Environmental archives of contaminant particles

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Abstract

Particulates in the environment may be contaminants or pollutants. They may affect climate through the absorption of energy in the atmosphere and by reducing the albedo of ice and snow surfaces; may enhance the transfer and distribution of pollutants such as trace metals and persistent organic pollutants via absorption and adsorption to their surfaces; may adversely impact the health of aquatic life and consequently other biota that depend upon it; in the atmosphere they may have direct effects on human health via respiratory disease and the transfer of substances deep into the respiratory system. Therefore, it is important to be able to determine temporal trends in particulate emissions and deposition. Natural archives such as ice, sediment and peat cores can provide well-resolved records but research has mainly focussed on a few particle types, and predominantly black carbon. In this chapter we review the environmental records of black carbon and other industrially-derived particles, their analysis, interpretation and relative strengths and weaknesses. Finally we consider two emerging particle types: microplastics and nanoparticles. These latter groups have, so far, received little attention from palaeoecological perspectives but their direct impacts on aquatic biota and ability to transport pollutants within the atmosphere and aquatic ecosystems is becoming increasingly apparent in the literature and are predicted to further increase in coming decades.

Keywords: black carbon; charcoal; fly-ash; ice cores; microplastics; nanoparticles; sediments

Introduction

The distinction drawn between a contaminant and a pollutant relates to the scale of its impact. A contaminant is a substance introduced into the environment, either directly or indirectly, such that levels that might naturally exist are exceeded (Frid and Dobson 2013) whereas a pollutant may be defined as a contaminant that causes harm or damage to an organism or ecosystem. In the atmosphere particles are often pollutants. Pope and Dockery's work in the 1990s (e.g., Pope et al. 1991, 1995; Pope and Dockery 1992; Dockery et al. 1993) highlighted the effects of fine airborne particulate matter, PM_{10} (defined as particles with an aerodynamic diameter ≤ 10µm) on a range of human health issues including asthma, bronchitis and mortality while more recently the emphasis has shifted to finer particulate fractions ($PM_{2.5}$; $PM_{1.0}$) and their role additionally in lung cancer and cardiopulmonary disease (e.g., Pope et al. 2002; Pope and Dockery 2006). The earlier health impact studies led to national assessments; for example, in the UK (COMEAP 1995; POST 1996; Pearce and Crowards 1996) and the Netherlands (Buringh and Oppenhuizen 2002), and also at the larger scale by the World Health Organisation (1999). These resulted in the instigation of regularly revised Air Quality Standards also at national and international levels (e.g., WHO guidelines: www.who.int/topics/air_pollution/en/). As an example, the current US EPA standards, revised in December 2012, lowered the annual mean $PM_{2.5}$ concentration from 15.0 to 12.0 µg m^{-3}, while maintaining the 24-hour value of 35 µg m^{-3} (www.epa.gov/pm/2012/decfsstandards.pdf). Interestingly, PM_{10} are now referred to as the coarse particle fraction.

The standards for airborne particulates, and most of their defined impacts, relate to undifferentiated particulate mass, i.e. it is the total particle load that is considered. Hence despite there being considerable interest in the long-term exposure of particulates for health issues (e.g., Hodgson et al. 2009) palaeorecords have so far not been employed to generate useful data. However, where impacts from more specific particle types can be identified, such as black carbon (Anderson et al. 2001; Roemer and van Wijnen 2001; Janssen et al. 2012; Künzi et al. 2013) or oil fly-ash (Ghio et al. 2002) there may be a role to play. In this sense, black carbon is of particular importance because its impacts are not only directly related to human and environmental health, but it has a further indirect effect via its climate change impacts (Löndahl et al. 2010; Shindell et al. 2012). Consequently, knowledge of long-term changes in black carbon emissions would be a benefit to determining (i) health effects from aerosol exposure, (ii) climatic effects of aerosols and (iii) health effects of climate change. It should be no surprise then, that the estimated economic value of damage from fossil-fuel combustion is enormous (Barbir et al. 1990) with the impacts to human health in the United States alone calculated at \$361 – 886 billion (or 2.5 – 6% GDP) annually (Machol and Rizk 2013) and for the UK £6 – 62 billion (0.4 – 3.5% GDP) (Yim and Barrett 2012).

In aquatic and terrestrial environments, as well as the atmosphere and cryosphere, a further significant impact from particles derives from their ability to transport toxic pollutants attached to their surfaces. These adsorbed (also absorbed) substances are distinct from emissions of pollutants in particulate form (e.g., metal fume (Pires et al. 2006)) and include trace elements such as lead (Pb), cadmium (Cd) and arsenic (As), which are preferentially concentrated onto the respirable fraction of airborne particles emitted from coal-fired power plants (Natusch and Wallace 1974). Mercury (Hg), zinc (Zn) and polycyclic aromatic hydrocarbons (PAHs) are also transported in this way and the scale of PAH absorption can be related to the carbon content of the emitted fly-ash (Wey et al. 1998). Dioxins and furans (PCDD/Fs) have also been linked to ‘soot black carbon’ (Persson et al. 2002; Lohmann et al. 2005) as have acidifying ions (Guazzotti et al. 2001). Similarly, Ghosh et al. (2003) showed that carbonaceous particles extracted from harbour sediments preferentially accumulated both PAHs and polychlorinated biphenyls (PCBs), while Chen et al. (2009) demonstrated the affinity of oil-derived black carbon for perfluoroctane sulphonate (PFOS). PFOS is an emerging pollutant with known multiple toxicities including endocrine disruptive, reproductive and developmental effects.

Particles, and in particular the carbonaceous component, therefore have direct pollutant effects in a number of environments and, furthermore, may be used as indicators of contamination sources for other deposited substances (see examples later in this chapter). For these reasons, it is important to be able to ascertain the long-term records of particulates in the environment via the use of natural archives. These archives make it possible to distinguish between natural and anthropogenic sources in order to interpret environmental impacts appropriately.

There is a long record of natural particulate contamination. Black carbon has been reported in sediments since the Devonian (c. 415 M yr; Schmidt and Noack 2000) and Graseby et al. (2011) describe carbon-rich char particles with a passing resemblance to the morphologies of modern-day fossil-fuel derived particulates from Permian age rocks (c. 250 Myr BP) in the Canadian High Arctic. It is speculated that these were produced by combustion of Siberian coal and organic-rich sediments by basalts before being widely dispersed (see also Sanei, this volume). Ancient carbonaceous particles have also been observed at the Cretaceous – Paleogene (K-P) (formerly Tertiary) boundary c. 65 Myr BP with suggested sources from both wildfires triggered by a bolide impact (Wolbach et al. 1985) but also from the impact itself into organic-rich geology (Harvey et al. 2008). Interestingly, these latter particles, while carbon-rich have a “bubble texture” and a light brown colour. Harvey et al suggested that these features result from the particles “boiling” at low temperatures (300 – 800 °C) but not igniting. They are therefore distinguishable from modern industrially derived carbonaceous particulates, which ignite at higher temperatures and produce a black porous ‘cenosphere’ (e.g., Rose 2001). Morphologically and chemically, however, these K-P carbon cenospheres are remarkably similar to particles observed from a peat core taken from Misten in eastern Belgium (50°33'44.33"N; 6°9'50.70"E) and dated to c. AD 550 (Jérémie Beghin, Université de Liège; pers. comm.). The colouration, the bubble texture and the carbon-rich composition are the same (Figure

1), but here it is suggested that the source is from some smelting-type activity. Further study is required to determine the formation processes for this intriguing particle type.

