Bioaccumulation Surveillance in Milford Haven Waterway Phase II (2010)

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Executive Summary

Biomonitoring of contaminants including metals Ag (silver), As (arsenic), Cd (cadmium),Co (cobalt), Cr (chromium), Cu (copper), Fe (iron), Hg (mercury), Mn (manganese), Ni (nickel), Pb (lead), Se (selenium) and Zn (zinc); organotins (OTs), polyaromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs) was previously carried out by the MBA ecotoxicology team at a series of sites along the Milford Haven Waterway (MHW) and at a reference site in the Tywi Estuary during 2007-2008. The species used as bioindicators encompassed a variety of uptake routes; i.e. seaweed, (*Fucus vesiculosus*: dissolved contaminants); winkles, (*Littorina littorea*: a grazer); mussels and cockles, (*Mytilus edulis* and *Cerastoderma edule*: suspension feeders that accumulate from both dissolved phase and suspended particulates); and the ragworm, (*Hediste* (=*Nereis) diversicolor*: an omnivore which often reflects bioavailable contaminants in sediment).

The purpose of the current project was to resurvey, using consistent protocols, a similar range of species and sites in 2010 and to consider the short term variation in contamination trends in the intervening period. Thus, are trends in bioaccumulation in the waterway stable over periods of ~ 2 years and, if so, would bioaccumulation surveillance at such intervals (or longer) provide an adequate integrated picture of contamination? In the current survey we have also extended sampling upstream in the Daucleddau Estuary (Picton, Hook) and included a further (regional) reference site at Appledore in the mouth of the Taw/Torridge Estuarine system, in order to provide a broader baseline against which the scale of any contamination in MHW can be judged. It should be noted, however, that the selection of Appledore as a near-pristine, baseline site is now debatable given recent exposure of old landfill material closeby (see footnote, page 24).

There were species differences in metal bioaccumulation due to feeding strategy and habitat preference, physiological and ecological attributes, and chemical properties of the different elements, which have subtle implications for monitoring trends. *M. edulis* and *C. edule* are considered the best all-round indicators and draw the clearest distinction between MHW and reference sites and illustrate trends along the waterway. Both Appledore and Tywi sites provide reasonable baselines, generally, though as indicated above there are some reservations regarding the former, with respect to some contaminants, due to possible influence of leachate from an old landfill. A gradient in bioaccumulation (increasing upstream in MHW) was evident for most metals and in the mid- and upper- estuary, Ag, Cd, Co, Cr, Fe, Hg, Mn, Ni, and to a lesser extent As, Cu, Pb, Se and Zn exceeded background concentrations in cockles and mussels. *Fucus* showed enrichment for Co, Cr, Cu, Fe, Mn, Ni and Zn; *Littorina* for Co, Cu, Fe and Mn; *Nereis* for Ag, Ni, (and to a small extent Pb, Cu, Hg). Increases in metal bioavailability at upstream sites reflect the influence of geogenic or other land-based sources, enhanced by lower salinities. However enrichment is seldom more than an order of magnitude and, towards the mouth of MHW, there was a good deal of overlap with reference values and little indication of localised impact. For the majority of samples (94%), metal concentrations in Milford Haven biota were at the lower-middle part of the UK range. Exceptions were Mn, Ni in mussels, Mn, Ni, Co, Fe, Se in cockles, Co, Mn, Se and As in seaweed, Mn in winkles and Ni in ragworm. Spatial trends for metals in biota were similar overall to those observed in the earlier survey (2007/8).

One of the main objectives of this project was to begin to establish temporal trends. Metals data reveal a number of changes between surveys, both increases and decreases. Reductions were observed for As (*Fucus, Mytilus, Cerastoderma*); Hg, Se (*Mytilus*, *Cerastoderma*); Cu, Pb (*Littorina*). Of these, the most notable trends were for As and Hg where all species exhibited lower values in the current survey. Significant increases were seen for Ag (*Littorina*, *Cerastoderma*) Cr and Fe (*Mytilus* only). Both decreases and increases were observed for Co (*Nereis* and *Fucus, Cerastoderma, Mytilus*, respectively) and for Ni (*Fucus* and *Mytilus* respectively) implying these may represent natural variability rather than changes in anthropogenic contributions. There were no changes in Cd or Zn.

