EPA Public Access

Author manuscript

Sci Total Environ. Author manuscript; available in PMC 2018 September 20.

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Published in final edited form as:

Sci Total Environ. 2017 February 15; 580: 509–517. doi:10.1016/j.scitotenv.2016.11.205.

Quantification of carbon nanotubes in different environmental matrices by a microwave induced heating method

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Abstract

Carbon nanotubes (CNTs) have been incorporated into numerous consumer products, and have also been employed in various industrial areas because of their extraordinary properties. The large scale production and wide applications of CNTs make their release into the environment a major concern. Therefore, it is crucial to determine the degree of potential CNT contamination in the environment, which requires a sensitive and accurate technique for selectively detecting and quantifying CNTs in environmental matrices. In this study, a simple device based on utilizing heat generated/temperature increase from CNTs under microwave irradiation was built to quantify single-walled CNTs (SWCNTs), multi-walled CNTs (MWCNTs) and carboxylated CNTs (MWCNT-COOH) in three environmentally relevant matrices (sand, soil and sludge). Linear temperature vs CNT mass relationships were developed for the three environmental matrices spiked with known amounts of different types of CNTs that were then irradiated in a microwave at low energies (70–149 W) for a short time (15–30 s). MWCNTs had a greater microwave response in terms of heat generated/temperature increase than SWCNTs and MWCNT-COOH. An evaluation of microwave behavior of different carbonaceous materials showed that the microwave measurements of CNTs were not affected even with an excess of other organic, inorganic carbon or carbon based nanomaterials (fullerene, granular activated carbon and graphene oxide), mainly because microwave selectively heats materials such as CNTs that have a higher dielectric loss factor. Quantification limits using this technique for the sand, soil and sludge were determined as low as 18.61, 27.92, 814.4 µg/g for MWCNTs at a microwave power of 133 W and exposure time of 15 s.

Graphical abstract

Keywords

Carbon nanotubes; Quantitative analysis; Microwave method; Quartz sand; Soil; Anaerobic sludge

1. Introduction

Carbon nanotubes (CNTs) are molecular-scale cylindrical tubes of graphitic carbon (Iijima, 1991). Their unique structures give them a large surface area, good electronic conductivity, excellent thermal stability and strength. CNTs have been successfully applied in various fields such as drug delivery system (Liu et al., 2009), aerospace (Baur and Silverman, 2007), construction (Lee et al., 2010) and incorporated into numerous consumer products (Vance et al., 2015, De Volder et al., 2013), with potential uses in everything from tennis racquets and bulletproof vests to electronic components and energy storage devices. The size of global CNTs market is estimated to reach \$5.64 billion by 2020 from \$2.26 billion in 2015 (www.marketsandmarkets.com). Therefore, the likelihood of CNTs being released into the environment during the manufacture, use and disposal of products containing CNT has definitely increased (Nowack et al., 2013). Despite exceptional properties that are valuable in many applications, there is a concern regarding their potential negative influence on environmental and human health (Wiesner et al., 2006, Oberdörster et al., 2005). Information on the amounts of CNTs accumulated or deposited in various environmental matrices is required before any risk or hazard assessment can be conducted. Typical methods that can be used for determining carbon content such as total organic carbon (TOC) analysis simply provide a nonspecific measurement of carbon, and are not able to distinguish CNTs from other carbon sources in environmental matrices. Therefore, a quantitative method that is specific for CNTs is needed.

Quantification of CNTs in complex environmental media remains a challenge. Nevertheless, there have been several detection techniques that focus on quantifying CNTs in real environmental and biological samples. In past studies, an ultraviolet-visible (UV-vis) spectrophotometer was used to determine the concentration of SWCNTs and MWCNTs in water and in electrophoretic suspension samples at a wavelength of 660 or 800 nm (Ye et al., 2013, Li et al., 2006), while a UV-vis-near infrared spectrometer was used to determine the concentration of SWCNTs in heavy water (Jeong et al., 2007). However, components from real water samples such as dissolved organic matter in surface water could also make contributions to the UV absorbance, leading to imprecise measurements. In addition, absorbance in CNT suspensions could be affected by several factors such as the type and concentration of surfactants, sonication and centrifugation conditions, and interactions between surfactants and CNTs (Angelikopoulos et al., 2010). Near-infrared fluorescence based techniques have been utilized in detecting SWCNTs in blackworm (Yang et al., 2011) and wastewater samples (Schierz et al., 2012), but this method was shown to be valid only for well dispersed SWCNTs, and not for the full range of CNTs (MWCNTs, functionalized CNTs, aggregates of CNTs, etc.). For solid samples, thermal oxidation methods such as thermogravimetric analysis coupled with mass spectrometry (Plata et al., 2012), chemothermal oxidation at 375 °C (Sobek and Bucheli, 2009) and programmed thermal analysis (Doudrick et al., 2012) were also used to quantify SWCNTs and MWCNTs in soil,

sediments, air and cyanobacteria due to their high thermal stability, but the degradation of other natural carbon materials in environmental samples that are not as thermally stable as CNTs could potentially interfere with the quantification of CNTs in such matrices. Recently, several studies used single stranded DNA (ssDNA) with magnetic fluorescence spheres to capture CNTs in water and soil samples, which relied on a decrease in fluorescence because of quenching to quantify the CNTs in the samples (Mota et al., 2013, Jeong et al., 2015). However, the ssDNA method was quite complicated to use, and there is a lack of information on the performance and efficiency of the method. Overall, the presence of different types of carbon (e.g., natural organic matter) in environmental samples interfered with the analysis and prevented the accurate determination of CNT concentration using the methods described previously (Herrero-Latorre et al., 2015, Petersen et al., 2011). Moreover, most current methods are appropriate for the detection of pristine CNTs only; these methods have not been shown to successfully quantify functionalized CNTs. Since the ratio of SWCNTs to MWCNTs production is reported to be 1:280 (Herrero-Latorre et al., 2015), the majority of CNTs released into the environment is expected to be MWCNTs and functionalized MWCNTs rather than SWCNTs. Therefore, it is very important to develop a selective and reliable methodology to detect and quantify the different types of CNTs, including MWCNTs and functionalized CNTs in the environment.

