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Supplementary material for

Links between the size fractionation, chemical speciation of dissolved copper and chemical speciation of dissolved organic matter in the Loire estuary

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Table S1: Copper speciation data and associated standard errors (in italics) used in this study.

Salinity	dCu (nmol.kg-1)	dLCu (nmol.kg-1)	$logK_{dCu2+}$	pCu	sCu (nmol.kg-1)	sLCu (nmol.kg-1)	$logK_{sCu2+}$	cCu* (nmol.kg-1)	cLCu** (nmol.kg-1)	$logK_{cCu2+***}$
0.1	**80.3** *1.2*	**147.1** *2.4*	**13.0** *0.1*	**12.9**	**76.6** *1.4*	**120.2** *4.1*	**10.6** *0.1*	**3.7** *2.4*	**26.9** *6.5*	**13.7** *0.1*
0.2	**25.6** *0.7*	**71.3** *1.1*	**12.1** *0.2*	**12.3**	**20.6** *0.5*	**62.5** *4.3*	**11.0** *0.2*	**4.9** *1.2*	**8.8** *5.4*	**13.0** *0.3*
4.48	**36.4** *1.1*	**102.2** *7*	**12.3** *0.1*	**12.7**	**17.5** **0.9**	**60.4** *3.6*	**11.0** *0.1*	**18.8** *2*	**41.8** *10.6*	**12.9** *0.2*
7.11	**28.5** *1.2*	**83.8** *9*	**12.7** *0.1*	**13.0**	**16.1** *2*	**47.9** *3.6*	**11.1** *0.1*	**12.4** *3.2*	**35.9** 12.6	**13.1** *0.1*
17.19	**13.1** *0.3*	**23.8** *0.9*	**11.8** *0.1*	**11.7**	**8.3** *0.5*	**17.1** *0.9*	**11.2** *0.3*	**4.8** *0.8*	**6.7** *1.8*	**12.2** *0.4*
29.6	**5.0** *0.4*	**8.4** *0.1*	**11.4** *0.1*	**11.2**	**3.4** *0.5*	**6.0** *0.4*	**10.5** *0.2*	**1.6** *0.9*	**2.4** *0.5*	**11.9** *0.3*

* Estimated as cCu = dCu – sCu

** Estimated as cLCu = dLCu – sLCu

*** Estimated using equation 8 of the manuscript

Table S2: Dissolved organic matter speciation data and associated standard errors (in italics) used in this study.

Salinity	Dissolved eHS mg eq SRFA.kg^{-1}	Soluble eHS mg eq SRFA.kg^{-1}	DOC mg C .kg^{-1}	sOC* mg C.kg^{-1}	cOC* mg C.kg^{-1}
0.1	**4.1** *0.12*	**3.4** *0.10*	**3.7** *0.11*	**3.2** *0.10*	**0.5** **0**.*21*
0.2	**2.6** *0.08*	**2.7** *0.08*	**2.3** *0.07*	**2.2** *0.07*	**0.1** *0.14*
4.48	**2.6** *0.08*	**2.4** *0.07*	**3.5** *0.11*	**2.6** *0.08*	**0.9** *0.19*
7.11	**2.2** *0.07*	**1.9** *0.06*	**3.2** *0.10*	**2.4** *0.07*	**0.8** *0.17*
17.19	**1.0** *0.03*	**0.7** *0.02*	**2.0** *0.06*	**1.7** *0.05*	**0.3** *0.11*
29.6	**0.6** *0.02*	**0.5** *0.01*	**1.2** *0.04*	**1.0** *0.03*	**0.2** *0.07*

* see section 3.3 for definition of sCO and cOC

Table S3: Dissolved copper concentrations measured by Waeles et al., 2004 along the salinity gradient of the Loire Estuary during winter 2001

Salinity	dCu (nmol.L-1) winter 2001
31.4	**6.99**
26.6	**13.52**
22.2	**18.13**
18	**21.12**
12	**20.89**
9.1	**19.31**
5.3	**18.56**
2.1	**17,26**

