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Assessment of the risk posed by toxic contamination to waterbirds on Special Protection Areas (SPAs)

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Cover note

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Executive summary

English Nature has a statutory role to assess the condition of Special Protection Areas (SPAs) and to advise relevant authorities, such as the Environment Agency about risks to site integrity associated with plans and projects (eg. from discharges). This project was commissioned by EN inform decision-making when discharging these responsibilities. Environment Agency Wales previously commissioned a screening level ("tier 1") study by Crane and others (2005) into the potential risks to shorebirds from contaminants in the Severn Estuary SPA. The present project further investigated the risks associated with the exposure of SPA waterbirds to chemical contaminants (through direct toxic effects), by:

1. carrying out a screening risk assessment using new measurements of concentrations in prey items (supplied by the Environment Agency, EA) to determine the key contaminants which could have toxic effects on waterbirds;

2. developing, for the identified key contaminants, a detailed probabilistic assessment of the ratio of predicted concentration in prey to the concentration at which no observable adverse effects on reproductive endpoints in birds would be observed (PEC[1]/PNEC[2] ratio). This detailed assessment was made on the basis of improved data on: prey contaminant levels, habitat use, foraging behaviour, and toxicity endpoints.

The study was conducted on two SPA sites: the Severn Estuary and Poole Harbour.

The results of the analysis were as follows:

1. Of the organic and inorganic contaminants studied in the screening analysis of *Nereis diversicolor* samples, seven were found to potentially lead to PEC/PNEC values which exceeded 1 and hence presented a potential risk to birds. These compounds were all metals or semi-metals: zinc (Zn), lead (Pb), mercury (Hg), selenium (Se), iron (Fe), arsenic (As), and chromium (Cr).

2. Of these seven contaminants, four were rejected from more detailed modelling following more critical examination of available toxicity data:

   - for Zn, the endpoint was not ecologically relevant;
   - for Fe, Cr, there was insufficient NOAEL[3] data available;
   - for As, recalculation using improved NOAEL data gave PEC/PNEC <1.

Detailed probabilistic modelling showed that

- there was a high probability that PEC/PNEC for Pb significantly exceeded 1 in both harbours for all species;

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[1] Predicted environmental concentration
[2] Predicted no effect concentration
[3] No observed adverse effect level

- there was a high probability that PEC/PNEC for Hg significantly exceeded 1 for Hg in the Severn Estuary and a significant (>5%) probability that PEC/PNEC exceeded 1 for Poole Harbour;
- there was a high probability that PEC/PNEC significantly exceeded 1 for Se in the Severn Estuary. There was no Se residue data available for Poole Harbour.

3. The major source of uncertainty in predicting PEC/PNEC values for Pb was the large uncertainty in no observable adverse effect level (NOAEL) values for this element. Predictions for Hg and Se were less uncertain than for Pb, but uncertainty in both were significantly influenced by NOAEL. Presence of Hg in the form of methyl mercury (MeHg) was also an important source of uncertainty for Hg, and food intake rate (FIR) and prey concentrations were an important source of uncertainty for both Hg and Se.

4. The attribution of contaminant residues to current point sources remains problematic and further measurements would be required before confident conclusions could be made concerning this. It appears likely, however, that Pb and Hg contamination of both estuaries is dominated by historic rather than current sources. We have insufficient information on Se sources to draw any conclusions for this element.

5. There may be "hot spots" of contamination in both estuaries which could lead to high concentrations of contaminants to a small proportion of the bird population which could feed in these areas, though birds in general feed from a variety of sources in both estuaries.

The results of the probabilistic modelling suggest that both of the study areas, Poole Harbour and the Severn Estuary, ingestion of Pb, Hg and Se residues within prey items poses a potentially significant toxic risk to wading birds, based on ecologically relevant endpoints.

Recommendations

The approaches used in this study, which has focused on Poole harbour and the Severn Estuary SPAs, could be used to assess the risk of toxicants to shorebirds in any UK estuary. Although many uncertainties have been noted, for a number of substances (at least in the two estuaries assessed here), the risk of significant exposure has been shown to be very low. For a number of other substances, risks may be higher, but the review of toxicity data indicates that detailed probabilistic modelling is not possible due to the paucity of data. Finally, for the three substances considered in detail here (Pb, Hg, Se) a significant toxic risk is predicted with a high probability, though it should be noted that the risk relates to sub-lethal effects only.

The approach could be improved by further research as follows:

1 Work should be carried out to better quantify impacts of current point sources and existing "hot spots" of contamination in the estuaries;

2 Further measurements in a range of prey items, including earthworms, should be made to improve estimates of PEC.

3 There may be little prospect of reducing uncertainty in NOAEL values since we think it unlikely that significant new toxicological data will appear in the near future. Uncertainty in model outputs could, however, be reduced by species specific estimates of FIR, and improved measurements of contaminants in prey items.

4 There is merit in extending contaminant characterisation and estimation of PEC/PNEC ratios (using acute toxicity and reproductive toxicity endpoints) to other UK sites which are important because they either support large breeding populations or large numbers of overwintering birds. This work would involve review of published data for other sites and targeted new measurements of contaminant residues. Selecting sites which represent a gradient of toxic exposure would also be beneficial.

5 If there are a significant number of sites where PEC:PNEC ratios are >1 there is a case for attempting to validate the probabilistic models applied in this report. This is likely to require measurement of metal residues in the tissues (of dead) and blood (of live) birds, and possibly even more detailed studies to relate individual reproductive success/overwinter survival to predicted dietary metal intake. In deciding whether to move on to this next level of investigation it has to be noted that predicted exposure of overwintering birds at levels associated with reproductive effects may have little bearing on their post- exposure reproductive success at the breeding grounds.

Contents

1 Introduction

English Nature has a statutory role to assess the condition of Special Protection Areas (SPAs) and to advise relevant authorities, such as the Environment Agency about risks to site integrity associated with plans and projects (eg from discharges). This project was commissioned by EN to inform decision-making when discharging these responsibilities. Environment Agency Wales previously commissioned a screening level ("tier 1") study by Crane and others (2005) into the potential risks to shorebirds from contaminants in the Severn Estuary SPA. The present project further investigated the risks associated with the exposure of SPA waterbirds to chemical contaminants (through direct toxic effects). The study was conducted on two SPA sites: the Severn Estuary and Poole Harbour, and the potential for using the methodology more widely is discussed.

The main objectives of the study were to:

1. Carry out a screening risk assessment based on the approach outlined in the previous Crane and others (2005) study and using new measurements of concentrations in prey items (supplied by the Environment Agency, EA) to determine the key contaminants which could have toxic effects on waterbirds in these estuaries;

2. On the basis of existing data, assess the habitat utilisation and feeding behaviours of shorebirds in the two estuaries;

3. Collate and review toxicity endpoints (LD50, LC50 and NOAELs) for the identified key contaminants, select the most appropriate endpoints for use given the likely exposure scenarios, and, where possible, determine probability distributions for these endpoints to be used in the models;

4. For the identified key contaminants, carry out a detailed probabilistic PEC/PNEC assessment on the basis of improved data on: prey contaminant levels (provided by EA and additional literature data), habitat use and foraging behaviour (derived from activity 2 above), and toxicity endpoints (derived from activity 3 above).

5. Fully discuss the benefits and limitations of the approach applied, in the context of both the study sites and more widely across SPAs.

The main steps carried out in the assessment are illustrated in a flow diagram (Figure 1).

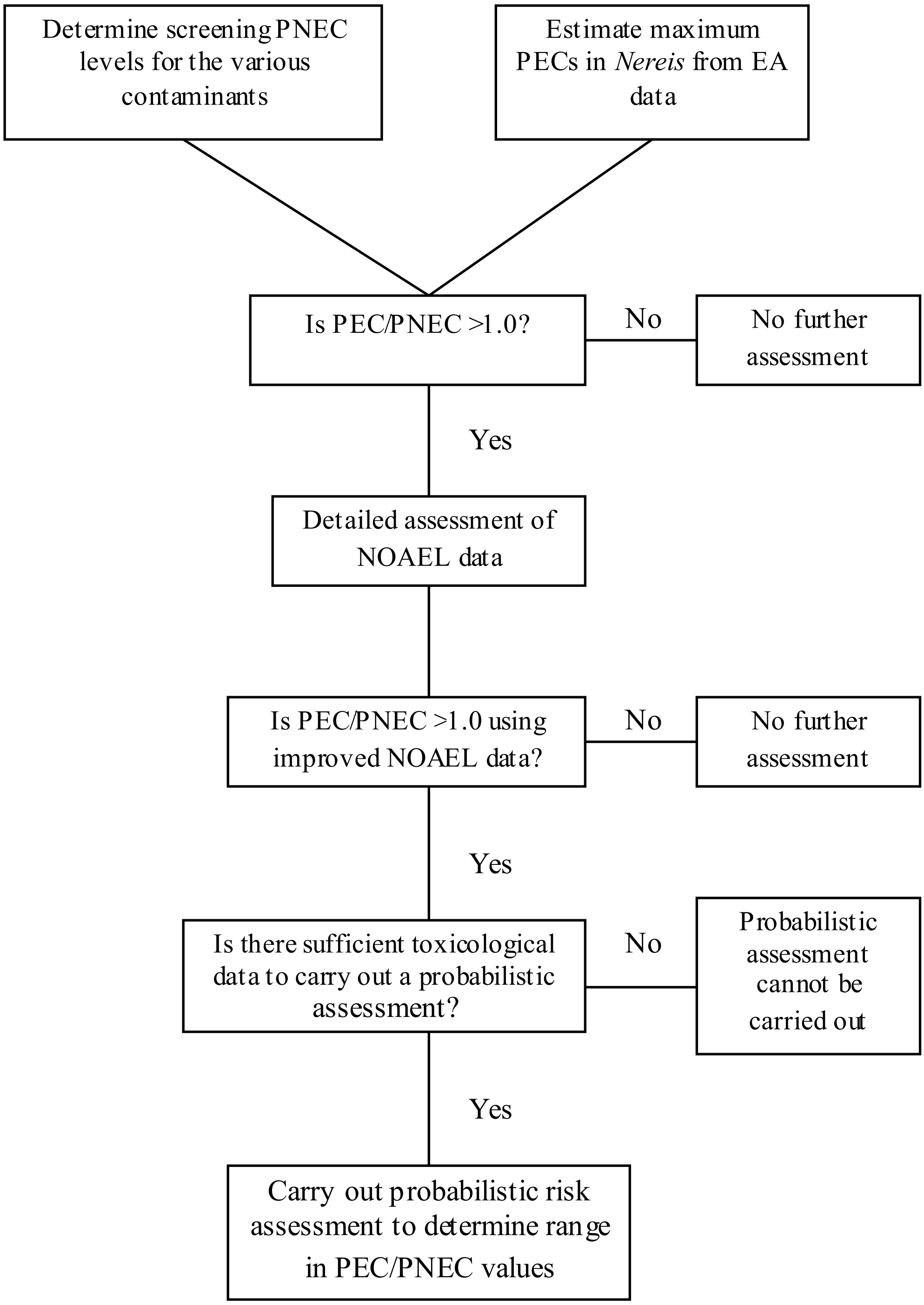


Figure 1 Flow diagram to show steps in the risk assessment process

2 Screening risk assessment

2.1 Data sources

The screening risk assessment was carried out using measurements of contaminant residues in prey in the Severn Estuary and Poole Harbour supplied by the EA. Ragworms *Nereis diversicolor* were sampled from 12 sites in Poole Harbour and 13 sites in the Severn Estuary. In addition, one sample of *Scrobicularia plana* (Peppery furrow shell) was taken from Poole Harbour. Subsequently, additional measurements of contaminant residues in *Nereis* were provided from 10 sites in the Severn Estuary. Due, however, to time constraints, these latter data could not be included in the initial screening risk assessment, but they were used in the more detailed probabilistic model. Finally, additional data on common mussels *Mytilus edulis* were provided for one site (Cardiff Flats) in the Severn Estuary.

The no observed adverse effect levels (NOAELs) used in this risk assessment were sourced from published studies in refereed journals. The NOAELs were empirically derived values equivalent to the highest dose level in each study at which no adverse effects were observed. Therefore, the precision of the estimated NOAEL was dependent upon the dosing regime employed in the study. For example, if a dosing regime of 0, 1 and 100 mg/kg/d was used in a study which demonstrated adverse effects at 100 mg/kg/d then the NOAEL reported would be 1 mg/kg/d. However, the actual NOAEL could be anywhere between greater or equal to mg/kg/d and less than 100 mg/kg/d.

In studies where adverse effects were observed in the lowest dose level employed, which consequently was the lowest observe adverse effect level (LOAEL), then the NOAEL was calculated as 10% of the lowest dose employed in the study.

2.2 Methods

The screening risk assessment was carried out by calculating the ratio of the predicted concentration of the contaminant in prey (PEC) to the Predicted No Effects Concentration (PNEC), the predicted concentration in prey (ie mean concentration in the bird diet) that causes no observed effect in the bird:

$$\frac{PEC}{PNEC} \qquad (1)$$

Contaminants for which PEC/PNEC <1 were considered to have no significant impact on shorebird health and were therefore excluded from further consideration. Contaminants for which PEC/PNEC >1 were considered to be a potential threat to shorebirds and were therefore considered in greater detail.

The predicted concentration in prey (PEC) was equal to the measured concentrations in *Nereis* at the different sites in the two estuaries. For the screening study, the highest value of PEC measured in each estuary was used. The PNEC is given by multiplying the No Observable Adverse Effect Level (NOAEL) of the contaminant in birds by the bird body weight (to get the actual mg of contaminant ingested per day) then dividing by the FIR (to get the actual mg of contaminant ingested per kg of prey ingested):

$$\text{PNEC} = \frac{\text{NOEL(mg/kg BW/day)} \times \text{BW (kg)}}{\text{FIR (kg fresh or dry weight/day)}} \quad (2)$$

BW Body Weight of bird (kg)

FIR Food intake rate of the bird (kg d^{-1}; kg fresh or dry weight of prey per day)

NOAEL No Observable Adverse Effect Level; this is the contaminant *intake rate* of the bird that causes no observed effect. (mg kgBW^{-1} d^{-1}; mg of contaminant ingested per kg BW per day)

PNEC Predicted concentration in prey (ie concentration in the bird diet) that causes no observed effect in the bird (mg kg^{-1}; mg of contaminant per kg of prey fresh or dry weight)

PEC Predicted/measured concentration of contaminant in prey (mg kg^{-1}; mg of contaminant per kg of prey fresh or dry weight)

The daily food intake rate was estimated using empirical relationships between predicted food intake rate and body weight (BW) for different groups of birds (Nagy, 2001). For shorebirds, gulls and auks, the daily intake (fresh weight, kg d^{-1}), FIR is estimated (Nagy, 2001) using:

$$\text{FIR} = 0.388 \times (\text{BW})^{0.769} \quad (3)$$

where the coefficients have been altered from those given in Nagy (2001) to change the units of weight and intake rate from grammes to kilogrammes.

Table 1 Body weights of 3 bird species and calculated food intake rates using Equation (1) from Nagy (2001)

Species	Body Weight kg f.w.	FIR kg(f.w.)/d	FIR as % of BW	BW/FIR
Curlew (big)	0.88	0.35	40.0	2.50
Curlew (small)	0.75	0.31	41.5	2.41
Oystercatcher (big)	0.62	0.27	43.4	2.30
Oystercatcher (small)	0.49	0.22	45.8	2.18
Dunlin (big)	0.055	0.042	75.8	1.32
Dunlin (small)	0.048	0.038	78.2	1.28

The PNEC values were calculated using the mean and the range of BW/FIR values over different species/sizes (BW/FIR: 1.28 – 2.5) presented in Table 1. For the Poole Harbour sites, measurements of metals in *Nereis* were given per unit dry weight. These were converted to fresh weight using a f.w./d.w. ratio of 4.4 for *Nereis* (Crane and others 2005).

2.3 Results

Estimates of PEC/PNEC were made for each of the 12 sites in Poole Harbour and 13 sites in the Severn Estuary for which residue data in *Nereis* were available. The predicted PEC/PNEC values for metals at each site in Poole Harbour and the Severn Estuary are shown in Appendix 1. There were no clear trends in the data for metals in either estuary: PEC/PNEC ratios were relatively evenly spread across different sites, though the highest metal concentrations tended to be observed at just a few sites in each estuary (Table 2 and Appendix 1).

