Supporting Information For:

Water-soluble iron correlation to speciated organics in low-emitting vehicle exhaust

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Summary of Supporting Information:

11 Pages (excluding cover): SI1- SI8

Figure SI1: Linear correlation plots representing EF in mg kg-fuel^{-1} for sulfate, organic carbon (OC), CO_2 and EF in µg kg-fuel^{-1} for water-souluble iron. Correlation lines and R^2 values for all elements are shown.

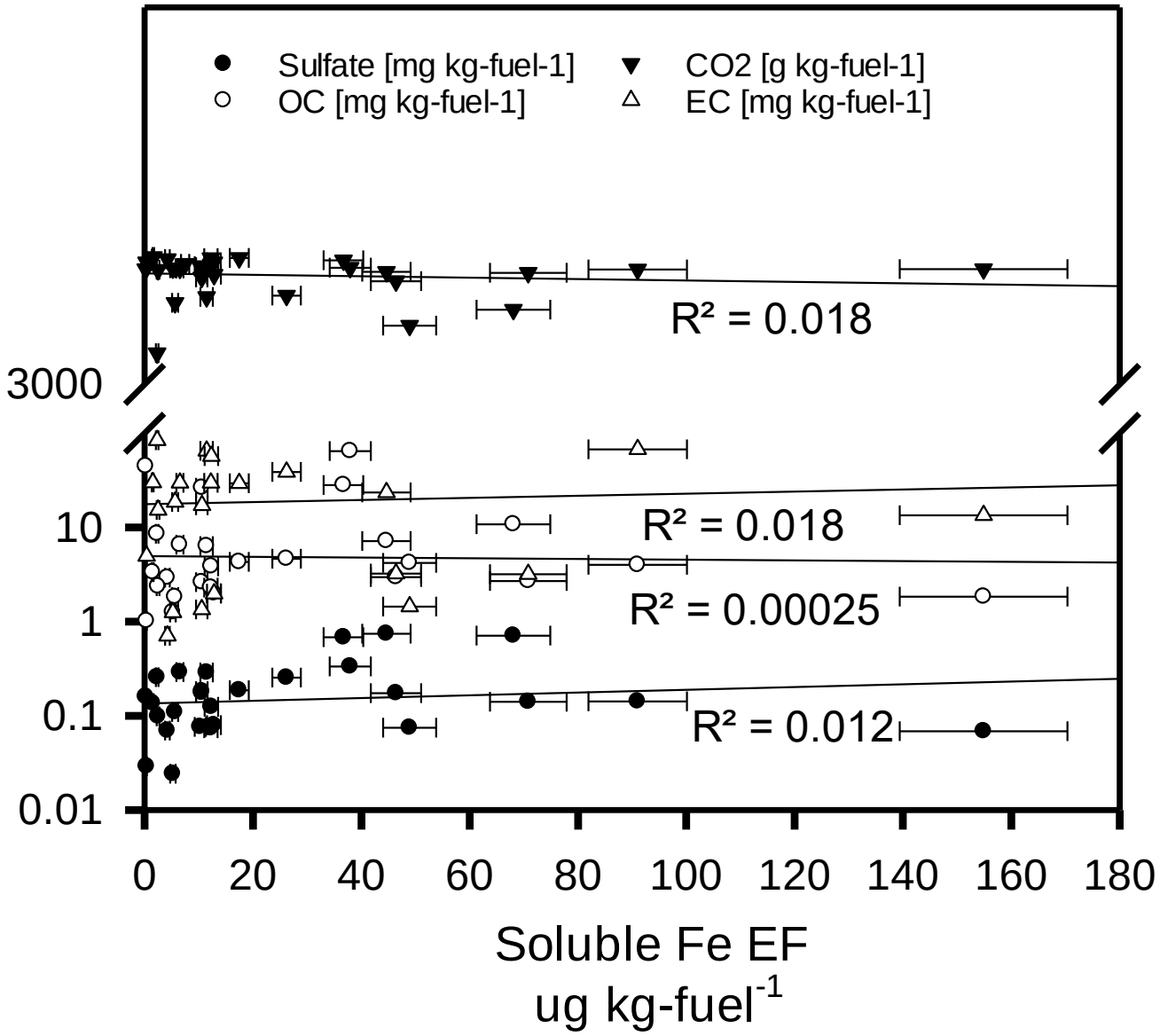

Figure SI2: Linear correlation plots representing EF in µg kg-fuel^{-1} for water-souluble iron and total iron. Correlation lines and R^2 shown.

