













NORTHERN RIVER BASINS STUDY PROJECT REPORT NO. 47 ENVIRONMENTAL CONTAMINANTS IN MINK PEACE AND ATHABASCA RIVERS DECEMBER, 1991 AND JANUARY, 1992















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PREFACE:

The Northern River Basins Study was initiated through the "Canada-Alberta-Northwest Territories Agreement Respecting the Peace-Athabasca-Slave River Basin Study, Phase II - Technical Studies" which was signed September 27, 1991. The purpose of the Study is to understand and characterize the cumulative effects of development on the water and aquatic environment of the Study Area by coordinating with existing programs and undertaking appropriate new technical studies.

This publication reports the method and findings of particular work conducted as part of the Northern River Basins Study. As such, the work was governed by a specific terms of reference and is expected to contribute information about the Study Area within the context of the overall study as described by the Study Final Report. This report has been reviewed by the Study Science Advisory Committee in regards to scientific content and has been approved by the Study Board of Directors for public release.

It is explicit in the objectives of the Study to report the results of technical work regularly to the public. This objective is served by distributing project reports to an extensive network of libraries, agencies, organizations and interested individuals and by granting universal permission to reproduce the material.

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ENVIRONMENTAL CONTAMINANTS IN MINK, PEACE AND ATHABASCA RIVERS, DECEMBER, 1991 AND JANUARY, 1992

STUDY PERSPECTIVE

In recent years, much concern has been expressed about the potential harmful effects of pulp mill discharges into the aquatic ecosystems of the northern river basins. Evaluating wildlife for exposure to contaminants originating from industrial sources in the Peace, Athabasca and Slave River systems has been identified as one of the objectives of the Northern River Basins Study. The mink was chosen as a good candidate species for monitoring pulp mill contaminants in wildlife because it is associated with aquatic ecosystems, it is widespread throughout the study area and aquatic prey comprise a large portion of its diet. The mink is considered to be a particularly sensitive indicator of ecosystem health because it is a top trophic level

Related Study Questions

- 4a) What are the contents and nature of the contaminants entering the system and what is their distribution and toxicity in the aquatic ecosystem with particular reference to water, sediments and biota?
- 11) Have the riparian vegetation and riparian wildlife in the river basins been affected by exposure to organochlorines or other toxic compounds?

species that readily accumulates environmental pollutants.

In an earlier NRBS project, mink were collected for contaminant analyses by trappers with traplines in the Peace-Athabasca delta and adjacent to the Wapiti, Smoky, Peace and Athabasca rivers. On the mainstem rivers, efforts were focused on areas within 100 km upstream and downstream of pulp mill effluents. Samples collected were submitted to laboratories for contaminant analyses, including dioxins/furans, PCBs, chlorinated phenolics, polyaromatic hydrocarbons, metals and other persistent organochlorines. The purpose of this project is to provide an interpretation of these analytical results.

A total of 13 mink were obtained from three general collection sites in December, 1991 and January, 1992. Mink liver homogenates were combined at these three collection sites, producing composite samples for the Wapiti River downstream of the Weyerhaeuser Canada pulp mill, the Athabasca River downstream of the Hinton-Weldwood combined effluent, and the Peace-Athabasca delta. Most contaminants were not detected in composite mink liver samples, and those found were at very low concentrations. 2,3,7,8-tetrachlorodibenzo-*p*-dioxin was found at very low concentration near the Wapiti River (0.2 pg/g) and the Athabasca River (0.6 pg/g), but was not detected in the Peace-Athabasca delta sample. PCBs and DDE were slightly higher in the Wapiti River sample (total PCB <0.05 μ g/g; DDE 0.014 μ g/g) than in the Athabasca River and delta samples. Mercury was also somewhat elevated in the two river sites when compared with the delta site.

Because of the small sample sizes, it is not possible to draw inferences from these data about regional patterns of contaminant exposure in mink in the northern river basins. Nonetheless, the mink trapped in the upstream reaches of these river systems near point sources contained higher levels of contaminants than animals trapped far downstream in the Peace-Athabasca delta. Further sampling of mink would be required to determine if the slight variation in contaminant levels is the result of regional differences in contaminant exposure. Contaminant levels found in mink form this study were significantly lower than levels known to cause adverse effects in experimental mink.

