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Nanotoxicity and Life Cycle Assessment: First attempt towards the determination of characterization factors for carbon nanotubes

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Abstract. Carbon materials, whether at macro, micro or at nanoscale, play an important role in the battery industry, as they can be used as electrodes, electrode enhancers, bipolar separators, or current collectors. When conducting a Life Cycle Assessment (LCA) of novel batteries manufacturing processes, we also need to consider the fate of potentially emitted carbon based nanomaterials. However, the knowledge generated in the last decade regarding the behavior of such materials in the environment and its toxicological effects has yet to be included in the Life Cycle Impact Assessment (LCIA) methodologies. Conventional databases of chemical products (e.g. ECHA, ECOTOX) offer little information regarding engineered nanomaterials (ENM). It is thus necessary to go one step further and compile physicochemical and toxicological data directly from scientific literature. Such studies do not only differ in their results, but also in their methodologies, and several calls have been made towards a more consistent approach that would allow us model the fate of ENM in the environment as well as their potentially harmful effects. Trying to overcome these limitations we have developed a tool based on Microsoft Excel® combining several methods for the estimation of physicochemical properties of carbon nanotubes (CNT). The information generated with this tool is combined with degradation rates and toxicological data consistent with the methods followed by the USEtox methodology. Thus, it is possible to calculate the characterization factors of CNTs and integrate them as a first proxy in future LCA of products including these ENM.

1. Introduction

Energy storage systems play a major role in the transition towards a more environmentally sustainable society, being critical for both increasing the production of electricity through renewable energies and to end a fossil fuel dependent mobility [1]. As such, a wide variety of technologies and an even wider range of material are now used or studied for the storage of electricity. One of those materials is carbon, used extensively in electrochemistry due to its good chemical stability and high electrical conductivity [2]. The importance of this element has increased in the last decades due to the apparition of carbon based nanomaterials. Carbon nanotubes (CNT) are rolled sheets of graphene with a diameter in the range of nanometers (nm) [3]. They can be used as electrodes, electrode enhancers, bipolar separators, or current collectors [2, 4–6]. Previous studies have shown the use of CNT on traction batteries can reduce the overall environmental profile of electric vehicles [7]. However, similarities between the structure of CNT and that of asbestos fibers have raised the awareness of the potential toxic effects of these substances and although there is ample literature on the subject [8], systematized information is still scarce.

Life Cycle Assessment is an ISO standardized methodology used to study the environmental effects of products and processes through their entire life cycle; this is, from the moment they are extracted from nature until they are disposed as waste (or return to a production cycle). In the Impact Assessment stage, all potential emissions which could cause a harmful impact are classified according to the impact categories they could potentially affect (Global Warming, Ozone Layer Depletion, Human Toxicity…) and relate them to a reference unit (e.g. kg CO_2 equivalents in the case of Global Warming) using characterization factors (CF) [8,9].

Due to the aforementioned relative scarcity of literature on CNT toxicity, there are no CF for CNT yet and, as a result of this, the effect of these nanomaterials in the environment is not included when conducting the LCA of their production process. Consequently, our objective was to test the capability of current impact assessment methodologies when assessing CNT and calculate the CF of single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNT).

2. Materials and methods

Commercially available MWCNT, Baytubes 150HP, were chosen based on the availability of data regarding their behaviour in the environment and their toxicological effects [10,11]. For comparative purposes, SWCNT of the same dimensions as the MWCNT (Ø13nm, length 1µm) were selected.