Table 2 The highest concentrations* of residues in prey were observed at 3 out of 12 sites in Poole Harbour and 3 out of 13 sites in the Severn Estuary. Sampling sites are shown in Figures 4 and 5 below

Metal	Site with highest conc. in *Nereis*	Metal	Site
	Poole Harbour		
Pb	4 (Mouth, R. Frome)	V	4, slightly elevated
As	2 (Sandbanks)	Cr	4, slightly elevated
Cd	3 (Holes Bay)	Mn	4, slightly elevated
Zn	3, slightly elevated	Fe	4 (Mouth, R. Frome)
Cu	2 (Sandbanks)	Ni	3 (Holes Bay)
Hg	3, slightly elevated		
	Severn Estuary		
Pb	16 (Northwick)	Cu	16, slightly elevated
As	8 (Beachley)	Ag	8, slightly elevated
Cd	11 (Purton) slightly elevated	Cr	8 (Beachley)
Zn	8, 11 slightly elevated	Se	8, slightly elevated
Hg	16, slightly elevated		8, slightly elevated

* In many cases no one site had significantly higher concentrations of a given metal than others – we have termed these "slightly elevated".

The initial PEC/PNEC screening exercise only used the toxicity data from the screening study summarised in the Crane report (Crane and others 2005), with additional values taken from two US EPA reports (Sample and others 1997; US Environmental Protection Agency, 1999), while the PNEC were calculated based upon EA chemical residue data for *Nereis diversicolor* from Poole Harbour (Table 3) and the Severn Estuary (Table 4). It identified seven compounds that had maximum PEC/PNEC ratios that equalled or exceeded 1. These compounds were all metals or semi-metals: zinc (Zn), lead (Pb), mercury (Hg), selenium (Se), iron (Fe), arsenic (As), and chromium (Cr). At one site (Poole Harbour, Parkstone Bay), a sample of *Scrobicularia plana* was measured. This was also assessed in the screening (assuming a hypothetical bird eating only *Scrobicularia*). As with the *Nereis* data, this sample showed Zn, Hg, Pb, As as having PEC/PNEC >1. Fe was not determined in the Severn Estuary and Se was not determined in Poole Harbour. In the Severn Estuary, several more organic contaminants were determined than in Poole Harbour.

It should be noted that in *N. diversicolor*, zinc is regulated, so concentrations may not reflect concentrations in other species which may regulate zinc to a lesser extent (Burt and others 1992).

Table 3 Maximum PEC/PNEC from Poole *Nereis* data

Contaminant	Max. PEC/PNEC	NOAEL mg/kgBW/d	Notes
Copper	0.073	47.0	
Silver	<0.12	>2.3	Used LC50*FIR/1000
Zinc	**3.15**	11	
Cadmium	0.08	1.45	
Mercury	**3.1**	0.0064	Assume NOAEL = LOAEL/10 Used a NOAEL for mercury as organo-metal (methylmercury). There is a large disparity between NOAELs for mercuric chloride and methylmercury (0.45 cf. 0.0064 mg/kg bw/d respectively); the chemistry reports only give a total mercury concentration. Using the NOAEL for methyl mercury should over estimate the risk to the wader while using the mercuric chloride figure may underestimate the risk.
Lead	**14**	0.021	
Vanadium	0.25	1.5	
Arsenic	**822**	0.0057	
Chromium	0.37	1.0	
Manganese	0.0029	977	
Iron	**216**	1.03	Used LC50*FIR/1000. But NOAEL lower than daily iron requirement.
Nickel	0.015	77.4	
PAHs	All <1	1.43 Benzo(a)pyrene	Checked each individual PAH against NOAEC for Benzo(a)pyrene, the most toxic PAH.
Tributyl tin	-	6.8	All measured values were below limit of detection. One *Scrobicularia* sample had 0.0647 mg/kg d.w. = 0.015 mg/kg f.w. – PEC/PNEC <1.

Table 4 Maximum PEC/PNEC from Severn *Nereis data*

Contaminant	Max. PEC/PNEC	NOAEL mg/kgBW/d	Notes
Copper	0.33	47.0	
Silver	<0.53	>2.3	Used LC50*FIR/1000
Zinc	**3.9**	11	
Cadmium	0.13	1.45	
Mercury	**22.5**	0.0064	Assume NOAEL = LOAEL/10. Used a NOAEL for mercury as organo-metal (methylmercury). There is a large disparity between NOAELs for mercuric chloride and methylmercury (0.45 cf. 0.0064 mg/kg bw/d respectively).
Lead	**34.2**	0.021	
Arsenic	**670**	0.0057	
Chromium	**1.0**	1.0	
Nickel	0.013	77.4	
Selenium	**4.9**	0.5	Assume NOAEL = LOAEL/10
PAHs	All <1	1.43 (Benzo(a)pyrene)	Checked each individual PAH against NOAEL for Benzo(a)pyrene, the most toxic PAH.
PCBs	Sum <1	0.18 (Arochlor 1254)	Checked sum of PCBs vs NOAEL for Arochlor 1254.
Tributyl tin	-	6.8	All measured values were below limit of detection
a,b,d,g-hexachlorocyclohexane			All measured values were below limit of detection
Aldrin, Dieldrin, Endrin, Isodrin			All measured values were below limit of detection
op-DDT, pp-DDT			All measured values were below limit of detection
pp-DDE			LC50 = 825 mg/kg. Max 1.19 µg/kg in prey. Only 2 out of 13 samples above L.O.D[4]
pp-TDE			1 out of 13 samples above L.O.D. Measured value 3.2 µg kg^{-1}. LD50 = 386 mg kg^{-1} BW acute dose.
Hexachloro-butadiene, Hexachloro-benzene			All measured values were below limit of detection

In the CEH tender, it was argued that we would need to restrict full probabilistic modelling effort to a limited number of compounds. We therefore examined the toxicity data used to calculate the initial PEC/PNEC ratios to determine if:

i. the toxicity data were experimentally sound
ii. the endpoints were ecologically relevant.

The following are summary notes to explain the outcome of that initial examination:

[4] L.O.D – limit of detection in chemical analysis

a. **Zinc (Zn)**

PEC/PNEC ratios were in the range of 3-4.

The reference used in the report by Sample and others (1997) for the toxicity data (Stahl and others 1990) did not actually indicate a lowest observed adverse effect level (LOAEL). There was no significant effect on hens or reproductive performance and the top dose of 2028 ppm diet equated to a no observed adverse effect level (NOAEL) of >140 mg/kg bw/day; this contrasts with the value derived by Sample and others (1997) of 14.5 mg/kg bw/day. This would suggest that the NOAEL is at least 10 fold higher than given in the Sample report.

Other toxicity studies that we have looked at suggest that LOAECs may be in the region of 2000-3000 ppm (Dewar and others 1983), equivalent to approximately 140 mg/kg bw/day. If it is assumed that NOAELs can be estimated as 0.1 * LOAELs, then the NOAEL is about 14 mg/kg bw/day. However, this is not for reproductive endpoints, but rather reflect physiological changes. Thus, although the PEC/PNEC ratios of 3-4 may actually be correct, these are for endpoints that are highly sensitive and do not have obvious ecological relevance. Zn was therefore not included in the probabilistic risk assessment.

b. **Lead (Pb)**

PEC/PNEC ratios range up to about 34.

The derivation of the toxicity value (estimated NOAEL of 0.021 mg/kg BW/d) used in the US EPA (1999) report was not clear and could not be verified because the source document was not cited. The detail given in the US EPA 1996 report (Sample and others 1997) gave full details of its source reference and was based on a study that we examined and agreed with its conclusions. This toxicity value was a LOAEL of 1 mg/kg BW/day, based on effects on egg production, and we estimated (on the basis of a NOAEL = 0.1 × LOAEL) this to be equivalent to a NOAEL of 0.1 mg/kg bw/day. This compares with the EPA 1999 toxicity figure of 0.021 mg/kg bw/day that was actually used to calculate the PEC/PNEC ratio in the Crane and others report.

Even if the US EPA 1999 toxicity data was incorrect, the verifiable US EPA 1996 toxicity data would result in PEC/PNEC ratios of more than 1 in many cases. Therefore, lead was included in the probabilistic risk assessment.

c. **Mercury (Hg)**

The PEC/PNEC ratios were approximately in the range 3-22. The toxicity data were based on NOAEL data for methyl Hg dicyandiamide, and there was concern that the cyanide may contribute to the toxicity of the compound. However LC_{50} value for methyl Hg dicyandiamide and for mercury chloride are similar (22-25 mg/kg cf. 24-40 mg/kg respectively; (Hill and others 1984; Hudson and others 1984)) and so we have assumed that the toxicity associated with methyl Hg dicyandiamide is due to mercury and not cyanide.

The likely toxicity of mercury is highly dependent on whether mercury is in a methylated form. NOAELs for reproductive endpoints for mercury (mg/kgbw/day) are:

mercury chloride	0.45 mg/kg/day
methyl Hg dicyandiamide	0.0064 mg/kg/day

For the Severn estuary, PEC/PNEC ratios would exceed 1 even if the *Nereis* contained only 10% of mercury in methylated form, and so it would seem reasonable to include Hg in the probabilistic modelling of PEC/PNEC ratios.

d. **Selenium (Se)**

The PEC/PNEC ratio for the Severn estuary was approximately 5.

The US EPA (1999) report is unclear as to the source of its toxicity NOAEL of 0.5 mg/kg/day. Further examination of the literature suggested that the NOAEL should be 0.4 mg/kg BW/day (Heinz and others 1989) rather than 0.5 mg/kg BW/day. The resultant change to the maximum PEC/PNEC ratio was marginal and in either case the ratio exceeded 1, and so it seems reasonable to include selenium in the probabilistic risk assessment.

e. **Iron (Fe)**

The PEC/PNEC ratio was in the range of approximately 200.

There was no toxicity data available from the Crane and others (2005) report. Search of the literature located LC_{50} and LD_{50} data from the US EPA ECOTOXicology database (US Environmental Protection Agency, 2002). There were no LOAEC or NOAEC data available for Fe for reproductive endpoints. All iron salts had LC_{50} values that exceeded the top experimental doses that were used. The only available LC_{50} value, which we were unable to verify, was for an iron complex and was 2940 ppm diet (US Environmental Protection Agency, 2002). On the basis that a NOEC can be estimated as three orders of magnitude below the LC_{50} value, the NOEC value was estimated to be 2.9 ppm diet; this is equivalent to a NOAEL of approximately 1 mg/kg bw/day. This value was used to generate the above PEC/PNEC ratio.

There were major uncertainties with using the LC_{50} data for iron in terms of:

a. the toxicity of iron complexes is poorly understood;
b. the conversion from LC to NOEC by using an uncertainty factor of 1000, although a recognised methodology, may contain large-scale errors;
c. the NOAEL that we estimated was below the dietary requirements for galiformes.

Given these uncertainties in the calculation of the NOAEL, iron was excluded from the probabilistic risk assessment.

f. **Arsenic (As)**

The PEC/PNEC ratio was in the range of approximately 1000.

This was based on the NOAEL value given in the EPA 1999 report for arsenate (As^{5+}). This value was 0.0057 mg/kg bw/day (US Environmental Protection Agency, 1999). This appeared to be very low and when the source document was examined (Stanley and others 1994), the data in this study suggested that the dietary NOEC for mallard was 100 ppm. Diet intake by mallards was 0.1 kg diet/kg bw/day and so the NOAEL appeared to be 10 mg/kg bw/day, more than 3 orders of magnitude higher.

The EPA 1996 report gives a NOAEL for arsenite (As^{3+}) of approximately 5 mg/kg bw/day, similar to our estimate above for arsenate (Sample and others 1997).

The *Nereis* PEC values were on average 4.9 mg/kg and the recalculated PEC/PNEC ratios were in the range of 0.5-1 (upper range). Therefore it was concluded that a probabilistic risk assessment would not be carried out. However it should be noted that the initial screening calculations indicated that As concentrations measured in Nereis samples from the Severn are close to a level that would potentially pose a threat to bird populations.

g. **Chromium (Cr)**

Although a maximum PEC/PNEC ratio of 1 has been assigned to chromium, this was based on unpublished data which can not be verified. In addition, only one Nereis sample (out of 13) from the Severn samples had a Cr concentration high enough to exceed PEC/PNEC ratio of 1.

Given the paucity of toxicological information available it is unlikely that a rigorous risk assessment could be carried out for chromium. Therefore it was concluded that a probabilistic risk assessment was not be carried out. However it should be noted that the initial screening calculations indicated that Cr concentrations measured in Nereis samples from the Severn are close to a level that would potentially pose a threat to bird populations.

2.4 Conclusion

Based on the above, the metals of importance in terms of potential toxicity (PEC/PNEC ratios greater than 1) and for which there was likely to be reasonable toxicity data were

1. Hg
2. Pb
3. Se

Arsenic was considered to be border-line in terms of likely PEC/PNEC ratios, iron and zinc and chromium data were too uncertain or the endpoints were considered inappropriate. Therefore it was concluded that further effort in terms of detailed examination/search of the toxicity data and in terms of modelling should proceed with Hg, Pb and Se.

3 Probabilistic risk assessment

Following the screening risk assessment, three metals (Pb, Hg, Se) were studied in greater detail using:

1. Site specific data on habitats and feeding behaviour of three shorebird species
2. A detailed analysis of available information on LD_{50}s, LC_{50}s and NOAELs
3. A probabilistic PEC/PNEC risk assessment using a Monte-Carlo model.

Three shorebird species, dunlin, oystercatcher and curlew were chosen for the study as they represented a range of body sizes and lifestyles. Brief background information on each of these species is given in Appendix 2.

3.1 Modelling

The model was (as with the screening risk assessment) based on calculating the PEC/PNEC value, though this time the analysis was based on more detailed information, and on estimated probability distributions of parameter values.

The PEC was predicted using:

$$PEC = \sum_i f_i C_i \qquad (4)$$

where f_i is the fraction of the birds' diet composed of prey item i and C_i is the concentration (mg kg^{-1} DW) of the metal in prey item i.

The PNEC was estimated as before, using

$$\text{PNEC} = \frac{\text{NOAEL(mg/kg BW/day)} \times \text{BW (kg)}}{\text{FIR (kg dry weight/day)}} \qquad (5)$$

where NOAEL is the no observable adverse effects level, BW is the bird body weight and FIR is the average daily food intake rate. Note that we have (for convenience) here calculated PEC/PNEC on the basis of dry weight of prey, whereas in the screening assessment, PEC/PNEC was calculated on a fresh weight basis. Dry mass basis was used here because most of the available data on prey concentrations and feeding rates was on a dry mass basis. This makes no difference to the (dimensionless) final PEC/PNEC estimate.

A Monte-Carlo model was used to estimate ranges in possible PEC/PNEC values, given the available data and the observed variation in that data. For each variable, 10,000 random values were generated based either on a normal (or lognormal) distribution about a mean, or a uniform distribution within a range of possible values. Where data was available to determine mean and standard deviation of parameter values, either a normal or lognormal distribution was used according to the distribution of data. In some cases there was insufficient data to give distributions, so a uniform distribution was assumed between the range in observed parameter values. These parameter values were then input to the model to generate 10,000 values of PEC, PNEC and the ratio PEC/PNEC using the model described above. Figures 2 and 3 show an illustration of a model run for methyl-mercury in Dunlin, Poole Harbour.

Mercury can be found in prey items either as inorganic mercury (IOM) or as methylmercury (MeHg) (Muhaya and others 1997). IOM and MeHg have widely differing toxicities: the NOAEL of MeHg is more than two orders of magnitude greater than that of IOM. For mercury, therefore, an additional step was introduced into the model to estimate the fraction of total mercury which is in the form of MeHg.

Modelling was carried out in both estuaries for two scenarios: the "Average Scenario" and the "Worst Case" scenario. The Average Scenario represents the best estimate and range of possible PEC/PNEC values for the average bird of a particular species which is assumed (over a season) to have a dietary intake of contaminants equal to the mean concentration in prey across all the sites studied. The Worst Case scenario assumes a juvenile bird (which has lower BW:FIR ratio hence higher PEC:PNEC) feeding exclusively at the most contaminated site in each estuary.

Available data for *Nereis* was relatively good, but current data for other prey species (primarily molluscs and earthworms) is relatively sparse. As discussed in the model parameterisation section below, the values and ranges of contaminants in molluscs and earthworms had to be estimated on the basis of a literature review. For Hg and Se, however, there was insufficient information available to estimate these contaminants in earthworms, so the model for Hg and Se could only be applied to Dunlin (which consume no, or very low, fractions of earthworms in their diet).

