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Review of the Predatory Bird Monitoring Scheme (PBMS) 2006

RF Shore, LA Walker, GO Thomas, JL Barber, FR Martin, KC Jones, NA Beresford, P Rowland & RW Pickup

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For further information please contact:
Surveillance Team
Joint Nature Conservation Committee
Monkstone House, City Road
Peterborough, PE1 1JY, UK
www.jncc.gov.uk

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Campaign for Responsible Rodenticide Use

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Contents

1 Executive Summary

The Wildlife and Pollution contract supports the long-term monitoring programme called the Predatory Bird Monitoring Scheme (PBMS) which monitors selected pollutants, pesticides and biocides in predatory birds in Britain. The programme was started in the early 1960s and was instrumental in securing the phased withdrawals of the permitted uses of organochlorine (OC) insecticides. It has since provided a measure of the effectiveness of regulatory bans in reducing the exposure of wildlife. The PBMS subsequently expanded to encompass a range of other contaminants and pesticides (specifically polychlorinated biphenyls (PCBs), mercury (Hg) and second-generation anticoagulant rodenticides, thereby reflecting contemporary conservation and regulatory concerns. The PBMS is run by the Centre for Ecology & Hydrology (CEH). The other long-term funding stakeholder is the Joint Nature Conservation Committee (JNCC) and the yearly results of the PBMS monitoring are reported to the JNCC. The data from the scheme enables the JNCC and Country Agencies to monitor trends, asses risk to wildlife, and advise on the effectiveness of measures to restrict the use and entry into the environment of particular compounds.

The Wildlife and Pollution contract has been subject to a number of scientific assessments within JNCC's rolling programme of peer review and as a result has undergone some refocusing of monitoring effort to ensure that it addresses current concerns. The current report is submitted as part of the latest review. Its aim is to review the key activities and data of the PBMS and identify existing and new monitoring activities that can be delivered and that will meet the key needs of the stakeholders. The report therefore summarised the key findings of the long-term monitoring programme, describes the sample archiving conducted by the PBMS and current associated research, and collates the key findings of various short-term PBMS studies that informed future monitoring. The report also highlights the potential for future cooperation between the PBMS and other UK schemes that monitor chemicals in vertebrates. The report also describes a horizon-scanning review to identify new and/or currently unmonitored chemical threats to wildlife, and, in particular, those compounds that can be monitored through the existing PBMS capability and through collaboration with Lancaster University. This collaboration will be facilitated through the forthcoming (2007-8) relocation of the PBMS from CEH Monks Wood site to CEH Lancaster.

The key recommendations from this report are: (i) the curtailment of reporting of OC insecticide in samples monitored by the PBMS except in sea eagle (*Haliaeetus albicilla*) eggs; (ii) coupling the monitoring of PCB congener and TEQ concentrations with that of new persistent organic pollutants of concern that can be analysed using similar methods; (iii) expanding the analysis of mercury to a wider suite of metals [for the same cost] so as to provide a wider assessment of toxic risk and a measure of health status based on trace element status; (iv) expanding the range of anticoagulant rodenticides monitored [at no extra cost] through transfer of analysis to mass spectrometry monitoring; (v) the focusing of annual one-off studies to develop new monitoring for new POPs and other priority chemicals of concern. Mechanisms to develop closer integration of different UK monitoring schemes and foster the dissemination and adoption of best practice are also outlined.

2 Introduction

2.1 Background

The Wildlife and Pollution contract supports the long-term monitoring programme called the Predatory Bird Monitoring Scheme (PBMS). The PBMS monitors the levels of certain pollutants in selected predatory birds in Britain. The programme was started in the early 1960s, when there were major concerns about the impacts of organochlorine (OC) insecticides and organomercury fungicides on wild birds and mammals. The early monitoring, accompanied by experimental and ecological studies, demonstrated the adverse effects of OC insecticides on predatory bird populations in Britain (Newton, 1986; Ratcliffe, 1980). This work contributed to the ban on the agricultural use of these insecticides in Britain and elsewhere. The PBMS subsequently assessed the effectiveness of these bans by measuring whether there was a decline in OC concentrations in the livers and eggs of predatory terrestrial and freshwater birds.

The PBMS subsequently expanded to encompass a range of other contaminants and pesticides, thereby reflecting contemporary conservation and regulatory concerns. Monitoring of the assimilation of industrial polychlorinated biphenyls (PCBs) by predatory birds was begun in 1966 after these compounds were identified as pollutants that were potentially toxic to birds. PCBs have been measured in the livers or eggs of a range of birds of prey and in the eggs of a marine predator, the gannet (*Morus bassanus*). Mercury (Hg), which may derive from past agricultural and from both past and current industrial sources, has been monitored in various bird species from approximately 1970. Second-generation anticoagulant rodenticides (SGARs) have been monitored in barn owls (*Tyto alba*) since 1982.

The PBMS is run by the Centre for Ecology & Hydrology (CEH) which is one of the principle long-term funding stakeholders for the scheme. The other long-term funding stakeholder has been the Joint Nature Conservation Committee (JNCC) and the yearly results of the PBMS monitoring are reported to the JNCC in the form of annual reports. Long-term trends are currently also evaluated in these reports, but at three year intervals rather than annually; the most recent long-term reviews were reported by (Shore *et al.*, 2005a; Shore *et al.*, 2006c). The Environment Agency became a funding stakeholder of the PBMS in 1998 and the Campaign for Responsible Rodenticide Use (CRRU) began funding support for the PBMS in 2006; this support is administered through the Wildlife and Pollution Contract. The financial contributions of all funding stakeholders are reviewed on an annual basis.

The Wildlife and Pollution contract has been subject to a number of scientific assessments within JNCC's rolling programme of peer review. As a result, some monitoring has been curtailed. Long-term monitoring of OC insecticides, PCBs and Hg in common kestrels (*Falco tinnunculus*) was stopped in 1998 and a reduction (from analysis of all birds received to a stratified random sample) in the number of sparrowhawks analysed annually for the same compounds was implemented in 2002. The carcasses and eggs of a range of other predatory bird species (peregrine falcon (*Falco peregrinus*), common buzzard (*Buteo buteo*), long-eared owl (A*sio otus)*, little owl (*Athene noctua*), common kingfisher (*Alcedo atthis*), great crested grebe (*Podiceps cristatus*), and bittern (*Botaurus stellaris*) which were monitored in the past for OCs in some years were excluded from the core monitoring of the PBMS from 1998 onwards. However, post-mortem examinations are carried out the carcasses of all the predatory birds submitted to the PBMS, relevant information is recorded and the cause of death is determined (and reported back to the volunteer who submitted the carcass). Samples of the egg contents and body tissues from all birds are stored at -20°C as part of the PBMS long-term frozen tissue and egg archive. The nature, value and uses for this archive are described in Section 4 of the current report.

The curtailing of certain monitoring has meant that the PBMS has already undergone significant refocusing in recent years to ensure that it addresses current concerns. This has involved conducting specific short-term pilot studies which, in some cases, have identified a need for new monitoring.

Thus, after initial pilot studies (Shore *et al.*, 2000; Shore *et al.*, 2001), monitoring of SGARs was widened in 2001 to include red kites (*Milvus milvus*) and kestrels (*Falco tinnunculus*) as well as barn owls, although red kites thought to have actually died as a result of poisoning are usually examined by the Department of Environment and Rural Affairs (DEFRA) Wildlife Incident Investigation Scheme (WIIS). (eg., Barnett *et al.*, 2005, 2006). Similarly, after review of PBMS activities (Shore *et al.*, 2005c), measurement and reporting of PCBs on an individual congener, sum congener and Toxic Equivalents (TEQs) (Ahlborg *et al.*, 1994; Van den Berg *et al.*, 1998; van den Berg *et al.*, 2006) was started in 2002. This was done so that the likelihood of toxic effects due to specific PCB congeners, and in particular by non-*ortho* and mono-*ortho* substituted coplanar congeners that can exert additive toxicity via the *Ah* receptor, could be more accurately assessed. The current long-term monitoring activities undertaken by the PBMS are summarised in Table 2.1.

Table 2.1: Current monitoring carried out under the PBMS

compound	species		tissue type	start of monitoring
PCB congeners	sparrowhawk	*Accipter nisus*	liver	1963
sum congener and total PCBs	heron	*Ardea cinerea*	liver	1963
PCB-TEQs and sum TEQs	merlin	*Falco columbarius*	egg	1963
DDE[1]	golden eagle	*Aquila chrysaetos*	egg	1963
HEOD[2]	sea eagle	*Haliaeetus albicilla*	egg	1986
total mercury[3]	gannet[4]	*Morus bassanus*	egg	1971
second-generation rodenticides	barn owl	*Tyto alba*	liver	1982
	kestrel	*Falco tinnunculus*	liver	2001
	red kite	*Milvus milvus*	liver	2001

[1]DDE is dichlorodiphenyldichloroethylene, the liver metabolite arising from exposure to DDT (dichlorodiphenyltrichloroethane)
[2] HEOD is hexachloro-epoxy-octahydro-dimethanonaphthalene, the liver metabolite arising from exposure primarily to aldrin and dieldrin
[3]not monitored in birds collected in 2001
[4]contaminants primarily monitored in eggs from two colonies, Ailsa Craig and Bass Rock

2.2 Aims and structure of the current report

The overall aim of the current report is to identify existing and new monitoring activities that can be delivered through the PBMS and that meet the key needs of the stakeholders. The findings from the long-term monitoring (Section 3), the sample archiving and associated research (Section 4), and the various short-term studies conducted under the Wildlife & Pollution contract (Section 5) are therefore summarised and collated with a view to informing future PBMS activities. Other UK national schemes that monitor pesticides and pollutants in vertebrates are briefly described in Section 6, with the aim of identifying the potential for future cooperation between the PBMS and these schemes. Chapter 7 describes a horizon-scanning review to identify new and/or currently unmonitored chemical threats to wildlife, and, in particular, those compounds that can be monitored through the existing PBMS capability and through collaboration with Lancaster University. This collaboration will be facilitated through the forthcoming (2007-8) relocation of the PBMS from CEH Monks Wood site to CEH Lancaster. Recommendations for future monitoring by the PBMS are summarised in Section 8.

3 Summary of the findings from long-term monitoring

3.1 Organochlorine (OC) insecticides

Sparrowhawks and herons generally have similar levels liver concentrations of DDE but herons have higher liver HEOD residues than sparrowhawks; kestrels typically have lower liver concentrations of both compounds compared with the two other species. There have been general long-term declines in liver residues of DDE) and HEOD in sparrowhawks, kestrels and herons (Shore *et al.*, 2006c). These declines largely levelled off during the 1990s. Currently, both compounds are detected in most birds that are analysed, which reflects their high environmental persistence. However, mean DDE and HEOD concentrations are well below 10 µg/g wet weight (wet wt) and 1 µg/g wet wt respectively, and insufficient to cause acute toxic effects in individuals or adverse effects on populations (Newton, 1988; Peakall, 1996; Walker & Newton, 1998, , 1999). Gamma –hexachlorocyclohexane (g-HCH), the other OC insecticide reported by the PBMS, is currently detected in a minority of the birds that are analysed. Concentrations are typically orders of magnitude below those associated with acute mortality (Wiemeyer, 1996).

Average DDE and HEOD concentrations in the eggs of eggs of peregrine falcons (not monitored since 1998), merlins, golden eagles and gannets have also declined during the monitoring period. Currently, concentrations in most eggs are unlikely to be directly embryotoxic, although occasional eggs have high concentrations that may cause adverse effects (Shore *et al.*, 2006c). The log-term decline has been accompanied by a recovery in shell index to approximately pre-DDT levels in peregrine falcons and merlin eggs, although there has been no clear pattern of change in the shell index of eggs of the other species that are monitored(Shore *et al.*, 2005b; Shore *et al.*, 2006c). Peregrine falcon and merlin populations have also increased as their exposure to and assimilation of OC insecticides has declined (Newton *et al.*, 1999a; Newton & Haas, 1988; Ratcliffe, 1980). OC concentrations in eggs vary regionally and this most probably reflects variation in the degree of dietary contamination.

Only 10 or so white-tailed sea eagle eggs have been monitored for OC insecticides by the PBMS. Lowest Observed Effect Levels (LOEL) for DDE-induced effects on eggshell thickness and on productivity have been estimated for this species (Helander *et al.*, 2002) and four of the eggs analysed by the PBMS exceeded the LOEL for eggshell thickness and two of these also exceeded the LOEL for productivity. Thus, although the sample size is small, a relatively large proportion of the addled eggs that have been analysed contained DDE concentrations that may have caused with adverse effects.

3.2 PCBs

The use of PCBs in open systems has been prohibited in many countries since 1972 and their production in most industrial countries was terminated by the late 1970s (Hoffman *et al.*, 2001). The long-term pattern of changes over time in liver PCB concentrations is not as consistent across species as for DDE and HEOD. PCB liver residues in the piscivorous heron have declined significantly since the late 1970s, although there is little evidence of much change in liver residues from the mid 1980s onwards. Likewise, there has been a significant downward trend in liver total PCBs in sparrowhawks that also occurred predominantly before the mid-1980s, but this decline was relatively small-scale compared to that in herons. In contrast, there is no evidence that liver PCB concentrations declined in kestrels throughout the period over which they were monitored (Shore *et al.*, 2006c).

Changes in PCB concentrations in eggs over time have been variable both within and between species. PCB concentrations in merlin eggs have fluctuated since the 1970s over and there has been no clear change in magnitude. Gannet eggs from Ailsa Craig and Bass Rock have likewise been monitored for PCBs since the early 1970s and while PCB concentrations have declined overall in eggs from Ailsa Craig, there has been no significant change in eggs taken from Bass Rock. Average concentrations in merlin and gannet eggs are both below the concentration range (8-25 µg/g wet wt) associated with bill deformities and decreased hatching success in a range of avian species, including some raptors (Hoffman *et al.*, 1996). However, some merlin and gannet eggs have Toxic Equivalence Concentrations that are within the range of those associated with adverse effects (see section 5.3 of this report).