In addition to optical and thermal properties, CNTs have other exceptional properties that could be leveraged to provide a solution to the CNTs quantification problem. For example, CNTs are reported to display strong microwave absorption at 700 W and 2.45 GHz, resulting in the evolution of a large amount of heat (Imholt et al., 2003). Previous studies have shown that microwave energy can selectively induce materials with higher dielectric loss factor (Robinson et al., 2008). Based on this unique property, a novel microwave induced heating method was established to quantify CNTs in root samples by Irin et al. (Irin et al., 2012). Their results indicated that if microwave conditions (power and exposure time) remained constant, the temperature increase (ΔT , °C) due to the release of heat energy upon irradiation will be a function of the mass of CNTs present inside a sample. This microwave technique has been successfully used to quantify CNTs in earthworm and amphibian larvae samples (Li et al., 2013, Bourdiol et al., 2015), but has not been used to determine concentrations of CNTs in the environment (e.g. soil and sludge) to date. It is believed that this microwave heating technique will be capable of quantifying CNTs in complex environmental samples as it is selective enough to distinguish CNTs from other background carbon sources in environmental samples of complex composition. Thus, the main objective of the study is to make use of this microwave induced heating system to quantitatively detect CNTs in three matrices of environmental relevance including sand, soil and anaerobic sludge. Additionally, the potential interferences from inorganic, organic and other carbon based nanomaterials (e.g., fullerene, granular activated carbon and graphene oxide) will be assessed, which is one of the main challenges in the area of CNTs quantification in environmental matrices. To meet the objective, linear mass-heat relationships were developed for SWCNTs, MWCNTs and carboxylated MWCNTs in the three environmental samples.

2. Materials and methods

2.1. Materials

SWCNTs, MWCNTs and —COOH functionalized CNTs (MWCNT-COOH) were purchased from US Research Nanomaterials Inc. As characterized by US Research Nanomaterials Inc., SWCNTs had purity > 90%, with a diameter of 1–2 nm and a length of 5–30 μm . The outer diameter of MWCNTs ranged from 10 to 30 nm, while their length ranged from 10 to 30 μm . The purity of MWCNTs was higher than 90%. The outer diameter of MWCNT-COOH ranged from 10 to 20 nm, while their length ranged from 10 to 30 μm . The purity of MWCNT-COOH was higher than 95%. All CNTs used in the study had < 1.5 wt% ash content. Fullerene (C_{60} , CAS#99685–96-8) was obtained from BuckyUSA Inc. with purity > 98%. Graphene oxide (GO) with purity > 99% was obtained from CheapTubes Inc. Granular activated carbon (GAC, CAS# 7440–44-0), hexadecyltrimethylammonium bromide (CTAB, CAS#57–09-0), humic acid(HA, CAS#1415–93-6) and sodium carbonate (Na_2CO_3 , CAS#497–19-8) were obtained from Sigma Aldrich. Quartz sand (whole grain silica, plant: Ottawa, Illinois, silicon dioxide content > 99.8%) was obtained from US Silica Company with an average size of approximately 0.3 mm. All materials and chemicals were used without any further purification. The surface soil sample (top ~ 10 cm) used in our study was collected from Wilmington, Ohio, U.S. (Xenia series silty loam soil: 74% silt, 17% clay and 9% sand (<http://ncsslabsdatamart.sc.egov.usda.gov>), and the total organic carbon content of the soil analyzed using a total organic carbon analyzer (Shimadzu TOC-L with solids sample module SSM-5000A) was 1.15%. Roots, grass and leaves were removed from the soil, and the aggregates were mixed thoroughly and passed through a 2 mm sieve. Anaerobic sludge was collected from Fairfield Wastewater Treatment Plant, Fairfield, Ohio, U.S. (total organic carbon content 41.08%).

2.2. Microwave device setup

A microwave generator (Ophos GMP150) was used to deliver a uniform microwave field. The frequency of the generator was 2450 MHz (microwave wavelength = 12.24 cm). A rectangular WR-284 waveguide was made of copper with an inner width of 7.21 cm and a height of 3.40 cm. A hole was drilled on the wall of the waveguide so that a Teflon® sample holder with a diameter of 1 cm could be inserted through the hole for microwave irradiation. To avoid microwave leakage, a shielding enclosure with a side access door was also built. The microwave field setup that was used in this study can be either open or closed. The open microwave system is able to provide a stable and uniform microwave field so that the temperature readings are consistent, while a closed system can provide more intense microwave field because of the reflections within the microwave. An open system was used for this study, which is different from the configuration in Irin et al.'s study. An infrared (IR) temperature probe (with close-focus optics) from Omega was used to measure the temperature change in the samples. Since the microwave heating is a local heating process, the IR probe was installed to detect temperature changes after the microwave irradiation, instead of thermocouple used in Irin et al.'s study. The IR setup offered more consistent and accurate temperature measurement. A custom-built data acquisition and control system was established to allow for remote control and data logging of the Ophos GMP150 microwave generator and the IR temperature probe. A schematic of the microwave device used in this

study is depicted in Supplementary Data (SD, Fig. SD 1), and calibration checks for the IR probe are presented in Table SD 1.

