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Remediation methods for white phosphorus contamination in a coastal salt marsh

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Summary

With the closure of many military bases worldwide and a closer scrutiny of practices on remaining bases, the environmental impact of the military is now an important consideration in the operation of bases. Many previously-unknown environmental problems related to chemicals are surfacing. White phosphorus, a chemical commonly used as an obscurant, is a chemical previously thought to be innocuous after use. In 1990, however, it was linked to the deaths of thousands of waterfowl at the Eagle River Flats impact area on Ft Richardson near Anchorage, Alaska, USA, and shortly after, a series of remedial investigations was initiated. This paper describes three of the remedial methods currently under investigation, namely enhanced in-situ remediation, pond draining through ditching or pumping, and dredging. These three approaches are best applied in different environments, but they can be used together or in conjunction with other strategies. Their impacts on the environment will vary as well.

Experience with these remediation strategies has proven very useful in determining the direction that the clean-up effort at Eagle River Flats (ERF) should take. Dredging, an effective means of removing contaminated sediments for off-site remediation, has been shown to be too slow and expensive at the ERF because unexploded ordnance is present. Enhanced natural remediation is effective under favourable climatological conditions in areas that experience intermittent flooding, but desaturation of the sediments is critical to its effectiveness. Pond draining by blasting a ditch effectively removes waterfowl feeding habitat, but attenuation of the contaminant is inhibited because the ditch increases flooding frequency, and the habitat alteration is permanent. Pond pumping, where feasible, has shown great potential for the desaturating of wide areas of ERF, enabling the natural attenuation mechanism to progress. Further investigation will be necessary to confirm these initial conclusions and determine the overall effectiveness of all three methodologies. Methods developed over the course of this work may be applied to other remediation projects where in-situ volatilization can occur and limited disturbance of wetlands is critical.

Keywords: attenuation, contaminated land, contamination, draining, dredging, Eagle River Flats, military activities, military bases, military impacts, pumping, remediation, wetland functions, wetland values, white phosphorus

Introduction

Salt marshes are valuable ecosystems, serving as habitat for numerous plants and animals, but as with many wetlands, human activities such as filling, draining, and/or chemical contamination, have eliminated or degraded many of them. Efforts to conserve and restore salt marshes are an important part of any land stewardship programme, including those of the military in the post-cold war era. In the USA, the regulatory process guiding the actions for clean-up of contaminated sites is the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) of 1980, also known as Superfund. It was under this guidance that the investigation and alternative remediation methods described in this report were formulated.

The Eagle River Flats (ERF, or the Flats) is an 865-ha subarctic coastal salt marsh located at the mouth of the Eagle River along the edge of the Knik Arm of Cook Inlet (Fig. 1). For over 50 years, this area, located on the US Army's Fort Richardson near Anchorage, Alaska, has been used by the military as an aerial and artillery impact area. The Flats are also heavily used by migrating waterfowl as a staging area. In 1981, US Army biologists discovered numerous waterfowl carcasses during seasonal migration periods. Mortality, however, was confined mostly to dabbling ducks and swans. Extensive ground surveys indicated that very few surface feeding birds or shorebirds were affected (Steele *et al.* 1997). A series of investigations culminated in the discovery in 1990 of the cause of the mortality, namely the ingestion of white phosphorus particles (Racine *et al.* 1992).

Incidents of white phosphorus contamination of the environment have been documented in the past. Idler (1969) and Jangaard (1972) discuss contamination at Long Harbour, Newfoundland, Canada. Dacre and Rosenblatt (1974), in their extensive review of munitions toxicity, mention Muscle Shoals, Alabama, USA. Blumbergs *et al.* (1973) discuss contamination at the Pine Bluff Arsenal in Arkansas, USA. All of these cases involved contaminant release through wastewater. Simmers *et al.* (1995) documented the contamination of a fir-

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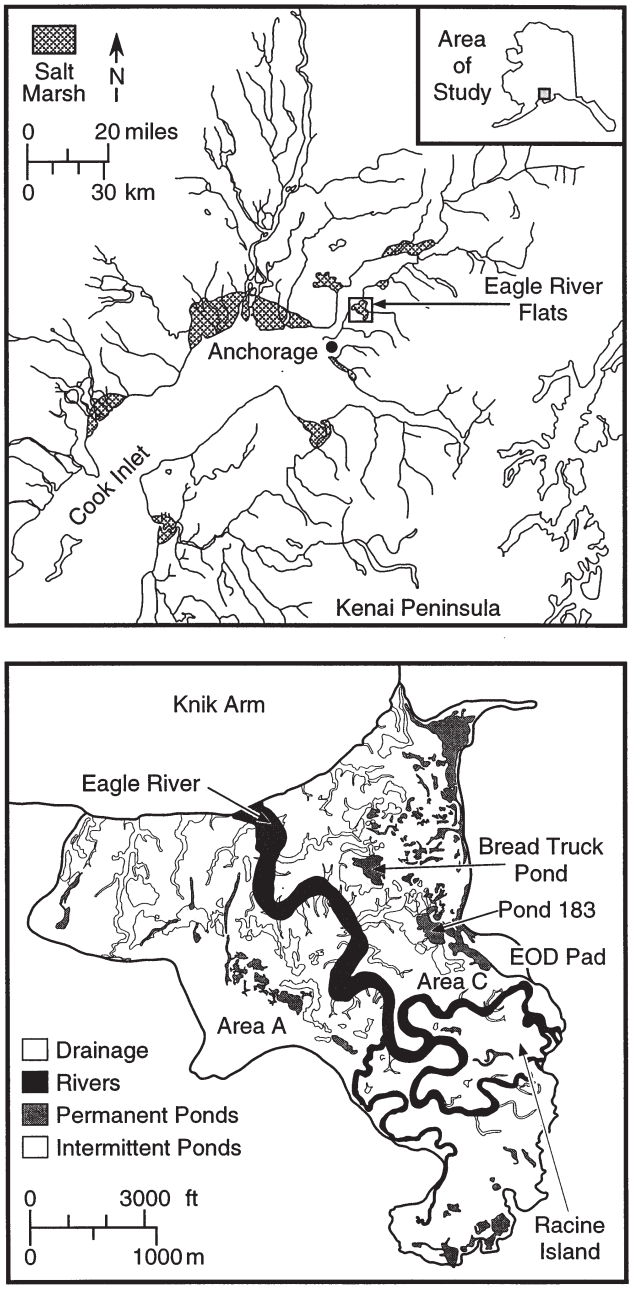


Figure 1 Eagle River Flats, Fort Richardson, Alaska.

ing range at Ft McCoy (Wisconsin, USA), one of nine military sites surveyed that contained residual white phosphorus. The effects of white phosphorus ingestion on waterfowl are documented in Coburn *et al.* (1950).

