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► **To cite this version:**

Yubing Pu, Bertrand Laratte, Rodica Elena Ionescu. Freshwater Sediment Characterization Factors of Copper Oxide Nanoparticles. International Conference on Environmental Engineering and Sustainable Development, Dec 2016, Sanya, China. pp.012020, 10.1088/1742-6596/51/1/012020 . hal-01489243

**HAL Id: hal-01489243**

**<https://hal.science/hal-01489243>**

Submitted on 29 May 2017

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# Freshwater Sediment Characterization Factors of Copper Oxide Nanoparticles

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**Abstract.** Wide use of engineered nanoparticles (ENPs) is likely to result in the eventually accumulation of ENPs in sediment. The benthic organisms living in sediments may suffer relatively high toxic effects of ENPs. This study has selected copper oxide nanoparticles (nano-CuO) as a research object. To consider the impacts of spatial heterogeneity on ENPs toxicity, the characterization factor (*CF*) derived from life cycle assessment (LCA) methodology is used as an indicator in this study. A nano-specific fate model has been used to calculate the freshwater sediment fate factor (*FF*) of nano-CuO. A literature survey of the nano-CuO toxicology values has been performed to calculate the effect factor (*EF*). Seventeen freshwater sediment *CF*s of nano-CuO are proposed as recommended values for subcontinental regions. The region most likely to be affected by nano-CuO is northern Australia (*CF* of  $21.01 \cdot 10^3$  CTU<sub>e</sub>, comparative toxic units) and the least likely is northern Europe and northern Canada (*CF* of  $8.55 \cdot 10^3$  CTU<sub>e</sub>). These sediment *CF*s for nano-CuO could be used in the future when evaluating the ecosystem impacts of products containing nano-CuO by LCA method.

## 1. Introduction

The volume of production of nanomaterials (NMs) have grown extensively over the last decade.[1] NMs are widely used in many household products including cosmetics, sunscreens, textiles etc.[2] Although people benefit a lot in using NMs, the potential negative impacts of NMs are also raised concerns. Many researches demonstrated the toxicity of NMs to environment.[3, 4] As a principal member of NMs, the engineered nanoparticles (ENPs) are widely used and likely to be released into ecosystem.[1] It was reported that the ENPs are usually released into the freshwater through the wastewater treatment plant.[5] Freshwater sediment is one of the main fate of suspended ENPs in freshwater.[6] Thus, the benthic organisms living in sediments may suffer relatively high toxic effects of ENPs.[7]

Generally, the bio-experiment is one effective way to investigate the toxicity of ENPs on organisms. However, most experiments have difficulty in assessing the impacts of spatial heterogeneity on ENPs toxicity. A recently published article indicated that the hydrogeology has significant influences on the impacts of ENPs because of the different residence time of ENPs in different freshwaters.[6] In order

to assess the impacts of hydrogeology on nanotoxicity to sediment, characterization factor ( $CF$ ) is used as an indicator in this study. The  $CF$  is derived from life cycle assessment (LCA) and reflects the relative importance of each component in life-cycle inventories.[8] It can be calculated under the framework of a scientific consensus environment model, USEtox model, which is recommended by many international organizations (e.g. European Commission, etc.).[9]

This study has selected copper oxide nanoparticles (nano-CuO) as a research object due to their relatively high toxicity than other metal oxide nanoparticles (e.g. nano-ZnO, nano-TiO<sub>2</sub>, etc.)[10] The aim of this study is to propose the freshwater sediment  $CF$ s of nano-CuO for different regions. A nano-specific fate model with 17 regional-specific input parameters has been applied to calculate the sediment fate factors ( $FF$ s) of nano-CuO.[6] In addition, a literature survey of nano-CuO toxicology values has been performed to calculate the effect factor ( $EF$ ). Finally, seventeen freshwater sediment  $CF$ s of nano-CuO are proposed as recommended values for subcontinental regions.

