CRREL REPORT 95-23

Persistence of White Phosphorus Particles in Sediment

Marianne E. Walsh, Charles M. Collins
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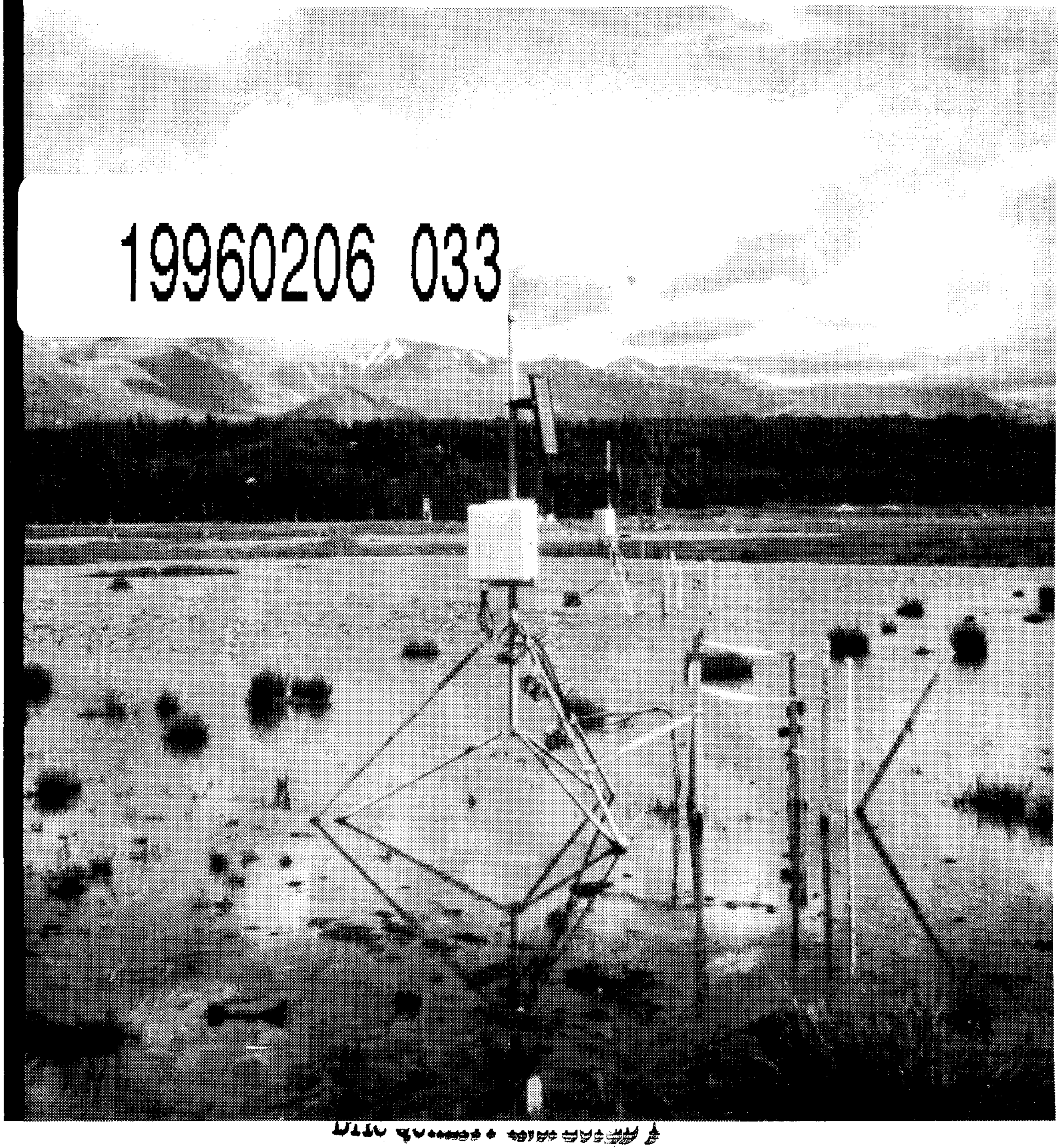

Abstract

Remediation of sediments at Eagle River Flats, a salt marsh contaminated with particles of white phosphorus (P_4), may require severe alterations of the wetland by dredging, draining or covering. However, some sediments may undergo decontamination naturally in areas that are seasonally exposed to air. To predict the persistence of white phosphorus particles in sediments, a literature review was conducted for the physical and chemical properties of white phosphorus. The persistence of millimeter-size white phosphorus particles was studied by laboratory and field experiments. White phosphorus particles were found to be persistent indefinitely in saturated sediments. In unsaturated sediments, loss was rapid (within 24 hours) at 20°C and retarded by low temperatures.

Cover: *Looking east along a transect across the main pond in Area C. Sediment temperature and moisture were monitored at these study sites during the summer of 1994.*

For conversion of SI units to non-SI units of measurement consult *Standard Practice for Use of the International System of Units (SI),* ASTM Standard E380-93, published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.

CRREL Report 95-23

US Army Corps
of Engineers
Cold Regions Research &
Engineering Laboratory

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Prepared for
U.S. ARMY ENVIRONMENTAL CENTER

PREFACE

This report was prepared by Marianne E. Walsh, Chemical Engineer, Applied Research Division; Charles M. Collins, Research Physical Scientist; and Charles H. Racine, Research Ecologist, Geological Sciences Division, Research and Engineering Directorate, U.S. Army Cold Regions Research and Engineering Laboratory.

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Persistence of White Phosphorus Particles in Sediment

MARIANNE E. WALSH, CHARLES M. COLLINS AND CHARLES H. RACINE

INTRODUCTION

Since 1990, CRREL researchers have been conducting field studies at Eagle River Flats, Alaska, the impact area at Ft. Richardson (Racine et al. 1992a,b,c, 1993). Eagle River Flats was contaminated by the detonation of projectiles containing white phosphorus, a smoke-producing munition. Eagle River Flats is the first Army training area identified with white phosphorus contamination. Recent surveys at other army training areas have revealed white phosphorus contamination (Simmers et al. 1994). Previous to our findings at Eagle River Flats, white phosphorus was thought to be nonpersistent in the environment.

The discovery of white phosphorus residues from smoke rounds at Eagle River Flats has shown that the current understanding of the environmental fate of white phosphorus is poor. Much of the basic research on the chemistry of white phosphorus was conducted prior to 1950 and was not concerned with environmental fate. More recent work on the environmental impact of training with white phosphorus munitions concentrated on downwind deposition of aerosols from the smoke cloud (Marchetti 1979, Van Voris et al. 1987). These studies examined white phosphorus particles much smaller than the millimeter-size particles (Fig. 1) found by examination of highly contaminated Eagle River Flats sediments. Lack of understanding of the environmental fate and transport of white phosphorus residues precludes accurate ecological assessments and efficient cleanup. This report will review literature describing the chemical and physical properties of white phosphorus. Then laboratory and field experiments will be described in which white phosphorus particles were incubated in Eagle River Flats sediments at various temperatures and moisture contents.

Figure 1. Particles of white phosphorus (P_4) isolated from Eagle River Flats sediment in 1994. These particles were deposited from smoke munitions fired into Eagle River Flats during army training. They were deposited prior to February 1990 when artillery training was suspended at Eagle River Flats. Lead shot, shown for scale, is 2.7 mm in diameter.

CHEMICAL AND PHYSICAL PROPERTIES OF WHITE PHOSPHORUS

History

As with many scientific discoveries, white phosphorus was discovered by serendipity, in 1669 in Hamburg, when Hennig Brand distilled urine with sand and coal while attempting to isolate metals for alchemy experiments (Mellor

1928). Phosphorus was subsequently named from the Greek word for "light bearer" since it glowed in the dark.

Properties of white phosphorus

Phosphorus occurs in both organic and inorganic forms in nature almost exclusively in oxidation state +5. Mean phosphorus concentrations in soil and crustal rocks are 430 and 1000 mg/kg, respectively (Sposito 1989), making it the twelfth most abundant element in the lithosphere. Phosphorus plays vital roles in biological systems in compounds such as ATP (adenosine triphosphate), phospholipids, DNA (deoxyribonucleic acid) and phosphate buffers, and it is found in the bones and teeth of vertebrates as calcium phosphate.

Elemental phosphorus (oxidation state 0) does not exist in nature; it is prepared commercially by heating phosphate ores [$Ca_3(PO_4)_2$] with sand (SiO_2) and coke in an electric furnace. White phosphorus is a wax-like solid that ignites spontaneously in air between 30 and 40°C. Its molecular structure is that of a regular tetrahedron with a phosphorus atom at each apex and a P–P distance of 0.22 nm. Since its molecular formula is P_4, its molecular weight is 124 amu. The high reactivity of white phosphorus is attributed to the extreme bond strain involved in the bonding of four phosphorus atoms in a tetrahedral configuration (Van Wazer 1958). Some chemical and physical properties of white phosphorus are given in Table 1.

Elemental phosphorus exists in several allotropic forms: white, red and black. White phosphorus is sometimes referred to as yellow phosphorus since the commercially available grade has a slight yellow color due to trace amounts of red phosphorus as an impurity. Pure white phosphorus is colorless. The crystal structure is cubic; a unit cell (a = 1.85 nm) contains 56 P_4 tetrameric molecules. The structure of red phosphorus is variable. Several polymeric forms exist. Red phosphorus, which is less reactive than white phosphorus, is also used by the Army as a smoke munition. Red phosphorus is nontoxic. Black phosphorus is similar in structure to graphite. It is the most stable form of elemental phosphorus; it does not spontaneously ignite under normal temperatures and humidities.

The oxidation of P_4 has been studied extensively (Mellor 1928, Van Wazer 1958). The final product of P_4 oxidation is phosphorus pentoxide (P_4O_{10}) via lower oxidation state oxides P_4O_n, where n = 1, 2,...9. Lesser amounts of phosphorus trioxide (P_4O_6) and phosphorus tetraoxide (P_4O_8) are products, depending on the availability of oxygen. Phosphorus trioxide is responsible for the garlic-like smell immediately noticeable when P_4 is exposed to air. Phosphorus pentoxide is one of the most hygroscopic substances known. It will extract moisture from the atmosphere; the dense white cloud formed following the bursting of a P_4 projectile is actually moisture condensing on oxidized white phosphorus. Phosphorus oxides hydrolyze in water to form various oxyacids.

The reaction between P_4 vapor and oxygen has several anomalies that have intrigued scientists for over three hundred years (Semenov 1959). The reaction is characterized by a greenish glow that occurs between two sharply defined limits of oxygen pressure, which diverge as P_4 pressure increases. Outside the limits, the rate is so slow that it is undetectable. The lower limit is affected by the size and surface condition of the reaction vessel and the presence of other gases.

Table 1. Chemical and physical properties of white phosphorus.

Property	*Value*	*Source**
Molecular structure	P_4	a
Molecular weight	124 amu	a
Physical state at STP	Solid	a
Melting point	44°C	a
Boiling point	280°C	a
Appearance	Waxy Transparent Colorless (pure)	a
Mohs hardness	0.5	a
Density (20°C)	1.8 g/cm^3	a
Vapor pressure (25°C)	0.043 torr	a
Viscosity (50°C)	1.69 cP	b
Solubility		
in water (15°C)	2.4 mg/L	c
	3 mg/L	d
in carbon disulfide (20°C)	13 × 10^6 mg/L	a
in diethyl ether (20°C)	7,000 mg/L	a
in benzene (20°C)	26,000 mg/L	a
in mineral oil	12,000 mg/L	d
Octanol–water partition coefficient	1200	c
Autoignition temperature	20–40°C	e
Latent heat of fusion (44°C)	20 J/g	a
Latent heat of sublimation (25°C)	455.2 J/g	a
Latent heat of vaporization (287°C)	545 J/g	a
Heat of combustion	24,000 J/g	a
Critical point	675°C, 80 atm	a

* a–Mellor (1928) d–Stich (1953)
b–Kirk Othmer (1982) e–Dainton and Bevington (1946)
c–Spanggord et al. (1985) f–Van Wazer (1958)

The lower limit is not a function of temperature, while the upper limit decreases with increasing temperature. These observations led to the theory of branching-chain reactions. The reaction mechanism proposed by Dainton and Kimberley (1950) is:

(1) $P_4 + O_2 \rightarrow P_4O + O$	initiation
(2) $P_4 + O + M \rightarrow P_4O + M$	propagation
(3) $P_4O_n + O_2 \rightarrow P_4O_{n+1} + O$ ($n = 1, 2, ...9$)	branching
(4) $O + O_2 + M \rightarrow O_3 + M$	termination
(5) $O + X \rightarrow$ stable product	termination
(6) O + wall $\rightarrow$ adsorbed oxygen	termination

where M is a third body and X is an inhibitor. The rate equation given by Dainton and Kimberley (1950) is:

$$\frac{d[P_4O_{10}]}{dt} = k_1[P_4][O_2] \left(1 + \frac{10k_2[P_4][M]}{k_4[O_2][M] + k_5[X] + k_6 - 8k_2[P_4][M]}\right) \qquad (1)$$

where $k_{1,2...6}$ are reaction constants for the six equations for the reaction mechanism. The lower limit of the glow reaction is due to "wall termination," reaction (6). The constant for reaction (6) is a function of the diffusivity of oxygen atoms in the gas mixture, the diameter of the reaction vessel and the concentrations of P_4, O_2 and M. The upper limit is due to homogeneous termination, reactions (4) and (5). The constant for reaction (4) is a function of a frequency factor for third-body reactions, temperature, activation energy (4.3 kcal) and the concentrations of P_4, O_2 and M. The reaction between P_4 and O_2 is rapid when the denominator of the term in the parentheses approaches zero. Dainton and Kimberley (1950) stated that within the limits of the glow reaction the "rate appears only to be limited by the supply and interdiffusion of the reactants."

Solid and liquid P_4 may ignite spontaneously in air. The autoignition temperature at atmospheric pressure for solid or supercooled liquid P_4 in dry air is 38°C (Dainton and Bevington 1946), and for a range of temperatures below 38°C (Fig. 2), P_4 will slowly oxidize, producing a greenish glow. Below 5°C, there is no reaction, unless the pressure is reduced to less than atmospheric.

In 1681, Slare (Mellor 1928) made the following seemingly paradoxical observation:

> It now being generally agreed that the fire and flame of phosphorus have their pabulum out of the air, I was willing to try this matter in vacuo. To effect this I placed a considerable lump of phosphorus under a glass, which I fixed to an engine for exhausting the air: then presently working the engine, I found it to grow lighter (i.e., the phosphorus to become more luminous), though a charcoal that was well kindled would be quite extinguished at the first exhaustion; and upon the third or fourth draught, which very well exhausted the glass, it much increased in light, and continued to shine with its increased light for a long time; on re-admitting the air, it returned again to its former dullness.

White phosphorus does not glow in oxygen at 1.5 atmospheres unless the temperature is raised above the melting point (Mellor 1928). Several researchers gathered evidence that the oxidation of P_4 occurs in the vapor phase. If a stream of air is blown over the oxidizing P_4, the glow appears

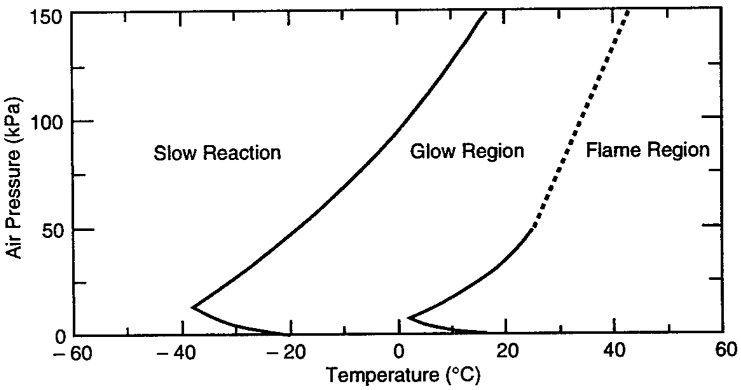


Figure 2. Effect of temperature and air pressure on the oxidation of solid P_4. (After Dainton and Bevington 1946).

downstream (Van Wazer 1958). Rayleigh (Mellor 1928) observed that P_4 is slightly volatile at room temperature and that the increased luminosity when the atmosphere is rarefied is due to the increased volatilization of the P_4. Thorpe (Mellor 1928) concluded that P_4 reacts with oxygen only under conditions where the P_4 volatilizes and that

> the glow itself is nothing but a slowly burning flame, having an extremely low temperature, caused by the chemical union of oxygen with the vapours of phosphorus and phosphorus oxide. By suitable means this glow can be gradually augmented until it passes by regular gradation into the active vigorous combustion which we ordinarily associate with flame.

The transition to burning with a bright yellow flame occurs when the temperature is raised to the ignition point or the pressure lowered below a definite limit (Fig. 2). Autoignition may also occur at room temperature if white phosphorus is covered by cotton (Mellor 1928). Since the oxidation of P_4 occurs by a reaction that occurs in the vapor phase immediately adjacent to the solid phase, activities that result in higher concentrations of P_4 vapor lead to autoignition. Dainton and Bevington (1946) observed surface melting as a solid piece of P_4 underwent transition from glow to flame. They speculated that not all the heat of reaction is dissipated as light and that the glow reaction is slightly exothermic. The heat causing the melting came from the oxidation reaction in the spatially adjacent vapor phase, which in turn raised the surface temperature of the solid P_4, leading to increased vapor pressure, more heat and finally ignition.

Dainton and Bevington (1946) described the greenish glow in terms of "width, intensity, and distance from the phosphorus." They concluded that the rate of consumption of P_4 vapor and oxygen was limited by the rate of diffusion of either reactant into the reaction zone. The conclusion of later work by Dainton and Kimberley (1950) was that "the glow reaction is only limited in velocity by the supply of phosphorus molecules to the reaction zone." White phosphorus exposed to dry air may form a layer of oxides that greatly reduces or stops the rate of oxidation (Russell 1903, Dainton and Bevington 1946). White phosphorus exposed to moist air forms a film of moisture that may stop oxidation (Russell 1903). The development of the film is due to the formation of the hygroscopic phosphorus pentoxide (P_4O_{10}).

White phosphorus will react with other oxidizing agents such as the halogens, sulfur and acids (e.g. nitric and sulfuric). The surface of solid P_4 is oxidized by aqueous solutions of metal salts such as copper sulfate, reducing salts of copper to the metal via copper phosphide. In the past, first aid for P_4 burns included bathing the P_4 in aqueous copper sulfate (Konjoyan 1983), which coated the P_4 particles with black copper phosphide (Mellor 1928) and prevented the P_4 from reigniting. White phosphorus stored under tap water will blacken due to reaction with copper cations dissolved in the water from copper pipes (Rae 1916).

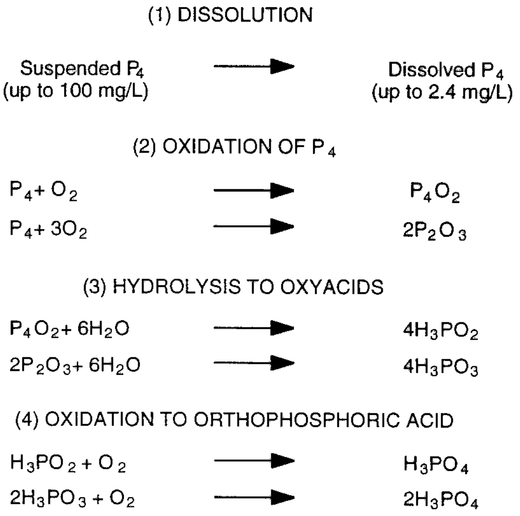


Figure 3. Oxidation pathway for white phosphorus in water. (After Sullivan et al. 1979.)

