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Do estuaries pose a toxic contamination risk for wading birds?

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Abstract

The impact of potentially toxic chemicals on wildlife is commonly assessed by comparing the intake of the contaminant with the "no observable effects level" (NOAEL) of intake. It is known, however, that there are considerable uncertainties inherent in this method. This study presents a Monte-Carlo based model to assess the degree of risk posed to birds (dunlin, *Calidris alpina*) from important estuarine habitats, and to show the limitations of such risk assessments, particularly with regard to data availability. The model was applied to predict the uptake of metals (Hg, Pb) in this shorebird species in Poole Harbour and the Severn Estuary/Bristol Channel, UK, two internationally important shorebird habitats. The results show that in both areas, Pb and Hg concentrations may pose an ecologically-relevant toxic risk to wading birds. For Pb, uncertainty in NOAEL values dominates the overall uncertainty. Use of lethal toxicity data (LD50/100) was investigated as a method for assessing sub-lethal impacts from Hg. It was found that this method led to a significant under-estimate of the potential impact of Hg contamination, compared with direct estimation of NOAEL.

Key words: mercury, lead, probabilistic modelling, estuaries, reproductive toxicity, dunlin.

1. INTRODUCTION

Analysis of uncertainty in environmental risk assessments is becoming increasingly important (e.g. Verdonck et al., 2005). To our knowledge, however, modelling approaches have not yet been developed for the assessment of uncertainty in contaminant uptake and risk in wading birds. Here we present a probabilistic modelling approach for risk assessment that employs ecologically relevant toxicological endpoints and, crucially, data inputs (bird behaviour, metal content of prey items, toxicity endpoints) that are realistic for typical environmental impact assessments. The Monte-Carlo based model is used to assess the degree of risk posed to birds from important estuarine habitats, and to show the limitations of such risk assessments, particularly with regard to data availability.

Estuaries are typically important feeding areas for wading birds but are also often subject to historic and current chemical contamination by heavy metals. Estuarine sediments commonly form major sinks for contaminants released during industrial activity. Many industrial processes lead to the release of metals initially in solution, which can then be adsorbed on to, for example, Fe hydroxides or clay minerals (Pirrie et al., 2003) and are subsequently deposited onto estuarine sediments. Both past mining activity and present industrial discharges have resulted in the accumulation of metals in estuarine sediment.

The Severn Estuary/Bristol Channel and Poole Harbour (Figure 1) are two major UK estuaries and are classified as Special Protection Areas (SPAs) under the European Wild Birds Directive. During the winter, they support nationally and internationally important numbers of overwintering shorebirds (Pickess and Underhill-Day, 2002; Pollitt et al., 2003). However, both areas are typical of estuaries in that they have previously been subject to significant metal contamination. Much of the metal contamination has been adsorbed onto estuarine sediments and as a consequence concentrations of heavy metals in sediments usually exceed those of the overlying water by between three and five orders of magnitude. With such high concentrations, the bioavailability of even a small fraction of the total sediment metal can lead to uptake by filter-feeding and burrowing organisms (Bryan and Langston, 1992). Furthermore, several metals, including mercury and lead, may be transformed in sediments to organometallic compounds which have greater bioavailability. These factors can result in accumulation of heavy metals by wading birds feeding in these areas (Bryan and Langston, 1992; Ferns and Anderson, 1997). Although there is evidence that metal contamination is declining in both Poole Harbour (Langston, 2003a) and the Severn Estuary (Duquesne et al., 2006; Langston et al., 2003b), the current levels of contamination suggest that they could still potentially have an impact on wildlife.

Assessment of the potential risk to wading birds posed from contamination has rarely been carried out, except where there have been specific spills or industrial incidents (Bull et al., 1983); (Pain et al., 1998). The aim of the current paper is to use the Severn Estuary and Poole Harbour as model systems (for which relatively good empirical data are available) to assess the potential risk posed to wading birds from long-term metal contamination in estuaries. A Monte Carlo analysis will be carried out to estimate the probability that the wading bird population is over-exposed to Pb and Hg in the two estuaries.

METHODS

The <u>variability</u> in population-averaged risk to dunlin, *Calidris alpine,* was assessed using a scenario approach. This species was selected because data on its diet selection and habitat use are available for both estuaries. 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 PPC/PNEC (predicted prey concentration/predicted no effect concentration in prey) values for the average bird, 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 a lower ratio of body weight to food intake rate and hence a higher PPC/PNEC) feeding exclusively at the most contaminated site in each estuary.

For each of these scenarios, the uncertainty in predicted PPC/PNEC value was determined by Monte Carlo analysis after assigning uncertainties to each model input parameter based on evaluation of empirical data.

Selection of contaminants to be modelled

An initial screening exercise was carried out to determine which contaminants to focus on in subsequent modelling. This was carried out by calculating the Predicted Environmental Concentration (PEC) and the Predicted No Effect Concentration (PNEC) in birds for each contaminant. The PEC in this case was the predicted concentration of the contaminant in the prey of the birds and is in this paper termed the PPC. The ratio of the PPC to the PNEC was calculated as:

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

where values of this ratio above 1 imply a toxic risk. A key prey item, ragworms (*Nereis diversicolor*), were sampled from 12 sites in Poole Harbour and 13 sites in the Severn Estuary (Environment Agency, unpubl. res.). It was assumed (for the purposes of the initial screening exercise only) that contaminant concentrations in *Nereis diversicolor* were representative of those in the range of different prey items in each estuary, though in the full uncertainty analysis below, other prey types (earthworms, molluscs and crustaceans) were also considered. Estimates of PPC/PNEC were made for each of the organic and inorganic contaminants measured in *Nereis*. The results of this screening exercise are presented in the Supplementary Material (Tables S1 and S2). Seven compounds (all metals or semi-metals) had maximum PPC/PNEC ratios ≥ 1: zinc (Zn), lead (Pb), mercury (Hg), selenium (Se), iron (Fe), arsenic (As), and chromium (Cr) for at least one of the sites. Fe was not determined in the Severn Estuary and Se was not determined in Poole Harbour. The source toxicity data used in calculating the screening PPC/PNEC ratios were then examined in detail to determine if they were experimentally sound (if they fulfilled the criteria set out in the *Toxicity Data* Section below) and if the endpoints were ecologically relevant. Using these criteria, only Pb and Hg were selected for subsequent detailed modelling.

Model input data

Bird distribution and diet

Bird habitat use and feeding behaviour were estimated using a combination of a foraging model which accounts for the different utilisation of feeding sites within an estuary (Stillman et al., 2005; Durell et al., 2006), the Wetland Bird Survey (WeBS) data and other literature data (Goss-Custard et al., 1988; Worrall, 1984). The proportion of different prey types taken by the birds and their associated uncertainty estimates are shown in Table 1. Earthworms comprise a significant part of the diet for some shorebird species, but in these estuaries dunlin do not consume significant proportions of earthworms in their diet. In Poole Harbour, dunlin have not been observed to eat earthworms (Durell et al., 2006), the major proportion of the diet of adult dunlin being marine worms, the rest being made up of molluscs and crustaceans. In the Severn Estuary, earthworms are estimated to form less than 10% of their diet. Juvenile dunlin (Table 1) take similar food types to adults.

Dietary lead and mercury concentrations

The data on Pb and Hg concentrations in *Nereis diversicolor* used in our model comprised not only new measurements (Environment Agency, unpubl. res.)) but also data from reviews of contamination in Poole Harbour and the Severn Estuary (Langston et al., 2003b), Supplementary Material, Tables S3-S6). Assumed ranges and estimates of uncertainty in metal concentrations used in the model are summarised in Table 2. For prey items other than *Nereis*, uncertainties in metal concentrations were estimated from data in the reviews, taking account of the known decline in metal contamination over time.

