17. TEMPORAL AND SPATIAL PATTERNS OF SPHEROIDAL CARBONACEOUS PARTICLES (SCPs) IN SEDIMENTS, SOILS AND DEPOSITION AT LOCHNAGAR

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Introduction

Spheroidal carbonaceous particles (SCPs) (Figure 1) are produced by industrial, high temperature combustion of fossil-fuels such as coal and oil. They are a component of fly-ash, the particulate matter emitted to the atmosphere with flue gases, and hence their dispersal and deposition are controlled by the meteorological conditions the dispersing plume encounters. SCPs are not produced by any natural process and consequently their presence in the environment represents an unambiguous indication of atmospherically deposited contamination from sources such as the electricity generation and other industries (Rose 2001). However, whilst there is no direct evidence for SCPs being harmful to biota *per se*, they are considered an important means by which toxic pollutants may be transported and deposited. Trace metals (e.g., Davison et al. 1974; Coles et al. 1979; Seigneur et al. 2005) and persistent organic pollutants (POPs) including polycyclic aromatic hydrocarbons (PAHs) (Griest and Tomkins 1984; Wey et al. 1998; Ghosh et al. 2000), polychlorinated biphenyls (PCBs) (Bucheli and Gustafsson 2003; Persson et al. 2005) and dioxins and furans (PCDD/Fs) (Ohsaki et al. 1995; Persson et al. 2002) may be adsorbed to the surfaces of the particles in the emitted plume or during transport. Such transport mechanisms and coincident sources explain the similarities in spatial and temporal trends between SCPs and these other pollutants in lake sediment studies (e.g., Broman et al. 1990; Boyle et al. 1999; Fernández et al. 2002).

N.L. Rose (ed.), Lochnagar: The Natural History of a Mountain Lake
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In environmental research, SCPs have been used in three main ways. First, as a means to identify and quantify trends in atmospherically deposited contamination, for example as concentrations in bulk deposition monitoring (Rose 2001) or as temporal trends in lake sediment (e.g., Renberg and Wik 1985a; Rose et al. 2002; Rose et al. 2003) or soil cores (Yang et al. 2001). Second, as a means of providing a chronology for lake sediment cores (Renberg and Wik 1984; 1985b; Rose et al. 1995; Rose and Appleby 2005) and third, as a method of source apportionment for deposited contamination, either simply as an indicator of fossil-fuel derived pollutants or by using the chemistry of the SCPs themselves to differentiate them into their original fuel sources (Rose et al. 1996; 1999).

This chapter deals with SCPs in the deposition, soils and sediments of Lochnagar as a means to determine temporal trends in the contamination of this remote site; assess the relative storage of SCPs in loch sediments and catchment soils; explore the possibilities for transfer between the catchment and lake; and consider how climate change may affect the movement of SCPs and the toxic pollutants adsorbed to their surfaces within this mountain ecosystem.

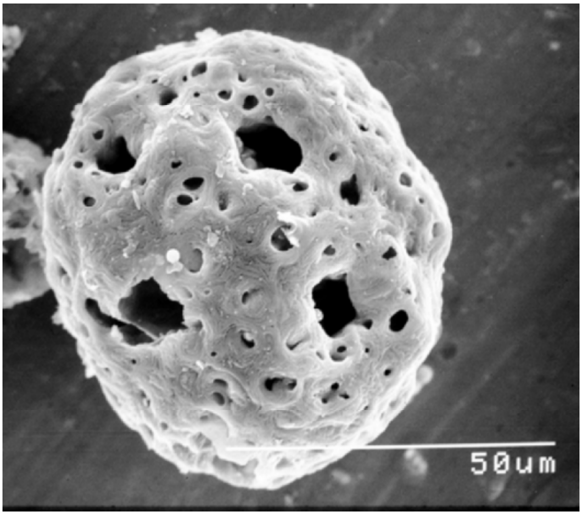

Figure 1. Scanning electron micrograph of a spheroidal carbonaceous particle (SCP) derived from the high temperature combustion of fossil-fuels. (Micrograph: Neil Rose)

Atmospheric deposition of SCPs

Bulk deposition

Sampling of bulk deposition for SCP analysis at Lochnagar began in August 1996 as part of the EU funded MOLAR project and has continued to the present. Data up to the end of 2003 are included in this chapter. NILU (Norwegian Institute of Air Research)-type bulk deposition collectors were used and, where weather conditions permitted, were sampled weekly until November 1997. Since then, samples have been taken every two weeks. The collector is located to the east of the loch near the Automatic Weather Station c. 15m above the loch and 2m above ground level. The position is shown on Figure 7. For SCP analysis, known volumes (as large as possible, but typically c. 2 litres) of the bulk deposition sample were filtered through Whatman GF/C filters. These were then digested and analysed as described on the CARBYNET website (http://www.ecrc.ucl.ac.uk/carbynet/). SCP concentrations can then be expressed as number of SCPs per litre of deposition, or more usefully given the variable length of sampler exposure, transformed to fluxes using site specific rainfall data from the Automatic Weather Station (Chapter 5: Thompson et al this volume).

Figure 2a shows the record of SCP flux in bulk deposition at Lochnagar from 1997 through to the end of 2003. There is considerable variability in the record although there are a higher number of elevated SCP fluxes in the earlier period compared to later in the record. Interestingly, despite the earlier samples being at a higher temporal resolution and thus generally being of lower volume, there are fewer samples below the limit of detection suggesting a more continuous input of SCPs to the site at this time. In the latter half of the record individual high fluxes are separated by periods where SCP

