Progress Report 4th Quarter 1993
Prepared for Directorate of Public Works
U.S. Army Garrison, Alaska
by USACRREL

Between May and September 1993, CRREL, USDA, AEHA and USFWS conducted laboratory and field studies related to the contamination of ERF by white phosphorus. Under a request from 6th ID, Ft. Richardson Dept. of Public Works, we have obtained brief progress reports from each agency and organized them into the following brief report.

I. DATA MANAGEMENT - COORDINATION
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2. Analytical Support (M. Walsh)
3. Salt Marsh Ecosystem Dynamics

II. WHITE PHOSPHORUS EVALUATION/CHARACTERIZATION
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5. Plants/Vegetation (1st Year) (M. Walsh, C. Racine)

VI. TREATABILITY STUDIES (Separate Report?)
1. Repellents/hazing, etc. (3rd Year) (J. Cummings, L. Clark, P. O'Neal)
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3. Cover/Capping Geotextiles (2nd Year) (C. Collins, K. Henry, C. Racine)
4. Cover/Capping Bentonite product (1st Year) (P. Pochop, J. Cummings,)
5. Pond Drainage (1st Year) (C. Collins)

I. DATA MANAGEMENT/COORDINATION

1. Data Management: CRREL (Racine and Collins)

CRREL serves as a clearing house and repository of all information collected in ERF by CRREL and other contractor agencies, maintaining a data base and a Geographic Information System of all sampling and work done in ERF.

All locations sampled for WP contamination are surveyed in and UTM locations, concentrations are entered into a data base. Locations sampled by AEHA and USGS-Patuxent were also partially surveyed in. Other sites were located by using a differential GPS unit. Some information on site locations for these two agencies still needs to be obtained from them. A new set of aerial photos of ERF were obtained on July 7, 1993 during a period of particularly low pond water levels. Large color infra-red enlargements of these photos were obtained from Aeromap and facilitated field work during the summer. Prior to flight to obtain the photos, a series of photo panel points were surveyed in. These were then used to photogrammetrically correct the aerial photographs into orthophotos. These orthophotos are being used to directly digitized terrain features in ERF into the Geographic Information System. The CIR's allow interpretation of vegetation and water patterns within ERF. Maps are being produced of sites sampled this year and additional environmental information obtained in the field and interpreted from the aerial photography.

2. Support for DWRC and AEHA CRREL (Walsh)

In May, 30 sediment samples were analyzed for white phosphorus in support of DWRC's pen experiments. In July, AEHA collected 25 sediment, 44 water and 15 fish samples in conjunction with the Ecological Risk Assessment. These samples were shipped to CRREL and analyzed for white phosphorus residues. AEHA conducted a bioassay and in support of this bioassay, 27 sediment samples and 42 water samples were analyzed at CRREL for white phosphorus residues.

3. ERF Ecosytem Components, Processes-Dynamics (ALL)

Over the past four years, while conducting field work in Eagle River Flats, we have gained insight into the biological (animal and plant species), chemical and physical characteristics of this ecosystem. Because Eagle River Flats is an estuarine salt marsh, physical, chemical and biological processes are extremely variable and change rapidly over daily and seaonal time scales. At Eagle River Flats both extreme variations in coastal tides (11 m+) and river flow rates (glacial melt) influence and control these processes. An understanding of the baseline composition, structure and function of this 865 ha ecosystem is crucial to predicting and monitoring the impacts of future remedial actions. We have all been accumulating information over the past four years on how this system operates and changes in terms of flooding, sedimentation, habitat and vegetation processes. Actions such as dredging, draining or filling of ponds or other contaminated areas could have unforseen or undesirable effects on the entire salt marsh and its viability as a wildlife habitat. We have therefore employed a network of several monitoring devices and sampling sites to understand these dynamic processes.

II. WHITE PHOSPHORUS DISTRIBUTION IN EAGLE RIVER FLATS

1. <u>Distribution of WP in ERF-CRREL</u> (Racine, Walsh and Collins)

During 1993, we developed new field sampling and detection methods for WP involving screening composited or single sediment samples through a standard Wildco 30 mesh (0.59 mm) bucket sieve. In addition rapid field screening of sediment samples was tested using a 'smear' of the sediment sample on a pie plate which was then heated and dried over a camp propane stove. WP particles burned or appeared as black specks in the gray dried sediment on these pans.

A new pond-bulrush marsh area, not previously sampled or recognized as a waterfowl use area was also visited for the first time and found to contain high levels of WP. The area is located on a helicopter-accessable island formed by two branches of Eagle River which divide immediately after entering the Flats and then rejoin a short distance downstream. An old truck target and craters are located on this island. In June four out of twelve sediment samples collected here tested positive for WP, with one sample containing over 3000 µg/g, (higher than any sediment sample ever collected in ERF). An additional 12 samples were collected in August with eight of these testing positive for WP. In additon over 40 waterfowl carcasses were counted in this area during two days in August.