Studies of the oxidation of P_4 in water are summarized by Sullivan et al. (1979). Dissolved P_4 reacts with dissolved oxygen to form phosphinic (H_3PO_2) and phosphonic (H_3PO_3) acids, which in turn oxidize to orthophosphoric acid (H_3PO_4) (Fig. 3). Phosphine is also produced, probably by hydrolysis (Spanggord et al. 1985). When solid P_4 is introduced into water containing dissolved oxygen, a film of oxidation product forms on the surface. This film, the formation of which is accompanied by hydrogen evolution, was identified by Nikandrov and Smirnov (1983) as $(P_4OH)_2$, an intermediate to the formation of phosphorus pentoxide.

Factors that affect the environmental fate of white phosphorus

At equilibrium, P_4 does not exist in oxygenated aqueous or soil media. The thermodynamic instability of P_4 is illustrated in the potential-pH equilibrium diagram for phosphorus in water at 25°C (Fig. 4). The domain of stability for P_4 is

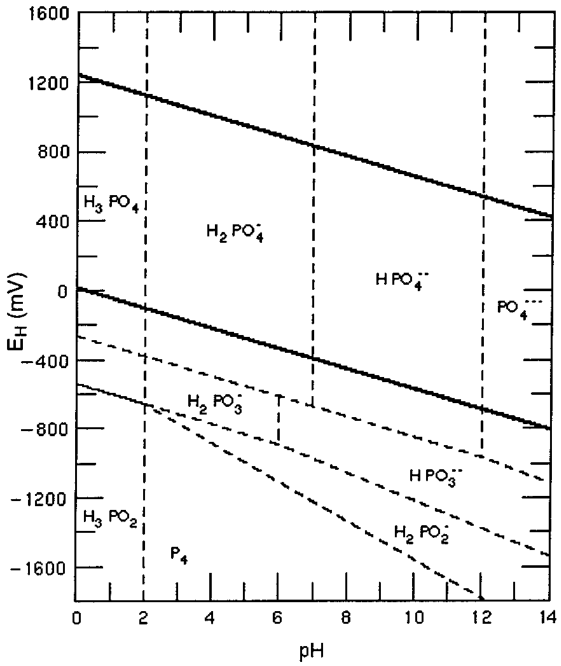


Figure 4. Pourbaix diagram for P_4 in water showing that P_4 is not thermodynamically stable in water. The region bordered by the heavy lines is the stability field of water. No substance outside this field is stable in the presence of water and atmospheric oxygen. (After Pourbaix 1966.)

well below the domain of the stability of water (Pourbaix 1966); that is, it can theoretically reduce water with the evolution of hydrogen. However, this diagram is for the state of *thermodynamic equilibrium* and does not indicate the rate at which equilibrium is achieved. Several factors must be taken into account to assess the persistence of a chunk of solid P_4 introduced into water or saturated sediments.

Spanggord et al. (1983) reviewed the properties and processes associated with the environmental fate of P_4. These included aqueous solubility, vapor pressure, sorption partition coefficient, octanol–water partition coefficient, leachability, Henry's constant and rates of dissolution, hydrolysis, oxidation, reduction and biotransformation.

Dissolution and aqueous solubility

White phosphorus is nonpolar, so it does not dissolve readily in water. Spanggord et al. (1985) measured the dissolution rate of a piece of P_4 that had a surface area of 1.25 cm^2 exposed to 25°C oxygen-saturated and nitrogen-purged water flowing at 0.14–3.00 mL/min. Dissolution rates ranged from 1.5 µg/hr for the slowest flow rate to 6.7 µg/hr for the highest flow rate. There was no difference in dissolution rate for white phosphorus exposed to oxygen-saturated or nitrogen-purged water.

Using these data and assuming that the rate of dissolution per unit area is constant, we can calculate the time for a spherical particle with an initial diameter of 1 mm (surface area of 0.0314 cm^2 and a mass of 953 µg) to dissolve from

$$\frac{dM}{dt} = \frac{1.5\,\mu g}{1.25\,cm^2 \cdot hr} \times 4\pi r^2. \tag{2}$$

Since

$$dM = \rho dV = \rho \frac{4}{3}\pi d r^3 = \rho 4\pi r^2 dr \tag{3}$$

then dM in eq 2 may be replaced:

$$\rho 4\pi r^2 dr = \frac{1.5\,\mu g}{1.25\,cm^2 \cdot hr} 4\pi r^2 dt \tag{4}$$

$$\int_{r=r_0}^{r=r} dr = \left(\frac{1.5\,\mu g}{1.25\,cm^2 \cdot hr}\right)(1/\rho) \int_{t=0}^{t=t} dt \tag{5}$$

$$\int_{r=r_0}^{r=r} dr = \left(\frac{1.5\,\mu g}{1.25\,cm^2 \cdot hr}\right)(1/\rho) \int_{t=0}^{t=t} dt. \tag{6}$$

Based on the amount of time for the radius to go to zero, a P_4 particle with an initial diameter of 1 mm would take about 8 years to dissolve at a constant temperature of 25°C (Fig. 5) in slowly flowing water.

Despite the slow dissolution rate, there is ample evidence that water becomes contaminated by contact with P_4. In industrial settings, P_4 is fre-

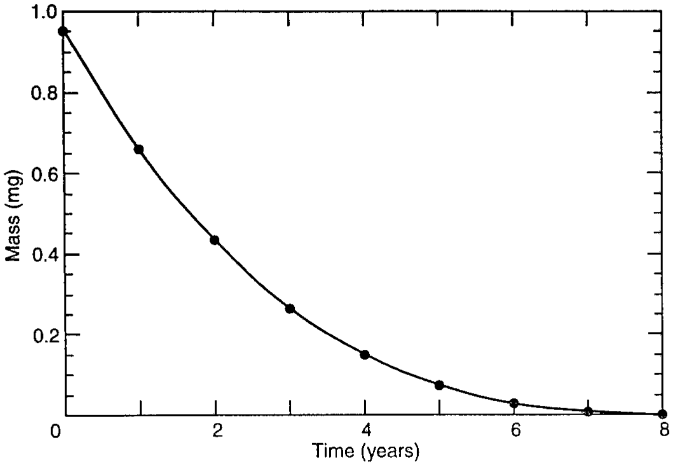


Figure 5. Calculated dissolution of a 1-mm-diameter P_4 particle in 25°C water assuming the rate of dissolution per unit surface area is constant [1.2 μg/(cm^2 hr)]. The rate is based on the data from Spanggord et al. (1985) for the slowest flow rate tested.

quently held above its melting point so that it may be poured and molded. Because the melting point exceeds the autoignition temperature, large quantities of water are used commercially either for storage and handling of P_4 or for washing equipment that has been in contact with P_4. This "phossy water" contains suspended (colloidal) and dissolved P_4 (Dacre and Rosenblatt 1974). Larger particles may also be suspended (Peer 1972). Release of phossy water has caused fish kills in Canada (Idler 1969) and the United States (Dacre and Rosenblatt 1974).

The aqueous solubility of P_4, as measured by Stich (1953), is 3 mg/L at 15°C, and this is the value reported in the *Handbook of Chemistry and Physics*. However, colloidal suspensions have concentrations up to 100 mg/L (Sullivan et al. 1979).

Spanggord et al. (1985) measured the aqueous solubility of P_4 by placing excess P_4 in deoxygenated water, heating to 45°C, sonicating for 30 minutes, then stirring for 48 hours. Solutions were then centrifuged at 7000 rpm for 60 minutes at three temperatures. Measured P_4 concentrations were 2.4, 4.1 and 5.0 mg/L at 15, 25 and 35°C.

Because P_4 is not an electrolyte, solubility in saline solutions will decrease as salinity increases, a process known as "salting-out" (James 1986). The effect is expressed mathematically by the Setschenow equation:

$$\log \frac{M_s^o}{M_s} = K_s M_{salt} \qquad (7)$$

where M_s^o is the solubility of the nonelectrolyte in pure water and M_s is the solubility of the nonelectrolyte in the saline solution with a salt concentration of M_{salt}. K_s is a constant, known as the Setschenow or salting-out constant (James 1986). A value for K_s has not been published.

Octanol–water partition coefficient

The octanol–water partition coefficient (K_{ow}) is the ratio of the concentration of a solute in the organic phase (octanol) to the concentration of a solute in water at equilibrium and is often used as an indicator of the bioaccumulation potential of an organic substance in fatty tissue of organisms and of mobility and sorption in the environment. High K_{ow} values (>1000) mean a tendency for bioaccumulation, low mobility and sorption to organic matter. Spanggord et al. (1985) measured K_{ow} using the method of Leo et al. (1971), where white phosphorus concentrations were measured in both the water and octanol phases. The mean of seven determinations was 1200 ±100, indicating that P_4 is lipophilic and has the potential to bioaccumulate.

Following the release of wastewater from a white phosphorus production facility in Newfoundland, numerous studies were performed on the bioaccumulation of P_4 in marine animals (Fletcher 1971, 1973, 1974). In animals exposed to aqueous solutions of P_4, white phosphorus was found to concentrate in fatty tissues. However, if the animals survived the exposure and were placed in uncontaminated water, the P_4 concentrations dropped below detectable levels. Similarly Clarkson (1991) reported that white phosphorus has been detected in the tissues of people who died within a few days following ingestion of white phosphorus but not in those that die after longer periods. These results are similar to those obtained in studies related to the P_4 contamination at Eagle River Flats. In carcasses of ducks from Eagle River Flats, P_4 concentrations were highest in the fat and skin (Racine et al. 1992a,b,c, 1993, Roebuck et al. 1994). Predators exposed to P_4-contaminated meat initially accumulated P_4 in fatty tissues; when contaminated meat was replaced by uncontaminated meat, P_4 concentrations in tissues dropped below detectable levels (Nam et al. 1994). Thus, P_4 is eliminated and does not bioaccumulate in the same manner as other lipophilic toxicants such as PCBs, which concentrate in upper trophic levels.

Vapor pressure

The vapor pressure of a liquid or solid is the pressure of the gas phase in equilibrium with the liquid or solid phase at a given temperature and is used to assess the tendency of a substance to evaporate.

The vapor pressure of solid P_4 has been measured over the temperature range –23 to 41°C and ranged from 0.0004 to 0.13 torr (Dainton and Kimberley 1950, Nesmeyanov 1963). At room temperature (20–25°C) the vapor pressure is 0.025–0.04 torr.

Van Wazer (1958) claimed that the following equation for vapor pressure of solid P_4 agrees with experimental data:

$$\log_{10}P\ (\text{torr}) = 1.9198 - (3.084\times10^{-3})T + 2.7763\log T - (2.641\times10^{3})/T - (3.258\times10^{4})/T^{2} \qquad (8)$$

which yields a pressure of 0.04 torr at 25°C (Fig. 6).

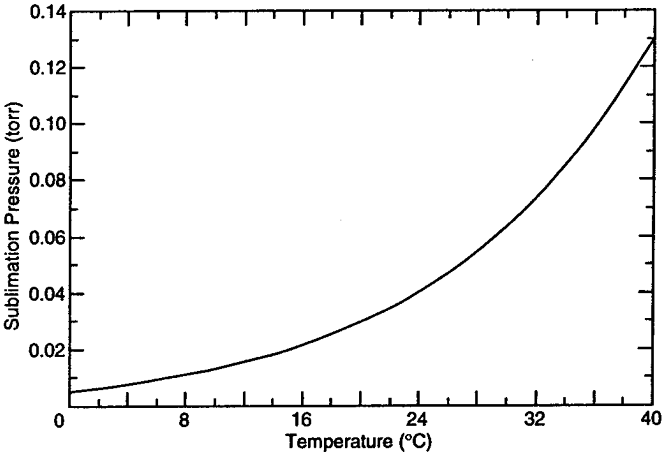


Figure 6. Calculated sublimation pressure for P_4.

At 25°C the vapor pressure of P_4 is on the same order of magnitude as many semi-volatiles such as naphthalene. Thus, sublimation could be a significant process in the environment, depending on temperature. In fact, sublimation of P_4 from soil was observed by Warnock (1972) when he investigated the potential use of white phosphorus as a source of plant-available phosphoric acid. During field studies, P_4 was observed to escape through the soil surface (concentrations higher than 0.01 mg/m^3, the threshold limit value, were measured in a vapor cloud above soil containing P_4). In the laboratory, 35 mg of P_4 as "pellets" (size not reported) were placed at depths of 2.5 and 10 cm in pots containing 750 g of two types of soil (acid and calcareous) of approximately 9% moisture. The air above each pot of soil was monitored for P_4 vapor for three days. The cumulative mass of P_4 in the air after three days was approximately 9.5 µg for the P_4 at 2.5-cm depth and 1.5 and 4.6 µg for the acid and calcareous soils with P_4 at the 10-cm depth (Table 2). In a second experiment the effect of soil moisture on the amount of P_4 vapor escaping from soils containing 35 mg of P_4 pellets at 5-cm depth was monitored for seven days. In all cases, P_4 was detected in the air above the soil (Table 2). There is no clear pattern as to the effect of soil type, soil moisture or length of time P_4 was monitored. Unfortunately soil temperatures were only measured intermittently and

Table 2. Mass of P_4 recovered as a vapor above soils containing 35 mg of P_4 pellets. (After Warnock 1972.)

Soil type	*Depth (cm)*	*Soil moisture (%)*	*Mass (µg) of P_4 recovered*						
			1	*2*	*3*	*5*	*6*	*7 days*	*Total*
Acid	2.5	8.6	6.4	2.5	0.5	*	*	*	9.4
Calcareous	2.5	9.3	3.1	4.9	1.6	*	*	*	9.6
Acid	10	8.6	1.1	0.2	0.2	*	*	*	1.5
Calcareous	10	9.3	1.8	1.6	1.1	*	*	*	4.6
Acid	5	4.3	2.3	1.0	0.5	2.2	1.2	0.3	7.5
Acid	5	11.2	2.2	0.6	5.0	0.3	1.7	0.9	10.7
Acid	5	18.1	1.3	2.8	0.5	0.5	0.7	0.2	5.8
Acid	5	31.9	1.8	0.8	0.3	0.6	1.1	0.3	4.7

* Not measured.

varied between 18 and 24°C. Given that the vapor pressure would vary between 0.025 and 0.041 torr over this temperature range, temperature effects could dominate the effects of soil type, moisture or time. In any case, the important observation is that there is experimental evidence for P_4 sublimation and escape from unsaturated soils.

Henry's constant

The Henry's Law constant is the ratio, at equilibrium, of the concentration (partial pressure) of an analyte in the vapor phase to the concentration (mole/L) in aqueous solution. It may be used to assess losses due to the transfer of P_4 from water to the atmosphere. Spanggord et al. (1985) measured the Henry's Law constant for P_4 as 2.1×10^{-3} atm-m^3/mole, so the mass transfer of P_4 from water to the atmosphere could be significant. Spanggord et al. (1985) estimated the volatilization half-life of dissolved P_4 in a turbulent stream to be 0.8 hours, which is faster than the oxidation half-life. This estimate is consistent with the results of Xulong et al. (1987), who found that agitation was the most significant factor contributing to the loss of P_4 in a treatment process for P_4-contaminated water.

Summary

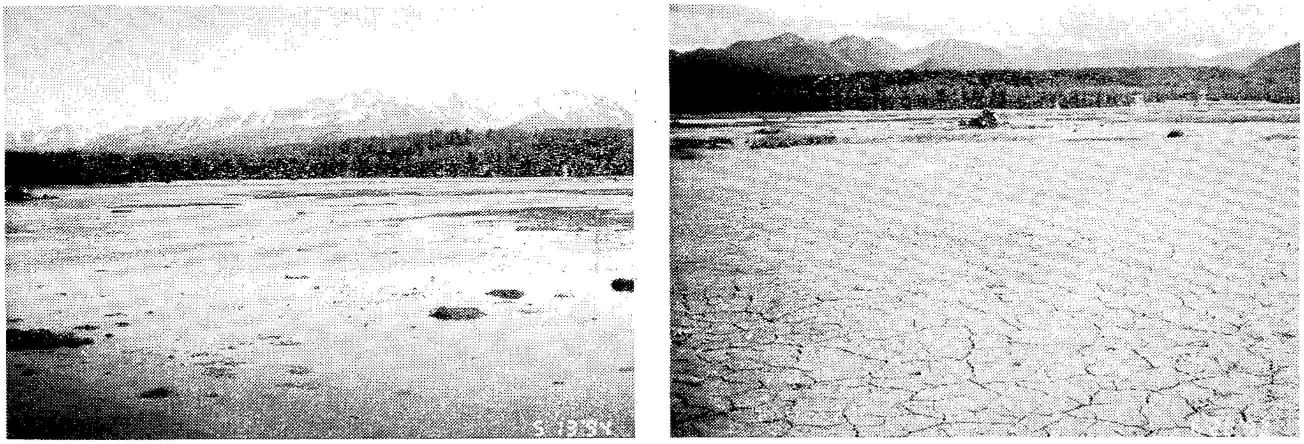
White phosphorus (P_4) is thermodynamically unstable in the presence of oxygen. In nature, phosphorus is found in oxidation state +5 as orthophosphate (PO_4^{-3}). When white phosphorus (oxidation state 0) is introduced into the environment, it will ultimately oxidize to orthophosphate, but the rate at which it oxidizes depends on the availability of oxygen and the state in which P_4 is introduced (vapor, solid or aqueous solution). Solid P_4 introduced into anoxic, saline aquatic environments is likely to persist indefinitely.

NATURAL SIZE REDUCTION OF WHITE PHOSPHORUS PARTICLES IN EAGLE RIVER FLATS SEDIMENTS

Background

Since 1990, when we identified white phosphorus as the cause of waterfowl deaths at Eagle River Flats (Racine et al. 1992a,b,c), methods have been discussed for decontaminating the sediments. Remedial techniques currently under investigation at Eagle River Flats (ERF) include dredging, covering and pond draining. To preserve as much habitat as possible and make the remedial process cost efficient, these techniques will most likely be used only in those areas where white phosphorus is persistent and will continue to threaten waterfowl.

While white phosphorus is extremely toxic (Clarkson 1991), it has the potential to form nontoxic phosphates. In the anoxic, saline sediments of permanently ponded areas of ERF, phosphate formation from solid, millimeter-size white phosphorus particles (Fig. 1) will be extremely slow. However, not all ponded areas of ERF are permanently covered with water. During some summers with extended periods between flooding high tides, the size of some ponds may be reduced significantly (Fig. 7). If exposed sediments become unsaturated and the sediment temperature rises, some in-situ decontamination may be occurring. Identification of these areas may reduce the total area that needs to be treated by some other remediation strategy.



a. Pond with water. *b. Same area with sediments exposed to air.*

Figure 7. Intermittent ponded area of Eagle River Flats.

In this work, natural decontamination of ERF sediments was investigated in three ways:

- A laboratory evaluation of the effect of sediment temperature and moisture on the persistence of P_4 particles in ERF sediments;
- A field investigation to determine if sediment moisture and temperature reach levels conducive to size reduction of P_4 particles in Eagle River Flats; and
- A field investigation of the pattern of P_4 contamination around previously tested sites in an intermittent ponded area to determine if the level of P_4 contamination had changed after exposure to air during the summer of 1993.

Incubation of P_4 particles at constant temperature and moisture content

Methods

To determine the effect of sediment temperature and moisture content on the persistence of P_4 particles in ERF sediments, P_4 particles of known diameter (approximately 2 mm) were placed at a depth of 3 cm in wet ERF sediment and the sediment was incubated in an environmental chamber at a constant temperature. Table 3 gives the experimental variables. The temperatures were selected to reflect sediment temperatures previously measured in Eagle River Flats. The moisture range was chosen to include unsaturated and saturated conditions. The sediment was contained in 8-×8-×6-cm plastic dishes, with one particle per dish. At discrete time intervals, samples were taken to determine if the P_4 particles had decreased in size. Particle sizes were measured directly with a micrometer, and gas chromatography (GC) was used to determine particle masses as well as residual P_4 that may be sorbed to the sediment or dissolved in the sediment moisture. Details of the methods used are given in Appendix A.