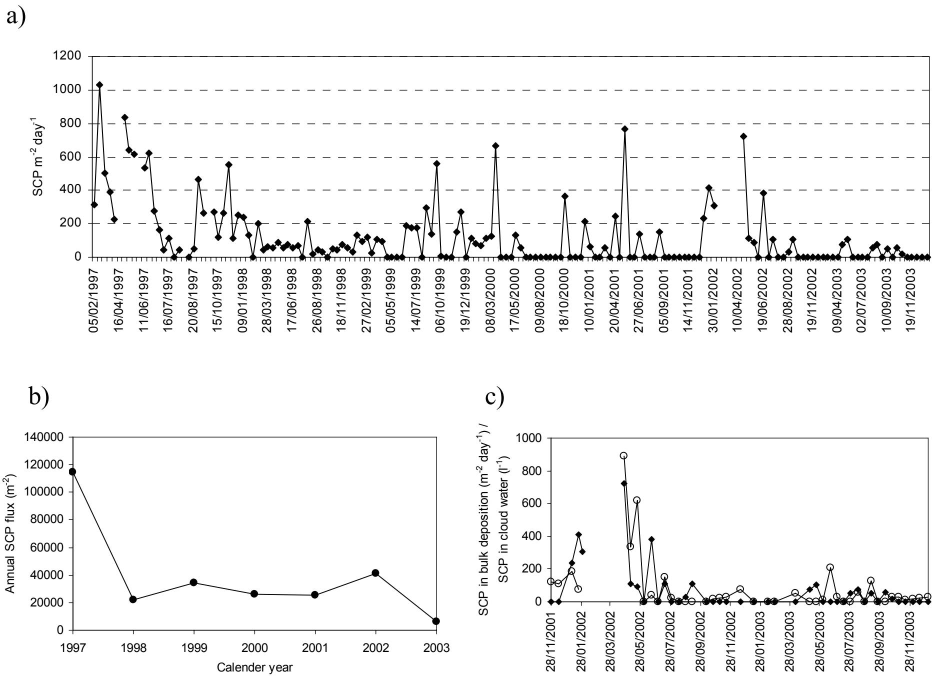

Figure 2. (a) SCP concentrations in bulk rainwater samples (as number of SCP m^{-2} day^{-1}); (b) The same data converted to annual fluxes (m^{-2} yr^{-1}) using rainfall data from the Lochnagar automatic weather station. (c) Expanded latter section of (a) with cloudwater data (○) for the same period (in SCP l^{-1}). The gap represents a period when the collectors were blown over by strong winds.

concentrations, and hence fluxes, fall below the limit of detection suggesting a more episodic input. Converting these data into annual (calendar year) fluxes (Figure 2b) translates the high values from 1997 into a high annual flux. This is followed by a stable period between 1998 and 2002 where annual fluxes vary little before declining again in 2003. Certainly this is in agreement with expected declining trends, although, as 1997 was the first full year of sampling, it is uncertain whether this was an unusually high year or the final year of a previous period of more elevated inputs. Future monitoring will confirm whether the lower flux in 2003 is a further permanent decline in SCP inputs or just a low value in an otherwise stable period since 1998.

Little similar long-term monitoring of SCPs in bulk deposition has been undertaken, either in the UK or elsewhere, although weekly sampling for SCPs over an 18 month period from August 1996 was undertaken at four other European mountain lakes as part of the EU funded MOLAR project (Rose et al. 2002). These four sites represented other studied mountain regions: Øvre Neådalsvatn (mid-Norway); Estany Redo (Spanish Pyrenees); Gossenköllesee (Austrian Alps) and Starolesnianske Pleso (Slovakian Tatras). Comparing the SCP deposition at these sites for the calendar year of 1997 showed that Øvre Neådalsvatn had considerably lower inputs than the other sites (c. 5700 m^{-2}), similar to the lowest Lochnagar annual value for 2003 (Figure 2b). The other sites, in a band across central Europe, showed annual fluxes of between 14000 and 31000 m^{-2}, considerably lower than the figure for Lochnagar over the same period, but comparable with annual Lochnagar fluxes for 1998 – 2002. Unfortunately, monitoring at these four mountain sites was not continued so it is not known whether 1997 was a year of high deposition across the whole of Europe, or whether the reduction in SCP deposition at Lochnagar in 1998 and subsequent years would have shown atmospheric inputs to be equivalent to these other remote European sites.

As SCPs are derived from high temperature fossil-fuel combustion it is interesting to compare trends in SCP deposition with those of deposited acid ions. Rose et al. (2001) undertook this comparison for the mountain lake sites described above, including Lochnagar. Correlations between SCP concentrations and those of the acid ions SO_4^{2-}, NO_3^- and NH_4^+ at Lochnagar were found to be low, but positive, whilst correlations of SCPs with (SO_4^{2-} + NO_3^-) were more positive than for SCPs with (SO_4^{2-} + NO_3^- + NH_4^+) as might be expected given the differing sources of SCPs and the mainly agriculturally derived NH_4^+. The positive correlations between SCPs and NH_4^+ were therefore thought to be an artefact of the high positive correlations of the ions SO_4^{2-} and NO_3^- with NH_4^+, as a result of the formation of the secondary aerosols $(NH_4)_2SO_4$ and $(NH_4)NO_3$, and the positive correlation of SCPs with SO_4^{2-} and NO_3^-.

Occult deposition

As cloudwater in upland UK can demonstrate a tenfold enrichment of fossil-fuel derived elements over bulk rainwater (Wilkinson et al. 1997) a collector was set-up at Lochnagar in October 2002, near the bulk deposition monitoring site, to sample intercepted cloudwater for subsequent chemical and SCP analysis. This cloudwater collector is a passive 'lidded-harp'-type as described in Neal et al. (1997) and shown schematically in Reynolds et al (1996). Briefly, the collector consists of a low density polyethylene-coated frame over which an inverted cone of nylon filaments is stretched. Beneath this cone, a funnel directs the intercepted moisture into a collection bottle. The whole assembly is protected from direct rainfall by a 1.2 m diameter lid mounted on a tubular steel framework, but some rainwater and snow contamination can still occur in windy conditions (Neal et al. 1997). These collectors have been used extensively for cloudwater studies in the UK (e.g., Fowler et al. 1988) and have been used to collect particles in orographic cloud including fly-ash (Crossley 1988). Samples are collected every two weeks, filtered for SCPs and the filters treated as described above for bulk deposition. For the sampling period October 2002 to the end of 2003, cloudwater SCP concentrations were episodic (Figure 2c) with more continuous inputs occurring during autumn and winter and only two samples showing SCP concentrations above detection limit between the end of June and early October 2003. Over the sampling period a cloudwater SCP input of 2970 m^{-2} yr^{-1} was determined (Jennifer Muller and David Fowler, Centre for Ecology and Hydrology, Edinburgh pers. commun.) corresponding to 46.8% of the bulk deposition input for the same period. Therefore, cloud inputs provide significant additional atmospheric deposition of SCPs to Lochnagar and its catchment.

SCPs in sediments and sediment traps

The first sediment core from Lochnagar analysed for SCPs (NAG3) was taken in 1986 using a mini-Mackereth corer (Mackereth 1969) as part of a study on acidification in the Cairngorm region (Jones et al. 1993). Since then, SCPs have been analysed on a number of sediment cores (NAG6, 8 – 23, 25 and 26) and, because of the slow sediment accumulation rate (Chapter 8: Rose this volume), these have all been short sediment cores taken by gravity corer (e.g., Glew 1991). Of these cores, NAG3, 6, 8 and 23 were ^{210}Pb dated.

