A novel passive sampler for monitoring nanosilver in aquatic matrices

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ABSTRACT

As a result of expanding use, nanomaterials such as nanosilver (AgNP), are being continuously released into the environment through production, usage, and disposal. Research is needed to develop cost-effective and sensitive methods to quantify AgNP in various environmental compartments in order to fully evaluate the exposure and risks associated with the presence of these nanomaterials in the environment. This work is hampered by the lack of sensitive methods to detect AgNPs and other nanomaterials in environmental matrices. The present study focused on the development, calibration and application of a passive sampling technique for detecting AgNP and estimating low concentrations of these nanomaterials in aquatic matrices. This thesis work included the design, calibration and application of the designed sampler to the detection of silver in nano-form in surface waters and wastewater. The Carbon Nanotube Integrative Sampler (CNIS) developed in this study was deployed in an experimental lake dosed with AgNP in order to demonstrate the applicability of these samplers for monitoring in natural surface waters. The time weighted average (TWA) concentrations of "CNIS-labile" Ag estimated from deployments of the sampler in the dosed lake varied between 1-10 ppb, which were similar to the concentrations of total Ag determined from grab samples collected in the lake. The samplers were then applied to monitoring AgNP in a wastewater treatment plant (WWTP), as well as the quantification of AgNPs in surface waters. Results of monitoring in the WWTP for the city of Peterborough, ON showed an estimated TWA concentration of CNIS-labile Ag of 0.2 ppb in the treated effluent, but there was no evidence of an increase in CNIS-labile Ag in receiving waters of the Otonabee River, ON, downstream of the wastewater discharge. Deployments of CNIS in two nearshore areas of Lake Ontario situated near discharges of municipal wastewater also showed estimated TWA concentrations of CNIS-labile Ag that were lower than 1 ppb. These monitoring results are consistent with recent literature showing that much of the Ag in municipal wastewater will settle out of the suspension as Ag₂S before final discharge into receiving waters. This thesis provided an assessment of the presence of AgNP in environmental waters and demonstrated the potential of the CNIS samplers as a tool to monitor concentrations of nanomaterials in surface waters and wastewater.

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RESUME

En raison de leur utilisation croissante, les nanomatériaux tels que les nanoparticules d'argent (AgNP), sont relâchées en continu dans l'environnement suite à la production, l'utilisation et la disposition de divers produits. Des recherches sont donc nécessaires pour le développement de méthodes économiques et suffisamment sensible pour la quantification de AgNP dans diverses matrices environnementales et ce, afin d'évaluer l'exposition réelle et les risques associés avec la présence de AgNP sur l'environnement et la santé publique. La présente étude a porté sur le développement, l'étalonnage et l'application d'un échantillonneur passif à la détection de AgNP et la mesure de faibles concentrations dans des matrices complexes. Les travaux de la présente thèse ont permis de concevoir un échantillonneur passif basé sur les nanotubes de carbon (nommé ici CNIS) et de l'étalonner pour le suivi de l'argent sous forme de nanoparticules. Le CNIS a ensuite été appliqué à la détection de AgNP dans les eaux de surface et les eaux usées. L'échantillonneur développé dans cette étude a été déployé dans un lac expérimental dosé avec des AgNP afin de démontrer l'applicabilité du CNIS pour la suivi d'eau de surface. Les concentrations moyennes pondérées d'argent déterminées à partir des déploiements de CNIS dans le lac dosé variaient entre 1-10 ppb, des valeurs comparables aux concentrations d'argent total déterminées à partir d'échantillons ponctuels. Les échantillonneurs ont ensuite été appliqué à la quantification de AgNP dans une usine de traitement des eaux usées (STEP), ainsi que la quantification de AgNP dans les eaux de surface naturelles. Les résultats de suivi à la station d'épuration de la ville de Peterborough, ON ont démontré une concentration estimée d'argent de 0.2 ppb dans l'effluent traité, mais n'indiquaient aucune augmentation dans les eaux réceptrices de la Otonabee River, ON, en aval de la décharge des eaux usées. Les déploiements de CNIS dans deux zones littorales du lac Ontario situées à proximité rejets d'eaux usées municipales a également montré des concentrations estimées d'argent inférieures à 1 ppb. Ces résultats de suivi sont conformes à la littérature récente qui montre que la majeure partie de l'argent contenue dans les eaux usées municipales est précipitée sous forme de Ag₂S avant décharge dans les eaux réceptrices. Cette thèse a fourni une évaluation de la présence de AgNP dans les eaux environnementales et démontré le potentiel

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LIST OF ABBREVIATIONS

Abbreviation	Meaning
AgNP	Silver nano particle
AFM	Atomic force microscopy
Cit-AgNP	Citrate acid coating silver nano particle
CNIS Carbon nanotubes integrative sampler	
CNT	Carbon nanotube
CNT-SS	Carbon nanotube growing on stainless steel 316
COOH-CNT Carboxyl functionalized carbon nanotube	
COOH-CNT-SS	Carboxyl functionalized carbon nanotube growing on stainless steel 316
DGT	Diffusive gradient in thin-films
EDX	Energy Dispersive X-ray Spectroscopy
ELA	Experimental lakes area
GA-AgNP	Gum Arabic coating silver nano particle
HDPE	Heavy duty polyethylene
ICPMS Inductively coupled plasma mass spectrometry	
ICP-OES	Inductively coupled plasma –optical emission spectrometer
IEP	Isoelectric point
ISA	Ionic strength adjustor
ISE	Ion selective electrodes
NH ₂ -CNT	Amine functionalized carbon nanotube
NT-WWTP	North Toronto wastewater treatment plant
PA-AgNP	Polyacrylate coating silver nano particle
PES	Polyethersulfone
PS	Poly sulfone
PTFE	Polytetrafluoroethylene
PVP-AgNP	Polyvinylpyrollidone coating silver nano particle
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
TWA	Time-weighted average
WWTP	Wastewater treatment plant
XPS	X-ray photon spectrometer

1 Introduction

Silver has been used since ancient times for jewellery, monetary currency, utensils, high-value tableware, etc. Due to its high light reflection, electrical conductivity and thermal conductivity, silver and its salts have also been used for a long time in electrical conductors, in mirrors, for catalysis of chemical reaction, and in photography. Because of the fungicidal, bactericidal and algicidal properties of silver, ancient Greeks used silver containers to kill harmful bacteria contaminating various commodities, including milk and water (Senjen, 2009). However, the high value of silver has limited its widespread application in low-cost consumer products. The worldwide production of silver reached 28,000 metric tons in 2007. The majority of silvers is still used in industry (38.2%), for jewellery and silverware (32.5%), and in the photographic industry (23.8%) (Hund-Rinke et al. 2008).

However, with the more recent development of nanotechnology, there is increasing use of nano-scale silver (i.e. AgNPs) in commercial products because of: 1) high surface area per unit mass, resulting in increased reaction rates and enhanced the particle mobility (Hoque et al. 2012; Smetana et al. 2008), and 2) powerful antibacterial and anti-fungal properties. Because of the latter anti-microbial properties, AgNPs are now used in food, packaging, odour resistant textiles, household appliances, children's toys, cleaning agents, paints and varnishes, water disinfectants, room sprays, cosmetics, personal care products and medical devices (Senjen, 2007; El-badawy et al. 2010; Kulinowski, 2008, Hund-Rinke et al. 2008). In 2015, there were 442 products (out of 1827 nanotechnology products in the inventory) containing nanosilver listed in the Nanotechnologies Consumer Products Inventory (Project on Emerging Nanotechnologies 2015). In 2013, the market for nanosilver materials and coating products has reached \$682 million and it is expected to grow to \$1.8 billion in 2020 (Transparency Market Research, 2014). As a result of expanding usage of AgNP, there is potential for the release of these products into the environment through production, usage, and disposal. Because of the rapid increase in production and use of nanosilver products, a lot of attention is currently given to the environmental fate, transport, and toxicity of AgNP. For example, Senjen (2007) reported that

AgNP adversely affects beneficial bacteria in soil and water and has the potential to enhance the development of antibiotic-resistant strains of harmful bacteria. AgNPs were also shown to alter microbial communities in natural waters presumably by selecting for more resistant strains of bacteria (Das et al., 2012).

Some research has been done on the quantification of total silver in environmental matrices, including relatively high concentrations of 38 ppb detected in the Colorado River (Wijnhoven et al. 2009) and low concentrations of 0.01 ppb detected in pristine water (WHO 2002). However, assessing the fate and effects of AgNP in the environment is currently challenging, partly due to the lack of methodology for distinguishing AgNP from other forms of silver, such as dissolved silver and silver complexes (El-badawy et. al., 2010). The development of trace analysis methods targeted at solid phase species present at low concentrations in complex environmental matrices is a challenge for analytical science with a long history of determining dissolved species (Howard, 2010). Some analytical methods, such as single particle ICP-MS (spICP-MS) and asymmetric flow field flow fractionation coupled to ICP-MS (AF4-ICP-MS) show promise as techniques for analyzing nanoparticles in aquatic matrices (Furtado et al., 2014), but these methods typically have detection limits in the low ppb range and require specialized instrumentation. Therefore, analytical tools are needed that provide sensitive methods to quantify AgNP in various environmental compartments.

One emerging technique to monitor xenobiotics in the environment is based on the use of passive samplers, which offer the advantages of simple operation, rapid field sample collection, and low operating costs (Kot-wasik et al. 2007). Current passive sampler techniques used for detecting dissolved silver in marine waters use anion exchange or chelating sorbents (Fones et al. 2011), which are not suitable for monitoring AgNP. This project thus focuses on describing the development of a novel passive sampling device, which we call the "Carbon Nanotubes Integrative Sampler" (CNIS) for monitoring the presence of AgNPs in aquatic matrices. In order to account for the co-occurrence of dissolved silver along with AgNPs, a widely used passive

sampling technique with "diffusive gradient in thin-films" (DGT) samplers were deployed in tandem with the CNIS.

2 Background

2.1 Introduction to silver nanoparticles

2.1.1 Definition of nano technology

Nano technology is the research and manufacturing of materials occurring at the atomic, molecular or macromolecular levels, in the length scale of approximately 1-100 nm in at least one dimension (BSI, 2007; SCE-NIHR, 2008). A visual size comparison between materials and biological structures at the nano-scale and visible scale is presented in Figure 2-1.



Figure 2-1 Size comparison of nano scale things to natural things (NSM, http://www.nanosilver.com.my/nanotech.asp)

2.1.2 Production, application and exposure pathways of AgNP

Due to the different applications, several nanomaterials are used in commercial products, such as carbon nanotubes, nanosilver, nanogold, nano-titanium dioxide and nanocopper. Among these, nanosilver is the most widely used nanomaterial, due to its high electrical and thermal conductivity and antimicrobial properties. In 2015, around 750 tons of AgNP were produced in the world and the market growth is predicted up to 2000 tons in 2022 (Grand View Research, 2015) (Figure 2-2). Nano silver suspensions consist of nano-scale elemental silver (Ag^o) that is typically coated with organic stabilizers to promote the suspension of the particles in aquatic matrices, and these suspensions typically contain more than 80% silver nanoparticles. Although there are similarities in the size distribution of both colloidal silver and AgNPs, colloidal silver consists of natural aggregations of loose silver atoms forced by the tensions of the water to adhere together as clusters in suspension, and the particle size of silver colloid is typically from 10 nm to 1 micron (Laroo H., 2013).

Nanosilver can be produced in various sizes from 1- 100 nm and shapes including spheres, rods, cubes, tubes, wires, plates, films, and multifacets, depending on the fabrication method (Wijnhoven et al. 2009). Due to the unique properties of AgNPs, more than 400 consumer products incorporating AgNP are available in the market in 2015 (Project on Emerging Nanotechnologies 2015). The major applications for AgNPs include water filtration, catalysis, food, textiles, clothing, health and fitness, household goods, children goods, medical, appliances, computer keyboards, and toothpaste, etc. (Shaw and Handy, 2011; Fauss, 2008; Kulinowski, 2008). Among these, healthcare is the largest application of AgNPs and is likely to be the fastest growing application (Figure 2-2).



Figure 2-2 Global silver nanoparticles market, by application, 2012 – 2022 (Tons) (Grand View Research, 2015)

Nano silver is synthesized through chemical and physical methods following stabilization of the particles to avoid coalescence (Kunhikrishnan et al. 2015). Metallic silver has been engineered into ultrafine particles consisting of about 20-15,000 silver atoms (Warheit et al. 2007) by a few methods, including spark discharging, electrochemical reduction, solution irradiation, cryochemical synthesis, and biological reduction (Chen et al. 2008; Li et al. 2011). Because of the high reactivity of nano-silver and its tendency to aggregate attributed to its high ratio of surface area to volume, bare nanosilver particles are not stable in suspension. Therefore, AgNP suspensions are typically stabilized using compounds such as citrate acid, sodium polyacrylate, tannic acid, gum Arabic (GA) and polyvinylpyrollidone (PVP) (Figure 2-3). The most commonly used capping agents for AgNPs in consumer products are citrate and PVP. Citrate weakly associates with the nanoparticle surface, providing stability, but is readily displaced by a range of other molecules, including thiols, amines, polymers, antibodies, and proteins (nanoComposix). PVP capped AgNP provides greater long term stability than citrate, due to strong binding to the silver particle surface and being difficult to displace. PVP coated AgNPs (10 nm) were stable for more than a year in natural surface water, and a week in chlorinated or chloramine-treated drinking water respectively (Tugulea et al. 2014). Sodium polyacrylate is a less commonly used capping agent, but it offers another route to stabilization by providing

carboxyl functional groups on the surface of AgNP. Gum Arabic (GA) which is an exudate from Acacia trees owns a combination of excellent emulsifying properties and low solution viscosity (Yadav et al. 2007). It is a branched-chain, complex polysaccharide, either neutral or slightly acidic. AgNP coated with GA (GA-AgNP) shows high stability in the water (Rao et al. 2010). Therefore, AgNP expresses different behaviours of aggregation and distribution in aquatic matrices due to the choice of coatings used to stabilize the AgNP. Based on studies by Hendren et al. (2013), the predicted nanosilver concentration in wastewater effluent range from 0.06 μ g/L to 0.24 μ g/L, in the order of bare AgNP<PVP-AgNP<citrate-AgNP<GA-AgNP. In contrast to the results for effluent concentrations, the predicted AgNP concentrations in sludge are in reverse order, from 4.3 μ g/kg for GA-AgNP to 13.03 μ g/kg for bare AgNP.



Figure 2-3 PVP, tannic acid, gum Arabic, citrate and sodium polyacrylate capping agents used as stabilizers for AgNPs

Due to the large number of AgNP-containing commercial products (Figure 2-2) available in the market, significant amounts AgNP may be released in wastewater and subsequently in surface waters during production, use and disposal. According to Wijnhoven et al. (2009), there are 300,000 kg of silver released into ecosystems every year worldwide. Direct discharge of AgNP

from manufacturing processes is potentially the largest portion of AgNP reaching wastewater streams (Kunhikrishnan et al. 2015). The other routes of AgNP entering into wastewater include direct disposal of consumer products incorporating AgNP, as well as release from wastewater treatment plants, and decomposition of consumer products discarded in landfill and natural bodies (Kang et al. 2009). Based on the data provided by Samsung, the amount of silver release from a washing machine is 0.05 mg/L during washing (Hund-Rinke et al. 2008). About half to two thirds of AgNP and Ag⁺ end up in the sewage system. Benn and Westerhoff (2008) indicated that commercially available socks containing 1360 µg-Ag/g-sock can leach 650 µg of Ag in 500 mL of distilled water. Another study by Geranio et al. (2009) showed that 0.3-377 ug-AgNP/g-textiles can be released during washing of nanotextiles and a significant amount of Ag⁺ is released when bleach is added. The portion of Ag making its way into sewer systems may be reduced by sedimentation through aggregation and settling in the WWTP (Blaser et al. 2008; Gottschalk et al. 2009; Mueller et al. 2008). According to Kim et al. (2010) and Kaegi et al. (2011), more than 90% of the silver in the wastewater will transform into silver sulfide (Ag₂S) nanoparticles during wastewater treatment and will be retained in the sludge. AgNP stabilized with polyoxyethylene fatty acid ester was also observed to transform into Ag₂S in a non-aerated tank in a wastewater treatment plant (Kaegi et al. 2011). Yang et al. (2012) illustrated the removal of Ag in a WWTP by comparing the total Ag concentration in wastewater influent, ranging from 1.78 to 105 μ g/L, with the Ag concentration in effluent, which ranged between 0.028 and 5.5 μ g/L. The model estimates of Ag in wastewater sludge of 7 – 39 mg Ag/kg further illustrate the potential for sedimentation of AgNP into sludge in a WWTP (Mueller et al. 2008). If biosolids from WWTPs containing AgNP were applied onto agricultural land as a soil amendment, it is estimated that AgNP could be transported into surface waters during heavy rainfall (Howard, 2010). Slow oxidation of AgNP may create a separate pathway for release of silver ion (Ag⁺) into the environment (Kaegi et al. 2011). Dumont et al. (2015) estimated through models a long-term average AgNP concentration in European rivers, lakes and wetlands ranging from 0.002 ng/L to 0.3 ng/L.

Another route of exposure to human is by inhalation and direct ingestion. For example, people may inhale the AgNP by using medical masks incorporating AgNP or other health products containing AgNP that may lead to ingestion of tiny amounts directly into human body. This exposure may lead to possible discharges of AgNP into wastewater treatment plant or environmental waters by human metabolism and excretion (Lamb et al. 2010). Food packaging materials is the largest category of current nanotechnology applications for the food sector. The AgNP incorporated in the food packaging materials appears to be released from the surface and through oxidative dissolution of silver under conditions of high temperature and low pH (Echegoyen, 2013), but the amount released is below the permitted limit of 0.05 mg Ag/kg food under the EU Regulation (EFSA, 2006). The routes by which AgNP may enter the environment are illustrated in Figure 2-4.



Figure 2-4 Routes of release of silver nanoparticles to the environment

2.1.3 AgNP fate in the environment

Silver is a naturally occurring earth metal, often found deposited as a mineral in association with other elements. It may be released into the air and water by natural processes, such as the weathering of rocks, as well as through human activities including processing of ores, cement manufacture and combustion of fossil fuels. Silver is present in aquatic environments in three forms: Ag⁰, ionic Ag and Ag complexes. Ionic Ag can be present in three oxidation states: Ag⁺, Ag²⁺, and Ag³⁺, but Ag⁺ is the most abundant ion present in natural waters, as the latter two

states are unstable in water (Smith et al. 1977). In the environment, ligands for Ag⁺ include sulfide, bicarbonate or sulfate and dissolved and particulate organic matter (WHO, 2002). When AgNPs present in the aquatic matrix, Ag⁺ has tendency to be adsorbed on the AgNPs surface through electrostatic attraction (Liu et al. 2010; Chao et al. 2011). That's because silver nanoparticles are usually coated by stabilizers (citrate acid, PVP, and GA etc.) on the surface and exhibit negative surface charge in environmental matrices (Jin et al. 2010).

