Supporting Information for

Environmental processes and toxicity of metallic nanoparticles in aquatic system as affected by natural organic matter

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Table S1. ZPCs and solubility (at neutral pH) of typical MNPs in water.

MNPs	Zero Point of Charge (ZPC)	Solubility at neutral pH (Percentage of dissolved metal ions, MNPs concentration, pH)
CuO	7.4 (Paschoalino et al., 2008)	Soluble (0.7%, 20 mg/L, pH 7) (Adeleye et al., 2014)
ZnO	9.3 (Zhou et al., 2010) 9.0 (Kumar et al., 2010)	Soluble (0.98%, 500 mg/L, pH 7.8) (Mudunkotuwa et al, 2011)
Ag	<3 (Lin et al., 2015)	Soluble (0.94%, 2000 mg/L, pH 7.5) (Fabrega et al., 2009)
Cu	2.0 (Adeleye et al., 2014)	Soluble (1.1%, 20 mg/L, pH 7.0) (Adeleye et al., 2014)
nZVI	7.0 (Lv et al., 2011)	Not available
Fe_3O_4	8.4 (Moharami and Jalali, 2014)	Not available
Fe_2O_3	7.9 (Daou et al., 2007) 7.5 (Yu and Chow, 2004)	Not available
Al_2O_3	7.0 (Moharami and Jalali, 2014) 7.9 (Ghosh et al., 2008)	Soluble (0.25%, 100 mg/L) (Wang et al., 2010)
CeO_2	~7.6 (Li et al., 2011)	Soluble (0.3%, 500 mg/L) (Cornelis et al., 2011)
SiO_2	~2.2 (Liang et al., 2011)	Not available
TiO_2	5-6 (Thio et al., 2011) 6.2 (Loosli et al., 2013) 4.2 (Mudunkotuwa and Grassian, 2010)	Insoluble (Schmidt and Vogelsberger, 2009; Wang et al., 2010)

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Table S2. Properties of representative NOM.

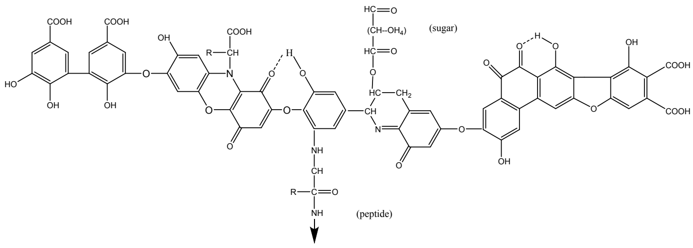
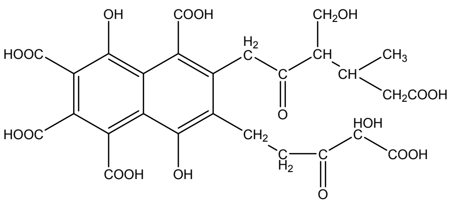
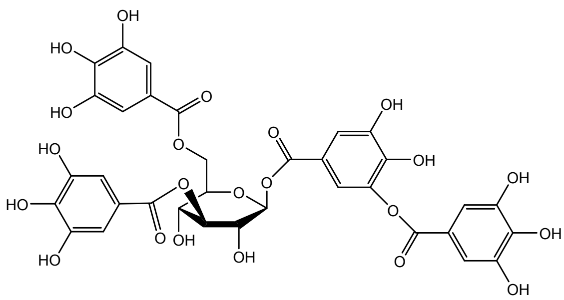
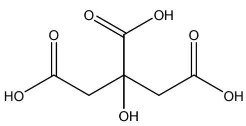
Species	Possible structure	Solubility (water)	Charge (4＜pH＜10)	Molecular Weight (kDa)
Humic Acid	 (Stevenson et al., 1982)	Well soluble at high pH	Negative (Yang et al., 2009)	1-10 (Thurman et al., 1982)
Fulvic Acid		Well soluble	Negative (Piccolo et al., 2001)	0.5-2 (Thurman et al., 1982)
Tannic Acid		Well soluble	Negative	1.70
citric acid		Well soluble	Negative	0.192

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Table S3. Adsorption of NOM on different types of MNPs.