Simple cylindrical sediment traps are employed for the annual sampling programme of the UK Acid Waters Monitoring Network (UK AWMN). These comprise arrays of three tubes attached to the corners of triangular plastic frames, thus providing triplicate samples. The internal diameter of each tube is 5.2 cm with an aspect ratio (length: diameter) of ≥ 7 to maximise trapping efficiency (Bloesch and Burns 1980; Blomquist and Håkanson 1981). Details of the sampling procedures are given in Rose and Monteith (2005) but at Lochnagar arrays of traps are deployed in the deep water area (> 20m) at c. 1m above the sediment-water interface while an upper trap is located at c. 2m water depth. All SCP analyses of lake sediments and sediment trap material have been undertaken using the method described in Rose (1994) except NAG3 which was analysed using the technique from Renberg and Wik (1984; 1985b).

Temporal trends

The regional diversity of the temporal record of SCPs in lake sediments across the UK is well characterised and now extensively used for providing sediment chronologies (Rose et al. 1995; Rose and Appleby 2005). The historical profile of SCP concentrations from Lochnagar is quite typical for Scotland and shows all the expected features (Figure 3a) associated with documented historical changes in fossil-fuel combustion, industrial development and pollution control (Rose 2001). The first presence of SCPs occurs in the mid-19th century as a result of developments in the industrial use of coal. Initially, this was not for electricity generation as the first public 'power station' in the UK was not commissioned until 1882. However, this early industrial coal combustion was both inefficient and lacking in any emission controls. Thus, the rapid spread of this technology quickly provided numerous point sources and the SCP record begins within a decade or two across the whole of the UK (Rose and Appleby 2005).

The SCP record for the following century at Lochnagar is also typical and shows a slow, but steady increase in concentration resulting from the growth in industrial coal consumption. However, starting in the 1950s, a major increase in SCP concentration is observed at Lochnagar, across the UK and throughout Europe. This is due to two factors. First, a major expansion in the consumption of fossil-fuels at power stations increasing rapidly in size (Laxen 1996) as a result of a dramatic increase in demand for electricity following the end of the Second World War, and second, the availability, for the first time, of cheap fuel oil leading to the development of the first large-scale oil-fired power stations. This rapid increase continued until the late-1970s when an increase in combustion efficiency and the introduction of particle arrestors at source, in addition to the implementation of successively more rigorous control legislation, meant that despite the continued increase in fuel consumption, particulate emissions started to decline. In addition, changes in policy led to a decline in heavy industry which was particularly acute in some areas of central Scotland, emissions from which are known to impact the Lochnagar region (Chapter 13: Rose et al. this volume). This led to a reduction in emissions both directly and indirectly (via a reduced demand for electricity) and was exacerbated by a move away from the use of 'traditional' fuels such as coal and fuel-oil to natural gas. In the lake sediment record, these changes are recorded as a SCP concentration peak and subsequent decline to the sediment surface. This concentration peak occurs in 1978 ± 2 in Lochnagar and is similar throughout northern and central Scotland (Rose and Appleby 2005). Such is the reliability of this temporal record that SCP concentration profiles are widely used for dating lake sediments. In Lochnagar, there is an additional benefit that four cores have been independently dated by ^{210}Pb allowing a reliable calibration. Therefore, there is considerable confidence in the use of SCP profiles to date sediment cores in Lochnagar and this approach has been used to provide dates for cores throughout this volume.

Similarities exist between the historical sediment record of SCPs and that of some atmospherically deposited trace metals such as Hg and Pb (Yang et al. 2002a) and to a lesser extent Cd, Zn and Cu (Yang et al. 2002b). This is most probably due to fossil-fuel combustion also being a major source of these trace metals. However, it is now apparent that metals, previously deposited from the atmosphere and stored in the catchment are being released into the loch such that the sediment basin flux of metals is not declining as would be expected as a result of emission reductions (Rose et al. 2004). It has been hypothesised that this additional catchment input could be due to increased peat erosion or leaching of the metals from the soils. SCPs are not leached but could be input from soils as a result of catchment erosion. The comparison of the SCP and metal mass balance will therefore help to ascertain the relative roles of these processes.

Following the determination of the full historical SCP record in all the UK AWMN sites, including Lochnagar, a programme of annual deep-water sediment trapping was introduced in 1990 in order to monitor the continued input of SCPs as a marker for atmospherically deposited pollutants. These data, although at a greater temporal resolution than the sediment core, show considerable inter-annual variability in SCP flux (Figure 3b Δ) (Rose and Monteith 2005) emphasising the 'smoothing' that occurs once the depositing sediment is incorporated into the full-basin record. However, despite this 'noise' the decline in SCP flux remains evident over the monitoring period and emphasises the remarkable reduction in deposition that has taken place since the peak in the late-1970s. Fluxes to the sediment in the deep-water area of Lochnagar are now at levels previously only observed prior to the 1930s in agreement with other UK AWMN lakes (Rose and Monteith 2005) and with levels in modelled non-marine sulphate deposition (Fowler et al. 2005).

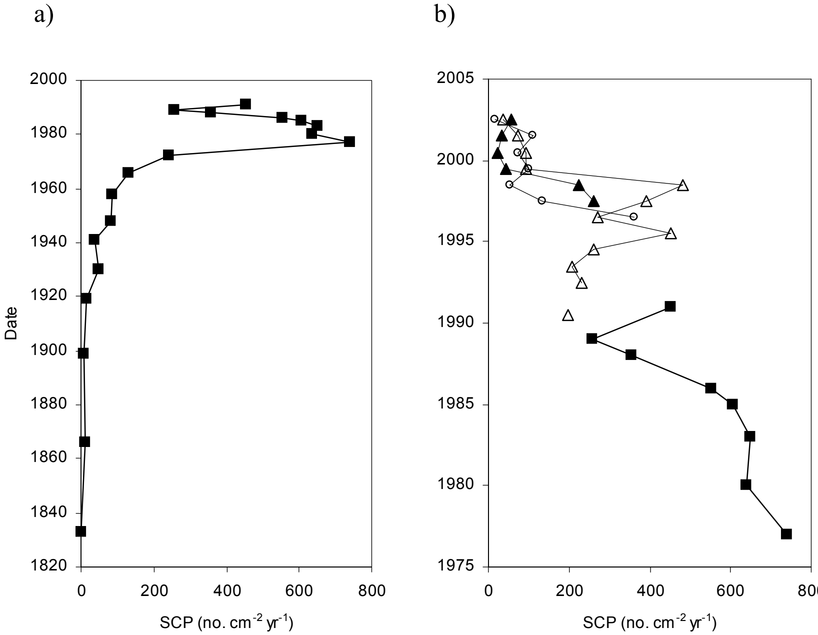

Figure 3. SCP fluxes (in SCP cm^{-2} yr^{-1}) from (a) a dated sediment core (■) from Lochnagar (NAG6) showing the full SCP record since the mid-19th century, and (b) the post-1975 SCP flux record from this sediment core (■) with more recent data from deep (△) and shallow (▲) water sediment traps and bulk deposition (○). The location of NAG6 is shown on Figure 4.