The fate of AgNP is determined by several physicochemical processes, which include dissolution, deposition, sedimentation, agglomeration, coating, association, reaction, and decomposition (Weinberg et al. 2011). As was mentioned before, the majority of AgNP entering into wastewater streams tend to accumulate in the solid sludge during centralized treatment (Kiser et al. 2012, Wang et al. 2012), as shown in Figure 2-5. The remaining portion of AgNP are discharged into rivers, lakes, and the ocean, contributing the exposure of aquatic organisms to AgNP (Brar et al. 2010, Nowack and Bucheli 2007). Ag⁺ and AgNP can be naturally transferred between each other through redox and precipitation reactions, depending on the environmental chemistry, including pH, ionic strength, and dissolved organic carbon (DOC) concentration (Lok et al. 2007, Bolan et al. 2011, Kunhikrishnan et al., 2012). According to a recent report on the equilibrium partitioning of AgNP in natural waters, silver (Ag^o) particles tend to be oxidized by dissolved oxygen to form Ag⁺ and silver complexes at ultra-low concentration (Liu et al. 2010). However, Ag⁺ in turn is more likely to be transformed to colloidal silver in the presence of humic acids (Akaighe et al. 2011). Furtado et al. (2014) showed that very little Ag⁺ was present when AgNPs were added to natural lake water, as the majority of Ag was present as complexes with organic material. When exposed to UV light, all silver salts such as silver nitrate, silver sulphate and silver acetate will transform into colloidal material (Laroo, 2013). Moreover, as long as the zeta potential of the surface of AgNP is greater than 20 mV or below -20 mV, AgNP will have sufficient electrostatic repulsion to remain stable in a simple matrix. Jin et al. (2010) reported that a high salt environment and the presence of divalent cations enhances aggregation of silver nanoparticles. With increasing ionic strength, AgNP aggregation tend to increase as well as the dissolution of silver to Ag_(aq), which causes an

increase in toxicity (Chambers, et al. 2013). As the concentration of chloride increases, the AgNP aggregation increase by forming AgCl⁰_(s) bridging of AgNPs. Furthermore, AgNPs dissolution greatly increases with increased chloride concentration, but the dominant aqueous silver species become $AgCl_x^{(x-1)}$ species, which is less toxic to E. coli (Chambers, et al. 2013; Levard, et al. 2013). According to the prediction of AgNP and chloride concentration in environmental waters from available data, it is most likely that the soluble AgCl_x^{(x-1)-} species is dominant over the formation of solid AgCl (Levard, et al. 2013). DOC also has a significant impact on the fate of AgNP, as DOC increases AgNP stability in surface waters (Furtado et al., 2014). AgNP was reported to be highly unstable in ground water, with Ag⁺ precipitating out of the water phase due to low DOC and high ionic strength (Tugulea et al. 2014). Therefore, the presence, stability and transformation of AgNP in environmental aqueous phase are complex and difficult to model and predict. Current models predicting concentrations of AgNP are based on probabilistic substance flow analysis that consider emission scenarios and partitioning parameters (Mueller, et al. 2008; Gottschalk, et al. 2009; Hassellov, et al. 2008). All models pointed out the difficulties to obtain the partitioning parameters because the models require validation through measurement of actual environmental concentrations. The current lack of methods for quantitative measurements of AgNPs and other Ag species is an impediment to the accurate assessment of the risk associated with the presence of AgNP in environmental waters.



Figure 2-5 Concentrations of silver in wastewater influent, effluent and biosolids (Wang et al. 2012)

2.1.4 AgNP toxicity

The antibacterial properties of silver ions are due to suppression of the metabolism of bacteria and inhibition of the transport of substrates across the microbial cell membrane. The main mechanism of Ag⁺ toxicity is that it causes oxidative stress through overproduction of reactive oxygen species (ROS) and results in damage to cellular components including DNA damage, activation of antioxidant enzymes, depletion of antioxidant molecules (e.g., glutathione), binding and disabling of proteins, and damage to the cell membrane, inhibition of replication (Reidy et al. 2013; McShan et al. 2014). When AgNPs come into contact with bacteria, it is hypothesized that Ag⁺ released from nanoparticles kills the bacteria by inhibiting cell growth due to AgNP penetrating the cells. Moreover, silver ion can react with nucleophilic amino acid residues in proteins and causes cell death through denaturing of protein (Dastjerdi and Montazer 2010). All factors indicate that the free silver ion is the most toxic form of the substance. The US EPA has regulated silver's discharge into water system as priority pollutant in 1977 (Luamo 2008). In comparison to other heavy metals, silver can inhibit microbial growth at extremely low concentrations (Braydich-Stolle et al., 2005). Sensitive aquatic organisms and insects, trout and flounder can be killed by exposure to 1-5 ppb of free silver ions (Bryan, et al. 1992; Wood et al. 1994). Therefore, free silver ions play an important role in the antibacterial activity and eukaryotic toxicity of AgNP. The released ionic silver and AgNPs form complexes with thiol groups in biological macromolecules due to strong affinity of silver to sulfur (Liu et al. 2010). By reviewing available data in 290 studies, Notter et al. (2014) concluded that most AgNPs are far less toxic than the inherent toxicity of the dissolved silver. Therefore, it has been hypothesized that the toxicity of silver nanoparticles is mainly due to the generation of the dissolved free silver ions. Even though silver ion concentrations in the environment have not reached toxic level (WHO, 2002), the gradual release of Ag⁺ from AgNPs in the aquatic environment may increase silver ion levels and pose a threat to human health (Lee at al. 2007). The role of free Ag^+ in the toxicity of AgNP to algae was demonstrated by Navarro et al. (2008). Others have reported that during the storage of silver nanoparticles, the toxicity of citrate and PVP capped AgNP increased over time due to slow dissolution to silver ion (Kittler et al. 2010). Another study indicated that toxicity is related to the size of AgNP because the dissolution rate

is more rapid for smaller particles (Heithmar, 2011). The coating of AgNP should also be taken into account for the size-dependent toxicity of AgNP since it was observed that larger AgNPs with PVP coating were more toxic than a smaller size of bare AgNP (Ellegaard-Jensen, et al. 2012).

Despite the evidence that the toxicity of AgNPs is mediated by dissolution to toxic Ag⁺, there appears to be some intrinsic toxicity related to exposure to the nanoparticle itself. For instance, Das et al. (2012) showed that exposure of natural bacteria to AgNPs caused changes to microbial community structure that were different from the community changes observed for bacteria exposed to AgNO₃. The proposed mechanisms for AgNP toxicity include the release of toxic silver ion in the cell by a Trojan-horse type mechanism, or interactions of AgNP with the surface of cells, or penetrating inside the bacterial cell, or interaction with respiratory chain by local proton depletion, resulting in disordering of cell function (Lubick 2008; Navarro et al. 2008; Li et al. 2008; Cao et al. 2011) (Figure 2-6). The mechanisms for (nano) silver toxicity could be loss of DNA replication (Feng et al. 2000, Yang et al. 2009), deactivation of essential proteins (Yamanaka et al. 2005), deactivation of membrane bound enzymes (Sondi and Salopek-Sondi, 2004), and inhibition of a respiratory enzyme (Pal et al. 2007). The main mechanism of AgNPs antimicrobial effect is considered as the damage of bacterial membrane to induce bacteria apoptosis and inhibit newborn DNA synthesis (Joshi et al. 2012; Khan et al. 2011; Bao et al. 2015). Some other factors seem to affect the toxicity of AgNP suspension, because Gao et al. (2009) found no linear relationship between the toxicity of AgNP and the concentration of the particles in the suspension. This can probably be attributed to the different uptake mechanisms for AgNPs and Ag⁺ in the cells. Several studies have indicated that AgNPs themselves can generate ROS and oxidative stress in vitro, as well as Ag ions, which can trigger the cellular antioxidant mechanisms and is considered to be closely related to cytotoxicity of AgNPs (George et al. 2012; Arora et al. 2009; Cheng et al. 2014; Gaiser et al. 2014; Kawata et al. 2009).

The main determinants of the toxicity of nanoparticles include the inherent toxicity of the materials, reactivity, mobility and shape (Bystrzejewska-Piotrowska et al. 2009). The length of silver nanofibers is an important parameter governing the inflammogenicity and toxicity of nanofibers (Wang et al. 2014). The large surface area of nanoparticles results in faster chemical reactions, biological activity and catalytic behaviour. However, these properties also lead to greater bioavailability, mobility and increased toxicity compared to the same unit of mass of larger particles (Hoet et al. 2004, Oberdorster et al. 2005, Oberdorster et al. 2005). Because of its extremely small size, AgNP can easily pass through or destroy the bacterial membrane, causing death of both harmful and beneficial bacteria. AgNP at a 1 mg/L concentration can inhibit autotrophic bacterial growth by 86%, which could influence organic and nutrient removal during wastewater treatment (Choi et al. 2008). In vitro and in vivo toxicity studies indicate that AgNP may have a toxic effect on mammalian (mouse) spermatogonial germline stem cells (Bray-dich-Stolle et al. 2005), zebrafish embryos (Lee et al, 2007; Laban et al. 2010; Yeo and Kang 2008), Daphnia (Lee et al. 2011), E. coli bacteria (Sondi and Salopek-Sondi, 2004), BRL 3A rat liver cells (Hussain et al. 2005), neuroendocrine cell lines (Hussain et al. 2006), rat alveolar macrophage cell lines (Carlson et al. 2008), and rainbow trout (Oncorhynchus mykiss) gill cells (Farkas et al. 2011). The cytotoxicity of AgNPs for hemocytes and gill cells are in the range of 10 to 100 mg Ag/L and 1 to 100 mg Ag/L, respectively (Katsumiti et al. 2015).

Some studies have indicated that DOC has a significant influence on the toxicity of AgNP. Adsorption of DOC on the surface of nanoparticles is likely to form a protective coating, thereby decreasing the deposition and attachment of bacteria on the surface of particles (Choi et al. 2009). AgNP at moderate concentrations (<40 mg/L) have minor effect on anaerobic digestion and methanogenic assemblages in wastewater treatment plants, which is attributed to adsorption of AgNPs by DOC (Yang et al. 2012).



Figure 2-6 Known mechanisms for antibacterial action of AgNPs and released Ag⁺. Grey circles indicate AgNPs and Ag⁺ implies ionic Ag released from AgNPs (Reidy et al. 2013)

2.1.5 Analytical techniques for AgNPs

A variety of analytical methods have been developed for characterization of nanoparticles, including AgNP. Scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM) have been used to characterize AgNP size, sorption, dispersion, aggregation, structure and shape (Klein et al. 2011, Emamifar et al. 2010, 2011), but these microscopy techniques cannot be used for quantification. The current methods for quantification of silver in suspension or solution include inductively coupled plasma atomic emission spectrometry (ICP-AES), inductively coupled plasma mass spectrometry (ICP-MS) and

inductively coupled plasma – optical emission spectrometry (ICP-OES) (Matyjas-Zgondek et al. 2008; Liu et al. 2009; Lin et al. 2011). The instruments used to characterize AgNP or quantify silver, along with their advantages and disadvantages, are summarized in Table 2-1. For all these methods except ICP-MS and ICP-OES, the limit of detection in the ppm range is the main limitation for quantification of silver in natural waters. Additionally, all of these methods quantity total silver and do not differentiate the forms of silver. Therefore, single particle inductively coupled plasma mass spectrometry (spICP-MS) and asymmetric flow field flow fractionation coupled to ICP-MS (AF4-ICP-MS) were developed to analyze AgNP concentration and particle size distribution (Furtado et al. 2014). AF4 was used for analysis of particle size distribution, and when coupled with ICP-MS, offers elemental specificity and sensitivity (Hoque et al. 2012; Poda et al. 2011). AF4-ICP-MS monitors the hydrodynamic size of AgNP and AgNP agglomeration < 0.2 μ m by separating particles as well as quantifies AgNP concentration in ng/L level. spICP-MS measures the particle concentration and mass concentration of AgNP as well as particle size based on mass of Ag (Laborda et al. 2011; Mitrano et al. 2012). Both of analytical methods are versatile tools for monitoring the AgNP transformation. However, spICP-MS is limited to analyze particle >30nm and AF4-ICP-MS needs to compromise between resolution of particle size separation and recovery (Furtado et al. 2014). Therefore, the techniques currently available for monitoring AgNPs in aquatic matrices all have limitations, including lack of sensitivity and specificity of analysis, or the need for specialized analytical instrumentation.

Techniques	Features	Applicability
SEM/TEM	Visualization and semi-	Can discriminate particle shapes and
	quantitative chemical	types, difficult to determine mass
	analysis	concentration
Dynamic light	Non intrusive, rapid and	Gives average size (hydrodynamic
Scattering (DLS)	accurate measurement of	diameter), but has a bias towards
	particle size	larger particles, not sensitive (ppm)
Ultrafiltration/	Provides elemental size	Incomplete passage of particles
centrifugation	distribution when coupled	through filter lead to results biased
	to chemical analysis, very	to larger size, centrifugation has low
	sensitive (ppb)	resolution for size separation, not
		sensitive (ppm)
UV-visible	Widely used for size	Unsuitable as other species present
	analysis of metal	in the complex matrix
	nanoparticles	
Field flow	High resolution, size	Detection limits in the 10-100 ppm,
Fractionation (FFF)	separation with wide	need sample pre-concentration
	dynamic range	
ICP-MS/ICP-OES	Fully chemical quantitative	Cannot be used for size distribution
	analysis, detection limits in	analysis and do not differentiate
	the range of 1 ppt -1 ppb	metallic particles from ions

Table 2-1 Summary of techniques used for AgNP analysis (adapted from Howard, 2010)

2.2 Passive sampling technique

2.2.1 Theory of passive sampling

The most common approach for water quality monitoring is grab sampling, which involves collection of a sample of surface water at a defined time and location, followed by analysis in the lab using various instruments (Mills et al. 2010). The disadvantage of this approach is that the concentration of analytes in the grab sample is not necessarily representative if large

variations in concentrations can be expected from one sampling time to another, so that episodic pollution events can be missed. Therefore, low frequency, grab sampling strategies are not considered as optimal method for detecting contaminants in surface waters (Bundschuh et al., 2014). Contaminant discharges in domestic wastewater may vary daily and seasonally (Ort et al., 2010), also limiting the effectiveness of grab sampling as a strategy for detecting contaminants discharged from wastewater treatment plants into surface waters.

Increasing the sampling frequency for grab samples or setting up automatic sampling systems over a given period of time is an alternative option to obtain data on representative average concentrations of pollutants (Bundschuh et al., 2014). Another alternative to estimate pollutants concentration in water is measuring concentrations in benthic sediments and subsequently using equilibrium distribution coefficients to estimate levels of target analytes in water (Vrana et al. 2005). This approach is limited by calibration of equilibrium of coefficients between sediments and water, and other organic carbon effects, which are not considered in the equilibrium-partition model. To overcome these issues and obtain an easy approach, passive sampling technologies have been developed over the last 30 years. This method collects analytes *in-situ* without power assistance and provides estimates of time-weighted average (TWA) concentrations of contaminants in water over the period of time that the passive samplers are deployed in the field. Passive sampling has been proved to be a reliable, robust and simple tool to monitor a range of priority and emerging pollutants (Vrana et al., 2005).

Passive samplers are devices in either diffusive or permeative forms that accumulate chemicals of interest through diffusion and partitioning between ambient media and a receiving phase, separated by a diffusion-limiting membrane (Chimuka et al. 2008; Kot-Wasik et al. 2007). Passive sampling devices can be used for either organic compounds or inorganic contaminants. The receiving phase can be a solvent, chemical reagent or a porous adsorbent. The movement force for the passive sampler based on the chemical potential between those two compartments can be diffusion, gravitation, electrostatic or Van der Waals force (Soltani, 2011). The membrane adsorption ability, which is defined as rate limiting step, directly determines the passive sampler working performance. For a single phase sampler, the target compound accumulation is a competition between uptake and offload processes (Darryl, 2010):

$$\frac{dCs}{dt} = K_1 C_w - K_2 C_s$$
(2-1)

where C_s is the concentration in the sampler after time t exposure, C_w is the concentration in the water assuming constant, and K_1 , K_2 are uptake and offload rate constant (time⁻¹), respectively. During the sampler operation period, two main accumulation regimes, either kinetic or equilibrium can be distinguished. The processes of exchange kinetics and contaminants behavior in different stages are illustrated in Figure 2-7. The exchange kinetic follows the first order mathematical model:

$$C_s(t) = C_w \frac{k_1}{k_2} (1 - e^{-k_2 t})$$
 (2-2)

Those samplers that do not reach equilibrium with surrounding water over the deployment time are defined as non-equilibrium samplers, as showed in Figure 2-7A and 2-7B right. Theoretically, these passive samplers work in the kinetic regime and have high capacity to collect contaminants on the receiving phase, which ensures that the pollutants can be enriched continuously throughout the sampling period. When the contaminants pass through the membrane and accumulate in the receiving phase in the early stages of uptake, the elimination process is negligible, and the rate of mass transfer to the receiving phase is assumed to be linearly proportional to time (Vrana et al. 2005), and can be represented as

$$C_{s}(t) = K_{1}C_{w}t$$
 (2-3)

Rearranging equation (2-3) provides the equivalent relationship:

$$M_{s}(t) = C_{w}R_{s}t \qquad (2-4)$$

Where M_s (t) is the mass of analyte accumulated in the receiving phase after exposure time (t), and Rs is sampling rate (volume of water cleared of analyte per unit of exposure time).

When the sampling rate is known, the TWA concentration of contaminants in the water C_w can be calculated based on equation 2-4. Most passive samplers are employed as kinetic or integrative samplers over a deployment duration of 2 weeks to 3 months. The advantages of non-equilibrium samplers are that they sequester pollutants from episodic events which are

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usually not detected by grab sampling, and can be used to monitor variable water concentrations. They can be used to monitor for ultra-trace, toxicologically relevant contaminants over extended periods (Vrana et al. 2005).

Based on the concentration gradient of contaminants between water and the receiving phase, contaminants can diffuse into passive sampling devices until the equilibrium is reached. Upon the achievement of equilibrium, the adsorption and desorption of contaminants takes place equally on/from the receiving phase, and thus, there is no more enrichment of contaminants on the samplers, as shown in Figure 2-7 A and 2-7 B left. The time span to reach equilibrium depends on the capacity of collection phase for the contaminant of interest. At the equilibrium regime, the exposure time is sufficiently long, and thus accumulation is the result of competing uptake and dissipation processes (Hawker, 2010), which reduces from equation 2-2 to:

$$C_{s} = C_{w} \frac{k1}{k2} = C_{w} K$$
(2-5)

Knowledge of the receiving phase-water partition coefficient (K) allows estimates to be made of the dissolved analyte concentration. The basic requirements of equilibrium samplers are that a stable concentration is achieved after a known response time. The sampler capacity is kept well below that of the sampler to avoid depletion during extraction and the device response time needs to be shorter than fluctuations in the environmental medium. Solid-phase microextraction (SPME) (Pawliszyn, 1997; Kraaij et al. 2003; Mayer et al. 2000; Verbruggen et al. 2000), passive diffusion bag samplers (PDBS) (Harte, 2002; Denis et al., 2008) and diffusive multi-layer sampler (DMLS) have all been used as equilibrium samplers in different matrices.


Figure 2-7 (A) Exchange kinetics between the sampler and the water (B) equilibrium (left) and kinetic (right) behaviours of passive samplers (Kot-Wasik et al. 2007).

Whether a passive sampler behaves as a kinetic or equilibrium sampler is highly dependent on the partitioning properties of the target chemicals. Some pollutants have reached equilibrium in the same sampler, while other contaminants are still in non-equilibrium phase (Vrana et al. 2005). Passive samplers in water can be classified as equilibrium and non-equilibrium samplers, based on the partitioning behaviour of the target compound. Environmental factors such as turbulence, temperature and biofouling (Chimuka et al. 2008; Mills et al. 2010) have to be considered when determining rates of accumulation of contaminants on passive samplers. Water turbulence affects the thickness of the unstirred layer of water that forms part of the diffusion limiting barrier near the sampler surface, and consequently impacts the mass transfer of contaminants. The rate-limiting step depends on the type and properties of the membrane, the environmental conditions prevailing during sampling and the properties of contaminants being sampled. Sampling rates in passive samplers are generally faster at greater flow rate and higher temperature (Huckins et al. 2002; Smedes and Booij, 2012). Uptake rates for hydrophobic organic contaminants by semi-permeable membrane devices (SPMDs) were found to increase by a factor of 2 for each 10°C increase in temperature (Huckins et al. 1999; White, 2014). Biofouling is another important factor affecting the sampling rate. Unprotected solid surfaces in contact with water eventually become colonized by microorganisms that ultimately form a biofilm. Biofouling can affect the overall resistance to mass transfer by increasing the barrier thickness and by blocking any water-filled pores in the diffusion limiting membranes. The thickness of biofilm varies from spot to spot on the same membrane. The organisms colonized on the membrane may damage the surface of membrane, if it is made of degradable materials. In describing mass transfer of contaminants into SPMDs colonized with biofilm, Huckins et al. (2006) was of the opinion that biofilm behaves like an immobilised water layer with a resistance to uptake of contaminants that is independent of their hydrophobicity. Reductions of 20 -70% in uptake rates of polyaromatic hydrocarbons (PAHs) were reported for SPMDs colonized with biofilm (Huckins et al., 2006). To reduce the impact of biofouling, it is essential to select a suitable membrane such as polyethersulphone or solvent-filled membrane, or to cover the device with protective screen such as copper or bronze mesh (Alvarez et al. 2005).

Solid-phase sorbents with high adsorptive capacity are highly recommended for use in passive samplers to provide infinite sinks for contaminants. For this project, multiwall carbon nanotubes were selected as a potential adsorbent. Due to the low concentration of AgNP expected in natural waters, the uptake capacity of AgNP was calculated based on the non-equilibrium regime. Since Ag is a heavy metal, only passive sampling devices for inorganic species will be considered in the literature review on passive sampling devices (Table 2-2).

