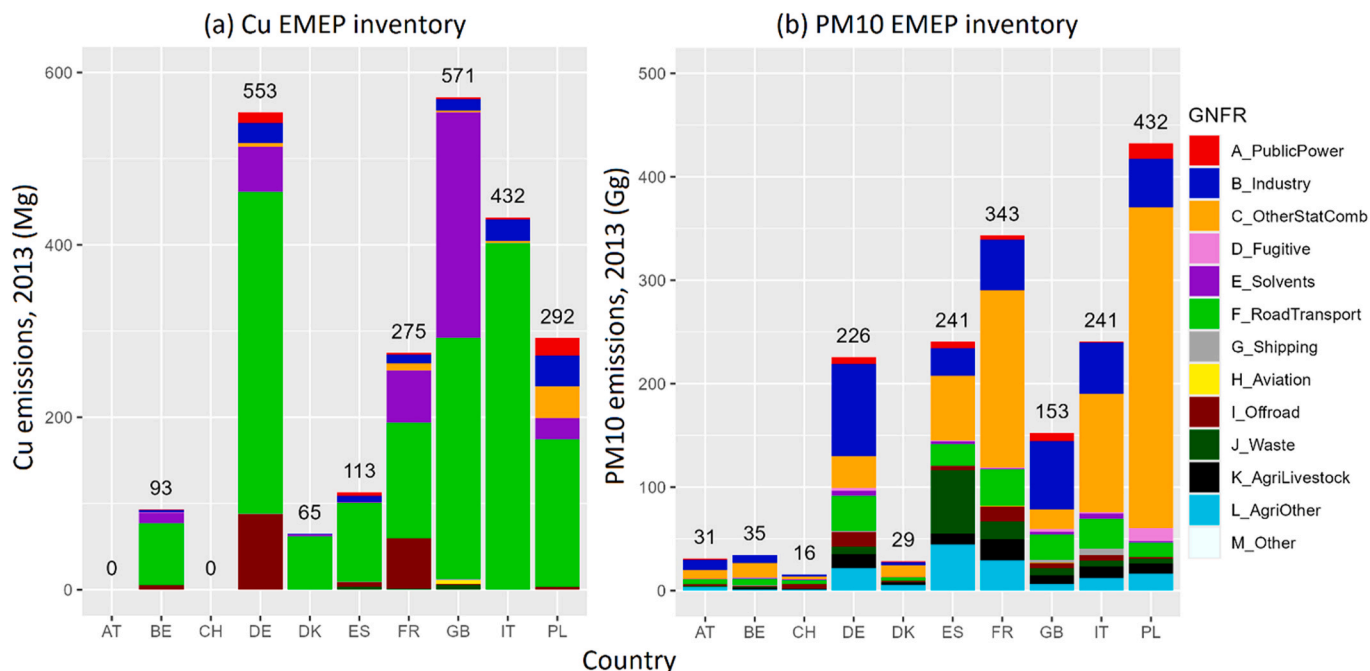


Fig. 2. (a) Cu emission (Mg) and (b) PM<sub>10</sub> emission (Gg) for the year 2013, from EMEP.

engine. All these qualitative differences most likely do not reflect real differences in emissions, but rather disparities in accounting methods.

If we look at the PM<sub>10</sub> emissions for the same year in Fig. 2 (b) and for the same countries, we see that the sources are much more similar between the different countries than they are for Cu. There is no dominant source in one country that is absent in another, although the relative abundance of the different sources varies between countries, both in absolute and relative terms. We mainly attribute this to the fact that Cu emissions are not uniformly reported (and therefore estimated) by countries as is the case for regulated pollutants such as PM<sub>10</sub>, PM<sub>2.5</sub> or NO<sub>x</sub> emissions, for which reporting protocols are harmonized.

In France, Citepa produces an inventory of Cu emissions, available at [www.citepa.org](http://www.citepa.org). The CEE-NU, Ominea and Secten reports present the main sources of Cu emissions in France (Citepa, 2024a, 2024b; 2024c). The main source is brake abrasion in the road traffic transport (130 Mg yr<sup>-1</sup>, 47 % of total emissions). Brake pads linings can contain high amounts of Cu (Hulskotte et al., 2007), because of its heat absorption and transmission properties. The non-energy combustion of lubricants in four-stroke engines is also a major source (61 Mg yr<sup>-1</sup>, 22 % of total emissions). These lubricants contain heavy metals and can also capture wear particles from different parts of the engine, which then end up in the exhaust emissions inventory (Coufalik et al., 2019). Another major source is the wear on train catenary wires, which are made of Cu and emit friction-related particles (59 Mg yr<sup>-1</sup>, 21 % of total emissions). There are other minor sources, such as the combustion of oil, coal or biomass, with a total of 28 Mg yr<sup>-1</sup> (10 % of total emissions).

### 3.2. Development of a new EU Cu inventory

Large differences in emissions between countries often reflect missing sources and gaps in inventories. This can have a significant impact on modelled concentrations. In our study, we assume that these anthropogenic emissions exhibit limited variations between countries with similar socio-economic characteristics and technological levels. This assumption is supported by the PM<sub>10</sub> inventories, which show a rather homogeneous sectoral distribution between the different countries (Fig. 2 (b)). Therefore, the choice is made to harmonize these Cu inventories, or to extrapolate them from existing inventories when input data are lacking. For the major emission sources, we evaluated the calculation methods used by activity sector in the main emitting countries where data was available. We then applied adjustments to obtain more harmonized emissions and consistency between countries.

The most detailed Cu emission inventory available to us was that of France, and it already considers the most important sources of Cu: brake wear, catenaries wear, combustion in general and engine lubricant combustion in particular, while other countries miss some of them. We therefore used French emissions as a reference in order to harmonize emissions in other countries. These processes concern brake wear emissions for Germany and the UK, lubricants emissions from the UK, emissions from combustion and abrasion in the road transport sector for Italy, and the creation of emissions for countries that did not report any of these sources, such as Austria or Switzerland. We have also added two missing sources for French emissions: open green waste fires and railway wheels, rails and brake abrasion.

It should be noted that the aim of this work is to provide a first estimate of Cu emissions on a European scale, and thus to identify the main weaknesses of the inventory and to correct them using simple methods. At this stage, the aim is not to develop harmonized systematic methods such as those developed by EMEP. Emphasis was therefore given on the countries and sources with the highest emissions, without being completely exhaustive.

#### 3.2.1. Homogenization of the Cu inventory

##### 3.2.1.1. German braking emission factors (NFR 1A3bvi). The Cu

inventory provided by EMEP (Fig. 2 (a)) shows a significant discrepancy in road transport emissions between France and Germany with a ratio between those two countries close to 3 (130 Mg for France, 373 Mg for Germany), stemming from a difference in NFR 1A3bvi (tyre and brake abrasion). However, the mileage data for France and Germany show only a slight difference: for the year 2013, according to the data available on the EMEP website ([www.ceip.at/webdab-emission-database/officially-reported-activity-data](http://www.ceip.at/webdab-emission-database/officially-reported-activity-data), last consulted in June 2024), they correspond to  $5.58 \times 10^{11}$  veh.km for France and  $7.32 \times 10^{11}$  veh.km for Germany, a difference of about 30 %. We investigated the reasons for this difference in emissions.

The methods used to calculate emissions, as well as the emission factors (EFs) applied, can be found on the website of the Umweltbundesamt (UBA) German Informative Inventory Report ([iir.umweltbundesamt.de](http://iir.umweltbundesamt.de), last accessed: June 2023). The EFs used for French emissions are available in Citepa, 2025 Ominea database (<https://www.citepa.org/donnees-air-climat/methodologie-de-linventaire-omeinea/>, last consulted: March 2025). The emission factors (EF) for France are presented in Table 2 (a) and those for Germany in Table 2 (b). Table 2 (b) shows that the German emission factors do not vary by road type, whereas we would expect variations associated with the frequency of vehicle braking, which changes depending on the road type. For example, the EF is expected to be higher for urban roads, where there is frequent braking over short distances, than for highways, where there is little braking over long distances (see Fig. 3 in the EMEP report, 2024).

The EFs applied for all type of roads in the German inventory are close to those for cities in France, which are the highest. This explains why Cu emissions from road abrasion are higher in Germany than in France. We therefore created corrected emission factors for roads and highways in Germany, using the French road/city and highway/city ratios for each vehicle type. The distance data by vehicle type and road provided by the UBA were then used to calculate the new Cu emissions for this sector in Germany. The calculation is detailed in Equation (3), where EF stands for emission factor. The results of the emission factors are presented in Table 2 (c). Their application leads to a reduction of Cu emissions from road traffic in Germany from 373 to 183 Mg for the year

**Table 2**  
Cu emission factor ( $\mu\text{g km}^{-1}$ ) for brake and tyre abrasion in the road sector, for (a) France (from Citepa Ominea database), for (b) Germany (from the UBA), for (c) Germany with our correction, and for (d) UK with our calculation.

Cu emission factor, $\mu\text{g km}^{-1}$		(a) French	(b) German	(c) German, new	(d) UK, new
<b>Passenger cars</b>	Motorway	45.5	385	45.4	45.4
	Rural	146	385	146	146
	Urban driving	386	385	385	385
<b>Light-duty vehicles</b>	Motorway	66.1	601	68.5	67.3
	Rural	204	601	211	208
	Urban driving	580	601	601	590
<b>Buses and coaches</b>	Motorway	560	1680	556	558
	Rural	876	1680	870	873
	Urban driving	1690	1680	1680	1680
<b>Heavy-duty vehicles</b>	Motorway	539	1680	556	547
	Rural	1020	1680	1051	1040
	Urban driving	1630	1680	1680	1650
<b>Mopeds &amp; motorcycles</b>	Motorway	22.3	190	22.3	22.3
	Rural	115	190	115	115
	Urban driving	190	190	190	190

2013.

$$\left[ \text{new } EF_{(DE,road)} = \text{old } EF_{(DE)} \times \frac{EF_{(FR,road)}}{EF_{(FR,urban)}} \right]_{(vehicle,road)}$$

Equation (3): Calculation of new Cu emission factors (EF) from braking for Germany; the calculation is made for the two other types of road: motorway, and rural driving, and for every type of vehicle.

3.2.1.2. *UK braking emissions (NFR 1A3bvi)*. There are also large differences between UK and French road transport emissions, with a ratio of 2, also due to a difference in NFR 1A3bvi. However, according to the data available on the EMEP website, there is only a small difference of 10 % in road traffic between France and the UK ( $5.58 \times 10^{11}$  veh.km for France and  $5.09 \times 10^{11}$  veh.km for the UK). This suggests that, as for Germany, this difference is not related to a difference in traffic intensity, but rather due to a difference in calculation methods.

For the UK, we only have access to total mileage data, without detailed information on road typology and vehicle type. To refine our estimates, we therefore averaged French and German emission factors by road type and vehicle type. The total mileage data for the UK were then allocated to different vehicle and road types based on the average proportions observed in France and Germany, to calculate particulate emissions from road abrasion for the UK. The results are presented in Table 2(d). This modification lowers the mass of Cu emitted from 279 Mg to 124 Mg for the year 2013.

3.2.1.3. *Italy road transport emission (GNFR F\_RoadTransport)*. There is also a marked difference between Italian and French road transport Cu emissions, with a ratio of 3. It is very unlikely that Italy has 3 times higher road transport emissions than France. Unlike the case for Germany and the UK (see section 2.1.2.2), mileage data for Italy are not available on the EMEP website. Therefore, we calculated an average Cu/PM<sub>10</sub> emission ratio for the road sector, by averaging this ratio for France, Germany and the UK, at the GNFR level. This averaged ratio is then multiplied by the amount of PM<sub>10</sub> emitted in Italy (Equation (4)). This step reduces the Italian Cu emissions from road transport in 2013 from 401 Mg yr<sup>-1</sup> to 182 Mg yr<sup>-1</sup>.

$$Cu_{(Road,IT)} = PM10_{(IT)} \times \frac{1}{3} \times \left( \frac{Cu_{(Road,DE)}}{PM10_{(Road,DE)}} + \frac{Cu_{(Road,FR)}}{PM10_{(Road,FR)}} + \frac{Cu_{(Road,GB)}}{PM10_{(Road,GB)}} \right) \quad (3)$$

Equation (4): Calculation of new Cu emissions from road transport in Italy; Road stand for the GNFR F\_RoadTransport emissions.

