



Cite this: *Environ. Sci.: Nano*, 2018, 5, 2500

# Environmental transformation of natural and engineered carbon nanoparticles and implications for the fate of organic contaminants

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Environmental transformation of carbon nanoparticles can significantly affect their transport, fate, and effects. The last decade of environmental nano-science has often focused on understanding the behavior of well-defined engineered carbon nanoparticles (eCNPs) in the natural environment. However, more complex pyrogenic/petrogenic carbon nanoparticles (pCNPs), including those derived from soot, fossil coal, wildfire charcoal, and biochar, are more than four orders of magnitude more abundant in the environment. This paper aims to review findings from investigations into eCNPs and to consider their transferability to pCNPs, in order to improve our understanding of pCNPs and identify gaps in our knowledge. Findings from previous investigations into the chemical, physical and biological transformation of larger carbonaceous particles, as well as of eCNPs, can help us to understand the transformation of pCNPs. The transformation of soot during atmospheric transport is relatively well documented, whereas the transformation of pCNPs in soil, sediment, and aqueous systems remains poorly understood. To bridge findings on particulate transport, contaminant binding, and contaminant transformation from eCNPs to pCNPs, the complex compositions of pCNPs need to be taken into account. We therefore suggest that future research on pCNP transformation should focus on changes in intrinsic porosity and on interactions with non-carbonized phases, tar phases, and mineral phases, as well as with organo-mineral complexes in soils, sediments and water bodies.

Received 22nd June 2018,  
Accepted 30th September 2018

DOI: 10.1039/c8en00676h

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## Environmental significance

Both natural and anthropogenic sources release large quantities of carbon nanoparticles (CNPs) into the environment. CNPs have strong adsorption affinities for organic contaminants and the accumulation of contaminants onto CNPs may significantly alter the effects of the CNPs, as well as the transport, reactivity, and bioavailability of environmental contaminants. Once released into the environment, CNPs can undergo physical, chemical and biological transformation, resulting in significant changes to their physicochemical properties, consequently altering their transport in natural environments and their interactions with contaminants through sorption and catalysis. Bridging findings from well-defined and well-studied engineered CNPs to the more complex, much more abundant and much less studied pyrogenic/petrogenic CNPs is critical for assessing the environmental impact and exploring applications of CNPs.

## 1. Introduction

Carbon particles are released into the environment from both natural and anthropogenic sources.<sup>1,2</sup> Forest fires, fossil fuel combustion and fossil coal transport all release large quantities of carbon into the environment<sup>2</sup> including carbon nanoparticles (CNPs), which have at least one dimension be-

tween 1 and 100 nm. Those CNPs that derive from pyrogenic or petrogenic sources (pCNPs) have been released into the environment for millennia. Engineered CNPs (eCNPs), including carbon nanotubes, fullerenes and graphene (oxides), have also been commercialized over the last decade and are used in a range of consumer products and industry applications.<sup>3</sup> Both eCNPs and pCNPs have strong adsorption affinities for a range of organic contaminants and are likely to be the predominant media with which contaminants are associated in many natural environments. The accumulation of organic contaminants onto CNPs may significantly alter the effects of the CNPs (e.g., their toxicity), as well as the transport, reactivity, and bioavailability of environmental contaminants.<sup>4–6</sup>

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Once released into the environment CNPs can undergo physical, chemical and biological transformation, resulting in significant changes to their physicochemical properties (e.g., their size, morphology, and surface functionality). The transformation of CNPs can have a marked effect on their surface charge, hydrophobicity, and reactivity, and may thus alter their aggregation and transport in natural environments and their interactions with contaminants through sorption and catalysis.

The formation and dispersal of carbonaceous particles,<sup>1,2,7</sup> the transport of CNPs,<sup>7–10</sup> and the sorption of organic contaminants by CNPs<sup>11–13</sup> have all been extensively investigated and reviewed. The transformation of CNPs in natural environments has also recently been receiving increasing

attention.<sup>14–17</sup> However, the last decade of research has focused mainly on understanding the behavior and implications of well-defined eCNPs, whereas those of the more complex, naturally occurring pCNPs of pyrogenic and petrogenic origins, which comprise the dominant fraction of CNPs in natural environments, remain largely unexplored. A key aim of this review is therefore to compare findings from investigations into pristine eCNPs and consider their transferability to pCNPs, in order to improve our understanding of pCNPs as well as of how transformation of pCNPs can affect the fate of contaminants. This will allow identification of future research needs in the field of naturally-occurring CNPs. A good understanding of the sources, transport, and transformation of pCNPs and the associated implications for contaminant



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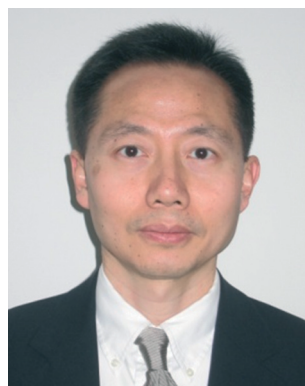
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fate is critical for identifying risks associated with colloidal CNPs and may also shed light on possible uses of CNPs in remediation.

## 2. Sources of CNPs in the environment

Sources of CNPs found in the natural environment include fossil coal transportation (petrogenic origin from geological transformation of organic carbon), forest fires, fossil fuel combustion, biochar application for agricultural and remedial purposes (pyrogenic origin from incomplete combustion of organic carbon), the use of activated carbon for filtration and remediation purposes, and unintended releases of eCNPs from industrial processes or during the resulting products life-cycles.<sup>2,5,7</sup>

### 2.1 Fossil coal

Fossil coal is a major energy source in many industrial countries including the USA, China, and India, where fossil coal combustion remains a key factor for power production. Although there has been a recent decrease in global coal-based energy production, fossil coal production still amounts to approximately 6.5 Pg per year and no complete phase-out of coal-based power plants is foreseeable in the coming decades.<sup>18,19</sup> The formation of pCNPs from fossil coal combustion residuals, which consist mainly of mineral phases, is negligible; pCNPs are, however, released during the mining and transport of fossil coal, where a mass loss of 1% has been reported.<sup>19</sup> The decomposition of fossil coal depends on its rank (which is associated with its aromaticity) as well as on its volatile matter and O content. Coal stability decreases in the following order: anthracite > bituminous coal > subbituminous coal > lignite.<sup>20,21</sup> Assuming that, on average, fossil coals disintegrate physically at a similar rate to biochar (see section 2.3) suggests a pCNP release of approximately 6.5 Tg per year from fossil coal.

