

UC Santa Barbara

UC Santa Barbara Previously Published Works

Title

Long-term colloidal stability and metal leaching of single wall carbon nanotubes: Effect of temperature and extracellular polymeric substances

Permalink

<https://escholarship.org/uc/item/7ph7w0d9>

Authors

Adeleye, Adeyemi S
Keller, Arturo A

Publication Date

2014-02-01

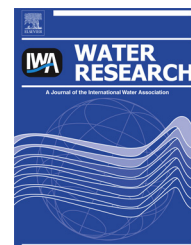
DOI

10.1016/j.watres.2013.11.032

Peer reviewed

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/watres

Long-term colloidal stability and metal leaching of single wall carbon nanotubes: Effect of temperature and extracellular polymeric substances

Adeyemi S. Adeleye^{a,b}, Arturo A. Keller^{a,b,*}

^aBren School of Environmental Science & Management, University of California, Santa Barbara, 3420 Bren Hall, Santa Barbara, CA 93106-5131, USA

^bUniversity of California Center for Environmental Implications of Nanotechnology, Santa Barbara, CA 93106-5131, USA

ARTICLE INFO

Article history:

Received 28 September 2013

Received in revised form

13 November 2013

Accepted 15 November 2013

Available online 28 November 2013

Keywords:

Carbon nanotubes

Colloidal stability

Aggregation

Metal leaching

Extracellular polymeric substance

ABSTRACT

Long term (90 day) stability, aggregation kinetics in the presence and absence of natural organic materials (NOM), and metal leaching of five commercial single wall carbon nanotubes (SWCNTs) in waters (e.g. freshwater, seawater, stormwater, wastewater, and groundwater) were studied, as well as the effect of temperature on SWCNT stability and metal leaching. Zeta (ζ) potential of SWCNT decreased in magnitude with increase in temperature. In wastewater, SWCNT sedimented from the water column to below detectable levels after 30 days when kept at 40 °C, but at 20 °C 19% suspension was still observed after the same exposure time. Addition of 0.1 mg-C L⁻¹ EPS shifted the critical coagulation concentration (CCC) of SRNOM-stabilized SWCNT from 15 mM to 54 mM NaCl via additional electrostatic and possibly steric stabilization. Attachment efficiencies (α) of SWCNT in waters ranged from ~0.001 in DI with 10 mg L⁻¹ SRNOM to 1 in seawater. However, sedimentation of SWCNT in seawater (and other high ionic strength conditions) was not as fast as expected due to improved buoyancy and/or drag. Purified forms of SWCNTs exhibited better dispersibility and stability in most waters, but as expected, the total metal leached out was higher in the raw variants. Metal leaching from CNT in these studies was controlled by metal and water chemistries, CNT pretreatment, leachable metal fraction, exposure time, and presence of NOM.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Carbon nanotubes (CNTs) are insoluble and not easily biodegradable (Lam et al., 2004), hence, they tend to persist in the environment. In order to assess the long-term impact of CNTs

released into surface waters, there is a need to understand how CNTs will partition between surface waters and sediment phases (Schwyzer et al., 2012). The hydrophobic surfaces of CNTs makes them interact readily with natural organic matter (NOM), which is abundant in the environment (Saleh et al., 2010). Hyung et al. (2007) demonstrated improved CNT

* Corresponding author. Bren School of Environmental Science & Management, University of California, Santa Barbara, 3420 Bren Hall, Santa Barbara, CA 93106-5131, USA. Tel.: +1 805 893 7548; fax: +1 805 893 7612.

E-mail addresses: keller@bren.ucsb.edu, arturo.keller@gmail.com (A.A. Keller).

stability in the presence of Suwanee River natural organic matter (SRNOM). In water bodies with significant amounts of NOM, such as humic acid, alginate or extracellular polymeric substances (EPS), the stability of CNTs may be enhanced. As such, CNTs may be mobile in natural aquatic systems, and available to pelagic organisms (Schwyzer et al., 2012). EPS are composed of a wide range of organic polymers such as polysaccharides, proteins, nucleic acids and phospholipids excreted by microorganisms (Flemming et al., 2007); and they may affect the fate and transport of engineered nanomaterials (ENMs) in natural systems (Miao et al., 2009).

Colloidal stability of CNTs in aqueous media has been investigated (Lin et al., 2010; Schwyzer et al., 2011, 2012). Schwyzer et al. (2012) investigated the stability of CNTs in aqueous media and concluded that surface functionalization and size correlates with stabilization. Bennett et al. (2013) monitored the dispersibility and stability of SWCNTs in freshwaters for 72 h and found that stability varies widely based on physicochemical properties of SWCNTs. However, long-term stability of CNTs in natural waters has not been examined. More so, the potential effect of temperature and EPS on stability of CNTs has not been reported to date.

As-prepared CNTs usually contain a significant amount of impurities, including metal catalysts (Bennett et al., 2013; Ge et al., 2012). These impurities are commonly removed in order to obtain purified CNTs. However, some of the metals are protected by graphitic shells, and may remain even after rigorous purification processes (Ge et al., 2011). Residual metal impurities may be mobilized upon introduction of CNTs into aquatic systems (Bennett et al., 2013; Ge et al., 2012). The water chemistry may or may not be favorable for dissolution of metal catalysts attached to CNTs (Ge et al., 2012) so leaching of metals may vary widely in different waters. Metal leaching from CNTs when dispersed in natural waters has only been investigated on a short term basis and no significant toxicity to algae was reported within the study period (Bennett et al., 2013). However, a 14-day study (Mwangi et al., 2012) reported that nickel leached out from CNTs suspensions at levels that were toxic to amphipods. As such, it is important to quantify the levels of metal impurities that may leach out of CNTs in natural waters over a long period of time.

The goals of this study were to experimentally measure the fate of SWCNT, applied from dry powders to natural waters, and investigate:

1. Long-term stability and partitioning of SWCNTs;
2. Long-term leaching of metals from SWCNTs; and
3. Effect of temperature variations on SWCNT surface characteristics, stability, and metal leaching.

2. Materials and methods

2.1. Materials

Five SWCNTs were used for dispersibility and stability studies, which include (1) raw (HP-R) and (2) purified (HP-P) forms of high-pressure carbon monoxide SWCNTs (HiPCo, Nano-Integris, IL); (3) raw (P2-R), and (4) purified (P2-P) forms of arc

discharge SWCNTs (Carbon Solutions, CA); and (5) SG65, a purified SWCNT prepared using the CoMoCat process (SouthWest NanoTechnologies, OK). All five SWCNTs were used as received. P2-P was selected as a model commercial SWCNT, and was used for all the temperature-dependent and aggregation studies. Some physicochemical properties of these SWCNTs have been described previously (Bennett et al., 2013). Additional characterizations done in this study include zeta (ζ) potential analysis (Zetasizer Nano-ZS90, Malvern, UK), transmission electron microscopy (FEI Titan 300 kV FEG TEM), and scanning electron microscopy (FEI XL30 Sirion equipped with an EDAX APOLLO X probe for energy-dispersive X-ray spectroscopy, EDS).

Waters used for this study include NANOpure water with or without 10 mg L⁻¹ SRNOM (denoted DI and DINOM respectively), freshwater with 0.1 mg L⁻¹ (FW0.1) or 1.0 mg L⁻¹ SRNOM (FW1.0), groundwater (GW), lagoon (LW), stormwater (STM), wastewater (WW), and seawater (SEA). Basic characteristics of the waters are shown in Table 1 and additional information is provided in the Supplementary material. Soluble EPS was isolated from an axenic culture of a phytoplankton, *Isochrysis galbana*. Details on EPS isolation are in the Supplementary material. EPS was characterized by measuring carbohydrate and protein concentrations using anthrone method (Morris, 1948), and modified Lowry Protein Assay Kit (Pierce Biotechnology) respectively. Hydrodynamic diameter (HDD) of EPS was determined using the Zetasizer Nano-ZS90.

2.2. Effect of temperature and natural organic materials on zeta (ζ) potential

10 mg L⁻¹ P2-P suspensions were made in the waters by probe-sonication with a Misonix Sonicator S-4000 (QSonica LLC, Newtown, CT). Sonication was done in ice-bath to reduce defect. ζ potential of an aliquot was then determined from 1 to 60 °C in DTS 1060 cells (Malvern) using the temperature controlled chamber of the Zetasizer Nano-ZS90. At each temperature, a 120 s equilibration period was allowed before ζ potential data were collected in triplicate measurements—with each measurement reflecting 12–15 runs. Trend experiments were not done in LW, SEA and WW because the ionic strength (IS) of those conditions was too high for the cells to function properly across the temperature range.

To see the effect of NOM on ζ potential, SWCNT stock suspensions were made with SRNOM or EPS or neither (see Section 2.3 for details). Aliquots were taken from the three stock suspensions, diluted to make a final [SWCNT] of 10 mg L⁻¹, and analyzed for ζ potential at different NaCl concentrations. All ζ potential measurements were done at pH 7.

2.3. Aggregation and sedimentation kinetics

Stabilized SWCNT stock suspensions (100 mg L⁻¹) were made by dispersing P2-P in NANOpure water (Barnstead) in ice-bath by probe sonication using the Misonix Sonicator S-4000 in the presence of 3 mg L⁻¹ SRNOM. Sonicated SWCNT stock was allowed to stand overnight and stable aqueous phase was removed for characterization and analyses. SWCNT stock was diluted by a factor of 10 for aggregation and sedimentation

Table 1 – Characteristics of water samples used in this study. ND = non-detect.