2.3. Sample preparation

Individual 0.3 mg/ml CNT dispersions were prepared for SWCNTs, MWCNTs and MWCNT-COOH by dispersing 6 mg of each CNT into a 20 ml aqueous solution containing 0.1% w/v CTAB as a positively charged surfactant, and sonicating the dispersion in a bath sonicator (100 W, Fisher Scientific, FS30) for 4 h. A 0.3 mg/ml GO dispersion was prepared by adding 2.4 mg GO into 8 ml of water followed by sonication for 4 h. All dispersions were prepared before use for each experiment to assure their stability.

For the generation of mass-temperature-increase calibration curves, an aliquot of each dispersion was added into each of the three environmental matrices considered in this study. To keep the volume of the sample that is exposed to microwave energy the same between each environmental matrix, 130 mg quartz sand, 100 mg soil or 5 ml sludge (dry weight: 15.3 mg) were spiked with 0–2 ml of a given 0.3 mg/ml CNT dispersion to yield samples with CNTs that varied from 0 to 0.6 mg within each type of sample. These samples were then tumbled end-over-end for 10 min, frozen at – 80 °C overnight and freeze dried (MillRock, Benchtop Manifold Freeze-Dryer BT48) for several days to eliminate water before microwave measurement. The CNT containing freeze dried samples were exposed to a constant microwave energy for a given length of time, and the resulting temperature increase (T , °C) was plotted against the mass of CNTs to yield each calibration curve. All samples were prepared in triplicate, each sample was measured 3 times, and the average value of the 9 measurements was used as a representative value for each sample. Error bars in all figures indicate standard deviation. All mass-temperature calibration curves were generated using SAS software (SAS Institute Inc., Cary, NC), and t -test was conducted to compare the slopes of calibration curves for each combination of matrix and type of CNT.

For the inorganic carbon test (in section 3.5), 0.1–1 ml of 6 wt% Na_2CO_3 solution was added to soil samples containing 0.3 ml of 0.3 mg/ml CNTs. All samples were freeze dried before microwave measurement (133 W/15 s). For the organic carbon test (in section 3.5), soil-HA mixture samples were prepared by mixing 80, 160, 240 and 320 mg HA in 2 g soil in a tumbler for 7 days. The organic carbon content of the soil-HA mixtures were in the range 1.15–7.75 mg/100 mg soil as obtained by TOC analysis. Each of the soil-HA samples was spiked with 0.3 ml of 0.3 mg/ml CNTs.

For experiments in Section 3.6, soil mixtures were prepared by mixing 2 g soil with 60, 90, 180 mg C60, and 30, 60, 90 mg GAC, respectively, in a tumbler for 7 days. Then, 100 mg soil samples were taken from each soil mixture, and mixed with 0.3 ml of 0.3 mg/ml CNTs. For the experiment with GO, each soil sample (100 mg pure soil) was mixed with 0.3, 0.6 or 0.9 ml of 0.3 mg/ml GO dispersion and 0.3 ml of 0.3 mg/ml CNTs. All samples were freeze dried and exposed to a microwave field (133 W/15 s).

3. Results and discussion

3.1. Microwave conditions

Microwave heating is a result of the conversion of microwave energy to heat, and the conversion is described in Equation (Eq. (1)) (Clark et al., 2000),

$$\frac{\Delta T \rho C_p}{\Delta t} = 2 \pi f \epsilon_0 \epsilon_{\text{eff}} E^2 \quad (1)$$

where ΔT is the temperature increase ($^{\circ}\text{C}$), t is exposure time (s), C_p is the heat capacity (J/K), ρ is the density (kg/m^3), E is the electric field (N/C), ϵ_0 is the permittivity of free space ($\text{C}^2/\text{N}\cdot\text{m}^2$) and ϵ_{eff} is the complex component of the relative permittivity of the dielectric of a material, also known as dielectric loss factor (F/m). Therefore, all other variables being constant, ΔT is influenced by microwave conditions and the properties of the material exposed to the microwave field. In this section, the relationship between ΔT and microwave conditions is discussed. Microwave power and exposure time are chosen such that the heat produced is detectable, but is not high enough to damage the CNTs. Fig. 1(a) shows the ΔT grid that is obtained upon microwaving 0.09 mg MWCNTs in sand at varying microwave power (70–149 W) and time (15–30 s). It can be seen that a higher temperature rise was obtained when greater microwave power and longer exposure time were provided, and that power is the more important variable of the two (as the temperature rise was larger at high power/low exposure duration than vice versa for a given amount of microwave energy (power $\times$ time, J)). The results indicated that CNTs were more active in absorbing microwave energy at higher power (Fig. 1(b)), which was in agreement with the results obtained previously (Irin et al., 2012). Thus, considering energy savings and a moderate, yet detectable temperature rise, all environmental samples were either exposed to 100 W/20 s and/or 133 W/15 s in all subsequent experiments.

3.2. Development of calibration curves

Prior to the development of the calibration curves, a few control experiments were conducted at 133 W/30 s, including those with control environmental samples (CNTs-free quartz sand, soil, and sludge samples), surfactant CTAB and CNT alone. These baseline results indicated that CNTs were more sensitive to microwave energy than environmental samples and surfactant alone (Fig. SD 2), which made it possible to differentiate CNTs from sand, soil and sludge samples.

