NO$_2$ and natural organic matter affect both soot aggregation behavior and sorption of S-metolachlor†

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Soot is an important carbonaceous nanoparticle (CNP) frequently found in natural environments. Its entry into surface waters can occur directly via surface runoff or infiltration, as well as via atmospheric deposition.

Pristine soot is likely to rapidly undergo aggregation and subsequent sedimentation in aquatic environments. Further, soot can sorb a variety of organic contaminants, such as S-metolachlor (log $K_D = 3.25 \pm 0.12$). During atmospheric transport, soot can be chemically transformed by reactive oxygen species including NO$_2$. The presence of natural organic matter (NOM) in surface waters can further affect the aquatic fate of soot. To better understand the processes driving the fate of soot and its interactions with contaminants, pristine and NO$_2$-transformed model soot suspensions were investigated in the presence and absence of NOM. NO$_2$-oxidized soot showed a smaller particle size, a higher number of particles remaining in suspension, and a decreased sorption of S-metolachlor (log $K_D = 2.47 \pm 0.40$). In agreement with findings for other CNPs, soot stability against aggregation was increased for both pristine and NO$_2$ transformed soot in the presence of NOM.

Environmental significance

Soot is an important carbonaceous nanoparticle (CNP) frequently found in natural environments with abundances up to $10^4$ times higher compared to widely studied engineered CNPs. Although soot CNPs are highly relevant to surface water systems, to date, the nano-particle properties of soot in the natural environment have received only a little attention. Here we investigate the effects of atmospheric transformation with NO$_2$ on soot aggregation and contaminant sorption using the widely found herbicide S-metolachlor as a model contaminant. The findings of this study will help to better understand the colloidal behavior of pristine soot compared to atmospherically transformed soot and bring forward hitherto underexplored aspects of soot as a naturally occurring CNP.

1. Introduction

Due to climate change and shifting land usage, wildfires have increased in abundance and intensity in recent years and are expected to further increase in the future.¹ Wildfires and incomplete combustion of biomass and fossil fuel can form a considerable amount of carbon nanoparticles (CNPs). One type of CNP is soot, the finest fraction of incomplete combustion residues formed via re-condensation and nucleation of organic compounds from the gas phase during the combustion process.² Annual production of soot transportable via the atmosphere is estimated to be 17 Tg per year.³ Thus, soot emissions are expected to be at least $10^4$ times more abundant compared to widely studied engineered CNPs including graphene oxides, fullerenes and carbon nanotubes.⁴

Once released into the atmosphere, soot can undergo chemical transformation, resulting in changes in the surface chemistry. Key processes for atmospheric soot transformation are photochemical redox reactions with NO$_2$, SO$_2$, O$_3$ and other reactive oxygen species in the atmosphere.⁵,⁶ Over time NO is predominantly oxidized to NO$_2$ in the atmosphere, thereby making NO$_2$ the most abundant NO$_x$ reactive oxygen species in the atmosphere. The reaction of NO$_2$ with soot was previously elucidated using spectroscopic techniques where infrared bands were attributed to acidic functional groups (C(=O)O–R, R–NO$_2$, and R–ONO are the main functionalities).⁷,⁸

