SURVEY OF CONTAMINANTS IN SOILS AND BIOTA AT THE SENEY NATIONAL WILDLIFE REFUGE

DAVID A. BEST
TIMOTHY J. KUBIAK
DIANE E. BOELLSTORFF

FEBRUARY 1995

STUDY IDENTIFIERS: 88-3-113 & 88-3-115

ENVIRONMENTAL CONTAMINANTS PROGRAM
DIVISION OF ECOLOGICAL SERVICES
EAST LANSING FIELD OFFICE
U.S. FISH AND WILDLIFE SERVICE

Table of Contents

List of Figures

List of Tables

Background

A survey was conducted in 1987 to assess the presence and degree of contamination in soils and various biota at Seney National Wildlife Refuge, located in the east-central Upper Peninsula of Michigan. While the refuge is well removed from the traditional "end-of-pipe" industrial sources of contamination, the refuge is still potentially threatened by historic onsite management activities, as well as by aerial deposition from distant sources.

There are two known onsite activities which historically took place that may pose continued risks to Service trustee resources. First, to suppress dust, various roads and dikes throughout the refuge were oiled (Figure 1) in the 1960s with waste products derived from the K. I. Sawyer and Kincheloe Air Force Bases in the Upper Peninsula and local businesses. Among the waste liquids sprayed were jet fluid (IP-4), kerosene, fuel oil, STP, antifreeze, hydraulic fluid, crankcase oil, and barrels of unknown fluids. In addition to the toxicity that might result from these petroleum products, there was the additional fear that this material might have contained dioxin-like compounds, as was the case at the Times Beach sites in Missouri. The second activity of concern was the past use of pentachlorophenol as a wood treatment and preservative on fence posts for the refuge. The primary area of interest was the Bone Yard work site where the posts were dipped into vats of hot preservative and open air-dried. Of concern was the presence of dioxin-like compounds, which are known contaminant byproducts in the manufacture of pentachlorophenol.

Aerial transport and deposition of inorganic and organic contaminants have been suggested to be measurable phenomena in the Great Lakes basin. The primary sources of these contaminants are believed to be combustion processes at industrial facilities within and outside the basin. However, evaporation of the more volatile of the compounds from industrial sites, as well as ponds, lakes and other natural areas with inplace pollutants, may be secondary or intermediate sources. Deposition of these compounds at Seney may augment natural onsite sources, particularly in the case of certain heavy metals derived from parent soils/bedrock.

This survey was designed to evaluate whether contaminants used onsite were still present at or near the sites of use or application, and to evaluate whether biota have been exposed to and affected by contaminants via aerial or onsite pathways. Biota were selected to evaluate contaminant exposure and accumulation through trophic levels, and assess effects to known or suspected sensitive species. Species were also collected to evaluate potential human consumptive risk through sports fishery and waterfowl hunting. Overall, the survey was directed to assist in refuge management.

Methods

A total of 48 soil and sediment samples were collected on the refuge and at background sites on the refuge and along US Highway 2 and the Lake Michigan shoreline. The background sediment sample was a surface grab in the Manistique River at the Michigan Highway 77 bridge. Ten soil