3.2 Estimation of parameter values and ranges

Bird distribution and diet

Poole Harbour

Bird distributions and diets in Poole Harbour were determined using the Poole Harbour bird behaviour model (Stillman and others 2005). Model birds are assigned different levels of foraging efficiency and dominance which influence where and for how long they need to feed. These birds then distribute themselves over the six available habitat patches in order to maximise their food intake rates. As in real life, Dunlin fed most in upshore, muddy areas in the west and south of Poole Harbour, whilst oystercatchers and curlew fed most in the northern bays and Sandbanks areas. Figure 4 shows a map of Poole Harbour with relevant places marked.

The model used for Poole Harbour is a new individuals-based model, MORPH, described in detail in Durell and others (in press). As with previous models, MORPH tracks the location, behaviour and ultimate fate of each individual in a population and incorporates variation in the foraging and competitive abilities of different individuals. The model predicts how individual animals will respond to environmental change by altering their feeding location, consuming different food or by adjusting the amount of time they spend feeding.

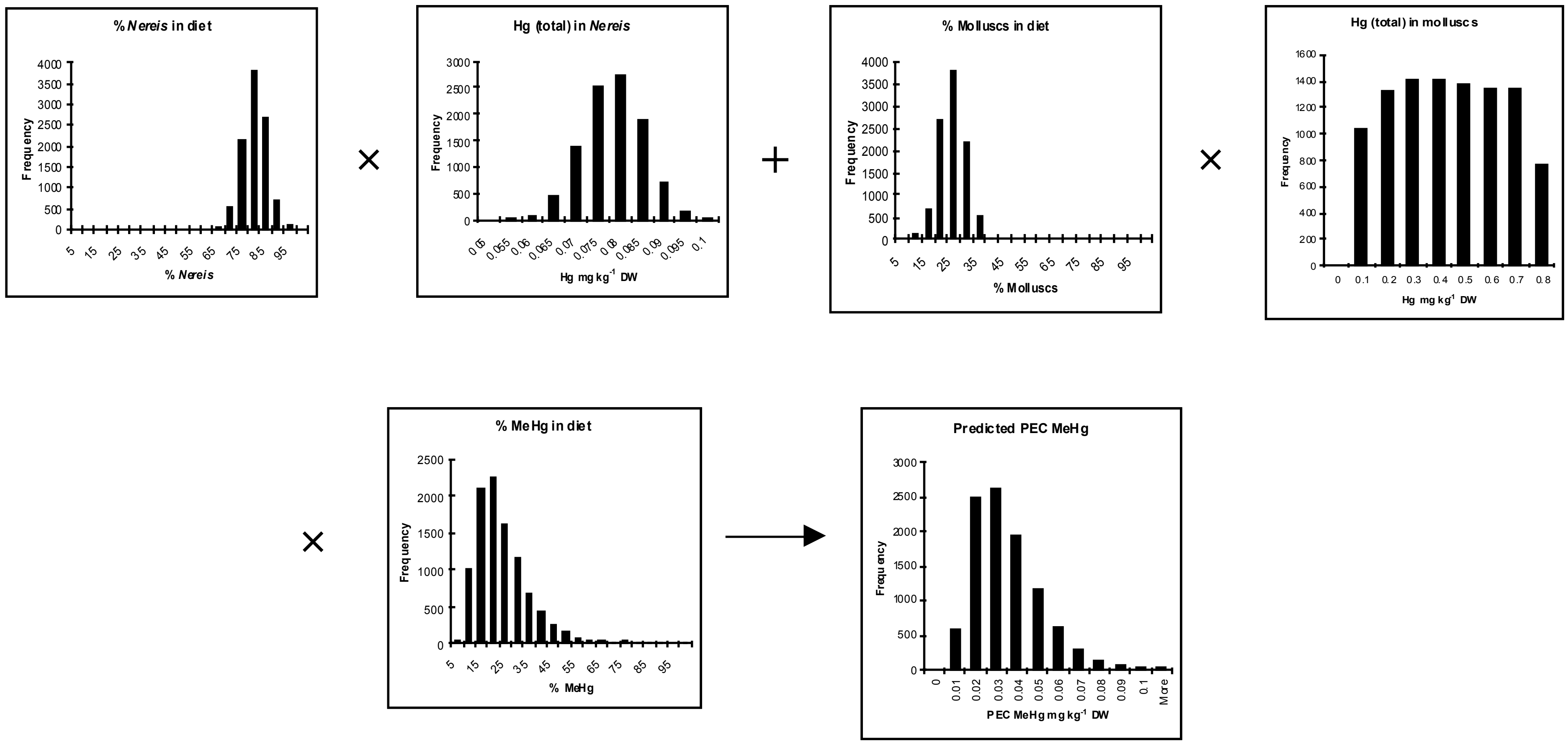


Figure 2 Illustration of the Monte-Carlo model PEC prediction for methyl-mercury in Dunlin (Average Scenario), Poole Harbour.
The graphs show the probability distributions of each input parameter and the figure illustrates the steps in the calculation of predicted PEC

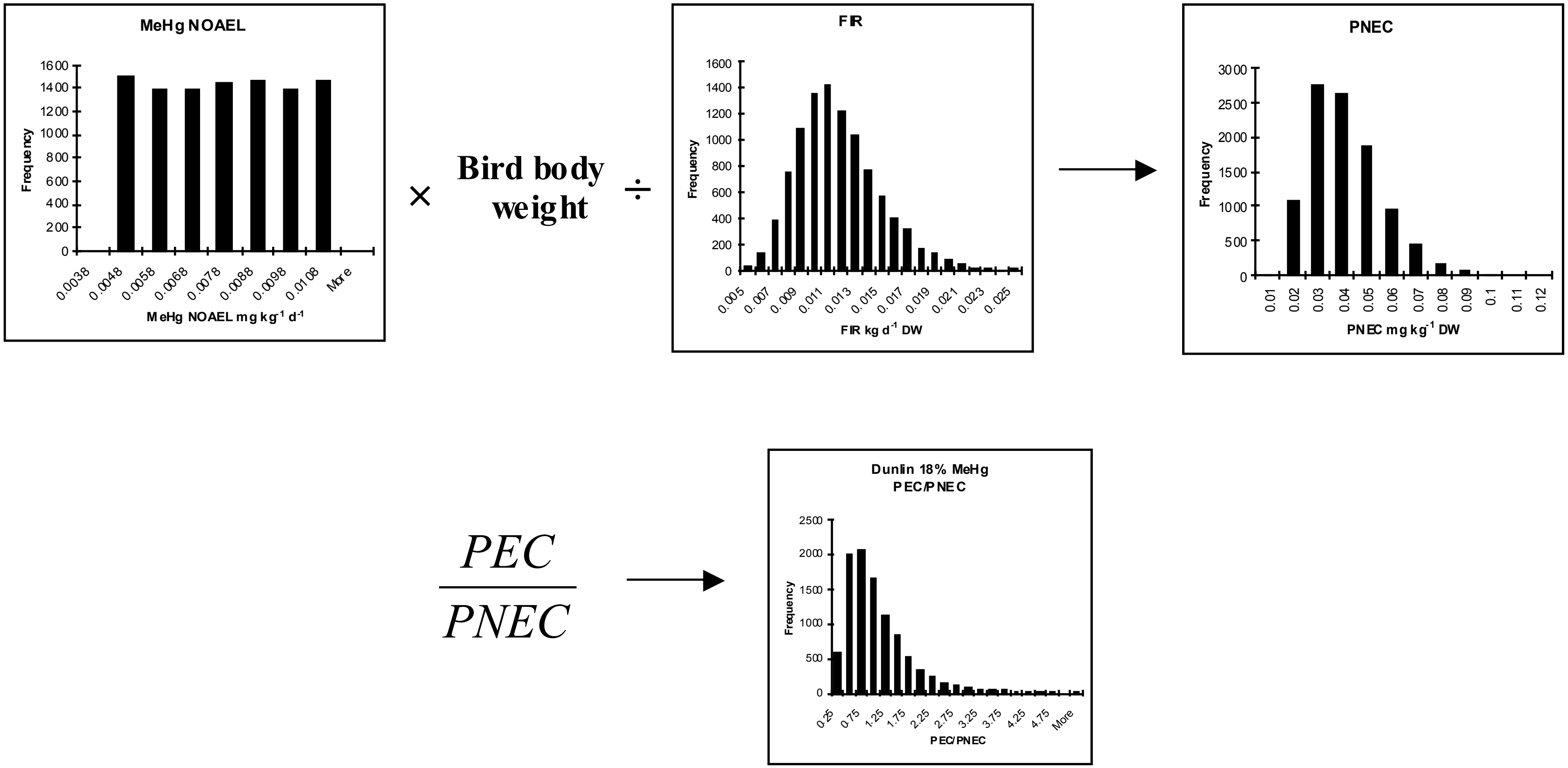


Figure 3 Illustration of the MC model PNEC and PEC/PNEC prediction for methyl-mercury in Dunlin (Average Scenario), Poole Harbour.
The graphs show the probability distributions of each input parameter and the figure illustrates the steps in the calculation of predicted PEC/PNEC.

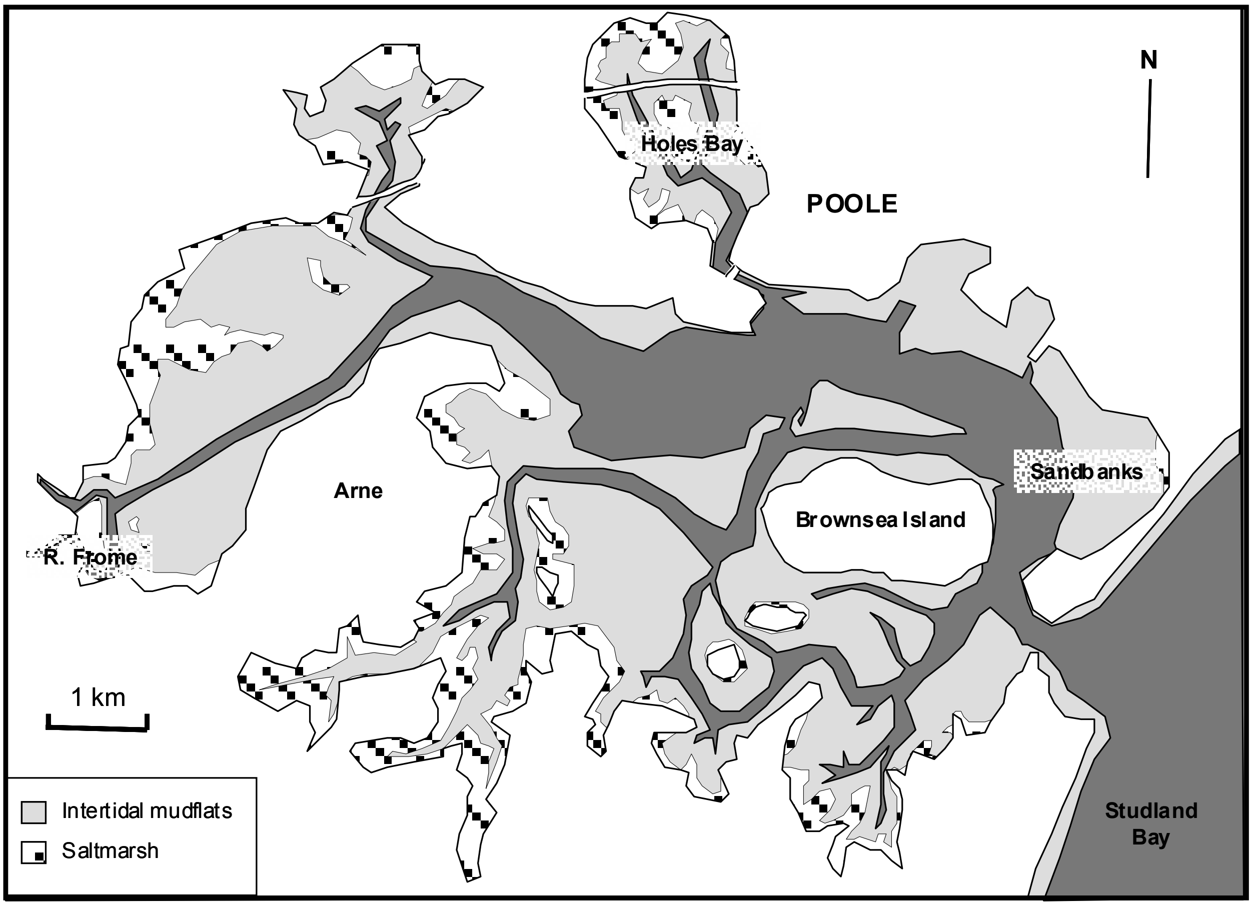


Figure 4 Poole Harbour

An example of the model output is given in Table 5 showing the division of feed types and associated uncertainty estimates. For dunlin, 78% of the diet was marine worms and 22% molluscs and crustaceans. The uncertainty in proportion of diet as marine worms was assumed to be normally distributed about the mean 78% with standard deviation 5%. Juvenile dunlin and curlew (Table 6) take similar food types to adults, so the same distribution of prey type was assumed as for the average scenario. Juvenile oystercatchers feed exclusively on marine worms and earthworms. It was assumed that 50% of the diet was marine worms and 50% earthworms.

Table 5 Percentage of different food types taken by Dunlin, Oystercatchers and Curlew in Poole Harbour – Average Scenario

	Dunlin	**Oystercatcher**	**Curlew**
Marine worms	78 % S.D. 5%	3.5% S.D. 1.2%	43% S.D. 4.4 %
Molluscs	100% minus % of marine worms	100% minus Σother	1.2% S.D. 0.34%
Crustaceans		0	0
Earthworms	0	20% S.D. 3%	100% minus Σother

Table 6 Percentage of different food types taken by juvenile Dunlin, Oystercatchers and Curlew in Poole Harbour – Worst Case Scenario

	Dunlin	Oystercatcher	Curlew
Marine worms	78 % S.D. 5%	50% S.D. 10%	43% S.D. 4.4 %
Molluscs	100% minus % of marine worms	0	1.2% S.D. 0.34%
Crustaceans		0	0
Earthworms	0	100% minus % marine worms	100% minus Σother

Bird distributions and diets (Tables 7 and 8) in the Severn estuary were determined from the Wetland Bird Survey (WeBS) data and a literature search. Dunlin are distributed widely around the estuary on muddy substrates, with particular concentrations at Bridgewater Bay, Berrow, New Grounds Slimbridge and Severn Beach (close to Avonmouth) (Figure 5). They feed mostly on polychaete worms, and also on the molluscs *Hydrobia* and *Macoma* (Worrall, 1984; Goss-Custard and others 1988). Proportions of each type of prey in dunlin diets were taken from Worrall (1984).

Oystercatchers feed mostly downstream from the Severn Bridge, with the largest concentrations being on the Welsh side of the estuary between Cardiff and Newport. Other concentrations are found at Berrow and at Severn Beach. As populations of bivalve molluscs are low on the Severn estuary, the majority of oystercatchers wintering there are worm-feeders (Goss-Custard and others 1988).

Curlew are found distributed throughout the Severn estuary, but by far the largest concentrations are found in Bridgewater Bay and on the Welsh side of the estuary near Collister Pill. The main diet of curlew in intertidal habitats is large marine worms (Goss-Custard and others 1988).

All three shorebird species are known to feed in fields around the Severn estuary, with curlew, in particular, feeding throughout the winter on the Gwent Levels (P. Ferns, D. Worrall and N. Burton pers. comm.). Earthworms, therefore, form a part of the diets of all three shorebirds. For Hg and Se, we did not have sufficient data to assess concentrations in earthworms (see below), so (in order to have at least one species represented in the Severn Estuary), for these metals we assumed that Dunlin consumed no earthworms. Because of their intake of earthworms, we could not assess intake of Hg, Se for Oystercatchers or Curlew in either Poole Harbour or the Severn Estuary.

