CHAPTER 6

PATTERNS OF METAL DISTRIBUTION IN CONTEMPORARY FLOOD SEDIMENTS

6.1. INTRODUCTION

The previous chapters have demonstrated that, as a result of the long history of lead mining in the Swale catchment, large quantities of metal-rich sediment have been released into formerly mined tributaries and the floodplain of the trunk channel. Periods of high flow have long been recognised as important agents of metal transport in historically-mined rivers (*e.g.* Grimshaw *et al.*, 1976; Bradley and Lewin, 1982; Bird, 1987; Ciszewski, 2001). During flood events, sediment-associated metals are washed into the river system from normally stable sources such as spoil tips and the bed and banks of the channel, and subsequently deposited across the floodplain surface further downstream (*e.g.* Bradley, 1982; Bradley and Cox, 1986; Leenaers, 1989; Foster and Charlesworth, 1996). Flood sediments therefore play an important role in the cycling of metals through a river system, and are an invaluable indicator of sediment quality at their time of deposition (Leenaers *et al.*, 1988). Indeed, the transfer of metal-rich sediment from tributary and floodplain stores to the active channel and floodplain surface may have important implications for environmental quality, and may pose a serious hazard to crops and grazing livestock in agricultural catchments, particularly since they are exposed on the floodplain surface.

Previous geomorphological investigations in the Swale catchment reveal a long history of geomorphologically effective floods (Merrett and Macklin, 1999; Merrett, 2001). Severe floods recorded in the Swale catchment during the nineteenth and twentieth centuries caused extensive slope and bank erosion, and remobilised large volumes of metal-rich sediment (Pounder, 1989; Newson and Macklin, 1990; Macklin, 1997). It is likely that contemporary high flow events continue to remobilise metal-rich sediment from formerly mined tributaries and the bed and banks of the trunk channel and redeposit it on floodplain surfaces further downstream. Metal concentrations in these flood sediments are likely to be strongly influenced by the magnitude of the flood event, primarily through controlling the input of both metal-rich and 'clean' material from tributary and channel bank sources. However, previous investigations have demonstrated that the relationship between flood magnitude and metal concentrations in flood sediments is not simple, with concentrations both increasing (*e.g.* Williams *et al.*, 1966; Williams *et al.*, 1973) and decreasing (*e.g.* Bradley and Lewin, 1982; Bradley, 1984) with increasing discharge. This apparent variation is likely to be a function of variations in the supply of metal-rich sediments and in the degree of dilution with material from unmineralised sources.

This chapter aims to determine whether, more than a century after the cessation of mining, lead extraction and processing continue to have an impact on the River Swale catchment. Patterns of metal dispersal in overbank and channel-edge sediments deposited during flood events will be identified, and the potential sources of metal-rich sediment will be evaluated. The relationship between flood magnitude and metal concentrations in associated flood sediments will be evaluated, and the relative importance of metal-rich and uncontaminated sediment supply will be considered.

6.2. METHODS

6.2.1. Recent floods in the Swale catchment

In order to evaluate the influence of periods of high flow on metal dispersal in active fluvial sediments, it is necessary to consider events of varying duration and intensity. It is fortunate that a particularly severe period of flooding occurred during the course of this study, in autumn 2000. These events were selected for investigation due to their intensity and long duration, while two less severe periods of high flow were selected for comparison.

Severe flooding during the autumn of 2000 caused widespread damage throughout the British Isles, with southeast and northern England being particularly badly affected (Kelman, 2001). Discharge recorded at York on 4th November was the greatest for 375 years, with waters rising almost 5.5 m above normal levels (Rennard, 2000). The autumn 2000 floods were notable not only for their high discharge, but also for their duration. The most severe instances of flooding in the Yorkshire Ouse catchment occurred between 10th – 15th October, 28th October – 12th November, and 8th – 14th December 2000 (Kelman, 2001). The River Swale catchment was badly affected by the autumn 2000 floods; discharge data from Catterick Bridge (NGR SE 226993, catchment area 499 km^2), in the piedmont reach shows a maximum daily discharge of 350 m^3s^{-1} on 2nd November (Figure 6.1). However, this peak discharge is in itself not exceptional, with several larger events (50 - 120 m^3s^{-1} greater) recorded in the Catterick Bridge discharge data between 1993 and 2002. The frequency of large flood peaks and the duration of high flows are more exceptional, however, with the first flood peak on 7th October and the last on the 13th December (Figure 6.1).

Two less severe periods of flooding were selected for comparison to the autumn 2000 floods. The first period occurred between 21st November and 5th December 2001, and consisted of several distinct flood peaks in rapid succession (Figure 6.1). A maximum daily discharge of 210 m^3s^{-1} was recorded at Catterick Bridge on 5th December. The second, more severe period occurred between 20th January and 26th February 2002 (Figure 6.1). At least six distinct flood peaks occurred during this period, with a maximum daily discharge of 270 m^3s^{-1} recorded at Catterick Bridge on 25th February. These floods provided a range of erosional and depositional conditions, ranging from the short and moderate November-December 2001 events to the long and severe autumn 2000 floods.

6.2.2. Flood sediment: sampling and analysis

Samples of fine-grained overbank and channel-edge flood sediment were collected at 35 regularly spaced sites along the River Swale (Figure 6.2). Field sampling was undertaken as soon after the flood event as possible, to ensure that the sediment collected was deposited during the events in question. In the case of the autumn 2000 floods, there was a delay of several weeks before sampling could be undertaken. Sampling of deposits from the other two events was undertaken within two days of the flood waters receding. In the upland and piedmont zones, samples were taken between each tributary to enable sources of contaminated material to be identified. In the lower reaches of the river, where no new contaminated sediment is introduced by tributaries, the sampling interval was increased to *c.* 5 km.

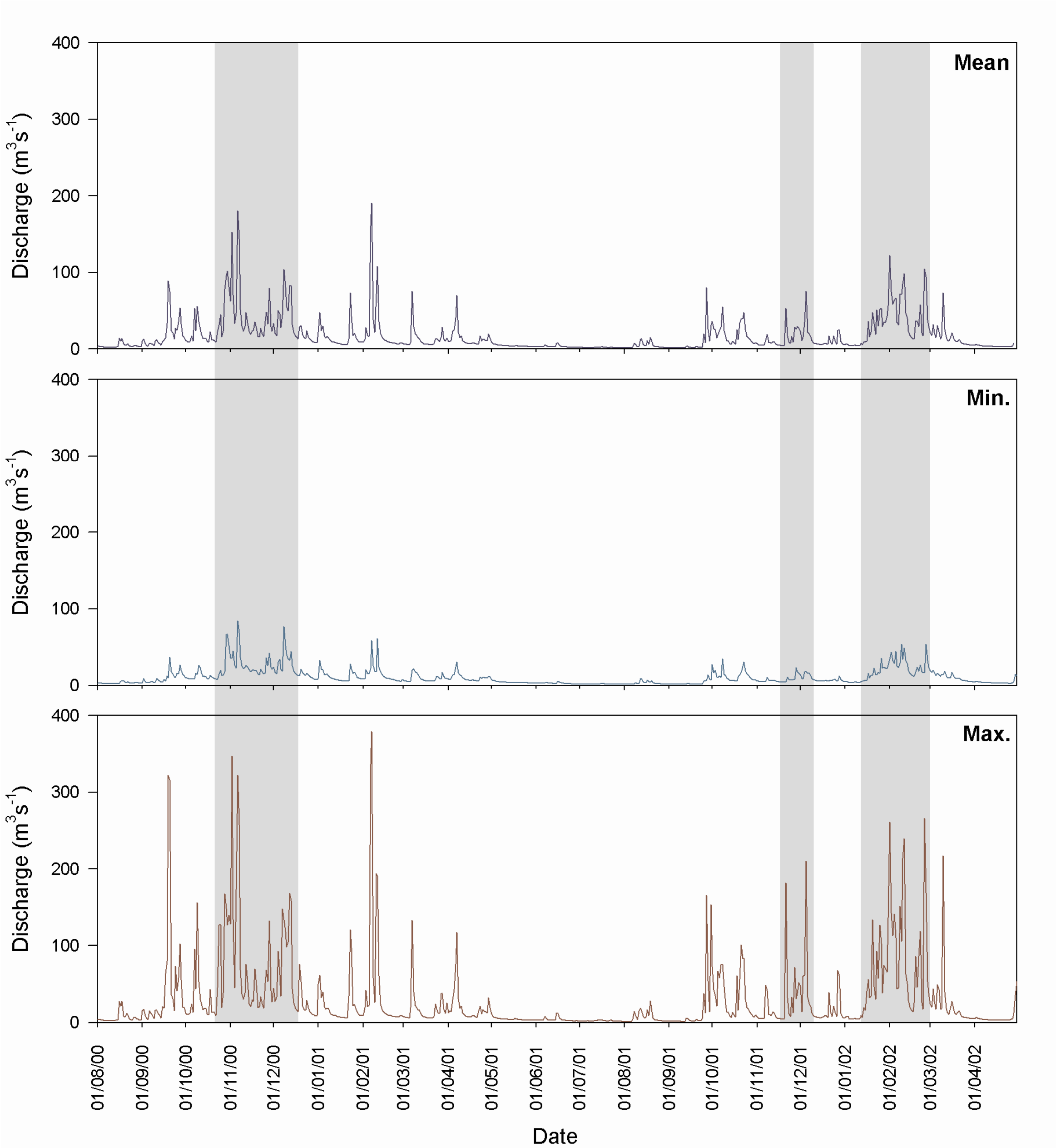

Figure 6.1: Mean, minimum and maximum daily discharge at Catterick Bridge gauging station. The periods of flooding included in this investigation are highlighted in grey

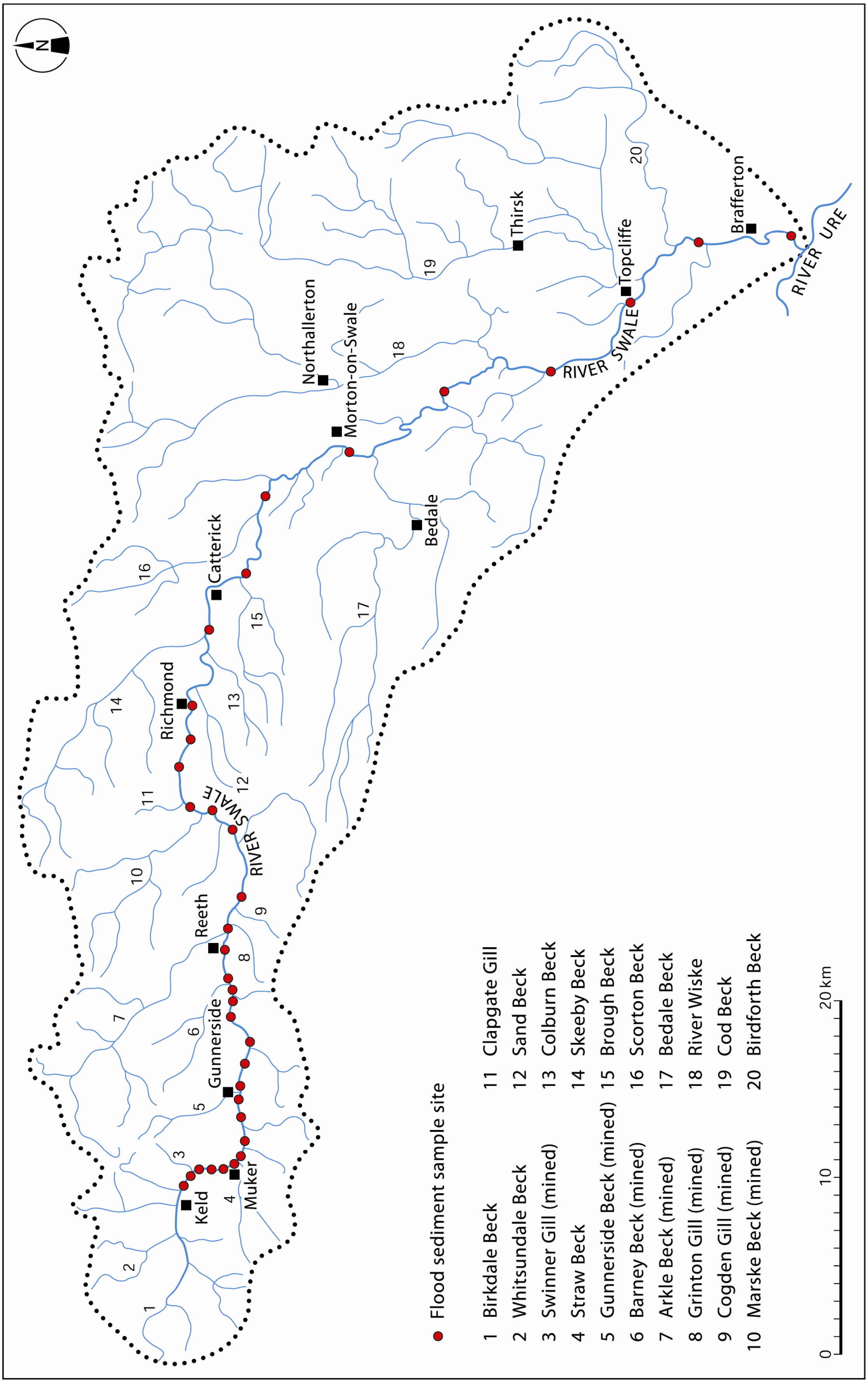

Figure 6.2: Map of the River Swale catchment, showing flood sediment sampling sites and the location of major tributaries

Overbank sediment deposited during the flood events was easily identifiable, since it was located on top of the riparian vegetation (Plate 6.1). This technique has been applied in a number of previous investigations into the characteristics of flood deposits (*e.g.* Walling *et al.*, 1998a). All overbank sediments were collected from within 10 metres of the bank line. The isolation of channel flood sediments was less simple, however. Many investigations into riverine metal transport have focussed on suspended sediment (*e.g.* Leenaers, 1989; Blake *et al.*, 2003; Nagorski *et al.*, 2003) or channel bed sediments (*e.g.* Moody *et al.*, 2000; Ciszewski, 2001; Marcus *et al.*, 2001). However, the need for a rapid and cost-effective technique to collect channel sediments at a large number of sites precluded the use of suspended sediment or bedload samplers. Instead, channel-edge sediment was collected from the edge and surface of gravel bars at each of the sampling sites. This material is likely to represent sediment that was active in the channel during high flow conditions, and deposited above the normal flow level on the receding limb of the flood event (*cf.* Swennen *et al.*, 1994). It is recognised, however, that this technique has a greater potential for uncertainty than automated flood-sediment sampling procedures.

