

Industrially synthesized single-walled carbon nanotubes: compositional data for users, environmental risk assessments, and source apportionment

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Abstract

Commercially available single-walled carbon nanotubes (SWCNTs) contain large percentages of metal and carbonaceous impurities. These fractions influence the SWCNT physical properties and performance, yet their chemical compositions are not well defined. This lack of information also precludes accurate environmental risk assessments for specific SWCNT stocks, which emerging local legislation requires of nanomaterial manufacturers. To address these needs, we measured the elemental, molecular, and stable carbon isotope compositions of commercially available SWCNTs. As expected, catalytic metals occurred at per cent levels (1.3–29%), but purified materials also contained unexpected metals (e.g., Cu, Pb at 0.1–0.3 ppt). Nitrogen contents (up to 0.48%) were typically greater in arc-produced SWCNTs than in those derived from chemical vapor deposition. Toluene-extractable materials contributed less than 5% of the total mass of the SWCNTs. Internal standard losses during dichloromethane extractions suggested that metals are available for reductive dehalogenation reactions, ultimately resulting in the degradation of aromatic internal standards. The carbon isotope content of the extracted material suggested that SWCNTs acquired much of their carbonaceous contamination from their storage environment. Some of the SWCNTs, themselves, were highly depleted in ¹³C relative to petroleum-derived chemicals. The distinct carbon isotopic signatures and unique metal ‘fingerprints’ may be useful as environmental tracers allowing assessment of SWCNT sources to the environment.

1. Introduction

Single-walled carbon nanotubes (SWCNTs) are promising new materials noted for their exceptional electrical properties, mechanical strength, and thermal stability. Due to their unique characteristics and novel synthetic methods, there is a great deal of uncertainty surrounding the possible influence of SWCNTs on the environment [1] and human health [2]. Previous efforts to assess the risks associated with the industry have considered production reagents and energy use [3], but there is a distinct lack of information regarding the environmental influence of the produced nanomaterials

themselves. Two recent reports [1, 4] highlighted the need for such analyses, outlining challenges to the safe advancement of the SWCNT industry. Explicitly, the authors call for the development of (1) methods to assess the environmental fate of engineered nanomaterials and (2) nanomaterial-specific toxicity data for dependable risk assessment modeling. Wiesner *et al* [1] emphasize that surface chemistry and morphology may influence the toxicity and environmental mobility of a given nanoparticle.

SWCNTs, which are formed from a variety of synthetic techniques, will have variable chemistries and physical properties resulting from their different metal catalysts or

Table 1. United States single-walled carbon nanotube manufacturers and purchase information.

SWCNT supplier name ^a	Symbol ^b	Production location ^c	Purchase price (g ⁻¹)	Purified? ^d	Purchase date
SES Research	SES	Houston, TX	\$375	Yes	1/14/06
Carbon Solutions Inc.	CSI	Riverside, CA	\$50		2/15/06
CarboLex, Inc.	CLex	Broomall, PA	\$100		2/14/06 ^e
Materials & Electrochemical Research Corp.	MER	Tucson, AZ	\$60		1/13/06
Helix Material Solutions	Helix	Richardson, TX	\$83		1/13/06
Manufacturer X ^f	ManX	Renton, WA	\$69.95	Yes	1/23/06
Nanocs Inc.	Nanocs	New York, NY	\$250	Yes	2/13/06
Nanostructured & Amorphous Materials	NanoAm	Houston, TX	\$210	Yes	2/13/06
SouthWest NanoTechnologies Inc. (SWeNT, Inc.)	SWPurified ^g	Norman, OK	\$500 ^g	Yes	3/9/06
	SWIntermed. ^h		\$200 ^h		
Carbon Nanotechnologies Inc.	CNI	Houston, TX	\$275		9/29/05 ⁱ

^a Companies that manufactured single-walled carbon nanotubes (SWCNTs) for commercial sale in the United States during September 2005 and March 2006 are listed. Companies that manufactured SWCNTs for direct incorporation into end-use products (i.e., flat-panel displays, bicycles, atomic force microscopes, polymer composites) are not listed.

^b Symbols used in the tables, figures, and text of this paper do not represent notations employed by the manufacturers.

^c SWCNT production location is shown. CarboLex, Inc. and Nanostructured and Amorphous Materials have affiliate offices in Lexington, KY, and Los Alamos, NV, respectively.

^d Select manufacturers reported removal of metal catalysts, inorganic supports, and/or amorphous carbon.

^e CLex SWCNTs are available for purchase through Sigma-Aldrich.

^f Manufacturer closed on 26 April 2006 and requested that we protect the identity of the business name.

^g Purified SWCNTs are routinely available from SWeNT, Inc.

^h SWIntermed. = SWIntermediate. This material represents an intermediate product in the manufacture of purified SWCNTs.

These SWCNTs are only available by special request from SWeNT, Inc., who provided us the opportunity to examine the SWCNT material mid-process.

ⁱ These nanotubes are synthesized using the HiPco[®] process and are often referred to as such in the literature. This sample is from lot number R0511C.

amorphous carbon coatings [5]. The latter can have environmental and toxicological impacts. For example, fluorescent fractions of the amorphous carbon associated with arc-produced SWCNTs impaired the development of estuarine copepods, whereas purified materials showed no remarkable toxicity [6]. Preliminary studies indicate no clear relationship between SWCNT metal content and respiratory impairment [7, 8]; however, the metal composition may dictate the environmental transport of, and ultimate biological exposure to, SWCNTs. For instance, oxides of the selected catalyst could confer charge on the nanomaterials. As surface charges control the aggregation of submicron-sized particles [9], SWCNTs with different metal catalysts may exhibit differing environmental lifetimes in air and water. Additionally, associated impurities could control SWCNT participation in photochemical processes and interactions with biological membranes [2, 10, 11]. Metal catalyst and amorphous carbon impurities can account for up to 70% of a bulk SWCNT material [12–14], yet these fractions are largely uncharacterized. Thus, our ignorance of the diversity of compositions of SWCNTs prohibits a mechanistic understanding of SWCNT electronic character, environmental transport, transformation, and ecotoxicology. Consequently, no predictive risk assessment models can be constructed at this time. Maynard *et al* [4] warn that this lack of information could result in eroded public confidence through real or apparent dangers, impacting market growth during this critical time of expansion, as well as unintended environmental and public health consequences.

To begin to rectify this situation, we determined the metal, carbon, nitrogen, stable carbon isotopic, and solvent-extractable aromatic hydrocarbon content of SWCNTs produced by ten companies in the United States (US) (table 1). Our specific goals were to (1) identify metal catalysts and aromatic hydrocarbons that would be released with and affect the properties of SWCNTs, (2) seek compositional data suited to pursuing environmental exposure modeling of SWCNTs, and (3) find properties that would be helpful for detecting, and perhaps apportioning the sources of, SWCNTs in environmental matrices. By pursuing these objectives while the SWCNT industry is developing large-capacity facilities, we seek to provide feedback to the manufacturers so as to avoid human health and environmental damage.

2. Experimental methods

2.1. Samples

SWCNTs were purchased from all known, US-based manufacturers between September 2005 and March 2006 (table 1). Advantageously, the materials represent a variety of fabrication techniques and include both purified and unpurified SWCNTs. As-produced SWCNTs (AP-SWCNTs) contain metal catalyst and amorphous carbon impurities and range in price from \$50 to \$275 g⁻¹. Purified SWCNTs are thermally and/or chemically treated and cost between \$70 and \$500 g⁻¹. To compare the differences in purified and unpurified SWCNTs, we analyzed nanotubes from one

manufacturer, SWeNT, Inc., before (SWIntermediate) and after purification (SWPurified) (table 1).

