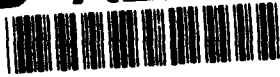


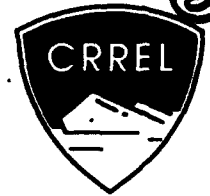
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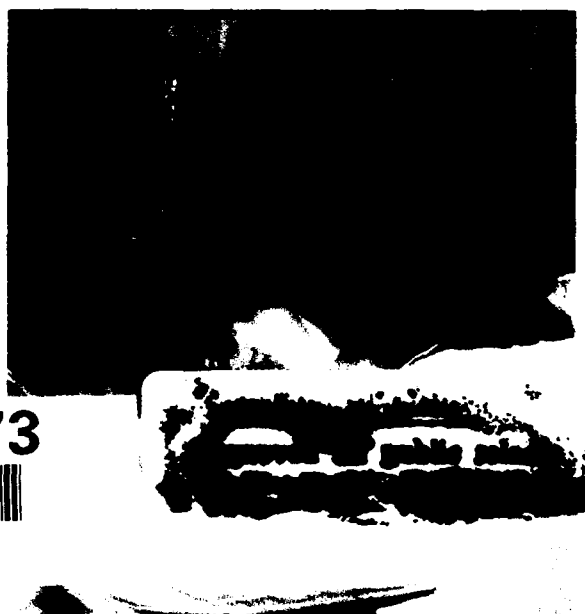
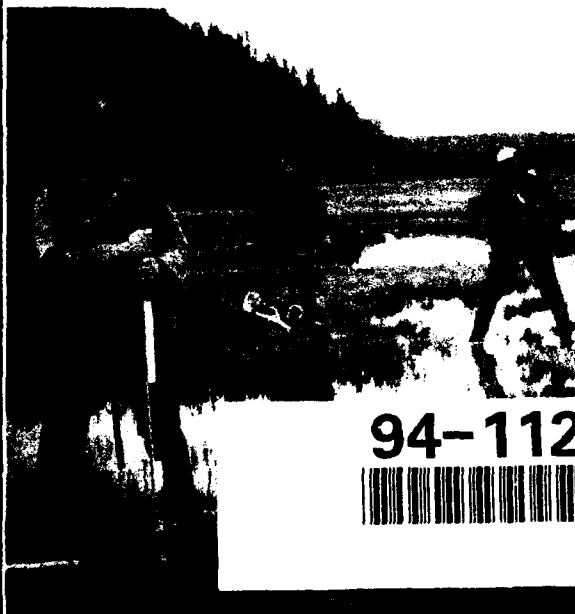
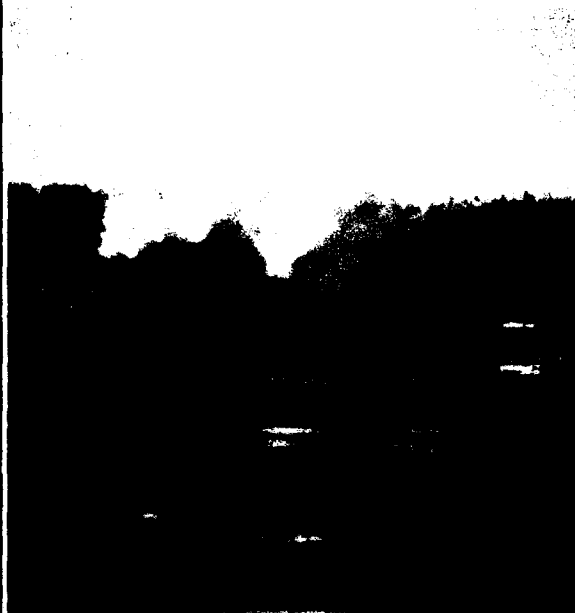
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# White Phosphorus Contamination of Salt Marsh Pond Sediments at Eagle River Flats, Alaska

Charles H. Racine, Marianne E. Walsh, Charles M. Collins,  
Susan Taylor, Bill D. Roebuck, Leonard Reitsma and Ben Steele

October 1993



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**Abstract**

In 1990 we proved that an annual waterfowl dieoff involving thousands of waterfowl at Eagle River Flats (ERF), a 1000-ha estuarine salt marsh at Ft. Richardson, Alaska, was due to the ingestion of highly toxic particles of white phosphorus that entered the bottom sediments of shallow ponds as a result of training with white-phosphorus smoke munitions. The anoxic conditions of the bottom sediments preserved the normally highly reactive white phosphorus. In 1991 we delineated the extent of white phosphorus contamination in the ponds of Eagle River Flats and further investigated the biological effects of WP contamination. Over 360 sediment samples were collected from six ponds where ducks were observed to feed and become sick and where carcasses of poisoned waterfowl were found. These ponds cover about 50 ha of the 1000-ha salt marsh. Sediment and tissue samples were analyzed for white phosphorus by gas chromatography. White phosphorus was found in 101 surface sediment samples and in sediment cores to depths of 20 cm. The distribution and highest concentrations of white phosphorus were localized in two of the six feeding pond areas, covering about 15 ha. We hypothesize that these two areas represent the major sources of waterfowl poisoning in ERF. While the locations in ERF where various species of waterfowl become sick showed close correlation with white phosphorus contamination in the sediments, dead waterfowl were also found in uncontaminated areas of ERF. No WP was found in over 300 gizzards of ducks harvested by hunters from various Cook Inlet marshes. Evidence for the transport of white phosphorus up the food chain from prey to predator was obtained in relation to the heavy feeding by bald eagles on WP-containing duck carcasses and in the presence of WP in the tissues of one dead eagle found in ERF. We predict that white phosphorus will persist in ERF sediments and continue to poison waterbirds until remedial actions are implemented.

*Cover (clockwise from upper left):*

*White phosphorus explosion in Eagle River Flats.*

*Duck tipping up in Eagle River Flats pond to feed in bottom sediments.*

*Laboratory preparation of gizzard contents for white phosphorus analysis.*

*Sediment sampling in Eagle River Flats.*

For conversion of SI metric units to U.S./British customary units of measurement consult ASTM Standard E380-89a, *Standard Practice for Use of the International System of Units*, published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.



**U.S. Army Corps  
of Engineers**  
Cold Regions Research &  
Engineering Laboratory

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## PREFACE

This report was prepared by Charles H. Racine, Research Ecologist, Geological Sciences Branch, Research Division; Marianne E. Walsh, Research Physical Scientist, Applied Research Branch, Experimental Engineering Division; Charles M. Collins, Research Physical Scientist, Geological Sciences Branch; Susan Taylor, Research Physical Scientist, Geological Sciences Branch, U.S. Army Cold Regions Research and Engineering Laboratory; Bill D. Roebuck, Toxicologist; Leonard Reitsma, Avian Ecologist; and Ben Steele, Avian Ecologist, Dartmouth College.

Funding for this effort was provided by the U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland (Installation Restoration Division). Captain Steven Bird, Project Officer, provided valuable assistance.

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The Eagle River Flats Interagency Task Force, composed of representatives from the U.S. Army 6th I.D., U.S. Fish and Wildlife Service, Alaska Dept. of Fish and Game, Alaska Dept. of Environmental Conservation and U.S. Environmental Protection Agency, offered valuable suggestions and helped with field work. Daniel Rosenberg (Alaska Dept. of Fish and Game) was responsible for collecting gizzard specimens from hunters in salt marshes neighboring Eagle River Flats. William Eldridge (U.S. Fish and Wildlife Service) harvested ducks from ERF. Clare Jaeger of the U.S. Army Engineer District, Alaska, graciously provided chemistry laboratory facilities and equipment. Leroy W. Metker of the U.S. Army Environmental Hygiene Agency provided valuable information for assessing human risk. CRREL personnel provided considerable assistance: Darryl J. Calkins provided administrative assistance and offered technical advice; Patricia Weyrick was responsible for the gizzard analysis, and Elizabeth Nadeau provided assistance. Robert Harris isolated white phosphorus particles. Dartmouth students also participated in the study. Sae Im Nam, graduate student in toxicology, analyzed many tissue samples and worked on the tissue method. Gregory Goldfarb, undergraduate biology major, assisted in field work.

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# White Phosphorus Contamination of Salt Marsh Pond Sediments at Eagle River Flats, Alaska

CHARLES H. RACINE, MARIANNE E. WALSH, CHARLES M. COLLINS, SUSAN TAYLOR,  
BILL D. ROEBUCK, LEONARD REITSMA, BEN STEELE

## INTRODUCTION

Since 1990, an interdisciplinary team of scientists from CRREL and Dartmouth College has been investigating the cause and extent of an annual waterfowl dieoff documented since 1982 on Eagle River Flats (ERF), a 1000-ha estuarine salt marsh on Cook Inlet at Ft. Richardson, Alaska (Fig. 1). During the first year of the study (1990), evidence was presented that the cause of the annual dieoff of an estimated 1000–2000 migrating dabbling ducks (*Anas* sp.) and 10–50 swans (*Cygnus* sp.) at Eagle River Flats was the ingestion of white phosphorus (WP) particles deposited in the sediments during artillery and infantry training with smoke munitions (Racine et al. 1992). Evidence that the smoke munition white phosphorus ( $P_4$ ) is the cause includes the following:

- Farm-reared adult mallards dosed with WP showed almost identical behavioral symptoms to those of wild ducks observed to become sick and die in Eagle River Flats;
- WP is highly toxic to waterfowl at ingestion levels on the order of 1 mg/duck;
- WP was detected by gas chromatography in the gizzard contents and fat of all 11 dabbling ducks and 8 tundra swan carcasses collected in Eagle River Flats in 1990 but in none of five healthy teal collected in a nearby salt marsh; and
- WP was similarly detected in several sediment samples from the bottom of a pond in which ducks feed and were observed to become sick.

ERF is the first documented case of WP deposition and of wildlife poisoning in a U.S. Department of Defense training area. Before our work at ERF, white phosphorus was dismissed as a possible environmental contaminant because it is thermodynamically unstable in the presence of oxygen (Pourbaix 1966). Because of this instability, as recently as December 1990, in a Health Advisory prepared by the EPA (Gordon et al. 1990), the

following statement is made: "It is considered unlikely that elemental phosphorus from smoke devices would deposit to any significant degree into terrestrial or aquatic environments." However, Berkowitz et al. (1981), while assessing the potential health hazards associated with the use of phosphorus smoke munitions, made the following observation:

Because of the extremely toxic nature of  $P_4$  residues in aquatic systems, deposition/wash-out of any undegraded  $P_4$ , especially to small water bodies, may create exposure risks to resident finfish, invertebrates, and/or waterfowl, even if resultant  $P_4$  concentrations are in the low ppb range. Unfortunately, there is no information available on the range and frequency of occurrence of  $P_4$  deposition to aquatic systems from...phosphorus...smokes in training or other field use. An area receiving repeated deposition (i.e., training) would be expected to be most vulnerable.

Because salt marsh sediments are highly reduced (Patrick and DeLaune 1977), they are more conducive to storage of the highly reactive WP.

## 1991 objectives

The main purpose of the 1991 effort was to obtain sufficient data to substantiate results from past investigations, to determine the effects of WP contamination on avian species in ERF and to characterize WP contamination in ERF sediments. The specific objectives of the year's work were to:

- Refine analytical techniques for detecting WP in pond sediments and tissues;
- Determine the spatial distribution and forms of WP particles in the sediments (and water) of waterfowl feeding areas or ponds of Eagle River Flats;
- Develop a better understanding of the form of WP in the salt marsh pond environment;
- Determine if waterfowl are ingesting chronic

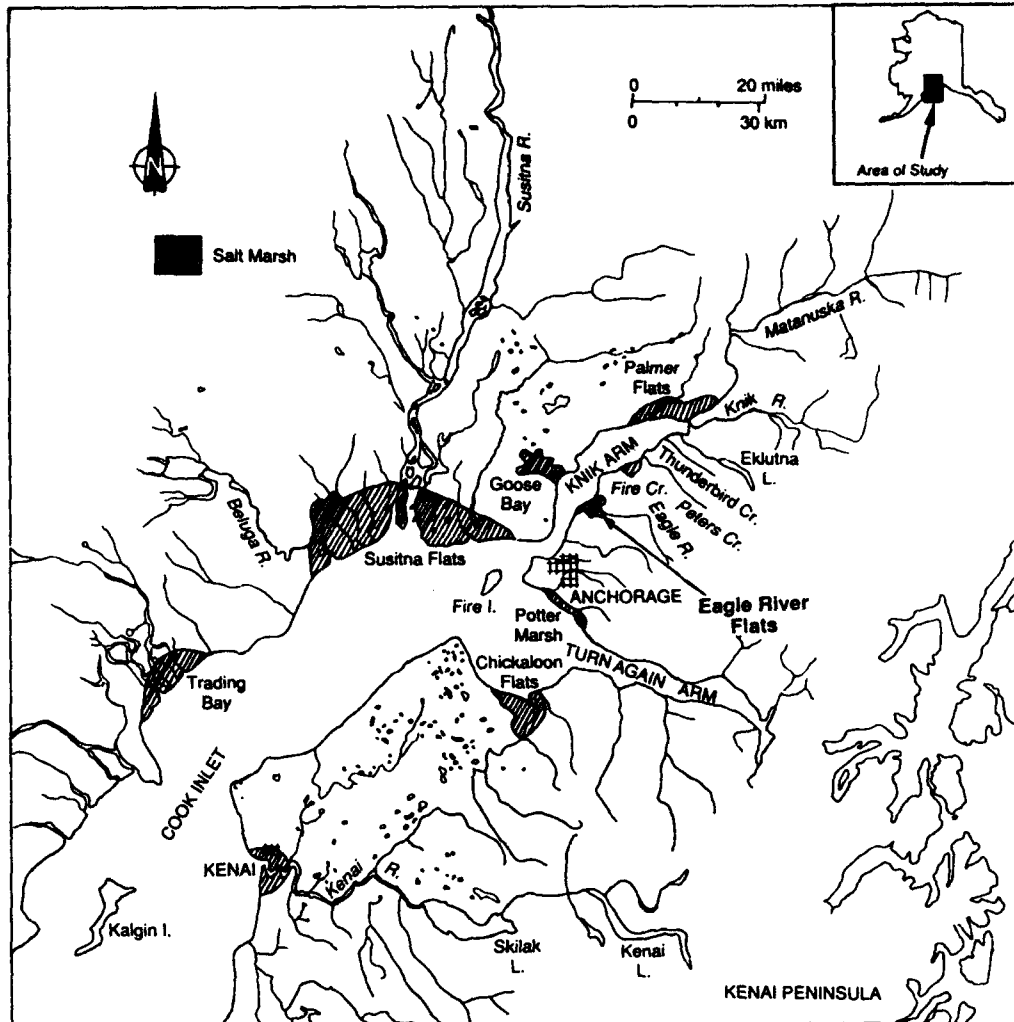


Figure 1. Map of the Upper Cook Inlet area in southcentral Alaska, showing the location of Eagle River Flats and other estuarine salt marshes used by migrating waterfowl.

or sublethal doses of WP at one site and flying into other areas of Eagle River Flats or out of Eagle River Flats into other Cook Inlet salt marshes;

- Determine if other sediment-feeding species such as shorebirds are being poisoned by WP and document the use of the area by other species;
- Obtain a better estimate of mortality in Eagle River Flats and devise a simple but repeatable technique or index to monitor mortality rates from year to year; and
- Determine the types and rates of predation of poisoned waterfowl and the possible effects on predators.

#### Study design and approach

From the beginning of the study we recognized the need to adopt an integrated, multi-disciplinary approach for the study. We felt that only a study that closely integrated biological, chemical and physical studies as well as field and laboratory tests could provide some understanding of the complex environment of Eagle River Flats and the extent of the white phosphorus contamination, as well as providing basic information for remediation options.

The parts of this integrated study included:

- An avian field study program to observe and measure waterfowl mortality, waterfowl behavior, predation, feeding habits, movement

- patterns and numbers of carcasses;
- A sediment sampling program to further define WP distribution in the shallow ponds used by the waterfowl and relate this distribution to observed patterns of mortality;
  - A field laboratory to quickly process and identify the presence of WP in field-collected sediment or tissue samples;
  - Measurements of physical, chemical and biological environmental variables associated with the ERF ponds in which waterfowl feed and in which WP is stored;
  - A remote sensing program to obtain imagery and to map sample sites and various environmental features; and
  - A field survey program to locate sampling and collection sites precisely for use in mapping and for eventual input into a GIS system.

All of the field work during both 1990 and 1991 was carried out during the last two weeks in May and August to coincide with the spring and fall waterfowl migration periods. The 1991 field sediment sampling and bird observation studies were centered on four observation towers or blinds constructed under the direction of the Army 6th ID in the major waterfowl feeding pond areas (designated as Areas A, C, C/D and D) (Fig. 2). Two additional ponded areas were recognized during the course of this study: Bread Truck Pond (named for a large yellow panel truck that had been placed here as an artillery target) and two small shallow ponds north of the Bread Truck pond designated here as the Pond Beyond (Fig. 2). The open water areas associated with all of these feeding areas comprise an area of about 50 ha (125 acres), or 5% of the 1000-ha ERF (Table 1).

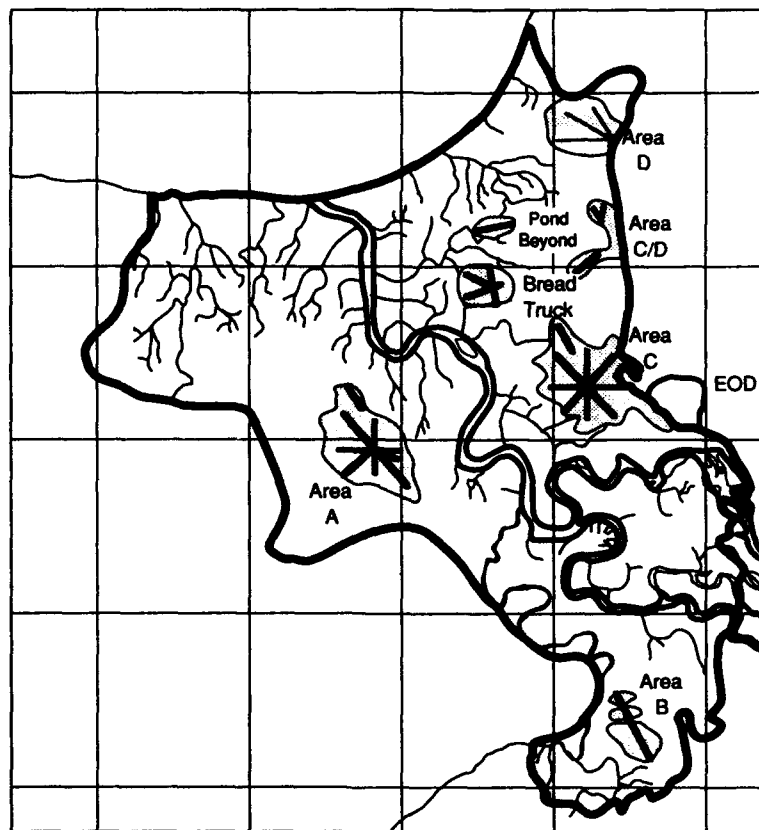


Figure 2. Map of Eagle River Flats salt marsh showing the Eagle River, distributary streams and waterfowl feeding ponds designated as Areas A, B, C, D and C/D, the Bread Truck Pond and the Pond Beyond. The approximate locations of sampling transects are also shown in each area. The UTM grid lines are 1000 m apart.

**Table 1. Poned areas in Eagle River Flats where 1991 integrated sediment and bird studies were conducted, including the area of open water (1 ha = 2.5 acres).**

Location	Area (ha)
<i>West of Eagle River</i>	
Area A	
Main Pond	14.52
Otter Pond	1.84
North End ponds	2.68
Total	18.04
<i>East of Eagle River</i>	
Area C	9.78
Area D	
Main Pond	10.69
Extension	0.90
Area C/D (Beaver Pond)	1.04
Bread Truck Pond	5.10
Pond Beyond	1.80
Total	29.31

The observation towers served as the focus of the sediment sampling and bird observation studies as well as providing a storage site for field sampling equipment and a site for surveying. Radios were used to communicate between towers and between the surveyor and sediment samplers. Sediment collection and bird observation transects were laid out and surveyed in a radiating pattern around each of the towers (Fig. 2). Sediment sampling sites were positioned at 25-m intervals along these transects and marked with numbered placards and 2-m-high stakes that allowed the bird observers to better estimate the location and distances to birds they were observing from the tower.

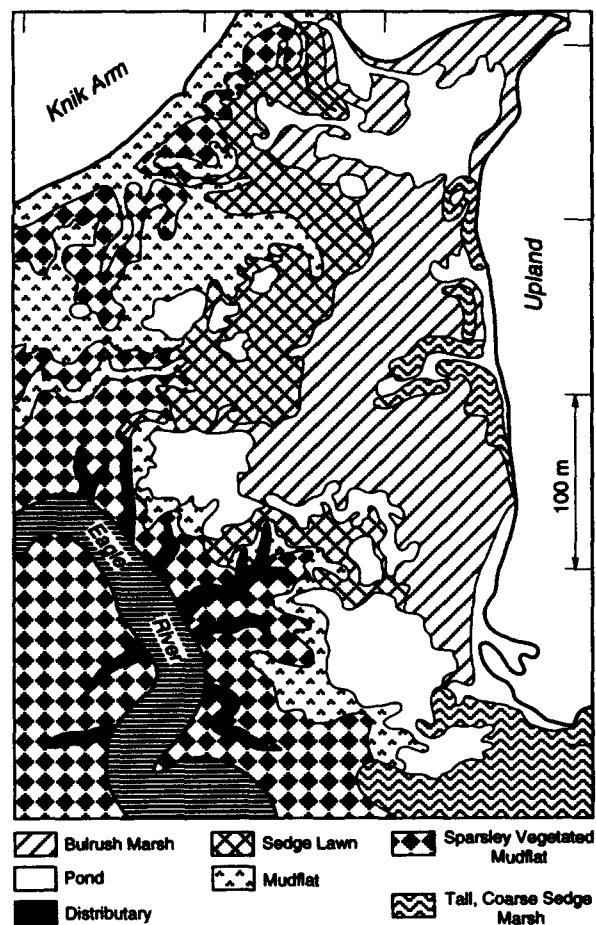
The avian study program involved investigations of waterfowl mortality, use, predation and movement patterns within and out of ERF. Most of the observations were made from the towers, but ground transects were also established for the purpose of counting carcasses and collecting tissue samples for WP analysis. Over 350 hours of bird observations were logged during the 1991 field season. Tissues were collected from over 60 bird carcasses as a part of this program.

Over 360 sediment samples were collected during the 1991 field season along transects radiating out from the blinds.

The surveying program allowed sediment sampling points, towers, mortality transects and other important features such as vehicle targets in ERF to be located precisely. Over 500 points were surveyed and assigned to a UTM coordinate system for mapping and future re-location.

A field laboratory was set up in Alaska at Elmendorf Air Force Base at the U.S. Army Corps Alaska District lab. This lab permitted the rapid "on-site" analysis of sediment and tissue samples for WP. The results were available within 24 hours after sediments were collected. The quick turnaround allowed areas that tested positive for WP to be resampled in more detail to confirm the presence of WP and to refine its distribution pattern. Over 600 samples (sediment and tissue) were analyzed during the 1991 field season.

A remote sensing program was established in



**Figure 3. Distribution of ponds and vegetation zones on the east side of Eagle River Flats.**

1991. A new set of color IR aerial photos and an eight-band multispectral scanner tape (CASI) was obtained of ERF feeding ponds on 21 July 1991 by Aeromap U.S., Inc. (Anchorage, Alaska). This imagery was used extensively for sediment sampling and bird observation studies in August and in the preparation of maps. An image processing system being developed at CRREL was used to map vegetation and habitat types and to calculate areas from the CASI tape.

## ENVIRONMENTAL SETTING

### Introduction

Eagle River Flats at the mouth of the Eagle River is an estuarine salt marsh on the south side of Knik Arm in upper Cook Inlet (Fig. 3). Estuaries are broadly defined as coastal zones where there is interaction of ocean water, fresh water, land and atmosphere. Beeftink (1977) defined a salt marsh as a "natural or semi-natural halophytic grassland and dwarf brushwood on the alluvial sediments bordering saline water bodies whose water level fluctuates either tidally or non-tidally." Numerous books and studies have been published on salt marsh ecosystems (Chapman 1977, Mitsch and Gosselink 1986, Day et al. 1989). Salt marshes are among the most important coastal wetlands in the world. They are dynamic, complex and highly productive, supporting fisheries, waterfowl and a myriad of other life forms. Salt marshes contain a complex zonation of plants, animals and microbes that is related to the stresses of salinity fluctuations and to the alternating drying and submergence.

In North America, most salt marsh studies have been conducted along the Atlantic (Teal 1986) and Gulf of Mexico (Gosselink 1984). Arctic and sub-arctic salt marshes in Alaska (MacDonald 1977) and Canada (Jeffries 1977) have received less attention, although they are extensive, particularly along the south shore of Hudson Bay (Glooschenko and Clark 1982, Earle and Kershaw 1989). While some salt marshes along the arctic coasts are strongly influenced by disruptive ice action, ERF is relatively sheltered, with little or no disruption from pack ice. In Cook Inlet, limited descriptions of salt marshes and their zonation are available for Susitna Flats (Snow and Vince 1984), Kenai Flats (Rosenberg 1986), Chickaloon Flats (Nieland 1971) and Potter Marsh (Batten et al. 1978). Below is a description of the zonation and habitats in ERF.

### Ecological zonation

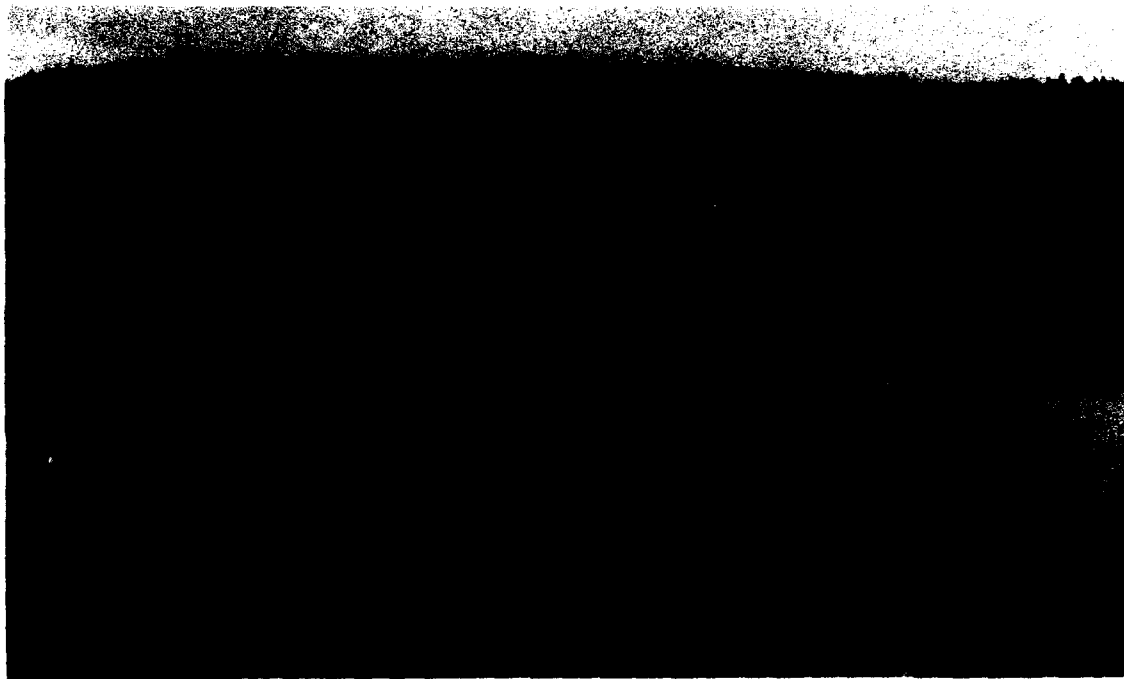
Vegetated and unvegetated mudflats and various types of marshes and meadows are arranged in zones in relation to the main channel of Eagle River, its many distributaries and two types of ponds (Fig. 3). These zones are presumably controlled by the surface elevation, as determined by sedimentation rates and the frequency of tidal flooding (and runoff), which controls the salinity of the soil and water. In addition the distribution and amount of fresh water from streams flowing into ERF affect salinity and the permanence of ponds.