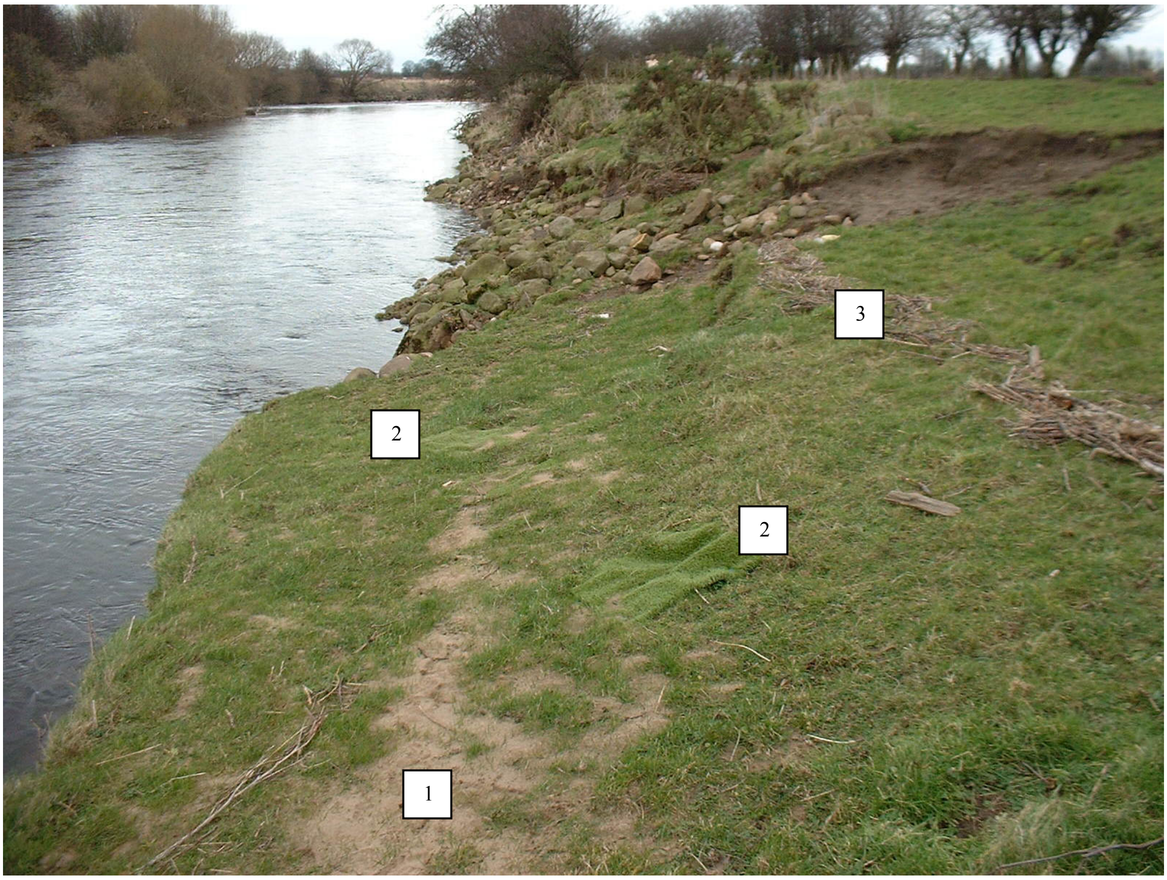

Plate 6.1: Overbank sediments deposited in January-February 2002 (1). Note the Astroturf sediment traps (2) and trash line indicating maximum water level (3)

The 2000-63 μm and <63 μm size fractions of each sample were digested in HNO_3 for one hour at 100°C prior to comprehensive geochemical analysis using ICP-MS. Full details of sample preparation and analysis can be found in Chapter 3. Full data are presented in Appendix 3. All geochemical data were incorporated into a GIS of the River Swale catchment to allow spatial trends of metal dispersal to be easily identified. Flood sediment data were compared to tributary metal concentrations (derived from BGS G-Base data and Chapter 4, this study) and floodplain metal concentrations (derived from various primary and secondary sources; see Chapter 5 for details) to allow the identification of potential sediment sources.

6.2.3. Measuring overbank metal deposition

A variety of techniques are available for use in the assessment of metal transport and deposition fluxes in fluvial sediments, including the sampling of suspended sediment (*e.g*. Horowitz, 1995; Walling *et al.*, 2003a) and the reconstruction of floodplain accumulation through dated sediment cores (*e.g*. Walling and Owens, 2002; 2003). An alternative approach is to measure the amount of sediment deposited during overbank flood events using sediment traps (*e.g*. Mansikkaniemi, 1985; Lambert and Walling, 1987; Asselman and Middelkoop, 1995). This technique has previously been applied to the calculation of overbank metal deposition rates in several U.K. river catchments (*e.g*. Walling and Owens, 2002; Walling *et al.*, 2003a). Sediment traps provide a simple and cost-effective method of measuring overbank metal deposition, and, unlike sediment cores, are not subject to complicating factors such as bioturbation and dating problems (*cf*. Foster and Lees, 1999; Walling *et al.*, 2003b). For these reasons, sediment traps were selected as the most suitable method of measuring metal deposition fluxes in the Swale catchment. A variety of different types of sediment trap have been employed in previous investigations, including plain plywood boards, plywood boards with 5 cm-long bristles attached to the surface, textured rubber mats, and Astroturf mats (*e.g*. Mansikkaniemi, 1985; Owens *et al.*, 2001; Walling and Owens, 2002; 2003; Walling *et al.*, 2003a). Astroturf mats with densely packed, 2 cm-long bristles were employed in this investigation, due to their ease of handling and efficient capture and retention of sediment (*cf*. Mansikkaniemi, 1985; Lambert and Walling, 1987).

In order to assess the metal deposition rates in the River Swale catchment, 50 by 50 cm squares of Astroturf were deployed at the 35 sites along the River Swale where flood sediment sampling was undertaken (Section 6.2.2 and Figure 6.2). Three sediment traps were attached to the floodplain surface at each site, adjacent to the river channel (Plate 6.1). The traps were put in place on 5th and 6th December 2001, and collected on 4th and 5th March 2002. Although there may have been several small overbank floods during this time period, the most significant events in terms of sediment delivery are likely to be the floods that occurred between 20th January and 26th February 2002 (Section 6.2.1 and Figure 6.1). Sediment traps were successfully recovered from 25 of the 35 sample sites. The remaining traps, primarily from the lower reaches of the river, were lost during the flood events.

Once collected, the sediment traps were stored individually in sealed polythene bags, and then oven dried at 40°C for 24 hours. The dry sediment was subsequently recovered from each trap using a stainless steel spatula (*cf.* Walling *et al.*, 2003a). All samples were passed through a stainless steel sieve with 2 mm aperture in order to remove vegetation fragments and (occasional) coarse particles. The <2 mm fraction was collected and weighed. Sub-samples from each mat were digested in HNO_3 at 100°C for 1 hour, prior to comprehensive geochemical analysis by ICP-MS. Full details of sample preparation and analysis can be found in Chapter 3. Total sediment accumulation for each sample site was calculated from the mean weight of sediment from each surviving mat. The resulting figure was then scaled up to provide a measure of sediment deposition in grams per m^2. The total amount of metal deposited at each site was calculated from the mean metal concentration (in mg kg^{-1}) and the amount of material deposited on the sediment traps (in g m^{-2}). Full data are presented in Appendix 3.

6.3. METAL DISTRIBUTION PATTERNS IN FLOOD SEDIMENTS

6.3.1. Introduction

The long history of metal mining in the Swale catchment (Section 2.2) suggests that channel-edge and overbank sediments deposited during periods of high flow are likely to contain high concentrations of metals such as Pb, Zn and Cd. This section aims to identify patterns of metal dispersal during the flood events that occurred during October-December 2000, November-December 2001 and January-February 2002.

6.3.2. October-December 2000 floods

6.3.2.1. Channel-edge sediment

Metal concentrations in channel-edge sediment associated with the October-December 2000 floods display a distinct downstream trend, characterised by a series of rapidly attenuating peaks followed by a more gradual downstream decline (Figure 6.3). Concentrations are initially low in the upper reaches of the Swale, before rising sharply 6 km downstream, close to the confluence with Swinner Gill. Two larger peaks can be observed 12 km and 20 km from the source, downstream of Gunnerside Beck and Barney Beck (reaching 20,300 mg kg^{-1} Pb in the <63 μm fraction and 1400 mg kg^{-1} in the 2000-63 μm fraction), respectively. Metal concentrations remain high further downstream, in a zone of the channel fed by Arkle Beck, Grinton Gill and Cogden Gill (8000 mg kg^{-1} Pb, 6500 mg kg^{-1} Zn and 29 mg kg^{-1} Cd in <63 μm sediments). A further peak, more pronounced in sediment from the <63 μm size-fraction, can be observed downstream of Marske Beck, approximately 40 km from the source.

Metal concentrations begin to fall and become less variable further downstream, as the river leaves formerly mined Swaledale and flows into the Vale of York (typically *c.* 1000 mg kg^{-1} Pb, <1000 mg kg^{-1} Zn and *c.* 3 mg kg^{-1} Cd in <63 μm sediments and <100 mg kg^{-1} Pb, <50 mg kg^{-1} Zn and <1 mg kg^{-1} Cd in 2000-63 μm sediments). This trend is most marked in the 2000-63 μm fraction. However, an extended zone of further metal enrichment can be observed 45 km downstream. At 80 km downstream, sediment from the <63 μm fraction displays a pronounced decrease in metal concentrations, while a small peak can be observed in material from the 2000-63 μm size-fraction. This site lies immediately downstream of Bedale Beck, an unmineralised tributary in the Vale of York.

6.3.2.2. Overbank sediment

Metal concentrations in overbank sediments deposited during the October-December 2000 floods display a similar pattern to those described for channel-edge deposits from the same events (Figure 6.4). Gradually rising metal concentrations are punctuated by a series of sharp peaks 6, 12 and 20 km from the source, downstream of Swinner Gill, Gunnerside Beck (5600 mg kg^{-1} Pb, 14,000 mg kg^{-1} Zn and 29 mg kg^{-1} Cd in <63 μm sediments) and Barney Beck (with Pb reaching 19,400 mg kg^{-1} in <63 μm sediments and 8500 mg kg^{-1} in

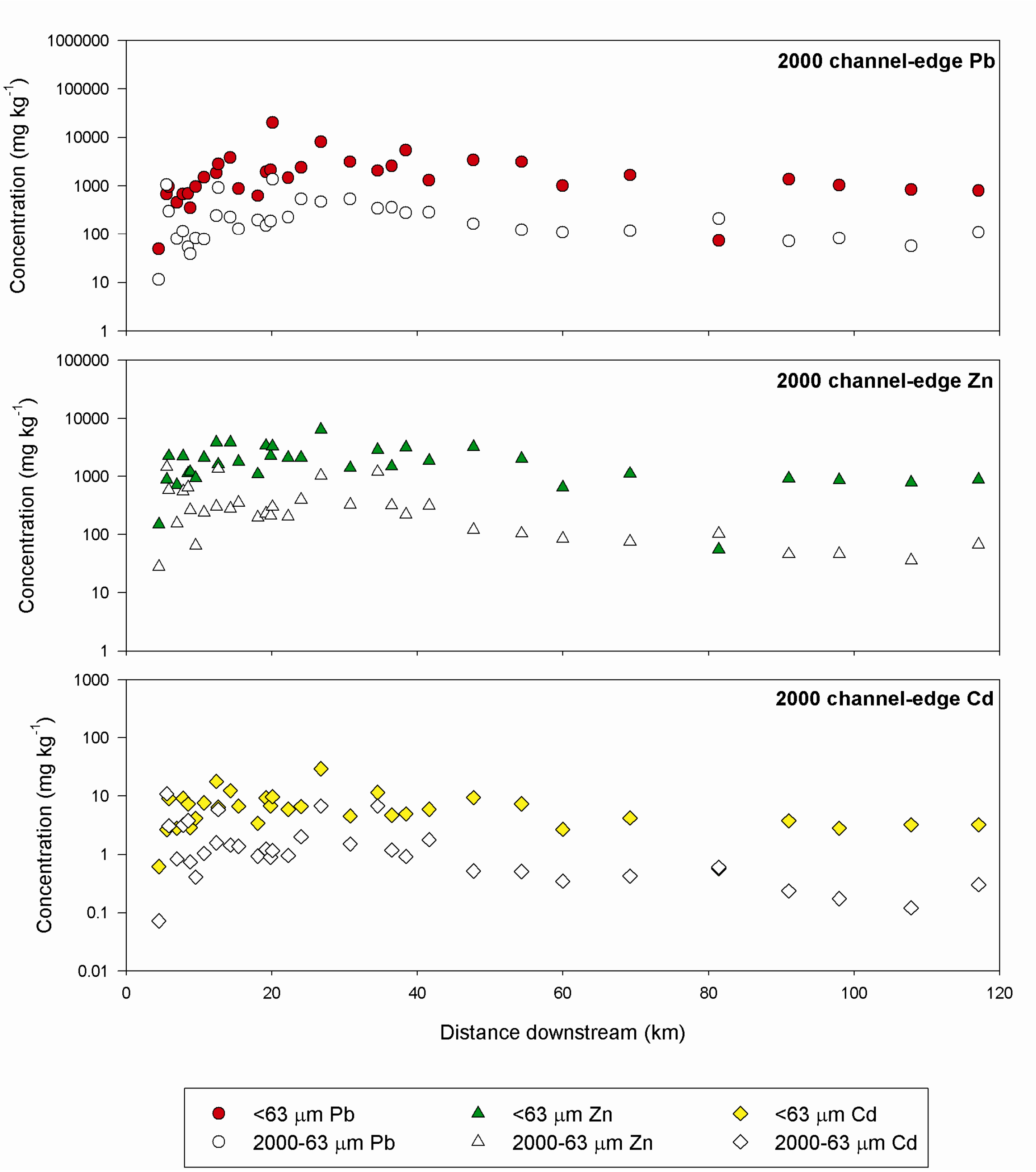

Figure 6.3: Pb, Zn and Cd concentrations in 2000 channel-edge flood sediment

2000-63 µm sediments), respectively. A prolonged zone of enriched metal concentrations can be observed in the <63 µm fraction downstream of Arkle Beck, Grinton Gill and Cogden Gill, approximately 25 km. This is manifested as a single peak in the 2000-63 µm fraction, however. Concentrations remain elevated further downstream, with a small peak at 40 km. Downstream of this point, metal concentrations begin to gradually decline (falling to <1500 mg kg^{-1} Pb, <1000 mg kg^{-1} Zn and *c.* 3 mg kg^{-1} Cd in the <63 µm fraction and <150 mg kg^{-1} Pb, <50 mg kg^{-1} Zn and <1 mg kg^{-1} Cd in the 2000-63 µm fraction). However, a further zone of enrichment can be observed approximately 60 km downstream, with a small peak in the 2000-63 µm size-fraction approximately 110 km from the source.