White phosphorus is not a naturally occurring substance and is highly unstable when exposed to air. The primary deposition mechanism in the ERF was through point-detonating military smoke rounds. Upon contact with water and saturated sediments, burning white phosphorus particles from detonated rounds are extinguished. The low temperatures and saturated sediments of the shallow ponds and associated mudflats are ideal storage environments for white phosphorus, so the embedded particles are highly persistent

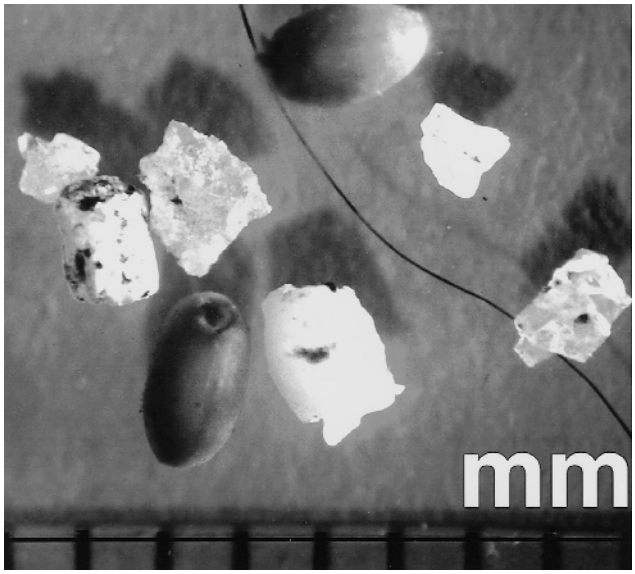


Figure 2 White phosphorus particles and seeds recovered from Eagle River Flats. The similar size and shapes of these items may lead dabbling waterfowl to sieve both from the fine sediments of the Flats when found together.

(M.E. Walsh *et al.* 1996). The particles thus became available to dabbling waterfowl, which, mistaking them for similarly sized and shaped food items (Fig. 2), sieved them from the fine sediments of the ERF (Steele *et al.* 1997). Investigations into the chemistry of white phosphorus (Racine *et al.* 1993*b;* M.E. Walsh 1993), the environmental fate of the contaminant (M.E. Walsh *et al.* 1995*a*), and the toxicological effects of avian ingestion of white phosphorus (Nam *et al.* 1994; Sparling *et al.* 1997) were conducted to determine the impact of the contaminant in this ecosystem and its properties. Food chain implications, especially with respect to raptors, were also investigated (Roebuck *et al.* 1998).

In 1992, work was started on strategies for remediating the white phosphorus contamination problem (Racine *et al.* 1993*a*). In 1993, work on artificial barriers to hinder waterfowl access to the contaminant was conducted to complement continuing studies of the mechanisms of natural attenuation (Henry 1994; Pochop *et al.* 1994). In 1994, further work on access barriers was conducted, and remediation through removal and treatment was begun. In 1995 and 1996, several remediation studies were initiated, looking into dredging, enhanced in-situ attenuation, pumping of water overlying contaminated areas, and draining of contaminated ponded areas (Cate & Racine 1996; Collins & Cate 1997, 1998).

In-situ remediation of white phosphorus is the most basic, least intrusive decontamination method considered. This method can occur only in sediments that naturally desaturate, allowing sublimation of the white phosphorus into the soil pore space. Elevating the soil temperatures will enhance this process. Manipulation of soil temperatures has become a common practice in agriculture where row covers use natural light to heat soils and enhance yield (Wells & Loy 1985). In cold regions, row covers improve plant growth through the

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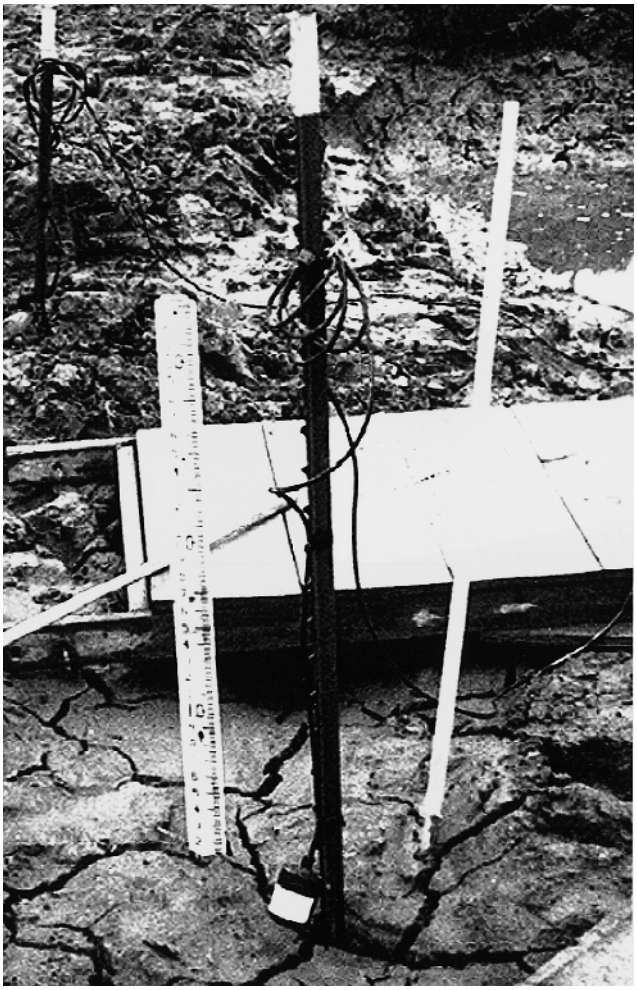


Figure 3 Crack development in desaturated sediment.

warming of soils in the early part of the growing season. In other parts of the world, they are used during fallow periods to heat soil up to over 45 °C. The most common row covers are polyethylene and polyester.