Samplers	Analytes	Deployment period	Advantages	Drawbacks	Sample preparation for chemical analysis
Chemcatcher	Cd, Cu, Ni, Pb, Zn	14 days – 1 month	Selectivity of the sampler can be adjusted using appropriate combination of membrane and Empore disks, and calibration data available for many chemicals		Acid extraction
Diffusion gradients in thin films (DGT)	55 metallic elements including the heavy metals, phosphorous, sulphide and ⁹⁹ T _c	1 week	Versatile, well documented	Complicated preparation of device	Acid extraction
Passive integrative mercury sampler (PIMS)	Neutral Hg species	Weeks - months	Membrane characteristics may be altered for control of sampling rates	Further development necessary for aquatic conditions	Direct analysis of the receiving phase
Permeation liquid membrane (PLM)	Cu, Pb	Hours	Selectivity of the sampler can be adjusted using appropriate combination of carrier media and receiving phase	Complicated preparation of device	Solvent extraction
Supported liquid membrane (SLM)	Doubly charged cations	Days	Versatile, Selectivity of the sampler can be adjusted		Direct analysis, can be coupled on-line for real time monitoring
Stabilized liquid membrane device (SLMD)	Divalent metal ions	Days - weeks		Early development stage	Acid extraction

Table 2-2 Overview of passive sampling devices for inorganic contaminants (Vrana et al. 2005)

2.2.2 Passive sampling of metal ions

As summarized in Table 2-2, the diffusive gradient in thin-films (DGT) sampler initially designed by Davison and co-workers in 1991 has been widely used for *in situ* estimates of TWA concentrations of dissolved metal ions and labile metal complexes, representing bioavailable metals concentration (Davison and Zhang, 1994; Wagner, 2004). It comprises of a resin gel incorporating a binding agent, a hydrated acrylamide diffusive gel creating a diffusion layer of well-defined thickness, and a 0.45 µm porous filter membrane, which are enclosed in a pistonlike plastic casting (Figure 2-8). The plastic casting consists of a base and a cap, which prevent water from entering the device when pressed together except through a 20 mm diameter opening in the cap. The first resin gel utilised ion-exchange resin as the receiving phase, but later, Zhang et al. (1994) demonstrated the utility of a high affinity chelating resin (i.e. Chelex-100) impregnated in a polyacrylamide hydrogel. Ions have to diffuse through the filter and diffusive layer to reach the resin layer. The membrane filter excludes the particulate matter and the diffusive layer builds a constant concentration gradient that eliminates the variations from flow and forms the basis of measuring metal concentration in solution quantitatively without separate calibration (Zhang and Davison, 1995). The maximum capacity of the binding gel depends on the amount of Chelex-100 resin used and can be determined based on the capacity of Chelex-100 resin, which is known to be 0.4 meq/mL.

DGT measures labile metal species *in situ*, including free metal ions and labile metal complexes by binding them on a resin gel, referred as "DGT-labile" metals (Leermakers et al., 2005). Free metal ions can easily diffuse into DGT device where they are bound and immobilized in the resin layer (Zhang and Davison, 1994). Although the filter membrane is able to eliminate the large particles entering the DGT device, labile metal complexes and particles less than 0.45 µm can still pass through the membrane and diffuse into the diffusive layer. Since the pore size of the open pore diffusive gel is in the range of 2-5 nm, only the labile metal complexes and particles smaller than 2 nm are able to diffuse sufficiently rapidly to be measured, whereas particles up to 5-6 nm diameter might be measured with reduced sensitivity (Davison and Zhang, 2012). The restricted pore gels allow much reduced quantities of particles and metals complexes associated with large organic ligands or DOC to be in contact with the resin (Allan et al., 2007). In order to prevent nanoparticles or colloids <2 nm in size from diffusing into the binding gel, a 1 KDa dialysis membrane can be placed in front of the diffusive gel layer (Pouran et al. 2014; Sekine et al., 2015). The detection of labile complexes depends on the stability and affinity to the binding agent. Less stable complexes undergo rapid dissociation during the time taken to traverse the diffusive layer and ligand exchange reactions during which the metal ions become available to bind with the resin gel. By changing the diffusive layer and binding agent, DGT has high affinity and sensitivity to different inorganic and organic complexed metal species (Zhang and Davison, 1995, 2000, 2001). DGT has been demonstrated to efficiently estimate the concentration and speciation of a range of trace metals (Cu, Pb, Ni, Zn, Cd, Fe and Mn) in surface water or seawater (Zhang and Davison, 1995; Allan et al., 2007; Zhang, 2004; Gueguen et al., 2011). For Ag, DGT has been deployed to detect the bioavailable Ag released from AgNPs in aqueous media (Navarro et al., 2008) and released from sediments spiked with ionic or nano particulate Ag (Dai, 2012). Non-labile Ag and labile Ag species in biosolids were also investigated by DGT devices (Sekine et al., 2014; Donner et al., 2015), but overall, the available literature on Ag analysis by DGT is limited.



Figure 2-8 DGT assembly (Wagner, 2004)

The DGT measures the amount of metal that diffuses into the device over a period of time per unit area. The mass of metal accumulated on the resin gel M (μ g) is calculated by equation 2-6:

$$M = C_e (V_{HNO3} + V_{gel})/f_e$$
(2-6)

Where C_e is the concentration of metals in the HNO₃ elution solution (μ g/L), V_{HNO3} is the volume of the elution solution (L), V_{gel} is the volume of the resin gel (L), typically 0.15 ml (which can be

negligible compared to the volume of the eluent), f_e is the elution factor which is given by the ration of the eluted metal to the total bound metal, typically 0.8.

Using the mass of metal accumulated in the DGT, the TWA concentration C_{DGT} in the bulk solution to which the DGT sampler was exposed can be calculated using the equation:

$$C_{DGT} = M\Delta g/(DtA)$$
(2-7)

Where Δg (cm) is the thickness of the diffusive gel (0.8 mm) plus the thickness of the membrane (0.14 mm), D is the diffusion coefficient of metal in the gel (to be calibrated) (cm²/s), t is the exposure time (s) and A is exposure area (cm²) (A = 3.14 cm²).

Like other passive samplers, DGT measurements can also be affected by temperature, flow rate, pH and ionic strength. As the diffusion coefficient is proportionally related to the temperature, the mass uptake rate is directly impacted by temperature. Low flow rate maintains the formation of a diffusive boundary layer (DBL) between the solution and the solid surface of the DGT sampler and increases the thickness of the diffusion layer, thereby interfering with the mass transfer (Gimpel et al., 2001). As long as the flow rate is greater than 0.02 m/s, the mass of metal measured by DGT is virtually independent of flow rate (Gimpel et al., 2001). Extreme pH conditions are not suitable for the metal sampling by DGT as the gel is not stable above pH 11 and competition occurs between metals and hydrogen ions for the binding agent below pH 2. Optimal conditions depend on the nature of the target metals. For example, Cd can be measured down to pH 4.5, while Cu is able to bind with resin down to pH 2 (Bio-Rad laboratories, 2000). DGT measurement is not accurate in very dilute solutions with ionic strength (i.e. Σ [Mg²⁺, Na⁺, K⁺, Ca²]) less than 0.2 mmol/L (Alfaro-De la Torre et al. 2000). This behaviour is thought to be caused by interference due to the counter-diffusion of Na⁺ across the diffusive layer. Peters et al. (2003) suggested that this unreliable performance is due to the ability of the diffusive gel to competitively bind cations with a low affinity for metal ions, and thus the binding of metal ions increases when there are insufficient excess cations present in the solution to saturate the binding sites.

DGT can be widely used for most of metallic elements measurement, whereas others introduced in Table 2-2 are mainly used for trace metals speciation measurement such as Cu, Pb, Zn, and Cd (Buffle et al. 2008; Allan et al. 2007). Among these samplers, Chemcatcher was studied intensively on trace metals adsorption by a few researchers (Knutsson, 2013; Allan et al. 2007; Allan et al. 2008; Petersen et al. 2015) and provided evidence of these trace metals presence in environment.

2.2.3 Carbon nanotubes (CNTs) used as adsorbent

Recently, carbon nanotubes (CNTs) have attracted great attention due to their special morphologies. Carbon nanotubes as one-dimensional materials have unique structural, electronic, optoelectronic, semiconductor, mechanical, chemical and physical properties, leading to applications in electronics, biomedical, aerospace and biosensor sectors, and for wastewater treatment (Khare and Bose, 2005; Park et al., 2002; Haddon, 2002; Rao et al., 2007; Zhao et al., 2011). CNTs could be visualized as a sheet of graphite that has been wrapped into a tube. Presently, the three main synthesis methods developed are arc-discharge, laser ablation, and chemical vapor deposition (CVD) (Cassell et al., 1999). Two types of CNTs are available in the market: (1) single-walled CNTs (SWCNTs) and (2) multi-walled CNTs (MWCNTs), which can grow on different support materials (e.g. glass fiber, silica gel, mullite or stainless steel) (Park et al., 2011; Yu et al., 2010; Tofighy and Mohammadi, 2015). The sidewalls of CNTs are not reactive, but the fullerene-like tips in the end of the tubes are more reactive, which causes the attachment of chemical groups on them (Zhang et al., 2011). Consequently, oxidation processes facilitate their dispersivity and create a great number of oxygen-containing functional groups on the surface of the CNTs (Shim et al., 2001). Bare CNTs can be easily functionalized by redox and noncovalent interaction methods (Rao et al., 2007; de la Cruz et al., 2012; Jiang and Gao, 2003; Wang, et al., 2006; Shi et al., 2011).

As mentioned before, the uptake capacity of passive samplers depends mostly on the adsorption rate of adsorbent in the receiving phase. Because the concentration of AgNPs in the environment is predicted to be lower than 20 μ g/L (Burkhardt et. al. 2010), choosing a highly

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efficient adsorbent becomes a great challenge. In the past few years, functionalized carbon nanotubes (CNTs) have been identified as a superior adsorbent, and have been widely used in removal of heavy metals and their salts from aqueous solutions, including cadmium, lead, nickel, zinc, chromium, aluminum, iron (III), manganese(II), and copper (II), as well as of organic compounds like dioxin, bisphenol A, naphthalene (NAP), atrazine, polycyclic aromatic organic compounds (PAH), 4-n-nonylphenol, phenanthrene, 1,2-dichlorobenzene, halogenated aliphatic compounds and 4-tertoctylphenol in environmental water samples (Pan et al. 2004; Long et al. 2001, Davis et al. 1998; Li et al. 2002; Cai et al. 2003; Li et al. 2005; Rao et al. 2007; Lu et al. 2006; Di et al. 2006; Cho et al. 2008; Gotovac et al. 2007; Peng et al. 2003; Yan et al. 2008; Yang et al. 2006, Ozcan, et al. 2010; Stafiej and Pyrzynska, 2007; Soylak and Ercan, 2009; Ghaedi et al., 2013; Yu et al., 2010; Apul et al., 2015; Wang et al., 2015). The CNT sorption mechanisms are governed by the surface features, ion exchange process and electrochemical potential (Gao et al, 2009). Normally chemical interaction and electrostatic attraction are main mechanisms occurring between the metal ions and the surface functional groups of CNTs. In multicomponent sorption, redox reactions likely occur, not only on the surface of adsorbents, but among the different adsorbates (Wang et al., 2005; Lu et al., 2006; Lu and Liu, 2006). Some literature indicates that CNTs oxidized by nitric acid has a great ability to adsorb metallic cation (Ag⁺ and Zn²⁺), which is attributed to the oxygen-containing surface functionalized groups leading to the isoelectric point (IEP) of CNTs shifting to the lower pH values and resulting negative zeta potential (Howard, 2010; Ding et al. 2007). Because of electrostatic force, negatively charged surfaces attract positively charge cations at relative high pH value. Especially in the pH range 3-7, the adsorption of Ag⁺ sharply increase to 100% Ag⁺ adsorption, with this increase due to less H⁺ competition at the sorption site of the CNTs (Ding et al. 2007). At low pH, the sorption is mainly driven by ion exchange by exchanging protons in carboxylic groups of CNTs with the metal ions in the aqueous phase. After sorption of metal ion on the CNTs, the solution pH decreases because H⁺ are released from the CNTs surface, as illustrated in Figure 2-9 (Rao et al. 2007).



Figure 2-9 Schematic of the main mechanisms for the sorption of divalent metal ions onto the surface of CNTs (Rao et al. 2007)

Generally, sorption of metal ions increases with time until equilibrium is reached between the bulk solution and the surface of the adsorbent. At initial stages, sorption takes place rapidly and gradually slows when reaching the equilibrium stage. There are a few factors impacting the adsorption capability, which are temperature, ionic strength, solution pH, and competitive sorption of other metal ions. The sorption is expected to increase with a rise in temperature due to an increase in the diffusion rate of metal ions and nanoparticles across the external boundary layer and within the pores of CNTs due to reduction of solution viscosity. Ionic strength, as a general solution property, has negative effect on sorption on CNTs by affecting the affinity between the solute and the aqueous phase (*Li et al., 2003). Lu and Chiu (2006) observed that Zn²⁺ sorption capacity was reduced with an increase of solution ionic strength. This decrease in sorption of metal ions by CNTs could be attributed to the increase in activity coefficients of metal ions, which retards their transfer to CNTs surface sites. However, the ionic strength effect became small when >0.05 mol/L NaClO₄ was present in the solution. As previously discussed, solution pH has a significant impact on the surface charge of CNTs and the degree of ionization and speciation of the sorbates (Chen and Wang, 2006; ^{*}Li et al., 2003; Li et al., 2002; Savio et al, 2011; Zhu et al., 2007). When the analyte of interest coexists with metal ions, competitive sorption will occur and decrease the sorption rate of the target analyte due to a decrease availability of sorption sites on the CNTs surface. It was observed that the

predominant cations and anions in natural water had a minor influence on the adsorption of Ag⁺ on CNTs (Ding et al., 2006).

Functional groups of CNTs play a dominant factor in sorption on CNTs. Several methods have been suggested to functionalize CNTs surface, including covalent and non-covalent methods (Pal et al. 2014). Non-covalent functionalization is the physical adsorption of surfactants or polymers onto CNT walls (Forati-Nezhad et al., 2015; Hirsch, 2002). The covalent ligands decrease the Van der Waals forces between the CNTs, which causes changes of the surface characteristics. A large number of articles have reported the superior adsorptive capability of CNTs after modification caused by exposure to acids, alkali or surfactants. The surface modification of CNTs changes the surface charge and properties of CNTs. Acid or alkali treated CNTs containing carboxyl functional groups can effectively adsorb heavy metals (Fe, Mn, Pb and Cu) salts and precious metal ions including Ag and Au (Ding, et al. 2007; Ozcan et al. 2010; Liang et al., 2008; Zhang et al., 2011). It was reported that CNTs were functionalized by poly (diallyldimethy-lammoniumchloride) (PDDA) (Shi et al. 2011) or N, N-dimethylformamide (DMF) (Xin and Li, 2011) via noncovalent route to form the positive surface charge of CNTs so that the negative surface charged AgNP can be attracted on the CNTs surface through electrostatic interaction (Figure 2-10). It has demonstrated that the carboxyl and carbonyl functional groups of CNTs are capable of reducing adsorbed Ag⁺ into zero valence silver nanoparticles on the external surface of CNTs (Wang et al., 2012; Song et al., 2011). When CNTs were treated with NH_3 gas, the zeta potential of CNTs with NH_2 functional group increased to a positive value and polyethyleneamine (PEI) coated CNTs reached more positive zeta potential due to the presence of cations (Jiang and Gao, 2003).





Most applications of carbon nanotubes as adsorbents are related to their use for varied applications, including electronics, bactericides, and adsorption of inorganic and organic compounds (Prodana et al. 2011; Goscianska et al., 2014; Tsai and Huang, 2008; Pal et al., 2014; Forati-Nezhad et al., 2015; Zhang et al., 2011; Park et al., 2011). There are no reports on the use of CNTs as an absorbent for the quantification of silver species in water. However, considering that previous studies indicated that CNTs can be used for the extraction of lead and nickel with a possibility for regeneration (Savioa et al. 2011; Wang et al. 2007), and that CNTs can be decorated with AgNP to increase the electrical conductivity of electronics components, we hypothesized that CNTs have the potential to act as an adsorbent in passive samplers for the quantification of AgNP in natural waters.

3 Objective

The overall objective of this PhD project was to develop a passive sampler for the determination of AgNP concentrations in natural waters and in wastewater. To achieve this objective, sub-objectives were defined as follows:

- 1. To identify the optimal surface functionalities of CNTs and the best support material to maximize the adsorptive properties of CNTs for AgNP in terms of efficiency of adsorption;
- 2. To determine the sampling rates of the developed CNT sampler for AgNP capped with citrate and evaluate the effects of water characteristics (temperature, pH, organic load, ionic strength) on the sampling rates;
- 3. To validate the use of the designed Carbon Nanotube Integrative Samplers (CNIS), for quantifying CNIS-labile Ag under environmental conditions;
- 4. To perform an *in situ* assessment using the calibrated CNIS and DGT samplers to quantify CNIS-labile Ag and DGT-labile Ag in surface waters and wastewater.

The following sections describe the approach used to meet these objectives.

4 Materials and Methods

The most significant part of this thesis work consisted in the design of the passive sampler and the validation of the technology under laboratory and field conditions. The following sections described the materials, analytical protocols and experimental methods used to evaluate diverse CNTs, either available commercially or synthesized at McGill, different surface functionalities, and various materials required to assemble the CNIS. These sections also describe the sites selected for the proof of concept and environmental assessment.

4.1 Chemicals and reagents

Reverse osmosis (RO) water made in the lab and trace-metal grade 67- 70% nitric acid (HNO₃) purchased from Fisher Scientific (Toronto, ON, Canada) was used throughout the experiments. PlasmaCAL 1000 µg/mL silver standards (AgNO₃ in 4% HNO₃, SCP Science Baie d'Urfe, QC, Canada) was used for calibration of the ICP-OES instrument. Dissolved Ag or free Ag ion (Ag⁺) solutions were prepared directly from standard stock solution of AgNO₃ by diluting appropriate amounts of silver nitrate standard in RO water or from 0.65 g/L silver acetate stock solution by mixing silver acetate powder (Sigma-Aldrich, Oakville, ON, Canada) in RO water. The solutions were stored in amber glass bottles at 4°C. Commercially available DGT passive samplers were purchased from (DGT research, UK). 10 nm and 50 nm of citrate (cit-AgNP) and PVP capped AgNP (PVP-AgNP) obtained from NanoComposix, San Diego, USA and polyacrylate (PA) capped AgNP (PA-AgNP) purchased from Sciventions, Toronto, Canada were used for optimization and calibration experiments.

4.2 Analytical methods

The expected concentrations of AgNP in the aquatic environment were estimated to be lower than 0.08 ppb (Mueller et al. 2008; Gottschalk et al. 2009). The methods described below are based on the use of ICP-OES for which limits of detection have been determined to be 0.5 ppb. Ion selective electrodes (ISE) were initially used to determine dissolved Ag concentrations in AgNP suspension. However, due to the high limits of detection (10 ppb) and instability of the ISE, this analytical method was rejected for this study (see Appendix 1). UV-visible spectrophotometry as a semi-quantification method was tested under diverse concentrations of AgNP in suspension and Ag⁺ in solution, but was rejected because of poor sensitivity (see Appendix 2). In order to reach lower detection limits, it was necessary to pre-concentrate the samples. Centrifugal ultra-filtration (Hadioui et al. 2013) was a pre-concentration method used in this project, as described below. After AgNP or Ag⁺ were adsorbed on the CNTs surface, Scanning Electron Microscope (SEM) with an Hitachi S-4700 FE-SEM, coupled with Energy Dispersive X-ray Spectroscopy (EDX) (Oxford 7200) and X-ray photonelectron spectrometry (XPS) (K-Alpha, Thermo Scientific) were conducted to characterize the surface of the CNTs (see Appendix 3).

4.2.1 Quantification of total silver

ICP-OES (iCAP 6000 Series, Thermo Scientific) was used to determine the concentration of total Ag. The optimized operating parameters for the instrument are listed in Table 4-1. The calibration of the instrument was done using multiple standard silver solutions prepared with 1% (v/v) nitric acid and PlasmaCAL silver standard at 1 ppb, 10 ppb, 50 ppb, and 500 ppb and a blank (1% HNO₃ without silver).

