1 **Carbon Nanotube Integrative Sampler (CNIS) for Passive Sampling**
2 **of Nanosilver in the Aquatic Environment**
3

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8 **Abstract**

9 Nanomaterials such as nanosilver (AgNP) can be released into the aquatic environment through
10 production, usage, and disposal. Sensitive and cost-effective methods are needed to monitor
11 AgNPs in the environment. This work is hampered by a lack of sensitive methods to detect
12 nanomaterials in environmental matrixes. The present study focused on the development,
13 calibration and application of a passive sampling technique for detecting AgNPs in aquatic
14 matrixes. A Carbon Nanotube Integrative Sampler (CNIS) was developed using multi-walled
15 carbon nanotubes (CNTs) as the sorbent for accumulating AgNPs and other Ag species from
16 water. Sampling rates were determined in the laboratory for different sampler configurations and
17 in different aquatic matrixes. The sampler was field tested at the Experimental Lakes Area,
18 Canada, in lake water dosed with AgNPs. For a configuration of the CNIS consisting of CNTs
19 bound to carbon fibre (i.e CNT veil) placed in Chemcatcher® housing, the time weighted average
20 (TWA) concentrations of silver estimated from deployments of the sampler in lake mesocosms
21 dosed with AgNPs were similar to the measured concentrations of “colloidal silver” (i.e. <0.22 µm
22 in size) in the water column. For a configuration of CNIS consisting of CNTs in loose powder
23 form placed in a custom made housing that were deployed in a whole lake dosed with AgNPs, the
24 estimated TWA concentrations of “CNIS-labile Ag” were similar to the concentrations of total
25 silver measured in the epilimnion of the lake. However, sampling rates for the CNIS in various
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matrixes are relatively low (i.e. 1-20 mL/day), so deployment periods of several weeks are required to detect AgNPs at environmentally relevant concentrations, which can allow biofilms to develop on the sampler and could affect the sampling rates. With further development, this novel sampler may provide a simple and sensitive method for screening for the presence of AgNPs in surface waters.

Keywords: *Silver, nanoparticles, passive sampling, carbon nanotubes, environmental monitoring*

1. Introduction

Silver nanoparticles (AgNPs) are being incorporated as an antimicrobial and anti-odour ingredient into a large number of consumer products, such as socks, sports clothing, deodorants, additives to washing machines, food packaging and wound dressings. There is growing concern that AgNPs can be released from these products into domestic sewage (Nowack et al., 2012). In wastewater treatment plants, a high proportion of AgNPs may be transformed into insoluble species (e.g. Ag₂S) and settle with sewage sludge, so that only small amounts of AgNPs are discharged from WWTPs into surface waters (Kim et al., 2010; Kaegi et al., 2013; Ma et al., 2014). Yang et al. (2012) predicted that AgNP concentrations in treated municipal wastewater would range between 0.028 and 5.5 µg/L. Model predictions for surface waters in Europe indicate that the long-term average concentration of AgNP will be in the range of 0.002 ng/L to 0.3 ng/L (Dumont et al., 2015). The low predicted concentrations reported in these studies show that measuring AgNP at environmentally relevant concentrations is a challenge using current analytical techniques, as also noted by Furtado et al (accepted).

Studies conducted in the laboratory have shown that the fate of AgNPs in the aquatic environment is influenced by a variety of factors, including temperature, ionic strength, pH, and the concentration of dissolved organic matter that control the rate of agglomeration of AgNPs to

form larger particles, and the rate of dissolution of the AgNPs to release silver ion into solution (Li et al., 2010; Delay et al., 2011; Chen and Zhang, 2012; Peretyazhko et al., 2014; Mitrano et al., 2014). However, no *in situ* studies have been conducted to date on the fate of AgNPs; primarily because there are few analytical methods to monitor for these nanoparticles at environmentally relevant concentrations. The International Council on Nanotechnology ranked the detection, quantification, and characterization of nanomaterials in environmental matrixes as a top research priority (U.S. EPA, 2011).

Passive sampling technologies have been developed over the last 30 years to provide a simple and cost-effective monitoring technique (Vrana et al., 2005). Passive samplers are deployed *in situ* in water for a period of days or weeks, and using data on the sampling rates for the device, it is possible to calculate time-weighted average (TWA) concentrations of contaminants in water over the deployment period (Kot-Wasik et al., 2007). The sorbents used in passive samplers are typically separated from the aqueous phase by a porous membrane through which the contaminant diffuses before binding with the receiving phase.

A variety of sorbents have been used to concentrate contaminants in passive samplers (Vrana et al., 2005). In this study, we selected multi-walled carbon nanotubes (CNTs) as a candidate sorbent for concentrating AgNPs in the passive sampler. CNTs are graphite sheets rolled up into a nanoscale tube, providing a large surface area of carbon atoms that can be functionalized with more reactive groups. CNTs have been shown to have a high adsorption capacity for silver ions (Ding et al., 2006; Yu et al., 2010) and have been used as a solid-phase extraction medium for a variety of metal ions (Stafiej and Pyrzynska, 2007; Soylak and Ercan, 2009; Ghaedi et al., 2013; Apul et al., 2015), as well as organic compounds (Wang et al., 2015; Li et al., 2013).

The objective of this study was to develop a Carbon Nanotube Integrative Sampler (CNIS) as a practical and cost-effective passive sampling device for monitoring AgNPs and other Ag species in aquatic matrixes. To do this, it was necessary to test in the laboratory various configurations of the samplers to determine the affinity of different CNT sorbents for AgNPs in different aquatic matrixes, and then to field test some of these devices to determine whether they can be used to estimate TWA concentrations of AgNP that are consistent with the concentrations of silver in water measured by conventional sampling techniques.

2. Experimental

2.1 Chemicals and Reagents

Ultra-pure 70 % (v/v) nitric acid (HNO_3) for digestion was purchased from either VWR International (Mississauga, ON, Canada) or Fisher Scientific (Toronto, ON, Canada). Milli-Q water (18.2 M Ω , Millipore, Billerica, MA, USA) was used to prepare all stock solutions and suspensions, unless specified as reverse osmosis (RO) water. PlasmaCAL metal standards of silver (Ag) and indium (In) used to prepare calibration standards for ICP-MS or ICP-OES analysis were obtained from SCP Science (Baie d'Urfé, QC, Canada). Dissolved Ag (Ag^+) solutions were prepared by dissolving the appropriate amount of crystals of silver nitrate (AgNO_3) purchased from Fisher Scientific in Milli-Q water or RO water, or by mixing silver acetate powder (Sigma-Aldrich, Oakville, ON, Canada) in RO water. Stock solutions of dissolved organic matter (DOM) were prepared in MilliQ water using Nordic Reservoir (IHSS, 1R105H) organic matter purchased from the International Humic Substances Society (St. Paul, MN, USA), which is widely used to simulate dissolved organic matter in water.

2.2 Nanosilver suspensions

The stock suspensions of AgNPs were purchased from NanoComposix, San Diego, CA, USA. All AgNPs were coated with an organic capping agent to promote dispersion in aquatic matrixes. The capping agents were either polyvinylpyrrolidone (i.e. PVP-AgNP) or citrate (i.e. CT-AgNP). The mean particle sizes of the AgNPs in the suspensions were 50 nm, according to the manufacturer and confirmed by analysis using Dynamic Light Scattering and spICP-MS instrumental methods. Working suspensions for laboratory experiments were prepared daily by diluting the stock suspensions with Milli-Q water or RO water. Stock suspensions were kept in a refrigerator when not in use.