The two types of ponds that serve as the major areas of waterfowl feeding are semipermanent and permanent ponds. Semipermanent ponds occur as transitional intertidal ponds from the outer mud flats and low marsh near Eagle River to the freshwater permanent ponds described below (Fig. 4). They are 3–10 cm deep on the outer mudflat side and deepen to 15–50 cm on the landward side. These ponds are best developed in Areas A and C. Both the Bread Truck Pond and the Pond Beyond represent semipermanent ponds. An intricate pattern of drainage channels can be seen connecting these semipermanent ponds to the main channel of the Eagle River (Fig. 4). These channels are probably formed by tidal and rainwater runoff. The ponds may have formed when the outlet of one of these drains became dammed by vegetation or shifting sediments. The pond also could drain if headward erosion were to cut back into a pond (Mitsch and Gosselink 1986). There are usually clumps and patches of low sedge lawn or tall, coarse sedge marsh in the pond (Fig. 4). On the deeper (landward) side of these ponds, emergent species such as *Hippurus tetraphylla* and bulrush appear. The area of these ponds may decrease by half during midsummer dry periods. Since the shallow outer areas of these semipermanent ponds (nearest the river) dry up, most of the submerged aquatic vegetation is located along the inner edge of these ponds.

Permanent ponds occur around the edge of Eagle River Flats where freshwater drainages occur (Fig. 5). Tidal distributaries generally do not extend into these ponds. The innermost ponds occur near the edge of the flats and are fed by freshwater streams but also occasionally flood during very high tides. The two major areas of permanent ponds include Area D and Area B, both located in embayments and upland edges of ERF. The beaver ponds and channels associated with



*Figure 4. View to the northeast across the Bread Truck Pond (named for the yellow panel truck visible on the far edge of the pond). This is a semipermanent pond connected to the Eagle River by the distributary and the bare mud bank of the Eagle River visible in the foreground. Water depths vary from 5 cm on the river side of the pond to 30 cm on the upland side.*



*Figure 5. Permanent pond in Area D with sediment sample transect markers and small patches of bulrush. Water depths here are 25–50 cm, and salinity is less than 7 ppt.*



Figure 6. Deep-water channel used by beavers and associated marsh vegetation (bluejoint grass and tall coarse sedge: *Carex lyngbyaei*) along the east side of ERF in Area C/D.

the transition area between areas C and D (C/D transition) are also well developed examples of permanent ponds (Fig. 6). These ponds tend to be deep (25–50 cm) and do not dry up during the summer. The vegetation of these ponds is highly productive and includes well-developed stands of emergent sedges and bulrushes as well as submerged aquatics (Fig. 7). Along the edges of the permanent ponds in Areas B, D and C/D there are stands of both the very tall, dark-green bulrush (*Scirpus validus*) and the lower, brown *Scirpus paladosus*, with occasional transition to tall productive stands of *Calamagrostis* sp. and the shrub *Myrica gale*, near the upland edge. Because of their high productivity and the relatively low input of glacial silts, the sediments of these ponds are highly organic and very reduced.

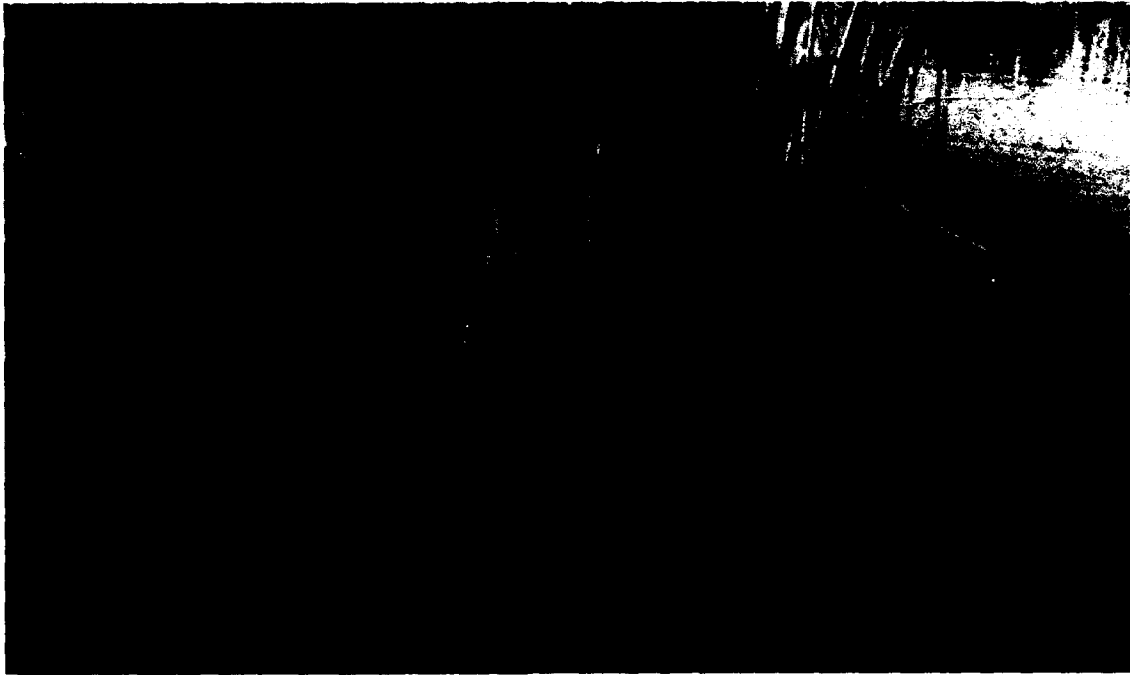
During warm, rainless summer periods without flooding high tides, water levels in the semi-permanent ponds may drop by 5–10 cm, exposing unvegetated open mudflats along the outer (shallow) edge of these pannes (Fig. 8). These mudflats are therefore subject to both flooding and drying, which prevent the establishment of vegetation.

Closest to the distributaries and Eagle River and interfingering along their edges are sparsely

vegetated mudflats dominated by arrowgrass (*Triglochin maritimum*) and alkali grass (*Puccinellia* sp.), goosetongue (*Plantago maritimum*) and glasswort (*Salicornia europaea*) (Fig. 9). Virtually all sediment samples that we screened for white phosphorus particles contained seeds of arrowgrass (*T. maritimum*). Closer to the higher edges or levees of some distributaries are tall stands of beach rye (*Elymus arenarius*).

Inside or landward of this sparsely vegetated mudflat zone is a low sedge lawn or dense sedge meadow, consisting of a tightly knit sedge sod dominated by the fine sedge *Carex ramenskii*. Other species here include *Potentilla egedii* and arrowgrass. This zone sometimes occurs as islands and isolated strips in the ponds, representing old levees.

The inner edges of ponds are bordered by a bulrush or tall, coarse sedge marsh dominated by *Carex lyngbyaei* (Fig. 10). The sedges are up to 1 m tall, and the roots form a very dense and tight mat (which made the collection of sediment samples particularly difficult). There is standing shallow water over the roots. A well-developed stand of this type borders the EOD pad and extends to the south end of the Area C ponds. It is also well

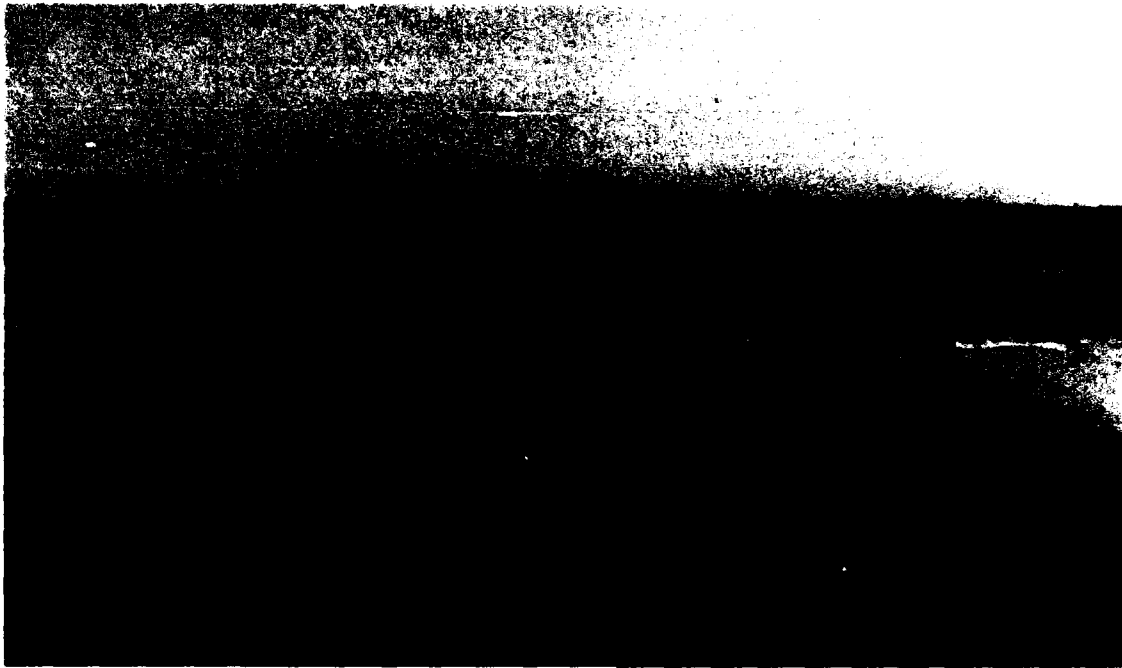


*Figure 7. Submerged aquatic vegetation (wigeon grass: Ruppia spiralis) in a permanent pond bordered by tall bulrush (Scirpus validus).*

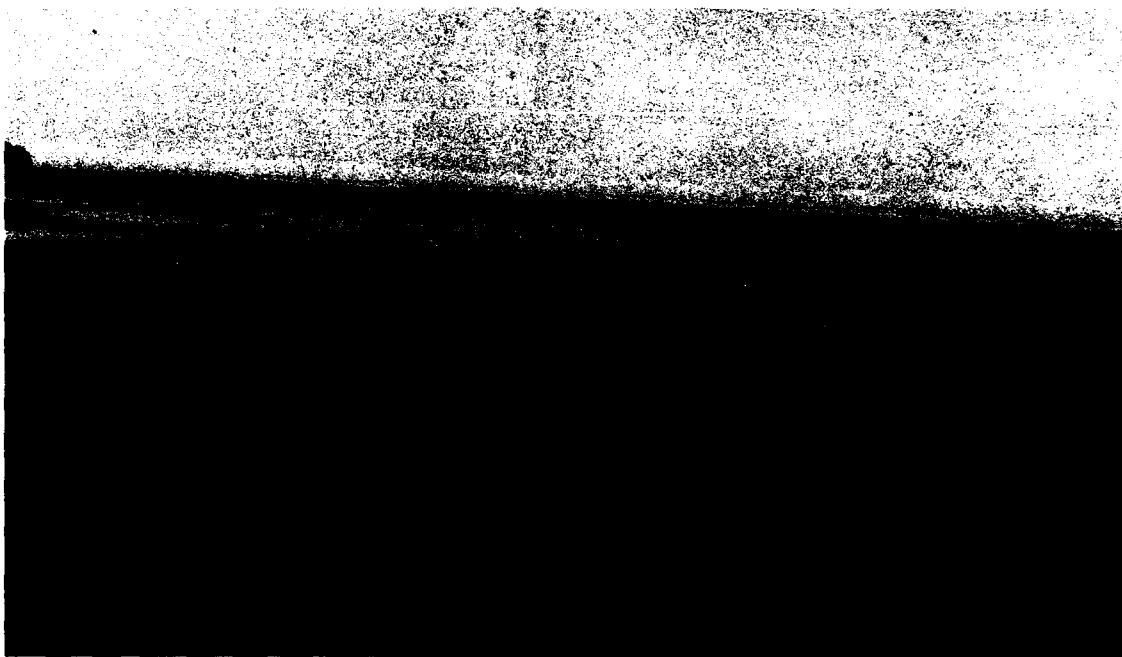


*Figure 8. Bread Truck Pond, showing the sparsely vegetated mudflat pock-marked with explosion craters and the open mudflat bordering the pond next to the sparsely vegetated mudflat. The vegetated islands and strips are low sedge lawn.*





*Figure 9. Area C pond viewed to the north with sparsely vegetated mudflat (foreground) and an old levee with low sedge lawn in the middle of the pond.*



*Figure 10. View to the northwest across Area C showing the observation blind and well-developed tall, coarse sedge (*Carex lyngbyaei*) vegetation (mixed with darker patches of bulrush) in the foreground.*

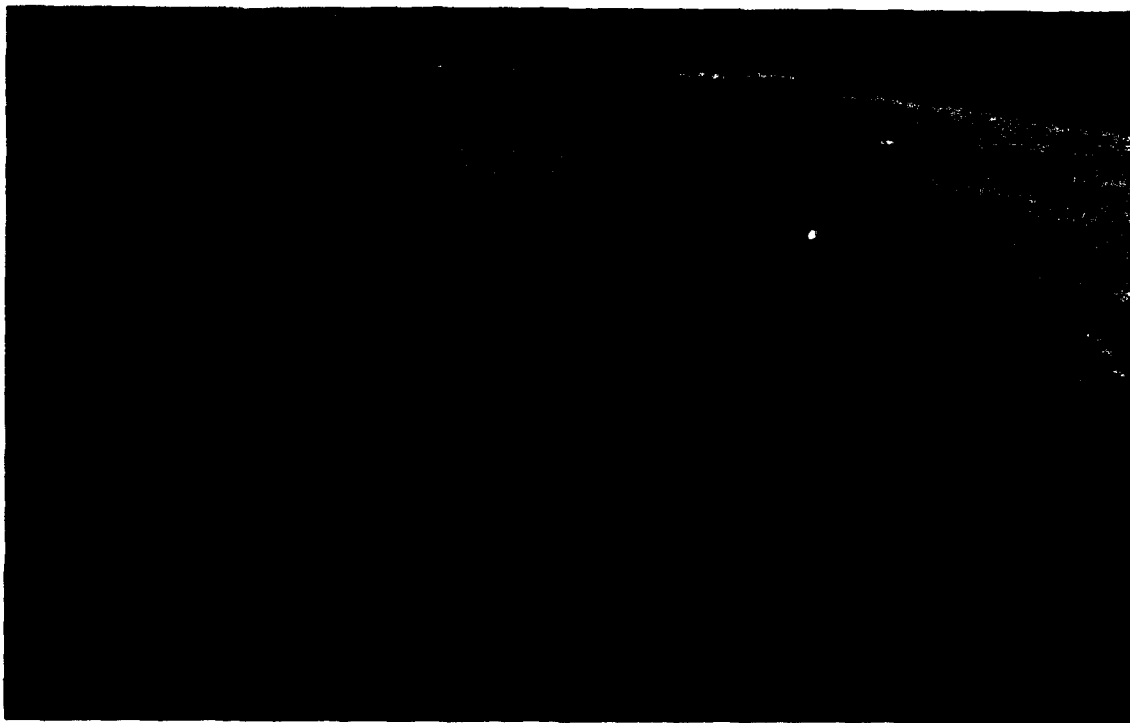


Figure 11. Pond in Area B showing the border of tall, coarse sedge marsh and bulrush (*Scirpus paludosus*) marsh in the deeper water pond.

developed around Otter Pond at the south end of Area A. This tall, coarse sedge zone is by far the most heterogeneous and varies greatly within ERF (Fig. 11).

The bulrush marsh zone occupies the inner edge of semipermanent ponds and forms extensive stands in and around permanent ponds. Bulrushes (*Scirpus* sp.) form almost closed stands or more open stands with small pools or ponds (Fig. 12). Two species of *Scirpus* occur in this zone (*S. paludosus* and *S. validus*) (Fig. 13), along with occasional patches of the tall coarse sedge *Carex lyngbyaei* (Fig. 10). *S. paludosus* is generally dominant and marked by extensive dead, brownish shoots (Fig. 11), in contrast with the tall and dark green stands of *S. validus* along the inner edge of this zone (Fig. 7, 13), particularly around the permanent ponds. Water depths here are 20–40 cm, but where small patches of bulrush occur in the permanent ponds the sediment surface is elevated 10–20 cm above the floor of the pond. These bulrush areas are particularly extensive between the semipermanent intertidal ponds and the permanent ponds east of Eagle River (Fig. 3, 12). In Area A, bulrush (*S. paludosus*) occurs extensively in the ponds but appears to be dying. These stands may

have been buried by silt because of ground subsidence caused by the 1964 earthquake. Nieland (1971) noted that in Chickaloon Flats the bulrush community was once far more extensive than at present. As in ERF, Nieland also found the most vigorous bulrushes at the edges of the wettest areas with coarse sedge marsh.

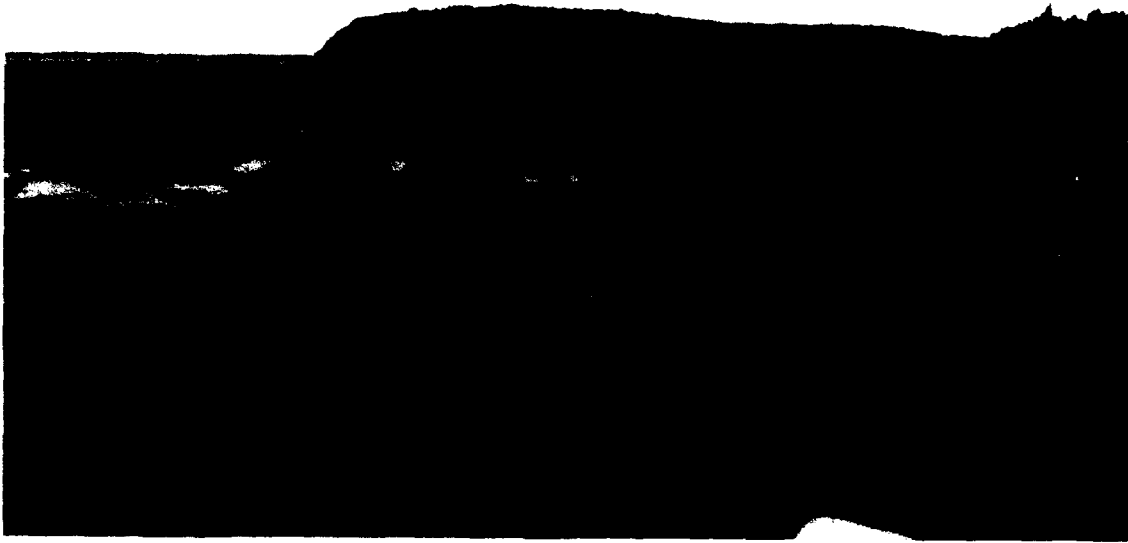
#### Factors controlling zonation

The biological zones in ERF develop because of the following factors: frequency and duration of tidal flooding, deposition and erosion of sediments, soil salinity and regional climate.

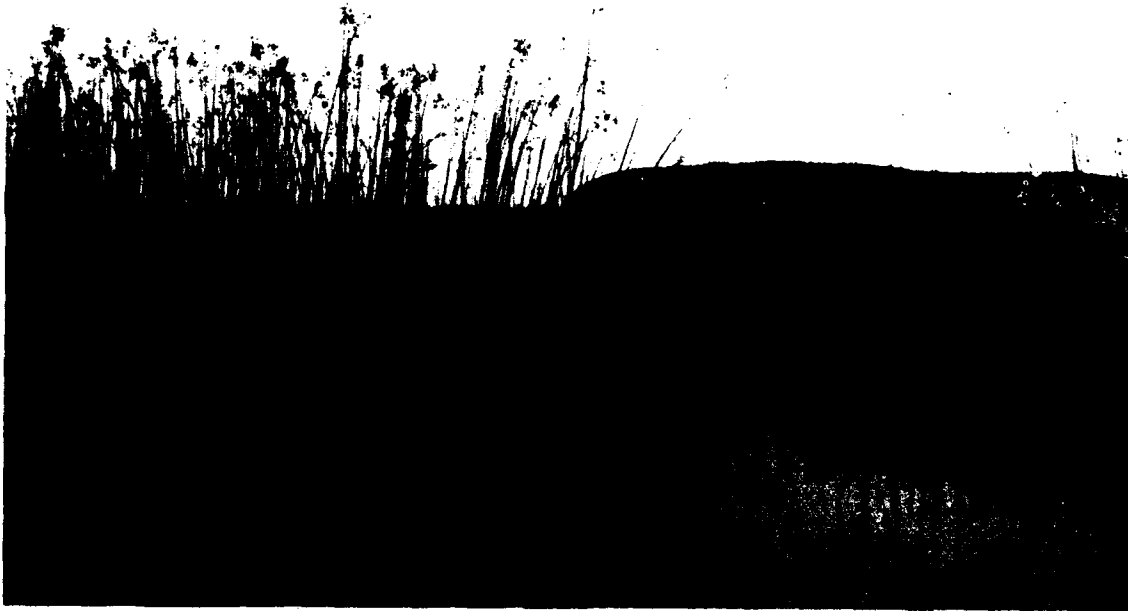
#### Tidal flooding

Eagle River Flats and other Cook Inlet and Knik Arm salt marshes are subject to large semidiurnal tidal fluctuations of 9.1–11 m (30–35 ft) during high tide. These represent the second highest tides in North America. Flooding of Eagle River Flats involves both tidal flooding from Knik Arm (Cook Inlet) and freshwater flooding from the Eagle River. The extent and type of flooding (fresh or salt water) depend on both the height of the high tide and the height of the river stage.

During the summer, when the discharge of



*Figure 12. Aerial oblique view to the north across the bulrush vegetation zone between Area C and Area D. Small open pools and ponds characterize this vegetation zone, which is used extensively by mallards.*



*Figure 13. Two species of bulrush around the edge of the permanent pond in Area C/D. The tall, dark-green bulrush on the left is *Scirpus validus*, and the lower, yellow-brown bulrush is *S. paludosus*.*



*Figure 14. Aerial view of Eagle River Flats in January 1991 viewed to the north, showing Knik Arm and ice-covered ERF. Otter pond is visible in the foreground.*

Eagle River is high due to snowmelt and glacial runoff, an incoming high tide acts to dam the river, causing it to overflow its banks and partially or completely flood the flats. This flooding appears to have occurred whenever the Anchorage tide tables reported tides greater than about 9.1 m (30 ft). Tides of this magnitude occurred at least five times in May 1991, nine times in June 1991, nine times in July 1991, 14 times in August 1991 and 18 times in September 1991. Between 16 August and 21 September 1990, eleven flooding events were recorded in an Area C pond.

During the winter, tidal flooding also plays a significant role in the formation of a continuous ice cover over ERF (Fig. 14). The ice not only forms in the ponds but also covers areas that at low tide during the summer are not normally flooded, such as mudflats, levees and sedge marsh or meadow. In February 1991, mudflat areas had a 30- to 60-cm layer of ice over frozen soils. Areas of standing water, such as the ponds, had ice thicknesses of 40-70 cm.

In February 1991, several 4-cm-diameter ice cores were drilled from an Area C pond out toward the river into a sedge marsh. Salinity and sediment concentrations were determined at 1-cm

intervals along the length of the ice cores.

Thin sections made from an ice core collected over a pond show that about 30% of the length of the core consisted of congelation ice (frozen pond water), 20% was thin ice layers with relatively high salt and sediment concentrations (frozen tidal events), and about 50% was snow ice (wetted and refrozen snow). Fresh water from streams entering ERF along the east side may flow out over the existing ice surface (aufeis) and thereby contribute to the ice thickness over some ponds.

An ice core collected over sedge marsh had standing vegetation incorporated within the ice. The ice appeared to be composed of about 50% tide-derived ice and 50% snow ice. The concentration of salt (3-6 ppt) and sediment (20-100 mg/g of ice) was fairly high near the base of the core and steadily decreased toward the top of the core. The correlation of high salinity with the presence of sediment bands (Fig. 15) indicates that sediment-containing salt water from Knik Arm flooded out over the surface of the ice or snow to form a distinct layer.

The mudflat and sedge marsh soils, as well as the bottom sediments of shallow ponds (<10 cm deep), freeze to depths of 30 cm. The depth of

seasonal freezing depends on the depth of the overlying snow cover, the frequency of tidal flooding and the average winter temperatures. Sediments at the bottoms of the deeper ponds (>50 cm) along the edge of ERF probably do not freeze.

It is not known when the ice buildup starts in Eagle River Flats and whether the ice thickness is similar from year to year. Weather factors such as the amount and timing of snowfall and air temperatures all affect the development of the ice cover at ERF.

In spring the ice appears to melt in situ. A 32-ft tide did not inundate the flats on 16 April 1991 but rather was mostly confined to the main river channel and a few adjacent low areas. Tides appear not to dislodge and remove ice from ERF. By 5 May 1991, ice remained only in the deeper ponds along

the edge of ERF, and most of the marker stakes placed in the sediments during summer 1990 were still standing.