Table 3. Experimental parameters for the laboratory study on the effect of sediment temperature and moisture on the persistence of white phosphorus particles.

Treatments
Temperatures: 4 , 15, 20°C
Approximate degree of saturation: 0.4, 0.6, 0.8, 1, >1

Results

Precision and accuracy of the measurement of particle mass. Eight replicate particles produced in the laboratory from molten white phosphorus were dissolved in 20 mL of isooctane by shaking for two hours. For the P_4 concentration in the extract to be within the linear range of the GC detector, these solutions had to be diluted by a factor of 5000. Such a large dilution factor can contribute to a systematic error. The masses of the particles (Table 4), as determined by GC, were in the range of 7.8–8.4 with a mean of 8.1 mg. The relative standard deviation (RSD) for these measurements was only 3.2%. Therefore, the measurements were very precise; however, the masses were higher than expected. For a 1.8-mm particle, the mass should be approximately 6 mg. Our calibration standard was checked against one prepared independently at the Waterways Experiment Station and was found to have the same GC response within experimental error.

Table 4. Masses (mg) of eight replicate white phosphorus particles.*

Mass		*Mass*
7.97	mean =	8.09
8.33	max =	8.39
7.77	min =	7.77
8.35	std. dev. =	0.26
8.39	RSD (%) =	3.21
8.18		
7.77		
7.97		

* Found following dissolution in isooctane, dilution with isooctane and gas chromatographic analysis.

Recovery from sediment at various moisture contents. Triplicate sediment samples were prepared at each of the five moisture contents used in this experiment. One P_4 particle was placed in each sample, and then each sample was extracted with isooctane. The P_4 mass found in each sample was determined by isooctane extraction and gas chromatography and compared with the mass found in samples without sediment (Table 5). The average P_4 mass found in the sediment samples was 7.99 mg, which yielded an average recovery of 97.8%, based on the samples without sediment (8.17 mg).

Physical appearance of particles following incubation. Following incubation the physical appearance was noted of each particle that could be located (Table 6). Initially the particles were spherical and had a smooth surface and a lustrous, translucent appearance. Following incubation the most noticeable change in those particles where there

Table 5. Mass of white phosphorus particles found following solvent extraction of sediment at various moisture contents *s* and gas chromatographic analysis.

s	*Rep.*	*WP mass (mg)*	*Recovery (%)*
0.45	1	7.05	86.4
0.45	2	7.96	97.5
0.45	3	7.92	97.0
0.64	1	8.46	103.6
0.64	2	8.13	99.6
0.64	3	7.92	96.9
0.82	1	6.21	76.0
0.82	2	8.53	104.5
0.82	3	8.86	108.5
1	1	8.19	100.3
1	2	8.60	105.3
1	3	8.16	99.9
>1	1	8.27	101.3
>1	2	7.90	96.8
>1	3	7.66	93.8
no sediment	1	8.48	
no sediment	2	7.85	
mean =		8.01	97.8
std dev. =		0.57	
%RSD=		7.16	
high =		8.86	108.5
low =		6.21	76.0
range =		2.65	32.5

was change was a pitting or dimpling of the surface, which gave the surface a whitish color (Fig. 8). This dimpling may correspond to empty sediment pores through which P_4 vapor diffused. With time, particles decreased in size and became irregular in shape. Several particles that had maximum linear diameters of approximately 1 mm appeared to have horn-like protrusions. Gross changes in surface texture and particle

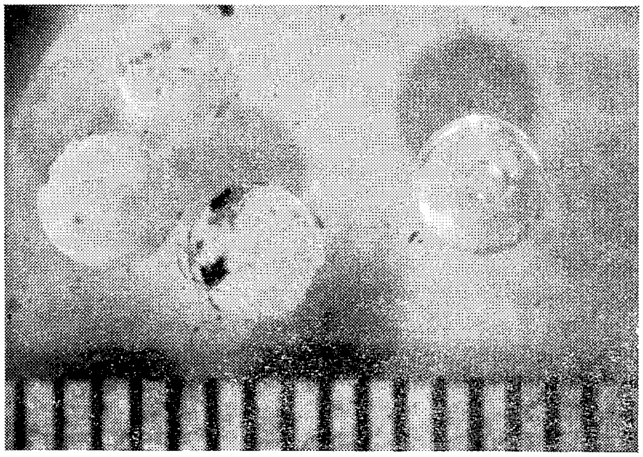


Figure 8. Surface texture of P_4 particles. The P_4 particle on the left is freshly made from molten P_4. Three particles on the right have been incubated in unsaturated sediment at 15°C for three days. Voids are visible on the surface of each particle, giving a dimpled appearance. Graduations on the ruler are 0.5 mm.

Table 6. Physical appearance of WP particles incubated at five moisture contents and three temperatures.

Temp (°C)	*No. of samples examined*	*No. of particles found*	*Surface appearance*								
			Spherical	*Smooth*	*Pitted*	*Lustrous*	*White*	*Orange*	*Colorless*	*Translucent*	*Smoking*
***s* = 0.45**											
4	14	14	10	7	13	10	6	0	11	14	0
15	13	11	9	1	9	3	8	0	2	11	0
20	6	0									
***s* = 0.64**											
4	14	14	13	10	5	13	3	0	12	14	0
15	13	10	10	2	8	4	5	0	5	10	0
20	6	0									
***s* = 0.82**											
4	12	12	12	12	1	12	1	0	12	12	0
15	15	6	4	3	2	6	0	1	3	6	0
20	10	6	5	5	1	5	0	0	4	6	4
***s* = 1**											
4	10	10	10	10	0	10	0	0	10	10	0
15	12	12	12	12	0	10	1	7	7	11	0
20	10	10	9	9	2	8	0	0	8	8	5
***s* >1**											
4	11	11	11	11	0	11	0	0	11	11	0
15	12	12	12	12	0	12	0	3	12	12	1
20	10	10	10	10	0	10	0	0	10	10	0

size were only evident in those particles incubated at moisture contents below saturation. Almost all particles were translucent, and there was no evidence of the oxidized coating that forms when P_4 is stored in water. Some particles developed an orange tinge over part of the surface, similar to the color that develops when P_4 is exposed to light. This color change may have been an artifact from the microscope light used to locate the particles.

The particles were difficult to locate. The moist sediment surrounding the particles was not visibly changed. Some unsaturated samples ($s = 0.64$) that were incubated at 20°C for 10 days were allowed to air-dry. Then a razor blade was used to slice through the region where the particle was planted. In each case, a small (1.8-mm), spherical void with smooth sides was found. Sediment surrounding the void was slightly lighter in color then the rest of the sediment. Previously we have observed the formation of a dark, wet, phosphate-rich halo around P_4 particles in very dry sediments (<10% moisture) (Racine et al. 1994) (Fig. 9). Sediments for this experiment were always moist; therefore, water-soluble oxidation products could freely diffuse away from the particle. Occasionally a whiff of "smoke" was visible when the sediments were probed (Table 6). In almost all cases, the sediment had to be sieved to find the P_4 particle. In three instances, one at each temperature tested, the particle was located without sieving, and the sediment in direct contact with particle was analyzed. P_4 concentrations in this associated sediment were 0.2 (4°C), 0.5 (15°C) and 6.6 µg/g (20°C).

Figure 9. Void in dry sediment formed as P_4 particle sublimed. Dark-colored hygroscopic oxidation products are visible in the sediment surrounding the void.

Residual mass of P_4 particles. P_4 particles were recovered from all samples incubated at 4°C. At this low temperature, there were no significant reductions of the masses of P_4 particles found, except the particles isolated at the last sampling interval (58 days) at the lowest moisture content (Fig. 10a), where the mass for each particle was approximately half that of the original mass.

For samples incubated at 15°C (Fig. 10b), there were no changes in particles incubated at saturation or above; however, there were significant reductions in particles incubated at the two lowest moisture contents ($s = 0.45$ and 0.64) during 30 days of incubation. Following incubation for 57 days at 15°C, no P_4 was detected in the samples at the two lowest moisture contents. At $s = 0.82$, P_4 loss was inconsistent. P_4 was undetectable in some samples after only one week of incubation but was persistent in other samples for 38 days, the last sample taken.

At 20°C (Fig. 10c) there were no changes in particles incubated at saturation or above; however, there were significant reductions in particles incubated at the two lowest moisture contents ($s = 0.45$ and 0.64) after only one day of incubation. Again at $s = 0.82$, P_4 loss was inconsistent. P_4 was undetectable in some samples after only 10 days of incubation but was persistent in other samples for over 20 days (the last sampling interval).

Based on the data obtained in the laboratory, persistence for 2-mm-diameter particles can be estimated. In a previous study, most particles isolated from Eagle River Flats sediments were smaller than 2 mm (Racine et al. 1993). For moist sediments that were well below saturation ($s < 0.6$) at 20°C, 99.9% of the mass was lost in one day and 99.999% was lost by 10 days. At 15°C, 99.9% was lost by 30 days and >99.999% was lost by 60 days. Only a 50% loss was observed at 4°C at the lowest moisture content after 56 days; thus, at this low temperature, particles can persist for several months or longer in unsaturated sediments. Since no loss of mass was observed in saturated sediments at any temperatures, P_4 particles can be assumed to persist indefinitely in saturated sediments. For sediments that have moisture contents slightly less than saturation, loss of P_4 mass can occur but at an unpredictable rate.

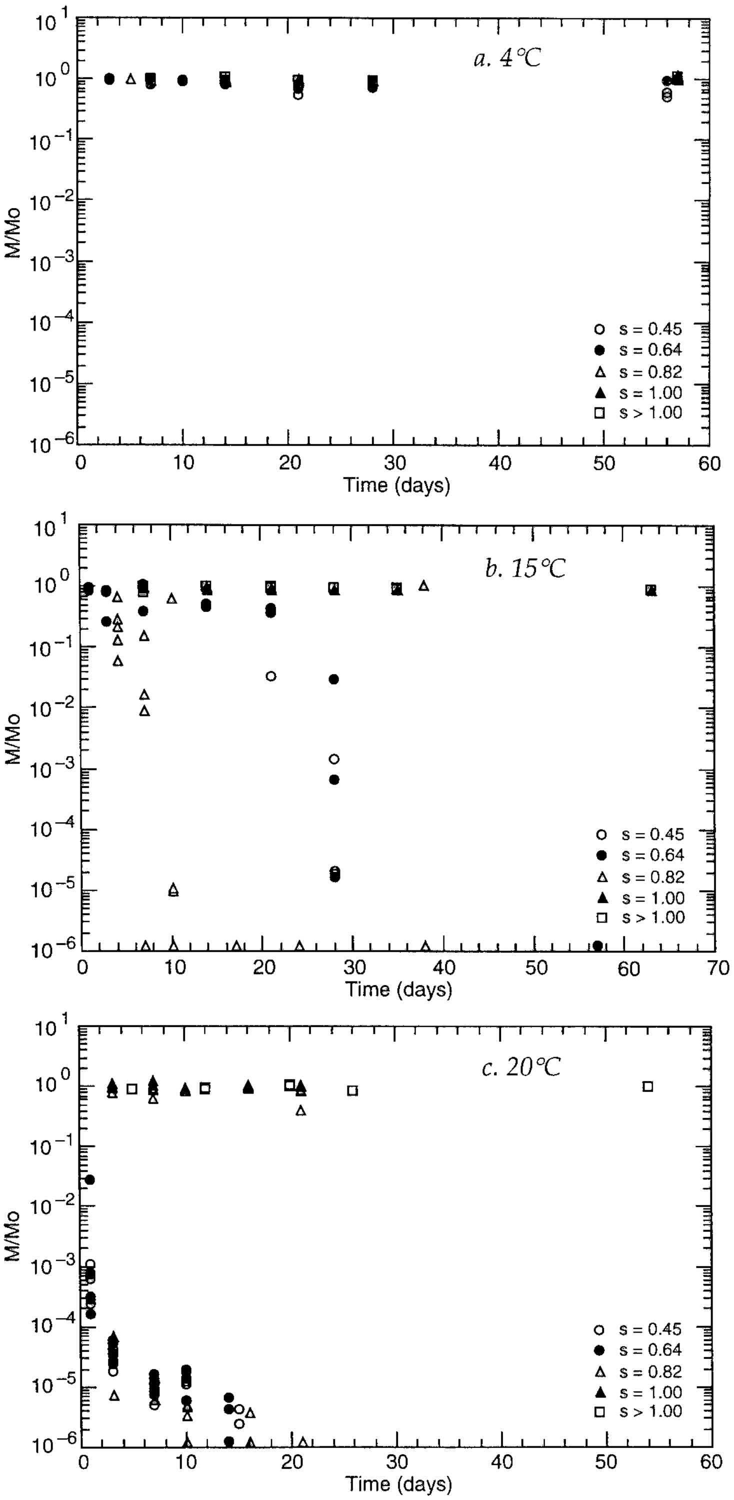


*Figure 10. Residual mass (*M*) of white phosphorus particles found following incubation in sediments at various moisture contents and temperatures normalized to the average initial mass (*Mo*) of white phosphorus.*

The difference in length of persistence at 20°C and 15°C in unsaturated sediments may be due to oxidation. As discussed earlier, P_4O_{10} is formed by a branching-chain reaction (Dainton and Bevington 1946, Dainton and Kimberley 1950). The reaction is slow unless the partial pressures of oxygen and P_4 vapor are within certain limits. Since the lower limit is inversely proportional to the pressure of P_4, the vapor pressure at 15°C may be below the critical pressure for a fast reaction. A value for the critical pressure is difficult to predict since it also depends on the diameter of the reaction vessel, in this case, the pore diameter. The "wall" of the vessel terminates the reaction by scavenging the oxygen atoms, which are the chain centers. The vapor pressure at 20°C may be high enough for a fast reaction. Since the oxidation of intermediate products (P_4O_n, $n = 2...9$) to P_4O_{10} is highly exothermic, the temperature surrounding the particle will rise. Any rise in temperature near the surface of the P_4 particle would be accompanied by an increase in vapor pressure, and therefore greater production of P_4O_{10} and more heat, until the supply of P_4 falls below the critical pressure as the particle diminishes in size.

Oxygen is not required for the loss of P_4 in unsaturated conditions. The vapor pressure is high enough that loss will occur as long as there is free pore space and hence gas exchange between sediment air and the atmosphere. For example, when field-contaminated sediments were dried at room temperature under nitrogen and under air, the loss was the same after 60 days (Walsh et al. 1993). The formation of oxidation products in the pore spaces surrounding P_4 particles may actually slow loss by forming a diffusion barrier.

In our laboratory experiment, sediment moisture was the more important of the two factors tested in terms of persistence of P_4 in ERF sediments. As a solid particle in saturated sediment, P_4 is persistent. However, in sediment with free pore space, P_4 can change to the vapor phase and diffuse away or be oxidized. Factors that slow the change of P_4 from a solid to a vapor are the same as those that limit diffusion. Diffusion continues as long as there is free pore space (Baver 1956). Free pore space, however, is reduced by compaction or increased wetness.

Monitoring sediment moisture and temperature in Eagle River Flats

Methods

Eagle River Flats (ERF) is an 865-ha estuarine salt marsh at the mouth of the Eagle River on Knik Arm in upper Cook Inlet (Fig. 11). As described by Racine et al. (1993), the main channel of the Eagle River meanders generally through the middle of 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 affects salinity, frequency of tidal inundation and sedimentation rate. Permanent ponds along the edge of ERF are also influenced by freshwater influx.

The field experiment to monitor sediment temperature and moisture was conducted in a part of ERF known as "Area C" (Fig. 12). Located on the east side of the Eagle River, Area C includes a single large pond and several interconnected smaller ponds and inlets (Fig. 13). The main pond (10 ha) is bordered by bulrush and sedge marsh to the east and south, mudflats to the west and deeper small pools with bulrush marsh to the north. Fresh water enters from the east edge, and three distributary channels drain the area to the west. Distributary channels also allow tidal inflow into the pond during flooding high tides. The frequency of flooding during the summer depends on the maximum height of the monthly series of peak high tides. Monthly peak high tides above about 31 ft at Anchorage (or about 4.79 m mean sea

Figure 11. Aerial view looking south across Eagle River Flats.

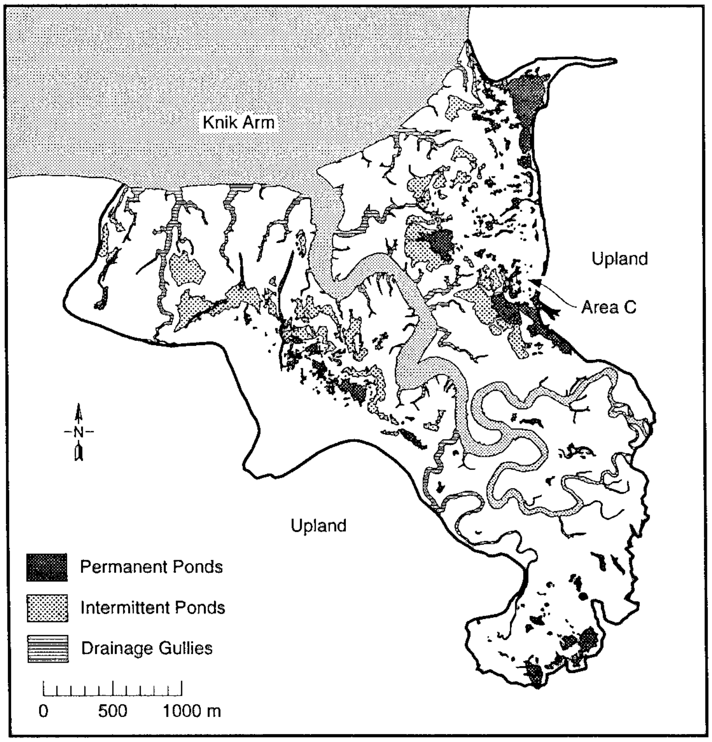


Figure 12. Eagle River Flats, showing the location of Area C, as well as the river, drainage gullies and intermittent and permanent ponds.

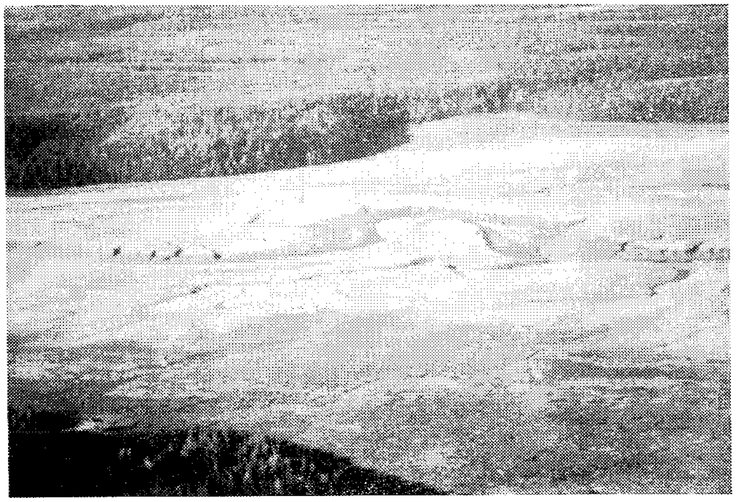


Figure 13. Area C, showing bulrush marsh, permanent ponds, intermittent ponds, mudflats and levees.

level) will fill the pond basin. During the summer of 1994, flooding high tides occurred on May 24–27, June 23–25 and September 6–9.

Area C contains several targets and impact craters and has been a focus of study for waterfowl mortality and sediment sampling (Racine et al. 1992a,b,c, 1993). Most of the white phosphorus contamination was detected in the permanently flooded sections (Fig. 14).