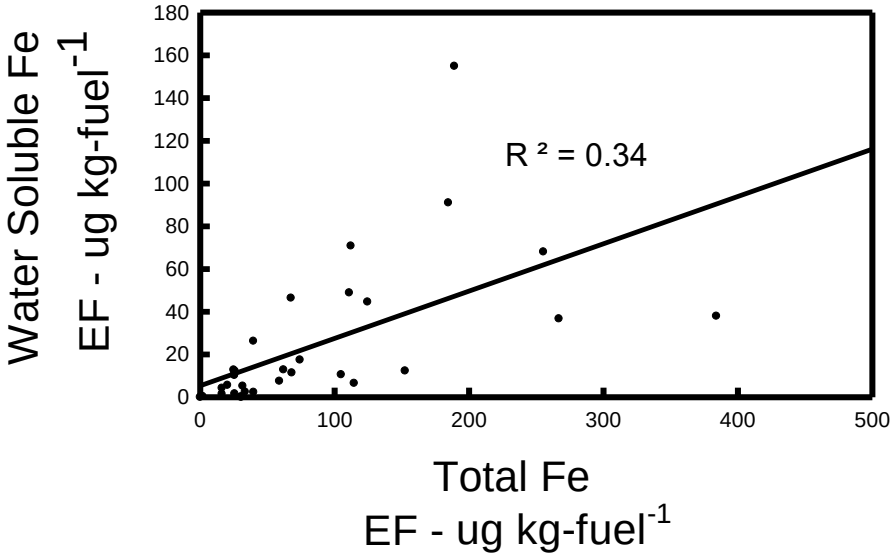

Figure SI3: Water-soluble irons correlation to organic species. (M = methyl, E = Ethyl, CY = Cyclo)

Organic Name	Relationship to water-soluble iron (R^2)
(1-ME)benzene	0.06
(1-Mpropyl)benzene	0.04
(2-Mpropyl)benzene	0.00
1,2,3,4-tetraMbenzene	0.04
1,2,3,5-tetraMbenzene	0.04
1,2,3-triMbenzene	0.05
1,2,4,5-tetraMbenzene	0.06
1,2,4-triMCYpentane	0.03
1,2,4-triMbenzene	0.07
1,2-butadiene	0.04
1,2-diEbenzene	0.03
1,2-diM-3-Ebenzene	0.03
1,2-diM-4-Ebenzene	0.06
1,2-propadiene	0.01
1,3,5-triMCYhexane	0.07
1,3,5-triMbenzene	0.09
1,3-CYpentadiene	0.00
1,3-butadiene	0.03
1,3-butadiyne	0.00
1,3-di-npropylbenzene	0.02
1,3-diEbenzene	0.08
1,3-diM-2-Ebenzene	0.00
1,3-diM-4-Ebenzene	0.05
1,3-diM-5-Ebenzen e	0.05
1,4-diEbenzene	0.03
1,4-diM-2-Ebenzene	0.07
1-(diME)-2-Mbenzene	0.00
1-(diME)-3,5-diMbenzene	0.03
1-E-2-npropylbenzene	0.03
1-E-tertbutylether	0.00
1-M-2-(1-ME)benzene	0.04
1-M-2-Ebenzene	0.05
1-M-2-n-butylbenzene	0.10
1-M-2-n-propylbenzene	0.05
1-M-3-(1-ME)benz ene	0.04
1-M-3-Ebenzene	0.08
1-M-3-n-propylbenzene	0.05