The Study's Science Advisory Committee reviewed the report and recognized that the samples are too small on which to base firm conclusions and should be considered only as exploratory. However, to the extent that this report indicates low levels of contaminants by comparison with rivers elsewhere, the findings are reassuring. Further studies will be necessary in the future.

REPORT SUMMARY

Among the guiding questions of the Northern River Basins Study, questions 4 and 11 ask about the nature and contents of the contaminants entering the system and about their effects on riparian wildlife, respectively. This report addresses those questions by focusing on contaminant levels in one riparian species, the mink.

Analyses were done on mink that were collected from three sites: 15 km downstream from the Weyerhaeuser Canada pulp mill about 2 km from the Wapiti River on Bear and Olsen Creeks; on Galoot Lake on the Athabasca Delta and on creeks about 5 km from the Athabasca River and approximately 40 km downstream from Hinton. Prior to analyses, 10 mink livers were homogenized and pooled into three pools, representing the Wapiti River site, the Athabasca River site and the Athabasca Delta site.

The three pools were analyzed for dioxins/furans, chlorinated phenolics, organochlorine pesticides and PCBs and metals. Most contaminants were not detected in pooled mink liver homogenates. Those that were, were found at very low concentrations. The dioxin, 2378-tetrachlorodibenzo-*p*dioxin (TCDD) was found at a very low concentration in the Wapiti and Athabasca River pools but was not detected in the Athabasca Delta pool. Other contaminants, including PCBs and DDE were slightly higher in the Wapiti River pool than in the Athabasca River and Athabasca Delta pools. Mercury was also somewhat elevated at the two river sites when compared to the Delta site. Because of the absence of replication, it is not possible to draw inferences from these data about regional patterns of contaminant exposure in mink in the northern river basins. Nevertheless, it is interesting that mink trapped in the upstream reaches of these river systems near point sources contained higher levels of contaminants than animals trapped far downstream from point sources in the Athabasca Delta. Further sampling is required to confirm whether these regional differences are, indeed, real. Despite difficulties attributing contaminants exposure in mink to point sources on these rivers, one result of this work emerges that is quite evident, namely that exposure of mink to contaminants in these river systems is minor and probably toxicologically irrelevant.

ACKNOWLEDGEMENTS

We thank the following individuals who provided mink for this study: D. Bredeson, A. Campbell, H. Matlock, L. Judd, O. Nodeland and J. Wilson. Mink collections were coordinated by Pecan Resources. E. Wilson and N. Manners provided logistic support for collections made in Wood Buffalo National Park. Tissue preparation and archiving was done at the Canadian Wildlife Service, National Wildlife Research Centre in Hull, Quebec. Laboratory analyses were done by Enviro-Test Laboratories (dioxins/furans), Zenon Environmental Laboratories (PCBs, organochlorines and chlorinated phenolics) and Chemex Labs Alberta (metals). Special thanks to D. Kennedy, Northern River Basins Study, for formatting the report.

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1.0 INTRODUCTION

Among the guiding questions of the Northern River Basins Study, questions 4 and 11 ask about the nature and contents of the contaminants entering the system and about their effects on riparian wildlife, respectively. To address these questions, many components of the ecosystem have been examined. This report deals with one species, the mink (*Mustela vison*).

Mink are predatory mammals associated with aquatic ecosystems, mainly marshes, lakes and streams. They have highly variable diets consisting of both terrestrial and aquatic prey (Gilbert and Nancekivell 1982). Their aquatic prey consists primarily of small fish such as cyprinids and sticklebacks as well as aquatic mammals (muskrats) and birds (ducks).

Mink were proposed as a bioindicator of contaminants exposure in riparian wildlife for three reasons. First, experimental data have shown that mink are among the most sensitive of animals to adverse effects of environmental contaminants, especially PCBs and dioxins (Aulerich and Ringer 1977, Wren 1991). Second, their predatory nature and use of aquatic prey make them a prime candidate for biomagnifying lipophilic organic contaminants such as PCBs which tend to accumulate in aquatic ecosystems. Third, there is extensive information on the toxicity of various contaminants to this species and on tissue concentrations of contaminants in mink from various locales in North America (reviewed by Wren 1991). This information could be compared to data from Alberta's northern rivers.