#### Siltation and sedimentation

During the summer Eagle River carries a moderate suspended-sediment load derived from glacial melt and runoff. Based on USGS data collected in the early 1970s, the summer mean daily suspended sediment load for Eagle River appears to range between 100 and 300 mg/L but increases to 400–700 mg/L during high discharge periods. The maximum recorded sediment load is 1810 mg/L (USGS 1990). These sediment loads are actually fairly low for glacially fed rivers in Alaska. In comparison the Knik River has a mean daily concentration during the summer of 1400 mg/L, con-

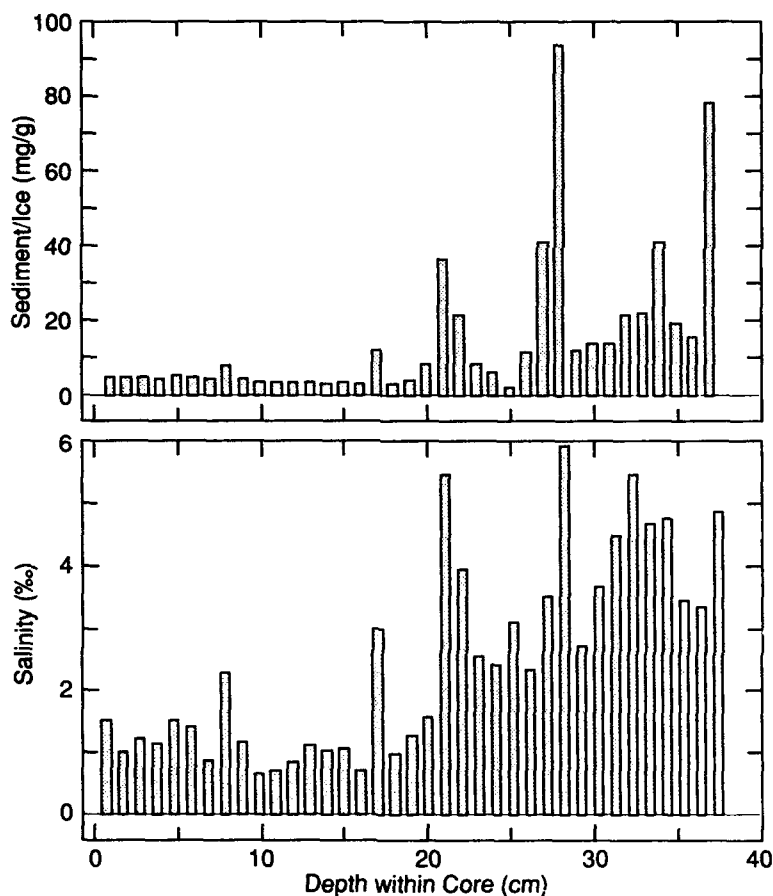


Figure 15. Salinity and sediment concentrations of ice at 1-cm intervals from the top to the bottom of an ice core obtained over a mudflat area. The correspondence between high salinities and sediments suggests that the ice here formed due to tidal flooding.

centrations near 4000 mg/L during high discharge periods and a maximum recorded sediment concentration of 6290 mg/L.

The waters of Knik Arm also contain a moderate suspended-sediment load derived from the glacially fed rivers emptying into it, such as the Matanuska and Knik rivers. Each time ERF is inundated, either by water from Eagle River or by tidal water from Knik Arm, silts and clays settle out of the water or ice covering the flats and are deposited, both on the mudflats and in the shallow ponds. In other areas sediment erosion is no doubt occurring. Sedimentation and erosion processes may play a role in the fate and future distribution of white phosphorus particles.

The 1964 earthquake caused the land to subside about 0.6 m along the shore of Knik Arm and probably increased flooding and the deposition of sediments at ERF (Small and Wharton 1972). We have not yet measured sedimentation rates at ERF, but rates determined on other mudflats in upper Cook Inlet (Vince and Snow 1984) are 5–12 mm per year.

The deposited sediments become the substrate of the ponds, mudflats and marshes. Here organic material is incorporated into the sediments as plant and animals die, causing a series of complex chemical reactions. The highly productive salt marsh produces large amounts of organic carbon, which becomes the basis of oxidation–reduction (respiration) reactions. Since oxygen is rapidly exhausted in these flooded organic-rich sediments, other electron acceptors such as sulfate become important. A major product of sulfate reduction is hydrogen sulfide, which has a characteristic odor that is pervasive in ERF. Since white phosphorus is highly reducing (it readily donates its electrons), the absence of an electron acceptor (i.e. oxygen) in the highly reduced salt marsh sediments means that WP will persist.

One measure of the relative availability of electrons in sediments is the redox potential ( $E_h$ ). The  $E_h$  is zero when there is no free oxygen in the sediments. The lower the redox potential, the slower WP would be oxidized. Over 200 measurements of sediment redox potential were made during the 1991 field season; these were from different vegetation zones, water depths and sediment types. All had negative values. In Area C,  $E_h$  varied from 0 mV on mudflat samples to –200 mV in the black organic sediments associated with bulrush areas. The sediments and water have pH values ranging from 7 to 8, or neutral to alkaline

(based on measurements of 36 water and sediment samples).

Phosphate tests were conducted on dried sediment samples, in hopes that this test could be used to screen for WP, since on drying the WP would theoretically be converted to phosphate ( $PO_4^{3-}$ ). Because the background levels of naturally occurring phosphates were high in the sediments, it was not possible to use this as a field screening test for WP. Other studies of salt marsh sediments in Georgia have shown that phosphorus (i.e. phosphate) accumulates in high concentrations and does not limit plant growth (Pomeroy et al. 1972).

#### *Salinity*

The salinity of the sediments and water varied seasonally within the flats, particularly in relation to the distance from freshwater inlet streams along the edge of ERF. In the permanent ponds of Areas B, D and C/D most likely fed by fresh water, the salinity of the water was less than 5 ppt. The salinity of the sediment pore water was usually higher than that of the pond water. In the semi-permanent ponds of Areas A, C and Bread Truck, salinities were higher (10 ppt). The highest salinities (20 ppt) were measured in shallow mudflat pannes and in craters during the winter and spring.

#### *Climate*

The Anchorage area is in the transitional climate zone between the extremes of the Continental and Maritime zones in Alaska. The Alaska Range north and northwest of Anchorage provides a barrier to the influx of very cold air from the interior. To the northwest and southwest, Anchorage is bounded by the waters of Cook Inlet and Turnagain and Knik Arms (Fig. 1), which provide a moderating influence on the climate. The average maximum temperature at Anchorage airport is 6.1°C (43°F), the average minimum temperature is –2.2°C (28°F) and the annual mean is 1.9°C (35.4°F). The highest and lowest recorded temperatures are 30°C (86°F) and –37°C (–34°F) (NOAA 1989). The Anchorage Bowl receives 33–51 cm (13–20 in.) of precipitation annually, with the heaviest precipitation in July and August, when the winds are often from the southwest. Air masses move in from the Gulf (southwest) and begin to rise over the Chugach Range east of Anchorage. This produces relatively heavy rainfall along the mountains and can contribute to high runoff events in the rivers draining the Chugach Range, including the Eagle River.

## Wildlife use

The interspersed and zonation of bulrush and sedge marshes, open water ponds and mudflats within ERF provide ideal habitat for large numbers of waterfowl, shorebirds, gulls, terns, raptors and other birds and mammals. Each of these groups is represented by a diverse array of species, as well as an abundance of several species. Because our field sessions were relatively short (two weeks in May and two weeks in August), the species listed in Table 2 represent only a sample of the species that use the area. Many more species would be included in a complete list.

Most waterfowl use ERF predominantly during the two migration periods: spring (late April to early June) and fall (mid-August to mid-October). During most years there are more waterfowl at ERF in the fall than in the spring. Small populations of ducks, cranes and shorebirds remain and breed in ERF throughout the summer.

## Waterfowl

ERF supports large numbers of green-winged teal, northern pintails, mallards, American wigeons, northern shovelers, Canada geese, greater white-fronted geese, tundra swans and trumpeter swans during the spring and fall migrations. The large number of species suggests that ERF is an important feeding and resting habitat during migration. In addition, some of these species, mallards at least, breed in ERF.

Less common species include blue-winged teal, ring-necked ducks, buffleheads, common mergansers and lesser scaup. These were seen occasionally in August; blue-winged teal were also seen in May 1991.

Sandhill crane flocks use ERF during migration, and several pairs nest and raise young.

## Shorebirds

The mudflats and shallow water at ERF are

Table 2. Bird species observed during field studies in May and August 1991.

Waterfowl		Shorebirds	
American wigeon	<i>Anas americana</i>	Red-necked phalarope	<i>Phalaropus lobatus</i>
Green-winged teal	<i>Anas crecca</i>	Lesser yellowlegs	<i>Tringa flavipes</i>
Northern pintail	<i>Anas acuta</i>	Short-billed dowitcher	<i>Limnodromus griseus</i>
Mallard	<i>Anas platyrhynchos</i>	Pectoral sandpiper	<i>Calidris melanotos</i>
Northern shoveler	<i>Anas clypeata</i>	Common snipe	<i>Gallinago gallinago</i>
Blue-winged teal	<i>Anas discors</i>	Wilson's phalarope	<i>Phalaropus tricolor</i>
Canada goose	<i>Branta canadensis</i>	Semipalmated plover	<i>Charadrius semipalmatus</i>
Tundra swan	<i>Cygnus columbianus</i>	Hudsonian godwit	<i>Limosa haemastica</i>
Trumpeter swans	<i>Cygnus buccinator</i>	Whimbrel	<i>Numenius phaeopus</i>
Greater white-fronted goose	<i>Anser albifrons</i>	Killdeer	<i>Charadrius vociferus</i>
Ring-necked duck	<i>Aythya collaris</i>	Lesser golden plover	<i>Pluvialis dominica</i>
Lesser scaup	<i>Aythya affinis</i>	Solitary sandpiper	<i>Tringa solitaria</i>
Bufflehead	<i>Bucephala albeola</i>	Western sandpiper	<i>Calidris mauri</i>
Common merganser	<i>Mergus merganser</i>		
Sandhill crane	<i>Grus canadensis</i>		
Gulls and Terns		Other Birds	
Herring gull	<i>Larus argentatus</i>	Violet-green swallow	<i>Tachycineta thalassina</i>
Mew gull	<i>Larus canus</i>	Rough-winged swallow	<i>Stelgidopteryx serripennis</i>
Arctic tern	<i>Sterna paradisica</i>	Tree swallow	<i>Tachycineta bicolor</i>
		Bank swallow	<i>Riparia riparia</i>
		Cliff swallow	<i>Hirundo pyrrhonota</i>
		Belted kingfisher	<i>Ceryle alcyon</i>
		Common northern raven	<i>Corvus corax</i>
		Rusty blackbird	<i>Euphagus carolinus</i>
		Savannah sparrow	<i>Passerculus sandwichensis</i>
		Lapland longspur	<i>Calcarius lapponicus</i>
Raptors			
Bald eagle	<i>Haliaeetus leucocephalus</i>		
Northern harrier	<i>Circus cyaneus</i>		
Merlin	<i>Falco columbarius</i>		
Peregrine falcon	<i>Falco peregrinus</i>		
Red-tailed hawk	<i>Buteo jamaicensis</i>		
Rough-legged hawk	<i>Buteo lagopus</i>		
Sharp-skinned hawk	<i>Accipiter striatus</i>		
Kestrel	<i>Falco sparverius</i>		
Northern goshawk	<i>Accipiter gentilis</i>		

valuable habitat for large numbers of shorebirds. Red-necked (northern) phalaropes, lesser yellowlegs, short-billed dowitchers and pectoral sandpipers occur in abundance. During May, aggressive mating behaviors were seen in the phalaropes, yellowlegs and pectoral sandpipers. Common snipe are less abundant in both May and August but appear to use ERF for breeding. Other species seen in small numbers in May include Wilson's phalaropes, semipalmated plovers, hudsonian godwits and whimbrels. In August (many shorebirds have migrated south before the last two weeks of August), semipalmated plovers, killdeer, lesser golden plovers, hudsonian godwits, solitary sandpipers and western sandpipers were seen. The abundance of the three species that use the area for mating plus the overall diversity of species indicate that this is an important habitat for shorebirds.

#### *Gulls and terns*

There are 5-10 herring gull nests in ERF. Most nests are in Area D, on hummocks of bulrush. Other pairs use the artillery targets as nesting platforms. In addition, numerous other herring gulls are seen on the flats, probably non-breeders feeding on salmon in Eagle River and on duck carcasses and aquatic organisms in the small ponds.

Mew gulls also breed in ERF. There are about ten nests in Area D. Arctic terns are common in May and are often seen diving for small fish in the open water.

#### *Raptors*

ERF supports a diverse community of hawks and eagles. Bald eagles are year-round residents. In May 1991 at least four adult and three immature birds used the flats. These probably include adults from nearby nests. Slightly fewer eagles were seen in August, presumably because some birds had moved to rivers to feed on spent salmon. Eagles often perch on targets and driftwood on the flats and on trees along the margins. Spruce trees used as perches on the northeast edge had well-worn, stunted tops, suggesting a long history of roosting by these eagles. These numbers represent a high concentration of eagles for a marsh this size. The abundance of eagles may result from the abundant food in the form of sick and dead ducks.

Both male and female northern harriers use ERF during spring and fall. Harriers are known to feed primarily on rodents in wet grassy areas but have been seen feeding on dead ducks at ERF. Merlins were seen regularly, eating the abundant

dragonflies in August. Peregrine falcons were seen during fall migration, presumably attracted by the abundant shorebirds. Other species seen include red-tailed hawks, rough-legged hawks, sharp-shinned hawks, kestrels and northern goshawks.

#### *Other birds*

Numerous other species use the Eagle River Flats marsh, the drier sedge areas, the open water and the margins of ERF. A diverse assemblage of swallows used ERF during May. Violet-green, rough-winged, tree, bank and cliff swallows were all seen in abundance. Belted kingfishers fished in the pools on the margins of ERF. Rusty blackbirds were seen in the bulrushes in May and August and may breed there. Savannah sparrows were common throughout the summer, and flocks of Lapland longspurs were common in August.

Common northern ravens also occur in abundance. Six to eight ravens use the flats regularly. Ravens also use dead ducks as their primary food resource, although they are subordinate to the eagles and are often chased away from carcasses.

#### *Other animals*

Several species of mammals add to the diversity of wildlife using ERF. Moose frequently wander out onto the flats from the edges. Three coyotes were seen on the flats, and muskrats inhabit bulrush areas.

Wood frogs were especially evident in August, probably representing a major source of food for sandhill cranes.

#### *Summary*

Each of these groups of animals considered alone represents a valuable wildlife resource; together these groups indicate that ERF has significant value to wildlife. Not only do large populations occur on the flats, but many species are represented. Thus, we conclude that ERF is an important wildlife resource for this part of Alaska.

The abundance of birds at ERF reflects a productive food chain providing resources to support the higher trophic levels. The great diversity of species results from the diversity of habitats. ERF contains large shallow ponds, sparse sedges, mudflats, craters and expansive bulrush stands interspersed with small ponds. Derelict trucks, placed as targets, provide perches that are not present in other marshes. As such, ERF has more diverse habitat features than surrounding marshes at Goose Bay and Fire Creek. In addition, ducks poisoned by white phosphorus represent an abun-



dant food source for predators not available in other areas.

## **ANALYTICAL METHODS FOR THE DETERMINATION OF WHITE PHOSPHORUS IN SEDIMENTS AND TISSUE**

### **Introduction**

A major objective of our 1991 work at ERF was to determine the spatial distribution of WP in ERF sediments. To meet this objective we needed an analytical procedure for determining WP concentrations in sediment. At present there is no standard method for the analysis of WP in soil or sediment, although there are published procedures (Sullivan et al. 1979), most of which are variations of the gas chromatographic method developed by Addison and Ackman (1970). Addison and Ackman developed their method to analyze sediments contaminated by the effluent from a WP production facility, so the mode of contamination was quite different from the contamination at ERF. The method we used was based on the work of Addison and Ackman (1970) in that we used isooctane to extract sediment and we used gas chromatography to determine WP concentrations. *However, we modified their method by changing the sediment-to-solvent ratio and the extraction procedure as described below.*

Also, as part of our 1991 field work, we planned to analyze tissues from carcasses of birds observed to die or found dead at ERF and surrounding areas. Therefore, an analytical method for WP in tissue was also required. Based on published procedures developed for fish tissue by Addison and Ackman (1970), we experimented with extraction conditions and storage procedures for duck tissue.

### **Sediment method**

#### *Soil-to-solvent ratio*

The method developed by Addison and Ackman (1970) was designed to detect WP in sediments contaminated with colloidal WP. Up to 5 g of wet sediment was extracted with 50 mL of solvent by swirling with 5-mm glass beads in a stoppered flask for 10–15 minutes. The samples were filtered, then extracted again. The filtrates were combined, and the isooctane layer was collected for analysis.

The sediments in ERF are contaminated with particulate WP, so the potential for subsampling error is high due to the heterogeneous distribution of WP particles within a sample. While extraction of a large subsample is desirable because it would

better represent the sample as a whole, the size of the subsample that can be efficiently extracted in the laboratory is limited by the mechanics of mixing the nonpolar solvent and the wet sediment.

We noticed that samples with low moisture content did not mix effectively with the isooctane; the soil formed a plug on the bottom of the extraction vial, and only the sediment surface was in contact with the solvent. However, samples with high moisture content (greater than 50%) appeared to mix well with the solvent since the sediment remained suspended when shaken. We found that efficient mixing could be obtained when approximately 20 g of wet sediment (50% moisture on a wet weight basis) was mixed with 10 mL of water and 10 mL of isooctane and shaken horizontally on a platform shaker.

#### *Extraction kinetics*

Addison and Ackman (1970) sequentially extracted spiked wet-sediment samples over two 10- to 15-minute intervals. Analyte recovery ranged from 77 to 90%. Since spiked samples do not realistically simulate field-contaminated samples (Jenkins et al. 1989), we performed an experiment using sediments collected at ERF to better define the length of time required to extract WP from wet sediments.

Four sediment samples with estimated WP concentrations ranging from 0.001 (barely detectable) to 1 µg/g were used. Sediments with a wide range of analyte concentration were tested, since extraction kinetics can vary with concentration (Jenkins and Grant 1987). Approximately 10 g of wet sediment were placed in a 40-mL vial containing 10 mL of isooctane and 5 mL of degassed water. Each sample was capped and then vortex-mixed for one minute. A Pasteur pipette was used to withdraw a 0.1-mL subsample of the isooctane layer. Then the samples were shaken horizontally on a platform for 48 hours, with subsamples of the isooctane layer taken at 0.5, 1, 1.5, 4, 7.75, 24 and 48 hours. Prior to sampling of the isooctane, each sample was briefly centrifuged, and after sampling each sample was vortexed to resuspend the sediment prior to being placed back on the platform shaker.

For the sample with the lowest analyte concentration, the highest concentration was measured after extended shaking (48 hours); WP was undetectable in the sample shaken less than 7.75 hours (Fig. 16a). For the two samples at the intermediate WP concentrations, the highest recoveries were at 24 and 7.75 hours (Fig. 16b,c). Extending shaking resulted in analyte loss. For the sample with the

highest WP concentration, WP was detectable after 1 minute of vortexing and reached equilibrium after 4 hours of shaking (Fig. 16d).

Based on these results, a shaking time between 7.75 and 24 hours is optimum. This situation is similar to that obtained for the extraction of explosives of soil (Jenkins and Walsh 1987). For practical reasons a shaking time of approximately 18 hours is convenient, since samples that are prepared for extraction in the afternoon are ready for analysis the following morning.

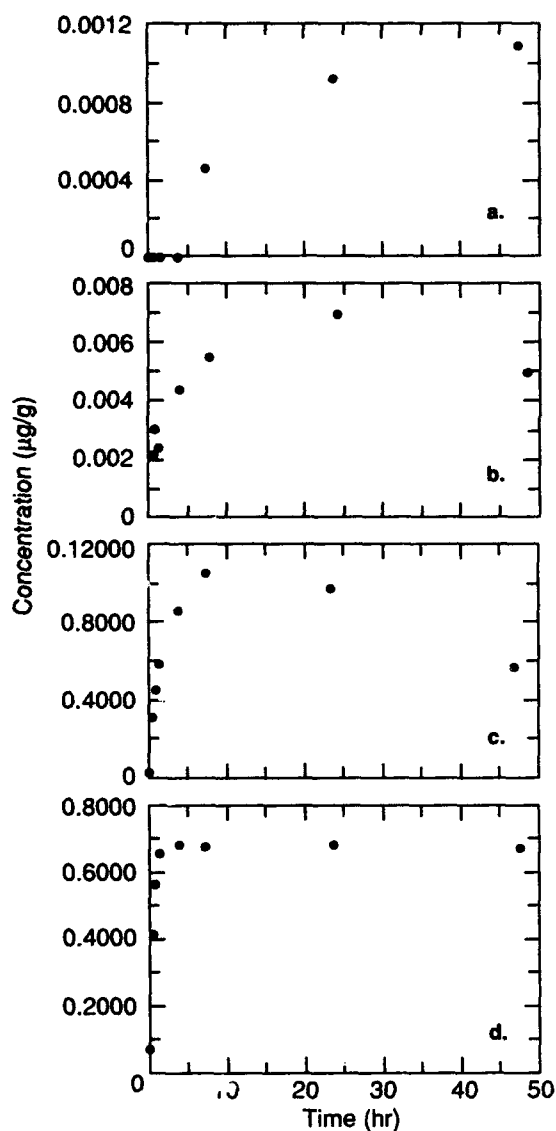


Figure 16. WP concentrations found in four sediment samples after various extraction times on a mechanical shaker.

#### Method certification

A spike-recovery study was conducted as described in the U.S. Army Toxic and Hazardous Materials Agency Installation Restoration Quality Assurance Program (USATHAMA 1990). Subsamples (10 g) of wetted (50% moisture on a wet weight basis) USATHAMA standard soil were spiked with isooctane solutions of WP to yield soil concentrations over the range of 0.004 to 0.08 µg/g. The samples were then treated as described below for field samples. Duplicate samples were prepared and extracted on four consecutive days. A certified reporting limit was calculated using 90% confidence bands about a linear least-squares regression model for found concentrations versus spiked concentrations. A reporting limit of 0.0009 µg/g (wet weight) was calculated; however, THAMA protocol does not permit a certified reporting limit less than the lowest tested concentration. When the calculated reporting limit is less than the lowest tested concentration, the certified reporting limit corresponds to the lowest tested concentration (0.004 µg/g for this case). Recovery was 97.2%. Certification data were approved by USATHAMA, and the method was assigned the number KN01.

#### Analysis of field samples

**Methods.** We set up a temporary field laboratory at the Alaska District Office (COE) on Elmendorf Air Force Base. On the same day as samples (500 cm<sup>3</sup>) were collected, they were brought to the field lab, and a subsample was taken for WP analysis. A plug of wet sediment was removed using a 20-mL corer (a plastic 20-mL syringe with the needle end cut off) and placed into a weighed 120-mL IChem jar containing 10 mL of isooctane and 10 mL of degassed distilled water. The jar was reweighed to determine the sample wet weight. The weight varied because the plug included sediment, vegetation, water and air in differing proportions. Each sample was shaken vigorously by hand and then placed horizontally on a platform shaker overnight. After shaking, the samples were allowed to stand vertically for about 15 minutes. Then a Pasteur pipette was used to transfer an aliquot of the isooctane layer to a 1.5-mL vial. This isooctane extract was then analyzed using gas chromatography (GC).

All samples were analyzed on a gas chromatograph (SRI Model 8610) equipped with a nitrogen-phosphorus detector. The GC conditions were as follows:

Column: J and WDB-1, 15-m, 3.0-µm film thick-

ness, 0.53-mm ID

Oven: 80°C (isothermal)

Injection: 1.0 µL, on-column

Carrier gas: Nitrogen, 30 mL/min

Data acquisition: Peak heights were measured and scored on an HP3396A digital integrator or measured on a linear strip-chart recorder.

A WP standard was analyzed during the course of the daily analysis to ensure that the sensitivity of the GC remained constant and to determine the mass of WP in the extracts. For each sample the mass of WP was divided by the wet sediment weight, and the concentrations were expressed as µg/g wet weight.

*Sources of Subsampling Error.* Because WP is present in the sediments as particles of different sizes, the mass of WP detected in a 20-cm<sup>3</sup> subsample from a 500-cm<sup>3</sup> jar would depend on the number and size of the particles in the subsample. We were concerned that if a sample jar contained only a few particles of WP heterogeneously distributed in the sediment, a negative result (i.e. no WP or below detection) might be obtained from a sample jar that contains WP. To test this possibility we subsampled five samples (collected in the vicinity of contaminated samples) that were negative when analyzed in the field lab.

Five subsamples from each of these five sample jars all tested negative. When the remaining contents (200–300 mL) of each jar was extracted, no WP was found. These results suggest that the risk of making a Type II error (false negative, or claiming a sample is blank when in fact WP particles are present) is low. We also took multiple subsamples from samples that we found were positive when analyzed in the field lab. None of the replicates from these samples presented in Table 3 gave a below-detection (or negative) result, which also supports the conclusion that the risk is low in our data set of claiming the absence of WP in a bulk sample where it is actually present.

The degree to which a single 20-cm<sup>3</sup> subsample represents the actual concentration of WP in a 500-cm<sup>3</sup> sample jar (bulk sample) was also investigated. Multiple 20-cm<sup>3</sup> subsamples taken from single jars show the high variability expected when sampling particulate contaminants (Grant and Pelton 1974), with the standard deviation being greater than the mean of the subsamples in some cases (Table 3). Out of four or five subsamples from a single jar, the highest-concentration replicate subsample was 2–50 times greater in concentration than the lowest-concentration subsample

**Table 3. Variability in WP concentrations (µg/g wet weight) of replicated 20- and 40-cm<sup>3</sup> subsamples (arranged from lowest to highest concentrations) from sample jars containing contaminated sediments from Eagle River Flats. A single 200-cm<sup>3</sup> sample was extracted from the contents remaining after removal of four 20-cm<sup>3</sup> subsamples from the last four jars. SD is the standard deviation of the mean; CV is the coefficient of variation, or SD × 100/Mean.**

Sample number	Size of subsample (cm <sup>3</sup> )	Conc. rep 1	Conc. rep 2	Conc. rep 3	Conc. rep 4	Mean conc.	SD	CV (%)
200	20	0.0055	0.0075	0.0081	0.0113	0.008	0.002	30
	40	0.0061	0.0063	0.0129	0.2620	0.072	0.127	176
382	20	0.0111	0.0113	0.0143	0.5475	0.146	0.268	183
	40	0.0118	0.0136	0.0159	0.0199	0.015	0.003	23
333	20	0.0088	0.0089	0.0125	0.0318	0.016	0.011	69
	40	0.0076	0.0077	0.0197	0.0318	0.017	0.012	71
278	20	0.0703	0.0903	0.0940	0.5237	0.195	0.220	113
	40	0.0934	0.101	0.1091	0.1478	0.113	0.024	21
561 core	20	0.334	0.449	0.460	0.795	0.510	0.199	39
494	20	6.36	26.3	33.4	43.9	27.5	15.8	57
223	20	0.0083	0.0090	0.005	0.011	0.008	0.003	38
	200	0.095						
496	20	0.0025	0.0031	0.0042	0.0063	0.004	0.002	50
	200	0.0048						
615	20	0.364	0.410	0.486	0.489	0.437	0.061	14
	200	0.521						
527	20	0.002	0.003	0.003	0.006	0.004	0.002	50
	200	0.005						

(Table 3). Therefore, one 20-cm<sup>3</sup> subsample taken from each sample jar in the field lab may or may not represent the true concentration in the entire jar. Doubling the size of the subsamples from 20 to 40 cm<sup>3</sup> decreased the replicate variation in only two of the four bulk samples (382 and 278) analyzed.

When four contaminated sample jars were subsampled with four 20-cm<sup>3</sup> subsamples and a 200- to 300-cm<sup>3</sup> sample (the remaining contents of the jar), the mean concentration of the five 20-cm<sup>3</sup> subsamples was very similar to that of the single large subsample in three out of four samples tested (Table 3). These results suggest that there are two size classes of WP particles: one class of very small particles that are homogeneously distributed and another class of significantly larger particles that are heterogeneously distributed. In any case a positive result for WP in a sample is evidence for the past use of WP munitions in the vicinity of the sampling point. If a positive result is found, even if the concentration is quite low (i.e., <0.004 µg/g), then areas near the sampling point could be contaminated with particles large enough to provide a toxic dose to a duck.