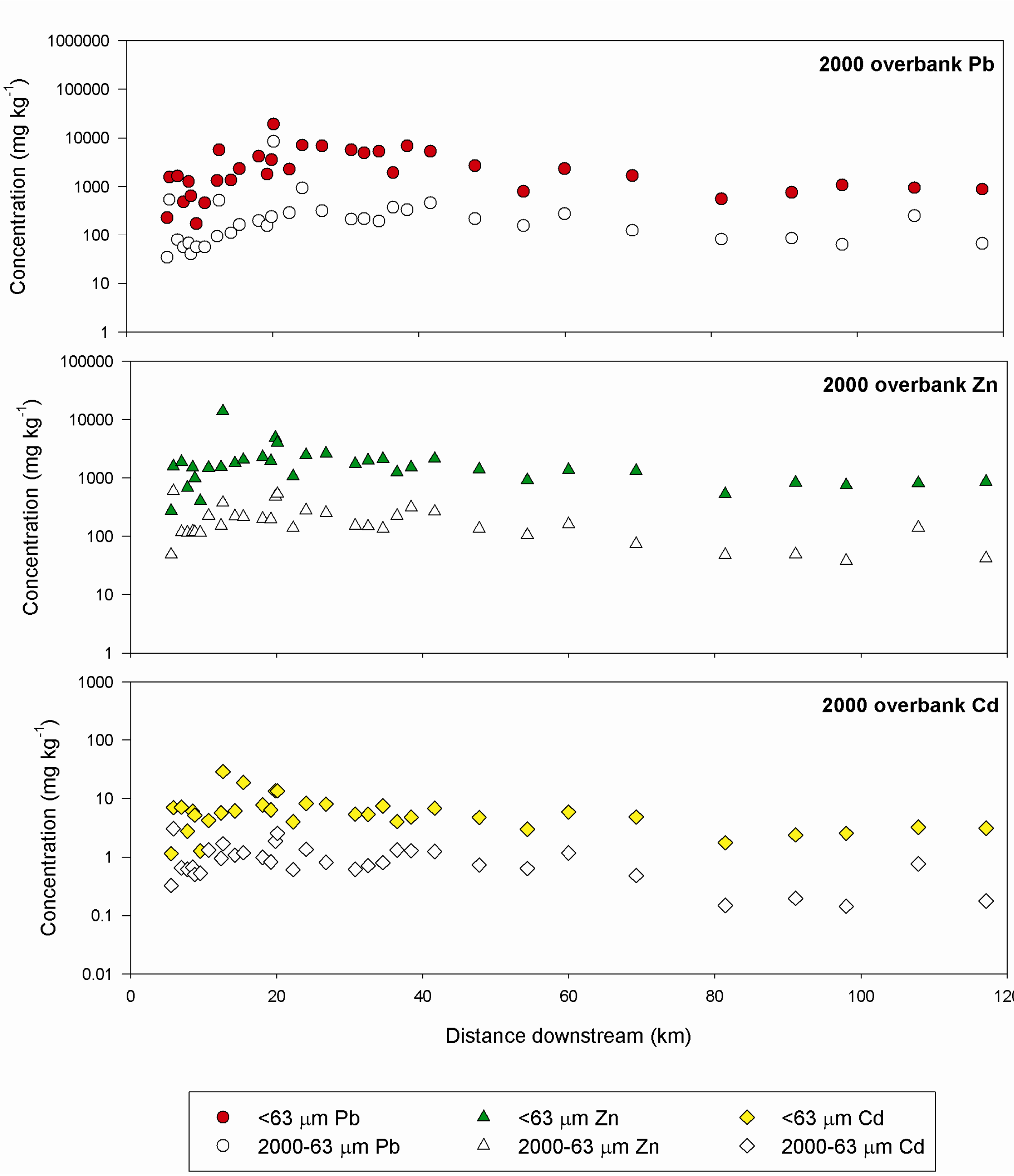

Figure 6.4: Pb, Zn and Cd concentrations in 2000 overbank flood sediment

6.3.3. November-December 2001 floods

6.3.3.1. Channel-edge sediment

Metal concentrations in channel-edge sediment deposited during the November-December 2001 flood events display broadly similar patterns of downstream variation as those associated with the October-November 2000 floods (Figure 6.5). Concentrations are low in the headwaters of the Swale, before reaching a small peak downstream of Swinner Gill, approximately 6 km from the source. A larger peak in metal concentrations can be observed 12 km downstream, shortly after the confluence between Gunnerside Beck and the main River Swale (reaching 24,800 mg kg^{-1} Pb and 12,500 mg kg^{-1} Zn in the 2000-63 μm fraction). Concentrations decline rapidly with distance downstream, before peaking once more approximately 20 km downstream, downstream of Barney Beck (12,800 mg kg^{-1} Pb, 6200 mg kg^{-1} Zn and 20 mg kg^{-1} Cd in <63 μm sediments and 4600 mg kg^{-1} Pb, 4200 mg kg^{-1} Zn and 34 mg kg^{-1} Cd in 2000-63 μm sediments). This peak is closely followed by another, considerably smaller, peak at 25 km, downstream of Arkle Beck, Grinton Gill and Cogden Gill. A final peak can be observed 40 km downstream, after which metal concentrations decline slightly and remain relatively stable in the upper part of the Vale of York.

6.3.3.2. Overbank sediment

Overbank sediments from the November-December 2001 floods again show a similar downstream pattern to that described for channel-edge sediment deposited during the same events (Figure 6.6). Low metal concentrations in the headwaters of the Swale increase further downstream, with a series of rapidly attenuating peaks observed at 6, 12 and 20 km, downstream of Swinner Gill, Gunnerside Beck and Barney Beck, respectively. The latter is most marked in the <63 μm fraction, with Pb, Zn and Cd concentrations reaching 95,100 mg kg^{-1}, 29,400 mg kg^{-1} and 97 mg kg^{-1}, respectively. A more sustained but considerably smaller increase in metal concentrations occurs 25 km from the source, downstream of Arkle Beck, Grinton Gill and Cogden Gill. Metal concentrations increase gradually further downstream, reaching a small peak at approximately 45 km. Concentrations gradually decline further downstream, and become less variable in the lower reaches of the Swale (<1500 mg kg^{-1} Pb, <1000 mg kg^{-1} Zn and *c.* 2 mg kg^{-1} Cd in the <63 μm fraction and <300 mg kg^{-1} Pb and Zn and *c.* 1 mg kg^{-1} Cd in the 2000-63 μm

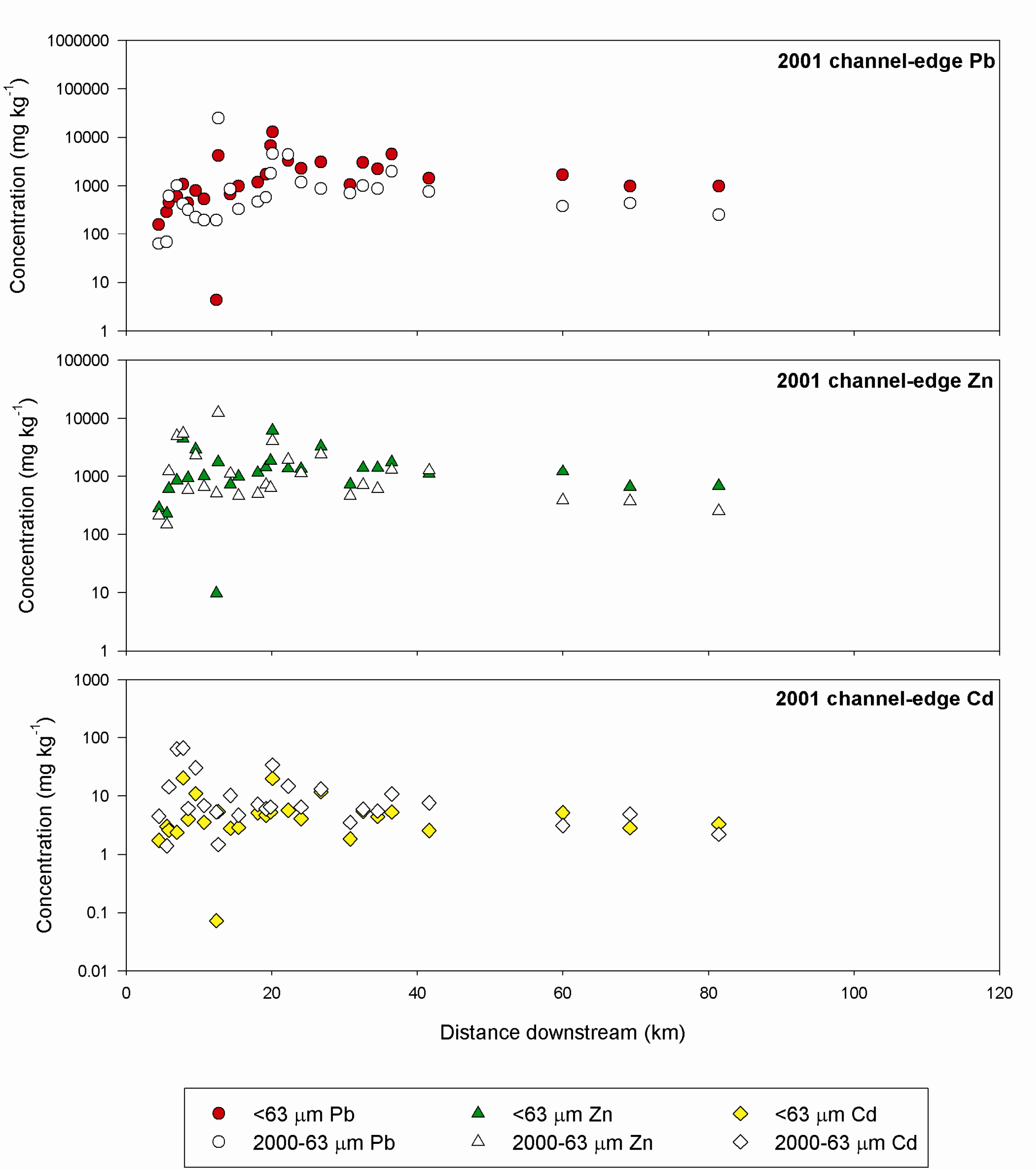

Figure 6.5: Pb, Zn and Cd concentrations in 2001 channel-edge flood sediment

fraction). A final peak in metal concentrations, most markedly for Cd, can be observed in the 2000-63 µm size-fraction 110 km downstream (5 mg kg^{-1}). Conversely, Pb and Zn concentrations decrease markedly in <63 µm sediments at this point.