Because contaminant levels had not previously been examined in Alberta mink, it was decided to conduct a preliminary survey of contaminant levels in this species based on pooled samples of their liver homogenates. If the pools indicated a large number of detectable levels, further work on individual samples would be considered. The results of the preliminary survey are discussed in this report.

2.0 <u>METHODS</u>

In December, 1991 and January, 1992, trappers with traplines in the Peace-Athabasca delta or adjacent to sections of the Wapiti-Smoky, Peace and Athabasca rivers were contacted and asked to provide mink carcasses taken on their traplines. On the mainstem rivers, only trappers with traplines within a 100-km section upstream and downstream from bleached kraft mill sites were canvassed. Trappers were asked to wrap the whole carcasses individually in tinfoil and label each with information about the trap location and date.

A total of thirteen mink were collected. Three were trapped about 15 km downstream from the Weyerhaeuser Canada (formerly P&G) millsite, about 2 km from the Wapiti River on Bear and Olsen creeks. Another was collected in an upland area about 22 km from the Smoky River near Debolt, AB. Five were trapped at Galoot Lake in the Athabasca Delta. Galoot Lake is a shallow basin located immediately to the north of the Embarras River, a tributary of the Athabasca. There are two

small creeks which, during high flows, may transport water and sediments into Galoot Lake from the Embarras River. However, in recent years such flooding has been infrequent and of low volume. One was collected at the mouth of the confluence of the Wabasca and Peace rivers. Another was trapped on a creek feeding into the McLeod River, located about 20 km upstream from the Athabasca River and about 100 km downstream from Hinton. Two were trapped on creeks about 5 km from the Athabasca River and approximately 40 km downstream from Hinton (Horstman and Code 1992).

Carcasses were sent to the Canadian Wildlife Service, National Wildlife Research Centre in Hull, Quebec for tissue preparation and archiving.

Because of the absence of existing information on contaminant levels in mink from Alberta's northern rivers, it was decided to analyze pooled mink liver homogenates in order to determine whether detectable levels of contaminants (especially those associated with bleached kraft mills) were present and to assess the need for further work. Individuals were pooled based on the locations where they were trapped. Three pools were analyzed: M1 consisting of the three mink about 15 km downstream from the Weyerhaeuser Canada pulp mill on the Wapiti River; M2 consisting of the five individuals from the Athabasca Delta; and M3 consisting of two mink trapped on a creek about 5 km from the Athabasca River and about 40 km downstream from Hinton. The trap sites for these pools are shown in Fig. 1.

The analyses followed procedures that were approved for all contaminants-related projects within the Northern River Basins Study. These procedures are described in detail in the laboratory reports (*e.g.*, Ralitsch 1993).

3.0 <u>RESULTS</u>

Analyses were made for 34 dioxin/furan congeners or homologues, nine metals, 39 chlorinated phenolic compounds, 53 PCBs including three coplanar PCBs, 15 PAHs and 24 organochlorines (OCs). Residues of two dioxin/furans, six metals, one chlorinated phenolic, 11 PCBs and seven OCs were detected. Table 1 lists the contaminants that were not detected in any of the pools.

Of the dioxins and furans, only 2378- tetrachlorodibenzo-*d*-dioxin (TCDD) was detected. It was found in two of the three pools, at 0.2 pg/g wet wt in M1 near the Wapiti River and at 0.6 pg/g in M3 near the Athabasca River downstream from Hinton (Fig. 2). 2378-TCDF was not detected. However, a TCDF homologue which did not include the 2378 isomer was detected in M1 at 0.3 pg/g. Of the chlorinated phenolics, only pentachlorophenol was detected. It was found in all three samples at 0.0032, 0.0032 and 0.0041 μ g/g in pools M1, M2 and M3 respectively (Fig. 3).