Soot – pristine or atmospherically transformed – can reach water bodies directly via atmospheric deposition and indirectly via surface runoff and infiltration. In suspension, soot can remain colloidaly stable, i.e. dispersed, and be transported in the aqueous phase, or it can aggregate and deposit. The
aggregation behavior of soot is expected to depend mainly on the
soot surface charge, the presence of natural organic matter
(NOM), and the ionic composition of the aqueous environment.²⁴
A recent study by Chen et al.²⁴ found that soot aggregation fol-
lowed classic Derjaguin–Landau–Verwey–Overbeek (DLVO)
theory,²⁵–²⁷ describing the aggregation behavior of particles as a
combination of van der Waals attraction and electrostatic
repulsion. Depending on the aqueous chemistry, soot particles
can remain stable against homo-aggregation in typical freshwater
environments but are likely to aggregate under saline conditions
(e.g., estuaries) due to the compression of the electrical double
layer at higher ionic strengths. The effect of chemical trans-
formation (e.g., with NO₂) on the aggregate size of soot particles
has to date received little attention. But with an increasing
negative surface charge and the presence of NOM soot particles
are expected to form increasingly stable suspensions.²⁴
In the water phase, soot has a strong adsorption affinity for a
range of organic contaminants,³³–³⁶ and because of its higher
abundance compared to other CNPs, soot may significantly alter
the fate of organic contaminants occurring in surface
waters. From other CNPs it is known that the presence of NOM
strongly affects particle aggregation and size and may also
influence the sorption of organic contaminants due to changes
in accessibility of sorption sites. For instance, a number of
studies have shown that the presence of NOM can decrease the
sorption affinity of carbon nanotubes for organic contaminants
by competing for sorption sites and blocking the accessibility
to micropores.³⁷–³⁹ In contrast, both Wang et al.³⁹ and Hou et al.⁴¹
found that NOM can increase the sorption affinity of organic
contaminants to fullerene (nC₆₀) aggregates. This can be
explained by an increase in accessible sorption sites due to
diminished aggregation of nC₆₀. However, it remains unclear if
similar effects occur with soot particle suspensions.

Pesticides are of environmental interest due to their wide-
spread use and subsequent occurrence in natural waters. The
herbicide S-metolachlor was selected as a model contaminant
because of its (i) structural similarities to several other mobile
organic contaminants, i.e., an aromatic ring substituted with
polar functional groups, (ii) widespread use since 1978 in the
USA and most European countries in corn and cotton produc-
tion, and (iii) ecotoxicity in several aquatic species and birds.²²,²³

Sorption of organic compounds to “soot in water” is gener-
ally weaker than that to “soot in air”, indicating that surface
coverage with water suppresses the sorption by soot.²⁴ Thus,
soot is expected to interact most strongly with organic
contaminants when it is not fully wetted. Investigations into
the pre-wetting kinetics of 1,2,4-trichlorobenzene and phenan-
threne sorption by Nguyen et al.⁴⁴ showed that the complete
wetting of soot requires more than 20 days and the corre-
sponding degree of water coverage of soot affects sorption of
organic contaminants. In addition, most soot particles are ex-
pected to be in suspension directly after their introduction into
water bodies, before they can sediment. Therefore, with the
intent to simulate environmentally meaningful scenarios, this
study tackled the behavior of soot freshly introduced into water.

With the aim to obtain a better understanding of soot
aggregation and interactions with organic contaminants,
pristine and NO₂-transformed model soot was investigated in
the presence and absence of NOM. We hypothesize that (i) NO₂-
transformation and interactions with NOM increase the aggre-
gation stability of soot and (ii) sorption of the model contami-
nant S-metolachlor is affected by changes in soot surface
chemistry and interactions with NOM.

2. Materials and methods

Analytical grade S-metolachlor, methanol, acetonitrile, HNO₃,
and CaCl₂ were purchased from Sigma-Aldrich (Germany).
Suwannee River NOM was purchased from the International
Humic Substances Society (USA). Milli-Q water was obtained
using a Millipore instrument (Elix 5 Milli-Q Gradient A10, USA).

2.1 Soot preparation

Printex U soot was purchased from Evonik Carbon Black GmbH
(Germany). Printex U is industrial soot with similarities to diesel
engine soot which has previously been well characterized and
used as a model soot sample.²⁶,²⁷ To approximate trans-
formation by NO₂, the soot was treated according to a protocol
adapted from Wei et al.²⁸ In short, a thin layer of soot (approx-
imately 2 mm) was exposed to saturated HNO₃ vapor containing
NO₂ within a sealed glass desiccator under vacuum for 24 h at
room temperature (25 °C) at a pressure of 200 mbar. The
experimental setup did not allow for the measurement of NO₂
and other radical species that could also have formed (i.e., OH’).
However, the degree of transformation was likely above the
short term soot transformation expected in the atmosphere.
Both pristine and NO₂-transformed soot were thereafter indi-
vidually rinsed with Milli-Q water (250 mL g⁻¹, Fisher Scientific
Phase Separating Filter Paper, Germany). Dry powdered soot
samples were weighed into the respective background solution
and vortexed for 30 s prior to any experiment.