Tributyltin (TBT) levels in MHW mussels remain highest in the seaward part of the waterway, reflecting port activities. Lowest TBT values, upstream in the Daucleddau, were comparable to local background. All were higher than the Appledore reference site. As in the previous MHW survey, all TBT concentrations were above the lower Environmental Assessment Criteria for mussels (sub-lethal effects possible) but below thresholds considered by OSPAR to be acutely toxic. TBT in *N. diversicolor* also indicated bioaccumulation in MHW as a result of the legacy of shipping/boating activity. Phenyltins (PT) were not accumulated appreciably in *Mytilus,* signifying restricted use in antifouling relative to butyltins (BT). However, PT residues in some *Nereis* populations in MHW suggest they may have been subjected to localized contamination in sediments, perhaps reflecting past agricultural use of TPT in the catchment. Mussel TBT concentrations in Milford Haven did not change significantly between surveys though the metabolite dibutyltin (DBT) was higher in 2010: monobutyltin (MBT) in contrast declined. TBT and DBT concentrations in *Nereis* increased slightly between 2007 and 2010 whilst MBT decreased. TPT increased slightly in mussels but in *Nereis* levels were similar in 2007 and 2010.

Biotic and metabolic variables result in different patterns of PAH bioaccumulation in *M. edulis* and the polychaete *N. diversicolor* with mussels being the better accumulators (by up to an order of magnitude). The majority of PAHs in Milford Haven mussels were above OSPAR Background and Tywi and Appledore reference values, but not excessively so, except at Angle and Pennar, where PAH concentrations exceeded baselines by an order of magnitude. Environmental Assessment Criteria were not exceeded for most PAHs in mussels, with the exception of anthracene. The stronger influence of fine-sediment contamination on *N. diversicolor* may account for different spatial profiles to those in mussels, accounting, for example, for a degree of PAH enrichment in Dale worms (sampled from a muddy creek – River Gann) not seen in mussels (rocky, sandy beach, Pickleridge). Though PAH body burdens in MHW *Nereis* were frequently higher than reference values, low levels were sometimes evident upstream, implying relatively light contamination. This is confirmed by comparison with Severn Estuary biota where PAH bioaccumulation was up to an order of magnitude higher than MHW. Environmental Assessment Criteria (EAC) would not be exceeded in MHW *Nereis,* though as with mussels, the actual extent of sublethal effects is uncertain. To place results in context, PAH levels in mussels (Angle and Dale) were of the order of 10^3-10^4 lower than at the time of the *Sea Empress* oil spill. Comparing our 2008 and 2010 surveys, PAHs have increased in mussels at Angle and Pennar, and an underlying increasing trend across sites is significant for fluorene, phenanthrene and anthracene, though not for other individual PAHs or ∑(sum of, or total) PAHs. Temporal changes in

Nereis were less obvious, apart from an increase in chrysene at Angle (the only PAH in worms for which there was a significant increase across the waterway). For phenanthrene, fluorene, fluoranthene and ∑PAHs the underlying trend, across sites was in fact downwards.

PCBs in MHW mussels were slightly higher than the Tywi reference site, but lower than at Appledore. Enrichment at the latter site was most notable for the more highly chlorinated penta- (CB101, 118), hexa- (CB138, 153) and hepta-chlorinated (CB180) congeners and may reflect the influence of landfill leachate. ∑PCB values (sum of the 'ICES 7' PCB congeners - IUPAC numbers 028, 052, 101, 118, 138, 153 and 180) for Milford Haven and Tywi mussels were below the OSPAR upper EAC threshold but were above the lower 'no-effects' threshold. Slightly different distributions were observed in sediment-dwelling *N. diversicolor*, compared with mussels: highest PCB concentrations in worms were those at Cosheston Pill and opposite Pennar where they exceeded the upper EAC (for mussels); lowest concentrations in worms were those at Dale and Angle in the mouth of MHW, where they were below the lower EAC threshold. PCB bioaccumulations in MHW biota were lower than known hotspots such as the Severn. Temporal comparison of PCB concentrations in 2010 with the earlier MHW surveys (2007/8) indicates that there has been no significant net change across the waterway as a whole.

The pattern of condition indices (CI) in bivalves (mussels and cockles) showed significant and consistent variation across the region. As in 2008, condition in these shellfish was highest at the Tywi reference site and at the mouth of Milford Haven (comparable also with the Appledore reference), and decreased upstream in the waterway. There were a number of significant (negative) relationships between CI of bivalves and body burdens of metals. The condition of mussels decreased in line with increasing metal concentrations according to the sequence Cr=Cu=Ni>Zn>Co>As>Hg. The corresponding sequence for metals in cockles was As>Hg>Ni>Co>Cd. It should be stressed however that these correlations are not proof of cause and effect. It is possible that a combination of contaminants (and natural factors) influence this pattern in the CI; a study of sub-lethal effects is needed to elucidate pollutant impacts.

The strategy for biomonitoring undertaken in this project builds on established sampling protocols and is a sound basis for a rolling program against which future change could be measured. Complementary, harmonised monitoring in which biological condition and environmental parameters are measured and interpreted alongside body burdens - using multivariate techniques – are also recommended for the future to help assess the status of the site more comprehensively.