Dissolution and aggregation kinetics of zero valent copper nanoparticles in (simulated) natural surface waters: Simultaneous effects of pH, NOM and ionic strength

Daniel Arenas-Lago, Fazel Abdolahpur Monikh, Martina G. Vijver, Willie J.G.M. Peijnenburg

* Institute of Environmental Sciences (CML), Leiden University, P.O. Box 9518, 2300 RA, Leiden, the Netherlands
b National Institute of Public Health and the Environment (RIVM), Center for Safety of Substances and Products, Bilthoven, the Netherlands

**Corresponding author. Van Steenis Building, Einsteinweg 2, 2333 CC, Leiden, the Netherlands.
E-mail address: f.a.monikh@cmi.leidenuniv.nl (F. Abdolahpur Monikh).**

**Check for updates**

**Contents lists available at ScienceDirect**

**Chemosphere**

**journal homepage: www.elsevier.com/locate/chemosphere**

**https://doi.org/10.1016/j.chemosphere.2019.03.190**

**0045-6535/© 2019 Elsevier Ltd. All rights reserved.**

**Dissolution and aggregation kinetics of zero valent copper nanoparticles in (simulated) natural surface waters: Simultaneous effects of pH, NOM and ionic strength**

**A B S T R A C T**

The combined effects of pH, dissolved organic carbon (DOC) and Ca\(^{2+}/\text{Mg}^{2+}\) on the dissolution and aggregation kinetics of zero valent copper engineered nanoparticles (Cu\(^0\) ENPs) were investigated. The dissolution and aggregation of the particles were studied in (a) synthetic aqueous media, similar in chemistry to natural surface waters, and (b) natural surface waters samples, for up to 32 or 24 h. The DOC stabilized the particles and prevented aggregation, and thus increased the available surface area. The higher available surface area in turn accelerated the dissolution of the particles. The presence of Ca\(^{2+}/\text{Mg}^{2+}\), however, changed the aggregation and the dissolution of the DOC-stabilized particles. The influence of Ca\(^{2+}/\text{Mg}^{2+}\) on DOC-stabilized particles was different at different pH's. In the absence of DOC, 10 mM of Ca\(^{2+}/\text{Mg}^{2+}\) induced charge reversal on the particles and caused particle stability against aggregation. This subsequently increased particles dissolution. The results obtained with regard to dissolution and aggregation of the particles in natural surface waters were compared with those determined for the synthetic waters. This comparison showed that the behavior of the particles in the natural surface waters was mostly similar to the behavior determined for media at pH 9. Overall, the current study provides some novel insights into the simultaneous effects of physicochemical parameters of water on particle stability against aggregation and dissolution, and provides data about how the processes of aggregation and dissolution of Cu\(^0\) ENPs interact and jointly determine the overall particle fate.

© 2019 Elsevier Ltd. All rights reserved.
1. Introduction

Many products containing engineered nanoparticles (ENPs) are currently on the market (Vance et al., 2015). Copper (Cu) ENPs are among the most commonly used ENPs with a wide range of applications, such as in electronics, textiles, ceramics, wood preservatives, inks, films and coatings, to name just a few of them (Vance et al., 2015). Upon production and application, Cu ENPs may enter the environment and end up in different environmental compartments such as natural surface water and sediment (Mudunkotuwa et al., 2012). Many studies nowadays focus on determining the fate and behavior of ENPs (Abdolahpur Monikh et al., 2018; Wagner et al., 2014), whereas only few data are available regarding the fate of Cu ENPs in the environment. In aquatic systems, the fate of Cu ENPs depends upon whether (a) the particles remain in dispersion, (b) processes that affect particle aggregation remove them from the water, or (c) dissolution changes their speciation (Johnson et al., 2011). Often these studies are limited to laboratory test conditions, although it is known that the natural conditions dramatically influence ENPs' environmental transformation and behavior (Conway et al., 2015). Understanding particle aggregation and dissolution kinetics under natural conditions is critical, since these processes have a decisive impact on the mobility and bioavailability of ENPs and, ultimately, on their toxicity in the aquatic environment (Li et al., 2012; Keller et al., 2010). Thus, dissolution/aggregation tests might be useful analytical tools for the regulatory assessment of not only Cu ENPs, but of dissolvable ENPs in general.