Parameter	Unit	DI water ^a	Storm	Groundwater	Freshwater ^a	Seawater	Lagoon	Wastewater
pH		7.1	7.7	7.5	7.3	7.3	6.6	7.6
Conductivity	$\mu\text{S cm}^{-1}$	0.44×10^1	3.86×10^2	9.71×10^2	0.97×10^2	4.94×10^4	5.08×10^4	2.29×10^3
TOC	mg L^{-1}	ND	6.49	ND	ND	ND	ND	2.38
UV ₂₅₄		0	0.242	0.002	0.002	0.002	0.041	0.098
UV ₅₅₀		0	0.001	0	0.001	0.007	0.001	0.005
Redox potential	mV	9.68×10^1	1.67×10^2	1.37×10^2	1.60×10^2	1.42×10^2	1.36×10^2	1.24×10^2
Na	mg L^{-1}	ND	4.93×10^1	1.58×10^2	ND	1.27×10^4	1.28×10^4	3.25×10^2
Ca	mg L^{-1}	0.03	3.61×10^1	4.95×10^1	0.15×10^1	4.90×10^2	4.93×10^2	1.20×10^2
Mg	mg L^{-1}	ND	1.0×10^1	2.75×10^1	0.35×10^1	1.65×10^3	1.69×10^1	7.8×10^1
Al	mg L^{-1}	ND	ND	ND	ND	ND	ND	ND
K	mg L^{-1}	0.48×10^0	0.75×10^1	0.86×10^1	0.12×10^1	4.61×10^2	4.64×10^2	3.86×10^1
Cu	mg L^{-1}	0.02	0.16	ND	0.01	ND	ND	0.08
Fe	mg L^{-1}	ND	0.25	ND	0.06	ND	ND	0.35
Ni	mg L^{-1}	ND	ND	ND	ND	ND	ND	ND
Y	mg L^{-1}	ND	ND	ND	ND	ND	ND	ND
Co	mg L^{-1}	ND	ND	ND	ND	ND	ND	ND
Mo	mg L^{-1}	ND	0.03	ND	ND	0.08	0.11	0.07

^a Measurements were done before the addition of SRNOM.

studies so the final [SWCNT] and [SRNOM] were 10 mg L^{-1} and 0.3 mg L^{-1} respectively. Aggregation kinetics was studied in (1) increasing concentrations of NaCl solution at pH 7, and (2) natural waters. As shown in Eq. (1), the initial aggregation rate constant (k) of SWCNTs reflects doublet formation and is proportional to the initial rate of increase in the intensity-weighted hydrodynamic radius, $a_h(t)$, with time, t , and the inverse of initial number concentration of SWCNT particles, N_0 (Saleh et al., 2008):

$$k \propto \frac{1}{N_0} \left(\frac{da_h(t)}{dt} \right)_{t \rightarrow 0} \quad (1)$$

k is obtained from the slope of the best fit line of $(da_h(t)/dt)_{t \rightarrow 0}$, which is determined via Dynamic Light Scattering (DLS) using the Zetasizer Nano-ZS90. The analysis requires that the final $a_h(t)$ be approximately 1.3 of initial a_h , where there are sufficient doublets formed and few higher-order aggregates (Zhou and Keller, 2010). Attachment efficiencies (α) of SWCNTs in aqueous NaCl were calculated by normalizing the measured k of a given concentration by the diffusion-limited aggregation rate constant (k_{fav}) determined in highly favorable aggregation conditions (Eq. (2)). Attachment efficiencies (α) of SWCNTs in each natural water was calculated by normalizing the measured k of a given natural water by the diffusion-limited aggregation rate constant (k_{fav}) determined in SEA:

$$\alpha = \frac{\left(\frac{da_h(t)}{dt} \right)_{t \rightarrow 0}}{\left(\frac{da_h(t)}{dt} \right)_{t \rightarrow 0, fav}} \quad (2)$$

To understand the role of naturally-occurring EPS in SWCNT stability, aggregation kinetics was also studied in SWCNT stock dispersed in 5 mg-C L^{-1} EPS. The final [EPS] in sample was 0.5 mg-C L^{-1} , which is within the range reported for colloidal carbohydrates in natural waters (Hung et al., 2001). Finally, an additional aggregation study was conducted in which 0.1 mg-C L^{-1} EPS was added to SWCNT initially stabilized with SRNOM just before measurements to see whether additional EPS might affect aggregation dynamics of

SRNOM-stabilized SWCNTs. Aggregation kinetics was measured using DLS as described elsewhere (Zhou and Keller, 2010). In summary a 532 nm laser source and a detection angle of 90° were used to do DLS measurements immediately after adding SWCNT stock and natural waters (or electrolyte, buffer, and NANOpure water). Data were collected until a 50% increase in the initial hydrodynamic radius was observed. The diffusion-limited (DLCA) and reaction-limited (RLCA) clustering aggregation regimes, and thus, CCC, can be identified in a plot of $\log_{10}[\text{NaCl}]$ versus $\log_{10} \alpha$. The dynamic aggregation process was monitored using a Biospec 1601 spectrophotometer (Shimadzu, Japan) measuring the sedimentation of the nanoparticles in natural waters and NaCl solution (pH 7) via time-resolved optical absorbency. Optical absorbency was measured every 6 min for 354 min, using aliquots of stabilized SWCNT stock in natural waters or a range of NaCl concentrations.

2.4. Stability experiments

SWCNT dry powder was added to the various waters to obtain concentrations of $10 \text{ mg SWCNT L}^{-1}$. The SWCNT suspensions were bath-sonicated (Branson 8210, Branson Danbury, CT) for 4 h to enhance dispersion without causing defects on the nanotubes (Islam et al., 2003). This form of low-power sonication better mimics naturally-occurring dispersive forces than probe ultrasonication. The sonicated suspensions were kept at 20°C and monitored for 90 days. To see the effect of temperature on CNT stability, suspensions of the model SWCNT, P2-P, were made in FW1.0 and WW, kept at 4, 20, and 40°C constant temperatures, and monitored for 30 days. To see how sudden temperature variation may affect stability, three sets of FW1.0 and WW suspensions of P2-P were kept at 20°C for 7 days, after which a set was moved to 4°C and another to 40°C . Stability was monitored at the new temperatures for the next 23 days, and compared with the set that remained at 20°C . Stability was monitored as described in previous studies (Bennett et al., 2013; Schwyzer et al., 2011). In summary, the concentration of suspended SWCNT was

determined via absorbance at 550 nm (Biospec 1601). SWCNT concentration was determined by constructing a calibration curve ($R^2 \geq 0.98$) of each SWCNT dispersed in the respective waters.

2.5. Metal leaching

Aliquots of the SWCNT suspensions were filtered with 0.2 μm -sized syringe filters (Millipore) to remove the nanotubes. The dissolved metal content of filtrate was determined as described elsewhere (Adeleye et al., 2013). In brief, a measured amount of the filtrate was digested using trace-metal grade nitric acid (Fisher Scientific), diluted with NANOpure water and analyzed via ICP-AES (iCAP 6300, Thermo Scientific) for: (1) nickel (Ni) and yttrium (Y) present in P2-P and P2-R; (2) iron (Fe) present in HP-P and HP-R; and cobalt (Co) and molybdenum (Mo) present in SG65. The temperature-dependent metal leaching study was only done using the model SWCNT, P2-P (at 4 °C and 40 °C). Metal leaching was monitored for 90 days.

2.6. Statistical analysis

Statistical significance between treatments was determined using analysis of variance (ANOVA). Tukey HSD test *post-hoc* was used to determine which treatments significantly differed. A *p* value of <0.05 was considered statistically significant. R statistical software (version 3.0.1) was used for all analyses.

3. Result and discussion

3.1. SWCNT and EPS Characterizations

The SWCNTs appeared as closely bound bundles and clusters (Fig. 1). This is primarily due to the strong interaction forces that exist in the nanotubes. Tubes of P2-R were not as densely packed, appearing as thin meshes of nanotubes interspersed with impurities. Morphology of the SWCNTs appeared to be affected by purification as seen in the physical differences between P2-R and P2-P, and HP-R and HP-P. SG65 appeared shorter and thicker compared to arc discharge and HiPCo SWCNTs. The raw forms of SWCNTs contained more non-CNT components than the purified variants. Most of the non-CNT components were metal impurities as confirmed by EDS (Fig. S1 in Supplementary material).

The EPS fraction had an average HDD of 203.95 ± 12.50 nm. Carbohydrate concentration was determined to be 12.19 mg L^{-1} glucose equivalent, while protein concentration was 3.63 mg L^{-1} using a Bovine serum albumin (BSA) standard.

3.2. Effect of temperature and natural organic materials on zeta potential

The ζ potential of all the SWCNTs indicated likely instability ($<\pm 30$ mV) in all the waters except in DI, DINOM and the freshwaters, all of which have low IS. ζ potential of the SWCNTs varied widely in different waters, with P2-P exhibiting the highest magnitude in most conditions (Fig. 2A). The presence of NOM increased the magnitude of the ζ potential in

natural waters, while the presence of salts decreased it. For instance ζ potential of P2-P, in mV, was -39.6 ± 3.0 , -32.8 ± 2.2 , and -35.5 ± 1.5 in DI, FW0.1, and FW1.0 respectively. Surface charge of carbonaceous ENMs may originate from surface oxidation (Sano et al., 2001), accumulation of hydroxides (Chen and Elimelech, 2009), defect and mechanochemistry (Saleh et al., 2010), or surface electron density distribution (Leys et al., 2003).

We observed that ζ potential of P2-P varied significantly with temperature. ζ potential became less negative as temperature increased in all the natural waters (Fig. 2B), and even turned positive at 60 °C in some waters. For instance, ζ potential of P2-P in STM increased in magnitude from -27.3 ± 1.0 mV at 20 °C to -32.7 ± 3.5 mV at 1 °C. At a typical summer temperature in tropical areas (40 °C or 104 °F), however, the ζ potential of the same sample decreased in magnitude to -19.3 ± 0.2 mV. In waters with significant amount of electrolytes (e.g. GW), ζ potentials at high temperature conditions were in the regions of maximum instability. This result suggests that stability of CNTs in natural waters will be influenced by temperature variation. At higher ζ potential induced by lower temperatures, electrostatic repulsion will be more significant and CNTs may have increased mobility in surface waters and groundwater. In hot temperature conditions, electrostatic repulsion will be significantly reduced. In addition, higher temperatures lead to increased evaporation, and thus higher salinity. Decreased surface charge of CNTs, coupled with higher salinity will enhance aggregation at high temperatures and SWCNT sedimentation.

The presence of SRNOM and EPS increased the magnitude of ζ potential of all SWCNTs (Fig. 2C, D). For example, ζ potential (in mV) of P2-P in 10 mM NaCl in the presence of EPS, SRNOM, and neither were -49.3 ± 0.4 , -44.7 ± 1.7 , and -39.1 ± 2.7 respectively. Similarly, in P2-R we observed -42.5 ± 1.3 , -35.7 ± 1.5 , and -28.2 ± 1.1 in the presence of EPS, NOM, or neither were respectively. This suggests that increased electrostatic repulsion is one of the mechanisms by which SRNOM and EPS improve the stability of SWCNTs in aqueous phase, possibly, in addition to steric hindrance. ζ potential values observed in SRNOM were not significantly different from observation in EPS in all the purified SWCNTs. In the raw SWCNT variants however, we observed that ζ potential was significantly higher in the presence of EPS than in SRNOM regardless of IS.