The CF were calculated with USEtox [13], a consensus methodology recommended by the ILCD handbook for the categories of Human Toxicity (HT) and Freshwater Ecotoxicity (FET) [10]. The parameters required for the CF are detailed in Table 1 and were introduced in USEtox using a spreadsheet tool previously developed by our research group [14]. For the calculation of the CF of MWCNT, the parameters found at the European Chemical Database (www.echa.eu) were used unless specified otherwise. Since no SWCNT are registered yet, the following assumptions and data were used:

- The molecular weight (MW) was calculated based on the diameter and length of the nanotube as in [15]. For the MWCNT, 27 layers were assumed based on its relative density.
- The octanol-water partition coefficient (K_{OW}) was calculated based on the chiral vector as suggested in [16].
- For both SWCNT and MWCNT the organic-carbon partition (K_{OC}) coefficient and the bioaccumulation factor in fish (BAF) were calculated based on their K_{OW} as recommended by the USEtox User's Manual [17].
- For both CNT types the vapour pressures were set to make their Henry Constants (K_H) equal to 10^{-20} as USEtox does for metals [17], since the vapour pressure of carbon at standard conditions is virtually none [18].
- For their two kinds of CNT the degradation rate in air was set to 10^{-20} as for metals in [17]. CNT are not degraded by free radicals, in fact, they induce the formation of free radicals and the oxidation of other substances [19].
- For both CNT the degradation rates in water and its derived degradation rates were calculated assuming they are recalcitrant substances [20].
- The aquatic ecotoxicity parameter was calculated based on the toxicity of these compounds for *Chlorella vulgaris* [21] and *Daphnia magna* [22].
- For HT, the ingestion non-cancer parameter was taken from a study conducted on mice [23] and the inhalation non-cancer one was taken from a study on rats [24]. Since the potential carcinogenity of SWCNT has not been established yet [25], no values were introduced for ingestion and inhalation cancer effects. Thr same review indicated certain MWCNT may

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induce malignant mesothelioma if inhaled. However, to the best of our knowledge, no NOEC[1] is available yet. As a result of this, no carcinogenic effects were assessed for MWCNT either.

Table 1. Parameters required for the calculation of the characterization factors

Physicochemical properties		**Degradation rates**		**Ecotoxicity**	
Molecular weight (MW)	g/mol	in air	s^{-1}	Aquatic ecotoxicity	EC_{50}
Octanol-water partition coefficient (K_{OW})	-	in water	s^{-1}		
Organic-carbon partition coefficient (K_{OC})	L/kg	in (aerobic) sediments	s^{-1}	**Human toxicity**	
Henry constant (K_{H25})	$Pa.m^3/mol$	in anaerobic sediments	s^{-1}	Ingestion, non-cancer	kg/kg/day kg/lifetime
Vapour pressure (P_{vap})	Pa	in soil	s^{-1}	Inhalation, non-cancer	kg/kg/day kg/lifetime
Solubility 25ºC (SOL)	mg/L	**Human exposure**		Ingestion, cancer	kg/kg/day kg/lifetime
		Bioaccumulation factor in fish (BAF)	L/kg_{fish}	Inhalation, cancer	kg/kg/day kg/lifetime

3. Results interpretation and discussion

3.1. Human Toxicity

Table 2 presents the CF for the USEtox methodology. To facilitate the comparison between the assessed substances and other compounds, the CF of Cu(II) are also presented, being this element a common negative current collector [6] and thus, substitutable by CNT.

Table 2. Human Toxicity (non-cancer) characterization factor ($cases/kg_{emitted}$)

Emission to	**Urban air**	**Rural air**	**Freshwater**	**Seawater**	**Natural soil**	**Agric. soil**
SWCNT	7.5E-05	6.7E-05	6.6E-04	6.4E-04	2.8E-07	2.9E-07
MWCNT	2.5E-03	2.6E-03	2.7E-03	9.2E-06	8.3E-04	1.4E-03
Cu(II)	1.3E-05	1.4E-05	8.6E-07	2.2E-07	4.6E-07	3.7E-05