## 2. Methods

### 2.1. General framework

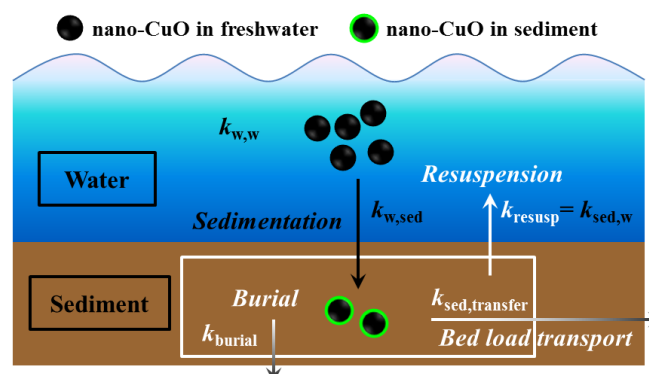
The USEtox model proposed a method to calculate the ecotoxicological characterization factor ( $CF$ ) of a substance for freshwater ecosystems. In this study, to calculate the  $CF$  for freshwater sediment, a small modification of the method is needed. The research object should be changed to the sediment compartment. The adapted characterization factor ( $CF$ , unit: PAF·m<sup>3</sup>·day·kg<sup>-1</sup>) of a substance for freshwater sediment is the product of three factors: fate factor ( $FF$ , unit: day), exposure factor ( $XF$ , unit: dimensionless) and effect factor ( $EF$ , unit: PAF·m<sup>3</sup>·kg<sup>-1</sup>):[9]

$$CF = FF \cdot XF \cdot EF \quad (1)$$

The  $FF$  represents the residence time of the substance in sediment and the  $XF$  is the bioavailability of a substance. The  $EF$  reflects the change in the potentially affected fraction (PAF) of species because of the change in substance concentration in sediment. In practice, the unit of  $CF$  is defined as comparative toxic units (CTU<sub>e</sub>) for ecosystem.

### 2.2. Calculation of fate factor

2.2.1. *Fate model concept* A nano-specific fate model with 17 regional-specific input parameters has been used to calculate the sediment fate factors ( $FF$ s) of nano-CuO.[6] Figure 1 shows the simplified fate model of nano-CuO in freshwater-sediment ecosystem. It was assumed that there is no direct ENPs emissions to sediment.[6] The following behavior as shown in figure 1 is considered as the removal processes for sediment: (1) resuspension from sediment to water; (2) burial into the deep sediment; (3) horizontal bed load transfer to other sediment compartment.



**Figure 1.** The behavior and transport of nano-CuO in freshwater and sediment with the corresponding rate constants accounted (Modified from Pu, et al.).[6]

2.2.2. *Sediment fate factor* The residence time of nano-CuO in freshwater sediment ( $FF_{sed, sed}$ , day) is calculated as equation 2:

$$FF_{sed, sed} = \frac{k_{w,w}}{k_{w,w} \cdot k_{sed, sed} - k_{w, sed} \cdot k_{sed, w}} \quad (2)$$

The total removal rate of nano-CuO in sediment ( $k_{sed, sed}$ ,  $s^{-1}$ ) is expressed as a sum of the rate constant for horizontal bed load transfer ( $k_{sed, transfer}$ ,  $s^{-1}$ ), burial ( $k_{burial}$ ,  $s^{-1}$ ) and resuspension ( $k_{resusp}$ ,  $s^{-1}$ ):

$$k_{sed, sed} = k_{sed, transfer} + k_{burial} + k_{resusp} \quad (3)$$

The detailed calculation methods and the input values for the above elements could be found in the study of Pu, et al.[6] The nano-CuO density of  $6320 \text{ kg} \cdot \text{m}^{-3}$  was used in the calculation. If not specified, the  $FF$  refers to  $FF_{sed, sed}$  in this study.

### 2.3. Calculation of exposure factor

In USEtox, the freshwater exposure factor ( $XF$ ) is defined as the fraction of a chemical dissolved in freshwater.[9] In this study, it is assumed that the CuO nanoparticles are all bioavailable and dispersed homogeneous in the freshwater sediment. Thus, here  $XF$  is set to be 1 to avoid significant errors in nano-CuO  $CF$  predictions.

