



Sorption kinetics and equilibrium of the herbicide diuron to carbon nanotubes or soot in absence and presence of algae



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ABSTRACT

Carbon nanotubes (CNT) are strong sorbents for organic micropollutants, but changing environmental conditions may alter the distribution and bioavailability of the sorbed substances. Therefore, we investigated the effect of green algae (*Chlorella vulgaris*) on sorption of a model pollutant (diuron, synonyms: 3-(3,4-Dichlorophenyl)-1,1-dimethylurea, DCMU) to CNT (multi-walled purified, industrial grade, pristine, and oxidized; reference material: Diesel soot). In absence of algae, diuron sorption to CNT was fast, strong, and nonlinear (Freundlich coefficients: $10^{5.79}–10^{6.24} \mu\text{g}/\text{kg}_{\text{CNT}} \cdot (\mu\text{g}/\text{L})^{-n}$ and 0.62–0.70 for K_F and n , respectively). Adding algae to equilibrated diuron-CNT mixtures led to 15–20% (median) diuron redissolution. The relatively high amorphous carbon content slowed down ad-/desorption to/from the high energy sorption sites for both industrial grade CNT and soot. The results suggest that diuron binds readily, but – particularly in presence of algae – partially reversibly to CNT, which is of relevance for environmental exposure and risk assessment.

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1. Introduction

Carbon nanotubes (CNT), a nano-scaled allotrope of carbon, can strongly sorb organic pollutants (OP) with a similar or higher affinity than other carbonaceous sorbents, depending on their high specific surface area (SSA), and their large delocalized electron systems (Pan and Xing, 2010b). Once released in the environment (Hendren et al., 2011), CNT may therefore change the fate and bioavailability of OP (Hofmann and von der Kammer, 2009; Pan and Xing, 2010b).

Numerous different sorption mechanisms are discussed to explain and predict the fate of chemicals in the presence of CNT in equilibrium (Chen et al., 2011, 2008; Pan and Xing, 2008, 2010b; Wang et al., 2010, 2009; Wu et al., 2013). Less attention has been given to the kinetics of ad-, ab-, and desorption of OP on/from CNT, which is important to understand the release of OP from CNT as a secondary water contamination source. Initial studies suggest that

many OP reversibly sorb to CNT on a time scale of hours (Chen et al., 2011, 2009; Oleszczuk et al., 2009; Pan and Xing, 2010a; Zhang et al., 2012). However, some pharmaceuticals' (Oleszczuk et al., 2009) and other OP's (Wu et al., 2013) sorption equilibrium to CNT was reached after 5 days only. It is currently not entirely clear why OP sorb that much slower to certain CNT than to others.

One of the first studies on desorption of OP from CNT was performed by Oleszczuk et al. who showed that desorption kinetics of oxytetracycline and carbamazepine from CNT followed a two-phase first order model consisting of a rapid and a slow desorbing fraction (Oleszczuk et al., 2009). Slightly slower desorption than sorption, and sorption hysteresis is proposed to be explainable by rearrangement of the CNT bundles, pore condensation, or the exothermic adsorption of OP to CNT (Pan and Xing, 2008). A more recent study suggested irreversible chemical reactions of the sorbate with carboxylic functional groups of the sorbent (Wu et al., 2013).

Little is known about sorption in more complex, environmentally relevant setups, e.g. sorption in presence of natural organic matter (NOM) (Pan et al., 2013), or sorption in presence of organisms (Xia et al., 2010). Competitively sorbed NOM (Shi et al., 2010;

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Zuttel et al., 2002), or surface oxidation (Pan and Xing, 2010b; Wang et al., 2010), may strongly reduce the CNT sorption capacity, especially for aromatic or planar OP (Shi et al., 2010; Wang et al., 2010, 2009; Zhang et al., 2011). Then again, the presence of NOM may increase OP sorption to CNT, because it may enhance dispersion of the CNT, and thus increase the available CNT surface area (Pan et al., 2013). We found just one study which investigated the influence of organisms on sorption. Xia et al. suggested that the presence of *Agrobacterium* probably promoted desorption of phenanthrene from CNT in soil, or that the bacterium utilized sorbed phenanthrene (Xia et al., 2010). It is unclear what led to the increased availability of the OP, and if phenanthrene desorbed before it became bioavailable. Because algae are the major primary producers in aqueous environments, it is of particular interest how OP sorption to CNT is affected by them. Again, there is no information available on such interactions. Any biological activity in aqueous sorption experiments is usually suppressed by adding a biocide such as NaN_3 (Shi et al., 2010). Information on the influence of organisms on OP sorption to CNT is needed to assess, for instance, the safety of applications aiming at removing OP from water by CNT. Generally, in view of the constantly growing CNT production volumes (Hendren et al., 2011), it would be useful to know the environmental exposure of micropollutants sorbed to CNT.