The amount of Ag^+ present in the stock suspensions of CT-AgNPs and PVP-AgNPs used for all the experiments was estimated by ultrafiltration with Centrifugal Filtration Units (CFUs) as described by Hadioui et al. (2013), using either Amicon Ultra-4 CFUs (Millipore, Etobicoke, ON, Canada) or Microsep Advance CFUs (Pall Science, Quebec, Canada). These filter units have a pore size of 3 kDa, corresponding to a size <1 nm. The percentage of Ag in the filtrate prepared from the stock suspensions of CT-AgNPs was always equivalent to $<2\%$ of the total Ag, but the percentage of Ag in the filtrate from the PVP-AgNPs stocks could be up to 20%, depending on the age of the stock.

2.3 CNIS

Several different types of functionalized and non-functionalized multi-walled CNTs were tested in this study as sorbents for CNIS devices. The CNT veil consisted of carboxy-functionalized or “bare” (non-functionalized) CNTs bound to a carbon fibre material that was purchased in 20 cm x 28 cm sheets from NanoLab (Waltham, MA, USA). This material was cut into smaller disks for use as a sorbent in CNIS devices. CNTs in powder form (30-50 nm particle size) purchased from MK Impex (Mississauga, ON, Canada) were either carboxy-functionalized

(i.e. COOH-CNT) or amide-functionalized (i.e. NH₂-CNT). Bare CNTs in powder form were initially tested but found to be ineffective as a sorbent for AgNP.

Various porous membranes were tested in order to select one that would allow AgNPs to diffuse through the pores to reach the CNT receiving phase. A polyethersulfone (PES) membrane with a 1 µm pore size (Environmental Sampling Technologies, St. Joseph, MO, USA), and a PES membrane with a 0.8 µm pore size (Pall Life Sciences, Montreal, QC, Canada) inhibited accumulation of silver on the sorbent. Therefore, most experiments in the lab and all trials in the field were conducted with CNIS constructed with a cellulose acetate membrane (0.8 µm pore size; 47 mm diameter) purchased from Pall Life Sciences, or a cellulose acetate membrane with the same pore size purchased from Sterlitech (Kent, WA, USA).

Different types of housings were used to construct the CNIS. In one of the CNIS configurations, the sampler was assembled in a Chemcatcher[®] housing made of polytetrafluoroethylene (University of Portsmouth, UK) by placing a disk of CNT veil (47 mm) on the Chemcatcher[®] backing, overlaid with a cellulose acetate membrane. This CNIS-Chemcatcher[®] sampler was then sealed with a locking ring and cap.

In the case of the CNIS assembled with a custom-made housing, 5 mg of the powder CNTs was placed between two porous membranes, and then secured together using two polyethylene rings with an opening of either 2 cm or 3.7 cm diameter that were fabricated by the machine shop for the Chemical Engineering Department at McGill University (Figure 1). The polyethylene material was used to minimize adsorption of silver to the surface of the rings during the laboratory exposures.

Figure 1: Assembled CNIS for sampling rate experiments, showing the configurations with the 2 cm diameter opening (left) and the 3.7 cm diameter opening (right).

In lake mesocosms dosed with AgNP, the CNIS-Chemcatcher[®] configuration with COOH-CNT veil and a cellulose acetate membrane (0.8 μm pore size) was used. During the whole ecosystem study, where an entire lake was dosed with AgNP, custom made CNIS containing NH₂-CNT powder sandwiched between two cellulose acetate membranes (0.8 μm pore size) were deployed in the lake. These CNIS were secured with 3.7 cm rings of stainless steel and placed in a stainless steel manifold constructed to hold three CNIS for field deployments (Figure 2). The stainless steel material was used for field deployments because of the robust design. Both of the stainless steel fittings were designed at McGill University.

2.4 Sampling rates

To determine the sampling rates expressed as the volume of water (mL) cleared of silver per day, static non-renewal experiments were conducted using procedures based on methods described by Li et al., (2010) and MacLeod et al., (2007). In one set of experiments with the CNIS-Chemcatcher[®] configuration, a 3 L volume of water was added to a glass test container spiked with solutions of silver nitrate (i.e. Ag⁺) or with stock suspensions of AgNPs. Four CNIS-Chemcatcher[®] samplers were added to each jar after 1 h of equilibration. The samplers were suspended in the test matrix with the sorbent facing the bottom of the bottle. Water pumps were used to maintain a low

circulation rate (about 60 mL/min) in the jars. All jars were covered with aluminum foil to reduce exposure to light and evaporation. Experiments were conducted at room temperature (i.e. $20 \pm 2^\circ\text{C}$).

Figure 2: Assembled CNIS for field deployments, shown in the manifold constructed to hold three samplers (left) and shown in stainless steel cage for field deployments (right).

In another set of experiments in the laboratory with the custom made CNIS configuration (2 cm and 3.7 cm opening diameters), the CNIS were suspended in 2 L of water placed in a beaker made of high density polyethylene (HDPE) and spiked with stock solutions of silver nitrate or suspensions of AgNPs. The water matrix was stirred with a magnetic stirrer at 75 rpm, and all beakers were covered with aluminum foil and parafilm to reduce light exposure and evaporation, respectively. Four CNIS were suspended in each beaker. Experiments were conducted at room temperature (i.e. $22 \pm 2^\circ\text{C}$) or in a bath maintained at $4 \pm 2^\circ\text{C}$. The HPDE beaker was found to adsorb lesser amounts of AgNPs to the inside walls over the course of the experiment than other materials tested (glass and Teflon).

In both sets of experiments, samples of water (5 mL) were removed from the exposure vessels at 0, 6, 24, 48, and 96 h to monitor the Ag concentration in the water over time. Spiked nominal concentrations of AgNPs or Ag^+ in the test containers ranged from 1 to 100 $\mu\text{g/L}$. A control treatment spiked with suspension/solution but containing no CNIS was run with each experiment to determine if there was loss of silver over time. A blank treatment (non-spiked)

containing CNIS was run with each experiment to determine if there was background silver contamination. One CNIS sampler was removed from the test container every 24 h (n=4) for a total experiment time of 96 hours. All experiments were conducted in triplicate.

The CNIS removed from the batch experiments were extracted as described below and the extracts analyzed for silver. The data obtained on the amounts of silver adsorbed by the CNIS were used to calculate the sampling rate (R_s) using the equation:

$$R_s = \frac{M_s(t)}{C_{w,t}}$$

Where $M_s(t)$ is the mass of Ag accumulated on the CNT over the experiment (4 days), $C_{w,t}$ is the concentration of Ag at time t , and R_s is the sampling rate in mL over the 4-day experiment.

