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Title: Sources, transport and deposition of iron in the global atmosphere

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Referee 1 (C. Pérez García-Pando)

Comment 1

The paper proposes a new emission inventory of Fe from combustion sources, and estimates and evaluates the global size-resolved Fe emission, concentration and deposition, including the contribution from natural dust sources using a recently published mineralogical soil database. In my opinion, this work is impressive and represents a significant step forward towards constraining the deposition of soluble iron into ocean waters. I only have some minor comments that intend to clarify a few aspects of the paper and allow the reproducibility of the method by other modelers.

Response

Thank you very much for the reviewer's positive comments. Please see a point-to-point response to specific comments in the following.

Comment 2

Section 2.1: With respect to equation 1 and its description, please provide in the form of table(s) in the Supplementary material the values and ranges of all the parameters included in the equation that are used to calculate the emissions. Some of these values and ranges appear in the text, but others are missing (for example A_y). Please provide a comprehensive table.

Response

Thank you for the good comment. According to the comment, we added in the revised manuscript a new Table, **Table 1** that lists all parameters used in estimating the emissions. A_y is computed by country and time using an empirical method. We describe the method in **Table 1**, but the parameters used in the functions are referred to a Table in the published paper (*Table S1* of Wang et al., 2014) to avoid repeating.

Table 1. Parameters used in the estimation of Fe emissions from combustion sources.

Parameter	Description	Values or data sources
<i>a</i>	Fuel consumption	The fuel data was taken from a global 0.1 °×0.1 ° fuel data set which is used to construct a global CO ₂ emission inventory (Wang et al., 2013; available at http://inventory.pku.edu.cn/home.html).
<i>b</i>	Completeness of combustion	<ul style="list-style-type: none">■ coal (98%);■ petroleum (98%);■ wood in stoves (88%);■ wood in fireplaces (79%);■ crop residues (92%);■ biomass burning (considered in van der Werf, 2010).
<i>c</i>	Fe content of the fuel	<ul style="list-style-type: none">■ coal: based on Fe contents in coal produced by country (Table S2) and an international coal-trading matrix (Chen et al., 2014);■ wood (a geometric mean of 0.036% and range in Fig. S1);■ crop residues (a geometric mean of 0.060% and range in Fig. S1);■ grass (a geometric mean of 0.027% and range in Fig. S1);■ dung cakes (0.13 ± 0.09 %);■ biodiesel (0.00024 ± 0.00023 %);■ heavy fuel oil (32 ± 2 ppm);■ diesel (13 ± 7 ppm);■ gasoline (3.3 ± 2.6 ppm);

		<ul style="list-style-type: none"> ■ liquefied petroleum gas (4.9 ± 3.3 ppm).
f	Fraction of Fe retained in residue ash relative to the amount of Fe in the burnt fuel	<ul style="list-style-type: none"> ■ coal used in industry and power plants (30-45%); ■ petroleum used in industry and power plants (43-58%); ■ solid biofuels used in industry and power plants (60-70%); ■ petroleum consumed by motor vehicles (2-12%); ■ anthracite coal used in the residential sector (99.2-99.8%); ■ bituminous coal used in the residential sector (91-97%); ■ straw used in the residential sector (79-95%); ■ wood used in the residential sector (89-99%); ■ forest fires (49-98%); ■ savanna fires (24-79%); ■ deforestation (43-50%); ■ woodland fires / peat fires (41-56%).
J_x	Fraction of Fe emitted in a particle size	<ul style="list-style-type: none"> ■ coal fly ash (0.1-0.3% in PM_1; 10-30% in PM_{1-10}; the remainder in $PM_{>10}$); ■ oil fly ash (80-95% in PM_1; the remainder in PM_{1-10}); ■ biomass fly ash (1-3% in PM_1; 50-60% in PM_{1-10}; the remainder in $PM_{>10}$).
A_y	Fraction of a specific control device	<p>A_y is computed for each country and each year using a function by Grubler et al. (1999) and Bond et al. (2007):</p> <p>$A_y = (F_0 - F_f) \exp[-(t - t_0)/2s^2] + F_f$, where F_0 and F_f are the initial and final fractions of the technology, t_0 is transition beginning time, and s is transition rate. Parameters were determined for developing or developed countries and listed in Wang et al. (2014a).</p>
$R_{x,y}$	Removal efficiency for each particle size by different control device (Zhao et al., 2008)	<ul style="list-style-type: none"> ■ cyclone (10% for PM_1; 70% for PM_{1-10}; 90% for $PM_{>10}$); ■ scrubber (50% for PM_1; 90% for PM_{1-10}; 99% for $PM_{>10}$); ■ electrostatic precipitator (93.62% for PM_1; 97.61% for PM_{1-10}; 99.25% for $PM_{>10}$).