Literature showed that the dissolution kinetics of ENPs are influenced by particles aggregation and by physicochemical parameters of the system, such as ionic strength, pH and natural organic matter (NOM) (Keller et al., 2010; Flemming and Trevors, 1989). Aggregation of ENPs decreases the volume specific surface area of particles and subsequently reduces the dissolution of the particles (Zhang et al., 2010; Axson et al., 2015). For instance, it is reported that a decrease in the particle size of aggregates increases the dissolution rate of Cu ENPs (Adleye et al., 2014) and silver (Ag) ENPs (Li et al., 2010a). Moreover, depending on their composition and the chemistry of the medium, NOM can stabilize (steric stabilization against aggregation) particles in suspension and through these mechanisms alter the dissolution rate and aggregation of ENPs (Conway et al., 2015; Wang et al., 2011). A decrease in the pH of an aquatic system may accelerate the dissolution of ENPs (Zhang et al., 2010). A study showed that at low pH, an elevated concentration of Ca\(^{2+}\) increases the stability of titanium dioxide (TiO\(_2\)) ENPs against aggregation due to charge reversal of the particles (Von Der Kammer et al., 2010). Although many studies are available that investigated the effect of NOM, pH and ionic strength on aggregation and stability behavior of ENPs (Kanel et al., 2015; Chowdhury et al., 2013; Louie et al., 2015), the simultaneous influence of these parameters on the dissolution of ENPs is still not well known. The underlying mechanisms are not straightforward, particularly when it comes to the behavior of these particles under natural field conditions. For example, previous studies reported inconsistent results when investigating the effect of NOM on two types of zero valent ENPs, including Ag\(^{0}\) ENPs (Gunsolus et al., 2015; Linlin and Tanaka, 2014; Linlin and Tanaka, 2014, 2014) and Cu\(^{0}\) ENPs (Wang et al., 2015). Gunsolus et al. (2015) reported that NOM decreases the dissolution rate of Ag\(^{0}\) ENPs, while Wang et al. (2015) reported that NOM increases the dissolution of Cu\(^{0}\) ENPs. These contrasting reports created the motivation for this study to understand in greater detail the chemistry of NOM interactions with Cu\(^{0}\) ENPs in simulated natural surface waters containing different pH and ionic strength, and to assess the dissolution rates and aggregation in dependence of the composition of the aqueous medium.

This study therefore first provides a large set of experimental data on dissolution and aggregation of Cu\(^{0}\) ENPs in a model system mimicking natural surface waters (reported as synthetic media in this study) to systematically gain insight into how NOM, pH and ionic strength in conjunction influence aggregation and the dissolution of the particles in natural conditions. Second, the dissolution kinetics of Cu\(^{0}\) ENPs are evaluated in samples from different natural surface waters by comparing the results obtained in these waters with the experimental data obtained from the synthetic media.

2. Material and methods

2.1. Chemicals and test materials

All chemicals were reagent grade and used without further purification unless noted. The water used was deionized by reverse osmosis and purified by a Millipore MilliQ (milliQ) system, making so-called milliQ water. Spherical bare Cu\(^{0}\) ENPs with a nominal size of 25 nm, a purity of 99.5% and a specific surface area of 30–50 m\(^2\)/g (according to the product information) were supplied from lolITec-Ionic Liquids Technologies GmbH. Optima grade hydrochloric acid (HCl, 30%) and nitric acid (HNO\(_3\), 65%) were purchased from Merck (Suprapure\textsuperscript{®}, USA). Sodium hydroxide (NaOH) was purchased from Sigma-Aldrich (Sigma-Aldrich Corp., St. Louis, MO, USA). Suwannee River NOM was supplied by the International Humic Substances Society (1R101 N).

2.2. Sampling areas and preparation of natural samples

The natural surface waters were collected from three different ditches, a lake (Valkenburgse Meer) and a river (Rijn) in the Netherlands (Fig. 1). Since the Ditches were shallow, to keep the sampling depth equal between all sampling area, the samples were collected from the first centimeters of the water column and brought to the laboratory of Leiden University on the same day. The physicochemical parameters of the samples (pH, concentration of NOM, concentration of Ca\(^{2+}\) and concentration of Mg\(^{2+}\)) were measured and the samples were kept in a climate chamber under controlled conditions at 18 °C. After 24 h, the samples were filtered using a 0.45 µm Whatman filter paper and used for the experiment.