1.1	**16.3**
0.4	**16.65**

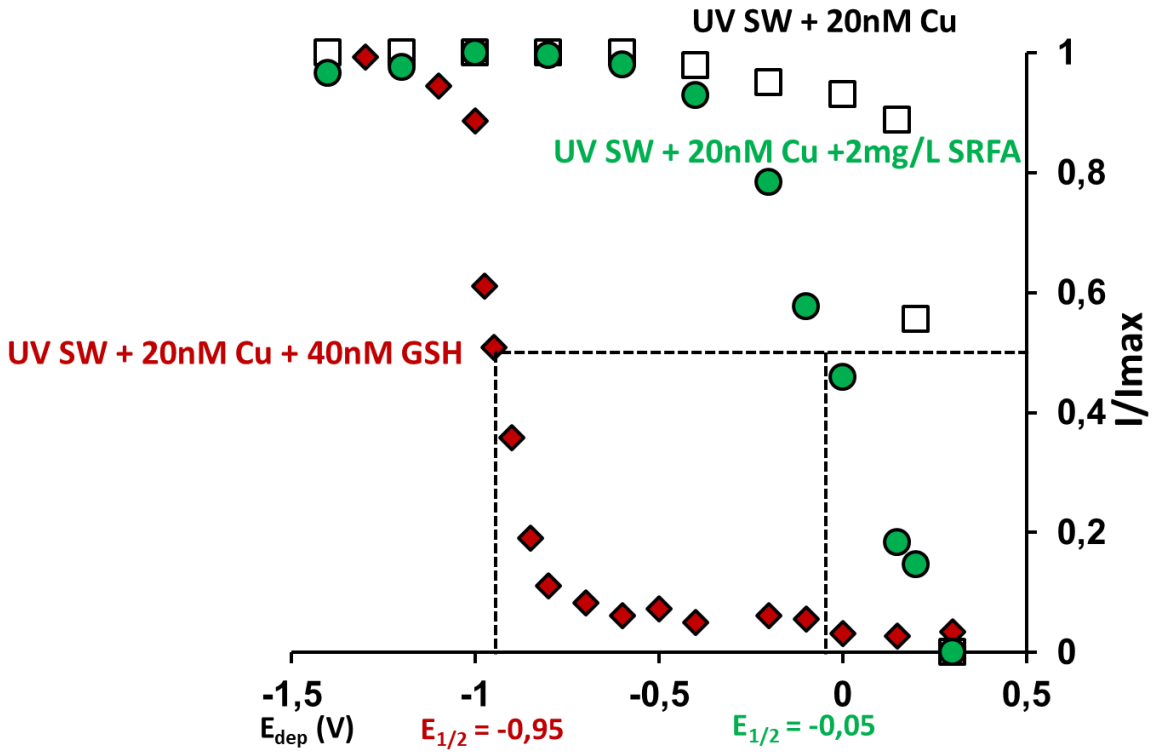

Figure S1: Pseudopolarographic experiments conducted on a UV seawater (Bay of brest) spiked with only 20nM of copper (white squares), 20nM of copper and 2mg/L of Suwannee River Fulvic Acid (SRFA, green dots) and 20nM of copper and 40nM of glutathione (GSH, red losanges). Half wave potentials are indicated.

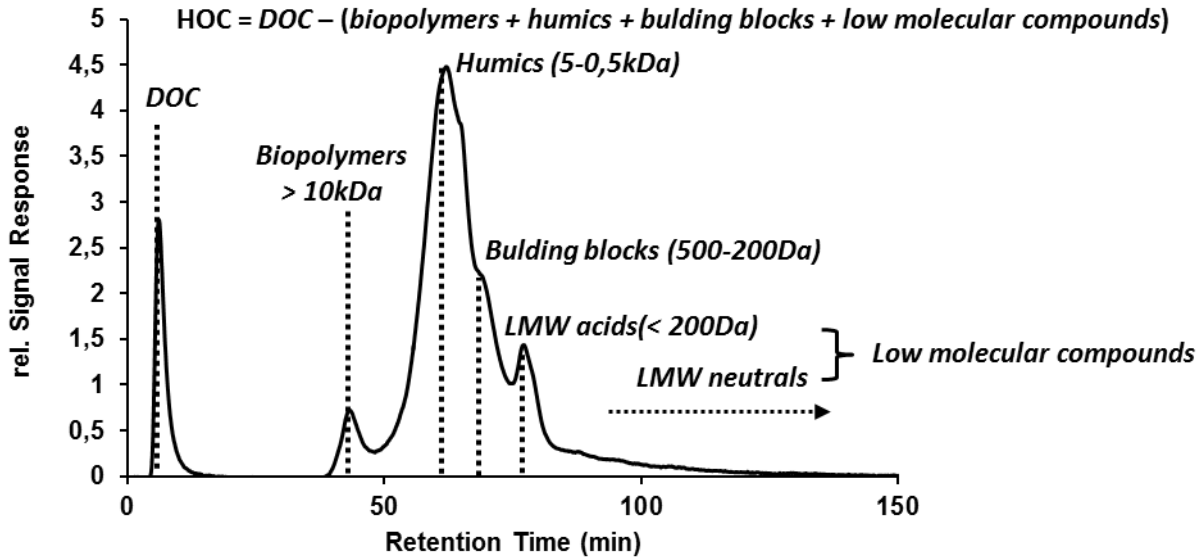

Figure S2: Typical chromatogram recorded by the organic carbon detector of the size exclusion chromatography coupled with organic carbon detection for an estuarine sample. The different fractions operationally defined by their retention time are indicated. In this study LMW acids and neutrals are combined as low molecular compounds. Hydrophobic DOC (HOC) is defined as the difference between DOC and the carbon content of the 4 other fractions.