2.5 Field studies

2.5.1 Mesocosms

Field trials for the CNIS-Chemcatcher[®] samplers were conducted between June 23rd and August 13th, 2012 in mesocosms installed in Lake 239 of the Experimental Lakes Area (ELA), ON, Canada as part of a larger study conducted by a research team from Trent University, ON, Canada. Lake 239 is an oligotrophic, dimictic lake. A total of 12 mesocosms were installed in a shallow embayment on the south side of the lake, as described by Furtado et al. (2015). The mesocosms were constructed of polyethylene sheeting and each measured 2 m wide and 2 m deep, with an approximate volume of 6 m³. The mesocosms were anchored to the bottom and open to the sediment at the bottom of the lake.

In this study, three of the 12 mesocosms were monitored using CNIS-Chemcatcher[®] (COOH-CNT) passive samplers. Two of the test mesocosms were spiked, respectively with CT-AgNP (50 nm) or PVP-AgNP (50 nm) purchased from NanoComposix, and the third mesocosm was a control treatment with no AgNPs added. The mesocosms containing AgNP were spiked

every other day with a 14.2 mL volume of a 1.0 mg/L stock suspension over 49 days, starting on June 23rd, 2012 and ending on August 8th, 2012. As described by Furtado et al. (2015), the additions of AgNPs were designed to yield a final nominal concentration of 66 µg/L, assuming no loss of silver from the water column over the treatment period. The total concentrations in the water column of the spiked mesocosms increased steadily to reach approximately 60% of the nominal concentrations.

Triplicate CNIS-Chemcatcher[®] samplers were deployed in the mesocosms for various overlapping time periods, with durations of 14, 28, and 49 days. As shown in Table 1, these time periods were chosen to evaluate the performance of the samplers deployed under conditions of: i) the same lengths of time in the mesocosms when there were different concentrations (W2i, W2ii, W2iii) and, ii) under different lengths of time in the mesocosms when deployed at the same initial time (W1, W2i, W4, W7). The samplers were deployed at a depth of 50 cm from the bottom of the mesocosm, facing down to reduce accumulation of sediment. Field blanks were exposed to the air during sampler deployment and retrieval to account for incidental contamination.

Bulk water samples were collected every 2-4 days from the mesocosms. The methods used to collect and analyze these samples are described in detail by Furtado et al. (2015). Briefly, a volume of water from each mesocosm was collected at 30 cm below the surface and passed through a 35 µm screen to remove macroplankton. A portion of the water sample was passed through a 0.22 µm polycarbonate filters to determine a fraction of silver that is defined as “colloidal silver”, which is operationally defined as any dissolved silver species that can pass through the 0.22 µm (i.e. 220 nm) filter. Another portion of the water sample was filtered through 3 kDa filter to determine the dissolved Ag concentration. Farmen et al. (2012) used a similar filtration approach to determine the size distribution of Ag in toxicological experiments and

defined “colloidal Ag” as the fraction passing through a 0.22 µm filter and retained by a 10 kDa membrane. It is recognized that this operational definition of “colloidal Ag” does not represent all colloidal material in suspension. Colloidal silver could include metal complexes up to 1000 nm in size (Geckeis et al., 2002). The water samples and filtrates were acidified with 70% HNO₃ to a final concentration of 4% (v/v) HNO₃ and heated at 70°C for 6 h for analysis by ICP-MS, as described by Furtado et al. (2015). Comparisons of this digestion protocol with more vigorous digestion overnight with 10% (v/v) HNO₃ showed no increase in Ag yields, so the shorter digestion protocol was used.

Table 1: Deployment periods for the CNIS-Chemcatcher[®] samplers in the three test mesocosms.

Time period	June 26 – July 2	July 3 – July 9	July 10 – July 16	July 17 – July 23	July 24 – July 30	July 31 – Aug. 6	Aug. 7 – Aug. 13
CT-AgNP mesocosm	W2i		W2ii		W1	W2iii	
	W4						
	W7						
PVP-AgNP mesocosm	W2i		W2ii		W1	W2iii	
	W4						
	W7						
Control mesocosm	W2i					W2iii	
	W7						

2.5.2 Whole lake additions

The field trials for the custom-made CNIS passive sampler were conducted during a whole lake addition study conducted by a research team at Trent University at ELA during the summer of 2014. Lake 222 at ELA was selected for this study. This is a small oligotrophic, dimictic lake containing ~600,000,000 L of lake water and with a maximum depth of approximately 6 meters. The lake stratifies during the summer to form an upper epilimnion and a lower hypolimnion, with a thermocline temperature gradient at about 3 meters depth. The lake was spiked during the 2014 field season with approximately 9 kg of PVP capped AgNP (30-50 nm), purchased as a powder

from NanoAmor (Houston, TX, USA). The powder was suspended in the lake water using a rotor-stator dispersion mill prior to addition to the lake. The methods used to suspend the AgNPs and the size characteristics of the particles in suspension are described in detail by Martin et al. (submitted). Every second day, 125 g of AgNPs suspended in 25 L of lake water was added to the Lake 222 with a peristaltic pump from a point source along the southwestern shore of the lake. The addition started on June 14, 2014 and was continued until October 23, 2014.

The CNIS had an opening of 3.7 cm in diameter and contained NH₂-CNT sorbent between cellulose acetate (0.8 µm) membranes held together with stainless steel rings. The CNIS were sealed in zip-lock bags and stored at room temperature prior to use. At each deployment period, three of the CNIS samplers were deployed together in a stainless steel cage (Figure 2), similar to those used to deploy POCIS passive samplers. The cages were placed at a site located approximately 75 meters northeast of the point of addition, and were suspended from a buoy in the epilimnion at a 1 meter depth. Three deployment periods of approximately 4-7 weeks were used during the study, from June 24-July 28 (32 days), July 28-August 25 (28 days) and August 25-October 19 (55 days). Note that water collected from a nearby reference lake, Lake 221 was used for calibration of CNIS samplers for the determination of sampling rates in Lake 222. The lakes are adjacent to each other and have very similar water quality parameters.

2.5.3 Diffusive gradient in thin film samplers

As the CNIS measure all forms of Ag with a size less than the membrane pore size, including dissolved Ag (dAg), diffusive gradient in thin films (DGT) samplers were used in the field study at Lake 222 to measure Ag⁺ or dissolved complexes with diameters <5 nm (as defined by the pore size of the diffusive gel) present in the water column. The DGT holders obtained from DGT Research (Lancaster, UK) consisted of a plastic molding with a front cap exposing a defined

area of 3.14 cm². A Chelex resin (25 mm diameter) was first placed on the molding and a disk of open pore (2-5 nm pore size) diffusive gel of the same diameter was placed over the resin layer. Finally, a 0.45 µm pore size polysulfone (PS) membrane (0.14 mm thickness) purchased from Pall Life Sciences was placed on the top of the diffusive gel, and the cap with a 20 mm diameter opening was fitted tightly over the assembly. The DGTs were sealed in zip-lock bags and stored at 4°C prior to use. For field studies, the DGTs were deployed either in the lake mesocosms, or in the dosed lake in a manifold designed to fit in the stainless steel cages with the CNIS. The diffusion coefficient (D) for estimating TWA concentrations of dAg from silver accumulated on the DGT was determined in lab experiments similar to those described for determining sampling rates for CNIS. The diffusion coefficient (D) was calculated using the equation.

$$\frac{M(t) \Delta g}{C_w A} = D t$$

Where C_w is Ag^+ concentration measured by ICP-OES, $M(t)$ is the mass of Ag^+ accumulated on the resin over time (adjusted for the extraction efficiency for Ag from the resin ≈ 0.8), Δg is the thickness of the diffusion layer and A is the open membrane area (3.14 cm²).