2.3. Characterization of the Cu\(^{0}\) ENPs

The hydrodynamic size (D\(_h\)) and the zeta potential of the Cu particles in milliQ water and the natural samples were measured using a Zetasizer Nano device (Malvern Panalytical, Netherlands and UK). The morphology and size of the Cu\(^{0}\) ENPs were also characterized by Transmission Electron Microscopy (JEOL 1010 TEM).

2.4. Preparation of synthetic water samples

The preparation of synthetic water samples containing NOM is described in Section 1 of the Supporting Information. The NOM was filtered (0.45 µm) and the filtered fraction, reported as dissolved organic carbon (DOC) in this study, was used. The stock DOC was used at four different concentrations, including 0, 5, 25, and 50 mg/L in milliQ water. Three concentrations of Ca\(_2\) and MgSO\(_4\) were selected in a fixed content ratio of 4:1 (Ca\(^{2+}\)/Mg\(^{2+}\)) (the sum of 0, 2.5 and 10 mM Ca\(^{2+}\)/Mg\(^{2+}\)). A ratio of 4:1 (Ca\(^{2+}\)/Mg\(^{2+}\)) simulates natural conditions, as reported by the OECD guidelines for stability testing of ENPs (Abdolahpur Monikh et al., 2018). To change the pH of the solution to three pH-levels ranging from 6 to 9, either 0.1 M NaOH or 0.1 M HCl was added. DOC served in these experiments as
a natural buffer to maintain a constant pH. The measured concentrations of DOC in the media with different conditions are reported in Tables 1–3 in the Supporting Information.

2.5. Developing the testing matrices

A stock suspension of Cu\textsuperscript{0} ENPs (250 mg/L) was prepared in milliQ water and tip sonicated using a SONOPULS ultrasonicator (BANDELIN electronic, Berlin, Germany) at 100% amplitude for 10 min. To investigate the influence of pH, ionic strength and DOC content on the aggregation and dissolution behavior of Cu\textsuperscript{0} ENPs, synthetic water samples were prepared using milliQ water. The different pHs, Ca\textsuperscript{2+}/Mg\textsuperscript{2+} concentrations and DOC contents were selected according to the most common features of the waters reported by the Geochemical Atlas of Europe ("The Geochemical Atlas of Europe") and a previous study (Abdolahpur Monikh et al., 2018) to cover the variance of natural surface water conditions that is typical for European waters. From the sonicated stock dispersion, the required volume was added to reach a final concentration of 1 mg/L of Cu\textsuperscript{0} ENPs in each testing medium. The dispersions were stored in a climate chamber under controlled conditions (20 ± 1°C). All tests were performed in triplicate.

2.6. Aggregation kinetics

Aggregation kinetics were measured using dynamic light scattering (DLS). For measurement of \( \text{Dh} \), dispersions (relevant for each testing medium) of 10 mg/L Cu\textsuperscript{0} ENPs were sonicated at 100% amplitude for 10 min and immediately measured using DLS for 30 min. It was selected 10 mg/L only for \( \text{Dh} \) measurement and not for exposure because measuring \( \text{Dh} \) of 1 mg/L of ENPs using DLS is problematic due to size detection limit of the DLS. The measurements using DLS were carried out every 1 min; 30 data points in total for each samples.

2.7. Dissolution testing

Aliquots of the samples were taken immediately after preparation to measure the total copper concentration ([Cu\text{total}]). To separate dissolved and particulate Cu, aliquots of each dispersion were

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu (µg/L)</th>
<th>DOC (mg/L)</th>
<th>pH</th>
<th>Ca (mM)</th>
<th>Mg (mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ditch 1</td>
<td>&lt; dl</td>
<td>18.5 ± 1.3</td>
<td>9.0 ± 0.2</td>
<td>2.1 ± 0.7</td>
<td>1.2 ± 0.2</td>
</tr>
<tr>
<td>Ditch 2</td>
<td>&lt; dl</td>
<td>16.2 ± 1.6</td>
<td>8.9 ± 0.02</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ditch 3</td>
<td>&lt; dl</td>
<td>16.9 ± 1.3</td>
<td>9.2 ± 0.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Lake</td>
<td>&lt; dl</td>
<td>13.3 ± 1.8</td>
<td>8.6 ± 0.01</td>
<td>1.4 ± 0.4</td>
<td>0.76 ± 0.2</td>
</tr>
<tr>
<td>River</td>
<td>&lt; dl</td>
<td>9.2 ± 1.3</td>
<td>7.67 ± 0.01</td>
<td>1.75 ± 0.1</td>
<td>9.0 ± 0.07</td>
</tr>
</tbody>
</table>