3.2.1.4. *UK engine lubricant combustion emission (NFR 2G)*. We also observe very different Cu emission levels for the NFR 2G sector (other solvent uses; for Cu, it consists only of the non-energy combustion of lubricants in 4-stroke engines) between Germany, France and the United Kingdom (9.5 %, 22 % and 45 % of total emissions respectively). These differences with the UK seem difficult to explain as the vehicle fleets are probably similar. We therefore decided to harmonize UK emissions with those of France and Germany. To do this, we calculated the mean ratio 2G/1A3bvi (brake and tyre wear) of Cu emissions for France and Germany. We apply this to the UK sector 1A3bvi. The new NFR 2G emission value for the UK is 86 % lower than the initial emissions for 2013, from 261 Mg to 36 Mg.

$$2G_{(UK)} = 1A3bvi_{(UK)} \times 0.5 \times \left( \frac{2G_{(FR)}}{1A3bvi_{(FR)}} + \frac{2G_{(DE)}}{1A3bvi_{(DE)}} \right) \quad (4)$$

Equation (5): Calculation of new Cu emissions from the 2G sector in the United Kingdom.

3.2.1.5. *Missing Cu emission for some countries*. Some countries, such as

Switzerland and Austria, do not report Cu emissions. This results in large geographical areas without Cu emissions. We therefore interpolate these emissions using information from neighboring countries, as described below: A Cu/PM<sub>10</sub> ratio is first calculated for all neighboring countries of each "zero emission" country and for each GNFR sector. This ratio is then averaged and applied to the PM<sub>10</sub> emissions of the targeted country. We used a ratio based on neighboring countries rather than a single average ratio calculated for the whole of Europe to try to better account for potential technological, socio-economic or geographical disparities between European countries. This calculation is described in equation (6), where N<sub>neighbors</sub> is the number of neighbors of the country under consideration. Then, in the same way as in the general procedure (section 2.2), these estimated national totals are distributed to the inventory grid cells proportionally to the EMEP GNF PM<sub>10</sub> emissions.

$$Cu_{(Country,GNFR)} = \left( \sum_{Neighbors} \frac{Cu_{(Neighbor,GNFR)}}{PM10_{(Neighbor,GNFR)}} \right) \times \frac{1}{N_{Neighbors}} \times PM10_{(Country,GNFR)} \quad (5)$$

Equation 6: Calculation of Cu emissions for countries with no reported emissions.

### 3.2.2. New sources for French emissions

3.2.2.1. *Open green waste fires in France (NFR 5C2)*. Among the sectors not assessed in the French emissions is that of "open fires of green waste". The EMEP 5C2 guide provides a Cu emission factor for this type of waste combustion (Table 3, EMEP, 2023). We combined the activity data available for France with this emission factor to obtain an estimate of emissions from open fires of green waste. The references used to estimate this source are available in Table 4. The new estimate is 0.19 Mg for the year 2013, which represents 0.07 % of the total emissions.

3.2.2.2. *Abrasion of railway wheels, rails and brakes in France (NFR 1A3c)*. Citepa database does not provide an estimate of Cu emissions for wheel, rail and brake abrasion related to rail transport. However, Burkhardt et al. (2008) provide a speciation of the amount of abraded material related to the rail sector including Cu, Fe and Mn. This speciation is then used with the PM<sub>10</sub> emissions for the same sectors to calculate the Cu, Fe and Mn emissions associated with this sector. The different references and emission ratios used to estimate this source are available in Table 4. This rises the 1A3c emission from 59.0 Mg to 61.5 Mg for the year 2013.

## 4. Fe and Mn inventories

### 4.1. Description of the method

There are no European inventories of anthropogenic emissions of Fe or Mn. Although some emission factors for Fe or Mn are available in the literature for specific sources (Skeaff and Dubreuil, 1997), they do not cover all sources that are relevant for these metals, such as road traffic

**Table 3**  
Description of the NFRs in the waste sector concerned by metals.

Waste NFR list	Description
5C1a	Municipal waste incineration
5C1bi	Industrial waste incineration
5C1bii	Hazardous waste incineration
5C1biii	Clinical waste incineration
5C1biv	Sewage sludge incineration
5C1bv	Cremation
5C1bvi	Other waste incineration
5C2	Open burning of waste
5E	Other waste

**Table 4**

List of ratios between metals and emission factors for the construction of the French metal inventory; for the SPECIEUROPE database, ID refer to the identification code of the different sources.

Category	NFR	Metal	ratio with Cu	Unit	Reference
<b>Road abrasion (brake)</b>	1A3bvi	Fe	4.1	Fe/Cu, g g <sup>-1</sup>	EMEP Guidebook 1A3bvi 1A3bvii: Road transport abrasion, Tables 3–12
		Mn	4.8 10 <sup>-2</sup>	Mn/Cu, g g <sup>-1</sup>	
<b>Road abrasion (tyre)</b>		Fe	9.8	Fe/Cu, g g <sup>-1</sup>	
		Mn	0.29	Mn/Cu, g g <sup>-1</sup>	
<b>Road abrasion (road)</b>	1A3bvii	Fe	28.5	Fe/PM <sub>10</sub> , mg g <sup>-1</sup>	Jandacka et al. (2021), Table 2
		Mn	1.3	Mn/PM <sub>10</sub> , mg g <sup>-1</sup>	
<b>Engine lubricant</b>	2G	Fe	5.8	Fe/Cu, g g <sup>-1</sup>	Coufalík et al., 2019, Table 2: Urania 5W, used & Castrol SLX 5W-40, used (mean)
		Mn	0.21	Mn/Cu, g g <sup>-1</sup>	
<b>Oil combustion (road)</b>	Several NFR	Fe	15	Fe/Cu, g g <sup>-1</sup>	SPECIEUROPE Database, ID 9, 10, 11, 86, 87, 88, 89, 140, 141, 214, 216, 217, 218 (mean)
		Mn	0.58	Mn/Cu, g g <sup>-1</sup>	
<b>Oil combustion (marine)</b>		Fe	72	Fe/Cu, g g <sup>-1</sup>	SPECIEUROPE Database, ID 205, 206, 207, 208, 209, 210, 211, 212, 213 (mean)
		Mn	0	Mn/Cu, g g <sup>-1</sup>	
<b>Oil combustion (heating)</b>		Fe	32	Fe/Cu, g g <sup>-1</sup>	SPECIEUROPE Database, ID 14, 35, 85, 124, 125, 153, 221, 266, 271 (mean)
		Mn	1.9	Mn/Cu, g g <sup>-1</sup>	
<b>Coal combustion</b>		Fe	303	Fe/Cu, g g <sup>-1</sup>	SPECIEUROPE Database, ID 25, 27, 28, 31, 32, 33, 34, 36, 69, 70, 81, 96, 97, 122, 123, 128, 129, 136, 137, 166, 279 (mean)
		Mn	5.7	Mn/Cu, g g <sup>-1</sup>	
<b>Biomass combustion (agricultural waste)</b>		Fe	8.5	Fe/Cu, g g <sup>-1</sup>	SPECIEUROPE Database, ID 23, 224 (mean)
		Mn	1.6	Mn/Cu, g g <sup>-1</sup>	
<b>Biomass combustion (wood)</b>		Fe	13.5	Fe/Cu, g g <sup>-1</sup>	SPECIEUROPE Database, ID 5, 6, 7, 8, 19, 20, 21, 22, 26, 67, 68, 118, 119, 184, 187, 188, 189, 190, 191, 225, 226, 248, 249, 250, 251 (mean)
		Mn	3.1	Mn/Cu, g g <sup>-1</sup>	
<b>Municipal waste incineration</b>	5C1a	Fe	18	Fe/Cu, g g <sup>-1</sup>	Abanades et al. (2002), Table 1 fly ash Argyropoulos et al. (2012), Table 2 wasteburn Bernasconi et al. (2022), Table S3 Bogush et al. (2015), table 2A & 2B, A3 A8 A10 1 2 4 5 9 Bogush et al. (2019), Table 2, APCR, XRF, TAD & AR

**Table 4 (continued)**

Category	NFR	Metal	ratio with Cu	Unit	Reference
					Chang et al., 2009, Table 3
					Cocis et al., 2012, Table 3, all samples
					Raclavská et al., 2017, Table 3, FA1, FA2 & FA3
					Weber et al. (2000), Table 3, waste I & waste II
					Zhou et al. (2015), Table 1 (mean)
					Internal Citepa data – accessible on request
<b>Hazardous waste incineration</b>	5C1bii	Mn	2.1	Mn/Cu, g g <sup>-1</sup>	Internal Citepa data – accessible on request
<b>Clinical waste incineration</b>	5C1biii	Fe	1.2	Fe/Cu, g g <sup>-1</sup>	EPA AP42 2.3: Medical Waste Incineration, Tables 2.3–6 & 2.3–7
		Mn	4.5 10 <sup>-2</sup>	Mn/Cu, g g <sup>-1</sup>	
<b>Sewage sludge incineration</b>	5C1biv	Fe	14	Fe/Cu, g g <sup>-1</sup>	EPA AP42 2.2: Sewage Sludge Incineration, Tables 2.2–5
		Mn	0.23	Mn/Cu, g g <sup>-1</sup>	
<b>Open burning of waste</b>	5C2	Cu	0.2	Cu/Burned waste, g Mg <sup>-1</sup>	EMEP Guidebook 5C2: Open burning of waste, Tables 3–1
		Fe	44	Fe/Cu, g g <sup>-1</sup>	
		Mn	13	Mn/Cu, g g <sup>-1</sup>	
<b>Vehicle burning</b>	5E	Mn	0.16	Mn/Cu, g g <sup>-1</sup>	ADEME report: improvement of knowledge of atmospheric emissions linked to vehicle burning, contribution of this source to the national emissions inventory, Table 3
<b>Building burning</b>		Fe	20	Fe/Cu, g g <sup>-1</sup>	EPA AP42 1.6: Wood Waste Combustion, table 7
<b>Train brake abrasion</b>	1A3c	Cu	4.3 10 <sup>-3</sup>	Cu/PM <sub>10</sub> , g g <sup>-1</sup>	Burkhardt et al. (2008), Table 1
		Fe	0.88	Fe/PM <sub>10</sub> , g g <sup>-1</sup>	
		Mn	5.2 10 <sup>-3</sup>	Mn/PM <sub>10</sub> , g g <sup>-1</sup>	
<b>Train wheel and rail abrasion</b>		Cu	6.7 10 <sup>-4</sup>	Cu/PM <sub>10</sub> , g g <sup>-1</sup>	
		Fe	0.97	Fe/PM <sub>10</sub> , g g <sup>-1</sup>	
		Mn	10 <sup>-2</sup>	Mn/PM <sub>10</sub> , g g <sup>-1</sup>	

and combustion (Birmili et al., 2006; Charron et al., 2019; Wang et al., 2015). These sources are often also important contributors to Cu emissions. Thus, for the selected sectors, we attempted to establish Fe/Cu and Mn/Cu ratios using available information (scientific literature or EMEP guidance). These factors were then applied to Cu emissions for France, considering the most precise level possible (NFR sector, or sub-NFR as

defined previously). These sectors were then summed up at the GNFR level. The sectors concerned are brake, tyres and roads abrasion, combustion of engine lubricants, fuel combustion and waste incineration. We also considered the abrasion of railway wheels, rails and brakes. All the different references used for the construction of the different sources of this inventory, including the emission ratios, are listed in Table 4. The next step is to calculate Fe and Mn emissions for other European countries, by applying the same Fe/Cu and Mn/Cu ratios derived for France at the GNFR level, to the Cu emissions for other European countries, still at the GNFR level.

This approach still has some limitations. Some sources, which may be locally important for Fe or Mn, do not emit (or very little) Cu. It should also be noted that for the industrial sector, we only considered emissions from combustion, and not emissions from processes (such as electric arc furnaces for steelmaking (Sylvestre et al., 2017) or cement production (Glojek et al., 2024)), which may have a local impact on metal concentrations in ambient air. As mentioned in the introduction, PM<sub>10</sub> emissions, and more specifically Fe and Mn emissions, can represent a significant fraction of total emissions (Alleman et al., 2010; Karagulian et al., 2015). In our case, only the fraction related to processes is not taken into account for Fe and Mn. Given the diversity of these processes, the approach of using ratios relative to Cu emissions in the same sector may not be appropriate. On the other hand, we have considered here that this source, particularly in Western Europe, remains rather local, as Weber et al. (2000) suggest for France.