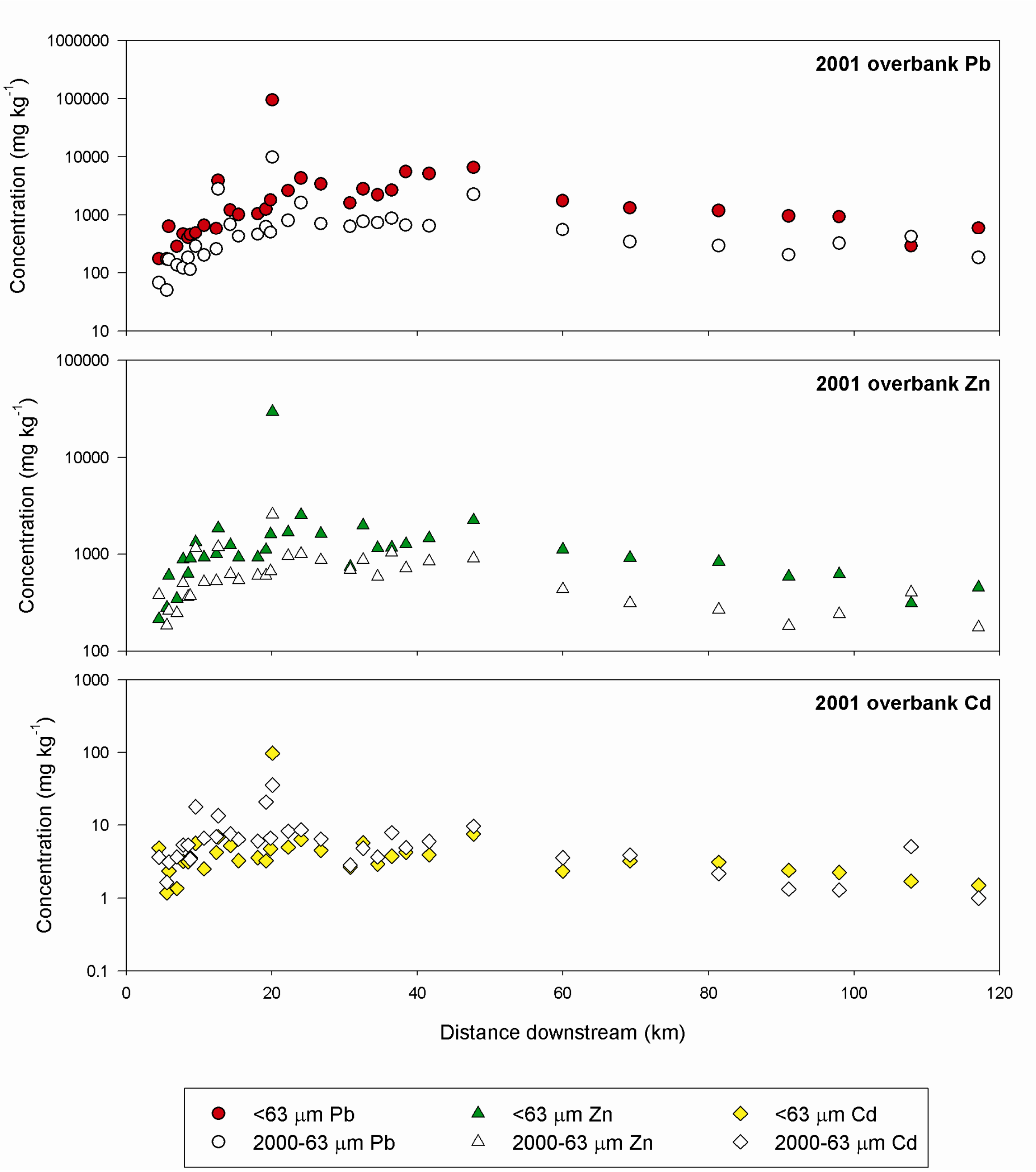

Figure 6.6: Pb, Zn and Cd concentrations in 2001 overbank flood sediment

6.3.4. January-February 2002 floods

6.3.4.1. Channel-edge sediment

Metal concentrations in channel-edge sediment deposited during the January-February 2002 floods display similar downstream patterns to those described for the 2000 and 2001 floods (Figure 6.7). Metal concentrations are low in the headwaters of the Swale, and

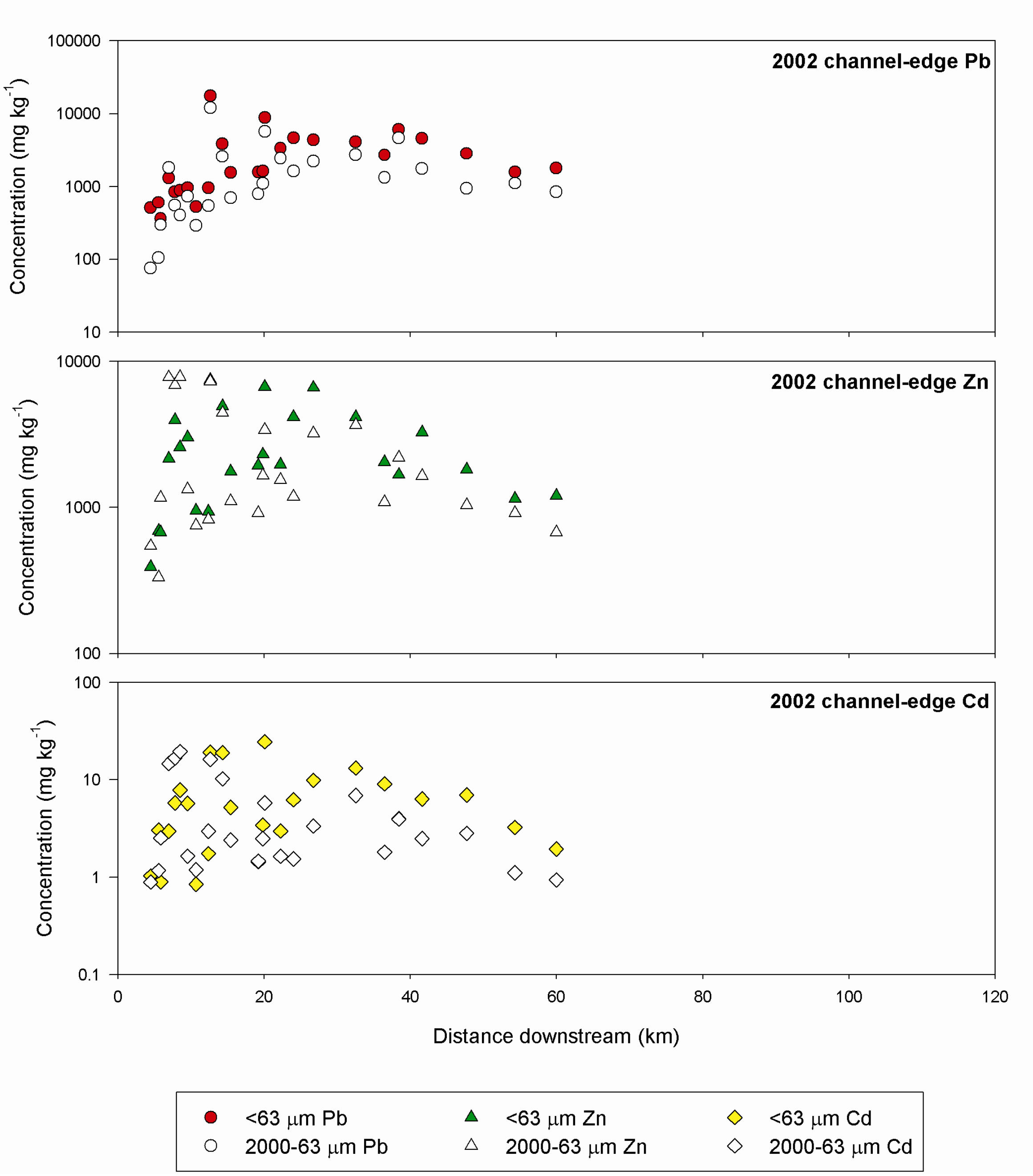

Figure 6.7: Pb, Zn and Cd concentrations in 2002 channel-edge flood sediment

increase markedly further downstream. Large, rapidly attenuating peaks in metal concentrations can be observed at 6, 12 and 20 km, downstream of Swinner Gill, Gunnerside Beck (reaching 17,400 mg kg^{-1} Pb, 7400 mg kg^{-1} Zn and 19 mg kg^{-1} Cd in <63 μm sediments and 12,100 mg kg^{-1} Pb, 7300 mg kg^{-1} Zn and 16 mg kg^{-1} Cd in 2000-63 μm sediments) and Barney Beck, respectively. A lower but more prolonged increase in metal concentrations can be observed 25 km from the source, downstream of Arkle Beck, Grinton Gill and Cogden Gill. A final peak can be observed approximately 40 km downstream, after which metal concentrations gradually decline as the river enters the Vale of York.

6.3.4.2. Overbank sediment

Metal concentrations in overbank sediment from the January-February 2002 floods display a broadly similar pattern to that described form channel-edge sediment from the same events (Figure 6.8). Concentrations are low in the uppermost reach of the Swale, rising steadily with distance downstream. Large, rapidly attenuating peaks in metal concentrations can be observed at 12 and 20 km, downstream of Gunnerside Beck and Barney Beck (22,600 mg kg^{-1} Pb, 6200 mg kg^{-1} Zn and 19 mg kg^{-1} Cd in the <63 μm fraction), respectively. Two lower, more sustained peaks in metal concentrations can be observed 25 and 35 km from the source, downstream of Arkle Beck, Grinton Gill and Cogden Gill, and Marske Beck, respectively. A much sharper peak in Zn concentrations can be observed in <63 μm sediment immediately downstream of Marske (6200 mg kg^{-1} in <63 μm sediments and 4000 mg kg^{-1} in 2000-63 μm sediments). Metal concentrations become less variable and gradually decline with distance downstream in the lower reaches of the river. Two small peaks in Cd concentrations in the <63 μm size fraction can be observed at 90 and 110 km (3 mg kg^{-1}). A corresponding peak in concentrations of Zn and Cd can be observed in 2000-63 μm sediments 110 km downstream.

6.3.5. Grain size partitioning in flood sediments

Channel and overbank sediments from the 2000, 2001 and 2002 floods are dominated by sand-sized material (2000-63 μm) (Figures 6.9 and 6.10). Proportions of silt and clay-sized sediment (<63 μm) are generally low; channel-edge sediments from the 2000, 2001 and 2002 flood events are comprised of between 0.15 – 56 %, 0.24 – 20 % and 0.25 – 10 % silts and clays, respectively. The finer fraction makes up 0.8 – 39 %, 0.26 – 19 % and 0.42 - 31 % of sediment from the 2000, 2001 and 2002 floods, respectively. These proportions are broadly similar to those reported by Walling *et al*. (1998a) for the wider Yorkshire Ouse catchment. These patterns show that overbank sediments are slightly finer than channel sediments, reflecting the preferential transport of silts and clays in the suspended load of the river (Horowitz, 1995). Material deposited during the 2000 floods contains a slightly higher proportion of <63 μm sediment than that deposited during the

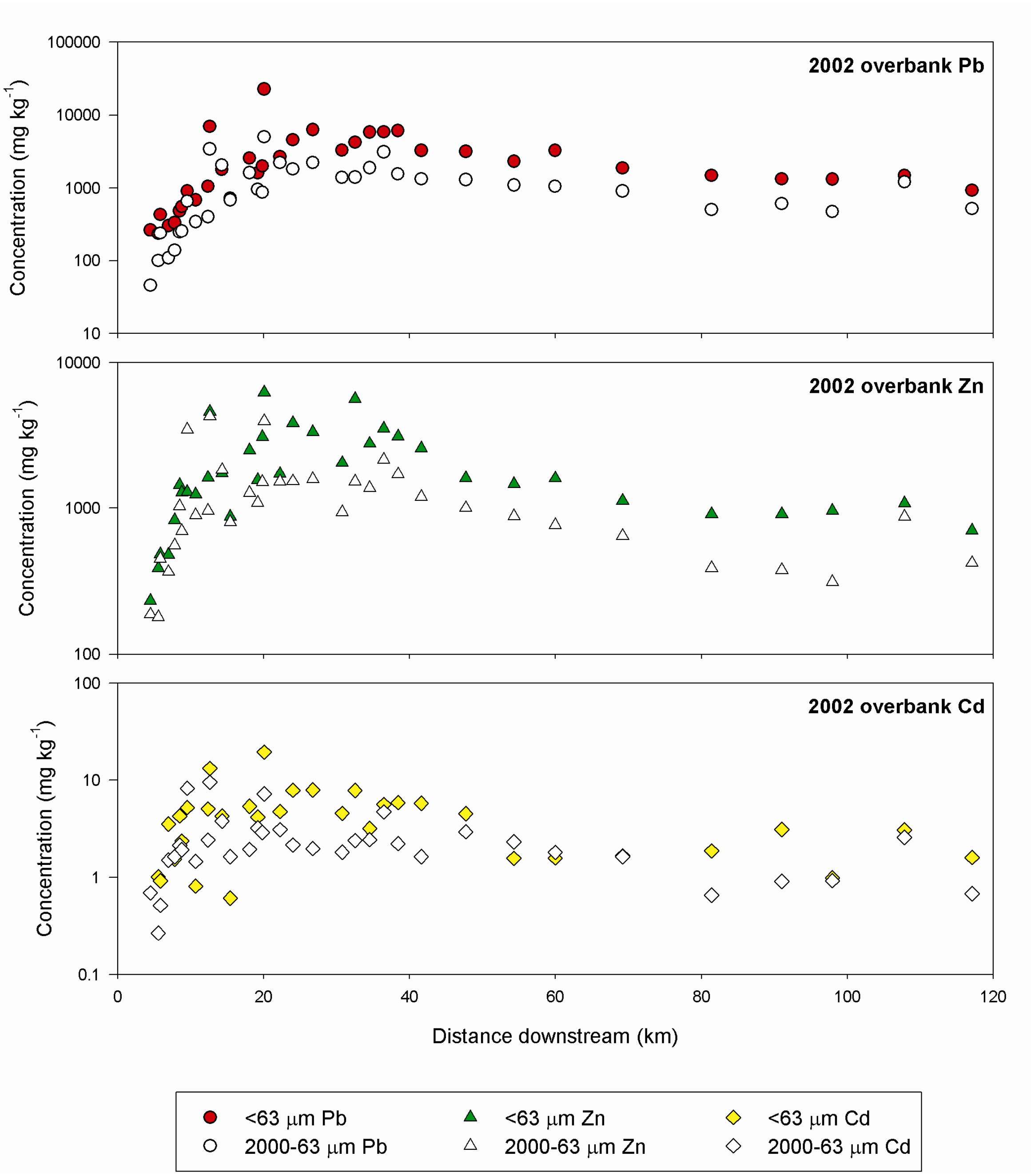

Figure 6.8: Pb, Zn and Cd concentrations in 2002 overbank flood sediment

later events. This is likely to reflect the greater in-wash of fine sediment from catchment sources during the larger floods, although it should be noted that, in the case of channel-edge sediments, the silt and clay-rich sediments from the lower reaches of the Swale are absent from the 2001 and 2002 data sets.