### 2.2 Soot

A very common type of pCNP is soot, which is the finest residual fraction from incomplete combustion; it results from natural processes such as forest fires as well as from anthropogenic processes such as fossil fuel combustion. Soot is formed through the re-condensation and nucleation of organic compounds such as acetylene and polycyclic aromatic hydrocarbons (PAHs) from a gas phase during combustion and is typically introduced into the environment *via* atmospheric transport.<sup>22</sup> It can be found throughout all environmental compartments, including extreme examples such as in a 10 000 year-old Greenland ice core.<sup>23</sup> Soot particles can vary greatly in their size distribution, surface chemistry, and morphology depending on the production conditions and other environmental factors. Soot generally contains large quantities of PAHs, which can become bioavailable.<sup>24,25</sup> Estimates for the annual production of soot transportable *via* the

atmosphere range from 6 to 28 Tg per year,<sup>26</sup> with the most recent estimates being 17 Tg per year.<sup>2,27</sup>

### 2.3 Biochar

Biochar is a product of biomass pyrolysis; it is used in agriculture to increase the nutrient- and water-holding capacity and pH of soils, and in remedial applications for sorption of contaminants. It also serves as a carbon sink for climate change mitigation.<sup>28</sup> In contrast to soot or wildfire charcoals, biochar is produced under more controlled conditions, resulting in a “cleaner”, more carbonized material. For instance, when comparing biochars with wildfire charcoals from the same feedstock, PAHs are generally found to be present at lower concentrations and to be less bioavailable in biochar than in wildfire charcoal.<sup>29</sup> Biochar particles produced by physical disintegration in soil are expected to be transported mainly by surface runoff and colloidal transport in pore water, rather than *via* the atmosphere.<sup>30</sup> Understanding the release of pCNPs from biochar in the field remains challenging as the fraction of pCNPs varies greatly depending on the biochar feedstock, pyrolysis temperature, and soil/sediment conditions.<sup>30–32</sup>

The application of biochar is currently limited globally to a number of test sites.<sup>28</sup> However, if biochar was to become globally accepted as a means of carbon sequestration and soil improvement, Woolf *et al.*<sup>33</sup> estimate that up to 220 Tg of biochar could be used every year, which would result in a considerable quantity of biochar-derived pCNPs being released into the environment. Spokas *et al.*<sup>30</sup> have reported particle release from disintegration of ten different biochars ranging from 1 to 47%. A conservative estimate of 10% was assumed for Fig. 1, resulting in the release of up to 20 Tg per year of biochar-derived pCNPs. It is not currently possible to quantify more precisely the overall potential release of pCNPs



Fig. 1 Major sources of CNPs in the natural environment with rough estimates of mass fluxes, as discussed in section 2.





from biochar due to the large differences in disintegration between different biochars.

## 2.4 Wildfire charcoal

Wildfires burn 30–46 million km<sup>2</sup> per year of the global land surface,<sup>34</sup> producing up to 241 Tg per year of wildfire charcoal,<sup>26</sup> the solid combustion residue of wildfires. Between 1 and 26% of the total carbon consumed during forest fires ends up as wildfire charcoal,<sup>35</sup> with a generally lower proportion for grassland (<3%).<sup>26</sup> The physicochemical properties of wildfire charcoal are strongly dependent on the feedstock, the maximum temperature of the fire, the heating duration, and the particle size of the feedstock.<sup>36,37</sup> It has recently been noted that the physical location within a tree (*e.g.*, base of main tree stem compared to the upper crown) also has a marked effect on the physicochemical properties of the wildfire charcoal produced.<sup>38</sup> de Lafontaine and Asselin<sup>39</sup> compared a large number of wildfire charcoals in different soils and found that soil type and climate only had a minor influence on their physical disintegration, indicating that disintegration mostly occurs soon after formation and is mainly driven by the physicochemical properties of the wildfire charcoal. Wildfire charcoals are typically less stable and more prone to transformation and physical disintegration than biochar.<sup>21,29</sup> For a rough estimate of pCNPs produced a slightly larger proportion has therefore been assumed for wildfire charcoal (15%) than for biochar (10%), yielding an estimated pCNP release of up to 36 Tg per year. This is of the same order of magnitude as a recent estimate of global charcoal particle transport to the oceans (26.5 Tg per year).<sup>40</sup>

## 2.5 Engineered CNPs

eCNPs include carbon nanotubes (CNTs), fullerenes, graphene, and graphene oxide (GO); they can be released into the environment both intentionally and unintentionally.<sup>5,7,41</sup> Global eCNP production was approximately 4.5 Gg in 2011<sup>3</sup> and is reported to have been approximately 20 Gg in 2016, with annual production predicted to increase by 20% per year until 2023.<sup>42</sup> The use of activated carbon may also result in the release of a significant quantity of CNPs into the environment. Recent predictions suggest that activated carbon production will reach 3 Tg per year by 2024.<sup>43</sup>

A significant fraction of eCNPs is incorporated into other matrices (*e.g.*, CNTs may be part of a composite) and/or used under highly controlled conditions (*e.g.*, activated carbon is used for water filtration) so that only a small proportion of eCNPs is expected to reach the natural environment, whether in wastewater streams or by direct introduction.

In summary, soot, fossil coal, and wildfire charcoal are important sources of naturally-occurring pCNPs (>99%; Tg per year range). In contrast, the better defined eCNPs, which have received the most attention over the last decade, make up a much smaller proportion of the CNPs in the natural environment (<1%; Gg per year range), as illustrated in Fig. 1. Although pCNPs and eCNPs share many molecular similari-

ties such as their high aromaticity and high electron donor-acceptor capacity, they differ significantly in terms of structural irregularities, surface functionality, inorganic phases and porosity. For example, pCNPs generally possess more negatively charged surface groups and smaller aromatic sheets and thus have a lower sorption affinity for most organic contaminants compared to eCNPs. These structural and molecular differences are expected to play an important role in fate, transport, and effects (*e.g.*, interactions with organic contaminants) of pCNPs. It therefore stands to reason that the scientific community needs to investigate in greater detail the often more complex and more abundant pCNPs described above. Although there is some current research into the transformation in natural environments of certain pCNPs, published literature on pCNPs and their transformation remains scarce. Therefore, findings for larger particles are taken into consideration in the subsequent discussion.

Recently, methods have been developed to identify and quantify some eCNPs in environmental matrices. For example, CNTs were quantified by measuring concentrations of characteristic metal catalyst impurities, laser fluorescence or microscopically by using the distinct shape of CNTs.<sup>44</sup> Unfortunately, these techniques are not directly applicable for the identification of pCNPs, as pCNP physicochemical properties are less distinct than for CNTs. One promising strategy for future studies on pCNPs in the laboratory will be the use of isotopically labeled particles. However, further development on separation, extraction and quantification of pCNPs in environmental matrices is necessary for all currently existing methods.