[FIGURE 1 NEAR HERE]

The record of charcoal particles in both palaeolimnological (Whitlock and Larsen 2001) and pedoanthracological (Nelle et al. 2013) natural archives extends over many millennia. In both lake sediments (e.g., Earle et al. 1996; Vannière et al. 2008; Higuera et al. 2009) and peat archives (e.g., Breitenlechner et al. 2010; Bindler et al. 2011) these records represent the complex interactions between climate, vegetation-type and human activity (Haberle 2001). Hence, charcoal as an indicator of fire frequency may be used to suggest where fires were natural or used as a land management tool. Natural fires may be less frequent (60 – 250 years) and irregularly spaced, while frequencies of 10 – 20 years are typical where controlled burning is used, for example, to maintain *Calluna vulgaris* dominated heathland (Birks 1997). Conversely where fire suppression is used as a management policy, a reduction in charcoal inputs may also result (Willis and Birks 2006).

Fire size, intensity and severity affect the production and also the transport of charcoal particles as they may be carried to great heights and over large distances in the process of dispersal (Whitlock and Larsen 2001). Aerial transport is affected by particle size with charcoal > 1000 µm in diameter being deposited close to the fire (Clark and Patterson 1997), while particles smaller than 200 µm are not expected to be deposited within approximately 6 km of a fire column (Whitlock and Larsen 2001). Taphonomic processes are an important consideration when interpreting charcoal records and include not only atmospheric dispersal and deposition but also transport from catchments via soil erosion (secondary charcoal) or via inflowing streams. These transfer processes may result in a considerable lag in the timing of a fire ‘event’ in a sediment record (Whitlock and Larsen 2001), and may also affect charcoal concentrations as sediments taken from near a stream inflow may be several times higher than those from deeper ‘offshore’ sediments (Patterson et al. 1987) as a result of movement from higher in a catchment (see also Rosen this volume).

Records of charcoal particles over tens of thousands of years have been used as an indicator of climatic change with warmer, drier climates leading to increased fire frequency (Vannière et al. 2008; Higuera et al. 2009). However, these changes also remain a key signature of human impacts through the Quaternary. For example, records over 40,000 years in Papua New Guinea have been interpreted as indicative of changes in human occupation (Hope 2009) while increased fire-frequency in the Mediterranean is equated with the development of human settlements, slash-and-burn agriculture, and mineral exploitation (Vannière et al. 2008). Distinguishing between climatic and anthropogenic charcoal signals is largely dependent on context. Supporting information most frequently pertains to pollen (e.g., Haberle et al. 2001; Whitlock and Larsen 2001; Vannière et al. 2008; Higuera et al. 2009; Breitenlechner et al. 2010) or macrofossil data (Willis and Birks 2006) to indicate vegetational changes, but also widely uses archaeological, dendrological and geochemical data to indicate, for example, metallurgical indicators of human expansion (Bindler et al. 2011; Pichler et al. 2013).

The need to distinguish between natural and anthropogenic sources of particles is not restricted to charcoal. Fossil-fuel combustion-derived inorganic ash spheres (IAS) (Rose 2001) appear morphologically similar to microspherules of volcanic (e.g., Lefèvre et al. 1986) or micrometeoritic origin (e.g., Handy and Davidson 1959; Hodge and Wright 1964). Natural sources of particles morphologically similar to IAS become less significant in more recent records as anthropogenic sources swamp those that are naturally produced. However, in areas where industrial particle inputs are low or infrequent, such confusions may still arise and as a result the records of unambiguously anthropogenic and / or industrial particles, such as spheroidal carbonaceous particles (SCPs), become exceedingly useful as environmental change markers.

Carbonaceous particulates, often termed ‘black carbon’ are therefore very important in toxicological, pollutant transfer and environmental change studies especially in archives that include periods after the Industrial Revolution when emissions increased dramatically. The remainder of this chapter focusses on the particle record of the industrial period and in particular the environmental records of black carbon particles. Finally, we consider some of the environmental impacts and archives of two new and emerging particle types: microplastics and nanoparticles.

Black carbon

What is black carbon?

The term ‘black carbon’ (BC) covers a range of particulates with a composition of > 60% carbon and with accessory elements including hydrogen, oxygen, nitrogen and sulphur (Goldberg 1985). It is formed by the incomplete combustion of biomass such as grasslands or forest fires, anthropogenic industrial combustion of biomass or fossil fuels, diesel and gasoline engines, and small-scale domestic fires. Emissions from these sources are large. According to ‘bottom-up’ inventories, total global emissions of BC were estimated to be 7500 Gg for the year 2000 but with a large uncertainty range of 2000 to 29000 Gg (Bond et al. 2013).

‘Black carbon’ therefore encompasses a wide spectrum of charred material and despite 30 years of research there is still no single accepted definition, especially between disciplines (Masiello 2004; Andreae and Gelencsér 2006). Terms such as black carbon, elemental carbon, soot, graphitic black carbon, pyrogenic carbon and refractory black carbon are often used interchangeably, and definitions for these are based on source processes, morphological characteristics, chemical composition and the optical properties of the material in question. Recently, for atmospheric sciences, Bond et al. (2013) defined black carbon very specifically as being a distinct type of carbonaceous material formed in flames and having a unique combination of physical properties. However, this definition does not cover all BC particles included in soil and sediment studies. In general, the term elemental carbon is used in atmospheric sciences while black carbon is used in soil and sedimentary disciplines (Hammes et al. 2007).

One way of understanding the myriad of particles under the BC umbrella is by considering the “black carbon combustion continuum model” first presented by Hedges et al. (2000). All components of the continuum (Figure 2) are black particles that have formed as incomplete combustion products. These particles range from slightly charred biodegradable biomass, char and charcoal through to industrial particles formed at high temperatures, but there are no clear boundaries between these classes (Seiler and Crutzen 1980). Generally, they can be grouped into larger chars, which are residues reflecting the structure of the burned material, or the nature of the burning process, and smaller particles, such as soots, which are combustion condensates, i.e. formed from the vapour phase (Novakov 1984). Both types can form simultaneously from a single combustion source (Goldberg 1985).

[FIGURE 2 NEAR HERE]

Soot BC is slightly different from the rest of the BC continuum because it is produced from the vapour phase as a condensation product rather than as a combustion residue. These are the particles that are mostly considered by atmospheric scientists as BC (e.g., Bond et al. 2013), probably due to their small size and well-known optical (light absorbance) properties. Although soot BC may be produced in large natural fires if sufficient temperature is attained, it is common in industrial processes and during the combustion of natural gas, gasoline and diesel, which do not produce any other BC forms. It is generally recognized that soot forms through the production of polycyclic aromatic hydrocarbons (PAHs), which continue to form larger structures, eventually condensing into solid spheres (Kennedy 1997). The size of soot particles may vary from a single to hundreds of nanometres. Although incomplete combustion of organic material always produces PAHs in addition to BC particles, PAHs are not included in the BC continuum because they do not share other properties such as light absorbance.