From 1997, an additional sediment trap was installed at 2m water depth in Lochnagar and included in the UK AWMN annual sampling programme. The SCP fluxes from these upper traps are also shown in Figure 3b (▲) and, whilst showing similar trends to those of the deep water traps, the fluxes are lower except for the most recent available data (2002 – 2003) where the upper trap samples show comparable SCP fluxes. The higher SCP flux in the deep water traps over the earlier part of this record may represent sediment 'focussing' or the movement of sediment material, including SCPs, from shallow water to deep water areas as a result of resuspension and transport within the body of the loch (Chapter 8: Rose this volume). However, the continued decline in SCP deposition, evident from both Figure 2b and 3b has led to very low depositional levels and the differences between shallow and deep water sediment trap fluxes are now much reduced.

An alternative hypothesis to explain the difference between upper and lower SCP trap fluxes is that the settling velocity of SCPs through the water column of a lake (6 – 8 cm day^{-1}; Punning et al. 2003) would require half a year for SCPs to reach the deeper trap in Lochnagar, but only a few weeks to reach the upper trap. Under this scenario, the upper trap always represents a more recent sampling interval and over a period of declining deposition, fluxes would always be lower in the more recent samples. Such a temporal disparity would also preclude a straightforward comparison between the two sets of trap data. However, Punning et al. (2003) also suggest that their empirically determined rate was probably "reduced substantially" as the result of the presence of a strong thermocline. As no strong thermocline exists at Lochnagar and the water column is generally well mixed (Chapter 5: Thompson et al. this volume) settling rates are probably higher than 6 – 8 cm day^{-1} reducing the difference in the collection intervals of the upper and lower traps, especially on an annual sampling time-scale.

Spatial distribution

As part of a study into the distribution and storage of trace metals in the sediment basin of Lochnagar (Yang 2000; Yang et al. 2002a; c; Chapter 15: Tipping et al. this volume), 17 sediment cores were taken in 1997 along five transects radiating from a central point (NAG9). These cores were all analysed for the full historical record of SCPs and are shown in Figure 4. It is immediately obvious that there is considerable variability in the sediment record of SCPs across the loch basin. Cores from near the centre of the loch (but not, necessarily from the deepest area) show profiles typical of the 'standard' UK pattern (NAG9, 12, 19, 21, 22) whilst 'marginal' cores near the edge of the area of accumulating sediment (e.g., NAG11, 14, 15, 16, 18, 25) show profiles that are markedly different, having surface concentration maxima, short records or unusual temporal patterns. Cores from locations in the deepest areas (e.g., NAG17, 23) seem quite variable; NAG23 shows many of the usual temporal SCP features in good agreement with ^{210}Pb-derived dates and NAG17 appears to have more in common with the nearby marginal SCP profiles of NAG15 and 16. Therefore, there seems to be a central area of sediment where a full SCP profile can be replicated (marked area, Figure 4) but whilst this area is not over the deepest part of the loch it does seem to be spatially central to the basin. This area is the same as that of maximum post-1850 sediment accumulation (Chapter 8: Rose this volume).

A comparison between the nearest core to the outflow within the main basin (NAG25) and the core from the first outflow pool (NAG26) is also of interest. NAG25 shows a typical marginal profile, with low concentrations and a short record, whereas NAG26 shows higher concentrations and a fuller profile. The sediment within this outflow pool is very organic and composed mainly of eroded peat fragments from the surrounding area. The differences between these two cores may, therefore, result from the erosion of SCPs from recent peats in this part of the catchment, highlighting the role that this process may play in the input of previously deposited pollutants to the loch from catchment soils. The difference in the records of NAG25 and 26 may therefore serve as a record of catchment peat erosion rather than a record of SCPs leaving via the outflow.