PCB concentrations have been monitored in golden eagle eggs since the 1970 and again there has been no clear pattern of change. There has been a significant long-term decline in the eggs of birds from inland western Scotland but not in eggs from elsewhere and PCB concentrations have generally been higher in the eggs of coastal birds. Approximately 6% of all the golden eagle eggs analysed had concentrations within or exceeding the 8-25 µg/g wet wt range. Whether golden eagles are as sensitive to PCBs as species that have been tested is unknown and but it is possible that the relatively high PCBs residues detected in some eggs may have contributed to their failure. There have been too few analyses of PCBs in sea eagle eggs from western Scotland to determine if there has been any change in residue magnitude over time. However, six of the ten eggs analysed had total PCB lipid concentrations above 300 µg/g, the concentration associated with adverse effects on productivity in other sea eagle populations (Helander *et al.*, 2002). All but two eggs had PCB residues of between 8 and 25 µg/g wet wt. However, DDE concentrations were also high in sea eagle eggs with high PCB concentrations and so it is uncertain whether PCBs were likely to have caused the failure of the eggs.

3.3 Mercury (Hg)

Herons generally have higher liver Hg concentrations than sparrowhawks. This may reflect greater bioconcentration through aquatic compared with terrestrial food-chains. Liver Hg has declined significantly over the whole course of the monitoring programme in both herons and sparrowhawks, although there is some evidence that average concentrations may have increased slightly in both species during the 1990s. Average liver concentrations and the concentrations in most individuals are below those associated with toxic effects in birds of prey (Thompson, 1996).

Egg concentrations of Hg, as with PCBs, show no consistent patterns of change over time within or between species. Regression analysis did not detect any significant change over time in Hg concentrations in merlin eggs, but concentrations appear to have increased to some extent since the mid 1980s. However, this may reflect variation in the proportion of eggs that came from Shetland, Orkney and other parts of north-west Scotland; some eggs from these areas have unusually high Hg residues. In golden eagles, Hg concentrations were generally higher in eggs from the west coast than elsewhere and levels in eggs from inland birds are higher in the west than the east. Birds from western areas have a relatively diverse diet and take seabirds that often contain high concentrations of Hg (Newton & Galbraith, 1991). There has not been any significant long-term change in Hg residues in eagle eggs from western coastal or eastern inland areas but concentrations have risen significantly in eggs from western inland areas. In gannets, egg Hg concentrations were higher at Ailsa Craig than Bass Rock during the 1970s and early 1980s. However, concentrations in eggs from Ailsa Craig have declined over the last 30 years whereas concentrations in Bass Rock eggs have significantly increased. Overall, total Hg concentrations greater than approximately 2 µg/g wet wt have been associated with impaired hatching in laboratory studies on some species, although the extent to which this effect level can be extrapolated to other species is uncertain as there appears to be considerable variation in sensitivity between species (Thompson, 1996). The geometric mean Hg concentrations in merlin, golden eagle and gannet eggs are all lower than 2 µg/g wet wt. Mercury concentrations in the sea eagle eggs that have been analysed were also below the toxic level.

3.4 Second-generation anticoagulant rodenticides (SGARs)

The monitoring of barn owls and kestrels, together with results from other studies, indicates that there is widespread exposure of predatory birds in Britain to SGARs, mainly difenacoum and bromadiolone. In barn owls, the proportion of birds exposed to either difenacoum or bromadiolone has increased over the time period in which monitoring has occurred, and currently approximately 40% of barn owls are exposed to one or more SGAR. Kestrels have been monitored for too short a period to allow analysis of time trends but 64% of all the kestrels analysed since monitoring of this species started had detectable liver residues of one or more SGAR. Of birds known to have died 2001 and 2005, 42% of barn owls and 65% of kestrels had detectable liver SGAR residues. The difference between the species in these proportions is statistically significant (Fisher's Exact test, $P<0.0001$), although it is unclear why there is more widescale exposure in kestrels than barn owls.

A "potentially lethal range" for SGAR residues in barn owls is thought to be > 0.1-0.2 µg/g wet wt (Newton *et al.*, 1998; Newton *et al.*, 1999b). This is based in two sets of observations. These are that almost all owls diagnosed at post-mortem of having died from rodenticide poisoning (because they had characteristic signs of haemorrhaging from such organs as the heart, lungs, liver, brain and/or subcutaneous areas) had liver residues >0.1 µg/g wet wt, and, secondly, that owls that had been experimentally poisoned had residues of the range 0.2-1.72 µg/g wet wt (Newton *et al.*, 1999b for review). Between 5% and 11% of all barn owls that have been examined had liver SGAR concentrations in the "potentially lethal range", but only approximately only 1% of the birds examined have been diagnosed as having been directly poisoned by SGARs. There is no evidence to date of the magnitude of liver residues of difenacoum and bromadiolone increasing over time and there is no evidence that the exposure of barn owls to SGARs is currently causing any population decline.

Residues associated with lethality in kestrels have not been determined. Mean sum liver SGAR concentrations are approximately two fold higher in kestrels than in barn owls for birds that died over the same time period.

3.5 Implications for future monitoring

The long-term monitoring data indicate that there have been declines in the liver and egg concentrations of the OC insecticides in all the species that are monitored. Current concentrations may be considered "background" and are below concentrations associated with acute toxic effects in all monitored species except sea eagles, in which egg DDE concentrations still often occur in embryotoxic concentrations. It can be argued that there is little conservation or scientific rationale for continued long-term monitoring of OC insecticides within the PBMS, apart from that for sea eagle eggs. Stopping the analysis of OC insecticide residues in PBMS monitoring except sea eagle eggs would result in little saving in analytical resource because these compounds are detected as part of the same analytical process used to quantify PCBs. However, it would represent a saving in resources in terms of data collection, analysis and reporting. Long-term archiving of analytical spectra and traces is a routine part of the PBMS activities and retrospective analysis of these spectra could be carried out if there was a subsequent need to quantify OC insecticide residues in specific samples, provided that they had been analysed for PCBs. This would require that standards and spiked samples for the OC insecticides were run simultaneously with those for PCBs, but would represent minor analytical costs for safeguarding the potential retrieval of long-term data.

As with OC insecticides, there have also been declines in total PCB concentrations in the livers and eggs of some species. However, declines have not occurred consistently across species and there has been little change in liver or egg concentrations in any species over the last 20 years. Egg total PCB concentrations, and associated TEQ concentrations, are within the embryotoxic range in a proportion of most species analysed. These findings indicate a need to continue monitoring PCBs in predatory birds

in Britain. Furthermore, the changes instituted in 2002 to the PBMS enabled determination and reporting of specific congener PCB and TEQ concentrations. This has greatly increased the capacity of the PBMS to determine if concentrations of individual PCBs, and the toxicity associated with a mixture of congeners, are declining over time. This gives a means of assessing whether significant toxic risk to individuals and populations is declining, and has further policy relevance as it provides a measure of whether EU directives (eg., Directive 96/59/CE; RD 1378/1999) to reduce and finally eliminate environmental contamination by PCBs by 2010 are likely to be met.

Mercury concentrations in livers and eggs either appear to be relatively stable or rising. Mercury liver and egg concentrations are currently below concentrations associated with acute toxicity but it is unknown whether the rise in mean annual concentrations detected in some species will be sustained. A recent study has demonstrated that liver Hg concentrations have risen over the last 15 years in pipistrelle bats (*Pipistrellus spp*) from rural areas of south-west Britain (Walker *et al.*, in press) and increases in mercury contamination have been noted in Arctic biota (Braune *et al.*, 2005). It is therefore possible that rising Hg contamination may be widespread in top predators in parts or all of of Britain. Further monitoring of Hg is required to determine whether rises in contamination in some species will continue.

The potential risk to predatory birds and mammals from SGARs in Britain is well documented (Newton *et al.*, 1999b; Shore *et al.*, 2003; Shore *et al.*, 2006a) and the monitoring of SGARs remains a key activity of the PBMS. The PBMS is a key tool to determine whether the Campaign for Responsible Rodenticide Use is successful in promoting best practice for outdoor use of rodenticides and results in a decrease in SGAR contamination in wildlife.

4 Long-term tissue and egg archiving: developments and summary of collaborative and allied research

4.1 Background

As part of the core monitoring programme, the PBMS has archived tissues from the birds that are submitted. Sub-samples of egg contents are likewise archived. All samples are stored at a constant -20°C. Archiving of material has been carried out since the PBMS started but most samples date from the 1970s onwards. Based on the current annual running costs of the PBMS, the value of the accumulated archive can be estimated to be in the region of £4 million.

There archive is used for three main purposes.

(i) *the development of new monitoring.* Pilot studies use archived material to determine the merit of initiating long-term monitoring for new chemicals or monitoring existing compounds of concern in new species. Such pilot studies provide information on whether compounds of interest are assimilated by predatory birds, which tissues accumulate the greatest concentrations (and so may be the most suitable for future monitoring), and the degree of variability in measured concentrations between individuals and species. Information on variability is required to determine the sampling intensity needed in any new monitoring programme, and the associated power that the monitoring programme would have to detect spatial and temporal changes in contamination.

(ii) *retrospective applied and fundamental studies.* Such studies are used to refine our existing monitoring methodologies, to develop our understanding about the transfer of chemicals through different trophic pathways, and to inform us about the risks posed by a range of contaminants that may be accumulated by predatory birds (for example, Erry *et al.*, 1999; Shore *et al.*, 2001; Shore *et al.*, 2006a).

(iii) *to provide material for collaborative and allied studies* run by stakeholders and research colleagues.

4.2 Developments

The long-term archiving of samples has involved retaining samples (where available) of liver, kidney, brain, muscle, fat, and gizzard contents from carcasses and egg contents from eggs. The archiving effort was expanded in 2005 to retain femurs, which can be used for monitoring accumulation of specific contaminants such as lead (Pain *et al.*, 2005; Scheuhammer *et al.*, 2003; Scheuhammer & Templeton, 1998), and used to determine whether bone strength and integrity is affected by compounds that interfere with calcium metabolism. In 2006, the archiving of specific feathers (10^{th} primary, 1st secondary and breast feathers) was also started. This was done to facilitate future evaluation of whether feather contaminant concentrations can be used to monitor spatial and temporal variation in exposure, and even predict the magnitude on internal tissue organ concentrations (Dauwe *et al.*, 2005; Martinez-Lopez *et al.*, 2005).

The PBMS archive currently consists of approximately 30,000 samples. Unique traceable codes are assigned to each sample so that they can be related to source data for each carcass or egg. However, as the archive has expanded, some samples have been completely or partly used for one-off studies.

Records of how much of each sample remains were not systematically kept. As the archive has grown, it has also been relocated several times. It is currently now housed in a dedicated freezer, but records of the exact location of every sample within the freezer is not known. Management of the archive resource and easy accessing of the samples can be problematic and time consuming. A project is currently underway to produce a readily interrogated catalogue of samples that are currently held, their exact location and a quantitative estimate of the amount of sample present. The procedures used to develop the catalogue and the progress of the project was reported by Shore *et al.* (2006b). The work will be completed by 2007.

4.3 Summary of collaborative and allied research

The PBMS archive presents a valuable resource for a range of other conservation-orientated research work. Current projects that utilise the archive, and others that involve collaboration using PBMS data and expertise, are listed in Table 3.1. It is apparent from this table that the PBMS, and its archive in particular, provides a valuable conservation resource nationally and internationally. The archive facilitates assessment of the exposure to and effects of chemicals in predatory birds than is wider in scope than the work that is supported under the PBMS core activities. It also provides a resource for projects that aim to assess the impacts of a range of non-chemical threats. These include illegal capture and hunting, potential threats from global warming, and assessment of how road design influences the likelihood of birds being killed by traffic.

Table 3.1: Current collaborative and allied research projects

Project Title	Collaborator	Project aims	PBMS role
Campaign for Responsible Rodenticide Use	British Pest Control Association	Provide advice on best practice for use of rodenticides for pest control	Provide data on incidence of exposure of wildlife to rodenticides. Involvement in press launch of campaign
Lead in red kites	RSPB, English Nature, Institute of Zoology, & Aberdeen University	Assess the exposure and likely effects of lead in red kites, and identify the likely sources of lead	Provision of samples and analysis of lead levels in kite bones
Effects of anticoagulant rodenticides on calcium homeostasis	Canadian Wildlife Service	To determine whether sub-lethal exposure to rodenticides affects bone density or breaking strength	Provision of bones from barn owls for density and strength determinations, and data on liver concentrations of anticoagulant rodenticides in the owls
NSAIDs detection methods	Anglia Ruskin University	Development of methods for the detection of Non-Steroidal Anti-Inflammatory Drugs in raptors	Provision of carcass material for analysis
Radio-chemicals in predatory birds	CEH Lancaster	Determine the baseline levels and activity of radionuclides in wildlife from natural sources	Provision of tissue samples for analysis of natural levels of radionuclides
PBDEs in wildlife[1]	Bromine Science and Environmental Forum (BSEF)	Monitor PBDEs in biota, including predatory birds	Initial provision of archive samples for analysis, and currently contribution of sparrowhawk eggs for monitoring
DNA Profiling of raptors	Wildlife DNA Services Ltd, University of Wales	Develop genetic markers to be used to determine if captive raptors are captive-bred or illegally taken from the wild	Provide samples for genetic typing
Illegal shooting of predatory birds	University of Bristol	Determine the prevalence of illegal shooting in predatory birds in Britain	Data held on proportion of birds submitted to the PBMS that were killed by being shot, or that contained gunshot pellets. Provision of carcasses for X ray analysis for shot.
Barn Owl road casualties	Countryside Council for Wales	Identification of main areas in which barn owl road casualties occur in Wales	Provision of data on provenance, age, class sex and year for barn owls which had killed on the road in Wales and submitted to the PBMS
Moult in relation to climate change	CEH	Determine if onset of reproduction and moult in predatory birds changes in response to warming climate	Analysis of long-term post-mortem data on reproductive and moult status of sparrowhawks and kestrels
Egg pigmentation & contaminants	EGI, University of Oxford	Determination of exposure to OC pesticides affected eggshell pigmentation	Provision of data on OC concentrations in eggs and eggshells for pigmentation analysis
Display material and reference collection	Natural History Museum (NHM) Tring and National Museums of Scotland (NMS)	Provision of reference material for rare GB species (NHM) and display eggshells for Scottish birds (NMS)	Provision of carcasses and eggshells

[1] see Shore *et al.* (2006b)

5 Review of the findings of one-year PBMS studies

5.1 Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are mainly released to the environment from point or diffuse natural and anthropogenic sources. These compounds are transferred to eggs and can be highly embryotoxic (Malcolm & Shore, 2003), and eggs may potentially be good biomonitors of environmental PAH contamination. Measurement of PAH concentrations in eggs was identified as one potential area of new monitoring for the PBMS (Shore *et al.*, 2005c) and so a pilot study was carried out in which 52 individual PAHs were measured in gannet, golden eagle, merlin and sea eagle eggs received by the PBMS in 2002.