The purest form of black or elemental carbon is graphite, which consists of sp^2–bonded carbon in planar layers. Graphite is formed over geological time-scales under conditions of high temperature and pressure. It is therefore not a combustion product and is not considered further here.

Black carbon effects on climate

In addition to the toxicological impacts and pollutant transport properties of particles described at the start of this chapter, BC also has a strong warming effect on climate where its potency is based on its colour and surface characteristics (Ramanathan and Carmichael 2008). BC absorbs solar radiation and so warms the atmosphere prior to deposition (e.g., Bond and Bergstrom 2006; Bond et al. 2013) but also darkens surfaces once deposited (Warren and Wiscombe 1980), thereby significantly reducing the albedo of snow and ice (Clarke and Noone 1985) and hastening the melting process. The strong warming effect of small BC concentrations in snow results from the more rapid growth of snow grain size following BC deposition (Bond et al. 2013). Coarse-grained (old) snow has lower albedo than fine-grained (new) snow and this leads to a positive feedback process accelerating melting (Flanner et al. 2007). Due to its properties in the atmosphere and this feedback process, BC is considered to be the second most important component of global warming after carbon dioxide (e.g., Jacobson 2001; Ramanathan and Carmichael 2008; Bond et al. 2013). It has been suggested that up to 40 % of current net warming is attributable to BC as well as 30 % of Arctic melting (Baron et al. 2009), making it potentially a more important factor than greenhouse gases for climate warming in this region (e.g., Hansen and Nazarenko 2003; Bond et al. 2013 and references therein).

Climatic impacts of BC are not restricted to the Arctic. It has recently been suggested that increasing deposition of industrial BC forced the climatologically premature end of the Little Ice Age in the European Alps around 1850. Glaciers in the region started to retreat in the latter half of the 19th century when according to temperature and precipitation records they should have continued to grow until c. 1910 (Painter et al. 2013). In the Himalayas, the warming of the atmosphere by BC and the darkening of ice surfaces is thought to be a major contributor to the accelerating retreat of glaciers (e.g., Ramanathan and Carmichael 2008; Xu et al. 2009), while its contribution to “atmospheric brown clouds” across southern Asia (Ramanathan and Crutzen 2003; Lawrence 2011) affect evaporation and long-range moisture transport responsible for the monsoonal circulation. As a consequence precipitation trends over many regions of the tropics, particularly Africa, south Asia and northern China, have been negative over the last 50 years (Ramanathan and Carmichael 2008). Atmospheric heating by BC and ozone has also occurred at mid-latitudes resulting in a poleward shift of the tropospheric jet, thereby moving the main division between tropical and temperate air masses and expanding the tropical zone in the northern hemisphere (Allen et al. 2012).

Environmental archives of black carbon

Methods most commonly used for the quantification of BC from environmental archives can be divided into five different categories: (i) optical; (ii) thermal (for both of these categories see references in Watson et al. 2005); (iii) microscopic (e.g., Stoffyn-Egli et al. 1997; Thevenon and Anselmetti 2007; Rose 1994; 2008); (iv) chemical (e.g., Masiello and Druffel 1998); and (v) indirect (e.g. molecular markers; Glaser et al. 1998). Additionally, some mixed methods have been employed such as the thermo-optical (e.g., Chow et al. 1993) or chemo-thermal (e.g., Gustafsson et al. 1997; 2001). Optical methods are usually used in atmospheric sciences for the quantification of elemental carbon and rely on its light-absorbing properties (see Watson et al. 2005 and references therein). By contrast, thermal methods developed for BC in sediments and soils rely on its resistance to degradation, in particular oxidation (Hammes et al. 2007). Many of these methods use a two-step approach in which the carbon oxidising below a certain temperature (≈350 - 550 °C) is termed organic carbon, while that at higher temperatures (≈650 to 1100 °C) is termed elemental carbon (Watson et al. 2005). Chemical methods determine BC as that which resists chemical extraction (e.g. removal of organic material and inorganic minerals with acid treatments) and this may be followed by microscopic techniques for specific particle types, such as charcoal and SCPs, which are counted after the chemical extraction has removed unwanted components of the surrounding matrix (Renberg and Wik 1984; Rose 2004).

Unfortunately there is no standard method for BC quantification for any environmental matrix. Watson et al. (2005) summarized over 50 inter-laboratory and inter-method comparisons for BC and elemental carbon determination. Analyses of identical samples showed typical differences by a factor of 2 between methods, but higher discrepancies (of a factor of up to 7) were measured in some cases and Schmidt et al. (2001) reported variability by a factor of 500 between measured concentrations of BC in an inter-comparison study of soil samples. For most methods it is not possible to precisely define which components of the BC continuum (Figure 2) are being measured. No single method measures the whole range and it is likely that overlap between particle types within the continuum results in much of the discrepancy between analytical approaches. Such deficiency makes comparisons between studies using different analytical methods problematic and even inappropriate, as illustrated later in this chapter. Exceptions are where particle types can be more precisely defined by their morphology with specific identification criteria. In these cases, comparisons between measurements and analysts are more robust (e.g., Rose 2008).

There are numerous studies on the presence of BC in the environment, including the atmosphere (e.g., Ogren and Charlson 1983; Kaneyasu and Murayama 2000; Hitzenberger and Tohno 2001; Bae et al. 2004; Sharma et al. 2004), snow (e.g., Forsström et al. 2009; Hadley et al. 2010; Hegg et al. 2010; Doherty et al. 2010), ice (Cachier and Pertuisot 1994; Chylek et al. 1992a; b), soils and lake sediments (e.g., Song et al. 2002; Cornelissen et al. 2005; Rumpel et al. 2006), fluvial sediments (e.g., Elmquist et al. 2008; Mitra et al. 2002) and marine sediments (e.g., Gustafsson and Gschwend 1998; Masiello and Druffel 1998; Middelburg et al. 1999). However, historical records are still relatively scarce. Models of concentrations and climatic effects of BC in the past have been mainly based on emission inventories and atmospheric circulation data (Shindell and Faluvegi 2009; Skeie et al. 2011). They are typically not directly constrained by measurements of BC deposition, which tend to be used only for validation of the model output. Published historical global BC emission inventories are based on estimates of different fuel consumption and changes in combustion technologies (e.g., Novakov et al. 2003; Bond et al. 2007). According to these inventories global BC emissions have increased 7-fold from pre-industrial levels (Bond et al. 2007), but these are, of course, not uniform around the world. Emissions from industrialized countries in Europe and North America have declined during the last few decades as a result of employing particle arrestor technology, increasing combustion efficiency and switching to cleaner fuels. Emissions from developing countries, especially China and India, have only started to increase rapidly during the last two or three decades (Novakov et al. 2003; Bond et al. 2007) (Figure 3) resulting in a southward latitudinal shift in global BC emission sources since the last decades of the 20th century (Skeie et al. 2011).