#### Tissue method

An analytical procedure for the analysis of WP in fish tissues was developed by Addison and Ackman (1970) in which up to 10 g of tissue was homogenized in a blender for two minutes with 50 mL of iso-octane. Then the iso-octane was analyzed by gas chromatography. Based on this analytical approach, we used tissues from farm-reared mal-

**Table 4. Concentration of WP in tissues homogenized under nitrogen and room air.**

Tissues	WP Concentration (µg/g)			
	Duck 1	Duck 2	Duck 3	Duck 4
<b>Breast Muscle</b>				
Nitrogen Atm.	0.033	0.025	0.120	0.038
Room Atm.	0.025	0.018	0.065	0.038
<b>Liver</b>				
Nitrogen Atm.	0.150	0.040	0.680	0.365
Room Atm.	0.045	0.430	0.530	0.080
<b>Fat</b>				
Nitrogen Atm.	3.30	2.04	3.52	1.41
Room Atm.	NA	2.76	3.50	1.99
<b>Skin</b>				
Nitrogen Atm.	1.02	1.16	2.22	1.42
Room Atm.	NA	1.04	2.28	1.53

**Table 5. Concentration of WP measured in tissues homogenized in a blender and tissues cut into small pieces.**

Tissues	WP Concentration (µg/g)		
	Teal	Sandpiper	Mallard
<b>Muscle</b>			
Blended	0.0056	0	0.0045
Cut	0.022	0.006	0.0043
<b>Fat</b>			
Blended	0.55	0.19	NA
Cut	1.30	0.47	NA
<b>Skin</b>			
Blended	0.24	0.14	0.024
Cut	0.44	0.33	0.065

lards dosed with WP and from wild birds that died of WP poisoning to better define extraction conditions and tissue storage methods. Additionally the method was used to determine the distribution of WP in the tissues of ducks.

#### Homogenization conditions

Since pure WP oxidizes when exposed to atmospheric oxygen, we were concerned that the air introduced when homogenizing tissues in a blender would result in reduced recovery of WP. We compared WP concentrations in tissues (fat, muscle, skin and liver) homogenized in a nitrogen atmosphere to those homogenized in room air using tissues from mallards gavaged at a dose level of 12 mg/kg as described elsewhere (Racine et al. 1992). Excised tissue was placed in a 40-mL glass vial (Supelco), and the vial was placed in the nitrogen glove bag. Under the nitrogen atmosphere, the collected tissue was cut into small pieces and placed in a Waring blender with 10 mL of degassed water. The tissue was homogenized for about 30 seconds, and the contents were emptied into a glass vial. Another 10 mL of degassed water was poured into the blender, homogenized for 30 seconds and added to the original vial. This was followed by the addition of 10 mL of iso-octane into the vial. Then the tightly capped vial was removed from the nitrogen bag and placed on a rotating shaker for 24 hours. For comparison, tissues were collected and homogenized as described above but were homogenized in room air. The WP concentration in each tissue sample was measured by gas chromatography (Table 4). No significant difference was found when the results were compared using a paired t-test at the 95% confidence level.

The tissue homogenization process described above was problematic in two important ways. First, it was difficult to recover all of the tissue from the blender container, and cleaning the blender to prevent cross contamination between samples was very time consuming. We used tissues from waterbirds (one green-winged teal, one mallard and one sandpiper) that died of WP poisoning at ERF in May 1991 to compare WP concentrations in tissues homogenized in a blender as described above to tissues that were simply cut into small pieces followed by extraction with iso-octane. The latter procedure is easily performed in the field. WP concentrations were consistently higher in tissues that were cut, not blended (Table 5).

#### Storage of tissues

While we planned to analyze some tissues in our field lab in Alaska, we also proposed to ship some tissues back to CRREL for more detailed analyses. Therefore, we needed to test some tissue storage methods. Two tissue storage procedures were tested prior to the May field trip using tissues collected from mallards dosed in the laboratory. Some of the tissue samples excised from the treated mallards were placed in a nitrogen-purged vial prior to being frozen and stored at  $-20^{\circ}\text{C}$  for one

week. Other samples were simply placed in a vial, frozen and stored at  $-20^{\circ}\text{C}$  for one week prior to extraction. Additionally, to simulate tissues collected from a carcass that is not fresh, approximately half of the duck was wrapped with wet paper towels and left at room temperature for 24 hours exposed to the atmosphere prior to tissue collection. All these tissue samples were collected and homogenized under a nitrogen atmosphere.

Freezing the WP-containing tissue had no significant effect on the WP concentration (Table 6). This finding agrees with the results of Dyer et al. (1972); they concluded that WP decomposition was very slight in cod muscles that had been frozen. Additionally the WP concentrations in tissues collected from the carcasses aged for 24 hours at room temperature were not significantly different from tissues collected and extracted immediately after death.

#### Distribution of WP in tissues

Prior to the May field trip, we wanted to identify which tissues are likely to have the highest WP concentration. Identifying such a tissue would facilitate sampling of carcasses for WP poisoning. For all four birds dosed in the laboratory (Table 7), the highest WP concentration was found either in the lower intestine or in the fat. WP concentrations

**Table 6. Concentration of WP measured in tissues stored under various conditions prior to extraction.**

Tissues	WP Concentration ( $\mu\text{g/g}$ )			
	Duck 1	Duck 2	Duck 3	Duck 4
<b>Breast Muscle</b>				
No storage	0.033	0.025	0.120	0.038
Nitrogen/Frozen	0.043	0.020	0.073	0.028
Air/Frozen	0.040	0.028	0.045	0.035
Air/Room Temp.	0.038	0.025	0.013	0.027
<b>Liver</b>				
No storage	0.15	0.040	0.68	0.36
Nitrogen/Frozen	0.020	NA	0.60	0.18
Air/Frozen	0.020	NA	0.50	0.095
Air/Room Temp.	NA	NA	NA	NA
<b>Fat</b>				
No storage	3.3	2.04	3.5	1.4
Nitrogen/Frozen	NA	NA	3.4	1.1
Air/Frozen	NA	NA	3.7	1.5
Air/Room Temp.	2.0	2.03	NA	NA
<b>Skin</b>				
No storage	1.0	1.2	2.2	1.4
Nitrogen/Frozen	NA	NA	1.8	1.2
Air/Frozen	NA	NA	2.0	1.1
Air/Room Temp.	1.2	1.0	1.5	1.2

**Table 7. Concentrations of WP in various duck tissues from mallards dosed in the laboratory.\***

Tissue samples	WP concentration ( $\mu\text{g/g}$ )			
	Duck 1	Duck 2	Duck 3	Duck 4
Brain	0.030	0.050	0.060	0.050
Breast Muscle	0.033 $\pm$ 0.007	0.025 $\pm$ 0.003	0.120 $\pm$ 0.045	0.038 $\pm$ 0.009
Body Fat	3.30	2.04	3.52 $\pm$ 0.495	1.41 $\pm$ 0.070
Heart	0.145 $\pm$ 0.045	0.150 $\pm$ 0.010	0.290 $\pm$ 0.050	0.265 $\pm$ 0.015
Kidney	0.270	0.130	0.150 $\pm$ 0.010	0.050
Lower Intestine	0.390	5.29	1.91	4.58
Upper Intestine	0.700	0.180	0.820	0.420
Proventriculus	0.220	0.250	0.920	0.470
Leg Muscle	0.360 $\pm$ 0.240	0.350 $\pm$ 0.050	0.330 $\pm$ 0.190	0.215 $\pm$ 0.045
Liver	0.150 $\pm$ 0.090	0.040	0.680 $\pm$ 0.020	0.365 $\pm$ 0.005
Skin	1.020 $\pm$ 0.090	1.16 $\pm$ 0.009	2.22 $\pm$ 0.015	1.42 $\pm$ 0.015
Gall bladder		0.320	0.360	
Testes	0.050 $\pm$ 0.010	0.040		
Egg Yolk			0.300	0.040 $\pm$ 0.020
Blood	0	0	0	0

\*The majority of the tissue samples were taken in duplicates, but some were taken in singles, triplicates or quadruplets. Duck 1 was a 1.05-kg male; duck 2 was a 1.1-kg male; duck 3 was a 1.2-kg female; and duck 4 was also a 1.2-kg female.

in the skin nearly equaled the fat concentrations. This finding was consistent with expectations, since WP is very lipid-soluble. The lowest concentrations were in the breast muscle. All tissues that were sampled for WP were positive, except for the blood samples.

Accumulation of WP in the tissues of marine animals has been studied extensively (Sullivan et al. 1979). WP concentrations were directly correlated with lipid content. For example, the liver of cod had the highest WP concentrations for that species. For ducks, collection of fat or skin with subcutaneous fat would provide a sample suitable for WP analysis.

#### Sample processing and analysis during the May and August field trips

Tissues from some birds found dead or observed to die at ERF during the May and August field trips were excised in the field, cut into small pieces, and then placed directly into weighed vials containing 10 mL of isooctane. These samples were returned to the field lab, shaken overnight on

a platform shaker, and then analyzed using the same chromatographic conditions as for sediment samples. Some whole birds were frozen and shipped to the Dartmouth Medical School for detailed analysis. Samples from these birds were processed as soon as the carcass thawed sufficiently to allow tissue collection.

## DISTRIBUTION AND CONCENTRATIONS OF WP IN ERF POND SEDIMENTS

### Introduction

Before any remediation efforts can begin in ERF, it is critical to know the location of the source of WP poisoning. Thus, a major objective of the 1991 field season was to determine the spatial extent and concentrations of WP contamination of ERF sediments in each of the waterfowl feeding pond areas. Shallow ponds cover about 50 ha (125 acres) of the 1000-ha ERF (Table 1). Although dead waterfowl and WP-containing carcasses have been collected from ponds in all four areas (A, B, C and

D), WP is not necessarily contained in the bottom sediments of all four areas; waterfowl may ingest WP in one area and fly into another pond where death takes place due to WP poisoning or predation. Because dabbling ducks that feed in the bottom sediments of ponds are the major victims, we assume that WP particles are located in the top 5–10 cm of bottom sediments where water depths are shallow enough (<25 cm) to allow the ducks to feed on the bottom by tipping up.

In May 1991 a sediment sampling program was initiated to systematically sample the bottom sediments of all the pond areas in ERF. By integrating the sediment sampling design with the waterfowl observation studies, it was also possible to identify areas where birds displayed early symptoms of WP poisoning and where sediment sampling should therefore be concentrated. Waterfowl observation blinds or towers 5 m tall were constructed by the Ft. Richardson DEH in the fall of 1990 and served as the center of waterfowl observations and the sediment sampling program during May and August 1991.

## Methods

### *Transect layout*

Sediment samples were collected every 25 m along transect lines radiating from the observation towers near the centers of Areas A and C and from the blind along the edge of Area D. Transect lines radiated in each of the compass directions (N, NE, E, SE, S, SW, W and NW). The lines ended at the edge of the ponds or on occasion extended into adjoining mudflats subjected to frequent flooding. The transect lines were marked every 50 m with 2-m-tall posts with numbered placards. The placards were marked with the compass direction and sequential numbers for the bearing and distance from the tower (for example, N-1 for the north transect 25 m from tower and E-3 for the sample point 125 m from the tower on the east transect). Sample sites at intermediate locations along the transect line were marked with 1.2-m-tall survey lath.

In August several "close-interval" samples were collected at a distance of 1–10 m from the 25-m-interval sample sites that tested positive for WP in May. In addition, several sediment cores were obtained (as described below) to determine the depth of WP contamination. The 25-m-interval was selected to sample the pond areas in ERF. This interval should be of sufficient resolution to detect WP particles dispersed by an explosion, although the extent of ejecta generated by a detonation

depends on a variety of factors, including height above the ground, projectile size and wind conditions. The imprint from such an event is probably on the order of 50 m.

### *Access*

We used an Army UH-1H helicopter provided by Ft. Richardson to gain access to Areas A and B and the Bread Truck Pond. Access to Areas C and D and the C/D transition was mainly by foot or canoe from the east side of ERF. In all cases the sampling party was escorted by EOD personnel because of concern about unexploded ordnance or duds.

### *Sample collection*

At each sample point a surface sediment sample was scraped up with a rubber-glove-covered hand from beneath the water. The sample was packed into a 500-mL I-Chem jar to exclude all air and was tightly capped. At each sample point the water depth was recorded and the vegetation-habitat type and species noted. Two or more people made up the sampling party, including one person to collect the sample and another to hold the survey range pole and carry the sample jars.

### *Sediment cores*

In August, several sediment cores were obtained to determine the depth of WP contamination. Coring soft bottom sediments is problematic. A coring device was designed and constructed at CRREL. It was made of 3-in.-diameter clear Plexiglas pipe. The non-coring end could be capped following insertion of the corer in the sediments. The vacuum provided by the cap permitted removal of an intact core. When the cap was removed, water that had been collected along with the sediments would pour out and then the sediment core was pushed out the end, cut into segments and placed in individual sample jars. Sediment cores were obtained from four sample sites in Area C and two in the Bread Truck Pond, both areas that had previously tested positive for WP.

### *WP analysis in the field laboratory*

The filled sample jars were brought to the laboratory at the COE District soils lab for analysis within a few hours of collection. Several measurements were made as described below, and a 20-cm<sup>3</sup> core was taken out of each jar with a cut-off syringe. This core was placed in a preweighed jar containing isooctane solvent and additional water, reweighed and placed on a mechanical shaker

overnight. In the morning an aliquot of the iso-octane above each sample was placed in a vial and then injected into the gas chromatograph. The WP mass from the 20-cm<sup>3</sup> sample was calculated and the concentration expressed as the weight of WP per unit weight of the wet sediment.

#### *Measurement of environmental parameters*

Salinity, pH, redox potential and temperature were measured for about half the samples collected during the 1991 field season. In May, salinity and redox potential were measured in the laboratory within a few hours of collection. The measurements were therefore made on the pore water in the sediment sample jars collected from the beginning, middle and end of each transect. At this time the salinity of the pore water was measured using a Hach digital titrator (mercuric nitrate titration method of chloride analysis). The redox potential was measured with a Hach One pH meter (in mV mode) with an oxidation-reduction (ORP) electrode. During August a YSI Salinity-Temperature and Conductivity meter was used in the field to determine the salinity, temperature and conductivity of the water column overlying each sediment collection site. The redox potential was again determined in the laboratory using the same method as that used in May.

#### *Surveying*

Each sample site was surveyed using an electronic Leitz SET4 Total Station (a theodolite with a built-in laser distance-measuring device) and a range pole with a three-prism reflector. The Leitz Total Station provides a direct digital readout of horizontal and vertical angles, as well as horizontal and vertical distances between the instrument and the prism being sighted on.

Three permanent survey control points, with known coordinates and elevations, were established prior to 1991 on high points around the perimeter of ERF (Fig. 2). "Ruth" is located on the bluff overlooking Area D near the northeast edge of the flats. "Point Cole" is located on the southwest side overlooking Area B. "Tank" is at the observation point overlooking the EOD pad and Area C. A fourth control point, "Point Crane," surveyed and established in 1990, is on the edge of the EOD pad, immediately adjacent to Area C. During 1991, additional survey control points were established to provide survey control during the detailed sampling in the shallow ponds in Areas A, B, C and D. The locations of each of the towers and the blind were precisely surveyed from the

known control points. Points were marked on the center of the upper decks of the towers and surveyed in. The UTM coordinates and the elevations for each of these survey points were computed. These new control points were then used to provide horizontal and elevation control when sample locations in the vicinity were surveyed.

Almost all the sampling areas were visible from at least one of the original control points or one of the newly established tower control points. The survey point for Area A was the top of the observation tower in A; the survey point for Area C was either Pt. Crane or the observation tower in C; for Area B the tower at Cole Point was used; the surveyed point for Bread Truck Pond was the observation tower in C; Area D was surveyed from the blind in D.

The three-prism reflector on the range pole was placed over each sample point, and the horizontal angle and horizontal and vertical distances from the Leitz Total Station to the sample point were determined. Based on the horizontal azimuth and distance from the control point, a set of UTM coordinates for the sample point could be calculated. Horizontal accuracies are on the order of  $\pm 0.01$  m. Elevations of the sample points were calculated based on the vertical distance directly measured between the instrument and the prism, the height of the instrument above the control point, and the height of the prism above the ground.

Small ponds north and south of the main pond in Area A and a pond on the west side of Area D were not directly surveyed, either because of the distance to the nearest control point or because there were not enough people to do both the sampling and the surveying. In these cases sampling points were located on large-scale color infrared aerial photographs while the sampling party was in the field. UTM coordinates for the sample points were later scaled from known, surveyed locations on these photographs. The accuracy of plotting sampling points on the photographs was quite good. The detail and clarity of the photography allowed the plotting of locations on the photo to within an estimated  $\pm 2$  m. The accuracy of scaling the UTM coordinates from known locations on the map adds an additional estimated error of  $\pm 2$  m, for a total estimated positional error of  $\pm 4$  m.

#### *Preparation of detailed maps*

The calculation of UTM coordinates for the sample sites, observation blinds and other features visible on a set of color infrared aerial photos



**Table 8. Results of WP analyses of sediment samples collected in Eagle River Flats at 25-m intervals and at closer intervals (1–10 m) along transects during May and August 1991.**

Feeding area	Date collected	Number of samples	Positive for WP		Concentration range ( $\mu\text{g/g}$ )
			Number	Percentage	
A	May 91 (25 m)	51	8	16	0.0001–0.06
	Aug. 91 (25 m)	43	4	7	0.0004–0.05
	Total (25 m)	94	12	13	
	Close Interval	9	4	44	0.0004–0.05
B	May 91 (25 m)	0	0	0	—
	Aug. 91 (25 m)	15	0	0	—
C	May 91 (25 m)	86	36	42	0.0002–6.3
	Aug. 91 (25 m)	38	13	34	0.0004–1.1
	Total (25 m)	124	49	40	
	Cores (4)	14	12	86	0.0035–19.8
C/D	May 91 (25 m)	0			—
	Aug. 91 (25 m)	23	2	9	0.001–0.01
D	May 91 (25 m)	16	0	0	—
	Aug. 91 (25 m)	27	0	0	—
	Total	43	0	0	
Bread Truck	May 91	23	16	70	0.0004–57.6
	Aug. 91	20	13	65	0.003–7.7
	Total	43	29	68	
	Close interval	4	4	100	
	Cores (2)	6	5	83	0.0014–7.72
Pond Beyond	May 91 (25 m)	7	1	14	0.02
	Aug. 91 (25 m)	0	0		—
Total surface		362	101	28	0.0001–57.6
Total cores		20	17	85	0.0014–198

(obtained on 21 July 1991) permitted the precise mapping of WP contamination and sample sites in relation to the habitat–vegetation zones, distributaries, craters, waterfowl carcasses and other features. The resulting maps showing the distribution of WP contamination provide important information for remediation work. These maps were prepared by positioning a 100-m-interval UTM grid transparency over the photo of each area and mapping the various habitat types, distributaries and sample sites or transects onto these transparencies.

## Results

### Presence of WP

Of 362 surface sediment samples collected in all six ponded areas of ERF during 1991, 101, or 28%, tested positive for WP. Over 65% of the samples collected in the Bread Truck Pond were positive, compared with 40% in Area C (Table 8, Fig. 17). None of the samples collected in Areas B or D showed detectable levels of WP. In Area A about 13% of the samples (12 out of 94) were positive for WP, compared with 9% (2 out of 23 samples) of the samples in the C/D transition area. As empha-

sized earlier the level of confidence in the WP presence or absence results is high.

### Concentrations and mass of WP

In the sediment samples testing positive for WP, concentrations of WP were highly variable, both between and within samples from the ponded areas. Because of the variability due to subsampling error for particulates, the concentration and mass values are considered less reliable than the presence and absence data. Concentrations ranged from less than the certified reporting limits of 0.004  $\mu\text{g/g}$  up to 57.6  $\mu\text{g/g}$ , with most values less than 0.099  $\mu\text{g/g}$  (Table 8, Fig. 18a). However, when the frequency distribution of concentration and mass is plotted on a log scale, the values are normally distributed (Fig. 18a). The masses in the 20-cm<sup>3</sup> subsamples are included here (Fig. 18b) because WP is in a particulate form, and mass per volume of sediment is more relevant to waterfowl feeding behavior. WP mass values varied from 0.001  $\mu\text{g}$  up to 2 mg (2000  $\mu\text{g}$ ), with most less than 1  $\mu\text{g}$  per 20-cm<sup>3</sup> sample. This mass (1  $\mu\text{g}$  or less) could be produced by a single small particle in the 20-cm<sup>3</sup> subsample. Table 9 presents the mean WP

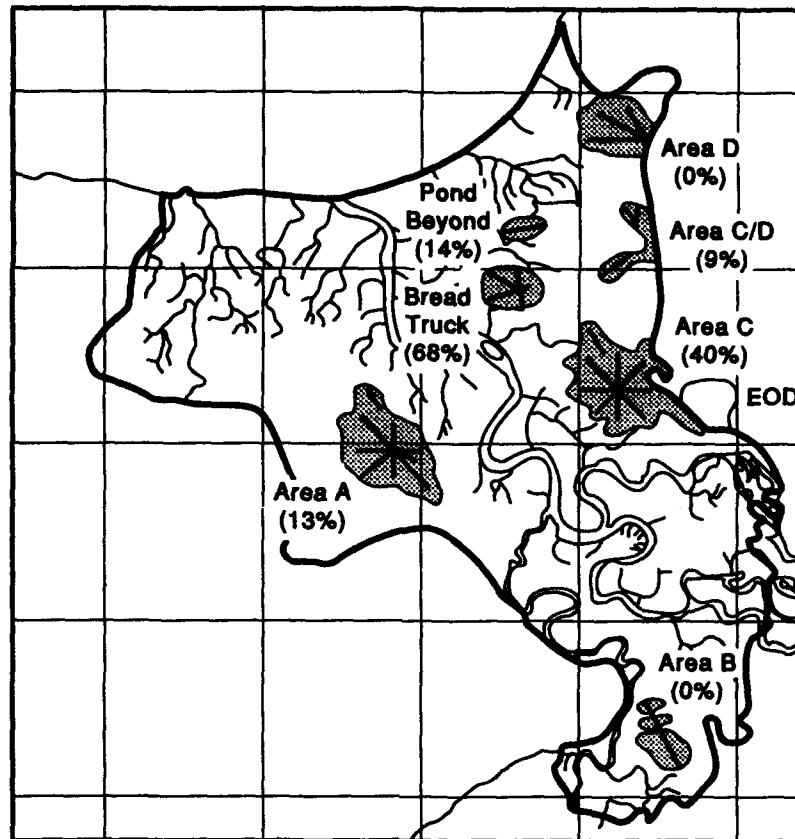


Figure 17. Map of Eagle River Flats showing the Eagle River and its distributaries and the percentage of sediment samples that tested positive for WP in each of the six waterfowl feeding areas. The UTM grid lines are 1000 m apart.

concentrations and masses for 20-cm<sup>3</sup> subsamples of the positive samples from ERF. Each area is discussed separately below.

#### *Distribution in feeding ponds*

Area A is the largest waterfowl feeding pond area (over 15 ha of open water) (Fig. 19). There are at least six or seven target vehicles with associated craters on the mudflats east of the feeding ponds. Only a limited number of samples (12 out of 94, or 12%) tested positive for WP (Table 8), and these were all located in the main pond area south and east of the tower (Fig. 19). Only one sample from north of the tower tested positive. No samples from the outlying ponds to the northwest and southeast of the main pond were found to contain WP.

The mean WP concentration (0.014 µg/g) from the 12 positives from Area A was relatively low compared with the other areas (Table 9). The sample with the highest WP concentration in Area A (333,

with 0.062 µg/g) was collected on the mudflat, which was unflooded on 28 May. Close-interval samples collected 1 m north, south, east and west of this sample site all tested negative. However, four out of five samples collected around sample 336 below water in the bulrush pond just southeast of the tower tested positive for WP.

Area B is in the extreme southwest corner of ERF and consists of a large number of fairly deep (0.1–0.5 m) small ponds and pools surrounded by lush, tall bulrush and coarse sedge vegetation. Since this area is in the buffer zone of the impact area, there are few craters and no targets, but dead waterfowl have been found here in the past. The salinities of the water were less than 4 ppt, and the redox potentials averaged about -300 mV, as expected of the highly organic black sediments collected here. None of the 15 sediment samples collected from a wide range of ponds and pools tested positive for WP.

Area C includes a large and diverse complex of

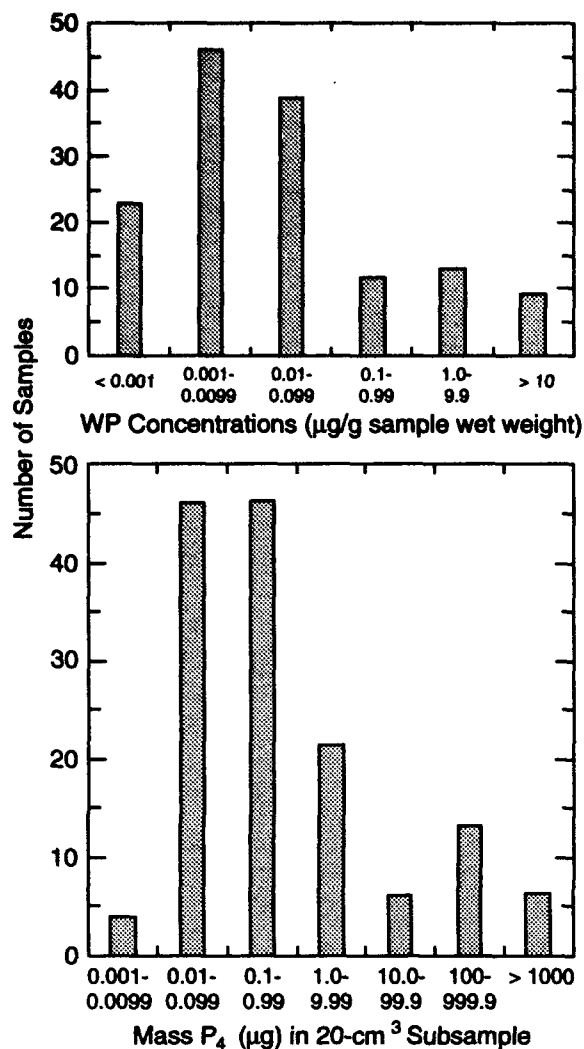


Figure 18. Number of sediment samples, from all six waterfowl feeding areas of Eagle River Flats, in each of several concentration or mass ranges. Only those samples testing positive for WP are included.

deep ponds and inlets (Clunie Creek) with tall bulrush and sedge vegetation along the upland (inner) edge of ERF that grades west out toward Eagle River into a shallow pond and mudflat (Fig. 20), where there are abundant craters and several targets. Of the 124 samples collected here, 49, or 40%, contained WP. Most of the positive samples are located in the northern half of the pond. There are four major areas of contamination in Area C:

- A large area about 300 × 200 m along the northern side of the pond;
- A bulrush area in the northeast part of the pond, which is highly contaminated, as are the deeper waters near the Clunie Creek inlet;
- The area around the tower and extending east to the shore and small inlet; and
- The mudflat area to the west and southwest of the tower, where at least four samples contained low levels of WP.