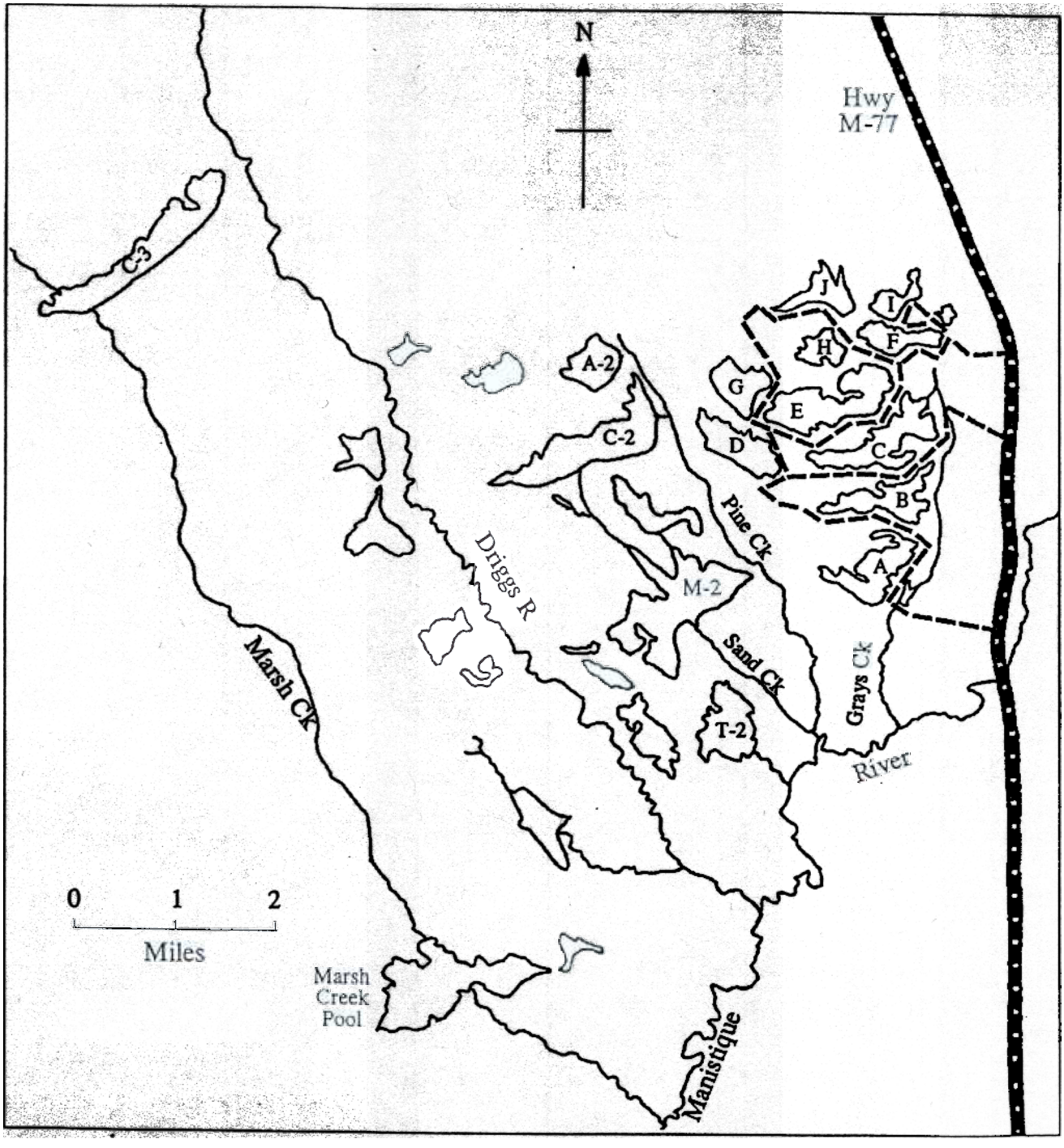

Figure 1. Location Pools, Sampling Sites and Oiled Roads (dashed line), Seney NWR.

samples were collected in 2 refuge work areas referred to as the Bone Yard and the Wood Burning areas. Equal sized portions of these samples were combined into 3 composite samples for analysis of dioxins and furans. The remaining soils were collected along roads dikes and spillways within the refuge, and represented background areas, as well as areas which were subject to oiling. At each of these sites, three individual samples were typically taken; center of the road/dike, side slope of the road/dike, and at the toe of the slope. Samples were obtained from a depth of 30-36 inches using a power auger. Each sample was deposited in a stainless steel pan for mixing before being transferred to a chemically clean glass jar. To eliminate any accidental spillage of cleaning solvents in the field, all collection and handling gear were washed with soap and water between sampling sites to cut any oil residue. Samples were placed on ice for shipment to the East Lansing Field Office (ELFO) where they were frozen prior to shipment to analytical laboratories. A subset of 25 soil/sediment samples were analyzed for organochlorine pesticides (OC) including total PCBs (gas-liquid chromatography), aliphatic and aromatic hydrocarbon compounds (gas chromatography/mass spectrometry (GC/MS) with selective ion monitoring) by analytical laboratories under contract to the Service's Patuxent Analytical Control Facility (PACF). The Regional Office would not approve the analysis of the 3 composite soil samples from the work areas for dioxins and furans. However, 2 of the 3 composite samples were later submitted for the H4IIE rat hepatoma bioassay to measure enzyme induction potencies of sample extracts expressed in units of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) equivalents. 2,3,7,8-TCDD is the most potent of the planar chlorinated hydrocarbon compounds to induce the cytochrome P-450 enzyme system. The bioassay was supervised by Dr. M. Mora, Pesticide Research Center, Michigan State University, East Lansing, MI.

The possible migration of contaminants from oiled areas to refuge impoundments via groundwater was evaluated in September 1987 by using Semi-Permeable Membrane Devices (SPMD) deployed at 18 sites by Dr. M. Zabik and M.A. Heindorf, Pesticide Research Center, Michigan State University. These 18 sites represented a subset of the 25 soil/sediment sites from which samples were collected and submitted for standard chemical analyses. A hand held power auger was used to bore through the roads, dikes, and work areas to reach the upper groundwater zone. Two isooctane-filled polypropylene bags were placed in each excavated hole at different depths ranging between 5-24 inches. The shallower bag was placed in the vadose zone while the deeper bag was situated in the upper saturated zone. Each hole was backfilled with the excavated soil. The 36 bags were retrieved after 7 days of exposure, rinsed with distilled water to dislodge adhering soil particles, and the solvent drained into chemically clean jars for transport back to the laboratory. Mass spectroscopy was used to qualitatively identify organic compounds.

All biota (except mink, river otter and muskrat) were collected by W. Bowerman through a Cooperative Agreement with Dr. T.J. Peterle with the Service's Cooperative Wildlife Research Unit, Ohio State University, Columbus, OH. Small mesh fyke nets were set for 4 trap nights each in Pools C-3, M-2, A, E and C-2. A total of 161 fish were collected between April 20 and June 18, 1988, representing northern pike (*Esox lucius*), yellow perch (*Perca flavescens*), white sucker (*Catostomus commersoni*), rock bass (*Ambloplites rupestris*), pumpkinseed (*Lepomis*

gibbosus), and black, brown and yellow bullhead (*Ictalurus melas*, *I. nebulosus*, and *I. natalis* respectively). In addition, 4 snapping turtles (*Chelydra serpentina*) and 7 crayfish (Order Decapoda) were caught and retained. Waterfowl were collected from all 3 management units with firearms using steel shot. Eleven birds were shot between May 13 and June 17, 1988, representing Canada goose (*Branta canadensis*), ring-necked duck (*Aythya collaris*), hooded merganser (*Lophodytes cucullatus*), and mallard (*Anas platyrhynchos*). All these specimens were wrapped whole in aluminum foil and frozen for shipment to ELFO.

All mink (*Mustela vison*), river otter (*Lutra canadensis*) and muskrat (*Ondatra zibethicus*) samples were obtained from existing specimens archived at the refuge. These samples were obtained between 1983-1989 from cooperative trappers operating on the refuge, and consisted of frozen skinned carcasses. Six mink, 5 river otter and 16 muskrat were transferred to ELFO. Two additional river otters were analyzed for background purposes. One otter was provided by D. Elsing, Forest Wildlife Biologist, Hiawatha National Forest. This otter was trapped on the Whitefish River in Delta County, at a site on the river accessible to anadromous fish migrating from Lake Michigan. The second otter was provided by Dr. K. Stromborg, USFWS, Green Bay Field Office. This otter was accidentally taken in a fyke net set along the Green Bay shoreline of Lake Michigan.