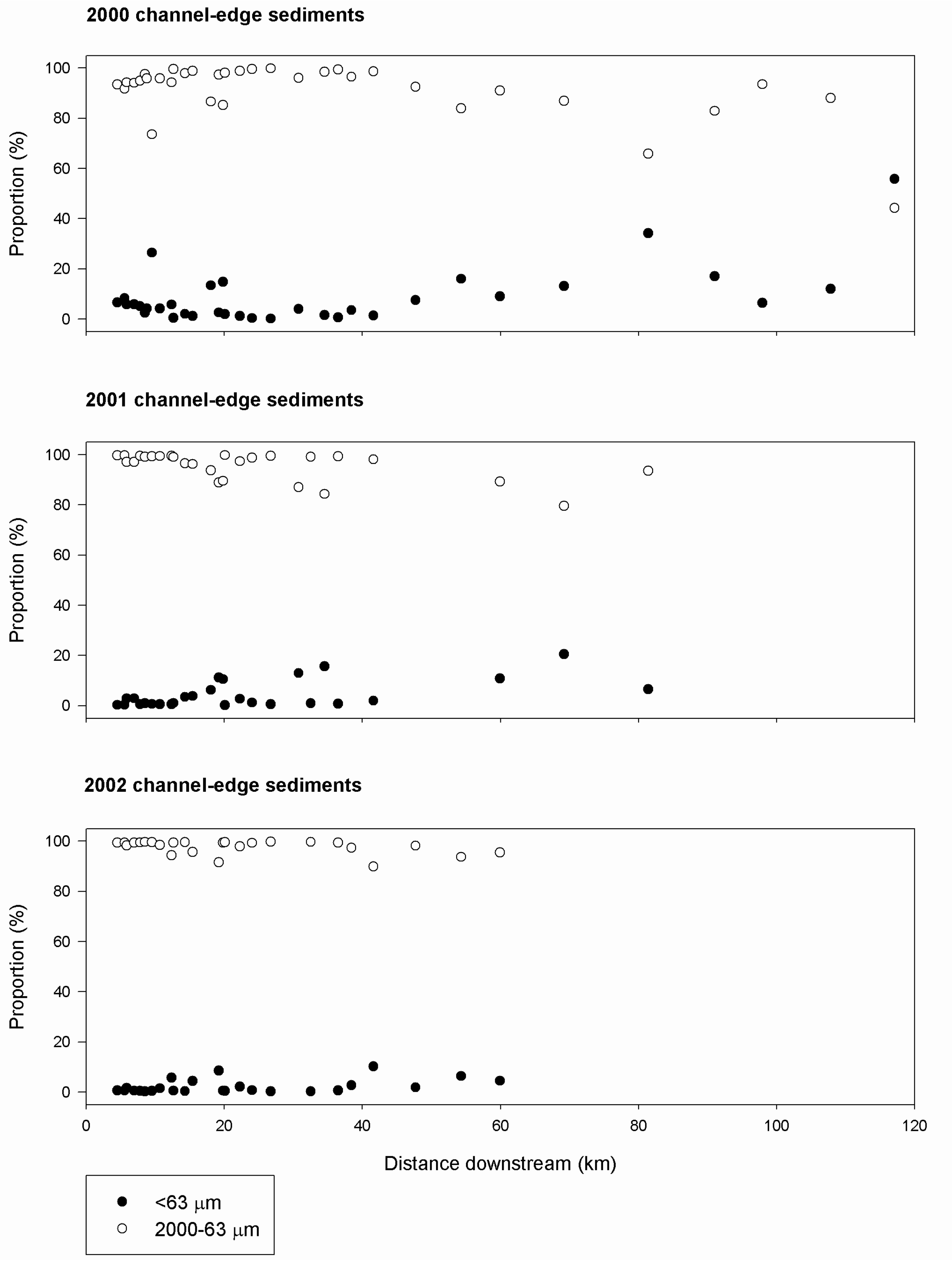

Figure 6.9: Grain size characteristics of channel-edge flood sediments

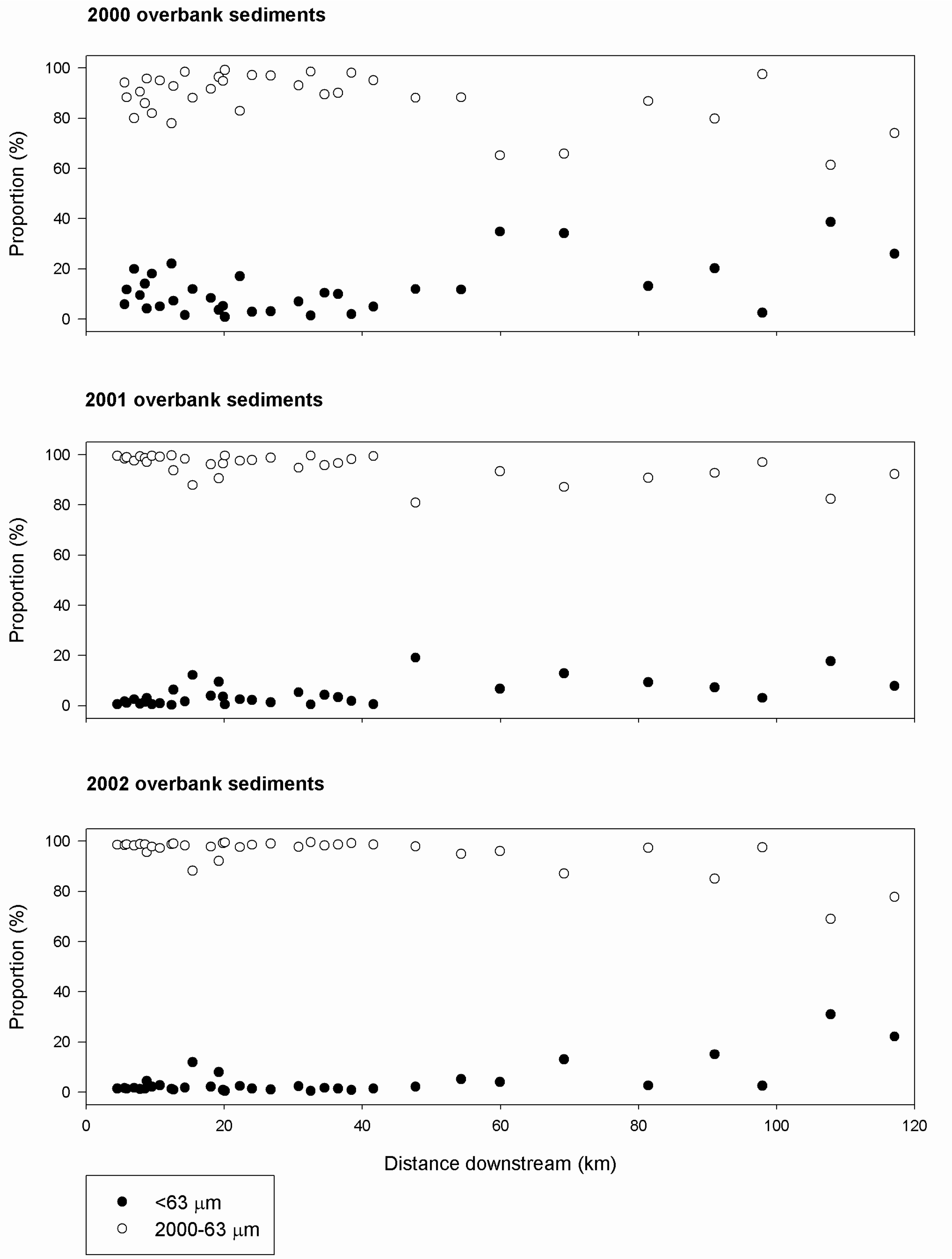

Figure 6.10: Grain size characteristics of overbank flood sediments

Despite differences in the proportions of silt and clay and fine sand, flood sediments from the 2000, 2001 and 2002 events display a similar downstream trend. With the exception of overbank sediments deposited between October and December 2000, flood sediments contain a low proportion of silts and clays in the upper reaches of the River Swale. Increases in the amount of sediment derived from the <63 μm fraction can be observed between 12 and 20 km downstream, approximately 35 km downstream, and in the lower reaches of the river, in the Vale of York. It is likely that the former two increases are a result of the input of fine-grained sediment from tributaries such as Gunnerside Beck, Barney Beck and Marske Beck, while the increase in the lower reaches reflects the operation of downstream fining processes such as selective deposition, abrasion and hydraulic sorting (*e.g.* Reid *et al.*, 1997; Rice, 1999; Moussavi-Harami *et al.*, 2004).

Metal concentrations in both channel-edge and overbank flood sediments are considerably higher in <63 μm sediments than in the coarser size fraction. A similar pattern has been widely documented (Macklin, 1996; Miller, 1997), and reflects the high affinity of metals to particles in this size fraction (Gibbs, 1973; Förstner and Wittmann, 1979; Salomons and Förstner, 1984; Horowitz, 1991). This pattern is most accentuated in sediment from the autumn 2000 floods, possibly reflecting the greater proportion of finer material in sediment deposited during these flood events. Some of the larger peaks in Zn and Cd concentrations in sediment deposited during the 2001 and 2002 floods, however, are observed in the 2000-63 μm size fraction. This may be attributable to the presence of coarse mineral grains and waste materials derived from dressing floors and spoil tips, and, in the case of Cd, an enhanced affinity for the sand size fraction (Jain and Ali, 2000). Such particles may have been dispersed further or diluted more during the larger 2000 floods.

6.3.6 Metal deposition on the River Swale floodplain

Volumes of overbank sediment deposition reconstructed from floodplain sediment traps suggest that there is a distinct downstream trend along the River Swale (Figure 6.11 and Appendix 3). Total sediment accumulation is generally low in the upper reaches of the river, and gradually increases with distance downstream. Localised peaks in sediment deposition can be observed approximately 12, 20 and 35 km from the source, downstream of Gunnerside Beck, Barney Beck, and Marske Beck, respectively. High deposition rates can also be observed in the most downstream sample, approximately 85 km from the source. This may reflect locally high deposition rates, but is more likely to reflect enhanced sediment accumulation in the lower reaches of the river. Low rates of overbank

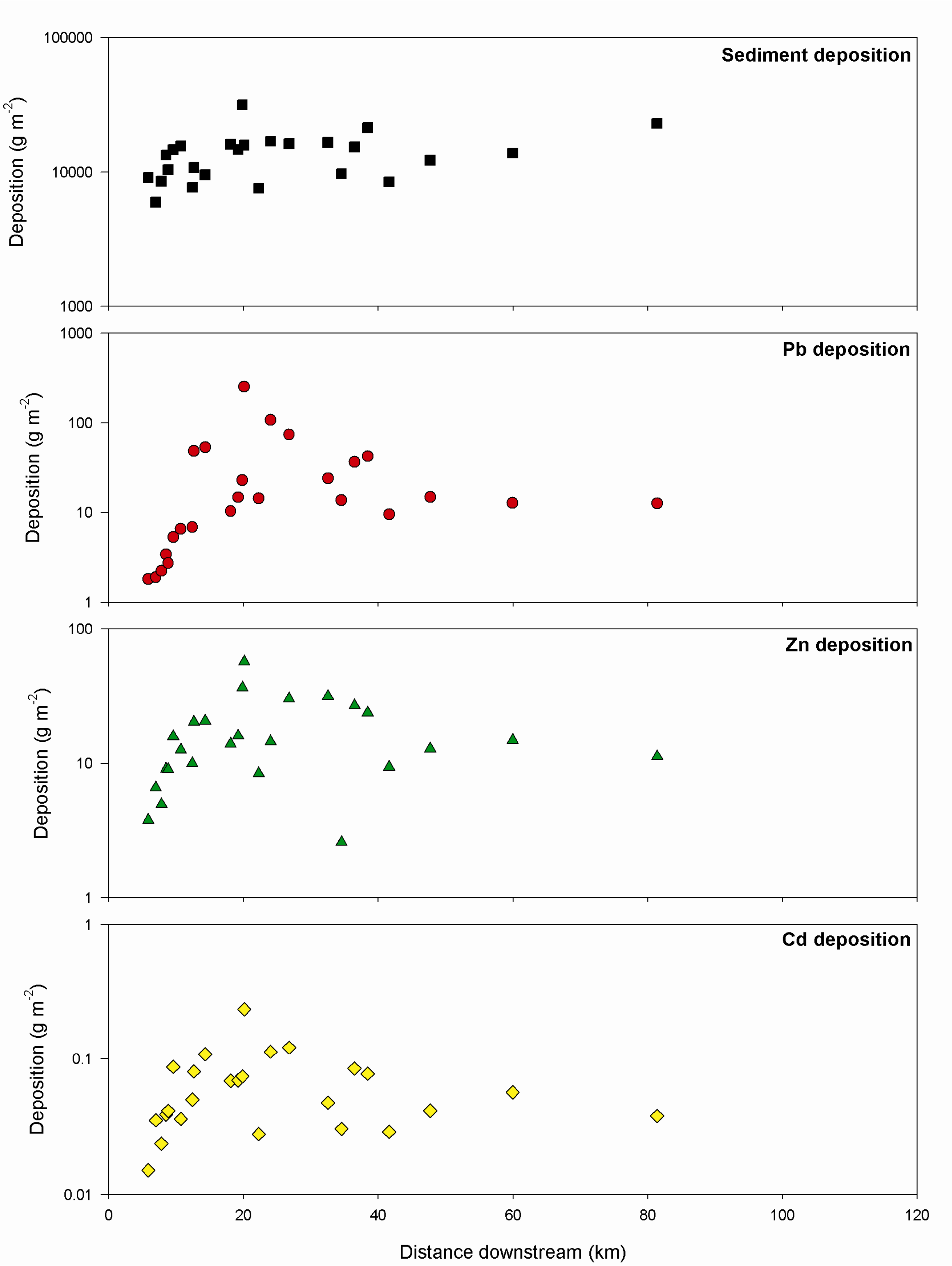

Figure 6.11: Overbank sediment and metal deposition along the River Swale (Dec. 2001 – March 2002)

sedimentation are apparent immediately upstream of Gunnerside Beck, *c*. 2 km downstream of Barney Beck, and between 40 and 50 km downstream. These troughs are coincident with locally narrow floodplain reaches.