The factors calculated for USEtox suggest MWCNT to be more harmful to human health than SWCNT when emitted to all compartments but seawater. If we take into account that the precision of the USETox CF for HT is usually of 2-3 orders of magnitude [13], the CF of both CNT could be considered identical. Similarly, for all emission compartments, the CF of one or both CNT are within 2-3 orders of magnitude of those of C. Hence, it is possible CNT are only marginally more toxic than the alternative. In order to explain the differences, both between CNT and of them with the reference substance, it is necessary to see how the parameters affecting the CF change between substances. According to [13]:

$$CF = FF \times XF \times EF \,, \tag{1}$$

or $$CF = iF \times EF \text{ , for human toxicity,} \tag{2}$$

being $$iF = FF \times XF \tag{3}$$

Where *FF* is the fate factor, how the chemical behaves in the environment, *XF* the exposure factor, the probability of being exposed to the chemical found in the environment, and *EF* the effect factor,

[1] No-Observed-Effect-Concentration: it is the parameter required to estimate the carcinogenity of substances in USEtox.

how the chemical behaves once it has reached the target organism. *iF* is the intake factor, which is the probability of being exposed to a chemical released to the environment.

Based on the calculated EF, SWCNT have almost 4 times more chances of affecting someone when inhaled than MWCNT (Table 3) but they still have a lower CF. This is because for all these three substances most of the impacts from their airborne emissions come from indirect sources. As indicated in section 2, the air-water partition coefficient of CNT is, as for metals, assumed to be negligible. As such, airborne CNT and Cu are going to be quickly deposited on water and soil, entering the human organism through drinking water or food rather than being inhaled. If ingested, MWCNT are the ones with a greater chance of causing damage, which is the reason why MWCNT's CF are higher than those of SWCNT for air, freshwater and soil emissions. The lower CF of MWCNT for seawater emissions is explained by means of their intake factors. The transfer of SWCNT from seawater to fish (the most direct route of exposure for seawater emissions) is 6 orders of magnitude higher than the one for MWCNT. Therefore, even when the latter are more toxic on a mass basis, they have a higher EF, the SWCNT have an overall greater chance of affecting a human body if released to the sea.

Table 3. Selected factors affecting Human Toxicity (non-cancer) CF

	EF (cases/kg$_{intake}$)		**iF (kg$_{intake}$/kg$_{emitted}$)**					
	inh	ing	Uair-air	Uair-other[1]	Fwater-fish	Swater-fish	Nat. soil-fish	Ag. soil-prod[2]
SWCNT	5.3E-02	1.1E-03	2.6E-05	6.5E-02	5.8E-01	5.7E-01	2.5E-04	3.0E-11
MWCNT	1.4E-02	1.3E+01	2.6E-05	2.0E-04	2.3E-05	7.2E-07	7.0E-06	4.7E-05
Cu(II)	9.1E-03	9.1E-03	2.6E-05	1.4E-03	6.7E-05	2.4E-05	3.6E-05	3.9E-03

[1] drinkig water+expected products+ unexpected products+meat+dairy+fish
[2] exposed produce+unexposed produce

The differences between the EF of CNT and Cu do not justify entirely the lower CF the latter showed in Table 2. Cu ingestion's EF 8 times larger than the one for SWCNT, should play an important role in defining the toxicity of its water and soil emissions. However, waterborne SWCNT are expected to transfer more easily from to fish than Cu (4 orders of magnitude more, see Table 3), hence their higher CF. For both SWCNT and Cu, fish is also the most direct route of exposure for natural soil emissions. However, in this case Cu is transferred more easily than SWCNT (14 times more) and therefore is the one presenting a higher CF. For agricultural soil, produce are the main route of exposure for Cu, enough to make them more dangerous than SWCNT, whose main route of exposure continues to be fish.

3.2. Data dependency of Human Toxicity CF: Current limitations and recommendations for future work

As seen in the previous section, there are two main factors affecting the differences in the CF calculated for the CNT and of these two with Cu: 1) their ingestion EF, and 2) their iF from several media, namely water, to fish.