[FIGURE 3 NEAR HERE]

It maybe expected that environmental archives should reflect these temporal trends, although local and regional transport and depositional processes may influence these records at the site-specific level (e.g., Ruppel et al. 2013). Past accumulation and fluxes of BC can be studied from sediments and soils as well as ice cores from continental ice sheets and glaciers. While ice sheets are invaluable archives of atmospheric pollutant deposition histories and may record inputs with seasonal resolution for thousands of years, their geographical distribution is limited and ironically it is the influence of BC on glacial melting that is now removing the record we would like them to preserve.

Black carbon in ice cores

One of the first studies to show historical trends in BC was from an ice core in the European Alps (Lavanchy et al. 1999). Black carbon concentrations were found to increase by a factor of 3.7 from pre-industrial (1755-1890) to modern times (1950-1975) and by considering BC emissions from Germany, France, Switzerland and Italy these trends were found to mostly reflect particulate carbon emissions from Western Europe. A second ice core from an adjacent site (Jenk et al. 2006) but covering the period 1650-1940, showed a six-fold increase in BC concentration starting from around 1870. Radiocarbon analysis of graphitic carbon dioxide generated during thermal BC quantification also showed an increasingly anthropogenic origin after this time (Jenk et al. 2006).

In 2007, McConnell et al. published the records of BC deposition since 1788 derived from two ice cores taken on the Greenland Ice Sheet. They found a seven-fold increase in BC concentrations from 1850, peaking in the early decades of the 20th century and followed by a decline to almost pre-industrial levels after 1950. Concentrations of BC prior to AD 1850 were found to closely match those of vanillic acid, used as an indicator for coniferous forest fires, but after 1850, BC concentrations reflected non-sea-salt sulphate indicating industrial emissions as the primary source (McConnell et al. 2007). North America was considered the most plausible source area for this contamination. However, McConnell et al. recognized that these high-altitude ice cores (2473 and 2713 m above sea level) were located in the free troposphere and hence BC deposition recorded there could not also be taken as representative of trends for lower altitude regions of the Arctic. Hirdman et al. (2010) confirmed that the source regions of BC for Summit on the Greenland ice sheet (3208 m above sea level) were representative only for this specific site and did not reflect the low-level atmospheric transport of pollution (Stohl 2006) from high latitude Eurasia that influences much of the rest of the Arctic (Quinn et al. 2011).

McConnell et al.'s (2007) highly influential paper was soon followed by other studies on the long-term records of BC in ice cores. Ming et al. (2008) reported elemental carbon concentrations in a Himalayan ice core while Xu et al. (2009) showed the records from five ice cores taken from glaciers on the Tibetan Plateau. Here, BC concentrations were relatively high in the 1950s-1960s but decreased during the 1970s-1980s, especially on glaciers influenced by long-range atmospheric transport from Europe (Xu et al. 2009). This pattern was seen to reflect decreasing emissions in Europe as a result of 'Clean Air' policies. However, during the 1980s-1990s and especially since the latter part of the 1990s, BC concentrations increased again, and this was thought to be due to industrialization in southern Asia. Ming et al. (2008) observed similar increases in BC concentrations after 1980 – 1990 in their core from the East Rongbuk Glacier near Mt. Qomolangma (Everest) (Figure 4a).

These European (Lavanchy et al. 1999; Jenk et al. 2006; Legrand et al. 2007) and Himalayan (Ming et al. 2008; Xu et al. 2009) studies used a filter based thermal-optical method, where comparably large amounts of ice are required in order to exceed the detection limit of the analysing instrument resulting in an annual to multi-year resolution. By contrast, McConnell et al. (2007) used a new method for BC analysis that had been developed for atmospheric samples (Stephens et al. 2003). In this method BC concentrations were determined with a single particle soot photometer or 'SP2'. This measures mass and size distribution of individual BC particles using laser-induced incandescence (Schwarz et al. 2006; McConnell et al. 2007) and thus only very small amounts of ice are required, thereby allowing a monthly resolution.

The SP2-method was also used for a study on BC deposition using an ice core retrieved from Mt Everest (Kaspari et al. 2011) close to the one collected by Ming et al. (2008) but the results of these two studies differed quite significantly. Firstly, the Kaspari et al. (2011) study did not observe the increase in BC concentrations after the 1990s evident in the Ming et al. (2008) core (Figure 4a, b); and secondly the concentrations in the later core were much lower than in the earlier one. Given the close proximity of the coring locations, it is unlikely that this variance is due to depositional differences alone but – as presented earlier in this chapter – is more likely due to the different analytical methods employed (Kaspari et al. 2011). Ming et al. (2008) collected BC for analysis by filtering the melted ice through a 1 µm pore-size filter prior to thermal-optical analysis, so particles smaller than this were most likely not quantified. However, the SP2 method employed by Kaspari et al. (2011) detected only BC particles with an estimated size of ≈80 - 500 nm. Hence, it is likely that these studies were measuring two quite different parts of the BC continuum possibly with little or no overlap. It is important, when comparing BC data from different studies, to be clear which analytical techniques are being used and which BC fractions are being quantified in order to make the appropriate interpretation. The analysis of these potentially different size-fractions for this area of the Himalayas is interesting in itself, as it may imply that emissions of larger particles (Ming et al. 2008) have increased in the source area (South Asia) since the 1990s, whereas emissions of smaller ones (Kaspari et al. 2011) have not. This may point to an increase in low-efficiency industrial coal and oil combustion in the region over the last 20 years.

Results of BC deposition in the Antarctic are also of great interest, because the region is the most remote from human influence. Bisiaux et al. (2012a; b) retrieved six ice cores from Antarctica with a maximum distance of ≈3500 km between them. The BC records showed considerable temporal variability at annual to decadal scales, but common features included relatively low concentrations from 1890 to 1910, higher concentrations 1910 - 1930 but, in particular, an increasing concentration trend at the end of the 20th century (1980-2000) (Figure 4c). These depositional patterns, especially in the latter part of the 20th century, were linked to changes in anthropogenic BC emission sources in the southern hemisphere and especially emissions from southern hemisphere grass fires and biofuel emissions, which were reduced over the 1950 -1980 period (Bisiaux et al. 2012b).

[FIGURE 4 NEAR HERE]

In summary, ice cores are able to provide considerable insights into BC depositional history, variability between regions and in providing historical estimates for radiative forcing in both the atmosphere and when deposited on snow and ice (Ming et al. 2008; Kaspari et al. 2011). Although the distribution of appropriate sampling sites is quite limited globally, ice cores do indicate the scale of long-range atmospheric transport of anthropogenic emissions to the remotest regions, albeit that physical constraints (McConnell et al. 2007), climatic variables (Bisiaux et al. 2012b) and methodological considerations (Kaspari et al. 2011) may significantly affect results and interpretation. Black carbon distribution and deposition globally is rather heterogeneous and, because BC has a relatively short atmospheric residence time (days to weeks), mainly linked to regional sources. Consequently, in order to get a better insight into the distribution and effects of BC in the past, measurements are required from many locations more widely distributed than is possible to achieve with ice cores alone. Here, lake sediments can play an important role.