The colour and opacity of the row cover influences solar heating efficiency (Lamont 1993). Black plastic absorbs most incoming radiation, then reradiates infrared (longwave thermal) radiation. Since most of this solar energy is reradiated back to the atmosphere, black plastic can either raise or lower soil temperatures, depending on the degree of its contact with the soil surface (Marion & Pidgeon 1992). Clear plastic and fabrics such as Reemay transmit up to 95% solar radiation, and trap longwave (thermal) radiation. Therefore, they are more effective than black plastic at raising soil temperatures. Fabrics such as Reemay are also self-ventilating. Slits or pores may be punched into plastic row covers to provide additional ventilation.

Preliminary results from natural attenuation studies, and knowledge of the characteristics of white phosphorus, indicated that removing water from permanently and intermittently ponded areas might reduce the presence of the contaminant. By removing the overlying water, the pond bottom sediments would desaturate, enabling the development of voids through which the white phosphorus could sublimate (Fig. 3). This was the basis for the two more active remediation methods, permanent pond draining and temporary draining by pumping.

Contaminated sites in large, deep, permanent ponds that are widely interconnected with other ponded areas are candidates for remediation by dredging. Dredging will have a long-term effect on the contaminated ponded areas at the ERF, altering them from a feeding area to a deeper-water loafing area for the dabbling waterfowl. Its usefulness to surface feeding waterfowl will also be affected, although floating seeds and vegetation still provide a limited source of food (Racine *et al*. 1992, 1993*a*). Dredging remediates the site by removing contaminated sediments and depositing them in a controlled environment where the white phosphorus can be exposed for sublimation.

Pumping was originally targeted at isolated contaminated ponds. Groundwater recharge, precipitation, and tidal flooding all affect the performance of this method, and an isolated pond is more easily addressed under these circumstances than a system of ponds. Experience gained with the system led to successful deployment of several pump systems in more extensive ponds. Pumping remediates through the temporary removal of water from above the contaminated sediments, allowing the in situ remediation of the contaminant. When remediation is complete, the pump can be removed and the pond can revert to its original state with the minimum of alteration.

In areas that cannot be feasibly addressed through pumping or dredging, the ponds are drained by blasting a ditch to the nearest drainage feature. Although this removes the contaminated pond from use by waterfowl, it is more susceptible to tidal flooding because the threshold has been lowered during the ditching operation. The result is a very slow attenuation of the contaminant.

Methods

Site description

The estuarine salt marsh (Fig. 1) is divided by the main channel of the Eagle River, which meanders through the middle of the ERF. On either side of the river, levees, mudflats, marshes, meadows, and intermittent and permanent ponds occur in zones determined by elevation, which in turn affect salinity, frequency of tidal inundation, and sedimentation rate. The deepest ponds are along the edge of the ERF; freshwater influx has made these ponds permanent.

The frequency of tidal flooding depends on the maximum height of the monthly series of peak high tides. Monthly peak high tides approximately 4.6 m above mean sea level or greater will fill the pond basins in the area. In some years, the Flats will flood over a series of consecutive days each month, leaving only three weeks for drying of the sediments. In other years, such as 1997, a flooding tide in early May and a flooding tide in July were separated by 72 days.

The three remediation methodologies discussed in this

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paper are driven by the physical characteristics of the ERF, as well as the chemical properties of white phosphorus. The three most common sites of contamination are intermittently flooded areas; adjacent, shallow (< 0.5 m), permanently ponded areas; and deep (0.5–1 m) permanently ponded areas along the edge of the marsh. The common characteristics of all three areas are the presence of water, either in the form of standing water or saturated sediment, and the presence of white phosphorus.

The most important condition for attenuation of white phosphorus particles in the ERF is the desaturation of the sediments, which takes place naturally in intermittently wetted areas of the ERF in summer during long periods between flooding tides (M.E. Walsh *et al.* 1996). A secondary factor is sediment temperature. Because the vapour pressure of white phosphorus increases exponentially with temperature, warming unsaturated sediments can significantly accelerate the loss of white phosphorus particles (M.E. Walsh *et al.* 1995*a*).

Enhanced in-situ attenuation

A field study was performed to see how effectively passive solar warming techniques could increase sediment temperature and promote the loss of planted white phosphorus test particles. A laboratory experiment was also conducted, using an active heating method to briefly warm sediments from 13–45 °C. The purpose of the laboratory experiment was to test the hypothesis that heating the sediments would increase the vapour pressure of the white phosphorus sufficiently to initiate oxidation, which in turn would generate heat to sustain continued sublimation and oxidation after the heat source was removed.

Field method

Three passive solar heating techniques were tested on the east side of the ERF known as Area C. The site was chosen because it had the potential to desaturate between the monthly flooding tides during the summer of 1995 (M.E. Walsh *et al.* 1995*a*).

Three treatments plus controls were evaluated on 1 m^2 (1m × 1m) plots arranged in a Latin Square design (Natrella 1966). In one treatment study, black sand was applied to the sediment to change the surface albedo at a thickness of 1 mm over each 1 m^2 plot (1 l m^{-2}). Also evaluated were two types of row covers. The first, Reemay, is a spun-bonded polyester. The second, Fast Start, is a porous polyethylene. Fabrics were held in place using wooden 2 × 4s (3.8 × 8.9 cm) and 20 kg sandbags. The wood maintained an air gap between the fabric and the surface of the sediment.

Within each plot, sensors were installed to monitor temperature and moisture conditions. Sediment temperatures were monitored at 5 cm depth using Campbell Scientific (Logan, UT) Model 107B soil/water thermistor probes. Sediment moisture status was monitored at 5 cm using Campbell Scientific Model 257 (Watermark 200) soil moisture sensors. Output from each sensor was taken every 10 min, and a Campbell CR10 Datalogger System recorded the hourly and 24 h averages. Three white phosphorus test particles were also planted within each plot at the same depth as the sensors. These particles, 1.8 mm in diameter with a mass of 5.56 mg, were fabricated in the laboratory by heating white phosphorus under water and pipetting 3 µl droplets into water-filled test tubes that were cooled to form waxy droplets (M.E. Walsh 1996). They were recovered four months later (September) to see if white phosphorus mass had decreased. One sediment sample from each plot containing a planted particle was sieved so that the white phosphorus particle could be physically examined. The remaining two samples containing particles were placed into isooctane to extract white phosphorus residue prior to analysis by gas chromatography.