Like total sediment deposition, metal accumulation rates also display a distinct downstream trend (Figure 6.11). Pb, Zn and Cd accumulation is generally low in the most upstream reach of the river. A series of peaks of increasing magnitude can be observed approximately 6, 12 and 20 km downstream. These rapidly attenuating peaks are likely to coincide with the input of metal-rich sediment from Swinner Gill, Gunnerside Beck and Barney Beck, respectively. More sustained metal deposition can be observed approximately 25 km from the source, downstream of Arkle Beck, Grinton Gill and Cogden Beck. A final peak in metal accumulation, attributable to the input of material from Marske Beck, can be observed approximately 35 km downstream. Rates of metal deposition generally become more stable in the lower reaches of the river, although there may be insufficient data to accurately identify large-scale trends.

This indicates that large quantities of metal-rich sediment continue to be deposited on the floodplain surface during periods of overbank flow. Indeed, the data suggest that, on average, the Swale floodplain received 31.85 g m^{-2} Pb, 16.89 g m^{-2} Zn and 0.07 g m^{-2} Cd between December 2001 and March 2002 (Appendix 3). Further downstream, the contribution of material remobilised from floodplain storage is likely to become more important. However, the data presented in this section are representative of floodplain metal accumulation over a three month period, during which a number of large overbank floods occurred. It is therefore not appropriate to extrapolate these results to produce detailed estimates that are representative of floodplain metal accumulation over longer time scales. However, Walling and Owens (2002; 2003) and Walling *et al*. (2003a) have produced annual estimates of floodplain storage and deposition in channel and overbank sediments from the catchment. A series of sediment traps and ^{137}Cs cores were used to reconstruct annual deposition fluxes between December 1997 and December 1999. The results of this procedure suggest that, as might be expected, metal deposition fluxes generally increase with distance downstream. However, maximum deposition occurs in the middle reaches of the river (*cf*. erosion, Lawler *et al.*, 1999). The Swale floodplain as a whole has received on average 24.49 t a^{-1} Pb and 17.50 kg a^{-1} Zn, which account for 45 and 35 % of the total load, respectively (Walling and Owens, 2002; 2003). Within individual reaches, mean annual metal deposition fluxes for Pb are between 5.67 and

16.70 g m^{-2}, while Zn fluxes range from 9.44 to 13.90 g m^{-2} (Walling *et al.*, 2003a). These rates are considerably lower than those recorded along much of the floodplain between December 2001 and March 2002, suggesting that the flood events that occurred during this period were considerably larger than any that occurred between December 1997 and December 1999. Despite these apparent discrepancies, these data confirm that significant quantities of metal-rich sediment are removed from storage in tributaries and the floodplain and redeposited on the floodplain surface during overbank flood events.

6.3.7. Summary: Metal distribution patterns in flood sediments

This section demonstrates that overbank and channel-edge sediment deposited during floods in 2000, 2001 and 2002 contains high concentrations of Pb, Zn and Cd. Both metal concentrations and deposition rates are low in the uppermost reaches of the Swale, followed by a series of large, rapidly attenuating peaks in the mining area of Swaledale. Concentrations and accumulation rates remain elevated for a considerable distance downstream, although a gradual decline can be observed as the river flows through the Vale of York. Sediment-associated metals from the three flood periods display a similar downstream dispersal pattern, particularly in material from the <63 μm fraction (Figures 6.12 to 6.14). More pronounced, however, are the variations in metal concentrations between the three sets of flood deposits. These are greatest in sediment from the 2002 floods, and lowest in 2000 flood sediment.

It is likely that downstream patterns of metal transport and deposition in flood sediments are controlled by factors such as the location of metal-rich and uncontaminated sediment inputs, downstream transport mechanisms, and the geomorphological characteristics of the channel and valley floor. However, the differences in metal concentrations between each set of flood deposits suggest that variations in flood magnitude may influence the operation and interplay of these controls. The likely influence of these controlling factors will be discussed in subsequent sections.

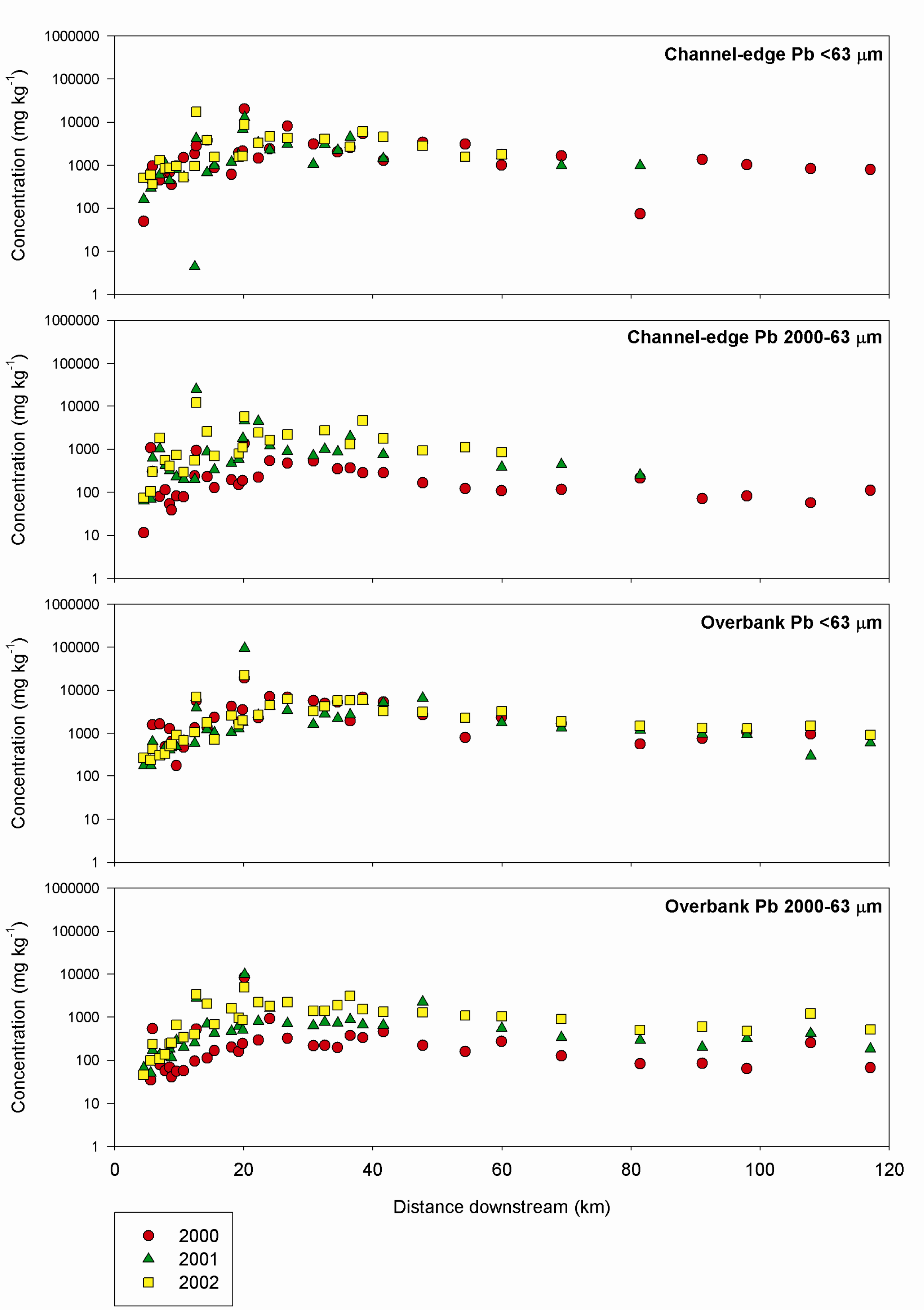

Figure 6.12: Pb concentrations in 2000, 2001 and 2002 flood sediments

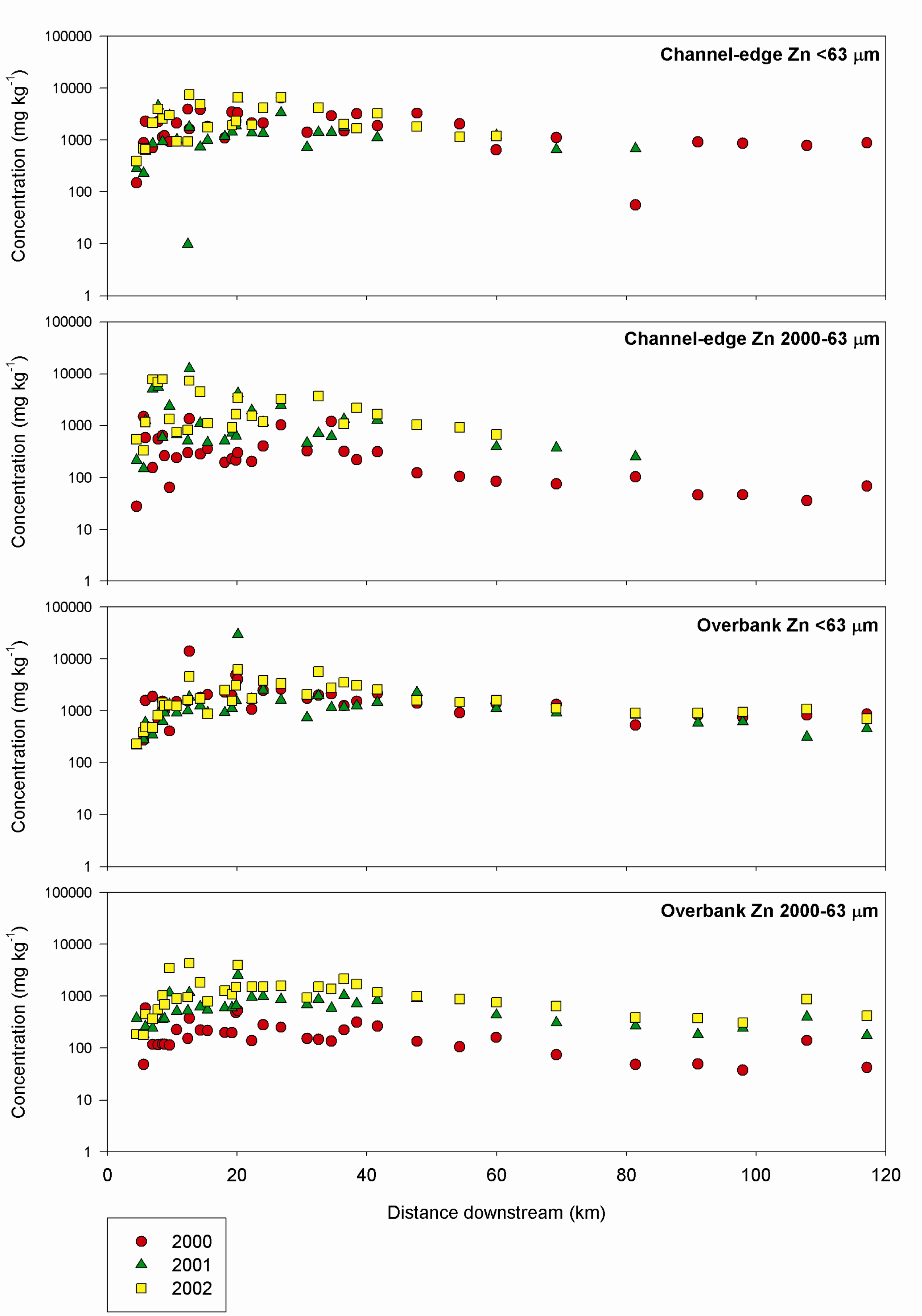

Figure 6.13: Zn concentrations in 2000, 2001 and 2002 flood sediments

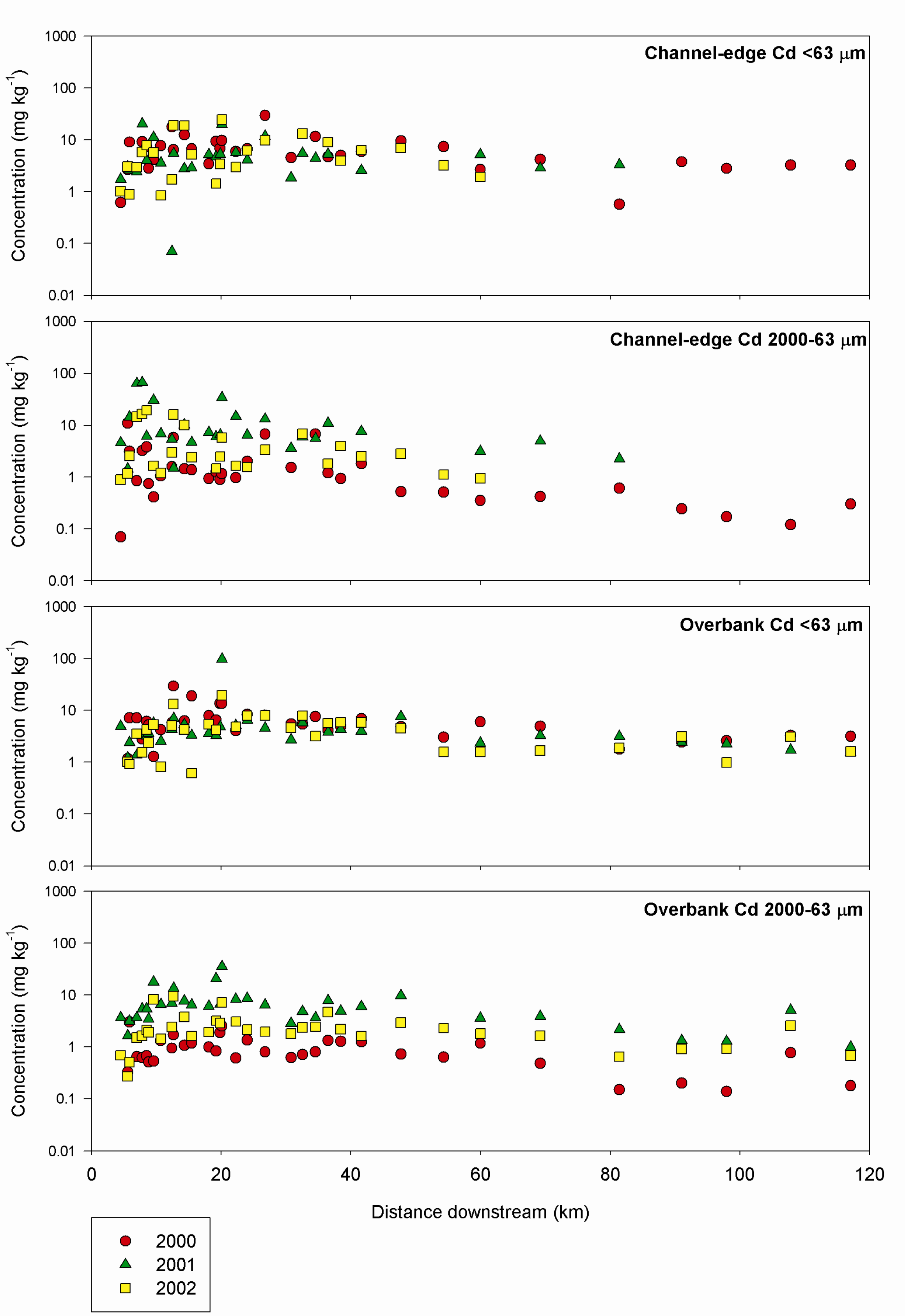

Figure 6.14: Cd concentrations in 2000, 2001 and 2002 flood sediments

6.4. CONTROLS OF DOWNSTREAM METAL CONCENTRATIONS IN FLOOD SEDIMENTS

6.4.1. Introduction

Section 6.3 demonstrates that metal concentrations in overbank and channel-edge sediments deposited during periods of flooding contain high concentrations of Pb, Zn and Cd. Metals in these deposits display a distinctive downstream trend, with rapidly attenuating peaks in Swaledale and a more gradual decrease in concentrations with distance downstream in the Vale of York. This section aims to identify the geomorphological controls on downstream metal dispersal during flood events. Factors affecting the physical distribution of metals along the river system will be discussed, alongside factors that influence differences in metal concentrations between the three events.