In August additional sediment samples were collected in several Area A ponds both north and west of A-Tower to try again to locate contaminated areas responsible for sick and dead waterfowl observed in that area. None out of 17 samples tested positive for WP in several ponds north of the tower. However, two out of five samples collected in a pond west of the tower tested positive.

Three small wet areas with targets and craters located near Eagle River east and south of Area A were sampled during August. These had very small localized semipermanent to permanent standing water areas near targets that had numerous craters around them. Only one sample out of four or five samples at two of these sites tested positive with none out of eight testing positive at the third target area. . There are still a number of such small wet areas within ERF that have not yet been tested for WP.

Twenty sediment samples were collected at various locations within the gully systems draining the ponds in Area C and the Bread Truck pond. These were collected from pools and depressions within the gullies where sediment washed from the ponds may have collected. None of the samples tested positive for WP.

2. Analysis of Water and Plant Tissue for White Phosphorus CRREL, (Walsh, Racine)

In June, several water samples were collected and analyzed for white phosphorus. White phosphorus was found above 0.2 μg/L (the method detection limit) only in those samples collected from highly contaminated confined areas (i.e., Site 110 (the smoke hole) and Miller's hole) and in the water column above contaminated pond sites after the sediment was disturbed. Several salt marsh plants were collected and analyzed for white phosphorus. Like the water samples, white phosphorus was found only in plants collected from highly contaminated sites (smoke hole, Miller's hole).

3. Contaminant Evaluation and Screening AEHA (Bouwkamp)

Sediment and water samples were collected from ponds, distributaries and Eagle River. These samples were analyzed for WP, explosives, nutrients, target analytes, and target compounds. In addition, the water was field tested for temperature, dissolved oxygen, pH, oxygen-reduction potential, conductivity, and salinity. The results are back from the laboratories except for explosives in the sediment, ammonia in water, total nitrogen and sulfates in sediment, and the final report from the sediment toxicity study.

Distributaries. (drainage gullies connecting the ponded areas to the river). Since the massive diluting capacity of the Eagle River made detection of any contaminants unlikely the distributaries were sampled before entering the Eagle River to determine if possible contaminants were detectable before dilution. Water and sediment samples were collected from distributaries that drain ponded areas known to be contaminated with WP. The water was sampled during the low tide following the first ERF inundating high tide that occurred 21 July. This tide flooded only portions of ERF. Therefore, water samples were only collected from four distributaries that were receiving drainage from the ponded areas that fully flooded. Sediment and invertebrates had already been collected from six distributaries. A seventh distributary was added on 21 July when the WP contaminated ponded area on Racine Island completely flooded and the flooding of the Bread Truck Area and Area C was not enough to discharge during the low tide. Distributary samples were analyzed for the same parameters as the ponded areas. Fish were not collected from the distributaries.

Eagle River. There were two sample sites on the Eagle River, one above the one below ERF. Water and sediment was collected from both locations as well as collecting a duplicate below ERF. They were analyzed for the same parameters as the ponded areas and distributaries. No fish or invertebrates were collected from the Eagle River because of the difference in habitat types and enormous flow rate.

Field Measurements. The dissolved oxygen was generally high except for Racine Island and one sample in Area CD. Salinity/conductivity ranged from fresh water to 150 percent that of sea water. Temperature ranged from 7.7° C in Eagle River to 30.9° C in the Bread Truck Area. The pH was generally above 7 but ranged from 6.6 to 9.2 standard pH units. The oxygen reduction potential ranged from -118 to 147 in the water and -406 to 114 in the sediment samples.

White Phosphorus. White phosphorus was detected in six of the water and sediment samples. The WP concentration ranged from 0.0143 - 1,740 mg/kg in the sediments. The total WP concentration ranged from 0.013 - 0.069 mg/L in the water. The dissolved WP concentration ranged from 0.005 - 0.048 mg/L in the water. There was no WP detected in any of the fish samples from the ponded areas even though it was detected in six of the corresponding water and sediment samples.

Nonmetal Inorganic Compounds. Complete analysis of the data will be done in the draft report when all of the data is back from the laboratory. Preliminary analysis of the data indicates that there is nothing that would need to be discussed at this time.

Metals. The metals data just arrived from the laboratory on 21 October. Complete analysis of the data will be done in the draft report. Preliminary analysis of the data indicates that there is nothing outstanding enough to require discussion here.