Adjacent to the plots, near-surface groundwater levels were monitored using submersible pressure transducers placed within piezometer wells. Output was recorded using Campbell CR10 dataloggers. A set of tensiometers was installed to provide another measure of near-surface sediment moisture. Two tensiometers equipped with dial gauges were installed, one at 10 cm depth and another at 25 cm depth. At the 5 cm depth, we installed a soil moisture probe equipped with a current transducer instead of the dial gauge. The current transducer converted soil moisture tension measurements into an analog output that was recorded on a datalogger every hour.

Laboratory

A laboratory experiment was also performed using a more aggressive method to heat sediments containing planted white phosphorus particles. Unsaturated sediments collected from an intermittent pond at the ERF were blended in duplicate 50 × 30 × 7 cm aluminium pans with sufficient water to saturate them. The mud samples were gently agitated for 24 h, consolidating the sediments. The two samples were then placed in an environmental chamber at 13 °C (typical average temperature for the ERF sediments during early June). Tensiometers were inserted to monitor moisture contents and four thermistors were inserted into one sample to monitor temperature. When tension reached 10 kPa, white phosphorus particles were planted at 3 cm depth. A hot air gun was used to heat one sample briefly to 45 °C. The heated sediment sample was then cooled to 13 °C and the white phosphorus particles recovered 24 h later. The other sample served as a control.

Pond pumping and draining

Two different strategies for active remediation were developed and tested: temporary pond draining by pumping and permanent pond draining by ditching. Pumping removes water by mechanical means without destroying or altering the habitat over the long term. Ditching entails excavating a drainage ditch with explosives from the contaminated pond area to a nearby tidal gully or the river. The ditch then erodes

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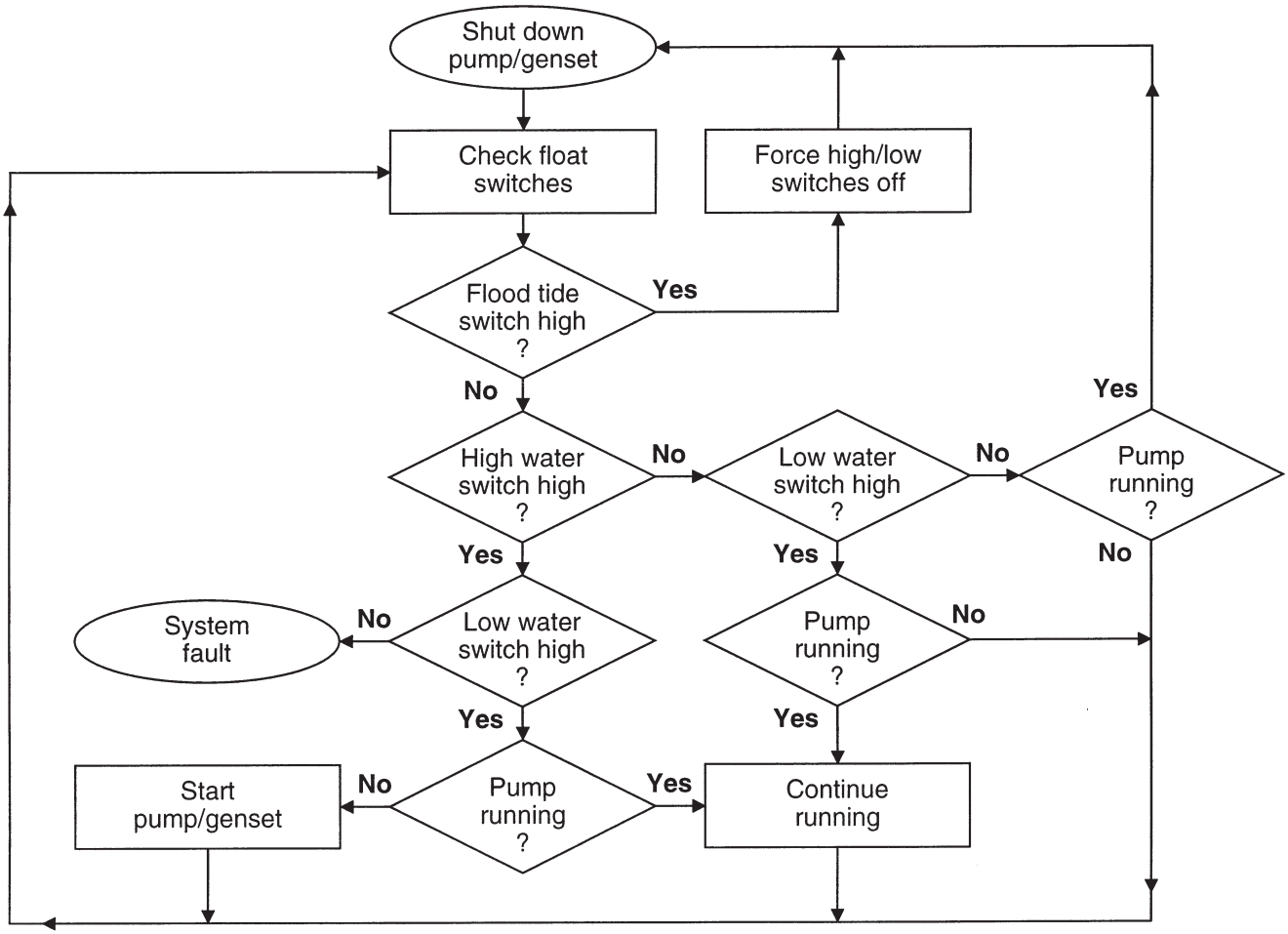


Figure 4 Pump float switch logic diagram.

channels to low-lying areas within the previously ponded area. Because of the degree of erosion of the ditch, restoration of the habitat is not feasible.

Pond pumping

In 1993, preliminary studies were conducted to determine the effects of draining ponded areas on the parameters critical to the natural attenuation of white phosphorus (Collins 1994). Candidate areas for either pumping or draining were surveyed to determine the scale at which these strategies could be applied.

A siphon was designed and deployed in the Bread Truck Pond (Fig. 1) in 1994 (Collins 1995). The surface area of the pond is 3.3 ha. A series of monitoring stations was installed, and white phosphorus test particles were planted. Automated measurements taken included water surface elevation, and air and sediment temperatures, all recorded on a solar-powered datalogger system. Manually recorded measurements included near-surface soil moisture, groundwater elevation (using 1.9 cm diameter slotted and screened PVC pipe), gravimetric soil moisture/resistance, and contaminant presence. The sediment samples for soil moisture and contaminant analysis were obtained using a 2 cm diameter soil sampling tube. Tensiometers were placed at the 10 and 25 cm depths, while sediment moisture and temperature sensors were placed at the 5, 10, 20 and 30 cm depths.