# 3. Environmental transformation of CNPs

Following their formation and/or release into the natural environment, various processes including (photo)chemical (redox) reactions, biological interactions, and interactions with environmental constituents (*e.g.*, natural organic matter, clay minerals) can alter the physicochemical properties of CNPs, in dependence of environmental conditions.<sup>31,45–47</sup> These transformations can be categorized as chemical, physical, or biological transformations.<sup>45</sup>

## 3.1 Chemical transformation

Chemical transformation of CNPs refers to surface reactions (including direct and indirect photolysis and redox reactions), which can change the chemical structure of CNPs as well as the abundance and species of surface functionality.<sup>45</sup> Research on eCNPs including CNTs,<sup>48</sup> graphene,<sup>16</sup> and GO,<sup>16,49</sup> has shown that pre-existing functional groups, structural defects, mineral phases (*e.g.* residual metal catalysts), and the edges of the aromatic sheets forming the eCNPs, are sites that favor chemical transformation. These observations indicate that the pCNPs discussed above may be more prone to transformation than eCNPs as they generally contain



Although the carbonized phase of pCNPs is generally very stable, transformations in the natural environment can increase the electron donating capacity and polarity of pCNPs due to the formation of oxygen-containing functional groups on the outer carbonized surface.<sup>31,70</sup> In aqueous suspensions CNPs often carry a surface charge due to the presence of dissociable O- and occasionally N- or S-containing functional groups (including carboxyl, amine, and sulfonic groups), and to the adsorption of charged solutes from the aqueous media. The degree of oxidation thereby increases from the interior of the particle to the exterior surface, and also with the particle density.<sup>71</sup> Under oxic conditions pCNPs therefore develop a more negative surface charge over time accompanied by a reduction in the release of positively charged ions from the soluble mineral phase. There have, however, been no sys-

While general trends and processes for chemical CNP transformation are reasonably well understood, the overall current state of knowledge remains incomplete for pCNPs derived from fossil coal, biochar, and wildfire charcoal. For instance, chemical transformation of the carbonized phases can be influenced by co-occurring mineral phases and non-carbonized NOM phases within the pCNPs, as well as by external factors such as soil type and pH; none of which are to date well understood.<sup>72,73</sup> Future research therefore needs to build on the current understanding of the chemical transformation of soot during atmospheric transport based on work by other scientific communities, and to focus on closing the gaps in our understanding of the transformation of pCNPs in soil, sediment, and aquatic systems.

In contrast to other pCNPs, soot particles are formed by nucleation of organic compounds such as acetylene and

PAHs from the gas phase. Soot particles are oxidized by O<sub>2</sub> and ROS both during and after their formation, which counteracts the growth of pCNPs. Following their initial formation, pCNPs coagulate to form larger particles that are initially spherical but can subsequently form chain-like fractal clusters.<sup>1,60</sup> Both during soot particle formation and during atmospheric transport, interactions with other constituents of the gas phase can have a marked effect on particle size and shape.<sup>59–63</sup> Over time, soot particle fractal dimensions tend to increase because they become either coated or entirely embedded within other aerosol components including sulfates, nitrates, sea salt, mineral dust, fly ash, and NOM.<sup>59,60,63</sup> In aqueous suspensions all CNPs can interact with the surrounding environmental matrix, including NOM and mineral particles contained therein, which can affect the size, surface charge, and aggregation of particles (see section 4.2).

Naturally-occurring pCNPs such as wildfire charcoal and biochar contain a complex network of micropores and mesopores, as well as differently bound mineral phases including organo-mineral complexes. The chemical processes described in section 3.1 can increase the accessibility of CNP pores by dissolution, or block pores through the formation of precipitates and/or the binding of large NOM molecules onto the biochar surface (“fouling”).<sup>70,76,77</sup> Changes in temperature, physical stress, and humidity can also lead to the disintegration and collapse of pore-networks.<sup>30,75</sup> Changes in the composition and porosity<sup>70</sup> of individual particles therefore need to be taken into account when investigating pCNP transformation. For instance, Liu *et al.*<sup>75</sup> found that pCNP derived from biochar disintegration contain more oxygen and less aromatic structures compared to the original biochar.

### 3.3 Biological transformation

Biological transformation of CNPs refers to changes in the physicochemical properties of CNPs due to interactions with organisms, individual cells, and enzymes.<sup>45</sup> For instance, the role of fungal hyphae in the physical breakdown of large fossil coal and biochar particles and of fungal extracellular enzymes in their chemical decomposition is widely recognized,<sup>21</sup> but they have to date not been investigated with regard to the transformation of pCNPs, even though certain microorganisms (*e.g.*, fungi) are capable of using highly aromatic structures such as lignin as carbon sources.<sup>78</sup> The extracellular enzymes produced by these fungi, as well as by certain bacteria, include Mn-peroxidase, lignin-peroxidase and laccase,<sup>20,79</sup> all of which are expected to oxidize pCNPs. Specifically, Hilscher *et al.*<sup>80</sup> found that O-alkyl/alkyl-C groups are microbially transformed to carboxyl/carbonyl-C groups. These authors observed a reduction in aromaticity for some carbonaceous materials through the transformation of aryl-groups and the associated opening and partial oxidation of aromatic ring structures. Saquing *et al.*<sup>81</sup> recently demonstrated that quinone groups in the carbonized phase of biochar can act both as electron donors and as acceptors for

microbiota, thereby being oxidized or reduced, respectively. The biological transformation of pCNPs through redox processes is generally expected to result in changes in surface chemistry similar to those in non-biological systems (see section 3.1).

Enzymatic transformations of CNPs are unfortunately often investigated using only pure enzymes and under laboratory conditions; they are consequently not very representative of enzymatic transformations in the natural environment. For instance, further investigation is required for the transfer and possible cellular-uptake required for the CNPs to reach degrading enzymes within the cells, as well as factors that drive the production and the associated gene expression of CNP-degrading enzymes (both intracellular and extracellular). Other factors influencing CNP degradation (*e.g.*, microbial community composition, nutrient availability) also remain poorly understood. The enzymatic transformation of pCNPs has hardly been investigated to date but investigations into the enzymatic transformation of eCNPs can help to understand key enzymatic transformation processes that are also relevant to pCNP transformation. For instance, the horseradish peroxidase enzyme is able to catalyze the formation of oxygen radicals that are capable of degrading a range of eCNPs, including CNTs<sup>82,83</sup> and GO,<sup>84</sup> and are thus expected to also be capable of degrading pCNPs. O-functionalized CNPs are generally more degradable than non-functionalized CNPs because the associated structural irregularities facilitate (bio) degradation.<sup>82</sup> However, Zhang *et al.*<sup>85</sup> found that manganese peroxidase was able to transform CNTs but not O-functionalized CNTs. This was explained as being possibly due to the bridging of Mn<sup>2+</sup> with carboxyl groups on the surface of O-functionalized CNTs, which interfered with the Mn<sup>2+</sup>/Mn<sup>3+</sup> catalytic cycle, thereby suppressing transformation. The generalization that “more O-functionalization will result in more biological transformation” is therefore not always valid.