Contaminant Group Dioxins/ Chlorinated PAHs **PCBs** OCs Metals Phenolics Furans 27-DiCDD 2346+2356 Naphthalene 5/8 Aldrin As TeCP(henol) 28-DiCDD 2345TeCP Acenaphthy-lene 15 Cd BHC, a 237-TriCDD 234TriCP Acenaph-16/32 BHC, β Vn thene 12378PCDD 235TriCP Fluorene 31 BHC.o 123478HxCDD 236TriCP Phenanth-rene 28 Chlor-dane, a 123678HxCDD 245TriCP Anthracene 33 DDD Fluoranth-ene 22 123789HxCDD 246TriCP DDT 1234678 24DCP Pyrene 52 Dieldrin HpCDD OCDD 26DCP Benz(a)-49 Endosulfan I anthracene 28-DiCDF TCG(uaiacol) Chrysene 44 Endosulfan SO, Benzo(b+k)fluor 238TriCDF 345TriCG 40 DDT, o'p' anthene 2378TCDF 346TriCG Benzo(a)-pyrene 70/76 Endrin 65/95 12378PCDF 456TriCG Indeno(123-Heptachlor cd)pyrene 23478PCDF 45DiCG Dibenz(ah) 56/60 Heptachlor anthracene Epoxide 46DiCG Benzo(ghi)-84 Lindane 123478HxCDF perylene 4CG 89 Methoxy-chlor 123678HxCDF 234678HxCDF TeCC(atechol) 101 Mirex 345TriCC 87 Nonachlor 123789HxCDF 85 1234678 34DiCC Toxaphene

Table 1: Contaminants that were below detection limits in the three pools of mink liver homogenates.

110

HpCDF 1234789

HpCDF

35DiCC

Dioxins/ Chlorinated Furans Phenolics		PAHs	PCBs	OCs	Metals
OCDF	45DCC		151		
DiCDD	4CC		149		
TriCDD	TeCV(eratrole)		118		
TCDD	345TriCV		105		
PeCDD	45DiCV		141		
HxCDD	345TriCS (yringol)		137		
HpCDD	56DiCV(anillin)		129		
DiCDF	6CV		185		
TriCDF	2346+2356 TeCA(nisole)		174		
PeCDF	2345TeCA		177		
HxCDF	234TriCA		191		
HpCDF	235TriCA		201		
	236TriCA	<u> </u>	189		
	245TriCA		195/ 208		
	246TriCA		207		
	24DiCA		205		
	26DiCA		206		
			209		
			77		
			126		
			169		



trapping locations in Alberta.



Fig. 3. Pentachlorophenol levels in pooled mink liver homogenates (n=1) from 3 trapping sites in Alberta.











		•	Conc. ((ppm)	
РСВ	Tissue	Region	Mean	Range	Reference
1254/1260	Whole body	Lake Erie		0.05-7.4	Proulx <u>et al.</u> 1985
1254/1260	Whole Body	James Bay		0.04-0.32	81
1254/1260	Liver	Lake Ontario		0.08-1.02	C. Weseloh, unpubl. data
РСВ	Liver	New York		0.03-7.9	Foley et el. 1988
1254	Liver	Maryland	1.4	0.62-2.4	O'Shea et_al. <u>1981</u>
РСВ	Liver	Oregon	1.0	0.55-1.6	Henny <u>et al.</u> 1981
1254	whole body	Minnesota	0.12	0.01-0.23	Ensor, 1991
1260	whole body	Minnesota	0.12	0.01-0.46	Ensor 1991
Total	whole body	Minnesota	0.15	0.01-0.46	Ensor 1991
1254/1260	liver	New York	0.3		Foley et al. 1991
РСВ	muscle	Wisconsin	1.3	ND-5.4	Meyer & Hurley 1991

Table 2: Trends in PCB tissue levels from mink in other regional studies within North America.

Most PCB congeners, including the coplanars, were not detected (Table 1). Those that were detected were quite low (Fig. 4 & 5). One interesting finding was for PCB 18 which was detected in all three pools and constituted 25-50% of the total PCB load. This PCB congener has not generally been found in wildlife tissues before, although it is possible that the results for PCB 18 are not accurate. Total PCBs were less than 0.05 μ g/g in all pools.

Organochlorines were also low, with DDE being the highest (0.014 μ g/g) (Fig. 6).

Mercury, methyl mercury, chromium, lead, copper and zinc were detected in the pooled mink samples (Fig. 7).