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 each harbour with uncertainty being normally distributed with coefficient of variation of 25%. Based on the review of data in Tables S3 – S6, for molluscs and crustaceans it was assumed (for the worst case scenario) that the average concentration at the most contaminated site was 3-10 times higher (Pb, Hg - Poole Harbour; Pb - Severn Estuary) or 1-3 times higher (Hg - Severn Estuary) than the maximum measured value in *Nereis*.

Metal concentrations in earthworms (Lumbricus terrestris)

Dunlin in Poole Harbour do not consume earthworms (Durell et al., 2006) and we assumed that this was also true for most dunlin in the Severn Estuary (Table 1). Data on Pb concentrations in earthworms is limited but a study of the Avonmouth smelter found concentrations in worms at an unaffected site distant from the smelter to be 27 mg kg^{-1} (dw) (Spurgeon, 1994). Concentrations in worms on a control site from a separate study were 4 – 12.3 mg kg^{-1} dw (Morgan and Morgan, 1991).

Concentrations of Hg in earthworms measured by (Bull et al., 1977) at a site uninfluenced by industrial activity (range 0.031-0.048 mg kg^{-1} dw, n = 18) were generally lower than those measured in estuarine biota (see Tables S4 and S6). This suggests that, in contrast to Pb, Hg in earthworms may have little effect on Hg intake in shorebirds.

Proportion of dietary mercury as methylmercury

The NOAEL of methylmercury (MeHg) is approximately two orders of magnitude lower than that for inorganic Hg. It is therefore important to estimate the proportion of total Hg in prey items which is in the form of MeHg. Muhaya et al. (1997) determined that the mean proportion of Hg as MeHg in *Nereis* across 13 sites in the Netherlands was approximately 18%, but the distribution of values was highly skewed. We therefore log-transformed these data (mean (±SD) log transformed proportion: 1.28 ± 0.22) and used this transformed distribution to generate random values for our Monte-Carlo model. The values were then back-transformed for use in the model.

Toxicity data

A literature search was conducted to identify studies from which avian NOAELs could be derived for inorganic and organic Pb and Hg. We used 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 (U.S. Environmental Protection Agency, 2002), and a number of US EPA reports (Sample et al., 1997; U.S. Environmental Protection Agency, 1999; U.S. Environmental Protection Agency, 2005) as reference sources. Where possible, the original papers or reports were assessed, and three criteria were used to decide whether the NOAEL values could be included in our models. These were:

(i) effects on reproduction and growth are more likely to affect population densities than lower order effects and in some cases are the integrated response to a range of physiological and biochemical effects. Thus, NOAELs based on reproduction and growth end-points were included but those based on physiological, metabolic, biochemical and other lower level end-points were rejected. This selection procedure also increased the likelihood of finding sufficient toxicity data for our model as there were unlikely to be multiple studies that used exactly the same physiological and biochemical endpoints.

(ii) use of only one NOAEL from a study when multiple NOAELs were derived from the same test, thereby avoiding pseudo-replication (when multiple NOAELs were derived in the same study but from different tests, all values were included).

(iii) studies in which the highest exposure level was assumed to be the NOAEL were excluded because no effects were observed at any exposure level.

The value of a NOAEL and Lowest Observed Adverse Effect Levels (LOAELs) is partly determined by the experimental design of the study if, in the case of NOAELs, no effect is observed at the highest dose administered or, in the case of LOAELs, an effect is observed at the lowest dose administered. Using NOAELs derived in such studies may give an over-estimate of the toxicity of a contaminant while using LOAELs may under-estimate the toxicity. NOAELs were used in this study as a precautionary approach in assessing risk to wading birds. Even the studies reporting NOAELs for the effects of Pb and Hg on reproduction and growth are sparse in number. Therefore, we also included studies which reported chronic Lowest Observed Adverse Effect Levels (LOAELs) for appropriate endpoints and also investigated the use of LD50 values. Chronic LOAELs were divided by 10 and LD50s were divided by 100 to approximate them to chronic NOAELs, following (USACHPPM, 2000).

The ranges in NOAEL used in our models are summarised in Table 3, and the individual data are presented in Table S7 in the Supplementary Material: this table also gives information on the species on which the tests were conducted. For Pb, we found only four studies that met our selection criteria for NOAELs. There are few avian lethality tests for inorganic Pb and, for those test that have been done, LC50 values typically exceed the highest experimental dose (≥ 5000 mg Pb/kg food). Although we found two avian LD50 values for tetraethyl lead, there appear to be large differences in toxicity between tetraethyl Pb and Pb salts and so we did not use the data for tetraethyl Pb in our model. For Hg, we found five values (two for inorganic Hg, three for Me-Hg) of chronic NOAELs. Seven further NOAELs (six for MeHg, one for inorganic Hg) were 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 100 to convert them to chronic NOAELs. The range of NOAELs derived in this way was 0.195 to 0.378 mg kg^{-1} day^{-1}, at least one order of magnitude higher than experimentally-derived chronic NOAELs for methyl mercury dicyandiamide based on reproductive end-points.

Modelling

The PPC/PNEC approach was used for the more detailed modelling of Hg and Pb impacts. The PPC was predicted using:

$$PPC = \sum_i f_i C_i \qquad (2)$$

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 using

$$\mathrm{PNEC} = \frac{\mathrm{NOAEL(mg/kg\ BW/day)} \times \mathrm{BW\ (kg)}}{\mathrm{FIR\ (kg\ DW/day)}} \qquad (3)$$

where NOAEL is the no observable adverse effect level, BW is the bird body weight and FIR is the average daily food intake rate. PPC/PNEC ratios are calculated on a dry weight basis. .

A Monte-Carlo model was programmed in Microsoft Excel using, where appropriate, Microsoft Visual Basic macros. Using the available data, we ran the Monte-Carlo model to estimate ranges in possible PPC/PNEC values. A total of 10 000 random values were generated for each variable. These were based on a normal (or lognormal, as appropriate) distribution about a mean where data were available to determine the mean and uncertainty. When there were insufficient data to estimate probability distributions, a uniform distribution across the range in observed parameter values was assumed. An additional step was introduced into the model for Hg which was to estimate the fraction of total Hg made up by MeHg. A model sensitivity analysis was carried out by first assigning to each of the input parameters its mean value (c.f. Cox et al., 2006). 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 predicted PPC/PNEC value.

The daily food intake rate (FIR) was estimated using empirical relationships between food intake rate and body weight (BW) (Nagy, 2001). For shorebirds, gulls and auks the daily food intake (FIR; DW, kg d^{-1}) is estimated by regression from data for 15 species in (Nagy, 2001) giving:

$$\mathrm{FIR} = 0.11 \times (\mathrm{BW})^{0.77} \tag{4}$$

($n=15$, $R^2=0.86$, $p < 0.001$). The residuals in this model were approximately lognormally distributed with mean (of logged ratios model:measured) 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 FIR for dunlin.

Results

The model gives the probability distribution of estimated PPC/PNEC values based on 10 000 model runs for each estuary and scenario. An example of the model output for Pb in Poole Harbour ('Average' Scenario) is shown in Figure 2, and for Hg in the Severn Estuary in Figure 3. All of the model outputs were summarised as the median, 5^{th} and 95^{th} percentile values of PPC/PNEC in Poole Harbour and the Severn Estuary (Table 4).

Lead

For the 'Average' Scenario, median PPC/PNEC values for Pb were 2.0 and 6.5 for Poole Harbour and the Severn Estuary respectively (Figure 4). The lowest 5 percentile value was less than 1 in both estuaries, but the highest 95 percentile values were 22 and 75 in Poole Harbour and the Severn Estuary respectively. For the 'Worst Case' scenario, median

PPC/PNEC values were only slightly higher than for the ‘Average’ Scenario; however, 95 percentile values were significantly higher, ranging up to 121.