Table 7 Percentage of different food types taken by Dunlin, Oystercatchers and Curlew in the Severn Estuary – Average Scenario

	Dunlin	Oystercatcher	Curlew
Marine worms	58 % S.D. 10%	100% minus Σother	43% S.D. 4.4 %
Molluscs	100% minus Σother	15% S.D. 5%	1.2% S.D. 0.34%
Crustaceans	0	0	0
Earthworms	0-10%	10% S.D. 5%	100% minus Σother

Table 8 Percentage of different food types taken by juvenile Dunlin, Oystercatchers and Curlew in the Severn Estuary – Worst Case Scenario

	Dunlin	Oystercatcher	Curlew
Marine worms	58 % S.D. 10%	100% minus Σother	43% S.D. 4.4 %
Molluscs	100% minus Σother	15% S.D. 5%	1.2% S.D. 0.34%
Crustaceans	0	0	0
Earthworms	0-10%	10% S.D. 5%	100% minus Σother

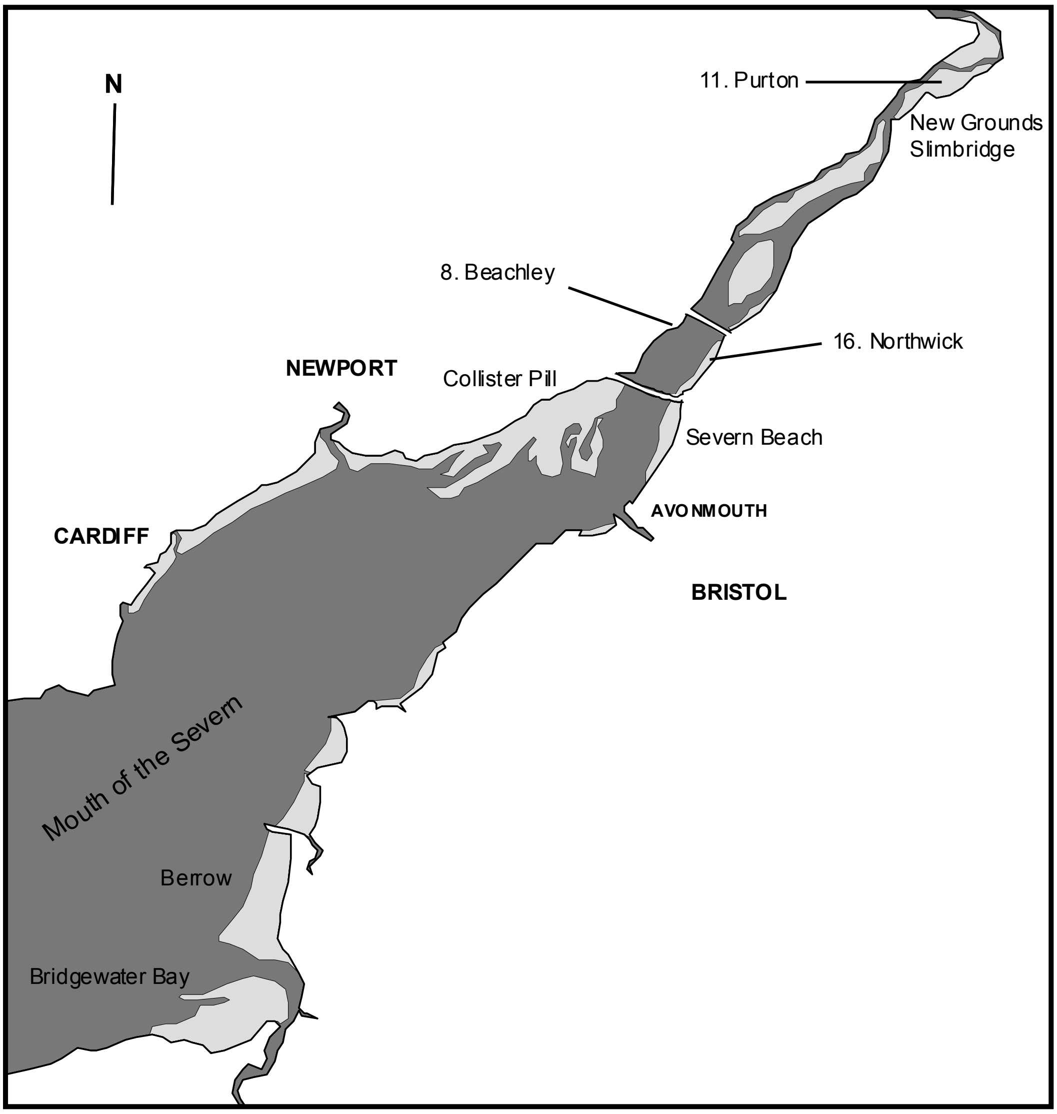


Figure 5 Map of the Severn estuary showing places mentioned in the text

Food intake rates

Average bird weights and dry matter intake rates (DMIs) for 15 species of shorebirds, gulls and auks were obtained from data presented in Nagy (2001). The dry matter intake rates were plotted against bird weight (Figure 6) and the best fit regression equation was determined.

The ratios:

$$\frac{Measured\ DMI}{\Pr edicted\ DMI} \tag{6}$$

were approximately lognormally distributed with mean (of logged ratios) 0 and standard deviation (of logged ratios) 0.123. The regression equation and distribution of residuals was used to determine the best estimate and uncertainty in the three shorebird species used in this study (Table 9).

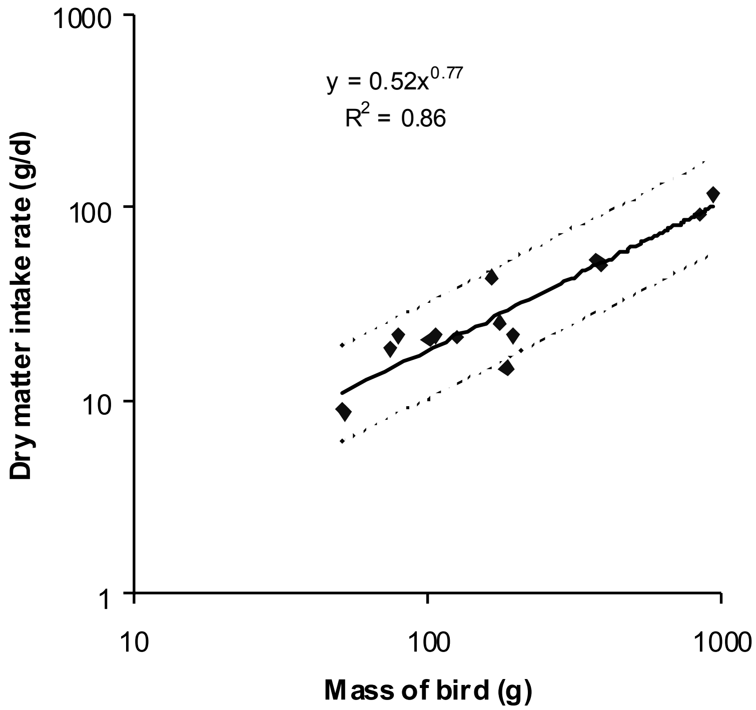


Figure 6 Regression of dry matter intake rate vs. mass of bird for 15 species (data from Nagy, 2001). Dotted lines show 2 S.D. uncertainty about the best estimate

Table 9 Bird masses and estimated dry matter intake rates (DMI) as used in the model

Species	Mass of bird, kg	DMI kg/d	S.D. kg/d
Adult Dunlin	0.0522	0.0109	0.0031
Juvenile Dunlin	0.0508	0.0107	0.0030
Adult Oystercatcher	0.537	0.0655	0.018
Juvenile Oystercatcher	0.492	0.0612	0.017
Adult Curlew	0.848	0.0931	0.026
Juvenile Curlew	0.800	0.0890	0.025

Metal concentration in diet – Poole Harbour

The data on contaminant residues in prey items supplied by EA were supplemented by a survey of literature, in particular the reviews of data on Poole Harbour (Langston, 2003a) and the Severn Estuary (Langston and others 2003b). Table 10 summarises some feeding characteristics of typical prey items.

For the average scenario, the metal content of *Nereis* was assumed to be normally distributed about the mean of the measured values for all sites in the harbour. In this case the uncertainty in the mean value (the standard error) was calculated as it is assumed (for the average scenario) that over a season the average bird will ingest prey at the mean metal concentration. The standard error in the mean is therefore appropriate. Where values were below the limit of detection, they were included in analyses of means and ranges of data by assuming that the value was equal to half the limit of detection.

Table 10 Prey species' feeding behaviours*

Species	Feeding behaviour	Feeding type
Nereis (Hediste) diversicolor Ragworm	Omnivorous, scavenging, filter feeding on suspended particles, deposit feeding on sediment materials.	Mud, sand, detritus, phytoplankton and plankton, other macrofauna.
Scrobicularia plana Peppery furrow shell	Active suspension feeder	Suspended/surface sediment particles
Cerastoderma edule Common cockle	Active suspension feeder	Phytoplankton, zooplankton, organic particulate matter.
Mytilus edulis Common mussel	Active suspension feeder	Bacteria, phytoplankton, detritus, dissolved organic matter.
Ostrea edulis Native oyster	Active suspension feeder	Suspended organic particles.
Crassostrea gigas Portuguese oyster	Active suspension feeder	Phytoplankton and protests
Macoma balthica Baltic telling	Active suspension feeder Surface deposit feeder	Diatoms, deposited plankton, suspended phytoplankton and detritus
Hydrobia ulvae Laver spire shell	Surface deposit feeder	Detritus, periphytic microalgae

*(MBA, 2005).

For Poole Harbour, we calculated the mean Pb in *Nereis* as 0.71 mg kg^{-1} DW, S.E. 0.11. and Hg in *Nereis* as mean: 0.076 mg kg^{-1} DW; S.E.: 0.0068.

Pb and Hg in molluscs and crustaceans was estimated by considering the available data on these organisms. Data on Pb and Hg in molluscs in Poole Harbour is summarised in Tables 11 and 12. We found no data on crustaceans so it was assumed that the range in crustaceans was equal to that in molluscs.

The data in Table 11 suggests that the Pb concentration of molluscs tends to be significantly higher than that in *Nereis*, though it is noted that the data was obtained over various different time periods. It is also clear from Table 11. that there is significant uncertainty in Pb concentrations in molluscs. We have assumed that the average Pb concentration in molluscs and crustaceans lies with equal probability (ie uniform probability distribution) between 3 × lower than and 10× higher than the average for *Nereis*, therefore in the range 0.24 – 7.1 mg kg^{-1} DW.

Table 11 Pb in various biota in comparison with *Nereis*, Poole Harbour

Pb mg kg^{-1} DW	Holes Bay	Brownsea/main harbour	Notes
Nereis (Hediste) diversicolor Ragworm	<0.5 – 1.6 Mean: 0.71 S.E.: 0.11		EA supplied data, 2004 range for Poole Harbour
	3.6		Langston and others. unpubl. Mean over 25 yr period.
Scrobicularia plana Peppery furrow shell	18		Langston and others unpubl. Mean over 25 yr period.
		5.8	EN supplied data 2004 Parkstone Bay
Cerastoderma edule Common cockle	14	5	Boyden (1975) samples from 1973-4
Mytilus edulis Common mussel	19	7	Boyden (1975) samples from 1973-4
		10.5*	MAFF (1998) Main harbour, site not specified.
Ostrea edulis Native oyster	1.2	0.35	Langston and others (2003a). Data from 1983.
Crassostrea gigas Portuguese oyster		2.5	Langston and others (2003a). Data from 1983.

* converted to DW basis using a FW/DW ratio of 7 for bivalves.

Table 12 Hg in various biota in comparison with *Nereis*, Poole Harbour

Hg mg kg^{-1} DW	Holes Bay	Brownsea/main harbour	Notes
Nereis (Hediste) diversicolor Ragworm	0.038 – 0.11 Mean: 0.076 S.E.: 0.0068		EA supplied data, 2004 range for Poole Harbour
	0.24		Langston and others unpubl. Mean over 25 yr period.
Scrobicularia plana Peppery furrow shell	1.08		Langston and others unpubl. Mean over 25 yr period.
		0.14	EN supplied data 2004 Parkstone Bay
Mytilus edulis Common mussel		0.413*	MAFF (1998) Main harbour, site not specified.
Ostrea edulis Native oyster	0.49	0.16	Langston and others (2003a). Data from 1983.
Crassostrea gigas Portuguese oyster		0.26	Langston and others (2003a). Data from 1983.

* converted to DW basis using a FW/DW ratio of 7 for bivalves.

The data in Table 12 suggests that the Hg concentration of molluscs tends to be significantly higher than that in *Nereis*, though it is noted that the data was obtained over various different time periods (metal contamination is expected to decline over time). It is also clear from Table 12 that there is significant uncertainty in Hg concentrations in molluscs. We have assumed that the average Hg concentration in molluscs and crustaceans lies with equal probability (ie uniform probability distribution) between 3× lower than and 10× higher than the average for *Nereis*, therefore in the range 0.025 – 0.76 mg kg^{-1} DW.

For the worst-case scenario, it was assumed that the mean concentration of Pb and Hg in *Nereis* was equal to the highest value measured at any of the sites in the harbour. For Pb this was 1.6 mg kg^{-1} DW measured at the mouth of the Frome and for Hg this was 0.113 mg kg^{-1} DW measured in Holes Bay near Creekmoor. There is not sufficient data to determine the accuracy of this worst case estimate, but a normal distribution of values with coefficient of variation of 25% is a reasonable conservative estimate. For molluscs and crustaceans, it is assumed, for the worst case scenario, that the average concentration at the most contaminated site is from 3-10 times higher than the maximum measured value in *Nereis* (ie for Pb, 4.8-16 mg kg^{-1} DW; for Hg, 0.34-1.1 mg kg^{-1} DW).

Metal concentration in diet – Severn Estuary

For the Average Scenario, the metal content of *Nereis* was assumed to be normally distributed about the mean of the values measured at all the different sites in the harbour. In this case, the uncertainty in the mean value (the standard error) was calculated as it is assumed (for the average scenario) that over a season the average bird will ingest prey at the mean metal concentration. The standard error in the mean is therefore appropriate. Where values were below the limit of detection, they were included in analyses of means and ranges of data by assuming that the value was equal to half the limit of detection.

For the Severn Estuary, we calculated the mean Pb in *Nereis* as 1.51 mg kg^{-1} DW, S.E. 0.32. Hg in *Nereis:* mean: 0.48 mg kg^{-1} DW; S.E.: 0.10. Se in *Nereis* has mean 8.42 mg kg^{-1} DW, S.E. 1.75 mg kg^{-1}.

Pb and Hg in molluscs and crustaceans was estimated by considering the available data on these organisms. Data on Pb and Hg in molluscs in the Severn Estuary is summarised in Tables 13 and 14 We found no data on crustaceans so it was assumed that the range in crustaceans was equal to that in molluscs.

The data in Table 13 suggests that the Pb concentration of molluscs tends to be significantly higher than that in *Nereis*, though it is noted that the data was obtained over various different time periods. It is also clear from Table 13 that there is significant uncertainty in Pb concentrations in molluscs. We have assumed that the average Pb concentration in molluscs and crustaceans lies with equal probability (ie uniform probability distribution) between 3× lower than and 10× higher than the average for *Nereis*, therefore in the range 0.50 – 15.1 mg kg^{-1} DW.

There is little evidence from the data in Table 14 to suggest that the Hg concentration of molluscs is significantly different to that in *Nereis* in the Severn Estuary. It is noted that the data was obtained over various different time periods (metal contamination is expected to tend to decline over time). It is also clear from Table 14 that there is significant uncertainty in Hg concentrations in molluscs. We have assumed that the average Hg concentration in molluscs and crustaceans lies with equal probability (ie uniform probability distribution) between 3× lower than and 3× higher than the average for *Nereis*, therefore in the range 0.16 – 1.44 mg kg^{-1} DW.

Table 13 Pb in various biota in comparison with *Nereis*, Severn Estuary

Pb mg kg^{-1} DW	Avonmouth	Severn Estuary	Notes
Nereis (Hediste) diversicolor Ragworm	0.55-2.3* Mean: 1.51 SE: 0.32		EA supplied data, 2004 range for Severn Estuary
	44.9	11.4; 17.0	Ferns and Anderson (1997), samples from 1979/80
	3.56		Langston and others (2003b). Mean over 25 year period
Scrobicularia plana Peppery furrow shell	43.5		Langston and others (2003b). Mean over 25 yr period.
Mytilus edulis Common mussel		10.0	Cardiff Flats EA data 2001-05
Macoma balthica Baltic tellin	40.6	19.5 – 27.5	Ferns and Anderson 1997. Samples from 1979/80.
Nephthys hombergi Catworm	91.9		Ferns and Anderson 1997. Samples from 1979/80.
Hydrobia ulva Laver spire shell	44.5		Ferns and Anderson 1997. Samples from 1979/80.

* converted to DW basis using a FW/DW ratio of 4.4 for *Nereis*.

