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A whole-basin, mass-balance approach to paleolimnology

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Abstract Lake sediments record the flux of materials (nutrients, pollutants, particulates) through a lake system both qualitatively, as changes in the composition of geochemical and biological tracers, as well as quantitatively, through changes in their rate of burial. Burial rates provide a direct link to contemporary (neo-) limnological studies as well as management efforts aimed at load reductions, but are difficult to reconstruct accurately from single cores owing to the spatial and temporal variability of sediment deposition in most lakes. The accurate determination of whole-lake burial rates from analysis of multiple cores, though requiring more effort per lake, can help resolve such problems and improve our understanding of sediment heterogeneity at multiple scales. Partial solutions to these problems also include focusing corrections based on ^{210}Pb flux, co-evaluation of concentration profiles, trend analysis using multiple lakes, and trend replication based on a small number of cores from the same lake. Recent multi-core studies demonstrate that no single core site faithfully records the whole-lake time-resolved input of materials, but that as few as five well-placed cores can provide a reliable record of whole-lake sediment flux for morphometrically simple basins. Lake-wide sediment fluxes can be coupled with reconstructed outflow losses to calculate historical changes in watershed and atmospheric loading of nutrients, metals, and other constituents. The ability of paleolimnology to accurately assess the sedimentary flux and extend the period of reference into the distant past represents an important contribution to the understanding of biogeochemical processes and their response to human and natural disturbance.

Keywords Multiple cores · Sediment focusing · Atmospheric deposition · Eutrophication · Erosion · Trace metals

Introduction

Over the last several decades lake-sediment records have assumed an increasingly important role in quantifying the magnitude of human impact on aquatic ecosystems and informing management and policy decisions aimed at mitigating those effects and restoring ecosystem function and services (Smol 2008). The impacts of interest range from nutrient enrichment, inorganic and organic contaminants, soil erosion, acidification, climate change, and exotic species, among others. Most commonly the paleolimnological approach is aimed at determining the relative

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magnitude of change, its timing and trajectory, and likely causation. Sediments also have the potential for reconstructing the rate of material flux (nutrients, metals, etc.) to a lake from its catchment or the atmosphere. However, sediment records are complex recorders of environmental change such that it is difficult to quantify actual fluxes through the system from analysis of a single sediment core—taken most commonly in the deep center of a lake basin. As has been clearly shown by many multiple-core studies, sediment deposition within a lake basin varies both spatially and temporally, such that accumulation trends in any individual core can be quite different from that for the lake as a whole (Bloemendal et al. 1979; Dearing 1983; Dearing et al. 1981). Despite such evidence, most studies still employ single-core approaches, often resulting from limitations in resources. However, the additional information obtained from, and interpretative power of, multiple-core studies should make them more widely used. Multiple-core studies allow spatial heterogeneity across all scales to be addressed (Blais and Kalff 1995; Evans and Rigler 1983). Furthermore, they permit the whole-basin time-resolved inputs of materials to be identified, allowing better between-site comparison (Dillon and Evans 1982; Swain et al. 1992), the identification of the role played by catchment inputs via a mass-balance approach (Foster et al. 1985; Rippey and Anderson 1996), and an assessment of increases in catchment inputs from storage via re-mobilization (Yang et al. 2002a).

In recognition of such issues, several recent studies have advanced a multi-core, mass-balance approach to quantify actual changes in material flux to and from a lake system. These studies begin with the reconstruction of whole-basin sedimentation so as to distinguish lake-wide burial from a core-specific rate (which varies spatially), and then go on to estimate one or more of the remaining fluxes to ultimately derive external inputs by simple mass balance of gains and losses over time. This approach has been aimed principally at problems involving atmospheric contaminants, nutrients, and biological productivity, as applied to single-lake investigations as well as comparative studies involving multiple lakes. The principal aim of this paper is to review the multi-core, mass-balance approach to paleolimnology, its assumptions, strengths, and uncertainties and to suggest ways that it might be streamlined to make it more efficient and tractable for future work. At its core, this paper is a tribute to the pioneering work of R.W. Battarbee, who through his scientific career has endeavored to make paleolimnology more rigorous and quantitative and to promote its integration with contemporary (neo-) limnology to better understand environmental change over the long course of time. Battarbee's early work on sedimentary dynamics in Lough Neagh (Northern Ireland) (Battarbee 1978a, b) along with efforts by others to derive whole-lake sedimentation from multiple cores (notably, Bloemendal et al. 1979; Dearing et al. 1981; Evans and Rigler 1980) are key to the development of the mass-balance approach highlighted in this review.

General methods

Whole-lake sediment accumulation

A key component of the whole-basin, mass-balance approach is a lake-wide sediment burial rate, calculated as a whole-lake flux (e.g. kg $year^{-1}$) or mean areal flux (e.g. g m^{-2} $year^{-1}$). In theory, the average burial rate could be established from a single well-dated core, provided the site from which the core was collected represented the average rate for the lake as a whole. But because sediment deposition patterns vary in complex ways that are difficult to predict a priori, it is usually necessary to collect multiple cores to establish a lake-wide average flux.

The physical transport of fine-grained sediments within a lake (focusing) typically results in higher than average burial rates in the deep central basin and below average rates in shallow sites or on steep slopes (Evans and Rigler 1980, 1983). However, the pattern of deposition varies from lake to lake depending on basin size, morphometry, and complexity (shape, inflows, embayments), and not all sediment components focus in the same manner. In small lakes, particle resuspension during overturn and peripheral wave action appear to be the dominant processes driving sediment focusing (Hilton et al. 1986). In addition to particle size and density, the spatial pattern of delivery to the lake along with in-lake chemical processes can produce different depositional patterns for different constituents. For example, clastic mineral particles delivered by streams or diffuse runoff from the lake margin will focus differently than constituents such as atmospheric pollutants or algal detritus deposited more evenly across the lake surface—not just because of density differences, but because of differences in transport distance between point of entry and site of burial. This is especially so for indicators of littoral productivity (e.g. epiphytic diatoms or macrofossils), which are notoriously underrepresented in deep-water cores (Anderson 1990b). In addition to these processes of physical redistribution, some sedimentary components undergo chemical transformation within the water column (or surface sediments) whereby they may be enriched (or depleted) by adsorption to particulates (e.g. organic or metal pollutants), redox cycling (e.g. Fe and associated metals), dissolution (e.g. carbonates), or mineralization (e.g. organic matter) (Engstrom and Swain 1986). This point is well illustrated by the study of Rippey et al. (2008) in which fluxes from a deep central core were compared with lake-wide values established from 43 cores taken from a small morphometrically-simple lake basin. The bias of the central core varied from 25 % for major elements, to 50 % for heavy metals and phosphorus, to 85 % for organic carbon.