ICP-OES working conditions					
RF power	1150 w				
Pump rate	50 rpm				
Auxiliary gas flow	0.5 L/m				
Nebulizer gas flow	0.5 L/m				
Coolant gas flow	12 L/m				
Purge gas flow	Normal				
Wash between samples	30 s				

Table 4-1 Optimized ICP-OES conditions for analysis of Ag

Sample preparation

Prior to injection on the ICP-OES, 100 µl of 70% nitric acid was added to a 5-ml sample placed in a plastic Digitube. The tube was then capped and placed in the digestion system (Digi Prep Jr digestion system, SCP Science, Baie-D'urfe, QC) and heated to approximately 95°C for 1 hour. When extract silver from DGT resins and CNTs, the temperature is higher than 95°C and the glass Digitube rather than plastic Digitube was chosen to avoid loss of Ag during acid digestion. The digested solutions, referred to as acid-digested samples, were then allowed to cool to room temperature prior to ICP-OES analysis.

This optimized nitric acid digestion was determined by testing the effect of nitric acid digestion on ICP-OES measurements of three types of 10 nm AgNP; AgNP capped with citrate or PVP (NanoComposix, San Diego, USA) and AgNP capped with polyacrylate (PA) (Sciventions, Toontor, Canada). 5 mL aliquots of AgNP stock suspension were diluted to 500 ppb. Some aliquots were not subjected to any treatment, referred to as non-digested samples, while 100 μ l of 70% (v/v) HNO₃ (Fisher, CA) was added to others aliquots, referred to as HNO₃ treated samples and another group of aliquots were treated with the same amount of nitric acid and then heated at 80°C for 60 minutes, and cooled down to room temperature, referred to as acid digested samples. The results obtained are presented in Appendix Table A.5. Based on these results, all three sample preparation approaches were comparable for cit-AgNP and PVP-AgNP suspension, but the acid treatment worked better for the PA-AgNP and this approach provided more consistent results from one run to another. It was thus decided to perform the acid digestion for all samples collected.

4.2.2 Quantification of dissolved silver

Multiple methods of quantification of Ag⁺ from AgNP release were reported by Hadioui et al. (2013). Centrifugal ultrafiltration was selected as a pre-concentration method for Ag⁺ in this project due to limitations on sample volume, particle size, sample concentration, and instrument availability. The centrifugation procedure conducted in this project was developed based on the method reported in Hadioui et al. (2013). The method was optimized for the quantification of dissolved silver in presence of 50 nm AgNP, capped with either citrate or PVP.

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The optimized method to quantify dissolved Ag was based on the use of ultrafiltration using Microsep Advance Centrifugal devices with 3 kDa (1 nm) average pore diameter (Pall Science, Quebec, Canada). 4 mL of 500 ppb AgNP stock suspension (or sample) was added into the filter vial, centrifuged in the Sorvall Legend X1R instrument (ThermoFisher Scientific, MA, USA) at 4000 g for 30-min centrifugation cycle and for 4 consecutive cycles. The centrifugal force and time were optimized to reduce the amount of retentate above the membrane in the tube to 50 μ L. As dissolved Ag needs to equilibrate with ultrafiltration membrane, the first three cycles of centrifugation are regarded as membrane equilibration steps. The final filtrate was then digested and analyzed by ICP-OES after centrifugation.

In order to get the optimal working conditions, a few tests on pre-conditioning and the duration of the centrifugation step were conducted. Silver nitrate solutions were centrifuged without pre-treatment and it was found that 50% of the original Ag⁺ concentration was lost in the membrane after 4 cycles of centrifugation. Therefore, at the beginning, 0.1 M of copper nitrate was chosen as pre-conditioning solution (Cornelis et al., 2010) to equilibrate with the membrane. However, as discussed by Cornelis et al. (2010), membrane pre-treated by Cu(NO₃)₂ did not allow significant amount of Ag⁺ to pass through the ultrafiltration membrane, which is proved by same percentage (50%) of Ag⁺ losses in untreated ultrafiltration tubes using the same Ag⁺ solution. In addition, membrane clogging was observed during the ultrafiltration, so that there was no solution passing through the membrane. Therefore, using the sample solution itself to equilibrate the membrane was suggested by Hadioui et al. (2013). Samples were centrifuged in four cycles for 30 minutes per cycle to establish an equilibrium on ultrafiltration membrane. Suspensions of 500 ppb of 50 nm cit-AgNP and PVP-AgNP prepared from stock suspensions following a standard procedure showed Ag⁺ concentration gradually increase in PVP-AgNP after 4 cycles of centrifugation, as presented in Appendix Figure A.3. Ag⁺ concentration in cit-AgNP had insignificant change within 4 cycles' centrifugation due to extreme low level of Ag⁺ existing in cit-AgNP. PVP-AgNP contained 18.3% ± 4.4% of dissolved Ag and cit-AgNP comprised negligible Ag^+ in the suspension (Appendix Figure A.11).

4.2.3 Analysis of water matrix characteristics (DOC, pH and conductivity)

Prior to analysis, all samples of natural waters collected in the field were filtered through medium flow rate P6 filter paper with 1 μm porosity (Fisher Scientific, Toronto, ON, Canada) to eliminate large particles. Then 20 mL of each water sample placed in a small beaker were directly analyzed for pH value by pH/ISE meter (Orion Dual Star, Thermo Scientific, Canada) without any further preparation. A 10 mL aliquot of the water sample was placed in a vial and acidified with 4% (v/v) nitric acid to pH below 2 prior to DOC analysis using a total organic carbon analyzer (TOC-V CPH, Shimadzu Corp., Japan). The TOC-V detection limit is 4 μg/L, which is far below the DOC concentrations in the tested field water samples. In general, the measurement of conductivity is regarded as a rapid and inexpensive way to determine the ionic strength of a solution (Radiometer Analytical Resource Center, 2004). Therefore, around 25 mL of water was transfered into a small beaker without any preparation for conductivity measurements using a Portable DiST[®] Waterproof EC/TDS/Temperature Tester (Hanna Instruments, Woonsocket, Rhode Island, USA). Prior to measurement of conductivity, the conductivity meter was calibrated using a conductivity calibration solution purchased from Hanna Instruments (Laval, QC, Canada).

4.3 Passive sampler assembly

4.3.1 CNIS lab testing assembly

Different designs and configurations were tested in the development of the Carbon Nanotube Integrative Sampler (CNIS). Multi-wall CNTs (MWCNTs) with different functionalities (COOH or NH₂), deposited on carbon fibres, grown on mesh or in powder form, were considered as potential adsorbent. Carboxyl-functionalized (COOH-CNT) and bare MWCNT deposited on carbon fibre veil were purchased from Nanolab, MA, USA. Carboxyl functionalized (COOH-CNT-SS) and bare MWCNT grown on stainless steel 316 (CNT-SS) were produced in the laboratory of Dr. Sylvain Coulombe at McGill University. Carboxyl (COOH-CNT) and amide functionalized MWCNTs (NH₂-CNT) powder, with diameter 30-50 nm, were purchased from MK Impex Corp., Mississauga, Canada. The CNTs with carbon fibre veil and CNTs grown on stainless steel (CNT-SS) were cut into 3 cm × 3 cm squares and placed between two membranes. Various membranes were tested in order to select one that would allow AgNP to pass through and reach the receiving phase. Polyethersulfone (PES) microporous membranes acting as a semipermeable barrier between the sorbent and surrounding aquatic environment have been successfully applied for Polar Organic Chemical Integrative Samplers (POCIS). Therefore, 1 μ m porous PES membrane squares with 9 cm × 9 cm dimensions (i.e. 1 μ m PES) were obtained from EST Labs (St. Joseph, MO, USA), and 0.8 μ m porous PES membrane disks of 47 mm diameter (i.e. 0.8 μ m PES) were purchased from Pall Life Sciences (Quebec, Canada). These membranes were tested with varied functionalized CNTs for uptake using cit-AgNP in suspension and silver acetate in solution. Cellulose acetate filter membrane is also a wide used membrane employed in passive samplers, such as DGT. Therefore, 0.8 μ m porous cellulose acetate disks of 47 mm diameter were purchased from Pall Life Sciences (Quebec, Canada) for testing with CNTs.

In the case of the CNT powders, 5 mg of the powder were weighed using a Mettler XP26 micro balance (Mettler Toledo, Mississauga, Canada) equipped with an antistatic device and placed between the membrane filters. Around 110 mg to 130 mg of COOH-CNT-SS and 13 mg to 14 mg of COOH-CNT veils were placed between the membrane filters. The CNTs sandwiched between the two membranes were then clipped together using two polyethylene rings (2 cm or 3.7 cm open diameter) that we designed and had fabricated by the McGill Engineering machine shop. Polyethylene was selected to minimize adsorption of AgNP to the rings during the lab experiments performed to calibrate the samplers, which was discussed in section 4.4 and proved in Table A.6. The CNIS assembled for lab testing is illustrated in Figure 4-1.

The CNIS measures all forms of Ag with sizes smaller than the pore size of the membrane (i.e. < 800 nm) including AgNP, colloidal silver, dissolved Ag and Ag complexes. Since AgNPs are defined as manufactured particles of silver with sizes between 1-100 nm, and colloidal silver is defined as natural particles with diameters between 1-200 nm, the Ag sequested by the devices was defined as "CNIS-labile" Ag.



Figure 4-1 Assembled CNIS for lab experiments. Left figure shows all the components of CNIS and assembly orders using a CNT-SS mesh. Right figure is the completely assembled CNIS with the 2 cm opening and 3.7 cm opening.

4.3.2 DGT assembly

As our designed CNIS measures all forms of Ag with a size less than the membrane pore size, including dissolved Ag, DGT devices were used to simultaneously monitor the amount of silver present as dissolved silver and small particles or complexes < 5 nm (defined by the pore size of diffusive gel). The concentration of AgNP and colloidal can then be estimated by the difference between the CNIS-labile and DGT-labile silver. The DGT holders obtained from DGT Research (UK) comprised a piston-like molding with a front cap exposing a defined area of 3.14 cm². A Chelex resin (25 mm in diameter) with the smooth side down was first placed on the piston. A disk of open pore (2-5 nm pore size) diffusive gel of the same diameter was placed over the resin gel. Finally, a 0.45 µm pore size polysulfone (PS) membrane (0.14 mm thickness) purchased from Pall Life Sciences (Quebec, Canada), which was recommended by DGT research for field sampling, was placed on the top of diffusive gel, and the piston cap with a 20 mm diameter circular window was fitted tightly to ensure good contact between all the layers, as illustrated in Figure 4-2. The assembled DGTs were sealed in zip-lock bags and stored in the fridge at 4°C prior to use. For lab experiments, the DGTs were suspended in the experimental tank using steel wires.



Figure 4-2 Assembled DGT for lab experiments and field deployments.

4.4 Sampling rates for CNIS

Preliminary experiments indicated that working at low concentration of AgNP in suspension requires the selection of containers made of materials with limited affinity for AgNP and silver ion. Three containers were tested, constructed of Teflon, heavy duty polyethylene (HDPE) plastic and amber glass. Results presented in Appendix Table A.6 indicated that amber glass bottles and HDPE plastic beakers show slight retention of cit-AgNP (7.5% and 9% of retention, respectively) and HDPE showed negligible adsorption of Ag⁺, while Teflon had a high AgNP adsorption (30% retention). Therefore, a 2 L HDPE plastic beaker was used to perform the lab experiments for the determination of the sampling rates.

According to the theory of passive sampling, a sampling rate (R_s) must be determined in the laboratory. The method used is based on the monitoring of the target analyte in the bulk solution or on the adsorbent as a function of time. Sampling rates were first used to determine the best material to use for the passive sampling device and then used to determine the sampling rates in all the natural waters in which CNIS and DGTs were deployed in this thesis work. For lab experiments, four CNIS (2 cm open diameter or 3.7 cm open diameter) were placed in the 2L HDPE beaker (Fisher Scientific, Toronto, ON, Canada) containing the silver solution or suspension (See Figure 4-3). Constant stirring at 75 rpm was maintained over the duration of the experiment, performed at room temperate (19 - 23°C) except in a few cases where calibration was performed at a lower temperature (4°C) to mimic the deployment conditions. Considering the expected low concentration of silver in natural waters, while taking

into account the limit of detection on the ICP-OES, the initial concentration of the suspension used in the lab experiments were varied from 10 ppb to 200 ppb, depending on the experiments.



Figure 4-3 Schematic of the experimental setup for the sampling rate determination

In order to determine the sampling rate for AgNP and evaluate the potential absorption of dissolved silver on the CNIS, 2L of water was added to HDPE beakers and spiked stock solutions of sliver nitrate (Ag⁺) or cit-AgNP. Prior to the start of the uptake experiment, stirring (75 RPM) was maintained for 1 h to allow the solution to equilibrate, and then an initial concentration was measured. Static, non-renewal experiments were conducted in triplicate with four CNIS suspended by stainless steel wires in each beaker, as well as one blank control Ag⁺ or cit-AgNP solution without CNIS sampler to account for other mechanisms of removal of silver from the solution. The beakers were covered with aluminum foil and sealed with parafilm to avoid exposure of AgNP to light, which might increase dissolution or aggregation. One CNIS sampler was removed from the solution or suspension every 24 h for a total experiment time of 96 hours. A fairly short exposure time was chosen for the sampling rate determination in order to reduce the influence of dissipation, as suggested by Li et al. (2010). Duplicate aliquots of Ag⁺ solution or cit-AgNP suspension (2×5mL) were collected from the solution or suspension to the amount of silver retrieved on the CNIS.

The data obtained from batch experiments were used to calculate the sampling rate by rearranging equation 2-4:

$$R_{s} = \frac{Ms(t)}{Cw t}$$
(4-1)

Where M_s(t) is the mass of Ag accumulated on the CNT after deployment.

When the sampling rate and mass of silver accumulated are known, the TWA concentration of Ag in the bulk will be estimated by equation 4-2.

$$Cw = \frac{Ms(0) - Ms(t)}{Rs t}$$
(4-2)

Where $M_s(0)$ is the mass of Ag retaining on the receiving phase before the exposure.

Blank CNTs without Ag adsorption in both laboratory and fields are extracted to determine $M_s(0)$ for sampling rate calculation.

4.5 Determination of the DGT diffusion coefficient

Similar experiments to the ones described for the determination of the CNIS sampling rates were used to determine the DGT diffusion coefficients (D). Instead of 2 L cit-AgNP, 1 L solutions of silver nitrate were used for DGT exposure. Similarily to CNIS, ion adsorption by DGT can also be affected by temperature, flow rate, pH and ionic strength. Considering the different water conditions where the samplers were deployed, DGT diffusion coefficient calibration were performed in each natural water relevant to this study. The diffusion coefficient (D) was obtained by normalizing Ag⁺ mass accumulation using water concentrations measured, referring to the equation 4-3. The bulk concentration of Ag⁺ was calculated using equation 2-7, as presented in Chapter 2.

$$\frac{M(t) \Delta g}{Cw A} = D t$$
 (4-3)

Where C_w is measured Ag⁺ concentration, M(t) is the mass of Ag⁺ accumulated on the resin over time, and A is the open membrane area (3.14 cm²).

4.6 Statistical analysis

To understand which parameters within the water matrix has a significant impact to CNIS sampling rate and DGT diffusion coefficient, statistical analyses were conducted using XL stat software and Microsoft Excel. A linear regression approach in Excel was used for modeling the relationship between DGT diffusion coefficient and other variables, including DOC, pH and conductivity. Since CNIS sampling rates appear to be affected by multiple water parameters including DOC, pH and ionic strength, multi-variate statistical analysis approaches were used with XL stat software, including nonlinear multiple regression analysis and discriminant function analysis of both diffusion coefficient and sampling rates.

4.7 Extraction of silver from samplers

4.7.1 Extraction of CNTs powder, veil and DGT

According to the EPA acid digestion method 3050b, HNO₃ has a strong ability to recover all types of Ag as well as other heavy metals from solid substrates (Savio et al. 2011; Wang et al. 2007; Benn et al. 2008). CNT powders (5 mg) or CNT veils or DGT resin were extracted in glass Digitubes using 10 mL of 70% (v/v) HNO₃ and heating at 120°C for 120 minutes. The Digitubes were capped by watch glass to prevent samples from drying during the initial heating process. Then the watch glasses were removed and a temperature of 150 °C was maintained to evaporate down the sample to 1 mL. Finally, samples were diluted to 5 ml, filtered using 0.45 μ m polytetrafluoroethylene (PTFE) syringe filter (Fisher Scientific, Toronto, ON, Canada) and placed into 10 mL graduated cylinders to measure the volume. Samples were then transferred to polypropylene test tube (Fisher Scientific, Toronto, ON, Canada) for cooling to room temperature prior to ICP-OES analysis.

Various Ag recoveries from CNTs were evaluated by submerging triplicate CNT powder with amine functionality (NH₂-CNTs) and carboxy-functionalized CNT powder (COOH-CNTs) along with the cellulose membranes together in 40 mL of 10 ppb cit-AgNP suspension in the centrifuge tubes. The centrifuge tubes were capped tightly and shaken in a shaker (Infors AG,

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Switzerland) at 75 rpm for 1 day to ensure that the CNTs had sufficient exposure. Initial and final suspension concentration were recorded and CNTs with membranes were extracted following the procedures described above. The acid digestion procedure provided acceptable extraction efficiencies for both NH₂-CNTs and COOH-CNT powders at 72% (Appendix Table A.7) and 74% (Appendix Table A.8) recovery rates, respectively.

To obtain the recovery factor for Ag^+ extracted from the DGT Chelex resin, known amounts of Ag^+ were spiked onto the resin and allowed to adsorb. Using the extraction procedure described above to recover the Ag^+ from resin, a 77% recovery was obtained (Appendix Table A.9).

4.7.2 Extraction of carboxyl functionalized CNT grown on the stainless steel (COOH-CNT-SS)

No standard methods were available to extract silver from the carboxyl functionalized CNTs grown on stainless steel, so some method development was required. In all cases, CNTs meshes were dried in a desiccator for an hour after exposure to AgNP and then subjected to one of the following recovery approaches: sonication, acid treatment or dry ashing.

For the sonication approach, COOH-CNT-SS were submerged into 50 ml of water and placed in a sonicator for an hour. The aqueous solution was recovered and prepared for ICP-OES analysis, as previously described, to measure the concentration absorbed on the CNTs. The use of sonication in an ultrasonic bath (Branson 2510, Danbury, CT) led to low recoveries (about 6.7% of recovery). SEM analysis also confirmed the presence of residual AgNP on the surface of the CNTs after sonication (Figure 4-4 a). Some losses of CNTs were noted, as observed by the formation of a black residue at the bottom of the vials. This might be expected considering that sonication is used to purify CNTs after synthesis (Rinaldi et al. 2011).

The other approach was based on the use of 4% nitric acid applied in varied amounts and 10 ml concentrated nitric acid. Volumes of 4% nitric acid solution (from 10 μ l to 30 ml) were added to 50 ml of water containing the CNTs in order to obtain pH values in the range of 3.78 to 0.44.

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The solution was then heated at 80 °C for an hour. The use of 4% nitric acid to recover the silver resulted in similar low recoveries, compared to sonication (i.e. 1.5%, 5.6% to 18%, for 10 μ l, 30 μ l and 30 mL, respectively). SEM images (Figure 4-4) showed that 10 μ l of 4 % HNO₃ has similar ability to recover silver with sonication, as indicated by the presence of bright spots on both Figure 4-4a and 4-4b. These bright spots included AgNPs presented in the suspension and Ag crystal or small silver particles transferred from Ag⁺ by electron of defect sites of CNT surface (Maley et al. 2011). Increasing the amount of nitric acid from 10 μ l to 30 μ l of 4% HNO₃ (corresponding to a pH of 3.3) increased the recovery by more than 3 fold. However, a white deposit started to form on the surface of CNTs, as observed by SEM (Figure 4-4 c). When the amount of HNO₃ was further increased to 30 ml (pH 0.44), the CNTs was completely covered by a white deposit of unknown nature (Figure 4-4d), while higher recovery was obtained. The use of 10 ml concentrated nitric acid following the CNTs powder extraction procedure resulted in the highest recovery of COOH-CNT-SS, at 27%. However, this recovery was not satisfactory and was highly variable at 27±27% (Appendix Table A.10). The low efficiency and great variability is probably because large amounts of other elements (Fe, Ni, Cr, etc.) from the stainless steel were dissolved in the solution after reacting with HNO₃ and these elements interfered with the Ag signal in ICP-OES. In addition, inconsistent adsorption and uncontrollable dissipation of AgNPs in the vessels may have contributed to high variability. Therefore, acid digestion was not suitable for CNT-SS extraction.