References:

Wang, R., Tao, S., Shen, H. Z., Huang, Y., Chen, H., Balkanski, Y., Boucher, O., Ciais, P., Shen, G. F., Li, W., Zhang, Y. Y., Chen, Y. C., Lin, N., Su, S., Li, B. G., Liu, J. F., and Liu, W. X.: Trend in global black carbon emissions from 1960 to 2007, Environ. Sci. Technol., 48, 6780–6787, doi:10.1021/Es5021422, 2014.

Comment 3

Section 2.4: The gridded fuel data (PK-FUEL) doesn't seem to be available from the web page announced in the text. If is announced as available, please make it available.

Response

Sorry for the misleading information. Unfortunately, we cannot release original fuel data in our web page at present due to policies using some data products developed by other groups, but the fuel data can be converted from the CO₂ emissions in the PKU-CO₂ inventory with CO₂ emission factors. The sentence on line 22 page 7653 was revised as: “*The annual emissions of Fe were estimated based on the 0.1° gridded fuel data which is used to construct a global CO₂ emission inventory (Wang et al., 2013; available at <http://inventory.pku.edu.cn/home.html>).*”.

Comment 4

Section 2.6: Emissions of Fe from mineral sources. Please provide in the text the assumed Fe content for each mineral.

Response

Thank you for the comment. The content of Fe in each mineral is listed in the revised manuscript, and the following sentence was added on line 22, page 7654: “*Then, a global 0.5° × 0.5° map of Fe content in clay fraction was obtained (Fig. S2) with the Fe content of each mineral (4.3% for illite, 2.6% for smectite, 0.23% for kaolinite, 12.5% for chlorite, 6.7% for vermiculite, 0.34% for feldspars, 62.8% for goethite and*

69.9% for hematite) measured in Journet et al. (2008) and compiled in Journet et al. (2013).”.

Comment 5

In contrast to combustion sources, the uncertainty calculated for Fe from dust only accounts for the uncertainty in the emission. I would suggest (at least) acknowledging that the elemental composition (and therefore the iron content) in each of the minerals can be regionally variable in nature, which adds additional uncertainty.

Response

Thank you for the comment. Due to lack of a global distribution of elemental composition in minerals, we acknowledge this uncertainty in the revised text. Accordingly, the following sentence was added in Section 2.6: “*Note that we only account for the variation of dust emissions when assessing the uncertainty in Fe emissions from dust. However, there is also a variation of elemental composition of minerals in nature. For example, the Fe content can vary from 0.8 to 8.4% in illite depending on the environmental condition (Murad and Wagner, 1994), and from 0.02 to 0.81% in kaolinite (Mestdagh et al., 1980). This uncertainty is not accounted for in our study due to lack of a global distribution of elemental composition in minerals.*”.

Comment 6

Section 2.7: Please clarify and detail the following issues: What is the assumption behind your treatment of sedimentation, dry and wet deposition for Fe in PM₁₋₁₀ and PM_{>10} as if it was dust? Are you assuming the same density as dust? Are you treating the combustion Fe as hydrophobic in those size ranges? Is there heterogeneous chemistry for dust (and therefore they can be in-cloud scavenged)? Please provide further details and justification.

Response

Sorry for missing these informations. According to the comment, hygroscopic growth, density of particles, and hygroscopic properties of Fe are described in the revised manuscript. Accordingly, the third paragraph in **Section 2.7** was re-written as: “*The emitted Fe from combustion sources were partitioned into three particulate modes with the following characteristics: Fe in PM₁ as a fine mode (MMD = 0.34 μm, geometric σ = 1.59); Fe in PM₁₋₁₀ as a coarse mode (MMD = 3.4 μm, geometric σ = 2.0); Fe in PM_{>10} as a super coarse mode (MMD = 34.0 μm, geometric σ = 2.0) (Mamane et al., 1986; Querol et al., 1995; Valmari et al., 1999). Hygroscopic growth, sedimentation, dry and wet deposition accounted for Fe in PM₁₋₁₀ and PM_{>10}, as for dust, and Fe in PM₁ as for BC (Balkanski et al., 2004, 2010, 2011). Hygroscopic growth of particles in the model is treated as a function of ambient relative humidity and the composition of soluble aerosol components based on Gerber’s experiment work (Gerber, 1988). The uptake of water on aerosols increases the particle size of Fe, while the loss of water on aerosols decreases the particle size of Fe. For the particle density, the fraction of low density mass in coal fly ash is found to increase with decreasing particle size (Furuya et al., 1987). The major fraction for particles with a diameter less than 10 μm is composed by mass with a density of 2.4-2.8 g cm⁻³, and by mass with a density of 1.6-2.4 g cm⁻³ for particles with a diameter from 10 to 100 μm. Therefore, we applied a density of 2.6 and 2.0 g cm⁻³ for Fe transported in PM₁₋₁₀ and PM_{>10} respectively in the model. For Fe in PM₁, we assumed that the density is the same as BC (1.5 g cm⁻³). For the hygroscopic properties of Fe, it is found that Fe in large-size coal ash is dominated in aluminosilicate glass, similar to that in dust (Chen et al., 2012), and thus we assume that the Fe in PM₁₋₁₀ and PM_{>10} can be treated as insoluble dust, which is removed by sedimentation, dry deposition and below-cloud scavenging. For the Fe in PM₁, it is found that approximately 25% of Fe in fine particle (diameter < 0.61 μm) is bound to organic matter and thus insoluble (Espinosa et al., 2002). Thus, we assumed that 25% of Fe in PM₁ was hydrophobic, which is removed by sedimentation, dry deposition and below-cloud scavenging, but not by in-cloud scavenging. The remainder Fe in PM₁ was hydrophilic, which is removed by sedimentation, dry deposition, below-cloud scavenging, and in-cloud scavenging. Due*