6.4.2. Downstream decline of metals on flood sediments

A number of studies have identified a strong downstream decline in metal concentrations with distance from the source of metal-rich sediment (Sections 1.2.3 and 4.4.5). This decline, attributable to factors such as hydraulic sorting, dilution with uncontaminated sediment, and loss to overbank storage, chemical solution and biological uptake, has frequently been found to conform to a negative linear, power or exponential decay pattern (Wolfenden and Lewin, 1978; Lewin and Macklin, 1987; Macklin, 1996). Flood sediment from the River Swale clearly exhibits the downstream decline observed in other catchments (Figures 6.3 to 6.8 and 6.11), but patterns do not generally conform to the simple decay curves suggested by other authors. When linear, power and exponential equations are fitted to flood sediment from the Swale, the resulting r^2 values are generally less that 0.01. This suggests that while it is probable that factors such as hydraulic sorting and dilution play an important role in determining metal dispersal patterns in Swale flood sediments, simple indicators of their influence are complicated by complex conditions within the catchment (*cf.* Macklin and Dowsett, 1989). Potential complicating factors will be discussed in the subsequent sections.

6.4.3. Sediment inputs

The location of metal-rich sediment inputs is likely to be an important factor in determining downstream patterns of metal dispersal in channel-edge and overbank flood sediment. As important is the location of 'clean' sediment inputs, which serve to dilute metal concentrations in flood sediments (Marcus, 1987; Miller *et al.*, 1999). Both metal-rich and 'clean' sediment is derived from two primary sources; tributaries, and channel bed and bank deposits.

During periods of high discharge, large amounts of sediment are likely to be transferred from tributaries into the trunk river system. In the case of the Swale catchment, this material is likely to include metal-rich sediment from historically mined tributaries in the upper reaches (*cf.* Chapter 4), and sediment with low metal concentrations from unmineralised tributaries in the piedmont and lower reaches of the river. Major peaks in both metal concentrations and sediment deposition can be observed downstream of tributaries such as Swinner Gill, Gunnerside Beck, Barney Beck, Arkle Beck and Marske Beck, all of which have a long history of metal mining and ore processing (Section 6.3.6 and Figures 6.15 and 6.16). Individual peaks in metal concentrations attenuate rapidly, suggesting that a large proportion of the dense, metal-rich sediment is deposited soon after it is transferred from a high gradient tributary to the lower gradient trunk channel (*cf.* Lewin and Macklin, 1987). On a wider scale, however, metal concentrations remain elevated for a considerable distance. This is likely to reflect both the greater downstream transport of finer particles and the remobilisation of coarser metal-rich sediments. Large, unmineralised tributaries such as Bedale Beck, the River Wiske and Cod Beck enter the Swale in the Vale of York. These are likely to be important sources of fine sediment to the trunk stream; indeed, more than half of all the fine sediment measured at Leckby Grange, in the Vale of York, has been identified as coming from these tributaries (Smith *et al.*, 2003b). These inputs are likely to have a considerable dilution effect on metal concentrations observed in flood sediments, although the effects of individual tributaries are difficult to identify with the data available (*cf.* Marcus, 1987).

Considerable erosion of channel bed and bank material is likely to occur during periods of high flow (*e.g.* Smith *et al.*, 2003b). As demonstrated in Chapter 5, these deposits contain appreciable amounts of metal-rich sediment. It therefore follows that floodplain sediment is likely to be a major source of the metals that are observed in overbank and channel-edge flood sediments (*e.g.* Rang *et al.*, 1987; Leenaers, 1989; Miller *et al.*, 1999; Davis *et al.*, 2001). Channel bed and bank material is also likely to be a major source of 'clean' sediment, diluting metal concentrations in flood deposits. As might be expected, metal

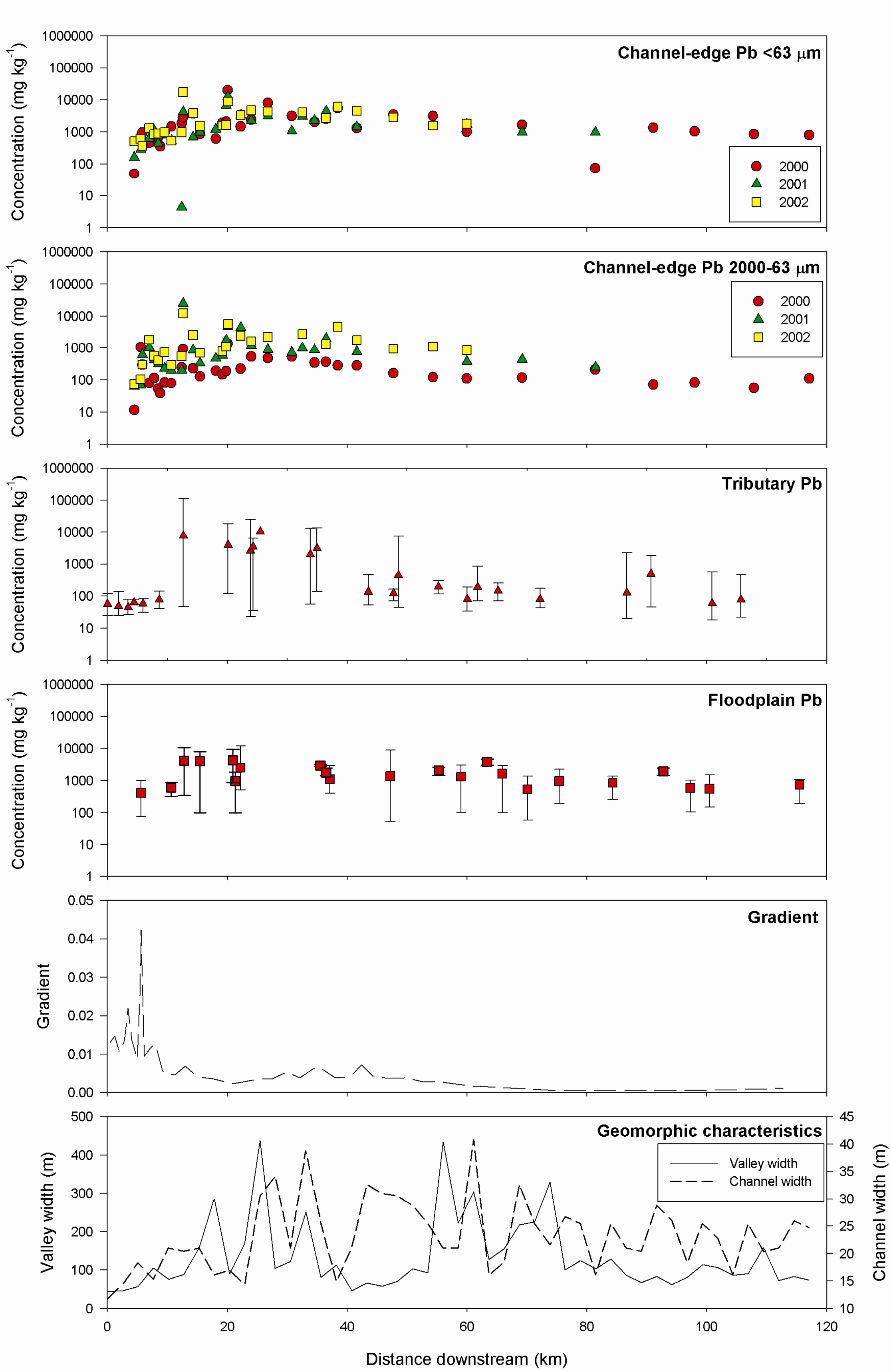

Figure 6.15: Pb concentrations in channel-edge flood sediment, tributaries and floodplain sediment (mean, minimum and maximum concentrations are shown), and geomorphological characteristics

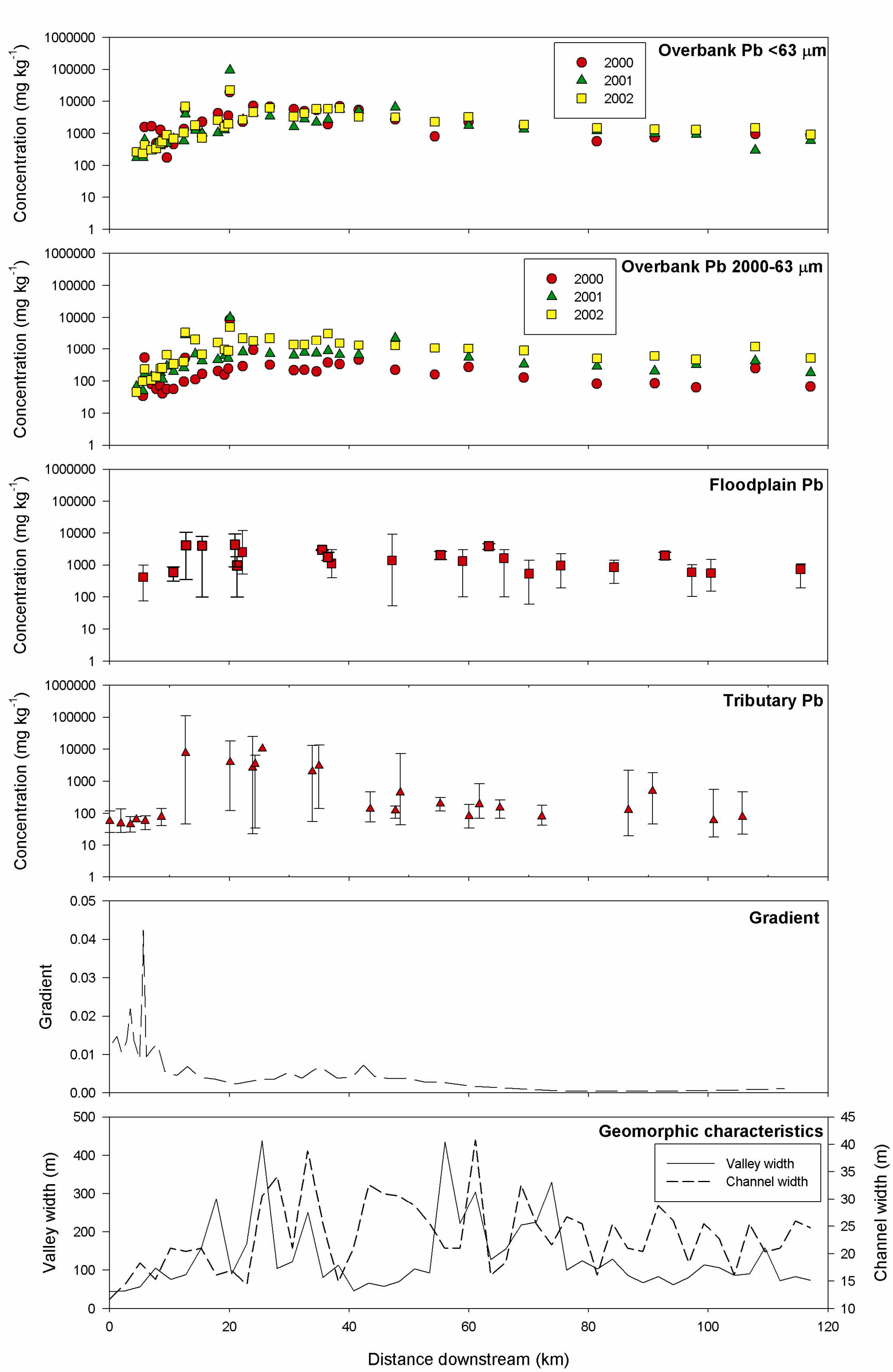

Figure 6.16: Pb concentrations in overbank flood sediment, tributaries and floodplain sediment (mean, minimum and maximum concentrations are shown), and geomorphological characteristics

concentrations observed in floodplain sediments are broadly similar to those observed in fresh flood sediment (Figures 6.15 and 6.16). However, it is difficult to determine the true influence of the floodplain as a source of metals. Although a number of peaks in sediment and metal deposition are coincident with areas of floodplain that have high metal concentrations, these peaks are all located downstream of tributary inputs, which are likely to be the dominant cause of enhanced metal accumulation. This may account, for example, for the zone of metal enrichment approximately 45 km downstream, and for peaks in metal concentrations observed in the lower *c.* 60 km of the river that do not coincide with tributary inputs of material. The maintenance of relatively high volumes of metal deposition in the lower reaches of the river suggests that fresh material is introduced from the bed and banks of the channel (Figure 6.11). Indeed, bank erosion rates are at their greatest in the piedmont and lower reaches of the river (Grove and Sedgwick, 1998; Lawler *et al.*, 1999), and erosion from the lower reaches is likely to be considerably enhanced during flood events (Smith *et al.*, 2003a; 2003b). Furthermore, investigations by Walling *et al*. (1999) suggest that approximately 28.2 % of suspended sediment in the River Swale is likely to be derived from the bed and banks of the channel. The supply of sediment from floodplain sources in the middle and lower reaches of the river is also likely to contribute to the dilution effects that are apparent in these reaches.