Fig. 2(a) and 2(b) show the calibration curves that were obtained for SWCNTs, MWCNTs and MWCNT-COOH in sand at 100 W/20 s and 133 W/15 s exposure, respectively. Although the samples were exposed to the same microwave energy (2000 J), the slopes of curves for all CNTs at 133 W/15 s exposure were larger than those observed at 100 W/20 s, confirming that CNTs were more sensitive to power than exposure time as discussed in Section 3.1. In addition, the sensitivity of the CNTs (higher slope) to microwave exposure decreased in the order: MWCNTs, SWCNTs and MWCNT-COOH. Fig. 2(c) and 2(d) show similar calibration curves that were obtained for soil and sludge at 133 W/15 s exposure,

respectively, and the observed trends were similar to those observed for sand. Similarly, the calibration curves obtained at 100 W/20 s exposure for both soil and sludge had smaller slopes than the ones obtained at 133 W/15 s, which are shown in Fig. SD 3.

At 133 W/15 s exposure, the slope of MWCNTs was $1.38 \times$ and $2.37 \times$ the slopes of SWCNTs and MWCNT-COOH in sand samples, respectively, while the corresponding values were higher in soil ($1.63 \times$ and $2.47 \times$, respectively) and sludge ($2.11 \times$ and $3.76 \times$, respectively) samples. The microwave response mechanism(s) for the different types of CNTs are not completely understood by the scientific community, and there are no systematic studies investigating the effect of microwave energy on the different types of CNTs. Dielectric heating is commonly considered as the major mechanism behind the observed temperature rise in CNT-containing samples when exposed to a microwave field, as shown in Eq.(1). Since “perfect” CNTs (no defects) do not exhibit an electric dipole, it is theorized that structural imperfections in CNTs hinder transport of electrons when exposed to a microwave field, thus allowing dielectric heating to occur, which in turn converts microwave irradiation into local heating (Vázquez and Prato, 2009). Since the structural defects are random within the CNTs, a uniform microwave field is required to maintain consistent response (temperature rise). The dielectric loss factor (ϵ_{eff} in Eq.(1), the imaginary component of the dielectric constant, specifies the ability of a material to convert electromagnetic energy to heat. The dielectric loss factors at 2.45 GHz are ~ 100 for SWCNT (Li and Juh-Tzeng, 2007) and $\sim 200\text{--}300$ for MWCNT (Wang and Deng, 2005) which is relatively large compared to other materials. The higher dielectric loss factor for MWCNTs could be the reason why MWCNTs exhibit better sensitivity to microwave energy when compared to SWCNTs. The dielectric loss factors for functionalized CNTs have not been reported in the literature. However, Paton et al. found that functionalized MWCNTs were less efficient at absorbing microwave energy at 700 W, 2.45 GHz compared to pristine MWCNTs (Paton and Windle, 2008). Similarly, Hu et al. reported a decrease in microwave energy (160 W, 30 s) absorption capacity with increased number of oxygens on graphene (Hu et al., 2012). The sensitivity of CNT response to microwave irradiation is thought to be dependent on the π -electron system. The presence of functional groups on the walls of CNTs diminish the size of π - π conjugated region in the CNTs, leading to less energy absorption by the functionalized CNTs (Hu et al., 2012, Schwenke et al., 2015) and causing MWCNT-COOH to be less sensitive when exposed to the same microwave energy than pristine CNTs.

Results on the influence of different environmental matrices (sand, soil and sludge) on microwave absorption are shown in Fig. 3. To obtain the subtracted ΔT values shown in the Figure, the ΔT values for the CNT + matrix was subtracted from their respective control samples (CNT-free matrix samples). For each type of CNTs, the slopes in different medium have been compared by t -test, and all p values were < 0.001 , indicating that slopes in different matrices were significantly different for the same type CNTs.

For the same amount of CNTs, the greatest temperature increases were observed in sand, while the increases were the smallest in the sludge samples. Soil and sludge samples, which contain 1.15% and 41.08% of organic carbon, respectively, can also absorb microwave energy, potentially resulting in less energy being available for the CNTs. The amount of

microwave energy available for absorption by the CNTs seems to be related primarily to the amount of organic matter in the environmental matrices as shown by the slope of soil samples (lower organic carbon content) being closer to sand (no organic carbon content) when compared to sludge (high organic carbon content). Therefore, the lower available energy for the soil and sludge samples could result in lower response for these samples when compared to sand. In addition, the effect of organic matter on MWCNT-COOH is more pronounced, likely because of its poor efficiency in microwave energy absorption when compared to non-functionalized CNTs.