A subset of 25 of the largest individual fish were processed by ELFO for analysis. The largest fish were selected to best estimate risk from human and wildlife consumption. Five of the smallest fish remained as whole fish samples. The remaining 20 fish were weighed whole prior to the preparation of a skinless fillet. A scale was removed from each fish for aging purposes. The fillet and the remaining carcass (including the fillet skin) were reweighed, wrapped separately in aluminum foil and refrozen. Fourteen northern pike, 4 yellow perch and 2 white sucker were processed in this manner. Three snapping turtles were processed by the removal of muscle tissue and abdominal fat samples. Each sample was weighed, placed in chemically clean glass jars and refrozen. Nine of the eleven waterfowl were processed. Each bird was weighed whole before the removal of breast muscle and liver samples. Each sample was weighed, placed in chemically clean jars and refrozen. All mink and river otters were sexed and their livers processed in a similar manner to the above samples. Skulls were retained for future aging.

All of these biota samples were submitted for an OC scan and mercury (Hg - cold vapor atomic absorption) analysis by analytical laboratories under contract to the PACF. Quality Assurance/Quality Control (QA/QC) of the contract laboratories was monitored by PACF through analysis of duplicate samples, matrix and reagent blanks, spiked samples, calibration checks, standard reference material samples, method blacks and GC/MS confirmation. Based on the QA/QC program, PACF determined that the results for the organic analyses (OCs, aliphatic and aromatic hydrocarbons) were acceptable. However, the results of the Hg analyses were deemed unacceptable. Based on these results, ELFO and PACF had 15 samples (those with the highest Hg results reported from the analytical laboratory) reanalyzed by the PACF. Based on these results, a correction factor (1.45) derived as the mean of the ratios of the results (PACF:contract laboratory) was calculated. This number was used by ELFO to correct those

contract laboratory's results which were not reanalyzed by PACF. Therefore, the Hg results contained in this report should be considered approximations only. The 6 river otter liver samples were also submitted for the H4IIE rat hepatoma bioassay of 2,3,7,8-TCDD equivalents by Michigan State University, as described above.

Results and Discussion

Soils

The results of the soil analyses showed surprisingly little contamination considering the potential threats from road oiling and wood preservative use. Only 3 of the 25 samples had measurable levels of *p,p'*-DDE, and then only at the method level of detection (0.01 *u*g/g). No other OC compounds were detected on or off the refuge by the standard scan methodology.

Of great interest was the detection of aliphatic and aromatic compounds on the refuge (Table 1). While both of these groups of compounds were detected at all sites on and off the refuge, concentrations were decidedly higher at 3 sites on the refuge; Bone Yard #2 and Wood Burning Areas #2 & #3. At these 3 work area sites, nearly every individual aliphatic and aromatic compound contributed to the total value. However, the bulk of the total aromatic hydrocarbon values was derived from 3 compounds; the carcinogen chrysene and the non-carcinogens pyrene and 1,2-benzanthracene. There was less variability in the concentrations of the individual aliphatic compounds contributing to the totals. Outside of the work areas, what little aliphatic and aromatic contamination was detected in soils on oiled roads and dikes, was found at levels similar to background sites on and off the refuge. In fact the Manistique River sediment sample at Highway M-77, up gradient of the refuge, showed higher concentrations of aliphatics and aromatics than samples from oiled roads and dikes.

The analysis of the SPMDs confirmed the presence of straight chain aliphatic hydrocarbons at various sampling sites (Heindorf 1992, M. Zabik pers. comm.). Those SPMDs with higher qualitative measures of hydrocarbons (coloration of isooctane) were associated with primarily sandy soils containing less humic materials. Hydrocarbons tend to bind with humic materials, which should limit their uptake by the SPMDs. The data showed relatively higher hydrocarbon levels in the shallower SPMDs when compared to those in the deeper saturated zone. The interaction of the hydrocarbons and the surface soils was believed to have limited the downward migration of hydrocarbons into the groundwater. It appears from these data that the refuge impoundments have not been compromised by hydrocarbons via shallow groundwater discharge.

Few criteria or standards have been promulgated for aliphatic or aromatic compound for the protection of sensitive aquatic organisms or wildlife. The Michigan Department of Natural Resources has promulgated cleanup criteria for certain aromatic hydrocarbons, under Public Act 307, Michigan Environmental Response Act of 1982. One set of promulgated soil cleanup criteria are designed to protect surface waters via discharge of contaminants from groundwater. Two aromatic compounds, chrysene and benzo(a)pyrene, exceeded soil cleanup standards at only

2 of the 25 soil sampling sites, Bone Yard #2 and Wood Burning Area #2. Both compounds are listed as carcinogens.

A variety of chlorinated organic compounds can induce some measure of enzymatic response from the H4IIE bioassay through their ability to mimic the molecular configuration of 2,3,7,8-TCDD. Among these compounds are various dioxin and furan congeners, planar PCBs, polychlorinated-napththalenes, -diphenyl ethers and -diphenyl toulenes (Jones *et al.* 1993). The results of the bioassay showed only relatively low levels of TCDD-EQ in soils at the Bone Yard and Wood Burning Areas (Table 2). These levels are extremely low when compared to the biologically productive sediments contained within the North and South Cells of the Grassy Island Confined Disposal Facility (CDF) in the Detroit River at Wyandotte NWR (Best *et al.* 1992). However, the Seney values are elevated when compared to sandy offshore sediments collected off Alpena in Thunder Bay, Lake Huron (Jones *et al.* 1993). These sandy sediments, with low organic binding potentials, in a high energy shoreline environment, would likely induce little bioassay response. The absence of detectable levels of total PCBs at these Seney NWR sites, as evaluated by the OC scan, is consistent with the relatively low TCDD-EQs. The results of the SPMD exposures further confirmed the qualitative absence of chlorinated organic compounds (M. Zabik pers. comm.). Despite past practices, the soils at the Bone Yard and Wood Burning Areas should be considered relatively free of dioxin-like contamination.

Fish

As might be expected from the soil analyses, there were few detectable OCs in the fish collected in the refuge pools. Only 1 sample, a northern pike skinless fillet from Pool C-3, had levels of *p,p'*-DDD and *p,p'*-DDT at detection limits (0.01 *u*g/g). No other OCs were detected. Low levels of OCs in fish are expected from inland areas of Michigan removed from point source discharges and protected by dams blocking the runs of anadromous Great Lakes fish (Giesy *et al.* 1994a).