### 2.4. Calculation of effect factor

The aquatic ecotoxicological effect factor ( $EF$ ) is calculated based on geometric means of single species  $EC50$  value in USEtox.[9]  $EC50$  ( $\text{kg} \cdot \text{m}^{-3}$ ) is the effective concentration of a substance at which 50% of a population (e.g. fish) displays a phenomenon (e.g. mortality). In this study, due to the research object is sediment, the  $EC50_{ref}$  from reference has a unit of  $\text{kg}$  nano-CuO per  $\text{kg}$  sediment. Therefore, a unit conversion is necessary to obtain the  $EC50$  in unit of  $\text{kg}$  nano-CuO per  $\text{m}^3$  sediment. In addition, when chronic  $EC50$  value is unavailable, an acute to chronic ratio ( $ACR$ , 15 in this study) will be used to derive the chronic-equivalent  $EC50$ .

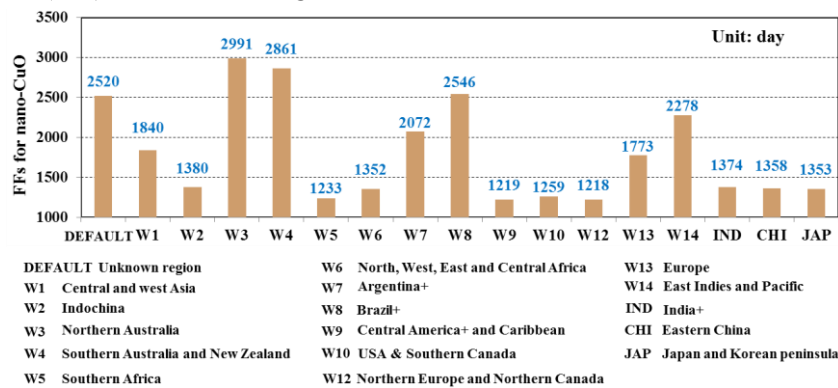
$$EC50_{chronic} = \frac{EC50_{ref} \cdot \rho_{sed}}{ACR} \quad (4)$$

where  $\rho_{sed}$  ( $\text{kg}$  sediment per  $\text{m}^3$  sediment) is the bulk density of freshwater sediment. Here, the value of  $1230 \text{ kg} \cdot \text{m}^{-3}$  has been applied.[6, 9] The obtained  $EC50_{chronic}$  was used to calculate the sediment  $EF$  of nano-CuO. The detailed calculation methods of  $EF$  could be found in the study of Pu, et al.[6]

## 3. Results and discussions

### 3.1. Fate factors of nano-CuO

As shown in figure 2, a low persistence of nano-CuO in the sediment ( $\sim 1218$  day) occurs in northern Europe and northern Canada regions (W12), while high  $FF$  values ( $\sim 2991$  day) is observable in northern Australia (W3). In the following calculation of  $CFs$ , these values of  $FFs$  were used.



**Figure 2.** The recommended values of sediment  $FFs$  for nano-CuO in 17 subcontinental regions. (Further details of the countries within each region can be found in the study of Shaked.[11])

The transport rate constants of nano-CuO between freshwater and sediment for 17 subcontinental regions are listed in Table 1 to explain the differences of *FFs*. For example, the transport rate of nano-CuO from freshwater to sediment ( $k_{w, \text{sed}}$ ) for W3 region is more than 5 times faster than that for W12 region ( $2.07 \cdot 10^{-5}$  versus  $3.77 \cdot 10^{-6} \text{ s}^{-1}$ ), while the inverse transport rate ( $k_{\text{sed}, w}$ ) for W3 region is less than one third of that for W12 region ( $3.32 \cdot 10^{-9}$  versus  $1.00 \cdot 10^{-8} \text{ s}^{-1}$ ). It's the apparent reason of longer residence time in sediment of W12 region than W3 region. The underlying cause is the the subcontinental difference of freshwater-sediment parameters.