The mean concentration of WP in the positive samples from Area C was 0.291 µg/g (Table 9), which is significantly lower ( $p = 0.05$ ) (using a non-parametric Mann-Whitney U test) than the mean concentration (3.70 µg/g) of positive samples from the Bread Truck Pond (Fig. 21). The highest WP surface concentrations in Area C were found along the transect running northwest from the tower. However, 20-cm<sup>3</sup> subsamples from a sediment core at the end of the east transect near the shore contained WP masses of 3700 and 5500 µg (the highest of any samples collected in 1991). The four core samples obtained in Area C all showed that WP contamination extended to depths greater than 10 cm, and in some cases concentrations were greater at depth than nearer the surface (Table 10).

The Area C/D transition, a small permanent pond area along the east side of ERF, is a complex

Table 9. Means and standard deviations for concentrations and mass (in 20-cm<sup>3</sup> subsamples) for white phosphorus in the sediment samples testing positive from the bottom of three feeding pond areas.

Area	No. testing positive	Geometric mean	Mean concentration (SD)		Mean mass (SD)	
			µg/g	Log	per 20 cm <sup>3</sup>	Log
Bread Truck	29	0.025	3.70 (12.2)	-1.60 (1.48)	115 (401)	-0.111 (1.47)
C	49	0.006	0.29 (1.03)	-2.25 (1.15)	7.67 (24.6)	-0.759 (1.13)
A	12	0.003	0.014 (0.02)	-2.48 (0.90)	0.473 (0.657)	-0.985 (0.912)
All areas†	93	0.009	1.31 (6.97)	-2.07 (1.26)	40.1(228)	-0.582 (1.24)

Mann-Whitney U: ( $p = 0.05$ ) BT/C Conc.

† Excluding close-interval samples

area of deeper narrow ponds and channels where beavers are active (Fig. 22). The bulrush and sedge vegetation surrounding these channels and ponds is very productive and over 2 m tall, affording concealment for waterfowl. Water depths are generally greater than 0.4 m, suggesting that feeding by dabbling ducks here is limited. The bottom sediments are black organics with very

low redox potentials ( $-300$  mV). The salinities of the pond water are less than 4 ppt. Two pond areas were sampled (Fig. 22). Thirteen samples at the bottom of the largest pond all tested negative for WP. However, two out of nine samples from a smaller pond area to the north contained WP ( $0.001$  and  $0.012$   $\mu\text{g/g}$ ).

Area D consists of a fairly deep (0.3–0.5 m)

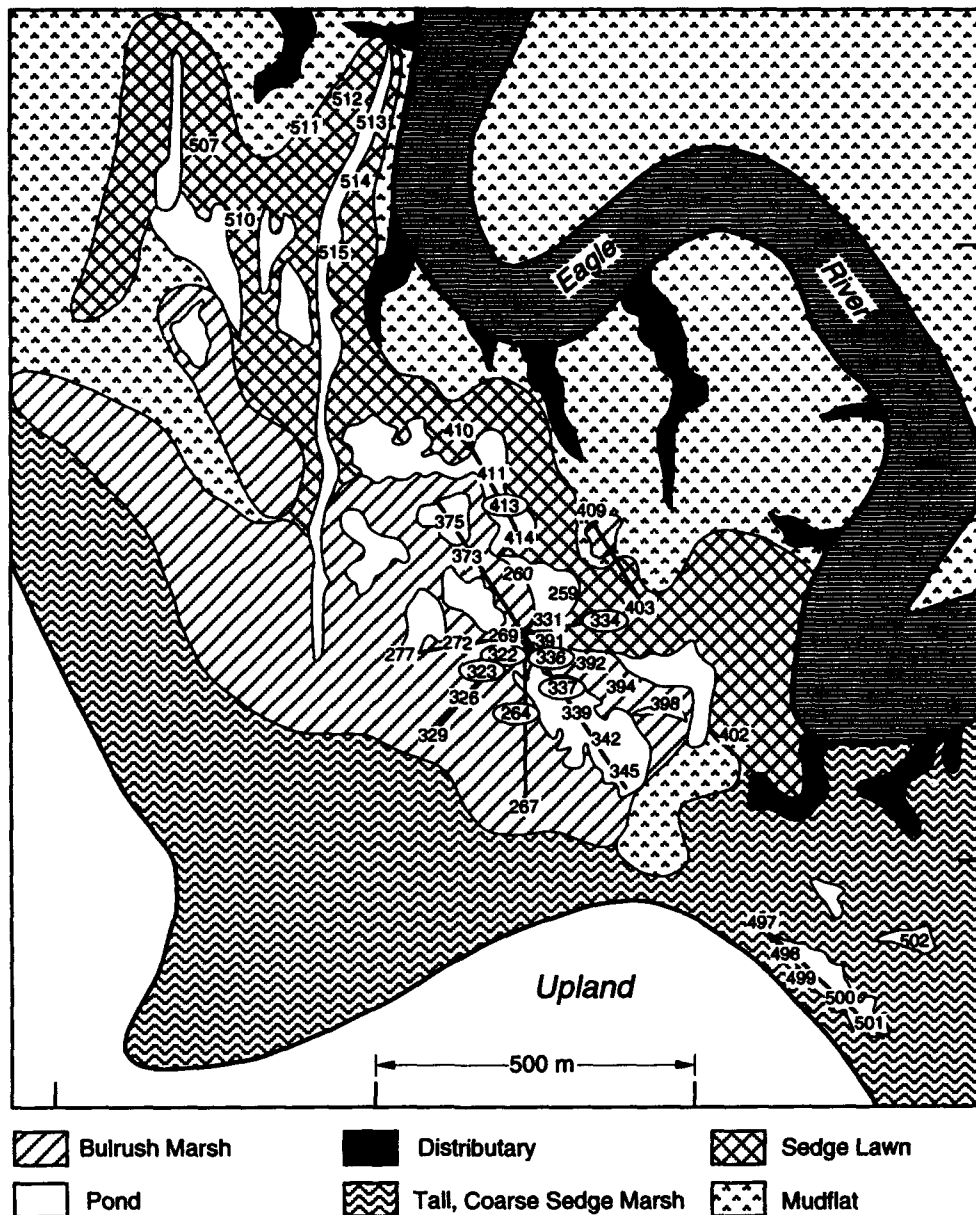


Figure 19. Vegetation-habitat map of Area A on the west side of ERF showing the location of sediment sample sites by numbers or transect lines. (Not all numbers are shown along the transects.) Samples that tested positive for white phosphorus are circled. This area is not highly contaminated relative to Area C and the Bread Truck Pond. Two connected ponded areas to the northwest and southeast (Otter Pond) were also sampled.

permanent pond in an embayment in the north-east corner of ERF (Fig. 23). Small islands and patches of bulrushes are scattered throughout the pond. To the northwest the pond grades into shallow ponds, mudflats and distributary streams out toward Knik Arm. The salinities here were about 7 ppt, and the redox potentials were extremely low ( $-300$  to  $-500$  mV) in the highly organic black bottom muck. Although the 43 samples collected in Area D represented both the deeper pond and the shallow ponds to the west, none of the samples were positive for WP. This area is in the buffer zone of the impact area, and there are few craters.

The Bread Truck Pond is a 5-ha semipermanent pond located near Eagle River, about 500 m west of Area C/D and 200 m northwest of Area C. Craters are dense on the west side of the pond, and there are several target vehicles (including the yellow panel truck for which we named the pond). Water depths vary from 1 cm along the mudflats near Eagle River to 30 cm along the east side of the pond, where it grades into the vast bulrush area on the east side of ERF (Fig. 3). Redox potentials here were always between  $-250$  and  $-350$  mV, with higher salinities (10–20 ppt) than in the other ponds sampled.

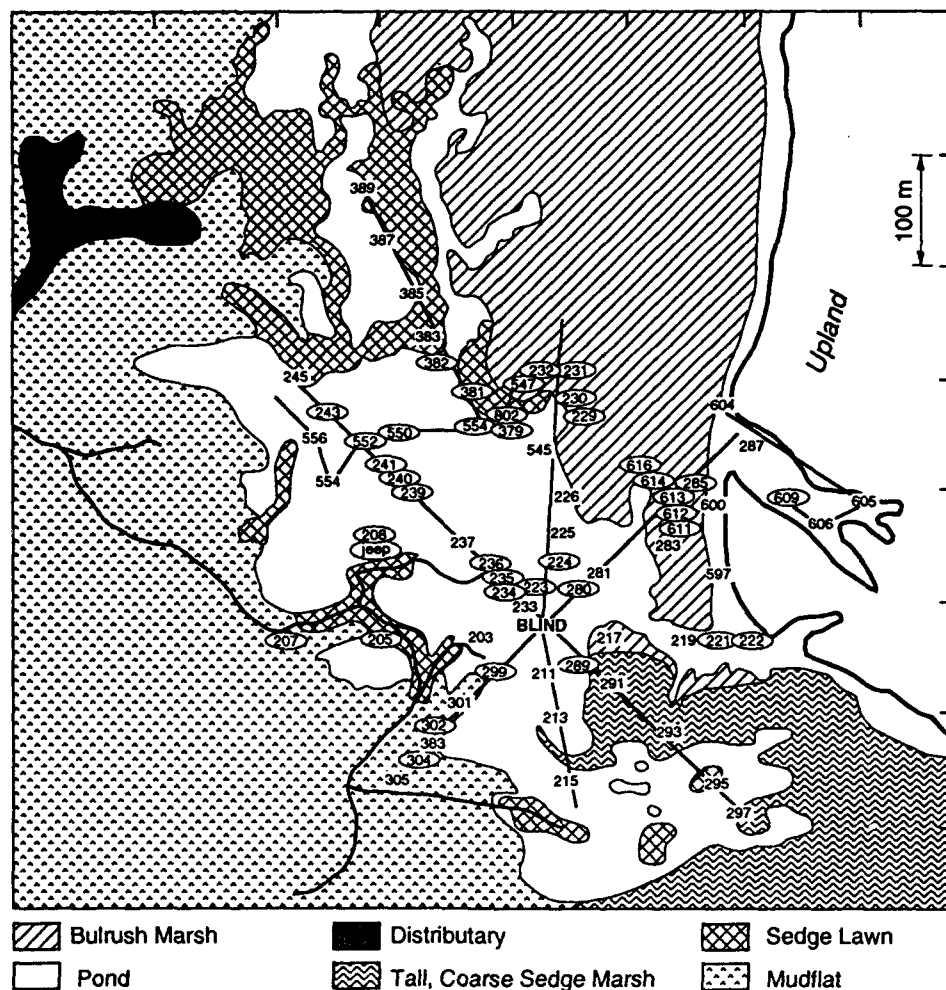


Figure 20. Vegetation-habitat map of Area C waterfowl feeding pond area showing the locations of sediment sample numbers along transects lines. The sediment samples testing positive for white phosphorus are circled. The sediments of this pond area are highly contaminated with WP. This semipermanent pond is located on the east side of ERF and grades from deeper water along the shore to shallow water on the mudflat or outer edge.

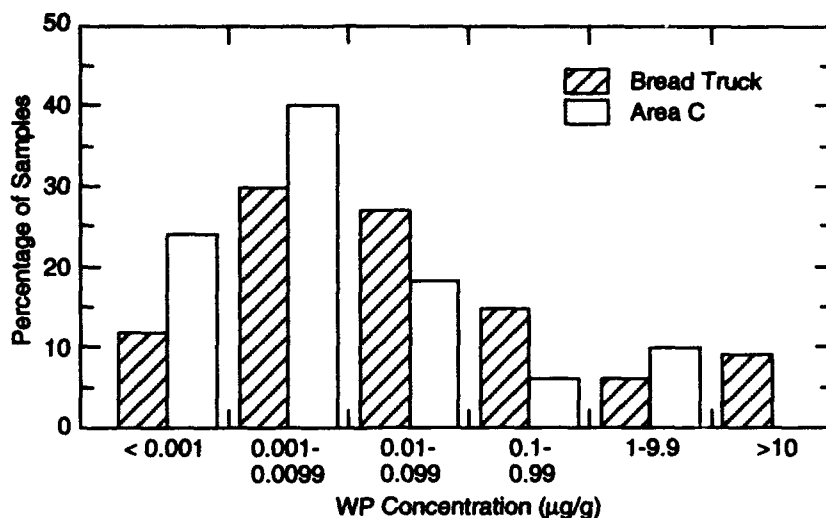


Figure 21. Percentage of positive-WP sediment samples from the Bread Truck and Area C ponds in each concentration range.

The Bread Truck Pond (Fig. 24) was not originally recognized as an area of waterfowl feeding and mortality, but it was identified as a site of high mortality and predation in the spring of 1991 by our avian ecologists making observations from the tower in Area C. At their recommendation we

initially collected sediment samples at 25-m intervals along a north-south transect across this pond (Fig. 24), with 10 of the 11 samples collected along this transect running south from the yellow panel truck testing positive for WP; one of these samples contained the highest level of WP found to date in

Table 10. WP analysis of sediment cores from Area C and the Bread Truck Pond obtained in August 1991.

Site number	Depth increment (cm)	Sample size (g)	WP mass (µg)	WP conc. (µg/g)	Water depth (cm)
<i>Area C</i>					
221 (E+150m)	0-7	25.6	0.253	0.0099	50
	7-14	36.0	0.128	0.0035	
	14-24	35.3	not detected	not detected	
	24-28	23.9	not detected	not detected	
222	0-3	22.9	225	9.83	45
	3-7	20.7	3700	179	
	7-11	12.0	1.55	0.129	
	11-13	27.9	5520	198	
240	0-3	19.0	0.912	0.0480	35
	3-6	28.4	104	3.66	
	6-10	39.0	118	3.02	
	10-17	28.0	161	5.78	
235	0-5	35.3	2100	59.5	
	5-13	21.7	0.738	0.0340	
<i>Bread Truck Pond</i>					
248	0-3	23.9	185	7.72	9
	3-6	30.3	0.0468	0.0015	
	6-10	52.9	not detected	not detected	
248	0-3	44.3	0.191	0.0043	8
	3-6	45.8	0.0120	0.0003	
	6-9	27.6	0.0384	0.0014	

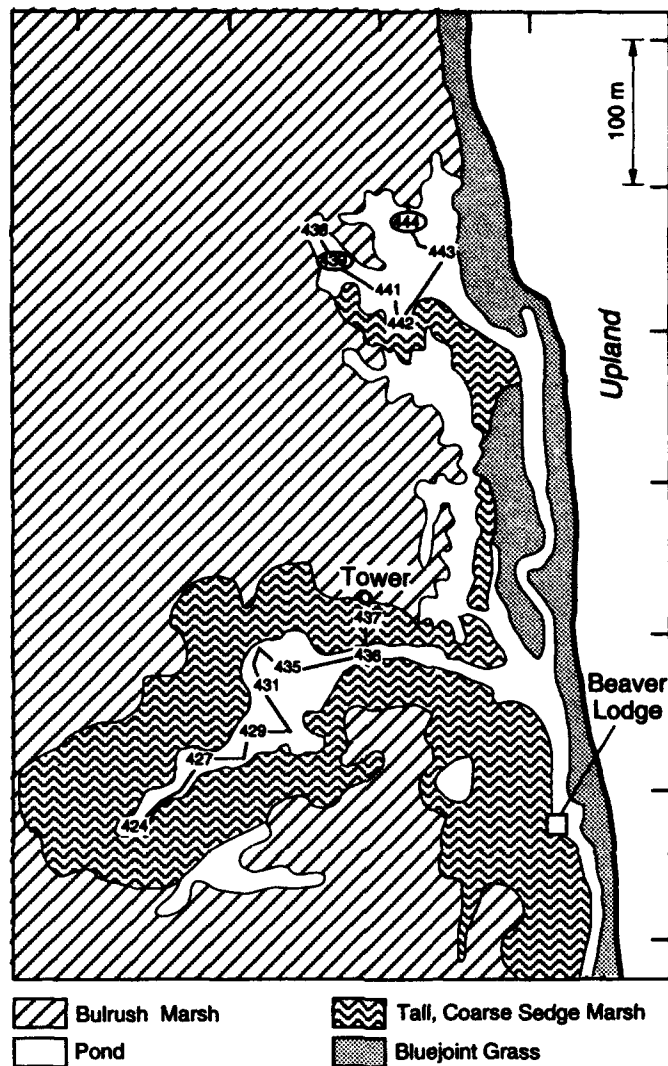


Figure 22. Map of Area C/D on the east edge of ERF between Areas C and D, where there is beaver activity and tall bulrush and sedge marsh surrounding two small, deep pond areas. The locations of sediment samples are shown by black dots. Two samples tested positive for WP.

surface sediment samples at ERF ( $57.6 \mu\text{g/g}$ , or  $2 \text{ mg}/20 \text{ cm}^3$ ).

The mean concentration and mass of WP in the surface sediment samples testing positive from the Bread Truck Pond ( $3.70 \mu\text{g/g}$  and  $115 \mu\text{g}$ ) (Table 9) were significantly higher (using non-parametric tests on the mean and parametric tests on the mean log) than those in either Area C or Area A. The main area of contamination and highest WP concentrations is near the center of the

pond in 8–10 cm of water (Fig. 24). Additional close-interval samples collected in the center of this pond were all positive, with high concentrations of WP. Two sediment cores collected near the pond's center showed that WP was present to depths of at least 10 cm in the sediments (Table 10), although the levels here were lower than in the cores from Area C.

Several sediment samples were collected in a nearby shallowly flooded mudflat pond about 200

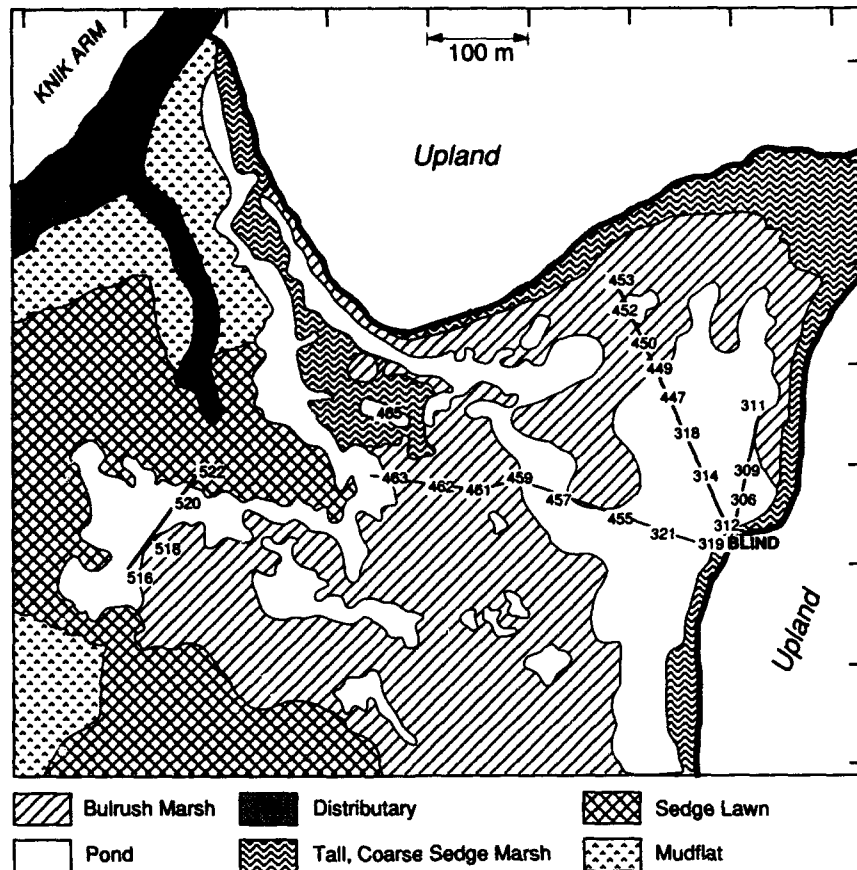


Figure 23. Map of Area D permanent pond in the northeast corner of ERF, showing the distribution of sediment sample transect lines and points in relation to the various types of habitat. The main pond here is fairly deep (40 cm) and surrounded by bulrush marsh. A gull nesting area is also located here. Not all sample numbers are shown, and none of the 43 samples collected here tested positive for WP.

m north of the Bread Truck Pond (called here the Pond Beyond) (Fig. 24). There are a target truck and abundant craters on the west edge of this pond. Seven samples were collected here, with one of these samples testing positive at a concentration of  $0.022 \mu\text{g/g}$ .

#### Discussion

Both the high percentage of positive samples and the relatively high concentrations of WP found in Area C and the Bread Truck Pond strongly suggest that these two areas (15 ha, or 37 acres) may be a major source of waterfowl poisoning in Eagle River Flats. A starting point for remediation should be treatment of the sediments or exclusion of waterfowl feeding in the center of the Bread Truck Pond. However, our sediment sampling was confined to the bottoms of the major waterfowl feeding ponds, representing an area less than

5% of Eagle River Flats. The other areas of ERF, representing 95% of ERF, should not be labeled as "uncontaminated." WP probably occurs elsewhere in the flats, particularly in wet mudflat sediments, which may in the future become ponded and used as feeding areas for dabbling ducks.

Despite the uncertainties at both large and small sampling scales and the subsampling error, we think that we have identified the important hot spots in relation to the five major ponded areas where the bulk of migrating ducks feed.

The majority of sediment samples that tested positive for WP have very low concentrations or mass of WP, and although ingestion of a large number of very small particles could poison a duck, a  $1\text{-}\mu\text{g}$  particle about  $0.082 \text{ mm}$  in diameter is smaller than food items usually selected (Nudds and Bowlby 1984). Contaminated sediments probably contain many small particles and a very few





Figure 24. Map of the Bread Truck Pond (center) and Pond Beyond (top of map) near the east bank of the Eagle River. The Bread Truck semipermanent pond was found to have the most highly WP-contaminated sediments of the six ponded areas. The pond is bordered by mudflats along the outer (or river) side and bulrush marsh along the inner side.

large WP particles so that when a duck processes large amounts of contaminated sediments, the ingestion of a large particle is likely.

Although WP was found in a limited number of sediment samples in Area A, the concentrations or extent of contamination did not seem sufficient to

be a major source of poisoning. Area C/D also contained two sediment samples with low levels of WP, and virtually no craters are located near this ponded area. One non-munition source of indirect WP contamination may be the decomposition of a WP-poisoned duck that ingested WP in

the Bread Truck Pond or Area C and flew into the nearby sheltered Area C/D to die. A preliminary study of WP fate in decomposing carcasses conducted during 1991 showed that WP persisted in rotting carcasses and could therefore be redeposited in the sediments.

The mechanisms by which an exploding WP smoke round deposits unburned WP particles into the sediments might include airburst residues, groundburst ejecta, delayed detonation deep within the sediments, leakage from WP-containing duds and low-level redistribution by ducks themselves when contaminated carcasses rot and are incorporated into the sediments. Both Area C and the Bread Truck Pond have high crater densities and a number of target vehicles on the mudflat (river) side. This fact, coupled with the observation that positive samples tend to be clustered in three to five successive 25-m-interval sample sites along a transect, suggests that WP is derived from airburst residues or groundburst ejecta or both. Targeting errors probably explain the contamination of bulrush areas along the east (landward) side of Area C.

There was no clear relationship between the distribution of WP in the bottom sediments and the redox potential, salinity or pH of the sediments. However, all the sediments in Eagle River Flats are highly reduced, with a redox potential  $E_h$  in the 0- to -200-mV range. WP, once deposited in these anaerobic sediments, would be protected from oxidation.

## CHARACTERIZATION OF WHITE PHOSPHORUS IN SEDIMENTS

Because sediment-feeding waterfowl are the principal victims of the poisoning at ERF, we hypothesized (Racine et al. 1992) that the white phosphorus is ingested by ducks as a particle in a manner similar to the ingestion of lead shot (Friend 1987). WP particles ingested by waterfowl should be in the size range of other food items selected by dabbling ducks (Nudds and Bowlby 1984). We also hypothesized that the source of these particles is WP-containing incendiary munitions fired into ERF. The bursting charge ignites the WP, and burning particles fall onto the water surface, where they are extinguished and settle onto the sediments. During winter tests of obscurants, Cragin (1984) observed "globules" of partially burned WP on the snow surface within a 60-m radius after a static ground-level detonation of a 12.7-cm Zuni rocket containing 8.9 kg of WP. While we hypothesized that particles generated by the WP cloud and burning globules are the source of contamination as measured in extracted sediment samples, the sizes, shapes and other characteristics of these particles that result in their consumption by waterfowl were unknown.

Several forms of WP have been recognized, including colloidal (fine particles suspended in water), dissolved and particulate (Table 11). WP has very low solubility in water (3 mg/L). Most of the research on WP has concentrated on the collo-

Table 11. Forms of WP contamination previously described in the environment.

<i>Activity</i>	<i>Form of WP</i>	<i>Location of contamination</i>	<i>Mode of transport to environment</i>	<i>Reference</i>
Manufacture of WP	1) Colloidal (0.45 -1 $\mu$ m) 2) Dissolved (3 mg/L)	1) Long Harbour, Newfoundland 2) Muscle Shoals, Alabama	Wastewater	Jangaard (1972)
Manufacture of WP munitions	1) Colloidal 2) Dissolved	Pine Bluff Arsenal, Arkansas	Wastewater	Blumbergs et al. (1973)
Training	1) Particles from unburned WP ? 2) Particles deposited from smoke cloud ?	ERF first documented case	Deployment of smoke rounds	Racine et al. (1992)

dal form that occurs in wastewater from the manufacture of WP and WP munitions. We may have detected this form when a fine-mesh net was towed through the pond water in Area C as described below. Such very fine particles of WP could have been deposited from the smoke cloud resulting from the deployment of the WP munition.

To gain some understanding of the form of the WP present in contaminated sediments, in the laboratory, we:

- Dropped a burning WP particle into water and measured the residual WP;
- Sieved contaminated sediments from ERF to isolate WP particles; and
- Used a fine-mesh plankton net to collect suspended material in the water column of contaminated ponds.

#### **Estimate of unreacted WP in burn residue**

We estimated the amount of unburned WP remaining when a burning WP particle drops into water by performing the following experiment.

#### *Methods*

An approximately 30-mg piece of WP (Aldrich

Chemical Co) was held in a spatula over a jar containing 250 mL of water. A match was used to ignite the piece of WP, which melted upon inflammation. The spatula was then inverted, dropping the brightly burning WP onto the surface of the water (Fig. 25). As the particle hit the surface of the water, it splattered into several smaller pieces. Some pieces sank and were immediately extinguished; other pieces floated on the water surface, where they continued to burn for about 30 seconds (Fig. 26). When all burning had stopped, isooctane was used to extract the residual WP from the water. For comparison, we ignited another particle of WP and dropped it into an empty jar. The particle was allowed to burn to completion on the glass surface of the bottom of the jar. When the residue had cooled, it was extracted with isooctane.