The gradual change in elevation along the east–west transect from the main pond in Area C to the levee next to the Eagle River results in a gradient in the duration of exposure of the sediments to air (i.e. lower elevations are covered with standing water for a longer time than higher elevations). Exposed sediments have the potential to become unsaturated during periods without standing water. In this study, sediment

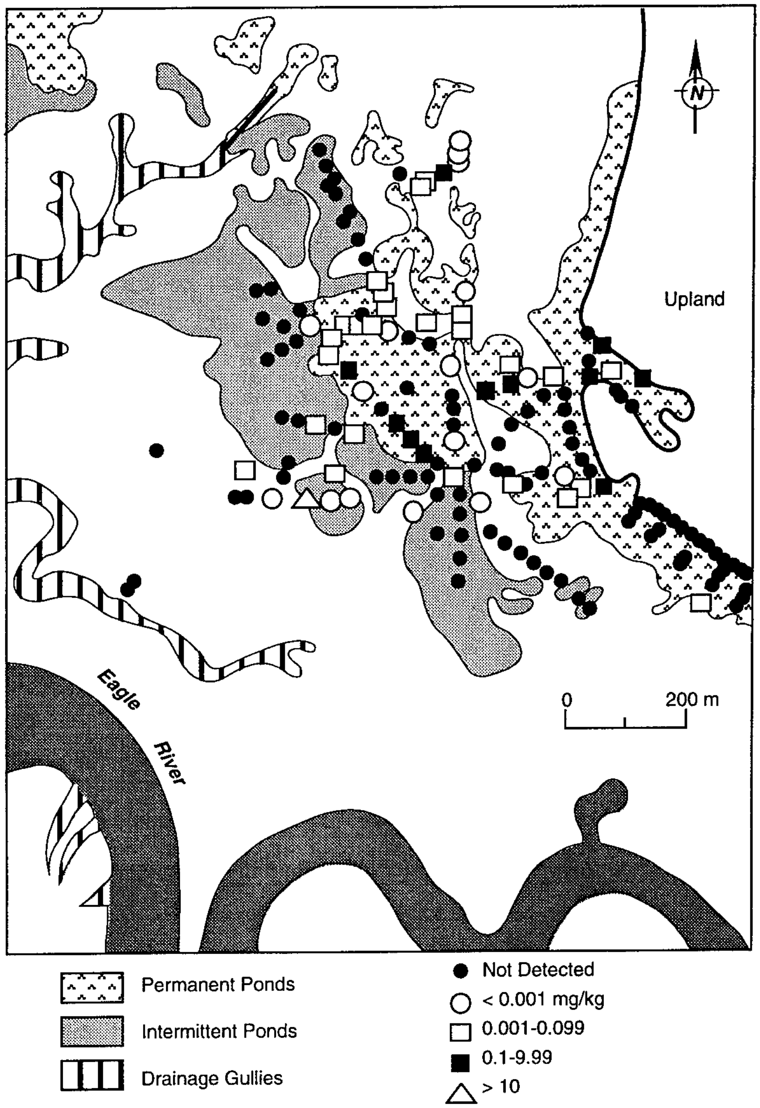


Figure 14. Sampling locations in Area C and results of sediment analyses for white phosphorus.

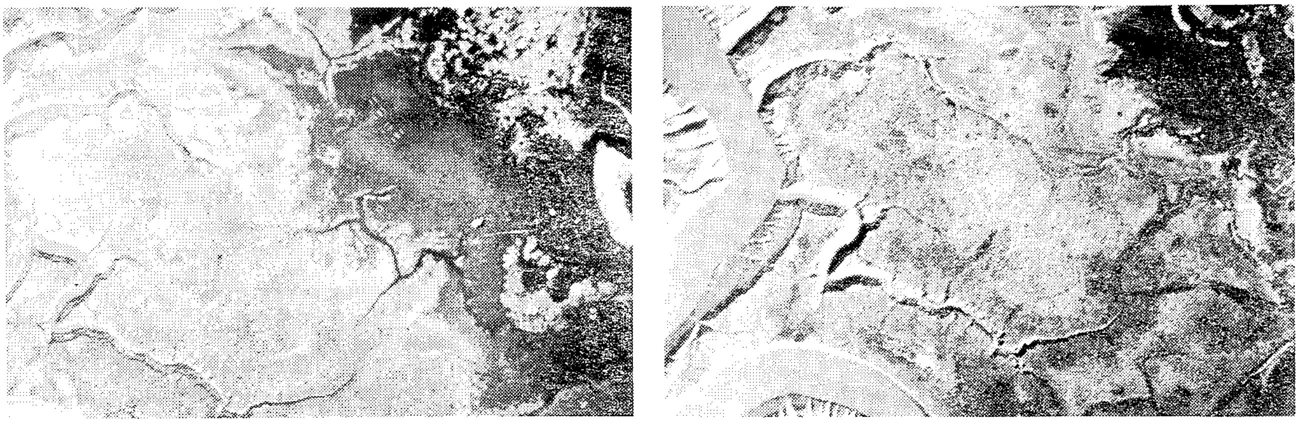
moisture and temperature at ten sites along the east–west transect (Fig. 15, 16 and 17) were monitored to see if conditions are conducive to natural attenuation of P_4 during some part of the summer. Universal Transverse Mercator coordinates and elevations for the ten study sites in Area C are given in Table 7. The overall length of the transect was 636 m, with a total elevation change of 0.52 m (Fig. 16). Water quality measurements were made in May when the ponds were full (Fig. 18), and vegetation was recorded in August (Fig. 18).

In addition, P_4 particles, produced in the laboratory as described above, were planted at each site and recovered at the end of the summer to see if the mass of the P_4 particles decreased. Details of the procedures used are given in Appendix B.

Results

Site characteristics. The conductivity of the water in the ponded sites increased towards the west (towards the river) (Table 8). The water at each site was slightly alkaline, and reducing conditions (i.e. low redox potentials) were found in the sediments at each site.

Vegetation varied significantly between sites (Table 8). The permanently flooded site (site 1) had a dense stand of mare's tail (*Hippurus tetragona*) (Fig. 19). The intermittent pond sites (sites 2–5) were mostly bare, with a few arrowgrass seedlings and glasswort (Fig. 20). Mudflat sites (6 and 7) were sparsely vegetated with alkali grass and arrowgrass (Fig. 21). The density of vegetation was higher at the mudflat site closest



a. In May 1992, when ponds were full.

b. In August 1994, when ponds were low. The transect is visible as a thin line running east–west from a permanently flooded zone to the east through the intermittent ponded area, across the mudflat zone to the levee adjacent to the Eagle River.

Figure 15. Aerial view of Area C.

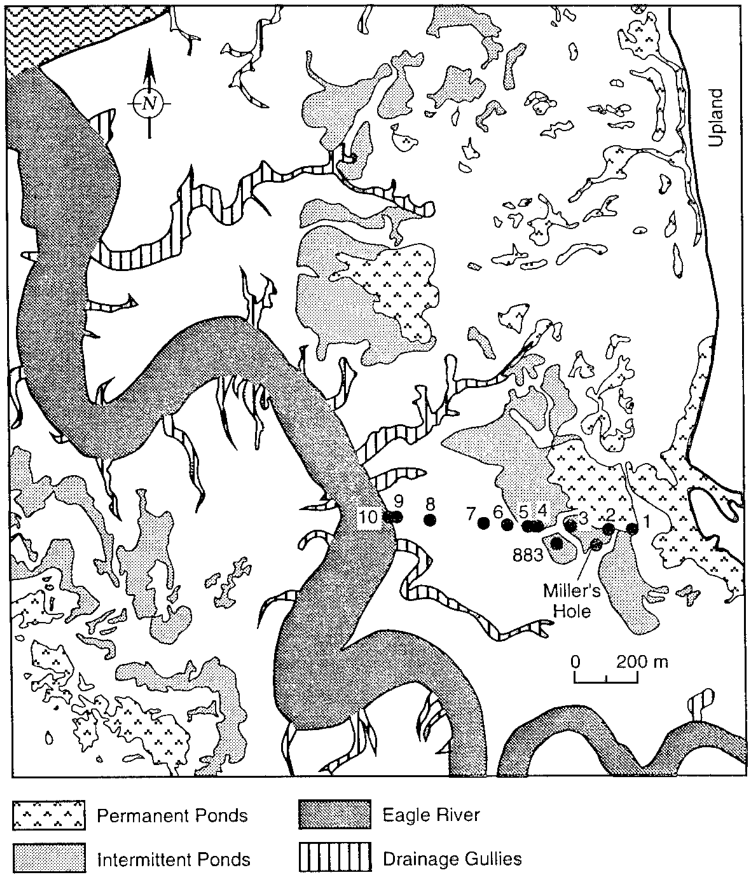


Figure 16. Locations of study sites in Area C. Sediment temperature and moisture were monitored and white phosphorus particles incubated between May and August at sites numbered 1 to 10. Sites 883 and Miller's Hole are field-contaminated sites which were sampled to determine P_4 concentrations.

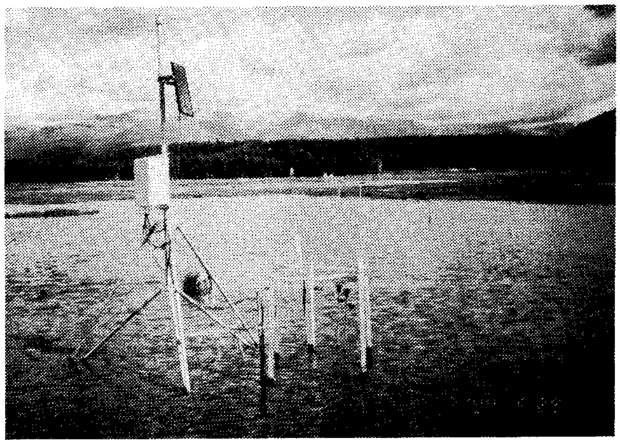
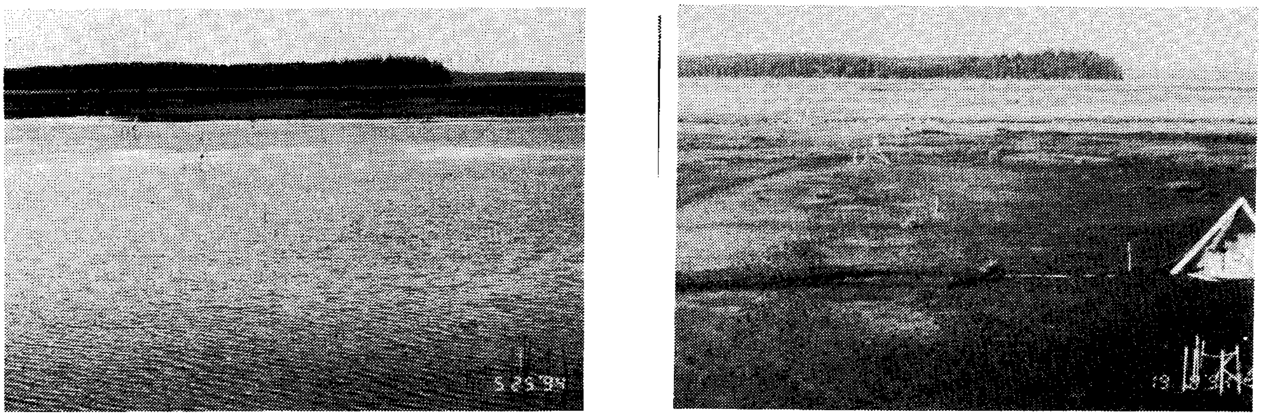


Figure 17. Study site in an intermittent pond area showing the datalogger with a solar panel mounted on a tripod. Data for sediment moisture and temperature were recorded every 10 minutes and averaged hourly from May 25 to August 26. Lath surrounds area where P_4 particles were planted. Tensiometers and the piezometer are also visible.



a. May.

b. August.

Figure 18. View looking west along transect across an intermittent pond area.

Table 7. UTM coordinates and elevations of sites in Area C where sediment temperatures and moisture levels were monitored and white phosphorus particles incubated, May–August, 1994.

Field site	*UTM coordinates* *Easting*	*Northing*	*Distance between sites (m)*	*Elev. (m)*	*Elev. change between sites (m)*	*Site descriptor*
1	355,171.6	6,801,180.4		4.70		Permanently saturated
2	355,105.8	6,801,192.5	66.9	4.74	0.04	Intermittent pond area
3	355,013.4	6,801,197.7	92.5	4.78	0.04	Intermittent pond area
4	354,917.7	6,801,208.1	96.3	4.80	0.02	Intermittent pond area
5	354,893.5	6,801,212.1	24.5	4.85	0.05	Intermittent pond area
6	354,836.9	6,801,216.9	56.8	4.87	0.02	Mudflat
7	354,713.4	6,801,230.2	124.2	4.92	0.05	Mudflat
8	354,593.0	6,801,243.0	121.1	4.99	0.07	Mudflat
9	354,553.3	6,801,247.3	39.9	5.06	0.07	River levee
10	354,539.1	6,801,248.7	14.3	5.22	0.16	River levee

Table 8. Water quality measurements and vegetation at sites in Area C where sediment temperatures and moisture levels were monitored and white phosphorus particles incubated, May–August, 1994.

	Water quality (May 1994)				
Site	*Depth (cm)*	*Cond. (mmho/cm)*	*Redox (mvolts)*	*pH*	*Vegetation (August 1994)*
1	12	17.1	–177	7.7	Mare's tail (*Hippurus tetraphylla*)
2	8	17.6	–169	8.3	Unvegetated
3	4.5	18.6	–182	8.5	1% arrowgrass (*Triglochin maritima*) seedlings
4	2	24	–111	8.6	1% glasswort (*Salicornia europea*)
5	1	24	–55	8.7	1% glasswort, arrowgrass seedlings
6	0				Alkali grass (*Puccinelia hultenii*), arrowgrass
7	0				Alkali grass, arrowgrass, 40% bare ground
8	0				Goose tongue (*Plantago maritima*), alkali grass, arrowgrass, kenipod (*Atriplex gmelini*), cinquefoil (*Potentilla egedii*), 20% bare ground
9	0				Beach rye (*Elymus arenarius*), cinquefoil
10	0				Goose tongue, beach rye (40%), cinquefoil

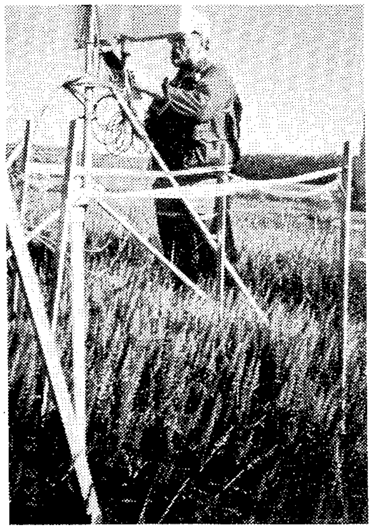


Figure 19. Permanently flooded site (site 1) with a dense stand of Hippurus tetragona.

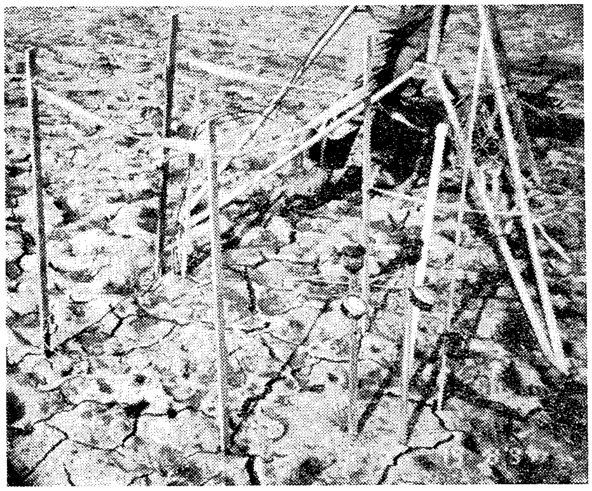


Figure 20. Site in an intermittent pond in August. The surface is cracked and covered with precipitated salt. A few glasswort and arrowgrass seedlings punctuate the mostly bare sediment.

to the river levee (site 8) with the addition of goose tongue, kenipod and cinquefoil to the stand of alkali grass and arrowgrass. The two river levee sites were densely vegetated with a tall stand of beach rye (Fig. 22).

Gravimetric moisture content measurements were obtained in May (Table 9) while sediments were saturated at the pond and mudflat sites. River levee sediments did not appear to be saturated when sampled. Samples were taken again in June just prior to a flooding high tide, then again in August. At the two later sampling times, the moisture contents were less than in May at all sites except the permanently flooded site. The dry bulk density generally increased with depth, mostly likely due to consolidation from freeze–thaw cycles, earthquakes, wet–dry cycles etc. Tensiometer and moisture probe resistance measurements were plotted vs. moisture content for depths of 10 and 25 cm (Fig. 23) to determine the moisture contents for saturation for undisturbed sediments under field conditions. Both measurements indicate saturation for sediments with moisture contents above 40% (dry weight basis) at 10 cm and above 35% at 25 cm. These moisture contents are lower than that determined for the homogenized sediment in the laboratory, most likely due to consolidation in the field.

The highest temperatures were measured at a depth of 5 cm, and temperatures at 10 cm were only slightly less than at 5 cm (Fig. 24). The average temperatures at 5 cm deep were between 16

Figure 21. Site on a mudflat vegetated with alkali grass and arrowgrass.

Figure 22. Site on a river levee with a tall stand of beach rye.

Table 9. Measurements of moisture contents obtained in May, June and August 1994, and measurements of dry bulk density obtained in August 1994.

Site	Depth (cm)	Moisture content (% dry weight basis) May 14	May 19	June 21	August*	Dry bulk density* (g/cm³)
Permanently flooded						
1	5	124	119		107	0.72
1	10		61		88	0.87
1	20	59	44	34	35	1.41
1	30	39	39	33	33	1.53
Intermittent pond						
2	5	56	78	64	46	1.18
2	10		61	48	39	1.27
2	20	42	47	39	33	1.32
2	30	36	36	30	31	1.38
3	5	45	63	48	42	1.21
3	10		49	48	38	1.25
3	20	44	46	40	36	1.27
3	30	35	41	30	30	1.40
4	5	63	62	42	37	1.27
4	10	48	50	38	37	1.24
4	20	42	46	37	34	1.28
4	30	42	41	34	29	1.39
5	5	54	62	43	37	1.28
5	10	49	48	43	35	1.25
5	20	42	39	37	34	1.32
5	30	44	38	34	31	1.41
Mudflat						
6	5	50	44	40	35	1.34
6	10	42	41	35	35	1.36
6	20	42	41	36	33	1.38
6	30	39	38	36	34	1.31
7	5	48	49	38	40	1.26
7	10	46	41	39	35	1.32
7	20	39	38	33	33	1.40
7	30	42	37	34	34	1.31
8	5	45	48	36	37	1.19
8	10	41	41	34	30	1.25
8	20	38	39	32	29	1.38
8	30	38	37	32	31	1.38
River levee						
9	5	35	35	30	31	1.19
9	10	31	36	30	29	1.11
9	20	31	36	30	27	1.16
9	30	31	33	30	29	1.39
10	5	36	36	31	30	1.30
10	10	35	35	29	25	1.26
10	20	32	32	27	26	1.21
10	30	31	32	28	29	1.35

* Site 3 on Aug. 20, Sites 7, 8, 9 and 10 on Aug. 22, Sites 2, 4 and 5 on Aug. 23, Site 1 on Aug. 24.

and 17°C for the ponded and mudflat sites and 15°C on the river levee. The date of the maximum average hourly temperature at 5 cm occurred in June in the ponded sites and in June or July in the mudflat sites (Table 10). Each of these days had over 10 hours of sunshine (NOAA 1994). The average temperatures were lowest at 30 cm deep (15°C for ponded and mudflat sites and 13°C for levee sites), and the date of maximum temperature occurred later than at shallower depths.