Volatile, and Base/Neutral/Acid Extractable Organic Compounds. Except for two low level detections of bis (2-ethylhexyl) phthalate and one methylene chloride there were no volatile, base/neutral or acid extractable organic compounds detected in any of the water or sediment samples. Both compounds are often laboratory contaminants. Therefore, their detection may be questionable.

Pesticides/PCB's and Herbicides. There were no pesticides or herbicides detected in any of the water or sediment samples.

Explosives. No compounds of explosives were detected in any of the water samples. The sediment analysis is incomplete at this time.

III. WHITE PHOSPHORUS TRANSPORT/BURIAL

Studies of Physical Processes: Sedimentation, Erosion and WP Transport CRREL (Lawson, Bigl, Bodette, and Weyrick)

Beginning in late May 1993, studies of the physical processes active in Eagle River Flats were continued. Sedimentation and erosion rates were measured at points along perpendicular transects through the site using techniques established in 1992. Sedimentation stakes and paint layers on the mudflats, and sedimentation stations in ponds with flat plate and cup samplers, provided measurements of primary and secondary sedimentation rates. The rate at which gully headwalls and lateral walls are receding during high tidal cycles was measured relative to fixed points established in 1992 on adjacent stable locations. Measurements in late May provided data on winter rates (since 1 October 1992) and subsequent measurements in June, August and September provided data on this summer's activity.

Discharge characteristics including suspended sediment concentrations during the August and September flood and ebb cycles were analyzed in two gullies; one draining "C" pond and one draining Bread Truck pond. CTD's with Campbell data loggers in small pools within the gullies measured a suite of parameters related to WP and sediment transport: temperature, pH, salinity, dissolved oxygen, redox, water depth, and turbidity. During August and September flooding events, an ISCO suction sampler collected water specimens for analysis of suspended sediment concentration and WP content. Because sampling of WP suspended in distributary drainage water had not been attempted previously, a variety of sample volumes, timing, and positions of withdraw were used in each gully. Bedload sediments deposited in gullies after the high September tides and flooding events were also sampled to determine if WP is in transport in this mode.

A wave and tide gauge recorder positioned offshore at Knik Arm monitored the tide heights during the August and September tidal cycles. These data will be correlated with more water depths measurements to define timing and height of inundation on the flats relative to tides in the Arm. Temperature, salinity, and turbidity were also monitored at this location during the September tidal cycle. Suspended sediment concentrations measured in Knik Arm will be correlated with measured concentrations in Eagle River and the gullies to define sediment sources. The incoming discharge from the Eagle River was characterized using a CTD and Campbell data logger positioned just downstream of Route Bravo bridge. An ISCO suction sampler collected water for analyzing the suspended sediment concentrations during part of the September high tide events. It should be noted that the primary process studies were delayed until the August flooding cycle because of the late arrival of funding.

IV. WP EVALUATION/CHARACTERIZATION

CHEMISTRY

1. Literature Review CRREL (Walsh)

Over the last three years, we have collected literature describing the physical and chemical properties of white phosphorus. This literature was reviewed for factors that influence the persistence of white phosphorus in the environment. While a summary will be included in the draft report, the conclusions based on the literature is that solid white phosphorus introduced into the environment must either dissolve in water or vaporize in air in order to react with oxygen. Any factor that slows these processes will limit the rate at which white phosphorus oxidizes.

TOXICOLOGY

1. Acute Toxicity Investigation Patuxent Wildlife Research Center (D. Sparling)

We conducted an acute toxicity study of WP on mallards during July, 1993. Adult mallards were obtained from a game farm and housed at the Center for several months before testing. Most birds were in late stages of molting. Birds were individually housed in 1-m2 pens provisioned with a water pan for drinking and bathing, and fed commercial pelletized food ad lib until dosing. The night before dosing each test bird was taken off of food. WP was dissolved in corn oil (0.5 g in 250 ml with final concentration verified by gas chromatography) and administered via gavage and prescribed doses based on individual body weight. Doses were at 2, 4.1, 5.3, 6.1, 7.1, 8.0 and 9.1 mg/kg body weight. Most birds received 3 ml solution/kg body weight but those at the highest dose and two controls received 4.5 ml solution /kg body weight. From 3 to 5 birds of each sex were tested at each dosage level (see below). Birds were observed every hour for the first 7 hours past dose, every 2-3 hours on the subsequent day, and every 4 hours thereafter for signs of intoxication. Upon death or at euthanasia at 1 week following dose, each bird was examined for pathological signs including overt necroses, lesions, and weight loss; several of these necropsies were conducted by a wildlife veterinarian. Livers (flash frozen for enzyme analyses, formalin for histopathology, and isooctane for WP), kidneys (flash frozen and formalin), brains (cholinesterase activity), skin (WP), fat (WP), heart (formalin), and blood (whole blood for WP, hematocrit and hemoglobin; and plasma for enzyme analysis) samples were collected as feasible. Work-up on these samples will occur during the next several weeks or months.