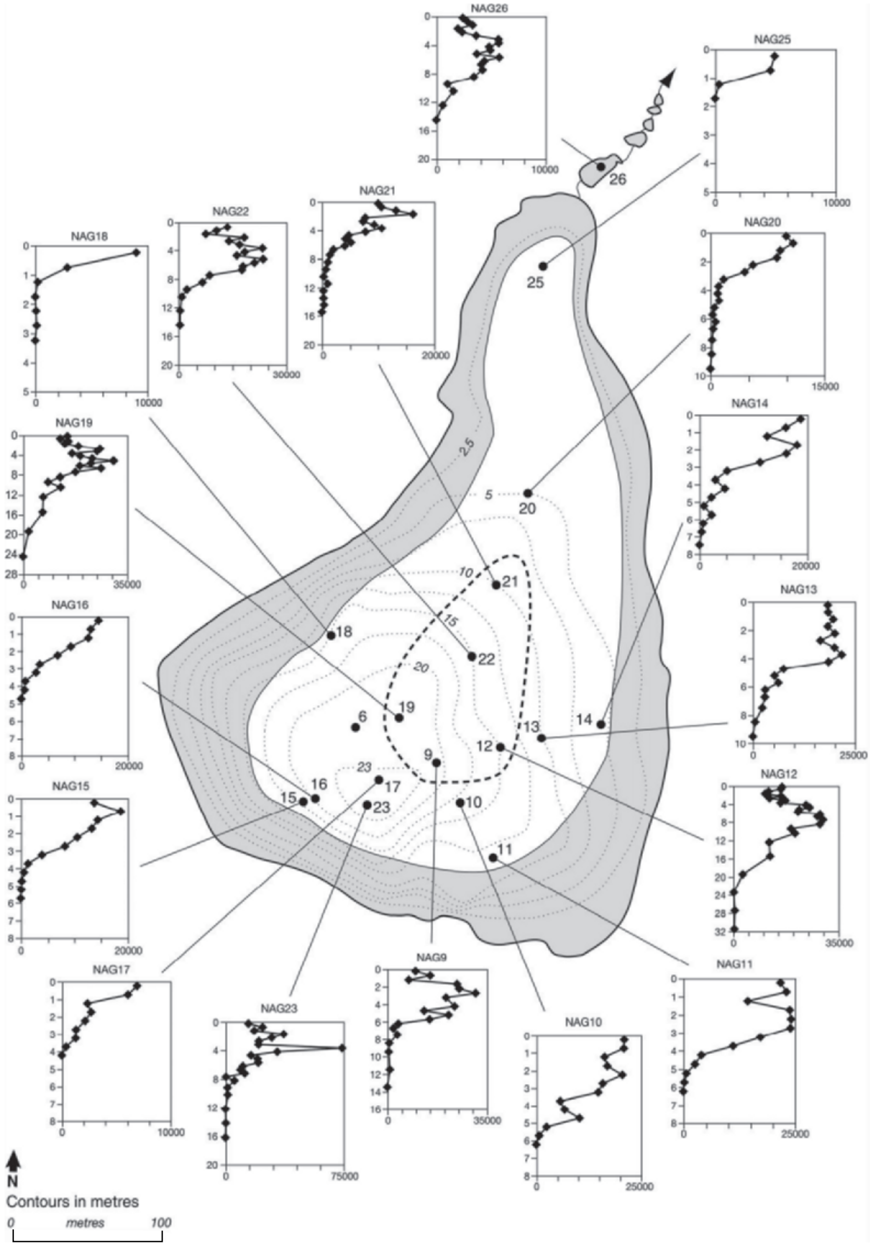

Figure 4. SCP concentration (SCP gDM^{-1}) profiles from sediment cores taken across the Lochnagar basin and from the first outflow pool. Depth contours are in metres. Dotted line denotes region within which maximum sediment accumulation occurs (Chapter 8: Rose this volume). Shaded area represents the empirically estimated region of little or no sediment accumulation.

As well as temporal profiles, SCP concentrations also vary across the loch. Surficial sediment (0– 0.5 cm) concentrations shown in Figure 5a, appear to show little spatial pattern although concentrations in the southeast are slightly higher. However, from Figure 4, this seems to be due to these southeastern cores failing to show the recent decline in SCP concentrations observed in the ‘full’ profiles seen in more central cores. Furthermore, SCP concentration maxima for individual cores are seen to be highest in this central region. Given these differences, a better spatial comparison, in terms of SCP accumulation within the Lochnagar sediment basin, can be made by converting the concentration profiles from Figure 4 into full-core SCP inventories (Figure 5b). From this it can be clearly seen that SCP accumulation is greatest in the central area and that, in general, inventories increase with depth along the radiating transects. These inventory data also highlight the variability of the record within the deep area (NAG17 and 23) whereas the surface sediment concentrations for these two cores (Figure 5a) were similar. It is uncertain why this is the case, although similar results are obtained for metals data, (Yang 2000) and it maybe that the sediment record in this area of Lochnagar is affected by rockfalls either directly from the backwall or via ice-rafting (Chapter 8: Rose this volume). Similarly, the surface concentrations of NAG25 and the ‘outflow pool’ core NAG26 show much closer agreement than do their inventories, which show considerably more SCP deposition in the outflow pool, supporting the hypothesis that this additional SCP input is from eroded peats around the outflow area.

The spatial distribution of SCP inventories shown in Figure 5b is close to that observed for inventories of the anthropogenic fraction of trace metals (i.e., ‘total’ minus ‘pre-industrial’) over the full industrial period (Yang et al. 2002b) and Figure 6 shows the relationships between SCP inventories with those for the anthropogenic fractions of Hg, Pb and Zn in the Lochnagar cores. The correlations between these are remarkably good with R^2 values of 0.84, 0.91 and 0.63 respectively. This suggests that mechanisms for transport and deposition of trace metals and SCPs within the loch are the same and, given the estimated depth of post-1860 sediment accumulation within the loch (Yang et al. 2002b), are related to the distribution of SCPs and particle-bound metals with the bulk sediment within the basin.

These core inventories can also be used to estimate the number of SCPs stored within the sediment basin. The area of accumulating sediment within Lochnagar can be sub-divided by depth and location so that each analysed core is representative of one of these smaller areas. These are described in Yang (2000) and vary between 1800 and 11000 m^2. The total inventory of SCP within the accumulating sediment basin (I_{tot}) can therefore be calculated from:

$$I_{tot} = \Sigma I_i . A_i \qquad (1)$$

where I_i is the SCP inventory for core i and A_i is the area of accumulating basin represented by core i. This results in the estimate of 6.18 x 10^{12} SCPs in the sediment basin of Lochnagar. Rose (2001) estimated that the mass of a 20 μm SCP would be in the region of 4.2 x 10^{-9} g and given this value an estimated 26 kg of SCPs is stored in the Lochnagar sediment basin. This compares with the total masses of anthropogenic Hg and Pb stored in the sediment basin of 71.4 g and 93.8 kg respectively (Yang et al. 2002a).