Apart from (bio)chemical transformation, cells can also physically interact with CNPs including soot,<sup>86–88</sup> biochar particles,<sup>89</sup> and CNTs.<sup>90,91</sup> In such cases the CNPs are immobilized by aggregation or ingestion, while at the same time inducing negative biological effects on the cells (such as cytotoxicity). These interactions of CNPs with cells can reduce their stability and lead to aggregation (see section 4), thus affecting their transport.

The formation of a biofilm on the surfaces of larger carbonaceous particles has previously been reported,<sup>68</sup> but it remains unclear if biofilms would also form on pCNPs. However, pCNP aggregates may well be susceptible to biofilm formation, which can have a variety of effects on the physicochemical properties of the pCNPs including changing their surface chemistry, increasing the particle size, and blocking pores.

Investigation of the biological transformation of pCNPs is challenging and a large number of factors need to be taken into account including their physicochemical properties, aggregation, and interactions with soil minerals, as well as the



presence of NOM, microbial compositions, microbial activity, and nutrient accessibility. This may be the reason why systematic investigations into CNP transformations in conditions that are close to those found in natural environments remain so scarce. Such studies are, however, essential to achieving a better understanding of the effects that biological transformation processes have on the fate of, and possible risks associated with, CNPs. Ideally such investigations need to reflect the complexity of the investigated systems by combining the expertise of specialists from different fields, including microbiologists, environmental chemists, and colloidal scientists.

## 4. Effects of transformation on the colloidal stability and transport of CNPs

The colloidal stability, aggregation, and transport of CNPs are all significantly affected by their surface chemistries. Changes in surface chemistry are typically caused by chemical and biological transformation processes and by changes in the surrounding environment.

### 4.1 Surface charge and surface potential of CNPs

The electric surface potential resulting from surface charges on CNPs affects the distribution of ions in aqueous solutions and is an important factor controlling the colloidal stability of CNPs in aqueous suspensions. Ions with opposite charges to the CNP surfaces (counterions) will accumulate around the CNPs and form an electrical double layer (EDL), which can be sub-divided into the Stern layer and the diffuse layer (see review by Wagner *et al.*<sup>92</sup>). The electric potential at the imaginary slipping plane between these two layers is referred to as the zeta potential ( $\zeta$ -potential), which is indicative of the electric surface potential. The pH at which the measured  $\zeta$ -potential approaches 0 mV is the isoelectric point (IEP) of a given CNP. In the absence of specific adsorption of charge-determining species onto the particle surface, the measured IEP is equal to the point of zero charge (PZC), *i.e.*, the pH at which the net surface charge of the CNP is zero.

The surface charge depends on the CNP functional groups and thus varies with the chemistry of the CNP surface, as well as with that of the solution. In natural environments most surfaces, including those of minerals, are negatively charged due to their crystallographic properties and/or the sorption of anionic polyelectrolytes such as NOM.<sup>47</sup> Nevertheless, the PZC of pCNPs, at which particles tend to aggregate, can cover a wide range of pH values between 2 and 12.<sup>93,94</sup> Both the surface functionalization and the composition of the mineral phases within the pCNPs can change upon environmental transformation (see section 3), which will in turn affect the  $\zeta$ -potential, IEP and PZC of the pCNPs. For instance, the formation of O-functional groups and the leaching of positively charged mineral phases from pCNPs would render their sur-

face charges more negative and reduce their  $\zeta$ -potential, IEP and PZC.

### 4.2 Colloidal stability and aggregation of CNPs

The colloidal stability of CNPs in aqueous suspensions is typically controlled by their EDL and van der Waals interactions, as described by the classic Derjaguin–Landau–Verwey–Overbeek (DLVO) theory.<sup>10,92,95,96</sup> Attractive van der Waals interactions cause the CNPs to aggregate, while the electrostatic repulsion between like-charged nanoparticles promotes stable colloidal systems. For example, Wang *et al.*<sup>32</sup> found that biochars produced at 350 °C formed more stable pCNPs than biochars produced at 550 °C, which have lower negative surface charges. Further, the DLVO theory was extended to also include hydrogen bonding/electron donating–accepting capacity by van Oss *et al.*, extending its predictive capability.<sup>97</sup> Still, DLVO might not be able to predict environmental aggregation behavior in complex matrices.

For CNPs with adsorbed organic molecules (such as, for example, NOM) steric repulsion is another important mechanism for colloidal stabilization. For instance, humic acid (a NOM fraction) has been found to increase the colloidal stability and mobility of biochar-derived pCNPs, which was explained as being due to an increase in electrostatic and steric repulsive interactions.<sup>98,99</sup> The colloidal stability and aggregation of CNPs are not only influenced by surface functionality and water chemistry (*e.g.*, pH, ionic strength and composition, NOM),<sup>95,96,100</sup> but may also depend on morphological CNP properties. The effect that the physical properties of pCNPs have on their aggregation has not been investigated to date. However, the colloidal stability of GO in NOM-containing water has been found to depend on the morphology of the GO, with NOM stabilizing crumpled GO more effectively than flat GO, regardless of surface chemistry of these different GOs,<sup>100</sup> indicating that the aggregation of pCNPs may also be influenced by their morphology.

CNPs with highly hydrophobic surfaces (*e.g.*, pristine soot particles and reduced GO) are prone to aggregation in aqueous media due to the minimal electrostatic repulsion between the CNPs. Strong aggregation can even occur in CNPs with a higher surface charge (*e.g.*, aged soot and GO) under certain conditions through one or more of the following mechanisms: (i) EDL compression induced by high ionic strength, (ii) adsorption and charge neutralization, where the surface charge is neutralized by adsorbed counterions within the Stern layer, (iii) bridging by NOM or other polymer chains and multivalent ions such as divalent  $\text{Ca}^{2+}$ , and (iv) sweep flocculation, in which large particle aggregates enmesh individually dispersed nanoparticles.