Table 14 Hg in various biota in comparison with *Nereis*, Severn Estuary

Hg mg kg^{-1} DW	Severn Estuary	Notes
Nereis (Hediste) diversicolor Ragworm	0.08 – 0.89*	EA supplied data, 2004 range for Severn Estuary
	1.42	Langston and others (2003b). Mean over 25 yr period.
Scrobicularia plana Peppery furrow shell	0.64	Langston and others (2003b). Mean over 25 yr period.
Mytilus edulis Common mussel	0.61 0.5	Langston and others (2003b). Date not known. Cardiff Flats EA data 2001-05

* converted to DW basis using a FW/DW ratio of 4.4 for *Nereis*.

There is much less information on selenium concentrations in biota than on the other metals. Table 15 shows the data on Se supplied by the Environment Agency for the Severn Estuary. Se in *Nereis* has mean 8.42 mg kg^{-1} DW, S.E. 1.75 mg kg^{-1}. The range in measured values for *Mytilus edulis* is similar to that of *Nereis*, though it is noted that only data from one site (Cardiff Flats) was available for *Mytulis edulis*. We have assumed that the average Se concentration in molluscs and crustaceans lies with equal probability (ie uniform probability distribution) between 3× lower than and 3× higher than the average for *Nereis*, therefore in the range 2.81 – 25.26 mg kg^{-1} DW.

For the worst-case scenario, it was assumed that the mean concentration of Pb, Hg and Se in *Nereis* was equal to the highest value measured at any of the sites in the estuary. For Pb this was 2.3 mg kg^{-1} DW measured at Beachley Point, for Hg this was 0.89 mg kg^{-1} DW measured at Northwick and for Se this was 17.4 mg kg^{-1} DW measured at Hills Flats. There is not sufficient data to determine the accuracy of this worst case estimate, but a normal distribution of values with coefficient of variation of 25% is a reasonable conservative estimate. For molluscs and crustaceans, it is assumed, for the worst case scenario, that the average concentration at the most contaminated site is from 3-10 times higher (for Pb) and from 1-3 times higher (for Hg and Se) than the maximum measured value in *Nereis* (ie for Pb, 6.9-23 mg kg^{-1} DW; for Hg, 0.89-2.67 mg kg^{-1} DW; for Se, 17.4-52.2 mg kg^{-1} DW). These ranges are estimated from consideration of the ranges in measured values presented in Tables 13-15.

Table 15 Se in various biota in comparison with *Nereis*, Severn Estuary

Se mg kg^{-1} DW	Severn Estuary	Notes
Nereis (Hediste) diversicolor Ragworm	1.2-17.4	EA supplied data, 2004 range for Severn Estuary
Mytilus edulis Common mussel	7.2-16.5	Cardiff Flats EA data 2001-05

Metal concentrations in earthworms

A significant proportion of the diet of oystercatchers and curlew is made up of earthworms from fields surrounding the estuaries (Tables 5-8).

Measurements of Pb in earthworms have been made in the vicinity of the Avonmouth Smelter and at a control site 110 km away (Spurgeon, 1994). Measurements 1.3 km from the smelter were up to 391 mgPb kg^{-1} DW, dropping to 28 mgPb kg^{-1} DW at 9.7 km distance. At the control site, the lead concentration was 27 mg Pb kg^{-1} DW. Concentrations at Dinas Powys close to Cardiff were in the range 4 – 12.3 mg kg^{-1} DW ((Morgan and others 1991). For both Poole Harbour and the Severn Estuary, we assumed that the concentration of Pb could take any value with in the observed range for "control" sites (ie not close to the Avonmouth smelter): 4-27 mg kg^{-1}. The mean for "control" sites was 16.7 mg kg^{-1} DW with S.E. 4.7.

In the time available we could not find sufficient data on Hg or Se in earthworms to estimate concentrations and ranges, so we have not carried out modelling of Hg in oystercatchers and curlew. The best estimates of mercury concentrations in earthworms comes from a paper by (Bull and others 1977) where they measured residues in two sites. A polluted site, near a chlor-alkali plant, had a mean dry weight Hg concentration in *Lumbricus terrestris* of 1.29 +/- 0.32 (+/- SE; n=18; range 0.27-3.27 mg kg^{-1}). A control site, 10-30 km from the chlor-alkali plant, had a mean dry weight Hg concentration in *Lumbricus terretris* of 0.041+/- 0.006 (+/- SE; n=18; range 0.031-0.048 mg kg^{-1}). The concentrations of Hg in earthworms at the control site are generally significantly lower than those measured in estuarine biota suggesting that (in contrast to Pb), Hg in earthworms may not play an important part in determining Hg concentrations in shorebirds. This would imply that the PEC/PNEC values for Oystercatchers and Curlew would be significantly lower than for Dunlin (for which we were able to calculate PEC/PNEC for Hg).

For Se, in a brief literature review, we found only one study on earthworms (Beyer and others 1987a; Beyer and others 1987b). Based on this paper we calculated the average Se conc. in a range of earthworm species as 0.39 +/- 0.15 (+/- SEM) mg/kg dry weight, N=9 (assuming a limit of detection of 0.05 mg/kg). As with Hg, this is lower than concentrations observed in

Nereis and *Mytilus edulis* suggesting that Se in earthworms may not play an important part in determining the exposure of shorebirds to Se. This would imply that the PEC/PNEC values for Oystercatchers and Curlew would be significantly lower than for Dunlin (for which we were able to calculate PEC/PNEC for Se).

Proportion of mercury as methylmercury

The NOAEL of methylmercury (MeHg) is approximately two orders of magnitude lower than that of inorganic mercury. It is therefore important to estimate the proportion of Hg in prey items which is in the form of methylmercury. A study (Muhaya ., 1997) measured the proportion of Hg as MeHg in *Nereis* at13 sites in the Netherlands. From these measurements, the mean proportion of Hg as MeHg is approximately 18%. Since the distribution of values was highly skewed, these data were log-transformed to give a mean log transformed proportion of 1.28 with SD 0.22. This log-transformed distribution was used to generate random values for the Monte-Carlo model; the values then being back-transformed for use in the model.

3.3 Thresholds for observable effects of contaminants on birds

A literature search was conducted to identify studies from which No Observed Adverse Effect Level (NOAEL) data for avian effects could be derived for Hg (both inorganic and organic forms), Pb and Se. This literature search was conducted using the web of knowledge (ISI, 2005), environmental health criteria (World Health Organisation, 1989a; World Health Organisation, 1989b; World Health Organisation, 1990; World Health Organisation, 1991), US EPA ECOTOXicology database (US Environmental Protection Agency, 2002), and a number of US EPA reports (Sample ., 1997; US Environmental Protection Agency, 1999; US Environmental Protection Agency, 2005). Where possible the original papers or reports were assessed. A number of criteria were used to decide whether the NOAEL values could be included in the risk assessment and are listed below.

1. NOAEL data for effects on reproduction and growth were included in the risk assessment while those studies that established NOAELs for effects at the physiological, metabolic, biochemical and lower levels of organisation were excluded. This distinction was made because effects on reproduction and growth are more likely to affect population densities than those lower order effects.

2. To avoid pseudo-replication within the risk assessment only one value was used from studies where multiple NOAELs were derived from a single exposure. However, where NOAEL values were derived in the same paper but from distinct exposures these values were included.

3. Studies in which the highest exposure level was assumed to be the NOAEL because no effects were observed in any exposure level were excluded from the risk assessment. NOAELS were only included in the risk assessment from studies where effects were observed at exposure levels higher than the estimated NOAEL.

The NOAEL values that passed the above criteria are listed in Table 16; while those that were identified but failed the criteria are listed in Table 17.

The ranges in NOAEL used in the model (derived directly or using LD50/100) are summarised in Table 18. For MeHg, NOAELs could also be derived from LD50 values. For MeHg, there are LD50 values for Hg for six species of bird (multiple values for most species). We calculated a geometric mean LD_{50} for each species, then divided these figures by a factor of 100 to convert them to NOAELs. This factor has been taken from the USEPA approach (USACHPPM, 2000). The range of NOAELs derived in this way is 0.195 to 0.378 mg/kg bw/d, approximately 30 to 60 times higher than that reported for methyl mercury dicyandiamide (Table 16).

The LD_{50} data for lead is even more sparse than that for mercury. We were only able to find two LD_{50} estimates, both using tetraethyl lead (TEL) which was used in leaded petrol. We calculated the LD_{50} values in terms of lead rather than the whole compound (this is the approach we have taken throughout this study). The LD_{50}s were then converted to NOAELs by multiplying by a factor of 0.01 (as with Hg). These values fall within the range of experimentally derived reproductive NOAELs for lead (Table 16). Use of these LD_{50} derived values may, however, be open to question because the data were for TEL rather than an inorganic salt. Inorganic salts have not been extensively tested on birds because they are not seen to pose a significant environmental risk; typical LC_{50} values exceed 5000 mg Pb/kg food. We have therefore not used the $LD_{50}/100$ values for lead in the probabilistic model.

A brief literature search (WoS, Environmental Health Criteria No. 58, and ecotoxdatabase search) did not yield avian LD_{50} data for selenium. We do not believe that a more protracted search would yield many values so, as with lead, we simply used the directly measured NOAEL data for selenium.

Table 16 Summary of avian no observed adverse effect levels (NOAELs) for selected contaminants that were included in the probabilistic risk assessment

Metal	Form	Species	Exposure Duration (d)	Critical Endpoint	NOAEL[1] (mg/kg BW/day)	Reference
Pb	Lead acetate	Chicken (*Gallus domesticus*)	28	Egg Production	1.63	[7]
	Lead acetate	Japanese quail (*Coturnix c. japonica*)	84	Progeny Counts	0.019*	[7]
	Lead acetate	Japanese quail (*Coturnix c. japonica*)	35	Egg Production	0.194	[7]
	Lead acetate	Japanese quail (*Coturnix c. japonica*)	84	Egg Production	0.011*	[32]
Se	Sodium selenite	Mallard (*Anas platyrhynchos*)	78	Embryo Deformities	0.5	[11]
	Selenomethionine	Mallard (*Anas platyrhynchos*)	100	Duckling Survival	0.4	[24]
	Selenomethionine	Eastern Screech Owl (*Megascops asio*)	96	Egg Production and Hatchability	0.44	[33]
	Selenomethionine	Mallard (*Anas platyrhynchos*)	124	Reproductive Effects[2]	0.1*	[4]

[1] Values with a * superscript are based on a LOAEL divided by a factor of 10, those with a # superscript are based on a LD_{50} value divided by a factor of 100.

[2] Reproductive effects include embryo deformities, hatching success and duckling growth, mortality and production.

Table 16 Summary of avian no observed adverse effect levels (NOAELs) for selected contaminants that were included in the probabilistic risk assessment

Metal	Form	Species	Exposure Duration (d)	Critical Endpoint	NOAEL[1] (mg/kg BW/day)	Reference
Hg (inorganic)	Mercury sulphate	White leghorn hen (*Gallus domesticus*)	21	Egg Hatchability	5.5	[34]
	Mercuric chloride	Japanese quail (*Coturnix c. japonica*)	140	Egg Production	0.45	[9]
	Mercuric chloride	Japanese quail (*Coturnix c. japonica*)	N/A	Mortality	0.30#	[35]
Hg (organic)	Methyl mercury chloride	Great Egret (*Ardea albus*)	91	Growth	0.0038	[36]
	Methyl mercury chloride	Great Egret (*Ardea albus*)	91	Growth	0.0108	[36]
	Methyl mercury dicyandiamide	Mallard (*Anas platyrhynchos*)	>365	Egg and Duckling Production	0.0064*	[20]
	Methyl mercury dicyandiamide	Mallard (*Anas platyrhynchos*)	N/A	Mortality	0.289#	[37]
	Methyl mercury	Bobwhite quail (*Colinus virginianus*)	N/A	Mortality	0.239#	[37]
	Methyl mercury	Japanese quail (*Coturnix c. japonica*)	N/A	Mortality	0.195#	[35, 37]
	Methyl mercury	Fulvous whistling duck (*Dendrocygna bicolour*)	N/A	Mortality	0.378#	[37]
	Methyl mercury dicyandiamide	House sparrow (*Passer domesticus)*	N/A	Mortality	0.219#	[37]
	Methyl mercury dicyandiamide	Pheasant (*Phasianus colchicus*)	N/A	Mortality	0.253#	[37]

[1] Values with a * superscript are based on a LOAEL divided by a factor of 10, those with a # superscript are based on a LD_{50} value divided by a factor of 100.

Table 17 Summary of avian no observed adverse effect levels (NOAELs) for selected contaminants that were excluded from the probabilistic risk assessment

Metal	Form	Species	Exposure Duration (d)	Critical Endpoint	NOAEL (mg/kg BW/day)	Reason for Exclusion	Reference
Pb	Lead acetate	Chicken (*Gallus domesticus*)	70	Progeny Numbers	0.326	NOAEL not reliable figure because no dose-dependentr relationships defined	[7]
	Lead oxide	Chicken (*Gallus domesticus*)	30	Albumen Weight	2.69	Endpoints not ecologically relevantt	[38]
	Lead acetate	Japanese quail (*Coturnix c. japonica*)	7	Total Production	0.931		[39]
	Lead acetate	Japanese quail (*Coturnix c. japonica*)	32	Egg Production	125	Egg production too low and variable in control group.	[40]
Se	Selenomethionine	Black-Crowned Night-Heron (*Nycticorax nycticorax*)	94	Reproduction	>1.8	NOAEL is top dose group and therefore underestimate of value	[2]
	Sodium selenite	Japanese quail (*Coturnix c. japonica*)	32	Egg Production	>0.1	NOAEL is top dose group and therefore underestimate of value	[40]
Hg (inorganic)	No studies were excluded for this contaminant						
Hg (methylated)	No studies were excluded for this contaminant						

The ranges in the NOAEL values used in the model (derived directly or using $LD_{50}/100$) are summarised in Table 18.

Table 18 Ranges and assumed probability distributions of NOAEL and LD50/100 values for Pb, Hg and Se

Metal	Endpoint	Range mgMetal/kgBW/d	Assumed probability distribution*
Pb	NOAEL	0.011-1.6	Uniform distribution of log-transformed values
MeHg	NOAEL	0.0038-0.0108	Uniform
MeHg	LD50/100	0.195-0.378	Uniform
IOM	NOAEL	0.45 – 5.5	Uniform
Se	NOAEL	0.1-0.5	Uniform

* A uniform distribution assumes that the endpoint can take any value between the upper and lower bounds with equal probability.

3.4 Results

The model output is presented as histograms of the probability distribution of estimated PEC/PNEC values for each model run (Appendix 3). We have also summarised these data to give the median, 5th and 95th percentile values of PEC/PNEC for Poole Harbour (Table 19) and the Severn Estuary (Table 20).

Table 19 Median, 5 and 95 percentile PEC/PNEC values for Poole Harbour

Metal	Species	Basis for PNEC	PEC/PNEC 5%	PEC/PNEC 50%	PEC/PNEC 95%
Average scenario					
Pb	Dunlin	NOAEL	0.18	1.97	21.8
Pb	Oystercatcher	NOAEL	0.45	4.97	55.9
Pb	Curlew	NOAEL	1.22	6.86	28.7
Hg	Dunlin	NOAEL	0.23	0.79	2.41
Hg	Dunlin	LD50/100	0.0061	0.02	0.055
Worst case scenario					
Pb	Dunlin	NOAEL	0.48	5.62	58.0
Pb	Oystercatcher	NOAEL	0.67	7.24	83.4
Pb	Curlew	NOAEL	0.65	7.52	85.1
Hg	Dunlin	NOAEL	0.45	1.39	4.34
Hg	Dunlin	LD50/100	0.012	0.035	0.10

Table 20 Median, 5 and 95 percentile PEC/PNEC values for the Severn Estuary

Metal	Species	Basis for PNEC	PEC/PNEC 5%	PEC/PNEC 50%	PEC/PNEC 95%
Average scenario					
Pb	Dunlin	NOAEL	0.58	6.45	74.6
Pb	Oystercatcher	NOAEL	0.33	3.37	35.5
Pb	Curlew	NOAEL	0.58	6.70	82.7
Hg	Dunlin	NOAEL	1.01	3.37	10.7
Hg	Dunlin	LD50/100	0.035	0.084	0.19
Se	Dunlin	NOAEL	***3.07***	7.70	21.7
Worst case scenario					
Pb	Dunlin	NOAEL	1.11	11.7	121
Pb	Oystercatcher	NOAEL	0.47	4.77	50.6
Pb	Curlew	NOAEL	0.69	7.43	85.3
Hg	Dunlin	NOAEL	2.31	6.94	21.9
Hg	Dunlin	LD50/100	0.060	0.18	0.51
Se	Dunlin	NOAEL	7.72	17.9	48.5

Pb

An example of the model output for Pb in Dunlin in Poole Harbour (Average Scenario) is shown in Figure 7, illustrating the wide range in estimates. This (as discussed in the *Uncertainty Analysis* section, below) is due to the very high uncertainty in estimation of the NOAEL.