A series of studies has established that a relatively small number of cores (5–10) is needed to derive an accurate estimate of whole-lake sediment accumulation (Engstrom et al. 1994; Rippey et al. 2008; Rowan et al. 1995a, b)—at least in morphometrically simple basins and so long as the cores are collected from a representative set of sites. A simple arithmetic mean of core-specific fluxes appears to work nearly as well as more complex calculations such as areal weighting by depositional zone, depth contours, or nearest-neighbor delineation. However, more cores may be desirable/required for complex lake basins (those with multiple basins and embayments) (Bindler et al. 2001) or those with major river inflows and pronounced depositional gradients (Engstrom et al. 2009). Finally, non-depositional areas of the lake bottom—shallow areas and steep slopes where fine-grained sediments are not permanently buried—need to be delineated so that mean areal accumulation can be propagated to a lake-wide flux. Approaches to this problem include semi-empirical models based on basin depth, exposure, and slope (Blais and Kalff 1995; Rowan et al. 1992, 1995a, b) and reconnaissance coring and field observation of sediment lithology (Fitzgerald et al. 2005; Rose et al. 2012), aided in some cases by seismic-reflection profiling (Engstrom et al. 2009).

Whole-basin sediment studies all require dating and cross-correlation among multiple cores, which adds considerably to the effort required to characterize burial rates for even a single lake. Various approaches have been used, from dating all cores by ^{210}Pb to dating only a single 'master core' and using supplementary stratigraphic information to correlate among cores. Among methods for stratigraphic correlation, non-destructive, whole-core scans of magnetic susceptibility, pioneered by Molyneux and Thompson (1973) and Thompson et al. (1975), have proven very effective, as have diatom biostratigraphy (Battarbee 1978a), pollutant markers (e.g. spheroidal carbonaceous particles (SCPs) (Rose and Yang 2007) and lithostratigraphy (Rippey et al. 2008). Lead-210 dating has the advantage of high temporal resolution, and although cost is often a limiting factor, several studies have used a multiple-core approach to assess for focusing (Appleby et al. 2003) or a modified approach in which a small number of 'primary' cores are dated in detail, augmented spatially by a suite of 'secondary' cores dated at coarse resolution (Engstrom et al. 1994; Fitzgerald et al. 2005). Ultimately, a combination of ^{210}Pb dating, magnetic stratigraphy, and other dating markers is recommended for overcoming uncertainties in each of the individual dating tools (Engstrom et al. 2009).

Corrections for sediment focusing

Many studies have used single sediment cores to estimate whole-basin accumulation by applying a correction factor for sediment focusing based on the inventory (or flux) of ^{210}Pb in the core relative to the atmospheric ^{210}Pb flux for the region in which the lake is located. This method embodies several critical assumptions: (1) the atmospheric ^{210}Pb flux is known with some level of certainty (2) the sediment constituent of interest is focused to the same degree as ^{210}Pb, and (3) focusing to the core site has remained relatively constant over the period of interest.

Regarding the first assumption, atmospheric ^{210}Pb deposition, which varies as a function of latitude, rainfall, and proximity to continental land-mass, has been explicitly measured in relatively few locations worldwide (Appleby 2008; Baskaran 2011; Graustein and Turekian 1986; Lamborg et al. 2012), although modeled approximations for global distribution (Appleby 2008) have been used in the absence of actual measurements. Atmospheric ^{210}Pb deposition rates have also been estimated from ^{210}Pb inventories in ombrotrophic peat cores—although lead is now known to be mobile in peat (Biester et al. 2007)—and from soil cores collected from the vicinity of the lake (flat areas not subject to soil redistribution). Fitzgerald et al. (2005) derived atmospheric ^{210}Pb deposition from a whole-basin, multi-core study of five arctic lakes. In this case, the uniformity of the ^{210}Pb fluxes among the five sites provided independent confirmation of the multi-core estimates of whole-lake sediment accumulation. By contrast, Appleby et al. (2003) in a 16-core study from Blelham Tarn in the UK Lake District identified significant variability across the lake basin as a result of erosive catchment inputs near a major inflow stream, compared with the dominant atmospheric deposition elsewhere in the basin.

The second assumption for focusing correction requires similar input functions and deposition patterns for ^{210}Pb and the sediment component under consideration. Lead-210 input to most lakes is predominately atmospheric and thus arealy uniform, while in-lake transport is controlled by physical redistribution of fine-grain particulates to which ^{210}Pb strongly adsorbs. Sedimentary constituents with similar behavior (e.g. atmospheric metals) should focus similarly, whereas other constituents, such as organic matter from littoral areas, might be expected to focus differently (Bindler et al. 2001).

The third assumption, that focusing has remained constant over time, is critical to the interpretation of accumulation trends from single cores, yet we know from many multiple-core studies that this condition is seldom met. Changes in sediment focusing over Holocene time scales were first described by Davis and Brubaker (1973), but it was work by Battarbee (1978a, b) on diatom stratigraphy in Lough Neagh, that showed clearly how sediment deposition patterns can shift within a lake basin over very short time periods. This observation has been confirmed by subsequent multi-core studies that show asynchronous changes in accumulation rates among cores, even as they show an overall trend in lake-wide flux (Anderson 1990a; Dearing 1983; Engstrom et al. 2009; Fitzgerald et al. 2005; Rose et al. 1999; Triplett et al. 2009). Because focusing-correction adjusts accumulation rates in a single core uniformly, any trends or changes in flux that are an artifact of shifting sedimentation patterns are retained. One way around this problem would be to analyze a small number of representative cores (say three or so) to determine the predominant trends in accumulation, while at the same time applying a ^{210}Pb focusing correction to adjust core-specific fluxes to a lake-wide mean.