Hg, on the other hand, was detected in all but one of the submitted samples (Table 3). In general, the larger, and presumably older fish had the highest levels of Hg. Several of the largest northern pike from Pools M-2 and A had Hg levels in skinless fillets, as well as whole body, which exceeded State and/or Federal health standards.

The anticipated effects of these levels of Hg on fish-eating birds can be estimated by employing forage fish:avian egg Biomagnification Factors (BMF). In the mid-1980s, ELFO cooperated with the Ottawa National Forest, in the western Upper Peninsula of Michigan, in assessing the level of contamination in forage yellow perch and addled eggs of the common loon (*Gavia immer*). Unpublished data from that study yielded Hg BMFs of 4.8 and 6.1 for the 2 lakes where fish and eggs were both available. Using the mean BMF of 5.45 and the smallest yellow perch collected from Pool A as appropriate forage for a loon (Table 3), one would expect loons to accumulate Hg within their eggs ranging between <0.22-1.7 *u*g/g, wet weight. The effects of Hg on other larger fish-eating birds, such as the osprey (*Pandion haliaetus*) or bald eagle (*Haliaeetus leucocephalus*), can be similarly estimated by assuming a similar BMF for those

species, and using the Hg results from the larger fish. This results in estimated Hg residues in birds eggs for various fish species and refuge pools as follows:

northern pike - 2.3-4.1 *ug*/g (M-2), 1.6-3.2 *ug*/g (A), 0.55-0.71 *ug*/g (C-3), 0.87-1.4 *ug*/g (E),
yellow perch - 0.76-1.3 *ug*/g (C-3) and
white sucker - 0.49-0.93 *ug*/g (A).

These calculated residues fall within the range of 0.79-2.0 *ug*/g associated with impaired reproduction in various bird species (as reviewed in Eisler 1987). In feeding experiments, adverse reproductive effects were noted at 0.85 *ug*/g Hg in mallard eggs (Heinz 1979), and 0.5-1.5 ug/g in ringed-necked pheasant (*Phasianus colchicus*) eggs (Fimreite 1971).

Specific to fish-eating birds, Eisler (1987) cites Hg residues in eggs of 1.3-2.0 *ug*/g, fresh weight associated with reduced hatching success in the white-tailed sea-eagle (*H. albicilla*) and the common loon (*Gavia immer*). For the common tern (*Sterna hirundo*), Fimreite (1974) noted reduced hatching and fledgling success at Hg levels in eggs within the range of 1.0-3.6 *ug*/g, wet weight. Similarly, Conners *et al.* (1975) reported poor reproductive success at a common tern colony in Hamilton harbor, Ontario, Canada, associated with egg residues of 1.1 *ug*/g Hg, wet weight. However, this study concluded that Hg and other detected metals did not appear to be the primary cause of the reproductive failure. In a Finnish study of ospreys, addled egg Hg residues of 0.1-0.4 *ug*/g, fresh weight were considered not to be the cause of the eggs' failure to hatch (Hakkinen and Hasanen 1980), a range of no effect values below the above cited effect levels.

Barr (1986) suggests that Hg may have impaired loon reproduction in northwestern Ontario through reduced egg production and aberrant adult behavior related to nest and territory fidelity, rather than through embryotoxic effects. In feeding studies with chickens, Scott *et al.* (1975) observed significant reductions in adult production of eggs, as well as egg hatchability resulting from methylmercury. However, these effects were noted at total Hg concentrations in the egg several times greater than the levels cited by Barr (1986). Methylmercury is not known to be teratogenic, but causes neurologic injury in both adults and developing embryos (Peereboom-Stegeman 1987). Therefore, in the case of the common loon, the effects of Hg on adult behavior and egg production may be manifested at lower exposure levels than embryotoxic effects. Little is known about the relative sensitivity among fish-eating bird species to Hg. However, in the period 1981-1993, Seney's bald eagles exhibited measures of reproduction characteristic of a healthy expanding population. The bald eagles on the refuge had a 67% success rate producing a mean 1.03 fledged young per occupied breeding area (ELFO unpublished data). Although no samples were specifically collected from Seney NWR, addled bald eagle eggs from inland and Great Lakes shoreline sites in Michigan and Ohio (1986-1989) had Hg residues in the range of 0.06-0.31 *ug*/g, fresh weight (ELFO unpublished data). These Hg residues are not considered to affect eagle egg hatchability, and are well below the above cited effect levels for other species. This suggests that productivity of Seney's bald eagles has not been impacted by long term exposure to Hg or other onsite contaminants through the forage fish base. A similar conclusion

was reached by Bowerman et al. (1994) for bald eagles throughout the Great Lakes basin, as monitored by Hg in feathers.

Based on the approximate nature of the Hg results (see Methods), it would be premature to alter the management direction of the refuge for fish-eating birds or sports fishing access. However, the poor QA/QC performance of the contract laboratory and the exceedence of the public health standards, suggest that the Service should resample the fish populations on the refuge to adequately document the Hg levels in fillets and whole fish.

Waterfowl

As was previously seen in sediments and fish, there were few OCs detected in skinless breast muscle or liver samples from waterfowl. *p,p'*-DDE was the compound most often detected, but only at or marginally above wet weight detection limits (Table 4). Oxychlorodane and heptachlor epoxide were also detected in the mallard liver, and in the muscle and liver of the hooded merganser. Mirex was also detected in both hooded merganser samples. It is of interest to note that the hooded merganser, a fish-eating species highest in the food web of the sampled waterfowl, had the highest residues of those OCs detected. Conversely, the Canada goose, being the most herbivorous of the waterfowl and lowest in the food web, had no detectable OCs.

The results for Hg in the waterfowl samples showed little accumulation in muscle or liver tissue, except for both hooded merganser samples which possibly reflects the higher trophic web position (Table 5). Overall, the Hg residues are similar to the results from waterfowl surveys over broad geographical areas in Canada (Vermeer and Armstrong 1972, Pearce *et al.* 1976) where the most likely source of mercury would be via aerial deposition. The Seney results were surprisingly similar, although lower, than those found in the waterfowl collected at the Grassy Island CDF, Wyandotte National Wildlife Refuge in the Detroit River (Best *et al.* 1992). Given the historical Hg problems in the St. Clair-Detroit River system, the waterfowl from the Grassy Island CDF were unexpectedly low in Hg. High Hg residues were encountered in waterfowl from northwestern Ontario and Lake Paijanne in Finland, where poor water quality was related, in part, to improper disposal of Hg from pulp and paper mills or chlor-alkali plants (Vermeer and Armstrong 1972, Vermeer *et al.* 1973, Fimreite 1973, 1974, Sarkka *et al.* 1978).