Hence, the overall aim of our study was to systematically quantify the sorption processes in a pollutant-CNT-biota model system, and to test the hypothesis that algae may attenuate sorption similar to NOM. Experiments were performed with the widely used herbicide diuron (Cornelissen et al., 2005; Knauer et al., 2007), different types of CNT, soot as a reference sorbent, and the freshwater green alga *Chlorella vulgaris*. The specific goals were to a) quantify sorption thermodynamics and kinetics of diuron and CNT, b) quantify the impact of algae on the ongoing sorption processes in the pollutant-CNT-biota system, and c) compare the sorption of industrial, purified, oxidized and pristine CNT and the reference sorbent Diesel soot. Further, this paper aimed at providing mechanistic explanation for diuron sorption in a companion study showing enhanced toxicity of the herbicide in presence of CNT (Schwab et al., 2013).

2. Experimental section

2.1. Chemicals

3-(3,4-Dichlorophenyl)-1,1-dimethylurea (diuron, DCMU) and 3-(3,4-dichlorophenyl)-1,1-dimethyl(D6)urea (D6-diuron), both >99% pure, were purchased from Labor Dr. Ehrenstorfer (Germany). For structures, see Table S1. Acetonitrile (99.99%) was obtained from SCHARLAU CHEMIE S.A. (Spain). All other chemicals were *per analysis* grade and obtained from Merck or Sigma-Aldrich, Switzerland. Ultra-pure water (Milli-Q) was produced by a gradient A10 water purification system from Millipore (Volketswil, Switzerland). Nitrogen (99.99995%) was obtained from PanGas (Dagmarsellen, Switzerland).

2.2. Carbonaceous nanoparticles

Purified pristine and oxidized CNT (ppCNT and poxCNT) were synthesized by catalytic chemical vapor deposition by EPFL Lausanne, Switzerland. Industrial pristine CNT (ipCNT) of similar size and shape were purchased from Cheap Tubes Inc., Brattleboro, VT 05301, USA. The average CNT diameter as determined by transmission electron microscopy ranged between 8 and 15 nm, and the length as determined by scanning electron microscopy between 0.5 and 2.0 μm . As native black carbon reference sorbent, a forklift Diesel soot standard (soot) with spherical primary particles in the range of 35 nm (Gustafsson et al., 2001) was used (Standard Reference Material 2975, National Institute of Standards and Technology, USA). Transmission electron microscopy images and detailed characterization data for all materials, and synthesis details are given in Fig. S1, Table S2, and in Schwab et al. (2011). The sorbent suspensions were prepared in 2-[4-(2-hydroxyethyl)piperazin-1-yl]ethanesulfonic acid (HEPES) buffered OECD algal test medium (OECD, 2006) 1.00 mM, pH 7.0 \pm 0.3. Further details are provided in the supporting information (SI, sections "Preparation of Sorbent Suspensions", and "Notes on the Sterile Preparation of the Particle Suspensions").

2.3. Green algae cultivation

Chlorella vulgaris, strain 211-11b (Culture Collection of Algae, SAG, University of Göttingen, Germany), was cultivated in the OECD algal test medium (OECD, 2006). In short, axenic cultures grew at 24 ± 0.5 °C, 100 rpm, an illumination of $80 \pm 15 \mu\text{Em}^{-2} \text{s}^{-1}$ (daylight lamps, Sylvania Gro-Lux F15W/Gro T8, Infors, Switzerland), and under a light:dark regime of 16:8 h. Algae used for tests were harvested in the exponential growth phase, and the cell density was counted using a haemocytometer chamber. More details on the incubation conditions are available elsewhere (OECD, 2006; Schwab et al., 2011).