Reconstructing other fluxes

In addition to whole-basin burial rates, an historical mass-balance requires the reconstruction of other inputs and outputs to the lake. For some constituents, sedimentation is the dominant sink, and other loss terms (e.g. outflow) can be ignored. Such is the case for eroded mineral matter, which is efficiently trapped in most lake basins, such that sediment burial is equal to catchment input. This can also include constituents, such as certain heavy metals (e.g. Pb) and hydrophobic organic contaminants (e.g. polychlorinated biphenyls; PCBs), which adsorb strongly to particulates and are effectively co-sedimented. Other chemicals that absorb less strongly (lower Kd) (e.g. Zn, Cu, Cd, Hg, polycyclic aromatic hydrocarbons (PAHs), chlorophenols) may have a significant dissolved phase and higher outflow losses (Rippey 2010). In-lake burial efficiency also depends on hydraulic residence time as well as particle settling rates, such that lakes in more arid regions or those draining small catchments and thus lacking substantial outflows will be more effective traps than lakes in regions with high rainfall or those with large contributing watersheds (Yang et al. 2002a). The latter is particularly true in the case of reservoirs on large rivers, which often infill rapidly with sediment and in so doing become progressively less efficient as sediment traps (Brune 1953).

Other constituents of interest, such as phosphorus (P), cycle between dissolved and particulate phases and are far less efficiently sedimented than clastic mineral matter. Unless lake residence time is very long ($>\sim 1$ year) outflow loss must be included in the mass balance. In the case of P, historical outflows may be derived from diatom-based P reconstructions of water-column total-P and recorded river flows (Triplett et al. 2009). Contemporary flow measurements may be used in the absence of historical flow data (Rippey and Anderson 1996) or modeled from meteorological records. Errors associated with numerical diatom reconstruction (Juggins et al. this issue) as well as those for flow estimation may well exceed the uncertainty of the sedimentation term and must be considered in the overall reliability of the reconstructed nutrient budget.

Water-column concentrations for many constituents (e.g. silicon, Si) cannot be readily reconstructed from fossil diatoms or other biotic assemblages (but see Kratz et al. 1991). In such cases outflow losses and in-lake burial (retention) may be reconstructed from contemporary measurements of inflow and outflow loads together with estimates of relative changes in catchment Si export (Triplett et al. 2012). Similarly, other fluxes that are difficult to reconstruct directly (e.g. gaseous exchange) may be derived from modern measurements and treated as constants in the past thereby simplifying the mass-balance (Fitzgerald et al. 2005). This latter approach is most robust when the assumed fluxes are relatively small, or when there is supplemental evidence that the flux was likely unaltered by environmental change. However, as with sediment focusing, the caveat on the assumption of no change through time needs to be carefully considered.

Finally, some fluxes can be determined from the mass-balance comparison of multiple lakes with different sized catchments (relative to lake surface area). Catchment/lake area ratios (C/L) are well-established, empirical predictors of watershed loading of runoff constituents such as phosphorus and mercury (Hg). In the case of Hg, Swain et al. (1992) were able to derive estimates of preindustrial atmospheric deposition as well as catchment Hg loading by use of lake-wide Hg burial rates arrayed against C/L (Fig. 1). In this representation, direct atmospheric deposition was derived from the intercept—a theoretical lake with no catchment (C/L = 0), while the proportion of deposition exported from the catchment (∼20 %) was determined from the slope of the relationship divided by the atmospheric deposition rate (Hg burial at C/L = 0). This approach has been applied in other studies of Hg deposition where lake-wide rates of Hg accumulation were derived from single cores in which ^{210}Pb inventories indicated little sediment focusing (Drevnick et al. 2012b; Kamman and Engstrom 2002).

Case studies

We have selected three examples of whole-basin, mass-balance studies to illustrate the range of environmental questions that have been addressed using this approach. These include atmospheric pollutant deposition to remote Scottish lochs, point-source nutrient enrichment of a small lake in Northern Ireland, and large-scale land-use impacts on two contrasting natural impoundments on the upper Mississippi River. Each of the case studies represents a synthesis of several component investigations that together reveal the power of the multi-core investigation to enhance understanding of sedimentary processes, biogeochemical cycles, and limnological change resulting from human activity.

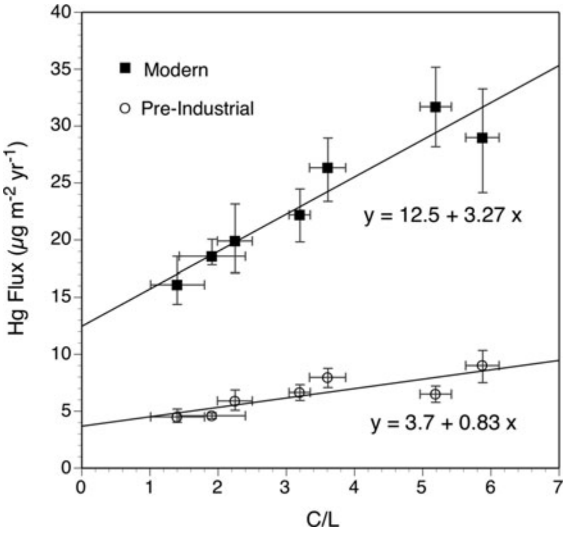
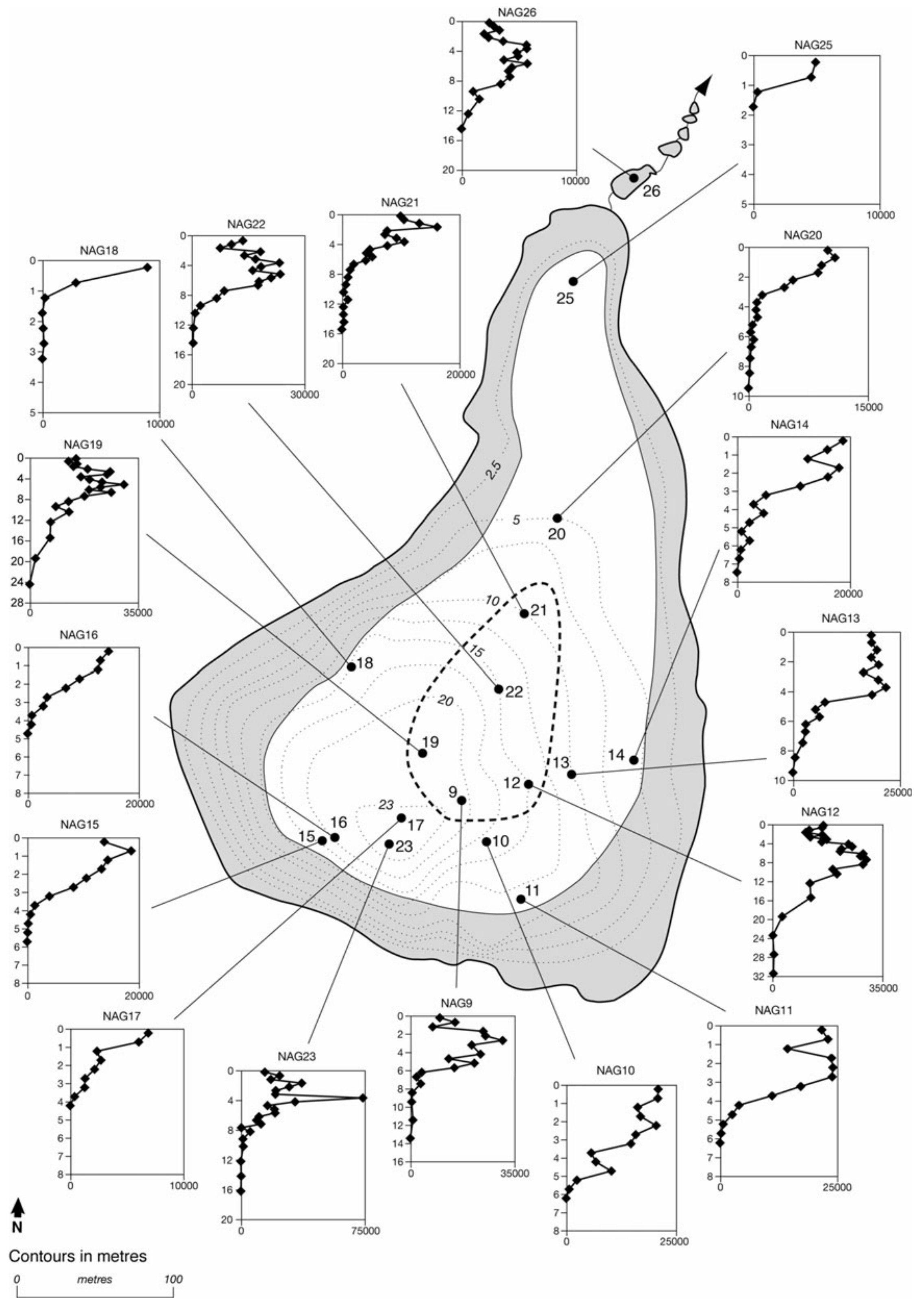