Hg does not appear to be a threat to waterfowl at Seney NWR. There are currently no State or Federal guidelines regarding Hg in edible portions of avian or mammalian wildlife for human consumption. However, if one were to consider the edible portion of a fish as an analogous situation, all of the waterfowl samples would fall well below both the State of Michigan level of public concern (0.5 *u*g/g, wet weight) and the US Food and Drug Administration tolerance level (1.0 *u*g/g, wet weight) for Hg in fish.

Furbearers

As was seen in other sampled media, there was little OCs detected in livers from mink or otter. Only *p,p'*-DDE was detected in 1 mink liver at the lower limit of detection (0.01 *u*g/g, wet

weight). The absence of detectable amounts of total PCBs is consistent with the low TCDD-EQs detected in the otter livers from Seney (Table 6). The otter livers from background sites contained higher levels of TCDD-EQ relative to the Seney samples. Both of these sites, Green Bay shoreline and the Whitefish River, have the potential for otters being exposed to Great Lakes fish containing dioxin-like contamination. The Whitefish River in Delta County supports runs of anadromous fish from Green Bay and Lake Michigan at various times of the year, while the Green Bay site would provide potential year round exposure.

The low residues of total PCBs and TCDD-EQs in the livers of Seney mink and otter should not result in reproductive impairment. In a recent feeding study using 3 different percentages of Great Lakes fish in mink diets, all 3 diets caused reproductive impairment at liver residues as low as 2.19 *u*g/g, wet weight total PCBs and 380 *p*g/g, wet weight TCDD-EQs (Heaton 1992). Only the control diet (0.09 *u*g/g total PCBs, <5 *p*g/p TCDD-EQ) containing no Great Lakes fish yielded normal reproduction in mink. Similar results were reported by Wren *et al.* (1987a,b). An even earlier feeding study on mink (Platonow and Karstad 1973) showed reproductive impairment at liver residues as low as 0.39 *u*g/g, wet weight total PCBs from a diet containing 0.30 *u*g/g, wet weight total PCBs. Several field studies have documented PCB residues from mink and otter livers in excess of these effect levels in areas where reproductive impairment is known or suspected (Henny *et al.* 1981, Foley *et al.* 1988).

The data suggests that Seney otters and mink are not currently being exposed to PCBs and other dioxin-like compounds to the levels which would affect reproduction. However, the background sites may be experiencing reproductive impairment at the detected levels of TCDD-EQ exposure. This has implications to the future condition at Seney NWR. Planned modifications to the Manistique Papers Dam near the mouth of the Manistique River may result in the deliberate or accidental upstream passage of anadromous fish, currently blocked by the dam. The upstream movement of contaminants via fish has been identified by ELFO as an unacceptable risk to the bald eagle (Kubiak and Best 1991), as well as other sensitive species such as the mink, on river systems in the Lower Peninsula of Michigan (Giesy *et al.* 1994b). The Service should continue to seek modifications to the Manistique Dam which would result in no passage of anadromous fish into the Seney NWR.

Hg levels in livers from mink and otter (Table 6) indicated bioaccumulation consistent with the levels detected in fish, a major component of the prey base for both species. In controlled feeding studies with, mink, Wren *et al.* (1987a,b) demonstrated no overall reproductive impairment at administered diets of 1 *u*g/g Hg, wet weight. This dietary level resulted in Hg residues in livers of dead or euthanized adults of 30-44 *u*g/g, wet weight. In addition, there was some indication of acute Hg toxicity to females at this dietary level in combination with cold stress. However, this study further demonstrated reproductive impairment via reduced kit survival from synergistic effects between PCBs and Hg at dietary levels of 0.5 *u*g/g, wet weight for each compound. In our evaluation at Seney NWR, 6 of 25 whole fish samples exceeded this 0.5 *u*g/g Hg level. Fortunately, no PCBs were detected in any of the fish samples. This demonstrates again the need to keep anadromous Great Lakes fish out of the Seney NWR.

Snapping Turtles

Samples from snapping turtles contained little OC residues (Table 7). No OCs were detected in muscle samples. In all 3 fat samples, *p,p'*-DDE was detected at or near the detection limit. Oxychorodane, heptachlor epoxide, and *t*-nonachlor were also detected in 1 or 2 samples at similar levels. The absence of PCBs in snapping turtles bodes well for this species at Seney NWR. PCBs and other dioxin-like compounds are known to result in reproductive impairment in Great Lakes snapping turtles, including hard and soft tissue anomalies (Bishop *et al.* 1991).

Unlike the fish-eating hooded merganser, the snapping turtles did not accumulate comparable levels of Hg in muscle fat tissues (Table 7). Livers were not evaluated for comparison to the furbearers. The detected levels probably have little impact on the health of this long-lived, upper trophic level species.

Recommendations

The suggestion that dioxin-like contaminants or other organic compounds may have been introduced into the Seney NWR via road oiling and/or use of wood preservatives in work areas is not substantiated by this assessment effort. Aliphatic and aromatic hydrocarbon compounds are largely restricted to the 2 refuge work areas and do not exceed State of Michigan promulgated cleanup standards. Furthermore, the detected hydrocarbons do not appear to have migrated from the work areas. PCBs, TCDD-EQs and other OC compounds were only minimally detected in all media sampled and pose no current threat to fish and wildlife resources on the refuge. This situation could change if anadromous Great Lakes fish are allowed to pass into the refuge as a result of planned modifications to the Manistique Papers Dam near the mouth of the Manistique River. The introduction of PCBs, and other dioxin-like compounds, could threaten to affect the reproductive health of fish and wildlife as a complex mixture, as well as interact synergistically with current Hg tissue burdens. These Hg burdens may already be affecting the health of some individuals and species. The interpretation of the Hg data is hindered by the estimated results presented in this report, due to the poor QA/QC of the contract laboratory. This needs to be resolved prior to proceeding onto issues of potential sources and refuge management options. No site specific remedial actions are recommended at this time.