2.2. Metal, metalloid, and rare earth element analysis

Plastic and quartz ware were cleaned by soaking for two weeks in 3 M hydrochloric acid (HCl) and two days in 8 M nitric acid (HNO₃) at room temperature (acids were Fisher trace metal grade). SWCNTs were delivered to 10 ml quartz (Type IV) beakers in ethyl acetate (EtOAc) suspensions, evaporated to dryness, and combusted for 6 h at 850 °C. Samples were then digested by refluxing in 1 ml 16 M HNO₃ (Fisher optima) for 30 min, evaporated to dryness, dissolved in 3 ml 12 M HCl (Fisher optima), evaporated to dryness again, and finally re-dissolved with 1.2 M HCl. Solutions were filtered through 0.2 μm filters and analyzed in quadruplicate (duplicate measurement of two distinct dilutions) by inductively coupled plasma mass spectrometry (ICP-MS). Samples were analyzed for Al, Ag, Au, Ba, Be, Bi, By, Ca, Ce, Cd, Co, Cr, Cs, Cu, Er, Fe, Ga, Gd, Hf, Ho, Hg, Ir, La, Li, Lu, Mo, Nb, Nd, Ni, Os, Pb, Pr, Pt, Re, Rh, Ru, Sb, Sm, Sn, Sr, Ta, Tb, Te, Th, Ti, Tm, U, V, W, Y, Yb, and Zr. Only elements present above the detection limit are reported here. Detection limits (all in ppm) were 100 (CNI), 50 (Helix, Nanocs), 20 (CLex, CSI, MER, ManX, SES, SWPurified, SWIntermediate), and 7 (NanoAm), varying between samples due to differences in SWCNT sample size.

Silica was measured in two samples thought to contain SiO₂ as a growth substrate (SWPurified and SWIntermediate). Briefly, samples (5–10 mg) and LiBO₃ (~70 mg) were added to graphite crucibles and heated at 950 °C for 15 min [15]. The hot liquid was poured into a Teflon beaker, stirred with 10 ml of 0.8 M HNO₃ for 15 min, transferred to a tared plastic vial, and diluted with Milli-Q water to a final mass of 20 g. After filtration through a 0.45 μm filter, solutions were analyzed by ICP emission spectroscopy.

2.3. Determining the bulk carbon and nitrogen content of SWCNTs

SWCNTs were delivered to silver capsules (15 mm × 7.5 mm) in EtOAc suspensions using 1 ml, glass gas-tight syringes. The syringes were rinsed seven times between sample replicates and were disassembled and sonicated for 20 min in EtOAc between different SWCNT samples. After drying overnight (60 °C), the residue was analyzed for carbon (C) and nitrogen (N) content using an Elementar CHN Analyzer. Samples were analyzed in triplicate, except for CNI and CSI ($n = 6$).

EtOAc was used to deliver the SWCNTs to the silver capsules, as it improved precision by reducing sample loss and sample-to-sample contamination due to electrostatic interactions. To confirm that EtOAc did not affect our results, we compared the C content of the National Institute of Standards and Technology Standard Reference Material 1649a 'Urban Dust' delivered with and without EtOAc; both gave values that matched the certified C content.

In order to distinguish SWCNT-C from amorphous C and other carbonaceous impurities, we performed a temperature-programmed oxidation using thermogravimetric

analysis (TGA, TA Instruments Q50). The initial sample mass was 3–3.5 mg, except for SWIntermed., whose initial mass was much larger (15 mg) to compensate for the low expected C content. Each sample was heated at 5 °C min⁻¹ to 950 °C (10 min hold) in dry air. The differentiated thermogram was fit assuming a bimodal Gaussian distribution using a non-linear least squares technique. Co-oxidizing phases can bias the analysis, giving higher-than-actual measured C content. These phases were present in SES (giving an overestimate of amorphous C), CSI (giving an overestimate of SWCNT-C), and MER samples.

2.4. Determining the stable carbon isotopic content of SWCNTs

Dry SWCNTs were transferred to a 9 mm cylindrical quartz insert, which was then inverted into a 12 mm quartz tube containing roughly 2 g of cupric oxide. The tubes were evacuated on a vacuum line, flame sealed, and combusted for 5 h at 850 °C. Carbon dioxide was isolated through a series of cold traps and ¹³C/¹²C was measured by isotope ratio mass spectrometry (IRMS) [16]. The ¹³C/¹²C content is reported relative to the ¹³C/¹²C of Vienna Pee Dee Belemnite (VPDB) as

$$\delta^{13}\text{C}_{\text{VPDB}} (\text{‰}) = \left(\frac{(\text{^{13}C/^{12}C})_{\text{sample}} - (\text{^{13}C/^{12}C})_{\text{VPDB}}}{(\text{^{13}C/^{12}C})_{\text{VPDB}}} \right) \times 1000. \quad (1)$$

Each sample was measured in quadruplicate, except for SES, MER, SWIntermed., Helix ($n = 2$), and CLex ($n = 3$).

2.5. Dichloromethane and toluene extraction

2.5.1. Extractable polycyclic aromatic hydrocarbons (PAHs).

Dry SWCNTs were added to 50 ml glass centrifuge tubes containing 50 ml of dichloromethane (DCM) or toluene. To gage the extraction efficiency and sample recovery, 5 μg each of *d*₁₀-acenaphthene, *m*-terphenyl, and *d*₁₂-perylene were added as internal standards. The solutions were then equilibrated over eight days at room temperature. After a 5 h, 2250 rpm (680 g) centrifugation, 10 ml subsamples of the extracts were transferred to pear-shaped flasks and concentrated by rotary evaporation. Each extract was spiked with calibration standards (*d*₁₀-anthracene, *d*₁₀-fluoranthene, and *d*₁₂-benz[*a*]anthracene) and analyzed in triplicate by gas chromatography mass spectrometry (GC-MS). Detection limits (table 2) vary between SWCNTs due to differences in the initial mass of SWCNTs extracted and reconstructed ion chromatogram noise.

The dichloromethane extraction was performed twice and the toluene extraction was performed once. To ensure the validity of the comparison, data shown here are from toluene and dichloromethane extractions that were performed simultaneously.

2.5.2. Stable carbon isotope content of extractable carbonaceous material.

Another 10 ml subsample of each DCM extract was concentrated by rotary evaporation and

Table 2. Polycyclic aromatic hydrocarbon (PAH) detection limits in toluene extracts (unless otherwise noted).

SWCNT supplier	Detection limit of analyte ($\mu\text{g}_{\text{PAH}} (\text{g}_{\text{SWCNT}})^{-1}$)		
	Naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene	Fluoranthene, pyrene, benz[a]anthracene, chrysene	Benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, perylene, indeno[1,2,3-c,d]pyrene, dibenz[a, h]anthracene, benzo[g, h, i]perylene
SES	0.1	0.2	0.1 (4) ^a
CSI	0.2	0.2	0.2 (1)
CLex	0.5	0.3	0.07 (2)
MER ^b			
Helix	1	0.5	0.1 (2)
ManX	0.1	0.3	0.05 (7)
Nanocs ^c	2	2	2
NanoAm	0.5	1.2	0.3 (10)
SWPurified	0.1	0.2	0.1 (2)
SWIntermed.	0.02	0.06	0.03 (0.1)
CNI	0.4	0.2	0.1 (4)

^a Parenthetical value gives recovery-corrected detection limit (i.e., the quantity of the PAH that would have to be present initially in order to persist following the eight day degradation). This was calculated assuming that the listed analytes are recovered with the same efficiency as *d*₁₂-perylene in toluene (see figure 4, section 3).

^b Sample not analyzed.

^c Nanocs detection limits are from a DCM extraction, as the toluene sample was lost during preparation.

transferred to a pre-combusted 1.5 ml amber vial. Samples were passively evaporated in a laminar flow hood and re-dissolved in chloroform (CHCl₃). The ¹³C content of the non-volatile material was analyzed in triplicate by moving wire IRMS (MW-IRMS) [17]. MW-IRMS gives accurate $\delta^{13}\text{C}_{\text{VPDB}}$ values on nanogram quantities of material. Briefly, 1 μl of liquid sample was deposited on a nickel wire, and as the wire moves through a drying oven (60 °C), the solvent evaporates and non-volatile compounds remain on the wire. The sample is then combusted and dried, and the resultant CO₂ is analyzed by IRMS.