The time periods when sediments were unsaturated are indicated by an increase in the moisture probe resistances (Fig. 25 and 26). The length of time the top 5 cm of sediment was unsaturated increased with increasing elevation (Fig. 27). Over the time period monitored, site 1, with the lowest elevation, was always saturated, while site 10, the highest elevation, was always unsaturated (Table 10). Unsaturated sediments were detected at 5 cm deep at the two intermittent ponded site

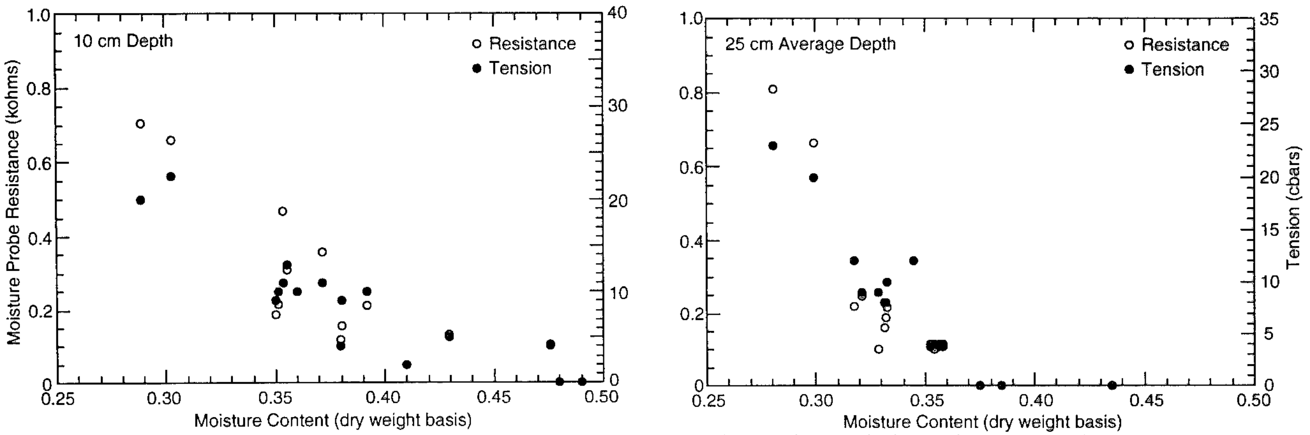
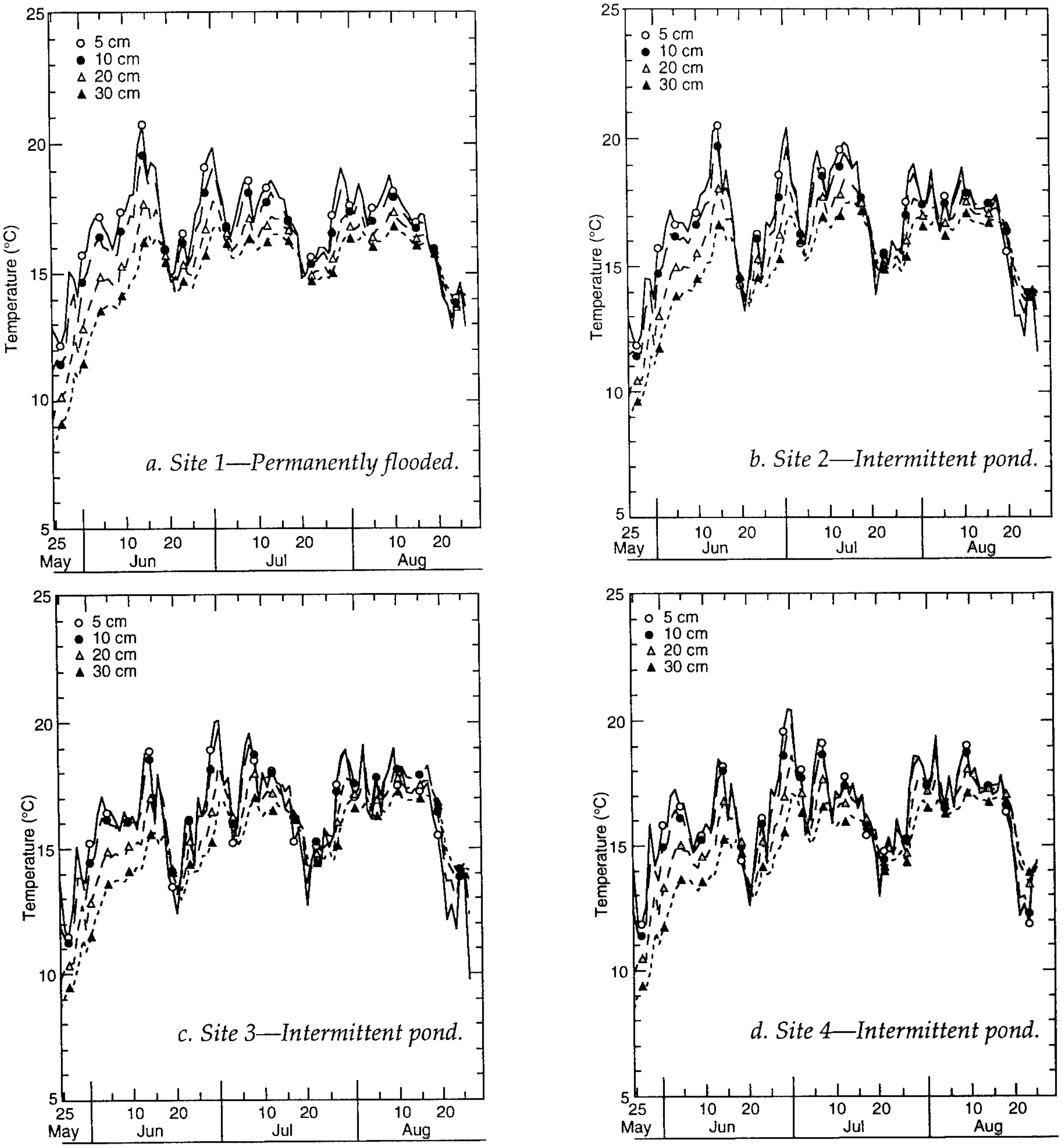


Figure 23. Moisture probe resistance and tensiometer readings obtained along the transect in Area C.



a. Site 1—Permanently flooded.

b. Site 2—Intermittent pond.

c. Site 3—Intermittent pond.

d. Site 4—Intermittent pond.

Figure 24. Daily (24-hour average) temperatures at 5, 10, 20 and 30 cm deep at each site.

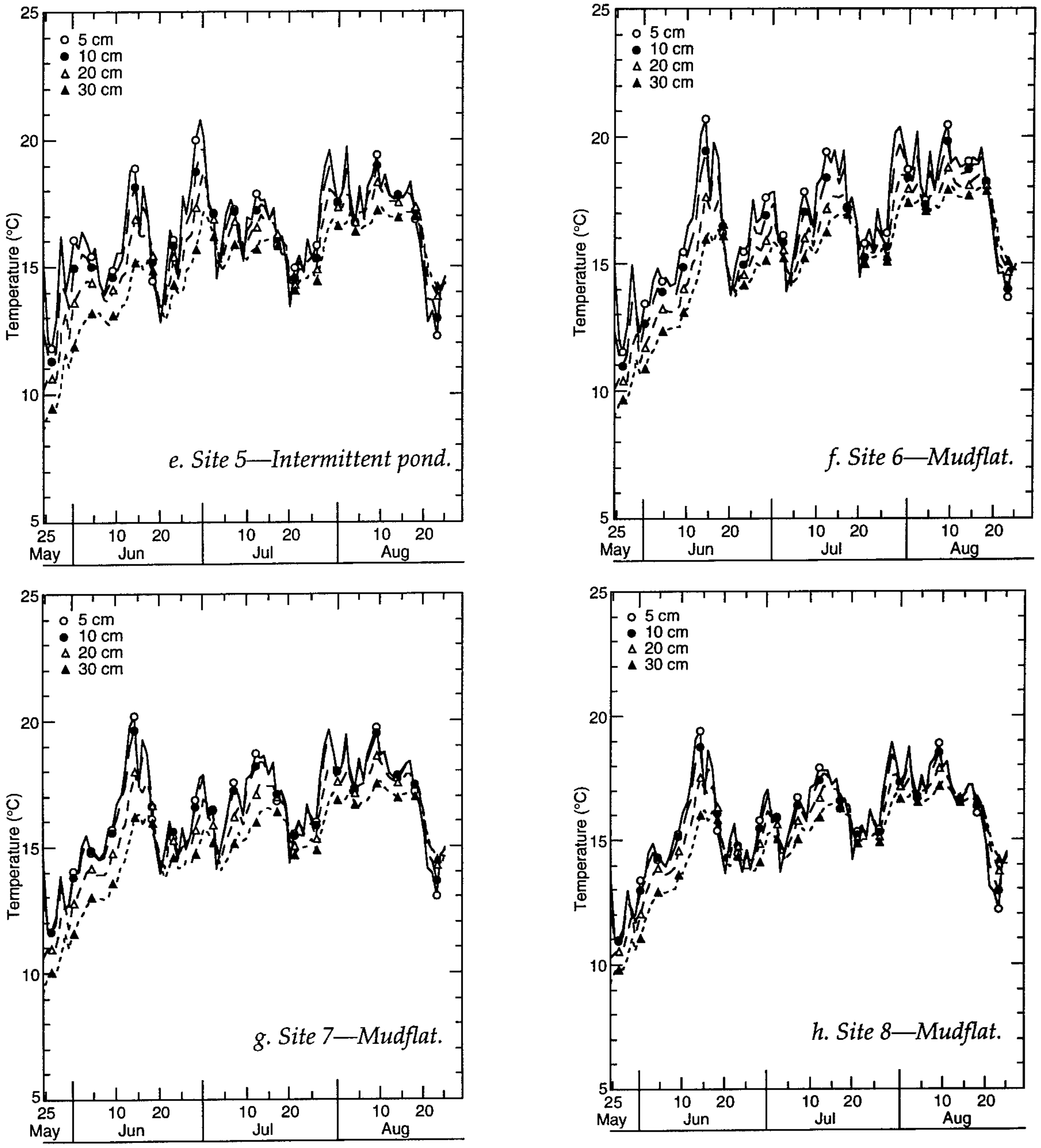
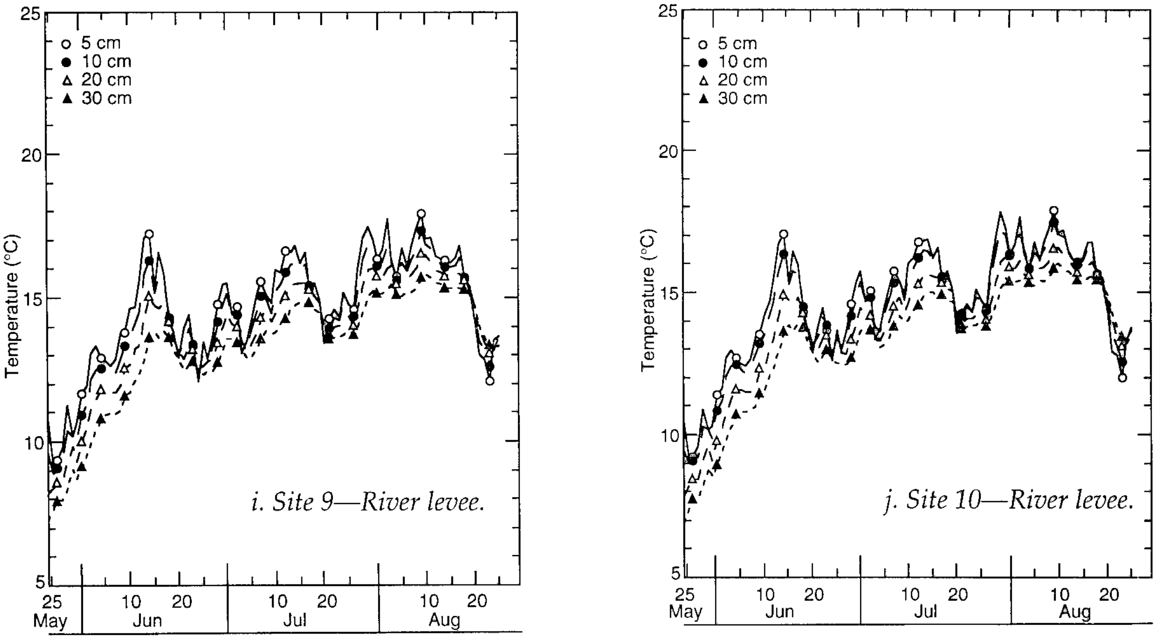


Figure 24 (cont'd).

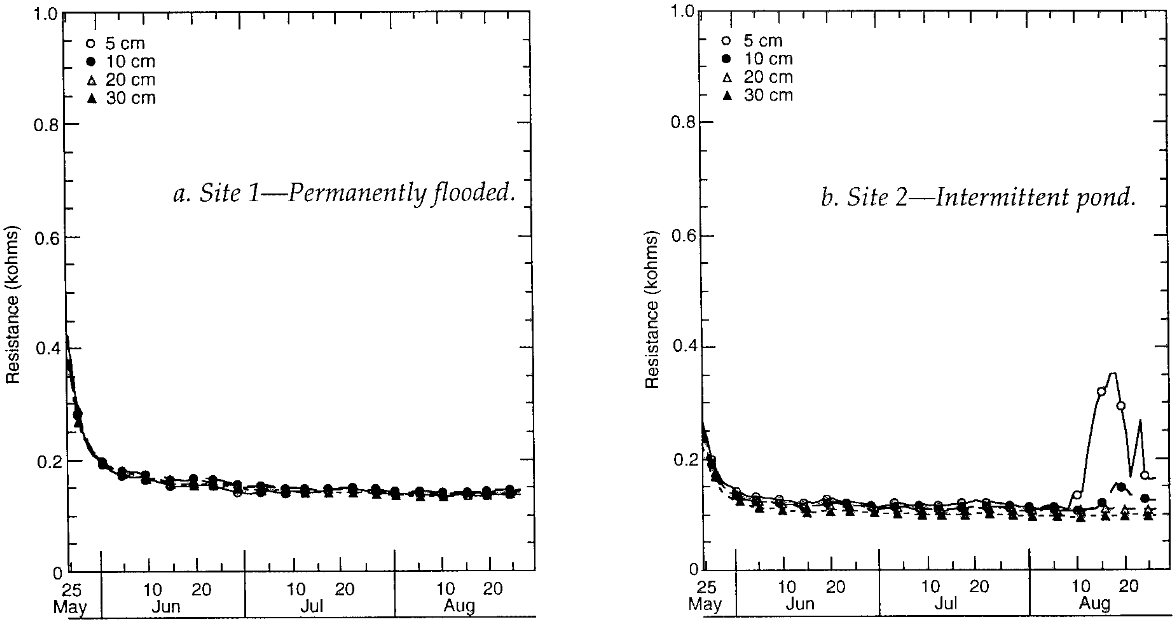
closest to site 1 (sites 2 and 3) starting August 12 and July 31, respectively. The remaining mudflat and intermittent ponded sites became unsaturated at 5 cm deep in June but were rewetted by the flooding high tides of June 23–25. Because of this rewetting, most of these sites were saturated during the part of the summer when the potential solar radiation is at its maximum. Unsaturated conditions were detected again in July and persisted over the period monitored. Unsaturated conditions were detected later with increasing depth. Unsaturated conditions were detected down to 30 cm deep at sites with elevations of ≥4.8 m (sites 4–10) (Fig. 25, Table 10).

Air-entry pressure. Based on the moisture characteristic curve for a sample collected from the intermittent pond area (Fig. 28), the air-entry pressure was approximately 5 cbars for this fine-grained sediment. In the field a pressure of this magnitude can occur by a drop in water table such that the equivalent head pressure between the surface of the sediment and the surface of the water table is 5 cbars. By expressing pressure in units of "cm of water" (10.2 cm of water = 1 cbar), we can estimate that a drop in the water table of 51 cm would result in air entry or desaturation of


i. Site 9—River levee.

j. Site 10—River levee.

Figure 24 (cont'd). Daily (24-hour average) temperatures at 5, 10, 20 and 30 cm deep at each site.


a. Site 1—Permanently flooded.

b. Site 2—Intermittent pond.

Figure 25. Daily (24-hour average) moisture probe resistance at 5, 10, 20 and 30 cm deep at each site.

Table 10. Maximum, average, median and minimum temperatures and periods below saturation measured at 5, 10, 20 and 30 cm deep at each site between May 25 and August 26 or 27, 1994.

Site	*Maximum temperature (℃)*	*Date of maximum temperature (℃)*	*Average temperature (℃)*	*Minimum temperature (℃)*	*Hours > 20℃*	*Dates below saturation*	*Hours > 20℃ and unsaturated*
5 cm deep							
1	23	June 15 20:00	17	11	191	none	0
2	24	June 14 20:00	17	8.9	357	Aug. 12–end*	44
3	26	June 30 18:00	16	6.8	392	July 31–end	88
4	26	June 30 18:00	16	6.6	381	June 18, July 20–21, July 28–end	150
5	27	June 30 17:00	16	8.1	412	June 18, July 20–end	169
6	26	July 29 18:00	17	7.2	491	June 18–20, July 20 – end	258
7	26	June 14 18:00	16	7.3	354	June 18–21, July 15–end	217
8	24	June 14 18:00	16	6.7	239	June 12–24, July 9–end	209
9	21	July 29 18:00	15	5.5	39	May 31–June 24, June 27–end	39
10	20	Aug. 3 17:00	15	6.3	30	May 31–end	0
10 cm deep							
1	21	June 15 23:00	16	10	47	none	0
2	22	June 14 22:00	17	10	193	Aug. 18–end†	0
3	22	June 30 21:00	16	10	175	Aug. 16–end	23
4	23	June 30 20:00	16	9.5	194	July 29–end	88
5	23	June 30 20:00	16	9.8	194	July 29–end	103
6	23	June 15 20:00	16	8.6	283	June 18–20, July 20 – end	186
7	23	June 15 19:00	16	9.0	232	June 18–21, July 15–end	159
8	21	June 15 20:00	16	9.0	49	June 12–24, July 9–end	49
9	18	Aug. 3 20:00	14	7.5	0	May 31–June 24, June 27–end	0
10	19	July 30 20:00	14	7.6	0	May 31–end	0
20 cm deep							
1	19	June 16 02:00	16	9.0	0	none	
2	19	July 16 24:00	16	9.4	0	none	0
3	19	July 1 23:00	16	9.2	0	none	0
4	19	July 1 24:00	16	9.1	0	Aug. 8–end†	0
5	20	July 1 24:00	16	9.2	10	Aug. 1–end	0
6	20	Aug. 10 22:00	16	9.2	3	July 30 – end	3
7	19	Aug. 10 22:00	16	9.2	0	June 20–21, July 16–end	0
8	19	June 15 23:00	16	8.7	0	June 12–24, July 9–end	0
9	17	Aug. 10 22:00	14	7.3	0	May 31–June 24, June 27–end	0
10	17	Aug. 10 23:00	14	7.0	0	May 31–end	0
30 cm deep							
1	17	July 2 07:00	15	8.1	0	none	0
2	18	July 16 04:00	15	8.8	0	none	0
3	18	Aug. 19 02:00	15	8.5	0	none	0
4	18	Aug. 11 03:00	15	8.3	0	Aug. 13–end	0
5	18	Aug. 11 02:00	15	8.4	0	Aug. 4–end	0
6	18	Aug. 19 02:00	15	8.8	0	Aug. 5–end	0
7	18	Aug. 11 03:00	15	8.9	0	July 17–end	0
8	18	Aug. 11 02:00	15	9.0	0	June 15–24, July 11–end	0
9	16	Aug. 11 04:00	13	7.1	0	May 31–June 24, June 29–end	0
10	16	Aug. 11 04:00	13	6.7	0	May 31–end	0

* End of time period in which data were recorded (Aug. 26 for Sites 4-10, and Aug. 27 for Sites 1–3). Flooding tide occurred on Sept. 6.