Fig. 1 The derivation of mercury (Hg) fluxes from whole-lake Hg accumulation rates for seven Minnesota and Wisconsin lakes plotted as a function of catchment:lake area ratio (C/L). Modern rates represent 1980–1990, while preindustrial rates are those prior to 1850. The intercept of the lines (C/L = 0) predicts atmospheric Hg deposition to the lake surface while the fraction of catchment deposition transported to the lake (∼20 %) is the slope of the *line* divided by the intercept. Redrawn from Swain et al. (1992)

Case study 1: Scottish lakes

Small-scale spatial variation of pollutant records within a lake basin were assessed by Rose et al. (1999) at Loch Coire nan Arr, a small upland loch in the northwest of Scotland, using spheroidal carbonaceous particles (SCPs) (Rose 1994). SCPs are a component of fly-ash, the particulate product of high-temperature industrial combustion of heavy fuel-oils and coal-series fuels. The sediment record of SCPs is robust and shows repeatable temporal trends across large geographical areas making it a useful sediment chronological tool (Renberg and Wik 1985; Rose et al. 1995). Multiple cores were taken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◀ **Fig. 2** SCP concentration profiles from 17 sediment cores taken across the Lochnagar basin and from the first outflow pool (26). Depth contours in meters. *Dotted line* denotes region of maximum sediment accumulation; *shaded area* indicates empirically estimated region of little or no sediment accumulation. From Rose and Yang (2007). Reprinted with permission from Springer

from a small (~ 20 × 20 m), deep, flat area of the loch. Although each core showed the basic SCP profile used for sediment dating, considerable variation was observed with a range of patterns superimposed on the familiar features of the SCP concentration profile, suggesting considerable localized short-term sediment focusing over small distances. Although good repeatability may be expected over short distances in small, simple lake basins, wind-stress in these upland lakes may add an additional level of complexity to sedimentation patterns. Modeling studies at Llyn Conwy, North Wales (Morales et al. 2010) show how complex flows driven by strong prevailing winds combined with seasonal variation of thermal structure and the lake basin morphology can inhibit sediment accumulation in the deepest parts of a lake and lead to preferential accumulation in mid-depth zones. Multiple sediment core studies at Loch Fleet, a wind-stressed lake in Scotland (Anderson 1990c; Cameron 1995), show how resuspension of sediments leads to re-working of old material and hence potential mis-interpretation of the record. However, in general, short-term variability on a small spatial scale does not usually affect temporal interpretation of the individual cores (Anderson 1990c; Rose et al. 1999), but greater variability may be expected at the full-basin scale.

Very few multiple-core SCP studies have been undertaken across a full basin. Vukić and Appleby (2003) analyzed five sediment cores from a small Czech reservoir and found considerable differences as a consequence of wind and current effects on sediment distribution. To our knowledge, the only other full-basin, multiple-core SCP study was undertaken at another Scottish loch, Lochnagar, located in the Grampian Mountains. Rose and Yang (2007) undertook SCP analysis of 17 sediment cores along five transects radiating from a central point (Fig. 2). Cores from near the center of the loch (but not, necessarily from the deepest area) exhibited profiles typical of the familiar UK pattern, whereas ‘marginal’ cores near the edge of the accumulation zone showed profiles that were markedly different, having surface concentration maxima, short records or unusual temporal patterns. Cores from locations in the deepest areas (e.g. NAG 17, 23) were variable and, whereas NAG 23 showed many of the usual temporal SCP features, NAG 17 appeared to have more in common with nearby marginal profiles. Therefore, there seems to be a central zone of accumulation where a full SCP profile may be replicated (marked area, Fig. 2). Although this area is not entirely coincident with the deepest part of the lake, it does seem to be spatially central to the loch basin.