EF are a direct consequence of the HT parameters, higher in the case of SWCNT for inhalation and for MWCNT in case of ingestion. For both CNT these parameters were obtained directly from experimental data. However, the ingestion factor of SWCNT is based on a study where a single bolus was administered, assessing then acute and sub-chronic effects [23]. This could potentially underestimate the oral toxicity of SWCNT and thus, in order to increase the validity of this parameter, future studies need to administer repeated doses so the chronic effects of the ingestion of SWCNT can be better known. Regarding EF, it is also necessary to mention that the size of the SWCNT used to define the inhalation and ingestion toxicity factors are not the same and that none of them are consistent with the one chosen for the comparison with MWCNT. As for MWCNT [26], it could be possible the behaviour of SWCNT in the organism to change with size, increasing thus the uncertainty of the calculated CF.

The intake factors from fish might, on the other hand, overestimate the availability of SWCNT for human consumption. According to the calculated results, fish consumption would be the main route of exposure to SWCNT, irrespectively of where they are emitted. The transfer of a substance to fish is affected by several factors, including the exchange between the media where they are emitted and water. For SWCNT, the most significant parameter is the BAF. As mentioned in section 2, for both CNT, this parameter is not measured directly but calculated instead based on the $\log K_{OW}$. This latter parameter is based on experimental data for MWCNT (2.42) but its value is estimated for SWCNT (12.42) which might be the reason for the the large differences between the two CNT. Due to the critical importance of these two parameters, BAF and $\log K_{OW,}$ in defining the behaviour of CNT in the environment, we recommended that for future calculations of CF at least one of them is based on empirical data.

Finally, as previously mentioned, there are no reports of SWCNT being carcinogenic [25] and as such no carcinogenic effects have been included in the CF presented here. However, if SWCNT are ever confirmed to cause cancer, those factors would need to be recalculated. Regarding MWCNT, there carcinogenity is relatively well known but we will require more data, in the form of NOEC, before their CF can be calculated.

3.3. Freshwater Ecotoxicity of Single-walled and Multi-walled Carbon Nanotubes

Regarding the FET results presented in Table 4, MWCNT are clearly more dangerous than SWCNT irrespectively of where they are emitted, since the differences between them are much larger than the precision of 1-2 orders of magnitude given by USEtox for FET CF [13]. Following the same reasoning, MWCNT are probably less dangerous than Cu, since most of the differences between them are in the range of 2 orders of magnitude. The exceptions are seawater emissions, where Cu is clearly more toxic than any CNT.

Table 4. Freshwater ecotoxicity characterization factor (PAF.m^3.day/$kg_{emitted}$)

Emissions to	**Urban air**	**Rural air**	**Freshwater**	**Seawater**	**Natural soil**	**Agric. soil**
SWCNT	4.85E-03	3.04E-03	1.25E-01	2.83E-30	5.32E-05	5.32E-05
MWCNT	1.91E+02	1.88E+02	7.40E+02	2.44E-21	2.26E+02	2.26E+02
Cu(II)	2.31E+04	2.33E+04	5.52E+04	1.03E-16	2.92E+04	2.92E+04

In the same way as HT CF, EF alone does not explain the differences between the FET CFof CNT, being 2 orders of magnitude higher for SWCNT than for MWCNT (Table 5). It is the XF, the possibility of being taken in by the objective organism (algae, daphnia, fish, etc.), the factor affecting the final value of the CF the most, being 6 orders of magnitude higher for MWCNT than for SWCNT. EF is however, the main responsible for the differences between MWCNT and Cu since it is 3 orders of magnitude lower for the former than for the latter. Nevertheless, the FF play an important role in defining the CF for seawater emissions. Contrarily than for the other compartments, where the FF to freshwater present the same tendency as the XF (MWCNT>Cu>SWCNT), in this case Cu and MWCNT exchange positions (Cu>MWCNT>SWCNT), which can explain partially why Cu is more toxic than CNT when emitted to seawater. Another factor affecting this discrepancy is that for both SWCNT and Cu, the transfer from seawater to freshwater is not as direct as it is for MWCNT (data not shown). Most of the SWCNT and Cu emitted to seawater would not exchange directly to freshwater, but would transfer there after moving to a different compartment, i.e. air and soil.