3.3. Aggregation and sedimentation kinetics

Probe sonication dispersed the SWCNTs which were then stabilized by SRNOM or EPS (Fig. 3). HDD (in nm) was 246, and 252 in SRNOM-stabilized, EPS-stabilized SWCNT respectively, compared to 1.49×10^4 nm with neither stabilizer. SWCNT fractions obtained in the presence of SRNOM and EPS were also monodispersed with average PDI < 0.4 (Fig. 3C). Attachment efficiency (α) and aggregation kinetics of P2-P in waters are presented in Fig. 4. The smallest α , observed in DINOM, was three orders of magnitude smaller than α in SEA. α in LW was similar to SEA, reflecting similarities in IS. An α of 0.92 was observed in GW, which had lower amounts of electrolytes than SEA and LW. α was an order of magnitude lower in WW

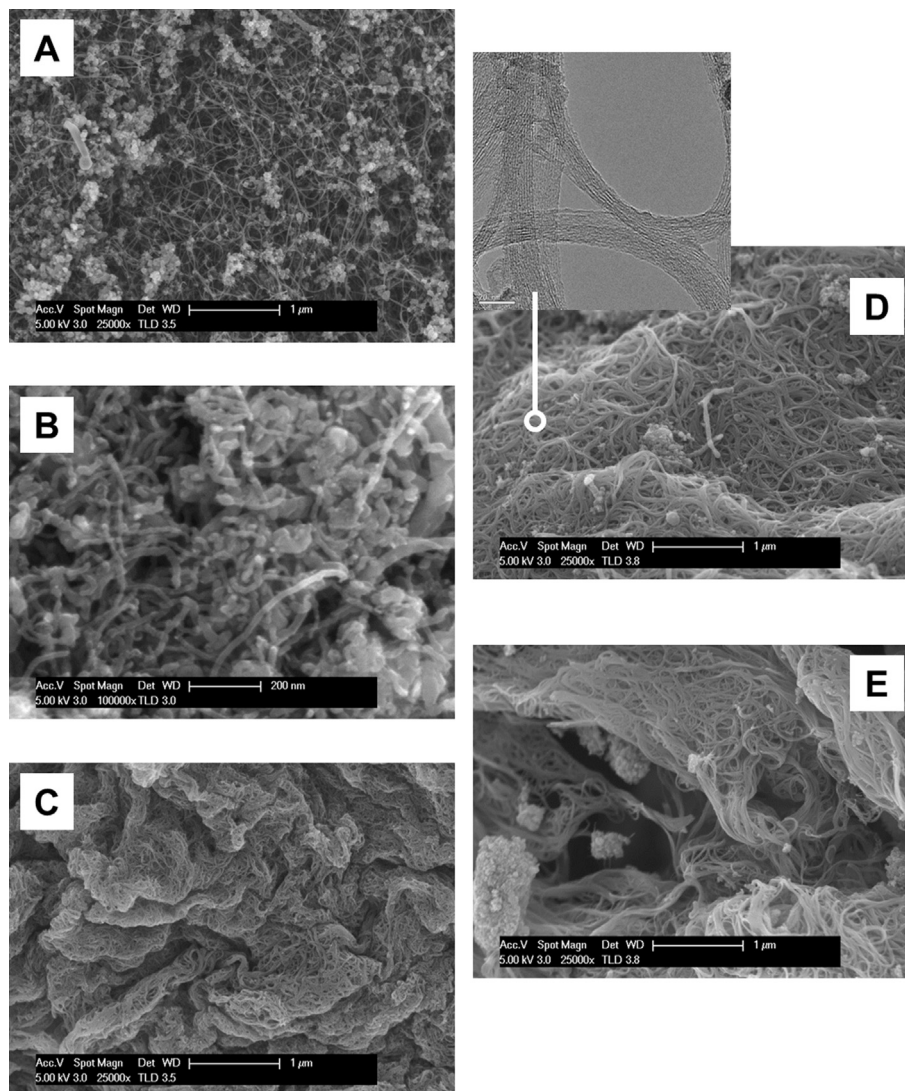


Fig. 1 – SEM micrographs of (A) P2-R, (B) SG65, (C) HP-R, (D) P2-P with inset showing a bundle of tightly packed tubes obtained via TEM, and (E) HP-P.

and at least two orders of magnitude lower in the rest of the waters.

At low [NaCl] (RLCA region), increased [NaCl] screened the electrostatic repulsion between nanotubes to a higher degree, leading to increase in α . At high [NaCl] (DLCA region), the charge of SWCNT was completely screened and the energy barrier between nanotubes was eliminated. The critical coagulation concentration (CCC) of P2-P stabilized with SRNOM was about 15 mM (Fig. 4C). A CCC value of 20 mM was reported in NaCl for a different type of SWCNT that was stabilized via successive sonication (Saleh et al., 2010). When EPS was used to stabilize P2-P stock instead of SRNOM, the CCC shifted to about 100 mM in NaCl, suggesting that EPS stabilized the nanotubes better than SRNOM in the conditions of this experiment. Finally, when additional 0.1 mg-C L⁻¹ EPS was added to SRNOM-stabilized P2-P just before analysis, a CCC of 54 mM NaCl was obtained. The presence of EPS in aqueous media has been suggested to affect the stability of ENMs (Miao

et al., 2009). Like other types of NOM, EPS may contain some hydrophobic polysaccharides with vast surface areas with which it can interact with other hydrophobic materials (Flemming et al., 2007) like CNTs, thereby creating steric repulsion between nanotubes. More so, the functional groups present in EPS such as hydroxyl, phosphoryl, and carboxylic groups (Pal and Paul, 2008) are able to enhance the negative charges on CNT, increasing electrostatic repulsion as indicated by ζ potential data.

Sedimentation of stabilized P2-P in natural waters was strongly dependent on the interplay of electrolyte concentration and presence of NOM (Fig. 4D). Significant sedimentation was not observed in DI, DINOM, FW0.1, FW1.0, and STM after 6 h as indicated by their normalized concentrations, C/C_0 (C = concentration and C_0 = initial concentration). In these waters, α was less than 0.01, so P2-P aggregation was unfavorable. Acute exposure of SWCNTs in surface waters with relatively low salt concentrations may therefore be mostly to

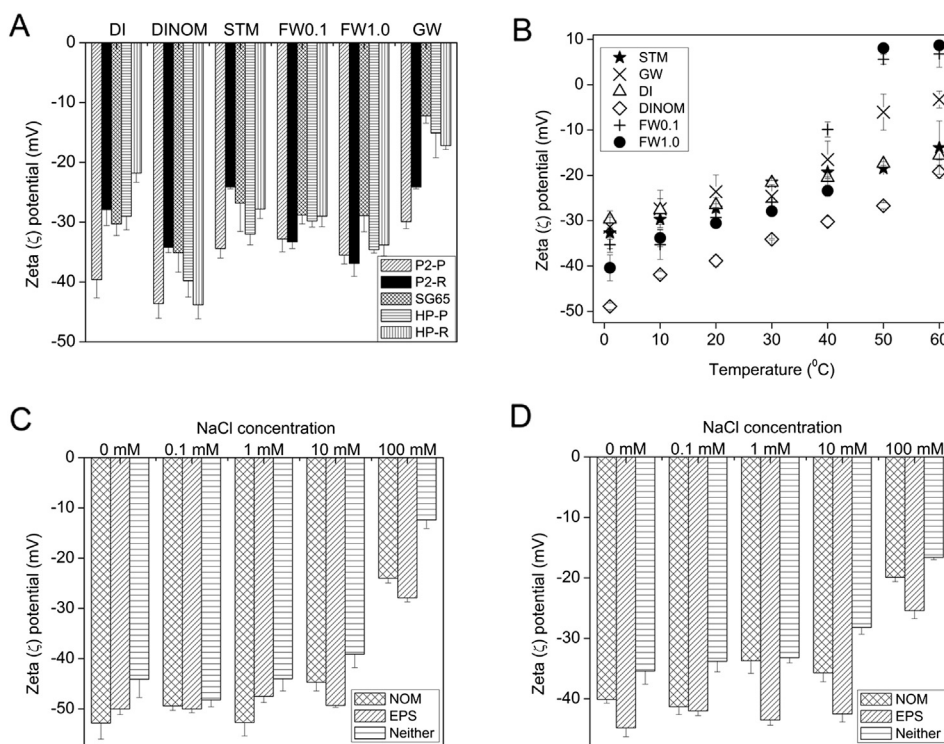


Fig. 2 – Zeta (ζ) potential of SWCNTs. (A) ζ potential of SWCNTs in selected waters. (B) ζ potential of P2-P in waters as a function of temperature. ζ potential of (C) P2-P and (D) P2-R as a function of NaCl concentration at pH 7 and in the presence of NOM, EPS or neither.

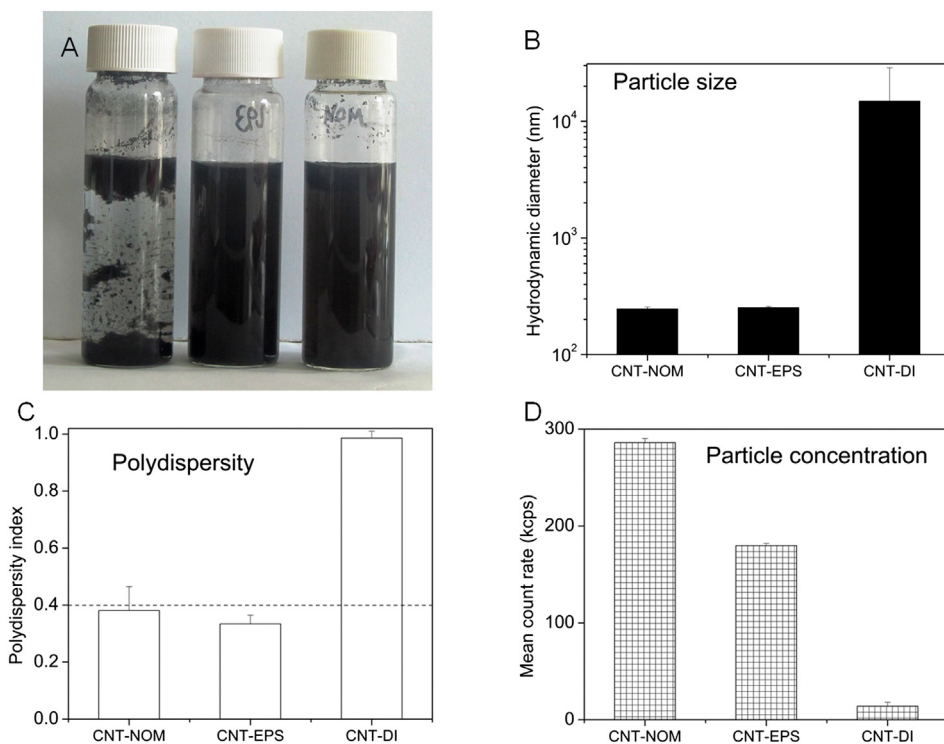


Fig. 3 – Characterization of SWCNT dispersed via probe-sonication in ice-bath. (A) Front view of stocks after 24 h settling, (B) Hydrodynamic diameter, (C) Polydispersity, and (D) Mean count rate of aqueous phase of SWCNT dispersed in SRNOM, EPS or neither.