The number of birds dying at each dose is listed in Table 1. The 24-hour median lethal dose for males is 6.5 mg/kg body weight (95% confidence interval 5.3 - 7.8 mg/kg) and is statistically valid. Even at the highest dosage less than 50% of the females succumbed to the treatment within 24 hours. A rough estimate of the median lethal dose in females is 15-20 mg/kg. Females had recently passed breeding condition at the time of dosing and were appreciably thinner with less abdominal or subcutaneous fat than males. We suspect that either body condition or interaction between hormones and WP metabolism may have resulted in the observed difference in sensitivity between the sexes. Additional studies are warranted in FY94 to further elucidate the differences between males and females.

Table 1. Response of mallards to dosing with white phosphorus.

	Number of birds dying/tested	
Dosage (mg/kg)	Males	Females
2.0	0/5	0/5
4.1	0/5	1/5
5.3	1/4	0/3
6.1	1/4	0/3
7.1	3/4	1/4
8.0	4/4	1/3
9.1	3/4	1/4

Overt signs of toxicity included lethargy, overall trembling which was especially pronounced in the legs, intense drinking, and eventually sporadic bouts of convulsions ending in death. Upon necropsy, birds occasionally showed necroses of the liver and small, multiple foci in various internal organs including pancreas, heart, and gizzard lining. The duration from dosing to death varied from 3 hours to more than 36. Some birds showed no signs of toxicity for several hours and then died an hour to two after the last check. We suggest that many intoxicated birds could leave ERF after being exposed to a lethal dose of WP only to die somewhere else. Analysis of brain cholinesterase levels revealed a dose-response relationship in cholinesterase depression in adult males (but not females). Maximum depression was approximately 30%, which is insufficient for lethality but may be useful as an indicator of exposure at ERF.

In October we dosed 14 male and 14 female juvenile mallards with 6.5 mg/kg WP to compare their sensitivity to adult males. Five of the males and 9 of the females died within 24 hours; there was no statistical difference in sensitivity between the two sexes of juvenile birds or between either group of juvenile and adult males. If you combine the mortality observed in the juvenile birds, exactly 50% died at the adult male LD50.

We are currently conducting a study on lowest effects levels of WP by giving juvenile mallards with a single dose of WP at the putative LD 1 (3.7 mg/kg) and LD0.01 (2.6 mg/kg). Birds will be weighed periodically and maintained for three weeks and then euthanized to determine if any physiological effects have occurred. Next week we will start a repeated dose study in which male and female juvenile mallards will be given 4 doses of WP at the LD30, LD20, LD10, and LD1 levels over a 4 day period.

<u>2. The Role of Phosphine in White Phosphorus Toxicity</u> Dartmouth Medical School (Bill Roebuck, S.I. Nam)

White Phosphorus has been implicated in thousands of waterfowl deaths in Eagle River Flats, Anchorage, Alaska. Lethality, however, could not be correlated with the level of P_4 found in the gizzard, nor in the fatty tissues of these ducks. It has been hypothesized that the toxicity of WP may be due to its metabolite(s) rather than the parent compound. In vitro studies were undertaken to determine if phosphine (PH_3), a toxic gas, was generated from WP by various rat tissues. Liver and small intestine tissues and cecum contents of the gastrointestinal tract of the F344 rat were used. Tissue homogenates were made with 0.3M Tris (pH 7.4) and placed in 40 ml vials. One set of samples was boiled for 10 minutes to denature enzymes and microbes. Samples were incubated in 37°C water bath prior to and subsequent to the addition of WP (1 mg). Phosphine was determined and quantified by GC at times up to 2 hours after WP exposure. By 2 hours, all samples produced phosphine close to toxic concentrations (3-65 ppm). PH_3 concentrations in boiled and non-boiled samples were similar, thus indicating that the formation of PH_3 from WP may be a non-enzymatic reaction. Furthermore, the toxicity of WP-exposed waterfowl may be due to PH_3 rather than WP.