However, this work provides a first estimate of the fluxes of anthropogenic emissions of these metals at the European scale. Implications of our hypothesis and limitations of our method will be considered in hereafter results' discussions.

#### 4.1.1. Sector-wise description of the procedure

**4.1.1.1. On-road abrasion.** Measurement campaigns carried out in environments heavily influenced by traffic generally show high concentrations of Fe and Mn (Charron et al., 2019; Miazgowiec et al., 2020). Non-exhaust emissions consist of three main sources: brake, tyre wear and road abrasion. Brake and tyre wear are the two sub-NFRs that make up the 1A3bvi NFR sector, while road abrasion is represented in the 1A3bvii NFR sector. The EMEP guideline "1A3bvi&vii road tyre and brake wear" (EMEP, 2024), available on the European Environment Agency website ([www.eea.europa.eu/publications/emep-eea-guidebook-2023](http://www.eea.europa.eu/publications/emep-eea-guidebook-2023)) provides an elemental composition for brake and tyre wear particles, with the proportions of Cu, Fe and Mn. These values were used to calculate the Fe and Mn emissions from Cu. For France, it represents 533 Mg for Fe and 6.28 Mg for Mn for the year 2013.

No information on road abrasion was found in this guideline. Janacka et al. (2021) provided a series of analyses of the elemental composition of several road types, including the amounts of Cu, Fe and Mn. The mean of these values was used to calculate Fe and Mn emissions for road abrasion. For France, it represents 142 Mg for Fe and 6.62 Mn for the year 2013.

It should be noted that other sources have different Fe/Cu and Mn/Cu ratio for these sources. For example (Hulskotte et al., 2014), calculated emissions factors for brake emissions, with a Fe/Cu ratio of 20 (instead of 4.1 for the EMEP guidebook), and a Mn/Cu ratio of  $1.4 \cdot 10^{-1}$  (instead of  $4.8 \cdot 10^{-2}$ ). Using these ratios would increase the amounts of Fe to 2600 Mg and Mn to 18.3 Mg. However, in the remainder of this work, we will use the EMEP guidebook ratios.

**4.1.1.2. Engine lubricants.** In 4-stroke engines, crankcase lubricant may enter the combustion chamber during engine operation. This lubricant is not intended to be burned during its initial use, unlike the lubricant in 2-stroke engines, which will necessarily be burned and is therefore part of

the fuel introduced into the vehicle. Inside an engine, friction between parts can produce metal particles. These can then be captured by the engine lubricant, and enter the combustion chamber where they are burned and end up in the exhaust. This emission source is at the sub-NFR level, and is included in the 2G NFR sector.

The metal concentration of some of these lubricants was assessed by Coufalík et al. (2019) with concentration values for Cu, Fe and Mn. The average of the ratios of these concentrations (e.g. Fe/Cu and Mn/Cu) was used with the Cu emissions from this source to calculate Fe and Mn emissions. For France, this corresponds to 356 Mg for Fe and 12.6 Mn for the year 2013.

**4.1.1.3. Combustions.** To assess the relative amounts of Fe and Mn - compared to that of Cu - emitted by combustion processes, we used the SPECIEUROPE database developed by Pernigotti et al. (2016). This database contains source profiles for more than 287 sources from many works, including combustion sources. The origins of the profiles we used are diverse, but most come from measurements in the atmosphere. For the latter, measurements were carried out with different strategies, such as near-source measurements or source apportionment studies. For each profile, detailed information is available on the SPECIEUROPE website.

Combustion processes, which may all emit metals, are numerous and many sectors of the NFR nomenclature are combustion sources. For coal combustion, 21 different profiles are available. The Fe/Cu and Mn/Cu ratios for these profiles were calculated, averaged and used to calculate the Fe and Mn emissions from this source using the Cu emissions from coal combustion. For oil combustion, the different profiles were divided into three classes: road fuels with 13 profiles, marine fuels with 8 profiles and other combustion fuel oils (for heating or electricity production) with 9 profiles. This allowed the construction of three different average Fe/Cu and Mn/Cu ratios combined with the corresponding Cu emissions from which the Fe and Mn emissions were derived. For biomass combustion, the profiles were divided into two classes: wood with 25 profiles and agricultural waste with 2 profiles. The two average Fe/Cu and Mn/Cu ratios were used as before to estimate the Fe and Mn emissions. For France, the emissions from combustion represents 670 Mg for Fe and 37.4 Mg for Mn for the year 2013.

**4.1.1.4. Waste incineration.** Emissions from waste incineration are classified into 9 NFRs, as reported in Table 3. For sectors 5C1a and 5C1bii, corresponding to municipal waste and hazardous waste, we used internal Citepa data for Mn, and data from a literature review for Fe (Abanades et al., 2002; Argyropoulos et al., 2012; Bernasconi et al., 2022; Bogush et al., 2015, 2019; Chang et al., 2009; Nicula et al., 2012; Raclavská et al., 2017; Weber et al., 2000; Zhou et al., 2015). EPA AP42 data (available at [www.epa.gov/air-emissions-factors-and-quantification/ap-42-compilation-air-emissions-factors-stationary-sources](http://www.epa.gov/air-emissions-factors-and-quantification/ap-42-compilation-air-emissions-factors-stationary-sources)) were used for sectors 5C1biii, 5C1biv and part of sector 5E, corresponding to medical waste, sewage sludge and building fires, to obtain Cu, Fe and Mn ratios. For the part of sector 5E corresponding to car fires, an ADEME report (ADEME, 2013) was used for Mn, and no data were found for Fe. Finally, for sector 5C2, corresponding to open vegetable waste fires, a report was used from the work of (Turn et al., 1997). For France, it represents 15.6 Mg for Fe and 3.01 Mg for Mn for the year 2013.

**4.1.1.5. Railways.** The various NFRs related to the railway sector include combustion sources in locomotives, as well as abrasion on wheels, rails, brakes and catenaries. Since combustion has already been discussed in section 2.2.2.3, brakes, wheels and rails, and catenaries are the three NFR sub-sources considered here, and are included in the NFR 1A3c sector.

In their work, Burkhardt et al. (2008) provide the metal composition of wheels, rails, and brakes for the Swiss railway infrastructure. These

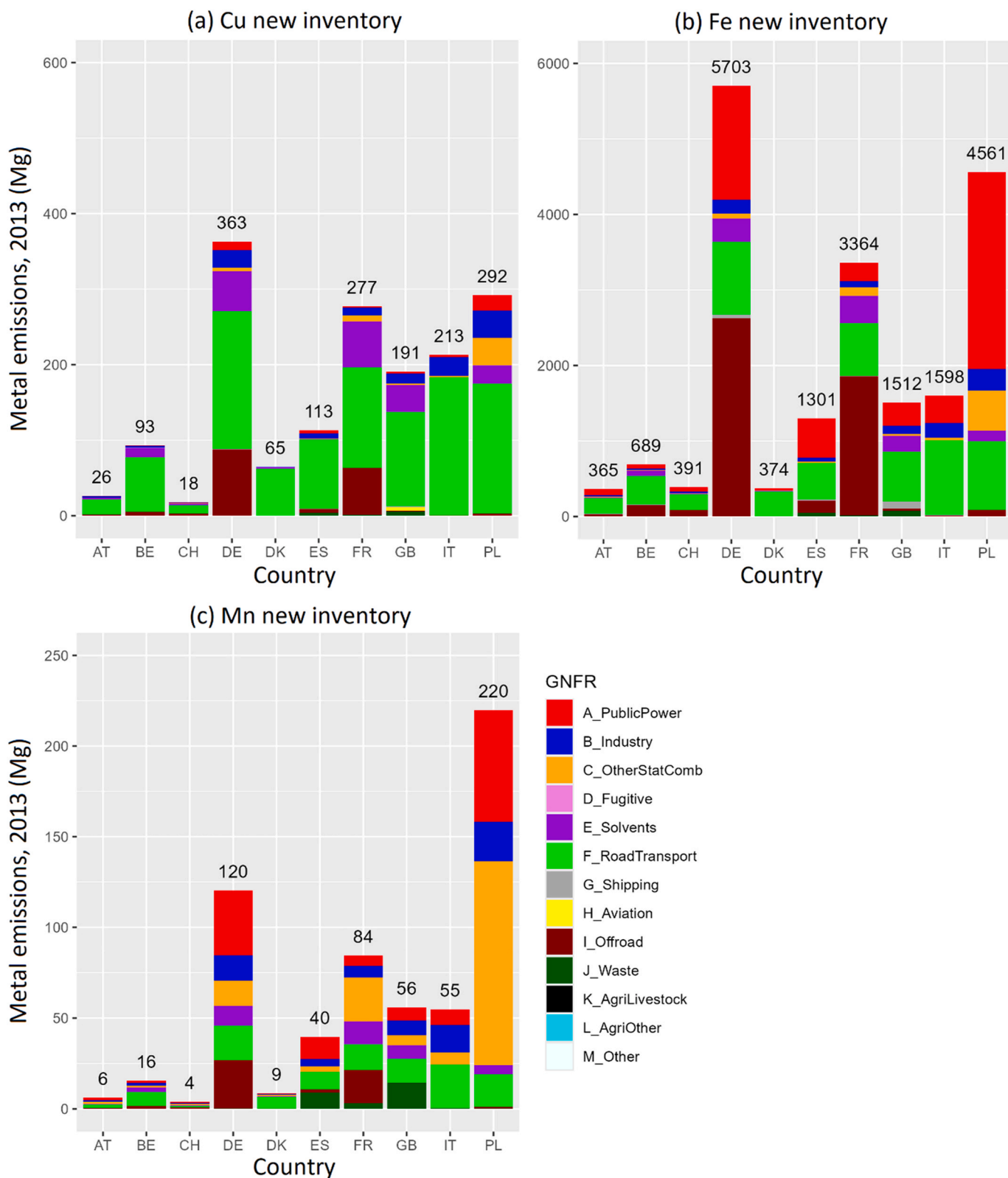


Fig. 3. Metal emissions (Mg) for the year 2013, from (a) our new Cu inventory with the modifications developed in this article in the upper half, and from (b) our Fe inventory and (c) our Mn inventory, calculated with the method developed in this work.

specifications were used directly with PM<sub>10</sub> emissions for these sectors to estimate Fe and Mn emissions. For France, this represents 1842 Mg for Fe and 18.6 Mg for Mn for the year 2013.

## 5. Results and discussion

### 5.1. Modification of the EMEP Cu inventory

The results of the new Cu emission inventory are shown in Fig. 3 (a) for 10 European countries, while emissions for other countries are presented in the supplementary material. Compared to the original EMEP emissions inventory shown in Fig. 2 (a), the heterogeneity of emissions between individual countries has been greatly reduced. Differences in total emissions between countries are smaller, and emissions have been created for countries that did not previously report emissions. The ratio between the lowest and highest emitting countries is now 23, compared to 69 previously; the ratio between German and French emissions is 1.3, compared to 2 previously, which is closer to the population ratio between the two countries, which was 1.27 in 2013.

In addition, the relative shares of each sub-sector in the country total are also more homogeneous between the main emitting countries. For example, the combustion of engine lubricants in the UK now accounts for 19 % of the country's emissions (compared to 45 % previously), which is comparable to France (22 %) and Germany (15 %).

As far as French emissions are concerned, the addition of open fires of green waste and abrasion of brakes, wheels and rails in the rail sector did not significantly increase total emissions (0.7 %), which rose from 275 to 277 Mg year<sup>-1</sup>.

However, there are still unexplained differences between certain countries. While catenary abrasion is a major source of Cu emissions for France and Germany, accounting for 21 % and 16 % of total emissions respectively, few other countries, even those with fully electrified rail networks, provide estimates of these emissions. Similarly, the source corresponding to the non-energy combustion of engine lubricants, present in the solvent sector, is not assessed for most countries. To improve the Cu emissions inventory, it would be necessary to systematically collect data and harmonize estimation methods, sector by sector and country by country, in order to standardize them.