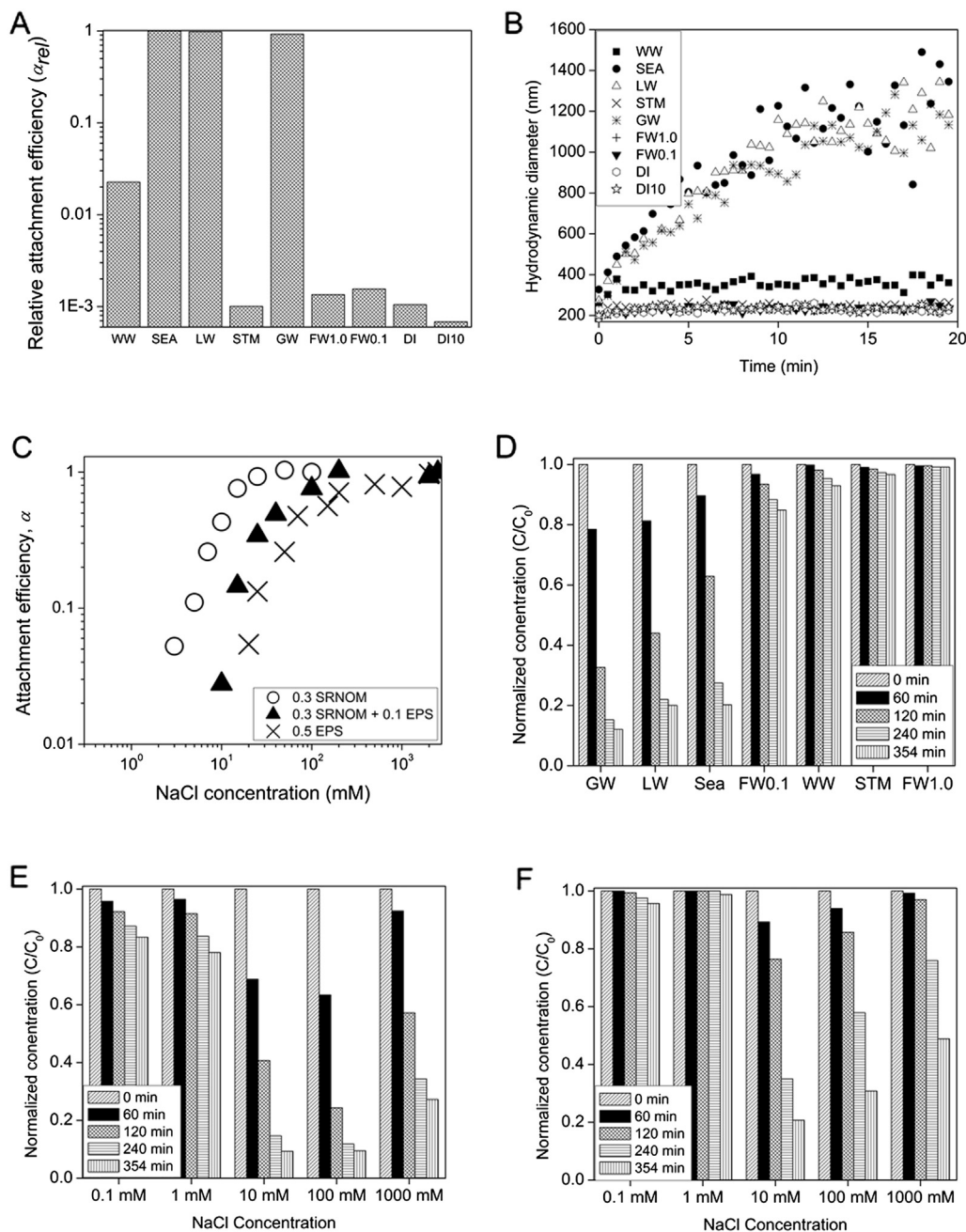


Fig. 4 – Aggregation kinetics of SWCNT. (A) Attachment efficiencies (α) of P2-P in waters. (B) Aggregation of P2-P in waters as a function of time. (C) Attachment efficiency of P2-P as a function of $[\text{NaCl}]$. Sedimentation of P2-P in (D) natural waters, (E) NaCl + SRNOM, and (F) NaCl + EPS.

epipelagic organisms, including phytoplankton, pelagic fish, and birds.

The concentration of suspended P2-P, $[\text{CNT}]_{\text{susp}}$, detected in GW (Conductivity = 971 μS) after 6 h ($C/C_0 = 0.12$) was surprisingly lower than in SEA (Conductivity = 49,400 μS) and LW (Conductivity = 50,800 μS). Both SEA and LW had C/C_0 of about 0.20 after 6 h. Since α of P2-P in GW was lower than SEA and LW, P2-P aggregation in GW was not as fast as in SEA and LW. Decreased sedimentation (despite faster aggregation) of SWCNT in SEA and LW may be due to higher viscosity, and

decreased difference in density between particles and medium ($\Delta\rho$) resulting from higher levels of salts compared to GW. Density and viscosity are higher in seawater than freshwater by about 3% and 10% respectively (El-Dessouky and Ettouney, 2002). In the presence of salts (hydrated ions), water molecules are organized around the ions via ion–dipole interactions, mostly leading to increased viscosity (Chandra and Bagchi, 2000). Increased viscosity results from increased ion concentration, especially for ions of higher valence (Chandra and Bagchi, 2000), which are abundant in SEA and

LW (Table 1). Decreased sedimentation of SWCNTs at high IS conditions was also observed in NaCl solution (Fig. 4F). For instance, C/C_0 of EPS-stabilized P2-P suspended in 10 mM NaCl was 0.21 after 6 h, while in 100 and 1000 mM NaCl, C/C_0 were 0.31 and 0.49 respectively after 6 h settling. Salts may also bridge SWCNTs in a network-like manner, decreasing sedimentation temporarily due to low density of network (Schwyzer et al., 2013), and/or increased drag from media.

Sedimentation of SWCNT was slower in the presence of EPS than in SRNOM at all [NaCl] studied (Fig. 4E, F). C/C_0 for EPS-stabilized P2-P after 6 h were 0.21 and 0.31 at 10 mM and 100 mM respectively. Meanwhile, at the same salt concentrations and settling time, C/C_0 values were 0.09 and 0.10 for SRNOM-stabilized P2-P.

3.4. Stability experiments

Sedimentation velocity of rod-like particles like SWCNTs depends on particle size, $\Delta\rho$, medium viscosity, and aspect ratio (Herzhaft and Guazzelli, 1999). Dispersibility and long term stability of SWCNTs in natural waters is also influenced by the presence and concentrations of salts and NOM, wettability of the SWCNTs, and the presence of impurities (Hyung et al., 2007; Li et al., 2011; Saleh et al., 2008). Dispersibility is defined as the initial nanomaterial concentration suspended in the media (Bennett et al., 2013), and it serves to determine the potential acute exposure of aquatic organisms to ENMs. As shown in Fig. 5, P2-R showed the least dispersibility (<17% by mass) in all tested waters, as a significant fraction remained aggregated in the air–water interface (AWI) after 4 h bath sonication. This agrees with our earlier observation of loose clustering of P2-R, compared to dense and compact clustering in all other SWCNTs used in this study. Dispersibility of the purified variant, P2-P, was $\geq 50\%$ in all the waters, showing that changes in physicochemical properties brought about by purification significantly affect CNT dispersibility. GW had the lowest dispersibility for all the nanotubes while DINOM suspensions were well-dispersed.

The energy delivered by bath sonication is not expected to overcome the van der Waals attraction between SWCNT pairs, which is estimated at -0.9 eV nm⁻¹ (Huang and Terentjev, 2012). For the stability studies, however, no additional treatment was performed to increase the amount of SWCNTs dispersed, since our goal was to understand the fate of dry-powdered SWCNTs in natural aquatic systems. Three distinct layers were identified in the SWCNT suspensions after sonication (Fig. 5): In addition to being suspended in the water matrices, some SWCNTs aggregates adhered to the AWI due to low density and hydrophobicity. Density of CNTs is affected by tube diameter, wall structure and the weight fraction of constituent elements (Thostenson and Chou, 2003). CNT density is estimated at 1.4 – 2.0 g cm⁻³ (Huang and Terentjev, 2012) with the lower end of the range more likely for SWCNTs, hence, $\Delta\rho$ is usually low compared to other ENMs. Except for P2-R, all the SWCNT had aggregates that also settled out during sonication, forming the third layer at the bottom of the vials. Additional settling was observed within a few minutes after sonication and throughout the study. Based on these observations, the introduction of SWCNTs presents

exposure risks to organisms in all the phases of aquatic systems—AWI, water column, and sediment phases.

The stability of SWCNTs in waters over a period of 8 days is shown in Fig. 6A–D. Although ζ potential indicated instability in most of waters, some stability was observed in STM and WW on the order of days (Fig. 6E), and in DINOM on the order of weeks. The stability observed may be due to steric repulsion from adsorbed NOM (Saleh et al., 2008). By Day 8, the order of $[CNT]_{\text{susp}}$ of P2-P was DINOM > WW > STM > FW1.0 > DI = SEA > FW0.1 > GW. SWCNTs were expected to be completely unstable in SEA and LW, and sediment out within hours as commonly observed for other ENMs (Keller et al., 2010). However, $[CNT]_{\text{susp}}$ of 0.78 – 2.71 mg L⁻¹ was observed in SEA by Day 8. Stability of SWCNTs in SEA and LW may be improved by high water density and viscosity and other factors discussed previously.

SWCNTs were only detectable in DINOM (lowest α) by Day 60, as suspended CNTs had fully sedimented in all the other waters by then. Thus, the long term fate of most SWCNTs in aquatic systems is the sediment phase. Fluctuations were observed in $[CNT]_{\text{susp}}$, and this may be due to resuspension of sedimented CNTs during sampling, even though considerable care was taken to minimize mixing. Their low density and weak attachment to other CNTs may result in easy resuspension. This may be different in a natural environment where clays and other sediments are present, and the CNTs can mobilize into pore water. Resuspension may still occur though, due to storm events and bioturbation. Settling of nanotubes to the sediment phase of natural waters implies that exposure of benthic organisms may increase significantly over time in the event of a CNT release. This may be a considerable concern as a recent study (Velzeboer et al., 2013) demonstrated that the structure of benthic communities in natural systems is sensitive to environmentally relevant levels of CNTs.