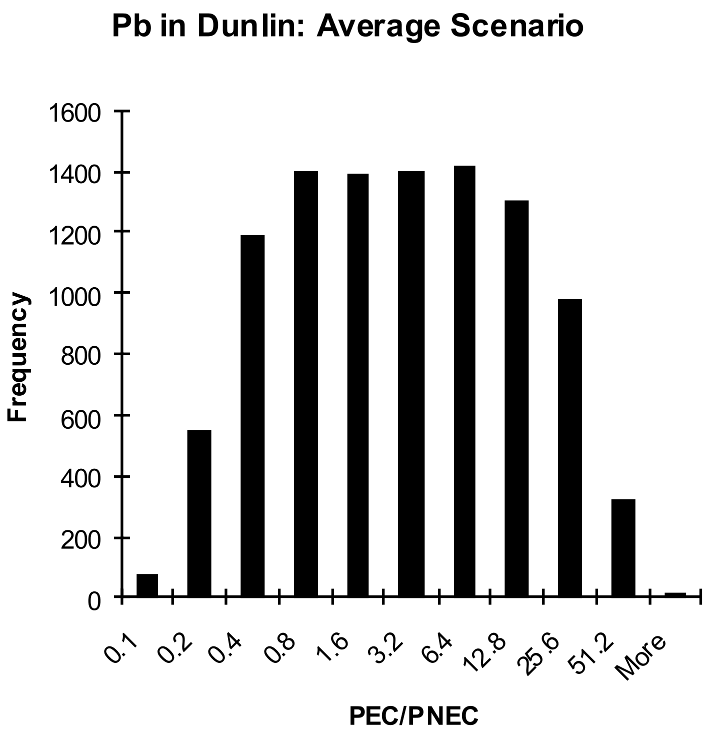


Figure 7 Lead in Dunlin, Poole Harbour (Average Scenario)

For the Average Scenario, median PEC/PNEC values for Pb ranged from 2-7 for all species in both estuaries. The lowest 5% value was of order 1 or less in all cases, but the highest 95% values ranged from 22-83. For the Worst Case scenario, median PEC/PNEC values were only slightly higher than for the Average Scenario, but 95% values were significantly higher, ranging up to 121.

In Poole Harbour, PEC/PNEC values for Pb tended to be higher in Curlew and Oystercatchers than in Dunlin. This was primarily due to the high consumption of earthworms in these species, and the relatively high estimated content of Pb in earthworms. This contrasted with the Severn Estuary where the Pb PEC/PNECs ratios were relatively high in Dunlin compared with the other species, primarily as a result of the high Pb in molluscs and high FIR:body mass ratio in these small birds.

Hg

Mercury contamination was assessed in both estuaries, though only one species, Dunlin, could be assessed owing to the paucity of data on mercury in earthworms. Note (as discussed in the Methods section) that although Dunlin in the Severn Estuary eat a small proportion (0-10%) of earthworms in their diet, we have assumed that they do not eat earthworms as we have insufficient data on Hg content of earthworms. This is likely to very slightly over-estimate the PEC/PNEC values since the limited evidence we have found suggests that Hg in earthworms are in most cases lower than in estuarine prey species.

There was sufficient ecotoxicological data to compare the PEC/PNEC for methyl mercury (MeHg) based either on the NOAEL, or on the calculated LD50/100. The range in NOAEL for MeHg is 0.0038 to 0.0108 mg Hg/kgBW/d. The range of derived NOAELs using LD50/100 is 0.195 to 0.378 mg/kg bw/d, approximately 30 to 60 times higher.

As is evident from Tables 19 and 20, the NOAEL gave significantly higher PEC/PNEC values than the LD50/100. Based on the LD50/100, Hg would not be predicted to have any environmental impact on either estuary since PEC/PNEC values are significantly lower than 1. There is a significant (ie >5%) probability that PEC/PNEC values for Hg (based on the NOAEL) are greater than 1 in both Poole Harbour and the Severn Estuary. Nevertheless, PEC/PNEC values for Hg (MeHg, based on NOAEL) are much lower than for Pb: in Poole Harbour, median PEC/PNEC is close to 1 for both Average and Worst Case scenarios.

Mercury toxicity is strongly dependent on the fraction present as MeHg. The range in NOAEL for inorganic mercury (IOM) is approximately two orders of magnitude higher than that for MeHg: 0.45 to 5.5 mg Hg/kg/d. We have assumed that 18% (log transformed: 1.28 with SD 0.22) of Hg is present in prey as MeHg (Muhaya ., 1997). If it was assumed that all Hg was present as IOM, then PEC/PNECs would be significantly less than 1 in all cases. If, however, a higher proportion was present as MeHg, PEC/PNEC values would be significantly greater than those presented here.

Se

Selenium data were available for prey in the Severn Estuary, though relatively few data were available for prey species other than *Nereis*. Only one species, Dunlin, could be assessed owing to the paucity of data on selenium in earthworms. Note (as discussed in the *Methods* section) that although Dunlin in the Severn Estuary eat a small proportion (0-10%) of earthworms in their diet, we have assumed that they do not eat earthworms as we have insufficient data on their Se content. This is likely to very slightly over-estimate the PEC/PNEC values since it is likely that Se in earthworms are in most cases lower than in estuarine prey species.

The predicted Se PEC/PNEC values (Table 20) are significantly greater than 1: values are predicted to be in the range 3.1 – 22 for the Average Scenario and in the range 7.7 – 49 for the Worst Case Scenario. Thus (as with Pb) there is predicted to be a very high probability that PEC/PNEC for Se significantly exceeds 1.

3.5 Sensitivity analysis

We have evaluated the sensitivity of the model to uncertainty in different input parameters. The sensitivity analysis was carried out by first assigning to each of the input parameters its mean value. Individual input parameters were then assigned random values within their uncertainty distributions for 10,000 model runs to determine the impact of uncertainty in each input parameter on the model outcome. Illustrative results of different sensitivity analyses are discussed here.

Pb

There is a very large uncertainty in the NOAEL for Pb: this varies uniformly over a range spanning two orders of magnitude. As shown in Figure 8, this uncertainty in NOAEL dominates the uncertainty in PEC/PNEC for Pb: when all other parameters are assigned their mean value, the predicted PEC/PNEC when only NOAEL varies spans a similar range to that predicted when all parameters are allowed to vary. When the sensitivity analysis was carried out for other parameters (ie other individual parameters varied whilst all other parameters assigned their mean) the variation in predicted PEC/PNEC was minor (Figure 8).

Hg

The sensitivity analysis for Hg is illustrated in Figure 9. The PEC/PNEC is predicted with significantly greater certainty than that for Pb – PEC/PNEC values for Hg are predicted within a range of approximately one order of magnitude. The percentage of Hg as MeHg is the most important source of uncertainty in predicted PEC/PNEC, though uncertainty in Hg content of molluscs, FIR and NOAEL all contribute significantly to model uncertainty.

Se

As shown in Figure 10 the PEC/PNEC for Se is predicted to be significantly less uncertain than that of Pb: PEC/PNEC values are predicted to vary within a range of approximately one order of magnitude. Uncertainty in Se content of molluscs, FIR and NOAEL all contribute significantly to uncertainty in PEC/PNEC.

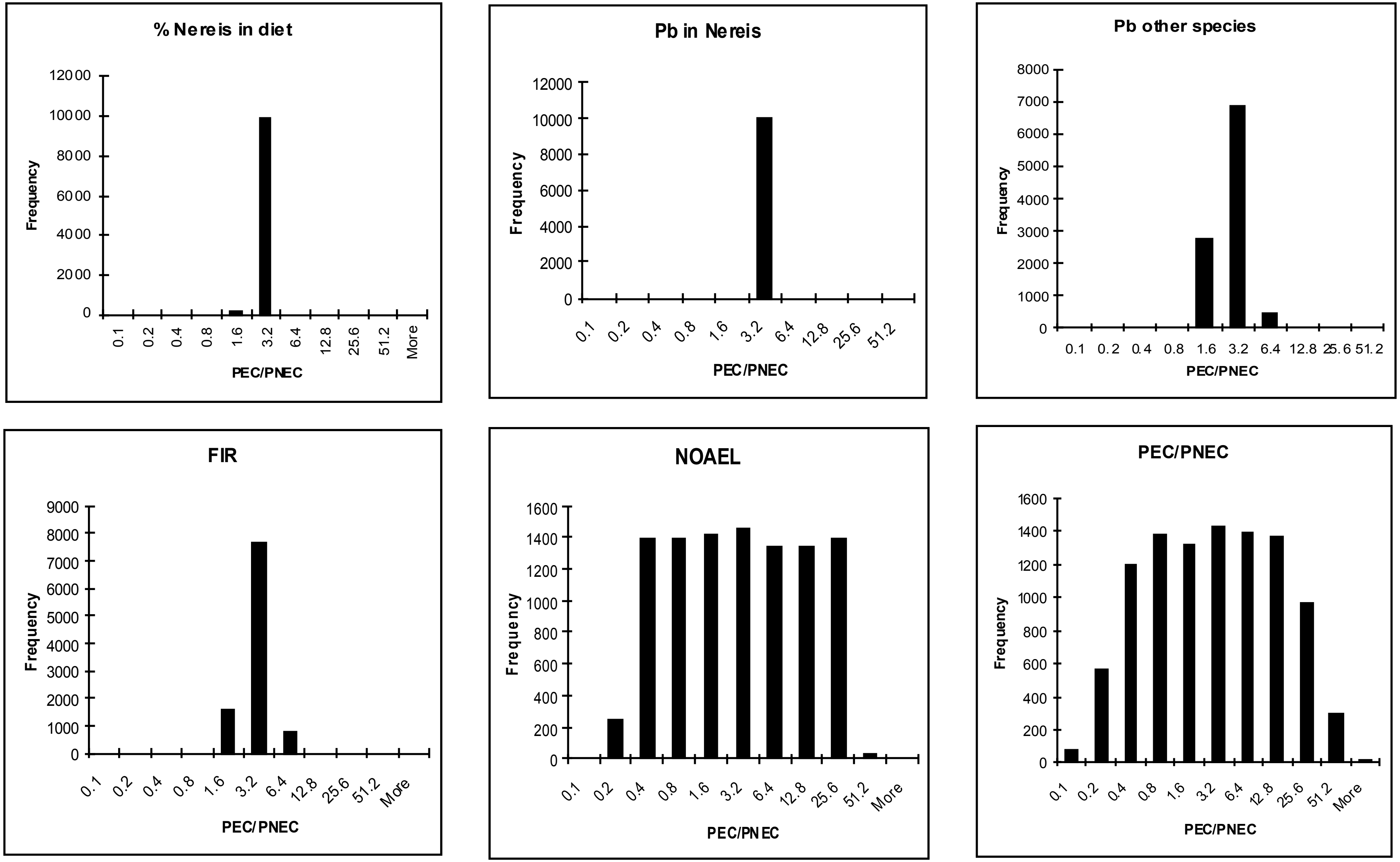
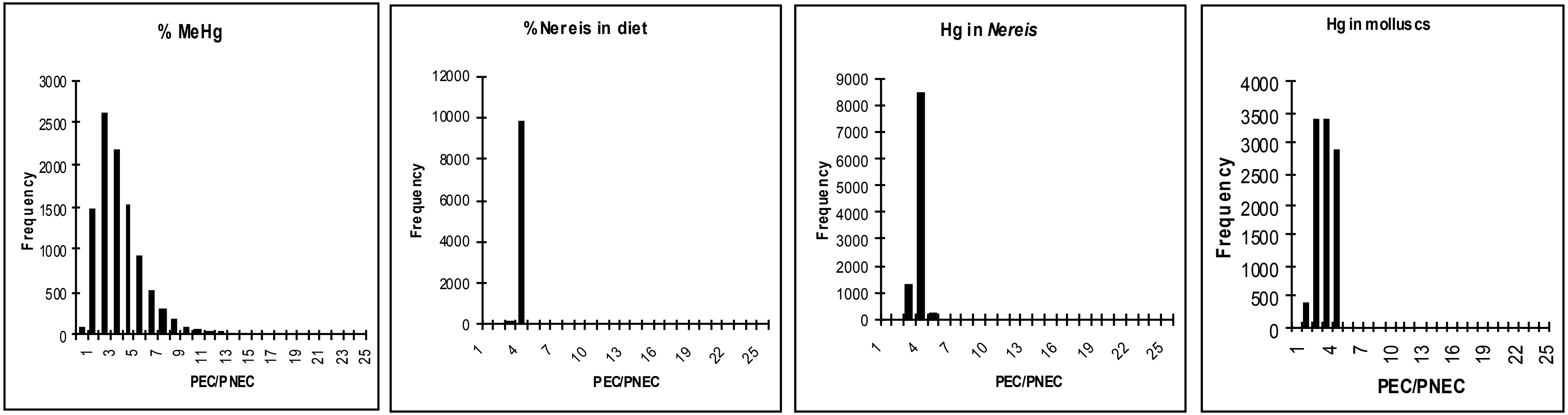
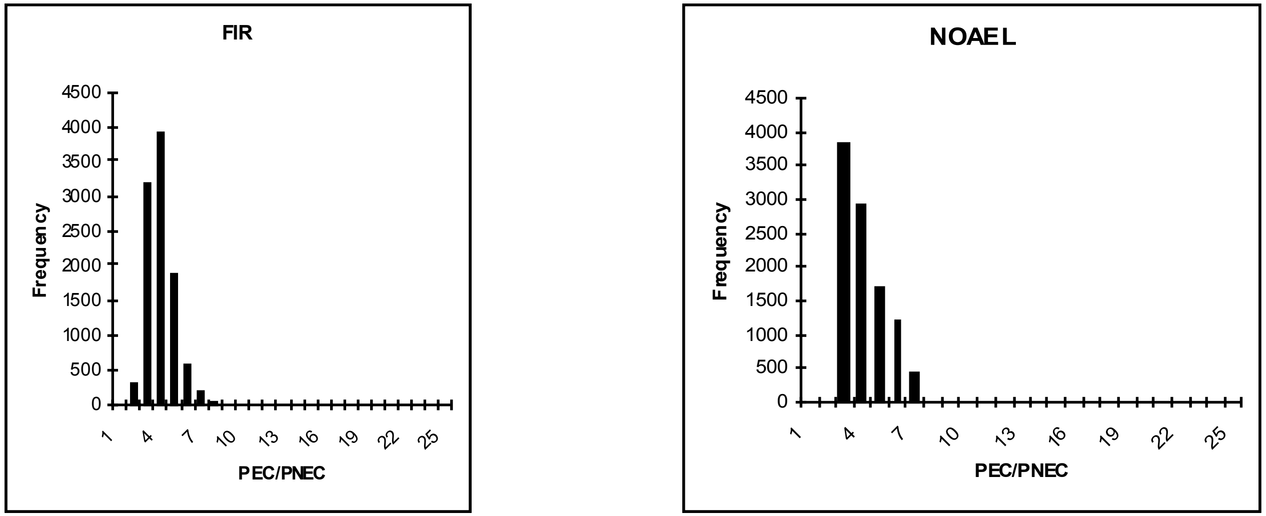


Figure 8 Sensitivity analysis: Pb in Dunlin, Poole Harbour (Ave. Scenario). Uncertainty in NOAEL for Pb dominates uncertainty in PEC/PNEC