Mercury

PPC/PNEC estimates for both estuaries are shown in Figure 5. There were sufficient ecotoxicological data to compare the PPC/PNEC ratios for MeHg based either on experimentally-derived NOAELs or on the much higher approximated values calculated as LD50/100 (Table 3). The predicted PPC/PNEC ratios were much higher when based on experimentally derived NOAELs than when based on the LD50/100 (Figure 5). When the PNEC was estimated using the LD50/100, Hg would not be predicted to have any environmental impact on birds in either estuary, since PPC/PNEC values were lower than 1 (with a probability of > 95%). In contrast, there is a significant (i.e. >5%) probability that PPC/PNEC values for Hg based on the experimentally derived NOAEL are greater than 1 in both Poole Harbour and the Severn Estuary. Nevertheless, PPC/PNEC values for Hg (18% MeHg, based on NOAEL) are much lower than for Pb in Poole Harbour with the median PPC/PNEC being close to 1 for both ‘Average’ and ‘Worst Case’ scenarios.

Sensitivity Analysis

We have evaluated the sensitivity of the model to uncertainty in different input parameters. Illustrative results of different sensitivity analyses are discussed here.

There is a very large uncertainty in the NOAEL for Pb; this varies approximately uniformly over a range spanning two orders of magnitude (Figure 6). As illustrated in Figure 6, this uncertainty in NOAEL dominates the uncertainty in the PPC/PNEC ratio for Pb when all other parameters are assigned their mean value. The predicted PPC/PNEC ratio, 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 (i.e. other individual parameters varied whilst all other parameters assigned their mean) the variation in the predicted PPC/PNEC was minor (Figure 6).

The sensitivity analysis for Hg is illustrated in Figure 7. The PPC/PNEC ratio for Hg is predicted with significantly greater certainty than that for Pb with predicted PPC/PNEC values for Hg being within a range of approximately one order of magnitude. The percentage of Hg in the form MeHg is the most important source of uncertainty in the predicted PPC/PNEC ratio, though uncertainty in Hg content of molluscs, FIR and NOAEL also contribute significantly to model uncertainty.

The outputs of the sensitivity analysis for different estuary scenarios showed very similar patterns to the illustrative examples we have given for Pb and Hg in Figures 6 and 7 respectively.

Discussion

This assessment of two estuaries showed a potential impact of Hg and Pb contamination on shorebird communities. For the Average Scenario, there was estimated to be a greater than 50% probability that PEC/PNEC values exceeded 1 for Pb in both estuaries and for Hg in the Severn Estuary (Table 4). There was an approximately 40% probability that PEC/PNEC exceeded 1 for Hg in Poole Harbour. For the “Worst Case” scenario, probabilities of PEC/PNEC > 1 were 95% or greater for both metals in the Severn Estuary and 68 and 75%

for Hg and Pb (respectively) in Poole Harbour. For Hg, where PNEC was calculated on the basis of LD50/100, PEC/PNEC values were not predicted to exceed 1 in either estuary (Table 4).

The study on two model estuaries for which relatively strong empirical data on shorebird (dunlin) feeding habits and metal concentrations were available demonstrates that intakes of these metals in metal contaminated estuaries are at levels which may have adverse effects on ecologically-relevant endpoints. This conclusion is based on an assessment of the food uptake pathway. We will, however, briefly consider the potential importance of other uptake pathways for these metals.

Alternative Uptake Pathways

Because the water-prey bioaccumulation factor is high for these metals, the direct ingestion of water by birds is a much less important uptake pathway than the food pathway we have modelled here. It therefore plays no significant role in predictions of PEC and uncertainty in those predictions (Crane et al., 2005).

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. For different species of birds, the USEPA (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 (taken from the same sites as *Nereis* were sampled; Environment Agency, unpubl. res.), we have estimated the potential uptake via contaminated sediments in comparison with direct uptake from food. The calculation assumed that either 2% of dry matter intake (DMI) is sediment, or 30% of DMI is sediment. This assumption is based on the USEPA (USEPA, 1993) 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 Pb, the amount of ingested metal per day via sediment was in the range 0.01 – 0.15 mg d^{-1} (for DMI in the range 2-30%) compared to 0.039 mg d^{-1} via food. For Hg, the ingestion rate via sediment was in the range 7.4×10^{-5} to 1.1×10^{-3} mg d^{-1} compared to 1.6×10^{-3} mg d^{-1} via food. It should be noted, however, that: (1) the upper range of sediment ingestion rate of 30% may be unrealistically high: for sandpipers the range was estimated to be in the range 7.3-30% (USEPA, 1993) and; (2) metals adsorbed to sediments may be less bioavailable than those in prey (Sheppard et al., 1995). It is, however, possible that direct ingestion of sediment could lead to higher PPC/PNEC values than those determined for the food pathway alone, although uncertainties in metal bioavailability and sediment uptake make the role of the sediment pathway difficult to quantify.

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 (a limitation of all environmental and ecological models). 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 PPC/PNEC values may be different to the predicted ranges. For example, the NOAEL values used for this study 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.

Reducing uncertainty

Further field studies of metal concentrations in prey and (to the extent which it 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 (i.e. validate predictions). For Pb, as shown above, the uncertainty in NOAEL is the dominant factor in model sensitivity, so reducing this uncertainty will have a much greater impact than reducing uncertainty in other parameters. For Hg, uncertainty in NOAEL is also important, but the study has also identified uncertainty in Hg content of prey items, FIR, and relative presence of MeHg as being important sources of uncertainty on which future research should be focussed.

Overwintering birds

In the context of this modelling study, 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 or Hg may have on subsequent breeding success. Some of the contaminants accumulated over winter may be remobilised. For example, Pb sequestered in bone may be remobilised as bone (and calcium) turnover increases during egg production, or MeHg 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 to Pb and Hg 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 principal way in which metal intake on overwintering grounds could have ecologically significant effects is their potential contribution to direct over-winter mortality or decrease in 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 and Hg in birds. We did not attempt to use acute toxicity endpoints in most of the probabilistic models but had sufficient ecotoxicological data for methyl-mercury to carry out an assessment using a NOAEL for survival. This was derived by dividing the LD_{50} data by 100. When this endpoint was used, the modelled median PPC/PNEC ratios were all extremely low, the 95th percentile for the worst case scenario being 0.5. Thus, from this limited assessment, there is no evidence that overwinter dietary intake of Pb or Hg poses an <u>acute</u> toxic threat to dunlin on the Severn Estuary or Poole Harbour.

Conclusions

The Monte-Carlo based model presented here is able to assess the degree of risk posed to birds feeding on important estuarine habitats, and also shows the limitations of such risk assessments, particularly with regard to data quality and availability. This modelling study indicates that internationally important feeding grounds for waders such as Poole Harbour and the Severn Estuary may pose an ecologically-relevant toxic risk to wading birds. It was found that there was a high probability that PPC/PNEC for Pb significantly exceeded 1 in both areas for dunlin. There was also a high probability that PPC/PNEC for Hg significantly exceeded 1 in the Severn Estuary and a significant (>5%) probability that PPC/PNEC exceeded 1 in Poole Harbour.

The model largely used data sets which would be typically available and necessary for assessing the impacts of contamination of large estuaries, although data describing feeding preferences and foraging patterns for waders are rarely site-specific. Whilst acknowledging the inevitable limitations in using such data sets (which are made up of data from a number of sources), their use gives a realistic estimate of uncertainty in environmental impact assessments. Such an uncertainty based assessment gives important insights into the limitations of real environmental impact assessments.