2.5.4 Estimated TWA Concentration

Using the sampling rate determined in laboratory experiments and data on the mass of silver accumulated on the CNIS by the end of the deployment period, the TWA concentration of Ag in water was estimated using the equation:

$$C_w = m_s / R_s * t$$

Where: C_w is the estimated TWA concentration in water (µg/L); m_s is the mass of the target analyte accumulated on the sorbent of the CNIS over the deployment period (µg), R_s is the experimentally determined sampling rate (mL/day), and t is the deployment time (days).

2.6 Extraction of samples

2.6.1 Extraction of CNIS

Upon recovery, CNIS were rinsed with Milli-Q or RO water (lab studies) or lake water (field studies) and stored at 4°C or lower in the dark. The CNIS-Chemcatcher[®] samplers were opened and the membrane and CNT were removed and placed in separate vials. To each vial, 15 mL of 10 % HNO₃ was added and the solution was heated at 60°C in an ultrasonic bath overnight. The extracts turned dark brown to black, and were filtered through 0.45 µm nylon filters (Fisher Scientific, Toronto, ON, Canada) and then diluted to a 4% HNO₃ solution using Milli-Q water in order to ensure that there was no corrosion of the analytical instruments. All samples were spiked with indium to a concentration of 5 µg/L prior to ICP-MS analysis. Procedural blanks were extracted with each batch of CNIS-Chemcatcher[®] samples.

Other configurations of CNIS were extracted by placing the sorbent and the membrane together in a glass test tube and adding 10 mL of 70% (v/v) HNO₃. The mixture was heated at 120°C for 120 minutes with the tubes covered with a watch glass or glass marble to prevent samples from drying during digestion. After digestion, the cover was removed and a temperature of 150°C was maintained to evaporate the sample to ~1 mL. The evaporated sample was diluted to 5 mL and filtered using 0.45 µm polytetrafluoroethylene (PTFE) syringe filter (Fisher Scientific). Samples were then made up to 10 mL and transferred to polypropylene test tubes prior to analysis by ICP-OES or ICP-MS. Procedural blanks were extracted with each batch of CNIS samples.

2.6.2 Extraction of Water Samples

The water samples collected in lab experiments were acidified in 10% HNO₃ and allowed to digest for a minimum of 24 h. The samples were then diluted to maintain a 4% HNO₃ concentration and spiked with indium to a concentration of 5 µg/L in preparation for analysis by ICP-MS or ICP-OES. A more vigorous digestion of samples using 10% HNO₃ heated at 85°C for

24 h gave the same analytical results, so the simpler method was used routinely for the preparation of water samples.

2.7 Analysis of silver

Analysis of extracts from CNIS or water samples was conducted using either ICP-MS or ICP-OES instrumentation. Samples were analyzed by ICP-OES using an iCAP 6000 Series instrument (Thermo Scientific). The optimized operating parameters for the instrument were: RF power, 1150 W; Pump rate, 50 rpm; Auxiliary gas flow, 0.6 L/min; Nebulizer gas flow, 0.5 L/min; Coolant gas flow, 12 L/min; Purge gas flow, 1 L/min. The calibration of the instrument was done using standard silver solutions prepared daily by serial dilutions of a Ag stock in 1% (v/v) nitric acid at concentrations from 1 to 500 µg/L. The method detection limit for Ag was 2 µg/L.

ICP-MS analysis was conducted with an X-Series instrument (Thermo Scientific, Nepean, ON, Canada). The quadrupole ICP-MS was operated in peak hopping scan mode with a dwell time of 25 ms for monitoring of ^{107}Ag and ^{115}In , with data acquired in steady-state mode and processed using the Thermo PlasmaLab (Thermo Scientific) software. The operating parameters were manually optimized using 5 µg/L tuning solution containing Ag and In. External calibration using standard solutions from 0.1 to 200 µg/L of Ag spiked with In as an internal standard was the method used to generate a calibration curve. Standard solutions were prepared daily from a Ag stock by serial dilution in 4% nitric acid. The method detection limit for Ag was 0.07 µg/L.

Grab samples of water collected in the whole lake experiment were also analyzed to determine the number and size distribution of AgNPs using a single particle ICP-MS (spICP-MS) analytical technique. Other sampling techniques such as composite samples were not practical, considering the absence of electricity at the site. Analysis was carried out with the XSeries 2 ICP-MS using an isotope dilution method with ^{109}Ag internal standard, as previously described by

Telgmann et al. (2013). The limit of particle sizes detectable under the operating conditions with this instrumentation was 45 ± 5 nm.

3. Results and Discussion

3.1 CNIS-Chemcatcher[®]

3.1.1 Sampling rates of CNIS-Chemcatcher[®]

The sampling rates (R_s) were determined for the CNIS-Chemcatcher[®] (COOH-CNT) for CT-AgNP and PVP-AgNP (50 nm) suspended in different aquatic matrixes (Table 2). In all cases, silver accumulation was linear over the time of the experiment (i.e. 96 h). Note that in these experiments with the CNIS-Chemcatcher[®] configuration, the porous membrane was separated from the CNT veil receiving phase, and R_s values were calculated using only the data on uptake in the receiving phase, excluding any accumulation on the porous membrane. Analysis of the membrane showed that up to 18% of PVP-Ag and up to 37% of CT-AgNP was retained on the filter during uptake experiments, but the amount on the filter was variable over time. Because of the variability of the adsorption on the filter, a decision was made to use only extracts from the CNT-veil receiving phase to calculate R_s for the CNIS-Chemcatcher[®] configuration. In later versions of the CNIS sampler, as discussed in the following sections, adsorption to the membrane was more consistent and so the membrane was digested with the sorbent.

Sampling rates for AgNPs suspended in MilliQ water were 4.5 and 6.6 mL per day for the CT-AgNP and PVP-AgNP, respectively (Table 2). The sampling rate for CNIS-Chemcatcher[®] in solutions of Ag^+ was also investigated, and was calculated as 18.0 mL per day (Table 2). These results indicate that the Ag^+ sampling rate is 3-4.5 times greater than the sampling rate for AgNPs. The diffusion of AgNPs across the porous membrane may be limited by electrostatic repulsion within the pores, even though the pore size is larger than the nanoparticle dimensions.

The sampling rate for Ag^+ under the conditions tested is lower than those reported for other

metals using chelating Empore™ sorbents in a Chemcatcher® housing that were between 84.0 to 127.2 mL per day for cadmium, copper, nickel, and zinc (Allan et al., 2007) and between 29 - 91 mL per day for mercury (Aguilar-Martínez et al., 2009). Although CNIS sampling rates for Ag⁺ are somewhat lower than those reported for sorption of other metals by Empore™ disks, they are within the same order of magnitude; giving some confidence in the performance of the CNIS as a passive sampler.