Based on the above data and discussions, we offer the following recommendations for Service consideration:

> Due to the elevated and estimated nature of the Hg results, biota should be resampled at Seney NWR and reanalyzed for Hg, with emphasis on fish and fish-eating wildlife. In the short term, this should be accomplished as a Service effort between ELFO's Environmental Contaminants Program and Seney NWR. If Hg continues to be a problem, then an expanded long term assessment of fish and wildlife exposure and source identification may be incorporated into the

Biomonitoring of Environmental Status and Trends Program being developed by the National Biological Service.

2. The Service should continue to seek modifications to the Manistique Papers Dam structure which will block all upstream passage of Great Lakes anadromous fish into the refuge vicinity. If there is evidence or suggestions that Great Lakes fish are passing the modified control structure, then any further assessment of biota at Seney NWR, as resulting from recommendation #1, will need additional analyses for OCs and TCDD-EQs.

Literature Cited

Barr, J.F. 1986. Population Dynamics of the Common Loon (*Gavia immer*) Associated with Mercury-Contaminated Waters in Northwestern Ontario. Canadian Wildlife Service, Occasional Paper No. 56. 23 pp.

Best, D.A., T.J. Kubiak and D.E. Boellstorff. 1992. Survey of Contaminants in Sediment and Biota within the Grassy Island Confined Disposal Facility, Wyandotte National Wildlife Refuge. U.S. Fish Wildl. Serv., East Lansing Field Office. 28 pp. + appendices.

Bowerman, W.W. IV, E.D. Evans, J.P. Giesy and S. Postupalsky. 1994. Using Feathers to Assess Risk of Mercury and Selenium to Bald Eagle Reproduction in the Great Lakes. Arch. Environ. Contam. Toxicol. 27:294-298.

Bishop, C.A., R.J. Brooks, J.H. Carey, P. Ng, R.J. Norstrom and D.R.S. Lean. 1991. The Case for a Cause-Effect Linkage between Environmental Contamination and Development in Eggs of the Common Snapping Turtle (*Chelydra serpentina*) from Ontario, Canada. J. Toxicol. Environ. Health. 23:521-547.

Connors, P.G., V.C. Anderlini, R.W. Risebrough, M. Gilbertson and H. Hays. 1975. Investigations of Heavy Metals in Common Tern Populations. Can. Field-Nat. 89:157-162.

Eisler, R. 1987. Mercury Hazards to Fish, Wildlife, and Invertebrates: A Synoptic Review. U.S. Fish Wildl. Serv. Biol. Rep. 85(1.10). 90 pp.

Fimreite, N. 1971. Effects of Dietary Methylmercury on Ringed-Necked Pheasants. Canadian Wildlife Service, Occasional Paper No. 9. 39 pp.

Fimreite, N. 1973. Mercury Contamination of Aquatic Birds in Northwestern Ontario. XIth. International Congress of Game Biologists, National Swedish Environmental Protection Board. p 479-489.

Fimreite, N. 1974. Mercury Contamination of Aquatic Birds in Northwestern Ontario. J. Wildl. Manage. 38:120-131.

Foley, R.E., S.J. Jackling, R.J. Sloan and M.K. Brown. 1988. Organochlorine and Mercury Residues in Wild Mink and Otter: Comparison with Fish. Environ. Toxicol. Chem. 7:363-374.

Giesy, J.P., D.A. Verbrugge, R.A. Othout, W.W. Bowerman, M.A. Mora, P.D. Jones, J.L. Newsted, C. Vandervoort, S.N. Heaton, R.J. Aulerich, S.J. Bursian, J.P. Ludwig, M. Ludwig, G.A. Dawson, T.J. Kubiak, D.A. Best and D.E. Tillitt. 1994a. Contaminants in Fishes from Great Lakes-Influenced Sections and above Dams of Three Michigan Rivers. I: Concentrations of Organo Chlorine Insecticides, Polychlorinated Biphenyls, Dioxin Equivalents, and Mercury. Arch. Environ. Contam. Toxicol. 27:202-212.

Giesy, J.P., D.A. Verbrugge, R.A. Othout, W.W. Bowerman, M.A. Mora, P.D. Jones, J.L. Newsted, C. Vandervoort, S.N. Heaton, R.J. Aulerich, S.J. Bursian, J.P. Ludwig, G.A. Dawson, T.J. Kubiak, D.A. Best and D.E. Tillitt. 1994b. Contaminants in Fishes from Great Lakes-Influenced Sections and above Dams of Three Michigan Rivers. II: Implications for Health of Mink. Arch. Environ. Contam. Toxicol. 27:213-223.

Hakkinen, H. and E. Hasanen. 1980. Mercury in Eggs and Nestlings of the Osprey (*Pandion haliaetus*) in Finland and its Bioaccumulation from Fish. Ann. Zool. Fennici. 17:131-139.

Heaton, S.N. 1992. Effects on Reproduction of Ranch Mink Fed Carp from Saginaw Bay, Michigan. MS Thesis, Michigan State University. 152 pp.

Heindorf, M.A. 1992. Two Topics in Trace Analysis: The Development of a Passive Water Sampling Device and the Development of a Ketone-Selective Derivatizing Reagent. PhD Dissertation, Michigan State University. 274 pp.

Heinz, G.H. 1979. Methylmercury: Reproductive and Behavioral Effects on Three Generations of Mallard Ducks. J. Wildl. Manage. 43:394-401.

Henny, C.J., L.J. Blus, S.V. Gregory and C.J. Stafford. 1981. PCBs and Organochlorine Pesticides in Wild Mink and River Otters from Oregon. In: J.A. Chapman and D. Pursley (Eds.), Worldwide Furbearer Conference Proceedings, August 3-11, 1980, Vol. III. Worldwide Furbearer Conference, Inc., Frostburg, MD. p 1763-1780.