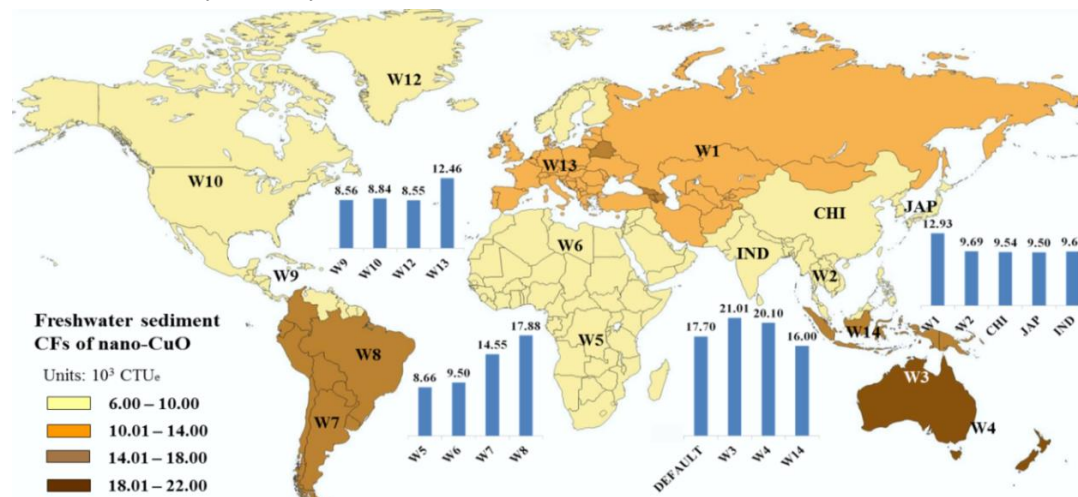
**Table 1.** The transport rate constants of nano-CuO between freshwater and sediment for 17 subcontinental regions (Unit:  $\text{s}^{-1}$ ).

	$k_{w,w}$	$k_{w,\text{sed}}$	$k_{\text{sed},\text{sed}}$	$k_{\text{sed},w}$		$k_{\text{sed},w}$	$k_{\text{sed},w}$	$k_{\text{sed},w}$	$k_{\text{sed},w}$
<b>DEF</b>	$2.57 \cdot 10^{-5}$	$2.07 \cdot 10^{-5}$	$1.17 \cdot 10^{-8}$	$8.87 \cdot 10^{-9}$	<b>W9</b>	$8.14 \cdot 10^{-6}$	$3.11 \cdot 10^{-6}$	$1.33 \cdot 10^{-8}$	$9.97 \cdot 10^{-9}$
<b>W1</b>	$9.99 \cdot 10^{-6}$	$4.97 \cdot 10^{-6}$	$9.43 \cdot 10^{-9}$	$6.30 \cdot 10^{-9}$	<b>W10</b>	$8.12 \cdot 10^{-6}$	$3.11 \cdot 10^{-6}$	$1.28 \cdot 10^{-8}$	$9.33 \cdot 10^{-9}$
<b>W2</b>	$9.83 \cdot 10^{-6}$	$4.78 \cdot 10^{-6}$	$1.32 \cdot 10^{-8}$	$9.87 \cdot 10^{-9}$	<b>W12</b>	$8.78 \cdot 10^{-6}$	$3.77 \cdot 10^{-6}$	$1.38 \cdot 10^{-8}$	$1.00 \cdot 10^{-8}$
<b>W3</b>	$2.60 \cdot 10^{-5}$	$2.07 \cdot 10^{-5}$	$6.51 \cdot 10^{-9}$	$3.32 \cdot 10^{-9}$	<b>W13</b>	$9.05 \cdot 10^{-6}$	$4.04 \cdot 10^{-6}$	$9.20 \cdot 10^{-9}$	$6.00 \cdot 10^{-9}$
<b>W4</b>	$2.58 \cdot 10^{-5}$	$2.07 \cdot 10^{-5}$	$7.21 \cdot 10^{-9}$	$3.93 \cdot 10^{-9}$	<b>W14</b>	$2.58 \cdot 10^{-5}$	$2.07 \cdot 10^{-5}$	$1.23 \cdot 10^{-8}$	$9.00 \cdot 10^{-9}$
<b>W5</b>	$6.36 \cdot 10^{-6}$	$1.35 \cdot 10^{-6}$	$1.10 \cdot 10^{-8}$	$7.80 \cdot 10^{-9}$	<b>IND</b>	$9.80 \cdot 10^{-6}$	$4.78 \cdot 10^{-6}$	$1.32 \cdot 10^{-8}$	$9.87 \cdot 10^{-9}$
<b>W6</b>	$6.36 \cdot 10^{-6}$	$1.35 \cdot 10^{-6}$	$1.00 \cdot 10^{-8}$	$6.93 \cdot 10^{-9}$	<b>CHI</b>	$9.80 \cdot 10^{-6}$	$4.78 \cdot 10^{-6}$	$1.34 \cdot 10^{-8}$	$1.00 \cdot 10^{-8}$
<b>W7</b>	$1.28 \cdot 10^{-5}$	$7.77 \cdot 10^{-6}$	$9.18 \cdot 10^{-9}$	$5.93 \cdot 10^{-9}$	<b>JAP</b>	$9.82 \cdot 10^{-6}$	$4.78 \cdot 10^{-6}$	$1.35 \cdot 10^{-8}$	$1.02 \cdot 10^{-8}$
<b>W8</b>	$1.31 \cdot 10^{-5}$	$7.77 \cdot 10^{-6}$	$6.64 \cdot 10^{-9}$	$3.53 \cdot 10^{-9}$					