The results of this study were reported by (Shore *et al.*, 2006b). Detectable concentrations of each PAH that was quantified were found in one or more sample apart from naphthalene, although various methylated naphthalenes were identified and were among the most frequently occurring and highest concentrations of any of the PAHs. The overall pattern of PAH contamination was broadly similar in the eggs of different species.

Median sum PAH concentrations in the gannet, golden eagle and merlin eggs ranged between 92.6 and 159 ng/g lipid wt, and the sum PAH concentration in the single sea eagle egg analysed was 44.3 ng/g lipid. There was no significant difference between species in the sum PAH concentrations detected in eggs, nor was there a significant difference in PAH contamination between different gannet colonies. The sum concentrations for sixteen PAHs measured in the 1990s in herring gull (*Larus argentatus)*, cormorant (*Phalacrocorax carbo*), shag (*Phalacrocorax aristotelis*) and chough (*Pyrrhocorax pyrrhocorax*) eggs collected from around the coast of Britain (Shore *et al.*, 1999) were also similar to equivalent concentrations detected in the PBMS pilot study of gannet, golden eagle, merlin and sea eagle eggs. The concentrations of individual compounds detected in the eggs were considered to be below those likely to be associated with embryotoxic effects.

The broad comparability in egg PAH concentrations between species and the relatively low concentrations suggested that the measured egg residues were likely to have been the result of background levels of exposure to diffuse PAH sources.

5.2 Spatial variation of liver PCB concentrations in terrestrial predatory birds

Liver total PCB concentrations measured each year as part of the core PBMS monitoring are characterised by large scale variation between individuals. In part, this is due to differences between individuals in their physiological state (see section 5.4), but geographical variation in dietary contaminant intake is also thought to be a major factor (Hoshi *et al.*, 1998; Newton *et al.*, 1993) PCBs are transported around the globe in the atmosphere (Bard, 1999; Sweetman *et al.*, 2002; Vallack *et al.*, 1998), but local sources (waste disposal, landfill sites and open sources such as plastics, paints and adhesives) are also likely to be important. A pilot study, which built on earlier work (Broughton *et al.*, 2003), was conducted to determine whether geographical hotspots of PCB contamination (that might be due to local sources) could be identified, and to determine whether liver PCB concentrations varied with larger-scale geographical factors, such as latitude and longitude, rainfall and land cover. The results of this work are given in detail by Shore *et al.* (2006b).

Spatial analysis at the micro-scale indicated the presence of a statistically significant cluster of total liver PCB concentrations in sparrowhawks at a search radius of 15-20 km. This was on Merseyside. No other clusters were detected in sparrowhawks and there were no statistically significant clusters at all for liver total PCB concentrations in kestrels.

Wider scale spatial analysis found a positive association between rainfall and liver PCB concentrations in sparrowhawks and kestrels (although only statistically significant for sparrowhawks), a significant negative association between latitude and liver PCB concentrations in sparrowhawks, and a significant positive association between degree of urban land cover and liver PCB concentrations in kestrels. In all cases, the strength of these relationships was relatively weak.

5.3 Analysis of unknown compounds and determination of Toxic Equivalence (TEQ) concentrations using a CALUX assay

During the analysis of OC insecticides and PCBs in the livers of birds of prey submitted to the PBMS, a number of unidentified peaks occur on the analytical traces produced by gas chromatography. These peaks represent unidentified compounds. These may be PCB congeners that are not present in analytical suite that is determined but could also be other organic xenobiotics. A pilot study was conducted on a number of bird livers using gas chromatography coupled with mass spectrometry (GC-MS) to determine what proportion of the identified compounds were, in fact, other PCB congeners and, where possible, to identify any non-PCB compounds that were present.

The results from this study were reported by Shore *et al.* (2006b). Typically, most (> 60%) of the unidentified peaks were PCBs not present in the Aroclor 1254 analytical standard. Several other compounds were also detected and were tentatively identified as metabolites of organochlorine insecticides. However, in livers with the highest total PCB concentrations, more than half of the unknown peaks on the analytical trace produced by gas chromatography were due to the presence of other compounds. The identity and potential toxicity of the compounds was unknown, but they were likely to be relatively non-polar and insoluble in water.

Given the presence of substantial numbers of unidentified compounds in more heavily contaminated birds, a follow up study was carried out (Shore *et al.*, 2006c). This focused on assessing the potential toxic threat to predatory birds from those persistent organic pollutants (POPs) that have a common mode of toxicity that is mediated through the aryl-hydrocarbon (*Ah*) receptor. These POPs are comprised of the coplanar, dioxin-like PCBs, which have been specifically quantified by the PBMS since 2002, and also suites of other POPs which may also be assimilated by predatory birds. Some of these compounds could be the unidentified peaks on chromatograms.

Methods have been developed to calculate the sum *Ah* receptor toxicity caused by exposure to multiple POPs. This is expressed as a sum Toxic Equivalence (TEQ) concentration, which is the toxicity equivalent to that caused by known concentration of 2,3,7, 8 -tetrachlorodibenzo-p-dioxin (TCDD). This can be measured directly in samples using a chemically-activated luciferase gene expression (CALUX) cell bioassay which measures the total TEQ concentrations which arise from the presence of *all* chemicals that act through the *Ah* receptor; these concentrations are termed CALUX-TEQs in this report.

The main objective of the follow-up study was to determine if the PBMS measured the relevant POPs to enable it to assess potential toxic impacts mediated via the *Ah* receptor. This involved quantifying CALUX-TEQ concentrations in selected PBMS samples using a CALUX bioassay, and comparing the CALUX-TEQs with TEQ concentrations due only to exposure to coplanar PCB congeners (termed here PCB-TEQ concentrations). The PCB-TEQ concentrations are determined chemically as carried out in the annual monitoring conducted by the PBMS.

Chemically determined PCB-TEQ concentrations were lower than CALUX-TEQ concentrations in merlin, peregrine falcon and gannet eggs that had relatively low levels of contamination, and in sparrowhawk, kestrel and heron livers that contained less than two detectable coplanar PCBs. In eggs and livers with relatively high levels of coplanar PCBs, PCB-TEQ concentrations were either similar to or exceeded CALUX-TEQ concentrations, suggesting that coplanar PCB congeners comprise most of the *Ah*-receptor mediated toxicity in these samples.

Chemical determination of PCB-TEQs appears likely, therefore, to underestimate total TEQ concentrations (as measured by CALUX assay) in eggs and livers, but only at low not high levels of contamination. This is unlikely to cause significant underestimation of likely toxicity, as the low CALUX-TEQ concentrations were below concentrations associated with adverse effects in birds. Overall, chemical and CALUX measurements suggested that TEQ concentrations in the livers of sparrowhawks, kestrels and herons and in the eggs of peregrines from Britain were not at toxicologically significant concentrations. However, TEQ concentrations in some merlin and gannet eggs can occur at levels that have been associated with adverse effects in other species.

5.4 The effect of nutritional state on liver contaminant concentrations

Wienburg & Shore (2004) observed that body condition, age, and sex can all affect the magnitude of liver PCB concentrations in raptors. Body condition appears to be the most important of these factors and is thought to affect liver residues because contaminants are remobilised from fat as starving birds deplete their body fat stores. Starvation would not be expected to have a major influence on liver concentrations of inorganic and non-lipophilic compounds, such as heavy metals, because these are not typically stored in fat in high concentrations.

To date, nutritional status has not been taken into account in any of the PBMS monitoring of long-term changes in OC insecticides and PCBs. Variation between years in the proportions of birds that were starving may have introduced considerable variation into the long-term dataset and potentially have masked long-term changes in liver concentrations or the rate of those changes. A study was conducted to determine whether taking nutritional state into account affected the detection of long-term changes in liver concentrations of three lipophilic compounds (DDE, HEOD and PCBs) in sparrowhawks, kestrels and herons. The effect of nutritional state on long-term trends in liver residues of mercury, a non-lipophilic compound, was also investigated. The results of this study were reported in Shore *et al.* (2006c).

Analysis of long-term trends in liver contaminant concentrations in starved and non-starved birds demonstrated that inter-year variation in the proportion of birds in different nutritional states can obscure the detection of changes in exposure to environmental contaminants. This was most apparent in the PBMS data for sparrowhawks, in which declines in liver PCB concentrations over time were only statistically significant once nutritional state was taken into account. Starvation was found to increase liver contaminant concentrations partly through remobilisation of residues from fat (and possibly other body tissues). This was the most important factor in sparrowhawks and herons but a relatively minor effect in kestrels for compounds such as PCBs. Liver contaminant concentrations were also increased in starving birds because of liver wastage. This alone elevated liver concentrations by two-three fold, and equally affected the measured residues of both organic and inorganic compounds.

5.5 Second generation anticoagulant rodenticides in tawny owls (*Strix aluco*) and other species

A one-off study into the degree of SGAR contamination of tawny owls, a species that appears to have undergone a shallow polopulation decline downward since the early 1970s that may have accelerated since 1999 (British Trust for Ornithology). Analysis of the data is currently ongoing but the percentage of birds currently exposed to one or more second-generation anticoagulant rodenticide is approximately 45%, similar to the scale of exposure currently observed in barn owls (Section 3.4 of this report).

5.6 Contaminant levels in sprats and sandeels from the North Sea

The breeding season in 2004 was the worst on record for many seabirds in the North Sea and was particularly critical for the common guillemot *Uria aalge*. Many chicks died before they left the colony, apparently of starvation, and it was notable that, in 2004, adult birds fed their chicks predominantly on sprats (*Sprattus sprattus*) rather than lesser sandeels (*Ammodytes marinus*), the normally preferred prey. Despite this, preliminary calculations of the energy intake of guillemot chicks at CEH's long term study site on the Isle of May off the southeast coast of Scotland did not differ from the long term average. However, the calculations were based on previously published data for energy values in the fish rather than measured values. Reproductive failure may therefore have occurred because the prey was of unusually poor nutritional quality. Another possibility was that the prey contained high levels of contaminants that adversely affected growth.

Sprats and sandeels were collected from seabirds on the Isle of May in 2004 and were analysed for organochlorine insecticides, PCBs, Hg and zinc (Zn—a key essential element for growth in chicks) to assess whether excessive contaminant or low Zn concentrations may have adversely affect growth in guillemots. This was done as part of the work undertaken for the current year of the Wildlife & Pollution contract. The nutrient content of the fish was also determined but this work was out-with of the Wildlife & Pollution contract.

OC insecticide, PCB and Hg concentrations in fish were relatively low and none of the dioxin-like PCB congeners were detected in any of the fish analysed. The major differences between sandeels and sprats were that sprats had significantly more HEOD and less zinc than sprats. Although sprats therefore appeared to be poorer diet than sand eels, there was no clear evidence that the Zn or contaminant concentrations in sprats and the unusually high dependence on sprats as prey accounted for the poor breeding success of guillemots in 2004. In contrast, the nutrient levels in *both* sprats *and* sandeels were significantly lower than expected based on analysis of fish from earlier years. It appeared from this wider nutrient analysis of the fish that poor food quality (in terms of its energy content) was the most likely proximate cause of the seabird breeding failure.

5.7 Implications of the findings of one-year studies for future monitoring

The incorporation of one-off annual studies that have been conducted as part of the PBMS since 2002 has increased the scope and flexibility of the scheme. Some of these studies have addressed specific issues of conservation concern, such as the degree of contamination in guillemot diet (eg., Section 5.6) and whether there are specific hotspots of PCB contamination that might be associated with particular waste-disposal or other practices (eg., Section 5.2). Other studies have particularly informed

monitoring practices and these are focussed on here in this discussion.

The PAH study was conducted following recommendations from the last major review of the PBMS (Shore *et al.*, 2005c). The results indicated that PAHs do occur in detectable but low (below embryotoxic) concentrations in gannet, golden eagle and merlin eggs and in similar concentrations to those measured in other species in Britain. The egg residues were thought likely to have been the result of background levels of exposure to diffuse PAH sources. Thus, it would seem possible that monitoring the eggs of these species at regular (not necessarily annually) intervals could be used to provide a measure of whether there is any change in background levels of PAHs in Britain. The sensitivity with which changes could be detected could be determined from power analysis of the data already collected. The value of conducting such monitoring would depend upon the priority given to monitoring PAHs compared with other compounds. Such monitoring would not identify whether other avian species are at risk from PAHs and a better understanding of inter-species variation in exposure is needed. This could potentially be done through a one-off study that focused on species likely to be at risk of high levels of exposure. Such species might include pigeon (*Columba livia*) in urban areas and eider (*Somateria mollissima*) and/or cormorant in and around relatively polluted and unpolluted estuaries. Eider ducks may be particularly at risk of exposure to PAHs in contaminated estuaries because they feed extensively on bivalve molluscs that are good PAH accumulators (Bender *et al.*, 1988; Naes *et al.*, 1995).