Despite much previous work on its ecotoxicological impacts, a major source of uncertainty in predicting PPC/PNEC values for Pb was the large uncertainty in NOAEL values. Generation of further experimental toxicity data for metals in birds is likely to be extremely limited because of the ethical concerns associated with such work, and it is doubtful that there will be significant reduction in the future in the uncertainty associated with these measures. For Hg, the amount of Hg present as MeHg, FIR and prey metal concentrations were also important sources of uncertainty and further studies to improve the precision of measurements of these parameters would reduce some of the uncertainty when estimating the risks of Hg to wading birds.

Use of lethal toxicity data (LD50/100) was investigated as a method for assessing sub-lethal impacts from Hg. It was found that this method led to a significant under-estimate of the potential impact of Hg contamination, as compared with direct estimation of NOAEL.

If significant toxic risk is still predicted following appropriate studies to reduce the uncertainty associated with contaminant levels in prey species, field studies to assess contaminant residues and relevant health indices in waterbirds should be undertaken. These should be focussed on high risk sites where inputs of relevant contaminants are ongoing. An approach which makes use of waterbird carcasses (found dead at relevant sites), similar to the UK's Predatory Bird Monitoring Scheme, should be considered, to provide further insight into the significance of the risk predictions made through the modelling work reported here. Application of non-invasive biomarkers to samples which could potentially be collected during routine ringing operations may provide useful supplementary information.

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Figure Captions

Figure 1. Map of Severn and Poole Harbour estuaries.

Figure 2. Predicted PPC/PNEC of Pb in dunlin, Poole Harbour: Average Scenario. The histogram shows the frequency of given PPC/PNEC output values out of 10,000 model runs. Percentage cumulative frequency is shown by the grey line using the right-hand vertical axis. The uncertainty is very high (note the logarithmic scale on the X-axis) due primarily to uncertainty in NOAEL (see Sensitivity Analysis section).

Figure 3. Hg in Dunlin, Severn Estuary, assuming mean fraction of MeHg = 18%. The histograms show the frequency of given PPC/PNEC output values out of 10,000 model runs. Percentage cumulative frequency is shown by the grey line using the right-hand vertical axis. Worst case scenario for PNEC based on (a) LD50/100 or (b) NOAEL based on reproductive endpoints. PPC/PNEC is predicted to be significantly greater than 1 based on NOAEL, but less than 1 based on LD50/100.

Figure 4. Median predicted values of PPC/PNEC for lead in dunlin in Poole Harbour and the Severn Estuary. Error bars show the range of 5-95 percentile predicted values.

Figure 5. Median, predicted values of PPC/PNEC for Hg in dunlin where PNEC is based either on an NOAEL or on LD50/100 in (a) Poole Harbour and (b) the Severn Estuary. Error bars show the range of 5-95 percentile predicted values.

Figure 6 Sensitivity analysis: Pb in dunlin, Poole Harbour (Ave. Scenario). The variation of predicted PPC/PNEC is shown given variation in different individual input parameters, and for variation in all parameters. Uncertainty in NOAEL for Pb dominates uncertainty in PPC/PNEC.

Figure 7 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 PPC/PNEC

TABLES

Table 1. Percentage of different food types taken by adult (Average Scenario) and juvenile (Worst Case Scenario) dunlin in Poole Harbour and the Severn Estuary.

Poole Harbour	**Percentage food type**
Marine worms	78 % S.D. 5%
Molluscs	100% minus % of marine worms
Crustaceans	
Earthworms	0
Severn Estuary	
Marine worms	58 % S.D. 10%
Molluscs	100% minus Σother
Crustaceans	0
Earthworms	0-10%

Table 2. Assumed distributions (mean ± S.E. or range) of lead and mercury in prey items for the Average Scenario based on measured data for ragworms and from a literature review for other species (see Tables S3-S6).

Prey type	**Pb – Poole H. mg/kg DW**	**Assumed distribution**	**Pb – Severn Est. mg/kg DW**	**Assumed distribution**
Nereis	0.71 ± 0.11	Normal	1.51 ± 0.32	Normal
Molluscs & crustaceans	0.24 – 7.1	Uniform	0.50-15.1	Uniform
Earthworms	4 – 27	Uniform	4 – 27	Uniform
Prey type	**Hg – Poole H. mg/kg DW**	**Assumed distribution**	**Hg – Severn Est. mg/kg DW**	**Assumed distribution**
Nereis	0.076 ± 0.0068	Normal	0.48 ± 0.1	Normal
Molluscs and crustaceans	0.025 – 0.76	Uniform	0.16 – 1.44	Uniform
Earthworms	Insufficient data		Insufficient data	

Table 3. Ranges and assumed probability distributions of NOAEL and LD50/100 values for Pb and Hg (see Table S7 for details of the studies on which these are based).

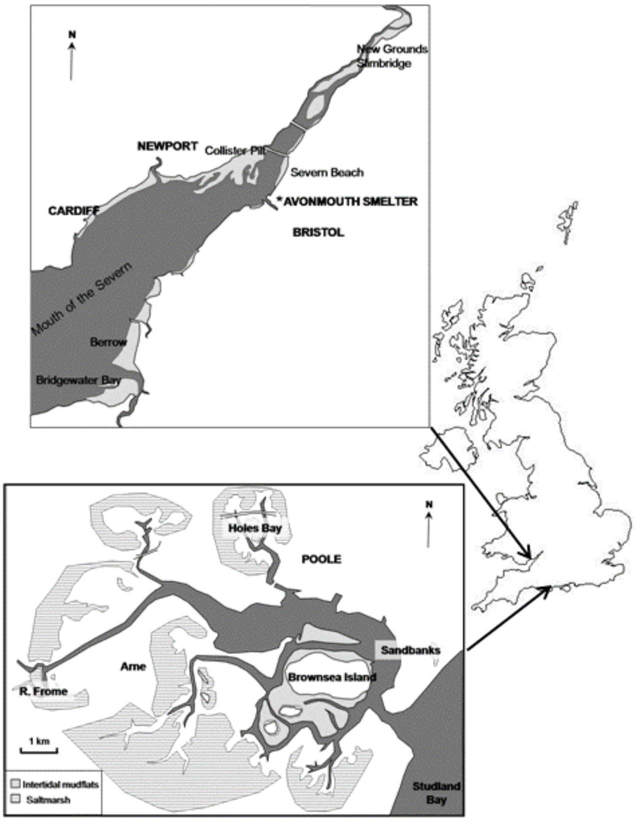
Metal	Endpoint	Range mgMetal/kgBW/d	Assumed probability distribution[a]
Pb	NOAEL	0.011-1.6	Uniform distribution of log-transformed values
MeHg	NOAEL	0.0038-0.0108	Uniform
MeHg	LD50/100	0.195-0.378	Uniform
IOM	NOAEL	0.45 – 5.5	Uniform