to limited understanding of the heterogeneous chemistry of Fe in the cloud, we did not account for the conversion of Fe from hydrophobic to hydrophilic in the atmospheric transport, and the ratio between the two phases varies due to their different removal rates in the atmosphere.”.

Comment 7

Section 3.5: I am confused by the last sentence of the section. Wouldn't it be desirable to have dust and plant material in the Fe emission estimates from biomass burning? Why would be Luo et al. overestimating? Perhaps just note that their estimates are larger than yours partly because their estimates implicitly include additional sources of Fe.

Response

Thank you very much for the good comment. Now, we realized that our lower estimates of the biomass burning emissions of Fe than previous studies is likely caused by the fact that previous estimates include the part by pyro-convection of Fe from soil and plant materials. In contrast, since we estimated the emissions based on the difference of Fe mass initially present in the fuel and that in the post-burn residues, rather than on the atmospheric concentration of Fe, we could miss the emissions of Fe by pyro-convection. Although our estimate provides a more explicit source attribution of Fe in the atmosphere, it could underestimate the total source. Accordingly, the sentences on line 20-24, page 7661 were revised as: *“Note that the dust and plant material entrained in fires can contribute to the Fe concentrations in the atmosphere, as noticed by Luo et al. (2008). As a result, their estimates include the pyro-convection of Fe from soils and plant materials. In contrast, our estimate is based on the mass balance of Fe from the burnt fuel. This might explain partly why our estimate of the biomass burning emission of Fe is lower than that in previous studies (Luo et al., 2008; Ito, 2013). Although our estimate provides an explicit source attribution of Fe, which is useful for modelling the Fe solubility, it underestimates the total sources. We propose that the emissions of Fe by pyro-convection in the fires should be estimated separately in the future.”.*

Comment 8

Section 4.2 Please note that the overestimation of iron from dust may not come (at least not all of it) from the assumption that the composition of dust resembles the composition of clay. Clay minerals form aggregates of larger sizes and the mineralogy database is mostly based on wet sieving that breaks the aggregates into small clay-sized particles.

Response

Thank you for the good comment. Accordingly, the following sentences were added on line 6, page 7664: *“In addition, when compiling data in the mineralogy database, Journet et al. (2014) noticed that wet sieving is used to determine soil texture, leading to loss of soluble minerals (e.g., calcite or gypsum) and a possible overestimation of the content of minerals rich in Fe such as hematite and goethite. This impact might also contribute to an overestimation of Fe content in dust.”.*

Comment 9

Section 4.6. This section needs further detail (this is connected to my previous comment on sedimentation, dry and wet deposition). The authors analyze the wet MMD. It would be very helpful to understand how this is treated in this specific model.

Response

Thank you for the good comment. The following paragraph was added on line 21-23, page 7667 to explain the mechanisms changing the size of Fe: *“According to Schulz et al. (2007), after the particles containing Fe are emitted into the atmosphere, there are three major processes that change the size distributions in the model. First, formation of sulphate increases the aerosol mass in the accumulation mode and, since the particle number is kept constant, the aerosol diameter increases for Fe in PM₁. Second, removing processes such as sedimentation removes the larger particles more efficiently, shifting the mode diameter to a smaller one for Fe in PM₁, PM₁₀ and PM_{>10}. At last, the hygroscopic growth creates instantaneous changes in the size of particles as a function of ambient relative humidity (Schulz et al., 2007), and the uptake of water on aerosols increases the size, while the loss of water on aerosols decreases the size. Therefore, the change of the size of Fe is dependent on the relative importance of the mechanisms increasing / decreasing the size.*

For example, the size of Fe in PM_{10} emitted from coal combustion increased from $0.3\ \mu\text{m}$ to $>2\ \mu\text{m}$ after being transported away from the source regions, because the hygroscopic growth by uptake of water on aerosol particles are more important. In contrast, the size of Fe in $PM_{>10}$ emitted from coal combustion in East Asia decreases over the southern Pacific Ocean, because sedimentation is the dominating process. The size of Fe in $PM_{>10}$ from coal combustion would decrease from $33\ \mu\text{m}$ in the source regions to $<10\ \mu\text{m}$ over the oceans.”. Please also refer to our response to **Comment 6** for a description of the treatment of Fe in the model.