1-M-4-(1-ME)benzene	0.03
1-M-4-ECYhexane	0.38
1-M-4-Ebenzene	0.07
1-M-4-n-propylbenzene	0.05
1-MCYpentene	0.00
1-buten-3-yne	0.15
1-butene	0.07
1-butyne	0.00
1-heptene	0.00
1-hexene	0.01
1-nonene	0.03
1-octene	0.00
1-pentene	0.04
1-propyne	0.00
1a,2a,3b-triMCYpentane	0.07
2,2,3-triMbutane	0.15
2,2,4-triMheptane	0.03
2,2,4-triMhexane	0.04
2,2,4-triMpentane	0.00
2,2,5-triMheptane	0.05
2,2,5-triMhexane	0.01
2,2-diM-octane	0.02
2,2-diMhexane	0.00
2,2-diMpentane	0.02
2,2-diMpropane	0.00
2,3,3-triMpentane	0.00
2,3,4-triMpentane	0.04
2,3,5-triMhexane	0.04
2,3-diM-1-butene	0.06
2,3-diM-2-pentene	0.01
2,3-diM-octane	0.00
2,3-diMbutane	0.02
2,3-diMheptane	0.01
2,3-diMhexane	0.08
2,3-diMpentane	0.03
2,4,4-triM-1-pentene	0.01
2,4,4-triM-2-pentene	0.31
2,4,4-triMhexane	0.07
2,4-diM-1-pentene	0.01
2,4-diM-2-pentene	0.00
2,4-diM-octane	0.01
2,4-diMheptane	0.07

2,4-diMhexane	0.04
2,4-diMpentane	0.04
2,5-diM-octane	0.05
2,5-diMhexane	0.04
2,6-diM-octane	0.00
2,6-diMheptane	0.01
2-M-1,3-butadiene	0.16
2-M-1-butene	0.11
2-M-1-pentene	0.12
2-M-2-butene	0.20
2-M-2-hexene	0.05
2-M-2-pentene	0.12
2-M-indan	0.05
2-M-octane	0.00
2-M-t-3-hexene	0.06
2-Mbutane	0.01
2-Mheptane	0.04
2-Mhexane	0.04
2-Mnonane	0.05
2-Mpentane	0.03
2-Mpropene	0.06
2-butyne	0.00
3,3-diM-1-butene	0.00
3,3-diM-octane	0.05
3,3-diMhexane	0.58
3,3-diMpentane	0.01
3,4-diM-1-pentene	0.03
3,4-diMhexane	0.03
3,5-diMheptane	0.06
3-E-2-pentene	0.05
3-Epentane	0.04
3-M-1-butene	0.06
3-M-1-hexene	0.00
3-M-1-pentene	0.01
3-M-c-2-hexene	0.25
3-M-c-2-pentene	0.00
3-Moctane	0.05
3-M-t-2-pentene	0.55
3-M-t-3-hexene	0.01
3-MCYpentene	0.02
3-Mheptane	0.03
3-Mhexane	0.04

3-Mpentane	0.02
4-M-1-pentene	0.01
4-M-c-2-pentene	0.00
4-M-indan	0.03
4-M-octane	0.06
4-M-t-2-hexene	0.01
4-M-t-2-pentene	0.05
4-Mheptane	0.04
5-M-indan	0.08
CYhexane	0.00
CYhexene	0.04
CYpentane	0.02
CYpentene	0.18
ECYhexane	0.10
ECYpentane	0.05
Ebenzene	0.09
Ethane	0.00
M-tertbutyl-ether	0.00
MCYhexane	0.02
MCYpentane	0.03
MEketone	0.00
Methane	0.00
Mpropane	0.00
acetaldehyde	0.03
acetone	0.06
acrolein	0.02
benzaldehyde	0.02
benzene	0.09
butyraldehyde	0.03
c-1,2-diMCYhexane	0.19
c-1,3-diMCYhexane	0.04
c-1,3-diMCYpentane	0.03
c-1-M-3-ECYpentane	0.00
c-2-butene	0.10
c-2-heptene	0.01
c-2-hexene	0.10
c-2-octene	0.02
c-2-pentene	0.04
c-3-hexene	0.16
crotonaldehdye	0.00
ethanol	0.06
ethene	0.07