V. RISK ASSESSMENT/FOOD CHAIN EFFECTS

1. Waterfowl Mortality NEILE (L. Reitsma)

A literature review was conducted on methods of measuring and estimating waterfowl die-offs. In addition, we consulted with a biometrician in order to design the best approach to measuring mortality at ERF. Waterfowl use was determined in order to adjust mortality rates in relation to the use. During the 1993 spring staging , the number of waterfowl feeding in the main pools was about 25% the number in May 1992 (actual numbers included in 1993 report). Use was estimated by Cole Point censuses at 0700 each morning, and from USFWS aerial censuses. Both methods indicate a reduction in the use of Eagle River Flats during spring staging. The low use, however, was comparable to the USFWS aerial censuses for the 1991 spring staging period. During fall staging from 15-30 August, the waterfowl use of ERF, particularly in Areas A, C, and the the Bread Truck Pond, was lower than in August 1992. The low numbers of waterfowl in Areas A, C. and the Bread Truck Pond continued throughout all of September. The continued low use of the areas with known contamination of WP is at least partly due to the hazing operation, which appeared to be effective at preventing use. We will soon complete our observations of waterfowl use when we are certain that fall staging is over. All census data will be compiled and compared to previous years.

During the spring migration, two separate measures of mortality were developed on the flats and in the bordering woods. These both indicate lower mortality in spring of 1993 than in 1992. However, due to the lower use in 1993 mentioned above preliminary analyses indicate that the mortality in spring 1993 was proportionally similar to the mortality in 1992. The surrounding woods was more extensively surveyed than in 1992 with a total of 30 transects randomly located around the entire perimeter of ERF. As predicted, the highest number of feather piles were found in the woods east of Areas C and CD.

One interesting finding pertains to bald eagle mortality. The number of eagles preying upon sick ducks was lower this spring than in 1992, most likely due to the lower number of ducks using ERF. However, we found evidence of at least three and possibly four eagle carcasses in the spring. Eagle feather piles were found in three widely separated locations in the bordering woods. Considering that our transects cover less than 1% of the bordering woods, the concern over eagle mortality bears further investigation.

The 1993 report will include ANCOVAs (analyses of covariance) of spring and fall waterfowl mortality using census data to calibrate death with use. We will also provide a compilation of USFWS aerial census data to illustrate annual fluctuations in the number and arrival schedule of waterfowl at ERF.

2. Waterfowl distribution and movements in Eagle River Flats Denver Wildlife Research Center (John Cummings)

We determined daily and seasonal movements, population turnover and site-specific exposure of waterfowl during fall migration, August and September 1993, at Eagle River Flats.

Seventy ducks of 5 species were captured mainly in areas C, C/D and Bread Truck with mist nets and swim-in traps. Of those, radio transmitters were attached to 12 mallards, 11 pintails, and 11 green-winged teals. Tracking data indicates that during August (pre-hazing) telemetry species ranged over the entire Flats. Mallards tended to concentrate in area A and B, Racine Island and the C/D transition area. Pintails used Area C and Bread Truck. Green-winged teal used the C/D transition area and shallow pools in Areas A and C. Post-hazing, most waterfowl concentrated in Area B and the C/D transition area. Preliminary data suggests that there was a 50% turnover of waterfowl species using the Flats during August and September. In addition, five telemetry ducks were found dead of ERF: Racine Island (1), Area A (2), Area C (1) and the C/D transition area (1).

3. Secondary hazards of white phosphorus to bald eagles. Denver Wildlife Res. Center (J. Cummings)

The objective of this study is to determine secondary hazards of waterfowl poisoned by WP pose to bald eagles on ERF. This study will be conducted April/May 1994.

4. WP Effects on Fish, Birds and Invertebrates Patuxent (D. Sparling)

To date, we have collected the following species and numbers from ERF. WP residues from all samples will be processed in the fall 1993. Residue analyses histopathology and physiological effects will be assessed over the next several weeks to months:

a. Sticklebacks - 27 samples including two species, three-spined sticklebacks (Gasterosteus aculeatus L), and nine-spined sticklebacks (Pungititus pungitius L).

b. Invertebrates - 19 samples, including odonates, snails, beetles and chironomids. Taxa included: Odonates (dragonflies and damselflies - Aeshna sp., Enallagma sp., Anomalagrion sp., Libellula sp., Dipterans (flies) - Chironomidae, Brachycera sp., Cyclorrhapha sp., Ephydra sp.; Coleopterans (beetles) - Agabus sp., Hydroporus sp.; Gastropods (snails) - Fossaria; and Amphipods - Gammarus sp..

c. Birds from ERF. Tissues collected from each bird sampled included liver (flash frozen and preserved in formalin), kidney (formalin), skin (preserved in isooctane for WP determination), and brain (frozen for cholinesterase determinations).