These sediment cores were also analyzed for a series of trace metals: Hg, Pb, Cd, Zn and Cu (Yang et al. 2002b). The spatial distribution of the anthropogenic fraction of these metals over the full industrial period was very close to that of the SCP inventories, with R^2 values of 0.84, 0.91 and 0.63 for Hg, Pb, and Zn, respectively (Rose and Yang 2007). 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-1850 sediment accumulation within the loch (Rose 2007), are related to the distribution of SCPs and particle-bound metals with the bulk sediment within the basin. Yang et al. (2002b) used these data to determine full-basin inventories for the trace metals and were able to determine that for Hg and Pb, the use of seven or more cores provided a >99 % estimate for the full basin, whereas using only four cores reduced this to 80–85 %. By contrast, the use of a single deep water core as a full-basin estimate varied greatly from 61–65 to 85–87 %. Here, therefore, deep water cores underestimate the full-basin record (i.e. <100 %) rather than overestimating it as a consequence of sediment focusing. This may be because the area of maximum sediment accumulation is not coincident with the deepest parts of the loch (Fig. 2), and serves to illustrate the risks associated with up-scaling from single cores to full basins.

Yang et al. (2002a) also used these data as part of a wider catchment-scale, mass-balance study to assess the relative roles of atmospheric and catchment inputs of Hg and Pb to the sediment record. For the study year 1998, the catchment of Lochnagar provided 3.5- and 10-fold the Hg and Pb, respectively, compared with direct atmospheric deposition to the loch surface. Furthermore, the full-basin accumulation profile derived from the 17 cores and resolved to a decadal resolution showed no decline in most recent decades in response to the dramatic emissions reductions since the 1970s. These profiles (Fig. 3) are of particular interest as they show a temporal profile that agreed well with expected emissions through to the 1970s, but failed in this agreement thereafter, when both emissions and deposition were known to be declining. This 'additional' Hg and Pb can only have been derived from the catchment, and most probably from inputs of eroded peat from the loch's eastern shore.

The results from these multiple core studies at Lochnagar led directly to a larger study involving multiple sediment cores from nine lakes across Scotland (Rose et al. 2012). In each of three regions, three lakes were selected to include a site with only thin soils in the catchment and/or little areal catchment soil coverage; a site with good soil coverage in the catchment but with no catchment soil erosion, and a site with significant catchment soil erosion. At each of these nine lakes, three cores were taken from across the lake basin representing deep-water, mid-depth and shallow-water accumulation. Each core was analyzed for Hg, Pb, Cd, Ni, Cu, Zn, and SCPs and full-basin accumulation calculated for each at decadal resolution. As SCPs are particulate they can only enter the lake from the catchment via soil erosion. Hence a comparison between the records of the metals and SCPs provided the means by which to assess the relative roles of soil erosion versus leaching in this transfer.

The full-basin accumulation of metals and SCPs for lakes with thin soils showed good agreement with temporal trends in metal emissions to the atmosphere and in deposition, indicating that in the absence of any significant catchment influence, full-basin records from these lakes faithfully recorded depositional trends. The recent decline in full-basin accumulation for Hg and Pb was only slightly less than that expected from emissions reductions (i.e. 60–80 % reduction in full-basin accumulation compared with ~80–90 % reduction in emission) (Fig. 4). Lakes with good catchment soil coverage but with no erosion also showed declines in full-basin accumulation in recent decades, but these declines were lower (40–50 % Pb; 20–30 % Hg) (Fig. 4), indicating a possible role for the transfer of metals by leaching, possibly concomitant with increasing dissolved organic carbon (DOC) (Monteith et al. 2007). The full-basin accumulation records for the lakes with eroded soils were quite different. Decadal patterns showed increases for metals and SCPs through to the most recent decades. However, variability among sites was quite high (Fig. 4), resulting from different degrees of erosion impact in the catchments.

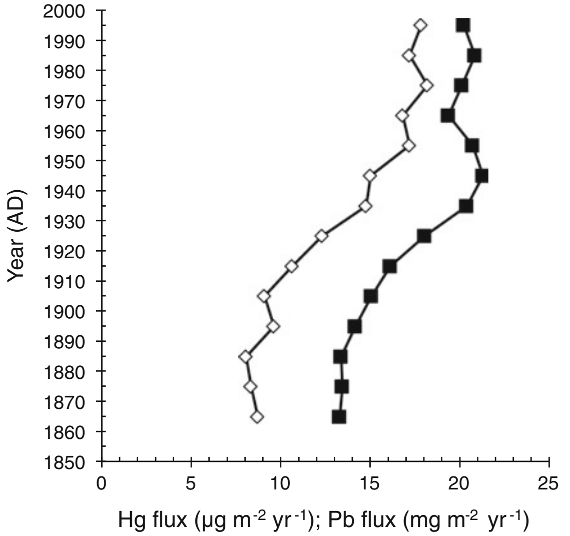


Fig. 3 Decadal mercury (*open symbols*; µg m^{-2} $year^{-1}$) and lead (*solid symbols*; mg m^{-2} $year^{-1}$) accumulation profiles for the whole sediment accumulation area of Lochnagar based on the analysis of 17 sediment cores. Redrawn from Yang et al. (2002a)

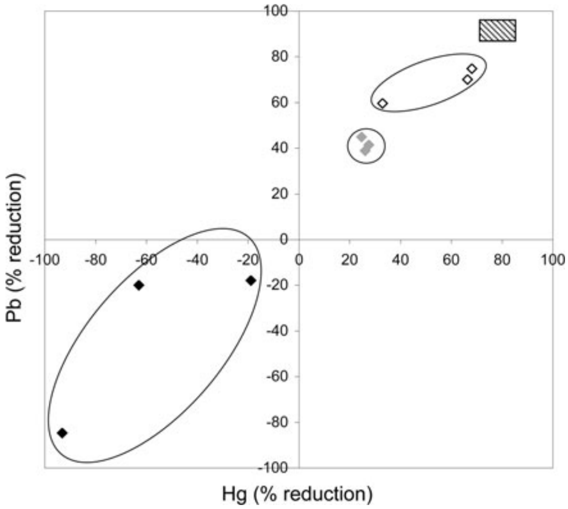


Fig. 4 Percentage reduction in decadal full basin inventory for Pb and Hg. *Black symbols* represent eroded soil sites; *grey symbols* sites with non-eroded soils and open symbols sites with thin soils. *Shaded box* indicates emissions reductions for the two metals (UK National Atmospheric Emissions Inventory data). Redrawn from Rose et al. (2012)

These Scottish multiple-core studies show the impact of catchment soil erosion as a mechanism for the transfer of atmospherically deposited pollutants stored in soils and now re-mobilized. The store within catchments is considerable, and the potential for further increases in inputs is high. This is important for two reasons. First, the full-basin accumulations observed for recent decades increased only slightly, but this must be viewed in the light of dramatic emissions and deposition reductions over the same period. Such reductions cannot continue, and emissions over recent years are now quite stable (RoTAP 2012). Hence continued or increased inputs from the catchment will result in more significant inputs to aquatic systems. Second, the processes that lead to soil erosion and leaching of DOC from the catchment are exacerbated by increased winter rainfall, prolonged summer drought and increased frequency of high intensity rain events. Hence, predicted climatic changes will increase pollutant transfer from catchment to surface waters, potentially for many decades.