### 5.2. Main sources contributing to Cu, Fe and Mn emissions

#### 5.2.1. French emissions

Details of Cu, Fe and Mn emissions for France, by NFR category, are given in Table 5. For Fe and Mn, the road abrasion sector (the sum of abrasion from brakes, tyres and the road surface itself) is a major source of emissions: 47 % for Cu, 23 % of the total for Fe and 18 % for Mn. As with Cu, tyre abrasion is negligible. On the other hand, unlike Cu, a significant proportion of Fe and Mn comes from road surface abrasion: 1

**Table 5**  
French Cu, Fe and Mn inventory, 2013 for various emission sectors.

Category	NFR	Cu (Mg yr <sup>-1</sup> )	Fe (Mg yr <sup>-1</sup> )	Mn (Mg yr <sup>-1</sup> )
On-Road abrasion (brake)	1A3bvi	129	531	6
On-Road abrasion (tyre)	1A3bvi	0.2	2	0.1
On-Road abrasion (road)	1A3bvii	2	286	10
Engine lubricant	2G	61	356.3	13
Biomass combustion	Several NFR	9.5	129	30
Coal combustion	Several NFR	1	300.5	6
Oil combustion	Several NFR	5	240	2
Waste	5C1(a, bi, bii, biii, biv, bv, bvi), 5C2, 5E	1	16	3
Railways	1A3c	61.5	1842	19

% of total abrasion for Cu, versus 35 % for Fe and 61 % for Mn. A large part of Fe and Mn emissions from brake abrasion. Non-energetic combustion of engine lubricants is also a major source of emissions for these metals, respectively 10 % for Fe and 14 % for Mn, but less than 22 % for Cu.

Combustion is the main emission sector for Mn (42 % of the total), an important sector for Fe (19 %) and makes only 6 % for Cu. We can take a closer look at the breakdown by type of combustion: Mn is very largely emitted by biomass (80 %), to a lesser extent by coal combustion (15 %), while oil accounts for a small share (5.1 %). Fe is more evenly distributed among the various sources: coal leads the way (45 %), followed by oil (36 %) and then biomass (19 %); finally, Cu is particularly emitted by biomass combustion (61 % of total combustion) and by oil (33 %), and little by coal (6 %). Our estimates show a predominance of the railway sector for Fe emissions, with 53 % of total Fe emissions. It is also an important sector for Cu and Mn, with 22 % and 21 % respectively. For Mn, waste incineration accounts for a small share of total emissions, within 3 %. This sector is almost negligible for Cu and Fe, with less than 1 % for each of these two metals.

#### 5.2.2. European emissions

Fe and Mn emission inventories for 10 European countries and for the year 2013 are presented in Fig. 3 (b) and (c) (see supplementary material for other countries). For most countries, the two main sources of anthropogenic Fe are the road transport sector and the public electricity and heat production sector. For Mn, the majority of anthropogenic emissions are due to the road sector, as well as industrial and non-industrial combustion, with different distributions between countries. As already found for Cu, there are large disparities between countries. This is partly explained by the poor representation of Cu emissions related to railway abrasion and the combustion of engine lubricants, which can be also important sources for Fe and Mn. As these sources are represented in only a limited number of countries, we did not systematically extrapolate values for countries where they are missing. This remains a weakness of the inventory that should be addressed in the future. In the emissions shown in Fig. 3, Poland is a special case. These differences can be explained by higher PM<sub>10</sub> emissions (Fig. 2) linked to the public and domestic energy production sectors and industry. As a result, higher Cu emissions associated with these sectors of activity are reported (Fig. 3). Table 4 shows that the Fe/Cu and Mn/Cu ratios can be significant for wood and coal combustion, which results in Fe and Mn emissions being particularly significant for Poland (Fig. 3). These data will need to be confirmed by observations.

#### 5.3. Spatialized emissions

Fig. 4(a), (b), and (c) represent the spatialized annual anthropogenic emissions of Cu, Fe, and Mn, respectively, while Fig. 4(d) shows the spatialized annual emissions of PM<sub>10</sub>. The native EMEP resolution of 0.1° × 0.1° has been used. For Cu, very significant emissions are observed in urban centers and along motorways. The most important hotspots are the Benelux, the North Rhine Valley, the Po Valley and England. The regions of Paris, Madrid and Berlin are also significant emitters. This is consistent with the fact that Cu is mainly emitted by road traffic via the abrasion process. Strong Cu emissions also appear over southern Poland. In France, urban emissions are about 3 kg km<sup>-2</sup> yr<sup>-1</sup>. Fe and especially Mn emissions have a spatial distribution partly similar to that of Cu due to the fact that traffic sources (roads and trains) account for a significant fraction of these emissions. However, there are differences, especially for Mn, with spatially more diffuse emissions and less marked gradients between rural areas and urban and road areas. This is mainly due to the importance of the biomass combustion sector which also affects urban areas. For Mn, we also observe high emissions in Poland. In France, these metals can reach emission levels in urban areas of the order of 20 kg km<sup>-2</sup> year<sup>-1</sup> for Fe, and of the order of 0.5 kg km<sup>-2</sup> year<sup>-1</sup> for Mn. The spatial gradients are overall, with the

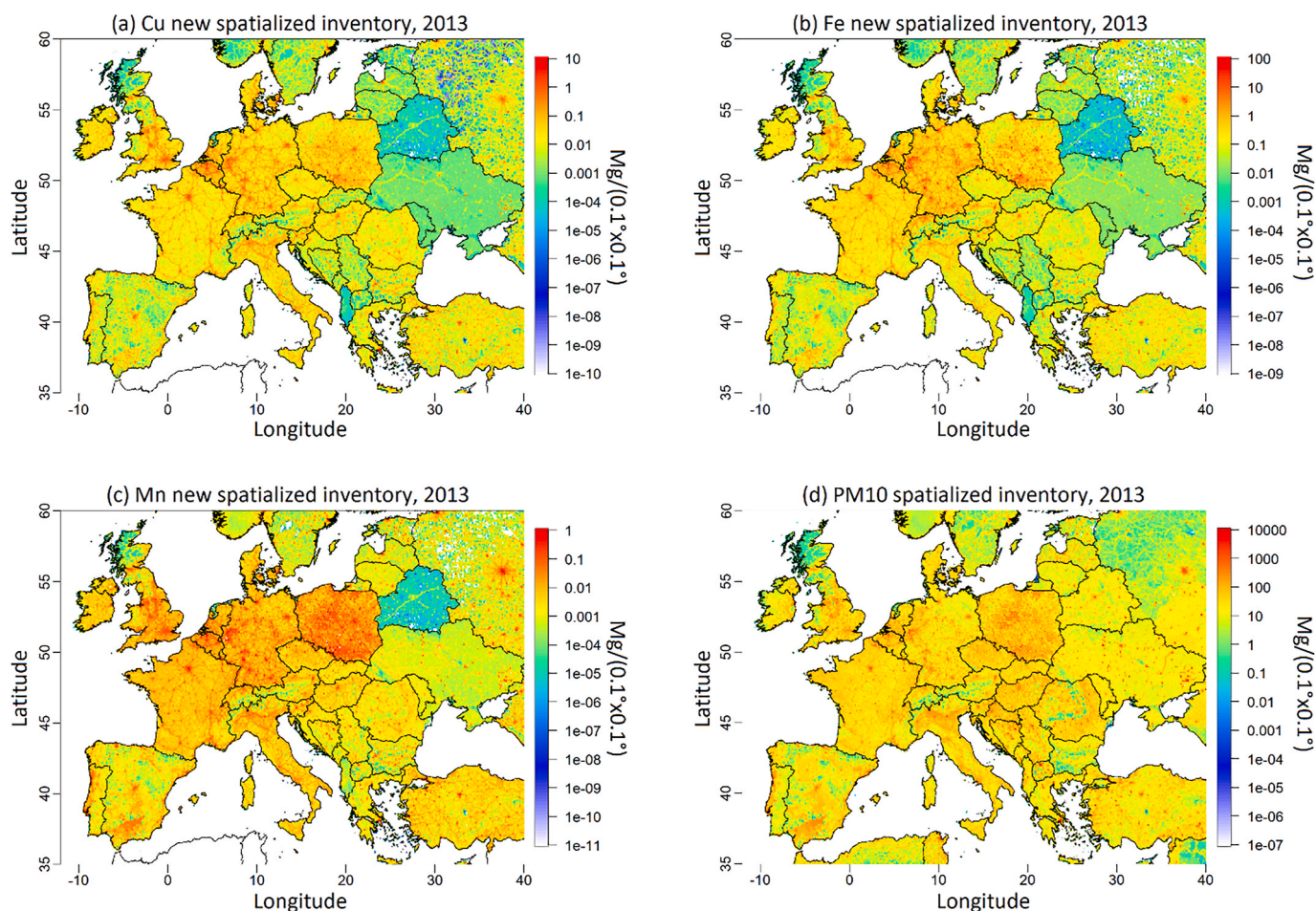


Fig. 4. Spatialized metal emissions for the year 2013, from (a) Cu, (b) Fe, (c) Mn, from this work, and (d) PM<sub>10</sub> from EMEP.

exception of Mn, more pronounced for these metals than for PM<sub>10</sub> emissions which have more diversified sources. We also note that some countries, notably Albania and Belarus, have significantly lower emissions than their neighbors, most likely due to unreported emissions for Cu.

#### 5.4. Comparison with measurements and other emission inventories

##### 5.4.1. Use of Fe/Cu and Mn/Cu ratios from measurements

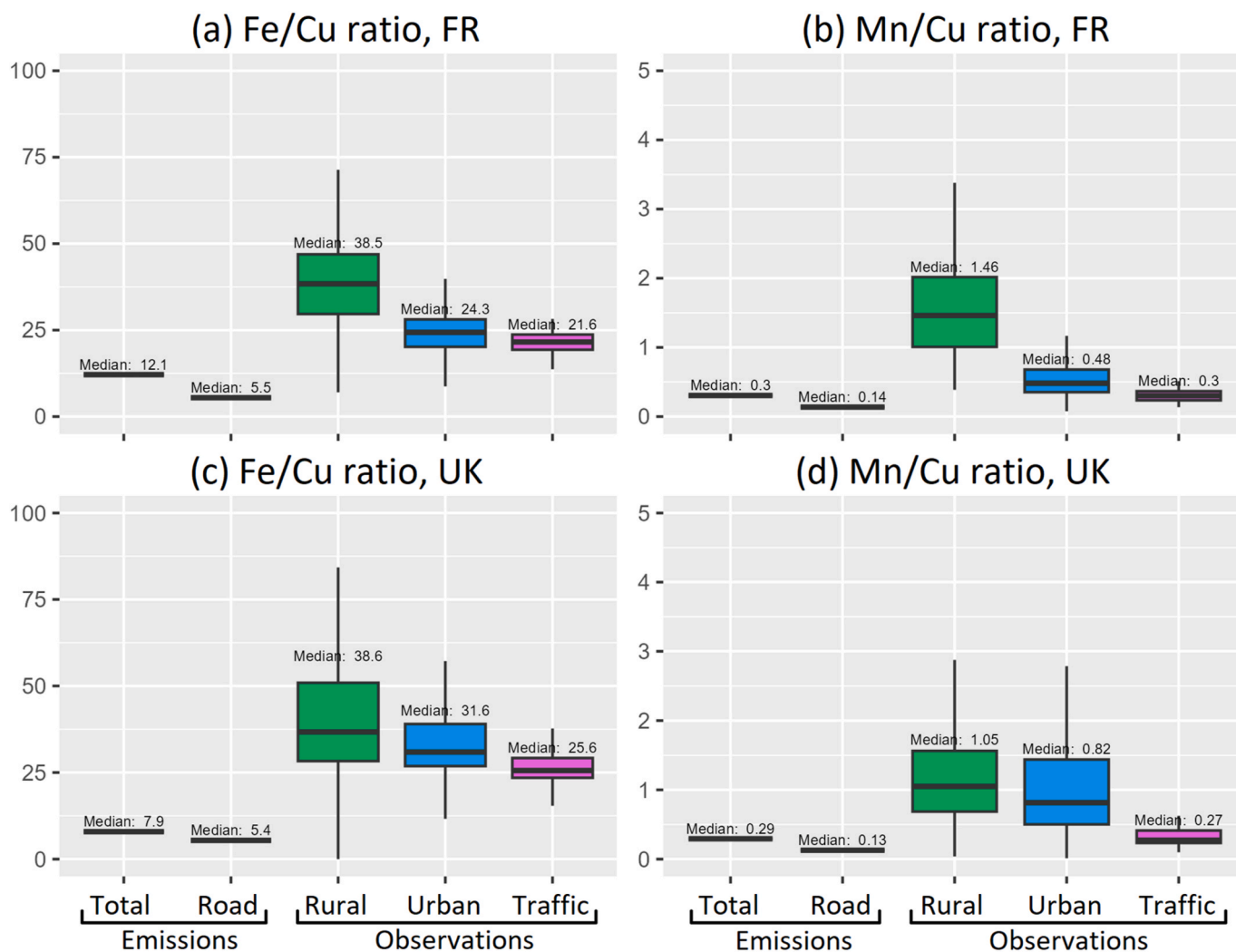
The Fe/Cu and Mn/Cu ratios were calculated from our emission inventories and in situ concentration measurements (described in section 2.3). Although the nature of the quantities compared is different, in the absence of direct flux measurements, these comparisons provide information to estimate the quality of our inventories, particularly for environments close to emission sources such as traffic and urban areas. The Fe/Cu and Mn/Cu ratios for total emissions and for road emissions are shown in Fig. 5, as well as the box plots of these ratios calculated from observations. Only data for France and the United Kingdom are shown, as these are the two countries for which the most data are available; the results for the other countries are presented in the supplementary material. For Fe, a significant difference is observed between the emission and the observation ratios. In France, the Fe/Cu ratio for total emissions is 12, while the median of the observations varies between 24 and 38.5, for urban and rural stations respectively, an underestimation by a factor of 2–3. For emissions related to road traffic only, the emission ratio is 5.5 and the median of the ratios of traffic stations is 21.5, an underestimation by a factor of 4. For the United Kingdom, the underestimation of emission ratios is even higher, by a factor of 4–5 for total emissions and 5 for road emissions.