3. Results and discussion

3.1. Metal and metalloid content

Residual metal catalysts are considered the principal components of metallic impurities in SWCNTs, accounting for up to 95% of the bulk material [12]. Commercial syntheses utilize diverse metals in variable proportions, and there are no purification procedures that successfully eliminate all metals from the SWCNTs. Since the abundance and oxidation state of associated metals can impact the charge carrying capacity of the SWCNTs and their reactivity, as well as their environmental fates and effects, one of our objectives was to identify all the metals and their abundances in commercial SWCNT materials. In addition, we sought to identify unique metal ‘fingerprints’ that might be applied to track SWCNTs in the natural world.

3.1.1. Expected and unexpected metals. Purified SWCNTs contain the reported metal catalysts at low abundances (1.3 to 4.1% total metal; table 3). Perhaps surprisingly, purified SWCNTs also have unexpected metals (Cr, Cu, Pb) at part per thousand levels (0.02–0.3 ppt). Comparing an intermediate product in SWCNT synthesis with a purified

material (SWIntermediate and SWPurified, respectively), SWIntermediate contains Co and Mo, as expected, while SWPurified has Fe, Cu, and Pb in addition to the known catalysts. Acid treatments are common in SWCNT purification procedures intended to leach metals from the bulk materials [12]. We speculate that SWCNTs, damp with residual acid, could come in contact with metallic manufacturing equipment, transferring trace quantities of metals to the SWCNTs. Carbon nanotube-associated metals can influence the charge transfer capacity [18], and unexpected metals may degrade the electronic performance of the materials. Unpurified SWCNTs contain the metals used as catalysts in their syntheses at weight percentages (14 to 29% total metal, table 3). Our results agree with those of Warheit *et al* [8] for the CarboLex and CNI samples and are generally similar to those reported previously for the catalysts [19]. Thus, SWCNTs will act as carriers of these metals to the environment. Such releases may have undesirable environmental consequences, acting as either toxic substances [2, 20] or nutrients [21] in niches where these substances are present at low levels. For example, Maynard *et al* [22] reported airborne levels of SWCNTs during handling near 50 $\mu\text{g m}^{-3}$; for nanotubes containing 10% cobalt catalyst, this would imply 5 $\mu\text{g Co m}^{-3}$, an exposure that is within a factor of 10 of OSHA’s time-weighted average exposure limit. Since it seems likely that greater concentrations of SWCNTs would occur in industrial settings [20], toxic exposures to metals like cobalt could result.

3.1.2. Unique metal ratios for SWCNT source apportionment.

While these expected and unexpected metals raise environmental concern, they may be valuable for detecting SWCNTs and apportioning them to diverse sources (both natural and synthetic), as the unique metal composition of an aerosol source

Table 3. Bulk metal and metalloid content of SWCNTs.

SWCNT supplier	Purified? ^a	Reported metal catalysts ^b	Metal Content (Weight %) ^c					Additional elements/SiO ₂ (ppt)
			Ni	Y	Fe	Co	Mo	
Arc ^d								
SES	Yes	Fe-based	nd ^e	nd	0.47 ± 0.01	2.80 ± 0.08	0.69 ± 0.02	
CSI		prop ^f	22.4 ± 0.5	6.0 ± 0.2	nd	nd	nd	
CLex		Ni, Y	24.3 ± 0.5	5.0 ± 0.1	nd	nd	nd	
MER		Co, Ni	3.53 ± 0.07	nd	nd	10.5 ± 0.2	nd	
Helix		Ni, Y	15.3 ± 0.4	5.3 ± 0.1	nd	nd	nd	
CVD ^d								
ManX	Yes	Fe-based	nd	nd	1.21 ± 0.03	nd	0.08 ± 0.01	Cu: 0.3 ± 0.1, Pb: 0.1 ± 0.01
Nanocs		Ni-based	20.3 ± 0.9	4.2 ± 0.2	nd	nd	nd	
NanoAm	Yes	Mg ^g , Co, Mo	nd	nd	0.24 ± 0.01	2.87 ± 0.06	1.00 ± 0.02	Cr: 0.02 ± 0.001
SWPurified	Yes	Co, Mo	nd	nd	0.07 ± 0.01	4.1 ± 0.2	6.9 ± 0.3	Cu: 0.1 ± 0.01, Pb: 0.2 ± 0.01, SiO ₂ : 2.5 ± 0.4
SWIntermed.		Co, Mo ^h	nd	nd	nd	0.50 ± 0.01 (6.4 ± 0.5) ⁱ	1.30 ± 0.04 (16.6 ± 0.5) ⁱ	SiO ₂ : 820 ± 30 SiO ₂ : 0 ^j
CNI		Fe	nd	nd	22 ± 3	nd	nd	

^a Manufacturer reported removal of metal catalysts and inorganic supports via SWCNT purification techniques. Note that Nanocs, Inc. reports purifying samples for amorphous carbon only, not for metal catalysts.

^b Here, we note the manufacturer-reported catalyst. Some manufacturers chose to limit the description to a single component of a mixed catalyst or a partial description (e.g., 'Ni-based' means the catalyst contains Ni and other metals, and Ni is not necessarily the most abundant component).

^c Data shown are the mean value and standard deviation on quadruple measurements (duplicate analysis of two distinct dilutions).

^d Arc = SWCNTs produced by arc-discharge. CVD = SWCNTs produced by catalytic chemical vapor deposition.

^e nd = not detected above the detection limits listed in section 2.

^f prop = proprietary information.

^g Magnesium (Mg) was not quantified due to high procedural blanks.

^h Manufacturer reports that the sample contains 82–87% SiO₂ support.

ⁱ Parenthetical value shows the calculated element content assuming no substrate is present and C, N, Co, and Mo are the only components of the sample (i.e., 100% recovery). This calculation relies on the measurement of SiO₂.

^j Value is assumed for the purposes of calculating SWCNT composition in the absence of the growth substrate.

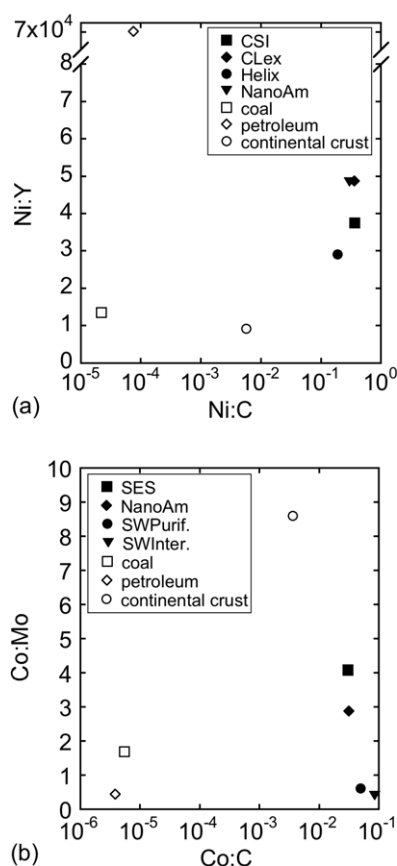


Figure 1. Metal ratios in SWCNTs and other aerosol sources. (a) Ni:Y ratios in SWCNTs are distinct from those in coal, petroleum, and continental crust. Furthermore, the metal abundance of these catalysts relative to the C content is much higher than Ni abundance in other materials. These distinct metal contents could be useful tracers of SWCNTs in environmental samples. (b) Co:Mo ratios in SWCNTs vary (see text) and overlap with some natural sources. However, the relative abundance of Co:C is distinct from coal, petroleum, and continental crust and could be used to identify SWCNTs in aerosol concentrates. The relative metal and carbon contents of coal, petroleum, and continental crust were calculated from data in Klee and Graedel [26].