Figure 4-4 SEM images of CNTs after: a. sonication with water, b. 10 μl of 4% HNO₃ digestion, c. 30 μl of 4% HNO₃ digestion, d. 30 ml of 4% HNO₃ digestion

Due to unreliable results with the previous two methods, a method of dry ashing was developed as a step prior to acid digestion in order to efficiently extract Ag from COOH-CNT-SS. In the extraction efficiency experiment, unlike CNT powders submerging in the cit-AgNP suspension, triplicate COOH-CNT-SS meshes were spiked with 400ng cit-AgNP directly on the surface in order to eliminate the AgNP dissipation in the tubes and produce consistent adsorption for all samplers. Mg(NO₃)₂ (300 µL) obtained from Fisher Scientific (Toronto, ON, Canada) as an ashing aid were spiked on the surface of CNT-SS after adsorption of Ag. The ashing aid is used to settle Ag on the mesh and prevent air and CO₂ flow from removing the Ag. Some research has shown that application of ashing aid and careful manipulation of the ashing temperature can greatly reduce the analytical losses associated with dry ashing (van Raaphorst et al. 1978; Adeloju et al., 1984; Gorsuch, 1959; Gorsuch, 1970; Abson and Lipscomb, 1957). The CNT-SS mesh was dried in the oven at 110°C for 30 min. Then CNT-SS was transferred to a microwave furnace, model MAS 7000 (CEM Corporation, Matthews, NC, USA) at 480°C for 1 hour. The carbon on the CNT-SS reacted with purged air as carbon dioxide and Ag remains on the surface of mesh. After dry ashing, CNT-SS were extracted by 5 mL of 70% HNO₃ at 95°C for 60 minutes. Samples were then filtered using a 0.45 µm pore size of polytetrafluoroethylene (PTFE) syringe filter and allowed to cool to room temperature prior to ICP-OES analysis. Finally,

82% of recovery rate was obtained for CNT-SS (Appendix Table A.4). The discussion related optimal conditions test of dry ashing was presented in Appendix 5.

4.8 Field deployments

4.8.1 Field assembly of CNIS and DGT

In order to validate the use of the samplers for quantification of AgNP in natural waters, the CNIS and DGT were placed in stainless steel cages and deployed at various locations for period deployment periods varying from one week to a few of months. CNIS plastic rings used in the lab were replaced by stainless steel rings with 37 mm open diameter in order to use materials resistant to field conditions. Two different sizes of stainless steel rings with a 58 mm outer diameter (OD) and 65 mm OD were used to fix the CNIS in the holder. To prevent the 5 mg CNTs losses during exposure, a 43 mm diameter rubber ring was placed between one membrane and the stainless steel ring before tightening up the two rings together. For field deployment, a holder for the CNIS was designed with three 60 mm opening diameter holes in two 146 mm diameter stainless steel disks in order to fit in the stainless steel cage. These cages have been widely used for deployments of POCIS passive samplers. Three other smaller holes were cut in both sides of the holder to allow the water to pass through the holder (Figure 4-5 left). A DGT holder was also custom designed consisting of 33 mm diameter holes drilled on one side and six same size holes on another side (Figure 4-5 middle). Triplicate CNIS disks and triplicate DGTs were assembled in the stainless steel holders, and then placed in a stainless steel cage for deployment, as shown in Figure 4-5 (right photo).





Figure 4-5 Assembly for field CNIS and DGT samplers in the holders and placement in the cage (right photo).

4.8.2 Sampler storage and transport

After retrieval, CNIS and DGT were placed in aluminum foil and sealed in zip-lock bags. The samplers were stored in a freezer. In the laboratory, CNIS and DGT were thawed and the samplers were rinsed lightly with RO water to remove biofouling material. The samplers were extracted as described previously and the extracts were stored in the fridge prior to analysis. CNTs and membranes or Chelex resins of DGT were placed in the glass Digitubes (SCP Science, Baie d'Urfe, QC, Canada) for extraction.

4.8.3 Deployment sites

Lake dosed with AgNP

The validation of the passive sampler for the quantification of AgNP in natural waters was performed during a whole lake addition study conducted by a research team at Trent University at the Experimental Lakes Area (ELA), ON, Canada. Lake 222 (49.694807, -93.723196) was selected for this study. This is a small lake containing ~600,000,000 L of lake water and with a maximum depth of 5.8 meters (Figure 4-6). 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 (30-80 nm), purchased as a powder from NanoAmor (TX, USA). The powder was suspended in the lake water using a rotor-stator dispersion mill (Kady[®] Mill) prior to addition to the lake. Every second day, 12 L of 2.5 g/L PVP-AgNP suspension were added in the Lake 222 with a peristaltic pump set at a delivery rate of 0.5 L per hour. The additions were located 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 total addition of PVP-AgNP was predicted to reach a concentration of AgNP of 15 ppb, if all AgNP remained in suspension and was evenly distributed in the lake.



Figure 4-6 Aerial photograph of Lake 222 of ELA (provided by ELA-IISD).

The NH₂-CNT and COOH-CNT were selected as the adsorbent for the CNIS in this deployment in L222. Five deployment locations were chosen, as indicated in the Figure 4-7. The cages were placed at all sites in the epilimnion at 1 meter depth, except at the center buoy where cages were also deployed in the hypolimnion at 4.5 meters depth. Four deployment periods of 4-6 weeks were used during the study, as described in Table 4-2.



Figure 4-7 Morphometric map of Lake 222 and deployment locations

Location	June 24 - July 28, 2014	July 28 - August 25, 2014	August 25 - October 19, 2014	Oct 19, 2014 - May 9, 2015
D2	\checkmark	\checkmark	\checkmark	
D3	\checkmark	\checkmark	\checkmark	
CB epilimnion	\checkmark	\checkmark	\checkmark	\checkmark
CB hypolimnion	\checkmark	\checkmark	\checkmark	\checkmark
West bay	\checkmark	\checkmark	\checkmark	
Outflow	\checkmark	\checkmark	\checkmark	

Table 4-2 Timelines for CNIS and DGT deployment at the Lake 222 of ELA

The lake temperature was relatively stable in the epilimnion over the periods of deployment, in the range of 16°C to 23°C, from June to August, except for the cage deployed in the hypolimnion (4.5 meters depth), where the temperatures ranged between of 5°C to 7°C. The dissolved organic carbon (DOC) concentration was also monitored and remained fairly constant at 11.2 \pm 1.3 mg/L. Note that water collected from a reference lake, L221 (Figure 4-6) was used

for calibration of CNIS and DGT samplers for the determination of sampling rates in L222. The lakes are adjacent to each other and have very similar water quality parameters.

Wastewater treatment plant and receiving waters

A deployment of the samplers was performed at the Peterborough wastewater treatment plant (WWTP), Ontario, Canada for a period of 7 days starting on September 11th, 2013. A period of 7 days was selected based on the common deployment period of other passive samplers and to avoid biofouling. The WWTP serving Peterborough (42.907625, -71.935055) is a secondary treatment facility with advanced chemical phosphorus removal and UV disinfection. It has a rated capacity of 68,200 m³/day. It is rated as a class IV Sewage Treatment Plant, which is the highest level for such a facility. In order to also evaluate the impact of the discharge on the receiving stream, samplers were also deployed in the Otonabee River, ON (42.906247, -71.934659), upstream and downstream of the wastewater discharge point. The Otonabee River begins at Katchewanooka Lake on the north side of the community of Lakefield in the municipality of Selwyn, and flows south over the Lakefield dams and locks. The length of the river is 55 kilometers, passing through the city of Peterborough to Rice Lake.

Four cages containing DGTs and CNIS using COOH-CNT-SS and NH₂-CNT powder as adsorbent were prepared to monitor the AgNP concentration in the influent, effluent and surface water upstream and downstream of the discharge point of the WWTP, as shown in Figure 4-8.



Figure 4-8 Peterborough WWTP: (1) Raw sewage pumping station. (2) Grit tanks. (3) Screen building. (4) Primary clarifiers. (5) Secondary treatment Plant One. (6) Secondary treatment Plant Two. (7) UV disinfection. Actual deployment locations downstream of discharging which is out of picture ---> flow of water within the plant (<u>https://esemag.com/wastewater/integrated-fixed-film-activated-sludge/</u>)

Lake Ontario nearshore sites

In collaboration with the Ontario Ministry of the Environment and Climate Change (OMOECC), DGT and CNIS samplers were deployed in western Lake Ontario at 6 locations. The sites were selected by OMOECC and are identified in Figure 4-9 as Toronto Harbour (43.639598, -79.379826), Don River (43.688641, -79.362140), Humber Bay near the Lakeview WWTP outfall (43.581355, -79.543140) and Humber Bay (43.616331, -79.476529). These sites were selected as these are known to be impacted by discharges from wastewater treatment plants. Humber River near Old Mill (43.652187, -79.492608) and the effluent of the North Toronto WWTP (43.700067, -79.357022) were also selected as deployment sites for the samplers. CNIS and DGT passive samplers were deployed in the water column at a depth of approximately 2 meters over two periods of approximately one month each, in June-July 2014 and October-November 2014.



Figure 4-9 Deployment locations in western Lake Ontario: (1) Humber Bay near Lakeview WWTP outfall, (2) Humber River near Old Mill, (3) Humber bay Index, (4) North Toronto WWTP effluent, (5) Downstream of North Toronto WWTP on Don River, (6) Toronto Harbour Index.

5 Results and Discussion

5.1 Design of the sampler

5.1.1 Membrane selection

In a passive sampler, the membrane filter plays an important role for the mass transfer, which may be a limiting step and greatly influence the capacity of sampler. Experiments were conducted to select an adequate membrane for the CNIS. The membrane selection criteria were resistance of the material to field conditions and minimal interference for the adsorption of the contaminant of interest, here AgNP, on NH₂-CNT and COOH-CNT.

Up to 8% cit-AgNP losses (initial concentration of 200 ppb) were observed in all controls (Appendix Table A.11, Table A.12). A summary graph was made in C_t/C_{o(t)} versus time including various combinations of membrane, CNT and solution (Figure 5-1). In this graph, Ct is residual AgNP or Ag⁺ concentration in replicates over time and C_o represents initial silver concentration in test solution. C_t/C_0 is referred to relative residual concentration of Ag. When it is close to 1, there is no adsorption of silver because no Ag losses occur in the solution. Lower ratio of Ct/Co showing higher adsorption, is more preferred. When compared to the control (no CNT or membrane), NH₂-CNT and COOH-CNT placed between 1 µm PES membrane did not adsorbed silver within the 4-5 days exposure (Figure 5-1), while NH₂-CNT placed between 0.8 μ m PES membrane led to a slight adsorption of about 1% of Ag (Figure 5-1). Further investigating the NH_2 -CNT with the 1 μ m PES membrane for the adsorption of dissolved silver (initial concentration of 10 ppb) showed that more than 50% of Ag⁺ was adsorbed on the NH₂-CNT while negligible dissipation of Ag⁺ was observed in the control (Figure 5-1). Suspending the 0.8 µm PES membrane alone in a solution of 200 ppb of silver nitrate led to no significant adsorption of silver over 24 hours (results not shown). PES was not ideal membrane of the CNIS design due to preventing AgNP entering into receiving phase of CNIS.



Figure 5-1 Summary graph of relative residual concentration of Ag over time for CNIS using various combinations of membranes, CNT material and silver solutions/suspensions.

The other membrane, 0.8 µm porous cellulose acetate membrane, was tested alone and with NH₂-CNT for the adsorption of cit-AgNP (initial concentration 80 ppb and 10 ppb, respectively). The cellulose membrane exhibited some adsorption of AgNP (29%), while the NH₂-CNT assembled with cellulose acetate membrane displayed a significant adsorption (87%), as shown in Figure 5-2. The membrane adsorption to AgNP was caused by chemical binding formation between cellulose acetate and Ag⁺ or polar molecule citrate which was coated on the AgNP surface (Liu and Bai, 2006; Kim et al., 2009). Based on these results as well as other characteristics of cellulose acetate membrane such as its high modulus, adequate flexural and tensile strength (Aoki, Teramoto, & Nishio, 2007), cellulose acetate membrane was selected for the CNIS assembly. There are also indications in literature of potential benefits of using this material. Cellulose acetate membrane was found that it highly resisted biofouling and mineral fouling because of smoothness of the membrane surface (Vrijenhoek et al., 2001).



Figure 5-2 Cit-AgNP residual concentration in control solution (no CNT and membrane) and in the suspension presenting NH_2 -CNT with 0.8 μ m cellulose acetate membrane and cellulose membrane alone

5.1.2 Selection of CNT materials

Adsorption of silver on CNT veil

Two types of CNTs veil firstly tested for their ability to adsorb dissolved Ag were based on bare CNTs and CNTs with carboxylate functional groups deposited on fiber veils. Prior to use, these veils were washed with RO water and dried in the oven to eliminate any residual material on the surface of the veil. Subsequently, the veils were placed in diluted silver nitrate solutions. Duplicate COOH-CNT veil placed in the solution without the membrane led to highly variable results (Table 5-1). Similar inconsistent results were observed for the bare CNT veils enclosed between two membranes (Table 5-1) while the COOH-CNT enclosed in two membranes led to more reproducible results but lower adsorptive efficiency (Table 5-1). The higher Ag⁺ adsorption of the bare CNT might be explained by the electron of the surface defects of CNT reducing Ag⁺ to Ag nanoparticles depositing on the CNT surface (Maley et al. 2011).
T (h)	COOH- veil dir expose	CNT rectly ed	COOH-CNT veil enclosed between two PES membranes			Bare CNT veil enclosed between two PES membranes						
Replicates	1	2	1	2	3	4	5	1	2	3	4	5
0	227.1	195.0	306.5	314.1	352.8	202.3	209.9	201.9	214.4	231.6	218.5	213.9
3	216.4	67.5										
6		19.5										
24	178.3	0.1	198.3	142.3	234.7	237.5	103.3	218.6	104.1	208.4	94.4	17.3

Table 5-1 Profile of concentration of Ag⁺ (ppb) in solution where CNT veils were deployed

The non-reproducible adsorptions observed on the CNT veil materials that were tested were attributed to: 1) Inconsistent amounts of CNT presenting on the surface of the fibers of the veil; 2) Non-homogeneous distribution of the CNT on the surface of the veil resulting in unequal amounts of sorbent in each run considering that the veil was cut in smaller pieces; 3) Weakly binding of CNT on the veil causing significant losses of CNT during handling; 4) Heterogeneous functionalization of CNT veil weakening the adsorption efficiency. Consequently, bare CNT and COOH-CNT veils were rejected as potential adsorbent in our CNIS and were not further tested for AgNP adsorption.

Adsorption of silver on COOH-CNT-SS

The CNT-SS were plasma-functionalized with covalent groups such as carbonyl (C=O), carboxyl (COOH), and hydroxyl (COH). Thus, these COOH-CNT-SS are heavily polar as opposed to their natural state and quite stable in aqueous solution, with more negative zeta potential around - 40 mV. All the preliminary CNT-SS (not functionalized) or COOH-CNT-SS exposure to Ag⁺ were carried out without a membrane. The direct exposure of CNT-SS and COOH-CNT-SS eliminated the mass transfer limitation, which might be associated with the membrane.

The unfunctionalized CNT-SS exposed to a silver nitrate solution for 24 h indicated a variable adsorption capability of Ag^+ in the range of 38% to 95%. The significant Ag^+ adsorption suggested that the electron of defect sites of CNT surface reduced Ag^+ to Ag^0 crystal or

nanoparticles and deposited on the surface (Maley et al. 2011), which was confirmed by SEM image in Figure 5-3. To avoid functionality formation on the bare CNT, the CNT-SS and COOH-CNT-SS were then tested in a silver acetate solution. CNT-SS resulted in adsorption of 6% to 42% over 24h while COOH-CNT-SS adsorption varied from undetectable to 42% over the first 24h and 3% to 94% over an extended period of exposure of 2 days. These results confirmed assumptions that CNT would adsorb all forms of Ag, including nano scale and dissolved Ag, and demonstrated the need of using DGT passive sampler along with CNIS to account for dissolved silver. However, it is important to point that the two samplers might not have the same adsorption efficiency of dissolved silver and direct comparison of the concentration estimated using the CNIS and DGT is not recommended.



Figure 5-3 SEM image shows Ag presence (white areas) on bare CNT-SS mesh after exposure to AgNO₃

COOH-CNT-SS exposure to AgNP was conducted using PA capped AgNP (PA-AgNP) suspension to evaluate the adsorption efficiency. The adsorption experiments were performed over 5 days but the process reached equilibrium within one day (Figure 5-4a) with a drastic decrease in total silver concentration in the solution (83%) declining almost linearly over the first 24 hours (Figure 5-4a, b). This profile (Figure 5-4a) corresponds to the one commonly observed in adsorption experiments reaching equilibrium (Kot-Wasik et al. 2007). To confirm the Ag presence on the COOH-CNT-SS surface, SEM coupled with EDX were used to analyze the surface of the CNT mesh (Figure 5-5). The white spots observed on the structure on the right SEM image of Figure 5-5 confirmed that silver was adsorbed on the surface of the COOH-CNT-SS. However, these spots are relatively large, up to a few µm in some cases. This is probably caused by the aggregation of AgNPs within the sampler considering that the membrane pore size is 800 nm. Another possibility is that the Ag⁺ contained in PA-AgNP suspension are reduced into Ag⁰ on the surface of the CNT-SS followed by aggregation on the CNT surface when a large amount of Ag⁺ diffuses through the membrane (Maley et al. 2011). The analysis by EDX of the white spots further confirmed the nature of this area as Ag (Figure 5-6a). XPS analyses of sections of the CNTs were also carried out to confirm the nature of the elements present on the CNTs surface. Figure 5-6b shows that silver was present on the CNTs mesh surface. XPS also indicated the presence of iron, which was attributed to the stainless steel mesh from which the CNTs are grown. The presence of the iron did not interfere with the adsorption experiment and no iron ions were detected by ICP-OES in the solution where CNT-SS were suspended. However, iron rust was observed after AgNP exposure.



Figure 5-4 PA-AgNP residual concentration during adsorption experiment and control experiment (no COOH-CNT-SS) for: a) 5 days and b) 24 hours



Figure 5-5 SEM images of COOH-CNT-SS mesh before and after exposure to PA-AgNP



Figure 5-6 EDX and XPS images of COOH-CNT-SS mesh after exposure to PA-AgNP

Adsorption of silver on CNT powder

Since the previously mentioned CNTs did not provide satisfied adsorption efficiency or reproducibility, CNTs powder draw our attention to be tested as CNIS adsorbent. The CNT powder with amine functionality (NH₂-CNT) and carboxyl functionality (COOH-CNT) were selected in this experiment. 5 mg of each CNT powder sandwiched between two cellulose acetate membranes and 2cm open diameter rings was submerged in 20 ppb diluted cit-AgNP suspension with RO water. Both of CNT powders presented consistent adsorption of AgNP (50% loss in solution) (Figure 5-7). Comparing with COOH-CNT-SS of 94% adsorption in 2 days, CNT powders adsorb AgNP gradually and slowly. However, CNTs powder provide more producible

adsorption of AgNP. Based on the adsorption efficiency and consistency, CNTs powder gave promise adsorption and became ideal CNIS adsorbent.



Figure 5-7 Cit-AgNP loss profile in the suspension during adsorption experiment of NH₂-CNT and COOH-CNT powder

5.1.3 AgNP effect on Ag⁺ adsorption by DGT

To validate the DGT adsorption efficiency of Ag⁺ in the presence of cit-AgNP, various experiments were conducted in pure silver nitrate solution, with 1:1 concentration ratio of Ag⁺ and cit-AgNP, 10:1 concentration ratio, and pure cit-AgNP suspension. These experiments were performed with the help of Stephane Liégey (Undergraduate stduent, McGill) who worked on this project with the support of a Summer Undergraduate Research (SURE) Award. Results are presented in Appendix Table A.13. It was noted that the presence of AgNP reduced the adsorption of Ag⁺ by the DGT (20% to 40%). The adsorption reduction was attributed to AgNP binding to the membrane or diffusive gels and preventing the uptake of silver ions. Previous analysis of the cit-AgNP suspension using centrifugal ultrafiltration showed that an insignificant amount of Ag⁺ is released from cit-AgNP. The accumulation of Ag on the DGT resin when exposed to cit-AgNP only is thus associated with the portion of AgNP which is smaller than 5 nm

(diffusive gel pore size limitation of 2-5 nm). Fortunately, negligible AgNP adsorption on the DGT was observed when the DGT was exposed to a cit-AgNP suspension. These results further support the idea of using DGT in tandem with the CNIS.