3.3. Method detection limit (MDL)

The MDLs for this method were determined for the three types of CNTs in the three environmental matrices using EPA 40 CFR part 136, Appendix B, revision 1.11 (Eq. (2)):

$$MDL = t_{(n-1, 0.99)} * STD \quad 2$$

where n is the number of replicates (7 for this study), $t_{0.99}$ is the t-statistic (3.14 at 99% confidence for 6 degrees of freedom), and STD is standard deviation of the 7 replicates (lowest concentration standard in this study). All MDLs (unit of μg CNTs/g environmental sample) were obtained at 133 W/15 s for each CNT-media combination, and are tabulated in Table 1. The MDL for soil was determined to be 40.09, 27.92 and 50.16 $\mu\text{g/g}$ soil for SWCNTs, MWCNTs and MWCNT-COOH, respectively, which was lower than those obtained using other methods (e.g., 100 μg SWCNT/g soil using thermogravimetric analysis coupled with mass spectrometry (Plata et al., 2012)). The MDLs of CNTs in sludge samples are reported for the first time. The MDLs were relatively high compared with the other two samples, because the high organic carbon content makes the less available microwave energy for CNTs. As we discussed in the Section 3.1, the temperature rises may be enlarged with a higher microwave energy input, especially the stronger microwave power. Therefore, it is worth noting that the MDLs in Table 1 were obtained at 133 W/15 s in current study, and the MDLs and sensitivity of the method could be improved by changing the microwave condition for complex matrices (e.g. sludge). More discussion and explanation are in Section 3.4. and 3.5.

The reliability and repeatability of the microwave method for quantifying CNTs in environmental samples were confirmed by conducting multiple analyses with known amounts of CNTs in the three environmental matrices (results summarized in Table SD 2).

3.4 Effect of environmental sample mass

The results in Section 3.2 were based on choosing a single amount of environmental sample (130 mg sand, 100 mg soil and 15 mg sludge) being used for each experiment. To study the effect of choosing varying amounts of environmental samples, freeze dried sand (130 and 60 mg), soil (100 and 45 mg) and sludge (15.3 and 10.3 mg) were exposed to 133 W microwave power for 30 s. The results (T vs. t) of using the two different amounts of each environmental sample are shown in Fig. 4(a). The two temperature curves for sand overlapped, and did not increase over 30 s of microwave irradiation, indicating that

variations in sand mass are not likely to affect CNT quantification using this method. However, the temperature curves were different for soil and sludge samples, with the variations for the sludge samples being more pronounced than those of the soil samples. To investigate the effect of soil and sludge sample masses, calibration curves were generated based on different mass of soil (100 and 45 mg) and sludge (15.3 and 10.3 mg). Fig. 4(b) shows that the temperature curves for MWCNT in 100 and 45 mg soil samples were parallel, indicating that the changes in mass of soil did not influence the microwave energy applied to MWCNTs. For sludge samples, the temperature curves for MWCNT were highly dependent on the mass of the sludge used (Fig. 4(c)), with lower sludge amounts yielding higher T .

Similar trends were observed for SWCNT and MWCNT-COOH in both soil and sludge samples (Fig. SD 4(a)–(d)). This could be explained by the amount of microwave energy taken up by CNTs vs. the other organic matter that is present in environmental samples. The total energy absorbed by the CNT-spiked environmental sample (Q) is represented as $Q = C_{pm} \Delta T$ (where C_p is the heat capacity and m is the mass of the material exposed to the microwave), which is the sum of energies absorbed by the CNTs and the environmental matrix (EM):

$$Q = Q_{EM} + Q_{CNT} = C_{p,EM} m_{EM} \Delta T_{EM} + C_{p,CNT} m_{CNT} \Delta T_{CNT}$$

At any given microwave condition (constant Q), when less sludge sample was used, a smaller ΔT_{EM} made Q_{EM} smaller, in turn leading to larger Q_{CNT} .

3.5. Microwave behavior of organic and inorganic carbon

A reliable methodology for determining CNTs in environmental samples should be able to overcome any interference from background material. In particular, as shown previously, background organic matter absorbs microwave energy and emits heat similar to CNTs. In this experiment, the effect of varying amounts of other forms of organic and inorganic carbon that are typically found in environmental matrices on CNT quantification using the microwave method was studied. For these set of experiments, Na_2CO_3 was chosen as the inorganic carbon source and HA was chosen as the organic carbon source. From Fig. 5(a), it can be seen that the addition of Na_2CO_3 did not have any influence on the microwave measurement of CNTs in soil, and that the temperature increase for all types of CNTs (0.09 mg) remained the same with increasing inorganic carbon to CNTs ratio from 7.5 to 75. The presence of inorganic carbon will most likely not interfere with CNTs quantification by using the microwave technique because these chemicals do not absorb microwave energy or release heat when exposed to a microwave field.

For the organic carbon test, all samples were exposed to 133 W microwave power for 15 s after they were freeze dried. Results indicated that the temperature of the soil samples containing HA (with no CNTs) increased between 1.35 and 1.63 °C with increasing amounts of HA (Fig. 5(b)), while ΔT generally decreased with increasing HA for the CNT spiked soil samples (3.84 °C to 3.31 °C for MWCNTs; 3.23 °C to 2.67 °C for SWCNTs; 2.72 °C to 2.15 °C for MWCNT-COOH). The increasing ΔT for CNT-free soil samples indicates that the HA could absorb microwave energy, thus contributing to the release of heat, while the

decrease in ΔT for CNT-containing soil samples may be due to the saturation of the microwave energy (133 W, 15 s), i.e., some of the energy is taken up by HA, leaving lower amounts of microwave energy for the CNTs. To test this hypothesis, higher microwave energy (149 W, 30 s) was provided to CNT-containing soil samples. Results from using the higher microwave energy show that the ΔT for the CNT-containing soil samples increases with increasing HA concentration (Fig. 5(c)) as expected, while the contributions by the CNTs remained the same (Fig. 5(d)) at the higher energy. These results indicate that the interference from background organic carbon can potentially be eliminated by adjusting the total microwave energy being imparted to the sample. In addition, from Fig. 5(b), the background subtracted ΔT of CNTs in soil-HA sample with 6.36 mg organic carbon was 1.97 °C (from 3.57 °C to 1.60 °C, Fig. 5(b)), while the background subtracted ΔT of the same amount of CNTs in 15.3 mg sludge sample with 6.27 mg organic carbon was 1.98 °C (calculated from previously generated calibration curve in Fig. 3(b) for MWCNT). The close results for the two types of samples indicate that the background subtracted ΔT would be very similar if the environmental samples contained similar amounts of natural organic carbon, and that the type of natural organic carbon without the special dielectric loss factors of CNTs may not be as important. This would also explain the differences in ΔT of soil and sludge samples for similar amounts of CNTs.