The sampling rates (R_s) were also determined from uptake experiments with surface water collected from two lakes with different water chemistries. Jack Lake, ON has a relatively high concentration of DOC and ionic strength, and intermediate pH relative to Leggat Lake, ON (Table 2). The mean sampling rates in Jack Lake water were 24.7, 5.6, and 7.3 mL per day for Ag⁺, CT-AgNP, and PVP-AgNP, respectively, which are all higher than the R_s values determined in experiments with MilliQ water (Table 2). The higher DOC in Jack Lake water may increase the stability of all Ag species (Chen and Zhang, 2012), reducing the degree of homo- or hetero-agglomeration, so that more nanoparticles are available for uptake by the CNIS. As an alternative explanation, less silver may be retained by the filter in the presence of high DOC. Ionic strength, pH and DOC concentration could affect the surface charge and stability of AgNPs, as well as influencing the surface charge of the CNTs (Chen and Zhang, 2012; Chen and Elimelech, 2007; Huynh and Chen, 2011; Song et al., 2011) but the data from experiments with the CNIS-Chemcatcher® indicate that sampling rates for AgNPs do not vary significantly with the water matrix. When comparing the sampling rates for citrate- and PVP-capped AgNPs, there were slight differences in sampling rates for AgNPs with different capping agents (Table 2).

Table 2: Mean ($\pm$ SD, n=3) sampling rates for CT-AgNP, PVP-AgNP, and Ag⁺ in experiments with the CNIS-Chemcatcher® in MilliQ water, and in surface water collected from Jack Lake and Leggat Lake, ON. The pH, DOC concentration and conductivity of the water matrixes are listed.

AgNP type	Mean sampling rates (R_s) mL per day
MilliQ Water pH 6.0, conductivity 10 μ S per cm	
CT-AgNP	4.5 ± 2.4
PVP-AgNP	6.6 ± 1.4
Ag ⁺	18.0 ± 3.1
Leggat Lake pH 7.4, DOC 4.1 mg per L, conductivity 60 μ S per cm	
CT-AgNP	4.7 ± 2.7
PVP-AgNP	7.0 ± 2.3
Jack Lake pH 8.3, DOC 7.9 mg per L, conductivity 122 μ S per cm	
CT-AgNP	5.6 ± 1.3
PVP-AgNP	7.3 ± 3.0
Ag ⁺	24.7 ± 3.1

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382 3.1.2 Field deployment of CNIS-Chemcatcher[®]

383 Water temperatures measured at the surface, 1 m and the bottom of the mesocosms ranged
384 from 21.3 to 25.7°C over the test period, while the dissolved oxygen ranged from 7-8 mg/L, and
385 the pH was 8 (Furtado et al., 2015). Water samples were collected over the 52 day mesocosm
386 study and three size fractions were analyzed, as previously reported by Furtado et al. (2015). In the
387 two mesocosms in which CNIS were deployed, the concentrations of total silver (TAg) steadily
388 increased over the course of the study as CT-AgNPs and PVP-AgNPs were added and reached
389 final concentrations that were approximately 60% of the predicted nominal concentration (Figure
390 3). Deviation from the estimated nominal concentration might be explained by losses in the water
391 column through sedimentation and adsorption to the mesocosm walls, as discussed previously by
392 Furtado et al. (2015).

Figure 3 Measured concentrations of total silver (TAg) in the mesocosms used for field experiments with the CNIS-Chemcatcher[®]. Data on TAg concentrations in 12 mesocosms were previously reported by Furtado et al. (2015), but this figure focuses on the TAg data for the two mesocosms in which the passive samplers were deployed and the control mesocosm.

The estimated TWA concentrations for silver measured in the TAg and the colloidal Ag (i.e. 0.22 μm filtrate) fraction over each deployment period were calculated by integrating the total area under the accumulation curves over various periods corresponding to the CNT deployments (Table 3). The levels of dAg in the <3 kDa filtrate were not included in this analysis because levels of dAg in the mesocosms were very low, as previously reported by Furtado et al. (2015).

To estimate the TWA concentrations from the CNIS-Chemcatcher[®] results, the sampling rates determined from experiments with CT-AgNPs and PVP-AgNPs spiked into Jack Lake water were used with respective values of 5.6 and 7.3 mL/day. The TWA concentrations estimated from CNIS-Chemcatcher[®] accumulation data (Table 4) are consistent with the calculated TWA concentrations from the measured colloidal Ag data in the 0.22 μm filtrate. This is to be expected, as the TAg concentrations include contributions from homo- and hetero-agglomerates that would not pass through the CNIS membrane and are therefore not sampled by the CNIS device. Pair-wise comparisons of the TWA concentrations estimated from the mass of Ag collected on deployed

CNIS-Chemcatcher[®] to the TWA calculated concentrations of the colloidal fraction (i.e. t-tests) showed that all of the estimated TWA concentrations from the CNIS deployed in the mesocosms spiked with CT-AgNP were not statistically different ($\alpha=0.01$) from the calculated TWA concentrations of measured colloidal Ag (Table 4).

Table 3 Estimated TWA concentrations ($\mu\text{g/L}$) calculated from measured concentrations in a time series of individual bulk water samples collected from mesocosms continuously spiked with CT-AgNP and PVP-AgNP and a control mesocosm. TWA concentrations were calculated by integrating the area under the curve for various deployment intervals, calculated for total silver (TAg) in unfiltered samples and for colloidal silver in the 0.22 μm filtrate. ND = Not detected.

Exposure period	TAg (TWA, $\mu\text{g L}^{-1}$)			Colloidal Ag (TWA, $\mu\text{g L}^{-1}$)		
	Control	CT-AgNP	PVP-AgNP	Control	CT-AgNP	PVP-AgNP
W2i	0.01	8.1	7.3	ND	3.7	3.7
W2ii	0.36	25.1	18.0	ND	2.5	2.6
W1	0.91	27.6	25.6	0.37	12.1	13.7
W2iii	0.87	36.8	30.9	0.26	20.6	20.2
W4	0.16	15.2	14.8	ND	5.4	5.4
W7	0.48	23.1	21.1	0.22	11.4	11.9

In the mesocosm spiked with PVP-AgNP, the TWA concentrations estimated from CNIS-Chemcatcher[®] deployed for shorter periods (i.e. 1-2 weeks) were not statistically different from the TWA concentrations calculated from measured colloidal silver (Table 4). However, there were statistically significant differences in the mesocosm dosed with PVP-AgNP between the TWA concentrations estimated from the CNIS-Chemcatcher[®] deployed for longer periods (i.e. 4 and 7 weeks) or at the end of the experiment (W2iii) and the TWA concentrations calculated from measured colloidal silver (Table 4). The lower TWA concentrations estimated from the passive samplers may have been due to biofouling of the CNIS. The TWA concentrations estimated from the CNIS samplers consistently slightly underestimated the concentration calculated from measured colloidal silver, with the exception of the W2i deployment in the mesocosm spiked with citrate-AgNP (Table 4).

Table 4 Estimated TWA concentrations ($\mu\text{g/L}$) for Ag determined from CNIS-Chemcatcher[®] samplers deployed in mesocosms spiked with CT-AgNP and PVP-AgNP compared to the TWA concentrations ($\mu\text{g/L}$) estimated from analysis of colloidal silver in grab samples collected from the mesocosms. Significance was determined by t-test ($\alpha = 0.01$). S.E. = statistically equivalent concentration; S.D. = Statistically different concentration.