The presence of a nonpolar hydrophobic organic contaminant (naphthalene) has been found to reduce pCNP mobility, probably due to the shielding of negative surface charges following naphthalene adsorption to the pCNPs.<sup>98,101</sup> Bisiaux *et al.*<sup>65</sup> found that pCNP pulses from wildfires and from urban runoff were rapidly attenuated in a river system,







Fig. 2 Transformation processes affecting CNP surface chemistry, aggregate size, and environmental behavior.

suggesting unexpected aggregation and/or disintegration of these particles. The presence of tar moieties formed during wildfires may partially explain high aggregation rates as the nonpolar tar components could shield the negative surface charges of the pCNP, thereby reducing electrostatic repulsion between the wildfire-derived pCNPs.

In addition to interactions between similar CNPs (homo-aggregation), CNPs can also aggregate with other nanomaterials and larger colloids (hetero-aggregation) and this will generally be the dominant process in natural environments. Both NOM and mineral phases (mainly Al- and Fe-oxides) will interact with pCNP surfaces as well as filling their intra-particle cavities, thus changing the size of the CNP aggregate, its porosity, and its density.<sup>95,102–104</sup> Yi *et al.*<sup>104</sup> investigated the hetero-aggregation of biochar-derived pCNPs with CeO<sub>2</sub> nanoparticles and found that at a pH where both particle groups are stable against homo-aggregation, hetero-aggregation occurred through a charge neutralization–charge reversal mechanism. In such cases primary hetero-aggregates are stable at both low and high pCNP concentrations due to electrostatic repulsion, but unstable at intermediate pCNP concentrations leading to secondary hetero-aggregation, which occurs through a charge-accumulation, core–shell stabilization mechanism. In this way pCNPs formed a negatively charged shell on the neutral surface of CeO<sub>2</sub> nanoparticles, stabilizing the core–shell hetero-aggregate at a size that decreased with pCNP concentration.<sup>104</sup> Similarly, the hetero-aggregation of biochar-derived pCNP with goethite/hematite increased at low pCNP concentrations and formed more stable suspensions with increasing pCNP concentrations.<sup>75</sup>

### 4.3 Transport of CNPs in porous media

The transport of CNPs in porous media is an important process affecting their fate and effects in terrestrial environments. When CNPs are exposed to soil and sediment they are

retained to some extent by physical sedimentation, straining, interception, or by attachment to collector particles through diffusion.<sup>105</sup> The attachment of CNPs to porous media surfaces is affected by electrostatic interactions and also by non-DLVO interactions such as steric hindrance, hydrophobic effects, hydrogen bonding, and cation/anion bridging. The transformation of CNPs in natural environments can significantly affect the size, density, surface charge, and functionality of the particles, and consequently the interplay between CNPs and the porous media (Fig. 2).<sup>52,106,107</sup>

CNP attachment generally decreases with increasing negative surface charge. Biochar-derived pCNPs, which contain the most O-functional groups and negative surface charge could therefore form more mobile pCNPs than less oxidized pCNPs.<sup>32</sup> Any alteration of CNP surface charge (*e.g.*, through an increase or decrease in surface O-functional groups, or adsorption of NOM) may significantly affect their transport. This is supported by Wang *et al.*,<sup>108</sup> who found that pCNP interactions with humic acids increased pCNP transport due to increased electrostatic repulsion, whereas pCNP interactions with positively charged iron oxyhydroxide reduced pCNP transport due to electrostatic attraction.

Reduction of CNPs generally reduces the concentrations of surface O-functional groups, thus increasing the hydrophobicity of the particles and resulting in increased aggregation. Such reduction-induced effects can in turn significantly reduce particle transport, for example through physical straining. Conversely, oxidation of CNPs typically enhances their transport by increasing their surface hydrophilicity and inhibiting aggregation.<sup>52,106,109</sup> It is important to note that the transformation of surface O-functional groups in natural environments is also critical to the mobility of CNPs. For instance, Xia *et al.*<sup>110</sup> observed that the inhibition of GO transport in saturated porous media by metal ions followed the Hofmeister series (*i.e.*, Na<sup>+</sup> < K<sup>+</sup> < Cs<sup>+</sup> and Mg<sup>2+</sup> < Ca<sup>2+</sup> < Ba<sup>2+</sup>), and that the Hofmeister effect was more significant for





reduced GO than for GO, probably due to the different quantities of metal complexing groups (including carboxyl and phenolic groups) in these different eCNPs. Furthermore, it has been reported that chloramine-treated GO (an oxidized form compared to pristine GO) exhibited greater mobility than pristine GO when  $\text{Na}^+$  was the dominant cation, whereas in the presence of  $\text{Ca}^{2+}$  its mobility was significantly lower than that of GO.<sup>106</sup> This surprising lower mobility was attributed to the stronger cation-bridging effect associated with this material, in that the chloramine treatment increased the concentration of surface carboxyl groups (a strong metal-binding moiety).<sup>109,111</sup>

When extrapolating the results reported for eCNPs to the transport of pCNPs, the particle shape, density, and complex composition (including mineral phases) also need to be taken into account, but these have received little attention to date. The mineral components of pCNPs may, for example, impart heterogeneous surface charges (e.g., localized positive surface charges) to particles, which can in turn enhance particle deposition onto negatively charged sand grains. Moreover, most of the studies on transport of CNPs have been conducted with column experiments using mainly saturated quartz sand as the porous media. A few studies carried out column experiments using soils or under unsaturated conditions indicated, as shown much earlier for natural colloids,<sup>112</sup> that heterogeneous soil components (e.g., iron oxides and clay minerals) and soil water content are important factors affecting transport of CNPs.<sup>99,113–115</sup> For example, it was reported that increasing ionic strength and switching background solution from NaCl to  $\text{CaCl}_2$  had more significant effects on the deposition of fullerenes in a sandy soil than in purified quartz sand, likely because the clay minerals (and possibly soil organic matter) in soil responded to changes of ionic strength and species differently than quartz.<sup>113</sup> In the natural subsurface environment (in particular, vadose zone) the effects of transformation on transport of CNPs are expected to be more complex compared to col-

umn tests using (purified) quartz sand, due to the non-stationary flow regimes and heterogeneity in porous media.

## 5. Effects of transformation on accumulation and release of organic contaminants by CNPs

Hydrophobic organic contaminants, as well as many ionizable organic contaminants, can sorb either reversibly or irreversibly onto CNPs.<sup>11,116</sup> The transformation of CNPs in natural environments leads to changes in their physicochemical properties and aggregation, thereby affecting the sorption of organic contaminants.<sup>11,116,117</sup> CNP transformation can therefore affect contaminant sequestration, enrichment, or release, depending on the properties of the particular contaminant involved, the properties of the CNPs, and the environmental conditions. Such alteration to the binding of organic contaminants to CNPs can in turn affect the transport of these contaminants, which is affected by colloidal CNPs.