### 3.2. Effect factor of nano-CuO

It is preferred to use toxicity data (EC50s in three trophic levels) reflecting the entire ecosystem in *EF* calculation.[12] Nevertheless, the toxicity values of nano-CuO to the organisms living in sediment were rarely reported. In this study, one toxicity value (EC50 = 868  $\mu\text{g} \cdot \text{g}^{-1}$ ) of nano-CuO on an estuarine amphipod, *Leptocheirus plumulosus*,[7] was found and used in the calculation of sediment *EF* of nano-CuO. The sediment *EF* value of 7.025  $\text{PAF} \cdot \text{m}^3 \cdot \text{kg}^{-1}$  for nano-CuO was calculated and applied to calculate the freshwater sediment characterization factors of nano-CuO.

### 3.3. Characterization factors of nano-CuO



**Figure 3.** World map of freshwater sediment characterization factors (CFs) of nano-CuO, with histograms indicating the variation between the numerical values (units:  $10^3 \text{ CTU}_e$ ) of 17 worldwide regions. The source of the underlying map was from Mapchart website.[13]

Based on the calculated *EF* and *FFs* of nano-CuO, the recommended world-wide nano-CuO sediment CFs were obtained and are depicted in figure 3. The deeper color on the map represents the larger *CF*

of nano-CuO for the related region. The values reflect the potential influences of nano-CuO on organisms. The larger *CF* value of nano-CuO, the more sensitive is the ecosystem of the related region. These *CF*s can be used in the future LCA, when assessing products containing nano-CuO. This map can show a general view of nano-CuO sediment *CF*s in the world despite of the imprecision.

The sediment most likely to be affected by nano-CuO is in northern Australia (*CF* of  $21.01 \cdot 10^3$  CTU<sub>e</sub>, comparative toxic units) and the least likely is in northern Europe and northern Canada (*CF* of  $8.55 \cdot 10^3$  CTU<sub>e</sub>). A *CF* of  $17.70 \cdot 10^3$  CTU<sub>e</sub> is proposed for the DEFAULT region, which is a large value among all the studied regions. It means the impacts of nano-CuO to sediment would probably be overestimated for an unknown region. In addition, due to the relatively high uncertainty in the calculation of fate, exposure and effects of nano-CuO, the *CF*s proposed in this study should be classified as “indicative”. [9]

#### 4. Perspectives

This work proposed the freshwater sediment characterization factors of nano-CuO in 17 subcontinental regions. Many limitations may affect the absolute values of the output: *CF*s of nano-CuO. The immature fate model of ENPs used in this study may bring uncertainties to *FF*s of nano-CuO. Moreover, *XF*, as a significant factor in *CF* calculation, may have big influences on the *CF* values. Thus, further investigation of *XF* is necessary. Furthermore, since the toxicity values of nano-CuO to the organisms living in sediment were rarely reported, just one toxicity value from literature was used in this study. The sediment *EF* of nano-CuO can be updated once more toxicity values are available. However, despite having defects, to the best of our knowledge, it is the first reports focusing on the sediment *CF* of ENPs. The method proposed in this study for calculating the sediment *CF*s of nano-CuO is promising. The recommended *CF*s for nano-CuO could also be used in the future when evaluating the ecosystem impacts of products containing nano-CuO.

#### Acknowledgement

Yubing Pu kindly thanks the Chinese Scholarship Council (CSC) for funding his PhD scholarship in France.

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