For France, the Mn/Cu ratio for total emissions is 0.3, while the median of the field observations varies between 0.5 and 1.5 for urban and rural stations, an underestimation by a factor of 1.5–5. For traffic-related emissions, the ratio is 0.15, while for traffic monitoring stations, the median measured ratio is 0.3, an underestimation of a factor of 2. For the United Kingdom, these underestimations of emission ratios are quite similar to those for France, with a factor of 3–3.5 for total emissions, and 2 for road emissions.

Assuming that Cu emissions are well estimated for both France and the UK, this means that there is a significant underestimation of Fe and Mn emissions. This "lack" of emissions may come either from sources not accounted for in our inventory or from a poor estimation of the intensity of sources already included.

For Fe, the difference in higher ratios for transport indicates that part of the emissions deficit may come from traffic. This could be associated with a poor estimation of emissions linked to combustion or abrasion, but it is particularly important to consider the fact that the resuspension of road dust is not directly represented in the inventories. This process is generally represented dynamically in chemical transport models. For Mn, this difference seems to be higher in rural areas and may therefore be associated with an emission deficit in rural areas, for example biomass burning, but also to other sources transferred by air mass transport. However, it is clear that the interpretation of the results for remote areas strongly influenced by transport of air masses, such as rural environments, is more complex due to the greater mixing of air masses of different origins.

The differences with the observations, can certainly be partly explained by the lack of mineral dust sources in the inventory (for both natural and anthropogenic origins), including the resuspension of



**Fig. 5.** Boxplot of (a) Fe/Cu and (b) Mn/Cu for France, and of (c) Fe/Cu and (d) Mn/Cu for UK, for (from left to right) total emissions for each country, emissions from to the road sector (made of the E\_Solvents and F\_RoadTransport GNFR sectors), observations from rural background stations (2 stations and 164 points for France, 12 stations and 477 points for UK), observations from urban background stations (4 stations and 328 points for France, 12 stations and 221 points for UK), observations from traffic station (1 station and 69 points for France, 5 stations and 110 points for UK); the upper whisker extends from the hinge to the largest value no further than  $1.5 \times$  inter-quartile range (IQR) from the hinge; the lower whisker extends from the hinge to the smallest value at most  $1.5 \times$  IQR of the hinge.

particles on road in urban environments. In the case of desert aerosols, Saharan dust episodes are frequent over Europe, and these particles contain Fe and Mn oxides, with an Fe/Cu ratio of 169 to 2,9, and a Mn/Cu ratio of 3–77 (Calzolari et al., 2015; Moreno et al., 2006). Pey et al. (2013) showed that over the period 2001–2011, African dust outbreaks in the European part of the Mediterranean basin happen between 17 % and 37 % of the annual days, depending on the sites, and that African dust is the largest source of PM<sub>10</sub> in these regions. As for resuspension, in some contexts, an urban aerosol can be composed of up to 60 % resuspended particles (Casotti Rienda and Alves, 2021). These resuspended dusts are composed of road abrasion and brake abrasion particles, which are important sources of metals (Amato et al., 2009, 2016), suggesting that resuspension can significantly increase ambient metal concentrations. It should be recalled that these two processes are generally not included in inventories estimating anthropogenic emissions. However, they can be accounted for in chemistry-transport models through the use of dedicated parameterizations as a function of specific dynamic variables, such as humidity and wind.

#### 5.4.2. Comparison with other inventories

To assess the quality of our emissions inventory, we compare it to the two main previous ones in this section. First, the National Atmospheric

Emissions Inventory (NAEI) details Mn emissions data for the United Kingdom on the UK-AIR website (naei.beis.gov.uk/data/data-selector, last accessed: June 2023), in NFR format. We have aggregated this inventory in GNFR format and compared it to the one from this work for the year 2013, in Fig. 6. Both inventories have a similar total amount of Mn emitted: 59 Mg for the NAEI inventory, 56 for this work. The main differences between the two inventories concern: emissions related to road transport (E\_Solvents & F\_RoadTransport) which are significant in our inventory (23 %) and negligible for the NAEI (1 %); emissions related to waste combustion (J\_Waste) which are significant in our inventory (25 %) and negligible for the NAEI (0.1 %); industrial emissions (B\_Industry), which are predominant in the NAEI (79 %), and almost 6 times lower in our inventory (14 %). It can be mentioned that the inventory produced in this work uses transport sources that have been updated more recently; moreover, the sources related to industrial processes are not taken into account in our inventory. These methodological differences partly explain the variability in sector-wise contributions.

Secondly, Ito and Miyakawa (2023) developed a global inventory for Cu, Fe and Mn in PM, subsequently named IM2023. This inventory consists of an anthropogenic component, a lithogenic component (mineral dust), and a pyrogenic component (open combustion of

## Comparison with the NAEI inventory

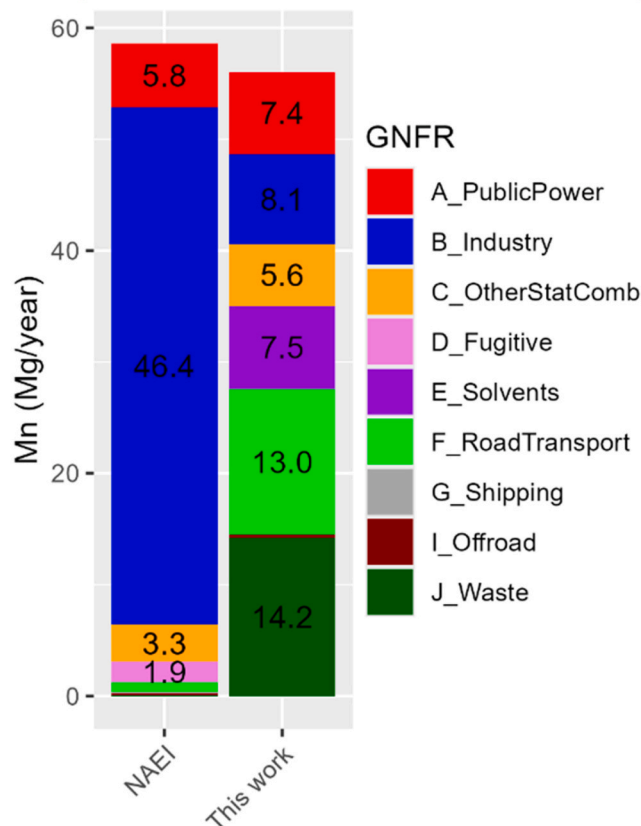


Fig. 6. Comparison of Mn emissions of the NAEI inventory (left column) and this work (right column), given in GNFR nomenclature, for the year 2013 in UK.

biomass). Since our inventory covers only anthropogenic emissions, we consider only the anthropogenic component of IM2023 for comparisons. The comparison of this inventory with the one developed in this work is shown on Fig. 7. As the particle sizes of the 2 inventories are not exactly the same, we compared our emissions in the PM10 fraction with the PM1 and TSP (Total Suspended Particles) fractions of IM2023. The Cu ratios between the IM2023 inventory and ours for different countries range from 0.2 to 1.4 for PM1 and from 0.9 to 6.7 for TSP. For Fe, these ratios range from 0.2 to 1.1 for PM1 and from 0.9 to 5.1 for TSP. For Mn, these ratios range from 0.2 to 2.7 for PM1 and from 1.0 to 16.0 for TSP. There are differences between these two inventories, which vary by country, but the values are of the same order of magnitude. For 21 out of 30 of the countries and emissions emission value shown in Fig. 7, the emissions from this work are between the values for PM1 and TSP of the IM2023 inventory: 6 times for Cu, 8 times for Fe and 7 times for Mn. It is difficult to determine a variation in these differences between the different metals.

As the country projection introduces errors (due to grid cells covering several countries), we also projected our emissions from the EMEP  $0.1^\circ \times 0.1^\circ$  grid onto the  $2^\circ \times 2.5^\circ$  grid of the IM2023 inventory (Fig. 8) for comparison (for the PM5 fraction). Generally, both inventories show common emission hotspots in Western Europe (the Netherlands and northwestern Germany), and Central Europe (southern Poland), and also Eastern Europe (southeastern Ukraine, Moscow region), but higher values are observed in the IM2023 inventory for these hotspots. There are also additional hotspots in Eastern Europe. For Cu, IM2023 emissions are somewhat higher than ours in most of Europe, notably at common hotspots displaying higher intensities for IM2023. For Fe, the hotspots are also much more pronounced for the IM2023 inventory than for ours, but the background levels are rather similar

match. Mn emissions from IM2023 are much higher than ours over most of Central Europe, and the hotspots are also more pronounced.

The results of these comparisons suggest that some of the initial assumptions can be questioned, especially the fact that industrial emissions associated with some processes are not considered. Since Cu emissions from the industrial sector are very low in the EMEP inventory for most countries (Fig. 2 and Fig. S5), and information on industrial processes is more limited, we have considered only the Fe/Cu and Mn/Cu ratios due to combustion in this sector, and have not taken into account metal emissions from specific industrial processes especially metallurgical processes that could exhibit very important values of these ratios (Alleman et al., 2010; Mbengue et al., 2017). However, in the NAEI inventory, the industrial source is important in England, and measurements in industrial environments in France and more generally in Europe confirm this (Liu et al., 2024). Part of the difference between observations and emissions could be explained by the absence of these emissions, at least in some regions where they would be significant. The comparison with the IM2023 inventory shows that our inventory for Fe is comparable for most countries, while our estimate for Mn is lower. However, it can be assumed that our inventory takes much better account of emissions from the road sector, which may explain the presence of Mn in urban and traffic stations. Finally, it is striking that all these inventories provide final annual total emissions of the same order of magnitude, although attributed to different sources. Since the emission ratios between other metals and Cu are lower than those obtained from observations, this calls for deeper investigations, including on-site measurements and emission factors, on the diversity of sources of these metals.