### 5.1 Effect of CNP surface chemistry on contaminant binding

The transformation of CNPs in natural environments can change their surface chemistry, and hence their hydrophobicity which has a major effect on the sorption of hydrophobic organic contaminants such as PAHs.<sup>31,116,118,119</sup> For instance, the number of O-functional groups on the surfaces of CNPs will either increase with oxidation, or decrease with reduction. If the number of O-functional groups increases, the CNP surfaces become more hydrophilic and hence thermodynamically less attractive to hydrophobic contaminants. Furthermore, the formation of water clusters around negatively charged O-functional groups has been proposed as an explanation for the observed reduction in sorption of organic contaminants onto CNPs.<sup>120–122</sup> Conversely, if the content of

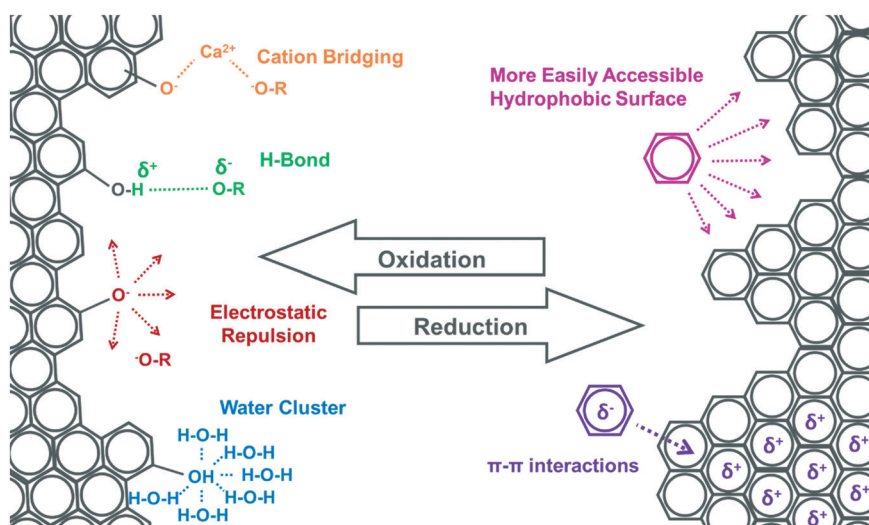


Fig. 3 Effect of chemical/biological transformation of CNPs on binding of organic contaminants.





Fig. 4 NOM loading can affect the pore structure and pore volume of fullerene ( $nC_{60}$ ) aggregates, thereby enhancing their ability to mobilize polychlorinated biphenyl (PCB) in porous media. Data adapted from Wang *et al.*<sup>138</sup>

O-functional groups decreases, the CNPs become more hydrophobic and less negatively charged.

The effects that changes in surface functional groups and surface charge have are more complex for polar ionic and ionizable contaminants, where the speciation of the contaminant, the pH, and the ionic strength are all important factors affecting their interactions with CNPs (see review by Kah *et al.*<sup>11</sup>). For instance, oxidation of CNPs can result in negatively charged contaminants being repulsed electrostatically from the negatively charged CNP surfaces.<sup>11,94</sup> However, polar compounds sorbed to CNPs by hydrogen bonds will become more strongly bound with an increase in surface O-functional groups (*e.g.*, following oxidation of the CNPs)<sup>107</sup> and sorption can decrease with the disappearance of these functional groups (*e.g.*, following reduction of the CNPs).<sup>11</sup> Such enhanced or inhibited polar interactions between polar contaminants (*e.g.*, 1-naphthol) and CNPs can then determine the extent of facilitated transport of contaminants by CNPs.<sup>107</sup> Aromatic organic contaminants are strongly bound to CNPs, mainly through  $\pi$ - $\pi$  electron-donor-acceptor interactions that occur between  $\pi$ -electrons of the aromatic surface of CNPs and  $\pi$ -electrons of the organic contaminants.<sup>123</sup> Depending on the region on the CNP and the functional groups of the contaminant, both can act as either  $\pi$ -electron acceptors or donors. The reduction of oxidized surfaces during CNP transformation in natural environments can increase the electron density on CNP surfaces, which can in turn enhance the  $\pi$ - $\pi$  interactions between CNPs and organic contaminants.<sup>6,124,125</sup> In addition, Wang *et al.*<sup>6</sup> found that reductions by sulfide can open the epoxy rings on GO surface to form hydroxyl and carbonyl groups. Because these two functional groups have the ability to form hydrogen bonds, the reduction could increase the sorption of a polar contaminant (1-naphthol). Again, such changes may affect the capability of CNPs as contaminant vectors of certain contaminants. Wang *et al.*<sup>117</sup> also found that reducing GO through  $Fe^{2+}$  enhanced their capacity for 1-naphthol adsorption by increasing the hydrophobicity of, and  $\pi$ - $\pi$  interactions with GO. However, reduction through  $Fe^{2+}$  reduced the adsorption capacity of hydroxylated CNTs for 1-naphthol. This can be

explained by the ability of  $Fe^{2+}$  to reduce the surface O-functional groups of the CNTs, which would also reduce hydrogen bonding and cation bridging. The adsorption capacity would consequently be reduced, even though hydrophobicity and  $\pi$ - $\pi$  interactions increased. These examples show that the importance of transformation-induced changes in contaminant binding depends on the relative contributions of different mechanisms to the overall sorption.

Similar effects can be expected for pCNPs derived from biochar and wildfire charcoal to those for eCNPs. Biochar transformation under oxidative conditions generally results in an increase in the number of oxygen-containing functional groups and the adsorption of partially oxidized organic matter and clay components, all of which reduce the number of accessible sorption sites resulting in a relative reduction in contaminant sorption with ageing.<sup>126–129</sup> In contrast, reductive processes have to date not been investigated in this regard for biochar, wildfire charcoal, and the associated pCNPs. Nevertheless, the general trends illustrated in Fig. 3 can be expected to apply for all CNPs.