The work conducted on "unknown" compounds and on determining TEQ concentrations using a CALUX assay has shown that many of the unknown peaks routinely detected on gas chromatograms are PCB congeners other than those specifically quantified as part of the standard analysis. However, more than 50% of the peaks were "unknowns" in the most highly contaminated livers and eggs. Despite this, PCB-TEQ concentrations in highly contaminated eggs and livers have been found to be comparable or even greater than CALUX-TEQ concentrations. This indicates that, though highly contaminated birds and eggs can contain a relatively large number of "unknown" compounds, there is no evidence to indicate that the presence of "unknowns" significantly add to toxicity mediated via the *Ah*-receptor. However, there remains a need to examine birds and eggs that contain the highest PCB concentrations to determine what other compounds are present. It is only possible to assess whether these compounds may exert toxic effects (other than that through the *Ah*-receptor) if their identities are known. The mechanisms and flexibility to undertake such studies are likely to be enhanced by the relocation of the PBMS to CEH Lancaster and are discussed more fully in Section 7. The results from the CALUX study also raise the question as to whether routine annual monitoring of PBMS samples using a CALUX bioassay would be worthwhile. Annual monitoring would provide a measure of the overall TEQ concentrations in liver and eggs samples that, in low and moderately contaminated samples, are probably currently underestimated by measurement of PCB concentrations alone. Routine CALUX-TEQ monitoring would also identify changes over time in assimilation of non-PCB compounds that act through the *Ah*-receptor, and that otherwise might not be detected. However, the maximum CALUX-TEQ concentration in the livers analysed in the one-off study was some 50 fold lower than the TEQ LOEL calculated for common tern (*Sterna hirundo*) chicks (Bosveld *et al.*, 2000). The value of annual monitoring of relatively low level TEQ concentrations in the livers of predatory birds is questionable. CALUX TEQ concentrations in the embryotoxic range do occur in some of the eggs monitored by the PBMS, but these appear to be largely attributable to the presence of dioxin-like PCB congeners which are chemically monitored, and additional annual CALUX monitoring is probably therefore not merited. However, characterisation of CALUX-TEQ concentrations in eggs currently collected by the PBMS and repeated monitoring at regular but not annual intervals may be merited to provide identification of changes in assimilation of non-PCB compounds that exert toxicity via the *Ah*-receptor.

The results from the study on the effect of nutritional state on liver contaminant concentrations have significant implications for the way in which long-term trend data should be analysed and reported by the PBMS. Starvation can elevate liver contaminant concentrations through remobilisation of contaminants from fat and other tissues and by causing loss in liver mass (but not contaminant burden). Nutritional state thus affects residue magnitude and may mask annual changes in exposure. It therefore needs to be incorporated as a factor into the analysis of long-term trends. It is currently

assessed using a six point visual post-mortem score of the fat depots in the body; a less subjective and continuous "condition index" variable, derived from the relationship between body mass and sternum length, has also been measured since 2005. Fat scores are only available for birds collected from approximately 1992, but analysis of changes in contaminant residues in birds from 1992 onwards should include fat score as a factor. Analysis of annual changes in liver contaminant concentrations should also include fat score as a factor or condition index as a co-variable. It is also likely to be worthwhile to report long-term data (over the whole of the monitoring period) for starved and non-starved birds as two separate groups, as was done in the one-off study (Shore *et al.*, 2006c).

The initial findings from the analysis of SGAR liver residues in tawny owls suggest that there is relatively large-scale exposure in this species that is similar to that observed in barn owls and kestrels. Unless woodland species are perceived to be particularly at risk from exposure, it is questionable whether the addition of a third species for annual monitoring for SGARs is merited. However, the one off-study provides a baseline set of data against which future exposure can be compared. Future one-off studies to determine whether there is evidence of changes over time in exposure in tawny owls may be merited.

In conclusion, many of the one-off studies conducted to date have provided information on how to improve the sensitivity of the monitoring that is currently conducted and provided pilot information for the development of future monitoring. The recommendations for future monitoring discussed in this section are further summarised in Section 8.

6 Brief overview of other schemes measuring chemicals in UK vertebrates

There is a small number of wildlife monitoring schemes that either have allied scientific objectives to the PBMS and/or generate samples that could be used by the PBMS. Such schemes and the PBMS could potentially derive mutual benefit from closer collaboration and co-ordination. Three such UK schemes, and the ways in which closer collaboration could or is currently being achieved, are outlined.

6.1 The Wildlife Incident Investigation Scheme (WIIS)

The Wildlife Incident Investigation Scheme (WIIS), run by the Department for Environment, Food and Rural Affairs (Defra), investigates the deaths of wildlife, including honeybees and some companion animals that may be related to pesticides. It provides scientific evidence that may be used to support cases that require a revision to the UK approval of particular products. The WIIS also provides a measure of the success of the pesticide registration process and helping in the verification and improvement of risk assessment processes. Evidence from the WIIS can be used to enforce legislation on the use of pesticides.

As with the PBMS, the WIIS relies on members of the public and interested organisations finding and reporting carcasses or suspected baits. This is investigated initially to determine whether pesticides may have been involved. Incidents are not typically investigated if they are not covered by the scheme, such as when pollutants, other "non-pesticides", or non-chemical factors are identified as the cause of death. When incidents are investigated further, carcasses are collected and examined by the Veterinary Laboratories Agency. Bacteriological and virological tests may be conducted to determine if death was due to disease, on-site visits may be made to investigate the circumstances related to the incident, and tissues are analysed chemically for pesticides. Death is generally confirmed as caused by a pesticide if tissue residues above concentrations thought to be lethal. In some cases, the presence of residues and other findings from the post-mortem may be used in combination to identify the cause of death.

The WIIS therefore differs from the PBMS in that although it examines a wider range of species, it typically only quantifies residues in animals thought to have been poisoned by pesticides and reports tissue concentrations for those pesticides that were the cause of death. Furthermore, the chemical analysis is focused on pesticides rather than any chemical contaminants. Thus, the WIIS is a post-registration pesticide incident monitoring scheme. In contrast, the PBMS is chemical exposure monitoring scheme that monitors a selected range of species for chemicals (pesticide and non-pesticide) of concern. The species selected for monitoring provide information on exposure routes through different pathways (terrestrial, freshwater and marine) and in some cases are species of high conservation concern.

The main area of similarity between the WIIS and the PBMS is the measurement of SGARs in predatory birds. This key area for potential collaboration has been recognized and a joint review of SGAR contamination in predatory birds using PBMS and WIIS data is currently underway. There is also potential for the PBMS to analyse samples collected by WIIS for non-pesticide contaminants and preliminary discussions about this have already been held. Incidents of suspected pesticide-related mortalities that are reported to the PBMS are automatically transferred on to the WIIS.

6.2 Monitoring of the Eurasian otter (*Lutra lutra*) for contaminants in the UK

The Environment Agency in the UK has conducted post-mortem analysis in otters found dead (mostly road traffic accidents) in England and Wales since 1992. The collection and post-mortem analyses for otters from EA management regions in the south are conducted by the Wildlife Veterinary Investigation Centre in Cornwall. Otters from the remainder of England and Wales are examined by the Cardiff University Otter Project (CUOP).

Various studies (for example, dietary, landscape genetics, parasites) are associated with the collection of otters. Specific contaminant related studies have involved monitoring otter livers for OC insecticides and PCBs (Bradshaw & Slater, 2002; Simpson *et al.*, 2000). A summary overview of UK data collected up to 2000 was conducted by Shore *et al.* (in press) and analysis of PCB and organochlorine concentrations in otter livers up to 2003 has been reported by Chadwick (2006). The characterisation of otters for exposure to OCs and PCBs is therefore similar to that conducted by the PBMS, particularly the monitoring of herons, another species with a diet that is largely composed of freshwater fish.

There is clear potential for collaboration between the otter monitoring and PBMS schemes, particularly as the EA is a current funding stakeholder of the PBMS. Comparison of contaminant trends over time and of liver contaminant profiles in herons and otters would provide an assessment of whether potential changes in environmental contaminant concentrations are equally reflected by both species. Closer coordination between the two schemes in planning future monitoring is also desirable. This could lead to sharing of resources dedicated to the development of analytical methods for new compounds of interest, and a coordinated programme in which some chemicals are monitored using herons and others using otters.

6.3 UK Cetacean Strandings Investigation Programme (CSIP)

A long-term programme that involves systematic post-mortem examination of cetaceans stranded in the UK was begun in 1990 by the then Department of the Environment (now Defra). The UK Cetacean Strandings Investigations Programme (CSIP) is currently coordinated by the Natural History Museum and involves a number of partners. The main aims of the work are to monitor trends in UK cetacean strandings, conduct standardised post-mortem investigations on stranded and by-caught cetacean and marine turtle carcasses, and thereby monitor the incidence of disease, determine causes of mortality, and investigate potential relationships between health status and pollutant exposure. The programme maintains a database of pooled data derived from these investigations and a national tissue archive for current and future scientific research purposes.

There is one immediate area in which collaborative links could be established between the Cetacean Strandings Investigation Scheme and the PBMS. This would be the comparison of contaminant trends and profiles in cetaceans with that detected in gannet eggs collected by the PBMS. As with comparisons with otters, this would allow evaluation of whether potential changes in environmental contaminant concentrations are equally reflected by gannets and cetaceans, and would inform future monitoring effort.

6.4 Conclusions

It is clear from this brief overview that there are at least four (including the PBMS) national-scale

schemes, supported through different funding agencies, that monitor contaminant levels in terrestrial, freshwater and marine vertebrates in the UK. These schemes differ to some extent in their objectives, priorities, size and scale but also have similarities in terms of some of the contaminants that they monitor and some of their methodological approaches. Although there is contact between the PBMS and the other schemes, there is greater potential for collaboration, as outlined above. There is also potential for greater communication between all the schemes, through workshops and other meeting fora. Such communication could facilitate the sharing of best practice, the initiation of new collaborative work, and the development of an overview of contaminant exposure and effects in vertebrates in terrestrial, freshwater and marine environments at a UK scale. The development and coordination of an initial workshop could form part of the annual "one-off" activities conducted by the PBMS.

7 Potential for monitoring of new chemical threats to predatory birds in the UK

7.1 Introduction

One of the main challenges for the chemical monitoring scheme is the identification of new chemical threats. This requires the identification of chemicals that are not currently monitored but are potentially of concern, and a flexibility to develop and test new monitoring protocols.

As part of the restructuring of CEH, the PBMS will be relocated to the CEH site at Lancaster in 2007-8. The site is located on the Lancaster University campus and forms part of the Lancaster Environment Centre (LEC). A key advantage of the relocation is that the PBMS will be more readily able to harness the expertise and skills present in the LEC to develop monitoring for new chemicals. In this section, we describe the potential to initiate future PBMS monitoring for a range of chemicals that are of current concern and for which there is expertise already established at the LEC. These include so called "new" persistent organic pollutants (POPs), radionuclides and heavy metals and include a range of chemicals listed on the Chemical Stakeholder Forum's list of priority chemicals. Chemicals that are not discussed in this report but are categorised as being of "highest concern" by the Chemical Stakeholder's Forum are also listed in Appendix 1. It is beyond the scope of this current report to review the potential threats to vertebrates from all of these chemicals or to assess the merits or feasibility of monitoring each of them. Reviews of particular compounds, or groups of compounds, may be merited in the future, depending upon the priorities of the PBMS stakeholders.

In addition to identifying potential new chemical monitoring, we briefly overview in this section the capability within the LEC to conduct screening of samples and sample extracts (that potentially contain a mixture of organic chemicals) for [genotoxic and biochemical] effects and for screening samples for disease and health status (Section 8.9).

7.2 Brominated flame retardants (BFRs)

7.2.1 Polybrominated diphenyl ethers (PBDEs)

PBDEs have been widely used as additive flame retardants in products such as paints, textiles and plastics to reduce fire risk. There are three main technical mixtures of PBDEs, the compositions and usage patterns of which are reviewed elsewhere (de Wit, 2002). Of these technical mixtures, the pentabromodiphenyl ether (PeBDE) and octabromodiphenyl ether (OcBDE) mixtures have been banned in the EU and Japan and are currently being phased out in the rest of the world (after being banned in some states of the USA). However, in the UK in particular, stringent fire retardancy regulations for furniture led to previously high use of PeBDE. The decabromodiphenyl ether (DeBDE) mixture, a high usage flame retardant (global annual usage of approx. 56,000 tonnes estimated in 2001; Law *et al.*, 2006) is almost entirely comprised of BDE 209, which has a high octanol-water partition coefficient (K_{OW}), a relatively high molecular weight (959 amu) and is relatively labile to heat and light (Soderstrom *et al.*, 2004). This chemical is used as a flame retardant in electrical equipment housing, rubber insulating materials and other applications. There is some uncertainty over whether DeBDE may enter the environment from products in use, or predominantly from production and application sites.

There are also uncertainties over its availability to biota. DeBDE has recently undergone a comprehensive risk assessment in the European Union (EU, 2002), performed by the UK Environment Agency, which concluded that its use can continue, but that it will remain under scrutiny because there are a number of unresolved concerns. These are that: (i) DeBDE has been found at low concentrations in a range of environment media; (ii) there is a possibility of loss of bromine to form other more toxic and bioaccumulative PBDE congeners; (iii) there is the possibility of neurotoxic effects in mice. The Environment Agency concluded that more information is required on the occurrence and behaviour of DeBDE in the environment, including temporal trends in environmental concentrations. The bromine industry has introduced a voluntary code of practice to attempt to limit emissions of DeBDE from production and application sites.

PBDEs from the PeBDE mixture have been reported in a wide range of environmental media (de Wit, 2002). DeBDE, despite its higher usage, has been found in a relatively small number of environmental studies, often linked to sediments near sites of production and use (Allchin *et al.*, 1999; Sellstrom *et al.*, 1998) and dust in offices and homes (Knoth *et al.*, 2002; Stapleton *et al.*, 2005). However, DeBDE has been found in animals in the terrestrial foodchain, including in wild birds of prey in Scandinavia (Lindberg *et al.*, 2004) and the UK. DeBDE presumably reaches the terrestrial foodchain through atmospheric emission and transport, although there is still some controversy over the relative importance of point source (i.e. factory) and diffuse (i.e. products in use) sources.

The first detection of PBDEs in biota was in fish from Sweden (Andersson & Blomkvist, 1981), and they have since been found in a wide range of biota, from all parts of the world. There are numerous reports of PBDEs in European biota, and they have been found in both bird tissues and bird eggs (Law *et al.*, 2006). A study of three (PeBDE-related) PBDEs in guillemot eggs from the Baltic showed concentrations peaking around the mid-late 1980s (Sellstrom *et al.*, 2003). However, there is recent evidence that there is a difference in the range of PBDEs accumulated by birds from different ecosystems; terrestrial species appear to be assimilate heavier PBDEs than species, and there are regional differences that are probably attributable to differences in prey availability (Law *et al.*, 2002; Lindberg *et al.*, 2004). Samples from the PBMS already analysed for PBDEs have shown a marked difference in PBDE patterns and concentrations between terrestrial and water birds, and generally lower concentrations of PBDEs in the UK than in Scandinavian birds (see Shore *et al.*, 2006b, for review).