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

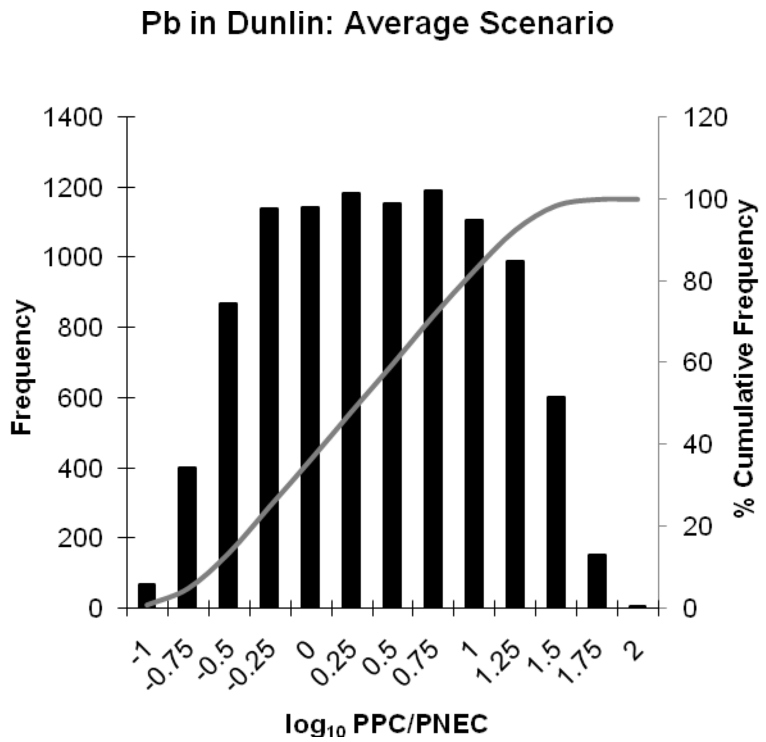
Table 4. Median, 5 and 95 percentile PEC/PNEC values for dunlin exposed to Pb and Hg in Poole Harbour and the Severn Estuary.

Metal	**Scenario**	**Basis for PNEC**	**PEC/PNEC 5%**	**PEC/PNEC 50%**	**PEC/PNEC 95%**
		Poole Harbour			
Pb	Average	NOAEL	0.18	1.97	21.8
Hg	Average	NOAEL	0.23	0.79	2.41
Hg	Average	LD50/100	0.0061	0.02	0.055
Pb	Worst Case	NOAEL	0.48	5.62	58.0
Hg	Worst Case	NOAEL	0.45	1.39	4.34
Hg	Worst Case	LD50/100	0.012	0.035	0.10
		Severn Estuary			
Pb	Average	NOAEL	0.58	6.45	74.6
Hg	Average	NOAEL	1.01	3.37	10.7
Hg	Average	LD50/100	0.035	0.084	0.19
Pb	Worst Case	NOAEL	1.11	11.7	121
Hg	Worst Case	NOAEL	2.31	6.94	21.9
Hg	Worst Case	LD50/100	0.060	0.18	0.51

Figure 1 Map of Severn and Poole Harbour estuaries.



FIGURES 2-7



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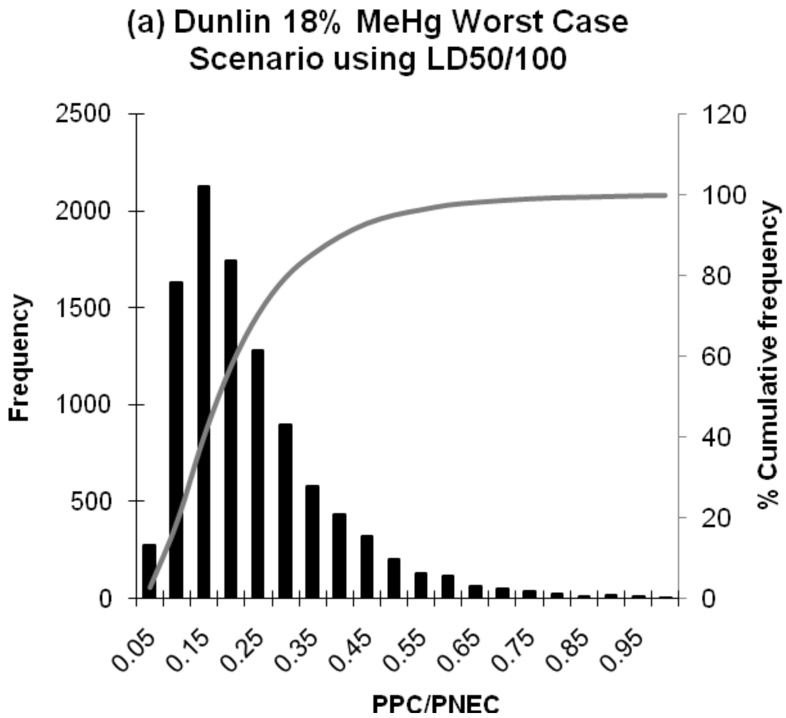

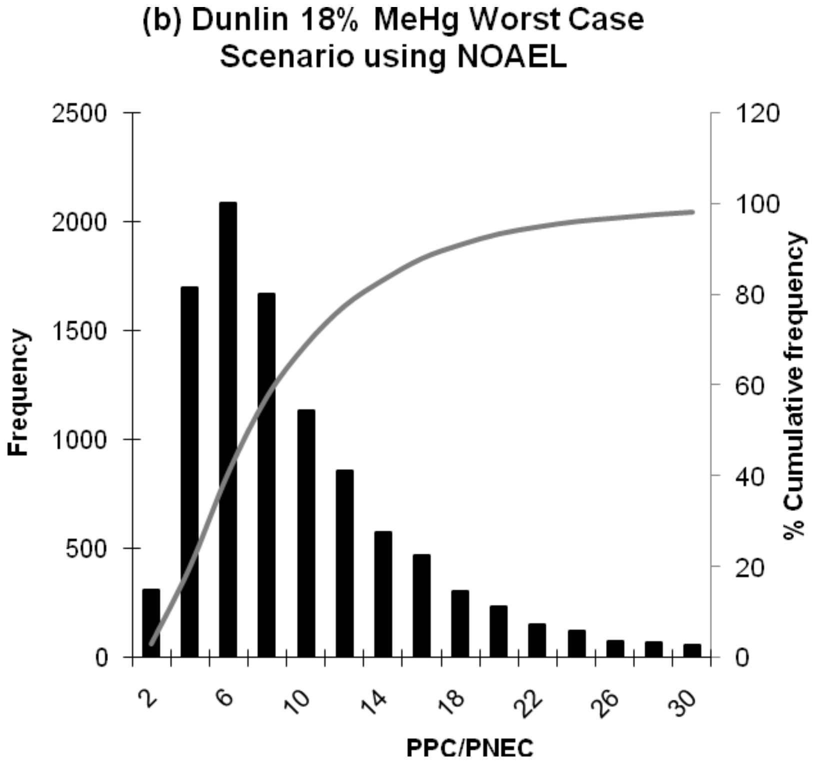

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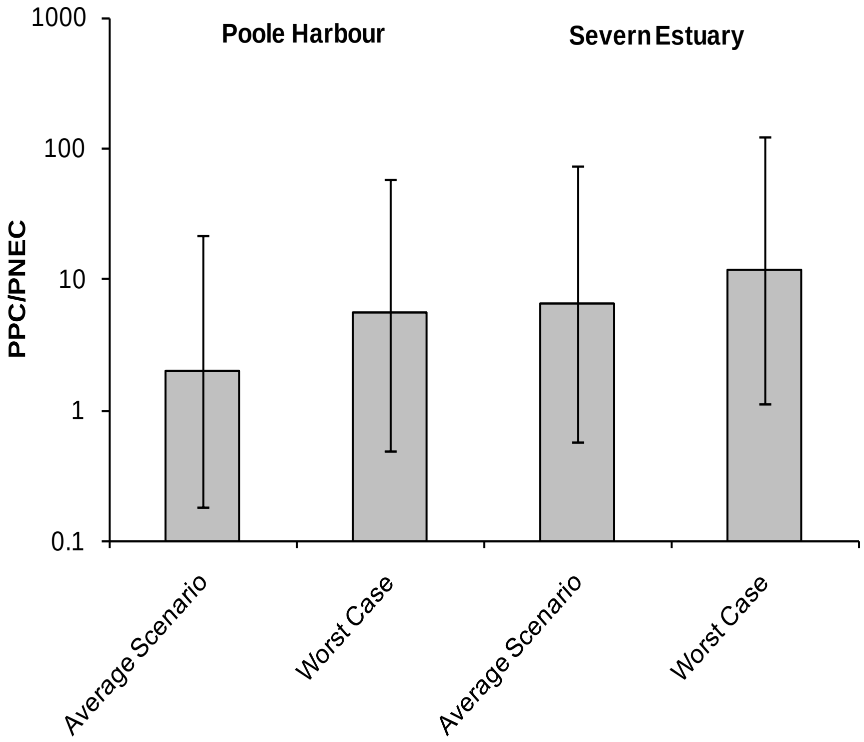