Black carbon in lake sediments

As with ice cores, analytical methodology is a critical consideration for BC determination in sediments and will affect which fraction of the BC continuum is being quantified. An additional factor for sediments, when compared with ice and especially atmospheric samples, is that BC comprises a very minor component and needs to be separated from the inorganic minerals and thermally unaltered organic carbon (such as plant/animal material and humic substances) that comprise the bulk of the sediment. This is often achieved by different chemical and/or thermal pre-treatments, which are based on the assumption that BC is more resistant to breakdown than other forms of organic carbon and some minerals (Hammes et al. 2007). These different methods may themselves result in the selection of differing fractions of the BC continuum, and analysis of the same samples with different methods can result in very different estimates for BC content (Hammes et al. 2007). However, where BC is quantified wholly or partly by visual methods, i.e.by identifying and counting particles using light (e.g., Goldberg et al. 1981; Odgaard 1993; Rose 2004; 2008) or scanning electron microscopy (e.g., Karls and Christensen 1998; Kralovec et al. 2002; Thevenon and Anselmetti 2007) then the fraction of the continuum is much more closely defined, albeit restricted to relatively large particles, > ≈2 μm (e.g., Rose 1994; Thevenon and Anselmetti 2007).

The early work on BC quantification in sediments was mainly based on chemical extraction and visual identification approaches (e.g., Goldberg et al. 1981; Renberg and Wik 1984; Odgaard 1993; Rose 1990; Stoffyn-Egli et al. 1997; Doubleday and Smol 2005), and while this work continues (e.g., Thevenon and Anselmetti 2007; Rose et al. 2012), there has been a recent escalation of interest in applying techniques developed for atmospheric research to sediment studies. These methods enable the quantification of smaller, high-refractory BC particles that cannot be assessed by visual methods (e.g., Gustafsson et al. 1997; 2001; Elmquist et al. 2007; Gelinas et al. 2001; Husain et al. 2008). The switch in focus towards smaller size fractions lies with the increasing interest in the climatic role of BC particles (longer atmospheric residence times and transport distances) and in advances in understanding the impacts of BC on human health (deeper penetration into respiratory tracts) (e.g., Hansen and Nazarenko 2003).

The chemo-thermal oxidation method (CTO-375) developed by Gustafsson et al. (1997; 2001) is one of the most widely used methods for this type of particle in sediments, but studies reporting the long-term accumulation trends of BC in sediments are still quite scarce. In Upper Mystic Lake in eastern North America (Gustafsson et al. 1997), the record for the period AD 1886-1989 showed low BC concentrations prior to industrialization, but increasing concentrations from c. 1940 to 1960 after which concentrations declined first slowly and later more rapidly. Combustion-derived PAH concentrations in the same core showed similar trends, as did records of sedimentary charcoal and spheroidal carbonaceous particles in Lake Michigan (Goldberg et al. 1981).

In Europe, Muri et al. (2006) also demonstrated a good agreement in the temporal records of BC, SCPs and PAHs in the sediments of three mountain lakes in the Slovenian Alps over the industrial period, peaking in the mid-20th century and declining through the following decades to 2000. A longer, 700-year record from Lake Aspvreten in Sweden (Elmquist et al. 2007) also compared BC and PAH fluxes. Pre-industrial fluxes of both contaminants varied little over the medieval period (Figure 5), but BC increased ahead of ΣPAH starting in the period prior to the industrial revolution and this was thought to be due to increased wood combustion (Figure 5). This trend continued with BC fluxes peaking in 1920 and ΣPAH peaking in 1960 at 50 times the pre-industrial flux value. Both then declined to pre-industrial rates in the most recent sediment levels. Elmquist et al. (2007) suggested that the driver for these changes was fuel-use patterns with the early record influenced by a lower BC/PAH emission factor for coal than for wood combustion. Recent declines could be linked to decreasing reliance on petroleum fuels and legislative control.

These studies not only highlight the need to specify the fraction of BC that is being analysed to interpret the resulting records accordingly but illustrate that a knowledge of the changing roles of various fuel-types, their efficiencies and the impact that legislative approaches will have upon them may also be required. For example, in New York City, the historical BC inputs to two lakes as observed from their sediment records were seen to differ markedly from published historical reconstructions based on fuel consumption and estimated emission factors (Louchouarn et al. 2007). Only when the changing role of oil as a combustion fuel and the increased vehicular emissions resulting from diesel usage were considered could the sediment records and emissions data be resolved.

[FIGURE 5 NEAR HERE]

A recent significant step forward has been the use of sedimentary elemental carbon to reconstruct atmospheric concentrations (Husain et al. 2008). Atmospheric elemental carbon concentrations measured at Whiteface Mountain, New York, from 1978 to 2005 were calibrated against those from a lake sediment record retrieved from nearby West Pine Pond. Both sample types were analysed using the thermal optical method commonly used for atmospheric samples and more recently ice core samples (e.g., Lavanchy et al. 1999; Ming et al. 2008; Xu et al. 2009). The results showed a good temporal agreement over the calibration period. This calibration was then used to reconstruct atmospheric elemental carbon concentrations from 1835 to 1978 using the sediment record (Figure 6), which showed good agreement with regional BC emissions. Such an approach emphasises the value of environmental archives and how they may be used to extend records where monitoring data are absent. These may become more important as historical records of BC are required to inform climate models.

[FIGURE 6 NEAR HERE]

Spheroidal carbonaceous particles (SCPs) in lake sediments

Spheroidal carbonaceous particles (SCPs) are the carbon-rich component of fly-ash, the particulate product of the incomplete combustion of coal-series fuels and fuel-oil at industrial temperatures. As such, SCPs form a discrete and well-defined fraction of the BC continuum (Figure 2). Although the historical records of SCPs have been used in peat and ice cores as indicators of atmospheric contamination (e.g., Isaksson et al. 2003; Hicks and Isaksson 2006; Barnekow et al. 2007) and additionally in peat cores as means of core dating (Yang et al. 2001; Kuoppamaa et al. 2009) they have most widely been used in lake sediments where they have been estimated to comprise up to 3% of BC, although this value is highly variable in space and time (Ruppel et al. 2013). A detailed introduction to the extraction and uses of SCPs in lake sediments has been included in previous volumes of this DPER series (Rose 2001; Rose and Yang 2007) and we will not replicate these here. However, as they have been so widely employed in sediment studies, for completeness, we will briefly outline their main uses with some examples.

The characteristic morphology of SCPs and their well-defined industrial source makes them useful and unambiguous indicators of atmospherically deposited contamination. They were first identified in marine sediments (Griffin and Goldberg 1979) and later in a freshwater sediment core (Lake Michigan; Griffin and Goldberg 1981) where their morphology was used to indicate changes in fuel use (wood to coal) while historical changes in concentration were used as an indication of intensity of fossil-fuel combustion. Their use in this regard became more important in the following decade when historical sediment records of SCP concentrations and fluxes in acidified lakes were used as supporting evidence for the acid deposition hypothesis in the surface water acidification debate (e.g., Battarbee 1990). Here, the SCP concentration record was found to mirror diatom-inferred pH reconstructions at many acidified lakes in the UK, Sweden and Norway and hence indicated a likely fossil-fuel combustion source for acidifying substances. They were used in a similar way in acidification studies in North America (e.g., Charles et al. 1990).