Case study 2. Lough Augher, Northern Ireland

Lough Augher is a small (9.25 ha) 14-m-deep eutrophic kettle lake in Co. Tyrone, Northern Ireland. Between 1900 and 1976 a local creamery discharged untreated effluent directly into the lake. In order to determine the lake response to this input and to assess diatom variability, 12 sediment profiles were analyzed across the full lake basin (Anderson 1989, 1990b). There are a number of parallels between the Scottish studies described above and the multiple-core work undertaken at Lough Augher, including: identification of small-scale variability; profile 'noise' superimposed on a basic identifiable temporal pattern; and the additional interpretative benefits of the multi-core approach, albeit with the inevitable loss of temporal resolution when producing full-basin records. However, the interpretation of multiple-core diatom data add an additional level of complexity while strongly making the case for a full-basin approach.

Small-scale spatial variability is important for multiple-core diatom studies. Diatom production in littoral areas of Augher was found to contribute more to littoral sediments and was underestimated in deep-water cores. Individual profundal cores also showed differences in both diatom percentages and accumulation rates for similar time zones (Anderson 1990b) and hence could not reflect changes in littoral production. Therefore, a whole basin approach was required to avoid the bias caused by using any one single core, whether deep-water or littoral. All Augher cores showed broadly similar compositional biostratigraphies, such that despite more strongly bioturbated plankton profiles in the littoral areas, the same approximate ecological interpretation of the eutrophication history of the lake could be made (Anderson 1989). A similar conclusion has been drawn from a more recent multiple-indicator (mites, chironomids, plant macrofossils) sediment study of five Norwegian lakes (Heggen et al. 2012). However, stratigraphic resolution and variability are functions of sediment mixing, accumulation rate and sampling interval (Anderson 1990b), and hence combining individual cores from Augher with higher sediment accumulation rates (and thereby greater temporal resolution) with those of lower resolution to produce a full-basin accumulation, resulted in the loss of temporal information. Indeed, although the Augher study found that a whole basin approach avoided the bias of single-core interpretation, no single core approximated to the basin mean (Anderson 1990b), emphasizing that generalization from a single core would be problematic.

A further development at Lough Augher involved the reconstruction of lake phosphorus loading using diatom-inferred total phosphorus concentration with the whole-lake-basin sediment accumulation rate as derived from these multiple cores (Rippey and Anderson 1996). This reconstruction is shown in Fig. 5. Lake phosphorus dynamics were also investigated, as changes to the efficiency of phosphorus sedimentation resulted from the increased loading from the effluent discharge. The multiple-core approach allowed an evaluation of whether littoral or profundal sedimentation was responsible for reduced sediment-P retention, with results identifying core sites shallower than 9.5-m depth being mainly responsible for lower sedimentation efficiency. The use of multi-core, whole-basin studies in this way to accurately record phosphorus retention in the lake indicates that problems arising from sediment diagenesis and phosphorus mobility were small.

Case study 3: Upper Mississippi River

Two natural impoundments on the upper Mississippi River provide an example of mass-balance paleolimnology applied on a much larger spatial scale than the

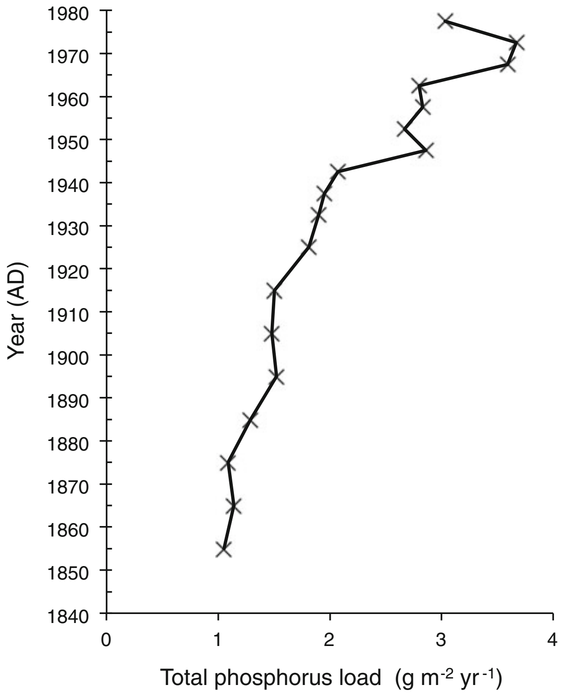


Fig. 5 Total phosphorus loading on Augher Lough from 1850 to 1980 reconstructed from the sediment record of seven cores. Redrawn from Rippey and Anderson (1996)

aforementioned case studies. The two lakes, formed at the end of the last glaciation by tributary alluvial damming (Blumentritt et al. 2009), provide an historic, paired-watershed experiment in which one (Lake Pepin) was strongly impacted by the combined effects of urbanization and extensive row-crop agriculture, and the other (Lake St. Croix), was affected by a far more limited set of land-use changes and is today a federally designated National Wild and Scenic River (Engstrom 2009). The combined watershed of these two river systems drains an area of 122,000 km^2, nearly half the state of Minnesota and a large portion of adjacent Wisconsin. The study of these large riverine lakes was initially aiming at quantifying historic inputs of sediment and phosphorus (Engstrom et al. 2009; Triplett et al. 2009), principally to establish natural background conditions (prior to Euro-American settlement) as a baseline for load reduction plans—technically known in the US as TMDLs (Total Maximum Daily Load). The investigations were ultimately expanded to include diatom productivity—as biogenic silica (bSi) (Triplett et al. 2008, 2012), heavy-metal pollution (Balogh et al. 1999, 2009, 2010), sediment-source fingerprinting (Belmont et al. 2011), and persistent organic pollutants including Triclosan (TCS) and TCS-derived dioxins (Buth et al. 2010).