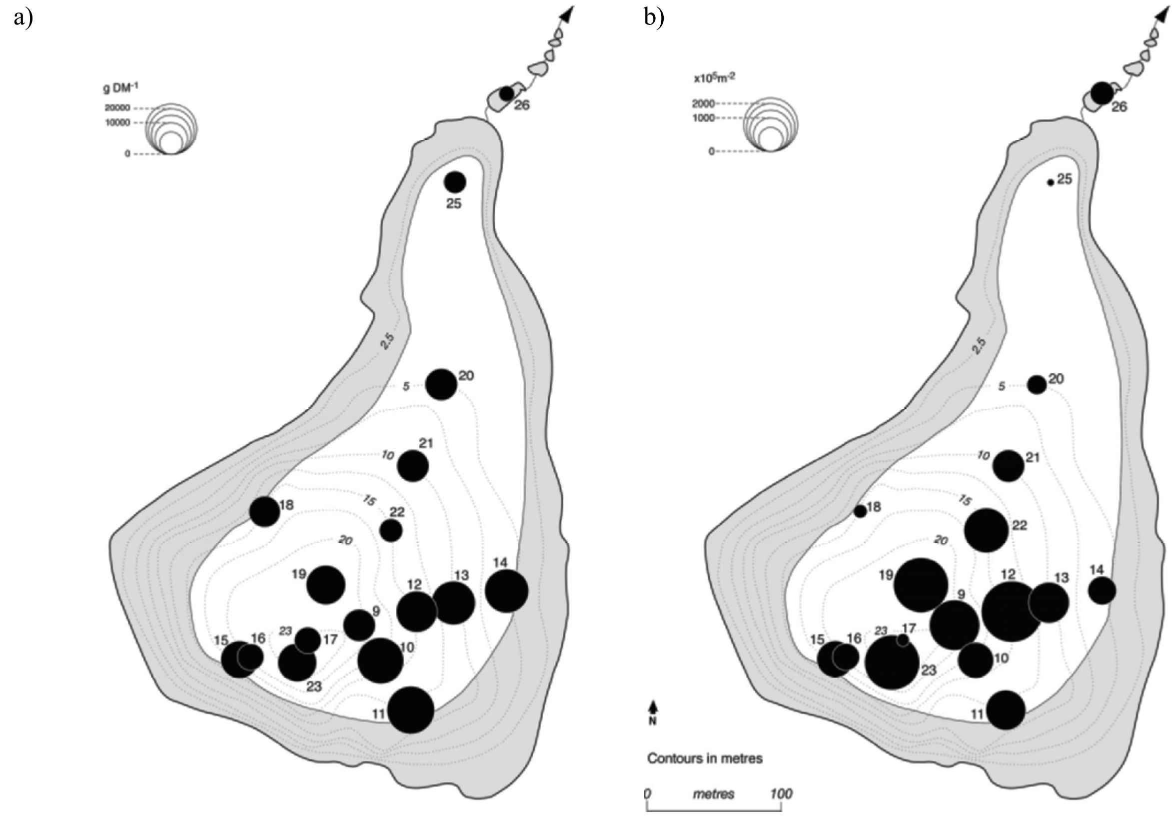

Figure 5. (a) SCP concentrations (SCP gDM^{-1}) in surface sediments and (b) full core SCP inventories (SCP x 10^5 m^{-2}) for cores taken across the Lochnagar basin. Shaded areas represent the empirically estimated region of little or no sediment accumulation.

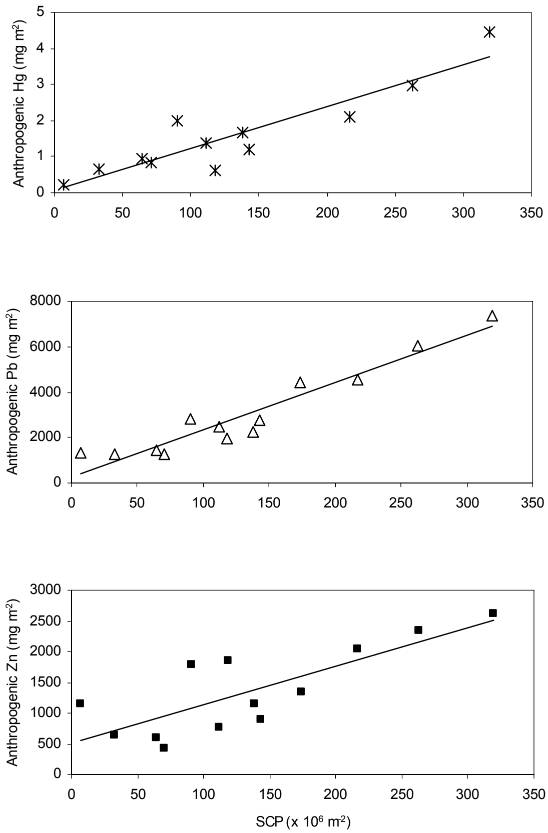

Figure 6. A comparison of SCP inventories (SCP x 10^6 m^{-2}) with those of the anthropogenic fractions of Hg, Pb and Zn from the Lochnagar sediment cores.

SCPs in catchment soils

In the same way that SCP and trace metal storage for the sediment basin of Lochnagar was estimated using a multi-coring approach, so the storage of these contaminants in the catchment soils has also been estimated. Ten soil cores (NAG50-52, 55-61) were taken from around the catchment of Lochnagar and analysed for SCPs as described in (Yang et al. 2001). The soil SCP concentration profiles (Figure 7) are generally short (less than 10 cm) except NAG51 which has a record of 15 cm. SCP profiles from areas of the catchment characterised by shallower slopes and greater accumulation of peats (Chapter 6: Helliwell et al. this volume) appear to show similar features to those of 'typical' SCP lake sediment profiles and as a consequence have been used to apply approximate chronologies to these soil cores (Yang et al. 2001). Maximum concentrations are lower than those of the sediment basin and reach c. 21000 gDM^{-1} on the eastern side of the loch (NAG56; Figure 7).

As with the sediment cores, SCP inventories for each soil core can be calculated. Inventories for the individual cores are lower than those of the sediment cores and range over about an order of magnitude between 6.8 x 10^6 (NAG52) and 6.7 x 10^7 m^{-2} (NAG56). In a similar way to the sediment cores, each soil core can be considered representative of an area of the catchment (Yang 2000) and used to estimate the total SCP storage. However, this requires an additional term in equation (1) i.e.

$$I_{tot} = \Sigma I_i.A_i.S_i \qquad (2)$$

where S_i is the fraction of area A_i covered by soil. This produces an estimate for the total SCPs in the catchment soils of 9.94 x 10^{12}. Comparing this value with that for SCPs stored in the sediment basin shows that of the SCPs deposited and accumulated in the loch and catchment over the industrial period, 61.7% are stored in the catchment soils and 38.3% in the loch sediment.

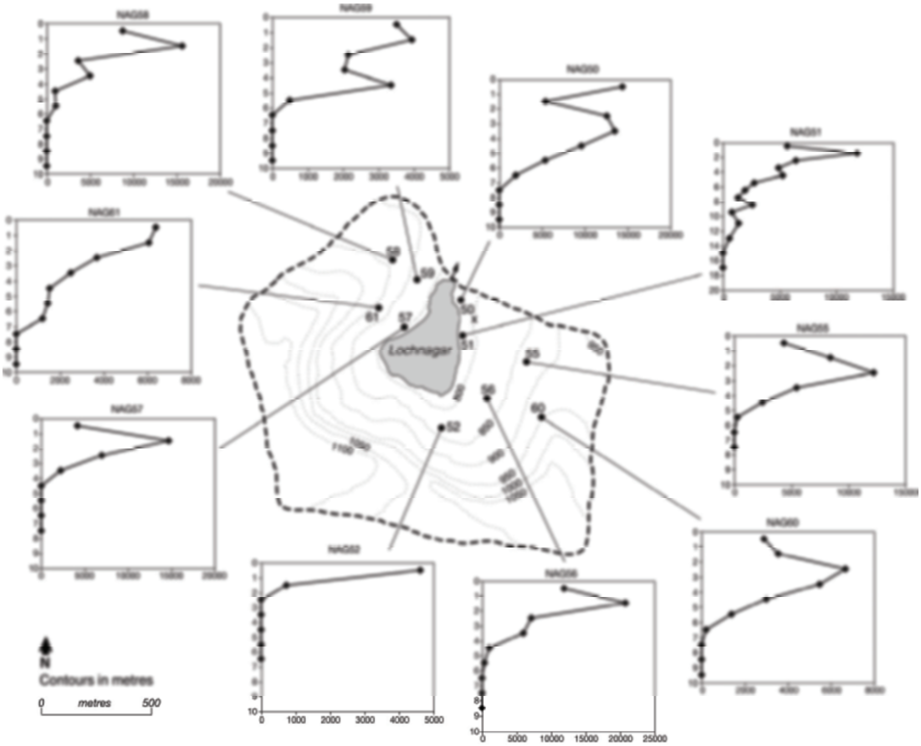

Figure 7. SCP concentration (SCP gDM^{-1}) profiles from soil cores taken across the Lochnagar catchment area. Contours are in metres above sea level. ‘X’ marks the location of the Automatic Weather Station.