In general, M1 and M3, which were trapped in the upstream reaches of these river systems near bleached kraft mills had the highest levels of contaminants. M2 consisted of mink in the Peace-Athabasca Delta, and had the lowest levels.

4.0 DISCUSSION

4.1 COMPARISONS WITH OTHER STUDIES

4.1.1 Dioxins and Furans

There is relatively little information on dioxin and furan levels in wild mink. A recent study on the St. Maurice River in Quebec found that mean 2378-TCDD levels ranged from non-detectable to 0.9 pg/g upstream and downstream from a bleached kraft mill (L. Champoux, CWS, *unpubl. data*). Mean TCDF downstream from the mill was 0.38 pg/g. 2378-substituted penta-, hexa- and hepta-congeners ranged from non-detectable up to 82 pg/g and were generally higher than the tetra-substituted congeners. 2378-TCDD, the only 2378-substituted dioxin or furan found in mink in this study was somewhat lower than in the Quebec study. This may reflect a lower degree of dioxin pollution originating from pulp mills in Alberta than on the St. Maurice River, or differences in diet and foraging times along the mainstems of these rivers. With the exception of 123678-hexa and 1234678-hepta, dioxins and furans were not found in mink trapped near pulp mills on the Columbia River in B.C (J. Elliott, CWS, *pers. comm.*).

4.1.2. <u>PCBs</u>

Although there have been many regional studies examining PCB trends in mink in North America, between study comparisons are difficult because of a lack of consistency in tissues analyzed, data reporting techniques and analytical approaches (i.e., PCBs reported as 1242, 1254, 1260 or simply as total PCBs). The data from this study suggest that PCBs in Alberta mink are consistent with background levels from other non-polluted sites. Table 2 summarizes trends in PCB tissue levels from other studies.

4.1.3. Metals

The levels for metals in this study were quite low and were consistent with background levels seen at non-polluted sites in other studies. Nevertheless, it is noteworthy that mercury and methyl mercury were 15 - 25 times higher in mink from the mainstem river sites near Hinton and Grande Prairie than in mink from the P-A Delta. It is unclear whether this is due to some artifact of the sampling such as age or sex-related differences in mercury exposure, or whether this represents a real difference in mercury pollution among the three study locations. Table 3 summarizes regional patterns of metal exposure in mink.

4.1.4. Organochlorines

Organochlorine levels in Alberta mink were low, as has been the case with mink trapped in other regions in the 1980s (Foley *et al.* 1991).

<u>Chlorinated phenolics and PAHs</u>: There do not appear to be comparative data for mink from other regions for these compounds.

4.2. TOXICITY OF CONTAMINANTS TO MINK

4.2.1. PCBs

Wren (1991) has summarized much of the information concerning PCB tissue levels associated with adverse health effects in experimental animals. Yet, as Wren (1991) notes, extrapolating these data to wild animals should be done cautiously because of the probable differences in exposure conditions between wild (long-term exposure) and experimental (short-term exposure) animals. Aroclor 1254 liver levels of 1.75 μ g/g were associated with reduced kit survival (Wren *et al.* 1987). Another study found that adverse reproductive effects occurred at higher levels; approximately 6.0 μ g/g (Hornshaw *et al.* 1983). PCB liver levels associated with death in adults ranged from 4.2 to 12.0 μ g/g as Aroclor

			Concentration (µg/g)		
Metal	Tissue	Region	Mean	Range	Reference
Hg	Liver	NW USA	0.66	0.02-2.6	Blus et al. 1987
Hg	Liver	Manitoba	3.2		Kucera 1983
CH ₃ Hg	Liver	NE USA	1.0	0.2-4.1	O'Connor & Nielsen 1981
Hg	Liver	Ontario	0.6	ND-7.5	Wren <u>et al.</u> 1986.
РЬ	Liver	Virginia	0.15	ND-12.7	Ogle et al. 1985
РЪ	Liver	NW USA	0.26	ND-22.0	Blus et al. 1987
РЪ	Liver	Idaho	2.5	ND-34.0	Blus & Henny 1990
Cd	Kidney	Virginia	1.2	0.1-16.0	Ogle et al. 1985
Cđ	Kidney	NW USA	0.37	ND-2.4	Blus et al. 1987
Cd	Kidney	Idaho	0.52	ND-2.9	Blus & Henny 1990
Zn	Liver	Virginia	102	64-194	Ogle et al. 1985
Zn	Liver	NW USA	23.4	13-48	Blus et al. 1987
Cu	Liver	Virginia	36.7	11-116	Ogle et al. 1985
Cu	Liver	NW USA	5.8	1.6-50.0	Blus et al. 1987

Table 3: Concentrations of metals in North American mink.