There is conflicting evidence on the bioavailability of DeBDE, with some laboratory studies showing low or negligible absorption by animals (El Dareer *et al.*, 1987; Kierkegaard *et al.*, 2001), and others reporting appreciable bioavailability (Sandholm *et al.*, 2003; Thomas *et al.*, 2005). Bioavailability may be linked both to species and dietary characteristics.

The less brominated PBDEs, generally originating from the PeBDE and OcBDE commercial products but potentially including debromination products of DeBDE, hve a range of proven or potential toxicological endpoints including hepatotoxicity (Darnerud *et al.*, 2001), neurodevelopmental effects (Muir, 2004), endocrine (particularly thyroid hormone) disrupting effects (Hall *et al.*, 2003; Hallgren & Darnerud, 2002; Zhou *et al.*, 2001; Zhou *et al.*, 2002), and cancer (McDonald, 2002). There are no proven toxic effects of the DeBDE commercial mixture, but there is some evidence that it may lose bromine atoms to produce more bioaccumulative and toxic PBDEs (Kierkegaard *et al.*, 1999; Soderstrom *et al.*, 2004; Stapleton *et al.*, 2004; Van den Steen *et al.*, 2006).

7.2.2 Hexabromocyclododecane (HBCD)

HBCD has been in use in the EU for more than 20 years in foam and expanded polystyrene products and textile coatings. In 2001 HBCD was the third most important BFR globally, and the EU accounted for over 50% of the global demand, making it the second most important BFR in the EU (Law *et al.*, 2006). The technical HBCD mixture contains a number of diastereomers which have different properties (Covaci *et al.*, 2006). An EU risk assessment is not yet complete, but some potential risks to human and environmental health have been identified, and further investigations are apparently underway.

The HBCD isomers are all bioaccumulative, but to different degrees, and they appear to have low acute toxicity. However, chronic toxic effects have been reported and include thyroid hormone disruption (Darnerud, 2003), carcinogenicity and neuro-developmental effects (Covaci *et al.*, 2006). High concentrations of HBCD have been found in top predators such as marine mammals and birds of prey, and concentrations in biota are apparently increasing slowly as demand for the product increases (Covaci *et al.*, 2006). There is a difference in the relative abundance of the diastereomers of HBCD between the technical product (dominated by γ-HBCD) and biota (dominated by α-HBCD), for which the most important causative factors (e.g. physical properties, uptake or metabolism) have not yet been determined (Covaci *et al.*, 2006).

There have been few studies of HBCD in birds, but those that have been performed have shown relatively high concentrations (in the low µg/g lipid range) in a range of marine and terrestrial species from northern Europe and the Arctic (Covaci *et al.*, 2006).

7.2.3 Tetrabromobisphenol-A (TBBP-A)

In use, TBBP-A differs from PBDEs and HBCD in that it is usually used as a 'reactive' BFR - i.e. covalently bonded (rather than 'dissolved', as in 'additive' BFRs) within the plastic structure (mostly electronic circuit boards). Annual worldwide production was estimated to be 120,000 tonnes/year in 2001, of which approximately 12,000 tonnes was used in Europe, although it is likely that much more is present in imported finished products (Law *et al.*, 2006).

An EU risk assessment of TBBP-A for human health has recently been released (Bureau, 2006), in which no risks to human health were identified. However, there is apparently some concern that there may be risks to surface water, sediment and soil ecosystems associated with the small number of additive uses, although the EU risk assessment for the environment is not yet available. There are concerns over the possibility of the breakdown of TBBP-A to bisphenol-A or the methyl ether derivative.

There are very few reports of TBBP-A in bird tissues or eggs, and these include finding TBBP-A at between the detection limit and 13 pg/g ww in Norwegian birds of prey (Herzke *et al.*, 2005) and at between 2.5 and 14 ng/g lipid (100-500 times lower concentrations than HBCD) in two cormorant livers from the UK (Morris *et al.*, 2004).

7.2.4 Polybrominated biphenyls (PBBs)

After a major accident in the USA in 1973, in which a commercial flame retardant containing PBBs was added to livestock feed, poisoning many animals and exposing over nine million people to PBBs in food, the effects of PBBs were found to be essentially the same as those of PCBs. Technical hexabrominated biphenyl (HxBB) is banned in North America and in Europe. Technical decabrominated biphenyl (DeBB) production in Europe was terminated in 2000 (de Wit, 2002).

7.2.5 Other BFRs currently in use

The Environment Agency has identified about 60 additional BFRs potentially that need to be reviewed on environmental grounds, but only the following have been shown to be supplied to the UK in significant quantities:

- Tetrabromobisphenol-A derivatives
- Tetrabromophthalic anhydride
- Ethylene bistetrabromophthalimide
- 1,2-Bis(pentabromophenyl) ethane (Decabromodiphenyl ethane)

There is very little published information on the use, environmental occurrence or toxicology of these

chemicals, although decabromodiphenyl ethane, which is used as an alternative to DeBDE, has been found in sewage sludge samples from Sweden and sediment samples from the Netherlands (Kierkegaard *et al.*, 2004).

7.2.6 BFR measurement capabilities at the LEC

The Lancaster University Environmental Organic Chemistry and Toxicology (EOCE) laboratories have been measuring PBDEs in environmental samples for over 6 years. The EOCE labs are well equipped with up-to-date analytical instrumentation, including liquid chromatography (LC) – mass spectrometry (MS), and a range of gas chromatography (GC) –MS instruments with a broad range of applications.

Twenty-two PBDE isomers are currently analysed, including the isomers which have been found in all three technical PBDE mixtures used and some isomers which may be breakdown products of these. More isomers can be added to the standard mixture easily for specific projects. The less brominated PBDEs (up to nona-BDEs) are currently analysed using GC – Electron capture negative ionisation (ECNI) low resolution (LR) MS, which gives a limit of detection of approximately 2 pg per analysis (i.e. 50 pg per sample, assuming a sample extract final volume of 25 µl). BDE209 (Decabromodiphenyl ether, the main component of the DeBDE mixture) is difficult to analyse due to its thermal and photolytic lability, and it's relatively high molecular weight. It is currently analysed in the Lancaster labs using 'cool on-column injection' GC – high resolution (HR) MS in order to obtain optimum sensitivity and selectivity. The detection limit obtained for this chemical is approximately 10 pg per analysis (250 pg per sample for a 25 µl final sample volume).

Current matrices which are routinely analysed in the Lancaster laboratory for PBDEs include adipose tissue, blubber, liver, blood, and milk-fat. Vegetation, soil, air and sediment is also analysed.

A variety of methods are used to prepare samples for instrumental analysis, depending on the nature of the matrix to be analysed, and the concentrations of PBDEs present. For animal tissues the methods used are similar to those used for PCBs, including sample homogenisation (and water removal), solvent extraction, and lipid separation (using concentrated sulphuric acid and/or gel permeation chromatography). Recovery and internal standards are used to monitor the performance of the method in all samples, and additional quality control measures include analysing an in-house reference material (at least one sample in 10).

If an estimate of 10 ng/g lipid is taken for the expected PBDE concentrations in UK birds of prey (one might expect actual concentrations of most PBDEs to be more than 10 times higher than this, based on previously published data for birds of prey in the UK and other European countries), a minimum sample size of 50 mg lipid would be required to achieve 10 times the detection limit for most PBDEs, and 250 mg lipid would be required for BDE209. As an estimate, assuming 10 % fat in eggs, a raw egg sample size of 2.5 g wet weight would be required to perform PBDE analysis (or 0.5 g excluding BDE209).

HBCD is not currently analysed on a routine basis in the Lancaster laboratories. However, the laboratory does possess the HBCD technical product standard, and analysis of this chemical can be achieved on the same extracts as for PBDEs and PCBs, with individual diastereomers analysed using LC-MS. A detection limit of approximately 100 pg per analysis is anticipated, so a slightly larger minimum sample size than for PBDEs would be preferred to achieve a reliable detection (100 ng/g lipid giving 10 x detection limit – previously reported concentrations in birds are 100-1500 ng/g lipid).

TBBP-A is not currently analysed on a routine basis in the Lancaster laboratories, but can also be analysed in the same extract as PBDE analysis. The acidic nature of this chemical means that it should be separated from a sample extract immediately after extraction. The analysis would preferably be performed by LC-MS or by chemical derivatisation and GC-MS. Using LC-MS a detection limit of approximately 50 pg per analysis is anticipated and this it is anticipated that the sample size required for reliable TBBP-A detection may be in the region of 2 g lipid per sample (equivalent to 20 g fresh egg). It is likely that egg samples would have to be pooled for such analyses.

PBBs are not currently analysed on a routine basis in the Lancaster laboratories, but can be analysed in the same extract as PBDE analysis using GC-MS (probably concurrently with PBDEs). Some PBBs have been reported at similar concentrations to PBDEs, and the achievable detection limit is likely to be similar to PBDEs, so the sample size suggested for PBDEs is likely to be sufficient for reliable PBB detection.

Tetrabromobisphenol-A derivatives are not currently analysed on a routine basis in the Lancaster laboratories labs, but should be able to be analysed in the same extract as PBDE analysis using LC-MS or GC-MS (depending on the derivative of interest). Similar detection limits to TBBP-A are likely to be achieved.

Tetrabromophthalic anhydride and ethylene bistetrabromophthalimide cannot be analysed in the Lancaster laboratories at the moment, although methods for the analysis of these chemicals using LC-MS could be developed.

1,2-Bis(pentabromophenyl) ethane (Decabromodiphenyl ethane) is not currently analysed on a routine basis in the Lancaster laboratories, but can be analysed in the same extract as PBDE analysis using GC-MS concurrently with BDE209). This chemical is likely to be present at up to 10 times lower concentrations than BDE209, and the achievable detection limit is likely to be similar to BDE209. The sample size suggested for PBDEs is likely to be adequate, but a slightly (Barber *et al.*, 2005; Peters *et al.*, 2000; Stevens *et al.*, 2003; Thomas *et al.*, 2006) larger minimum sample size than for PBDEs would be preferred to achieve reliable detection.

7.3 Chlorinated Paraffins (CPs)

Chlorinated paraffins (CPs) are technical mixtures of polychlorinated linear alkanes (PCAs), which have been produced since the 1930s for many uses, including in lubricants and cutting fluids, and as flame retardants in plastics and sealants. The technical mixtures of CPs are generally divided into three production and usage defined, groups: short chain CPs (abbreviated to SCCPs or sPCAs) comprising isomers with 10 to 13 carbon atoms; medium chain CPs (MCCPs / mPCAs) – isomers with 14 to 17 carbon atoms; and long chain CPs (LCCPs / lPCAs) – isomers with more than 18 carbon atoms. The many possible positions for the chlorine atoms and presence of chiral carbon atoms lead to a large number of potential positional isomers, enantiomers and diastereoisomers. For example, there are theoretically 122,161 positional isomers for MCCPs, assuming that only one chlorine atom will be bound to any carbon atom. The level of chlorination of CPs varies between 30 and 72% by weight. CPs are lipophilic, and have the potential to biomagnify. The log K_{ow} value ranges are: 4.39 and 8.69 for SCCPs, 5.5 and 8.2 for MCCPs, and 7.3 to 12.8 for LCCPs.

It is estimated that more than 200 commercial CP formulations have been produced (Alcock *et al.*, 1999). As a result of recent regulation of SCCPs, the major CPs in production are now MCCP and LCCPs (Stern & Tomy, 2000). Although China is the largest producer of CPs, with an output of 120,000 tonnes in 2002 (Yongjun, 2002), one of the major CP manufacturing facilities is in the UK.
CPs appear to be ubiquitous in the environment (Bayen *et al.*, 2006) and there is a need for better understanding of their environmental occurrence, fate and transport. SCCPs have been shown to be toxic to aquatic organisms and are potential liver, thyroid and kidney carcinogens in some vertebrates. The EU considers SCCPs to be priority hazardous substances (European Community, 2001), SCCPs have been proposed for inclusion in the international POPs protocol, and the International Maritime Organization (IMO) considers CPs a 'Severe Marine Pollutant'. There are only a small number of research laboratories worldwide capable of the analysis of CPs and these chemicals are not the subject of routine monitoring. Because of the complexity of the CP mixtures, the analysis and quantification of CPs is very demanding, and not as reliably quantitative as many other organohalogen chemicals. There is very little information on the occurrence of CPs in the environment, and most of the data that exists

is for the SCCPs and MCCPs. SCCPs have been detected in a range of environmental media, including in the UK (Barber *et al.*, 2005; Peters *et al.*, 2000; Stevens *et al.*, 2003; Thomas *et al.*, 2006).

The only data on CPs in birds that appear to be available are for liver and muscle concentrations in little auks (*Alle alle*) and kittiwakes (*Rissa tridactyla*) from Bjørnøya (Bear Island, Norway: 74 °N, 19 °E) in 2001. Concentrations of SCCPs and MCCPs ranged from 150 to 880 ng/g lipid and 450 to 3700 ng/g lipid, respectively, in little auks; concentrations in kittiwakes were between 41 and 860 ng/g lipid SCCPs, and between 41 and 730 ng/g lipid MCCPs (Reth *et al.*, 2006).

Similar isolation and cleanup procedures can be used for CP analysis as for other organohalogen compounds such as PCBs and PBDEs. However, the complexity of CP quantification has resulted in numerous cleanup stages being required to remove potential analytical interferences. A review of the analytical procedures for CP determination reported in the literature can be found in the literature (Bayen *et al.*, 2006).