SCPs have also been widely used in lake sediment studies, both as a measure of atmospheric contamination from specific sources, and as a means to provide chronologies to recent sediments either instead of, or to provide independent corroboration for, radiometric dating. The dating of sediments using SCPs was first developed by Renberg and Wik (1984; 1985) in Sweden. The approach relies on the robust and repeatable historical concentration profiles for SCPs across broad regions (e.g., Rose et al. 1999b) but requires the profile to be calibrated to other chronologies (e.g., varves, ^{210}Pb or emission statistics) in the first instance. Initially, three dates were identified; the start of the record in the mid-19th century; a rapid increase in concentration c. 1950, and a concentration peak, for which an ascribed date is more regionally variable but tends to occur in the 1960s – 1980s in Europe (Rose 2001). More recently, the use of SCP cumulative inventory profiles has allowed more dates to be ascribed to the lake sediment SCP record (Rose and Appleby 2005) although the mid-19th century remains the earliest dating horizon as this is when coal was first burned at the temperatures required for SCP formation. To date, there appears to be no evidence for the degradation of SCPs within natural archives and as a result they may continue to provide a useful means of providing chronologies to industrial-age records for centuries to come. As the limits of ^{210}Pb chronologies move forward in time (i.e. always the most recent c. 150 years) and are progressively unable to date the full industrial period, a combination of the two approaches should become a powerful and reliable technique for dating recent sediments.

Rose (2001) summarised the regions of the world (mainly Europe, and some areas of North America, China and north Africa) where historical SCP records had been produced, but in the time since that review, these have further expanded to include sites in south-eastern Europe, such as Bulgaria (Ognjanova-Rumenova et al. 2009) and Romania (Rose et al. 2009); the Ural Mountains of Russia (Solovieva et al. 2005; 2008); North Africa (Rose et al. 2003; Flower et al. 2009); western Greenland (Bindler et al. 2001); mountain lakes of the western United States (Landers et al. 2010); Chile (Chirinos et al. 2006; von Gunten et al. 2009); Japan (Yoshikawa et al. 2000; Tsukuda et al. 2006; Nagafuchi et al. 2009) and the Falkland Islands and Antarctica (Martins et al. 2010; Rose et al. 2012). Their presence has now, therefore, been recorded in most regions of the world. In almost all areas, the mid-20th century increase in SCP concentration is observable while the start of the record tends to depend on regional fossil-fuel combustion as well as site specific sediment accumulation rates. In regions of low SCP deposition, the start of the record may begin in the mid-20th century when the rapid increase in concentration surpasses the analytical limit of detection for the first time, rather than being the date of first SCP production. Post-1950, the SCP record is more variable in different regions of the world and this is dependent upon a number of factors including national and regional industrial development and decline, the introduction of policies leading to emission controls of industrial sources, and changing fuel-types such as the increase in the use of natural gas and renewable energy sources for power generation. Further development of regional SCP chronologies, such as that proposed for the UK (Rose and Appleby 2005), may therefore need work at a greater spatial resolution than might once have been required.

SCP sediment records have also been employed as proxies for other depositing contaminants. Fernández et al. (2002) considered the relationship between SCPs and PAHs in mountain lakes finding both gave consistent histories of pyrolytic emissions across Europe, but only when differing particle size fractions (PAH: < 1µm; SCP >5µm) and hence source regions were considered. Rose and Juggins (1994) used the SCP record in surface sediments to determine non-marine sulphate deposition across a broad geographical region. This was developed further by Rose and Monteith (2005) who used annual sediment trap SCP fluxes over a 12-year period from Round Loch of Glenhead in Galloway, Scotland, and measured non-marine sulphate deposition from an adjacent atmospheric deposition monitoring site at Loch Dee, to calibrate the SCP flux record. They then used this to reconstruct site-specific non-marine sulphate deposition for the lake over a 154 year period (1848 - 2002) providing a much improved record compared with previous modelled estimates (Figure 7). This relationship with other pollutants highlights the role of SCPs (and other BC) as a vector by which polluting substances such as trace metals and persistent organic pollutants can be transported (Wey et al. 1998; Chen et al. 2009). This property was also the foundation by which SCPs have been used in chemical source apportionment studies. Griffin and Goldberg (1979) used SCP morphology and surface texture to distinguish between coal, oil and wood derived particles, and this was developed further by Rose et al. (1996) in a chemical apportionment technique using the trace elements on SCP surfaces to distinguish between the main fuel types in the UK , and later continental Europe (Rose et al. 1999a). Although this was applied to regional surface sediments to determine geographical distribution of contaminants from fuel sources (e.g., Rose and Harlock, 1998; Fott et al. 1998) and historically down a sediment core (Rose et al. 1996) to our knowledge this approach has not been developed or applied further.

[FIGURE 7 NEAR HERE]

Other industrial particles: Inorganic fly-ash particles

While SCPs are produced from the incomplete combustion of the organic fraction of coals and fuel oil, the other component of fly-ash, inorganic ash spheres (IASs), are produced from the fusing of non-combustible components present within the fuel (Rose 2001). As a consequence IASs are almost solely derived from coal-series fuels as a result of mineral inclusions within coal seams and other non-combustible material from the seam edge. Because IASs derive from the melting of minerals, unlike SCPs, they are true spheres while their chemical composition is dependent upon the original mineral. This means that they are predominantly aluminosilicates, and this leads to additional difficulties in their extraction from sedimentary material (Rose 1990b), although iron-rich fly-ash particles in lake sediments may be identified and extracted by means of their magnetic susceptibility (Querol et al. 1993). Because IASs are also similar morphologically to some natural particulates (e.g., volcanic and meteoritic microspherules) and some chrysophyte cysts, they appear to have a background concentration in sediment records that is considerably higher in areas of volcanism (Nagafuchi et al. 2009). They have therefore been less widely used than SCPs in palaeolimnological studies.

As IASs are almost solely derived from the combustion of coal-series fuels and SCPs are from both coals and oil, the ratio of the concentrations of these two particle types (IAS:SCP) has been used as a means to distinguish fuel sources. IAS:SCP ratios exceeding 1.0 are usually ascribed a predominantly coal origin (Rose 1996). This has been used to indicate contaminant particle sources in remote regions (Nagafuchi et al. 2009; Rose et al. 2012) and as a comparison with results from SCP fuel-type characterisation (Rose 1996).

Recent and future developments

A number of studies indicate that total BC emissions in North America and Europe have already been declining for some time as a result of the successful implementation of clean air policies, such as the introduction of particle arrestor technology, more efficient combustion and a switch to cleaner energy sources (e.g., Novakov et al. 2003). SCP depositional fluxes are already at levels not seen since the 1930s in some regions (e.g., Rose and Monteith 2005). While total BC emissions from developed countries are expected to continue to decrease, BC emissions in Asia increased by 30% between 2000 and 2005 (Bond et al. 2013) and emissions are projected to increase further or stay the same over the next 20 years in China and India (Streets et al. 2004). Furthermore, emissions of finer fractions, too small to be removed by particle arrestor technology, and with longer atmospheric residence times, are not necessarily declining even in industrialized countries (e.g,. Elmquist et al. 2007) and may increase further during the 21st century as a result of increasing energy consumption and vehicular emissions (Streets et al. 2004). Hence, fine BC may well continue to reach sensitive Arctic and Himalayan areas and continue to perturb the monsoonal cycle in southern Asia despite changing source regions (Koch and Hansen 2005).