The siphon consisted of 165 m of 6.5 cm rigid PVC pipe with shut-off valves at either end, a 'Y' valve at the high point for priming, and an air bleed valve. A 30 m flexible section of 6.5 cm diameter hose was attached to the outlet end for discharge into a nearby drainage gully. The intake was placed in the deepest section of the pond in a modified 114 litre barrel to stop potentially contaminated sediments from being transported out. The vertical head change was approximately 2 m between the intake and discharge. The siphon was filled and started on 25 June, following a flooding tide. It ran for about 20 days, until a leak developed in the pipe, breaking suction. Repairing the pipe proved difficult, so the area was allowed to dry naturally. Monitoring of attenuation parameters continued, and at the end of the season, test particles were retrieved and sediment samples were taken for contaminant analysis.

Because of the slowness of and difficulties encountered with the passive siphon system, attention was redirected

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towards an active pumping system. In 1995, a system was specified and purchased based on calculations made for draining Bread Truck Pond in two days or less (Collins *et al.* 1996). This is a 450 m^3/hr autonomous floating pump and generator set (genset) system, based on a Crisafulli J-series 15 cm standard duty centrifugal pump and an 80 kW diesel-powered generator. It is designed to run continuously for 48 hours at full power. Both the pump and genset are affixed to floating barges for deployment in the ERF.

In May 1997, a 9 × 2 m sump was excavated with explosives at the edge of Pond 183 in Area C (Fig. 1). Two shaped and two cratering charges were used to create the sump. The pump was airlifted to the sump via a US Army UH-60H Blackhawk helicopter, and the genset was airlifted to the end of a channel dredged the previous year. (The channel was used to transport fuel to the genset via a barge). The genset and pump, located 70 m apart, were electrically connected. The 20 cm discharge pipe and hose were run from the pump to the nearest drainage gully, a distance of approximately 400 m. Shallow (15 cm) channels were dug through areas cleared by an unexploded ordnance detection specialist to help drain the ponded area into the sump. The equipment was operational on 21 May 1997 (M.R. Walsh *et al.* 1998).

In July, prior to the next flooding event at the Flats, a third float switch and associated circuitry were added to the system. This switch is used to shut the system down during flooding events by forcing the other two switches electrically low (Fig. 4). After flooding, when the area drains to the point where natural flow is confined to a few drainage channels, the flood switch drops, and the water level switches resume normal operation and pumping recommences. The upper water level float switch was also removed from the pump at this time and placed on the sump rim. This eliminated the need to adjust the start timing sequence prior to pumping when the sump is filling. These changes allow more autonomous operation of the system while also reducing fuel consumption during natural flooding and cutting down on the cycling of the equipment.

Before the start of pumping in May, an instrumentation station was installed in a connected area that would not fully drain. This station recorded water levels and air temperature (see previous descriptions). As part of the continuing natural attenuation study, three monitoring stations as described for the Bread Truck deployment, were installed along a transect through the area to be drained in Pond 183. Composite samples of the sediment in the area to be pumped were collected from the saturated sediments to establish a baseline of white phosphorus contamination. Ten white phosphorus particles previously made in the laboratory were planted adjacent to the instrumentation stations as part of the treatment effectiveness study. Tensiometer readings were periodically recorded to monitor progress in the drying of Pond 183.

At the end of the 1997 season, half of the planted white phosphorus particles in Pond 183 were retrieved and analysed to see if the pumping operation was promoting the attenuation of the contaminant. In addition, the areas that had shown contamination in the spring were resampled using a composite sampling method to broadly determine the remediation of in situ particles (M.E. Walsh *et al.* 1998). These results were compared to those of the Bread Truck Pond to assess the alternative remediation strategies.

Pond draining

Because of the difficulties with the siphon, and a shortage of funds that prevented the deployment of the pump system, a decision was made to excavate a ditch to permanently drain Bread Truck Pond. Owing to the dangers of unexploded ordnance, military engineers excavated the ditch using military explosives. Prior to deployment in April 1996, a route between an active drainage gully and one of the deeper sections of the pond was surveyed and marked. Military engineers then set up two sets of charges to form a ditch that was 1.5 m deep, 3–4.5 m wide, and 90 m long. The ditch drained the intersected pond. Instrumentation was installed to monitor the attenuation parameters within the newly exposed pond bottom sediments.

In 1997, a similar exercise was carried out at Racine Island (Fig. 1) to remove a highly contaminated pond in the centre of the island. In this case, a large ditch, 120 m long by 6 m wide by 2 m deep, was blasted between Racine Island Pond and a gully near a channel of the Eagle River. This ditch drained most of the contaminated pond, but water remained in some of the lower sections. Further ditching may yet be necessary to remove the water from these areas, as a high water table and frequent flooding will stop natural drying. Instrumentation was installed to monitor the attenuation parameters for white phosphorus.

In conjunction with the remediation effectiveness study, composite samples were taken along transects in the drained Bread Truck Pond. These samples were analysed and compared to similar samples taken from the pumped C-Pond area to determine the absolute and relative effectiveness of the two remediation methods. A description of the sampling and analysis protocols can be found in M.E. Walsh *et al.* (1997).

Dredging

In 1995, a small, remotely-controlled auger dredge with unique features developed for use at the ERF was leased for trials. The dredge system included an armoured dredgehead, separation of the pump from the augerhead, use of non-toxic vegetable-based hydraulic oil, an armoured shore-based cab, and video-assisted remote operation with overlaid sensor information (M.R. Walsh 1995; M.R. Walsh *et al.* 1996). The dredge weighed less than 6000 kg to allow helicopter deployment. The minimum width and depth of cut were 2.4 m and 0.5 m, respectively. A special maceration assembly was designed to cope with the tough, fibrous vegetation and debris ubiquitous throughout the Flats (M.R. Walsh & Lambert 1997).