Dowitchers (Limnodramus sp.) - 9
Red-necked phalaropes (Phalaropus lobatus) - 9
Greater yellowlegs (Totanus melanoleucus) - 5
Lesser yellowlegs (Totanus flavipes) - 5
Arctic tern (Sternus paradisaea) - 11
Mew gull (Larus canus) - 16
Bonaparte's gull (Larus philadelphia) - 1
Pintail (Anas acuta) - 3, found dead
Blue-winged teal (Anas discors) - 1 found in convulsions
Green-winged teal (Anas carolinensis) - 13 found dead
Mallards (Anas platyrhynchos) - 14 found dead

d. Birds from Susitna Flats. This area was used as a reference or "clean" site, 3 each of long-billed dowitchers, red-necked phalaropes, lesser yellowlegs, arctic terns, and mew gulls were collected.

e. Clutches from ERF. For each clutch, one egg was processed for WP determinations by taking 10 ml of yolk (5 ml for Arctic terns) and combining it with an equal volume of isooctane. The remainder of each clutch was incubated and pipped embryos were euthanized and preserved in formalin to determine if any developmental defects occurred. White phosphorus determinations and examination of the embryos will be conducted in fall.

Mew gulls - 12
Arctic tern - 2
Herring gull (Larus argentatus) - 1

5. Macroinvertebrate Samples from ERF AEHA (C. Bouwkamp)

The extended period between inundating tides (7 or 8 May until 21 July 1993) concentrated many of the possible contaminants to a yearly maximum and subjected invertebrates to extreme natural stress. The combination would show the maximum chemical and biological effect. Water, sediment, macroinvertebrates, and fish were collected from 10 locations in ponded areas in ERF, one duplicate, and two reference locations in Goose Bay just before the 21 July inundating high tide. The invertebrates were analyzed for community structure to see if WP or other contaminants were having an adverse effect. The fish were analyzed to see if they were bioaccumulating WP.

The macroinvertebrates were so stressed by the high salinity and low water that six species were the maximum found at any of the sample sites. This happened to be a reference site from Goose Bay. However, the sample site with the highest sediment concentration of WP had five species. Correlation coefficients will be calculated for WP, salinity, and a few other parameters with the macroinvertebrate diversity and taxa richness in the draft report. Preliminary analysis indicates salinity will have a higher coefficient than WP. However, the sample variability will likely make any difference statistically insignificant.

6. WP Sediment Toxicity Study (Sediment Bioassays) AEHA (C. Bouwkamp)

Since the benthic macroinvertebrate diversity in ERF was low, it became apparent that a change in community structure would not statistically determine a concentration of WP or other contaminants that showed an adverse biological effect. A sediment toxicity study was conducted to determine a no effect level for WP on the amphopod Hyallela azteca (1st test) and the midge larva Chironomus riparius (2nd test). A bulk sediment sample was collected from Racine Island and mixed with uncontaminated sediment to make 20, 40, 60 and 80% dilutions.

All the organisms in both bioassay tests died in all sediment concentrations with 20 percent WP contaminated sediment being the lowest concentration in the test. The sediment concentration in the 20 percent sediment dilution averaged 194.5 mg/kg. The water concentrations in the 20 percent dilution chambers were 23.7 µg/L total and 14.7 µg/L dissolved WP at the start and 2.54 µg/L total and 1.32 dissolved WP at the end of the 30 day test. These water concentrations were far in excess of field samples collected over undisturbed sediment with higher WP levels. This proves that the toxicity test does a poor job of mimicking what happens in the field. The toxicity study needs to be redone at lower WP concentrations to get a no effect level. But since organisms are obviously living over sediments in ERF with higher concentrations than those found to be toxic in the toxicity test, it becomes obvious that the level of WP in the sediments that effect the natural aquatic organisms cannot be answered in this laboratory test.

The remaining data should be completed with sufficient time to complete the draft report by the 6 December task force meeting. Preliminary analysis of the data indicate that WP is the only bad player identified in the aquatic system. Unfortunately, just what concentration of WP causes an adverse effect on the aquatic biota at ERF is unlikely to be fully answered by the macroinvertebrate data or sediment toxicity data. Extrapolating from laboratory or literature numbers to the real world has its limitations.

VI. TREATABILITY STUDIES

1. Landfarming and Thermal Treatment CRREL (Walsh)

Laboratory

During FY92, a laboratory experiment was conducted to determine the effect of air-drying on WP concentration in sediments collected from some of the most highly contaminated sites we had located in ERF. Moisture loss from these sediments resulted in loss of 99% of the WP after two weeks of air-drying at 20°C.

During FY93 additional laboratory drying experiments were conducted in which contaminated sediment from site 240 (Area C) was dried at elevated temperature for up to 10 days. Two temperatures were tested, 40°C and 100°C. WP concentrations decreased significantly at both temperatures.