can be used to study its transport in the environment [23]. For example, automobile emissions have been traced using platinum group element ratios, which reflect the composition of metal catalysts in catalytic converters [24, 25]. Given the diversity of metal catalysts used in nanotube synthesis, there is no universal metal ‘fingerprint’ for all SWCNTs. However, we suggest that metal abundances in environmental samples (e.g., aerosol concentrates), in combination with other elements, could be used to help determine if SWCNTs are present and potentially identify the source. For example, when Ni was used as a catalyst in SWCNT synthesis, the Ni:C ratio in the product was quite high, varying between 0.20 and 0.37 (figure 1(a)). These proportions are orders of magnitude higher than those of other common aerosol sources, such as coal (Ni:C = 2.2×10^{-5}), petroleum (Ni:C = 7.7×10^{-5}), and continental crust (Ni:C = 5.9×10^{-3}) [26]. If crustal-derived dust occurred in an air sample at $1 \mu\text{g m}^{-3}$ and has 1% carbon content, then the crustal Ni:C ratio implies 0.06 ng

Ni m^{-3} . If SWCNTs of interest contain 20% Ni, then only 0.3 ng SWCNTs m^{-3} would be needed to double the Ni in the air. Therefore, ng m^{-3} levels of SWCNTs would result in Ni levels six times higher than background. Thus, Ni measures can detect industrially produced SWCNTs at ng m^{-3} levels in air samples. Moreover, key metal ratios might be diagnostic. The Ni:Y ratio of the commercial SWCNTs varied between 2.9 and 4.9 (figure 1(a)), and these ratios are also distinct from coal (Ni:Y = 1.3), petroleum (Ni:Y = 66000), and continental crust (Ni:Y = 0.9) [26]. Hence, the proposed natural sources of carbon nanotubes (e.g., products of combustion processes [27]) could be distinguished from some industrial sources based on metal content. This will be particularly useful for identifying responsible parties if SWCNT manufacturers are called on to remediate SWCNTs found in the environment, as other users of industrially important materials have in the past (e.g., DuPontTM has paid \$108 million for perfluorooctanoic acid (PFOA) contamination in Parkersburg, WV [28]; General ElectricTM is liable for \$115 million for polychlorinated biphenyls (PCB) clean-up on the Hudson River, NY [29]; and W R GraceTM was fined \$58 million for asbestos contamination in Libby, MT [30]).

Currently, there is a narrow range of Ni:Y ratios used in commercial SWCNT production. There is more variability in the relative amounts of Co:Mo that successfully yield SWCNTs. When only Co and Mo were used as metal catalysts in SWCNT synthesis, the Co:Mo ratio was 0.31 ± 0.01 or 0.59 ± 0.04 (for SWIntermediate and SWPurified, respectively), whereas the ratio is much higher (2.9 ± 0.1 for NanoAm and 4.0 ± 0.2 for SES) for SWCNTs grown from Fe/Co/Mo catalyst mixtures. Thus, metal catalyst ratios may be used to distinguish SWCNTs produced by different SWCNT manufacturers.

Unlike Ni:Y abundances, the Co:Mo ratios in industrially synthesized SWCNTs (0.31 ± 0.01 to 4.0 ± 0.2) overlap with those of coal (1.67) and petroleum (0.43), making it difficult to identify natural and anthropogenic SWCNT sources using metal ratios alone. However, SWCNTs have relatively high Co:C content (0.31 and 0.88) compared to coal (Co:C = 5.6×10^{-6}), petroleum (Co:C = 4.0×10^{-6}), and continental crust (Co:C = 3.7×10^{-3}) [26]. If crustal-derived dust occurred in an air sample at $1 \mu\text{g m}^{-3}$ and has 1% carbon content, then the crustal Co:C ratio implies 0.04 ng Co m^{-3} . If SWCNTs of interest contain 3% Co, then only 1.3 ng SWCNTs m^{-3} would be needed to double the Co in the air. Therefore, 4 ng m^{-3} levels of SWCNTs would result in Co levels six times higher than background. This sensitivity for Co-containing SWCNTs is slightly less than that for Ni-containing SWCNTs and results from the higher Co content of continental crust and lower Co content of SWCNTs, as compared to the Ni content of the respective materials. Nevertheless, Co measures can detect industrially produced SWCNTs at several ng m^{-3} levels in air samples. Thus, the unique metal-to-carbon content of SWCNTs can be useful for tracing these emerging contaminants as they are released to and travel through the environment.

Table 4. Bulk carbon and nitrogen content of SWCNTs commercially available in the US.

SWCNT supplier	Carbon feedstock	Purified? ^a	Total C (%) ^b	SWCNT-C (%) ^c	Amorph. C (%) ^c	Total N (%) ^b	C + N + metals + SiO ₂ (%)
Arc							
SES	graphite	Yes	89 ± 1	58 ± 1	ms ^d	0.14 ± 0.06	93 ± 1
CSI	graphite		60 ± 3	44 ± 1	13.4 ± 0.3	0.17 ± 0.01	93 ± 3
CLex	graphite		66.3 ± 0.2	23 ± 1	34 ± 1	0.20 ± 0.04	96 ± 1
MER	graphite		84 ± 1	nm ^e	nm	0.19 ± 0.02	98 ± 1
Helix	graphite		78 ± 2	32 ± 1	33 ± 1	0.45 ± 0.01	99 ± 2
CVD							
ManX	C ₂ H ₅ OH	Yes	97 ± 2	81 ± 1	nd	nd ^f	98 ± 2
Nanocs	C _x H _y ^g	Yes	66.3 ± 0.8	nm	nm	0.48 ± 0.04	91 ± 1
NanoAm	C _x H _y ^g	Yes	88.6 ± 0.6	48 ± 1	41 ± 4	nd	93 ± 1
SWPurified	CO	Yes	81 ± 2	41 ± 1	37 ± 1	0.11 ± 0.02	92 ± 2 89 ± 3
SWIntermed.	CO		5.7 ± 0.2 ^h (76 ± 2) ^h	5.3 ± 0.2 ^h (71 ± 3) ^h	nd	nd	(100) ⁱ
CNI	CO		68 ± 5	28 ± 4	45 ± 4	nd	96 ± 3

^a Select manufacturers reported removal of metal catalysts, inorganic supports, and/or amorphous carbon.

^b Standard deviation on triplicate analyses, except for CNI and CSI ($n = 6$).

^c Calculated area under TGA curve with mathematical fit uncertainty on one sample (i.e., $n = 1$). Amorphous C and SWCNT-C are distinguished by their relative thermal oxidation temperatures. Other phases, such as multi-shell carbon, may exist as part of the bulk material.

^d ms = multi-shell carbon was measured in this sample at $31 \pm 1\%$.

^e nm = not measured. We could not resolve the contribution of SWCNT-C, amorphous carbon, and other carbon species, as their co-oxidation precluded an accurate model fit of the differentiated mass loss curve.

^f nd = not detected above 0.3 μg blank (0.02–0.04% N).

^g Typically, Nanocs uses ethyne (acetylene, C₂H₂) and NanoAm uses ethene (ethylene, C₂H₄), but both companies report using a variety of C_xH_y sources. Nanocs also manufactures arc-produced SWCNTs from graphite.

^h SWIntermed. contains inorganic substrate material, SiO₂, which is removed prior to sale. Parenthetical value shows the calculated C content assuming no substrate is present. This calculation relies on the measured quantity of the SiO₂ and assumes 100% sample recovery.

ⁱ Assumed recovery for calculation of C and metal content in substrate-free material.