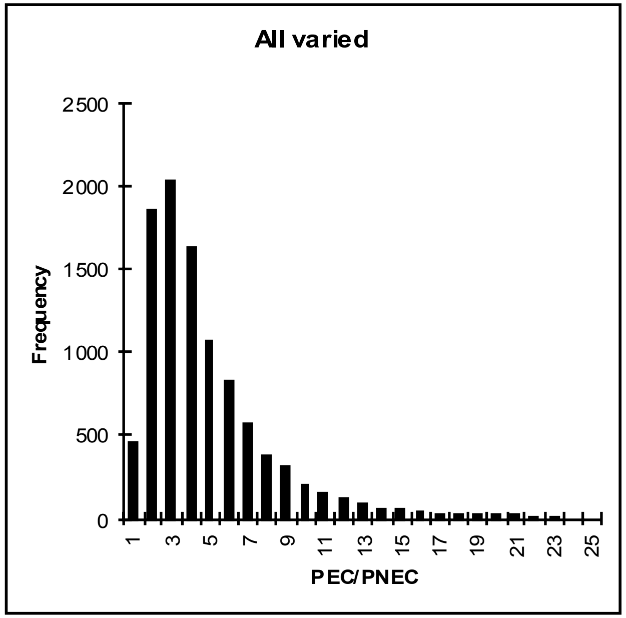
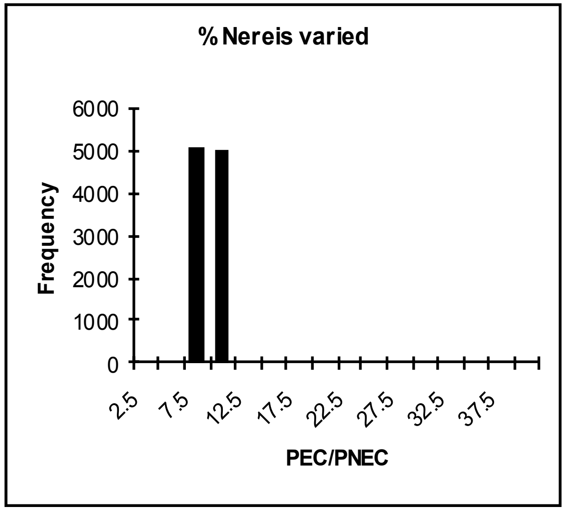
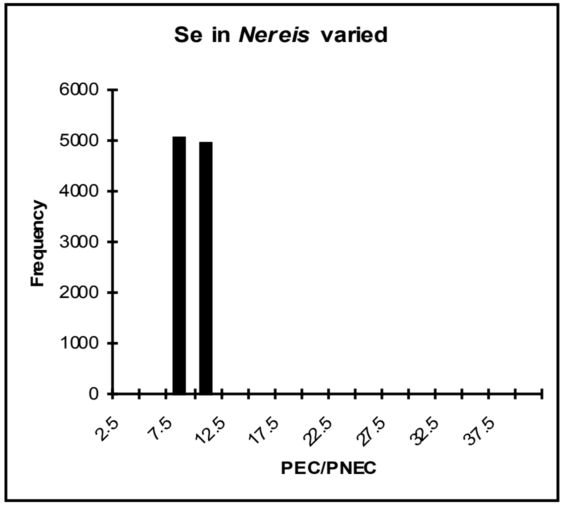
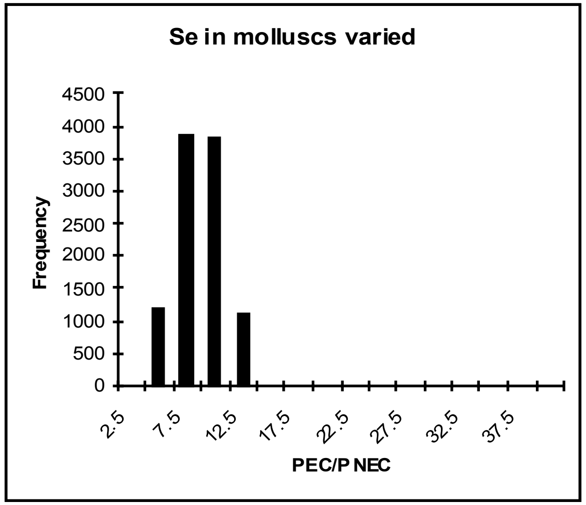
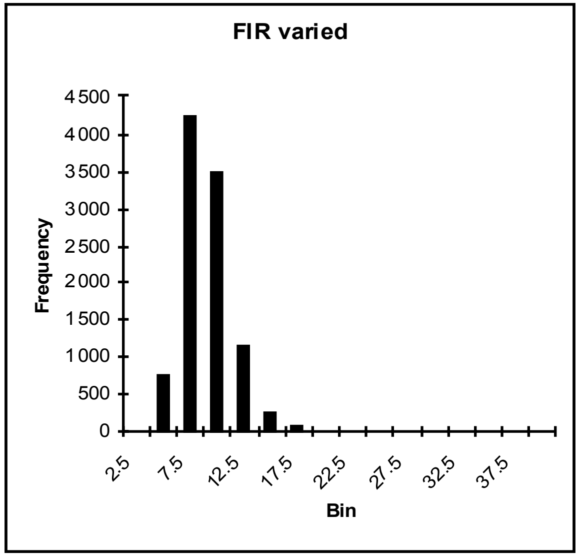


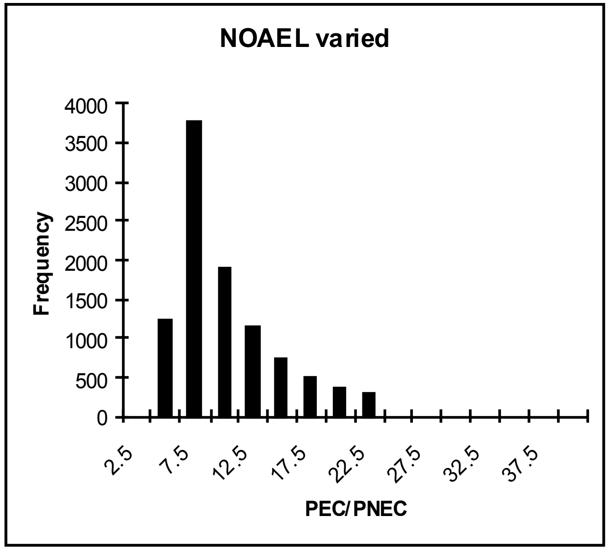
Figure 9 Sensitivity analysis: Hg in Dunlin, Severn Estuary (Ave. Scenario). Uncertainty in %MeHg in diet, Hg content of molluscs, FIR and NOAEL all contribute significantly to uncertainty in PEC/PNEC











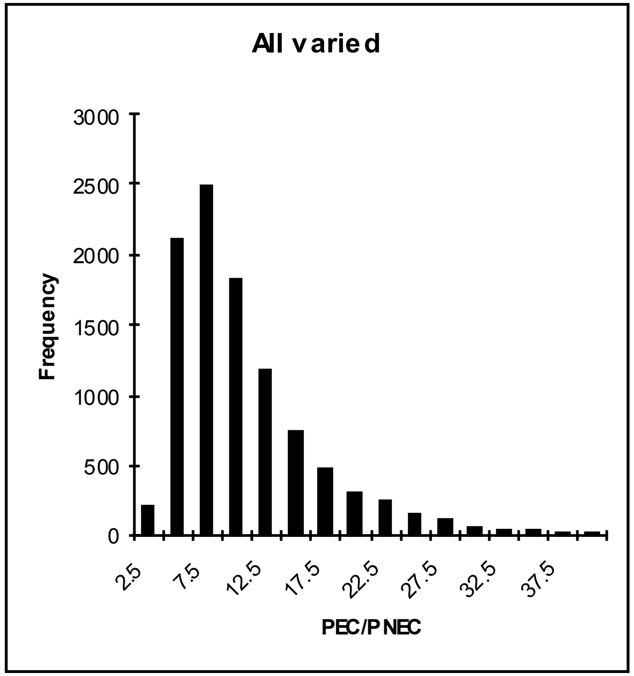


Figure 10 Sensitivity analysis: Se in Dunlin, Severn Estuary (Ave. Scenario). Uncertainty in Se content of molluscs, FIR and NOAEL all contribute significantly to uncertainty in PEC/PNEC

3.6 Uncertainty in model predictions

It should be noted that model sensitivity analyses, by definition, only give information on the uncertainty encompassed within the defined model. A sensitivity analysis does not necessarily encapsulate all sources of uncertainty. It is possible that due to unknown factors (which may make model parameters vary to a different extent than those assumed in the model) real PEC/PNEC values may be different to the predicted ranges.

Two examples illustrate this problem (which is common to all environmental models):

The Pb content of earthworms, for example, may in reality be different to the range we have assumed from the literature. This would significantly alter the predicted PEC/PNEC values for Pb in oystercatchers and curlew, both of which eat a significant proportion of earthworms in their diet;

The NOAEL values are necessarily estimated from data on laboratory birds of different species than those studied here. Actual NOAELs of the wild species studied here may be significantly different to those used in the model.

Thus sensitivity analysis (whilst being a powerful modelling tool) cannot alone determine predictive uncertainty of environmental models. Further field studies of prey concentrations or metal contents of birds, and (to the extent which is possible) field assessments of the impact of metals on bird health/populations would be required to further reduce model uncertainty and to improve assessment of that uncertainty (ie validate predictions). Improvement in estimates of NOAELs by further experiments on avian toxicity of these estimates could reduce the uncertainty in PNEC values.

3.7 Other uptake pathways

Water pathway

Inspection of the model used by Crane . (2005; Equation 6), rearranged below as Equation (7) shows that the direct ingestion of water plays a minor role in contaminant uptake by Dunlin:

$$\frac{PEC}{PNEC} = \frac{C_e \times DF \times \left(BAF + 0.059bw^{0.67} / bw\right)}{PNEC \times FMR} \tag{7}$$

where bw is the bird body weight, C_e is the concentration of the chemical in water and DF is the dilution factor and FMR is the extrapolation factor for metabolic rate. For all contaminants except vanadium, mean bioaccumulation factor in prey, BAF $\gg 0.059bw^{0.67}/bw$. (Here BAF is defined as in the Crane . study as the ratio of the concentration in the whole body of the prey to that in water.) Hence, from Equation 7, for all contaminants except vanadium, the water pathway plays no significant role in predictions of PEC and uncertainty in those predictions. According to the analysis of Crane . (2005) for the Severn Estuary and that carried out here for Poole Harbour, predicted vanadium concentrations in prey do not present a significant risk to birds in the Severn Estuary or Poole Harbour.

Ingestion of contaminated soil or sediment

Uptake by ingestion of contaminated soil or sediment may occur incidentally (as, for example, soil or sediment attached to food is ingested) or deliberately (some birds, for example, deliberately ingest grit).

Ingestion of contaminated soil or sediment is likely to vary significantly depending on the behaviour and diet of a bird. Ingestion rates for birds primarily feeding on earthworms, for example, could be estimated by measuring the average content of soil in earthworms. Estimates can also be made of the soil/sediment content of faeces. For different species of birds, the USEPA (1993) have estimated values of <2 % to 30% soil or sediment (per unit dry weight) in faeces of different birds. The highest values were observed in sandpipers which feed on mud-dwelling invertebrates.

Using data for Pb and Hg in sediments in Poole Harbour, we have estimated the potential uptake via contaminated sediments in comparison with direct uptake from food. The calculation in Table 21 assumes either 2% of DMI is sediment, or 30% of DMI is sediment. This assumption is based on the USEPA study of sediment in faeces, though this is likely to be somewhat over-estimated since dry mass of excreted food is lower than dry mass of ingested food. For Hg, the amount of ingested metal per day is significantly lower via the sediment pathway than by the food pathway, although when an extremely (and perhaps unrealistically) high sediment ingestion rate of 30% is assumed ingestion via the food pathway is only slightly higher than via sediments. For Pb, ingestion via food is higher than via sediment for the 2% sediment ingestion scenario, but is lower than via sediment for the (perhaps unrealistically high) 30% sediment ingestion scenario. It may be that in terms of total Pb ingested by birds, ingestion of sediment bound Pb is an important exposure pathway.

It should be noted that bioavailability of Pb and Hg attached to sediments may be much lower than that in prey items, so accumulation via the sediment pathway may be much less significant.

Table 21 Pb and Hg ingestion by Dunlin, Poole Harbour, via contaminated sediments and food

Metal	Mean conc. in sediment mg kg^{-1} DW	Metal ingestion rate via sediment mg d^{-1}		Mean conc. in food mg kg^{-1} DW	Metal ingestion rate in food mgd^{-1}
		$f_s = 2\%$	$f_s = 30\%$		
Pb	46.2	**0.010**	**0.15**	3.55	**0.039**
Hg	0.34	**7.4×10^{-5}**	**1.1×10^{-3}**	0.15	**1.6×10^{-3}**

3.8 Sources of Pb, Hg and Se

For metal contamination in particular, the attribution of risk to individual point sources is likely to be difficult since contaminant concentrations in birds will be caused by pollution from a number of sources. It should also be noted that (as discussed above) bird species which feed on sediment dwelling organisms may primarily ingest some contaminants bound to sediments. Thus, past discharges of contaminants that are now bound to sediments may strongly influence current contaminant concentrations in birds and their prey.

In the Severn Estuary, metal refining and steel production at Avonmouth and South Wales were significant sources of metal contamination of the estuary. In Poole Harbour, metal concentrations were highest in the Holes Bay area (particularly in the upper eastern part, Langston . 2003) as a result of inputs from (now closed) chemical industries and other inputs from Poole Sewage Treatment Work (STW). Both harbours are also subject to point source discharges from sewage treatment works and diffuse atmospheric and riverine sources of metals.

Pb

Pb contamination of both estuaries originates from multiple sources.

Data presented in Langston . (2003b) shows that direct industrial discharges to the Severn Estuary were not always the most important source of metals to the estuary. Atmospheric inputs accounted for 57.8 % of the lead in the estuary. These data are more than twenty years old, nevertheless, they give a useful indication of the sources of pollution to the estuary (Langston ., 2003b).

According to Langston . (2003b) “there is still some uncertainty about the scale of reductions [in metal concentrations] in recent years”, though these authors note that lead and cadmium “have generally decreased by up to a factor of two” between the 1970’s and 1990’s. The recent study by Crane . (2005) estimated PEC/PNEC values for Pb significantly greater than 1 at 9 of the 18 licensed discharge sites studied. This study (necessarily) was not based on direct empirical evidence of residue levels in prey items close to point source discharges. It should not therefore necessarily be concluded that these point sources are significantly damaging to shorebirds, particularly in the context of the widespread Pb contamination of the estuary from past point- and diffuse sources.

In Poole Harbour, 60 kg Pb per year was discharged directly into the harbour from STWs in 2001 compared to a riverine flux (which probably also contains point source contributions) of 300 kg (Langston . 2003a). It is likely that current Pb contamination of Poole Harbour is largely from past atmospheric deposition and past industrial effluents. There may be “hot spots” of contamination in parts of Holes Bay.

Hg

Data from the 1970s and early 1980s indicates that roughly half of the Hg contamination of the Severn Estuary originated in rivers and streams and half from industrial effluent. The Crane (2005) study did not identify any current licensed discharges as having significant PEC/PNEC values though this study was based on an NOAEL for IOM rather than the much lower NOAEL for MeHg. The Crane (2005) study identified 8 current licensed discharges of Hg to the Severn Estuary. From the information given in Crane (2005), it is likely that only one of these sources (Treated Landfill Leachate NGR ST3151043310) would have resulted in PEC/PNEC >1 had the MeHg NOAEL been used. Assuming 18% MeHg in prey (Section 3.2 above), it is likely that none of the sources would have resulted in a significant probability of PEC/PNEC >1. It is possible that the elevated PEC/PNEC values we have observed in the present study are largely due to historical contamination of the estuary and that current discharges are not significant sources of Hg, though further measurements of prey species close to discharge sources would be required to confirm this.

In Poole Harbour in 2001, 0.42 kg Hg per year was discharged directly into the harbour from STWs compared to a riverine flux of 2.58 kg (Langston . 2003b). It is likely that Hg contamination of Poole Harbour is largely from past riverine and industrial effluents. There may be “hot spots” of contamination in parts of Holes Bay.

Se

We have found little information on Se contamination of the Severn Estuary. According to the Crane (2005) report, there are no current licensed discharges of Se to the Severn Estuary. No information on Se is given in the Langston (2003b) review.

3.9 Wider implications of model outputs and potential future work

The rationale for the current project was to investigate suitable means of assessing the risk posed by toxic contaminants in invertebrate prey, when ingested by wading birds, to inform condition assessment of estuarine SSSIs and SPAs and the management of discharges (eg. through Regulations 48 and 50 of ‘the Habitats Regulations’). The results of the probabilistic modelling suggest that in both of the study areas, Poole Harbour and the Severn Estuary, toxic residues in prey (Pb, Hg and Se concentrations) may pose an ecologically-relevant toxic risk to wading birds. However, it needs to be borne in mind that this assessment is informed by models that predominantly used toxicity data based on reproductive endpoints.