## 5.2 Effect of CNP aggregation and porosity on contaminant binding

The effects of chemical and physical transformation of CNPs are interrelated. While changes in the surface properties of CNPs can affect their aggregation and adsorption potential, the aggregation of CNPs can in turn affect the kinetics of chemical transformation and the surface chemistry of the particles (*e.g.*, decreasing negative charge as a result of cation bridging between surface O-functional groups of CNPs).<sup>130,131</sup> Changes in aggregation of CNPs and in the pore structures of aggregates therefore affect their ability to sorb organic contaminants.<sup>132,133</sup>

The aggregation of CNPs can reduce the number of accessible sorption sites<sup>134</sup> and thereby reduce the binding capacity of CNPs.<sup>107</sup> The aggregation of CNPs can, however, also form micropores and mesopores, which can become important sorption sites for organic contaminants.<sup>135,136</sup> The structure formed by aggregation of tubular CNTs is relatively



open, which means that organic molecules entering open spaces within the aggregate can interact with multiple CNTs at the same time, resulting in enhanced adsorption.<sup>130</sup> In contrast, aggregation of spherical fullerenes can form a closed inner space that is not accessible to organic contaminants.<sup>134</sup> Changes in the intrinsic pore size distributions of pCNPs as a result of transformation and leaching of soluble phases can also affect the pCNP-contaminant binding potential.<sup>137</sup>

Changes in water chemistry, surface functionality, and NOM loading all affect the aggregation of CNPs.<sup>15,47,107</sup> Changes in CNP aggregation as a result of transformation in natural environments can alter the pore structure and pore volume, thus affecting the sorption and desorption of contaminants as well as their co-transport with the CNPs.<sup>130,134,138,139</sup> The adsorption of organic contaminants onto the outer surfaces of CNPs is generally reversible. However, due to the capillary condensation effect or aggregate structure rearrangement in the process of adsorption, contaminants can become trapped in the internal pore spaces of CNP aggregates and thus be more strongly bound.<sup>132,138</sup> For example, Wang *et al.*<sup>138</sup> found that fullerene aggregates that had been modified by NOM and surfactants had markedly different pore geometries, and possibly also greater pore volumes, than unmodified fullerenes. The sorption of polychlorinated biphenyl (PCB) in these physically transformed fullerene aggregates consequently exhibited a much higher level of desorption resistance and, as a result, enhanced co-transport with fullerene (Fig. 4).

The influence of NOM on sorption by CNPs is ambiguous. On the one hand NOM can improve the dispersion of CNPs, thereby increasing the number of available sorption sites, while on the other hand NOM can also bind to CNP sorption sites, thereby competing with organic contaminants for sorption sites. NOM can also block micropores in CNPs and their aggregates, with adverse effects on their binding capacity.<sup>130,140–143</sup> In addition, interactions between CNPs and NOM can result in the blockage of micropores and mesopores, thereby trapping contaminants within these pore spaces.<sup>132,137</sup>

Organic contaminants sorbed by CNTs, fullerenes, fossil coal, and biochar are generally not very bioaccessible because of their high contaminant-binding capacities.<sup>116,144,145</sup> However, when comparing these materials, which are generally produced under controlled conditions, with their counterparts from unintentional emissions (*e.g.*, soot,<sup>24,25</sup> biochar produced under poorly controlled conditions,<sup>146</sup> or wildfire charcoal<sup>29</sup>), the sorption and release of organic contaminants can differ considerably. To derive conclusions for contaminant release from soot, biochar, and wildfire charcoal on the basis of findings for eCNPs is therefore not advisable, as additional factors need to be taken into account. For example, the intrinsic porosity of these materials has been identified as a key factor affecting the sorption and desorption of organic contaminants. Many pCNPs –especially wildfire charcoal and biochars– contain intrinsic micropore networks

which can result in strong sorption hysteresis exceeding that of eCNPs, making these pCNPs potentially more effective contaminant vectors than eCNPs. Although preliminary results indicate that the micropore and mesopore size distributions of certain types of biochar may remain similar after transformation in the field,<sup>70,146</sup> this observation cannot be extrapolated to other types of biochar, soot, or wildfire charcoal, which may be transformed under different conditions in the natural environment (*e.g.*, under different temperatures, water saturation, or pH).

It is therefore important to complement findings from eCNPs with investigations into those additional factors that can affect contaminant binding and release by pCNPs in the natural environment. Additional factors to be considered include the intrinsic porosity, physical disintegration, non-carbonized phases, tar phases, and mineral phases of pCNPs.

## 6. Effects of transformation on catalytic efficiency of CNPs

The involvement of activated carbon in catalytic reactions under elevated temperatures has been well documented.<sup>147</sup> The involvement of pyrogenic carbons including soot, biochar, and wildfire charcoal in catalytic reactions under conditions encountered in natural environments has also more recently been discussed.<sup>116</sup> Pignatello *et al.*<sup>116</sup> subdivided reactions that can be catalyzed by CNPs into two groups: (i) reactions involving surface-mediated electron transfer (including surface-mediated hydrolysis), and (ii) reactions involving the generation of ROS.

### 6.1 Surface-mediated electron transfer

pCNPs typically contain both non-carbonized and mineral phases, in addition to the carbonized phase that reassembles eCNPs. Both the mineral phase and the non-carbonized NOM-like phase can interact with the carbonized phase, and can also participate in catalytic reactions. For instance, redox reactions and the hydrolysis of organic contaminants on mineral surfaces (*e.g.* Mn-oxides and Fe-rich minerals), which have been widely investigated, can both be affected by the presence of NOM. NOM can participate in and/or accelerate mineral dissolution and metal complexation, which in turn affects the catalytic capacity of minerals (see review by Polubesova and Chefetz<sup>56</sup>). All the phases of pCNPs, including carbonized, non-carbonized, and mineral phases, can be dissolved, exchanged, and transformed, which will affect their influences on the catalytic properties of the pCNPs. The catalytic properties of these phases in pCNPs and their transformation products have, to date, received little attention. However, results obtained for eCNPs may help understand the catalytic properties of the carbonized phase of pCNPs.

The catalytic efficiencies of CNPs in hydrolysis reactions are largely affected by the acidity/basicity of their surface O-functional groups. For example, deprotonated surface O-functional groups of CNTs and GO have been shown to act



as bases to catalyze the dehydrochlorination of chlorinated solvents.<sup>148,149</sup> Even though the total number of surface functional groups on the GO decreased following photochemical transformation, the number of carboxyl groups increased,<sup>148,150</sup> resulting in an increased catalytic efficiency for the dehydrochlorination of 1,1,2,2-tetrachloroethane compared with that of pristine GO.<sup>148</sup> Furthermore, Fu and Zhu<sup>54</sup> found that GO was reduced in the presence of Na<sub>2</sub>S and could therefore catalyze the reduction of nitrobenzene with Na<sub>2</sub>S. The edges of the reduced GO acted as the catalytic sites, while the basal plane of the reduced GO served as a conductor for the electron transfer during the catalytic process.

In addition to surface functionality, the aggregation of CNPs can also affect their catalytic efficiency. For example, oxidation increases the amount of O-functional groups on CNP surfaces, which can improve their catalytic efficiency for hydrolysis of organic contaminants. However, O-functional groups can form cation bridges with divalent cations (e.g. Ca<sup>2+</sup>) so that an abundance of O-functional groups can encourage aggregation of CNPs, thereby decreasing their catalytic efficiency. Furthermore, NOM can enhance the dispersion of CNPs leading to more surface functional groups becoming available as active catalytic sites.<sup>151,152</sup> However, NOM may also block a proportion of the sorption and catalytic sites on CNP surfaces by sorbing to the CNPs.<sup>148,151,153</sup> The effect of NOM on the catalytic properties of CNPs therefore needs to be carefully evaluated on a case by case basis.