2.2 Soot characterization

Sorbent suspensions of pristine and transformed soot were
prepared in 1 mM CaCl₂ with or without NOM (10 mg L⁻¹ DOC)
and shaken for 24 h to obtain similar conditions to those in the
sorption batch experiment (see Section 2.3). For selected
samples DOC concentrations were measured after 24 h of
shaking to determine the DOC loading on soot in the experi-
ments (centrifugation at 1000g for 30 min and filtration, <0.22
µm, Shimadzu L series TOC). The hydrodynamic diameter of
the particles was calculated by dynamic light scattering (DLS)
with a ZetaSizer Nano ZS (Malvern Instruments Ltd., UK) with
a laser of 632.8 nm wavelength at a fixed angle of 173°. Soot
suspensions were vortexed for 10 s after the soot was transferred
into the respective background solution. Including sample
transfer and automatic adjustment of measurement settings by
the instrument, the first measurement point was obtained after
80 s. Data for individual measurements of 10 s each for 30 min
and for 1 min after 24 h of shaking were collected automatically.
The autocorrelation function was fitted using the cumulant
method, assuming a refractive index of 2.4. The polydispersity
index (Pdi) ranged from 0.2 to 0.8. Thereafter, the

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electrophoretic mobility of the particles remaining in suspension after a settling period of 1 min was measured and converted to the ζ potential using 3 measurements with 20 runs each applying Henry’s equation. The electrical conductivity was above 200 μS cm⁻¹. All samples were run in duplicate. The ash content was determined by weighing samples before and after heating at 750 °C for 6 h. The total C, H, and N contents were determined using an elemental analyzer (Elementar Vario Macro, Germany), and the O content was calculated by mass balance: O% = 100 – (C + H + N + ash). The BET specific surface area and pore size distribution were determined using N₂ physorption following protocols previously described in Sigmund et al.²⁹ For scanning electron microscopy (Zeiss Sigma VP 300, acceleration voltage of 5 kV, working distance 3.6 mm, magnification 1.56k), single drops (20 μL) of the four soot suspensions after shaking for 24 h and settling for 1 min were placed on aluminum foil and dried in a desiccator. Fourier transform infrared spectra of dried samples (FTIR Bruker Tensor 27) were measured with a resolution of 4 cm⁻¹ and 128 scans.

2.3 Sorption experiments

Sorption experiments were conducted at room temperature using the batch method based on OECD guideline 106 at 1 mM CaCl₂ and at eight different S-metolachlor concentrations in the range of 1 to 50 mg L⁻¹ (remaining at least one order of magnitude below solubility).²⁸ Experiments for sorption of S-metolachlor and soot aggregation were carried out in suspensions comprising 10 mL aqueous phase loaded with 10 mg soot (i.e. 1 g soot per L), which is likely above most concentrations that may occur in the natural environment. The pH ranged between 6.8 and 7.4 throughout all experiments and did not significantly differ between pristine and NO₂-transformed soot. S-Metolachlor is a polar but non-ionizable compound and pH is thus not expected to strongly affect sorption even though functional groups on the soot surface may have been partially dissociated. The samples were spiked with S-metolachlor using a methanolic stock solution (volume < 1% to avoid co-solvent effects) and equilibrated on a shaker at 125 rpm for 24 h to reach equilibrium (pre-experiments showed that equilibrium was reached after 16 h; see Fig. S1 in the ESI†). Thereafter, a small volume of the suspension was filtered (<0.20 μm) and analyzed by HPLC (Phenomenex Luna C18 50 × 2.00 mm 5 μm column, detection at 210 nm with a Shimadzu DAD SPD-M20A detector). For the mobile phase a solvent mixture of Milli-Q water and acetonitrile was used (20/80 by volume). The limit of quantification for S-metolachlor was calculated to be tenfold the background noise and was 0.10 mg L⁻¹. Measured concentrations ranged between 0.4 and 40 mg L⁻¹ and recoveries were calculated based on control samples without soot and used for concentration correction (recoveries ranged from 90 to 115% over the concentration range investigated). Sorbent loading was calculated via mass balance and fractions of S-metolachlor sorbed ranged from 6.5 to 85%.