3.6. Microwave heating behavior of other carbon based materials

In addition to CNTs, the application of other carbon based nanomaterials, some of which have properties that are similar to CNTs, is also growing; so, these different carbon nanomaterials may enter the environment in conjunction with the CNTs. Therefore, to verify the reliability of the microwave quantification method, the effect of other carbon sources that are similar to CNTs on the microwave measurement of CNTs was examined. Similar to CNTs, fullerene (C_{60}) and GO are composed of sp^2 bonds, and GAC is widely used in filtration and purification during water and wastewater treatment. Hence, these samples were chosen as representative carbon-based materials, and soil was used as a model environmental matrix.

Control experiments were carried out to determine the effect of pure C_{60} , GAC and GO on the microwave heating response. Results indicate that C_{60} and GAC are not affected by the microwave energy (Fig. 6(a)). Although the ΔT for GO increased by 2.55 °C, it was still much smaller than that of CNTs, even though its mass (5 mg) was much more than that of CNTs (0.1 mg). In addition, the ΔT for GO did not increase with time, likely indicating that the amount of background ΔT contributed by GO will remain the same for all samples. CNTs had a stronger microwave response compared to these carbon materials. A comparison of some other sp^2 based carbon nanomaterials (graphene, functionalized fullerene, carbon black and graphite flakes) also showed similar results (Irin et al., 2012). Results for the CNT-spiked soil samples containing varying amounts of C_{60} , GAC and GO are shown in Fig. 6(b)–(d), respectively. These results (standard deviation < 6%) indicate that the three carbon sources did not have any effect on the quantifications of CNTs in environmental samples that contain these materials.

With significant increasing demand of CNTs worldwide, it is necessary to assess potential exposure during the production, use and disposal of the product containing CNTs, toxicity after exposure, and the fate and transport of CNTs in environmental matrices (Plata et al., 2016). Hence, a quantitative method for CNTs in some key environmental matrices (e.g. water, soil/sediment, biological samples) would be helpful in addressing some of the concerns and questions raised above.

The microwave heating method described in this paper can be used to selectively detect and quantify CNTs in environmental samples containing different other forms of carbon. This is a rapid, consistent and cheap method. For an unknown sample matrix, the amount of CNTs in the sample can be easily obtained from calibration curves generated for this matrix. However, if no information on the matrix is available, qualitative information such as the presence/absence of CNTs may still be obtained using this method by conducting spiking studies and monitoring ΔT after microwave irradiation since the ΔT for matrices containing CNTs were shown to be much higher than matrices containing other forms of carbon.

4. Conclusions

Since the substantial production and widespread applications of CNTs can potentially enhance the possibility of the release of CNTs into the environment, it is essential to develop a sensitive and reliable method to detect CNTs in different environmental matrices. In this study, a microwave induced heating system was applied to selectively quantify SWCNT, MWCNT and MWCNT-COOH from sand, soil and sludge samples, and even in the mixture with other carbon based nanomaterials. All three different types of CNTs tested released detectable amounts of heat under microwave irradiation, and the microwave heating behavior of CNTs was dependent more upon microwave power than exposure time. Environmental matrices with high organic content, like sludge, can absorb microwave energy, resulting in less energy being available to CNTs. Moreover, the heating behavior of CNTs was not affected by the excess presence of other carbon based materials (inorganic carbon, organic carbon, C₆₀, GAC and GO), indicating the method's selectiveness for heating CNTs. Additionally, the MDLs depended on the types of CNTs and organic content in the matrix. In future work, the microwave method used in this study will be used to investigate the interactions of CNTs with other environmental media, determine the toxicity of CNTs to various organisms, and study the fate and transport of CNTs in the environment. In addition, future work will also include the development of analytical techniques that can provide confirmatory analysis and analysis of blind sample matrices with known quantities of CNTs to verify the efficacy of this microwave-based method for quantitative results.

Supplementary Material

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Acknowledgements

This research was funded and conducted by the National Risk Management Research Laboratory of U.S. Environmental Protection Agency (EPA), Cincinnati, Ohio. This manuscript was subjected to EPA internal reviews and quality assurance approval. The research results presented in this paper do not necessarily reflect the views of the Agency or its policy. Mention of trade names or products does not constitute endorsement or recommendation

for use. The authors would like to thank Dr. Raghuraman Venkatapathy for valuable comments on the manuscript and Mr. Phillip Cluxton for technical and laboratory support.