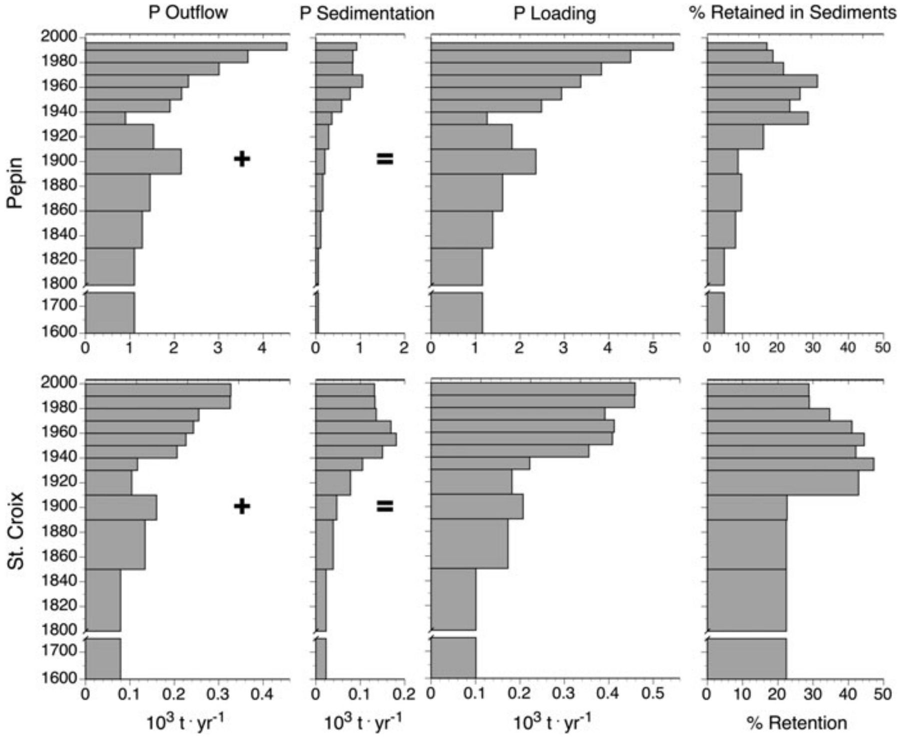
The first challenge for both lakes was to establish whole-lake sediment burial based on multiple cores (25 and 24 for Pepin and St. Croix, respectively) collected along sequential transects placed perpendicular to the linear flow axis of the basins. A selection of 8–10 master cores from each lake was dated using a combination of ^{210}Pb, ^{137}Cs, ^{14}C, pollen markers, and loss-on-ignition, and then cross-correlated with the secondary cores by whole-core magnetic susceptibility (Engstrom et al. 2009; Triplett et al. 2009). The use of multiple dating tools was essential for these systems given their extremely high sedimentation rates (1–2 cm year^{-1} in most cores) and the spatial and temporal complexity of deposition. Shifting patterns of sediment accumulation were clearly evident in both lakes, demonstrating the importance of the multi-core approach in quantifying actual sediment loads. The accuracy of these reconstructions was validated for recent decades by comparison with measured sediment loads from long-term river monitoring.

For Lake Pepin, present-day sediment accumulation approaches 10^6 t year^{-1}, exceeding pre-settlement rates (prior to 1830) by nearly an order of magnitude. Sediment fingerprinting showed that most (~85 %) of the sediment load, both past and present, originated in the Mississippi's highly agricultural tributary, the Minnesota River (Kelley and Nater 2000), but that the sources for the increased erosion had shifted over the last half century from predominantly agricultural fields to stream channels (Belmont et al. 2011), largely as a consequence of altered hydrology (agricultural drainage) and increased river flows. Lake St. Croix also showed increased sedimentation over time, but with modern rates (60,000 t year^{-1}) only a factor of 4× greater than pre-settlement rates, and lower by half than peak rates in the 1950s. More interestingly, and as revealed by the multiple-core approach, the 1950s peak in sediment accumulation was recorded only in the lower (downstream) half of the lake. The sudden input of these sediments was a consequence of channel destabilization and erosion of lithologically distinct sediments from small side-valley tributaries to the lake itself, as opposed to sediment delivered by the main-stem of the St. Croix River (Triplett et al. 2009). These tributary inputs have since abated, though the specific factors contributing to their initial mobilization are not clear.

As in the Lough Augher study, a phosphorus mass-balance was reconstructed for lakes Pepin and St. Croix by determining whole-lake sediment-P burial and P outflow losses and summing the two to determine historical P loads and in-lake retention (sedimentation) over time (Engstrom et al. 2009; Triplett et al. 2009). P burial rates were readily determined from whole-lake sediment accumulation and sediment-P concentrations, while P outflow was estimated from diatom-based TP reconstructions and more than a century of recorded river flows. Results show a 5× increase in P loads to Lake Pepin and a 2.5× increase to Lake St. Croix over the period of record (Fig. 6). However, the steepest rise in P loading was later than that for total sediment, especially in St. Croix where it began after 1940, likely owing to the mid-20th century introduction of industrial phosphate fertilizer. Phosphorus inputs have not abated in recent decades in either system, despite major reduction in P discharge from waste-water treatment plants, indicating the increasingly important role of non-point nutrient leakage from P-enriched agricultural soils. In both lakes, P sedimentation was a small part of the budget (10–40 %), with most of the influent P load exported through the outflow. Such results are expected given the short hydraulic residence times of these riverine systems (~7–30 days, depending on flow conditions). Both lakes showed approximately a doubling of sediment P retention over time, (a consequence of more rapid sediment burial), as opposed to the decrease in P retention in L. Augher, which was attributed to increased sediment-P release caused by eutrophication and bottom-water anoxia (Rippey and Anderson 1996).

The biological consequences of these increasing P loads were equally dramatic, with major changes in the composition of diatom communities (a classic shift from benthic to planktonic dominance) (Edlund et al. 2009; Engstrom et al. 2009) and a 10-fold increase in biogenic-Si (bSi) burial in Pepin and a 5× increase in St. Croix (Triplett et al. 2008, 2012). These bSi burial rates were combined with measured Si inflows (dissolved and bSi), and modeled estimates of catchment Si fluxes to determine historical changes in Si trapping (sediment burial). Results showed an exponential increase in Si trapping efficiency in each lake (2–5× in Lake St. Croix and 9–16× in Lake Pepin), indicating the extent to which eutrophication of riverine impoundments can reduce silica export to downstream coastal and marine systems.