2.4 Data analysis

Sorption isotherms were fitted with the Freundlich model:

\[
q = K_F \times C_{aq}^n
\]

where \( q \) (mg kg⁻¹) is the sorbent loading, \( C_{aq} \) (mg L⁻¹) is the aqueous concentration of the sorbate, \( K_F \) is the Freundlich coefficient, and \( n \) is the Freundlich exponent representing isotherm non-linearity (non-linearity increases as \( n \) deviates from unity). For a comparison among the soot suspensions and a prediction model, individual sorption coefficients (\( K_{F0} \), L kg⁻¹) were calculated with the Freundlich equation at a fixed aqueous concentration of 10 mg L⁻¹. Standard deviations (\( \sigma \)) of the Freundlich fit based \( K_F \) values at a given aqueous concentration were calculated using the uncertainty propagation equation.

\[
\sigma_q = \sqrt{(\frac{C_{aq}^n \sigma_K}{K_F C_{aq}^n})^2 + \left(\frac{K_F C_{aq}^n \ln(C_{aq}) \sigma_a}{K_F C_{aq}^n}ight)^2}
\]

Standard deviations for ppLFER-based \( K_F \) values at a given aqueous concentration were calculated using linear uncertainty propagation.

3. Results and discussion

3.1 Particle size decreased after transformation with NO₂ and interaction with NOM

The measured ζ-potential increased upon transformation from −8.5 ± 0.8 mV for pristine soot to −19.4 ± 0.4 mV for transformed soot (see Fig. 1), indicating the formation of negatively charged functional groups on the NO₂-transformed soot surface (e.g. R-C≡O and/or R-COOH as indicated in FTIR spectra; see Fig. S2 in the ESI†). The formation of nitrogen- and oxygen-containing surface functional groups (C(=O)O-R, R-NO₂, and R-ONO) has previously been reported in the literature²⁸ and is additionally confirmed by an increase in the nitrogen and oxygen content (Table 2).

The increase in negative surface charge induced a decrease in size of the suspended soot particles based on DLS measurements (Fig. 1A). The measurements presented were obtained after 24 h of shaking to be comparable with sorption batch experiments. In addition, aggregation kinetics for the first 30 min after introduction of the soot into the water phase were determined (Fig. S3†).

The exposure of soot to NOM did not significantly change the elemental composition of the material (\( p > 0.05 \)). This is consistent with the measured DOC loading of soot (17.7 ± 0.3 mg DOC per g soot). However, it increased the negative ζ-potential of soot to a similar degree as the NO₂ transformation, stabilizing the soot particles electrostatically against aggregation and decreasing their particle size (Fig. 1A). In contrast to the effect on pristine soot, NOM could not increase the negative surface charge of NO₂-transformed soot.

The number of particles remaining in suspension increased both after NO₂ transformation and after interaction with NOM (Fig. 1B), with the particle number concentration increasing up to 30-fold compared to pristine soot. The aggregate size decreased and the number of particles remaining in suspension was higher for NO₂-transformed soot with NOM compared to NO₂-transformed soot without NOM. This indicates that in
were more pronounced for pristine soot than for NO2-transformation and/or interaction with NOM. The Abraham solute parameters A, V, E, A and B are obtained from the UFZ-LSER database.\textsuperscript{25}