< dl: not detected, the concentration of Cu was lower than the detection limit of the instrument. *-- same.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(ng cm\textsuperscript{-2} h\textsuperscript{-1})</th>
<th>R\textsupscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ditch 1</td>
<td>26.1</td>
<td>0.99</td>
</tr>
<tr>
<td>Ditch 2</td>
<td>23.6</td>
<td>0.99</td>
</tr>
<tr>
<td>Ditch 3</td>
<td>24.2</td>
<td>0.98</td>
</tr>
<tr>
<td>Lake</td>
<td>21.2</td>
<td>0.98</td>
</tr>
<tr>
<td>River</td>
<td>16.0</td>
<td>0.98</td>
</tr>
</tbody>
</table>

Table 1

Average dissolution rates \( (k_{diss}) \) of Cu\textsuperscript{0} ENPs in the synthetic water samples up to 32 h.

Table 2

Physicochemical parameters of the samples collected from the natural surface water in the Netherlands.

Table 3

Average dissolution rates \( (k_{diss}) \) of Cu\textsuperscript{0} ENPs in the natural surface water samples up to 24 h.
taken at each time point (0, 4, 8, 24 and 32 h) and centrifuged at 4000 rpm for 30 min at 4°C (Sorvall RC5Bplus centrifuge, Fiberlite F21-8). Samples were taken from the supernatant (top 5 cm), digested by HNO3 and analysed for dissolved Cu ([Cu]dissolved) using a flame atomic absorption spectrometer (FAAS; Perkin Elmer AAAnalyst 100). Changes in the [Cu]dissolved concentrations in the samples allow to examine the dissolution kinetics within 32 h of exposure.

2.8. Dissolution rate and its rate constant

The measured mass of [Cu]dissolved versus time was examined to obtain the dissolution rate constant following the approach reported by Levard et al. (2013). In this study, the rate constants were calculated for all conditions where the initial [Cu]dissolved/[Cu]total at the first sampling time was less than 0.5. The samples with initial [Cu]dissolved/[Cu]total higher than 0.5 were considered as being reflective of very fast dissolution conditions that could not be reliably assessed by means of the methods employed in this study. The data showed that, as expected, the dissolution rate was not constant across all water samples tested. The calculation of the dissolution rate constants was carried out assuming pseudo-first-order kinetics.

2.9. Statistics and data analysis

Data were analysed statistically with the statistical program SPSS v. 19. Data are expressed as the average ± standard deviation (SD) of three replicates. Kolmogorov-Smirnov and Levene tests were performed by Levard et al. (2013) using a flame atomic absorption spectrometer (FAAS; Perkin Elmer AAAnalyst 100). Changes in the [Cu]dissolved concentrations in the samples allow to examine the dissolution kinetics within 32 h of exposure.

3. Results and discussion

3.1. Characterization of Cu0 ENPs

The Cu0 ENPs were characterized in milliQ water immediately after sonication. The DLS data showed that the Cu0 ENPs were well dispersed immediately after sonication. Rapid aggregation of the particles was however observed over time. After 1 h, the particle Dh was between 278 nm and 425 nm (Table 4, Supporting Information). TEM microscopy confirmed the intense aggregation of the particles in milliQ water immediately after sonication (Fig. 1, Supporting information). An averaged zeta potential value of about −3.4 ± 0.4 mV was measured by electrophoretic mobility. The point of zero charge (PZC) for Cu0 ENPs from alkalimetric titration was at pH of 8.5–9 and close to previously reported values for similar particles (Collins et al., 2012; Kosmulski, 2009).