A spoils-retention basin was constructed 450 m from the dredge site. The basin, which was designed to minimize

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percolation into the substrate, was used for decanting the supernatant from the spoils and the subsequent treatment of the contaminated sediments through natural drying and warming. Instrumentation was installed at four locations in the basin to monitor critical remediation parameters (soil and air temperature, water depth, and soil moisture). In addition, controlled studies were conducted within the basin sediments to determine the contaminant attenuation rate through the use of planted white phosphorus particles.

Dredging commenced in mid-October 1994, but was quickly stopped because of a heavy snowfall. However, dredge spoil samples were collected and analysed for white phosphorus. These initial analyses indicated that the dredging process was removing the contaminant from the ERF.

Dredging began again in late June 1995, but because of equipment problems and the time required to optimize the system, no serious dredging occurred until September. During each hour of dredging, a composite sample, made up of spoil subsamples collected every 15 min, was taken. In addition, supernatant was sampled at the end of each day to determine if colloidal white phosphorus was escaping during basin decanting. At the end of the dredging season (September 1995), several samples were taken of the deposited sediments in the basin and analysed. White phosphorus particles, six in each of four locations, were also planted in the retention basin sediment for the attenuation study (M.R. Walsh 1996).

Dredging operations were turned over to a private contractor in 1996 (M.R. Walsh & Collins 1997). Because of limited funding, there was very little sampling of spoils. However, the newly dredged area was sampled, and areas dredged from 1994–96 were sampled using a sieved compositing method for particulate contaminants developed by the US Army Cold Regions Research and Engineering Laboratory (CRREL) and the US Army Environmental Hygiene Agency (M.E. Walsh *et al.* 1995*b*). The planted white phosphorus particles in the basin were removed, half from each location in May and the other half in September, and analysed to determine in-situ attenuation.

Over the course of the 1995 and 1996 seasons, approximately 0.5 ha of one of the most contaminated permanent ponds at the ERF were dredged to an average depth of 0.6 m. During this period, 151 composited spoils line samples, 28 basin supernatant outflow water grab samples, and 31 post-dredging bottom composite samples were taken and analysed (M.R. Walsh & Collins 1998). Waterfowl use and mortality were also observed, although no rigorous analysis was performed. A total of 12 planted white phosphorus particles, three each from the four retention basin locations, were retrieved prior to the 1996 season in May (M.E. Walsh *et al.* 1998). In addition, 10 sediment grab samples from the previous year's dredging activities were collected from the accumulated basin sediment. Two basin sediment grab samples were collected near the spoils line discharge pipe after the 1996 dredging season.

Results

Enhanced in-situ attenuation

Field studies

The conditions during the summer of 1995, when we field-tested passive solar warming techniques, were expected to be unfavourable for in-situ attenuation because of predicted monthly high tides exceeding 4.6 m. Piezometers and tensiometers installed within Area C provided data on the actual flooding frequency. In June, prior to the flooding tides, groundwater surface elevation dropped to 0.6 m below the sediment surface. Surface sediments were dewatered as indicated by the rise in tension to almost 10 kPa (24-h average). After the series of flooding tides in June, frequent precipitation prevented the surface sediments from desaturating in the intervals between flooding tides.

All three treatments (Reemay, Fast Start and black sand) slightly increased sediment temperatures versus the controls (Fig. 5). From 28 May to 12 June (before the June flooding tides), the maximum increase was 2.5 °C for the black sand and 4 °C for each of the row covers, and the average increase was 1 °C for the black sand and 1.5 °C for each of the row covers.

The flooding tides covered the black sand with new sediment. After the tides, sediment temperatures in the treated plots were indistinguishable from those in the controls. Both

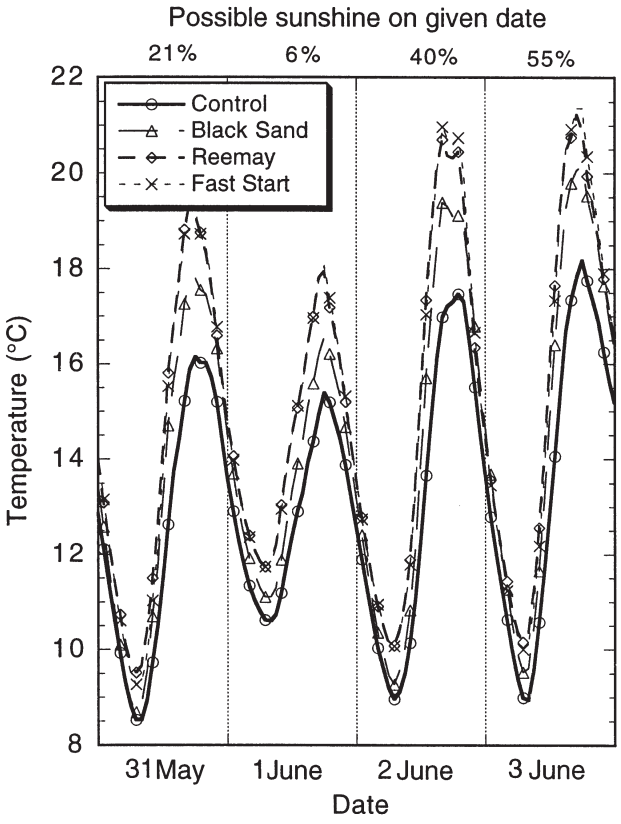


Figure 5 Diurnal variations in mean temperature ($n = 4$) in sediment (5 cm depth) under control (bare) and three treatments 31 May to 3 June and per cent possible sunshine.

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Table 1 Mass of white phosphorus residue found by solvent extraction and gas chromatography in sediments containing planted white phosphorus particles (nominal initial mass = 5.56 mg) under passive solar warming treatments. White phosphorus particles were planted in May and the residue recovered in September.

		White phosphorus mass (mg) remaining			
Row	*Duplicates*	*Control*	*Sand*	*Reemay*	*Fast Start*
1	1	2.09	5.25	5.47	4.72
1	2	4.45	4.02	5.11	5.21
2	1	0.48	4.70	5.82	5.28
2	2	5.11	3.75	0.001	6.20
3	1	5.58	5.48	4.62	4.27
3	2	5.87	5.29	2.58	4.67
4	1	5.65	5.48	1.26	5.75
4	2	4.50	5.68	5.14	5.73
	Mean:	4.22	4.96	3.75	5.23
	Standard deviation:	1.93	0.72	2.18	0.65
	Median:	4.81	5.27	4.86	5.24

fabric row-covers survived, but immediately after the flooding tides, the sediment temperatures under the row covers were less than the control. They then gradually became greater than the control. This cooling effect was caused by wet, new sediment being deposited on the top of the row covers, making them opaque. Once dry, wind removed the layer of sediment and warming resumed.