	Exposure period	TWA conc. calculated from Ag mass collected on CNIS ($\mu\text{g/L}$)	TWA conc. calculated from measured colloidal Ag in grab samples ($\mu\text{g/L}$)	Deviation (%)	P-value	$\alpha=0.01$
CT-AgNP	W2i	5.4 ± 0.6	3.7	45	0.019	S.E.
	W2ii	1.7 ± 0.6	2.5	-34	0.148	S.E.
	W1	9.8 ± 1.2	12.1	-19	0.076	S.E.
	W4	4.1 ± 0.3	5.4	-23	0.017	S.E.
	W2iii	13.8 ± 3.4	20.6	-33	0.072	S.E.
	W7	8.7 ± 0.7	11.4	-24	0.023	S.E.
PVP-AgNP	W2i	3.0 ± 0.2	3.7	-17	0.028	S.E.
	W2ii	2.3 ± 0.6	2.6	-13	0.422	S.E.
	W1	8.6 ± 2.2	13.7	-32	0.029	S.E.
	W4	2.7 ± 0.1	5.4	-49	0.001	S.D.
	W2iii	9.9 ± 1.3	20.2	-51	0.005	S.D.
	W7	5.4 ± 0.2	11.9	-54	0.000	S.D.

These were encouraging results for the development of a passive sampler using CNTs. However, the R_s values were relatively low compared to other Chemcatcher[®] devices and sampling rates were variable. It was concluded that further work is needed to improve the performance of the CNIS. Specifically, a sampler was needed with a higher density of CNTs and greater surface area for absorption. A more robust housing of the CNIS was needed that is resistant to damage under the more extreme conditions expected in surface waters (e.g. rivers, streams, lakes) and in wastewater streams. Finally, it was concluded that the membrane should be extracted along with the sorbent because of the potential for accumulation of silver on this part of the CNIS.

3.2 Custom CNIS

3.2.1 Receiving phase of CNIS

Two types of CNT veil were further tested for their ability to adsorb AgNP and dissolved Ag. Veils with bare CNTs and COOH-CNTs enclosed in cellulose acetate membranes were placed in CT-AgNP suspensions and silver nitrate solutions. Inconsistent results were observed for the bare CNT veils, while the COOH-CNT enclosed in two membranes showed more reproducible, but still variable results. The disadvantages of the CNT veil were the inconsistent amounts of CNT present on the fibers of the veil, especially after handling, and a non-homogeneous distribution of the CNT on the veil surface. Consequently, CNT veils were rejected as potential adsorbents for the improved CNIS.

Tests were conducted with CNT powder (30-50 nm particle size) with amine functionality (NH₂-CNT) and carboxyl functionality (COOH-CNT). CNIS were prepared for laboratory experiments with 5 mg of each CNT powder sandwiched between two cellulose acetate membranes with a 0.8 µm pore size and held together with rings with a 2 cm diameter opening. All experiments were conducted with a 20 ppb CT-AgNP suspension in RO water. Both of the CNT powders adsorbed AgNP with kinetics that were reproducible in replicate experiments. Based on their high adsorption efficiency and consistency, CNT powder was selected as a receiving phase for further study. In addition, because a significant amount of AgNPs and Ag⁺ is retained on the porous cellulose acetate membrane (10-20%), a decision was made to determine sampling rates for these CNIS by digesting both the membrane and the sorbent for analysis of silver.

The Ag accumulated on the CNIS sorbents was assumed to include any Ag species that are able to pass through the porous 0.8 µm membrane. In addition to AgNPs of 1-100 nm in size, species of Ag that could pass through the membrane may include colloidal Ag, as Geckeis et al. (2002) noted that colloidal material includes metal complexes that are <800 nm in size. Other Ag

species that pass through the membrane could include dAg species and some AgNPs in agglomerated state. In addition, significant amounts of Ag may have accumulated on the porous membrane and this material was also included in the total load on the CNIS. More work is needed to define the species of Ag that can pass through the membrane and are adsorbed on the membrane, as well as the kinetics of accumulation. Therefore, the CNIS samplers are not specific for sampling AgNPs alone. Analogous to the term “DGT-labile” commonly used to describe metal species that bind to DGT sorbent (Allan et al., 2008; Guéguen et al., 2011), it was decided that “CNIS-labile” Ag is the most appropriate term to describe the Ag that accumulates on the samplers over the deployment period.

3.2.2 *Sampling rates of small CNIS*

Sampling rates were determined at room temperature for the CNIS samplers constructed using NH₂-CNT and COOH-CNT powder between cellulose acetate membranes and held together with rings with a 2 cm diameter opening. Experiments were conducted with 20 ppb CT-AgNP suspension in RO water. The sampling rate calculation was based on the mass of silver accumulated on the CNT surface, while the AgNP residual concentration was also monitored over time in the test solution/suspension. The mass of Ag accumulated on the CNTs followed a linear uptake for 4 days, as illustrated in Figure 4. The NH₂-CNT and COOH-CNT sampling rates for CT-AgNP were 1.8 ± 0.4 mL/day and 3.0 ± 1.2 mL/day, respectively. The R_s value for the COOH-CNT powder (i.e. 3.0 ± 1.2 mL/day) is slightly lower than the mean R_s determined in experiments with CT-AgNP suspensions for the CNIS-Chemcatcher[®] (COOH-CNT) device of 4.5 ± 2.4 mL/day, but the sampling rates in replicate experiments with the CNT powder were more reproducible.

Figure 4: Mass of Ag accumulated every 24 h over a 96 hours experiment by CNIS with NH₂-CNT sorbent in an experiment with a 20 ppb CT-AgNP in RO water. Extracts from CNIS were analyzed by ICP-OES.

As previously shown, the sampling rate for adsorption of silver on the CNT is specific to the water matrix in which they are deployed. Therefore, sampling rates for CNIS must be determined for the specific aquatic matrix in which they are deployed. Sampling rates were determined for CNIS with small rings (2 cm opening) in experiments at room temperature in 6 different aquatic matrixes, including three different surface waters collected from lakes in ON, Canada and three wastewaters collected at two municipal wastewater treatment plants (WWTPs) in ON, Canada. For each experiment, 16 L of the matrix were filtered through medium flow rate P6 filter paper with 1 μ m porosity (Fisher Scientific) to eliminate large particles, and then aliquots were spiked with CT-AgNP at concentrations of 20 ppb. The mean sampling rates for AgNPs in each of these matrixes are summarized in Table 5. In all of these experiments, the accumulation of Ag on the sorbent was linear over time ($R^2 > 0.9$). The mean sampling rates ranged from 1.8 to 22.4 mL/day for the CNIS with NH₂-CNT sorbent (Table 5), although the sampling rate for WWTP influent was much higher than the other matrixes. The sampling rates for CNIS with

COOH-CNT sorbent were comparable to sampling rates for the NH₂-CNT sorbent in trials where both types of sorbent were tested (Table 5).

Table 5: Sampling rates (R_s) for Ag in CNIS (2.0 cm diameter opening) with NH₂-CNT and COOH-CNT sorbents determined in experiments with different water matrixes spiked with CT-AgNP suspension (20 ppb). The water quality characteristics of the aquatic matrixes are listed.