Fig. 6 Phosphorus mass-balance for lakes Pepin and St. Croix on the upper Mississippi River. Reproduced from Engstrom et al. (2009) and Triplett et al. (2009)



The whole-basin sediment budgets for the two lakes also provided a ready framework for the reconstruction of pollutant-metal fluxes and their dominant sources (Balogh et al. 1999, 2009, 2010). While both lakes showed large increases in accumulation rates for Hg, Pb, Cd, Cr, Zn, and Ag since preindustrial times, the rise in Lake Pepin was far greater than that for Lake St. Croix, and most of the increase could thus be attributed to industrial and municipal waste-water discharges. In contrast, the metal inputs to Lake St. Croix tracked closely those of a nearby lake with no point-source inputs and thus appeared be largely atmospherically derived. However, secondary inputs from catchment erosion of side-valley tributaries, evident in cores from the lower half of Lake St. Croix, dominated during the mid-20th century. Present-day metal inputs to Lake Pepin have declined by as much as 70 % from peak loads in the late 1960s and early 1970s, primarily as a result of industrial cleanup efforts and improvements in wastewater treatment technologies. Metal inputs to Pepin today still greatly exceed rates attributable to direct atmospheric deposition, largely because of sustained high rates of erosion and the enhanced delivery of metals deposited atmospherically to catchment soils.

Conclusions

The flux of materials (water, solutes, particulates) and energy through a lake system is a fundamental measure of its ecological state and its response to anthropogenic and natural disturbance (Leavitt et al. 2009). Lake sediments record these fluxes both qualitatively, as changes in the composition of geochemical and biological tracers, as well as quantitatively, through changes in their rate of burial. Paleoecologists recognized early on the power of knowing rates of accumulation (as opposed to relative concentrations) (Davis and Deevey 1964; Livingstone 1957), but soon realized the complexity of lake sedimentation and the challenges of deriving whole-lake fluxes from single cores. Many subsequent multi-core studies, including those reviewed above, have shown that problems can arise from equating flux in a single core with that for the lake as a whole. In almost all cases, no single core site faithfully records the whole-basin, time-resolved inputs of materials, but rather all are biased as to overall lake-wide rate or its fluctuation over time. Yet many paleolimnological studies (including some by the authors of this review) interpret single-core accumulation rates as though they represented the lake/catchment system as a whole. Such interpretations are not automatically flawed, but they do require some consideration of the sedimentary processes that may bias individual cores. Partial solutions to these problems include focusing corrections based on ^{210}Pb flux, evaluation of concentration profiles, trend analysis using multiple lakes, and trend replication based on a small number of cores from the same lake.

The basis for ^{210}Pb focusing correction is described earlier in this paper. What is important to keep in mind is that it provides only a rough approximation, the reliability of which depends on several assumptions that are difficult to verify. It does not correct for temporal changes in the spatial pattern of sediment deposition, and it may not be appropriate for sediment constituents that focus differently from ^{210}Pb. Nonetheless, it can correct to some degree for large differences among lakes in focusing intensity, allowing for a more accurate comparison of material fluxes among lakes. The correction is more reasonably made for lakes in the same geographic region where a similar rate of atmospheric ^{210}Pb deposition can be assumed.

Material fluxes derived from single cores can be driven by short-term changes in the pattern of sediment deposition, as opposed to changes in the flux of materials to/from the lake as a whole. Although this is difficult to verify from a single core, Engstrom et al. (1991) have proposed that lake-wide changes in material input to a lake should appear as both a change in flux and a change in sediment concentration. This is especially so for sediment constituents that are delivered to the lake through a process that is different from that of the bulk sediment matrix—atmospheric metals, for example. Thus if a situation arises in which accumulation rates change but sediment concentrations remain constant, this would suggest that inputs to the lake have not changed, but rather the pattern of sediment focusing have shifted. In more general terms, both accumulation and concentration profiles need to be consulted to verify the likely mechanism for changes recorded at a single core site.

In some situations multiple lakes with single cores may represent a more effective strategy for evaluating flux changes than multiple cores from one or a few lakes. This alternative approach relies on the statistical power that derives from multiple units of study for which uncertainty (error) in any single unit is less important than the variability among sites and the need to scale up to a larger population or geographic region. In such cases, the time-resolved trends in flux for any given lake may be of less interest than the overall magnitude of change and how that varies among sites or regions subjected to different levels of environmental disturbance. Examples of this approach include the evaluation of atmospheric mercury deposition across large geographic regions (Drevnick et al. 2012a; Muir et al. 2009) or among lakes subject to different degrees of land-use change and atmospheric loading (Engstrom et al. 2007). Other examples include rates of carbon burial associated with cultural eutrophication and land-use change (Heathcote and Downing 2011). In such studies the signals of interest are large and resolvable against the uncertainty inherent in any individual core record.

Finally, and as mentioned earlier, compromises can be made on the number of cores analyzed in each lake, whereby time-resolved trends can be verified among a few widely spaced core sites, with focusing correction applied as needed based on ^{210}Pb flux. Several multi-core studies have demonstrated that if lake morphometry is relatively simple, as few as five well-placed cores can provide an accurate picture of lake-wide material flux over time. Other efficiencies are also possible, including cross-correlation of a single well-dated 'master' core with secondary cores by use of whole-core magnetic susceptibility. Such advances are encouraging, as they indicate that a more rigorous mass-balance approach to paleolimnology should be feasible, even when multiple lakes are involved.

Ultimately, the purpose of the multi-core approach is to allow the quantitative reconstruction of material flux through a lake ecosystem. From a neo-limnological perspective, sediment burial is often a secondary consideration, estimated crudely or derived by difference from measured contemporary fluxes. The ability of paleolimnology to accurately assess the sedimentary flux and extend the period of reference into the distant past is a tremendous contribution to the understanding of biogeochemical processes and their response to human and natural disturbance. It also links directly the sister disciplines of paleo- and neolimnology by placing historical and contemporary measures of material flow in the same basic framework. Such linkages clearly strengthen our ability to understand and manage the long-term effects of human disturbance on our aquatic environs.

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