A SCP number balance

The SCP data described above can be used to compile a SCP 'number balance' (cf. 'mass balance' for other pollutants) for Lochnagar. This is done for the calendar year 1997, as there are most data available for this period.

SCP inputs via bulk deposition and cloudwater

Figure 2b shows that, for 1997, SCP deposition calculated from the bulk collectors was 114850 m^{-2}. If it is assumed that this is a reasonable estimate for deposition across the area of the loch and the catchment then the number of SCPs directly deposited to these areas in 1997 are 1.126×10^{10} and 1.056×10^{11} respectively (Figure 8).

In addition to bulk deposition inputs, cloudwater was estimated to add an additional c. 46% to SCP inputs from the atmosphere for 2002-03. Assuming a similar cloud enhancement for 1997 results in an input of 4.86×10^{10} SCP to the catchment from this source. The total SCP input to the Lochnagar catchment area is therefore 1.542×10^{11} for the year. These cloudwater estimates were made using a surface roughness appropriate for moorland vegetation and while the use of this same factor for direct deposition to a water surface is probably too high, the influence of the surrounding catchment on small water bodies such as Lochnagar is such that the same factor probably does not over-estimate cloudwater inputs to the Lochnagar surface too much (Jennifer Muller and David Fowler, Centre for Ecology and Hydrology, Edinburgh pers. commun.). Therefore, assuming a similar cloudwater enhancement for the loch as for the catchment results in an additional input of 5.18×10^{9} SCP (Figure 8) and a total input from the atmosphere to the loch surface of 1.644×10^{10} for the year.

SCP loss via the outflow

During 1997, the concentration of SCPs in outflow water was estimated bi-monthly. This was done by filtering large volumes of water (≥40 litres) and analysing the filters for SCPs (see CARBYNET: http://www.ecrc.ucl.ac.uk/carbynet/). The mean and standard deviation of these measurements were 1.6 l^{-1} and 1.46 respectively (N = 6). An estimate of the water volume lost via the outflow in 1997 was made from a calculated hydrological balance where:

$$\text{Outflow} = \text{Precipitation} + \text{Run-off} - \text{Evaporation} \qquad (3)$$

Here, 'Precipitation' is the volume of direct precipitation to the loch surface calculated from the Lochnagar automatic weather station data; 'Run-off' is the volume of precipitation to the catchment area multiplied by a factor of 0.9 (Jenkins et al. 2001) and 'Evaporation' from the loch surface is calculated from the Penman equation (Penman 1948). This provides an estimate of 1.75×10^{9} litres (Jonathan Tyler, University College London pers. commun.) for the volume of water leaving Lochnagar via the outflow stream in 1997. This is then combined with the mean SCP concentration data to give an estimate for the number of SCPs lost via the outflow in 1997 as 2.795×10^{9}. Further, if it is assumed that the loch water is well mixed, then the number of SCPs in the water column may be estimated from the loch volume. This number is 1.31×10^{9}

SCPs. However, for the purposes of this 1997 number balance calculation it is assumed that storage in the water column does not vary over the year and hence there is no net loss or gain via this compartment.

SCP loss to the sediment

Although annual sediment trap data exist for the years 1996/7 and 1997/8 their location in the deep water area c.1-2 m above the sediment surface may result in an over-estimate of the number of SCPs deposited to the sediment, as a result of focussing. The number of SCPs 'lost' to the sediment in 1997 was therefore estimated from the multiple cores taken from across the sediment basin in that year (NAG9 – 25).

The dry mass of sediment in the uppermost 0.5 cm for each core was estimated from the volume and the dry bulk density of the slice. Up-scaling these masses to the areas of the sediment basin for which each of these cores is representative, and combining these with the surface SCP concentrations for each core, provides an estimate for the number of SCPs in the uppermost 0.5 cm for each area of the basin. Further, the time period covered by this uppermost slice can be estimated from the depth of the SCP peak concentration (taken as 1978) or, where no peak is present (mainly in short cores from the more 'littoral' areas), from the depth of the first presence of SCPs (taken as 1860). The number of SCPs in the uppermost 0.5 cm from each area can then be divided by the number of years represented by this depth of sediment in each area to provide an estimate of SCP deposition to this area for a single year. These 'annual' values can then be summed to provide an estimate for one year across the whole accumulating sediment basin. This summed value can then be used as an estimate for 1997, i.e.

$$\text{SCPs 'lost' to sediment in 1997} = \sum\left(\frac{0.5A_i.\rho_i.C_i}{Y_i}\right) \qquad (4)$$

where A_i is the area of the accumulating sediment basin represented by core i (in cm^2); ρ_i is the dry bulk density of the 0 – 0.5 cm slice of core i in area i (in g cm^{-3}); C_i is the concentration of SCPs in the 0 – 0.5 cm slice of core i (in gDM^{-1}); Y_i is the number of years represented by the 0 – 0.5 cm slice in core i. This provides an estimate for the number of SCPs deposited to the sediment in 1997 of 5.1×10^{10}.

However, if this estimate is made from the deep-water sediment trap data, then the number of SCPs deposited across the sediment basin is estimated as 1.88×10^{11}, a factor of 3.7 higher than the estimate made using the multiple core approach. This supports the hypothesis that focussing is taking place within the loch and that the sediment traps are representative only of deposition to the deep-water area.

SCP transfer from the catchment

If 2.795×10^9 SCPs were lost from Lochnagar via the outflow in 1997 and 5.1×10^{10} were 'lost' to the accumulating sediment in that year, then the balance for this loss must come from inputs from the atmosphere and indirectly from the catchment. Subtracting direct atmospheric deposition (1.126×10^{10}) and cloudwater input (5.18×10^9) from the total loss thus provides an estimate for the transfer of SCPs from the catchment to the lake in 1997. Figure 8 shows a schematic representation of the loch and catchment system from which this number can be calculated as 3.735×10^{10}, a factor of 3.3 higher than the direct inputs from the atmosphere and a factor similar to that calculated for Hg (3.6; Yang et al 2002a). As the inflow streams are only very minor, these catchment SCPs could be transferred during snow-melt, deposited onto bare rock and transferred directly into the loch, or from SCPs previously deposited and stored in catchment soils and recently eroded. However, unlike Hg and other metals SCPs cannot be leached from the catchment. Figure 8 shows that the number of SCPs directly deposited to the catchment is more than enough to balance the number required in the loch and still allows a surplus of 1.168×10^{11} to be stored in the catchment. Some of these will presumably be in areas available to be transferred to the loch in subsequent years. This calculation suggests that catchment transfer is an important source of SCPs and, by implication, other associated contaminants.