ethyne	0.01
formaldehyde	0.04
hexanal	0.00
indan	0.10
m-tolualdehyde	0.01
m-xylene	0.07
methacrolein	0.03
methanol	0.00
n-butane	0.00
n-decane	0.02
n-dodecane	0.02
n-heptane	0.05
n-hexane	0.03
n-nonane	0.04
n-octane	0.04
n-pentane	0.01
n-pentylbenzene	0.03
n-propylbenzene	0.05
n-undecane	0.04
o-xylene	0.07
p-xylene	0.07
propane	0.01
propene	0.06
propionaldehyde	0.08
styrene	0.04
t-1,2-diMCYpentane	0.04
t-1,3-diMCYhexane	0.04
t-1,3-diMCYpentane	0.05
t-1,3-pentadiene	0.00
t-1,4-diMCYhexane	0.04
t-1-M-3-ECYpentane	0.05
t-2-butene	0.07
t-2-heptene	0.06
t-2-hexene	0.03
t-2-octene	0.08
t-2-pentene	0.04
t-3-heptene	0.10
t-3-hexene	0.02
t-4-octene	0.48
toluene	0.08
valeraldehyde	0.04

Figure SI4: Results of Least-square linear combination fitting (LCF) of Fe K-edge XANES. Spectra were fitted in the range 7090 to 7365 eV.

Sample	%	Component 1	%	Component 2	%	Component 3	Sum	*NSS* x10^{-4}
1	50	Biogenic FeIII oxyhy	32	Maghemite	18	NKT-1g basalt glass	100	0.74
2	59	FeIII sulfate	31	Biogenic Fe(III) oxyhy	10	Almandine	100	1.28
4	63	Hematite	14	Pigeonite	23	Roedderite	100	1.2
5	26	Coalingite	61	Hematite	13	Maghemite	100	1.06
6	49	FeIII dextran	14	Kaolinite	37	Lepidocrocite	100	0.7
7	19	FeIII sulfate	20	FeIII dextran	61	Ferrihydrite_2L	100	0.49
8	41	FeIII dextran	59	Maghemite	NA	NA	100	2.27
9	10	Almandine	83	FeIII sulfate	7	Roedderite	100	1.48
10	10	Almandine	84	Ferrihydrite_2L	6	FeSi	100	0.73
11	37	Awaruite	17	Fe3C	46	Fe3Si	100	2.07
12	25	FeIII phosphate hydrate	20	FeIII dextran	55	Ferrihydrite_2L	100	0.69
13	76	Hematite	24	Coalingite	NA	NA	100	1.59
14	56	FeIII sulfate	26	FeIII pyrophosphate	18	Goethite	100	0.94
15	28	Fe3C	33	Fe3Si	39	Aegirine	100	1.35
16	67	FeIII dextran	14	Goethite	19	Jarosite	100	1.13
17	7	Almandine	62	FeIII Kaolinite	31	Maghemite	100	1.32

Notes: Normalized sum-square value ($NSS=100\times[\sum(\mu_{exp}-\mu_{fit})^2/\sum(\mu_{exp})^2]$). Error on the percentages of species is estimated to be ±10%. Biogenic FeIII oxyhy is biogenic Fe(III) oxyhydroxide*

* Toner, B., Santelli, C. M., Marcus, M. A., Wirth, R., Chan, C. S., McCollum, T., Bach, W., Edwards, K. J. (2009) "Biogenic iron oxyhydroxide formation at mid-ocean ridge hydrothermal vents: Juan de Fuca Ridge" Geochimica et Cosmochimica Acta 73,388-403

Figure SI5: Classification of Fe-bearing standards found by LCF in pseudo-mineral groups