Table 1

| Parameter | Value | Structure |
|-----------|-------|-----------|
| log $K_{ow}$ | 3.13 (ref. 23) | |
| V | 2.28 (ref. 25) | |
| E | 1.11 (ref. 25) | |
| A | 0.00 (ref. 25) | |
| B | 1.25 (ref. 25) | |

addition to electrostatic repulsion, steric effects might also play a role in the aggregation of soot in the presence of NOM.\textsuperscript{4}

In good agreement with DLS measurements and particle mass remaining in suspension, scanning electron microscopy images confirmed the higher number and smaller size of suspended particles for NO2 transformed soot compared to pristine soot. The stabilizing effect of NOM on soot aggregation could also be observed when comparing suspensions with and without NOM (Fig. 2), where differences in particle aggregation were more pronounced for pristine soot than for NO2-transformed soot. It should be noted that relatively high soot concentrations were used in this study, and in many scenarios hetero-aggregation with other suspended particles in the natural environment is expected to outweigh the importance of the homo-aggregation investigated here.\textsuperscript{4,31,32} However, the investigation of hetero-aggregation was not in the scope of this study and may be an interesting subject of further investigations building on the results presented here.

3.2 Sorption of S-metolachlor decreased upon NO2-transformation and was not affected by the presence of NOM

Sorption ($K_{0}$) of S-metolachlor decreased by more than one order of magnitude after NO2-transformation of soot and was not significantly affected ($p > 0.05$) by the presence of NOM (see Fig. 3 and Table 3). The decrease in sorption of S-metolachlor upon NO2-transformation can be explained by a lower hydrophobicity of the soot surface and a less favorable accessibility of surface sorption sites.\textsuperscript{4,33} Therefore, the higher number of O-containing surface functional groups on the NO2-transformed soot is energetically favorable for H-bond interactions with water molecules, which increases the competitiveness of water molecules for sorption sites.\textsuperscript{14,35} A decrease of organic contaminant sorption with an increase of O-functional groups is in good agreement with the literature findings on other carbonaceous materials, including carbon nanotubes,\textsuperscript{36,37} fullerenes,\textsuperscript{33,37} and biochars.\textsuperscript{38,39}

The change in particle size was not reflected in the change in sorption of S-metolachlor. For instance, the particle size decreased for pristine soot after interaction with NOM, but did not significantly change the sorption. The BET specific surface area was $84.7 \pm 3.1$ and $89.9 \pm 4.0 \text{ m}^2 \text{ g}^{-1}$ for pristine and NO2 treated soot, respectively. Thus, the total specific surface area, which did not differ significantly between the materials, was not a limiting factor for S-metolachlor sorption under the conditions investigated. Also, under the conditions investigated, the presence of NOM did not suppress sorption due to competition for sorption sites, possibly because the high specific surface area offered enough sorption sites for both sorbates. This is consistent with previous observations on pyrene sorption to carbon nanotubes, which was only substantially suppressed by

Table 2

| Element | C [%] | H [%] | N [%] | O [%] | Ash [%] |
|---------|-------|-------|-------|-------|--------|
| pristine | 93.76 ± 0.11 | 0.04 ± 0.09 | 0.47 ± 0.08 | 0.69 ± 0.56 | 5.12 ± 0.31 |
| NO2 | 84.91 ± 0.11 | 0.07 ± 0.09 | 1.19 ± 0.08 | 9.36 ± 1.26 | 2.74 ± 1.01 |
NOM at concentrations > 20 mg L\(^{-1}\).\(^{40}\) It should be noted that both the salt (1 mM CaCl\(_2\)) and the NOM concentration (10 mg L\(^{-1}\) DOC) used in this study correspond to concentrations that can be found in natural aquatic environments,\(^{41}\) and a higher concentration of NOM (e.g. 100 mg L\(^{-1}\)) may have been able to suppress sorption to soot surfaces via competition for sorption sites.\(^{40}\)