MNPs	NOM	Adsorption isotherm modelling	Adsorption mechanisms	References
TiO_2	Six HA from different sources	The isotherms followed Freundlich model. Langmuir model was not appropriate here because HA is known to consist of a complex mixture.	High adsorption is related to high aromaticity and functional group (carboxylic and phenolic groups) content of HA.	Erhayem and Sohn, 2014
TiO_2, SiO_2, Al_2O_3, ZnO	HA	Langmuir type adsorption behavior was observed for all the MNPs.	HA adsorption on MNPs was pH-dependent. HA adsorption by MNPs was mainly induced by electrostatic attraction and ligand exchange between HA and MNPs surface. Adsorption is negatively related to MNPs hydrophilicity as indicated by H contents on MNPs surface (i.e., surface-bound water and hydroxyl groups).	Yang et al., 2009
SiO_2 (20, 100, 500 nm)	HA, FA	The adsorption of HA and FA were fitted much better to Langmuir model than Freundlich model.	HA sorption is higher than FA: (1) HA is more hydrophobic; (2) HA was facilitated to be adsorbed through cation bridging when cations were presented. (3) Hydrogen bonding is present. HA and FA may act as the hydrogen-bond donors.	Liang et al., 2011
TiO_2	Citric acid	-	Adsorption of citric acid at all the tested pHs was irreversible because of strong inner-sphere surface complexation.	Mudunkotuwa and Grassian, 2010
Ag	SRHA	Adsorption of HA on Ag MNPs followed a Langmuir model at neutral pH.	The authors did not deeply investigate the interaction mechanism.	Gao et al., 2012

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Table S4. Dissolution of MNPs in the presence of NOM.

MNPs	NOM	Dissolution alteration	Dissolution mechanisms	References
Ag	HA	HA suppressed the dissolution of Ag MNPs, and the dissolution was decreased with increasing NOM concentrations.	The mechanism was not investigated, but two reasons were speculated: (1) the reducing sites on Ag surface were blocked by HA; (2) the released Ag can be reduced to Ag MNPs via the reducing sites of HA molecules.	Linlin and Tanaka, 2014
Ag	SRFA	SRFA slowed down the dissolution of Ag NPs, probably due to the protective role of SRFA in reducing Ag NP dissolution.	-	Baalousha et al., 2015
Ag	HA, FA	SRFA and SRHA had little effect on Ag dissolution while PLFA significantly decreased the release of Ag^{+}.	The Ag-NOM interaction excluded molecular oxygen from active sites and thereby limited oxidative dissolution.	Gunsolus et al., 2015
Cu	HA, FA, BSA, sodium alginate	All the NOM could enhance the dissolution of Cu MNPs, and HA had the highest enhancement because of a higher amount of functional groups and lower molecular weight of HA, which facilitated the contact and complexion reactions.	Copper release mainly resulted from complexation reactions between Cu MNPs and functional groups of NOM.	Wang et al., 2015
CuO, Cu	Extracellular Polymeric Substances (EPS)	The presence of EPS correlated with higher dissolved Cu at pH 7 and 11, and lower dissolved Cu at pH 4. More dissolution was observed at higher I.S. (NaCl) due to complexation with Cl^{-}.	The enhancement may be attributed to improved stability, solubility of NOM-Cu complexes, and the strength of interactions between NOM and Cu-based MNPs. Decreased Cu^{2+} dissolution in the presence of EPS may be caused by (1) steric exclusion of water from the surface of the particles by NOM aggregates, (2) reduced availability of H^{+} which may bind to NOM	Adeleye et al., 2014

			molecules, and/or (3) adsorption of dissolved Cu by NOM aggregates.	
Cu, CuO	NOM	The presence of NOM decreased the concentration of Cu_{aq} and Cu_{dis}.	This reduction should be caused by a combination of chelation and surface coating.	Conway et al., 2015
ZnO	HA	The addition of HA into ZnO MNPs increased the dissolution only at high pH conditions (e.g., pH 9.0). The dissolution is size-dependent.	The increased dissolution of Zn MNPs is due to polydentate complexing of HA and the availability of a greater number of functional groups at high pHs (e.g., pH 9.0).	Bian et al., 2011
ZnO	Citric acid	The presence of citric acid significantly enhanced the dissolution of ZnO MNPs.	The enhancement was attributed to ligand-promoted dissolution.	Mudunkotuwa et al., 2011

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