## 6. Conclusion

In this work, we have built a spatialized European inventory of Cu, Fe and Mn emissions for year 2013, considering their main sources, road abrasion, combustion of engine lubricants, abrasion of railway tracks. As Cu reporting is suggested but not mandatory in EMEP reporting guidelines, and Fe and Mn are not mentioned, we had to work with incomplete and unharmonized inventories for Cu and without any for Fe and Mn. In particular, we have corrected and completed the existing Cu inventories. In addition, we have established one of the first European inventories of Fe and Mn from the Cu inventory and a meticulous work of collecting the emission ratios by sectors of activity of Fe and Mn compared to Cu. These inventories of total annual anthropogenic emissions, obtained at the country level, were then spatialized based on the distribution of EMEP PM<sub>10</sub>.

For Cu, emissions are mainly due to road brake wear, non-energy combustion of engine oils and rail transport (when data are available). For Fe particulate emissions, the dominant anthropogenic sources are abrasion in the railway sector, combustion for energy production and road transport with a significant share related to abrasion. For Mn, the main sources are biomass combustion and roads and rail abrasion. These new emission inventories for Fe and Mn still show inhomogeneities between countries that are not realistic and are partly related to differences already present in the PM<sub>10</sub> and Cu inventories. Some missing information prevents estimation of emissions for all sources, particularly for rail transport, which appears to be a key source and requires dedicated analysis.

To estimate the strengths and weaknesses of our inventories we also compared them with existing inventories. In the case of Mn, the comparison of our inventory with the one developed in the United Kingdom shows a good agreement of total emissions ( $\pm 20\%$ ), but with significant differences between sectors of activity, particularly linked to the share of industrial processes in emissions. In the case of global inventories, the inventory developed in this work is more complete and explicitly integrates the roads and rail abrasion, but once again the question of emissions linked to industrial processes may arise. This is clearly an issue that needs to be addressed in the future. We also used in situ

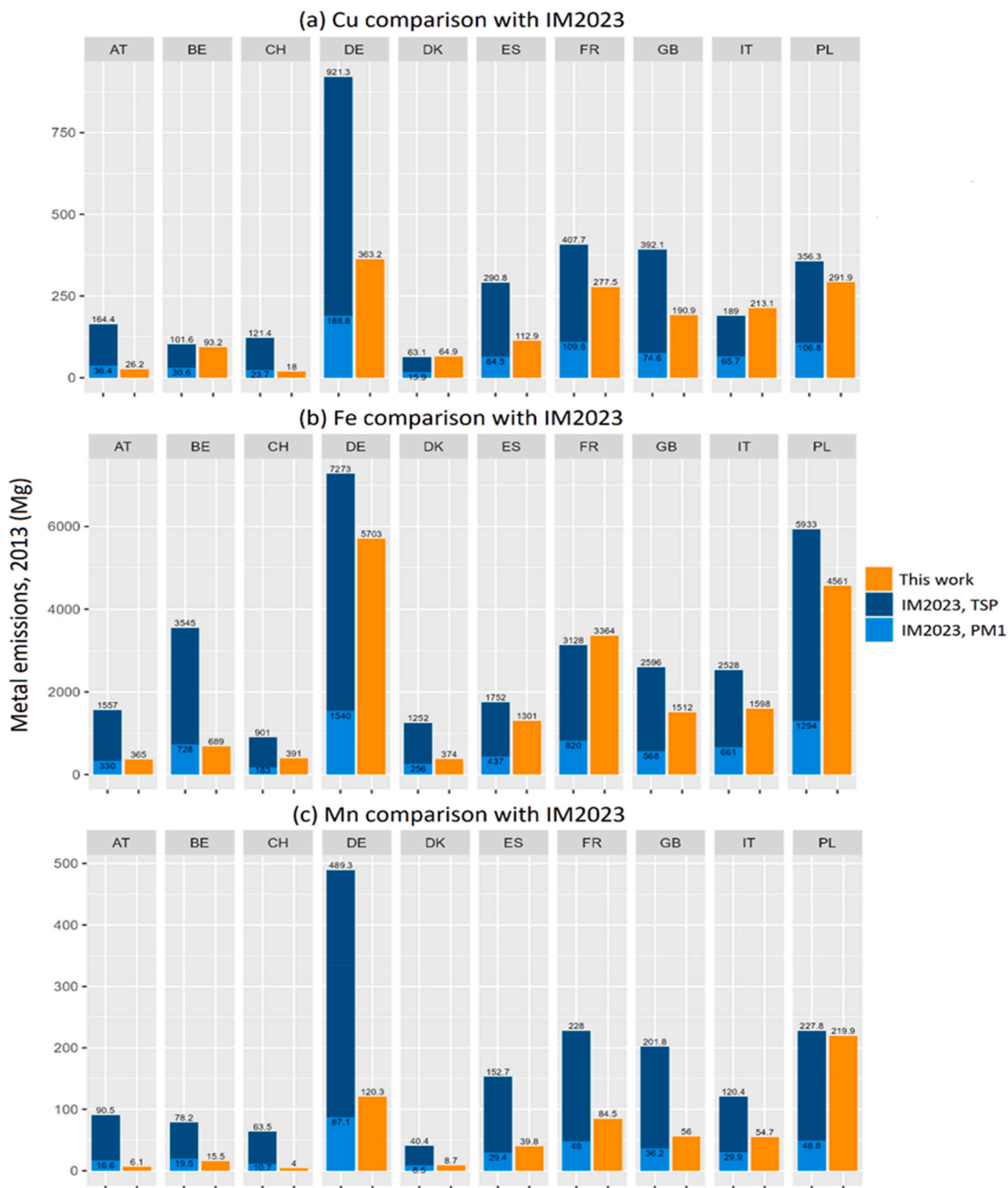


Fig. 7. Comparison of (a) Cu, (b) Fe and (c) Mn emissions from this work (right column) with the IM2023 inventory (left column: light blue for PM<sub>2.5</sub>, dark blue for PM<sub>5</sub>), for the year 2013, for 10 European countries. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

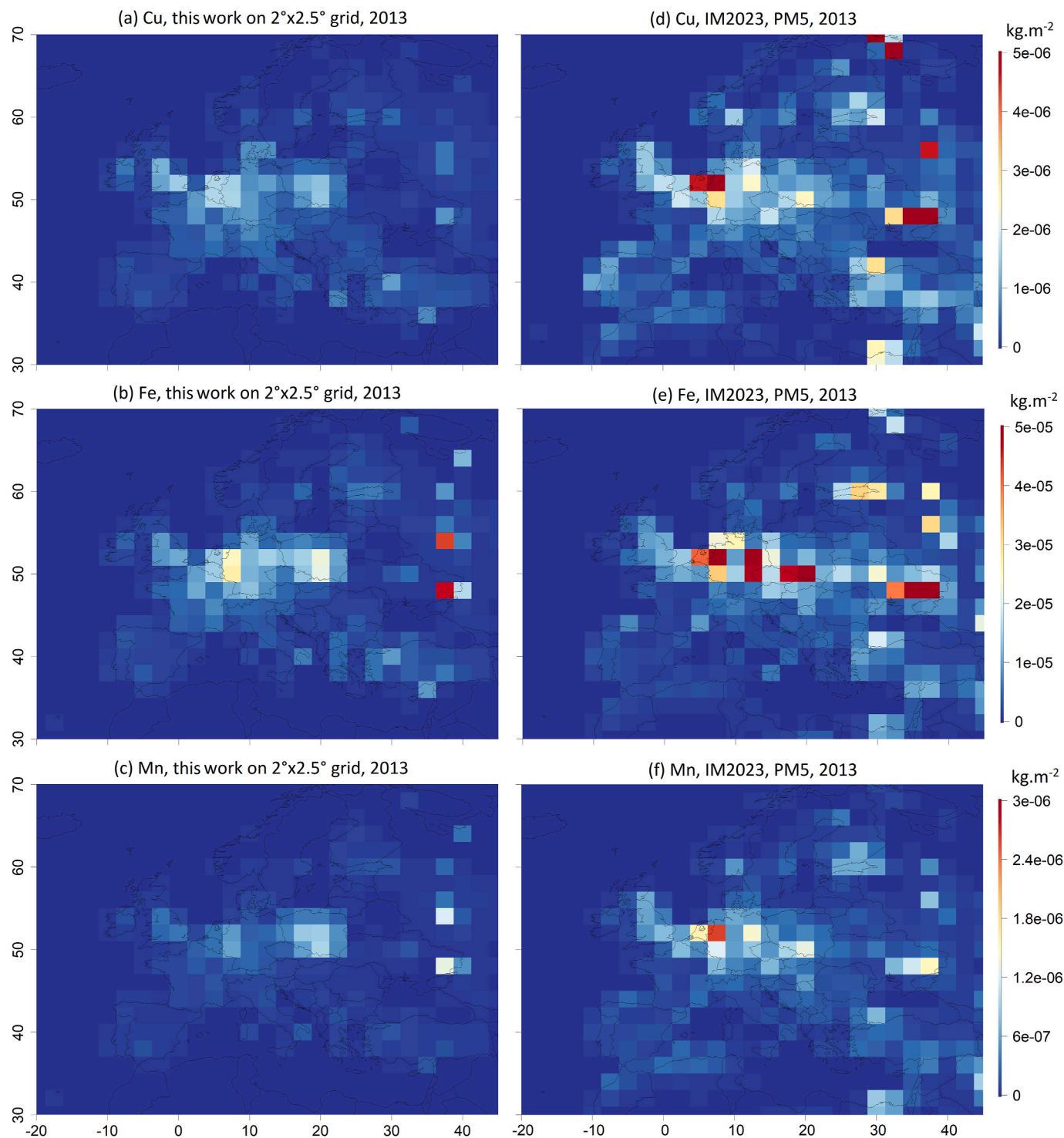


Fig. 8. Comparison of (a) Cu, (b) Fe and (c) Mn emissions from our inventory, plotted on a  $2^\circ \times 2.5^\circ$  grid, with the (d) Cu, (e) Fe and (f) Mn emissions from the IM2023 inventory over Europe, for the year 2013. (a) and (d) share the same scale, as do (b) and (e), and (c) and (f).

observations of concentrations for these 3 metals to assess our inventory. For this, we used the observed Fe/Cu and Mn/Cu ratios and compared them to those in our inventory. These ratios are lower for calculated emissions than for actual measurements, suggesting a significant underestimation of Fe and Mn emissions in our inventory. This can be explained firstly by the potential impact of sources not generally integrated in inventories such as mineral dust emitted by wind erosion or the resuspension of particles by traffic. This could also result from inaccuracies in existing European Cu inventories, such as the lack of railways

emissions in most countries, or from the reference data used to calculate the ratios applied in the Fe and Mn inventory. To go further in this direction, it will be necessary to use a transport chemistry model to compare simulated and observed concentrations. This could allow for sensitivity tests on emissions and help assess the importance of dynamic processes.

Finally, although many hypotheses remain to be tested, we have built a new European Cu inventory that is more reliable than the existing one, and we have established the very first European inventories of

anthropogenic emissions of Fe and Mn to date. These inventories can already be used to estimate the main European emission sources for Cu, Fe and Mn, and can also be used by chemical transport models. They could therefore lead to future works regarding these metals, and help to estimate the health impact of different source of particles based on their respective chemical composition.

#### CRediT authorship contribution statement

**N. Dubois:** Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Conceptualization. **G. Foret:** Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization. **G. Siour:** Writing – review & editing, Writing – original draft, Supervision, Software, Resources, Methodology, Investigation, Formal analysis, Conceptualization. **G. Uzu:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **F. Couvidat:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis. **M. Vida:** Software. **J.-M. André:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Data curation, Conceptualization. **S. Moukhtar:** Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **N. Sirina-Leboine:** Resources, Project administration, Funding acquisition. **Robin Aujay-Plouzeau:** Data curation. **L. Alleman:** Writing – review & editing, Writing – original draft, Formal analysis, Data curation. **S. Conil:** Writing – review & editing, Data curation. **C. Pallares:** Data curation. **G. Salque-Moreton:** Data curation. **E. Stratigou:** Data curation. **A. Alastuey:** Writing – review & editing, Data curation. **X. Querol:** Writing – review & editing, Data curation. **A. Ito:** Writing – review & editing, Writing – original draft, Data curation. **J.-L. Jaffrezo:** Writing – review & editing, Writing – original draft, Methodology, Data curation, Conceptualization. **O. Favez:** Writing – review & editing, Writing – original draft, Methodology, Formal analysis, Data curation, Conceptualization. **M. Beekmann:** Writing – review & editing, Writing – original draft, Supervision, Methodology, Investigation, Formal analysis, Conceptualization.