2.4. CNT and soot suspensions

The used CNT and soot in the standardized suspensions and their detailed behavior in the algal medium were characterized as described previously (Schwab et al., 2013, 2011). The polydispersity of the CNT suspensions was monitored using dynamic light scattering (DLS) in a range of 1–10 000 nm (Zetasizer Nano ZS, Malvern, UK) at the same experimental conditions as used for the ternary sorption experiments. Three replicates per treatment were measured. Finally, sorbent-algae suspensions were examined microscopically. For more details see SI, section "Dry and Suspended CNT Characterization."

2.5. Binary sorption experiments

All sorption isotherms with CNT or soot and diuron were obtained using a batch equilibration technique at 24 ± 2 °C. Screw cap glass vials (22 mL) were used. To each vial, well homogenized sorbent stock suspension was added and diluted with algal growth medium to obtain, after addition of the diuron stock solution, a final nominal concentration of 10.0 $\text{mg}_{\text{CNT}}/\text{L}$ and 5.00 $\text{mg}_{\text{soot}}/\text{L}$, respectively. The exact sorbent concentration in the stock suspensions was calculated in each experiment from the weighed in mass of CNT or soot. Nine to ten different initial diuron concentrations in a range of 0.73–2994 $\mu\text{g}/\text{L}$ were prepared by spiking different volumes of a diuron working stock solution to the CNT suspensions. The concentration range covered more than three orders of magnitude to account for the expected nonlinear sorption behavior of CNT. All concentrations were tested at least in duplicates, and control treatments at least in triplicates. We reduced the replicate number to two, for the sake of a higher number of tested concentrations. These test suspensions were prepared sterilely without biocide, despite of the increase of variability of the data this inflicts, to avoid killing the algae in the subsequent ternary sorption experiments (details in section "Notes to the sterile preparation of the particle suspensions" in the SI). Finally, the vials containing the sorbent-diuron mixture were sealed with polytetrafluoroethylene (PTFE) lined screw caps, additionally covered with Parafilm[®], wrapped in aluminum foil and then pre-equilibrated on an orbital laboratory shaker. The mixtures were kept for 20 h at 175 rpm (to keep the sorbents in full suspension; see OECD, 2000) in the dark at 24 ± 2 °C, and under equal conditions for 28 d to study sorption of diuron under non-equilibrium and equilibrium conditions, respectively.

2.6. Ternary sorption experiments

To examine the change of sorption after perturbation of the system by living green algae, $7\text{--}37 \times 10^4$ cells/mL of *C. vulgaris* were added to 20 h-, or 28 d-kept diuron-CNT mixtures (equilibration conditions alike the binary sorption experiments). The added algae culture volume was controlled to change the total volume in the vials by $\leq 1.8\%$. For incubation, all vials were placed vertically inside of an illuminated sterile bench ($15 \pm 5 \mu\text{Em}^{-2} \text{s}^{-1}$) at room temperature to prevent contamination of the samples and to provide light for the algae. These conditions were chosen to keep the viability (photosynthetic activity) of the green algae constant in the control treatments (Schwab et al., 2013). After incubation the diuron-CNT mixtures with green algae, the subsequent changes of the diuron concentration were measured after 3, 6, 15, and 24 h (sampling and quantification described in section "Diuron Analysis"). The robustness of this setup was verified by repeating some ternary sorption experiments under different incubation conditions (in 50.0 mL Erlenmeyer flasks at 100 rpm and $80 \pm 15 \mu\text{Em}^{-2} \text{s}^{-1}$).

2.7. Sorption isotherms

Sorbent diuron for both binary and ternary sorption experiments was calculated by mass balance using the initial and final quantified aqueous diuron concentrations (see section "Diuron Analysis"). The algae-affected "sorption isotherms" are denoted in this study by the term "perturbed isotherms", where the perturbation was the incubation with *C. vulgaris*. Five common isotherm models were evaluated for fit to the data (Pikaar et al., 2006; Xia and Ball, 2000). All details on the modeling are provided in the SI, Table S5, sections "Modeling of (Perturbed) Sorption Isotherms", "Details on the Different Sorption Models", and "Details on the Goodness of the Fit of the Different Sorption Models". Details on calculation of the fraction of additionally sorbed or re-dissolved diuron are provided in the SI.

2.8. Adsorption kinetics

Batch adsorption experiments (50.0 mL per replicate) were performed in 50 mL screw-capped glass vials. Pristine purified CNT, ipCNT, and soot were tested (poxCNT

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