5.1.4 Determination of CNIS and DGT sampling rates

Sampling rates of cit-AgNP were determined for the adsorbents that provided more reproducible and promising results for deployment under environment conditions investigated in this project. Sampling rates would have to determined for AgNPs coated with other materials considering that Fischer, 2013 mentioned that sampling rate of PVP-AgNP was slightly higher than cit-AgNP in the same water conditions. NH₂-CNT and COOH-CNT powders were verified previously as suitable sorbents, due to the high degree of adsorption of Ag in the lab. Even though data generated using COOH-CNT-SS were not very consistent, the configuration was still taken into account in the field deployment due to its easy manipulation and great adsorption efficiency. The following sections summarize the sampling rate determinations in RO water, as well as in the natural waters and wastewater in which the samplers were field deployed. Similarly, DGTs were calibrated in the various matrices to determine reliable diffusivity coefficients.

Determination of CNIS sampling rate in RO water

Sampling rates for CNIS exposed to cit-AgNP in RO water were determined at room temperature for the samplers constructed using NH2-CNT and COOH-CNT powders. Due to the limited availability and higher cost of COOH-CNT-SS, these were not calibrated in RO water and were solely calibrated in the natural waters where they were later deployed. The sampling rate calculation was based on equation 4-1 using data on the mass of silver accumulated on the CNT surface and AgNP residual concentration in solution/suspension. The mass of Ag accumulated on the CNTs followed a linear uptake for 4 days (Figure 5-8 a, b). This sampling period was carefully chosen to avoid the significant AgNP dissipation onto the labware (Hassellov et al. 2008) and allow the accumulation of a sufficient amount of silver on the CNTs surface to obtain measurable concentrations on the ICP-OES instrument (limit of detection of 0.5 ppb). The detailed sampling rate calculations for the NH₂-CNT sampler are presented in Appendix 4 as a

sample. Using this approach, the NH_2 -CNT and COOH-CNT sampling rates were determined to be 1.8±0.4 mL/day and 3±1.2 mL/day, respectively. These values are not significantly different when considering the standard deviation determined from triplicate data.

Using the accumulated mass of silver and calculated sampling rates, the time weight average (TWA) concentration of CNIS-labile Ag can be estimated and compared with actual concentrations of Ag measured in the solution/suspension. Figure 5-8 c,d summarizes these results for CNIS constructed with the NH₂-CNT and COOH-CNT sorbents. It can be noted that the measured initial Ag concentration, 14.3 μ g/L, is lower than expected nominal concentration of 21.5 μ g/L. This difference might be attributed to the adsorption of AgNP to the surface of the test vessel, as was reported in other studies (Hassellov et al. 2008). The TWA concentration estimated based on the CNTs sampling rate declined gradually over time and matched the concentration profile based on the measured AgNP concentration at each time point. For NH₂-CNT and COOH-CNT, the estimated TWA concentrations of silver were 15 μ g/L and 12 μ g/L, respectively, which corresponds well to the measured Ag concentration of 13 μ g/L and 12 μ g/L, respectively, indicating that the method of calibration gives good results.



Figure 5-8 Mass of cit-AgNP accumulated by a) NH₂-CNT b) COOH-CNT powder as a function of deployment time in RO water. Measured Ag concentrations and estimated TWA concentrations of CNIS-labile Ag for cit-AgNP in suspension for CNIS containing c) NH₂-CNT and d) COOH-CNT

Determination of DGT diffusion coefficient in RO water

A 1 L volume of solution spiked with Ag⁺ in RO water was used in the DGT calibration experiment. The Ag⁺ accumulation in the DGT was as expected linearly correlated to time (Figure 5-9 a). The calculation of the diffusivity coefficient D for Ag⁺ in RO water was then determined by the slope of the regression line, shown in Figure 5-9 a. The estimated Ag⁺ concentrations predicted using the diffusive coefficient calculated using equation 2-7 match the Ag⁺ concentrations measured over time (Figure 5-9 b).



Figure 5-9 The mass of Ag⁺ accumulated onto the Chelex resin in DGTs exposed in RO water, and the estimated TWA concentrations of DGT-labile Ag and measured Ag concentrations in solution.

Determination of CNIS sampling rate in other matrices

Considering that adsorption of silver on the CNT can be affected by characteristics of the water matrix such as pH, ionic strength, and DOC (Li et al. 2003), the CNIS with small rings (2 cm open) were calibrated at room temperature in each of the aquatic matrices where they were deployed. During each deployment, water (16 L) was collected and brought back to the lab for calibration of the samplers. The waters were filtered through medium flow rate P6 filter paper with 1 µm porosity (Fisher Scientific, Toronto, ON, Canada) to eliminate large particle matters, then spiked with known concentration of cit-AgNP (20 ppm) and then used for calibration of the CNIS.

The approach presented in the earlier section on calibration in RO water was applied to each of the other matrices. The various graphs obtained are presented in Appendix 5. A summary of the sampling rates as well as the corresponding estimated TWA concentrations of CNIS-labile Ag and measured Ag concentrations are presented in Table 5-2. The estimated TWA concentration of Ag was calculated from mass of Ag accumulation on CNT and sampling rate according to the equation 4-2. The measured Ag TWA concentration is based on the equation:

$$C_{TWA} = \frac{t1 C1 + t2 C2 + \dots + tn Cn}{t1 + t2 + \dots + tn}$$
(6 - 1)

Where C_i is Ag residual concentration in the solution at each time interval t_i .

The effluent of North Toronto WWTP (NT WWTP), Toronto Harbour surface water and Lake 221 water from ELA were collected for sampling rate calibration (Appendix Figure A.5, A.6, A.7). The water characteristics (pH, DOC and ionic strength) for these aquatic matrices are listed in Appendix Table A.14. All the calibrations presented stable adsorption ($R^2 > 0.9$) and relatively low variability among replicates. As a result, the estimated TWA concentrations of CNIS-labile Ag and measured concentrations of Ag were in good agreement.

Table 5-2 CNIS sampling rates (Rs) determined in different water matrices and with different types of CNTs in the presence of cit-AgNP suspension along with the estimated TWA concentration of CNIS-labile Ag and the measured Ag TWA concentration (E: estimated; M: measured).

								Α	g TWA		. (ppb)	
	Water characteristics			Sam	Sampling rate R₅ (mL/day)		N	H ₂ -	CO	OH-	COOH	I-CNT-
							CI	NT	Cl	١T	S	S
Water matrix	DOC	рH	Conductivity	NH ₂ -	COOH-	COOH-CNT-	Е	М	Е	М	Е	М
	(ppm)	P	(µs/cm)	CNT	CNT	SS						
NT WWTP	5.60	7.72	985	6.7±2.8	8.7±1.8		11	11	7	8		
Toronto Harbour	2.57	8.26	332	5.1±0.1	5.7±1.0		15	15	12	11		
PB WWTP influent				22.4±								
	8.00	7.62	908	8.6		16.6±9.6	5	6			7	7
PB WWTP effluent	4.23	7.84	702	8.7±1.7		14.5±6.5	9	8			5	6
PB WWTP discharging												
Disco	4.20	8.03	182	7.0±0.4		3.9±0.3	14	15			14	16
River												
RO water	0.91	6.15	7	1.8±0.4	3.0±1.2		15	13	12	12		
L221	12.08	6.55	43	1.7±0.5			16	16				

Compared to the sampling rate in RO water, the sampling rates in wastewaters and surface water were much higher (by at least a factor of 2), except for the sampling rates for Lake 221 water. The measured residual concentration of AgNP spiked in the wastewater declined more rapidly than the concentration estimated based on the rate determined using mass accumulated on the sampler. This difference between the accumulation on the CNIS and the rate of disappearance in the water is most likely due to loss of AgNP on the surface of the tank or through sedimentation (Appendix Figure A. 3, A. 4 d, e, f). In fact, the larger deviation between the two values occurred over the first few days of the calibration experiments was caused by slow accumulation of Ag on the surface of CNT at the beginning. After 2 days, the estimated Concentrations did not match the measured concentrations of AgNP at all time points, the estimated TWA concentration closely agreed with the measured TWA concentration. When comparing to COOH-CNT-SS uptake, NH₂-CNT presented higher sampling rate than COOH-CNT-SS, except for effluent. This observation is probably attributed to the non-uniform distribution of CNT on the mesh surface causing no adsorption on some sites.

For both NH₂-CNT and COOH-CNT-SS adsorbents in wastewaters, the Ag uptake rates are in the order of influent > effluent > surface water. Rapid uptake in the influent is attributed to the great presence of hydrophobic DOC and ionic strength, facilitating AgNP agglomeration and decreasing its mobility by displacing its capping agents to increase its irreversible capture on the CNTs membrane (Kanel et al., 2015; Joseph et al., 2011; Gao et al, 2012; lau et al, 2012; Jones and Su, 2012). This can be proved by presence of larger yellowish particles on the membrane surface. Even though AgNP may not pass through the membrane, membrane was digested with CNT together to extract silver so that mass accumulation of Ag increased.

As reported by Gao et al. (2009), the adsorption on CNTs is considered to be mainly driven by electrostatic attraction and chemical interactions. We had initially assumed that the positive surface charge of the NH₂-CNT would be preferable for the adsorption of the negative cit-AgNP on the surface by electrostatic attraction. However, by comparing the COOH-CNT and NH₂-CNT

sampling rate in the three different matrices tested with both types of CNTs, it was observed that the sampling rates were consistently higher for the COOH-CNT-based CNIS. A possible explanation is that the AgNP adsorption is driven by van der Waals forces, which is another non-covalent interaction that facilitates the AgNP adsorption (Rance et al., 2010, Pal et al., 2014). Although van der Waals forces act over short-range and are weak forces, these can play an important role. Larger CNTs diameters and nano particles size can enhance van der Waals force and increase AgNP affinity toward adsorption (Rance et al. 2010), which correspond to the relative large diameter COOH-CNT (30-50 nm) and AgNP particle size (50 nm) used in the present study. Another possible reason is that the functionalization level in COOH-CNT is higher than NH₂-CNT, which causes more COOH functionality available than NH₂ functionality.

To analyze the factors influencing the NH₂-CNT sampling rates determined at room temperature (summarized above in Table 5-2), XL Stat using both a linear regression model and non-linear multiple regression model with effect factor interactions (Appendix Table A.15) were used to identify potential correlations. The linear regression gave a poor fit of the data, where R² was only 0.509 and no significant effects were found, as all P values for variables were larger than 0.05 (Appendix Table A.15). Therefore, a judgement was made that the sampling rate may be related to the variables under a non-linear model. In non-linear model, R_s values gave a perfect fit, which is equal to 1 and there is a strong correlation between R_s and conductivity (0.697). To further verify the significant effect, Discriminant Analysis was performed, as presented in Table 5-3. In the Discriminant Analysis, pH showed significant effect on R_s value where P value was less than 0.05. Because factor 1 which is a combination effect of three variables (pH, DOC and conductivity) displayed a significant effect on R_s, and both pH and conductivity gave a highly positively correlation with factor 1, the pH and conductivity must both interactively affect the sampling rate. This interaction also gave us a good explanation of the poor linear relationship between R_s and the water quality variables.

In the acidic water, negatively charged cit-AgNP can be neutralized by the high concentrations of H⁺, which would result in repulsive interactions between cit-AgNP and the positive charged

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NH₂-CNT surface (Huynh and Chen, 2011). This phenomenon can limit the uptake of AgNP as observed in RO water and in L221 water having low pH and ionic strength. Although alkaline water may then be a preferred condition for AgNP uptake, positive zeta potential of NH₂-CNT gradually decreased to negative value with pH increase, which weakened electrostatic attraction between AgNP and NH₂-CNT (Jiang and Gao, 2003). That might explain the low R_s in Toronto Harbour water, which had the highest pH value.

Comparing uptake in the Peterborough WWTP effluent and in the receiving water suggested that there is an increase in R_s with ionic strength. Increasing ionic strength can cause competition with counter-ions and result in the contraction of the electrical double layer (Pokhrel et al., 2014), which could promote the transport of AgNP through the membrane to the CNT surface. However, strong ionic strength caused larger standard deviation of uptake rate by comparing all NH₂-CNT and COOH-CNT-SS sampling rate. In high ionic strength waters, the standard deviation for estimates of R_s can reach up to 10 mL/day.

As mentioned previously, DOC has a great influence on the uptake of AgNP. When DOC is present, it tends to complex with AgNP, which may promote irreversible binding of these complexes to the porous membrane (Kanel et al., 2015, Pokhrel et al., 2014). That can explain the yellowish precipitate observed on the membrane of CNIS placed in WWTP influent. When the membrane and CNT were digested together, the mass of Ag accumulation increased. Although the L221 water had high levels of DOC, the low pH and ionic strength tended to counteract the DOC influence and was the primary reason for the reduced rate of Ag uptake. The formation of DOC-AgNP complexes can also facilitate sedimentation of AgNP. Due to the limited number of different DOC levels tested, it is difficult to definitively determine the effect of DOC on R_s. However, the results indicated that the sampling rates in different water matrices are highly controlled by a combination of DOC, pH and ionic strength.

Table 5-3 Discriminant Analysis of R_s data relative to the water quality parameters of DOC, pH and conductivity (i.e. ionic strength).

Unidimensional test of equality of the means of the classes						
Variables	P value					
DOC	0.655					
рН	0.001					
conductivity	0.073					
Bartlett's test for eigenvalue significancy						
	Factor 1					
Eigenvalue	54.197					
Bartlett's statistic	14.038					
P value	0.003					
Variables / Factors	correlations					
Variables	Factor 1					
DOC	-0.210					
рН	0.962					
conductivity	0.717					

Determination of DGT diffusion coefficient in other matrices

Since CNIS were calibrated in several aquatic matrices, it was necessary to calibrate DGT in the same matrices, since these passive samplers were deployed together. Aliquots of 3×1 L of each type of water were filtered through 1 µm porous filter paper to eliminate large particles. Due to lack of sufficient volumes of water, DGT calibration at room temperature was conducted only in duplicate. Silver nitrate (5 ppm) was spiked into each water matrix. The calibration procedure was the same approach as the one used for the DGT calibration in RO water. The graphs presenting the results obtained for each water matrix are shown in Appendix 7. A summary of the DGT diffusion coefficients in the various aqueous matrices, as well as the corresponding estimated TWA concentrations of DGT-labile Ag and measured Ag concentrations are presented in Table 5-4.

Table 5-4 Summary of diffusion coefficients and water quality parameters in various water matrices where CNIS were deployed, as well as the estimated TWA concentrations of DGT-labile Ag and measured Ag concentrations.

	Water characteristics			DGT	Ag TWA conc. (ppb)		
	DOC (ppm)	рН	Conductivity (us/cm)	D (cm²/s)	Estimated	Measured	
NT WWTP	5.60	7.72	985	2.1E-06	44	42	
Toronto Harbour	2.57	8.26	332	7.8E-06	11	11	
Peterborough discharging River	4.19	8.03	182	4.5E-06	31	29	
Peterborough Effluent	4.23	7.84	702	3.4E-07	33	34	
Peterborough influent	8.00	7.62	908	3.6E-08	19	23	
RO water	0.91	6.15	7	1.7E-05	28	25	
L221	12.08	6.55	43	4.0E-06	40	38	

The mass of Ag⁺ accumulated on the DGT over time followed a linear trend ($R^2 > 0.9$) in all water matrices (Figure A. 8, A.9, A.10). The diffusion rate was the highest in RO water (1.7×10^{-5} cm²/s). The estimated DGT-labile Ag and measured Ag⁺ concentrations (by direct analysis of the spiked water) closely agreed with each other for Peterborough influent, which was attributed to the slow rate of absorption. In the other types of water, the estimated concentrations of DGT-labile Ag did not correspond to the measured Ag concentrations at the initial time points (Figure A.8 e, f, A.9, A.10 d), which can be explained by a rapid accumulation of Ag⁺ on the DGT initially and slower constant accumulation of Ag⁺ later on. Due to gradual accumulation on the DGT over the remaining days, the estimated DGT-labile Ag and measured Ag concentrations matched well later in the experiment. The TWA concentration of DGT-labile Ag was slightly under-estimated in the influent wastewater due to the complex matrix, but the values were still comparable with values of 19 ppb for the estimated concentration and 23 ppb for the measured concentration. Based on the D values measured for DGTs in different matrices and the water characteristics, a linear regression analysis was conducted using Excel (Table 5-5), yielding a significant linear relationship, as indicated by a high R² of 0.911. The P value for DOC is less than 0.05. Therefore, DOC has a significant effect on DGT diffusion coefficients (Table 5-5). The effect of DOC on the sampling rate might be caused through complexation of Ag⁺ with DOC, preventing it from entering into the Chelex resin. To evaluate the potential interaction effect of the wastewater characteristics, a Discriminant Analysis was used, as summarized in Table 5-5. This analysis showed that conductivity significantly affected D and presented strong correlation with factor 1 that is an interaction effect factor of pH, DOC and conductivity. The effect of conductivity might be due to ionic adsorption competition and decreased diffusion of Ag⁺. Therefore, experiments in RO water led to the highest diffusion coefficient (D) due to minimal interferences from ions. The experimental data of D presented an opposite tendency between ionic strength and D. Although North Toronto WWTP effluent owned the highest conductivity, the higher DOC in Peterborough influent played an import role to obtain the lowest D. The diffusion coefficient decreased with increasing DOC, except for experiments with effluent from the North Toronto WWTP and ELA water, in which ionic strength has significant effect. As a result, the combination effect of DOC and conductivity influenced diffusion coefficient of DGT. DOC and ionic strength both have negative effects on ion diffusion. More complex matrices reduced the Ag⁺ adsorption on the DGT resin.

Table 5-5 Statistical linear regression and Discriminant Analysis of D and water qualityparameters of DOC, pH and conductivity (i.e. ionic strength).

Linear regression of D									
Statistical analysis	DOC(ppm)	рН	conductivity(us/cm)						
P value	0.0395	0.1014	0.1620						
R square		0.911							
	Discriminant analysis of D								
Unidimensional test of equality of the means of the classes									
Variables		P value							
DOC		0.757							
рН		0.478							
conductivity		0.001							
Bartlett's test for eigenvalue significancy									
		Factor 1							
Eigenvalue		13.476							
Bartlett's statistic		9.354							
P value		0.025							
	Variables / Facto	ors correlations							
Variables		Factor 1							
DOC		-0.150							
рН		-0.336							
conductivity		-0.979							

5.1.5 Effect of temperature and CNIS size on sampling rate and diffusion coefficient

The effect of cross sectional area of the CNIS was evaluated considering that the samplers designed for field deployment had a larger diameter, 3.7 cm opening compare 2 cm for the sampler used in the laboratory. According to Vrana et al. 2006 and Kot-Wasik et al. 2007, the sampling rate can be represented as a function of the exposure area:

$$R_{\rm S} = k_{\rm o}A = k_{\rm e}k_{\rm DW}V_{\rm D} \tag{5-1}$$

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Where k_0 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 and V_D is the volume of the receiving phase. This suggests that the larger cross sectional area of the rings used during field work likely had higher sampling rates. To validate this and determine the rate for the larger CNIS, the calibration was repeated in L221 using plastic rings of the same dimension as the stainless steel rings used in the field. Due to limited materials, time and environmental water availability, the CNT sampling rates in other water matrices could not be re-evaluated using the larger CNIS.

The results obtained for the calibration of NH₂-CNT suspended in L221 water using both the small and large rings are presented in Figure 5-10a and Figure A.5a, respectively. With both sizes of CNIS, silver accumulated linearly over time. Because of the low variability and good agreement between estimated TWA concentrations of CNIS-labile Ag and measured Ag concentration, NH₂-CNT was judged to be a promising adsorbent for AgNP (Figure 5-10 b; Figure A.5 b). The NH₂-CNT uptake rates were 1.7 mL/day and 3.8 mL/day for CNIS having a diameter of 2 cm and 3.7 cm, respectively. The increase in surface area promoted the Ag uptake by a 2.2 fold.



Figure 5-10 a) Cit-AgNP accumulation by NH₂-CNT powder as a function of time in L222 water at room temperature in CNIS with 3.7 cm open diameters rings. b) Measured and estimated concentration of cit-AgNP at room temperature with 3.7 cm open diameters rings.

CNIS and DGT were deployed in Lake 221 at ELA throughout the year. In addition, these passive samplers were deployed in the warmer epilimnion and the colder hypolimnion of the lake during the summer. Therefore, the water temperature varied drastically from summer to winter, and with depth of deployment in the lake. Therefore, CNIS sampling rates were conducted at room temperature (22 °C to 24 °C) and at low temperature (1 °C to 6 °C), which correspond to the measured temperatures in the summer in the epilimnion (16 °C to 23 °C) and hypolimnion (5 °C to 7 °C).