3.5. Effect of temperature on stability

Colloidal stability of P2-P decreased significantly at 40 °C compared to lower temperatures (Fig. 7). However, they were either more stable at 20 °C than 4 °C (as observed in WW) or not significantly different (as observed in FW1.0). In WW, 36% of the SWCNT suspended after sonication had settled out after 48 h at 40 °C, compared to 31% and 24% sedimentation at 4 °C and 20 °C respectively. By Day 30, 81% had sedimented at 20 °C and 86% at 4 °C, while SWCNT was not detectable in the water column at 40 °C. The trend was similar in FW1.0, with C/C_0 of 0.12, 0.29, and 0.32 by Day 30 at 40 °C, 4 °C and 20 °C respectively. Increase in temperature corresponds to energy input into SWCNT suspensions, which may lead to disruption of weak interaction forces (Zhou et al., 2012), increased Brownian motion (and collision), and decreased ζ potential. Disagglomeration of ENMs due to disruption of weak forces may improve stability temporarily since smaller particles sediment slower. However, as collision of nanotubes continues due to increased kinetic energy, more nanotubes aggregate due to lower surface charge. As such, high temperature favors aggregation of ENMs in the long run, leading to faster sedimentation.

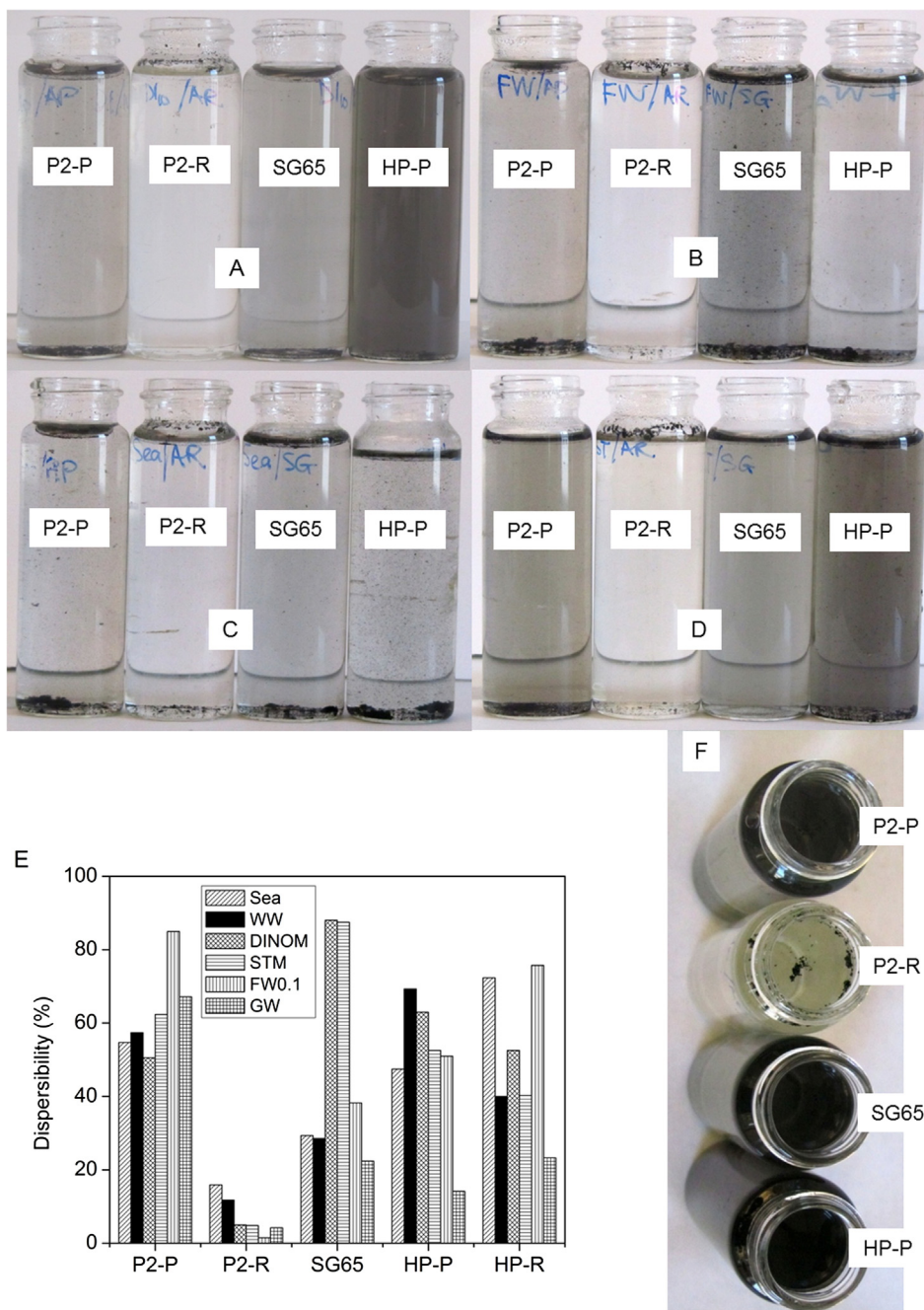


Fig. 5 – Dispersibility of SWCNTs after 4 h sonication in (A) DINOM, (B) FW1.0, and (C) SEA. (D) and (F) are top and side views of SWCNTs in STM respectively, and (E) mass percent of SWCNTs detected in suspension of selected waters immediately after sonication.

Changing the temperature of the P2-P suspensions from 20 °C to either 4 °C or 40 °C resulted in faster sedimentation relative to samples that remained at 20 °C (Fig. 7C, D). For WW, warming from 20 °C to 40 °C decreased $[CNT]_{susp}$ by 28% within three days (Day 7–10), but only by 13% within the same time frame when cooled to 4 °C. In SWCNT suspensions kept at a constant 20 °C, $[CNT]_{susp}$ only decreased by 7% between Day 7 and Day 10. The initial instability caused by temperature change decreased with time, especially at 4 °C, which shows that acute temperature changes may affect CNT stability more

than prolonged temperature variations. By Day 30 C/C_0 was 0.14 in both the constant 4 °C and when cooling from 20 °C to 4 °C for P2-P in WW. Neither 40 °C temperature treatments had detectable SWCNT in WW suspension by Day 30. Similarly, C/C_0 was 0.25 and 0.29 in constant 4 °C, and 20 °C to 4 °C treatments respectively for SWCNTs suspended in FW1.0. These observations imply that stability of CNTs in the natural environment may be affected as ambient temperatures change, especially with rapid temperature fluxes (e.g. those due to sunrise and sunset).

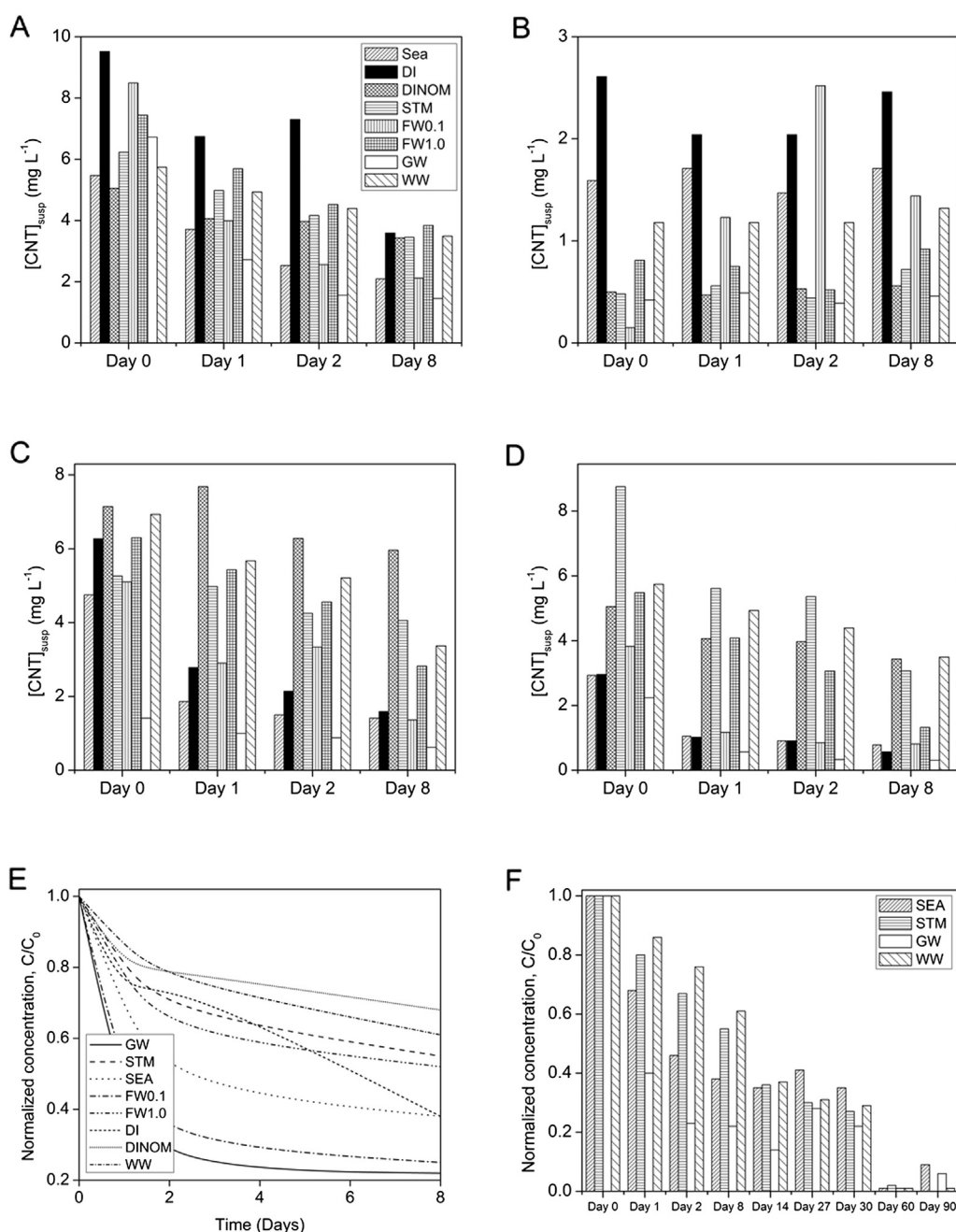


Fig. 6 – Stability of SWCNTs in waters. Suspended concentrations, $[CNT]_{susp}$, in waters of (A) P2-P, (B) P2-R, (C) HP-P, and (D) SG65 over 8 days. (E) and (F) are normalized concentration of P2-P in waters over 8 days and 90 days respectively.