A recently published sorbate-activity-dependent polyparameter linear free-energy relationship (ppLFER) for pristine diesel soot\(^{15}\) found that the difference in dispersive interactions with the soot versus with the water was the dominant factor encouraging adsorption, and H-bonding interactions discouraged this process. We applied the ppLFER proposed by Lu et al.\(^{15}\) using Abraham solute parameters for \(S\)-metolachlor from the UFZ-LSER database\(^{25}\) as presented in Table 1 (calculation in Table S1\(^{\dagger}\)). The ppLFER predicted that \(K_D\) value ranges were in good agreement with the values determined in this study but could not predict the differences observed between pristine soot and NO\(_2\) transformed soot (see Table 4). The discrepancy of \(K_D\) values between the ppLFER and this study may partially be explained by differences in the surface chemistry (e.g. oxygen containing surface functional groups); however, such data were not reported in the study by Lu et al.\(^{15}\)

4. Conclusion

Soot is an important naturally occurring CNP that can be found ubiquitously in the environment. During atmospheric transport, soot can be chemically transformed by reactive oxygen species, including NO\(_2\). Our results show that reaction of soot with NO\(_2\) has significant impacts on aggregation and sorption of soot in aquatic environments. Pristine soot is a strong sorbent for \(S\)-metolachlor, but is likely to rapidly aggregate when introduced directly into surface waters. In contrast, soot that is oxidized by NO\(_2\) shows a decreased sorption for \(S\)-metolachlor, but exhibits a higher stability against aggregation.

### Table 3

|          | \(K_F\) [mg kg\(^{-1}\) (mg L\(^{-1}\))] | \(n\) | \(R^2\) |
|----------|--------------------------------------|-------|--------|
| Pristine | 3382 ± 52                            | 0.72 ± 0.01 | 0.991  |
| Pristine + NOM | 3898 ± 70                          | 0.71 ± 0.02 | 0.991  |
| NO\(_2\)  | 475 ± 46                             | 0.90 ± 0.05 | 0.956  |
| NO\(_2\) + NOM | 198 ± 22                            | 1.17 ± 0.04 | 0.994  |

### Table 4

|          | log \(K_D\) from ppLFER | log \(K_D\) from Freundlich fit |
|----------|-------------------------|-------------------------------|
| Pristine | 2.86 ± 0.49             | 3.25 ± 0.12                   |
| Pristine + NOM | 3.31 ± 0.23            | 2.47 ± 0.40                   |
| NO\(_2\)  | 2.81 ± 0.49             | 2.47 ± 0.40                   |
| NO\(_2\) + NOM | 2.58 ± 0.40           | 2.58 ± 0.40                   |

The sorption coefficient (\(K_D\)) range calculated based on the ppLFER proposed by Lu et al.\(^{15}\) is in the same range as the coefficients derived in this study, but the ppLFER was not able to differentiate between pristine and NO\(_2\)-transformed soot. All parameters were calculated at an aqueous concentration of 10 mg L\(^{-1}\).

Fig. 2 Scanning electron microscopy images of soot particles with different surface chemistry and aggregate sizes for (a) pristine soot, (b) pristine soot with NOM, (c) NO\(_2\)-transformed soot, and (d) NO\(_2\)-transformed soot with NOM (same magnification of 1.56k for all).

Fig. 3 Sorption of \(S\)-metolachlor to NO\(_2\)-transformed soot was weaker than that to pristine soot. Filled symbols (●, ■) are sorption data, dotted lines are Freundlich sorption isotherm fits.
In agreement with findings on other CNPs, soot aggregation decreased in the presence of NOM. NO₂-transformed soot can act as a contaminant vector; however, due to the significantly lower sorption potential for S-metolachlor, the expected risk is lower than that for pristine soot or soot stabilized by NOM.

Future research on soot CNP properties should focus on additional transformations and changes in soot properties that can occur in the natural environment. For instance, hetero-aggregation of soot and NO₂-transformed soot with mineral particles remains an underexplored aspect and should be the subject of further investigations.

## Conflicts of interest

There are no conflicts to declare.

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