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#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.atmosenv.2025.121582>.

#### Data availability

All measurement and PMF data for this paper are archived at the IGE, and are available on request from the corresponding authors (JLJ and GU). The specific codes and modelling data produced within this work are available from the LISA authors (ND, GF, MB, GS). The reference model is available here: <https://www.lmd.polytechnique.fr/chimere>.

#### References

- Abanades, S., Flamant, G., Gagnepain, B., Gauthier, D., 2002. Fate of heavy metals during municipal solid waste incineration. *Waste Manag. Res.* 20, 55–68. <https://doi.org/10.1177/0734242X0202000107>.
- ADEME, 2013. Improvement of the Knowledge of the Atmospheric Emission from Vehicles Fires, Contribution of This Source to the National Emission Inventory.
- Alleman, L.Y., Lamaison, L., Perdrix, E., Robache, A., Galloo, J.-C., 2010. PM<sub>10</sub> metal concentrations and source identification using positive matrix factorization and wind sectoring in a French industrial zone. *Atmos. Res.* 96 (4), 612–625. <https://doi.org/10.1016/j.atmosres.2010.02.008>.
- Amato, F., Pandolfi, M., Escrig, A., Querol, X., Alastuey, A., Pey, J., Perez, N., Hopke, P. K., 2009. Quantifying road dust resuspension in urban environment by multilinear engine: a comparison with PMF2. *Atmos. Environ.* 43 (17), 2770–2780. <https://doi.org/10.1016/j.atmosenv.2009.02.039>. ISSN 1352-2310.
- Amato, F., Favez, O., Pandolfi, M., Alastuey, A., Querol, X., Moukhtar, S., Bruge, B., Verlhac, S., Orza, J.A.G., Bonnaire, N., Le Priol, T., Petit, J.-F., Sciare, J., 2016. Traffic induced particle resuspension in paris: emission factors and source contributions. *Atmos. Environ.* 129, 114–124. <https://doi.org/10.1016/j.atmosenv.2016.01.022>. ISSN 1352-2310.
- Argyropoulos, G., Manoli, E., Kouras, A., Samara, C., 2012. Concentrations and source apportionment of PM<sub>10</sub> and associated major and trace elements in the rhodes island, Greece. *Sci. Total Environ.* 432, 12–22. <https://doi.org/10.1016/j.scitotenv.2012.05.076>.
- Bernasconi, D., Caviglia, C., Destefanis, E., Agostino, A., Boero, R., Marinoni, N., Bonadiman, C., Pavese, A., 2022. Influence of speciation distribution and particle size on heavy metal leaching from MSWI fly ash. *Waste Manag.* 138, 318–327. <https://doi.org/10.1016/j.wasman.2021.12.008>.
- Birmili, W., Allen, A.G., Bary, F., Harrison, R.M., 2006. Trace metal concentrations and water solubility in size-fractionated atmospheric particles and influence of road traffic. *Environ. Sci. Technol.* 40, 1144–1153. <https://doi.org/10.1021/es0486925>.
- Bogush, A., Stegemann, J.A., Wood, I., Roy, A., 2015. Element composition and mineralogical characterisation of air pollution control residue from UK energy-from-waste facilities. *Waste Manag.* 36, 119–129. <https://doi.org/10.1016/j.wasman.2014.11.017>.
- Bogush, A.A., Stegemann, J.A., Roy, A., 2019. Changes in composition and lead speciation due to water washing of air pollution control residue from municipal waste incineration. *J. Hazard Mater.* 361, 187–199. <https://doi.org/10.1016/j.jhazmat.2018.08.051>.
- Burkhardt, M., Rossi, L., Boller, M., 2008. Diffuse release of environmental hazards by railways. *Desalination* 226, 106–113. <https://doi.org/10.1016/j.desal.2007.02.102>.
- Calzolari, G., Nava, S., Lucarelli, F., Chiari, M., Giannoni, M., Becagli, S., Traversi, R., Marconi, M., Frosini, D., Severi, M., Udister, R., di Sarra, A., Pace, G., Meloni, D., Bommarito, C., Monteleone, F., Anello, F., Sferlazzo, D.M., 2015. Characterization of PM<sub>10</sub> sources in the central mediterranean. *Atmos. Chem. Phys.* 15, 13939–13955. <https://doi.org/10.5194/acp-15-13939-2015>.
- Casotti Rienda, I., Alves, C.A., 2021. Road dust resuspension: a review. *Atmos. Res.* 261, 105740. <https://doi.org/10.1016/j.atmosres.2021.105740>.
- Chang, C.-Y., Wang, C.-F., Mui, D.T., Chiang, H.-L., 2009. Application of methods (sequential extraction procedures and high-pressure digestion method) to fly ash particles to determine the element constituents: a case study for BCR 176. *J. Hazard Mater.* 163, 578–587. <https://doi.org/10.1016/j.jhazmat.2008.07.039>.
- Charron, A., Polo-Rehn, L., Besombes, J.-L., Golly, B., Buisson, C., Chanut, H., Marchand, N., Guillaud, G., Jaffrezo, J.-L., 2019. Identification and quantification of particulate tracers of exhaust and non-exhaust vehicle emissions. *Atmos. Chem. Phys.* 19, 5187–5207. <https://doi.org/10.5194/acp-19-5187-2019>.
- Chen, L.-C., Maciejczyk, P., D. Thurston, G., 2022. Chapter 6 - metals and air pollution. In: Nordberg, G.F., Costa, M. (Eds.), *Handbook on the Toxicology of Metals*, fifth ed. Academic Press, pp. 137–182. <https://doi.org/10.1016/B978-0-12-823292-7.00004-8>.
- Citepa, 2024a. Rapport Secten Éd. 2024 Émissions de gaz à effet de serre et de polluants atmosphériques en France, pp. 1990–2023.
- Citepa, 2024b. CEE-NU Inventaire des émissions de polluants atmosphériques en France au titre de la convention sur la pollution atmosphérique transfrontière à longue distance et de la directive européenne concernant la réduction des émissions nationales de certains polluants atmosphériques.