3.2. Total carbon and nitrogen

The total carbon content of the SWCNTs ranged from 60–97% (table 4). The measured values agree with the manufacturer-reported carbon contents, except for SWPurified and Nanocs. SWPurified contained $81 \pm 2\%$ C when measured by elemental analysis, whereas 93% C was reported by the manufacturer. This offset may result from differences in analytical methods, as SWCNT, Inc. determines the elemental content using x-ray photoelectron spectroscopy (XPS). XPS is used to determine the chemical composition of a surface (typically the upper 10 nm or less). It is possible that thick (>10 nm) amorphous carbon coatings in the SWPurified sample biased the carbon content to an artificially high value. Nanocs contained $66.3 \pm 0.8\%$ C even though this product was listed as ‘high purity’. The Nanocs C content is quite low for traditionally purified SWCNTs; and when contacted, Nanocs, Inc. explained that they emphasize structural purity, eliminating amorphous carbon and retaining intact SWCNTs without removing metal catalysts. Metal analyses confirm that this sample was not purified of metal catalysts. Purified and unpurified SWCNTs are often difficult to distinguish without chemical analyses, and such subtleties in nomenclature may confound toxicity, environmental transport, and SWCNT application studies.

An intermediate product in SWCNT synthesis, SWIntermed., had an unusually low C content ($5.7 \pm 0.2\%$), primarily due to the presence of inorganic growth substrate (SiO₂). Correcting for the presence of the substrate gave a calculated C content of $76 \pm 2\%$. While this corrected result certainly puts the product in the range seen for other SWCNTs, it is clear that the carbon contents of these ostensibly carbonaceous materials were quite variable.

Similarly, there was a broad range in the SWCNT-C and amorphous C content of these materials, irrespective of the reported purity level (table 4). Arc-produced samples contained between 23 ± 1 and $44 \pm 1\%$ SWCNT-C, whereas CVD-generated SWCNTs contained between 41 ± 1 and $81 \pm 1\%$ SWCNT-C. Again, the SWIntermed. sample contains $82 \pm 3\%$ SiO₂ growth substrate (table 2), and correcting for the presence of this material gave $71 \pm 3\%$ SWCNT-C. Perhaps surprisingly, some purified samples, NanoAm and SWP, contained ‘amorphous C’ at or above the SWCNT-C content. We suspect that this was due to the formation of a partially oxidized carbon phase during the SWCNT purification process, which typically involves thermal and/or chemical oxidation steps. Clearly, these lower-thermal-stability (relative to SWCNT-C) phases were not removed during subsequent purification steps.

Given the diversity of procedures and metals used in SWCNT synthesis, and the influence of those choices on the thermal stability and relative abundance of SWCNTs [31, 32], it is difficult to compare our results with the literature directly. Nevertheless, we note that CarboLex samples analyzed by the same TGA method exhibited roughly 25% amorphous C and 30% SWCNT-C (by inspection of the mass-loss thermogram) [31], in agreement with our results. In addition, Itkis *et al* [33] report 31.8% SWCNT purity for the CSI sample, analyzed by near-infrared spectroscopy. Our TGA results indicate that this sample contained $44 \pm 1\%$ SWCNT-C. This discrepancy may reflect the differing analytical biases of the two methods. For example, the thermogram in this sample indicated the presence of purported multi-shell carbon [31] co-oxidizing with the SWCNTs. This co-oxidation could result in a mathematical overestimation (due to the curve fitting procedure) of the SWCNT content. Alternatively, the discrepancy could result from differences in the commercially available product over the time frame of the two studies.

Unfunctionalized SWCNTs are expected to have very low N contents. However, we found that all arc-synthesized SWCNTs contained measurable amounts of N, ranging from 0.14 to 0.45% (table 4). In contrast, catalytic chemical vapor deposition (CVD)-produced materials did not have detectable quantities of N (0.02–0.04% N), except for SWPurified and Nanocs. We hypothesize that the presence of N in SWPurified results from N incorporation during (1) SWCNT synthesis, (2) the purification process, especially if HNO_3 is used, or (3) post-manufacture processing and transport. Additionally, although Nanocs, Inc. currently employs CVD as their principal fabrication method, they also use arc-discharge synthesis. It is possible that this particular batch of SWCNTs was arc produced. The high-energy environment of arc-discharge synthesis may favor the incorporation of N, even if derived from atmospheric N_2 [34], into SWCNTs. The direct incorporation of N into the carbon-based skeleton can influence the helicity and, therefore, the conductivity of the nanotube [35]. Thus, manufacturers designing synthetic processes for a particular application may choose low- or high-energy fabrication depending on the desired tube chirality. If the N is incorporated into the nanotube itself, the added functionality may alter the SWCNT persistence in the environment by influencing the surface charging and increasing the susceptibility to transformations. Moreover, if the N occurs as part of the population of aromatic hydrocarbon side products (which will be discussed in more detail below), there is cause for concern regarding the toxicities derived from N-heterocyclic compounds [36].

From a mass balance perspective, the measured quantities of C, N, metals, and SiO_2 accounted for between 89 ± 3 and $99 \pm 2\%$ of the SWCNT materials (table 4). None of our analyses quantified the oxygen content of the SWCNTs, and so the remaining fraction of unaccounted material could contain oxygen. Such oxygen could be present as functional groups on the SWCNTs or, perhaps more likely, as metal oxides. If we assume that metal oxides are present at 50–100% of the SWCNT-associated metal content and in representative stoichiometries (i.e., NiO , Y_2O_3 , Fe_2O_3 , MoO_3 ,

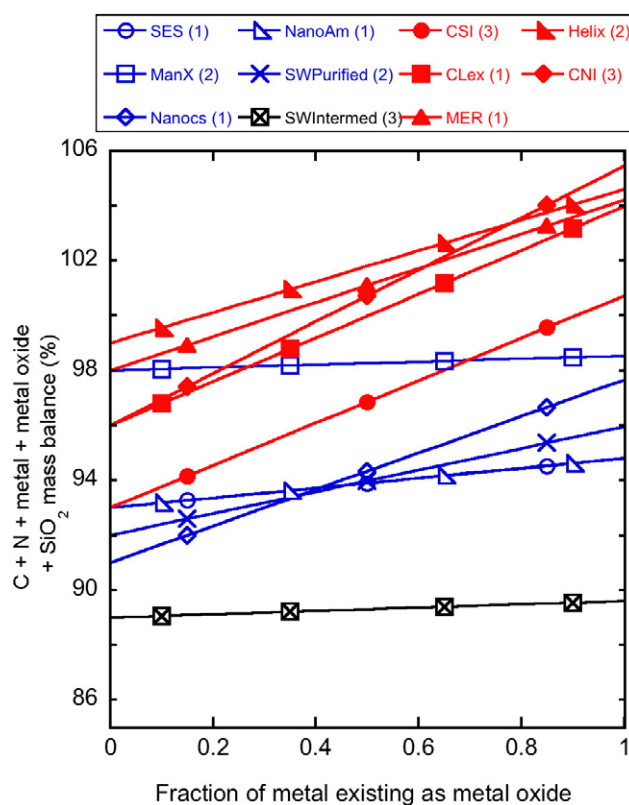


Figure 2. Total accounted SWCNT mass as a function of assumed metal oxide content. For this calculation, we assumed that metal oxides existed in representative stoichiometries (i.e., NiO , Y_2O_3 , Fe_2O_3 , MoO_3 , and CoO (or, equivalently, CoMoO_4)). Using the quantified metal abundances, we calculated the mass of oxygen that would be present as metal oxide. The uncertainty in the calculation is given in parentheses in the legend, next to the sample name. (Error bars are omitted for figure clarity.) For AP-SWCNTs (filled, red symbols), metal oxides easily account for the unidentified material if we assume that 50% of the SWCNT-associated metal is present as metal oxide. For purified materials, (open, blue symbols) oxygen present as metal oxides cannot account for the total mass of the SWCNT, and oxygen present in the SWCNT carbon lattice could explain the missing mass fraction. For the intermediate SWCNT product (black, hatched symbols), SWIntermed., no amount of metal oxide can explain the unaccounted fraction of material.