#### *Results*

For the WP particle dropped into water, we found 9.4 mg of residual WP, or approximately 30% of the original mass. For the particle burned on a glass surface, we found 3.7 mg of unburned WP, or about 10% of the original mass.



*Figure 25. Burning particle of WP prior to hitting the water surface.*



Figure 26. Particle of WP after hitting the water surface. Most of the WP sinks and is extinguished, but some of it floats and continues to burn.

#### *Discussion and conclusions*

Burning WP is extinguished when immersed in water, leaving a significant amount of unreacted material in the burn residue. Even when burned in air, some of the WP remains unreacted.

In experiments to identify the combustion products of WP-felt (WP impregnated in a felt matrix) munitions, Snelson\* reported between one part per million to one part per thousand by weight of the original WP remained unburned after test burns conducted at 50% relative humidity (Berkowitz et al. 1981). Spangford et al. (1985) measured the extent of conversion of WP to  $P_4O_{10}$  as a function of initial oxygen pressure using samples of WP-felt. They found that the upper limit of conversion was 92%, and they concluded that significant amounts of unreacted WP would remain unburned from WP-felt munitions.

The burned residue in both of our experiments was rusty-orange in color and flaky in appearance. We have observed similar flakes in sediments from ERF; however, the particles of WP we isolated from sediments, as described below, were translucent yellow. These particles may have been the cores of burning pieces of WP that were extin-

guished upon entering the ponds of ERF, and with time, the oxidized material has dissolved. The white oxidized coating commonly found on WP stored under water will slowly dissolve in water (Russell 1903). When Russell heated the oxidized coating, a red residue formed, part of which was identified as red phosphorus (amorphous). Thus, the rusty-orange color we observed may be due to the formation of some red phosphorus that forms when WP is heated to 250–350°C (VanWazer 1958).

#### *Isolation of WP particles from ERF sediment*

To characterize the WP particles in terms of their size and mass, seven WP-containing sediment samples collected in May 1991 from the Bread Truck Pond and Area C were examined.

#### *Methods*

Up to 30 mL of sediment was dispersed at a time with a Calgon solution (40 g/L of hexametaphosphate) and then rinsed through a 0.150-mm-mesh sieve. The material left on the sieve was placed in a petri dish with a calcium chloride solution to floc the suspended sediment and clarify the water. The material was then examined under a stereomicroscope. WP particles were recognized by their waxy, translucent-yellow appearance. White and pink

\* Personal communication cited in Berkowitz et al. (1981).

**Table 12. Particles isolated from ERF sediments.**

Sample number	Area	Conc. ( $\mu\text{g/g}$ )	Volume sieved (mL)	No. of particles isolated	Masses of particles (mg)		Lengths of particles (mm)	
					Range	Median	Range	Median
240	C	3.33	253	4	0.0049–3.4	0.59	0.37–2.9	0.96
248	BT	57.6	278	7	0.0001–0.75	0.10	not measured	
280	C	1.09	202	1	0.28		1.4	
359	BT	33.7	295	12	0.0073–0.83	0.13	0.29–1.4	0.61
361	BT	10.6	383	26	<0.0001–2.3	0.05	0.26–2.3	0.89
228	C	0.001	343	0	—		—	
224	C	0.0009	347	0	—		—	

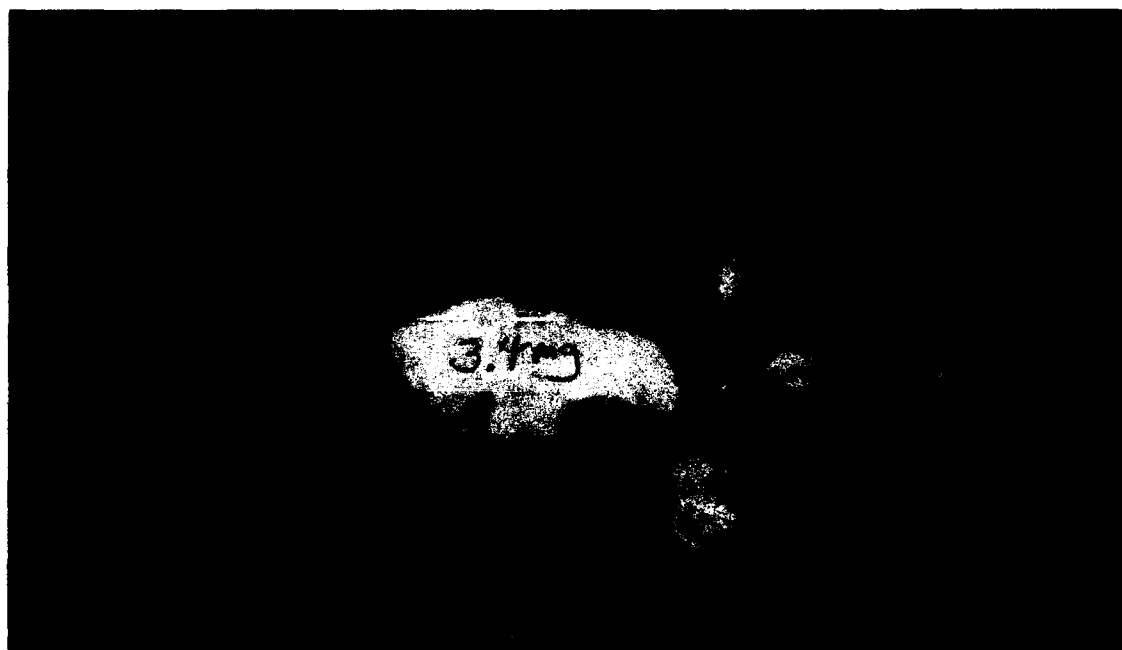
particles were also isolated. When a WP particle was found, its dimensions were measured to the nearest 0.01 mm, the particle was photographed, and then it was dissolved in isooctane. The isooctane was analyzed by GC to obtain an estimate of WP mass. Material that passed through the 0.150-mm sieve was dried in an aluminum pie pan.

#### Results

Particles of WP were recovered from five of the seven sediment samples examined (Table 12). These samples all had WP concentrations greater

than  $1 \mu\text{g/g}$  as determined by GC. The shapes of the particles varied considerably; some were angular while many were globular (Fig. 27). The particle masses ranged from less than  $0.1 \mu\text{g}$  to 3.4 mg, and the particle lengths ranged from 0.26 to 2.9 mm.

Particles were not recovered from the two samples with very low WP concentrations ( $0.001 \mu\text{g/g}$ ). However, when the dried material that had passed through the sieve was examined, small black specks were evident. We speculate that these specks are a result of WP oxidation to phosphorus



*Figure 27. Particles of WP isolated from a sample (240) collected in Area C. Counterclockwise from the large particle to the left of the glass bead, the estimated masses are 3.4, 0.73, 0.045 and 0.0049 mg. The glass bead is 0.72 mm in diameter.*

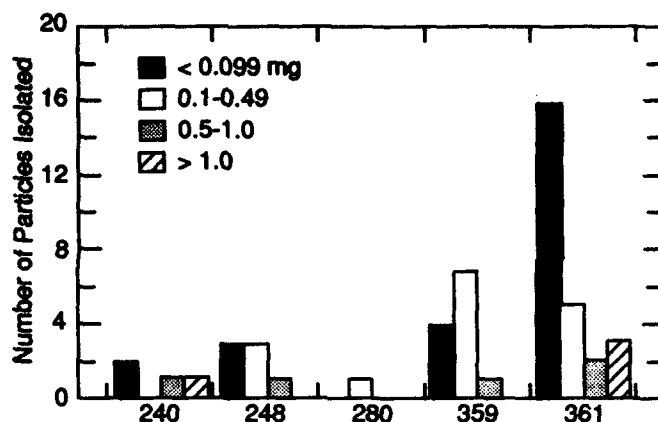


Figure 28. Ranges of masses of particles isolated from five ERF sediment samples.

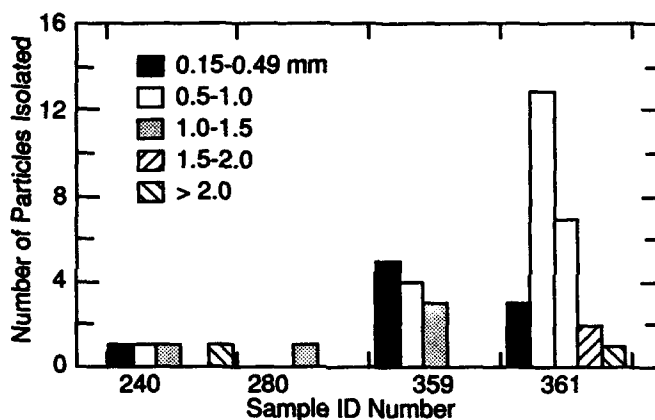


Figure 29. Ranges of lengths of particles isolated from four ERF sediment samples.

pentoxide ( $P_4O_{10}$ ). Phosphorus pentoxide is extremely hygroscopic, and the black specks are probably due to the wetting of the sediment surrounding each oxidized WP particle.

There is evidence that very small WP particles can be suspended in the water column (as colloidal particles) in Area C ponds. A 15-cm Wisconsin plankton tow net with a 0.076-mm mesh size was dragged through the shallow pond just north of the Area C tower on 28-29 August. Walking through these ponds stirs up a fine suspension of the bottom sediments. Of two samples taken before this walking disturbance, one contained a very low but measurable concentration of WP (0.0008  $\mu\text{g/g}$ ). Another sample taken in the same place after disturbance of the bottom sediments

yielded a concentration of 0.0224  $\mu\text{g/g}$ , suggesting that very small particles of WP are or may become suspended in the water column.

#### Discussion and conclusions

The isolation and characterization of WP particles in sediments provide information on the dose of WP a duck receives from the ingestion of a single particle. Within a sediment sample, the masses of the particles isolated varied considerably (Table 12). For example, in sample 240, four particles were isolated, the largest of which was 3.4 mg and the smallest, 0.0049 mg (Fig. 28). Of the 50 particles isolated, most were less than 0.49 mg, and only four were greater than 1 mg.

Most of the particles isolated were greater than 0.5 mm in length (Fig. 29) and thus are in the size range of food items (Nudds and Bowlby 1984) or gizzard material selected by ducks. The smallest particles isolated were around 0.25 mm in length. However, if the black specks observed in the dried sieved material from the two low-level samples are in fact the result of oxidized WP particles, the size class containing particles less than 0.150 mm is significant.

The source of very small particles (on the order of a few micrometers) in the sediment samples and water column could have been the smoke clouds that formed when WP projectiles were deployed at ERF. Van Voris et al. (1987) measured chemical and physical characteristics of airborne smokes in relation to relative humidity and wind speed. Smoke clouds were generated by the controlled burning of WP in a combustion chamber, and the products were passed into a wind tunnel, where various measurements were made, including particle size and WP deposition. WP deposition onto a water surface averaged  $2.6 \mu\text{g}/\text{m}^2$  for clouds generated at 35–90% relative humidity over 1–4 hours. Particles (composed of WP, combustion products and water vapor) ranged in size from 0.3 to 10  $\mu\text{m}$ . The particle size distribution was log normal. The largest particles were produced during tests run at the highest relative humidity, as was expected since the particles grow by moisture accretion. To relate this information to the data we obtained for ERF sediments, we must first convert our data to a mass per area basis. For samples 228 and 224, approximately 0.03  $\mu\text{g}$  of WP was determined in a 20-cm<sup>3</sup> subsample. Assuming the top 5 cm of sediment was sampled in the field, the area sampled would cover 0.0004 m<sup>2</sup>. Thus, on a mass per unit area basis, we found  $75 \mu\text{g}/\text{m}^2$ . Considering that the WP in the ERF sediments is found at depth due to the accumulation of deposited WP over an unknown number of years, this estimate is in reasonable agreement with Van Voris et al. (1987). Thus, deposition from the smoke cloud may account for some of the very low concentrations in samples we collected from ERF, and the particle sizes in these samples are probably on the order of micrometers.

Although the data are insufficient, samples with WP concentrations less than 1  $\mu\text{g}/\text{g}$  may not contain WP particles in a size range selected by ducks. However, other organisms may be affected. For example, at Pine Bluffs Arsenal, sediment concentrations above 0.002  $\mu\text{g}/\text{g}$  drastically altered the population of benthic organisms (Pearson et al.

1976). The finding of WP-poisoned phalaropes at ERF, which feed on zooplankton in the water of arctic ponds (Dodson and Egger 1980), also suggests that the water column may be a pathway of exposure to filter-feeding waterbirds in ERF.

## BIOLOGICAL EFFECTS

### Waterfowl movement and possible transport of WP

Following the initial ingestion of WP by a dabbling duck in a particular pond on ERF, the bird may be capable of flying to another area on ERF or out of ERF to another area of Cook Inlet. Such ingestion followed by flight would result in the transport or movement of WP and could pose a health hazard to hunters in other areas of Cook Inlet. Consequently we tried to determine the ability of poisoned waterfowl to move within or out of ERF, as well as the movement patterns of ducks within ERF.

The ability of birds to fly following ingestion probably depends on the size or mass (dose) of the particle ingested and the rate of absorption of the WP. The analysis of WP particle sizes and masses in the sediments described earlier in this report and the finding of a large number of sediment samples with low WP concentrations (<0.01  $\mu\text{g}/\text{g}$ ) suggest that there are abundant opportunities for exposure to sublethal doses of WP. No toxicological studies of sublethal or chronic, long-term effects of WP on waterfowl were conducted, although Coburn et al. (1950) gave two mallards and two black ducks doses of 1 mg/kg at irregular intervals over two weeks or until death. Both of the black ducks survived for two weeks, while one of the mallards died within three days and the other survived for 18 days.

A 1969 spill of water containing colloidal and dissolved white phosphorus (phossy water) into a marine bay at a Newfoundland WP-manufacturing plant resulted in a massive die-off of fish around the plant as well as the death of herring (*Clupea harengus*) and other fish as far as 80 km from the manufacturing plant (Idler 1969). Schools of fish, especially herring, swam through the relatively small plume of "phossy water" and died many kilometers from the source.

To understand the possible transport of WP within or out of ERF, several studies were conducted during the 1991 field season:

- Collection of tissues and dead waterfowl from Cook Inlet ponds and marshes out-

side ERF;

- Collection of flying (apparently healthy) waterfowl in ERF; and
- Monitoring of waterfowl movement patterns within and outside ERF by human observations, by trapping and banding, and by radiotelemetry.

#### Methods and results

##### Collection of dead waterfowl outside ERF

Four small lakes surround ERF: Gwen, Clunie, Waldon and Otter lakes (Fig. 30). In 1991 all four of these lakes were searched by canoe on a weekly basis in June and on a bi-weekly basis in July through September to see if any waterfowl died on nearby lakes from WP poisoning. Of the five waterfowl carcasses collected outside ERF in 1991, only one tested positive for WP (Table 13). This green-winged teal was found in the road bordering the southeast side of ERF. Over 1 mg of WP was found in the gizzard of this bird. In addition a

mallard found in 1988 in Gwen Lake and subsequently frozen was tested and found to contain WP. Gwen Lake is less than one km southeast of Area B of ERF.

Goose Bay and Fire Creek salt marshes (Fig. 1) were searched by helicopter on a monthly basis from May through August 1991. No carcasses were found in Goose Bay or Fire Creek, but carcasses in emergent cover are very difficult to see in aerial searches and may have been overlooked. During the first week of the 1991 Cook Inlet waterfowl hunting season, over 300 gizzards and skin samples were collected from hunter-harvested ducks at Goose Bay, Palmer Hay Flats, Susitna Flats and the Anchorage Wildlife Refuge by the Alaska Dept. of Fish and Game and by USFWS. WP was not detected in any bird.

##### Collection of flying waterfowl in ERF

On 28 August four teal were shot as they flew into the pond on Area C. Although they were clearly able to fly and were shot on the wing, all

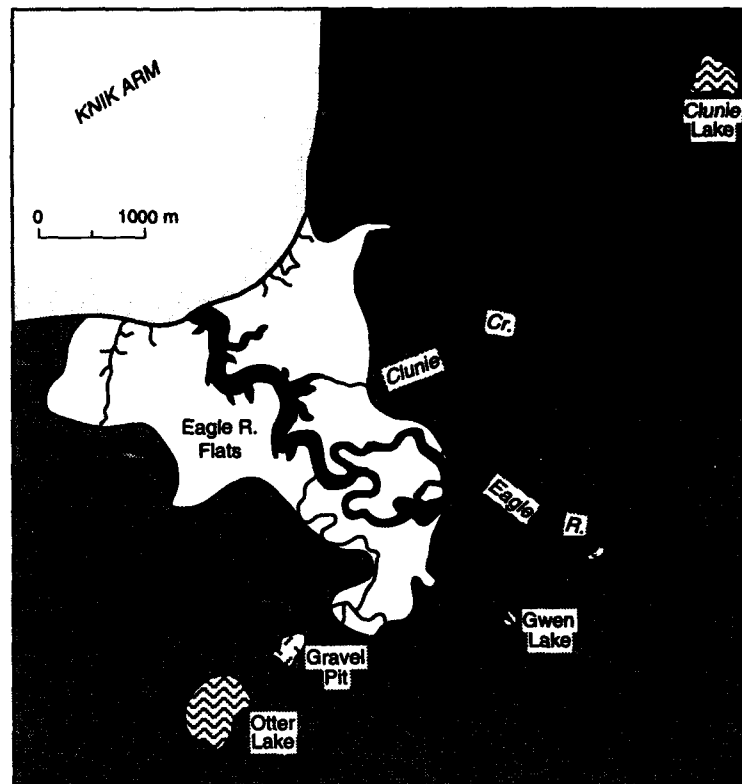


Figure 30. Map of the ERF area, showing the surrounding lakes (Gwen, Clunie and Otter) where searches for waterfowl carcasses were conducted to determine if WP-poisoned waterfowl were capable of leaving ERF. Two locations are marked where WP-containing waterfowl were collected.



**Table 13. WP analysis of tissues from dead waterfowl collected outside Eagle River Flats.**

Species	Location	Date collected	Tissue	Mass of tissue (g)	Mass of WP (µg)	WP Conc. (µg/g)
Green-winged teal	Road	8/26/91	Gizz. contents	0.33	1160	3500
			Fat	0.1	0.35	3.5
			Skin	1.3	5.80	4.46
			Breast muscle	3.5	0.47	0.13
Grebe Swan	Clunie Lake Elmendorf AFB	6/14/91 by B. Eldridge	Wing and skin	3.93	not detected	
			Skin	5.4	not detected	
Mallard	Gwen Lake	8/18/88 by mil. police	Gizz. contents	0.25	25.8	103
			Fat	0.39	0.15	0.39
			Skin	5.0	0.17	0.03
Loon chick	Otter Lake	7/9/91	Skin		not detected	
Grebe chick	Gwen Lake	8/14/91	Skin		not detected	

four contained WP (Table 14). Levels in one teal were similar to those in ducks found dead on the flats. Five mallards, two shovelers, one green-winged teal and one pintail were shot on September 18 near the C/D tower by Bill Eldridge (USFWS-Anchorage) and did not contain any WP.

*Collection of tissue from decaying waterfowl carcasses within ERF*

One possible mechanism by which WP may be transported from one area of ERF to another is by waterfowl that ingest WP and fly to another area where they die. Four decaying waterfowl carcasses were sampled for WP analysis. All four tested positive for WP (Table 15). Fly larvae feeding on the contaminated carcasses were also col-

lected and tested for WP. None tested positive.

*Waterfowl movement patterns*

On 24, 25 and 29 August 1991, one observer was stationed at each of four blinds. Each observer had a radio and communicated the movement patterns of ducks throughout the flats. Flying into and out of the flats was also documented. When ducks left an area, the size and species composition of the flock was described to the observers in the tower toward which the flock was flying. Maps were developed showing the movement patterns of these flocks within ERF.

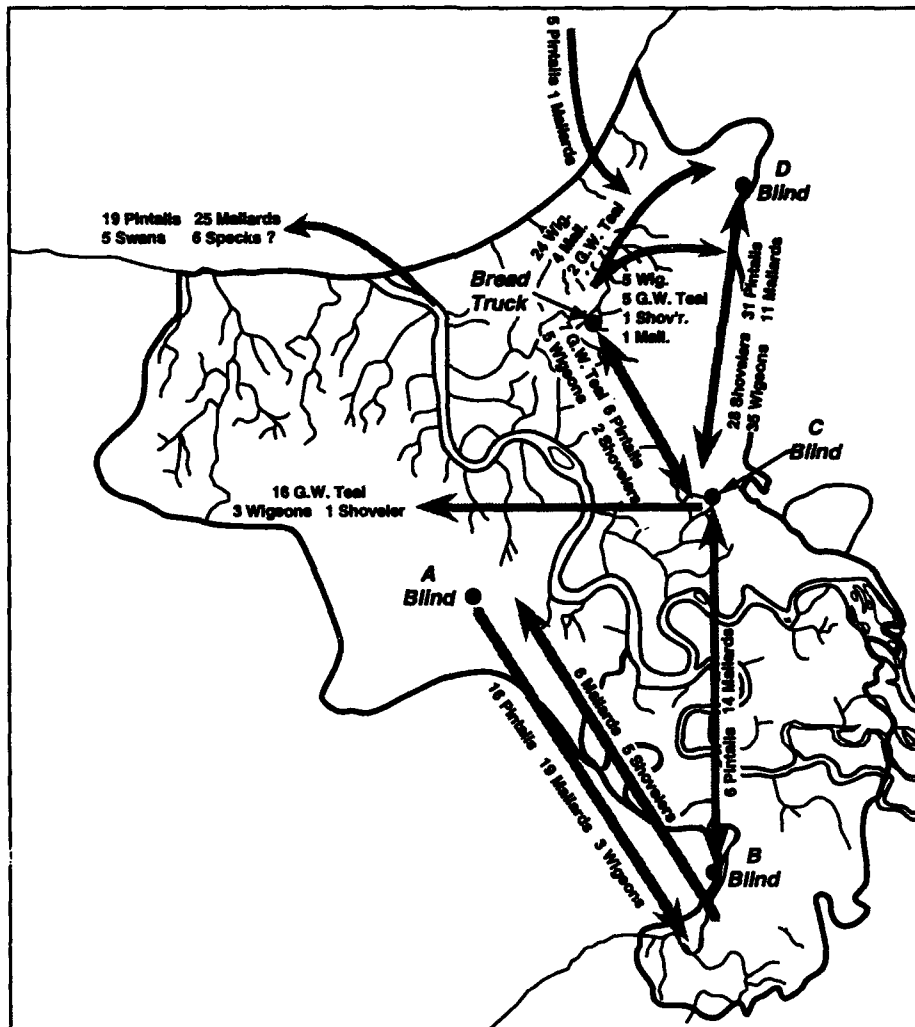
Ducks were observed routinely flying from one area to another. Of the 527 ducks seen flying during the three days of observations, only six

**Table 14. Waterfowl collected while flying in Eagle River Flats and analyzed for WP. All birds were shot in Area C or the C/D transition.**

Species	Date collected	Tissue	WP Conc. (µg/g)
Green-winged teal	8/28/91	Gizzard contents	0.0163
		Skin	0.0737
		Fat	0.0230
		Muscle	not detected
Green-winged teal	8/28/91	Gizzard contents	0.040
		Skin	0.070
		Muscle	0.011
		Fat	0.066
Green-winged teal	8/28/91	Gizzard contents	0.156
		Skin	0.150
		Fat	no sample
Green-winged teal	8/28/91	Gizzard contents	0.075
		Skin	1.14
		Fat	2.70
		Muscle	0.028

**Table 15. WP analysis of decayed carcasses collected on 30 August 1991.**

Species	Tissue	Tissue mass (g)	Mass of WP ( $\mu\text{g}$ )	WP Conc. ( $\mu\text{g/g}$ )
Mallard	Skin	2.90	0.217	0.0748
	Larvae	0.80	not detected	
Green-winged teal	Skin	1.90	0.868	0.457
	Larvae	0.20	not detected	
Mallard	Skin	6.60	0.213	0.0323
Green-winged teal	Skin	2.90	0.191	0.0660
	Larvae	0.10	not detected	



**Figure 31. Map of Eagle River Flats showing the movement patterns of various numbers of several waterfowl species as determined by observers stationed in four blinds (A, B, C and D) with radio communication during 24, 25 and 26 August 1991.**

(1%) were seen entering the flats from the northeast off the Knik Arm and 55 (10.4%) were seen leaving ERF. Most of the flying occurred between areas within ERF. The summary map (Fig. 31) shows that individuals of all the commonly seen waterfowl species move from Area C and the Bread Truck Pond, the areas with the highest concentrations of WP, to all the other areas on the flats. This summary map does not include all the recorded observations, only those in which the take-off and landing points were known. The map also does not show routes where the ducks took off or landed in an area on the flats other than the areas discussed (for example, Eagle River, Otter Creek Pond and other ponds north of the Bread Truck Pond). Also, many observations were made of ducks flying from one location to another location within an area. Excluding observations of movement within areas, 98 observations were recorded, with an average flock size of 18.6 ducks.

Seven times on 29 August, censuses were conducted of the number of ducks on the flats. The average number of ducks counted between 0700 and 1500 was 398, with the highest count being 481. A total of 234 flying ducks were seen on 29 August, representing 58.6% of the average number counted that day and 48.6% of the highest number counted. This indicates that at least half the ducks on the flats on a given day may move from one area to another.

An additional pattern we noticed was that ducks did not fly as frequently during certain periods of the day. Most of the documented flying occurred from 0700 (when the earliest observations were recorded) to 1100, with a steady decline from 1000 to 1100. Very little flying occurred from 1100 to 1330 or 1400. After 1400, activity began to increase again until about 1530. Some variation in this pattern exists between days, but the mid-day lull was evident each day. Because ducks feed heavily in the morning and then settle down to preen and wash during mid-day, there may be a greater tendency to see ducks get sick during mid-day when individuals are in one location for an extended time, especially after having eaten heavily. The flying that occurs in the morning also suggests that ducks could ingest WP in one area and relocate before the mid-day lull, when they may then get sick and die.

An immature male mallard (patagial tag 102) was captured using a dipnet on July 26, fitted with a 20-g backpack mortality-mode transmitter and released. It was subsequently located six times or more per week from 27 August through 25 Sep-

tember (Fig. 32). All locations were on ERF, and 48% were in the bulrushes between the large ponds in C and the Beaver Pond. On three occasions the bird was flushed from this area.

This mallard exhibited a home range of 350 ha (870 acres), with daily flight distances ranging from 0.1 to 1.9 km. This duck exhibited localized flights between and within different portions of ERF, often remaining in one location throughout the day. When last located, this mallard was still alive after spending at least 29 days on ERF.

#### *Discussion and conclusions*

This evidence suggests that during the August 1991 study period individual waterfowl spent considerable time within ERF and moved regularly between Areas A, B, C, C/D, D and the Bread Truck Pond. The results also show that a duck can survive on the flats for at least a month without dying of WP poisoning.

The movement of ducks between areas is understandable from an ecological point of view. By regularly moving to new areas, individuals or flocks reduce the chances of depleting food resources and reduce the risk of being preyed upon by predators restricted to a specific area. This movement, along with the finding of WP in waterfowl capable of flying and in carcasses found in Gwen Lake and on the road to ERF, substantiates the possibility that ducks may ingest WP in one area and fly to another area where they die. Limited data indicate that carcasses retain WP during decomposition, and this represents redistribution of WP in relatively small quantities to different areas within the flats. We have no evidence of the transport of WP by flying ducks to other salt marshes on the Cook Inlet.