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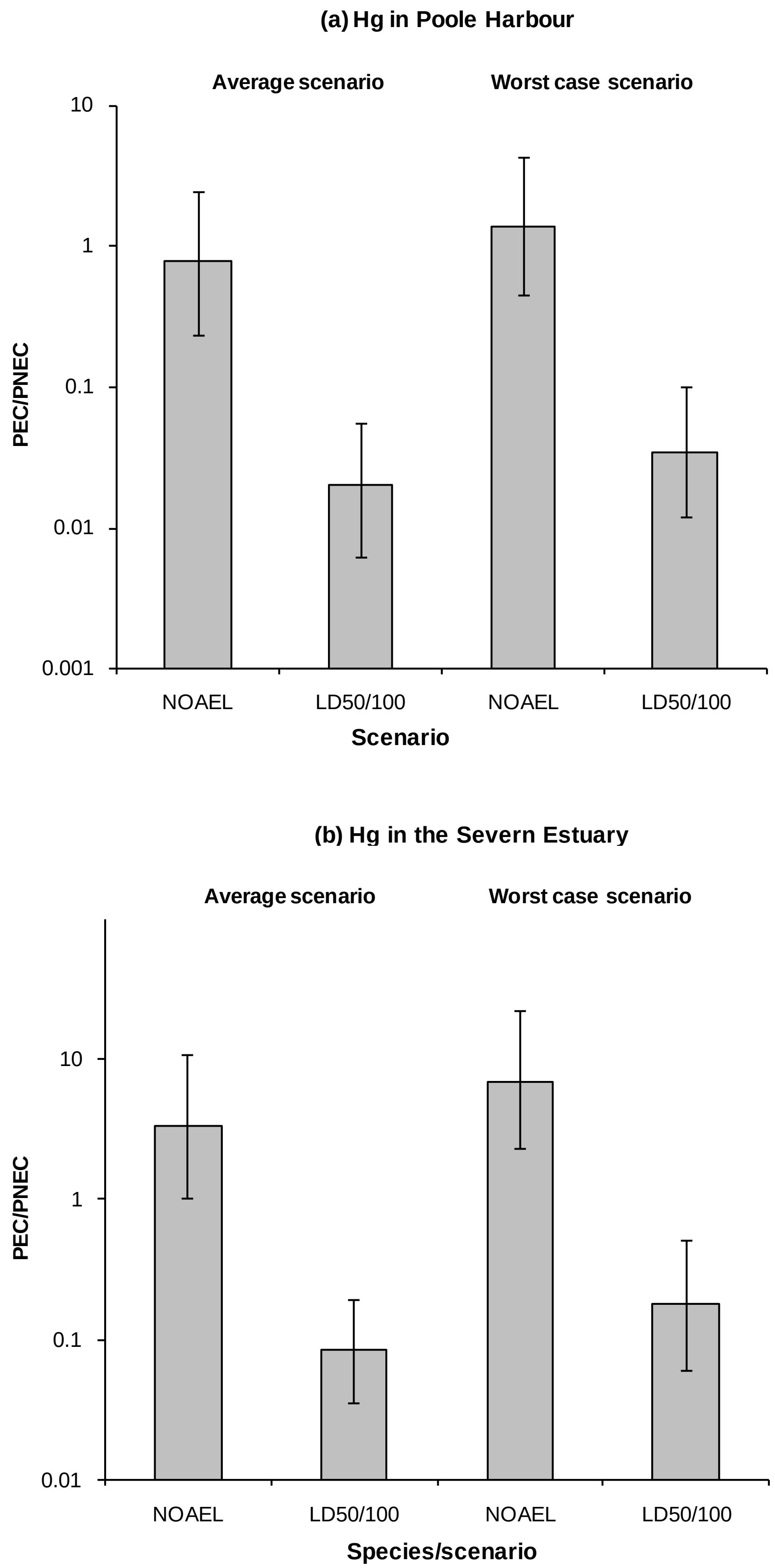

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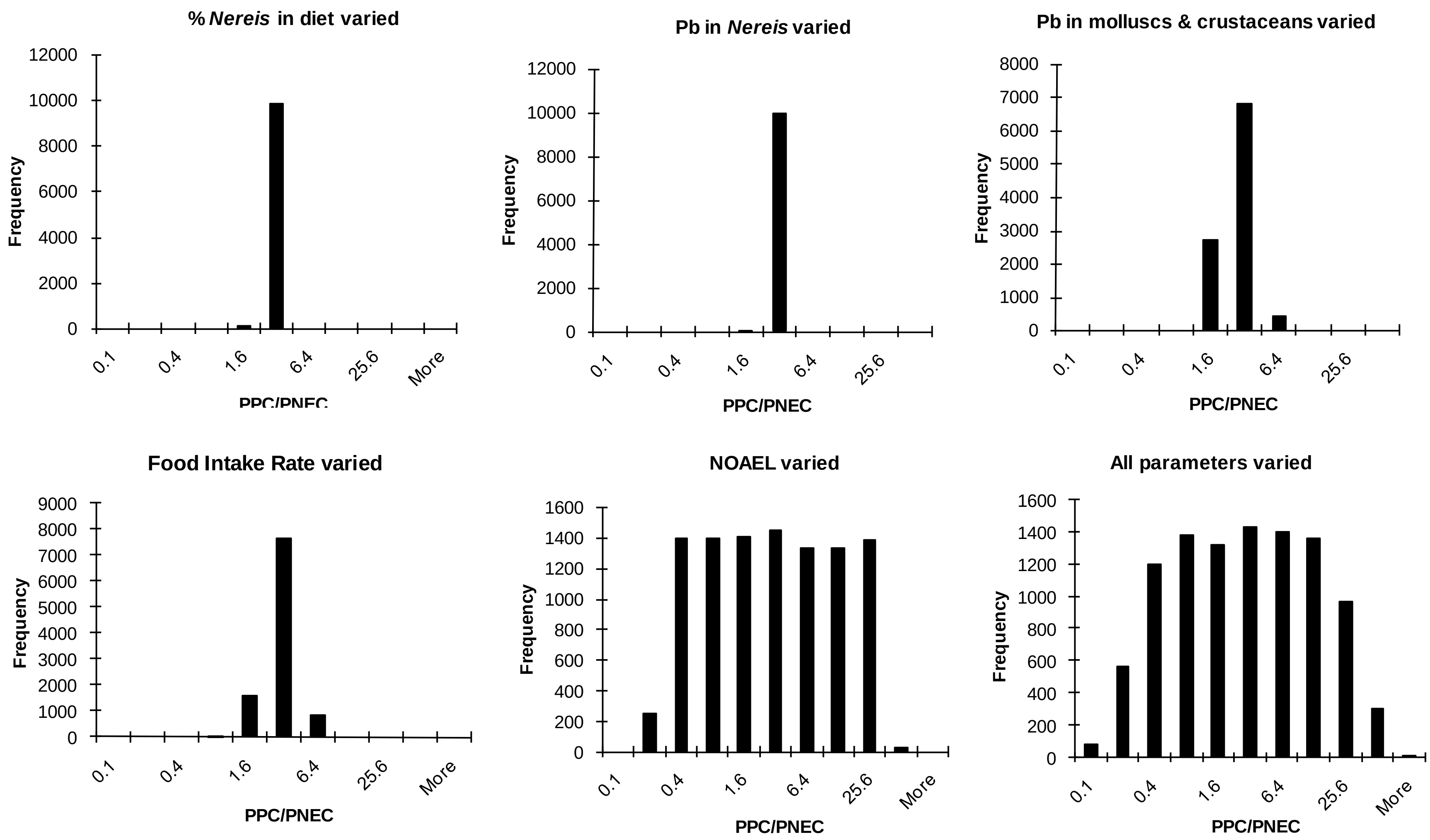