Water matrix	Water quality characteristics			Sampling rate R_s (mL/day)	
	DOC (ppm)	pH	Conductivity (μ S/cm)	NH ₂ -CNT	COOH-CNT
WWTP 1 effluent	5.6	7.7	985	6.7 $\pm$ 2.8	8.7 $\pm$ 1.8
WWTP 2 influent	8.0	7.6	908	22.4 $\pm$ 8.6	
WWTP 2 effluent	4.2	7.8	702	8.7 $\pm$ 1.7	
Toronto Harbor, ON ¹	2.6	8.3	332	5.1 $\pm$ 0.1	5.7 $\pm$ 1.0
Otonabee River, ON ¹	4.2	8.0	182	7.0 $\pm$ 0.4	
Lake 221, ON ²	12.1	6.6	43	1.7 $\pm$ 0.5	
RO water	0.9	6.2	7	1.8 $\pm$ 0.4	3.0 $\pm$ 1.2

1) Western Lake Ontario; 2) Experimental Lakes Area (ELA)

The high rates of accumulation of CNIS-labile Ag on samplers deployed in wastewater may be due to deposition of material on the membrane surface. There was visible accumulation of material on the membrane during the sampling rate experiments. Even though the Ag may not pass through, the membrane was digested together with the sorbent and contributed to the loadings of CNIS-labile Ag. Wastewater is a complex matrix with high ionic strength. Once ion concentrations exceed the critical coagulation concentration, rapid agglomeration of nanoparticles may occur (Metrevelli et al. 2016). There is high DOC in wastewater, which may improve stability of AgNPs by adsorbing to nanoparticles, but conversely, DOC may also induce bridging-determined aggregation (Metrevelli et al. 2016). In any event, more work is needed to

determine the behaviour of AgNPs in wastewater in order to understand their accumulation in CNIS devices.

As reported by Gao et al. (2009), adsorption on CNTs is mainly driven by electrostatic attraction and chemical interactions. In acidic water, negatively charged CT-AgNP can be neutralized by the high concentrations of H^+ , which could result in repulsive interactions with the positively charged NH_2 -CNT surface (Huynh and Chen, 2011). This phenomenon may limit the uptake of AgNP, as observed in RO water and in Lake 221 water with low pH. Therefore, alkaline water may be the preferred condition for accumulation of CT-AgNP by NH_2 -CNT sorbent. We had initially assumed that the positive surface charge of the NH_2 -CNT would promote adsorption of the negatively charged CT-AgNP. However, in comparing the COOH-CNT and NH_2 -CNT sampling rates (Table 5), the R_s values were comparable, if not slightly higher for the CNIS with the COOH-CNT sorbent. A possible explanation is that the AgNP adsorption is driven by van der Waals forces, which is a non-covalent interaction that could facilitate AgNP adsorption on CNTs with either functional group (Rance et al., 2010, Pal et al., 2014).

To identify the factors influencing the NH_2 -CNT sampling rates, the data were analyzed using both a linear regression model using Excel software and a non-linear multiple regression model with effect factor interactions using XL Stat software. The linear regression gave a poor fit of the data, but in the non-linear model, a strong correlation was observed between R_s and conductivity (0.697). Discriminant Analysis of the data indicated that pH and conductivity interacted to give a highly positively correlation with the sampling rate.

As mentioned previously, DOC is expected to influence the uptake of AgNP. When DOC is present, it tends to complex with nanoparticles (Kanel et al., 2015), which may promote binding of these complexes to the porous membrane. That can explain the yellowish precipitate observed

on the membrane of CNIS placed in WWTP influent. Although Lake 221 water had relatively high levels of DOC, the low pH and ionic strength may have counteracted the influence of DOC, resulting in a relatively low sampling rate for CNIS-labile Ag (Table 5). It is likely that the sampling rates in different water matrices are controlled by a combination of DOC, pH and ionic strength, as well as other water quality parameters. Therefore, it is advisable to determine R_s values for each aquatic matrix in which the CNIS are to be deployed.

3.2.3 *Sampling rates of large CNIS*

CNIS using NH₂-CNT sorbents with a larger ring size (i.e. 3.7 cm opening) were used for field deployments in Lake 222, so it was necessary to determine sampling rates for these larger CNIS. According to Vrana et al. (2006) and Kot-Wasik et al. (2007), the sampling rate is a function of the exposure area:

$$R_s = k_o A = k_e k_{DW} V_D$$

Where k_o is the overall mass transfer coefficient, A the cross-sectional area, k_e the overall exchange rate constant, k_{DW} the receiving phase/water partitioning coefficient, V_D is the volume of the receiving phase.

This indicates that the larger area of the rings used in CNIS for field deployments would increase sampling rates. The results obtained for the calibration of CNIS (NH₂-CNT) using both the small and large rings in uptake experiments conducted in Lake 221 water spiked with 20 ppb CT-AgNPs indicate that the sampling rates were 1.7 mL/day for CNIS with the 2 cm diameter opening and 3.8 mL/day for CNIS with the 3.7 cm diameter opening. Therefore, the increase in size of the CNIS promoted the Ag uptake by a factor of 2.2. This increase in sampling rate is not proportional to the difference in the surface area of the smaller and larger CNIS (i.e. 3.4). This

could be due to the fact that the same amount of CNT sorbent (i.e. 5 mg) was used in both configurations of the CNIS, even though the surface area was greater in the larger sampler.

CNIS were deployed in Lake 222 in the warmer epilimnion and the colder hypolimnion of the lake. Therefore, CNIS sampling rate experiments were conducted with 20 ppb CT-AgNP suspended in Lake 221 water at low temperatures ($4 \pm 2^\circ\text{C}$), which roughly corresponds to the temperatures in the summer in the hypolimnion (i.e. $5\text{--}7^\circ\text{C}$). In the low temperature experiment, the sampling rates were 0.7 mL/day and 1.1 mL/day for the smaller and larger sized CNIS, respectively. These are lower than the sampling rates determined at room temperature of 1.7 mL/day and 3.8 mL/day for the smaller and larger sized CNIS, respectively. Therefore, water temperature can have a significant effect on CNIS sampling rates.

Since DGT samplers were deployed along with CNIS in the field, diffusion coefficients for DGTs were determined in batch experiments similar to those described for CNIS uptake, but with Ag^+ solutions (20 ppb). In experiments with Lake 221 water spiked with AgNO_3 , diffusion coefficients were observed at room temperature and at low temperature of $4.0 \times 10^{-6} \text{ cm}^2/\text{s}$ and $4.3 \times 10^{-6} \text{ cm}^2/\text{s}$, respectively. Therefore, it appears that temperature is not a major factor affecting the accumulation of DGT-labile Ag and might have been compensated by other factors associated with the matrix.