3.6. Metal leaching

3.6.1. Effect of CNT purification

Significant release of metals was found in all conditions (Table 2). For arc discharge SWCNTs, the total amount of dissolved metals detected was higher in P2-R than in P2-P (Fig. 8A). However, in proportion to the amount of residual metals in each SWCNT, there was more leaching in P2-P than in P2-R. For instance, Day 90 dissolved nickel concentrations, $[Ni]_{diss}$, detected in WW were $158 \mu\text{g L}^{-1}$ in P2-R (representing 7.0% by mass of residual Ni) and $42 \mu\text{g L}^{-1}$ (representing 14.3%

by mass of residual Ni) in P2-P. Similarly, dissolved yttrium (mass %) by Day 90 in WW was 0.8% in P2-R and 5.6% in P2-P. A similar trend was observed between HP-R and HP-P. Removal of metal impurities from raw CNTs is commonly done by using strong oxidizers, which may weaken the attachment of some residual metals that remain attached. This may make it easier for metal leaching to occur in purified CNTs when exposed to aqueous media. $[Ni]_{diss}$ detected in P2-R increased over time in all waters as more of the residual metal was mobilized with time, but this was not observed in most P2-P suspensions suggesting that most of the leachable Ni in P2-P

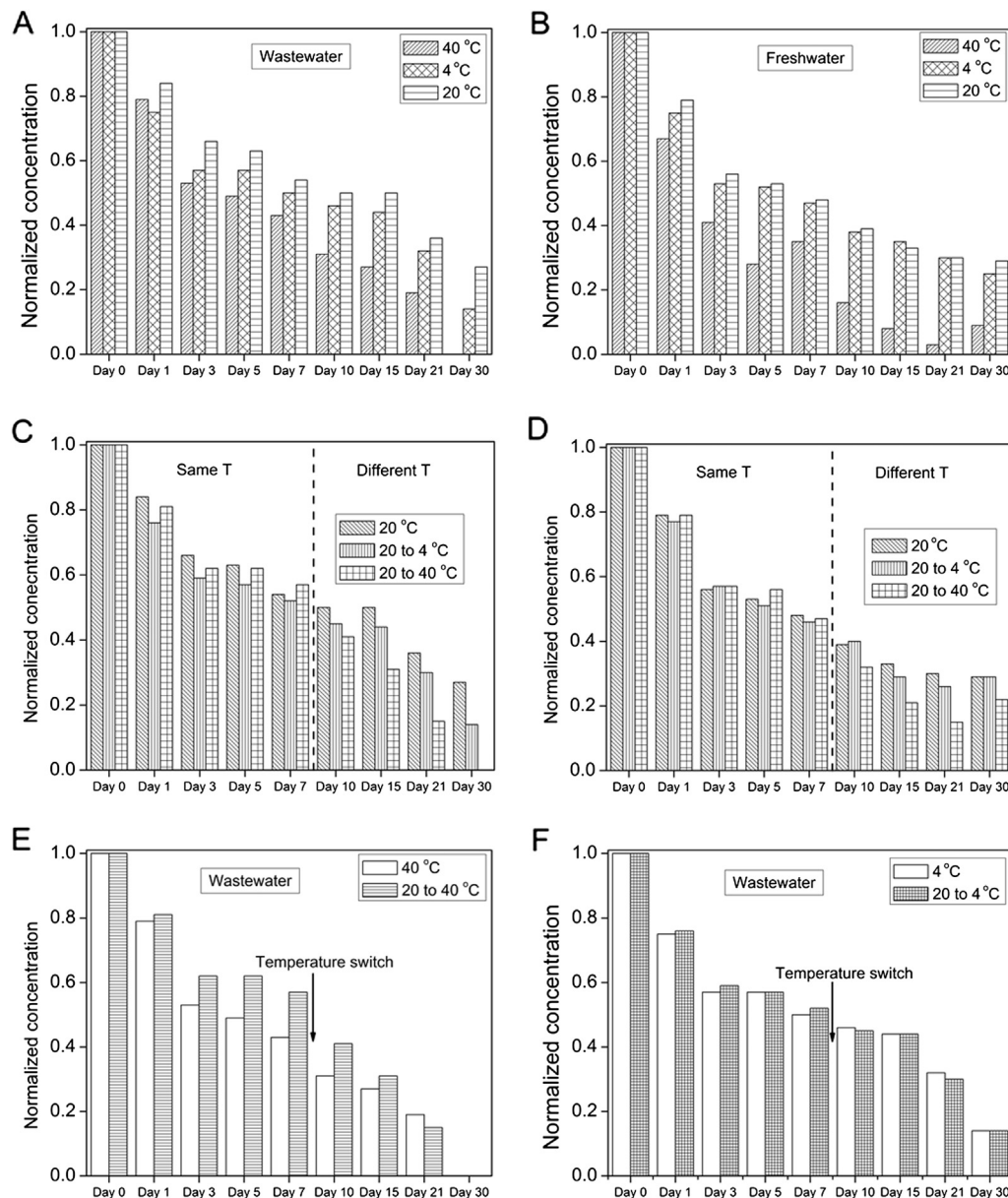


Fig. 7 – Effect of temperature on SWCNT stability. Stability of P2-P in (A) WW, and (B) FW1.0 at constant temperatures. Comparison of P2-P moved from 20 °C to either 4 °C or 40 °C after 7 days with P2-P kept at 20 °C in (C) WW and (D) FW1.0. Comparison of P2-P in WW kept at constant 4 °C or 40 °C with P2-P in WW moved from 20 °C to either 4 °C, or 40 °C.

leached out earlier on. Low amount of metals detected over 90 days (compared to total metals present in the SWCNTs) may be due to 1) re-adsorption of mobilized metals; and 2) the presence of metals in insoluble state. Both possibilities are discussed in later sections.

3.6.2. Effect of water and metal chemistries

The concentration of each dissolved metal detected in SWCNT suspensions varied widely in the different waters (Fig. 8A, Table 2), which shows that water chemistry plays a primary role in leaching and mobilization of metals from CNTs. For instance, observed Day 90 $[\text{Ni}]_{\text{diss}}$ in P2-R were 130 and $53 \mu\text{g L}^{-1}$ in GW and LW respectively. Similarly in SWCNTs

that contained two types of metals the level of each dissolved metal detected in waters did not follow the same trend, suggesting that the chemistry of individual elements also controlled their leaching. In P2-R for instance, the amount of dissolved Ni released into waters over 90 days ($p < 0.05$) was $\text{GW} > \text{WW} = \text{FW0.1} > \text{DINOM} > \text{SEA} = \text{STM} > \text{FW1.0} > \text{LW} > \text{DI}$. Meanwhile the order detected for Y was $\text{GW} = \text{SEA} > \text{DINOM} > \text{STM} = \text{LW} > \text{WW} = \text{FW1.0} = \text{FW0.1} > \text{DI}$ over the same period. The order was also different for Co and Mo that leached out of SG65. Dissolved Co was quite low and not significantly different in all the waters, except in FW where it was relatively high. Meanwhile, for Mo we found $\text{GW} = \text{LW} = \text{STM} = \text{SEA} > \text{FW0.1} = \text{FW1.0} = \text{WW} = \text{DI} > \text{DINOM}$.

Table 2 – Average concentrations of dissolved metal mobilized from five SWCNTs in $\times 10^2 \mu\text{g L}^{-1}$. ND = non-detect.

Natural water	SWCNT		P2-R		P2-P		HP-R	HP-P	SG65	
	[Me] ($\times 10^2 \mu\text{g L}^{-1}$)		Ni	Y	Ni	Y	Fe	Fe	Co	Mo
Groundwater	Day 0		1.291	0.180	0.075	0.041	1.116	0.020	ND	0.205
	Day 3		1.572	0.264	0.104	0.001	0.293	0.085	0.044	0.279
	Day 7		1.614	0.280	0.182	0.018	0.047	0.092	ND	0.273
	Day 21		1.613	0.259	0.078	0.011	0.298	0.048	0.023	0.412
	Day 30		1.767	0.286	0.090	0.002	0.009	0.027	0.001	0.437
	Day 60		1.741	0.256	0.128	ND	0.107	0.536	ND	0.488
Stormwater	Day 90		1.834	0.110	0.096	0.032	0.310	0.328	0.020	0.586
	Day 0		0.940	0.098	0.194	0.016	1.245	ND	0.012	0.273
	Day 3		0.957	0.059	0.258	ND	0.163	0.127	0.008	0.293
	Day 7		0.970	0.089	0.152	0.028	0.073	ND	0.012	0.315
	Day 21		1.051	0.066	0.229	0.018	0.297	0.515	0.014	0.439
	Day 30		1.015	0.102	0.156	0.014	0.266	0.434	0.018	0.445
Seawater	Day 60		1.161	0.074	0.172	ND	0.398	0.828	ND	0.534
	Day 90		1.064	0.053	0.172	0.031	0.248	0.532	0.008	0.547
	Day 0		0.842	0.155	0.271	0.038	0.922	0.292	ND	0.248
	Day 3		0.916	0.158	0.168	0.023	0.589	0.532	0.001	0.298
	Day 7		1.046	0.198	0.148	0.039	0.234	0.365	ND	0.286
	Day 21		1.133	0.204	0.255	0.063	0.063	0.103	0.003	0.426
Freshwater + NOM0.1	Day 30		1.023	0.216	0.211	0.052	0.055	0.129	ND	0.406
	Day 60		1.160	0.198	0.212	0.027	0.232	0.296	ND	0.516
	Day 90		1.157	0.257	0.221	0.059	0.094	0.188	ND	0.523
	Day 0		1.137	0.048	0.064	ND	13.574	0.172	0.080	0.172
	Day 3		1.272	0.022	0.121	ND	0.358	0.322	0.068	0.192
	Day 7		1.307	0.017	0.016	0.007	0.161	0.247	0.055	0.183
Freshwater + NOM1.0	Day 21		1.387	0.026	0.117	0.013	0.186	0.278	0.050	0.320
	Day 30		1.392	0.030	0.028	ND	0.146	0.406	0.024	0.293
	Day 60		1.675	0.039	0.093	ND	0.361	0.511	0.024	0.378
	Day 90		1.531	0.016	0.128	0.026	0.112	0.354	0.022	0.381
	Day 0		0.388	0.053	ND	0.025	1.101	0.330	0.033	0.215
	Day 3		0.447	0.037	0.001	0.011	0.402	0.485	0.025	0.212
DI	Day 7		0.491	0.032	0.020	0.008	0.414	0.296	0.023	0.201
	Day 21		0.555	0.029	0.065	0.037	0.303	0.237	0.029	0.311
	Day 30		0.688	0.064	0.120	0.024	0.217	0.483	0.028	0.310
	Day 60		0.775	0.017	0.186	ND	0.539	0.425	ND	0.395
	Day 90		0.844	0.051	0.109	0.025	0.254	0.544	0.053	0.420
	Day 0		0.031	0.028	ND	0.016	0.253	0.336	0.016	0.183
DI	Day 3		0.106	0.014	0.062	ND	0.193	0.170	0.003	0.213
	Day 7		0.178	ND	0.012	0.019	0.070	0.067	0.019	0.187
	Day 21		0.264	ND	0.001	0.019	0.208	0.033	0.051	0.278
	Day 30		0.045	0.012	0.042	0.007	0.015	ND	ND	0.274
	Day 60		0.244	0.019	0.076	ND	0.350	0.157	0.006	0.392
	Day 90		0.167	0.017	0.051	0.019	0.155	0.321	0.006	0.446

Fe leached from HP-R was not significantly different in all the waters over 90 days. There were similarities in the trend of metal leaching into waters between raw and purified SWCNT variants (Table 2). The chemistry of metal ions is dependent on the formation of complexes with ligands present in natural waters (Adeleye et al., 2013; Dries et al., 2005). Such complexes reduce the concentration of the free metal species in solution and thus affect solubility of metals (Dries et al., 2005).