Figure 6 Sensitivity analysis: Pb in Dunlin, Poole Harbour (Ave. Scenario). The histograms show the frequency of given PPC/PNEC output values out of 10,000 model runs. The variation of predicted PPC/PNEC is shown given variation in different individual input parameters, and for variation in all parameters. Uncertainty in NOAEL for Pb dominates uncertainty in PPC/PNEC.

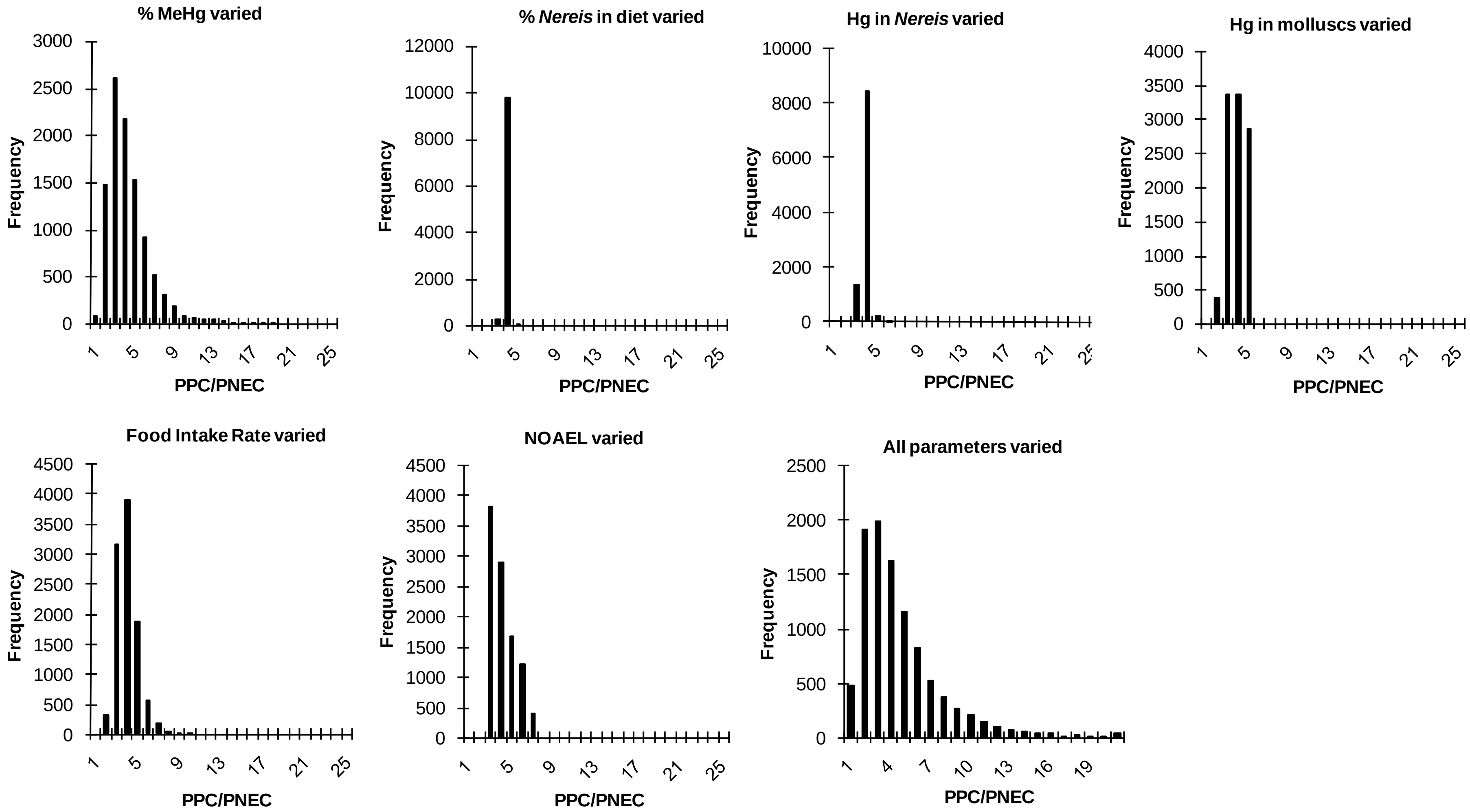

Figure 7 Sensitivity analysis: Hg in Dunlin, Severn Estuary (Ave. Scenario). The histograms show the frequency of given PPC/PNEC output values out of 10,000 model runs. Uncertainty in %MeHg in diet, Hg content of molluscs, FIR and NOAEL all contribute significantly to uncertainty in PPC/PNEC

SUPPLEMENTARY MATERIAL

Table S1. Maximum PPC/PNEC estimated from measurements of contaminants in *Nereis diversicolor* (Environment Agency, unpubl. res.) at 12 sites in Poole Harbour. Contaminants with PPC/PNEC > 1 are highlighted in bold font.

Contaminant	Measured concentration (Range) mg/kg f.w.	NOAEL mg/kgBW/d	Max. PPC/PNEC	Notes
Copper	1.8 - 6.8	47.0 [1]	0.073	
Silver	0.23 – 0.36	>2.3 [2]	<0.12	Used LC50×FIR/1000
Zinc	19 – 44	11 [3]	**3.15**	
Cadmium	0.011 – 0.36	1.45 [4]	0.08	
Mercury	0.0086 – 0.026	0.0064 [5]	**3.1**	Assume NOAEL = LOAEL/10 A NOAEL for mercury as organo-metal (methylmercury) was chosen.[a]
Lead	0.11 – 0.36	0.021 [6]	**14**	
Vanadium	<0.23 – 0.48	1.5 [7]	0.25	
Arsenic	1.5 – 6.0	10.0 [8]	0.47	
Chromium	<0.23 – 0.48	1.0 [3]	0.37	
Manganese	1.0 – 3.6	977 [9]	0.0029	
Iron	67 – 285	1.03 [2]	**216**	Used LC50×FIR/1000. But NOAEL lower than daily iron requirement.
Nickel	0.41 – 1.5	77.4 [10]	0.015	
PAHs	<0.0005 – 1.1	1.43 [11] Benzo(a)pyrene	All <1	Checked each individual PAH against NOAEC for Benzo(a)pyrene, the most toxic PAH.
Tributyl tin	n.d.	6.8 [12]	-	All measured values were below limit of detection.

a. There is a large disparity between NOAELs for mercuric chloride and methylmercury (0.45 cf. 0.0064 mg/kg bw/d respectively). Using the NOAEL for methyl mercury over estimates the risk. [1] (Mehring et al., 1960) ; [2] (U.S. Environmental Protection Agency, 2002); [3] (Sample et al., 1997); [4] (White and Finley, 1978); [5] (Heinz, 1979); [6] (Edens and Garlich, 1983); [7] (Romoser et al., 1961) [8] (Stanley et al., 1994); [9] (Laskey and Edens, 1985); [10] (Cain and Pafford, 1981); [11] (Hough et al., 1993); [12] (Schlatterer et al., 1993);

Table S2. Maximum PPC/PNEC estimated from measurements of contaminants in *Nereis diversicolor* at 13 sites in the Severn Estuary. The range of organic contaminants that were analysed for was greater than in the Nereis collected from Poole Harbour (Table S1).