- Citepa, 2024c. OMINEA - 21Ème Édition Organisation Et Méthodes Des Inventaires Nationaux Des Émissions Atmosphériques En France.
- Citepa, 2025. Rapport Secten - Émissions De Gaz À Effet De Serre Et De Polluants Atmosphériques 1990-2024.
- Coufalík, P., Matoušek, T., Krůmal, K., Vojtíšek-Lom, M., Beránek, V., Mikuška, P., 2019. Content of metals in emissions from gasoline, diesel, and alternative mixed biofuels. *Environ. Sci. Pollut. Control Ser.* 26, 29012–29019. <https://doi.org/10.1007/s11356-019-06144-4>.
- Deguille, L., Leriche, M., Desboeufs, K., Mailhot, G., George, C., Chaumerliac, N., 2005. Transition metals in atmospheric liquid phases: sources, reactivity, and sensitive parameters. *Chem. Rev.* 105, 3388–3431. <https://doi.org/10.1021/cr040649c>.
- EMEP, 2024. 1.A.3.b.vi Road Transport: Automobile Tyre and Brake Wear & 1.A.3.b.vii Road Transport: Automobile Road Abrasion.
- EMEP, 2023. 5.C.2 Open Burning of Waste.
- European Environment Agency, 2023. Harm to Human Health from Air Pollution in Europe – Burden of Disease 2023. Publications Office of the European Union.
- Fang, T., Guo, H., Zeng, L., Verma, V., Nenes, A., Weber, R.J., 2017. Highly acidic ambient particles, soluble metals, and oxidative potential: a link between sulfate and aerosol toxicity. *Environ. Sci. Technol.* 51, 2611–2620. <https://doi.org/10.1021/acs.est.6b06151>.
- Fang, T., Lakey, P.S.J., Weber, R.J., Shiraiwa, M., 2019. Oxidative potential of particulate matter and generation of reactive oxygen species in epithelial lining fluid. *Environ. Sci. Technol.* 53, 12784–12792. <https://doi.org/10.1021/acs.est.9b03823>.
- Favez, O., Weber, S., Petit, J.-E., Alleman, L.Y., Albinet, A., Riffault, V., Chazeau, B., Amodeo, T., Salameh, D., Zhang, Y., Srivastava, D., Samaké, A., Aujay-Plourzeau, R., Papin, A., Bonnaire, N., Boullang, C., Chatain, M., Chevrier, F., Detournay, A., Dominik-Sègue, M., Falhug, R., Garbin, C., Ghersi, V., Grignon, G., Levigoureux, G., Pontet, S., Rangognio, J., Zhang, S., Besombes, J.-L., Conil, S., Uzu, G., Savarino, J., Marchand, N., Gros, V., Marchand, C., Jaffrezo, J.-L., Leoz-Garziandia, E., 2021. Overview of the French operational network for in situ observation of PM chemical composition and sources in urban environments (CARA Program). *Atmosphere* 12. <https://doi.org/10.3390/atmos12020207>.
- Fussell, J.C., Franklin, M., Green, D.C., Gustafsson, M., Harrison, R.M., Hicks, W., Kelly, F.J., Kishta, F., Miller, M.R., Mudway, I.S., Oroumijeh, F., Selley, L., Wang, M., Zhu, Y., 2022. A review of road traffic-derived non-exhaust particles: emissions, physicochemical characteristics, health risks, and mitigation measures. *Environ. Sci. Technol.* 56, 6813–6835. <https://doi.org/10.1021/acs.est.2c01072>.
- Gao, D., Ripley, S., Weichenthal, S., Godri Pollitt, K.J., 2020. Ambient particulate matter oxidative potential: chemical determinants, associated health effects, and strategies for risk management. *Free Radic. Biol. Med.* 151, 7–25. <https://doi.org/10.1016/j.freeradbiomed.2020.04.028>.
- Gerlofs-Nijland, M.E., Bokkers, B.G.H., Sachse, H., Reijnders, J.J.E., Gustafsson, M., Boere, A.J.F., Fokkens, P.F.H., Leseman, D.L.A.C., Augsburg, K., Cassee, F.R., 2019. Inhalation toxicity profiles of particulate matter: a comparison between brake wear with other sources of emission. *Inhal. Toxicol.* 31, 89–98. <https://doi.org/10.1080/08958378.2019.1606365>.
- Gietl, J.K., Lawrence, R., Thorpe, A.J., Harrison, R.M., 2010. Identification of brake wear particles and derivation of a quantitative tracer for brake dust at a major road. *Atmos. Environ.* 44, 141–146. <https://doi.org/10.1016/j.atmosenv.2009.10.016>.
- Glojek, K., Thuy, D.N.V., Weber, S., Manousakas, M., Uzu, G., Elazzouzi, R., Džepina, K., Darfeuil, S., Jaffrezo, J.L., Zăbkar, R., Turšič, J., Podkoritnik, A., Močnik, G., 2024. Annual variation of source contributions to PM10 and oxidative potential in a mountainous area with traffic, biomass burning, cement-plant and biogenic influences. *Environ. Int.* <https://doi.org/10.1016/j.envint.2024.108787>.
- Goddard, S.L., Williams, K.R., Robins, C., et al., 2019. Concentration trends of metals in ambient air in the UK: a review. *Environ. Monit. Assess.* 191, 683. <https://doi.org/10.1007/s10661-019-7824-2>.
- Gonet, T., Maher, B.A., 2019. Airborne, vehicle-derived Fe-Bearing nanoparticles in the urban environment: a review. *Environ. Sci. Technol.* 53, 9970–9991. <https://doi.org/10.1021/acs.est.9b01505>.
- Grigoratos, T., Martini, G., 2015. Brake wear particle emissions: a review. *Environ. Sci. Pollut. Control Ser.* 22, 2491–2504. <https://doi.org/10.1007/s11356-014-3696-8>.
- Hulskotte, J., Denier van der Gon, H., Visschedijk, A.J.H., Schaap, M., 2007. Brake wear from vehicles as an important source of diffuse copper pollution. *Water Sci. Technol. : a journal of the International Association on Water Pollution Research* 56, 223–231. <https://doi.org/10.2166/wst.2007.456>.
- Harrison, R.M., Allan, J., Carruthers, D., Heal, M.R., Lewis, A.C., Marnner, B., Murrells, T., Williams, A., 2021. Non-exhaust vehicle emissions of particulate matter and VOC from road traffic: a review. *Atmos. Environ.* 262, 118592. <https://doi.org/10.1016/j.atmosenv.2021.118592>.
- Hulskotte, J.H.J., Roskam, G.D., Denier van der Gon, H.A.C., 2014. Elemental composition of current automotive braking materials and derived air emission factors. *Atmos. Environ.* 99, 436–445. <https://doi.org/10.1016/j.atmosenv.2014.10.007>.
- Ito, A., Miyakawa, T., 2023. Aerosol Iron from metal production as a secondary source of bioaccessible Iron. *Environ. Sci. Technol.* 57, 4091–4100. <https://doi.org/10.1021/acs.est.2c06472>.
- Jandacka, D., Kovalova, D., Durcanska, D., Decky, M., 2021. Chemical composition, morphology, and distribution of particulate matter produced by road pavement abrasion using different types of aggregates and asphalt binder. *Cogent Engineering* 8, 1884325. <https://doi.org/10.1080/23311916.2021.1884325>.
- Kajino, M., Hagino, H., Fujitani, Y., Morikawa, T., Fukui, T., Onishi, K., Okuda, T., Kajikawa, T., Igarashi, Y., 2020. Modeling transition metals in East Asia and Japan and its emission sources. *GeoHealth* 4, e2020GH000259. <https://doi.org/10.1029/2020GH000259>.
- Karagulian, F., Belis, C.A., Dora, C.F.C., Prüss-Ustün, A.M., Bonjour, S., Adair-Rohani, H., Amann, M., 2015. Contributions to cities' ambient particulate matter (PM) : a systematic review of local source contributions at global level. *Atmos. Environ.* 120, 475–483.
- Lakey, P.S.J., Berkemeier, T., Tong, H., Arangio, A.M., Lucas, K., Pöschl, U., Shiraiwa, M., 2016. Chemical exposure-response relationship between air pollutants and reactive oxygen species in the human respiratory tract. *Sci. Rep.* 6, 32916. <https://doi.org/10.1038/srep32916>.
- Lelieveld, J., Evans, J.S., Fnais, M., Giannadaki, D., Pozzer, A., 2015. The contribution of outdoor air pollution sources to premature mortality on a global scale. *Nature* 525, 367–371. <https://doi.org/10.1038/nature15371>.
- Lelieveld, S., Wilson, J., Douvrou, E., Mishra, A., Lakey, P.S.J., Shiraiwa, M., Pöschl, U., Berkemeier, T., 2021. Hydroxyl radical production by air pollutants in epithelial lining fluid governed by interconversion and scavenging of reactive oxygen species. *Environ. Sci. Technol.* 55, 14069–14079. <https://doi.org/10.1021/acs.est.1c03875>.
- Liu, X., Zhang, X., Wang, T., Jin, B., Wu, L., Lara, R., Monge, M., Reche, C., Jaffrezo, J.-L., Uzu, G., Dominutti, P., Darfeuil, S., Favez, O., Conil, S., Marchand, N., Castillo, S., de la Rosa, J.D., Stuart, G., Eleftheriadis, K., Diapouli, E., Gini, M.I., Nava, S., Alves, C., Wang, X., Xu, Y., Green, D.C., Beddows, D.C.S., Harrison, R.M., Alastuey, A., Querol, X., 2024. PM10-bound trace elements in Pan-European urban atmosphere. *Environ. Res.* 260, 119630. <https://doi.org/10.1016/j.envres.2024.119630>. ISSN 0013-9351.
- Maciejczyk, P., Chen, L.-C., Thurston, G., 2021. The role of fossil fuel combustion emissions in PM2.5 Air Pollution health associations. *Atmosphere* 12. <https://doi.org/10.3390/atmos12091086>.
- Mbengue, S., Alleman, L.Y., Flament, P., 2017. Metal-bearing fine particle sources in a coastal industrialized environment. *Atmos. Res.* 183, 202–211. <https://doi.org/10.1016/j.atmosres.2016.08.014>. ISSN 0169-8095.
- Miazgowiec, A., Krennhuber, K., Lanzerstorfer, C., 2020. Metals concentrations in road dust from high traffic and low traffic area: a size dependent comparison. *Int. J. Environ. Sci. Technol.* 17, 3365–3372. <https://doi.org/10.1007/s13762-020-02667-3>.
- Moreno, T., Querol, X., Castillo, S., Alastuey, A., Cuevas, E., Herrmann, L., Mounkaila, M., Elvira, J., Gibbons, V., 2006. Geochemical variations in aeolian mineral particles from the Sahara-Sahel dust corridor. *Chemosphere* 65, 261–270. <https://doi.org/10.1016/j.chemosphere.2006.02.052>.
- Nicula, E.-A., Soporan, V., Ilea, P., Imre-Lucaci, F., Soporan, B., Bere, P., Nemes, O., 2012. Characterisation of generated ash from hazardous waste incineration. *Stud. Univ. Babeş-Bolyai, Chem.* 57, 147–156.
- Park, M., Joo, H.S., Lee, K., Jang, M., Kim, S.D., Kim, I., Borlaza, L.J.S., Lim, H., Shin, H., Chung, K.H., Choi, Y.-H., Park, S.G., Bae, M.-S., Lee, J., Song, H., Park, K., 2018. Differential toxicities of fine particulate matters from various sources. *Sci. Rep.* 8, 17007. <https://doi.org/10.1038/s41598-018-35398-0>.
- Pernigotti, D., Belis, C.A., Spanò, L., 2016. SPECIEUROPE: the European data base for PM source profiles. *Atmos. Pollut. Res.* 7, 307–314. <https://doi.org/10.1016/j.apr.2015.10.007>.
- Pey, J., Querol, X., Alastuey, A., Forastiere, F., Stafoggia, M., 2013. African dust outbreaks over the Mediterranean Basin during 2001–2011: PM10 concentrations, phenomenology and trends, and its relation with synoptic and mesoscale meteorology. *Atmos. Chem. Phys.* 13, 1395–1410. <https://doi.org/10.5194/acp-13-1395-2013>.
- Raclavská, H., Corsaro, A., Hartmann-Koval, S., Juchelková, D., 2017. Enrichment and distribution of 24 elements within the sub-sieve particle size distribution ranges of fly ash from wastes incinerator plants. *J. Environ. Manag.* 203, 1169–1177. <https://doi.org/10.1016/j.jenvman.2017.03.073>.
- Reff, A., Bhavne, P.V., Simon, H., Pace, T.G., Pouliot, G.A., Mobley, J.D., Houyoux, M., 2009. Emissions inventory of PM2.5 trace elements across the United States. *Environ. Sci. Technol.* 43, 5790–5796. <https://doi.org/10.1021/es802930x>.
- See, S.W., Wang, Y.H., Balasubramanian, R., 2007. Contrasting reactive oxygen species and transition metal concentrations in combustion aerosols. *Environ. Res.* 103, 317–324. <https://doi.org/10.1016/j.envres.2006.08.012>.
- Shahpoury, P., Zhang, Z.W., Arangio, A., Celso, V., Dabek-Zlotorzynska, E., Harner, T., Nenes, A., 2021. The influence of chemical composition, aerosol acidity, and metal dissolution on the oxidative potential of fine particulate matter and redox potential of the lung lining fluid. *Environ. Int.* 148, 106343. <https://doi.org/10.1016/j.envint.2020.106343>.
- Shiraiwa, M., Ueda, K., Pozzer, A., Lammel, G., Kampf, C.J., Fushimi, A., Enami, S., Arangio, A.M., Fröhlich-Nowoisky, J., Fujitani, Y., Furuyama, A., Lakey, P.S.J., Lelieveld, J., Lucas, K., Morino, Y., Pöschl, U., Takahama, S., Takami, A., Tong, H., Weber, B., Yoshino, A., Sato, K., 2017. Aerosol health effects from molecular to global scales. *Environ. Sci. Technol.* 51, 13545–13567. <https://doi.org/10.1021/acs.est.7b04417>.
- Skeaff, J.M., Dubreuil, A.A., 1997. Calculated 1993 emission factors of trace metals for Canadian non-ferrous smelters. *Atmos. Environ.* 31, 1449–1457. [https://doi.org/10.1016/S1352-2310\(96\)00319-6](https://doi.org/10.1016/S1352-2310(96)00319-6).
- Sylvestre, A., Mizzi, A., Mathiot, S., Masson, F., Jaffrezo, J.L., Dron, J., Mesbah, B., Wortham, H., Marchand, N., 2017. Comprehensive chemical characterization of industrial PM2.5 from steel industry activities. *Atmos. Environ.* <https://doi.org/10.1016/j.atmosenv.2016.12.032>.
- Turn, S.Q., Jenkins, B.M., Chow, J.C., Pritchett, L.C., Campbell, D., Cahill, T., Whalen, S.A., 1997. Elemental characterization of particulate matter emitted from biomass burning: wind tunnel derived source profiles for herbaceous and wood fuels. *J. Geophys. Res. Atmos.* 102, 3683–3699. <https://doi.org/10.1029/96JD02979>.

- Vithanage, M., Bandara, P.C., Novo, L.A.B., Kumar, A., Ambade, B., Naveendrakumar, G., Ranagalage, M., Magana-Arachchi, D.N., 2022. Deposition of trace metals associated with atmospheric particulate matter: environmental fate and health risk assessment. *Chemosphere* 303, 135051. <https://doi.org/10.1016/j.chemosphere.2022.135051>.
- Wang, R., Balkanski, Y., Boucher, O., Bopp, L., Chappell, A., Ciaia, P., Hauglustaine, D., Peñuelas, J., Tao, S., 2015. Sources, transport and deposition of iron in the global atmosphere. *Atmos. Chem. Phys.* 15, 6247–6270. <https://doi.org/10.5194/acp-15-6247-2015>.
- Weber, S., Hoffmann, P., Ensling, J., Dedik, A.N., Weinbruch, S., Miehe, G., Gütlich, P., Ortner, H.M., 2000. Characterization of iron compounds from urban and rural aerosol sources. *J. Aerosol Sci.* 31, 987–997. [https://doi.org/10.1016/S0021-8502\(99\)00564-9](https://doi.org/10.1016/S0021-8502(99)00564-9).
- Wei, J., Fang, T., Lakey, P.S.J., Shiraiwa, M., 2022. Iron-facilitated organic radical formation from secondary organic aerosols in surrogate lung fluid. *Environ. Sci. Technol.* 56, 7234–7243. <https://doi.org/10.1021/acs.est.1c04334>.
- Weichenthal, S., Eric, Lavigne, Alison, Traub, Dana, Umbrio, You, Hongyu, Krystal, Pollitt, Shin, Tim, Kulka, Ryan, Stieb, Dave M., Jill, Korsiak, Barry, Jessiman, Brook, Jeff R., Hatzopoulou, Marianne, Evans, Greg, Burnett, Richard T., 2021. Association of sulfur, transition metals, and the oxidative potential of outdoor PM<sub>2.5</sub> with acute cardiovascular events: a case-crossover study of Canadian adults. *Environ. Health Perspect.* 129, 107005. <https://doi.org/10.1289/EHP9449>.
- West, J.J., Cohen, A., Dentener, F., Brunekreef, B., Zhu, T., Armstrong, B., Bell, M.L., Brauer, M., Carmichael, G., Costa, D.L., Dockery, D.W., Kleeman, M., Krzyzanowski, M., Künzli, N., Liousse, C., Lung, S.-C.C., Martin, R.V., Pöschl, U., Pope, C.A.I., Roberts, J.M., Russell, A.G., Wiedinmyer, C., 2016. What we breathe impacts our health: improving understanding of the link between air pollution and health. *Environ. Sci. Technol.* 50, 4895–4904. <https://doi.org/10.1021/acs.est.5b03827>.
- Zhou, J., Wu, S., Pan, Y., Zhang, L., Cao, Z., Zhang, X., Yonemochi, S., Hosono, S., Wang, Y., Oh, K., Qian, G., 2015. Enrichment of heavy metals in fine particles of municipal solid waste incinerator (MSWI) fly ash and associated health risk. *Waste Manag.* 43, 239–246. <https://doi.org/10.1016/j.wasman.2015.06.026>.