CPs are not currently analysed on a routine basis in the Lancaster labs. However, Lancaster staff have experience in analysing CPs, and have a long-standing collaboration with the Fisheries and Oceans Canada laboratories (one of the leading experts on CP measurement in environmental samples) for this analysis. The Lancaster labs also have collaborative links with other leading CP analysis laboratories, including ITM (Stockholm), RIVO (Netherlands), The Free University of Amsterdam, RECETOX (Brno, Czech Republic) and CEFAS (UK), amongst others. At the moment the Lancaster labs are in negotiation to obtain funding to establish an analytical facility for SCCPs, MCCPs and LCCPs. Analysis will be performed using GC-ECNI MS instrumentation already available in the Lancaster laboratory. The analysis of CPs can be achieved on the same extracts as for PBDEs and PCBs, although it is likely that larger sample sizes will be necessary for CP analysis. A detection limit of below 1 ng per analysis is anticipated for SCCPs, MCCPs and LCCPs so a minimum sample size of approximately 0.2 g lipid (i.e. 2 g fresh egg) would be preferred to achieve reliable detection, assuming that UK birds of prey will have CP concentrations at the upper end of those found in Bjørnøya.

7.4 Polychlorinated Naphthalenes (PCNS)

Polychlorinated Naphthalenes (PCNs) are a group of 75 chemicals (congeners) with similar chemical properties to polychlorinated biphenyls (PCBs), and with uses and a use-history similar to that of PCBs (but at approximately 10% of PCB production volumes). The production of technical PCN formulations began to decline in the 1960s, ceasing in the United States in 1977 and in Europe in the 1980s. PCNs can also be produced as by-products of combustion, metal refining, pyrolysis of chlorinated solvents, and chlorination of tap water. They can also be present as impurities in PCB technical mixtures. PCNs have not been restricted in their use and disposal, despite some congeners having dioxin-like toxicity (Hanberg *et al.*, 1990), and their wide usage. It has been shown that the toxic contribution (TEQ value) from PCNs can be greater in air than that of the coplanar PCBs (the most toxic PCB congeners) (Harner *et al.*, 1998). PCNs have been proposed for inclusion in the international POPs protocol by the EU (van de Plassche & Schwegler, 2002).

It has been suggested that, in the UK, a mixture of 'diffuse' (for instance, re-emission from soils) and 'non-diffuse' (i.e. predominantly primary) sources exist (Harner *et al.*, 1999), and PCN concentrations in UK air in the 1990s were approximately one-third those of PCBs (Harner *et al.*, 2000). It has also been suggested that the UK is a significant source of PCNs to the atmosphere (Harner *et al.*, 2000). Analysis of lake sediment core samples has suggested that peak UK environmental concentrations of PCNs occurred *circa* 1960, and that concentrations have declined by a factor of 2-3 since then (Gevao *et al.*, 2000). PCNs have been found in a range of biota (eg., Helm *et al.*, 2002), including glaucous gulls (*Larus hyperboreus*) in the Norwegian arctic (at 1.8-160 ng total PCN per g lipid in eggs) (Verreault *et al.*, 2005), and 83-2400 pg/g wet weight in cormorants and herring gulls from the N American Great Lakes (Kannan *et al.*, 2001b). There do not appear to be any measurements of PCNs in

animals reported from the UK.

There are a small number of research laboratories worldwide (probably <10, including the Lancaster laboratories) which regularly analyse PCNs in environmental samples, but these chemicals are not generally the subject of routine monitoring. Analytical procedures have generally used commercial PCN mixtures as analytical standards (see Harner & Kucklick, 2003), but in recent years individual PCN congener standards have become available. This has improved the ability to measure these chemicals in a truly quantitative manner. The Lancaster laboratories have participated in what is thought to be the only international inter-laboratory study on the analysis of PCNs (Harner & Kucklick, 2003). PCNs have been analysed in a range of environmental media (including sediment, vegetation and air) in the Lancaster laboratories for at least 6 years. The Lancaster labs have collaborative links with leading PCN analysis laboratories, including Meteorological Services Canada (Downsview, Toronto), ITM (Stockholm), and CEFAS (UK), amongst others.

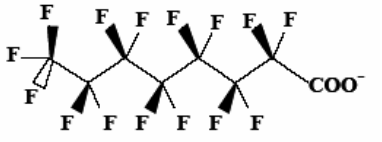
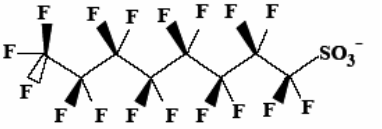
Analysis of PCNs is performed using GC-MS instrumentation in the Lancaster laboratories. The analysis of PCNs is achieved on the same extracts as for PBDEs and PCBs. A detection limit of approximately 1 pg per analysis is achieved, so the sample size suggested for PBDEs would be sufficient for reliable PCN detection.

7.5 Per- and polyfluorinated alkylated (PFAS) substances

Fluorinated organic chemicals (PFAS) have been industrially manufactured for over 50 years and total annual production is in the order of thousands of tonnes. Recently interest in has risen in perfluorinated chemicals since perfluorooctane sulfonate (PFOS) and perfluorinated carboxylic acids (PFCAs) were widely detected in human blood (Olsen *et al.*, 2003) and in high-trophic biota from remote areas such as the Arctic (Smithwick *et al.*, 2005). The environmental behavior of this class of chemicals differs from other known persistent organohalogens. Because of their hydrophobic and oleophobic nature, chemicals such as PFOS do not accumulate in lipids but are found at the greatest concentrations in the liver and in blood bound to serum proteins (Kannan *et al.*, 2001a). PFOS and its derivatives were produced commercially and used for surface treatment, paper protection and some performance chemicals, such as insecticides and fire-fighting foam. Perfluorooctanoic acid (PFOA) is a surfactant chemical used in fluoropolymer manufacturing processes (Kannan *et al.*, 2001a; Kissa, 2001; Schultz *et al.*, 2003). These compounds are ionic and possess very low volatility, and are thus unlikely to enter the atmosphere directly and undergo long range atmospheric transport. It is therefore unclear how they transported from densely populated application areas to remote places. PFOS, in addition to its presence in various perfluorinated products, is also a stable degradation product/metabolite of other PFAs. It has therefore been hypothesised that PFOS and PFCAs must be globally distributed via more volatile, neutral (perfluorinated) airborne contaminants that undergo long-range transport to remote areas, and then degrade to yield the free acid (Ellis *et al.*, 2004). Possible precursor compounds for PFCAs and PFOS are fluorotelomer alcohols (FTOHs), and fluorooctane sulfonamides/ethanols (FOSAs/FOSEs), respectively. It has also been suggested that fluorinated telomer olefins may degrade to form PFCAs. Manufacturing of FTOHs by the 'telomerisation' process began in the 1970s, and therefore PFCAs measured in the environment prior to this must come from 'direct' sources. The chemical structures of some key PFAS are shown in Table 7.1.

Table 7.1: Definitions of acronyms and structures of perfluorinated carboxylic acids (PFCAs) and perfluorinated sulfonic acids (PFSAs).

Acronym	Name	Molecular structure
PFCA	Perfluorinated carboxylic acid	$CF_3(CF_2)_nCOOH$ (n = 2, 3, 4….12)

PFSA	Perfluorinated sulfonic acid	$CF_3(CF_2)_nSO_3H$ (n = 3, 5, 7, 9)
PFOA	Perfluorooctanoic acid	$C_7F_{15}COOH$ 
PFOS	Perfluorooctane sulfonate	$C_8F_{17}SO_3H$ 
FTOH	Fluorotelomer alcohol	$CF_3(CF_2)_nCH_2CH_2OH$ (*n* = 3 , 5, 7….15)
FTO	Fluorotelomer olefin	$CF_3(CF_2)_nCH{=}CH_2$ (*n* = 3, 5, 7…13)
FOSA	Fluorooctanesulfonamide	$C_8F_{17}SO_2NHR$ (R=H, CH_3, or CH_2CH_3)
FOSE	Fluorooctanesulfonamidoethanol	$C_8F_{17}SO_2N\ (C_2H_5O)\ R$ (R= CH_3 or CH_2CH_3)

There is considerable interest in these chemicals at present. PFOS (and its derivatives) was submitted in 2005 under the Stockholm Convention as a candidate persistent organic pollutant (POP) for global banning of production. Indeed 3M, the company manufacturing most PFOS derived products, announced prior to this in 2000 that it was going to voluntarily withdraw all products based on this chemistry. PFOA has been listed as a 'Probable Carcinogen' by the US Environmental Protection Agency. PFCAs including PFOA will be the subject of an OECD meeting to be held in Stockholm in 2006.

Analysis of PFAS is technically more challenging than that of traditional POPs, with liquid chromatography-mass spectrometry (LC-MS) techniques being used for ionic species rather than gas chromatography-mass spectrometry (GC-MS). Key challenges in environmental trace analysis of PFAS include blank contamination issues, purity of reference standards and matrix effects in the ionization process of the mass spectrometer (Martin *et al.*, 2004). Blank contamination is most problematic for PFCAs, especially PFOA. It is associated with fluoropolymer materials used in the laboratory (e.g. Viton®, Teflon®) or in the analytical instrument, rather than field contamination. These materials must be avoided in trace analysis of PFCAs. Solvents (from the PTFE-lining in the cap) and nitrogen blow down have also been identified as additional sources. Matrix effects are known to be present when applying weak ionisation techniques, such as electrospray ionisation used in mass spectrometry of PFAS compounds. Measures have to be taken to control matrix effects in MS and a recently developed extraction method for biological samples has proven to be virtually free from matrix effects (Powley *et al.*, 2005). Samples are extracted using a methanol and sodium hydroxide mixture, and then cleaned using dispersive solid-phase extraction with Envi-Carb. Following addition of ammonium acetate buffer, extracts are analysed by LC/MS/MS with electrospray ionization. Biota samples may be frozen prior to analysis without any loss of target analytes, but care must be taken to avoid the use of Teflon-lined lids or containers. Aqueous samples stored in glass containers are susceptible to large losses by sorption to the glass surface, but this may be overcome by performing the solvent extraction in the glass storage container.

The available information on biological monitoring of PFAS was recently summarised by Houde *et al.* (2006), and a selection of the data is shown in Table 7.2. PFAS have been detected worldwide in

seabirds and in terrestrial birds and waterfowl. Few biomonitoring studies have been conducted for terrestrial mammals, but a comparatively greater number of studies have been conducted on marine mammals. Overall, PFOS is the predominant PFAS in biotic samples. Long-chain PFCAs (>8 carbons) have also been detected, as well as perfluoroalkyl sulfonate acids (PFSAs) with 4 to 10 carbons.

The toxicological effects of PFOA have been reviewed by Kennedy *et al.* (2004). PFOA is a peroxisome proliferator (PPAR agonist) and exerts morphological and biochemical effects characteristic of PPAR agonists. These effects include increased *β*-oxidation of fatty acids, increases in several cytochrome P-450 (CYP450)-mediated reactions, and inhibition of the secretion of very low-density lipoproteins and cholesterol from the liver. These effects on lipid metabolism and transport result in a reduction of cholesterol and triglycerides in serum and an accumulation of lipids in the liver. Tumours have been observed (liver, Leydig cell, and pancreatic acinar-cell), and are typical of many PPAR agonists in that they are believed to involve non-genotoxic mechanisms. However, in an exposed human population with some of the highest serum concentrations reported to date, there was no link between high exposure levels and biomarkers of liver or thyroid disease (Emmett *et al.*, 2006).

Similarly, known *in vivo* effects of PFOS in vertebrates are increased relative liver weight, induced peroxisomal liver fatty acid *β*-oxidation and lowered serum cholesterol and triglyceride concentrations (Seacat *et al.*, 2003). PFOS exposure also increases the serum alanine aminotransferase (ALT) activity, which is a marker for hepatic damage (Hoff *et al.*, 2003). Other in vivo effects are the inhibition of gap junction intercellular communication (Hu *et al.*, 2002), the induction of carboxylesterase expression (Derbel *et al.*, 1996), neuroendocrine effects (Austin *et al.*, 2003) and the occurrence of developmental effects (Lau *et al.*, 2004). Newsted *et al.* (2006) have performed the only studies evaluating the acute and chronic effects of PFOS on avian species, the mallard (*Anas platyrhynchos*) and the northern bobwhite quail (*Colinus virginianus*). Concentrations of PFOS in juvenile mallard and quail liver associated with mortality (Newsted *et al.*, 2006) are at least 50-fold greater than the single maximum PFOS concentration that has been measured in livers of avian wildlife.

Environmental monitoring data and temporal trends of PFAS are still relatively scarce, with only a few studies published to date (Bossi *et al.*, 2005a; Braune *et al.*, 2005; Holmstrom *et al.*, 2005; Smithwick *et al.*, 2006). Levels of PFAS show an increase from 1970s to late 1990s, with a doubling time of 7-10 years, followed by a leveling off in recent years. There is a need to expand existing databases in order to better understand the relationship between trends observed in the environment, possible sources of PFAS, and potential future risk to biota.