There are, of course, a great many assumptions in this SCP number balance and the errors for each estimated parameter are large. However, it does show that while known inputs from the atmosphere have been, and remain, important as a source of contamination, transfer from the catchment is required for a balance. While the mechanisms described above are all means by which SCPs could be transferred, catchment erosion is thought to be a major source of metals to Lochnagar (Yang et al. 2002b) and SCPs are undoubtedly also eroded into the loch during this process. However, although uncertainty remains as to the relative importance of these processes

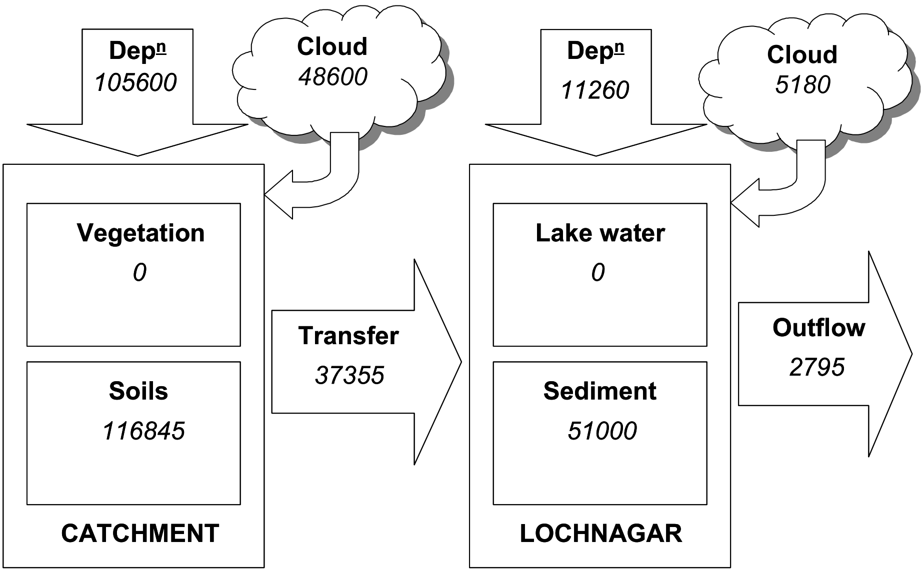

Figure 8. SCP 'number balance' for Lochnagar in 1997 showing: estimated inputs from bulk deposition (Dep^n) and cloudwater (cloud); loss via the outflow and loss via deposition to sediment basin and soils; calculated transfer from the catchment to the loch. All values in millions of SCP (e.g., loss via outflow is 2795 million or 2.795×10^9).

for SCPs compared with that of direct deposition, it is certain that a vast number of SCPs and other previously deposited contaminants remain stored in the catchment soils of Lochnagar with some potential for release as a result of enhanced transfer possibly as a consequence of climate change.

Impacts of climate change

While the SCP number balance raises some interesting questions with regard to the transfer of pollutants from the catchment to the loch, it is currently unknown whether this situation is unique to Lochnagar or typical for upland freshwaters across Scotland. As with many of the detailed studies outlined in this volume, the data for Lochnagar are unique in the UK and further work is required to determine how typical the situation at Lochnagar is. An EU funded project, Euro-limpacs, is currently (2004 – 2009) investigating the role of climate change in enhancing the transfer of contaminants from catchments to waters of upland lakes and it is hoped that the results of this study will help interpret the Lochnagar data still further. Current climate scenarios for Scotland (Chapter 18: Kettle and Thompson this volume) suggest prolonged drier and warmer periods in summers and heavier rainfall in winters with an increased frequency of severe meteorological events. These conditions are favourable for an increase in both erosion and leaching (Noda et al. 2001; Rose et al. 2004) and hence elevated transfer of contaminants, including SCPs, might be expected at Lochnagar as a result.

In terms of the impact of this on the ecosystem, the increased input of SCPs is unlikely to affect biota directly. However, an increase in the catchment input of SCPs to the loch serves as an indication of enhanced inputs of toxic compounds in two ways. First, as a marker for the erosion process thereby indicating that previously deposited toxic metals and POPs stored in catchment soils are similarly, and increasingly, being input via this means. Second, as SCPs bring with them trace metals and POPs adsorbed to the particle surface (e.g., Wey et al. 1998; Ghosh et al. 2000), possibly via complexation with large organic acids which themselves readily adsorb to elemental carbon particles (Seigneur et al. 2005). In this latter case, the porosity of SCPs increases the available adsorption surface making them particularly suitable for the transport of these pollutants via this route. The increase in transfer of SCPs from catchment to the waterbody would therefore indicate an enhanced input of toxic pollutants to Lochnagar regardless of any policy-driven reductions in emissions to the atmosphere.

Summary

- Monitoring of SCPs at Lochnagar has been ongoing since 1990 when the annual sediment trapping programme was initiated. Fortnightly monitoring of SCPs in bulk deposition began in 1996 and a full sediment basin and soil survey was undertaken in 1997.
- Bulk deposition data show a decrease in SCP deposition since 1997 with a stable period between 1998 and 2002. Further monitoring will determine whether a subsequent decrease in 2003 is a temporary reduction or a further decline in deposition.

- Inputs of SCPs from cloudwater at Lochnagar represent an additional c. 46% of bulk deposition inputs.
- Combined sediment trap and dated sediment core data show a continued decline since the late-1970s. SCP fluxes are now at their lowest levels since the 1930s, in agreement with modelled non-marine sulphate data.
- A multi-core survey across the basin of Lochnagar shows replicable temporal trends in an area central to the loch, but not its deepest area. SCP profiles outside this central region are truncated or show unusual trends.
- SCP profiles from the central area of Lochnagar are typical of those across the UK, with the start of the record in 1850 ± 25 and a concentration peak in 1978 ± 2.
- SCP inventory data for Lochnagar shows evidence of sediment focussing in deeper areas in good agreement with trace metals data.
- An SCP number balance for 1997 suggests that inputs can only balance outputs with additional transfer from the catchment. These additional SCPs are either transferred during snowmelt, in-washed from deposition on bare rock areas or enter the loch with eroded catchment peats.
- Predicted climate scenarios imply conditions favourable for increased catchment peat erosion suggesting SCP transfer from this store could increase in the future as a result. While SCPs are not known to be detrimental to freshwater biota, inputs of toxic trace metals and POPs, adsorbed to SCP surfaces, could be enhanced by this mechanism.

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