6.4.4. Geomorphological controls

Large-scale geomorphological parameters such as valley width, channel width and gradient have been shown to have a major influence on the storage and deposition of metal-rich sediment along a river system (Chapters 4 and 5). As observed in Gunnerside Beck and along the floodplain of the Swale, metals often accumulate in wider, low gradient ‘storage’ reaches, and are flushed from narrow, high energy ‘transport’ reaches (*e.g*. Macklin, 1996). It may therefore be reasonable to expect that overbank and channel-edge flood sediments are also strongly influenced by these geomorphological controls. However, multiple regression analysis suggests that this may not necessarily be the case. The results of the analysis suggest that only a small proportion of the variation in flood sediment metal concentrations is explained by variations in gradient, channel width and valley width (Tables 6.1 and 6.2). The influence of each geomorphological factor is highly variable between sediment from different flood periods, different depositional settings, and different size fractions, and no clear patterns are evident. Furthermore, none

Table 6.1: Multiple regression results: The relationship between metal concentrations in channel-edge flood sediments and geomorphological parameters

	Sediment	r^2	Significance level (p)	Individual parameters	
2000 floods	<63 µm	0.048	0.681	Gradient	0.004 (-)
				Channel width	0.000
				Valley width	0.044 (+)
	2000-63 µm	0.025	0.853	Gradient	0.008 (-)
				Channel width	0.000
				Valley width	0.017
2001 floods	<63 µm	0.088	0.583	Gradient	0.016 (-)
				Channel width	0.074 (-)
				Valley width	0.023 (+)
	2000-63 µm	0.099	0.487	Gradient	0.000
				Channel width	0.044 (-)
				Valley width	0.080 (+)
2002 floods	<63 µm	0.242	0.114	Gradient	0.144 (-)
				Channel width	0.105 (-)
				Valley width	0.066 (+)
	2000-63 µm	0.134	0.379	Gradient	0.057 (-)
				Channel width	0.057 (-)
				Valley width	0.066 (+)

of the relationships are statistically significant at normal confidence levels (p = >0.05). However, it may be possible to discern an indication of likely trends from the results of this analysis.

The results of the multiple regression analysis broadly suggest that, as observed in tributary and floodplain sediments from the Swale system, valley width has a positive relationship with metal concentrations and gradient has a negative relationship (Sections 4.4 and 5.4.2). Channel width also has a negative influence on metal concentrations. This contrasts with the patterns observed for Swale floodplain sediments, but corresponds with

Table 6.2: Multiple regression results: The relationship between metal concentrations in overbank flood sediments and geomorphological parameters

	Sediment	r^2	Significance level (p)	Individual parameters	
2000 floods	<63 µm	0.041	0.731	Gradient	0.001 (-)
				Channel width	0.024 (-)
				Valley width	0.024 (+)
	2000-63 µm	0.125	0.253	Gradient	0.031 (-)
				Channel width	0.041 (-)
				Valley width	0.052 (+)
2001 floods	<63 µm	0.083	0.452	Gradient	0.014 (-)
				Channel width	0.026 (-)
				Valley width	0.058 (+)
	2000-63 µm	0.182	0.106	Gradient	0.028 (-)
				Channel width	0.058 (-)
				Valley width	0.128 (+)
2002 floods	<63 µm	0.193	0.800	Gradient	0.056 (-)
				Channel width	0.128 (-)
				Valley width	0.052 (+)
	2000-63 µm	0.260	0.240	Gradient	0.042 (-)
				Channel width	0.133 (-)
				Valley width	0.139 (+)

those observed in channel sediments from Gunnerside Beck, suggesting that active channel sediments are subject to different controls to floodplain sediments. In most cases, channel width and valley width appear to have the strongest influence on metal concentrations in flood sediments.

The influence of these factors is evident along some reaches of the river. For example, metal concentrations in flood sediments are generally low in the narrow, high-gradient headwaters of the system; however, this may be attributable as much to the small scale of mining activities in this area as to the lack of suitable storage reaches and prevalent depositional conditions. Metal concentrations are high in reaches with a wide valley floor in the upper 40 km of the river, but are not exceptional when compared to adjacent, narrower reaches (Figures 6.15 and 6.16). Indeed, some of the larger peaks in metal concentrations occur in reaches with a narrow valley and channel, although these also coincide with the confluences of historically mined tributaries. Further downstream, the influence of valley and channel width may be masked by the large flood embankments that border the river channel, limiting sediment deposition to a relatively narrow corridor in all but the most extreme flood events, possibly reducing the strength of any relationships between metal concentrations and simple geomorphology. The influence of simple geomorphology on metal concentrations in flood sediment may be also be masked by inputs of metal-rich and uncontaminated sediment from tributaries and the bed and banks of the channel (Section 4.4.3).

This section demonstrates that the relationship between metal concentrations and fluvial geomorphology is complex and not easily explained by variations in simple geomorphological controls. However, it remains likely that downstream metal concentrations are strongly influenced by factors such as gradient, channel width and valley width, acting in conjunction with the input of metal-rich and uncontaminated sediments. Multiple regression analysis indicates that the degree of influence of each geomorphological control appears to be highly variable between depositional environment (*i.e.* channel-edge and overbank), sediment size fraction, and individual flood periods. This suggests that factors such as stream power, metal load and sediment transport capacity were different within each flood. It is therefore likely that these differences were at least partially caused by variations in discharge between each event. The influence of flood magnitude on metal concentrations in flood sediments will be discussed in the subsequent section.

6.4.5. The influence of flood magnitude on metal concentrations

A number of previous investigations have highlighted the importance of high discharge in the transport of sediment-associated metals through the fluvial system, largely through the ‘activation’ of sources of metals such as spoil tips and the channel bed and banks (*e.g.* Bradley and Lewin, 1982; Leenaers, 1989; Marcus *et al.*, 2001). However, while the total metal transport may be greatest during high flows as a result of increased suspended sediment load (Bradley, 1984; Horowitz, 1991; 1995), the relationship between flood discharge and metal concentrations may be more complex. A number of authors have recognised a positive relationship between discharge and metal concentrations in suspended sediments during a flood wave, due to increased remobilisation of bed and bank material during higher flows (*e.g.* Williams *et al.*, 1966; Williams *et al.*, 1973; Förstner and Wittmann, 1979; Foster and Charlesworth, 1996), or increased scavenging capacity and metal adsorption due to the greater sediment yield (Salomons, 1988). Conversely, a negative relationship has also been widely reported, as a result of dilution with 'clean' sediment and the flushing and exhausting of readily available metal-rich fines (*e.g.* Salomons and Eysink, 1981; Bradley and Lewin, 1982; Bradley, 1984; Salomons and Förstner, 1984; Bird, 1987; Bradley, 1988; Salomons, 1988; Blake *et al.*, 2003; Xue *et al.*, 2003). Finally, several studies have demonstrated that metal concentrations do not have any strong correlation with flood discharge (Leenaers *et al.*, 1988; Leenaers, 1989; Shiller, 1997; Nagorski *et al.*, 2003).

Metal concentrations in flood sediments from the River Swale display a distinct variation between the three periods of high flow that were sampled (Figures 6.12 to 6.14). In the 2000-63 μm fraction, metal concentrations are greatest in sediment from the January-February 2002 event, and lowest in sediment form the larger autumn 2000 floods. Concentrations observed in sediment from the smallest floods, in November-December 2001, fall between those observed in the two larger, more prolonged periods of high flow. Metal concentrations in the <63 μm fraction are less varied, but generally display the same pattern as the coarser-grained material. These patterns suggest that, while discharge is likely to have an influence on metal concentrations in flood sediments, this relationship is not straightforward (*cf.* Leenaers, 1989).

The effects of dilution during large flood events can clearly be seen when concentrations in autumn 2000 flood sediment are compared to those observed in material from the other flood periods. The amount of 'clean' material mobilised during the largest floods may have been sufficient to cause considerable dilution of sediment-associated metals, resulting in lower concentrations in comparison to smaller floods, where dilution was less pronounced. This may be reflected by the greater proportion of silts and clays in the 2000 flood sediments in comparison to material from the 2001 and 2002 events (Figures 6.9 and 6.10). However, if simple dilution was the primary control on metal concentrations, it would be expected that material from the smallest floods, during November and December 2001, would contain the highest metal concentrations. This is not the case, however; although sediment from the 2001 floods contains higher metal concentrations than sediment from the 2000 floods, these concentrations are not as high as those observed in material deposited during the larger 2002 flood events. This suggests that other factors work in combination with dilution effects to produce the patterns observed in flood sediments observed in the River Swale.

Seasonal variations in metal concentrations in flood sediments (*e.g.* Horowitz, 1995) are unlikely to be an important factor in this case, since the three flood events discussed in this chapter all occurred during the autumn-winter period. However, differences in the erodibility of material from vegetated slopes and largely unvegetated spoil tips and channel banks may help to explain the patterns observed in the Swale catchment. During the extreme autumn 2000 floods, heavy rainfall and high river flows over a prolonged period are likely to have mobilised large amounts of metal-rich sediment from spoil tips and channel banks, alongside uncontaminated sediment from hillslopes and unmineralised areas of the catchment. The contribution of the latter is likely to have been sufficient to considerably dilute metal concentrations in sediment deposited during the 2000 floods, resulting in the lowest sediment metal values observed during the study period. During the large 2002 flood events, rainfall and river flow may have been sufficient to mobilise material from easily erodible spoil tips and the bed and banks of the river channel, but not sufficient to erode more resistant, uncontaminated sediment from predominantly vegetated slopes. This relative lack of dilution effects may explain the high metal concentrations observed in sediments deposited during this period. Finally, precipitation and discharge during the smaller 2001 floods may not have been sufficient to mobilise large volumes of metal-rich sediment from spoil tips, resulting in concentrations that fall between those observed in sediments from the two more severe periods of flooding. Alternatively, the comparatively high metal concentrations observed in these sediments may be attributable to the relatively long period without large floods preceding these events, during which metals may have accumulated (*cf.* Ciszewski, 2001).

This shows that, while there is clearly a relationship between metal concentrations and discharge in flood sediments in the Swale catchment, this relationship is complex (*cf.* Leenaers, 1989). Metal concentrations do not simply increase (*cf.* Williams *et al.*, 1966) or decrease (*cf.* Bradley and Lewin, 1982) with increasing discharge; instead, metal concentrations observed in flood sediments are a result of the complex interaction of rainfall intensity, river flow and the 'activation' of sources of uncontaminated and metal-rich sediment.

6.4.6. Summary: Controls of downstream metal distribution in flood sediments

This section demonstrates that the downstream dispersal of metals in flood sediments from the River Swale is complex. While a distinct downstream decline associated with factors such as hydraulic sorting and loss to overbank storage can be observed, this simple trend is complicated by a range of factors. The input of metal-rich and 'clean' sediment from multiple tributary and floodplain sources along the length of the river complicates the pattern, as do geomorphic characteristics such as valley and channel width. The influence of each of these factors is difficult to determine. It is clear however, that they are strongly influenced by variations in flood discharge. Differences in discharge and the activation of sources of metal-rich sediment lead to marked variations in metal concentrations observed in each set of flood sediment.

6.5. CONCLUSION

This investigation has demonstrated that channel-edge and overbank sediment deposited during a series of floods in 2000, 2001 and 2002 contains extremely high concentrations of Pb, Zn and Cd. Metal concentrations exhibit a distinct downstream trend, with a series of large, rapidly attenuating peaks in the upper reaches and a gradual decline in the lower reaches. This downstream pattern is controlled by the complex interaction of factors, including hydraulic sorting, the location of metal-rich and uncontaminated sediment inputs, and geomorphological factors that influence the transport and deposition of sediment along the river valley. Of these, the input of sediment from tributaries and floodplains is likely to be the most important, controlling metal enrichment and dilution.

While the downstream patterns observed in each flood event are similar and subject to the same controls, the concentrations of metals in each set of flood sediment are markedly different. Variations in discharge between the three flood periods cause differences in the degree of dilution and activation of metal sources. As a result, metal concentrations are considerably greater in low to intermediate floods than in severe periods of flooding. This has considerable implications for environmental quality within the Swale catchment, since the sediment transported during more frequent, small events may be more harmful than that transported during larger floods. It is noted that the data presented in this chapter do not take into account the absolute volume of metal transport during each flood; this is likely to increase proportionally with discharge (Horowitz, 1995). However, the combined effects of repeated metal-rich sediment deposition during smaller floods may outweigh the impacts of less contaminated sediment deposition during larger floods.

The presence of high metal concentrations in flood sediments deposited more than a century after the cessation of lead mining suggests that mining continues to have a significant impact on the River Swale catchment. The metals cycled through the river system during contemporary floods are likely to be derived from the extensive tributary and floodplain stores described in Chapters 4 and 5. This raises several important questions:

- How much sediment is supplied from tributary sources?
- How much sediment is supplied from floodplain sources?
- How long will tributaries and floodplains continue to supply metal-rich sediment to the River Swale?
- What is the likely environmental impact of metal-rich sediment transport and deposition within contemporary flood sediments?

These issues will be explored in subsequent chapters. Sediment budgeting techniques will be employed provide an estimate of the relative importance of tributary and floodplain sources of metal-rich sediment. The likely impact of metal cycling during floods will be assessed by comparison with environmental quality guidelines suggested within U.K. legislation, and estimated background metal concentrations.