The low temperature experiment was set up in the isothermal container comprised of circulating coolant and ice slush inside a box that was placed on the top of stirring plates. The experimental beakers were put in the container surrounded with ice slush and the water in the beakers was stirred at 75 rpm. To reduce the thermal transfer to air, the top was covered with isothermal foam. The ice was added every 12 hours to keep the temperature below 6°C. In the low temperature experiment, the measured sampling rates were 0.7 mL/day and 1.1 mL/day for the smaller and larger sized CNIS, respectively (Figure 5-11). Previous sampling calibration in L221 at room temperature showed 1.7 mL/day and 3.8 mL/day sampling rate for 2 cm and 3.7 cm diameter open CNIS, respectively. Temperature increase facilitated AgNP adsorption on CNT surface by 2 to 3 times. In addition, when comparing the rates obtained for the small and large CNIS used at low temperature, the larger exposure area again increased the sampling rate, this time by 1.6 fold rather than the 2.2 fold observed at room temperature.



Figure 5-11 Mass of cit-AgNP accumulation by NH₂-CNT powder as a function of time in L222 water at low temperature with: a) 2 cm diameter rings b) 3.7 cm diameter rings. Measured and estimated concentration of cit-AgNP at low temperature with c) 2 cm open diameters rings d) 3.7 cm open diameters rings.

Temperature effect was also considered for DGT calibration, using the same conditions and setup as for the CNIS. Temperature had insignificant effect on the Ag⁺ diffusion onto DGT in L221, revealing similar diffusion coefficients at room temperature and low temperature, 4.0×10⁻⁶ cm²/s and 4.3×10⁻⁶ cm²/s, respectively (Figure 5-12 a; Figure A.9). That is probably because the effect significance of DOC is larger than the significance of temperature due to high DOC presence in L221. Therefore, higher DOC complexation with Ag⁺ interfere Ag⁺ accumulation onto DGT and counteract the effect of temperature.



Figure 5-12 a) Mass of Ag⁺ accumulated over time on DGT exposed in L222 water at low temperature b) Estimated TWA concentration of DGT-labile Ag and measured Ag concentrations determine over time using DGTs exposed at low temperature.

5.1.6 Desorption of Ag from CNIS

Given the long deployment time at the Centre Buoy location in L221 at ELA during the recovery phase after dosing of the lake (i.e. October, 2014 to May, 2015), it is possible that Ag initially adsorbed to the CNT sorbent in the CNIS may have experienced desorption over the 7 month deployment period. Previous studies have shown that there is no diffusion of sorbed material out of DGT samplers over time (Ernstberger et al. 2005) but similar studies are needed with CNIS. In order to evaluate whether Ag on the CNIS sorbent is labile, we conducted a desorption test in the laboratory. As described in the background section (2.2.1), when the desorption of analytes is larger than the adsorption, the uptake constant K₁ can be ignored and equation 2-1 is rearranged to:

$$\frac{\mathrm{dCs}}{\mathrm{dt}} = -\mathrm{K}_2\mathrm{C}_\mathrm{s} \tag{5-2}$$

From which the following equation is obtained:

$$\operatorname{Ln}\frac{Cs}{Co} = -\mathrm{K}_2 t \tag{5-3}$$

where K_2 is the desorption rate constant and C_s is the concentration in the sampler.

Nine (9) CNIS containing NH₂-CNT sorbent were exposed to 500 ppb cit-AgNP suspended in a HDPE beaker. CNIS were left in the beaker for 2 days in order to reach an equilibrium mass of

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Ag on the sorbent. Two (2) CNIS were extracted right after being removed from the suspension (t=0) in order to determine the amount of silver adsorbed on the samplers at time zero of the experiment. The other 7 CNIS were used for the desorption experiment and were placed in a flow through 8-L vessel fed with tap water flowing at a rate of 4 mL/min. A constant volume of water in the vessel was maintained using an overflow system. One or two samplers were removed from the water at 2, 4, 6, 8, and 10 days of the experiment and the sorbent was analyzed for the mass of Ag (Figure 5-13 a), from which the desorption rate was calculated using equation 5-3. Rapid desorption in the first two days and slow desorption after the second day indicated that there are two processes occurring for desorption over time. The AgNP desorption rate was determined from the slope of the two linear regressions shown on Figure 5-13 b, with two desorption rates of 0.146 d⁻¹ and 0.024 d⁻¹. The first rapid phase at high loads of silver on the sorbent could be rapid loss of Ag⁺ from the sorbent that is weakly binding to CNT, and the second slower phase corresponded to loss of Ag over time as a result of dissolution of AgNPs adsorbed to the CNTs to release Ag⁺.

Overall, these data indicate that there is loss of Ag from the CNIS over time when the rate of uptake exceeds the rate of loss. This must be taken into account when interpreting the data on estimated TWA concentrations of Ag determined from CNIS. The accumulation of Ag on the sorbent is a dynamic process, representing the balance between sorption and desorption (see Equation 5-3). If the concentration of Ag in the aquatic matrix declines markedly, then the desorption rate will exceed the sorption rate and the amount of Ag on the sorbent will decline over time. Additional studies are required to determine the mechanism for loss of Ag from the CNIS. It is possible that AgNPs are diffusing back into the aquatic matrix through the porous membrane, but it is more probable that there is dissolution of the sorbed AgNPs over time, and Ag⁺ is diffusing back into the medium during the slow phase of desorption.



Figure 5-13 a) cit-AgNP desorption profile from NH₂-CNT surface over 10 days. b) desorption rate calculation

5.2 Field deployments of CNIS and DGT passive samplers

5.2.1 Experimental Lakes Area L222

Four deployments of CNIS (NH₂-CNT and COOH-CNT) and DGTs were conducted during the summer of 2014 in the Lake 222 of ELA. The lake was dosed over the deployment period with ~9 kg of AgNP. Analysis of grab samples of lake water collected over the deployment period using spICP-MS analysis, as described by Telgmann et al. (2014) indicated that the range of particle sizes of AgNPs in lake water were consistent with the size range of nanoparticles in the suspension that was added to the lake; that is, the majority of the particles were <80 nm in size (C. Metcalfe, Trent University; unpublished data). Previous studies on the fate of AgNPs in

mesocosms deployed 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 lakes from this region (Furtado et al., 2014; Furtado et al., 2015). The mass of Ag accumulated on the samplers and the sampling rates determined at two different temperatures using water from L221 were used to calculate the TWA concentrations of CNIS-labile Ag. The sampling rates applied here were those determined in the laboratory using L221 water using CNIS with the same cross sectional area as those used in the lake deployments (i.e. 3.7 cm open diameter) to eliminate the exposure area effect. The deployment results are presented in Table 5-6.

Summary of estimated TWA concentration (ppb) per sampler								
	June 24 - J	uly 28 2014	July 28 - /	July 28 - August 25		– Oct. 19	Oct 19, 2014 - May	
			20	14	201	14	9,	2015
Site	COOH-	NH ₂ -CNT	COOH-	NH ₂ -CNT	COOH-	NH ₂ -CNT	COOH-	NH ₂ -CNT
	CNT		CNT		CNT		CNT	
Outflow	0.666±	1.199±	1.267±	0.992±	3.923±	1.082±		
	0.397	0.149	0.286	0.119	3.369	0.612		
West Bay	0.202±	0.630±	0.851±	1.072±	0.728±	1.342±		
	0.126	0.295	0.168	0.281	0.606	0.732		
CB hypo	2.593±	1.021±	9.255±	2.880±	15.004±	8.372±	1.446±	1.131±
	1.694	0.620	4.841	1.130	14.104	13.693	0.310	0.729
CB Epi	1.537±	2.369±	1.779±	2.526±	1.013±	1.476±	10.549	9.723±
	0.727	1.087	0.293	0.566	0.400	0.208	±7.376	0.241
D3	1.908±	2.075±	2.985±	8.995±	4.455±	7.412±		
	0.793	0.655	0.930	7.206	2.762	4.660		
D2	18.648±	48.295±	464.732±	176.632	774.446±	850.564		
	4.236	24.752	298.375	±47.782	151.838	±89.554		

Table 5-6 Estimated TWA of CNIS-labile Ag measured at the ELA sampling sites over time

The D2 station is located within one meter of the AgNP addition point, so it is not surprising that the estimated TWA concentrations of CNIS-labile Ag are always highest at D2 relative to all other locations (Table 5-6). The other locations have a trend of gradual decrease of Ag concentration with distance from the site of addition, with the lowest estimated concentrations

at the West Bay and Outflow sites. In most of case, NH₂-CNT displayed better adsorption than COOH-CNT. Because of continuous addition of AgNP, the first batch of CNTs gave less Ag concentration, then the Ag bulk concentration increased over time at most locations. This trend is obvious at the D2 close to the addition point, but there was no significant change over time in the estimated TWA concentration of CNIS-labile Ag at the West Bay and Outflow sites. It appears that AgNP transport was a slow process in Lake 222, but once suspended in lake water, the AgNP was fairly stable over time. The AgNP tended to settle down to through the water column to the sediment, which corresponded to the high concentrations in the hypolimnion during summer. The estimated concentrations in the hypolimnion increased markedly during the August to October deployment, which corresponds with the "lake turnover" (i.e. breakdown of the thermocline) that typically occurs in September every year. It is difficult to interpret the significance of the estimated TWA concentrations of Ag in the CNIS deployed at Centre Buoy over the 8 months period between October, 2014 and May, 2015. Our lab experiments indicate that desorption of Ag can occur over time from CNIS after exposure ceases. It is difficult to know if the CNIS-labile Ag observed on the samplers after retrieval in May, 2015 over this long period is due to an initial exposure at higher concentrations during the previous Fall, or represents a constant concentration of AgNP present in the water column over the winter months.

Grab samples of Lake 222 water were collected in the amber glass bottles at each location during deployment and retrieval and were shipped back to Trent University for analysis of total Ag by ICP-MS. The preparation and analysis of these water samples was conducted as described by Furtado et al. (2015).

Figure 5-14 shows a comparison between the total silver concentration determined by ICP-MS analysis of grab samples and the estimated TWA concentrations of CNIS-labile Ag determined from CNIS samplers with NH₂-CNT as absorbent during the first deployment period in June-July, 2014. The data show reasonable agreement between the CNIS-labile Ag concentrations and the measured concentrations of total Ag from the grab samples; especially for the grab samples

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collected in June at the time of deployment. However, the CNIS-labile Ag determined at site D2 (i.e. >48 ppb) shows a much higher concentration that the total Ag determined in the grab samples; possibly reflecting the patch distribution of the AgNP in suspension at this site very close to the point source. Aside from the D2 site, the grab samples show total Ag concentrations at sites in the lake ranging from <1 to <6 ppb, while the CNIS-labile Ag concentrations were estimated to be in the range of 1-2 ppb. Of course, total Ag concentrations could include forms of Ag that are larger than the 800 nm pore size of the PES membranes used to restrict uptake of Ag into the CNIS sorbent.



Figure 5-14 Comparison between total Ag concentration determined by ICP-MS analysis of grab samples at deployment (June) and retrieval (July) and estimated TWA concentrations of CNIS-labile Ag determined from CNIS deployed over this time period.

All DGT samplers were extracted and analyzed by ICP-MS at Trent University, and the estimated TWA concentrations of DGT-labile Ag are summarized in Table 5-6. Except for the DGT deployed near the AgNP addition point (D2), where the highest concentrations of DGT-labile Ag were measured (0.498 to 1.549 ppb), the concentrations of DGT-labile Ag were consistently low at all

the sampling points and sampling times (Table 5-7). Considering the continuous addition of silver at D2, an increasing concentration of Ag⁺ was expected over time. However, a decrease in concentration was observed for the period of July to August (0.128 ppb compare to the previous value of 0.498 ppb). This observation might be explained by an increased concentration of dissolved organic or particulate material in the water column, associated with optimal summer conditions for lake productivity that facilitated complexation of Ag⁺. Unlike AgNP, which might tend to settle down through the water column to the bottom of the lake, Ag⁺ was distributed uniformly between the different layers of lake resulting in similar concentrations in the epilimnion and hypolimnion. The very low concentrations of DGT-labile Ag measured in grab samples of L222 water by spICP-MS according to methods described by Telgmann et al. (2014). These measured concentrations of dissolved Ag were typically <1 ppb, except at the D2 station, where they were typically in the range of 2-5 ppb (C. Metcalfe, Trent University, unpublished data). 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 species pool.

Table 5-7 Estimated TWA concentrations of DGT-labile Ag measured at the ELA sampling sites over time

TWA (ppb)	June 24 - July 28 2014	July 28 - August 25 2014	Aug. 25 – Oct. 19 2014	Oct 19, 2014 - May 9, 2015
Site	DGT	DGT	DGT	DGT
Outflow	0.064±0.109	0.011±0.010	ND	
West bay	0.009±0.010	0.012±0.019	0.013±0.030	
СВ Нуро	0.018±0.018	0.019±0.025	0.051±0.095	0.013±0.005
CB Epi	0.019±0.016	0.001±0.001	0.057±0.097	0.015±0.006
D3	0.017±0.013	0.005±0.005	0.016±0.030	
D2	0.498±0.217	0.128±0.042	1.549±0.301	

5.2.2 Peterborough WWTP and receiving waters

Cages (n=3) containing DGT and CNIS (NH₂-CNT and COOH-CNT-SS) were placed for 1 week in the Peterborough WWTP influent and effluent and in the Otonabee River upstream and

downstream of the effluent discharge. As discussed in the section of ELA water sampling rate determination and equation 5-1, silver sampling rate is proportional to the cross sectional area. Higher exposure area gives larger uptake of analytes (Greenwood et al. 2007). Since only smaller cross sectional area was calibrated in the field deployment water, the sampling rates were adjusted for all field deployments by multiplying the ratio of sampling rates experimentally determined from two size of cross sectional area CNIS in L211 at room temperature (i.e. 2.2). The TWA concentrations of CNIS-labile Ag at these locations were estimated using the various calibrated and adjusted sampling rates (Table 5-8). There was a high degree of variability in the results. That can be explained by shorter deployment period during which accumulation of Ag was minimal. The TWA concentration of CNIS-labile Ag in the influent and effluent were not significantly different, which can be an evidence that AgNP or silver are not significantly removed by sedimentation during water treatment or that short deployment time might not be sufficient to allow enough silver to diffuse onto the CNIS. Apparently, COOH-CNT-SS showed the best adsorption in all four locations, with up to 20 folds higher than NH₂-CNT without considering variability or at lease higher adsorption in influent and effluent taking into account variability. That is because the COOH-CNT-SS unique surface properties, great CNTs accessibility, and large adsorption area allow it to adsorb Ag intensively.

Table 5-8 Estimated TWA concentrations of CNIS-labile Ag at the Peterborough WWTP and in the receiving waters.

TWA conc. (ppb)	upstream	downstream	influent	effluent
NH ₂ -CNT	0.410±0.281	0.088±0.101	0.047±0.037	0.016±0.027
COOH-CNT-SS	1.557±1.800	1.287±2.180	0.618±0.372	0.204±0.123

Because of the short deployment period, slow diffusion of Ag⁺ and the complex aqueous matrix, no DGT-labile Ag was detected in the Peterborough influent (Table 5-9). It is possible that there was no free Ag ions available in the influent due to interaction with DOC or suspended particles. Consistently low concentrations of DGT-labile Ag were detected in the river downstream and upstream, whereas 10 times higher level of dissolved silver was observed in the WWTP effluent. This latter observation may indicate that the UV disinfection process following the secondary clarifier process has a significant impact on the behaviour of dissolved Ag (see Table 5-9). As mentioned by Laroo, 2013, silver ions can be transformed into colloidal silver when expose to UV light. That can also explain the higher concentration of CNIS-labile Ag present in receiving surface water. Doolette et al. 2013 also suggested that AgNPs was more readily transformed into Ag₂S than Ag⁺ during biological treatment. This observation and the lower DOC and ionic strength in the effluent may explain the higher concentration of dissolved Ag in the effluent.

Table 5-9 Estimated TWA concentrations of D	OGT-labile Ag at the Peterborough WWTP and in
receiving waters	

	TWA concentration of
Peterborough	DGT-labile Ag (ppb)
Influent	ND
Effluent	0.122±0.153
Up stream	0.013±0.008
Down stream	0.011±0.010

Overall, these data showing low concentrations of DGT-labile and CNIS-labile Ag in the wastewater and in the receiving stream for wastewater discharges is consistent with studies that most of the AgNPs and silver salts present in municipal wastewater will be transformed into Ag₂S nanoparticles during aerobic and anaerobic treatment and be end up in the sludge (Kiser et al. 2012; Wang et al. 2012; Doolette et al. 2013).

5.2.3 Field deployment in western Lake Ontario

DGT and CNIS were deployed at nearshore locations in the western Lake Ontario in June and October, 2014 for periods of 1 month. The first batch of DGT and CNIS were extracted and analyzed by ICP-OES at McGill. The second batch of samplers were recovered and analyzed by ICP-MS at Trent in order to use the more sensitive instruments. During deployment, DGT and CNIS experienced extreme conditions in the Don River and the Humber River. Rapid water flow rate and large amounts of sediment accumulated in the sampler cages (see photos in Appendix Figure A.12) leading to membrane ruptures. In the June deployment, the CNIS deployed in the Don River were all broken and the CNIS deployed in the Humber River in October deployment were also ruptured. CNIS only accumulated detectable amounts of Ag in the Don River during the October deployment. The second batch of CNIS analysis was conducted VICP-MS which is 1000 times more sensitive than ICP-OES. Estimated TWA concentrations of CNIS-labile Ag at all locations were extreme low or below detection limits (Table 5-10). Once again, these results are consistent with studies that show that AgNPs present in municipal wastewater will settle out of suspension into the sludge (Kiser et al. 2012, Wang et al. 2012).

June deployment (ppb)	COOH-CNT	NH ₂ -CNT			
Toronto Harbour 1364	0.099±0.066	0.003±0.006			
Humber Bay near STP	ND	0.031±0.054			
Humber Bay Index 2047	ND	ND			
NT WWTP	0.007±0.005	0.007±0.009			
Humber River at old Mill	0.013±0.015	0.041±0.036			
Don River	All CNTs were broken				
October deployment (ppb)	COOH-CNT	NH ₂ -CNT			
October deployment (ppb) Toronto Harbour 1364	COOH-CNT ND	NH ₂ -CNT ND			
October deployment (ppb) Toronto Harbour 1364 Humber Bay near STP	COOH-CNT ND ND	NH2-CNT ND ND			
October deployment (ppb) Toronto Harbour 1364 Humber Bay near STP Humber Bay Index 2047	COOH-CNT ND ND ND	NH2-CNT ND ND ND			
October deployment (ppb) Toronto Harbour 1364 Humber Bay near STP Humber Bay Index 2047 NT WWTP	COOH-CNT ND ND ND ND	NH2-CNT ND ND ND ND			
October deployment (ppb) Toronto Harbour 1364 Humber Bay near STP Humber Bay Index 2047 NT WWTP Humber River at old Mill	COOH-CNT ND ND ND ND All CNTs	NH₂-CNT ND ND ND ND were broken			

Table 5-10 Estimated TWA concentration of CNIS-labile Ag in Lake Ontario (ND = not detected)

DGTs deployed in Lake Ontario showed levels of DGT-labile Ag below detection limits, except for DGTs deployed in Toronto Harbour and in the Humber River near Old Mill (Table 5-11). The low levels of DGT-labile Ag, may reflect low levels of dissolved Ag as a result of DOC interactions and competitive adsorption with the sorbent as a result of high ionic strength.

Table 5-11 Estimated TWA concentrations of DGT-labile Ag at sites in Lake Ontario (ND= Not detected)

TWA concentration (ppb)	Summer	Fall
	DGT	DGT
Toronto Harbour	0.002±0.002	ND
Humber Bay near STP	ND	ND
Humber Bay Index	ND	ND
NT WWTP	ND	ND
Humber River at old Mill	0.002±0.004	ND
Don River	ND	ND

6 Conclusions

We developed a passive sampler that is a simple *in situ* technique for monitoring Ag in the size range approximately corresponding to the size distribution of AgNP in aquatic matrices. However, the data presented here indicate that sampling rates for the CNIS samplers are specific to the matrix in which the samplers are deployed, and that pH and ionic strength have a significant impact on these sampling rates. The sampling rate is also proportional to the cross sectional area of the sampler. The sampling rates for the CNIS in its current configuration is relatively low (i.e. <0.01 litres per day). It is possible that sampling rates could be increased by increasing the cross-sectional area of the sampling surface and mass of absorbent placed in the sampler.