Abbreviations

CNT(s)	Carbon nanotube(s)
CTAB	Hexadecyltrimethylammonium bromide
C₆₀	Fullerene
GAC	Granular activated carbon
GO	Graphene oxide
HA	Humic Acid
MDL(s)	Method detection limit (s)
MWCNT(s)	Multi-walled carbon nanotube (s)
MWCNT-COOH	Carboxylated MWCNT
SWCNT(s)	Single-walled carbon nanotube (s)

References

- Angelikopoulos P, Gromov A, Leen A, Nerushev O, Bock H, Campbell EEB, 2010 Dispersing individual single-wall carbon nanotubes in aqueous surfactant solutions below the cmc. *J. Phys. Chem. C* 114 (1), 2–9.
- Baur J, Silverman E, 2007 Challenges and opportunities in multifunctional nanocomposite structures for aerospace applications. *MRS Bull.* 32 (04), 328–334.
- Bourdiol F, Dubuc D, Grenier K, Mouchet F, Gauthier L, Flahaut E, 2015 Quantitative detection of carbon nanotubes in biological samples by an original method based on microwave permittivity measurements. *Carbon* 81, 535–545.
- Clark DE, Folz DC, West JK, 2000 Processing materials with microwave energy. *Mater. Sci. Eng. A* 287 (2), 153–158.
- De Volder MFL, Tawfick SH, Baughman RH, Hart AJ, 2013 Carbon nanotubes: present and future commercial applications. *Science* 339 (6119), 535–539. [PubMed: 23372006]
- Doudrick K, Herckes P, Westerhoff P, 2012 Detection of carbon nanotubes in environmental matrices using programmed thermal analysis. *Environ. Sci. Technol.* 46 (22), 12246–12253. [PubMed: 22663014]
- Herrero-Latorre C, Alvarez-Mendez J, Barciela-Garcia J, Garcia-Martin S, Pena-Creciente RM, 2015 Characterization of carbon nanotubes and analytical methods for their determination in environmental and biological samples: a review. *Anal. Chim. Acta* 853, 77–94. [PubMed: 25467451]
- <http://ncsslabsdatamart.sc.egov.usda.gov> National Cooperative Soil Survey (NCSS) Soil Characterization Database.
- Hu H, Zhao Z, Zhou Q, Gogotsi Y, Qiu J, 2012 The role of microwave absorption on formation of graphene from graphite oxide. *Carbon* 50 (9), 3267–3273.
- Iijima S, 1991 Helical microtubules of graphitic carbon. *Nature* 354 (6348), 56.
- Imholt TJ, Dyke CA, Hasslacher B, Perez JM, Price DW, Roberts JA, Scott JB, Wadhawan A, Ye Z, Tour JM, 2003 Nanotubes in microwave fields: light emission, intense heat, outgassing, and reconstruction. *Chem. Mater.* 15 (21), 3969–3970.

- Irin F, Shrestha B, Canas JE, Saed MA, Green MJ, 2012 Detection of carbon nano- tubes in biological samples through microwave-induced heating. *Carbon* 50 (12), 4441–4449.
- Jeong J, Lee YJ, Hwang YS, Hong IS, 2015 Selective detection and quantification of carbon nanotubes in soil. *Environ. Toxicol. Chem.* 34 (9), 1969–1974. [PubMed: 25931381]
- Jeong SH, Kim KK, Jeong SJ, An KH, Lee SH, Lee YH, 2007 Optical absorption spec- troscopy for determining carbon nanotube concentration in solution. *Synth. Met.* 157 (13–15), 570–574.
- Lee J, Mahendra S, Alvarez PJJ, 2010 Nanomaterials in the construction industry: a re- view of their applications and environmental health and safety considerations. *ACS Nano* 4 (7), 3580–3590. [PubMed: 20695513]
- Li S, Irin F, Atore FO, Green MJ, Canas-Carrell JE, 2013 Determination of multi-walled carbon nanotube bioaccumulation in earthworms measured by a microwave-based detection technique. *Sci. Total Environ.* 445–446, 9–13. [PubMed: 23183125]
- Li Y-H, Juh-Tzenga a.L., 2007 Dielectric constants of single-wall carbon nanotubes at various frequencies. *J. Nanosci. Nanotechnol.* 7 (8), 1–4. [PubMed: 17455473]
- Li ZF, Luo GH, Zhou WP, Wei F, Xiang R, Liu YP, 2006 The quantitative character- ization of the concentration and dispersion of multi-walled carbon nanotubes in sus- pension by spectrophotometry. *Nanotechnology* 17 (15), 3692–3698.
- Liu Z, Tabakman S, Welsher K, Dai H, 2009 Carbon nanotubes in biology and medicine: in vitro and in vivo detection, imaging and drug delivery. *Nano Res* 2 (2), 85–120. [PubMed: 20174481]
- Mota LC, UrenÍfa-Benavides EE, Yoon Y, Son A, 2013 Quantitative detection of single walled carbon nanotube in water using DNA and magnetic fluorescent spheres. *Environ. Sci. Technol* 47 (1), 493–501. [PubMed: 23214724]
- Nowack B, David RM, Fissan H, Morris H, Shatkin JA, Stintz M, Zepp R, Brouwer D, 2013 Potential release scenarios for carbon nanotubes used in composites. *Environ. Int.* 59, 1–11. [PubMed: 23708563]
- Oberdörster G, Oberdörster E, Oberdörster J, 2005 Nanotoxicology: an emerging disci- pline evolving from studies of ultrafine particles. *Environ. Health Perspect.* 113 (7), 823–839. [PubMed: 16002369]
- Paton KR, Windle AH, 2008 Efficient microwave energy absorption by carbon nano- tubes. *Carbon* 46 (14), 1935–1941.
- Petersen EJ, Zhang L, Mattison N, O'Carroll D, Whelton A, Uddin N, Nguyen T, Huang Q, Henry T, Holbrook R, Chen K, 2011 Potential release pathways, envi- ronmental fate, and ecological risks of carbon nanotubes. *Environ. Sci. Technol.* 45 (23), 9837–9856. [PubMed: 21988187]
- Petersen EJ, Flores-Cervante D, Bucheli T, Elliott L, Fagan J, Gogos A, Hanna S, Kagi R, Mansfield E, Bustos ARM, Plata D, Reipa V, Westerhoff P, Winchester M, 2016 Quantification of carbon nanotubes in environmental matrices: current capabilities, case studies, and future prospects. *Environ. Sci. Technol.* 50 (9), 4587–4605. [PubMed: 27050152]
- Plata DL, Reddy CM, Gschwend PM, 2012 Thermogravimetry-mass spectrometry for carbon nanotube detection in complex mixtures. *Environ. Sci. Technol.* 46 (22), 12254–12261. [PubMed: 22283840]
- Robinson JP, Kingman SW, Onobrakpeya O, 2008 Microwave-assisted stripping of oil contaminated drill cuttings. *J. Environ. Manag.* 88 (2), 211–218.
- Schierz A, Parks AN, Washburn KM, Chandler GT, Ferguson PL, 2012 Characterization and quantitative analysis of single-walled carbon nanotubes in the aquatic envi- ronment using near-infrared fluorescence spectroscopy. *Environ. Sci. Technol.* 46 (22), 12262–12271. [PubMed: 22970987]
- Schwenke AM, Hoepfner S, Schubert US, 2015 Synthesis and modification of carbon nanomaterials utilizing microwave heating. *Adv. Mater.* 27 (28), 4113–4141. [PubMed: 26087742]
- Sobek A, Bucheli TD, 2009 Testing the resistance of single- and multi-walled carbon nanotubes to chemothermal oxidation used to isolate soots from environmental sam- ples. *Environ. Pollut.* 157 (4), 1065–1071. [PubMed: 18952329]
- Vance ME, Kuiken T, Vejerano EP, McGinnis SP, Hochella MF, Jr., Rejeski D, Hull MS, 2015 Nanotechnology in the real world: redeveloping the nanomaterial con- sumer products inventory. *Beilstein Journal of Nanotechnology* 6, 1769–1780. [PubMed: 26425429]