(This figure is in colour only in the electronic version.)

and CoO (or, equivalently, CoMoO_4)), we find that oxygen can account for the missing mass in all of the AP-SWCNTs (figure 2). In the case where we assume that 100% of the metal is present as metal oxide, the total mass balance is overestimated by as much as 2.5% (outside of the analytical error), whereas the mass balance is within the analytical error when we assume that 50% of the metal is present as metal oxide. (For the intermediate product (SWIntermed.), no amount of metal oxide can account for the missing material, suggesting that we have failed to quantify some portion of the material. TGA results confirm that we are not accounting for approximately 10% of the AP-SWCNT product.) In purified SWCNTs, metal oxides cannot account for the missing mass, and 2–6% of the material remains unexplained. We propose that purified materials contain oxygen functional groups within the SWCNT lattice, as oxidizing acids used

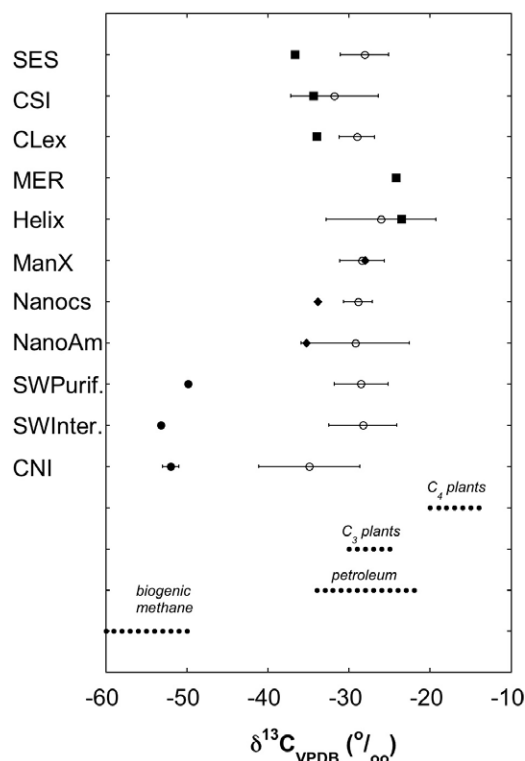


Figure 3. Stable carbon isotopic signatures of SWCNTs, SWCNT-associated solvent-extractable material, and selected carbon sources. SWCNTs synthesized from arc-discharge (■), CVD (◆), and CO-CVD (●) exhibit a broad range of $^{13}\text{C}/^{12}\text{C}$ ratios, primarily resulting from the distinct isotopic signatures of their respective starting materials (●●●). Graphite is industrially produced from petroleum coke ($\delta^{13}\text{C}_{\text{VPDB, petroleum-derived}} = -34$ to -22%) [40–42], and provides a carbon source for arc-discharge synthesized SWCNTs. A variety of carbon source materials are used for CVD-synthesized SWCNTs, including ethanol and carbon monoxide. Ethanol can be produced from the sugar derived from C_3 plants (woody plants, $\delta^{13}\text{C}_{\text{VPDB}} = -30$ to -25%) or C_4 plants (maize, grasses, $\delta^{13}\text{C}_{\text{VPDB}} = -20$ to -14%) [38]. Carbon monoxide is typically produced from methane ($\delta^{13}\text{C}_{\text{VPDB, biogenic methane}} = -110$ to -50%) [39, 42]. Error bars represent one standard deviation on quadruple analyses, except SES, MER, SWIntermed., Helix ($n = 2$), and CLex ($n = 3$). The ^{13}C content of dichloromethane solvent-extractable material (○) is consistent with petroleum-derived sources, characteristic of ambient hydrocarbons. Error bars represent one standard deviation on triplicate measurements. The larger relative error of the extracts (as compared to the SWCNTs) is due to the small quantity of extracted material.

during purification can induce such functionality, especially at SWCNT ends and defects. These oxygen functional groups, along with acid residues (e.g., HCl , HNO_3 , and H_2SO_3), could account for the unquantified proportion of the purified SWCNTs. Whether present as metal oxides or functional groups on the SWCNTs, oxygen functionalities contributing up to 10% by weight of the SWCNTs would dramatically affect the surface properties of these nanoparticles (e.g., conferring pH-dependent charging in aqueous suspensions), which will be important for many applications that rely on SWCNT adsorptivity (e.g., water filtration) and suspension stability.

3.3. Stable carbon isotope composition of SWCNTs

SWCNTs exhibited a wide range in $\delta^{13}\text{C}_{\text{VPDB}}$ values (-53.2 to -23.5% , figure 3, see section 2 for the definition of $\delta^{13}\text{C}$ notation). The observed ^{13}C abundances can result from either the C source material or isotopic fractionation during fabrication and post-production treatments. Carbon isotopic fractionation typically diminishes with increasing reaction temperature [37], and we expect that such effects are minor at SWCNT synthesis temperatures, which often exceed 700°C . Thus, we believe that the diverse ^{13}C abundances primarily reflect the varied ^{13}C content of their respective source materials (table 4). A variety of carbon source materials are used for CVD SWCNTs, including ethanol, carbon monoxide, and ethane [5]. Ethanol can be produced from the sugar derived from C_3 plants (woody plants, $\delta^{13}\text{C}_{\text{VPDB}} = -30$ to -25%) or C_4 plants (maize, grasses, $\delta^{13}\text{C}_{\text{VPDB}} = -20$ to -14%) [38]. Carbon monoxide is typically produced from methane, which can be depleted in ^{13}C ($\delta^{13}\text{C}_{\text{VPDB, biogenic methane}} = -110$ to -50%) [39]. Graphite (a carbon source for arc SWCNTs), ethene, and ethyne are all industrially produced from petroleum coke. Petroleum cokes and associated compounds can have a range of ^{13}C content, depending on the isotopic signature of the source reservoir, from -34 to -22% [40–42].

Arc SWCNTs have $\delta^{13}\text{C}_{\text{VPDB}}$ values ranging from -36.7 to -23.5% , indicative of graphitic sources. The ^{13}C abundance of ManX (-28.0%) is consistent with growth from a C_3 -derived ethanol [38]. Ethene-derived NanoAm (-35.2%) had a ^{13}C content similar to that of Nanocs (-33.8%), which has a proprietary C source. Given the broad and overlapping range of ^{13}C abundances, it is not possible to differentiate arc and CVD SWCNTs using C isotopic techniques. Conversely, CO-CVD SWCNTs have a distinct ^{13}C composition (-51.7 to -49.8%), reflecting growth from a ^{13}C -depleted feedstock. This unique isotopic signature may be another useful tracer of CO-SWCNTs and their metabolites in both laboratory and field studies. For example, the ^{13}C abundance of CO-SWCNT transformation products will be depleted relative to the bulk carbon of most systems (i.e., SWCNT-derived biomolecules will have a different isotopic signature than biomolecules from other carbon sources). In addition, CO-derived SWCNTs' isotope signature is distinct from the bulk isotopic content of marine seawater and sedimentary organic matter (-30 to -20%) [38]. This isotopic fingerprint may be particularly valuable for the development of analytical methods to quantify SWCNTs in complex environmental matrices, as the isotopic content of an artificial sample (e.g., a laboratory-generated aerosol sample containing CO-derived SWCNTs) could be used independently to calculate the quantity of nanotubes persisting through each step of the analysis (i.e., sample collection, separation, and quantification). A similar approach would allow one to quantify SWCNTs in mixture-based applications, such as polymer composites and pharmaceutical vectors.

3.4. Total solvent-extractable material (TSEM)

Amorphous carbon and graphitic nanoparticles are considered the principal components of C-based SWCNT impurities [12],

accounting for up to 45% of as-produced SWCNT material. In addition, amorphous carbon formation plays an important role in catalyst deactivation during CVD growth, resulting in suboptimal carbon nanotube formation [43], and influences the electronic character of the SWCNT [44]. The chemical composition of this amorphous carbon fraction is largely uncharacterized, and one of our objectives was to develop a more detailed description of the SWCNT co-products, their behavior, and their origin through solvent extraction.