3.2. Particle aggregation behavior in synthetic water

The aggregation kinetics of Cu0 ENPs nanoparticles were investigated over DOC, Ca2+/Mg2+ and pH ranges of 0–10 mM, 0–50 mg/L, and 6–9 respectively. The Polydispersity Index (PDI) was in the range of 0.02–0.48 for all the measurements. At pH 6, the trends in the patterns of aggregation over time were similar in almost all conditions (Fig. 2). Immediate aggregation in the first few minutes (up to 10 min) in the media without DOC and 0–2.5 mM Ca2+/Mg2+ was typically observed. A downward trend in aggregate size from 0 to 30 min was observed in some media. This trend was likely due to sedimentation of the largest aggregates (Conway et al., 2015) and due to fast dissolution of the particles. At pH 7.5, the particles showed a typical increase in sizes over time in the media without DOC and Ca2+/Mg2+. At pH 9, substantial aggregation was observed for media without DOC and at Ca2+/Mg2+ concentrations of 0 and 2.5 mM.

3.3. Particle dissolution behavior in synthetic waters

The concentrations of Cu ions (μg/L) were measured in the supernatant (top 5 cm) during 32 h of incubation in the synthetic media. The ratio of [Cu]dissolved/[Cu]total was calculated and plotted as a function of exposure time for the different media at pH 6, 7.5 and 9. The data show a good reproducibility, with generally low variations between the replicates.

As shown in Fig. 3, in almost all media the final amount (at 32 h) of [Cu]dissolved in the supernatant increased as compared to the initial concentration, except for the media contain 0 or 2.5 mM Ca2+/Mg2+ and 0 mg/L DOC at pH 9 (Fig. 3C). When introduced into the water, Cu0 ENPs were immediately oxidized, as previously reported (Collins et al., 2012; Conway et al., 2015). This resulted in an immediate increase in the concentration of [Cu]dissolved in the suspension at the first sampling time (measurement at exactly 0 h was not possible given the time needed for sample preparation, including sonication, centrifugation, etc.) and continued to increase up to 32 h. The dissolution over time was different across the different media. The initial concentrations of [Cu]dissolved in the media without DOC and without addition of Ca2+/Mg2+ were higher at pH 6 than at pH 7.5 and 9, whereas the concentration of [Cu]dissolved increased slightly at pH 6 during 32 h. As described by Wang et al. (2016), the dissolution of Cu0 ENPs in water is an oxidative process following the stoichiometry below (eq. (1)):

\[
\text{Cu}^0(s) + \frac{1}{2} \text{O}_2(aq) + \text{H}^+(aq) \rightarrow \text{Cu}^+(aq) + \frac{1}{2} \text{H}_2\text{O}
\]  

(1)

According to this stoichiometry, oxygen and Cu+ are the factors controlling the dissolution of the particles in the system. When Cu0 ENPs are dispersed in a solution containing dissolved oxygen, release of Cu ions is observed (Zou et al., 2017). Dissolution may continue for a long time, but eventually the [Cu]dissolved concentration typically reaches a plateau. Once the system has reached a state of equilibrium, the particles may persist dissolution even in the presence of free oxygen (Molleman and Hiemstra, 2017). This stability could be attributed to the formation of a layer of Cu oxide (CuO and Cu2O) on the surface of the particles (Mudunkotuwa et al., 2012). However, Cu oxide is highly soluble and will generally not be stable for a long time under different physicochemical conditions. At neutral and acidic pH, the solubility of Cu oxide is some orders of magnitudes higher than at pH > 8, which limits the persistence of a Cu oxide layer on the surface of the particles (Mudunkotuwa et al., 2012). This could explain the higher stability observed at pH 9 in comparison to the stability at pH ≤ 7.5. Similar results were reported by Jones and Su (2012) for dissolution of Cu0 ENPs as a function of pH, and Molleman and Hiemstra (2017) for dissolution of Ag oxide formed on the surface of Ag ENPs. In the latter study the authors reported that formation and persistence of Ag is highly unlikely, unless the pH is very high.

In the absence of DOC, the concentration of dissolved Cu decreased after 4 h of exposure at all pH values, except for media containing 10 mM Ca2+/Mg2+ at pH 6 and 7.5 (Figs. 3a and 3b). This decrease can be attributed to re-precipitation of Cu2+ on the surface of the Cu0 ENPs (Jones and Su, 2012) as reported for Ag ENPs by Levard et al. (2013). The final concentrations of [Cu]dissolved in the media without DOC were also lower than those in media treated with DOC, except in the presence of 10 mM Ca2+/Mg2+. This may result from the fast aggregation of particles which took place as the
Fig. 2. Aggregation kinetics of Cu⁰ ENPs as a function of DOC concentration, ionic strength and pH over 30 min of measurement using DLS.
particles were introduced in the media without DOC. This results in a lower available surface area and, subsequently, lower dissolution kinetics as reported by Li et al. (2010a,b). The aggregation results confirmed these observations (Fig. 2). Similar results were previously reported for Cu ENPs as aggregation was found to decrease the ion release from the particles (Adeleye et al., 2014).