- Vázquez E, Prato M, 2009 Carbon nanotubes and microwaves: interactions, responses, and applications. *ACS Nano* 3 (12), 3819–3824. [PubMed: 20025299]
- Wang L, Dang Z-M, 2005 Carbon nanotube composites with high dielectric constant at low percolation threshold. *Appl. Phys. Lett* 87 (4) 042903.
- Wiesner MR, Lowry GV, Alvarez P, Dionysiou D, Biswas P, 2006 Assessing the risks of manufactured nanomaterials. *Environ. Sci. Technol.* 40 (14), 4336–4345. [PubMed: 16903268]
- www.marketsandmarkets.com 2015. Carbon Nanotubes Market by Type (Single Walled- And Multi-Walled), by Application (Electronics & Semiconductors, Chemical & Polymers, Batteries & Capacitors, Energy, Medical Application, Advanced Materials, Aerospace & Defense, Others) - Global Forecasts to 2020.
- Yang M, Kwon S, Kostov Y, Rasooly A, Rao G, Ghosh U, 2011 Study of the biouptake of labeled single-walled carbon nanotubes using fluorescence-based method. *Environ. Chem. Lett.* 9 (2), 235–241.
- Ye Y, Cai S, Yan M, Chen T, Guo T, 2013 Concentration detection of carbon nanotubes in electrophoretic suspension with UV–vis spectrophotometry for application in field emission devices. *Appl. Surf. Sci.* 284, 107–112.

Fig. 1. Effect of (a) microwave power and exposure time on temperature rise of 0.09 mg MWCNTs in sand; (b) microwave energy on temperature rise of 0.09 mg MWCNTs in sand.

Fig. 2. Calibration curves for (a) CNT-spiked sand at 100 W for 20 s exposure; (b) CNT-spiked sand at 133 W for 15 s exposure; (c) CNT-spiked soil at 133 W for 15 s exposure; (d) CNT-spiked in sludge at 133 W for 15 s exposure.

Fig. 3.

Comparison of calibration curves generated in different environmental samples at 133 W/15 s exposure for (a) SWCNTs; (b) MWCNTs; (c) MWCNT-COOH.

Fig. 4. Effect of environmental sample mass. (a) Temperature profiles for different mass of environmental media; (b) Calibration curves based on different mass of soil for MWCNTs; (c) Calibration curves based on different mass of sludge for MWCNTs.

Fig. 5.

(a) Effect of inorganic carbon on microwave behavior of 0.09 mg CNTs in soil at 133 W/15 s exposure time; (b) Effect of organic carbon on microwave behavior of CNTs in soil at 133 W/15 s exposure time; (c) Effect of organic carbon on microwave behavior of CNTs in soil at 149 W/30 s exposure time; (d) Background corrected ΔT at 149 W/30 s exposure time.

Fig. 6. Effect of different carbon based materials on temperature rise of 0.09 mg CNTs. (a) Temperature profiles of some carbon based materials; (b) C_{60} ; (c) GAC; (d) GO.

Table 1.

MDL of different types of CNTs in three environmental matrices (unit: μg CNTs/g environmental sample) at 133 W/15 s exposure.

	SWCNT	MWCNT	MWCNT-COOH
Sand	22.70	18.61	32.16
Soil	40.09	27.92	50.16
Sludge	1222.40	814.40	2021.92