Because of monthly flooding tides during the summer of 1995 and frequent rainfall during July, August and September, sediments were saturated except for those few days before the June flooding tides. None of the treatments appeared to significantly inhibit evaporation during this brief period.

When the white phosphorus particles planted at each site were retrieved and examined, the only physical difference noted was dimpling on the surfaces. Particles under the Fast Start (porous plastic) had the most severe dimpling, with some voids appearing. However, the masses of the remaining particles, as determined by gas chromatography, were essentially unchanged, except for a few particles under the Reemay and one particle in the control plot (Table 1). The length of time that the sediments were unsaturated was too short to result in significant changes (Kruskal-Wallis test, $p = 0.478$) in the mean mass of these large particles. Since loss is from the surface of the particles, the initial loss of mass is small compared to the total mass of the particle, but it will accelerate as the surface area to volume ratio increases.

Laboratory

In previous experiments, we determined that loss of white phosphorus particles in unsaturated sediment was much slower at 15 °C (30 d) than at 20 °C (24 h). In the present experiment, we briefly warmed unsaturated sediments that were initially cool to see if one warming event would result in rapid loss of white phosphorus particles. The sediment of the treated sample was heated well above the autoignition temperature of white phosphorus, and the tension of the treated sample rose to 82 kPa after 24 h compared to 40 kPa in the control. Despite this increased heating and drying, the mean mass of remaining particles in the treated sample was 4.5 ± 1.2 mg, which is not significantly different from the control (5.7 ± 0.3 mg). For this experiment, the heat was focused on the centre of the sample, an area 17 cm in diameter. Approximately 3 kg of sediment actually reached 45 °C after an expenditure of 840 W-hr of electricity. Longer heating periods were not tested because the costs would be too high when scaled up to the volume of sediment needing treatment at the ERF.

Pond pumping and draining

Results to date show a sharp contrast in remediation effectiveness of pumping versus draining by ditching. Pumping was much more successful at drying the surface sediments, critical to the attenuation of white phosphorus, than permanent draining by ditching. Baseline composite sampling of drained areas in Bread Truck Pond and Pond 183 of Area C showed significant differences in attenuation. Bread Truck Pond, although breached for over a year, still contained significant amounts of white phosphorus. In Pond 183, drained only in late May of 1997, the contaminant's concentration decreased significantly (Table 2). Corroborating data can be found from the sediment moisture data that were collected over the long drying spell from 10 May through July 1997. There was significant drying in the Pond 183 at all depths monitored, while sediments in Bread Truck Pond continued to be at or near saturation (Table 3).

During what are normally considered non-flooding events, tides less than 3.75 m mean sea level, the Bread Truck Pond was temporarily flooding whereas Pond 183 remained dry (P. LeMay & M.E. Wong of CH2M Hill, personal communication July 1997). Because of the blasted ditch leading from Bread Truck Pond to the drainage gully, the flooding threshold level was lower, resulting in many more floods. This repeated flooding was inhibiting the drying of the pond sediments. Another wetting process is precipitation, which affected both areas equally in the short term, wetting the upper sedimentation layers but quickly drying and thus not

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Table 2 Results of 1997 season composite sampling of Pond 183 and Bread Truck Pond.

Site and Transect	*Date collected (1997)*	*Mean concentration (μg/kg)*	*Notes*
Bread Truck Pond			Means based on 5 replicates
North (BTN)	3 June	11.5	Elevation: 4.76 m
	3 September	7.9	Does not include one outlier
South (BTS)	4 June	4.9	Elevation: 4.76 m
	4 September	0.87	
Pond 183 (C)			Means based on 5 replicates
	2 June	61.2	Area never previously dry
	3 September	6.89	Elevation: 4.65 m

Table 3 Tensiometer readings and number of days sediments were unsaturated for in three drained ponds in 1997. Stations: C = Pond 183, BTN = Bread Truck Pond North, BTS = Bread Truck Pond South. Stations: 0, 100 and 200 are distances (m) from the start of the sampling transect.

Station	*Depth (cm)*	*Maximum tensiometer reading (kPa)*	*Number of days unsaturated*
C-0	5	44	38
	10	60	35
C-100	5	75	38
	10	80	41
C-200	5	65	40
	10	50	33
BTS-0	5	26	41
	10	6	34
BTS-100	5	8	12
	10	10	11
BTS-200	5	12	8
	10	10	9
BTN-0	5	13	6
	10	15	No data
BTN-100	5	10	18
	10	10	11
BTN-200	5	No data	26
	10	15	12

greatly affecting the attenuation process. Heavier rains, which cause pooling, were more quickly addressed by the pumping system, resulting in a quicker resumption of the drying and attenuation processes.

The Racine Island Pond continued to drain throughout 1997, although segments still contain water. This area is frequently wetted, and thus the objective here was to remove contaminated waterfowl habitat, which was accomplished. Contaminated habitat has also been removed at Bread Truck Pond, and no dead birds have been found in its vicinity since the pond was breached. However, the cessation of an active ground-based mortality count programme in 1996 and 1997 makes mortality comparisons with previous years subjective.

Dredging

White phosphorus was being effectively removed from the dredged area (Table 4). About 20% of the spoils line samples were positive for white phosphorus, a rate typical of the pre-dredging contamination rates found in the area by other researchers since 1990 (Racine & M.E. Walsh 1994). Some contamination may still have been present after dredging. However, the depth of dredging (0.5 m minimum) precluded bottom feeding by dabbling ducks, and no sick or dying waterfowl were observed in any of the dredged areas.

White phosphorus-contaminated sediments were deposited in the spoils retention basin, and these sediments were remediated through controlled draining and natural drying. Two samples were taken from the fresh sediment deposits in the basin, and both tested positive for white phosphorus. All those taken from sediments that had been through a partial or complete drying cycle tested negative. The planted particles, which were retrieved early in the field season, all showed significant changes in mass (Table 5).

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Table 4 Sampling data synopsis for the dredging project: 1994–96.