3.4.1. TSEM isotopic composition and hydrocarbon origin. The ^{13}C abundances of the DCM solvent extracts of all the SWCNTs were approximately -29% (range -35 ± 6 to $-26 \pm 7\%$, figure 3), irrespective of the ^{13}C content of the SWCNTs. This suggests most of the TSEM derived from a common source for all of the SWCNTs. The ^{13}C signature of the TSEM was consistent with that of ambient petroleum-derived compounds (-34 to -22%) [40, 41], and SWCNTs could be acquiring hydrocarbons through contact with industrial apparatus and packaging material, as well as through exposure to ambient vapors and aerosols. The presence of phthalates (ubiquitous organic compounds used in the manufacture of plastics) in all of the solvent extracts, as compared to our phthalate-free laboratory blanks, also supported the contention that SWCNTs have a tendency to sorb organic contaminants from their surroundings. Sorbed organic material influences the electronic properties of SWCNTs [19], and thus manufacturers concerned with the electronic integrity of their nanotubes should take care to minimize SWCNT contact with plastics, other organic-rich materials, and urban air. These data indicate that SWCNTs released to the environment may continue to sorb organic compounds, influencing the mobility and persistence of both natural and pollutant compounds. Depending on the strength of the sorptive interactions, SWCNTs will act either as a local sink for anthropogenic contaminants or as a vector for distributing them in the environment.

3.4.2. TSEM mass and metal reactivity. The quantity of solvent-extractable material was remarkably low ($<1\%$ in dichloromethane (DCM), $<5\%$ in toluene, table 5), suggesting that carbonaceous impurities were either (1) not soluble in DCM or toluene due to their macromolecular/particulate nature, (2) strongly sorbed to SWCNTs, or (3) degraded during the solvent extraction procedure. While we would not expect amorphous or graphitic nanoparticles to be soluble, it is somewhat surprising that small (<350 amu), soluble molecules contribute less than 5% of the SWCNT co-products [45, 46]. If such molecules are formed, preserved, and associated with the SWCNTs, we would expect that milliliter quantities of apolar solvent would efficiently extract them from milligram quantities of SWCNTs, based on our physical-chemical understanding of hydrocarbon sorption [47]. Thus, we hypothesized that a degradation reaction was consuming some of the low molecular weight compounds during extractions. As noted previously, both purified and unpurified SWCNTs contain substantial quantities of metals (table 3). Reduced metals are able to react with dichloromethane to form

Table 5. Mass of solvent-extractable material from SWCNTs.

SWCNT supplier	Total solvent-extractable material (TSEM)	
	DCM extraction GC ^a -amenable mass ^b (mg (g SWCNT) ⁻¹)	Toluene extraction GC-amenable mass ^b (mg (g SWCNT) ⁻¹)
Arc		
SES	0.23 ± 0.03	0.16 ± 0.03
CSI	0.13 ± 0.01	0.20 ± 0.03
CLex	0.052 ± 0.002	0.05 ± 0.01
MER	c—	c—
Helix	1.2 ± 0.8	23.6 ± 0.7
CVD		
ManX	0.25 ± 0.05	8.2 ± 0.3
NanoAm	0.8 ± 0.1	13 ± 3
Nanocs	0.3 ± 0.1	c—
SWPurified	0.11 ± 0.02	2.23 ± 0.09
SWIntermed.	0.07 ± 0.02	2.93 ± 0.02
CNI	0.8 ± 0.3	49.2 ± 0.1

^aGC = gas chromatography.

^b Mass determined by integrating total ion chromatogram and applying the response factor for pyrene.

^c Sample not analyzed.

chloromethyl radicals, and such radicals can react with expected components of the TSEM, such as PAHs [48]. These transformations would result in losses of PAHs in halogenated solvent extractions.

To test this hypothesis, we compared the recovery of three added PAH internal standards (d_{10} -acenaphthene, m -terphenyl, d_{12} -perylene) with toluene versus DCM extractions of the SWCNTs. DCM extractions of SWCNTs showed poor recoveries for all three internal standards (figure 4). In contrast, the toluene extractions were very efficient ($96 \pm 8\%$ to $114 \pm 8\%$) for d_{10} -acenaphthene and m -terphenyl from all SWCNTs, and the d_{12} -perylene was also recovered better by the toluene. Interestingly, DCM extractions of purified SWCNTs showed markedly worse recoveries of m -terphenyl and d_{12} -perylene than DCM extractions of unpurified SWCNTs. Purification processes typically remove the amorphous carbon coating of the SWCNT-associated metal catalysts [12], and while decreasing the overall metal abundance, purification could increase the effective surface area of available metal catalyst. The poor internal standard recoveries in purified SWCNT-DCM extracts are consistent with degradation of PAHs by radicals generated via metal-halogenated solvent reaction. These data suggested that metals are not 'inaccessible to the outside environment', [2] as some have suggested, but rather, the metals are available to participate in reactions.

Given the difficulty of removing metal catalysts from SWCNTs with 100% efficiency (table 3) and the apparent increase in metal reactivity with SWCNT purification (figure 4), manufacturers and users must consider the effect of metal catalysts in their products. For example, the metal content of SWCNTs designed to deliver pharmaceuticals to cell targets [49] will influence the lifetime of the drug in the body. Additionally, the presence of reactive metals will almost certainly influence the toxicity of the nanomaterial [10, 20, 21].

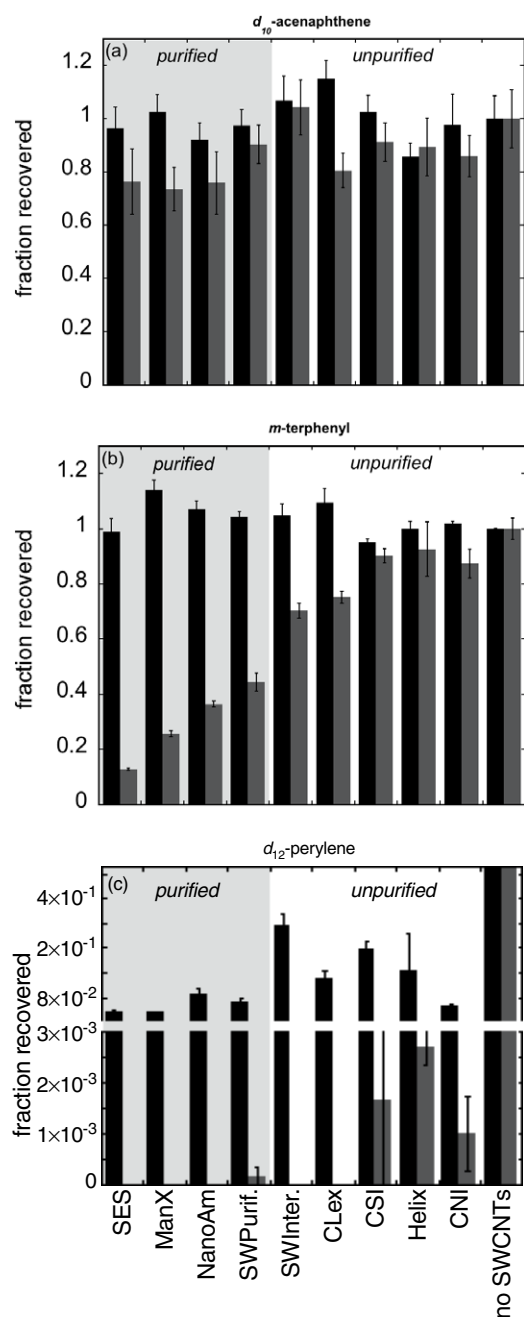


Figure 4. Polycyclic aromatic hydrocarbon internal standard recoveries. Recoveries of three PAH internal standards, d_{10} -acenaphthene (a), m -terphenyl (b), and d_{12} -perylene (c), varied significantly between samples. Additionally, dichloromethane (dark gray) extractions of SWCNTs gave poorer recoveries than analogous toluene (black) extractions, especially in the case of m -terphenyl and d_{12} -perylene. These two compounds exhibit higher recoveries from unpurified (white background) samples than purified (light gray background) samples. Note the different scale necessitated by the d_{12} -perylene data. Here, the 'no SWCNTs' recovery is off scale (fraction recovered = 1). Recoveries are reported relative to the SWCNT-free controls ('no SWCNTs'), and error bars represent one standard deviation on duplicate analyses.