An additional laboratory experiment was conducted in which contaminated sediment from site 240 was air-dried in an inert atmosphere (i.e., under nitrogen). This experiment was designed to test the hypothesis that oxygen is not necessary for loss of WP from contaminated sediments. Rather the loss may be a physical process where the solid particles sublime to form a vapor which then may diffuse to the atmosphere. After 60 days at 20°C, white phosphorus concentrations in the sediments dried under nitrogen were slightly less than those under air, and greater than 99% less than the initial concentration.

Field Tests

Based on the FY92 laboratory results, a field experiment was conducted starting in June 1993 in which contaminated sediment was excavated from a contaminated site near Canoe Point (Sample point 53 and 222) and placed on land on top of geotextile fabric. Six 1-m diameter test plots were made. A small greenhouse was placed over two of the plots to elevate sediment temperatures and to protect the plots from rain. Plots varied in thickness from 10 cm to 20 cm, and one of the plots was tilled periodically. Initial white phosphorus concentrations varied over several orders of magnitude (0.0089 to 2800 µg/g); the plot with the highest concentration was tilled and actually "smoked" when a shovel was used to turn over the drying sediment. The sediments in each plot was sampled after 28 days of air-drying, and WP was undetectable in five of the plots. The concentration in the sixth plot (the one that smoked) was reduced to 0.003 µg/g. During the August field study, the plots were intensively sub-sampled. Out of thirty samples taken, WP was undetectable in twenty-seven subsamples and just above the detection limit in three samples.

In August, a larger landfarm treatment test plot was set up to more closely replicate actual conditions that may occur with placement of dredge material on the EOD pad. This treatment plot consisted of a 2 m diameter walled cell with 35 cm of WP-contaminated sediment from Site 240. The test cell was instrumented with a tensiometer and piezometers to monitor in situ soil moisture. Samples were taken periodically for soil moisture and WP contamination determinations. The plot will be monitored through freeze-up and again next spring to determine rates of drying and loss of WP.

2. Cover/Capping with Geotextiles CRREL (Collins and Henry)

Geotextile test sections set out in August 1992 were evaluated in June 1993. The test sections in a low energy environment (Area B) were all still in place. Conversely the test sections set out in a high energy environment (near the coast, west of Area D) were all disturbed and moved by tidal action. The test sections in Area B all had sediment deposited on top of the fabric and aquatic vegetation rooted and growing in the sediment.

The optimal use of geotextile fabric as a barrier may require an anchoring layer of sediment or gravel applied on top of the geotextile during installation. The optimum time frame for placing such a cap or cover of material on a contaminated area still appears to be the early spring prior to breakup of the ice cover. The lateness of the start of the program this year precluded any attempt to further evaluate this procedure.

3. Response to waterfowl to Concover® and Bara-kade® USDA (Patty Pochop and John Cummings)

We evaluated the efficacy of two materials on contaminated sediments to provide a physical barrier to foraging waterfowl. One material was Concover®, a blend of recycled paper (99%) and cellulosic polymers (1%) and the other was Bara-kade®, a blend of calcium bentonite/organo clays, gravel adn polymers. Laboratory trials were conducted on both materials to determine if either product could be used in the field trials. Visual inspections indicated that Concover®, when applied to moist sediment and covered with 10 cm of water, separated from the sediment and began floating within 1/2 hour. Further, the Concover® was readily torn-up by mallard activity. In contrast, daily inspections of the Bara-kade® indicated the material appeard to maintain its structure under use by mallards.

From June 14-30, 1993, we evaluated the effectiveness of Bara-kade® to reduce mallard mortality on Eagle River Flats (ERF). Prior to the application of Bara-kade®, six mallards were placed in each of two test pens for eight days to establish a mortality baseline for each pen. Mortality was 50% and 100%, respectively. Following this period, one pen was covered with 907 kg of Bara-kade® material while the other remained as a control. Over a six day period, all mallards died in the control pen and none in the Bara-kade® pen.

4. Pond Draining CRREL (Collins)

A survey of the distributary channels and gullies on the east side of Eagle River was done in June. Detailed elevation measurements of the thalweg (the bottom elevations of the channel) were made to determine the controlling elevations for tidal flooding into the ponds. Channels leading to C Pond, the Bread Truck Pond, and the Pond Beyond were surveyed. This information will be used to evaluate the feasibility of pond draining as a treatability measure for WP-contaminated pond sediments.