The presence of Ca\(^{2+}/Mg\(^{2+}\) in the media accelerated the aggregation of the particles, which is in line with the Derjaguin Landau Verwey Overbeek (DLVO) theory. Enhanced aggregation is due to compression of the diffuse double electrical layer of Cu\(^{0}\).
ENPs. However, in the media containing 10 mM Ca\(^{2+}\)/Mg\(^{2+}\) and pH lower that 8, the particles were stable against aggregation and the rate of dissolution was high, in some cases even higher than in case of DOC-induced dissolution (Fig. 3). This finding also was in agreement with the zeta potential of the particles (Table 5, Supporting Information). At pH < 7.5 and without DOC, the particles are positively charged (Table 5, Supporting Information). An increase in the concentration of Ca\(^{2+}\)/Mg\(^{2+}\) increases the positive charge of the particles due to specific interactions of Ca\(^{2+}\) ions with the particles (Abdolahpur Monikh et al., 2018). This results in a high positive zeta potential. This thick double layer reduces the successful collision between particles, which in turn will decrease the aggregation rate. Consequently the particles remain stable against aggregation for a longer period of time and dissolution increases.

In agreement with previous studies (Wang et al., 2011, 2015), the presence of DOC increases the amount of dissolved Cu (Fig. 3). In the presence of DOC and absence of Ca\(^{2+}\)/Mg\(^{2+}\), the particles remain stabilized in the suspension and do not aggregate. This leads to a high dissolution rate of the particles. NOM can act as a ligand that effectively interacts with Cu ENPs (Wang et al., 2015). NOM induces both a negative surface charge and steric stabilization on the surface of Cu\(^{0}\) ENPs due to the interaction of carboxylic and phenolic functional groups with the particle surface. This could stabilize the particles electrostatically and sterically against aggregation (Jones and Su, 2012). In the presence of high concentrations of DOC, a higher amount of functional groups are available to form strong complexes with the Cu\(^{0}\) ENPs. The complexion of DOC with Cu ENPs (with CuO and Cu\(_{2}\)O present on the surface of the particles) weakens the surface Cu—Cu and Cu—O bonds (Korshin et al., 1998; Aiken et al., 2011; Wang et al., 2015), which leads to enhanced dissolution through ligand promoted processes (Misra et al., 2012). Dissolved Cu ions, independent of their release being induced by DOC, protons and/or hydroxide ions, have a greater affinity towards organic ligands to form insoluble complexes with DOC (Mudunkotuwa et al., 2012). Thus, after release, Cu ions can form strong complexes with the functional groups of DOC via intra- or intermolecular bidentate chelation (Wang et al., 2015). If the concentration of DOC in the system is high, the Cu concentration gradient between the particle surface and the functional groups acts as the driving force of particle dissolution, resulting also in a decrease of the mineral saturation index (the driving force for precipitation) (Aiken et al., 2011).

At pH 6 (Figure 3a) and 0 mM Ca\(^{2+}\)/Mg\(^{2+}\), there was no significant difference in the dissolution patterns of Cu\(^{0}\) ENPs between media containing 5, 25 and 50 mg/L DOC. The same results were observed in the media with 2.5 mM Ca\(^{2+}\)/Mg\(^{2+}\). However, in the presence of 10 mM Ca\(^{2+}\)/Mg\(^{2+}\), the highest and the lowest extent of dissolution were observed in the media containing 50 and 5 mg/L DOC, respectively. These results indicate that at a high concentration of Ca\(^{2+}\)/Mg\(^{2+}\), 5 mg/L DOC blocks the enhancement in the positive charge on the surface of the particles due to specific interaction of Ca\(^{2+}\) with particles, but also was not able to stabilize the particles against aggregation. Thus, the particles underwent aggregation, which led to a decrease in the dissolution rate.