Table 7.2: Concentrations of per- and poly-fluorinated chemicals (PFAS) in vertebrates

Species (common name)[1]	Locations	Sampling year	Tissue	PFOS (ng/g ww)	PFOA[2] (ng/g ww)	Reference
Arctic cod	Eastern Arctic	2000-2001	whole	1.3 ± 0.7	0.2 ± 0.006	(Tomy *et al.*, 2004)
Flounder	Denmark		liver	18 - 21	<0.4	(Kallenborn *et al.*, 2004)
Pike	Finland		liver	204 - 551	<0.4 - 1.4	(Kallenborn *et al.*, 2004)
Perch	Sweden		liver	169 - 432	<0.4	(Kallenborn *et al.*, 2004)
Black-legged Kittiwake	Eastern Arctic	2000-2001	liver	10 ± 4.6	nd	(Tomy *et al.*, 2004)
Black guillemot	Greenland	2000	liver	13 - 16	nd	(Bossi *et al.*, 2005b)
Glaucous gull	Eastern Arctic	2000-2001	liver	20.2 ± 3.9	0.1 ± 0.05	(Tomy *et al.*, 2004)
Common cormorant	Med. Sea, Italy	1997	liver	32 - 150	29 - 450	(Kannan *et al.*, 2002b)
Black-eared kite	Japan	1999	liver	180 - 450	<19 - 21	(Kannan *et al.*, 2002a)
Bald eagle	Midwestern USA	mid-1990s	liver	360	N/A	(Giesy & Kannan, 2001)
Osprey	USA	1996-1997	liver	42 - 959	N/A	(Kannan *et al.*, 2001a)
Carrion crow	Tokyo Bay	2000	liver	464	N/A	(Taniyasu *et al.*, 2003)
Polar bear	Greenland	1999-2002	liver	1285	<12	(Bossi *et al.*, 2005b)
Walrus	Eastern Arctic	1998	liver	2.4 ± 0.4	0.3 ± 0.09	(Tomy *et al.*, 2004)
Grey seal	Baltic Sea		liver	140 - 360	<19	(Kannan *et al.*, 2002b)
Grey seal	Sweden		liver	331 - 537	0.3 - 5.6	(Kallenborn *et al.*, 2004)
Ringed seal	Baltic Sea		liver	130 - 100	<19 - 39	(Kannan *et al.*, 2002b)
Long-finned pilot whale	Faroe Islands	2002	liver	88 - 336	0.4 - 1.7	(Kallenborn *et al.*, 2004)

[1]latin names available from references, [2]nd is not detected, N/A is not analysed

7.6 General investigation of contamination with organic chemicals

General methodologies for detecting unknown compounds in PBMS samples and some initial studies have been outlined in previous reports (Shore *et al.*, 2006b; Shore *et al.*, 2005c). GC-MS and LC-MS instruments now provide extremely sensitive analysis in full scan mode, in which it is possible to determine unknown compounds at concentrations in the pg range. Sample extracts can be comprehensively analysed for exogenous compounds using the full capabilities of the instruments (including different ionisation modes and different separations – based on polarity and structural moieties – afforded by different GC and LC columns), and the comprehensive mass chromatographic libraries and structure elucidation tools available both as part of the instrument software, and, increasingly, through online shared resources. A very broad range of exogenous chemicals can be identified using this approach, and sensitivity can be further enhanced by investigating the data acquired for known chemicals of interest (i.e. allowing the broadest range of chemicals to be investigated, without the restrictions of performing the most sensitive targeted chemical analysis). Chemicals identified in samples can be confirmed and quantified by comparison with reference standards (which may need to be purchased). Alternatively, if suitable reference standards are not available, semi-quantitative analysis can be performed against similar compounds.

The range of chemicals which can be investigated using this approach is broad, but limited by the extraction and treatment of samples used to prepare extracts for analysis. The identification of analytes is only restricted by the ability of the GC or LC to separate individual analytes, and for this it is

necessary to ensure that samples preparation techniques are optimised. A range of techniques can be used to prepare the samples, and with careful choice of the most suitable (least destructive) techniques, and modification to collect extract portions normally discarded, the widest range of potential identifiable analytes can be achieved, whilst maintaining optimum performance. Although the chemical classes which can be identified and investigated is not unlimited, some chemicals of potential interest that can be investigated using this approach include halogenated pollutants not discussed above; pharmaceutical chemicals; personal care product chemicals; phthalates.

The combined analytical facilities that will be available through the LEC will allow detailed scanning of selected samples for new compounds. The LEC, through its larger critical mass of analytical chemists, and the potential to involve post-graduate MSc and PhD in dedicated projects, will enhance the capability of the PBMS to undertaking this type of analysis and identify new chemical risks.

7.7 Toxic and essential metals

The Environmental Analysis Group, based at CEH Lancaster and part of the LEC, provides a range of analysis of inorganic chemicals. The Group was established in 2003 by combining the resources from two groups with experience in analysing materials from the aquatic and terrestrial environment and housing them in a modern purpose-built facility in the LEC. The new purpose-built suite of laboratories is specifically designed to handle soil, plant and animal material, and to perform trace-analysis of aqueous media in clean rooms. Analysers include an Inductively Coupled Plasma-Mass Spectrometer (ICP-MS), an Inductively Coupled Plasma-Optical Emission Spectrometer, hydride and cold-vapour fluorescence analysers. The laboratory is UKAS accredited to ISO 17025 for frequently performed analyses and regularly participates in proficiency testing schemes.

Currently, the PBMS monitors carcasses and eggs for Hg (Section 3.3) using cold vapour atomic absorption spectrophotometry. This monitoring is in the process of being transferred to the LEC and will be conducted in the future using ICP-MS analysis. The associated resource costs would be similar, and the new analysis would provide slightly improved detection limits for Hg and allow simultaneous detection and quantification of a suite of other inorganic essential and non-essential metals in the same sample digest. This element suite would include copper, zinc, iron, manganese, nickel, chromium, selenium, arsenic, cadmium and lead.

Data on current tissue concentrations of toxic heavy metals can be assessed against a large body of information available on the toxic effects associated with such residues. While the potential toxic risks associated with ingestion of lead shot has recently been assessed for red kites (Pain *et al.*, submitted), there is no systematic monitoring of exposure to lead or other toxic metals in a wider range of predatory bird species in the UK. Data on trace element status would be valuable as it is one potential means of gauging the health status of birds.

7.8 Radionuclides

The need for a system to protect the environment from ionising radiation is now generally recognised. There has been a considerable international and national effort on this issue over the last decade with a number of assessment models and frameworks developed. Some countries are now using these within their national regulatory frameworks for nuclear and other sites which may be releasing radioactivity to the environment (Beresford *et al.*, 2005). In England and Wales the Environment Agency is using a methodology(developed in collaboration with English Nature; Copplestone *et al.*, 2001) to undertake assessments of Natura 2000 sites which may receive discharges from authorised sites (e.g. Copplestone *et al.*, 2005)

The contribution that naturally occurring radionuclides make to the radiation dose received by non-

human species needs to be determined to compliment the impact assessment methodologies. Pentreath (2002) suggested that it may be useful to compare the potential impacts of artificially released radionuclides to that of the natural background radiation dose rate normally experienced by animals and plants and this concept is being considered further by the International Commission on Radiological Protection (ICRP, 2005). However, there are few relevant data for the United Kingdom to enable estimation of doses received by non-human species from natural radionuclides (Beresford *et al.*, 2006). To start to address this deficit a limited number of grey heron liver samples obtained from the PBMS sample archive were analysed to determine the activity concentrations of ^{238}U and ^{232}Th series radionuclides and ^{40}K (Beresford *et al.*, 2006).

Further analyses of samples collected from the PBMS for natural series radionuclides would enhance ability to determine background exposure of birds and, depending upon the number of samples analysed, how this varies throughout the country. Furthermore, whilst not the objective of the determinations, the analyses of the heron liver samples discussed above showed detectable levels of some anthropogenic radionuclides (^{137}Cs and ^{241}Am). The PBMS samples may, therefore, provide a source of materials to assess anthropogenic activity concentrations in birds distant from and/or close to nuclear licensed sites, and so provide a measure of the bioavailability and associated risk to top predators from anthropogenic sources of radionuclides.

7.9 Screening for contaminant-related effects and for disease status

7.9.1 Use of the PBMS to screen for contaminant-related exposure and damage

Dr Frank Martin's laboratory in the LEC specialises in the use of a range of short-term genotoxicity assays, primarily using immortalised or primary human cell lines. Historically, these have been mainly derived from hormone-responsive tissues of the breast (e.g. MCF-7) or prostate (e.g. PC-3, DU-145, LnCaP) but may be applied to other cell types. For example, the laboratory currently has a project investigating DNA-damage mechanisms in the earthworm which is used as a sentinel organism (Martin *et al.*, 2005). The assays include the alkaline single cell-gel electrophoresis ('comet') assay[1] and the cytokinesis-block micronucleus (CBMN) assay[2]. Rates of cell viability (clonogenic assay) can also be measured and quantitative real-time RT-PCR is employed to assess the quantitative expression of cytochrome P450 isoenzymes (*CYP1A1*, *CYP1A2* and *CYP1B1*), cyclin-dependent kinase inhibitor 1A (*CDKN1A* (*P21$^{WAF1/CIP1}$*)), B-cell leukaemia/lymphoma-2 (*BCL-2*) and Bcl-2-associated X (*BAX)*. Immunoblot analysis of protein expression may also be ascertained. The laboratory is also currently developing the novel technique of infrared (IR) micro-spectroscopy to assess biochemical and conformational alterations associated with contaminant exposures or to track bio-remediation. This can be applied to interrogate the biochemical composition of tissues (even archived such as paraffin-embedded) or sub-cellular components (e.g. DNA). This straightforward and inexpensive approach has been used to monitor bio-remediation as a function of decreasing conformational changes in DNA.

The PBMS tissues could potentially be screened to develop an understanding of adverse effects in wildlife that may be associated with contaminants and other stresses. Comet assay analysis of pre-existing damage in tissues/blood cells require fresh samples obtained as soon as possible post-

[1] The alkaline comet assay is a microelectrophoretic technique that facilitates the direct visualisation of DNA damage in the form of single-strand breaks (SSBs) in individual cell genomes. It is sensitive down to 25 SSBs per genome and is based on the fact that negatively-charged DNA migrate in a size-related fashion when an electric current is past across it i.e. the more SSBs, the more DNA migrates and this may be quantified and is proportional to the amount of damage. Tissue/cells need to be fresh (i.e. viable) and it may be applied to most cell types e.g. peripheral blood lymphocytes.

[2] The CBMN assay – this is a direct means of quantifying chromosomal damage in individual cells. As cells divide a piece of chromosome may break off or a whole chromosome may fall away – this may subsequently be visualised as extra-nuclear DNA material i.e. a micronucleus. Experiments may be conducted in using immortalised or primary human cell lines. The *in vivo* version of this assay employing erythrocytes is a core test; erythrocytes are anucleate but if damage occurs micronuclei are visible

mortem and would require significant assay development per tissue as different cell types would need to tailored to specific lysis/electrophoretic conditions. There is also a problem of dealing with heterogeneous cell populations as the comet assay will not distinguish the cells susceptible to a damaging stimulus. Similar problems exist for the CBMN assay and this would also require significant method development. However, both methods are routinely applied in a regulatory toxicology setting.

Spectral fingerprint analysis of tissues/blood cells using IR micro-spectroscopy is very straightforward and may be applied to frozen tissues or paraffin-embedded blocks. This technique is already applied in the US to interrogate spectral changes in DNA isolated from the livers of Dover Sole as a marker of contaminant exposure, and there is an increasing literature that this approach has strong potential to identify a range of pathological conditions including neurodegenerative, cancer, and hypertrophic/cirrhotic conditions in the liver.

It is also possible to test tissue extracts using a range of short-term assays so as to assess the potential effects that arise from cellular exposure to contaminant mixtures. This could provide a measure of additive toxicity or synergistic toxicity arising from exposure to mixtures. The tissue under investigation is put through a solvent and column extraction procedure to remove tissue components such as lipids that would be inherently toxic, and concentrate a class of chemicals of interest. Part of these extracts can be analysed chemically and the other fraction sent for biological testing using the alkaline comet assay, the CBMN assay or IR micro-spectroscopy. Cells in culture would be treated for a specified time period (2 h or 24 h) and then incorporated into the particular assay. The CBMN and alkaline comet assays could be used to assess genotoxic effects while IR micro-spectroscopy could be used to obtain a whole-cell biochemical fingerprint or one derived from an isolated component.

In all cases, baseline measures of pre-existing damage and biochemical spectra would have to be obtained and this is likely to require accumulation of datasets over approximately 3 years. Such baseline data could be used to determine the power of future monitoring to detect significant deviations. The major limitation is that these approaches would require developmental work for each particular purpose. The advantage is that they are relatively simple, very well validated, and would provide measures of effects that could, through chemical analysis, be linked to particular contaminants, or taken as measures of general health.

7.9.2 Microbiological screening

The relocation of PBMS to CEH Lancaster will give rise to the opportunity to screen tissue samples using the most up-to-date molecular methods that are not only exquisitely sensitive but allow quantification of the target microbial pathogens including viruses, bacteria, fungi and protozoa. Microbiological screening for pathogens can be used for both assessing avian health and human health.

With respect to avian health, the pathogen detected may give an insight into the health of the host who donated the tissues and therefore give insights into population health (e.g. Avian pox caused by several strains of Poxvirus). Furthermore, an assessment can be made of pathogens that would associate the host as a disease carrier (i.e. avian diseases not associated with predatory birds, e.g. mycoplasmal conjunctivitis caused by *Mycoplasma gallisepticumi*). Conversely, the bird may be a carrier of pathogens than may impact non-avian animal and human health (such as *Salmonella* spp., *Campylobacter* spp.). In addition, it is possible to assess whether birds are carriers of specific human pathogens such as the Lyme disease agent *Borrelia burgdorferii,* E. coli O157:H7 or *Mycobacterium avium* subsp. p*aratuberculosis*, which is linked to Crohn's disease in human, causes Johne's disease in animals, with rabbits and small rodents representing an environment sink for this organism.

The CEH Lancaster laboratories in the LEC have the facilities to culture bacterial pathogens at containment levels 1, 2 and 3 (the latter required for pathogens such as *E. coli* O157:H7). They have

extensive expertise in detecting and identifying pathogens using molecular methods such as polymerase chain reaction (PCR) amplification of DNA and real time PCR, which provides a quantitative assessment. Extensive literature exists on DNA sequences that can employed in the development of PCR based molecular tools for the detection of a wide range of microbial pathogens. Furthermore CEH Lancaster has experience in using computer software for the design of molecular primers necessary for PCR methodologies. For example, the laboratory has developed a PCR detection system for *Mycobacterium avium* subsp. *paratuberculosis* which has been used on both environmental samples and human colonic tissue and has allowed us to link environmental sources to human disease.

In conclusion, microbiological assessments can therefore be conducted on PBMS tissues as an indicator of bird health or to assess their impact as carriers of pathogens that may impact animal and/or human health. In addition, there is capability to respond to new an emerging disease and address issues as they arise.

8 Recommendations for future monitoring

8.1 Collection of carcasses

The potential risks associated with transport of birds via the post possibly contaminated with the H5N1 virus or other diseases were reviewed in 2006 and postal submissions of birds were suspended. At the time of this suspension, sufficient birds had already been collected to complete the core monitoring for 2006.

Collection of carcasses in 2007 will be achieved through collection via couriers and through a network of collection points, the development of which is currently ongoing. Information about new submission methods will be provided to major past submitters of carcasses through information posted on the website, through e-mail shot and through dissemination of information via he post. In all cases, potential submitters of single carcasses are encouraged to contact CEH in the first instance and the most appropriate means of carcass collection will be arranged.