3.2.4 Field deployments of large CNIS

Deployments of CNIS ($\text{NH}_2\text{-CNT}$) and DGTs were conducted during the summer of 2014 in Lake 222 at ELA. The lake was dosed over the deployment period with $\sim 9 \text{ kg}$ of AgNP. Analysis of water quality parameters showed that the DOC concentration was 11.3 mg/L , the pH was 7.1 and the conductivity was $41 \text{ }\mu\text{S/cm}$. The water temperatures in the epilimnion of the lake were in the range of $16\text{--}23^\circ\text{C}$ throughout the first two deployment periods in June to August, but

declined to 11°C by the end of the third deployment. Grab samples of lake water were collected at 1 m depth at the CNIS deployment site and subsamples were flash frozen in liquid nitrogen, then later stored at -80°C. These samples were thawed and analyzed by spICP-MS for nanoparticle sizes and dAg concentrations, as described by Telgmann et al. (2014). Subsamples were also acidified in 4% HNO₃ and analyzed by ICP-MS for total silver (TAg).

Analysis by spICP-MS indicated that the majority of the particles were <80 nm in size, and particle sizes were all < 200 nm (Figure 5). Therefore, all particles were smaller than the pores in the cellulose acetate membrane (0.8 µm) used with the CNIS and should have been able to pass through to reach the receiving phase of CNTs. Previous studies on the fate of AgNPs in mesocosms in a lake at ELA indicate that the nanoparticles are stable in suspension because of the low ionic strength and relatively high DOC concentrations in oligotrophic lakes from this region (Furtado et al., 2014; Furtado et al., 2015).

Figure 5: Size (particle diameter) distribution of AgNPs determined by spICP-MS analysis of a grab sample of lake water collected at 1 m depth on July 28, 2014 at the CNIS deployment site in Lake 222.

The mean (n=3) mass of Ag accumulated on the CNIS (NH₂-CNT) during the deployments in Lake 222 were 268 ng, 954 ng and 1,545 ng over the three deployment periods, respectively.

These were greater than the masses of AgNPs accumulated on CNIS during the 8-day laboratory experiments, which were typically <200 ng. The mass on the individual CNIS and the sampling rates (R_s) determined for CNIS with the same receiving phase in experiments at room temperature using water from Lake 221 (i.e. 3.8 mL/day) were used to calculate the TWA concentrations of CNIS-labile Ag over the three deployment periods (Table 6). The estimated TWA concentrations of DGT-labile Ag are also listed in Table 6. Since these estimated concentrations of DGT-labile Ag are very low, it is unlikely that dAg contributed significantly to the burden of silver adsorbed to the CNIS.

Table 6: Mean (n=3) estimated TWA concentrations ($\mu\text{g/L}$) of CNIS-labile Ag and DGT-labile Ag, and the measured concentrations of TAG, dAg and number of particles/mL in grab samples collected at the deployment site in Lake 222 over three deployment periods in the summer of 2014.

	Deployment 1 June 24 - July 28	Deployment 2 July 29 – August 25	Deployment 3 August 26 – October 19
CNIS-labile Ag	2.1 ± 0.7	9.0 ± 0.7	7.4 ± 4.7
DGT-labile Ag	0.017 ± 0.013	0.005 ± 0.005	0.016 ± 0.030
Measured TAG ¹	2.9 ± 0.4	9.3 ± 1.6	8.6 ± 1.2
Measured dAg ^{1,2}	0.08	0.22	Not analyzed
Measured particles/mL ^{1,2}	8,540	15,420	Not analyzed

1) Measured in samples collected at the end of each deployment period.

2) Analyzed by spICP-MS

There was good agreement between the measured concentrations of TAG in grab samples collected at the end of each deployment period and the estimated TWA concentrations of CNIS-labile Ag (Table 6). There was considerable variability in the estimates of TWA concentrations of CNIS-labile Ag from the third deployment, which was probably due to biofouling of the samplers over the 7 week deployment period. Estimates of TWA concentrations from CNIS deployed over the two shorter periods (i.e. 28-32 d) showed little variability (Table 6).

The very low concentrations of DGT-labile Ag in the lake over the deployment periods is consistent with the low concentrations of dAg measured in grab samples of water collected at the deployment site (Table 6). However, the concentrations of dAg measured by ICP-MS are 1-2 orders of magnitude higher than the DGT-labile Ag concentrations. It must be remembered, however, that DGT-labile Ag and dissolved Ag measured by ICP-MS may not represent the same fractions of the Ag pool. Previous studies on the fate of AgNPs in mesocosms deployed in a lake at ELA indicate that levels of Ag^+ are low because the silver ions bind to dissolved organic matter to form soluble complexes (Furtado et al., 2014). These complexes may not readily pass through the DGT diffusive layer to the sorbent gel, but are measurable as dissolved Ag by sp-ICP/MS. In any event, we can conclude from data on measured concentrations of dAg and estimated concentrations of DGT-labile Ag that dissolved silver did not contribute significantly to the Ag accumulated on the CNIS during deployment in the lake.

4. Conclusions

The Carbon Nanotube Integrative Sampler (CNIS) developed and tested in this study shows promise as a monitoring tool for AgNPs in aquatic matrixes. The configuration using CNT powder placed between cellulose acetate membranes has sampling rates for AgNPs in the range of 2-5 mL/day. This is lower than sampling rates reported for passive samplers using chelating Empore™ sorbents in a Chemcatcher® housing that were between 84-127 mL/day for metals (Allan et al., 2007) and between 29-91 mL/day for mercury (Aguilar-Martínez et al., 2009). However, this can be explained by the slower diffusion of nanoparticles across porous membranes than metal ions. This means that deployment periods of several weeks are needed to detect environmentally relevant concentrations (e.g. ng/L). Further study is needed to determine whether accumulation of CNIS-labile Ag is linear in CNIS deployed for several weeks, and also to evaluate

whether biofouling that could occur over an extended deployment period might impact sampling rates.

It must be stressed that we have assumed that the CNIS can accumulate any Ag species that are able to pass through the porous 0.8 μm membrane. In addition, digestion of the membrane with the receiving phase will include any Ag bound to the membrane. Therefore, CNIS-labile Ag will include AgNPs and a wide range of other Ag species, including dAg, AgNPs in agglomerated (<800 nm) state and colloidal Ag. However, the CNIS can be a useful screening tool to evaluate whether there is potential contamination of surface waters and wastewater by AgNPs. Once candidate sites for Ag contamination have been identified using CNIS, more sophisticated analytical techniques such as spICP-MS can be used to confirm whether nanoparticles are present in the aquatic matrix. Co-deployment of DGT devices with the CNIS can also indicate whether there is also contamination with DGT-labile Ag.

The sampling rates for CNIS vary with the aquatic matrix in which they are placed. In this study, we determined sampling rates for CNIS in laboratory experiments with water that had very similar water quality characteristics to the field sites where the samplers were to be deployed. This is an optimal strategy for monitoring using CNIS, but may not always be practical. The variable effect of physical and water quality conditions, as well as biofouling on sampling rates is a problem that is shared with all passive sampling devices (Allen et al., 2008; Gunold et al., 2008; Harman et al., 2012). One approach to compensate for variable conditions at the site of deployment may be to develop Performance Reference Compounds (PRCs) for the CNIS, as has been done for other types of passive samplers (Huckins et al., 2002; Mazzella et al., 2010). The rate of efflux of PRCs spiked onto the receiving phase back into the water matrix over the period of deployment is used to adjust the sampling rates to reflect conditions at the deployment site.

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