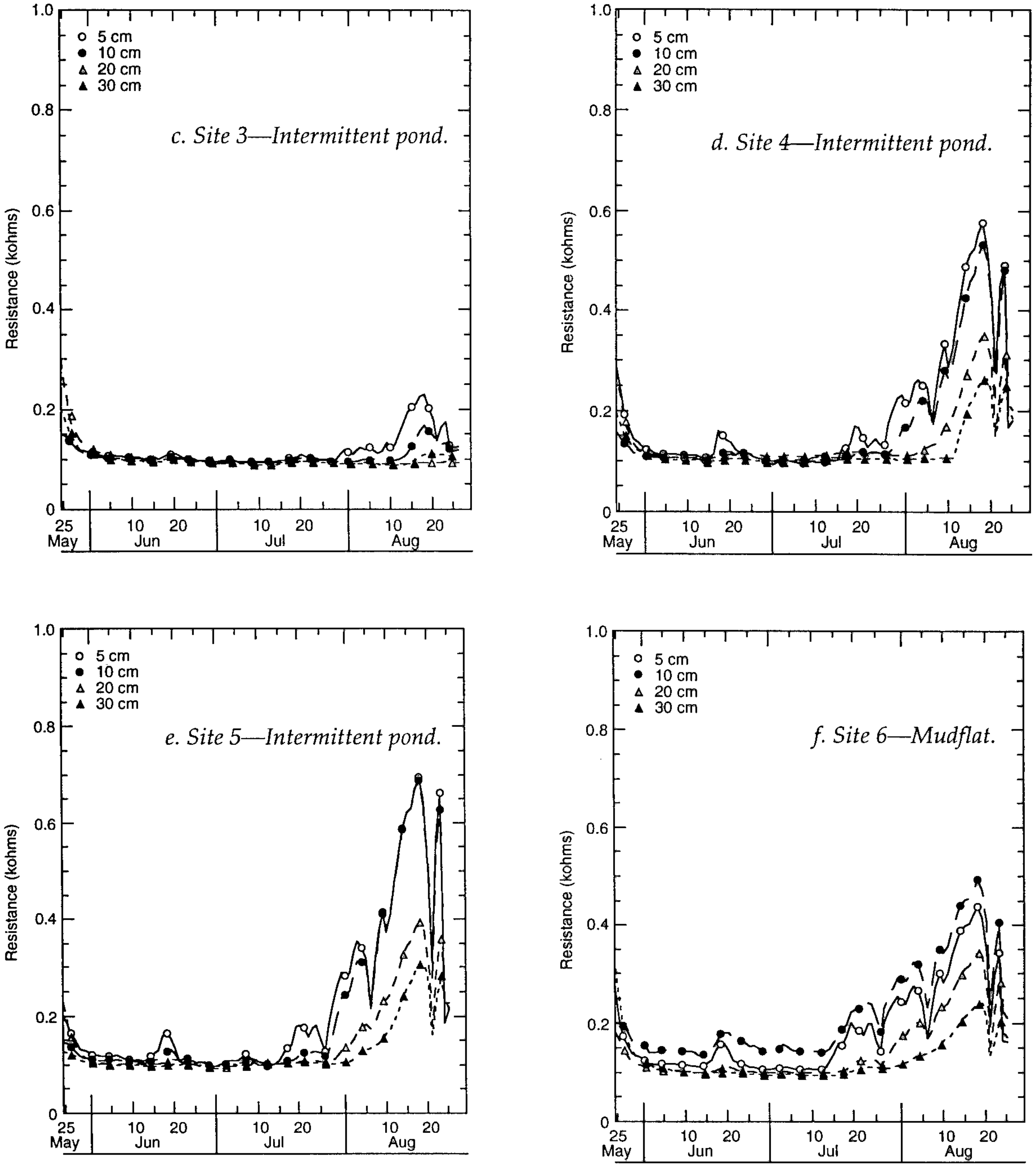


Figure 25 (cont'd). Daily (24-hour average) moisture probe resistance at 5, 10, 20 and 30 cm deep at each site.

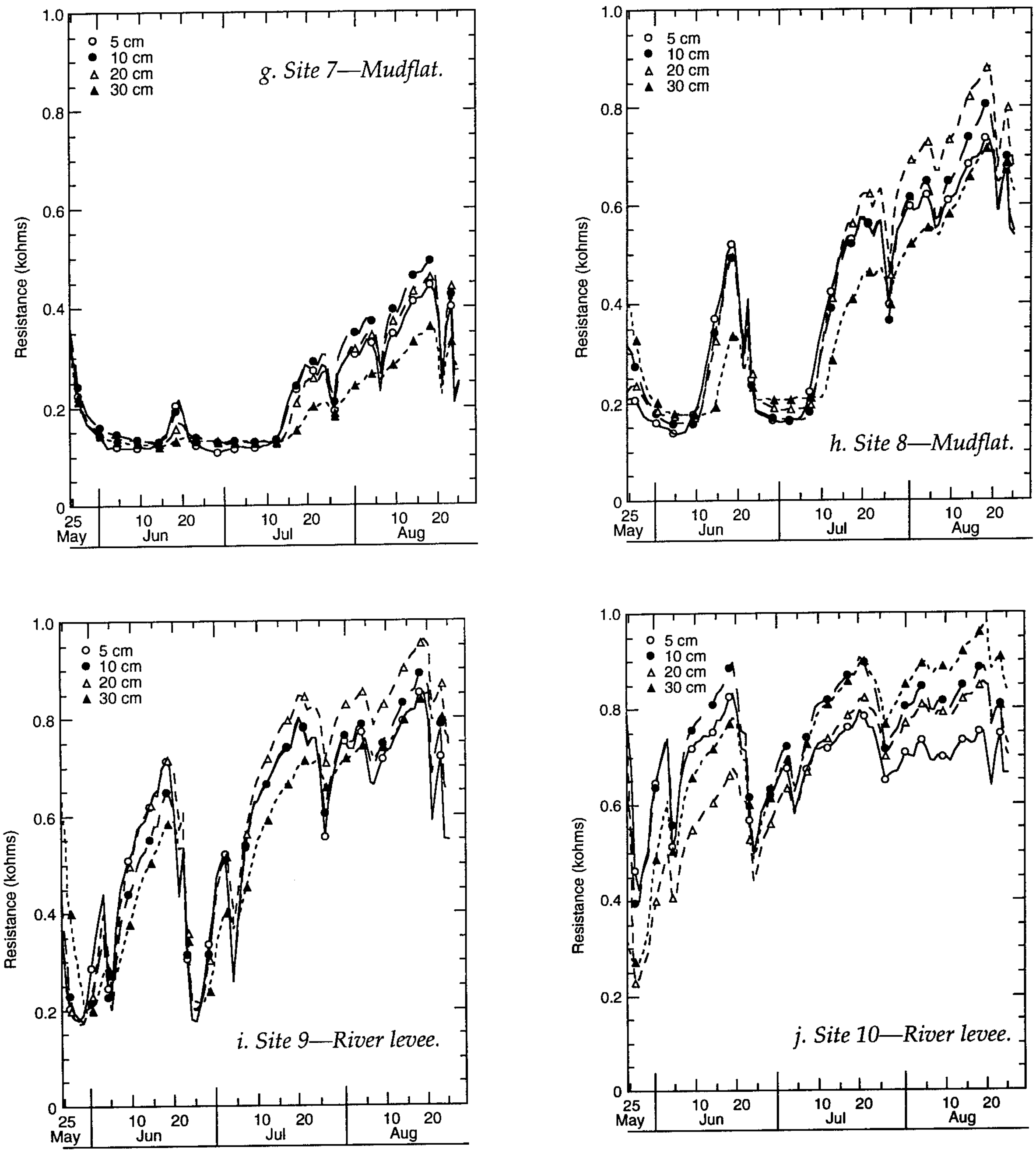
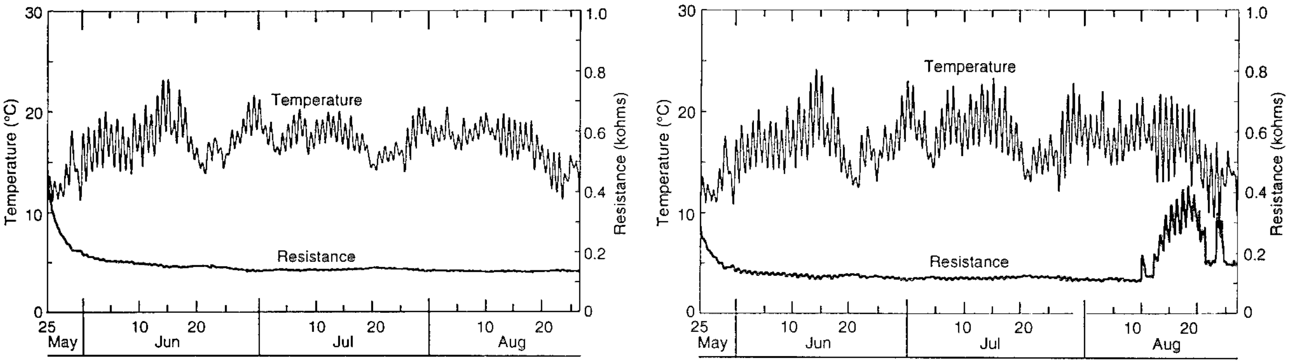
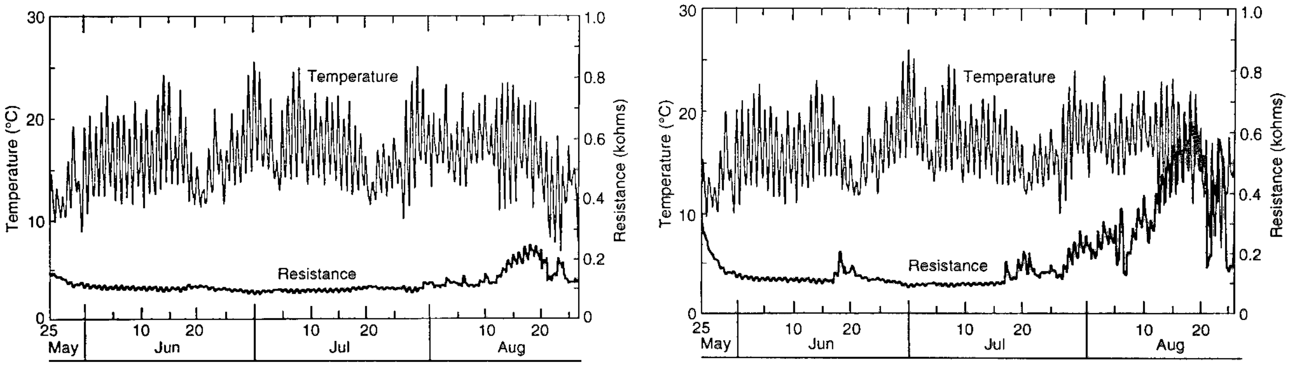


Figure 25 (cont'd).



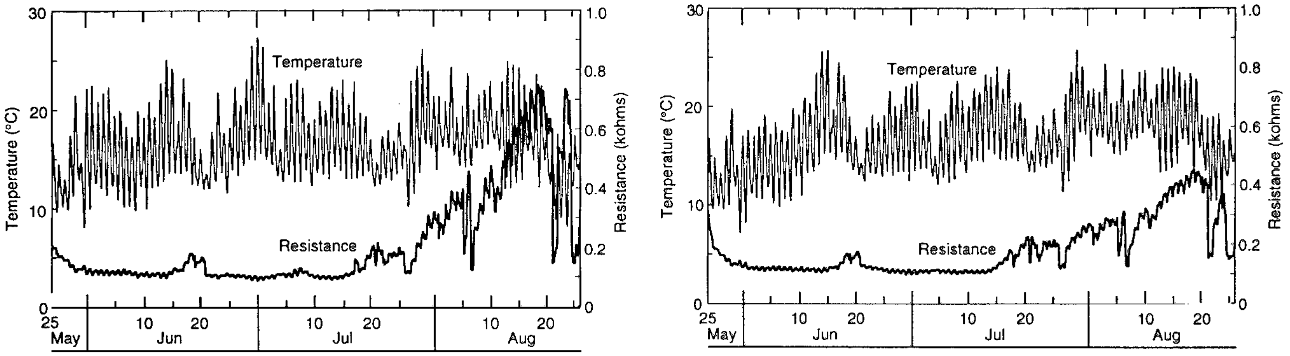
a. Site 1—Permanently flooded.

b. Site 2—Intermittent pond.



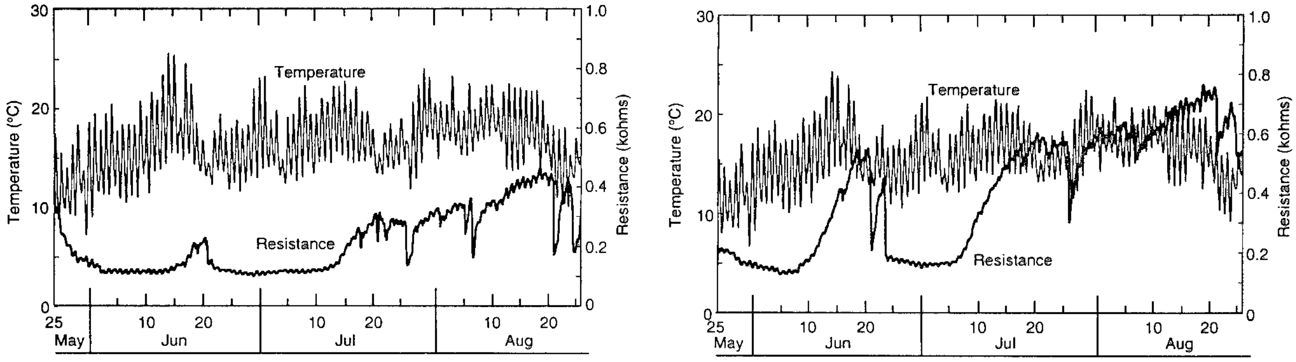
c. Site 3—Intermittent pond.

d. Site 4—Intermittent pond.



e. Site 5—Intermittent pond.

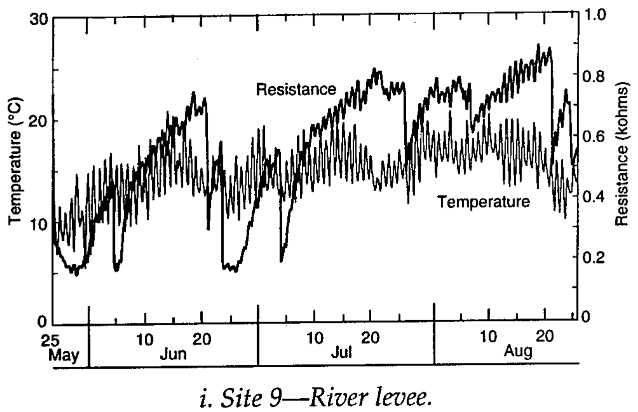
f. Site 6—Mudflat.



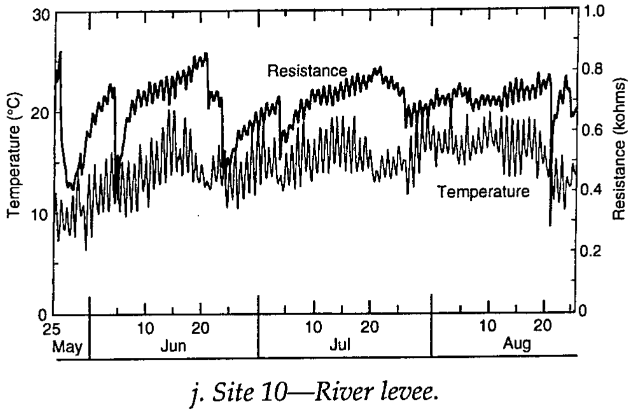
g. Site 7—Mudflat.

h. Site 8—Mudflat.

Figure 26. Hourly measurements of sediment temperature (℃) and moisture probe resistance (kohms) at 5 cm deep for sites 1–10.



i. Site 9—River levee.



j. Site 10—River levee.

Figure 26 (cont'd).

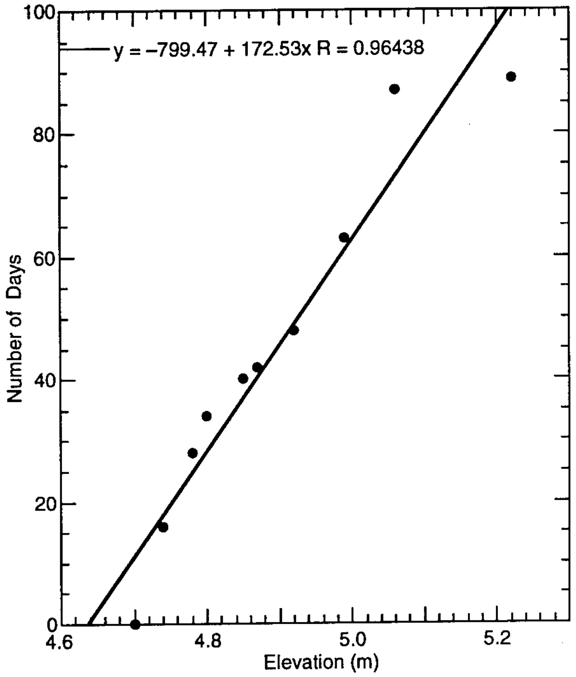


Figure 27. Number of days that sediments at 5 cm deep were unsaturated vs. elevation.

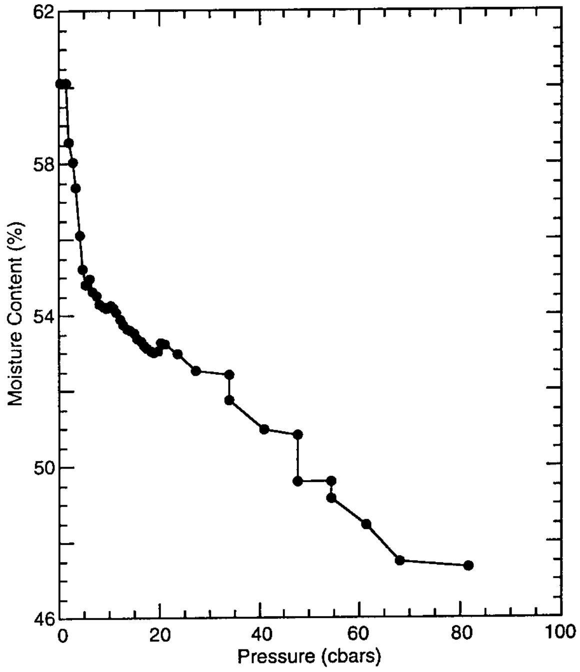


Figure 28. Moisture retention curve for a sediment sample collected 20 m south of the transect between sites 3 and 4 in the intermittent pond.

the surface sediments. The actual air-entry value in the field will vary with the heterogeneity of the sizes of sediment pores. Sediment with cracks and channels (macropores) would have a lower value (Hemond and Chen 1990).

Water surface elevations. Water surface elevations were recorded three times using piezometers. The first measurement was seven hours after a flooding high tide on May 24. The second measurement was on June 20, three and one-half weeks after a flooding tide and three days prior to the next series of flooding tides. The last measurement was on August 19, seven and one-half weeks after a flooding tide and two and one-half weeks before the next series of flooding high tides.