Jones, P.D., G.T. Ankley, D.A. Best, R. Crawford, N. DeGalan, J.P. Giesy, T.J. Kubiak, L.P. Ludwig, J.L. Newsted, D.E. Tillitt and D.A. Verbrugge. 1993.

Biomagnification of Bioassay Derived 2,3,7,8-tetrachlorobibenzo-*p*-dioxin Equivalents. Chemosphere. 26:1203-1212.

Kubiak, T.J. and D.A. Best. 1991. Wildlife Risks Associated with Passage of Contaminated, Anadromous Fish at Federal Energy Regulatory Commission Licensed Dams in Michigan. U.S. Fish Wildl. Serv., East Lansing Field Office. 24 pp. + appendices.

Pearce, P.A., I.M. Price and L.M. Reynolds. 1976. Mercury in Waterfowl from Eastern Canada. J. Wildl. Manage. 40:694-703.

Peereboom-Stegeman, J.H.J.C. 1987. Toxic Trace Elements and Reproduction. Toxicol. Environ. Chem. 15:273-292.

Platonow, N.S. and L.H. Karstad. 1973. Dietary Effects of Polychlorinated Biphenyls on Mink. Can. J. Comp. Med. 40:421-428.

Sarkka, J., M. Hattula, J. Janatuinen, J. Paasivirta and R. Palokangas. 1978. Chlorinated Hydrocarbons and Mercury in Birds of Lake Paijanne, Finland - 1972-74. Pestic. Monit. J. 12:26-35.

Scott, M.L., J.R. Zimmermann, S. Marinsky, P.A. Mullenhoff, G.L. Rumsey and R.W. Rice. 1975. Effects of PCBs, DDT, and Mercury Compounds upon Egg Production, Hatchability and Shell Quality in Chickens and Japanese Quail. Poultry Sci. 54:350-368.

Vermeer, K. and F.A.J. Armstrong. 1972. Mercury in Canadian Prairie Ducks. J Wildl. Manage. 36:179-182.

Vermeer, K., F.A.J. Armstrong and D.R.M. Hatch. 1973. Mercury in Aquatic Birds at Clay Lake, Western Ontario. J. Wildl. Manage. 37:58-61.

Wren, C.D., D.B. Hunter, J.F. Leatherland and P.M. Stokes. 1987a. The Effects of Polychlorinated Biphenyls and Methylmercury, Singly and in Combination on Mink. I: Uptake and Toxic Responses. Arch. Environ. Contam. Toxicol. 16:441-447.

Wren, C.D., D.B. Hunter, J.F. Leatherland and P.M. Stokes. 1987b. The Effects of Polychlorinated Biphenyls and Methylmercury, Singly and in Combination on Mink. II: Reproduction and Kit Development. Arch. Environ. Contam. Toxicol. 16:449-454.

Table 1. Dry Weight Concentrations of Organic Compounds (*ug*/g) in Terrestrial Soils and Aquatic Sediments, Seney NWR.

	Total Aromatics[1] (*ug*/g, dry wt.)	Total Aliphatics[2] (*ug*/g, dry wt.)
Oiled Sites		
Bone Yard # 1	0.24	0.05
Bone Yard # 2	7.8	370
Bone Yard # 3	0.15	0.04
Bone Yard # 4	0.03	0.15
Bone Yard # 5	0.15	0.27
Bone Yard # 6	0.02	0.10
Wood Burning Area # 1	0.02	0.07
Wood Burning Area # 2	4.3	48
Wood Burning Area # 3	2.2	38
Wood Burning Area # 4	0.11	0.27
Entrance Rd # 1, Shoulder	0.01	0.02
Entrance Rd # 2, Shoulder	0.10	0.99
F Pool Rd, Center	0.58	0.13
Rd, E/F Spillway, Center	0.01	0.01
J Pool Rd, Center	0.02	0.06
G Pool Rd, Center	0.04	0.14
Rd, E/D Spillway Center	0.02	0.03
A Pool Rd, Toe of Slope	0.04	0.06
B Pool Rd, Center	0.04	0.02
Rd, B/C Spillway, Center	0.01	0.06
Rd, E/C Spillway, Center	0.46	0.06
Background Sites		
Marsh Creek Pool Rd, Center	0.08	0.04
M-2 Pool Rd, Center	<0.01	<0.01
US-2, Lake Mich dune sand	0.04	0.01
Manistique R sediment, M-77	0.27	0.35

[1] Summation of 14 Polynuclear Aromatic Hydrocarbon compounds.
[2] Summation of 13 Aliphatic Hydrocarbon compounds.

Table 2. Dry Weight Concentrations of Dioxin Equivalents (*pg*/g) in Soils and Sediments from Seney NWR and Reference Sites.

		TCDD-EQ[1] (*pg*/g) dry weight
Seney NWR		
Bone Yard # 1-3	Soil Composite	387
Wood Burning Area # 7-10	Soil Composite	116
Wyandotte NWR[2]		
CDF-North Cell	Sediment-Fine	16591
CDF-South Cell	Sediment-Fine	1357
Thunder Bay-Alpena[3]		
Navigation # 1	Sediment Composite-Sand	18
Navigation # 2	Sediment Composite-Sand	8

1 H4IIE rat hepatoma bioassay measures enzyme induction potencies of sample extracts expressed in units of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin equivalents.

2 Best *et al.* 1992.

3 Jones *et al.* 1993.

Table 3. Approximate Wet Weight Concentrations of Mercury (*ug*/g) in Paired Skinless Fillet and Whole Body Fish Samples, Seney NWR.

				Hg (*ug*/g, wet wt.)	
	Pool	Length (cm)	Total Wt.(g)	Fillet	Whole Body
N. Pike	M-2	71	2571	1.4[1,2,3]	0.55[2,3]
		62	1684	0.96[2,3]	0.64[2]
		60	1272	1.1[1,2,3]	0.76[2]
		44	473	0.59[2]	0.43
	A	67	1637	0.44[3]	0.57[2]
		53	895	0.53[2]	0.31
		45	521	0.52[2,3]	0.58[2]
		46	489	0.40	0.30
		43	419	0.55[2]	0.31
	C-3	41	389	0.16	0.09
		38	272	0.17	0.10
		35	233	0.22	0.13
	E	56	1228	0.43	0.26
		55	1155	0.18	0.16
Y. Perch	C-3	30	318	0.45	0.14
		25	244	0.28	0.16
		27	228	0.39	0.20
		26	200	0.42	0.23
	A	18	61	-	0.17
		15	39	-	0.10
		16	35	-	0.10
		15	34	-	0.32
		11	13	-	<0.04
W. Sucker	A	40	937	0.19	0.17
		38	836	0.21	0.09

Table 3. - continued.