3.6.3. Effect of CNT exposure time

$[\text{Ni}]_{\text{diss}}$ from P2-R and $[\text{Mo}]_{\text{diss}}$ from SG65 increased with time in all waters. However, $[\text{Fe}]_{\text{diss}}$ from HP-R decreased with time, and there was no clear trend in other metals. In addition to water and metal chemistries, the amount of metals that were mobilized from SWCNTs appeared to also depend on proportion of residual metals that is leachable. For instance, the highest $[\text{Ni}]_{\text{diss}}$ from P2-R detected (on Day 90) was $183 \mu\text{g L}^{-1}$

(in GW) which represents only 8.1% of the total Ni in P2-R. Since $[\text{Ni}]_{\text{diss}}$ in P2-R increased throughout this study, we may have detected higher levels of $[\text{Ni}]_{\text{diss}}$ if we continued sampling beyond 90 days. In conditions where metal concentration decreased or remained steady with time, we can assume that total leachable metal from SWCNTs were obtained based on the conditions of this experiment or the solubility limits were reached. The proportion of residual metals that is leachable may also depend on pre-treatment of CNTs, and experimental conditions (e.g. pH, and temperature).

Decreased metal concentration with time may be due to sorption to SWCNT or NOM (Tian et al., 2012), and/or precipitation or complexation (Davis, 1984). In HP-R the highest levels of dissolved Fe were detected on Day 0, and then $[\text{Fe}]_{\text{diss}}$ decreased over time in all the waters. As an example, $[\text{Fe}]_{\text{diss}}$ in HP-R were $112 \mu\text{g L}^{-1}$ and $31 \mu\text{g L}^{-1}$ in GW on Day 0 and Day 90 respectively. This suggests that leachable Fe from HP-R was

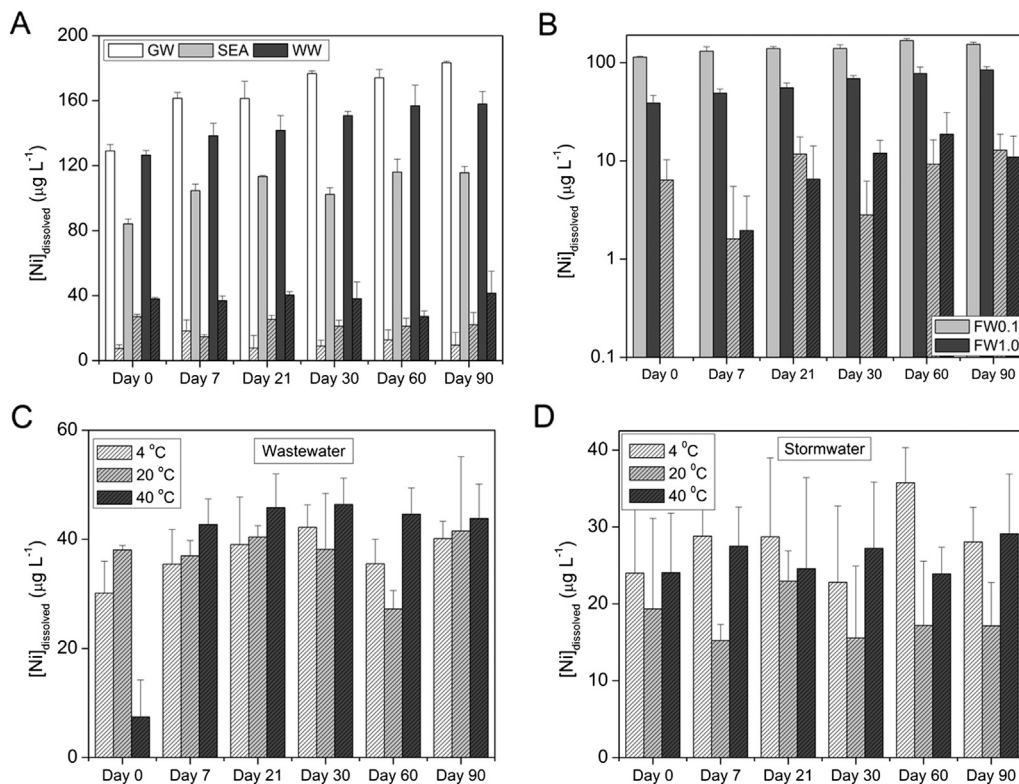


Fig. 8 – Metal leaching from SWCNTs. Block and patterned bars represent P2-R and P2-P respectively in all plots. (A) Comparison of dissolved Ni leached from P2-R and P2-P in selected waters. (B) Effect of NOM on metal leaching. Effect of temperature on metal leaching in (C) WW, and (D) STM.

released as the nanotubes were suspended and sonicated, probably due to high amount of loosely held soluble Fe. With time, released Fe adsorbed to SWCNT and/or NOM in the different waters or precipitated out. $[\text{Fe}]_{\text{diss}}$ increased with time in HP-P in some waters as seen in GW where Day 0 and Day 90 $[\text{Fe}]_{\text{diss}}$ were $2 \mu\text{g L}^{-1}$ and $33 \mu\text{g L}^{-1}$ respectively. This suggests gradual release of leachable Fe from HP-P suspension since most of the loosely attached Fe had been removed during purification.

3.6.4. Effect of natural organic matter

The presence of NOM appears to have significant effect for certain metals. $[\text{Ni}]_{\text{diss}}$ from P2-R in FW1.0 was a factor of 2 or 3 lower than in FW0.1, suggesting that Ni was adsorbed to NOM or perhaps, SWCNT-adsorbed NOM inhibited dissolution. $[\text{Ni}]_{\text{diss}}$ detected in P2-R right after sonication on Day 0 were $114 \mu\text{g L}^{-1}$ and $39 \mu\text{g L}^{-1}$ in FW0.1 and FW1.0 respectively. By Day 90 the proportion had not changed significantly with $[\text{Ni}]_{\text{diss}} = 153 \mu\text{g L}^{-1}$ in FW0.1 and $84 \mu\text{g L}^{-1}$ in FW1.0. Similarly, $[\text{Ni}]_{\text{diss}}$ from P2-P released into FW0.1 was slightly higher than in FW1.0. This is similar to the observation of another study (Tong et al., 2012) which recovered less metal species from solutions with higher amount of NOM. Both dissolved NOM and NOM bound to SWCNT may adsorb metals or precipitate them out via complexation (Lin et al., 2012; Tian et al., 2012). Surface-bound NOM with oxygen-containing functional groups improves metal adsorption onto CNTs (Lin et al., 2012). In addition, metal ions may be electrostatically attracted to

the diffuse layer of NOM-CNT complex (Lin et al., 2012), which is more charged at higher levels of NOM. In contrast $[\text{Ni}]_{\text{diss}}$ was much lower in DI than in DINOM in both P2-R and P2-P. The lowest metal concentrations were detected in DI for most of the metals (Table 2) perhaps due to lack of redox-active and/or complexing species. Similarly to Ni, higher $[\text{Co}]_{\text{diss}}$ was detected at lower levels of NOM. However, there was no significant correlation difference between Fe and Mo, and NOM levels. Lin et al. (2012) also detected lower amount of dissolved Co compared to Mo from a CNT in the presence of humic acid. Increased adsorption of metals in the presence of NOM will control their bioavailability when mobilized from CNTs into natural media (Tong et al., 2012).

3.6.5. Effect of temperature

We observed no significant difference between $[\text{Ni}]_{\text{diss}}$ detected over 90 days at 4°C and 40°C in all the waters. However, when $[\text{Ni}]_{\text{diss}}$ detected over 90 days at 20°C was compared with the levels detected at either 4°C or 40°C we confirmed that more dissolved Ni was present at both 4°C and 40°C in SWCNT suspensions of STM, DINOM, FW1.0. These are conditions with relatively high amount of NOM and low IS. As reported in subsection 3.6.4 for the 20°C conditions, NOM appeared to result in increased adsorption of dissolved metal, thus leading to detection of lower amount of dissolved metal at FW1.0 relative to the levels detected in FW0.1 over 90 days. In contrast, there was no significant difference in the $[\text{Ni}]_{\text{diss}}$ detected between FW0.1 and FW1.0 at either 4°C or 40°C . This

suggests that the adsorption potential of CNT-NOM complex for Ni is affected by change in temperature, and this effect is more pronounced in waters with relatively high NOM level.

4. Conclusion and environmental significance

Release of CNTs into water bodies will lead to immediate exposure of organisms in all phases. In the long run however, exposure of benthos will increase as CNTs sediment. In addition to electrolytes and natural organic matter (NOM), sedimentation of CNTs is also controlled by media density and viscosity, and temperature. Elevated temperatures decrease the magnitude of surface charge of CNTs, and may thus favor aggregation. As such, in hot temperatures, exposure risk of aquatic organisms to CNTs may be higher around the point of release. Temperature variation decreases CNT stability and the effect is less significant with time when the media is cooled down (e.g. from summer to winter temperatures) relative to when it is heated up (e.g. winter to summer temperatures).

This study demonstrated the improved stability of CNTs by EPS compared to SRNOM. EPS is a NOM synthesized by microbes growing under normal conditions and as a response to stress. Exposure of microbes to CNTs may trigger increased synthesis of EPS, a defense mechanism seen with other ENMs (Miao et al., 2009), which may further increase CNT stability (and thus organisms' exposure) in water matrix. Accounting for the role of EPS in ENM stability may improve the closeness of ENM fate and transport prediction to what may happen in reality. Also, adsorption of EPS and other types of NOM to CNTs and their leached metals may significantly change their bioavailability to organisms.