1254 (reviewed in Wren 1991). The total PCB levels seen in this study (maximum of 0.04 μ g/g) cannot be directly compared with those in the above studies because they have not been reported in Aroclor 1254 equivalents. However, studies on Great Lakes Herring Gull eggs have shown that total PCBs expressed as the sum of 41 congeners are equal to 0.44 to 0.48 of the PCB total when expressed as Aroclor 1254/1260 (Turle *et al.* 1991). The congeners analyzed in the Alberta mink and in the Herring Gull eggs were nearly identical. Therefore, if the total PCBs in Alberta mink are multiplied by 2, a rough approximation of the Aroclor 1254 estimate can be obtained. For the Alberta

mink, the maximum would be 0.08 μ g/g, substantially lower than PCB levels in mink liver known to be associated with adverse effects in experimental mink.

4.2.2. Mercury

Liver concentrations of 24 and 58 μ g/g mercury were associated with death in mink (Wobeser and Swift 1976). Mercury levels of approximately 20 μ g/g in adult liver were associated with reduce kit survival (Wren *et al.* 1987). In this study, mercury levels in liver were at least 10X lower than those reported above.

4.2.3. Other Substances

Toxicity information for the other contaminants in mink were not available. Nevertheless, it is noteworthy that the 28-d LD50 for adult mink was approximately 20,000 times lower for TCDD than for Aroclor 1254 (Hochstein *et al.* 1988, Aulerich *et al.* 1988). Extrapolating this to liver levels associated with reduced reproductive success, it can be calculated that reduced reproductive success would be evident at 87.5 pg/g TCDD. This is substantially higher than the levels seen in this study (Fig. 2). Because the mink in this study were trapped up to 5 km from the mainstems, it is possible that their contaminant levels may be lower than those in mink that feed exclusively on the mainstems. Consequently, potential toxicity to mink that feed exclusively on the mainstem rivers cannot be evaluated in this study. However it should be noted that the mainstem rivers offer poor habitat for mink when compared to creeks, streams and small ponds in the upland areas (Allen 1984). Thus, mink populations are probably low on the mainstems.

4.3. COMPARISON OF CONTAMINANTS IN POOLED SAMPLES IN THIS STUDY

In this study, M1 and M3 contained the highest 2,3,7,8-TCDD and mercury levels, while M2 was somewhat lower. However, because of the absence of replication, it is impossible to draw any inferences about geographical patterns of contaminant distribution in mink. Other factors, unrelated to where the mink were trapped, may have influenced the contaminant burdens. For example, age and sex information is lacking for the mink in this study. These factors often influence contaminant burdens and may have been a factor in this study.

Despite these problems, it is interesting that mink trapped in the upstream reaches of these river systems near point sources (M1 and M3) contained higher levels of contaminants than M2 animals which were trapped in the Peace-Athabasca Delta far downstream from any point source. Such exposure would require that mink have access to effluent-exposed prey, an uncertain assertion in this study. Foraging ranges are highly variable in mink. Adult males generally occupy up to approximately 6 km of shoreline while females occupy up to 3 km (Eagle and Whitman 1987). Thus, it is conceivable that the mink in this study may have had access to effluent-exposed prey, especially since some prey species may move into tributaries of the mainstem at certain times of the year (Swanson et al. 1993). It is possible that mink in the upstream reaches of these rivers are exposed to contaminants originating in effluents. However, the exposure is minor and probably toxicologically irrelevant.

5.0 **REFERENCES**

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APPENDIX A: TERMS OF REFERENCE

No contractual Terms of Reference were prepared for the work documented in this report. The work was undertaken by the author as a contribution in kind from his employing agency and represents a part of his responsibilities to the working committee of the Contaminants Component of the Northern River Basins Study.

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