At pH 7.5 (Fig. 3b) and pH 9 (Fig. 3c), the influence of DOC on the dissolution of the Cu\(^{0}\) ENPs decreases as the concentration of Ca\(^{2+}\)/Mg\(^{2+}\) increases in the media. The differences between media containing different DOC concentrations are also more pronounced in comparison to those at pH 6. At pH ~ 9, the zeta potential is close to zero and the particles are unstable and may aggregate relatively easy to form large particles. The larger aggregates influence the rate of release of ions in the media and the final [Cu\(_{\text{dissolved}}\) at 32 h. Previous studies also reported that dissolution of Cu ENPs (Adeleye et al., 2014) and Zn ENPs (Odzak et al., 2014) decreases as the pH of the system increases. Griffitt et al. (2007) reported that less than 0.1% of Cu ENPs dissolved in media at pH 8.2 after 48 h. However, the dissolution increased to 98% Cu ENPs at pH 6 after one week. Overall, the observation of higher rates of dissolution of the
particles in the presence of DOC compared to the rates of dissolution in the absence of DOC shows that even (a) the presence of high levels of Ca\(^{2+}/Mg\(^{2+}\) in the media, which can increase the aggregation and reduce the available surface area, and (b) the formation of Cu oxides on the surface of Cu\(^{0}\) ENPs at high pH values cannot overcome the DOC promoted dissolution of the particles. The interaction Cu-DOC-carboxylic groups is predominantly covalent, outweighing the electrostatic effect of Ca\(^{2+}/Mg\(^{2+}\), and at higher pH the polyionic DOC colloid is highly negatively charged, thus facilitating covalent bonding with Cu\(^{2+}\).

### 3.4. Dissolution rate in synthetic water

The dissolution rates (\(k_{\text{diss}}\)) of the Cu\(^{0}\) ENPs, determined from the slopes of the \([\text{Cu}]_{\text{dissolved}}\) versus time, for synthetic waters are reported in Table 1. Very fast dissolution and high values of \(k_{\text{diss}}\) were observed in some samples at rates that were too high to be assessed by means of the methods used in this study. No numerical values for the rate constants are included in Table 1 for these samples. As reported in Table 1, the \(k_{\text{diss}}\) differed between the media tested. At pH 6 and Ca\(^{2+}/Mg\(^{2+}\) concentration of 2.5 mM, increases in the concentration of DOC increased the \(k_{\text{diss}}\) of Cu\(^{0}\) ENPs dissolution. A similar trend was observed at pH 9 for sample containing 2.5 mM Ca\(^{2+}/Mg\(^{2+}\). Furthermore, the apparent \(k_{\text{diss}}\) of the particles increased as the pH value increased from 6 to 9 (Table 1). This is contradictory to what one would expect on the basis of eq (1) which could be due to the combined effects of pH, Ca\(^{2+}/Mg\(^{2+}\) and DOC. The \(k_{\text{diss}}\) of the Cu\(^{0}\) ENPs in the samples containing no Ca\(^{2+}/Mg\(^{2+}\) were higher compared to those in media containing 2.5 and 10 mM. The differences in the release behavior were discussed in the previous section. This results suggest that the rate of dissolution of ENPs is strongly dependent on the concentration of DOC and the pH of the media as reported in previous studies (Mitrano et al., 2014; Molleman and Hiemstra, 2017). It must be also mentioned that aggregation affects the \(k_{\text{diss}}\), especially for the high ionic strength suspensions. This explains the lower \(k_{\text{diss}}\) observed in high ionic strength media.

### 3.5. Particle dissolution behavior in natural surface waters

The physicochemical parameters of the samples collected from five different natural surface waters in the Netherlands were measured and reported in Table 2. The background concentration of Cu in the samples was lower than the detection limit of the instrument (<1 ppb). The concentration of DOC was between 9.2 and 18.5 mg/L with the highest concentration measured in Ditch 1 followed by Ditch 3 > Ditch 2 > Lake > River. The highest pH value was recorded for Ditch 1 and the lowest was recorded in the River. The pH of all samples was in the neutral — slightly basic range and exceeded 7.6. According to the data reported in the Geochemical Atlas of Europe the highest concentration of Ca\(^{2+}\) and Mg\(^{2+}\) are 4.12 and 1.06 mM respectively. From these results is may be deduced that the conditions in the natural waters sampled are mostly mimicked by the synthetic media contain 5–20 mg/L DOC, 2.5–10 mM of Ca\(^{2+}/Mg\(^{2+}\) and 7.5–9 pH.