#### **Risk of white phosphorus poisoning of waterfowl predators**

Evidence of predation on waterfowl in ERF include observations of predation events and numerous bird remains, consisting primarily of feathers from scavenged carcasses. These "feather piles" can be found both on the flats and on the forest floor in the surrounding woodland. Because WP is highly soluble in lipids [i.e. 1 g of WP is soluble in 80 mL of olive oil (Stecher 1968)] and therefore could accumulate in fatty tissue, we predicted that WP could pose a risk to both predators of ducks poisoned with WP and possibly to hunters should they consume a WP-poisoned duck.

A 1969 spill of water containing colloidal and dissolved WP (phossy water) into a marine bay at



Figure 32. Map of Eagle River Flats showing the movement patterns of an immature male mallard fitted with a radio transmitter on 26 August 1991, released and then located six or more times per week from 27 August to 25 September 1991.

a Newfoundland WP-manufacturing plant supports the case that WP is not particularly reactive once deposited in biological tissues and, like many other highly lipid-soluble chemicals, might be transferred from prey to predator (Idler 1969). In the vicinity of the plant there were massive fish kills and dead and dying herring (*Clupea harengus*), and other dead fish were found as far as 80 km from the manufacturing plant. Later studies by Fletcher (1973) showed that WP-contaminated cod liver was lethal when fed to brook trout, and the symptoms of WP poisoning were identical to those observed when WP is present in water. This type of transfer of WP from prey to predator could have

explained in part the finding of dead and dying fish at considerable distances from the Newfoundland spill site. Fletcher (1971) also showed that marine invertebrates and seaweed all accumulated WP. There is evidence that the distribution of WP was highest in organisms and organs with the highest lipid contents. WP-fed cod contained 194  $\mu\text{g/g}$  in the liver but only 4–11  $\mu\text{g/g}$  in the muscle (Fletcher 1973). Dyer et al. (1972) found that WP was still present in the edible muscle tissue of cod during processing, including icing, freezing and thawing, frozen storage, salting and cooking, and suggested that the WP was dissolved and protected from oxygenation by the tissue lipid.

To determine if WP poses a toxicological risk to predators at ERF, our approach was to carefully monitor the predation events and record the species of prey and predator. We recorded the frequency and circumstances of predation, the amount of tissue ingested from ducks poisoned at ERF, the concentrations of WP in the duck tissues being consumed, any evidence of the presence of WP in predator species, and any resultant obvious toxicity to those predators.

#### *Methods*

##### *Field observation of predation events*

Observations of waterfowl, waterfowl poisoning and predation of waterfowl were made at ERF during the spring (21–31 May) and fall (19–30 August) of 1991 from an observation tower in Area C (Fig. 10). These periods correspond to the major spring and fall migrations of ducks into and through Cook Inlet. Field observations usually started between 0700 and 0800 hours and ended between 1800 and 2000 hours. These hours encompassed the major times when ducks were feeding in ERF. Eighty hours of observations specifically looked at predation events. Of particular importance were the types of predators and whether the ducks were alive or dead when preyed upon. Particular attention was paid to the signs of WP poisoning in the waterfowl, especially with respect to those signs that attracted predators. As discussed previously (Racine et al. 1992), the signs of WP toxicity included extensive drinking, uncontrolled and frequent head shaking, lethargy and convulsions.

##### *Observation and collection of predators*

During May and June 1991 the U.S. Army 6th ID made helicopter flights over ERF to locate sick or dead bald eagles. In addition observations of predators were made from the blinds to detect any abnormal behavior that may be related to WP poisoning. Herring gulls and gull eggs were also obtained and analyzed for WP during the field season.

##### *Tissue sampling procedures*

To determine if predators were commonly exposed to WP, we routinely sampled the breast skin, breast muscle and body fat deposits of waterfowl that had been preyed upon in Area C. For each of these tissues, approximately 5-g samples were cut from the carcass, minced when necessary to produce pieces no thicker than 3 mm and added to a preweighed, 40-mL glass vial containing 10

mL of iso-octane. If available the entire gizzard contents were sampled. If a predator had fed on a carcass, we often were not able to obtain specific tissue samples or sample sizes. In those cases, we sampled whatever tissue was available to determine if the prey contained WP.

Several whole carcasses collected in ERF were frozen and shipped to the laboratory, where it was possible to make a more detailed sampling of tissue. To assess the amount of WP a "predator" could ingest by eating all or parts of WP-poisoned waterfowl, we weighed and sampled over 14 major organs and tissues of ERF ducks that had all shown signs of WP poisoning.

##### *WP analysis*

WP analyses were accomplished according to procedures used previously (Racine et al. 1992) and detailed elsewhere in this report. WP was determined by gas chromatography.

#### *Results*

A total of 24 predation events were observed in Area C during May 1991 (Table 16), from which carcasses were recovered and analyzed. Not included are events in which the prey could not be identified.

The majority of the ducks preyed upon were green-winged teal. The teal also represented the major species of duck in Area C during these observation periods. Of particular interest was whether the ducks were alive or dead when preyed upon, since WP toxicity involves sedation or lethargy in the ducks, allowing them to be easy prey. For example, on several occasions predator were observed to flush a flock of ducks and then wheel around to prey on an individual that did not flush. Another sign of WP poisoning is convulsions. This violent behavior attracted predators, especially eagles. Often bald eagles would perch on the trees on the eastern shoreline of Area C and watch the ducks feeding. Herring gulls were also attracted by ducks that were convulsing.

Predators of ducks include bald eagles, gulls and ravens (Table 17). During the May 1991 field season, immature bald eagles were more common than adults, and every day there were several eagles in ERF. Herring gulls and ravens often scavenged remains left by eagles, though this was not always the case. Herring gulls and occasionally ravens were observed to kill sick ducks and consume at least a portion of the duck.

Of the 24 predation events observed during May in ERF, about 20 of the preyed-on birds were

**Table 16. Predation events on ducks observed between 21 and 31 May 1991 from the blind in Area C.**

Prey species	Events	Sex	When preyed on:		
			Alive	Dead	Unknown
Green-winged teal	7	male	2	2	3
	4	female	2	1	1
Shoveler	1	male		1	
Pintail	1	male		1	
Unknown	11	unknown			11
<b>Total</b>	<b>24</b>				

carried by eagles out of the flats into the bordering woodland, where the carcasses were consumed. On 21 and 22 May 1991, over 40 fresh feather piles were identified by searching the dense woods to the east of Area C from the EOD Area, north along the margin of ERF to the C/D transition area. The species of duck could often be identified from the remains in the feather pile and were the species known to be susceptible to WP poisoning in ERF. Feather piles of shorebirds were also found, suggesting that they may also be victims.

Another important feature regarding predation was the observation of multiple predators feeding on a single carcass. This included both multiple individuals of the same species and a succession of eagles followed by gulls or ravens or both. On two occasions pairs of herring gulls were observed to feed on ducks. These pairs appeared to be offering bits of food to each other. On other occasions pairs of herring gulls were observed to search the flats together. We suspect that these represented breeding pairs of herring gulls.

On 21 May 1991 an immature bald eagle was observed to eat three ducks within three hours. This was the only time that an individual predator was seen consuming several ducks. The first duck was consumed in a tree near the C/D transition area. The second was a male green-winged teal convulsing in Area C, and it was carried to a tree and consumed. Finally a third duck was taken to a tree in this same area. It seems likely that a large predator would consume at least portions of several ducks in a single day.

Other predators, in addition to the ones we observed (Table 17), may also feed on poisoned birds in ERF. During the 1991 field season, coyotes, both singly and in small groups of four or five, were observed to hunt over a wide range of the flats. Whether they prey upon sick or dead ducks is not known. In August 1991 a northern harrier

(*Circus cyaneus*) was observed to feed upon a duck that had just died. The role of other less common or less commonly observed predators at ERF is not known.

Table 18 summarizes the concentrations of WP in the tissues of 15 duck carcasses randomly collected primarily in Area C during the 1991 field season. The gizzard contents had WP masses that ranged from 8820 to 0.021  $\mu\text{g}$ , a range of over five orders of magnitude. This wide range implies that the exposure to WP is quite variable and depends on the number and size of particles that are ingested, which in turn depends on where the duck feeds and the extent of foraging that occurs in the contaminated sediments. The gizzard contents indicate exposure to WP but not absorption and tissue deposition. These 15 ducks all contained WP in their tissues, with the highest concentrations being in the fat deposits, followed by skin and muscle. Tissue concentrations, both from a single bird and from bird-to-bird comparisons, varied considerably and may reflect variations in WP exposure, rates of WP absorption, amount of tissue fat, blood supply to the specific organ or tissue, or other factors. With the amount of WP found in gizzards varying by orders of magnitude, it is likely that differing exposures are the greatest

**Table 17. Major predators observed to feed on sick or dead ducks at Eagle River Flats between 21 and 31 May 1991.**

Primary predator	Number of predation events
Bald eagle	
Immatures	12
Adults	3
Herring gull	7
Common raven	2

**Table 18. Concentrations of WP in duck tissues from various carcasses collected between 21 May and 3 June 1991 in Eagle River Flats.**

Species	Gizzard contents ( $\mu\text{g WP}$ )	Tissue concentration ( $\mu\text{g WP/g wet weight}$ )		
		Fat	Skin	Muscle
Green-winged teal (male)				
WP range	1310-0.021	1.80-0.52	6.34-0.012	0.022-0.001
number =10	(8)	(5)	(9)	(8)
median value	0.48	0.187	0.0733	0.007
Green-winged teal (female)				
WP range	8820-37.8	5.92-0.235	1.37-0.142	0.560-0.006
number =3	(3)	(3)	(3)	(3)
median value	1084	2.04	0.214	0.010
Shoveler (female)				
WP level	0.751	0.047	0.067	0
number =1	(1)	(1)	(1)	(1)
Mallard (male)				
WP level	1.32	0.42	0.06	0.004
number =1	(1)	(1)	(1)	(1)

variable with respect to determining the tissue concentration.

Direct evidence that predators are being exposed to WP is provided by tissues (Table 19) collected from five scavenged carcasses left behind after an observed predation event (Table 16). Based on these data, there is no doubt that predators are ingesting ducks with WP in their tissues.

In late May an immature bald eagle carcass was collected in Area A. The fatty tissues of this eagle contained WP (Table 20). This immature female apparently did not die of a chronic condition, as it contained large quantities of adipose fat. In addition a mature bald eagle was seen exhibiting abnormal behavior on 28 and 29 May. It was ap-

proached to within 50 m and ran into a drainage channel with its wings dragging. Eventually it was able to fly, and we were not able to confirm the cause of its initial inability to fly.

Three herring gull eggs were collected in May and June 1991 from three nests in ERF (two in Area D and one in Area C). One of these eggs contained a small quantity of WP (Table 20). In August and September, two herring gulls were killed in ERF. Neither of these birds contained WP, and we do not know whether the gulls had eaten ducks at ERF. The gull collected in September was likely not eating many ducks as there were almost no dead ducks seen in the flats. The single gull egg with WP indicates that WP can move from ducks

**Table 19. Concentration of WP in various tissues of duck carcass remains that were observed to be partially consumed by various predators in Area C between 21 and 31 May 1991.**

Prey	Predator	Comment	Sample	Conc. ( $\mu\text{g/g}$ )
Teal (female)	Raven	Duck convulsed and killed by raven	Gizzard	1084*
			Fat	0.235
			Skin	0.142
			Muscle	0.006
Teal (male)	Immature eagle	Predation two days prior to collection	Wing tissue	0.022
Shoveler (male)	Herring gull		Muscle	0.060
Pintail (male)	Adult eagle	Fed on by five other eagles	Wing tissue	0.017
Teal (male)	Herring gull		Unknown tissue	0.521

\* The gizzard contents are cited as mass of WP in the contents and not on a concentration basis as with tissue.

**Table 20. Analysis of WP in tissues of predators or predator eggs collected during May or June 1991 in Eagle River Flats.**

<i>Prey</i>	<i>Source</i>	<i>Sample</i>	<i>Concentration (µg/g wet tissue)</i>
Bald eagle (immature female)	Found dead in flats	Fat	0.060
		Skin	0.010
Herring gull (2)	Shot in Area C	Fat	not detected
		Skin	not detected
Herring gull eggs (3)	Collected from two nests in Area D	Entire egg	0.003 (1)
		contents	not detected (2)

to gulls and to their eggs. This emphasizes the stability of this toxicant and, at least with respect to bioaccumulation, its similarity with other lipid-soluble toxicants.

#### *Discussion and conclusions*

These data support the hypothesis that predators can be poisoned by ingesting ducks and other waterbirds containing WP, but the risk of poisoning is not known. WP was found in tissues of ducks and other species, as well as in one of the predators feeding on the poisoned ducks. Generally WP was associated with fatty tissues, including skin and adipose fat. To date, except for the WP-containing eagle carcass, we have little evidence of toxicity to predators of ducks.

Of particular concern is the effect on a predator, such as an eagle or other large species, that ingests an intact gizzard and its contents of WP particles. In some duck gizzards, milligram quantities of WP are present. If the lethality of WP is in the range of 1 mg/kg of body weight for a wide range of predators, then the ingestion of a single, highly contaminated gizzard could be lethal. The lower concentrations of WP in the tissues of poisoned ducks makes ingestion of these tissues a more unlikely source of toxicity to a predator. It is not known, however, if the rate of accumulation of WP is greater than its rate of detoxification or elimination by the predator.

#### **Waterfowl mortality patterns and estimates**

During the 1991 field season, studies were initiated to measure the distribution and magnitude of WP poisoning of birds in ERF. The main goals of these studies were:

- To examine the spatial and temporal patterns of mortality in order to direct sediment sampling into areas of high mortality and to determine if there is a correlation between the distribution of WP in the sedi-

ments and the locations of waterfowl mortality;

- To determine what waterfowl species and sediment-feeding shorebird species are dying due to WP poisoning;
- To design a standardized mortality index technique with which to efficiently monitor the relative rates of mortality over time and make it possible to evaluate the effectiveness of future remediation efforts; and
- To apply and test this mortality index technique in several areas of ERF and use it to estimate the total number of dying waterfowl.

Various attempts to count the numbers and species of bird carcasses in various parts of ERF were made by previous researchers between 1983 and 1990. Both ground searches and observer inventories have been made. However, accurate estimates of waterfowl mortality are difficult to obtain in an area as large as the 1000-ha (2500-acre) ERF. These aerial and ground counts of dead ducks on ERF underestimated the actual mortality on the flats for three reasons:

- Predators such as bald eagles, gulls and ravens remove sick and dead ducks from the flats and carry them into the forest bordering ERF. In the spring these removal rates are high due to the large number of bald eagles feeding at ERF;
- Carcasses decompose and sink before they are found; and
- Most poisoned ducks seek shelter and eventually die in taller and denser clumps of vegetation, making them difficult or impossible to see from the air (or on the ground).

For example, on 27 August 1991 we found nine dead ducks in bulrushes in a 200- × 10-m area while a helicopter survey detected seven dead ducks on the entire flats. However, the size and



conspicuous white plumage of swans allow their mortality to be counted accurately from helicopters.

Past mortality counts were made on foot and often involved several individuals walking over certain areas of the flats during either the spring or fall (Racine et al. 1992). The most intensive count of dead birds involved 26 foot searches between 20 April and 7 October 1988 by two to four searchers along the east side of ERF from Area D through Area C/D into Area C. A total of 350 man-hours were spent on this 1988 count, and almost 1000 dead waterfowl were found (Racine et al. 1992).

#### Methods

##### *Observations of waterfowl mortality and symptoms of WP poisoning*

Intensive observations of waterfowl from towers in Areas A, C, C/D and the blind in D were used to locate and map sick and dying ducks, observe symptoms of WP poisoning, watch predation and count the numbers of each species using the ponds. Observations were made mostly in Area C during four migration periods: 9–16 September 1990, 18–31 May 1991, 18–30 August 1991 and 21–25 September 1991 (Table 21). In addition, Ft. Richardson personnel made occasional observations throughout the summer of 1991. Our observations usually extended from 0730 to 1800 each day.

##### *Ground counts of mortality*

Past ground searches and carcass counts in various areas of ERF have not been systematically carried out along marked and defined transects or areas. The actual ground area searched by individual searchers varied from week to week since no defined transects were established. In August 1991 a mortality sampling technique was designed that is based on counting carcasses and feather piles each time in exactly the same area using permanent transects of known length and width.

Transects in Areas A, C, C/D, D and the Bread Truck Pond were established, and counts made in each transect three or four times over a 10-day period in late August 1991. Dead ducks found on transects were labeled with metal tags to prevent recounting the same carcasses and to determine if carcasses are removed. Carcasses and feather piles were counted in two types of transects. The "D" or density transect is a 10-m-wide belt transect of known length and area for measuring the number of carcasses or feather piles per unit area. These D transects were located so as to include the four major vegetation-habitat types around each feeding pond area. These types were bulrush, sedge, mudflat and open water with clumps of vegetation (island-water complexes). We expected to find different numbers of carcasses in each of these four vegetation types because of the behavior of sick ducks as well as the rates of removal by predators. Predator removal is more rapid in open mudflats and the island-water complex than in tall bulrush vegetation, where sick ducks often hide to escape predators. We assumed that our transects represented typical mortality density in each area.

The second type of transect is the "E" or edge transect of undefined width, established along the edges of the main water bodies where we expected to find high concentrations of carcasses (because wind may push floating carcasses to the pond edge or because sick birds tend to seek cover along the pond edge) (Fig. 33); the larger carcass numbers in these transects permit easier measurement and detection of relative mortality of each species and changes in mortality in subsequent years.

#### Results

##### *Mortality of waterfowl species*

Of the 106 duck carcasses counted in all the mortality transects in ERF, 44 (42%) were green-winged teal, 27 (25%) were northern pintail, 18

**Table 21. Number of hours spent observing waterfowl and predators in the various areas of Eagle River Flats.**

Dates	Area A	Area C	Bread Truck			Total
			Pond	Area C/D	Area D	
10-16 September 1990	0	100	0	0	0	100
19-31 May 1991	6	163	4	6	4	183
19-30 August 1991	9	40	9	17.5	3	78.5
Total	15	303	13	23.5	7	361.5

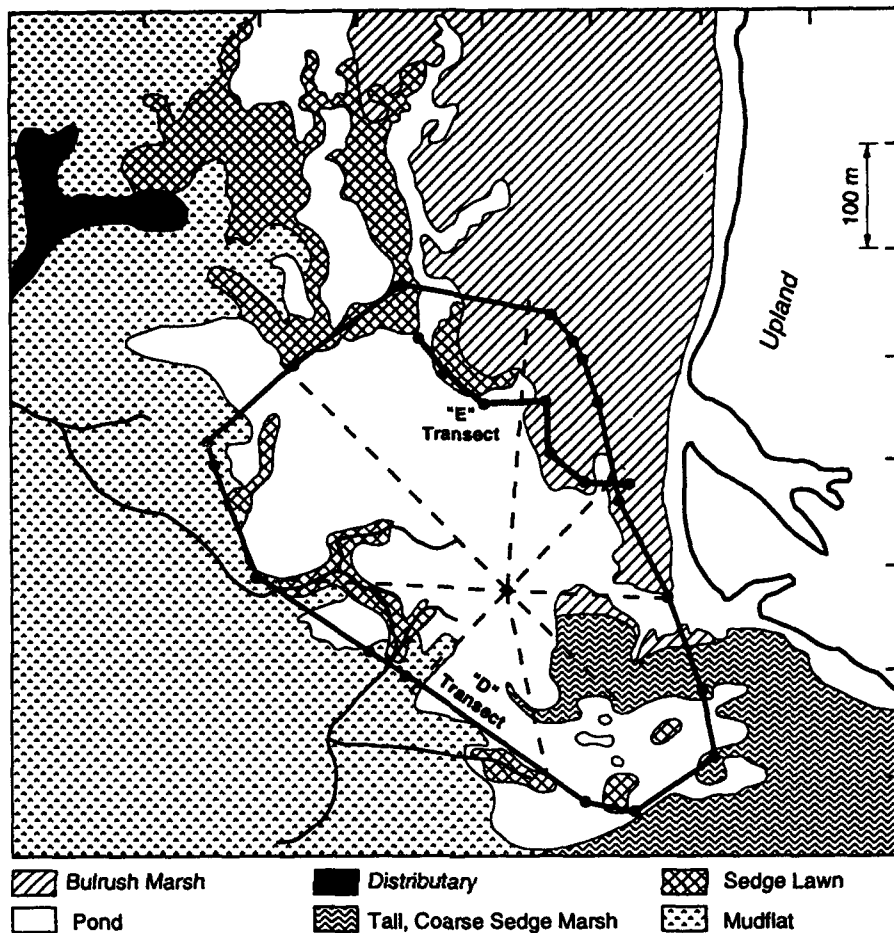


Figure 33. Map of Area C showing the location of the density or D transect surrounding the main pond area in which carcasses were counted in a 1400-m-long  $\times$  10-m-wide belt, and the edge or E transect where carcasses tended to accumulate in large numbers.

(17%) were mallards, 1 was a wigeon and the rest were too decomposed to identify. Green-winged teal, northern pintails and mallards are the most frequently found carcasses in ERF. When the percentages of carcasses of each species in Area C are compared with the percentages for the numbers of each species using the Area C ponds (as observed from the tower), mallards and pintails appear to be dying in proportionately greater numbers than other waterfowl using the area (Table 22). This suggests that they may be more susceptible than green-winged teal to WP poisoning. Of the dabbling ducks using Area C in August, wigeon are clearly the least susceptible to WP poisoning. The number of mallards using the pond may be underestimated due to their use of densely vegetated areas (bulrush vegetation) in Area C rather than the ponds that were being observed from the

tower. Although shoveler carcasses have been found, they did not comprise a significant percentage of the birds using the ponds.

#### *Mortality of non-waterfowl species*

During the 1991 field season we collected seven dead red-necked phalaropes (Table 23). All seven had WP in their gizzards and tissues, and the three females collected also had WP in eggs still within their bodies. In addition to these phalaropes, two sandpipers were collected, one in June and one in September. These birds also had WP in their gizzards.

Many shorebird species feed on the flats from spring to fall. The most common are short-billed dowitchers and lesser yellowlegs, although phalaropes are also abundant in spring and probably breed at ERF. The phalaropes appear to be the

**Table 22. Percentage of four species of dabbling ducks observed in Area C compared with the percentage of carcasses counted in the edge transect in Area C.**

Species	Ducks observed in Area C (%)	Carcasses in edge count of Area C (%)	Selectivity Index (%Dead-%Observed)
Green-winged teal	53	49	-4
Pintail	15	30	+15
Mallard	2	20	+18
Wigeon	27	1	-26
Shoveler	3	0	-3

only species that does not aggressively probe into the sediments for food, yet more dead phalaropes have been found than dead birds of any of the other shorebird species. It is possible that shorebirds die regularly from WP poisoning but are either too small to detect or fly off the flats and die somewhere else, for example on the edge of the Cook Inlet where they may communally preen and wash.

*Temporal patterns of mortality*

Mortality of waterfowl was observed during all

three observation periods, including September 1990, May 1991 and August 1991. However, during 21-25 September 1991, no mortality was noted by observers in either areas C, C/D or D. This absence of mortality correlated with the absence of waterfowl feeding in either Area C or the Bread Truck Pond. On 25 September 1991, over 1000 ducks were counted in Area D, while none were seen in Area C. Also during this time period, an average of 60 swans fed in Area D and none used Area C. These observations are interesting, but the mortality transects established in August were not

**Table 23. Tissue analysis for white phosphorus of shorebird carcasses from Eagle River Flats.**

Species	Sex	Area	Date collected	Tissue	Mass (g)	Mass of WP (µg)	Conc. of WP (µg/g)
Red-necked phalarope	F	C	5/27/91	Gizz. and cont.	0.46	0.0514	0.112
				Skin	1.21	0.546	0.451
				Egg yolk	1.39	0.0432	0.0311
Red-necked phalarope	F	C	5/27/91	Gizz. and cont.	0.78	0.848	1.09
				Skin	1.25	3.98	3.19
Red-necked phalarope	?	road to D	5/27/91	Gut pile	2.96	13.5	4.57
Red-necked phalarope	F	C	5/28/91	Gizz. and cont.	0.84	1.18	1.4
				Skin	0.43	1.32	3.06
				Yolk 1	2.48	0.036	0.015
				Yolk 2	0.71	0.104	0.146
Red-necked phalarope	F	C	5/28/91	Gizz. and cont.	0.97	263	271
				Skin	0.32	0.37	1.15
				Egg yolk	3.22	0.34	0.11
Red-necked phalarope	M	C	5/29/91	Gizz. and cont.	0.68	1.15	1.68
				Skin	0.46	0.27	0.59
				Testes	0.33	not detected	
				Gizz. and cont.	0.92	15,500	16,800
Red-necked phalarope	F	C	5/31/91	Skin	0.18	0.11	0.61
				Gizzard cont.	0.43	12.4	28.7
Sandpiper	F	C	6/18/91	Fat	0.74	0.35	0.47
				Fat	0.5	0.32	0.64
				Skin	1.05	0.35	0.33
				Breast muscle	4.98	0.03	0.006
				Gizz. and cont.	2.71	0.21	0.078
Sandpiper			9/90	Gizz. and cont.	2.71	0.21	0.078

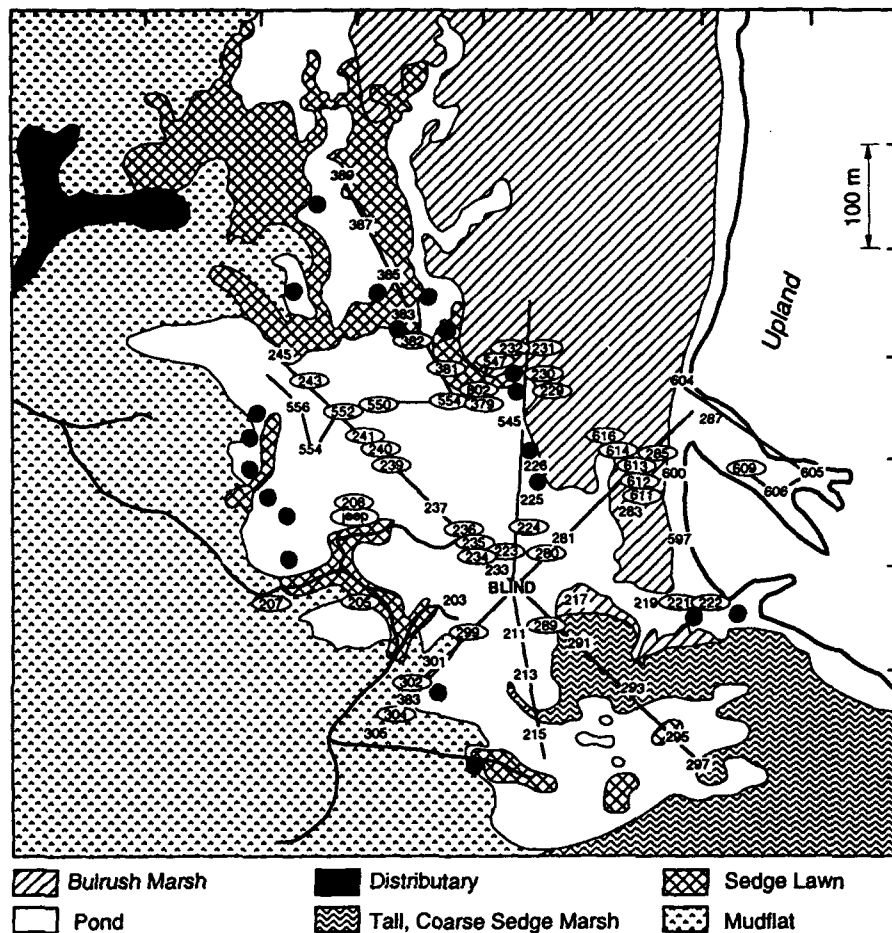


Figure 34. Habitat map of Area C showing the location of sediment samples testing positive for WP (239) and locations (black dots) where 22 waterbirds were observed to become sick and die during observation periods in September 1990, May 1991 and August 1991.

walked and no systematic observations were made in Area C or the Bread Truck Pond. Therefore, because there are no quantitative data from September, it is difficult to confirm the "suspicion" that the absence of mortality in September is related to the avoidance of the highly contaminated Area C and Bread Truck ponds. During this time waterfowl also often feed on an abundant crop of seeds floating on the surface of the water, not in the sediments.