Year	*Method*	*Type*	*Number of samples*	*Positive*	*Concentration (μg/l)*
1994	Composite[1]	Sediment	2	50%	
1995	Composite[1]	Sediment	137	19%	
	Grab	Water	23	4%	4.00
	Composite[2]	Sediment	6	0%	
1996	Composite[1]	Sediment	12	20%	
	Grab	Water	5	20%	0.12
	Composite[2]	Sediment	25	8%	

[1] 4 subsamples taken from spoils line, consolidated into one sample.
[2] Several sieved subsamples (#30 mesh/0.59 mm) taken along a transect.

Recontamination of the Flats from discharged supernatant was minimal, with only 2 of 28 water samples showing contamination at low levels (≤ 4 μg/l).

Discussion

Remediation studies have demonstrated that removal of persistent white phosphorus from the ERF is possible. The use of several different remediation strategies may be necessary because of the variability of the environment at the ERF. Each method has its strengths and weaknesses, and these must be carefully considered to ensure the most cost-effective resolution to the problem with a minimum of impact to the environment.

Field studies indicate that row covers or black sand may be used as a tool to raise sediment temperatures slightly, but they are not effective at removing white phosphorus unless sediments are desaturated for longer than a few days. Laboratory studies showed that a brief interval at high temperatures (up to 45 °C) failed to remove white phosphorus rapidly from the sediments. The average white phosphorus mass remaining in the heated sediments was not significantly different from the control, indicating that a longer period of heating would be necessary to accelerate white phosphorus loss. However, the energy requirements for prolonged heating in situ would be prohibitive.

Given that some parts of the ERF are remediating naturally in areas that desaturate, ways to enhance natural drying, such as temporary pond draining, are more important than active methods of raising sediment temperatures. Pond pumping has shown promise with a minimal impact to the environment. Planted particles, composite sampling, and monitoring of attenuation parameters over the 1997 field season all indicate that this method is very effective in enhancing the attenuation of the contaminant. Draining through ditching seems to be most effective in keeping the target species out of contaminated areas. However, the areas drained by this method are more prone to flooding, and the environmental impact is high as the area is no longer ponded. Based on planted particle, composite sampling, and tensiometer data, attenuation in ditched ponds is occurring at a very slow pace.

Dredging is an effective method for the removal of contaminated material and breaking the contamination pathway to the dabbling duck, especially in ponds that receive a large amount of groundwater recharge or surface runoff. Data indicate that some contamination remains behind after dredging to a depth of about 0.6 m, although the concentrations are low. The contamination may be attributable to 'edge effects', slumped material adjacent to the dredged area that was included in the composite samples. Attenuation studies conducted in the spoils retention basin show that this is an effective method for off-site remediation of contaminated dredge spoils. The results of the planted particle test were especially encouraging, as the remediation period covered less than eight months, most of that time during freeze-up. The recontamination of the ERF by white

Table 5 Planted white phosphorus particle mean residual masses (initial mass: 5.56 mg).
N/D = Not detected.

Area	*Location*	*Mass (mg)*	*Notes*
Retention Basin			3 Replicates/5 locations
	All locations	N/D	No detections
Pond 183 (Area C)	C-0	3.13	5 Replicates at each station
	C-100	2.64	Depth of all particles 5 cm
	C-200	2.57	Particles planted 31 May 1997
Bread Truck Pond	BTS-0	3.23	Particles retrieved 3–4 Sept. 1997
(South transect)	BTS-100	2.44	
	BTS-200	3.27	
(North transect)	BTN-0	2.77	
	BTN-100	3.05	
	BTN-200	2.28	

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Table 6 Alternative treatment methods summary. The environmental impact is determined by the permanence of the disruption to the environment.

Treatment method	*Applicable location*	*Approximate treatment cost and impact*	*Treatment effectiveness*
Sediment warming	Intermittently wetted areas	Cost – Low: US$10 000/ha Impact: Low	Marginal: reduction in contaminant level by elevating the sediment temperature was not found to be statistically significant.
Dredging	Deep ponds and ponded areas with high recharge rates	Cost – Very high: US$300 000/ha Impact: Moderate to high	Good: dredging removed the contaminated sediments to a controlled treatment area where the contaminant was fully removed. Edge contamination in dredged areas reduced overall effectiveness. Decrease in contamination was approximately 60% in the dredged areas.
Draining: Ditching	Permanent ponds that experience frequent flooding	Cost – Low: US$13 000/ha Impact: High	Poor to good: blasting ditches led to more frequent flooding of the area, suppressing the overall effectiveness. Very dependent on tides and precipitation. Reduction in contamination is from 1–75% (composite sampling method). Planted particle reduction range is from 30–80%.
Draining: Pumping	Any ponded area	Cost – Moderate: US$60 000 Impact: Low	Good to very good: composite sampling indicates approximately 90%/yr reduction in contamination. Planted particle masses reduced 65%/yr, greater in second year than first (79% versus 47%).

phosphorus in the supernatant is minimal. The environmental impact is significant, especially in the shallower ponds that are dredged. Sedimentation will eventually refill the ponds to their former levels, but this is a very slow process. A summary of the four remediation methods is given in Table 6.

Remediation of white phosphorus at the ERF is difficult and dangerous. The variability of the environment dictates that no one acceptable solution is applicable throughout the area, although initial pond pumping results strongly favour this strategy. Research into the environmental fate of white phosphorus allowed us to narrow the options and applications to specific areas and methodologies, thereby reducing the impact of remediation activities and minimizing human exposure to the UXO (unexploded ordnance) ubiquitous throughout heavily contaminated areas.

Pond pumping was the remediation method chosen in October 1998 by the Remediation Project Managers for the Eagle River Flats Superfund site clean-up. Six pumps, with capacities ranging from 63–190 l/s were deployed and operating in two areas of the ERF. Total area of contaminated permanent ponds drained was 12 ha, with an adjoining 10 ha of intermittent ponds affected. As part of the Record of Decision, a five-year deployment plan will be implemented with a goal of 99% reduction in waterfowl mortality.

This study has demonstrated that the remediation of white phosphorus in an environmentally-sensitive wetland can be accomplished in a manner that does not adversely impact the physical condition of the area. The ability to address the contaminant in situ greatly reduces the intervention required, and methods of enhancing the natural attenuation can be applied with minimal effort. The projected treatment period in this periodically-flooded northern estuarine salt marsh is three years for each pond. The deployment of several specialized systems throughout the contaminated area will greatly reduce the time required to complete the remediation effort.

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