Significant choices can already be made to reduce climate impacts of BC and these issues represent an opportunity to involve both developed and developing countries in a common air quality improvement effort.Choosing biomass rather than fossil fuels would reduce BC impacts, because BC particles resulting from fossil fuel combustion are thought to warm the atmosphere twice as much as those from biomass burning (Ramana et al. 2010). By bringing BC into climate negotiations the objective of developed countries to mitigate global warming could also meet the goals of developing countries for cleaner air (Grieshop et al. 2009) while additionally having significant health (Löndahl et al. 2010; Shindell et al. 2012) and economic benefits (Barbir et al. 1990; Machol and Rizk 2013).

New and emerging particle types

Although BC will continue to be a significant particulate pollutant for many decades to come, other new and emerging particle types may also have increasing environmental impacts.

Microplastics

Of the 230 million tons of plastics produced annually, more than 10% ends up in the oceans (Cole et al. 2011). Plastic can enter the environment by being intentionally or unintentionally discarded and also by being wind-blown from land-fill sites. Since the 1950s an estimated 1 billion tons of plastic have been discarded which may persist for hundreds of years (O’Brine and Thompson 2010; Bergmann and Klages 2012). Plastic resin pellets, the raw material for much manufacturing, may also be unintentionally released during manufacturing and transport. These are granules with a diameter of a few millimetres and may be carried by surface run-off and rivers to the ocean or to the ocean directly (Mato et al. 2001; Holmes et al. 2012). While “macro-litter” (Bergmann and Klages 2012) causes entanglement, suffocation and disrupts ingestion in many marine fauna (Derraik 2002), it may be broken down mechanically by UV radiation or by biological degradation (Imhof et al. 2012) into secondary particles, or microplastics, generally defined as being less than 1 mm in size (Imhof et al. 2012) or between 67 - 500 µm (Andrady 2011). Microplastics may also be derived from abrasives in personal care products or from shedding during laundry and may pass through standard wastewater treatment facilities unchanged (Engler 2012). As with BC described above, these particles can adsorb pollutants onto their surfaces including trace metals (Holmes et al. 2012), PAHs, PCBs, organochlorine pesticides (Mato et al. 2001; Cole et al. 2011) and brominated flame retardants (Zarfl and Matthies 2010; Engler 2012). Via ingestion, these can then enter the marine food web.

Research on these particle-types has mainly been focussed on their association with potentially toxic compounds, and the scale of contamination from the particles themselves, while seemingly ubiquitous, has not been wholly addressed. Microplastics were found in all samples taken from 18 beaches across six continents (Browne et al. 2011) with concentrations ranging from 8 L^{-1} in Australia to 124 L^{-1} in Portugal. These particles were mainly found to be polyester (56%) but also acrylic, polypropylene, polyethylene and polyamide fibres. Other studies have shown evidence for microplastics in all samples taken from Belgian (Claessens et al. 2011), UK (Holmes et al. 2012) and Singaporean (Ng and Obbard 2006) marine sediments and in Arctic surface waters (Zarfl and Matthies 2010).

In terms of temporal trends and environmental archives very little data exist to date, although such data would be very useful in terms of assessing rates and even directions of change, which are currently largely uncertain (Cole et al. 2011). Concentrations of plastic marine debris in the North Atlantic subtropical gyre showed very little trend over a 22-year period despite a strong increase in discarded material (Law et al. 2010), but the total number of microparticles (fibres, granules and films) taken from sediment layers of a Belgian beach section (Claessens et al. 2011) showed an increasing temporal pattern (Figure 8). However, continued degradation and weathering of microplastics results in the production of nanoscale particles and these may have a more significant future environmental impact.

[FIGURE 8 NEAR HERE]

Nanoparticles

A nanoparticle is defined as a substance having at least one dimension between 1 and 100 nm. It is particle size that gives these materials their unique properties, which are often quite different from larger versions of the same material (Klaine 2009). For example, carbon nanotubes have a higher strength-to-weight ratio than steel, are better thermal conductors than diamond and better electrical conductors than copper (Meo and Andrews 2001). The products of nanotechnologies are expected to increase exponentially and the environmental risks associated with their use are currently uncertain (Griffitt et al. 2008). The characteristics of these particles that play a role in their bioavailability, absorption, distribution, toxicity (Klaine 2009) and solubility (Misra et al. 2012) are also uncertain, although a recommended list of physical and chemical characteristics for toxicology studies on nanomaterials has been produced and includes size/shape/agglomeration; composition and structure; surface area, reactivity and charge; stability and solubility (MINChar 2008).

Although natural processes such as volcanic eruptions, forest fires, physical and chemical weathering of rocks may produce nanoparticles (Murr et al. 2004), these emissions are low compared with those produced by combustion processes (e.g., vehicular and stationary sources; hydrocarbon flames) (Utsunomiya et al. 2002; Sanchís et al. 2012). Current generation clean technology in coal-fired power plants has led to an unanticipated increase in emissions of particles 1 – 10 nm in diameter (Junkermann et al. 2011) resulting in higher concentrations of nanoparticles (e.g., C_{70} fullerene, Sanchís et al. 2012) in areas of industrial activity. Particles of this size are effective precursors of cloud condensation nuclei, which may cause a shift in precipitation patterns (Junkermann et al. 2011), while carbonaceous nanoparticles such as nanotubes, BC and soot from natural gas combustion have been found to be cytotoxic and may pose a variety of respiratory health problems (Murr and Garza, 2009; Scown et al. 2010). Further, the ability of nanomaterials to efficiently adsorb gases (SO_2, NO_x), trace elements (e.g., As, Mn, trace metals) and organic pollutants as well as viruses, bacteria and antibiotics (Khin et al. 2012; Yang et al. 2013), means they offer great potential for environmental remediation but also pose a more significant threat as carriers of toxic substances including PAHs (Hu et al. 2008), perfluorinated alkylated substances (e.g., PFOS) (Kwadijk et al. 2013) and other POPs such as PCBs (Andrady 2011) into the environment as noted above for BC and SCPs.

In addition to respiratory effects and their potential role as chemical 'carriers', a number of studies have now begun to explore the toxicological effects of nanoparticles on aquatic organisms and Scown et al. (2010) provide an excellent critical review. A number of different carbon-nanoparticles such as C_{60} fullerene and carbon nanotubes have been shown to exhibit antibacterial or antimicrobial activity with direct contact of the nanotube with the membrane being the likely cause of cell death, while the antibacterial properties of metal oxide nanoparticles (e.g., TiO_2, ZnO, CeO_2 and Al_2O_3) are well established (Scown et al. 2010). TiO_2 nanoparticles act as 'photocatalysts' and in the presence of UV light they react with oxygen and water to form highly reactive oxygen species (ROS) which damage cell membranes of bacteria. Hence, TiO_2 acts as an effective sewage disinfectant (Miller et al. 2012). However, ROS also inhibit growth of aquatic algae and clump on the surface of algal cells attacking membranes and limiting photosynthesis. The toxicity of metal oxides to algae shows a clear size relationship with larger particles exhibiting lesser effects (Navarro et al. 2008). However, Griffitt et al. (2008) found no toxic effects from TiO_2 on algae, daphniids (*Daphnia pulex*) or zebrafish (*Danio rerio*) although silver and copper nanoparticles were lethal to daphniids at concentrations of 40 and 60 $\mu g\ L^{-1}$ respectively. However, there is an apparent inconsistency in results between studies as TiO_2 has also been found to result in immobilisation and mortality to daphniids (Scown et al. 2010).