In May, water was present in all piezometers (Fig. 29). The water surface elevation was above or within 1 cm of the surface of the sediments at sites 1–7. At site 8, the mudflat site near the river levee, water was 20 cm below the sediment surface, and at site 9, on the river levee, it was 33 cm below the sediment surface. Between the May and June measurements, the water surface elevations dropped significantly at all sites except the permanently flooded site (site 1). On June 20, pi-

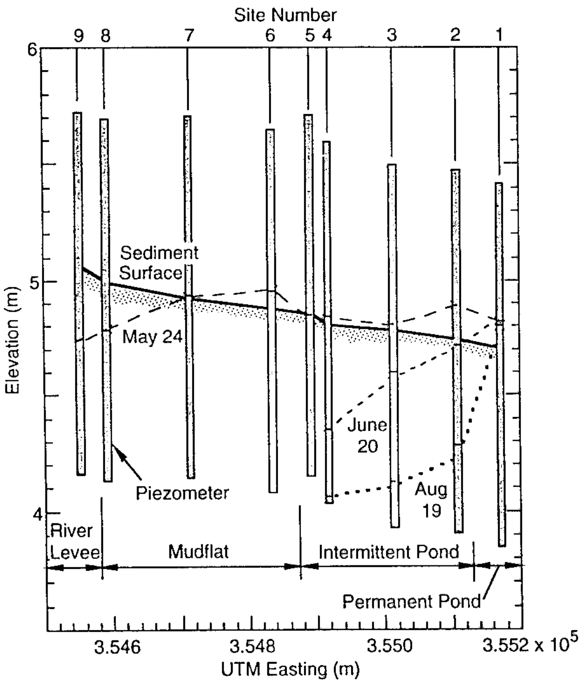


Figure 29. Water surface elevations (dashed lines) measured in piezometers at sites 1–9 on May 24, June 20 and August 19.

ezometers at sites 5–9 were dry, indicating that the water surface elevation was greater than 75 cm below the sediment surface at each of the mudflat and river levee sites, and greater than 68 cm below for site 5 at the edge of the intermittent pond. East along the transect across the intermittent ponded area, water surface elevations were 46, 21 and 4 cm below the sediment surface at sites 4, 3 and 2, respectively. At the permanently flooded site, the water surface elevation in the piezometer was 14 cm above the sediment surface and 4 cm higher than the pond surface elevation. At the time of the last measurement on August 19, piezometers at sites 5–9 were dry, and the water surface elevations were lower at the remaining sites. The depth to water was 75, 68 and 52 cm at sites 4, 3 and 2, respectively.* Based on the moisture retention curve, the water surface elevation at each of these sites is sufficiently below the sediment surface to desaturate the surface sediments. At site 1 the water surface elevation inside the piezometer was again 4 cm higher than the pond surface.

Tensiometer measurements were taken at six sites at the same time as piezometer measurements. The tension exceeded 5 cbar, the estimated air-entry value, at each site in August when the depth to water surface was over 50 cm, indicating that the surface sediments were below saturation (Table 11).

Table 11. Tensiometer measurements at 10 and 25 cm deep taken at the same time as piezometer measurements of water surface.

Site	*Date*	*Depth* (cm) to water surface in piezometer*	*Tension (cbars)*	
			*10 cm deep**	*25 cm deep**
Intermittent Pond				
3	June 20	21	4	4
3	Aug. 19	68	10	10
4	June 20	46	4	4
4	Aug. 19	75	30	20
5	June 20	>68	5	4
5	Aug. 19	>68	28	16
Mudflat				
6	June 20	>77	9	4
6	Aug. 19	>77	27	21
7	June 20	>76	10	8
7	Aug. 19	>76	25	23
River Levee				
9	June 20	>88	23	20
9	Aug. 20	>88	38	34

*Depth from sediment surface.

These data give some insight into the relationship between surface water and ground water along the transect and their influence on moisture levels in the surface sediments. At site 1, the permanently flooded site, upwelling of ground water appears to be high enough to prevent drying by evaporation. At the remaining sites, saturation of the surface sediments appears to be primarily the result of flooding high tides. Following a flood event, a combination of downward seepage and evaporation loss dewaters the surface sediments.

Measurement of water level at permanently flooded site. The elevation of the pond surface at site 1 was monitored hourly from June 15 to August 27 using an Ultrasonic Depth Gage interfaced with a datalogger. Given that the elevation of site 1 is 4.7 m, the sensor indicates that the 24-hour average water depth at this site was 7.9 cm on June 15 and declined by approximately 0.5 cm per day until June 21(Fig. 30). Then the series of flooding tides on June 23–25 deepened the pond to 25 cm. A full month passed before water levels returned to preflood levels. The first week after the last flood event (June 25–July 2), the drop averaged 1.5 cm per day. Once the pond surface elevation reached 4.85 m, which is the elevation of site 5 at the edge of the pond, the drop slowed to 0.5 cm per day until the water depth was 6 cm on July 21. The pond

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* Data obtained from Beth Nadeau indicated that water surface elevation continued to drop after our August measurements. On September 3, piezometers were dry at a depth of 80 cm in the intermittent pond near site 3.

level then fluctuated over the remaining time monitored, with the lowest water depth (3 cm) recorded on August 18.

Residual white phosphorus. On August 22–23, five samples were removed from each site to examine the physical appearance of P_4 particles. When particles were found, they appeared to be unchanged (i.e. they were lustrous in appearance). In the intermittent ponded sites, significant surface cracking of the drying sediment was observed. For all samples that were located within or adjacent to cracks, the P_4 particle was not found. In one sample, a spherical void space with a diameter of 1.8 mm (the original diameter of the P_4 particle) was observed.

The mass of P_4 in each of the five replicate samples remaining at each site on August 30 was normalized to the initial mass and plotted vs. site (Fig. 31). There was no change in the mass of P_4 particles removed from the permanently flooded site (site 1). The results for the intermittent ponded sites and mudflat sites were similar to those observed in the laboratory for the samples incubated at degree of saturation of 0.82 at 15 or 20°C. The mass of P_4 for at least one replicate was reduced by several orders of magnitude. According to a Kruskal–Wallis test (a nonparametric equivalent of one-way ANOVA), the length of time in which unsaturated conditions existed had a significant effect on the residual mass of white phosphorus found at each site ($p = 0.0027$) (Table 12). For those sites where unsaturated conditions were detected (sites 2–10), the length of time sediments were unsaturated *and* sediment temperatures were greater than or equal to 20°C at 5 cm deep also had a significant effect but less so ($p = 0.0234$) (Table 12).

Resampling of field-contaminated sites

Method

In August 1992 we examined the variability in P_4 contamination around a highly contaminated site in the intermittent pond of Area C (Racine et

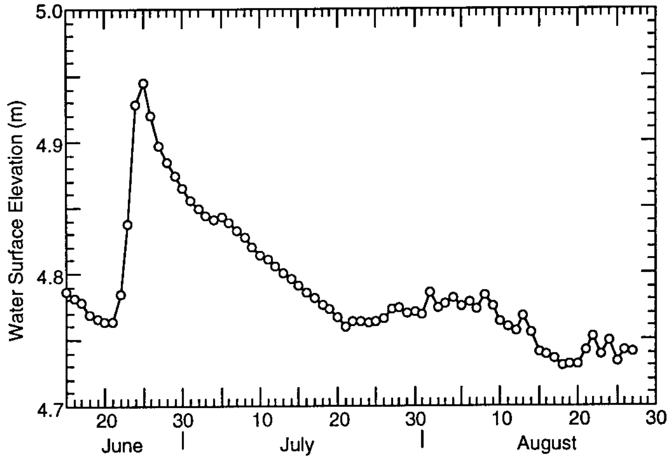


Figure 30. Average (24-hour) pond surface elevation at site 1.

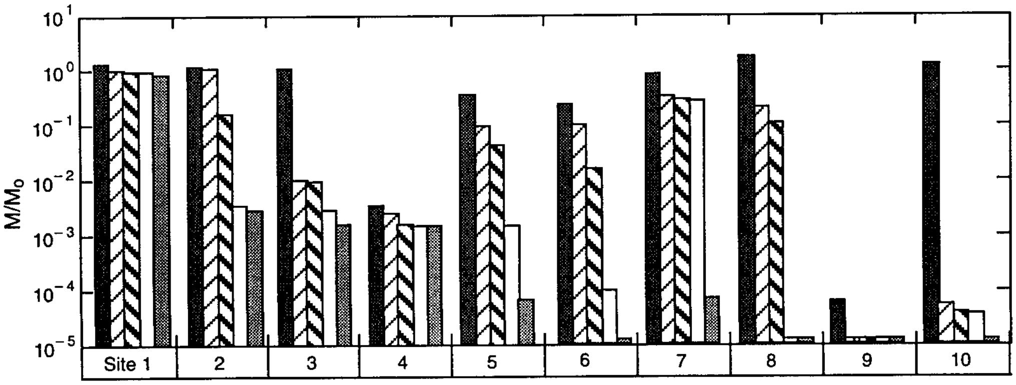


Figure 31. Residual P_4 found in five replicate samples normalized to initial mass from each site. Site 1 is permanently flooded, sites 2–5 are intermittently flooded, sites 6–8 are on the mudflat, and sites 9–10 are on the river levee.

Table 12. Results of Kruskal–Wallis test to determine if a) the length of time sediments were unsaturated at 5 cm deep or b) the length of time unsaturated and temperature greater than or equal to 20°C had an effect on residual WP found at each site.

Number of days unsaturated	*Site*	*Mean rank*
0	1	44.8
16	2	35.8
28	3	28.6
34	4	20
40	5	26.4
42	6	21.5
48	7	32.4
63	8	24.4
87	9	6
89	10	15.1

$H = 25.2; p = 0.0027$.

Number of days unsaturated and T>20°C	*Site*	*Mean rank*
0	10	21.5
39	9	1
44	2	6
88	3	34.2
150	4	27.8
169	5	20
209	8	26.4
217	7	23.6
258	6	32.4

$H = 17.7; p = 0.0234$.

al. 1993). Samples were taken at 1-m intervals out to 5 m along eight axes around the center point (Site 883) (Fig. 16). P_4 particles were isolated and measured from the sample collected at the center point (Racine et al. 1993). During 1993, Anchorage experienced an unusually warm and dry summer, and this area was above the water level through June and July 1993. We revisited this site on August 19,1994, and repeated the close-interval sampling to determine if the pattern and level of contamination had changed.

In addition, samples were collected from the crater (Miller's Hole) (Fig. 16) produced by the detonation of an 81-mm P_4 smoke round in May 1992. Samples were taken from the rim and center of the crater. Details of the procedures used to collect the samples are given in Appendix B.

Results

Sampling for white phosphorus contamination by various agencies continued at Eagle River Flats in 1994 (Racine and Cate 1995). Any white phosphorus detected by these field sampling efforts has persisted in ERF since at least February 1990, when training with white phosphorus munitions was suspended at Eagle River Flats. White phosphorus continues to be detected at high concentrations in the permanent ponds of Area C. In contrast, intermittent ponded areas and mudflats tend to have low concentrations or undetectable levels of white phosphorus. For example, the transect described above passed through a heavily cratered area (10–25% crater cover), yet no white phosphorus was detected in the mudflat and river levee samples, and trace amounts (near or below the certified reporting limit) were found in the intermittent ponded area. This pattern of contamination indicates that white phosphorus may be persistent only in the permanently flooded areas. However, one site in the intermittent pond of Area C (Site 883) was found in 1992 to have very high concentrations of white phosphorus (>200 µg/g) (Fig. 16). From tide table data for 1990 to 1994 (Fig. 32) and the assumption that the flats flooded every time the predicted high tide for Anchorage was greater than 31 ft, this site was mostly likely exposed to air each summer except for 1991 when the flats flooded each month. The longest period of exposure was in 1993, when Anchorage also experienced an unusually warm, dry summer. Given an elevation of 4.77 m and the drying data obtained along the transect described above, the moisture content of the surface sediments probably decreased below saturation during the summer of 1993. The water depth was approximately 8 cm when the site was sampled in August 1992, and the site was subaerially exposed when sampled in August 1994 (Fig. 33).

When sampled in 1992 and 1994, sediment was taken at 1-m intervals in a radial pattern (Fig. 34). Samples taken in 1994 showed that the moisture content ranged from 40 to 46% on a dry weight basis. The patterns of contamination for August 1992 and August 1994 (Fig. 34) show that there is a reduction in the number of samples in the highest-concentration group (>10 µg/g), from four to one (Fig. 35). There is also an increase in the number of samples in the lowest-concentration group (<0.001 µg/g), from 15 to 25. The results were compared using a sign test for paired observations. If the differences between

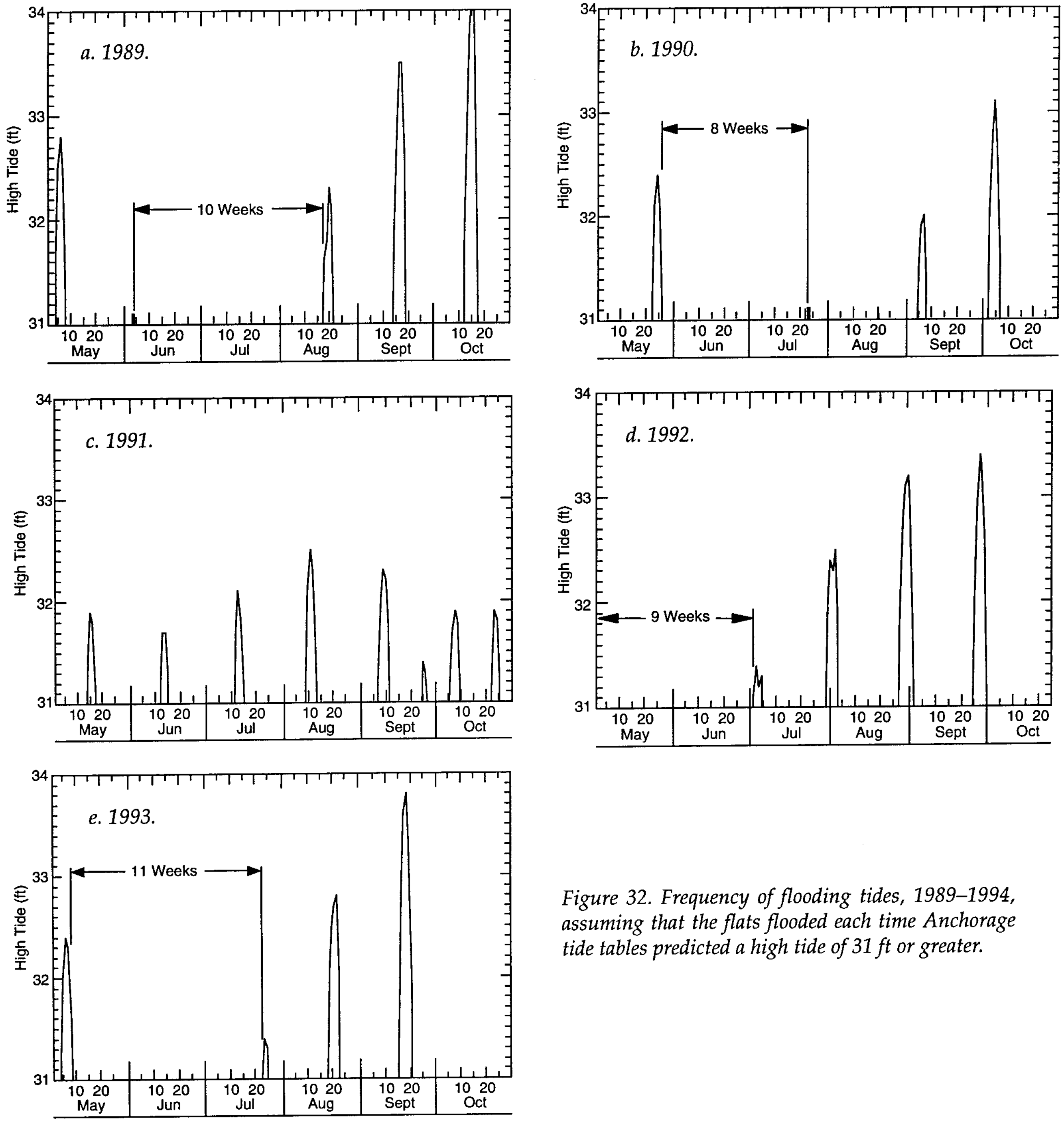


Figure 32. Frequency of flooding tides, 1989–1994, assuming that the flats flooded each time Anchorage tide tables predicted a high tide of 31 ft or greater.

the concentrations found in 1992 and 1994 were due solely to random error, the observation of an increase in concentration would be just as likely as an observation of a decrease. Of the 41 pairs compared, 22 showed a decrease, 7 showed an increase, and 12 were below the detection limit (Fig. 36). The number of samples showing a decrease between 1992 and 1994 is significant at the 0.05 significance level.

Sources of uncertainty about this field-contaminated site include the date it was contaminated, the type of round that produced the contamination (mortar or howitzer), where the round exploded, the type of fuse (point detonating or other) and the initial white phosphorus concentration. However, we do have this information for another site in the intermittent pond of Area C, a site where unexploded ordnance (UXO), an 81-mm mortar round

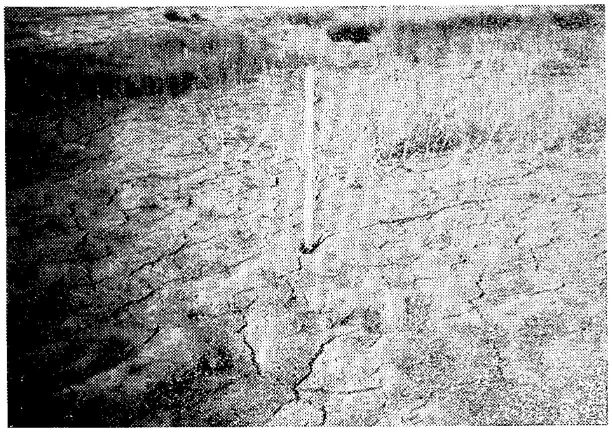
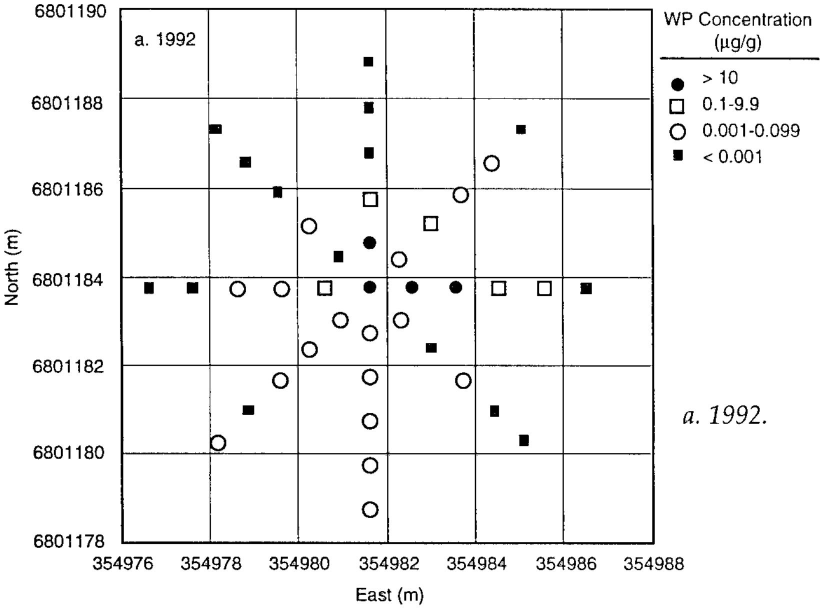
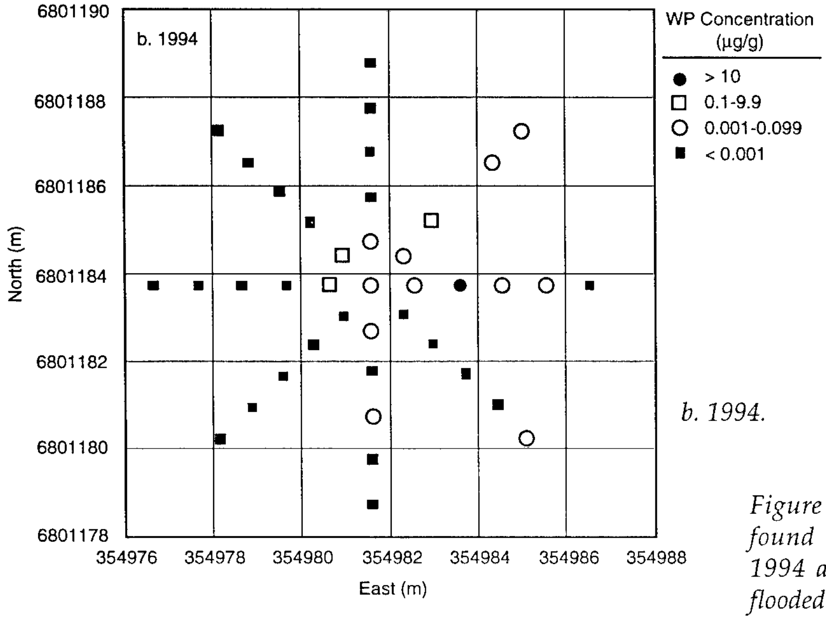


Figure 33. Site 883, in the intermittent pond of Area C, where high concentrations of white phosphorus were detected in 1992.



a. 1992.



b. 1994.