Exceeds USFDA Tolerance Level for Mercury in fish for interstate commerce, >1.0 *u*g/g, wet weight.

[2] Exceeds MDPH level of public health concern for Mercury in fish, >0.5 *u*g/g, wet weight.

[3] Actual result from PACF; others are estimates using correction factor (1.48) derived from mean of the ratios of the results (PACF:contract laboratory).

Table 4. Wet Weight and Lipid Weight Concentrations of *p,p'*-DDE (*ug*/g) in Skinless Breast Muscles and Livers from Adult Waterfowl, Seney NWR.

		p,p'-DDE (*ug*/g)			
		Muscle		Liver	
	Pool	Wet Wt.	Lipid Wt.	Wet Wt.	Lipid Wt.
C. Goose					
Ad. ♀	J/G Burn	ND[1]	ND[2]	ND[1]	ND[2]
Ad. ♀	C-3	ND[1]	ND[2]	ND[1]	ND[2]
Ad. ♂	J/G Burn	ND[1]	ND[2]	ND[1]	ND[2]
Mallard					
Ad. ♂	B	0.01	0.98	0.03	1.4
R.-N. Duck					
Ad. ♀	F	0.01	0.50	ND[1]	ND[2]
Ad. ♂	J	ND[1]	ND[2]	0.02	0.39
Ad. ♂	F	0.01	0.44	0.03	1.0
Ad. ♂	C-3	0.01	0.48	ND[1]	ND[2]
H. Merganser					
Ad. ♀	J	0.20	2.4	0.38	11.[3]

[1] *p,p'*-DDE not detected, <0.01 *ug*/g, wet weight.
[2] *p,p'*-DDE not detected, <0.051 *ug*/g (mean), lipid weight.
[3] Exceeds USFDA Tolerance Level for Total DDT in poultry for interstate commerce, >5.0 *ug*/g, lipid weight.

Table 5. Approximate Wet Weight Concentrations of Mercury (*ug*/g) in Skinless Breast Muscles and Livers from Adult Waterfowl, Seney NWR.

		Hg (*ug*/g, wet wt.)	
	Pool	Muscle	Liver
C. Goose			
Ad. ♀	J/G Burn	ND[1]	ND[1]
Ad. ♀	C-3	ND[1]	ND[1]
Ad. ♂	J/G Burn	ND[1]	ND[1]
Mallard			
Ad. ♂	B	0.14	0.32
R.-N. Duck			
Ad. ♀	F	0.14	0.14
Ad. ♂	J	ND[1]	ND[1]
Ad. ♂	F	ND[1]	0.11
Ad. ♂	C-3	ND[1]	0.12
H. Merganser			
Ad. ♀	J	1.3[2]	10.[2]

[1] Hg not detected, <0.043 *ug*/g (mean), wet weight.

[2] Actual result from PACF; others are estimates using correction factor (1.48) derived from mean of the ratios of the results (PACF:contract laboratory).

Table 6. Approximate Wet Weight Concentrations of Mercury (*ug*/g) and Dioxin Equivalents (*pg*/g) in Livers from Mink and River Otters, Seney NWR.

	Year Collected	Location-Trapper	Hg (*ug*/g)	TCDD-EQ[1] (*pg*/g)
Mink				
♀	1987	Unit 2, North B Fe(?)	2.2[2]	-
♂	(?)	Pool C-3, westend	0.22	-
♀	(?)	Driggs R. Bridge, R-3(?) Rd.	0.15	-
♀	1987	Unit 2, Lower Grey M(?)	2.4[2]	-
♂	(?)	Driggs R. Bridge to Pool C-3	0.89[2]	-
♂	(?)	Delta Creek	0.55	-
River Otter				
♂	1983	Unit 4(?)-Hankamp	0.54[2]	47.27
♀	1988(?)	Unit 2, Pool A-2 - England(?)	4.4[2]	21.39
♂	1983	Unit 4 - Spencer	2.3[2]	13.81
♀	1987	Unit 5 - Alberts	3.2[2]	ND[3]
♀	1989	B/A Spillway - (?)	-	26.89
♂	1989	Whitefish R., Hiawatha NF	-	133.74
(?)	(?)	Green Bay	-	150.35

Method: H4IIE rat hepatoma bioassay measures enzyme induction potencies of sample extracts expressed in units of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin equivalents, Pesticide Research Center, Department of Fisheries and Wildlife, Michigan State University.
Actual result from PACF; others are estimates using correction factor (1.48) derived from mean of the ratios of the results (PACF:contract laboratory).
Limit of quantification = 5 *pg*/g, wet weight.

Table 7. Approximate Wet Weight Concentrations of Mercury (*ug*/g) and Wet and Lipid Weight Concentrations of *p,p'*-DDE in Muscle and Fat Samples from Snapping Turtles, Seney NWR.

		Hg[1] (*ug*/g, wet wt.)		*p,p'*-DDE (*ug*/g, wet wt.)		*p,p'*-DDE (*ug*/g, lipid wt.)	
	Pool	Muscle	Fat	Muscle	Fat	Muscle	Fat
S. Turtle							
#1	C-2	0.07	<0.10	ND[2]	0.04	ND[3]	0.06
#2	J	0.10	0.07	ND[2]	0.02	ND[3]	0.05
#3	C-2	0.23	<0.11	ND[2]	0.02	ND[3]	0.03

Estimated result using correction factor (1.48) derived from mean of the ratios of the results (PACF:contract laboratory).
p,p'-DDE not detected, <0.01 *ug*/g, wet weight.
p,p'-DDE not detected, <2.63 *ug*/g (mean), lipid weight.