The \([\text{Cu}]_{\text{dissolved}}\) of Cu\(^{0}\) ENPs was determined in the natural surface waters (Fig. 4). After 24 h, the \([\text{Cu}]_{\text{dissolved}}\) in water followed this order; Ditch 1 > Ditch 2 > Ditch 3 > Lake > River. The concentration of DOC in the Ditches and Lake is higher than that in the River. The results, thus, also imply that a higher extent of dissolution of Cu\(^{0}\) ENPs in the Ditches and in the Lake than in the River is likely to occur. According to these results, it is likely that DOC-enhanced dissolution of Cu\(^{0}\) ENPs is occurring in the natural waters, as observed in the synthetic waters. One should also consider that the physicochemical parameters of natural surface waters are changing dramatically from place to place and season to season. Thus, these variations will modify the dissolution and aggregation behavior of the particles dramatically. The reported data herein are therefore to be considered a snapshot of what occurs under dynamic natural conditions. The rate constants measured in the natural samples provide a general overview of the range of dissolution/aggregation of Cu\(^{0}\) ENPs in natural conditions and show that the rate constants obtained in synthetic waters are indeed comparable to the rate constants in natural waters of similar compositions. Natural systems are inherently complex, which makes it difficult to directly compare the data with other published studies. Mitrano et al. (2014) reported that for most circumstances, the \(k_{\text{diss}}\) of Ag ENPs was higher in water originating from a creek as compared to the \(k_{\text{diss}}\) in distilled water and in tap water. It must be mentioned that chloride, Cl\(^{-}\), which is a common ligand in natural surface waters, may form a complex with Cu ENPs or with Cu ions released during particle oxidation, and thus may influence the

---

![Fig. 4.](image) Dissolved copper fraction and standard deviation over 24 h in natural surface water collected from the Netherlands.
dissolution rate of the particles (Levard et al., 2011; Mitran et al., 2014). In this research, the influence of Cl− was not investigated and this could be a motivation for future studies in which the impact of Cl− on particle dissolution is explicitly considered.

Measuring Dh using DLS to determine the aggregation kinetics of ENPs in natural water is challenging due to the limitation of the technique to deal with samples containing different natural particles (von der Kammer et al., 2012). In addition, it was noticed that there were natural particle settlements in the cuvettes which led to particle sedimentation as a consequence of heteroaggregation. Thus, reliably measuring the Dh using DLS to obtain the aggregation kinetics of Cu0 ENPs in natural samples was not possible in this study. The measured zeta potential values are reported in Table 6 in the Supporting information.

As can be seen in Fig. 4, a slightly higher extent of dissolution than in any of the other waters was observed for Ditch 1. The second highest [Cu\textsubscript{dissolved}] was observed in Ditch 3, followed by Ditch 2 > Lake > River. The concentration of [Cu\textsubscript{dissolved}] in the River sample was significantly lower than in the other natural waters samples. The initial level of [Cu\textsubscript{dissolved}] in all the natural waters, after addition of Cu0 ENPs, was around 0.1 μg/L which is similar to what was recorded for the synthetic media with 2.5 mM Ca\textsuperscript{2+}/Mg\textsuperscript{2+} at pH 7.5 and 9.

The values of k\textsubscript{diss} as calculated for the natural samples are reported in Table 3. The k\textsubscript{diss} in the investigated natural waters was similar to that calculated for the synthetic media. The k\textsubscript{diss} in Ditch 1, 2 and 3 was higher that the lake and the river. The rate constant in the river was similar to the rate constant obtained for the synthetic medium containing 10 mM Ca\textsuperscript{2+}/Mg\textsuperscript{2+}, 5, 25 and 50 mL/DOC and pH 7.5. Considering the physicochemical parameters of the river (Table 2), this constant rate is expected for the river.

4. Conclusions

The key finding of this study is that dissolution and aggregation of Cu0 ENPs are highly dependent on the DOC, ionic strength and pH of the aqueous medium. DOC can induce dissolution of Cu0 ENPs by controlling the aggregation, thus the available surface area, of the particles and by weakening the Cu−Cu and Cu−O bonds formed as a result of oxidation on the surface of the particles. Moreover, DOC can sorb the released Cu ions from the particles and, subsequently, accelerate the dissolution. Changes in the pH induced on particle dissolution is explicitly considered. Water Air Soil Pollut. 44, 143–158. https://doi.org/10.1007/s11270-015-2457-8.