Daphniids were used in the majority of nanoparticle aquatic toxicity studies reviewed by Baun et al. (2008)and, as filter feeders, they may be more susceptible than other aquatic fauna (Scown et al. 2010) with exposure concentrations of 2.5 – 5 ppm fullerenes resulted in delayed daphniid moulting and reduced number of offspring. However, uptake, depuration and bioaccumulation of carbon nanotubes by daphniids is not straightforward and may depend on many factors including organic matter content of the water (Petersen et al. 2009). In sediment dwelling invertebrates including amphipods (*Hyalella azteca*) and chironomids (*Chironomus dilutus*) carbon nanotubes added to water (1.00 g L^{-1}) were found to significantly reduce survival and growth over a 14-day period (Mwangi et al. 2012). These nanoparticles have also been found to be respiratory and neurotoxicants in rainbow trout (*Oncorhynchus mykiss*) (Smith et al. 2007), but while carbon-based nanoparticles are generally considered to have the capacity to induce toxicity in aquatic vertebrates, effects have (so far) usually been seen at concentrations unlikely to be found in many natural aquatic environments. By contrast, both carbon-based and metallic nanoparticles have been shown to exhibit developmental abnormalities in fish embryos (Scown et al. 2010). However, in all studies of 'natural' exposure, factors such as solubility, presence of other compounds and environmental parameters (e.g., pH, surface coatings, organic matter) are key considerations in confounding or exacerbating toxic effects to aquatic biota (Scown et al. 2010; Misra et al. 2012).

Nanoparticles therefore have the capacity to be significant and increasing environmental contaminants into the future, but to our knowledge there have, to date, been no studies considering long-term trends in engineered nanoparticles (ENPs; cf naturally produced nanoparticles) or attempts to extract these from environmental archives. Although Esquivel et al. (2004) demonstrated the possibility of extracting nanoparticles from a 10,000-year-old ice core sample from Greenland and found a range of carbon nanotubes and fullerene-type particles, no historical record was attempted, possibly because the method was described as "tedious". Standardised approaches, particle characterisations and an advancement of tools and techniques in order to assess and quantify these particles are urgently needed (Scown et al. 2010) as this particle type will undoubtedly become significantly more important in the coming decades.

Summary

Particulate contaminants may have a range of environmental impacts. In the atmosphere they can adversely affect human health via respiratory intake while those that are carbonaceous can additionally contribute to atmospheric warming, glacial and ice-cap melting and the transport of pollutants via absorption or adsorption to their surfaces. These pollutants include trace metals, PAHs and persistent organic pollutants such as PCBs, PCDD/Fs and brominated flame retardants. Determining temporal and spatial trends for particulates through the analysis of environmental archives can therefore provide useful information on a diverse range of issues.

The most common particle-type analysed from environmental archives is ‘black carbon’. This term covers a myriad of particles forming a combustion continuum from charred biomass through to high temperature refractory soots. There is a long record of black carbon in the environment, from natural Devonian and Permian sedimentary deposits, to charcoal records spanning tens of thousands of years and frequently used as an indicator of human influence. However natural and early human black carbon emissions are very much lower than those from industrial sources.

Black carbon records in ice, peats, soils, marine and lake sediments have been used to assess the scale, extent, onset and sources of contamination and also for providing chronological control for these sequences. There is no single quantitative analysis for black carbon and different methods assess different parts of the black carbon continuum. Care is therefore required when comparing temporal records and scales of contamination between studies that have used different approaches. While industrial black carbon emissions in Europe and North America have been declining for some years and are predicted to continue to do so over coming decades, emissions from vehicular sources, and industrial emissions from countries such as China and India are predicted to increase. As a consequence, while source regions may have altered, global black carbon emissions may continue to increase. Environmental archives will continue to play an important role in tracking the distribution and temporal trends from site-specific to international scales and in validating transport and deposition models.

Other emerging particle-types of concern include microplastics (< 1mm) particularly in the marine environment and also nanoparticles (defined as possessing at least one dimension 1 – 100nm). Both these particle-types have large capacities for pollutant adsorption to their surfaces, while nanoparticles maybe directly toxic to organisms in a number of environments. Currently, there are very few historical records published for these particle types and techniques for their extraction and analysis are urgently needed.

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Figure captions

Figure 1. (a) Scanning electron micrograph and (b) EDS-spectra of carbon-rich particles extracted from a peat core in Misten, eastern Belgium and dated to c. AD 550 (Both courtesy of Jérémie Beghin, Unité de Paléobiogéologie - Paléobotanique - Paléopalynologie (PPP), Département de Géologie, Université de Liège)

Figure 2. Black carbon combustion continuum model. (Modified after Hedges et al. 2000 and Masiello 2004).

Figure 3. Estimated historical fossil-fuel black carbon emissions. Redrawn from Novakov et al. 2003.

Figure 4. (a) and (b) Black carbon concentration data from two adjacent ice cores taken from the East Rongbuk glacier on Mount Everest using two different analytical methods. (a) Black line is raw data; red line is smoothed (redrawn from Ming et al. 2008); (b) Black line shows data re-sampled to 4 samples per year; red line is data smoothed with a robust spline (redrawn from Kaspari et al. (2011). Also for comparison, (c) the black carbon record for an ice core taken from Law Dome, Antarctica plotted on a monthly (thin black line) and annual (thick black line) resolution. Red line is 21 year smoothing (redrawn from Bisiaux et al. 2012b). Note the difference in y-axis scales between the three Figures.

Figure 5. Historical fluxes of BC and ΣPAH over 700 years from Lake Aspvreten, Sweden. The dominant combustion-based energy sources (i.e., wood, coal, and coke, or oil) are also displayed. Redrawn from Elmquist et al. 2007.

Figure 6. Atmospheric elemental carbon concentrations 1835 – 2005 reconstructed from a lake sediment core taken from West Pine Pond, New York. Redrawn from Husain et al. 2008.

Figure 7 SCP reconstruction of non-marine sulphate deposition at Round Loch of Glenhead, Galloway (1848 – 2002). Non-marine sulphate reconstructed from SCPs (●) and measured non-marine sulphate deposition for Loch Dee (🟥) compared with the estimated record based on a modelled historical national trend (▲) scaled to fit the geographically nearest available 1988 deposition figure and used in recovery models. Redrawn from Rose and Monteith (2005).

Figure 8. The total number of microplastic fibres, granules and plastic films found in different sediment layers at the high water mark of a beach section at Groenendijk, Belgium. The line indicates estimated annual global plastic production (right axis). Redrawn from Claessens et al 2011.