## 6.2 Generation of reactive oxygen species

During pyrolytic pCNP formation unshared electrons and electron pairs can form free radicals that can persist within the pCNP structures for prolonged periods of time. The abundance of these persistent free radicals within pCNPs depends on the pyrolysis conditions, the composition of the original feedstock, the abundance of oxygen groups in the pCNPs, and the presence of external metals (see review by Qin *et al.*<sup>154</sup>). The concentration of persistent free radicals in pCNPs can reach up to 10<sup>19</sup> spins per gram,<sup>116</sup> which is two orders of magnitude above the concentrations commonly found in humic acids.<sup>155</sup> When pCNPs are introduced into water these radicals can form H<sub>2</sub>O<sub>2</sub> and ROS, but most of these reactions typically take place within the first few hours after contact with water, as was recently observed for biomass-based chars where H<sub>2</sub>O<sub>2</sub> production peaked after approximately 1 hour and then declined.<sup>156</sup>

CNP aggregation and pore blockage can decrease the release of free radicals and their products, similar to the reduced release of organic contaminants discussed in section 5.2. ROS deriving from pCNPs are capable of inducing the transformation of a range of organic contaminants including sulfadimidine,<sup>157</sup> 1,3-dichloropropene,<sup>158,159</sup> *p*-nitrophenol,<sup>160</sup> trifluralin,<sup>161</sup> pendimethalin,<sup>161</sup> diethyl phthalate,<sup>162</sup> nitrobenzene,<sup>163</sup> and 2-chlorobiphenyl.<sup>164</sup> Some compounds can react directly with carbonaceous materials, as has been ob-

served for chloropicrin<sup>165</sup> and *p*-nitrophenol.<sup>156</sup> Pignatello *et al.*<sup>116</sup> suggested that the intrinsic reactivity of carbonaceous materials could be due to their redox behavior. The transformation of pCNPs is expected to have a strong effect on H<sub>2</sub>O<sub>2</sub> production, ROS release, and pCNP redox behavior. These aspects of pCNP-induced contaminant transformation remain largely unexplored and require further investigation.

Finally, it is important to note that the sorption of organic contaminants to CNPs can affect contaminant transformation. For example, sorption of nitroaromatics to CNPs favors electron transfer for redox transformation of these contaminants.<sup>166</sup> Thus, the effects of CNP transformation on contaminant sorption discussed in section 5 can also affect the catalytic efficiency of CNPs for contaminant transformation.

## 7. Further research required

Our review indicates that engineered carbon nanoparticles (eCNPs) comprise a very small proportion (<1%, Gg per year range) of the CNPs in the natural environment and are therefore largely of academic interest compared to the generally more complex pyrogenic or petrogenic carbon nanoparticles (pCNPs) that derive from forest fires, fossil fuel combustion, and biochar application (>99%, Tg per year range).

The translation of exiting findings on eCNPs to understand the behavior of pCNPs needs to carefully consider molecular differences between these materials. Generally, pCNP consists of smaller aromatic clusters and contains more structural irregularities and mineral phases than eCNPs, resulting in significant differences in surface chemistry, density, porosity, reactivity, and stability. Therefore, building on the knowledge obtained for eCNPs and soot, a special focus should be on changes in intrinsic porosity and on the transformation of the non-carbonized phases, the mineral phases, and the organo-mineral complexes of pCNPs. The complexity of these transformation processes calls for increased exchanges between different scientific communities, including atmospheric chemists, microbiologists, soil scientists, water chemists, and colloidal scientists.

Among the different pCNPs, soot and its transformation within the atmosphere are well understood because of a large body of research in atmospheric chemistry. In contrast, pCNPs deriving from fossil coal, wildfire charcoal, and biochar are less well understood. A strategy for future research could be to build on existing knowledge concerning the transformation of soot during atmospheric transport and focus on closing the existing knowledge gaps on the transformation of pCNPs in soil, sediment, and aquatic systems. Most of the reported findings have been obtained under oxidative conditions, while investigations under anoxic and reducing conditions are underrepresented in the scientific literature.

Investigations into the effects of transformation on CNP colloidal transport should take into account the geometry, porosity, and composition of pCNPs deriving from soot, fossil coal, wildfire charcoal, and biochar. Differences in





aggregation compared to commonly investigated eCNPs (including GO and CNTs) can be expected and will require further investigation. Thereby, the effects of the pCNP phases that differ from those of eCNPs are of special interest. For instance, non-carbonized phases, Al- and Fe-oxides, organo-mineral complexes, and tar can bind to pCNP surfaces and affect their surface chemistry, porosity, and aggregation. Incorporating these factors into systematic prediction tools for pCNP transformation and aggregation that can take into account chemical, physical, and biological transformation processes would be of great assistance in obtaining a better assessment of naturally-occurring pCNPs.

Contaminant binding and release can be affected by CNP transformation, however, the importance of transformation-induced changes in contaminant binding depends on the relative contributions of particular mechanisms to the overall sorption, which needs to be carefully considered. Future research needs to complement the findings for pristine eCNPs with investigations into additional factors that might affect the binding and release of contaminants by pCNPs. The additional factors to be considered include changes in the intrinsic porosity, physical decomposition, non-carbonized phases, tar phases, and mineral phases of pCNPs.

The catalytic properties of pCNPs are expected to be affected by all of the different phases of pCNPs including carbonized, non-carbonized, and mineral phases, which can all be dissolved, exchanged, and transformed in the natural environment. The influence that these phases and their transformation have on the catalytic activity of pCNPs has received little attention to date and warrants further investigation.

Systematic investigations are required into the relative contributions of specific mechanisms to the overall sorption in order to better predict transformation and transformation-induced changes to contaminant binding. The development of generalized approaches such as the use of poly-parameter linear free-energy relationships (ppLFER), while taking into account pCNP properties and transformation processes, will be required to predict the sorption of both neutral and polar organic contaminants to CNPs in the natural environment. However, such comprehensive predictive tools are unlikely to be developed in the near future as more fundamental open questions, such as those discussed in this review, will first need to be addressed.

## Conflicts of interest

The authors declare no conflict of interests.

## Acknowledgements

This project was supported by the National Natural Science Foundation of China (Grant 21425729), the Ministry of Science and Technology of China (Grant 2014CB932001), the Fundamental Research Funds for the Central Universities, and the 111 Program of the Ministry of Education of China (T2017002).

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