Comment 10

Page 7667, line 28: replace “of two mechanisms” by “of the two mechanisms” (this refers to mechanisms presented before and the omission of “the” creates confusion when reading.)

Response

Thanks for correcting the confusion, and “*of two mechanisms*” was revised as “*of the mechanisms increasing / decreasing the size*”.

Comment 11

Page 7670, line 5: “orders of magnitude” instead of “magnitudes”

Response

Revised accordingly.

Comment 12

Caption of Figure 1: the Fe emission is log-transformed but the x-axis is not on log-scale

Response

Sorry for the problem. Figure 1 is plotted on a log-scale x-axis (as below).

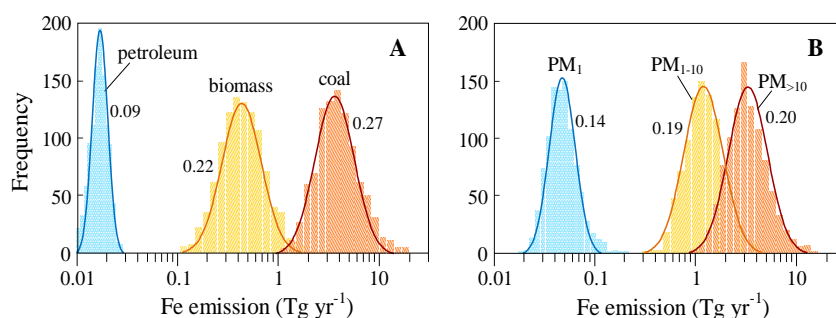


Figure 1. Frequency distributions of Fe emissions from different fuel types (A) and particle sizes (B). The distributions are derived from 1000 Monte Carlo simulations. The standard deviation of \log_{10} -transformed Fe emissions is shown for each distribution. The x-axis is plotted on a log scale.

Comment 13

Caption of Figure 7: measurement instead of measuring

Response

Thank you for the comment. Revised accordingly.

Comment 14

Figure 9: One cannot distinguish the colors for the dust and combustion contributions

Response

Sorry for the unclear figure. In the revised version, Figure 9 was plotted with contrasting colors for the dust and combustion contributions (as below).

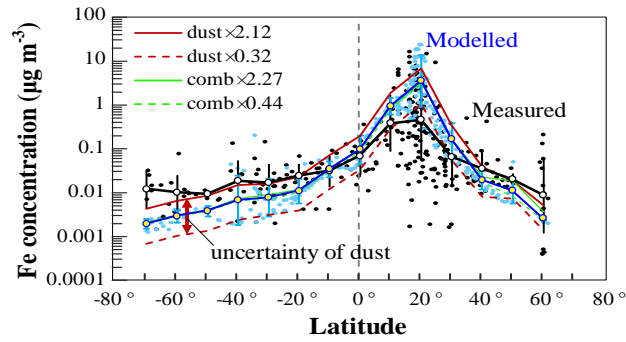


Figure 9. Zonal distribution of modelled (cyan dots) and measured (black dots) Fe concentrations attached to aerosols in surface air over the Atlantic Ocean from 70 °S to 60 °N. The solid lines with circles show the modelled (blue) and measured (black) Fe concentrations as geometric means in each band with error bars for the geometric standard deviations. As sensitivity tests, Fe concentrations from mineral sources were scaled by factors of 0.32 and 2.12 (solid and dashed red lines) as 90% uncertainties in dust emissions (Huneus et al., 2011) and Fe concentrations from combustion sources were scaled by factors of 0.44 and 2.27 (solid and dashed green lines) as 90% uncertainties in Fe emissions from combustion.

Comment 15

Figure 10: Why do you show the median of the observations? You also show the median of the model or the mean? Please describe

Response

Thank you for the comment. We were using the median concentrations in the measurements, because we were trying to minimize the impact of very high or low concentrations on a specific day measured during 1988-1994. In the previous version, the modelled concentration was computed as the monthly mean. To be consistent, we computed medians in the model in the revised version (the mean and median is very close in the model). To make it clear, the following sentence was revised in the capture of Figure 10: “*Modelled Fe concentrations are derived from all sources (Fe_{total}) and from mineral sources only (Fe_{dust}) as medians of all days for each month in 2005.*”.