Tensiometers and piezometers were installed in the shallow pond edge west of the C Tower. Information from these instruments, as well as from soil moisture samples collected in the same area, were used to determine the degree of soil drying that occurred during the extended dry spell from June to mid-July. This information is analogous to conditions that would exist if a pond was drained as a treatment for WP. The intent is to determine if bottom sediments would dry out sufficiently for WP to dissipate after a pond was drained. Even after draining, there is only a four to six week window in June and early July where a drained pond bottom would be continuously subaerially exposed. After that time frame, periodic high tides in conjunction with high river stage levels would inundate the drained pond on a regular basis, rewetting the sediment, and preventing any addition drying and further dissipation of the WP contamination.

Soil moistures below 35% by dry weight were measured in the upper 10 cm of the exposed pond sediments west of the C tower in early July. Moisture levels between 35 and 40% were noted down to 30 cm. These moisture levels may be low enough for at least some WP contamination to disappear. This in fact does appear to happen at the nearby "Miller's hole" where WP concentrations in the raised crater rim have gone from 997 µg/g in May 1992 to 0.017 µg/g in June 1993 and .0018 in August 1993. The center of the crater, which is inundated longer than the rim has gone from 5000 to 81 µg/g.

This year was warmer and drier than average. In June, the temperature was +1.9°F above average and the precipitation was 0.07" below average. In July the averages were +2.8°F above normal and 1.03" below normal. It is unclear if drained pond sediments would dry sufficiently in a wetter summer to significantly reduce WP concentration. This question may require a full scale test draining of a pond to answer.

A series of test cells was planned to be put out in June to help isolated the drying bottom sediments from high tides in July. These were not installed because of the lateness of obtaining funding and the subsequent late delivery of material. A couple of test cells were installed in August, but not under optimum conditions. Despite this, they proved useful in isolating localized area of pond sediment. The material will be used next year for addition tests.

5. <u>Waterfowl Repellants</u> USDA (John Cummings and Larry Clark)

In 1993, we continued to evaluate new bead formulations of methyl anthranilate in the laboratory and field to determine their effects on waterfowl feeding behavior. Modification in the wall characteristics, chemical concentration and size of beads were made to improve the overall repellency to waterfowl. In the laboratory, experiments designed to test the diffusion rate of MA through the bead wall showed that new formulations JR930413A and JR930725A retain MA 7 to 20 times longer than formulation JR920817C used during testing in 1992, respectively. The difference in diffusion rates among formulations is attributed to the addition of tannic acid to the bead structure and an improved cross-linking process which reduces the permeability of the bead shell.

We evaluated MA formulation JR930413A in a simulated pond setting to determine its effect on mallard feeding behavior. Equal numbers of male and female mallards were housed individually in eight 2 X 2 X 2 m test pens in an indoor aviary. A circular pool 1 m in diameter and 20 cm deep was installed in each pen so that water height was the same as the floor. The bottom of each pool was covered with 0.5 cm of fine sand. Following a 10 day acclimation period, mallards were tested for 17 days which included a 7 day pretreatment period. During the pretreatment period normal feeding from bottom sediment was noted. Each mallard averaged 135 minutes loafing and/or feeding daily in the pool. Following treatment of the bottom sediment with MA at an application rate of 21.7 kg/ha, use of the pools by mallards decreased significantly to an average of 34 minutes/bird/day. Pool use posttreatment was limited to quick entries and exits with no prolonged time spent in the pool as during the pretreatment period. Overall, there was no significant difference in use of pool by either male or female mallards.

In the field, we evaluated the effectiveness of MA formulations JR930413A and JR930725A to reduce mallard mortality on Eagle River Flats (ERF). Six 7 x 20 m test pens were constructed in Area C of ERF over areas of varying degrees of white phosphorus contamination. At the start of each test, 6 mallards were placed in each pen. An alternative source of food, a mixture of duck chow and grains, was placed in the center of each pen. During the spring (June 14, 1993) 3 pens were randomly selected for treatment with MA formulation JR930413A at an application rate of 21.7 kg/ha. Following the first 8 hours of exposure, duck mortality was greater in untreated pens (3 of 18), than MA treated pens (1 of 18). However, within 24 hours posttreatment, mortality was equal in treated and untreated pens (4 of 18), and did not vary significantly to the conclusion of the test. During the fall (August 6, 1993), a similar test was conducted with MA formulation JR930725A at an application rate of 43.4 kg/ha. After 24, 48 and 72 hours, accumulative mallard mortality in treated and untreated pens was 2, 3 and 6 and 5, 8, and 10 respectively. Similar results were noted at the conclusion of the test, 120 hours posttreatment. Mallards in control pens were 2.6 times more likely to die of WP than ducks from MA treated pens.

A field evaluation of MA formulation JR930725A was initiated following the pen tests. However, duck activity on 8 feeding sites on ERF dropped dramatically after 5 days of pretreatment observations. Further testing is scheduled for a later date.