Contaminant	Measured conc. (Range) mg/kg f.w.	NOAEL mg/kgBW/d	Max. PPC/PNEC	Notes
Copper	7.2 – 20	47.0 [1]	0.33	
Silver	0.25 – 1.6	>2.3 [2]	<0.53	Used LC50*FIR/1000 for NOAEL
Zinc	20 – 55	11 [3]	**3.9**	
Cadmium	0.024 – 0.25	1.45 [4]	0.13	
Mercury	0.039 – 0.20	0.0064 [5]	**22.5**	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	0.18 – 0.53	0.021 [6]	**34.2**	
Arsenic	1.4 – 4.9	10.0 [7]	0.38	
Chromium	0.20 – 1.3	1.0 [3]	**1.0**	
Nickel	0.32 – 1.3	77.4 [8]	0.013	
Selenium	1.2 – 3.1	0.5 [9]	**4.9**	Assume NOAEL = LOAEL/10
PAHs	< 0.0005 – 0.8	1.43 [10] (Benzo(a)pyrene)	All <1	Checked each individual PAH against NOAEL for Benzo(a)pyrene, the most toxic PAH.
PCBs	< 0.0001 – 0.0086	0.18 [11] (Arochlor 1254)	Sum <1	Checked sum of PCBs vs NOAEL for Arochlor 1254.
Tributyl tin	n.d.[b]	6.8 [12]	-	All measurements below L.O.D.[b]
a,b,d,g-hexachlorocyclohexane	n.d.			All measurements were below L.O.D.
Aldrin, Dieldrin, Endrin, Isodrin	n.d.			All measurements were below L.O.D.
op-DDT, pp-DDT	n.d.			All measurements were below L.O.D.
pp-DDE	< 0.001 – 0.0012			LC50 = 825 mg/kg. Max 1.19 µg/kg in prey. Only 2 out of 13 samples above L.O.D[2]
pp-TDE	<0.001 – 0.0032			1 out of 13 samples above L.O.D. Measured value 3.2 µg kg^{-1} f.w. LD50 = 386 mg kg^{-1} BW acute dose.
Hexachloro-butadiene, Hexachloro-benzene	n.d.			All measurements were below L.O.D.

a. n.d. – not detected; b. L.O.D – limit of detection in chemical analysis

[1] (Mehring et al., 1960) ; [2] (U.S. Environmental Protection Agency, 2002); [3] (Sample et al., 1997); [4] (White and Finley, 1978); [5] (Heinz, 1979); [6] (Edens and Garlich, 1983); [7] (Stanley et al., 1994); [8] (Cain and Pafford, 1981); [9] (Heinz et al., 1987); [10] (Hough et al., 1993); [11] (Dahlgren et al., 1972); [12] (Schlatterer et al., 1993);

Table S3. 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		This study, range for Poole Harbour
	3.6		Langston et al. unpubl. Mean over 25 yr period.
Scrobicularia plana Peppery furrow shell	18 	 5.8	Langston et al. unpubl. Mean over 25 yr period. This study, Parkstone Bay
Cerastoderma edule Common cockle	14	5	(Boyden, 1975) samples from 1973-4
Mytilus edulis Common mussel	19	7 10.5[a]	(Boyden, 1975) samples from 1973-4 (MAFF, 1998) Main harbour, site not specified.
Ostrea edulis Native oyster	1.2	0.35	(Langston, 2003a). Data from 1983.
Crassostrea gigas Portuguese oyster		2.5	(Langston, 2003a). Data from 1983.

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

Table S4. 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 et al. unpubl. Mean over 25 yr period.
Scrobicularia plana Peppery furrow shell	1.08		Langston et al. unpubl. Mean over 25 yr period.
		0.14	EN supplied data 2004 Parkstone Bay
Mytilus edulis Common mussel		0.413[a]	(MAFF, 1998) Main harbour, site not specified.
Ostrea edulis Native oyster	0.49	0.16	(Langston, 2003a). Data from 1983.
Crassostrea gigas Portuguese oyster		0.26	(Langston, 2003a). Data from 1983.

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

Table S5. 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[a] 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 et al., 2003b). Mean over 25 year period
Scrobicularia plana Peppery furrow shell	43.5		(Langston et al., 2003b). Mean over 25 yr period.
Mytilus edulis Common mussel		10.0	Environment Agency, unpul. res. 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.

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

Table S6. 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[a]	This study, range for Severn Estuary
	1.42	(Langston et al., 2003b). Mean over 25 yr period.
Scrobicularia plana Peppery furrow shell	0.64	(Langston et al., 2003b). Mean over 25 yr period.
Mytilus edulis Common mussel	0.61	(Langston et al., 2003b). Date not known.
	0.5	Environment Agency, unpubl. res., 2001-05

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

Table S7. 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 (mg/kg BW/day)	Reference
Pb	Lead acetate	Chicken (*Gallus domesticus*)	28	Egg Production	1.63	(Edens and Garlich, 1983)
	Lead acetate	Japanese quail (*Coturnix c. japonica*)	84	Progeny Counts	0.019[a]	(Edens and Garlich, 1983)
	Lead acetate	Japanese quail (*Coturnix c. japonica*)	35	Egg Production	0.194	(Edens and Garlich, 1983)
	Lead acetate	Japanese quail (*Coturnix c. japonica*)	84	Egg Production	0.011[a]	(Edens et al., 1976)
Hg (inorganic)	Mercury sulphate	White leghorn hen (*Gallus domesticus*)	21	Egg hatchability	5.5	(Scott, 1977)
	Mercuric chloride	Japanese quail (*Coturnix c. japonica*)	140	Egg Production	0.45	(Hill and Shaffner, 1976)
	Mercuric chloride	Japanese quail (*Coturnix c. japonica*)	N/A	Mortality	0.30[b]	(Hill and Soares, 1984)
Hg (organic)	Methyl mercury chloride	Great Egret (*Ardea albus*)	91	Growth	0.0038	(Spalding et al., 2000)
	Methyl mercury chloride	Great Egret (*Ardea albus*)	91	Growth	0.0108	(Spalding et al., 2000)
	Methyl mercury dicyandiamide	Mallard (*Anas platyrhynchos*)	>365	Egg and Duckling Production	0.0064[a]	(Heinz, 1979)
	Methyl mercury dicyandiamide	Mallard (*Anas platyrhynchos*)	N/A	Mortality	0.289[b]	(Hudson et al., 1984)
	Methyl mercury	Bobwhite quail (*Colinus virginianus*)	N/A	Mortality	0.239[b]	(Hudson et al., 1984)
	Methyl mercury	Japanese quail (*Coturnix c. japonica*)	N/A	Mortality	0.195[b]	(Hill and Soares, 1984; Hudson et al., 1984)
	Methyl mercury	Fulvous whistling duck (*Dendrocygna bicolour*)	N/A	Mortality	0.378[b]	(Hudson et al., 1984)
	Methyl mercury dicyandiamide	House sparrow (*Passer domesticus*)	N/A	Mortality	0.219[b]	(Hudson et al., 1984)
	Methyl mercury dicyandiamide	Pheasant (*Phasianus colchicus*)	N/A	Mortality	0.253[b]	(Hudson et al., 1984)

a. values based on a LOAEL divided by a factor of 10; b. values based on a LD50 value divided by a factor of 100. N/A indicates that duration of exposure is not applicable as single oral dose was used.

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