It is anticipated that the total submission of carcasses will be reduced from current levels but the PBMS will focus in particular on achieving target numbers of carcasses for its core monitoring work.

8.2 Existing monitoring

8.2.1 Organochlorine insecticides

The case for retaining annual monitoring of OC insecticides within the PBMS other than in the eggs of sea eagles from the west-coast of Scotland is weak. This is because current concentrations in all other samples are at relatively low levels and do not appear to be changing. It has been previously argued that terminating quantification of OC insecticides would save little resource for the PBMS because chemical analysis of OC pesticides and PCBs are carried out simultaneously in the same sample (Shore *et al.*, 2005c). This argument remains true but the reporting of the data in PBMS reports and statistical analysis of trends in all species does consume resources. Continued prominent reporting of low-level OC insecticide concentrations also obscures the ongoing refocusing of the PBMS towards other contaminants of current concern.

Contamination by OC insecticides may still potentially be significant in migratory species that over-winter in regions where these compounds are still in use, for example for malaria control operations. If OC insecticides are to be retained as part of the core PBMS monitoring, it may be more appropriate to refocus monitoring towards eggs of such species to determine if there is a significant risk from exposure to DDT and other OC insecticides, and whether assimilation is changing over time. Monitoring of failed osprey (*Pandion haliateus*) eggs and/or the eggs of Hirundines might be a better focus for OC monitoring than the current core PBMS species other than sea eagles. The potential for obtaining sufficient samples would have to be explored.

It is therefore recommended that the reporting of OC insecticides in the core PBMS monitoring species is stopped, other than for white-tailed sea eagle eggs in which DDE can still be present at embryotoxic levels. Standards for OC insecticides should still be included in the analytical process so that archived analytical scans can be re-examined and OC insecticide concentrations calculated in the future should there be a requirement for such data.

8.2.2 PCBs

The analysis and reporting of PCBs was modified for birds collected since 2002 so that congener-specific concentrations and TEQ concentrations were reported. The intensity of monitoring (number of sparrowhawk samples analysed) was also reduced. Long-term trends in specific congeners and TEQ concentrations cannot yet be determined because monitoring has not yet been conducted for long enough. Therefore, there are major uncertainties about long-term trends for specific congeners, sum PCB concentrations and TEQ concentrations in predatory birds. Current PCB and TEQ concentrations are at embryotoxic concentrations in some eggs.

We therefore recommend that the PBMS continues its current level of monitoring for PCBs. Data from these studies will help assess the risk to predatory birds from different PCB congeners and allow evaluation of EU objectives to eliminate PCB contamination by 2010. The analysis of PCBs is also likely to form part of a wider analysis that will be developed over the next five years for other POPs and for effects screening (see Section 7 and Section 8.3).

8.2.3 Anticoagulant rodenticides

Given the significant concerns over the potential risk to predatory and scavenging birds and mammals from anticoagulant rodenticides, monitoring for these compounds remains of high conservation value and a priority. The monitoring is also a key tool to determine whether the promotion through CRRU of best practice for use of anticoagulant rodenticides is successful in reducing the exposure of predatory birds. We recommend that monitoring of barn owls and kestrels should remain at the current level.

In the last report describing potential modifications to the PBMS (Shore *et al.*, 2005c), we highlighted that recent analytical developments that involve transferring quantification techniques to a mass spectrometry basis means that residues of some first-generation anticoagulant rodenticides, such as warfarin and coumatetralyl, were also likely to be reported in future years. It is intended that this transfer process will be completed when the PBMS is transferred to the LEC and so will provide a more complete picture of possible risk posed by anticoagulant rodenticides generally. This expansion in the range of contaminants analysed is unlikely to raise analytical costs and so will be an improvement in the amount of information provided per unit cost. Cross calibration of concentrations determined by current fluorescence methods and by LC-MS will be necessary to ensure continuity of long-term datasets.

8.2.4 Mercury and other metals

Concerns over long-term trends in Hg have been highlighted in Section 3.3. The potential to analyse a suite of other toxic and essential trace elements simultaneously with Hg (at no increased analytical cost), and the associated benefits of such analyses, have also briefly been described (Section 7.7). The only additional resources required would be associated with increased costs of reporting and analysis of long-term data for multiple metals, but these would be more than offset by termination of reporting of OC insecticides by the PBMS.

We therefore recommend that the current analysis of Hg conducted by the PBMS is continued but the analysis is conducted by ICP-MS and concentrations of other toxic metals and essential trace elements are reported as a wider means of assessing health status. Cross calibration of concentrations determined by cold vapour AAS and by ICP-MS will be necessary to ensure continuity of long-term datasets

8.2.5 Use of data on nutritional state when analysing long-term trend data.

Our recent studies on the impacts of nutritional state on liver concentrations of organic and inorganic contaminants (Shore *et al.*, 2006c; Wienburg & Shore, 2004) have demonstrated the

importance of including this measure as a factor in our analyses of long-term trends in contaminant concentrations over time and when relating tissue concentrations to potential toxic effects. We therefore recommend that information on the nutritional state of birds is provided when liver residue data are presented and that nutritional state is included as a factor in future long-term analysis of residue data.

8.3 Reporting

The annual and long-term Wildlife & Pollution contract reports have expanded in recent years to reflect wider contaminant reporting (for instance quantification of individual PCB congeners and TEQ concentrations), increasing interpretation of the biological significance of the residues that are reported, and the inclusion of distinct annual studies. This has substantially increased the information supplied in and the resources required to produce reports. However, some of the generic reporting of annual monitoring data has remained largely unchanged over a number of years and includes some repetition of information and statistical analyses that are less applicable than was the case previously. We recommend that the format of the annual reports is revised to reflect the refocusing of the PBMS. We recommend the proposed following changes are discussed with PBMS funding stakeholders and are implemented where they are deemed appropriate.

- Remove from the annual report the introductory background sections that are largely repeated each year. Provide a more succinct summary and refer readers to the PBMS website where fuller information can be made available.

- Provide a short description of the number of carcasses and eggs of each species received by the PBMS each year that are processed for analysis and/or archived.

- Streamline the annual report by providing in the main body of the report only summary data (% of birds with detectable residues, mean and variance data for residue concentrations) rather than tables of individual tissue and egg concentrations. Report individual tissue and egg contaminant concentrations in an appendix in the report or omit from the report completely and post the data annually on the PBMS website.

- In annual reports, terminate the comparison of residue data for the year with that for the previous year. This is because differences between pairs of years in average tissue and egg contaminant concentrations have little biological significance. Meaningful interpretation of changes over time is only really possible using longer time series of data; this analysis is conducted currently every three years.

- Residue data are currently reported on a species by species basis but could instead be grouped by contaminant type (for example, PCBs, Toxic and trace metals, Anticoagulant rodenticides) rather than by species, so that common trends across species are more readily apparent.

- The three-yearly analysis of long-term time trends will become increasingly complex and large when sufficient time series data are available to report such trends in specific PCB congeners, in other POPs (which often consists of numerous congeners as with PCBs), and in a suite of inorganic metals. There is likely to be a need for some prioritisation of which congeners and metals are analysed in detail for time trends which would be tailored to prevalence and magnitude of occurrence.

- Three yearly reviews of the long-term data are currently conducted for OC insecticides, PCBs and Hg together and for anticoagulant rodenticides separately. We recommend that

long-term trend analyses for the three major groups of compounds that we propose should be monitored (PCBs and other POPs, anticoagulant rodenticides, toxic and trace metals) are fully desynchronised so that each annual report will contain a long-term trend analysis for one of these groups of compounds. This will spread the effort required to prepare the reports more evenly across years.

- Details of collaborative studies that use the PBMS archive (Section 4) and a summary of the results of these studies should be included in annual reports. The provision of such information should be a precondition of access to archive material.

- A short newsletter that highlights the main findings and activities of the monitoring work could be produced each year. This would provide easy access to key information for stakeholders and the public who would not otherwise reference annual reports.

- CEH has recently developed a dedicated website for the PBMS. This should continue to be developed in consultation with stakeholders and be a key resource for dissemination of information.

8.4 Development of new monitoring studies in the future

The incorporation of annual one-off studies in recent years in the PBMS has increased the flexibility of the scheme to refine its existing activities and explore the potential and need for new chemical monitoring. We recommend that this structure is maintained so that the PBMS can remain flexible in approach and remain a key tool for assessing chemical threats and for developing a wider role in monitoring the health status of birds.

The current report has clearly highlighted the potential for further refocusing of the PBMS monitoring that will result from the relocation of the PBMS to the LEC. A wide range of possible new monitoring activities for priority chemicals (mostly new POPs) has been described in Section 7. A key question is which of what are already a list of priority chemicals should potentially be incorporated into the PBMS? We recommend that any new chemical monitoring should initially focus on "new" POPs of concern for which extraction and clean-up methods are similar or identical to that used for ongoing PCB analysis. This is likely to represent the most cost-effective means of rapidly incorporating into the PBMS monitoring for new chemicals. Prioritisation of which new POPs should be monitored is likely to be informed by the use of the annual one-off studies. These can be used to pilot potential new monitoring using PBMS archive tissue and egg samples. Such work would determine the presence and magnitude of different new POPs in samples, provide an initial estimate of likely chemical risk, and quantitative estimates of the power of any new monitoring to detect temporal changes.

We also recommend that consideration and priority be equally given to the development of effects screening tools, as described in section 7.9. Incorporation of such monitoring could be integrated with the measurement of trace element status and lead to the development of health indices. Linkage between monitoring of exposure/assimilation of chemicals and the occurrence of associated effects is key for understanding the risk posed by chemicals to wildlife and an essential development for the PBMS. Such effects screening and monitoring would have wider applications other than those solely associated with exposure to contaminants.

Clearly, there is a need for discussion between funding stakeholders as to the priorities for future monitoring. We recommend that such discussions should be informed by closer linkage with the EA priority setting for chemical monitoring in otters (Section 6.2), as it would provide a means of linking the otter monitoring work and the PBMS and the EA is a funder of both monitoring schemes. This

could be achieved by mutual attendance of project leaders and nominated officers at priority setting meetings for the two schemes. The development of workshops between the two schemes and between other national and international monitoring scheme (Section 6) is also recommended as it will foster better collaboration between the schemes, better coordination of UK-scale chemical monitoring, and general adoption of best practice.

8.5 Conclusion

Overall, the relocation of the PBMS to the LEC represents a major opportunity to develop and widen the PBMS largely within the constraints of current resourcing. The integration with the LEC is likely to provide significant additional flexibility to the PBMS in terms of exploring the need for new monitoring activities and assessment of risk to wildlife. The key recommendations for future monitoring discussed in this section of the report are summarised in Table 8.1.

Table 8.1: Summary of recommended future developments for the PBMS

Activity	Development
Collection of samples	Develop drop-off points and courier methods for collection of material
OC insecticides	Terminate except for sea-eagle eggs
PCBs	Continue to monitor on congener specific and TEQ basis
Anticoagulant rodenticides	Continue monitoring, transfer to mass spectrometry methods and include quantification of first generation compounds
Mercury	Continue monitoring Hg but transfer to ICP analysis and simultaneously report suite of essential and toxic metals
Measurement of nutritional status of birds	Report and include as factor in analysis of long-term trends
PBMS Reporting	Streamline and modify. Include more detail of projects utilising the PBMS archive. Further develop website
New chemical monitoring	Use one-off annual studies and expertise available through the LEC to develop monitoring for priority chemicals of concern. Focus initially on priority compounds that can be incorporated rapidly into existing analytical methodologies
Effects screening and health indices	Develop effects screening methods and link with measures of trace element status to develop health screening indicies
Closer integration of national monitoring schemes	Develop linkage with other national monitoring schemes to encourage better focus for coordinated UK monitoring, collaboration and sharing of best practice

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10 Appendix

Table A.1: Chemicals of highest concern from Chemical Stakeholder Forum (CSF) list of chemicals of concern that are not included in Section 7.

Chemical	CAS No	Category	Use	OSPAR listed
Bis(tributyltin) oxide (TBTO)	56-35-9	Biocide	It is still produced or used in the UK and exposure is expected to be widespread, although marketing and use restrictions exist.	Yes
6,6'-di-tert-butyl-2,2'-methylenedi-p-cresol	119-47-1	Cresol	Polymers and Adhesives	No
Anthracene, pure	120-12-7	PAH	Isolated anthracene is used as a chemical intermediate and has some minor uses (e.g. as a plasticiser in thermosetting resins). Other sources are creosote and coal tar derivatives, and fuel combustion.	Yes
Octamethylcyclotetrasiloxane	556-67-2	Siloxane		No
Triphenylphosphine	603-35-0	"Others"	Used in synthesis of organic and organometallic compounds. It is still produced or used in the UK, and exposure is expected to be widespread.	Yes
2-Ethylhexyl 10-ethyl-4,4-dioctyl-7-oxo-8-oxa-3,5-dithia-4-stannatetradecanoate	15571-58-1	Plastic additive	Plastic additive approved for food contact	No
Nonylphenol	25154-52-3	Phenol	Used to make nonylphenol ethoxylates, resins and plastic stabilisers.	Yes
Phenol, 4-nonyl-, branched	84852-15-3	Phenol	Used to make nonylphenol ethoxylates, resins and plastic stabilisers.	No
2-Ethylhexyl 10-ethyl-4-[[2-[(2-ethylhexyl)oxy]-2-oxoethyl]thio]-4-octyl-7-oxo-8-oxa-3,5-dithia-4-stannatetradecanoate	27107-89-7	Plastics Additive	Plastic additive approved for food contact. It is still produced or used in the UK, and exposure is expected to widespread.	No
Di(tert-dodecyl) pentasulphide	31565-23-8	"Others"	Still produced or used in the UK, and exposure is expected to widespread.	No
Vinyl neodecanoate	51000-52-3	"Others"	Used as an additive to paints and adhesives	Yes
1,4-Benzenediamine, N,N'-mixed phenyl and tolyl derivatives	68953-84-4	"Others"	Rubber and plastics additive	No
Dodecylphenol, mixed isomers (branched)	121158-58-5	Phenol	Used to make oil and lubricant additives, with a small amount used to produce phenol/formaldehyde resins, latex for rubber tyres, printing inks and other niche applications. Minor use for ethoxylate surfactants	No