#### *Observations and locations of sick and dying waterfowl in Area C*

During the three observation periods (September 1990, May 1991 and August 1991), a total of 19 ducks (17 green-winged teal and two pintails) and 3 shorebirds (phalaropes) were observed to get sick and eventually die in Area C (Fig. 34). WP was found in the gizzards of all these individuals. All

but four of these birds died in the northern half of the Area C pond, and most were located along the edge of the main pond. We also saw many other birds show early symptoms of sickness, but they flew to other areas and WP intoxication could not be confirmed as the cause of their behavior. In addition 15 other ducks were carried off by predators from Area C in May 1991.

In May 1991, during observations from the tower in Area C, we saw bald eagles and gulls consuming duck carcasses in the Bread Truck Pond. This resulted in the sampling and discovery of large amounts of WP in the bottom sediments of this pond.

#### *Transect mortality counts during August 1991*

From August 20 to 30 we performed 28 ground counts in density and edge transects in five areas and found 106 dead ducks and three dead swans

**Table 24. Number of dead ducks counted in each transect and in each area.**

Date	A		C		C/D	D	Bread Truck Pond
	D count*	E count**	D count	E count	E count	D count	D count
Aug. 20	—	—	Pt 1	GwT 7 Pt 10 Ma 1 unk. 9	—	—	—
Aug. 21	—	—	—	—	GwT 2 Swan 1 unk. 3	Pt 1	—
Aug. 22	—	—	—	—	—	—	GwT 5 Pt 1 Ma 1 unk. 3
Aug. 23	GwT 1 Pt 1 Ma 2 Swan 1	Ma 8 Pt 6	—	—	—	—	—
Aug. 24	—	—	—	—	GwT 1 Swan 1	—	—
Aug. 25	—	—	GwT 1 Pt 1	—	—	—	—
Aug. 27	—	—	GwT 5 Pt 2	GwT 6 Ma 3	GwT 1	—	GwT 3
Aug. 28	Pt 1	GwT 3 Pt 2 Wi 1	—	—	—	—	—
Aug. 30	0	0	GwT 3 Pt 2	GwT 4 Ma 1	0	0	GwT 2
Totals	Gwt 1 Pt 2 Ma 2 Swan 1	GwT 3 Pt 8 Ma 8 Wi 1	GwT 9 Pt 6	GwT 17 Pt 10 Ma 5 unk. 9	GwT 4 Swan 2 unk. 3	Pt 1	GwT 10 Pt 1 Ma 3 unk. 3
Area totals	6	20	15	41	9	1	17
Grand total = 109							

\*D counts = transects used for density measurements in estimating mortality

\*\*E counts = edge counts used only as indices of relative mortality (see text for details)

GwT - Green-winged Teal

Pt - Pintail

Ma - Mallard

Wi - Wigeon

unk. - unknown species, carcass too decomposed to identify species

— = no count made in this area on this date

(Table 24). Seventy (66%) of the ducks were counted in edge transects (E counts), with the remaining 36 in the density transects. Fifty-six of the ducks were found in Area C, 26 in Area A, 17 in the Bread Truck Pond, nine in C/D, and only one in Area D.

In Area C the density transect ran 1404 m in a circular course around the C tower (Fig. 33) and covered an area of 1.4 ha (Table 25). This transect crossed bulrushes to the northeast, tall sedge to the northwest and southeast, and mudflat to the west. The edge transect, varying from 10 to 15 m wide, ran along the northeast shoreline of the main pool

in Area C. Counts in Area C were made on 20, 25, 27 and 30 August (Table 24). A total of 56 carcasses were counted in both the density and edge transects, with 41 of these in the edge transect along the northeast edge of this pond. Counting the 15 carcasses from the density transect, we calculate a density of 10.7 carcasses/hectare (Table 25). This area probably contained high numbers of dead ducks, because ducks that feed in the main pool and become sick take cover in the tall bulrushes lining this section of the pool and because ducks that die in open water and are not removed

**Table 25. Total number of dead ducks counted on each density transect, the total area searched and the resulting density of dead ducks in Areas A, C, D and the Bread Truck Pond.**

Area	No. of dead ducks	Area searched (ha)	Density (ducks/ha)
A	6	0.64	9.4
C	15	1.40	10.7
Bread Truck Pond	17	1.05	16.2
D	1	0.60	1.7

by scavengers are likely to be pushed into this edge of the pond by the prevailing wind.

The Bread Truck Pond is a combination of open water with clumps of sedge forming many small islands (Fig. 25). There is also an area of sedge meadow along the north edge of the main 5.1-ha pond and some bulrush along the southeast edge of the pond. A density transect (10 m wide by 1054 m long) was established and marked; on 22, 27 and 30 August, both carcasses and feather piles (including enough body parts to be identifiable as a dead duck) were counted. A total of 17 carcasses were found in the Bread Truck Pond density transect, with 14 of these represented by feather piles only. The resulting density of 16.2 carcasses per hectare is the highest density measured in the various areas (Table 25). The high rate of predation here suggests that many more sick or dead ducks may have been removed from the Bread Truck Pond by predators and will result in a low estimate of the actual mortality if the mortality estimate is based on carcass counts. Few of the dead ducks in counts from other areas were represented by feather piles (in Area C, only four out of 56). The short-sedge meadow and mudflats that dominate this area make sick and dead ducks more visible to predators than in areas with taller bulrush.

Area A is an extensive area of interspersed bulrush and open water. We established a 530-m-long density transect following the marked grids where sediment samples had been taken (Fig. 20). We also established an edge transect and counted carcasses from a canoe along the perimeter of the larger open water areas south of the A tower. Both density and edge counts were obtained on 23, 28 and 30 August. The carcass density was only 9.4 per hectare. Twenty-six carcasses were counted, with 20 (77%) of these from the edge count.

Area C/D includes mostly bulrush interspersed

with small deep ponds. The deep water made it necessary to establish an edge transect that could be traversed by canoe (Fig. 23). Counts were made on 21, 24, 27 and 30 August. Only 10 carcasses were counted here.

Area D consists mainly of a fairly deep pond with islands of tall bulrush (Fig. 24). A 16-m-wide density transect ran for 375 m, and counts were made using a canoe. Counts on this transect were conducted on 21, 24 and 30 August. Only one carcass was found, so the density was only 1.7 carcasses per hectare.

#### *Estimates of August 1991 mortality*

The primary purpose of the mortality transects was to monitor relative mortality in the same area over time. However, mortality transect data can also be used to derive a total estimate of mortality by making several assumptions about the data. The main assumption is that the number of dead ducks found in each habitat type in the mortality density transect is representative of the density of dead ducks in that habitat type farther away from the transect. We realize that our transects are in close proximity to feeding areas that have higher mortality, but the transects are actually 20 m from the feeding ponds. For example, in Area C we found seven ducks in the bulrush habitat of the density transect about 20 m from the edge of the main pond. This contrasts with 41 duck carcasses counted in the edge transect for the main pond in Area C.

The method involves calculating the area of each of four habitat types that transects passed through. Then the number of carcasses or feather piles of each species in each vegetation type is determined. The number of dead ducks per area for each habitat is then applied to the total area in each vegetation type to obtain the total number of individuals of each species dying in each vegetation type (Table 26). For example, this is how mortality was calculated for green-winged teal:

1. Number of dead green-winged teal counted in tall sedge on D counts in Areas C, C/D, D and the Bread Truck Pond = 12.
2. Total area of sedge included in D counts = 1.33 ha.
3. Total area of sedge in Areas C, C/D, D and the Bread Truck Pond = 34.6 ha.
4. Number of green-winged teal that died in sedge in August =  $(12) \times (34.6) / 1.33 = 312$ .
5. The totals of each species in each vegetation type in Areas A, C, C/D, D and the Bread Truck Pond were then added to obtain the total number of ducks that died in August.

**Table 26. Number of dead waterfowl of each species in density mortality transects counted during August 1991 in each of three habitat types grouped by areas on the east side of Eagle River Flats (C, C/D, D and the Bread Truck Pond) and for Area A on the west side of ERF. The total area in each vegetation type was calculated from aerial photos.**

	Dead ducks counted			Area censused (ha)			Total area (ha)			Mortality estimate		
	Sedge	Bulrush	Island/ water	Sedge	Bulrush	Island/ water	Sedge	Bulrush	Island/ water	Sedge	Bulrush	Island/ water
<i>Areas C, C/D, D and the Bread Truck Pond</i>												
GwTeal	12	6	5	1.33	0.52	0.60	34.6	46.2	18.6	312	533	155
Pintail	2	5	1							52	444	31
Unknown	0	1	3							0	89	93
Subtotal	14	12	9							364	1066	279
<i>Area A</i>												
GwTeal	1				0.64			17.0				27
Pintail	2											53
Mallard	2											53
Subtotal	5											133
<i>Total for All Areas and Habitats</i>												
		40			3.0			116.5				1842

The total number of ducks estimated to have died between early August and the end of August 1991 in Areas C, C/D, D and the Bread Truck Pond is 1842 (Table 26). Our counts included old carcasses, so we assume that most of the early fall migrants are included. In addition, resident individuals may have died on our transects, so we consider our counts to estimate mortality for all of August, even though our counts did not begin until August 20.

#### Discussion

Our mortality estimate of 1842 dead ducks in August 1991 is not unreasonably high compared to previous estimates. In the spring of 1989, ESE (1990) estimated that 2500–3000 ducks were affected in a four-week period during the peak of migration in May. In August 1988, 232 dead ducks were counted by 3–4 people walking from Area D to Area C. Assuming that these ground searches covered about 20% of the 74-ha area represented by this search, the density of carcasses (16 carcasses per hectare) is similar to that obtained by our density counts in Areas C, C/D and D. A third piece of evidence supports the conclusion that mortality in ERF is much greater than the 1000–2000 waterfowl usually quoted: during May 1991 we observed that 80% of the dead or dying ducks preyed upon by eagles were removed from ERF and were therefore not counted in either the 1988 ground searches or 1991 transects. If this per-

centage is applied to the 573 feather piles (which represents ducks eaten in situ) counted in the spring of 1988, the estimated mortality for 1988 in a limited area of ERF is much greater than 1000.

If the density counts alone are compared, and if the counts are scaled by the amount of area covered, then the Bread Truck Pond had the highest density of dead ducks, followed by Area C and then Area A (Table 25). This pattern of mortality is consistent with the pattern of the distribution of WP in the sediments, with the highest occurrence and concentration of WP in Areas C and the Bread Truck Pond. The highest concentration of carcasses we have encountered anywhere on the flats is in the bulrushes along the northeast edge of the main pool in Area C, where high levels of WP were detected in the sediments. At two spatial scales (the entire ERF and within Area C), there is a correlation between the location of WP in the sediments and the location of dead ducks and high incidences of predation on ducks. Most ducks probably die near where they ingest WP. However, the fact that dead ducks are found in areas with little or no WP in the sediments (Areas D and B) demonstrates that some ducks ingest WP and then fly 1000 m or more before dying. Evidence for the ability of poisoned ducks to fly include the finding of WP in the gizzards of four flying teal in Area C and the observation of several ducks with presumed early symptoms of poisoning flying considerable distances, e.g., from Area C to Area A.

The finding of WP poisoning of shorebirds raises questions about the risk of mortality to these species. We have found feather piles both on the flats and in the bordering forest that were clearly shorebirds. We were puzzled after our initial observations in 1990 as to why these sediment-probing shorebirds did not appear to ingest WP or to suffer ill effects if they did. We are now aware that shorebirds are at some risk. Further observation and mortality counts are needed to determine the severity of the risk. In red-necked phalaropes, the source of WP may be suspended WP in the water column, where this species is known to feed (Dodson and Egger 1980).

#### Preliminary human health risk analysis

Since waterfowl displaying early symptoms of WP poisoning have been observed to fly, the potential for these birds leaving the flats is a concern from a human health risk standpoint. Because of this concern, Alaska state epidemiologist John Middaugh issued a warning in September 1991 to hunters not to take sick or dead ducks in Cook Inlet (Price 1991). Meanwhile, the U.S. Army Environmental Hygiene Agency (AEHA), in a memorandum to USATHAMA on 24 July 1991, described a statistical sampling plan for hunter-harvested ducks to assess the exposure risk to hunters in neighboring Cook Inlet salt marshes. Following their recommendations, on the opening day of hunting season, over 300 gizzards from hunter-harvested ducks were collected by personnel from the Alaska Department of Fish and Game and U.S. Fish and Wildlife Service for WP analysis. Collections were made from Palmer Hay Flats, Goose Bay, the Anchorage Coastal Wildlife Refuge and Susitna Flats (Fig. 1). The gizzards were primarily from dabbling ducks such as mallards, northern

pintails, green-winged teal, northern shovelers and American wigeon (Table 27). For most birds, a skin or fat sample was also taken. A limited number of gizzards from diving ducks were also collected.

#### Method for screening of gizzards for WP contamination

Following collection in the field, the gizzards were frozen and shipped to CRREL, where they were analyzed for WP. Our plan was to test the gizzard contents and, if WP was found, to analyze the fat or skin samples as well. We chose to analyze the gizzard contents first because we have found WP in the gizzard contents of every bird found dead or observed to die at ERF. While we do not know the residence time of WP in the gizzard, the analytical method as outlined below is sensitive enough to detect 20 ng (or 0.00002 mg) of WP in the gizzard contents. Thus, even a minute quantity remaining in the gizzard will be detected. We did not analyze the fat or skin from each bird because the chromatographic column used in the analysis degrades in performance with each injection of fat extract. Thus, the column would have to be changed frequently, adding to the time and expense required for the analysis.

Each gizzard was defrosted overnight in a cooler. Then a razor blade was used to slice the gizzard open. The gizzard contents were scrapped with a spatula into a preweighed vial containing 5 mL of isooctane. The vial was reweighed and the weight of the gizzard contents obtained by difference. The gizzard was rinsed with distilled water, and this rinse water was added to the vial with the scrapings. The sample was vortex-mixed for 30 s and then shaken overnight. The isooctane extract was analyzed by gas chromatography using the same parameters described previously in this report.

Table 27. Hunting areas and species of dabbling ducks from which gizzards were collected and analyzed for WP.

	Mallard	Pintail	GW Teal	Shoveler	Wigeon	Other	Total
Palmer Hay Flats							
Rabbit Slough	6	23	17	6	12	5	69
Cottonwood Creek	37	19	11	7	6	15	95
Kruk River	11	15	2	5	6	8	57
Anch. Coastal Wldlf. Ref.	26	2	14	4	9	0	55
Goose Bay	9	2	1	0	1	0	13
Susitna Flats							
Susitna River	16	3	0	0	0	0	19
Little Susitna River	2	3	2	0	0	0	7
<b>Total</b>	<b>107</b>	<b>67</b>	<b>47</b>	<b>22</b>	<b>34</b>	<b>28</b>	<b>305</b>



**Table 28. Maximum proportion of total population contaminated for various sample sizes and confidence levels for the case where no contaminated ducks are found.**

Sample size	Confidence level		
	90%	95%	99%
25	0.088	0.113	0.168
50	0.045	0.058	0.088
100	0.023	0.030	0.045
200	0.011	0.015	0.023
300	0.008	0.010*	0.015
400	0.006	0.007	0.011

\*Sample calculation:  
 $(1 - 0.95) = (1 - 0.010)^{300}$ .

**Results and discussion**

WP was not detected in the gizzard contents of any duck.

As outlined in the AEHA memorandum, a binomial distribution can be used to calculate the probabilities that a certain proportion of the duck population in neighboring salt marshes is contaminated with WP. The estimated maximum pro-

portion of the total population that could be contaminated varies with sample size and confidence levels (Table 28).

Since 305 gizzards were analyzed and no WP was detected, we can state that the proportion of contaminated ducks in the population is less than or equal to 0.010 at the 95% confidence level. In other words, the chances of selecting 305 uncontaminated individuals is only 0.05 (0.99 raised to the 305 power) if 1% of the population is contaminated.

Two exposure situations can be considered: chronic and acute. We have no evidence for either situation given that no WP was detected in the gizzard contents of any duck collected from other Cook Inlet salt marshes. We can, however, calculate a worst-case estimate of human health risk based on data for five ducks observed to die with symptoms of WP poisoning in ERF in August 1991. Using data for the most commonly consumed portions of the duck (i.e. breast muscle, thigh muscle, fat and skin), an estimate was made of the amount of WP that could be ingested by eating these five contaminated birds (two green-winged teal and three pintails) (Table 29). When

**Table 29. Estimate of total WP in edible tissues from five ducks that died in ERF.**

	Tissue	Total tissue mass (g)	Conc. of WP (µg/g)	Total WP (µg)
Green-winged teal	Breast muscle	62.1	0.0923	5.7
	Thigh muscle	12.0	0.277	3.3
	Fat	3.1	1.57	4.9
	Skin	53.6	0.891	47.8
	Total			61.7
Green-winged teal	Breast muscle	56.5	0.00792	0.4
	Thigh muscle	12.3	0.036	0.4
	Fat	3.7	0.0901	0.3
	Skin	41.5	0.0344	1.4
	Total			2.7
Pintail	Breast muscle	129.2	0.0169	2.2
	Thigh muscle	30.3	0.0234	0.7
	Fat	26.6	0.269	7.1
	Skin	115.3	0.176	20.3
	Total			30.3
Pintail	Breast muscle	129.8	0.00867	1.1
	Thigh muscle	28.2	0.049	1.4
	Fat	13.7	0.289	4.0
	Skin	109.4	0.211	23.1
	Total			29.5
Pintail	Breast muscle	143.0	0.0128	1.8
	Thigh muscle	35.2	0.031	1.1
	Fat	1.2	0.475	0.6
	Skin	160.6	0.0108	1.7
	Total			5.2
Average per duck				25.9

making this calculation we must stress that since hunting is not allowed in ERF these birds were not accessible to hunters.

The chronic oral reference dose (Rfd) is used to assess chronic exposure. The Rfd is an estimate of a daily exposure level that is not likely to pose a significant risk of adverse health effects. Rfd's typically are based on animal or human data or both and contain safety factors to provide an adequate margin of safety for all members of the population. The Rfd for WP has a safety factor of 1000. The chronic Rfd for WP is  $2 \times 10^{-5}$  mg/kg-day (Gordon et al. 1990). For a 70-kg adult, this amount represents a daily dose of about 1.4  $\mu$ g WP/day, or, on a yearly basis, the consumption of approximately 20 contaminated ducks per year. Since it is unlikely that birds able to leave ERF would be contaminated to the levels seen in the five birds used in this estimate, and it is unlikely that a single hunter would take this many contaminated birds, the risk of chronic exposure from hunter-harvested ducks is low.

There is no value comparable to an Rfd to assess acute exposure. Data from accidental poisonings show that the lowest recorded lethal dose of WP for humans is 1.4 mg/kg (Gordon et al. 1990). To ingest this amount of WP, a human would have to consume 3784 ducks at a single meal.

Based on the chronic and acute human health risk assessment data, Dr. John Middaugh, Alaska State Epidemiologist, stated in a letter on 28 August 1991 to John T. Toenes, Deputy Director, DEH, that, "while the risk of adverse health effects from potential exposure to elemental phosphorus in waterfowl cannot be said to be zero, based upon evidence from available scientific data and findings of the ongoing investigation, the risk can be said to be so low as to constitute no basis for public concern."

## DISCUSSION AND CONCLUSIONS

A high proportion of the sediment samples from the bottom of two of the six waterfowl feeding pond areas in ERF tested positive for WP. The mean WP concentration in one of these ponds was significantly higher than in the others. These results from the collection and analysis of over 360 sediment samples and over 350 hours of observations by avian ecologists resulted in the hypothesis that these two ponded areas, together covering an

area of 15 ha (37 acres), are the major sources of dabbling duck WP poisoning in ERF. The most heavily contaminated pond area was first identified by the avian ecologists, who noted intense duck predation by eagles, gulls and ravens in the vicinity of this pond.

The actual extent of WP contamination of non-ponded areas (i.e. mudflats, meadows and marsh) is not known since only the feeding ponds, covering an area of about 5% of the 1000-ha (2500-acre) ERF, were sampled. Although these unsampled areas are less used by waterfowl, mudflats are used extensively by shorebirds during migrations, and in the future, areas that are now mudflat could become areas of standing water (i.e. due to earthquakes, erosion, etc.). Although a high risk of WP ingestion by duck-eating predators was confirmed, along with WP-poisonings of shorebirds (particularly phalaropes), the effects of WP on other members of salt marsh food chains (invertebrates and fish) is unknown.

The WP particles in the sediments range in size from very small (<0.1 mm), which can become suspended in the water column, to larger particles of about 1 mm buried up to 20 cm deep in the sediments. There is evidence that the very small particles are abundant in contaminated ponds. The WP mass of each particle (or dose to a bird ingesting one of these particles) ranges from 0.0001 mg for the small particles up to 3.4 mg for the large particles. Ducks feeding in the bottom sediments probably ingest these particles as they feed on food items such as seeds and invertebrates. Since a lethal dose of white phosphorus is on the order of 1 mg/kg of body weight, the ingestion of one particle can be fatal to a small duck (0.25 kg), such as a green-winged teal. Whether the very small particles (<0.1 mm) and sediment concentrations (<0.001  $\mu$ g/g) represent a hazard to waterbirds or aquatic invertebrates is uncertain.

While the majority of WP particles were deposited by the explosion of WP smoke munitions, WP may also be indirectly deposited in the pond sediments by birds that ingest WP in a contaminated area and then fly to uncontaminated areas, where they die and decompose, with resulting WP deposition. Evidence for this mechanism is that:

- WP was found in the tissues of four green-winged teal harvested while flying in ERF and in two ducks found dead 250 m from ERF;
- Some of the uncontaminated ponds where

carcasses are found are too deep for dabbling ducks such as green-wing teal to feed; and

- Samples of tissue from floating duck carcasses in advanced stages of decomposition still contained significant WP levels.

Although poisoned ducks can fly short distances within ERF and just beyond its edge, long-distance transport of WP to other Cook Inlet salt marshes apparently did not occur during the 1991 fall hunting season based on the analysis of 305 gizzards from hunter-harvested ducks.

A large percentage of the waterfowl killed or disabled by WP poisoning are partially or completely eaten by predators (eagles, ravens, gulls) on or outside ERF, resulting in high risks of WP poisoning to predators. The risk is particularly high if the gizzard contents are ingested by the predator. Tissues of a dead eagle and a herring gull egg collected from ERF tested positive for WP. Since neither eagles nor gulls feed in the sediments and both feed on duck carcasses, we conclude that WP can be transferred from one trophic level to another via predation. WP deposits in fat-containing tissues in a way similar to DDT and other well-known food chain contaminants.

Previous to our work at ERF, WP was thought to be non-persistent in the environment because it is thermodynamically unstable in the presence of oxygen. However, the wet fine-grained clays and silts of ERF, even on non-flooded mudflats, remain sufficiently wet and anaerobic to prevent oxidation and sustain storage of WP particles. Most documented cases of WP environmental contamination and toxicity to biota involve colloidal forms (small particles suspended in water) of WP generated in the manufacturing of WP and WP munitions. Existing remediation techniques are therefore not easily applied to the WP contamination in ERF sediments. Future work will focus on identifying potential remediation techniques for treating WP-contaminated sediments. Whatever remediation techniques are used, it will be important to monitor and measure relative changes in mortality rates using methods developed here.

The major conclusions of this report are:

- Reliable analytical methods (solvent amounts, extraction times and subsample size) were developed to extract WP particulates from ERF sediment samples. In the field one 20-cm<sup>3</sup> extracted subsample

from each 500-cm<sup>3</sup> jar containing the sediment sample provided a reliable determination of the presence or absence of WP but was less reliable in representing the actual concentration of WP in the total 500-cm<sup>3</sup> sample.

- Procedures for processing waterfowl tissue samples were developed. WP was found in highest concentrations in the fatty tissues.
- Over 360 pond-bottom surface sediment samples were collected at 25-m intervals along transects in the six waterfowl feeding ponds in ERF (representing less than 5% of the area of ERF). The bottom sediments of two of the sampled waterfowl feeding ponds contained a high percentage of WP-positive samples. In addition the WP concentrations of samples from one of these ponds (Bread Truck Pond) were significantly higher than those from the other ponds. Area C and the Bread Truck ponds are hypothesized to be the major sources of WP poisoning in ERF.
- The bottom sediments of the two contaminated ponds in ERF likely contain a large number of very small WP particles (<80 μm) and a small number of much larger particles (1 mm). The larger particles could provide a lethal dose (around 0.25 mg) for a small duck such as a green-winged teal.
- The very small WP particles in the sediments can become suspended in the water column and could provide another source of exposure to waterbirds, fish or plankton.
- Following ingestion of WP particles, waterfowl are capable of flying to other feeding pond areas in ERF. Four green-wing teal out of 13 flying ducks harvested in ERF at the end of August contained WP.
- WP may be transported and redeposited in sediments from the decay of poisoned ducks.
- A method to monitor waterfowl mortality in permanent transects was tested and should be used to establish a baseline mortality index for evaluating the success of future remediation efforts. Observations of dying ducks and predation on them led to the discovery of the Bread Truck Pond as a major source of WP poisoning. Annual waterfowl mortality in ERF probably ex-

ceeds 2000 waterfowl and involves shorebirds as well as ducks and swans.

- Predators in ERF, such as eagles, ravens and gulls, are ingesting WP-contaminated duck tissues and are likely at risk. The tissues of a dead eagle and a gull egg contained WP.
- Human health risks through consumption of ducks shot in nearby Cook Inlet marshes were found to be minimal based on the analysis for WP in over 300 hunter-harvested duck gizzards collected in September 1991.
- WP is stable in wet ERF sediments and may persist indefinitely.

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