Significant leaching of CNT metals may occur in groundwater, seawater, and wastewater. The dynamics of leaching vary widely between the different CNTs and their respective metals. While most dissolved Fe was found right after exposure of a CNT to waters, dissolved [Ni] increased with time in another CNT. 6% of CNTs produced and used globally are currently estimated to end up in wastewater treatment plants (WWTP) and this may increase with novel applications (Keller et al., 2013). This represents about 180 t of CNTs or 4–45 t of metals that may potentially enter wastewater streams annually, based on global CNT production of ~3000 t/yr, and 2–25% metal content by weight as found in commercial CNTs. The chemistry of wastewater favors metal leaching from CNTs and this may portend a potential challenge to proper WWTP functioning since biota may be affected. In addition, WWTPs may only be an intermediate step for CNTs and their leached metals as they may transfer into surface waters with effluents, or biosolids.

Acknowledgment

This material is based upon work supported by the National Science Foundation (NSF) and the Environmental Protection Agency (EPA) under Cooperative Agreement Number DBI

0830117. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of NSF or EPA. This work has not been subjected to EPA review and no official endorsement should be inferred. We thank the MRL Central Facilities for the use of their ICP, SEM and TEM instruments. The MRL Central Facilities are supported by the MRSEC Program of the NSF under Award No. DMR 1121053. We also thank Jon Conway, Dongxu Zhou and the anonymous reviewers for their valuable comments, and acknowledge the lab assistance of Brittany Hall, Daniel Dunham, Sahar El-Abbadi, and Paige Ruten.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.watres.2013.11.032>

REFERENCES

- Adeleye, A.S., Keller, A.A., Miller, R.J., Lenihan, H.S., 2013. Persistence of commercial nanoscaled zero-valent iron (nZVI) and by-products. *J. Nanopart. Res.* 15 (1).
- Bennett, S.W., Adeleye, A., Ji, Z., Keller, A.A., 2013. Stability, metal leaching, photoactivity and toxicity in freshwater systems of commercial single wall carbon nanotubes. *Water Res.* 47 (12), 4074–4085.
- Chandra, A., Bagchi, B., 2000. Beyond the classical transport laws of electrochemistry: new microscopic approach to ionic conductance and viscosity. *J. Phys. Chem. B* 104 (39), 9067–9080.
- Chen, K.L., Elimelech, M., 2009. Relating colloidal stability of fullerene (C60) nanoparticles to nanoparticle charge and electrokinetic properties. *Environ. Sci. Technol.* 43 (19), 7270–7276.
- Davis, J.A., 1984. Complexation of trace-metals by adsorbed natural organic-matter. *Geochim. Cosmochim. Ac.* 48 (4), 679–691.
- Dries, J., Bastiaens, L., Springael, D., Kuypers, S., Agathos, S.N., Diels, L., 2005. Effect of humic acids on heavy metal removal by zero-valent iron in batch and continuous flow column systems. *Water Res.* 39 (15), 3531–3540.
- El-Dessouky, H.T., Ettouney, H.M., 2002. *Fundamentals of Salt Water Desalination*. Elsevier, Amsterdam; New York.
- Flemming, H.-C., Neu, T.R., Wozniak, D.J., 2007. The EPS matrix: the “house of biofilm cells”. *J. Bacteriol.* 189 (22), 7945–7947.
- Ge, C.C., Li, W., Li, Y.F., Li, B., Du, J.F., Qiu, Y., Liu, Y., Gao, Y.X., Chai, Z.F., Chen, C.Y., 2011. Significance and systematic analysis of metallic impurities of carbon nanotubes produced by different manufacturers. *J. Nanosci. Nanotechnol.* 11 (3), 2389–2397.
- Ge, C.C., Li, Y., Yin, J.J., Liu, Y., Wang, L.M., Zhao, Y.L., Chen, C.Y., 2012. The contributions of metal impurities and tube structure to the toxicity of carbon nanotube materials. *Npg. Asia Mater.* 4.
- Herzhaft, B., Guazzelli, E., 1999. Experimental study of the sedimentation of dilute and semi-dilute suspensions of fibres. *J. Fluid Mech.* 384, 133–158.
- Huang, Y.Y., Terentjev, E.M., 2012. Dispersion of carbon nanotubes: mixing, sonication, stabilization, and composite properties. *Polymers* 4 (1), 275–295.
- Hung, C.C., Tang, D.G., Warmken, K.W., Santschi, P.H., 2001. Distributions of carbohydrates, including uronic acids, in

- estuarine waters of Galveston Bay. *Mar. Chem.* 73 (3–4), 305–318.
- Hyung, H., Fortner, J.D., Hughes, J.B., Kim, J.-H., 2007. Natural organic matter stabilizes carbon nanotubes in the aqueous phase. *Environ. Sci. Technol.* 41 (1), 179–184.
- Islam, M.F., Rojas, E., Bergery, D.M., Johnson, A.T., Yodh, A.G., 2003. High weight fraction surfactant solubilization of single-wall carbon nanotubes in water. *Nano Lett.* 3 (2), 269–273.
- Keller, A.A., McFerran, S., Lazareva, A., Suh, S., 2013. Global life cycle releases of engineered nanomaterials. *J. Nanopart. Res.* 15 (6), 1–17.
- Keller, A.A., Wang, H., Zhou, D., Lenihan, H.S., Cherr, G., Cardinale, B.J., Miller, R., Ji, Z., 2010. Stability and aggregation of metal oxide nanoparticles in natural aqueous matrices. *Environ. Sci. Technol.* 44 (6), 1962–1967.
- Lam, C., James, J., McCluskey, R., Hunter, R., 2004. Pulmonary toxicity of single-wall carbon nanotubes in mice 7 and 90 days after intratracheal instillation. *Toxicol. Sci.* 77 (1), 126–134.
- Leys, F.E., Amovilli, C., Howard, I.A., March, N.H., Rubio, A., 2003. Surface charge model of a carbon nanotube: self-consistent field from Thomas–Fermi theory. *J. Phys. Chem. Sol.* 64 (8), 1285–1288.
- Li, Z., Lin, W., Moon, K.-S., Wilkins, S.J., Yao, Y., Watkins, K., Morato, L., Wong, C., 2011. Metal catalyst residues in carbon nanotubes decrease the thermal stability of carbon nanotube/silicone composites. *Carbon* 49 (13), 4138–4148.
- Lin, D., Liu, N., Yang, K., Xing, B., Wu, F., 2010. Different stabilities of multiwalled carbon nanotubes in fresh surface water samples. *Environ. Pollut.* 158 (5), 1270–1274.
- Lin, D.H., Tian, X.L., Li, T.T., Zhang, Z.Y., He, X., Xing, B.S., 2012. Surface-bound humic acid increased Pb²⁺ sorption on carbon nanotubes. *Environ. Pollut.* 167, 138–147.
- Miao, A.-J., Schwehr, K.A., Xu, C., Zhang, S.-J., Luo, Z., Quigg, A., Santschi, P.H., 2009. The algal toxicity of silver engineered nanoparticles and detoxification by copolymeric substances. *Environ. Pollut.* 157 (11), 3034–3041.
- Morris, D.L., 1948. Quantitative determination of carbohydrates with dreywoods anthrone reagent. *Science* 107 (2775), 254–255.
- Mwangi, J.N., Wang, N., Ingersoll, C.G., Hardesty, D.K., Brunson, E.L., Li, H., Deng, B.L., 2012. Toxicity of carbon nanotubes to freshwater aquatic invertebrates. *Environ. Toxicol. Chem.* 31 (8), 1823–1830.
- Pal, A., Paul, A., 2008. Microbial extracellular polymeric substances: central elements in heavy metal bioremediation. *Ind. J. Microbiol.* 48 (1), 49–64.
- Saleh, N.B., Pfefferle, L.D., Elimelech, M., 2008. Aggregation kinetics of multiwalled carbon nanotubes in aquatic systems: measurements and environmental implications. *Environ. Sci. Technol.* 42 (21), 7963–7969.
- Saleh, N.B., Pfefferle, L.D., Elimelech, M., 2010. Influence of biomacromolecules and humic acid on the aggregation kinetics of single-walled carbon nanotubes. *Environ. Sci. Technol.* 44 (7), 2412–2418.
- Sano, M., Okamura, J., Shinkai, S., 2001. Colloidal nature of single-walled carbon nanotubes in electrolyte solution: the Schulze–Hardy rule. *Langmuir* 17 (22), 7172–7173.
- Schwyzler, I., Kaegi, R., Sigg, L., Magrez, A., Nowack, B., 2011. Influence of the initial state of carbon nanotubes on their colloidal stability under natural conditions. *Environ. Pollut.* 159 (6), 1641–1648.
- Schwyzler, I., Kaegi, R., Sigg, L., Nowack, B., 2013. Colloidal stability of suspended and agglomerate structures of settled carbon nanotubes in different aqueous matrices. *Water Res.* 47 (12), 3910–3920.
- Schwyzler, I., Kaegi, R., Sigg, L., Smajda, R., Magrez, A., Nowack, B., 2012. Long-term colloidal stability of 10 carbon nanotube types in the absence/presence of humic acid and calcium. *Environ. Pollut.* 169 (0), 64–73.
- Thostenson, E., Chou, T., 2003. On the elastic properties of carbon nanotube-based composites: modelling and characterization. *J. Phys. D–Appl. Phys.* 36 (5), 573–582.
- Tian, X.L., Li, T.T., Yang, K., Xu, Y., Lu, H.F., Lin, D.H., 2012. Effect of humic acids on physicochemical property and Cd(II) sorption of multiwalled carbon nanotubes. *Chemosphere* 89 (11), 1316–1322.
- Tong, Z., Bischoff, M., Nies, L.F., Myer, P., Applegate, B., Turco, R.F., 2012. Response of Soil microorganisms to as-produced and functionalized single-wall carbon nanotubes (SWNTs). *Environ. Sci. Technol.* 46 (24), 13471–13479.
- Velzeboer, I., Peeters, E., Koelmans, A.A., 2013. Multiwalled carbon nanotubes at environmentally relevant concentrations affect the composition of benthic communities. *Environ. Sci. Technol.*
- Zhou, D., Bennett, S.W., Keller, A.A., 2012. Increased mobility of metal oxide nanoparticles due to photo and thermal induced disagglomeration. *Plos One* 7 (5), e37363.
- Zhou, D., Keller, A.A., 2010. Role of morphology in the aggregation kinetics of ZnO nanoparticles. *Water Res.* 44 (9), 2948–2956.