The NH₂-CNT sampling rate for CNIS with the smaller cross sectional area varied from 0.7 to 22.4 mL/day under various water quality conditions, indicating that DOC, ionic strength and pH significantly affect the Ag uptake onto CNTs. Increased pH and ionic strength together will largely promote Ag uptake by reducing repulsive interaction and particle size. The CNIS calibration showed good agreement between estimated and measured concentrations of Ag in all types of water. The selective adsorption of DGT provides an opportunity to quantitatively distinguish DGT labile Ag (i.e. dissolved Ag) from CNIS-labile Ag (i.e. AgNP, colloidal silver and dissolved silver). Increasing ionic strength, pH and DOC or a combination of these three variables may influence silver diffusion into the samplers. DOC ligands form large complexes with Ag⁺ to prevent diffusion through the membrane. More ions create adsorption competition with Ag⁺ to exclude silver ion on the resin. Temperature has a minor impact on diffusion rates when high DOC is present in the water.

Since the AgNP water concentrations fluctuate temporally or spatially due to changes in discharge, water flow or other parameters, passive samplers allow the advantage of giving estimates of TWA concentration over the entire deployment period. Grab samples do not take into account the fluctuations in concentrations over time, resulting in the over or underestimation of AgNP concentrations. That was illustrated by comparing the CNIS sampler

and grab sample results for L222 in June-July, 2014. At the beginning of the addition of AgNP, total silver level analyzed by grab water samples was similar to the TWA concentrations of CNIS-labile Ag. At the end of the deployment period, the grab sample concentration was lower, indicating a decrease due to sedimentation. DGT-labile Ag was present at much lower concentrations than CNIS-labile Ag in Lake 222, indicating AgNP spiked into the lake was relatively stable in the water column. AgNP tends to settle down to the sediments in the summer. CNIS constructed from COOH-CNT and NH₂-CNT gave similar results for CNIS-labile Ag validating the AgNP sampling concept.

The CNIS-labile Ag and DGT-labile Ag are extreme low or undetectable in Peterborough WWTP and western Ontario Lake. Especially the low value of dissolved Ag in both fields indicate that DOC and ionic strength play an important role to prevent Ag⁺ adsorbing onto DGT resins by forming complexes. The obtained CNIS-labile Ag in wastewater demonstrated that silver transformed into Ag₂S and removed with the biosludge and was sorted out, which is consistent with previous studies.

Overall, DGT provided promised results in Peterborough WWTP and ELA. However, quantification of dissolved silver in very complex matrix is a challenge due to water conditions effects. The use of CNIS samplers for uptake of AgNP gave prospect results in both laboratory and field work. Appropriate deployment period chosen was suggested to promote CNIS efficiency and capability in AgNP adsorption by analyzing water condition to predict it when unknown amount of AgNP present in the field. Some CNIS samplers experienced rupture in extreme weather conditions during deployment in Western Lake Ontario. More robust membrane or cage design is required to minimize sediment entering the cage and damaging the CNIS surface, which also lead to CNTs loss. Choosing CNTs deposited/grown on a support material (i.e. CNT-SS) is an alternative option to avoid membrane limitation and CNTs loss. In this project, only cit-AgNP was selected to calibrate CNIS sampling rate in different configuration. Due to the availability on the market of AgNPs with different coatings, the impact of coating material on AgNP fate in environment and CNIS efficiency need to be evaluated.
7 Future work

Although the current design of the CNIS was able to provide useful data on the presence of silver in environmental waters, further work is required to improve the design:

- 1) For practical reasons related to manipulation and assembly and the decreased risk of releasing CNT in the environment, the use of COOH-CNT-SS would be preferable. However, it is necessary to improve the production process in order to obtain reproducible and uniform distribution of the CNTs on the surface of the mesh and to stabilize the iron in order to prevent the formation of rust on the surface of the mesh.
- 2) Due to the low concentrations observed in environmental waters, it would be necessary to increase the sampling rate of the CNIS in order to limit the deployment time. A better understanding of the adsorption mechanism of AgNP on the surface of the CNTs would provide hints on possible ways to improve the sampling rates, for example, Increase surface area of CNIS or Increase the amount of sorbent.
- 3) Further testing of the CNIS includes evaluating effects such as biofouling, mineral fouling, flow rate and turbulence on the sampling rate of the designed CNIS.
- 4) Because the stabilizers of AgNPs can change AgNP behavior and fate in the environment, the sampling rate of AgNPs with different coatings need to be investigated. To better understanding the adsorptive mechanism involved in the CNIS, it is suggested to monitor the AgNP transformation during sampling rate determination.
- 5) Considering that under extreme field conditions the membranes were ruptured, it is also necessary to develop a more robust design of the sampler and cage in order to minimize damage of the CNIS. Investigating other membranes materials, the use of CNT-SS or CNT deposited on other support materials as well as decreasing the mesh size of cage are options to consider in order to minimize the damage caused to the sampler by sediments.
- 6) Due to powerful adsorption of CNTs to many metal ions and organic compounds, the potential of CNIS to monitor concentrations of other target analytes such as heavy metals and organic contaminants could be investigated.

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APPENDIX

Appendix 1: Quantification of dissolved silver by ISE

The use of a silver/sulfide ion selective electrode (ISE, 9616BNWP, Thermo Scientific, CA) equipped with pH/ISE meter (Orion Dual Star, Thermo Scientific, CA) was considered for the monitoring of Ag⁺. Standard silver nitrate (1000 mg/L, Thermo Scientific, CA) dissolved in 2% (v/v) nitric acid and ionic strength adjustor (NaNO₃) (ISA) at a volume ratio of 1:100 was used as standard solution for calibration of ISE in the silver concentration range 10 ppb to 300 ppb. Aliquots of samples were mixed with the same volume of ISA as the standard solutions to obtain comparable ionic strength. To minimize the effect of other cations and air on the measurements, samples were purged with nitrogen gas for 1 minute prior to measurement. The use of a nitrogen purge was shortened the response time by 50% and increased the linear range of the calibration. Figure A.1 presents the ISE calibration curve from 10 ppb to 300 ppb using this method. However, the linearity was lost for concentration below 40 ppb.



Figure A. 1 ISE calibration for Ag⁺ from 10 ppb to 300 ppb

The method was also tested to evaluate the adsorption of silver on COOH-CNT veil, bare CNT veil (without functionality) and COOH-CNT-SS. Results obtained using ISE were compared with ICP-OES results. Results shown in Table A.1 indicated the need to measure concentrations below 40 ppb and that for higher concentrations differences as high as 50% were observed

when using ISE. Therefore, ISE was abandoned due to its high detection limit, lower sensitivity, and longer responding time.

	Initial concentration (ppb)		Final concentration after adsorption	
Samples	ISE	ICP-OES	ISE	ICP-OES
Control blank	109.9	205.9	140.0	205.2
COOH-CNT veil	100.1	209.9	29.3	103.3
Bare CNT veil	125.2	213.9	32.1	17.3
COOH-CNT-SS	137.8	218.2	29.3	12

 Table A. 1 Comparison of ISE and ICP-OES results for measuring dissolved Ag

Appendix 2: Determination of Ag⁺ and AgNP by UV-Visible

UV-visible was evaluated as a semi-quantitative method for the different speciations of silver in cit-AgNP suspension. The stock solution of Cit-AgNP (20 mg/L) was diluted to 1000 ppb, 500 ppb and 100 ppb and 100 ppb solutions of silver nitrate were prepared directly from a silver standard (1000 mg/L). Figure A.2 summarizes the UV-visible responses obtained for each of the solutions prepared. High concentration of cit-AgNP (1000 ppb) generated a wide peak at a wavelength of 425 nm, whereas the low concentration of cit-AgNP (100 ppb) and all dissolved Ag solutions resulted in comparable flat signal. This indicate the inability of the method to detect concentration of cit-AgNP below 100 ppb. Considering the low concentrations involved in this PhD work, measurement by UV-visible was not an option for quantification of the various forms of silver.



Figure A. 2 UV-visible responses for various concentrations of cit-AgNP and Ag⁺

Appendix 3: Characterization of CNT surface

SEM (Hitachi S-4700 FE-SEM) was used to confirm the presence of silver particles on the surface of the CNTs. EDX (Oxford 7200) was coupled with SEM for using to confirm the nature of the particles observed by SEM. An XPS (K-Alpha, Thermo Scientific) was also used to confirm the elemental appearance of silver and other elements (contaminants) on the surface of the CNTs. The SEM and XPS do not require any sample preparation other than loading the CNT samples on a metal support. The operation conditions used for SEM and EDX are listed in Table A.2.

SEM operating conditions	
Operation mode	Ultra high resolution
Working distance	≤6 mm
Cond lens 1	6.0
SE detector	Upper
HV control voltage	10 kV
HV control current	10 μΑ
EDX working conditions	
Operation mode	Analysis
Detector	Upper
WD	12 mm

Table A. 2 SEM and EDX operating conditions

Appendix 4: NH₂-CNT sampling rate calculation:

Table A. 3 Measured mass of silver accumulation on NH₂-CNT and silver concentration in the solution to calculate sampling rate

Time (h)	Mass of Ag accumulated on the CNT (ng)	Silver concentration in solution (ppb)
0	1.4	19.7
23	33.6	17.0
48	48.9	14.8
72	49.7	12.9
96	109.3	11.0

Silver's TWA concentration in the solution is calculated by the equation 6-1:

$$C_{\text{TWA}} = \frac{t1 C1 + t2 C2 + \dots + tn Cn}{t1 + t2 + \dots + tn}$$

Where C_i is the silver concentration in the solution over time t_i interval. Therefore, silver TWA concentration within 96 h is calculated based on the data in Table A.3:

$$C_{\text{TWA}} = \frac{19.7 \times 0 + 17 \times 23 + 14.8 \times 48 + 12.9 \times 72 + 11 \times 96}{0 + 23 + 48 + 72 + 96} = 12.9 \text{ ppb}$$

According to the equation 4-1, the slop of Figure 5-6a is the interaction of silver TWA concentration C_{TWA} and sampling rate R_s presented in equation A-2:

$$Slop = C_{TWA \times} R_s \tag{A-2}$$

The sampling rate is calculated as follow:

$$R_{s} = \frac{0.9614 ng/h}{12.9 \frac{\mu g}{L} \times 1000 ng/\mu g} = 7.5 \times 10^{-5} L/h = 1.8 mL/day$$

Appendix 5: optimal conditions of COOH-CNT-SS dry ashing

Dry ashing is a method to remove carbon without interfering Ag deposit on the mesh. As mentioned before, utilization of ashing aid, ashing temperature and duration are mainly considered during dry-ashing as well as subsequent acid usage and digestion time. Before the recovery rate was determined by dry ashing, crucible adsorption of Ag is another important factor to be taken into account. Duplicate 40 μ L stock cit-AgNP suspension and 80 μ L 5 ppm of silver nitrate were spiked in the crucible, undergoing dry ashing in the microwave furnace. 100% of Ag was recovered from crucible, which indicated that crucible has minor influence on Ag extraction. Longer digestion and concentrated HNO₃ utilization increased the extraction efficiency by 50%. At higher ashing temperature 550°C, longer ashing caused recovery decrease 4 to 20 folds and greater than 95% of Ag losses after 2h ashing. During the same ashing period, low temperature of 480°C results in the significant increase of recovery rate to 2 fold, which can be explained by occurrence of Ag volatilization at temperature higher than 500°C (van Raaphorst et al., 1978). Finally, dry ashing conditions were determined that COOH-CNT-SS was extracted under 480°C for 1 h in microwave furnace and digested by 70% (v/v) HNO₃ at 95°C for 1h, which leads to 82% Ag recovered shown in Appendix Table A.4.

Table A.	4 Recovery rate of silver from COOH-CNTs-SS and membrane spiked with 400 ng cit-
	AgNP by dry ashing

	COOH-CNT-SS 1	COOH-CNT-SS 2
Spiked mass of AgNP (ng)	400	400
Extracted Mass of Ag from	334	324
COOH-CNT-SS (ng)		
Recovery rate (%)	83.5	81.0
Average recovery (%)	:	82.3





Figure A. 3 Cit-AgNP accumulation by COOH-CNT-SS as a function of time in Peterborough WWTP a) influent b) effluent c) discharging river. Measured and estimated residual concentration of cit-AgNP over time in d) influent e) effluent f) discharging river.



Figure A. 4 Cit-AgNP accumulation by NH₂-CNT as a function of time in Peterborough WWTP a) influent b) effluent c) discharging river. Measured and estimated residual concentration of cit-AgNP in d) influent e) effluent f) discharging river over time.



Figure A. 5 a) Cit-AgNP accumulation by NH₂-CNT powder as a function of time in ELA water at room temperature. b) Measured and estimated residual concentration of cit-AgNP at room temperature.



Figure A. 6 Cit-AgNP accumulation by COOH-CNT and NH₂-CNT in NT WWTP effluent and measured and estimated residual concentration of cit-AgNP over time



Figure A. 7 Cit-AgNP accumulation by COOH-CNT and NH₂-CNT in Toronto Harbour and measured and estimated residual concentration of cit-AgNP over time





Figure A. 8 Ag⁺ accumulation by DGT normalized by residual Ag⁺ concentration in Peterborough a) influent b) effluent c) discharged river and measured and estimated residual Ag⁺ concentration over time in d) influent e) effluent f) discharged river



Figure A. 9 Ag⁺ accumulation by DGT normalized by residual Ag⁺ concentration in ELA water and measured and estimated residual Ag⁺ concentration over time



Figure A. 10 Ag⁺ accumulation by DGT normalized by residual Ag⁺ concentration in a) Toronto Harbour b) NT WWTP and measured and estimated residual Ag⁺ concentration over time at c) Toronto Harbour d) NT WWTP

Appendix 8: Appendix Tables and Figures

 Table A. 5 Comparison of measured concentrations of 500 ppb solutions of Cit-AgNP and PVP

 AgNP and 100 ppb solution of PA-AgNP using different sample preparation strategies

AgNP samples	Concentration measured by ICP-OES (ppb)
Cit-AgNP	432.5
Cit-AgNP, HNO₃ treated	415.5
Cit-AgNP , acid digested	414.4
PVP-AgNP	437.7
PVP-AgNP, HNO ₃ treated	446.5
PVP-AgNP, acid digested	437.5
PA-AgNP	83.7
PA-AgNP, HNO₃ treated	95
PA-AgNP, acid digested	91.7

Table A. 6 Cit-AgNP or Ag⁺ losses in vessels made of various materials

	Teflon 1	Teflon 2	HDPE 1	HDPE 2	Amber	HDPE
	(AgNP)	(AgNP)	(AgNP)	(AgNP)	HDPE	(Ag+)
Vessels & solution					(AgNP)	
Initial conc. (ppb)	9.6	9.7	9.8	8.9	9.3	120.9
Final conc. (ppb)	6.4	7.2	8.3	8.7	8.6	120.1
Ag losses (ppb)	3.2	2.5	1.5	0.2	0.7	0.8
Retention %	33.4	25.8	15.3	2.2	7.5	0.7

Table A. 7 Recovery rate of silver from NH₂-CNT and membrane placed in 10 ppb cit-AgNP suspension (RO water)

	COOH-CNT 1	COOH-CNT 2	COOH-CNT 3
Initial conc. (ppb)		8.45	
Final conc. (ppb)	0.35	0.30	0.25
Mass of loss in the solution (ng)	405.0	407.5	410.0
Mass accumulated on CNT (ng)	283.6	292.9	298.1
Recovery rate (%)	70.0	71.9	72.7
Average recovery (%)		71.5	

	COOH-CNT 1	COOH-CNT 2	COOH-CNT 3
Initial conc. (ppb)		9.05	
Final conc. (ppb)	0.70	0.80	0.55
Mass of loss in the solution (ng)	417.5	412.5	425.0
Mass accumulated on CNT (ng)	320.7	309.2	297.0
Recovery rate (%)	76.8	74.9	69.9
Average recovery (%)		73.9	

Table A. 8 Recovery rate of silver from COOH-CNT and membrane placed in 10 ppb cit-AgNP suspension (RO water)

Table A. 9 Recovery rate of silver from DGT resin spiked with 513 ng AgNO₃

	Replicate 1	Replicate 2	Replicate 3
Spiked mass of Ag ⁺ (µg)	0.513	0.513	0.513
Recovered mass of Ag ⁺ (μ g)	0.412	0.385	0.395
Recovery rate (%)	80.2	75.0	77.0
Average recovery (%)		77.4	

Table A. 10 Recovery rate of silver from COOH-CNT-SS and membrane placed in 10 ppb cit-AgNP suspension when using concentrated acid digestion method

	Replicate 1	Replicate 2	Replicate 3	Replicate 4	Replicate 5
Initial conc. (ppb)	9.4	9.3	10.2	11.2	10.6
Final conc. (ppb)	7.1	6.7	5.0	9.5	3.2
Mass of loss in the	2300	2600	5200	1700	7400
solution (ng)	2000	2000	5200	1700	, 100
Extracted Mass of Ag	463.0	178 1	3803 8	337 3	1086 3
from COOH-CNT-SS (ng)	405.0	170.1	3093.0	552.5	1000.5
Recovery rate (%)	20.1	6.9	74.9	19.5	14.7
Average recovery (%)			27.2		
Standard deviation (%)			27.2		

		Concentration of aqueous silver (ppb) in the solution where NH ₂ -CNT was deployed (ppb)			
Time (h)	control	Replicate 1	Replicate 2	Replicate 3	
0	202.6	204.1	198.6	204.5	
18	194.3	189.4	197.0	203.2	
48	195.0	208.1	205.2	202.3	
116	186.5	205.5	203.8	233.4	
Samples		Trip	licate COOH-CNT (p	opb)	
Time (h)	control	Replicate 1	Replicate 2	Replicate 3	
0	195.5	190.7	188.7	188.4	
24	191.4	191.4	188.7	186.6	
48	189.8	190.6	185.7	186.5	
72	189.0	189.6	182.8	185.9	
96	188.1	186.7	177.4	186.7	

Table A. 11 Residual cit-AgNP concentration in control solution (no CNT and membrane) and in the solution presenting NH₂-CNT and COOH-CNT with 1 μm PES membrane

Table A. 12 Residual cit-AgNP concentration in control solution (no CNT and membrane) and in the solution presenting NH_2 -CNT with 0.8 μ m PES membrane

Samples	NH ₂ -CNT (ppb)			
Time (h)	Control	Replicate 1	Replicate 2	Replicate 3
0	194.0	192.5	192.3	189.3
20	185.9	185.1	187.0	185.8
45	186.2	185.4	184.8	187.0
120	182.6	177.6	173.5	162.4
Extracted Mass of Ag from CNT (μg)		0.64	0.63	1.07

Initial Ag ⁺ conc.	Initial AgNP	Initial total conc.	Final total conc.	Mass of Ag on
(ppb)	conc. (ppb)	(ppb)	(ppb)	Resin (µg)
10.4	0	10.4	8.6	1.16
10.5	0	10.5	8.8	1.39
10.8	1.1	11.9	9.9	1.14
10.9	1.0	11.9	10.2	0.89
10.6	8.9	19.5	16.8	0.85
10.6	9.1	19.7	16.4	0.71
0	8.9	8.9	8.5	0.38
0	10.3	10.3	9.4	0.65

 Table A. 13 The effect of different ratio of Ag⁺: AgNP on DGT adsorption

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	DOC(ppm)	рН	conductivity(us/cm)	Temperature (°C)
Don River	5.414	8.06	1197	20.1
NT WWTP	5.596	7.72	985	19.9
Humber River near mill	6.168	8.44	944	19.8
Humber Bay STP	2.808	8.28	319	19.6
Humber Bay Index	2.25	8.26	296	19.9
Toronto Harbour	2.572	8.26	332	19.9
Linear regression of R _s				
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Multiple R	0.713			
R square	0.509			
Adjusted R square	0.018			
Standard Error	0.00029			
variables	P value			
DOC	0.743			
рН	0.859			
conductivity	0.285			
Non-linear regression of R _s				
variable	R _s correlation			
DOC	0.199			
рН	0.398			
conductivity	0.697			
	Goodness of fit statistics			
R ²	1.000			

Table A. 15 Linear and non-linear regression analysis of factors influencing the CNIS samplingrate







Figure A. 12 Samplers retrieved from Humber River (left) and Don River (right) in June, 2014 deployment