Biogenic Fe(III) oxyhy	Fe(III) oxy+org
Maghemite	Fe(III) oxide
Basalt glass NKT-1	Fe(II) silicate
Fe(III) sulfate	Fe(III) sulfate
Almandine	Fe(II) silicate
Hematite	Fe(III) oxide
Pigeonite	Fe(II) silicate
Roedderite	Fe(II) silicate
Coalingite	Fe(III) carbonate
Fe(III) dextran	Fe(III) oxy+org
Kaolinite	Fe(III) silicate
Lepidocrocite	Fe(III) oxy+org
Ferrihydrite2L	Fe(III) oxy+org
FeSi	Native
Awaruite	Native
Fe3C	Native
Fe3Si	Native
Fe(III) pyrophosphate	Fe(III) phosphate
Goethite	Fe(III) oxy+org
Aegirine	Fe(III) silicate
Jarosite	Fe(III) sulfate

Note: “Org”: Fe(III)-organics

Figure SI6: Percentage distribution of the pseudo-mineral groups

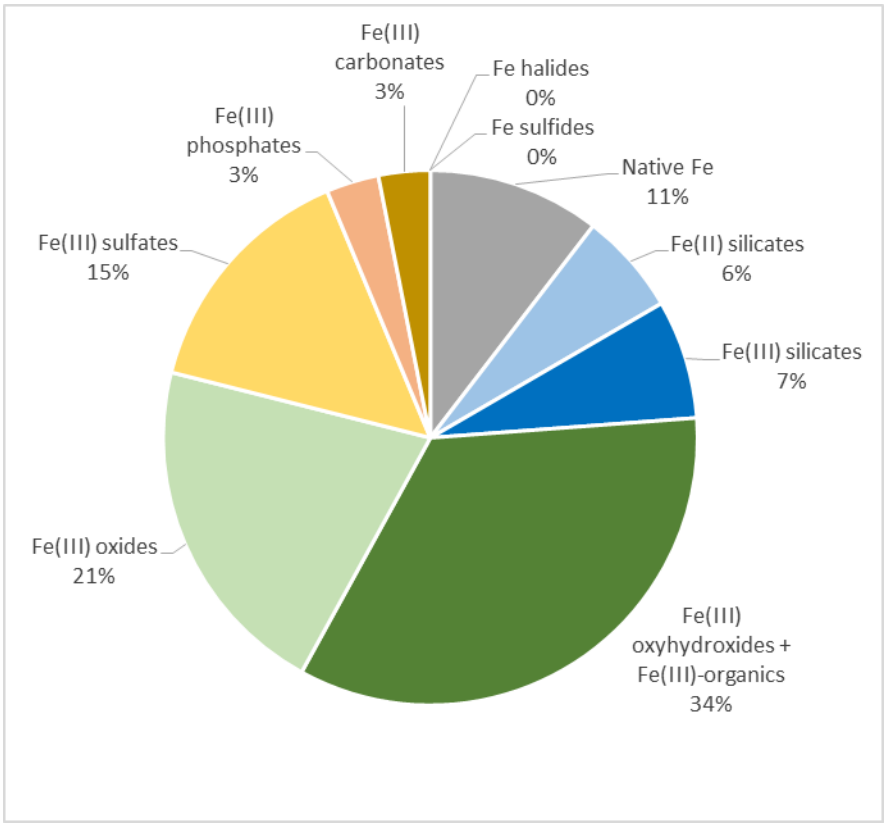

Figure SI7: R^2 Values of different carbon species and their correlation to water-soluble iron.

CARBON NUMBER	ALKANE	SINGLE RING AROMATIC	POLAR
12	0.04	0.00	0.25
13	0.06	0.03	0.17
14	0.23	0.37	0.33
15	0.37	0.13	0.33
16	0.37	0.13	0.56
17	0.23	0.26	0.28
18	0.05	0.23	0.10

Figure SI8: Linear correlation plots representing EF in µg kg-fuel^{-1} for water-souluble iron and vehical miles read from the vehical odometer. Correlation lines and R^2 shown.