SWCNTs released to the environment could also react with halogenated contaminants, generating radical species and degradation products with elevated toxicity [50, 51]. For

example, zero-valent metals are used to remediate chlorinated ethenes via reductive dehalogenation to produce toxic vinyl chloride [50]. Furthermore, such reactions result in oxidation of the metal catalyst, which will alter the solubility of the metal, the SWCNT's ability to carry and dissipate charge [18], and the charging of the nanoparticle surface. Consequently, risk assessment models must consider the presence of the reactive metal, and we cannot continue to ignore the presence of catalytic impurities in manufactured nanomaterials.

3.4.3. Solvent-extractable polycyclic aromatic hydrocarbons. SWCNTs are formed at elevated temperatures from reactive carbon species. PAHs share this formation mechanism, and we hypothesized that PAHs would be co-formed during SWCNT synthesis [49]. Based on the effectiveness of our toluene extractions for the low molecular weight (LMW)-PAHs (<200 amu), we determined the abundance and identity of such PAHs for the different SWCNT samples (table 6). All samples contained naphthalene (0.035 ± 0.002 to $112 \pm 4 \mu\text{g} (\text{mg SWCNT})^{-1}$), and some carried additional PAHs (CSI, Helix, ManX, NanoAm, SWPurified, NanoAm). CLex and CNI contained a full suite of PAHs, including benzo[*b*]fluoranthene (0.07 ± 0.03 and $0.28 \pm 0.01 \mu\text{g} (\text{g SWCNT})^{-1}$, respectively). Since the isotopic analyses indicated that the majority of SWCNT-associated hydrocarbons were derived from the environment rather than the SWCNT synthesis (figure 4), the same may be true of the PAHs. Naphthalene and phenanthrene are present in many of the extracts, and they often appear in the greatest abundance. These compounds are common air contaminants, and we suspect that the PAH composition reported here is largely a function of the lifetime of the SWCNT sample (e.g., quality of air and carbonaceous materials to which it was exposed during manufacture, transport, storage, and use). These results suggest that LMW-PAHs only contribute a small fraction of the amorphous material associated with SWCNTs.

4. Implications and conclusions

With an industry-projected doubling rate of more than once per year [52], the anticipated growth of the carbon nanotube industry is nearly unprecedented, and SWCNTs will soon be in broad use by the general public in a variety of different applications. These materials will appear in the environment in the near future, and there is an urgent need to develop methods to study SWCNT transport [4]. These data provide metal-to-metal, metal-to-carbon, and carbon isotopic information that can be used, independently or in concert, as forensic tools to identify SWCNTs in natural and artificial samples.

In addition, we have shown that SWCNTs, associated metals, and solvents can react to degrade aromatic hydrocarbons. This reactivity may be useful for chemical transformations. However, unintended reactions will affect the surface charge and conductivity of the nanomaterial, and thus the SWCNTs' suitability for a particular application.

Commercially available SWCNTs are highly diverse materials whose character and constituents vary with the production scheme and post-fabrication treatment. During

Table 6. Polycyclic aromatic hydrocarbons extracted from SWCNTs using toluene (unless otherwise noted).

SWCNT supplier	Naphthalene ($\mu\text{g}_{\text{PAH}} (\text{g}_{\text{SWCNT}})^{-1}$)	Acenaphthylene ($\mu\text{g}_{\text{PAH}} (\text{g}_{\text{SWCNT}})^{-1}$)	Acenaphthene ($\mu\text{g}_{\text{PAH}} (\text{g}_{\text{SWCNT}})^{-1}$)	Fluorene ($\mu\text{g}_{\text{PAH}} (\text{g}_{\text{SWCNT}})^{-1}$)	Phenanthrene ($\mu\text{g}_{\text{PAH}} (\text{g}_{\text{SWCNT}})^{-1}$)	Anthracene ($\mu\text{g}_{\text{PAH}} (\text{g}_{\text{SWCNT}})^{-1}$)	Fluoranthene ($\mu\text{g}_{\text{PAH}} (\text{g}_{\text{SWCNT}})^{-1}$)	Pyrene ($\mu\text{g}_{\text{PAH}} (\text{g}_{\text{SWCNT}})^{-1}$)
Arc								
SES	9.8 ± 0.6	nd ^a	nd	nd	nd	nd	nd	nd
CSI	2.3 ± 0.1	nd	nd	nd	0.31 ± 0.08	nd	nd	nd
CLex	52 ± 7	10.0 ± 0.5	2.9 ± 0.3	2.2 ± 0.4	7.8 ± 0.3	1.01 ± 0.05	5.4 ± 0.1	0.73 ± 0.07
MER ^b								
Helix	9 ± 4	0.90 ± 0.02	nd	nd	2.0 ± 0.2	nd	0.89 ± 0.04	nd
CVD								
ManX	1.1 ± 0.1	nd	nd	0.25 ± 0.01	1.1 ± 0.1	0.52 ± 0.09	nd	nd
Nanocs ^c	4.5 ± 0.6	nd	2.6 ± 0.3	nd	nd	nd	nd	nd
NanoAm	4.0 ± 0.4	nd	0.46 ± 0.05	0.70 ± 0.08	2.2 ± 0.2	nd	nd	nd
SWPurified	0.39 ± 0.05	nd	nd	nd	0.22 ± 0.04	nd	0.32 ± 0.04	nd
SWIntermed.	0.035 ± 0.002	nd	nd	nd	nd	nd	nd	nd
CNI	112 ± 4	7.8 ± 0.6	2.6 ± 0.2	1.4 ± 0.1	12.3 ± 0.5	3.12 ± 0.07	6.2 ± 0.1	9.1 ± 0.3

^a nd = not detected above detection limit. Detection limits (table 2) varied between samples due to differences in the initial SWCNT mass of the sample and reconstructed ion chromatogram background noise. In addition to the compounds given in the table, samples were analyzed for benz[*a*]anthracene, chrysene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*e*]pyrene, benzo[*a*]pyrene, perylene, indeno[1,2,3-*c,d*]pyrene, dibenz[*a,h*]anthracene, and benzo[*g,h,i*]perylene.

^b Sample was not analyzed.

^c Results reported were obtained from a DCM extraction, as the toluene extraction sample was lost during processing. DCM recoveries of *d*₁₀-acenaphthene varied between 74 and 100%, and we expect these naphthalene and acenaphthalene abundances reflect their presence in the sample. Higher molecular weight PAHs (>202 amu) may have been lost due to DCM–metal catalyst interactions (figure 4) and present in greater abundance than reported here.

these early stages of SWCNT research, investigators and regulators should be aware that there are significant differences in materials provided by different manufacturers, especially when cross comparing and interpreting toxicological studies [53]. Likewise, newly emerging nanomaterial risk assessments [54] must explicitly acknowledge these differences, as opposed to modeling the risk of a generic (i.e., over-simplified) SWCNT. Different SWCNTs will act as carriers of diverse metals and hydrocarbons to the environment. Furthermore, as both of these impurity classes affect the surface properties and reactivity of the SWCNTs, they will influence the overall environmental fate of the nanomaterials. Perhaps most importantly, SWCNT manufacturers can weigh the SWCNT-specific risk assessments and design synthetic processes to achieve environmental objectives while simultaneously considering performance and manufacturing cost. If we fail to use chemical understanding to strategically avoid unintended environmental consequences, the nanomaterial revolution may come to a halt with deteriorated public opinion, product bans, and expensive clean up efforts, such as those associated with other industrially important materials of the past (e.g., asbestos).

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