It is important to realise that, for waders that overwinter in Poole Harbour or the Severn Estuary and migrate to breeding grounds elsewhere, exposure to metal contaminants at the time of breeding may be quite different to that experienced during the winter. It is uncertain what, if any, impacts previous overwinter exposure(s) to Pb, Hg or Se may have on subsequent breeding success. Some of the contaminants accumulated overwinter may be remobilised. For example, Pb sequestered in bone may be remobilised as bone (and calcium) turnover increases during egg production, or methyl-mercury in fat may be remobilised as energy reserves are depleted during migration, immediately before breeding starts. There are no toxicological studies that we are aware of that specifically investigate the effects of prior exposures of Pb, Hg and Se on subsequent reproduction; exposure typically occurs prior to *and/or during* the reproductive cycle. Pharmaco-kinetic modelling would therefore be needed to estimate the likely extent of remobilisation of previously accumulated contaminants and how this might supplement the internal dose derived from dietary intake on the breeding grounds.

The other principle way that metal intake on overwintering grounds could have ecologically significant effects are if they cause or contribute to direct over-winter mortality or decrease the likelihood of survival during spring migration. There are no suitable toxicity test endpoints to assess whether survival during migration could be affected. Thus, the only available data are for acute toxicity data (LD_{50}/LC_{50}/NOAEL data), which are also sparse for inorganic Pb, Hg and Se in birds. We did not attempt to use acute toxicity endpoints in most of the probabilistic models but one methyl-mercury model did use a NOAEL for survival, derived by dividing the LD_{50} data by 100. When this endpoint was used, the modelled median PEC/PNEC ratios were all extremely low and even the 95th percentile for the worst case scenario was 0.5 (Tables 19 and 20). Thus, from the limited assessment that we have carried out, there is no evidence that overwinter dietary intake of Pb, Hg or Se poses an acute toxic threat to wading birds on the Severn Estuary or Poole Harbour.

The value and means of further developing the approach outlined in this report to assist in condition assessment of sites depends on the protection goal. The goal may be to assess risk of toxic contamination on either (i) overwintering wading birds, or (ii) resident breeding wading birds (see below).

(i) One of the most important findings of this project is that the dietary toxic element intake of waders in Poole Harbour and the Severn Estuary is not trivial, and appears to exceed levels that can cause major adverse effects, such as disruption of reproduction. Arguably, a pressing next step is to determine how contamination in Poole Harbour and the Severn Estuary compares with that in those other British estuaries that are classed as important overwintering feeding areas for waders. This could be achieved by measuring residue levels in *Nereis* or other key prey species in these estuaries and comparing the results with those available for Poole Harbour and the Severn Estuary. Similar probabilistic models to the ones used in the present study could be run for waders from any highly contaminated estuaries (in conjunction with appropriate reference sites) to determine whether the PEC/PNEC ratio exceeds one when PNEC values based on acute toxicity endpoints (where data allow); if so this would suggest that such estuaries might directly affect populations by causing mortality or possibly by reducing the likelihood that birds will migrate to their breeding grounds successfully. If PEC/PNEC ratios exceeded one for reproductive endpoints, this may also identify risks which require further investigation, though the significance to migratory species is less clear. It may also be valuable to obtain more direct measures of exposure in birds (for example through measurement of tissue residues, faeces or blood) across a range of sites with different predicted PEC/PNEC ratios. Such measurements would assist in validating model outputs that predict differences between estuaries in exposure.

Data may already be available for some estuaries, particularly those where there may be active shellfish fisheries, although such data may not be available for the key prey species of waders and the potential for extrapolating residue data across different prey species may need to be assessed. Repeated sampling from a stratified set of estuaries at appropriate time intervals would also allow assessment of whether risk from contamination to overwintering waders was changing over time. Such surveys might include estuaries subject to large-scale changes in catchment land-use (which may affect inputs into estuaries), permitted discharges, or permitted activities within estuaries (dredging etc). It may also be possible to compare whether change over time in contamination risk is correlated with changes in population numbers in estuaries, although the potential role of other confounding factors that affect population numbers would also have to be considered.

The development of pharmacokinetic models to predict residue remobilisation would only be merited if data on dietary metal intake on the breeding grounds were available. Even then, the models would require validation, presumably by experiment and non-destructive comparison of circulating metal levels in breeding waders that had come from different overwintering grounds.

(ii) In the case of resident waders and other waterbirds on the Severn Estuary and Poole Harbour, the outputs of the present study suggest that the toxic metals may adversely affect their reproductive success if their exposure is similar to that predicted for

Dunlin, Oystercatcher and Curlew. However, the probabilistic models would need to be modified to other particular species of concern and the PEC/PNEC ratio recalculated. Should the resultant ratios still exceed 1, a next logical step would be to validate the outputs of the model, to ensure that they are realistic. As in the case of overwintering birds, this could partly be done by analysing metal tissue concentrations in birds found dead to determine if they are consistent with concentrations expected from the predicted dietary metal intake and with residue levels associated with adverse effects in birds. Such sampling could be supplemented, if appropriate, with active monitoring achieved through non-destructive blood sampling of netted birds, although it would be important to have prior knowledge (experimentally derived from laboratory model species) of how blood metal concentrations and/or effects biomarkers are related to dietary intake. Ultimately however, true validation of the model prediction would require comparison of the reproductive success of individual birds in contaminated areas with that of birds from less contaminated areas. This potentially could be done within and between estuaries, though there are likely to be a number of confounding environmental factors which make such comparison difficult.

As argued for overwintering waders, it would be valuable to characterise the contamination of other UK estuaries and determine how they compare with that of the Severn estuary and Poole Harbour. However, sampling in this case would be focussed on estuaries that are important for breeding rather than overwintering wader population. Knowledge of the spatial variation in prey contamination within and between estuaries would inform condition assessment and estuary management at both a local and country-wide scale.

4 Conclusions

Of the contaminants studied in the screening analysis of *Nereis diversicolor* samples, seven were found to potentially lead to PEC/PNEC values >1. These compounds were all metals or semi-metals: zinc (Zn), lead (Pb), mercury (Hg), selenium (Se), iron (Fe), arsenic (As), and chromium (Cr).

Of these seven contaminants four were rejected from more detailed modelling following more critical examination of available toxicity data:

- Zn – the endpoint was not ecologically relevant
- Fe, Cr – there was insufficient NOAEL data available

As – recalculation using improved NOAEL data gave PEC/PNEC <1.

Probabilistic modelling showed that:

- There was a high probability that PEC/PNEC for Pb significantly exceeded 1 in both harbours for all species;
- There was a high probability that PEC/PNEC for Hg significantly exceeded 1 for Hg in the Severn Estuary and a significant (>5%) probability that PEC/PNEC exceeded 1 for Poole Harbour;

There was a high probability that PEC/PNEC significantly exceeded 1 for Se in the Severn Estuary. There was no Se residue data available for Poole Harbour.

The major source of uncertainty in predicting PEC/PNEC values for Pb is the large uncertainty in NOAEL values for this element. Predictions for Hg and Se were less uncertain than for Pb, but uncertainty in both was significantly influenced by NOAEL. Presence of Hg in the form of MeHg was also an important source of uncertainty for Hg, and FIR and prey concentrations were an important source of uncertainty for both Hg and Se.

The attribution of contaminant residues to current point sources remains problematic and further measurements would be required before confident conclusions could be made concerning this. It appears likely, however, that Pb and Hg contamination of both estuaries is dominated by historic rather than current sources. We have insufficient information on Se sources to draw any conclusions for this element.

There may be "hot spots" of contamination in both estuaries which could lead to high concentrations of contaminants to a small proportion of the bird population which could feed in these areas, though birds in general feed from a variety of sources in both estuaries.

5 Recommendations

The approaches used in this study could be used to assess the risk of toxicants to shorebirds in other UK estuaries. Although many uncertainties have been noted, for a number of substances (at least in the two estuaries assessed here), the risk of significant exposure is very low. For a number of other substances, risks may be higher, but the review of toxicity data has shown that detailed probabilistic modelling is not possible due to the paucity of data. Finally, for the three substances considered in detail here (Pb, Hg, Se) a significant toxic risk is predicted with a high probability, though it should be noted that this relates to sublethal rather than acute toxicity.

The approach could be improved by further research as follows:

Work should be carried out to better quantify impacts of current point sources and existing "hot spots" of contamination in the estuaries;

Further measurements should be made in a range of prey items, including earthworms, to improve estimates of PEC.

There may be little prospect of reducing uncertainty in NOAEL values since we think it unlikely that significant new toxicological data will appear in the near future. Uncertainty in model outputs could, however, be reduced by species specific estimates of FIR, and improved measurements of contaminants in prey items.

There is merit in extending contaminant characterisation and the estimation of PEC/PNEC ratios (using acute toxicity and reproductive toxicity endpoints) to other UK sites which are important because they either support large breeding populations or large numbers of overwintering birds. This work would involve review of published data for other sites and targeted new measurements of contaminant residues. Selecting sites which represent a gradient of toxic exposure would also be beneficial.

If there are a significant number of sites where PEC:PNEC ratios are >1 there is a case for attempting to validate the probabilistic models applied in this report. This is likely to require measurement of metal residues in the tissues (of dead) and blood (of live) birds, and possibly even more detailed studies to relate individual reproductive success/overwinter survival to predicted dietary metal intake. In deciding whether to move on to this next level of investigation it has to be noted that predicted exposure of overwintering birds at levels associated with reproductive effects may have little bearing on their post- exposure reproductive success at the breeding grounds.

6 Glossary

LOAEL – Lowest observed adverse effect level

The lowest daily contaminant intake rate of the bird that causes observable adverse effects. For this study this was taken to be the lowest tested dose of a substance that has been reported to have adverse effects on the bird, normalised for body weight (mg kgBW^{-1} d^{-1}; mg of contaminant ingested per kg BW per day).

NOAEL – No observed adverse effect level

The daily contaminant intake rate of the bird that causes no observed adverse effect. For this study this was taken to be the highest tested dose of a substance that has been reported to have no adverse effects on the bird, normalised for body weight (mg kgBW^{-1} d^{-1}; mg of contaminant ingested per kg BW per day).

Uncertainty factor

Mathematical adjustments for reasons of safety when knowledge is incomplete. For example, factors used in the calculation of doses that are not harmful (adverse) to birds. Uncertainty factors are used to account for variations in individuals sensitivity, for differences between species, and for differences between a LOAEL and a NOAEL. Uncertainty factors are used when one has some, but not all, the information from studies to decide whether an exposure will cause harm to birds [also sometimes called a safety factor].

PEC - Predicted environmental concentration

The expected concentration of a contaminant in the environment, taking into account the amount initially present (or added to) the environment, its distribution, and the probable methods and rates of environmental degradation and removal, either forced or natural. In this study the PEC is the predicted/measured concentration of contaminant in prey (mg kg^{-1}; mg of contaminant per kg of prey fresh or dry weight)

PNEC - Predicted no effect concentration

The concentration of a contaminant in an organism's environment that is expected not to cause an adverse effect on that organism. In this study the PNEC is the predicted concentration in prey (ie concentration in the bird diet) that causes no observed effect in the bird (mg kg^{-1}; mg of contaminant per kg of prey fresh or dry weight).

LD_{50} - Median lethal dose

The dose of a chemical which kills 50% of a sample population. In full reporting, the dose, treatment and observation period should be given. Further, LD_{50}, LC_{50}, and similar figures are strictly only comparable when the age, sex and nutritional state of the animals is specified. Nevertheless, such values are widely reported and used as an effective measure of the potential toxicity of chemicals (mg kgBW^{-1}; mg of contaminant per kg BW).

LC_{50} - Median lethal concentration

The concentration of a chemical which kills 50% of a sample population. This measure is generally used when exposure to a chemical is through the animal breathing it in or consuming the chemical in its diet over a specific time period. , while the LD50 is the measure generally used when exposure is by a single acute exposure either by swallowing, through skin contact, or by injection (mg kg^{-1}; mg of contaminant per kg of diet).

FIR - Food intake rate

The amount of food a bird is expected to consume each day normalised for body weight (kg d^{-1}; kg fresh or dry weight of prey per day).

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Research Information Note

English Nature Research Reports, No. 703

Assessment of the risk posed by toxic contamination to waterbirds on Special protection Areas (SPAs)

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Date: 1 September 2006
Keywords: Special Protection Areas, toxicity, heavy metals, wading birds, probabilistic risk assessment

Introduction

English Nature (EN) has a statutory role to assess the condition of Special Protection Areas (SPAs) and to advise relevant authorities, such as the Environment Agency, about risks to site integrity associated with plans and projects (eg. from discharges). To help fulfil this role, a desk-based risk assessment project was commissioned by EN to evaluate the significance of toxic contaminant residues in prey items with respect to the interest features of two South West Special Protection Areas, the Severn Estuary SPA and Poole Harbour SPA. The study builds upon a previous screening level study by Crane *et al.* (2005) commissioned by Environment Agency Wales.

What was done

The present project further investigated the risks associated with the exposure of SPA waterbirds to chemical contaminants (through direct toxic effects), by:

- carrying out a screening risk assessment using new measurements of concentrations in prey items (supplied by the Environment Agency) to determine the key contaminants which could have toxic effects on waterbirds);
- developing, for the identified key contaminants, a detailed probabilistic assessment of the ratio of predicted concentration in prey to the concentration at which no observable adverse effects on reproductive endpoints in birds would be observed (PEC[5]/PNEC[6] ratio). This detailed assessment was made on the basis of improved data on: prey contaminant levels, habitat use, foraging behaviour, and toxicity endpoints.

Results and conclusions

The results of the analysis were as follows:

- Of the organic and inorganic contaminants studied in the screening analysis of *Nereis diversicolor* samples, seven were found to potentially lead to PEC/PNEC values which exceeded 1 and hence presented a potential risk to birds. These compounds were all metals or semi-metals: zinc (Zn), lead (Pb), mercury (Hg), selenium (Se), iron (Fe), arsenic (As), and chromium (Cr).

[5] Predicted environmental concentration
[6] Predicted no effect concentration

Continued……

- Of these seven contaminants, four (Zn, Fe, Cr and As) were rejected from more detailed modelling following more critical examination of the limited toxicity data available:
- Detailed probabilistic modelling showed that:
  - There was a high probability that PEC/PNEC for Pb significantly exceeded 1 in both harbours for all species;
  - There was a high probability that PEC/PNEC for Hg significantly exceeded 1 for Hg in the Severn Estuary and a significant (>5%) probability that PEC/PNEC exceeded 1 for Poole Harbour;
  - There was a high probability that PEC/PNEC significantly exceeded 1 for Se in the Severn Estuary. There was no Se residue data available for Poole Harbour.
- The major source of uncertainty in predicting PEC/PNEC values for Pb was the large uncertainty in no observable adverse effect level (NOAEL) values for this element. Predictions for Hg and Se were less uncertain than for Pb, but uncertainty in both were significantly influenced by NOAEL. Presence of Hg in the form of methyl mercury (MeHg) was also an important source of uncertainty for Hg, and food intake rate (FIR) and prey concentrations were an important source of uncertainty for both Hg and Se.
- The attribution of contaminant residues to current point sources remains problematic and further measurements would be required before confident conclusions could be made concerning this. It appears likely, however, that Pb and Hg contamination of both estuaries is dominated by historic rather than current sources. We have insufficient information on Se sources to draw any conclusions for this element.
- There may be "hot spots" of contamination in both estuaries which could lead to high concentrations of contaminants to a small proportion of the bird population which could feed in these areas, though birds in general feed from a variety of sources in both estuaries.

The results of the probabilistic modelling suggest that on both of the study areas, Poole Harbour and the Severn Estuary, ingestion of Pb, Hg and Se residues within prey items poses a potentially significant toxic risk to wading birds, based on ecologically relevant endpoints. However, uncertainties in the risk assessment process make it difficult to accurately assess the risk posed to the integrity of the SPAs concerned. Opportunities for refining the risk assessment are discussed.

English Nature's viewpoint

The methodology applied provides a useful way of assessing which estuarine SPAs are potentially at risk from toxic pollution, with respect to food chain transfer to birds. However, in this study the significance of PEC:PNEC ratios >1 in relation to the integrity of the site is difficult to predict with confidence for a number reasons. The limitations of this method, given the available input data, are discussed in the report, together with opportunities for refining the risk assessment and the value of extending the approach to consider other relevant SPAs.

Further information

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Middle left: Co_2 experiment at Roudsea Wood and Mosses NNR, Lancashire.
Peter Wakely/English Nature 21,792
Bottom left: Radio tracking a hare on Pawlett Hams, Somerset.
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