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Table 5. Selected factors affecting Freshwater Ecotoxicity CF

	EF (PAF.m³/kg)	**XF (-)**	**FF to freshwater from (days)** Air[1]	Fwater	Swater	Nat. soil	Ag. Soil
SWCNT	6.5E+02	6.5E-06	6.4E-01	2.9E+01	5.5E-28	1.2E-02	1.2E-02
MWCNT	8.0E+00	1.0E+00	2.1E+01	9.2E+01	2.0E-14	2.8E+01	2.8E+01
Cu(II)	4.5E+03	3.3E-01	1.4E+01	3.7E+01	3.6E-20	1.9E+01	1.9E+01

[1] FF for Urban air and Rural air emissions present the same value

3.4. Data dependency of Freshwater Ecotoxicity CF: Current limitations and recommendations for future work

As for HT, two factors are the ones affecting the most the FET of CNT: 1) the EF and the 2) XF. Contrarily to how the HT EF are calculated, for FET several species, and potentially several studies for each species, can be considered. As indicated in section 2, two studies were used to calculate the EF of SWCNT, one for *Daphnia mangna* and another one for *Chlorella vulgaris*. Although the literature regarding the toxicity of engineered nanomaterials in fish is extensive [27], to the best of our knowledge no studies assessing the mortality caused by SWCNT are available yet. SWCNT are known respiratory toxicants in trout, producing gill pathologies at concentrations of 0.1 mg/L [28] but, partially due to the low solubility of these compounds, no LC_{50} has been determined for SWCNT yet. This kind of study would be required to achieve more robust FET CF. Nevertheless, all EC_{50} used in this assessment suggest SWCNT to be more harmful to aquatic life than MWCNT. Thus we consider there is only a small margin for error regarding their relative CF.

For FET, the XF is calculated as the truly dissolved fraction of a substance [29]. According to [17]:

$$XF = \frac{1}{1 + \frac{(Kp \cdot SUSP + K_{doc} \cdot BCF_{fish} \cdot BIOmass)}{10^6}} \tag{4}$$

Where *Kp*, *Kdoc*, and BCF_{fish} increase with K_{OC}, which is calculated based on K_{OW} thus the 6 orders-of-magnitude between CNT shown in Table 5. Contrarily to what happened to HT, the high K_{OW} of SWCNT makes them less available for aquatic life. Regardless, K_{OW}, calculated for SWCNT based on their chirality, has proven to affect significantly both human and freshwater toxicity CF. Accordingly, it should be a priority for the calculation of future CF to use experimental K_{OW}, as well as using BAF and K_{OC} not based on the water-octanol partition coefficient.

4. Conclusions

CNT are a promising material group with excellent technical performed which can be applied in the in the field of energy storage as well as in many others. Regarding known effects, they could potentially cause less environmental harm than alternative materials. However, their potential effects on human health might discourage its implementation. Important differences were found between the two CNT assessed, suggesting that 1) CNT are not a homogeneous group in terms of toxicity, 2) whether or not CNT should substitute current materials might depend on which particular nanotube is used.

This work shows that, despite current limitations, it is possible to calculate the CF of CNT for Life Cycle Impact Assessment with the existing information and methodologies. However, these CF should be considered as interim due to their dependency on estimated parameters, namely K_{OW}, and the lack of toxicity studies regarding certain effects such as carcinogenity. Overall, more research, both in the field of LCA and outside, will be required before the impact of engineered nanomaterials can be fully assessed over their whole life cycle.

Nomenclature

CF	Characterization factor(s)	HT	Human Toxicity
CNT	Carbon Nanotube(s)	iF	Intake factor(s)
EF	Effect factor	MWCNT	Multi-walled Carbon Nanotube(s)
FET	Freshwater Ecotoxicity	SWCNT	Single-walled Carbon Nanotube(s)
FF	Fate factor(s)	XF	Exposure factor(s)

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