Figure 34. Pattern of WP contamination found during August 1992 and August 1994 around a site in an intermittently flooded pond in Area C.

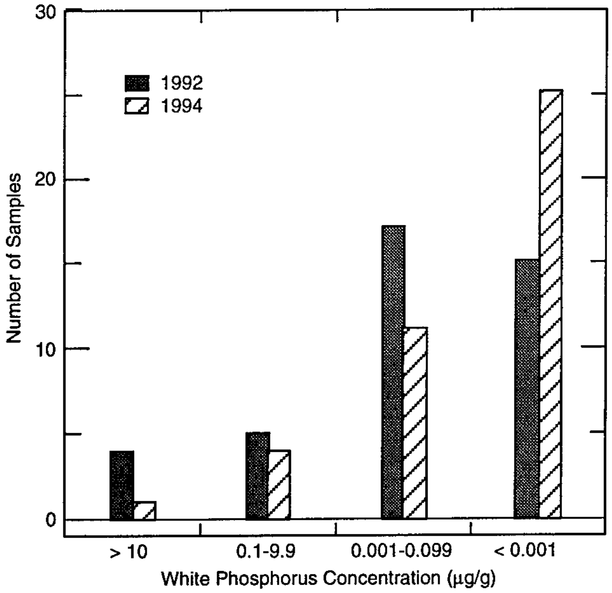


Figure 35. Number of samples in different concentration ranges in 1992 and 1994.

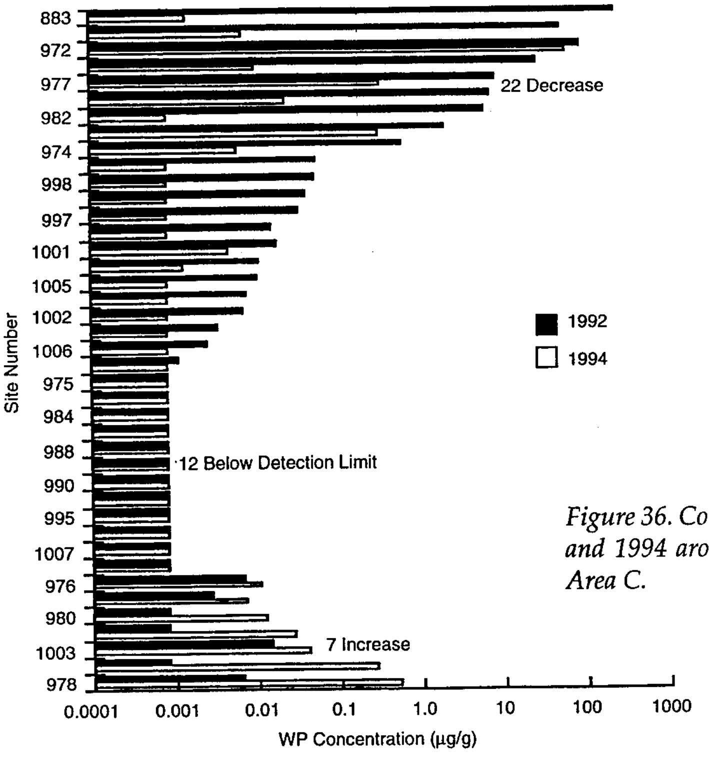


Figure 36. Comparison of WP concentrations found in 1992 and 1994 around site 883, an intermittent ponded site in Area C.

that contained white phosphorus, was exploded on 20 May 1992. The UXO was exploded for the safety of researchers. Since the shell of this UXO was extremely corroded, the filler material was not identified as white phosphorus until a dense white cloud formed when the round detonated (Fig. 37). The crater produced by this explosion has been called "Miller's Hole" (Fig. 38) for the EOD team member who detonated the round.

The crater produced has provided an opportunity for monitoring the persistence of white phosphorus in an intermittent pond. The elevation of the rim of the crater is 4.77 m, while the center is only 4.45 m. Because of this elevation difference, the rim is subaerially exposed for longer periods of time than the center. The initial white phosphorus concentrations in the center were over 2000 µg/g (Table 13). Over the summer of 1992, the concentration in the center appears to have decreased by one order of magnitude (approximately 90%). An-

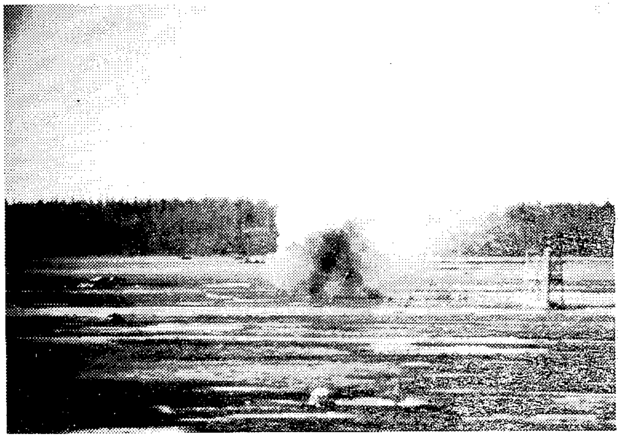


Figure 37. Detonation of a UXO, an 81-mm mortar round that contained white phosphorus, on May 20, 1992.

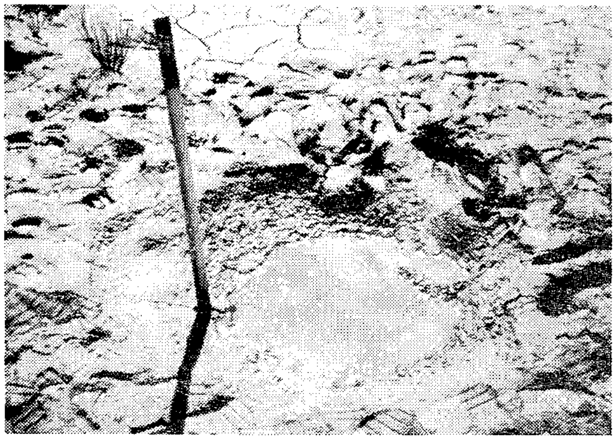


Figure 38. Crater, known as "Miller's Hole," produced by detonation of a UXO that contained white phosphorus. White phosphorus concentrations in sediment from the rim and bottom of the crater have been measured each spring and fall since the explosion.

other order-of-magnitude change (approximately 99% decrease) has taken two years. Even with the uncertainty associated with subsampling error, the general trend has been a decrease in P_4 concentration in the crater center since June 1992, with the majority of the change taking place over the summer. The white phosphorus concentration in the crater rim has changed in a different pattern. The initial white phosphorus concentrations were very high (980 µg/g). After 29 days the decrease was greater than 99.9% and after 93 days was greater than 99.999%. When sampled in June 1993 and May 1994 there has been an apparent increase in concentration from the previous August. Most likely some mixing of sediment may occur when the crater is underwater or by slight shifting of the ice at this site. When last sampled in August 1994, the surface sediment was exposed and cracked. White phosphorus was not detectable in the rim of the crater, showing that white phosphorus did not persist during subaerial exposure during the summer.

Table 13. White phosphorus concentrations found at Miller's Hole, a crater produced by the detonation of a UXO (81-mm mortar smoke round) in the intermittent pond of Area C.

Date sampled	*Days since explosion*	*Concentration (µg/g)*	
		Center	*Rim*
May 20, 92	0	2400	980 (silt), 34,500 (orange residue)
June 18, 92	29	5600	0.237
Aug. 21, 92	93	184	0.00427
June 23, 93	399	187	0.0175
Aug. 27, 93	464	81.5	0.00177
May 16, 94	726	49.5	34.1*
Aug. 30, 94	832	9.5	<0.00088

* Crater under water. Sediment very fluid.

CONCLUSIONS

In laboratory experiments where P_4 particles were incubated under constant moisture contents (degree of saturation = 0.45, 0.64, 0.82, 1 or >1) and temperatures (4, 15 or 20°C), P_4 particles were persistent at moisture contents at or above saturation. P_4 particles incubated well below saturation (s = 0.45 or 0.64) were lost within 24 hours at 20°C and within 30 days at 15°C, but they persisted over the time interval tested (approximately 60 days) at 4°C. For samples incubated slightly below saturation (s = 0.82), the results were variable, with significant loss in some samples and no change in other samples.

In field experiments where P_4 particles were incubated at a depth of 5 cm in salt marsh sediments, P_4 was persistent in the permanently flooded area, but there was loss of P_4 in areas with unsaturated sediments. Unsaturated conditions were detected down to 30 cm at monitoring sites on the river levee and mudflat and two intermittent pond sites, indicating that loss of P_4 is possible at depth. However, at depth, loss is likely to be slower due to consolidation, lower temperatures and longer periods of saturation.

Resampling of field-contaminated sites in an intermittent pond also showed loss of P_4 after the area was subaerially exposed. Continued monitoring of white phosphorus concentrations in field-contaminated sites will eliminate some of the uncertainty associated with the persistence of P_4 in near-saturated conditions and provide additional information about the rate of natural attenuation in intermittent pond areas. This understanding will enhance the ability to predict the fate of P_4 and its associated ecological risk within an estuarine salt marsh.

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APPENDIX A: METHODS FOR LABORATORY STUDY

Incubation of P_4 Particles at Constant Temperature and Moisture Content

PRODUCTION OF PARTICLES

White phosphorus was obtained as sticks (16.1 mm in diameter), stored in water, from Aldrich Chemical Co. (Milwaukee, Wisconsin). One stick of P_4 was placed in an 18.3-cm-diameter glass dish under 3 cm of reagent water, and a razor blade was used to obtain a 2-mm slice. The edges of the slice were cut away so that only P_4 from the interior of the stick was used. The mass of each slice was approximately 700 mg. The piece of P_4 was transferred under water to a test tube (13×100 mm), and the test tube was then placed in a 1-L beaker containing reagent-grade water. Additional test tubes containing reagent-grade water were placed in the 1-L beaker. These test tubes served to isolate the particles of P_4 once they are produced.

The 1-L beaker containing the test tubes and P_4 were placed on a Corning hotplate and the water heated to 54°C (10°C higher then the melting point of P_4). The beaker was removed from the hotplate; then 3-µL droplets obtained from the molten P_4 using a Gilson Microman Positive Displacement Pipet (size M25) equipped with disposable capillaries and pistons. Droplets of this size maintain a spherical shape. Each droplet was transferred under water to individual test tubes (only one droplet was placed in each test tube since molten P_4 droplets merge to form a larger droplet). The test tubes containing the P_4 droplets were cooled in a refrigerator (4°C). P_4 can supercool (i.e. remain liquid below the melting point); thus the water had to be cooled well below 44°C to ensure solidification of the P_4.

To measure the diameter of each particle, each particle was transferred to a glass petri dish containing reagent-grade water, and the diameter was obtained using an SPI (Swiss Precision Instruments) 6-in. caliper with 0.1-mm gradations. Previously we have measured diameters of 127 P_4 particles produced in this laboratory by the method described above. The mean (± standard deviation) diameter was 1.79 ± 0.06 (3.2% relative standard deviation). After the diameter was measured, each particle was transferred with a forceps from the petri dish to an amber vial containing cold reagent-grade water. Particles were placed in sediment samples within a few hours of production.

PREPARATION OF SEDIMENT SAMPLES

Sediments

Uncontaminated sediment from Eagle River Flats was air-dried and homogenized. A set of samples at one test temperature required approximately 40 kg of air-dried sediment. The sediment was air-dried in a fume hood at room temperature (22°C) for two weeks. Since ERF sediments are silt and clay size, the sediments hardened as they dried. During drying, the hardening sediment was broken apart with a large stainless steel spoon and mixed thoroughly. A mortar and pestle was used to break apart the hard clumps. To thoroughly homogenize the sediment, the sediment was processed in 1-L batches in a Cuisinart (Model DLC-X) processor. The moisture content of the air-dried, homogenized sediment was determined gravimetrically (difference in weight before and after heating at 105°C for 24 hours). The ERF sediment air-dried in our laboratory was approximately 2% moisture (on a dry weight basis).

Determination of moisture contents to be tested

The moisture content levels were chosen to reflect those that may be expected in exposed Eagle River Flats sediments. Following the thawing each spring of the ice covering Eagle River Flats, most of the flats is covered by water, and sediments throughout the flats are saturated. Following drainage through gullies and evapotranspiration, the area covered by water gradually shrinks in size until the flats is periodically reflooded by high tides exceeding 31 ft. Thus the area exposed to air shrinks and grows in a cyclic pattern throughout the summer. If the sediments are exposed for a sufficient length of time, their moisture content may fall below saturation. While unconsolidated pond bottom sediments in permanently flooded areas have moisture contents up to 200% on a dry weight basis, sediments in intermittent ponds have much lower moisture contents. For example, in the top 10 cm of exposed pond sediments in early July 1993, sediment moisture levels were between 30 and 35% (on a dry weight basis). Moisture levels between 35 and 40% were measured down to 30 cm deep. Since these moisture levels represent conditions that exist for extended periods between high tides, moisture levels in this range were chosen for this experiment.

The moisture content at saturation was estimated by a variety of techniques. One way was by making assumptions based on the properties of clay-size sediments. This approach is shown below:

> Assume 100 g of oven-dried clay, with 60% porosity and a density of 2.65 g/cm^3
>
> Then:
>
> Volume of solids = 100 g $\div$ 2.65 g/cm^3 = 37.7 cm^3 = (1 – 0.60) × Total Volume
>
> Total Volume = 37.7 cm^3 $\div$ (1 – 0.60) = 94.3 cm^3
>
> Volume of voids = 94.3 cm^3 – 37.7 cm^3 = 56.6 cm^3.
>
> If all voids are filled with water, then:
>
> % moisture = (56.6 cm^3 $\div$ 1 g/cm^3) $\div$ 100 g = 56.6%.

A tensiometer was also used to estimate the moisture content at saturation. Pore water tension, expressed as negative millibars, is zero at or above saturation and increases (actually becomes negative) below saturation. In the laboratory at CRREL, sediment samples from ERF were wetted to obtain moisture contents over the range of 35–60% moisture (using the procedure given below), and a tensiometer from Soil Measurements Systems was used to measure the pore water tension. Based on these measurements, the saturation was between 50 and 55% moisture (on a dry weight basis).

Another experimental approach was to gradually add water to a known amount of sediment until no further water was absorbed. In the lab at CRREL, 300 g of oven-dried ERF sediment absorbed 160 g of water, indicating that the saturation was 53%.

Based on these three estimates, the moisture level at saturation is in the range of 50–55% for the homogenized sediment in the lab. To simulate moisture levels that may be expected in air-exposed ERF sediments, the following levels were tested: 25% (s = 0.45), 35% (s = 0.64) (measured in field in July 1993), 45% (s = 0.82), 55% (s = 1), 65% (s >1), where s is the degree of saturation.

Labeling

At each temperature, sediments were moistened to one of five moisture contents (Table 3). At each moisture content, there were 25 replicates prepared. Therefore, each test at a given temperature required 125 sediment samples in individual plastic containers. Plastic (high-density polyethylene) containers (8 × 8 × 6 cm) were labeled with the incubation temperature, the desired moisture content and a number between 1 and 25 (for example: 20°C—55%—12).

Pretreatment of sediments

The equivalent of 300 g of oven-dried sediment was placed in each of 125 containers for each test temperature. The actual amount of sediment added depended on the moisture content of the air-dried sediment. For example, if the moisture content of the air-dried sediment was determined to be 1.75% (on a dry weight basis), then each dish was filled with 305 g of air-dried sediment (300 + 0.0175 × 300 = 305). Then reagent-grade water (MilliQ, Millipore Corporation) was added to the obtain the desired moisture content. For example, a sediment sample containing the equivalent of 300 g of oven-dried sediment wetted to 55% moisture (on a dry weight basis) required 165 g water (0.55 × 300 = 165). Since air-dried sediment had 5.25 g of water associated with it, only 160 g of water had to be added to obtain a sample at 55% moisture. Samples were wetted at least three days prior to placement of the white phosphorus particles. Samples were equilibrated at the appropriate temperature and rewetted daily to replace water lost by evaporation. Prewetting of the sediment served to compact the sediment to more closely approximate field conditions.

Placement of P_4 particles

At the two lowest moisture contents, a 3-cm-long core was removed from the center of each sediment sample using an 18.9-mm-diameter polypropylene corer (produced by cutting off the tapered end of a 20-cm^3 syringe). One P_4 particle was quickly transferred into the center of the hole in the sediment sample, and the core was quickly replaced. The sediment surrounding the core was gently compacted to fill in the voids around the core. An additional 5 g of water was added so that the wet sediment was sufficiently fluid to flow into the voids surrounding the core; this additional water increased the initial moisture content by 1.7%.

At the three higher moisture contents, a 2-mm-diameter hole was made using a wooden dowel, and the particle was pushed down to a depth of 3 cm. Then the sides of the sample were gently squeezed to seal the hole.

INCUBATION OF SEDIMENT SAMPLES

Samples incubated at 15 and 20°C were placed in a Labline Biotronette plant growth chamber. Since only one growth chamber was available, one experimental treatment was completed before the next one was initiated. Samples incubated at 4°C were placed in a coldroom at CRREL. Samples at each temperature were placed in random order and were rearranged on each working day. To maintain the moisture content, samples were weighed, and any water lost by evaporation was replaced with reagent-grade water. To prevent excessive loss of moisture overnight and over weekends, sample containers were placed in larger plastic containers (66 × 46 × 15 cm) and loosely covered with a plastic lid. This procedure maintained the relative humidity close to 100% and slowed evaporative losses.

RECOVERY OF PARTICLES

The residual P_4 was measured periodically during incubation. At each sampling interval, two samples were taken for microscopic examination. The sediment sample was placed on the stage of a Cambridge Instruments dissecting scope, and at a magnification of 10×, the sediment overlying the residual particle was gently removed and placed on a 30-mesh sieve. The material on the mesh was rinsed with distilled water to remove fine-grained sediment. Sediment was removed in 1-mm depth increments down to a depth of 4 cm or until the P_4 particle was found. If the particle was found, its diameter was measured using a micrometer, the appearance of the particle and the surrounding sediment was noted, and the particle and sediment were shaken separately in isooctane prior to gas chromatographic analysis.

If P_4 particles were not located by examining the samples, three additional samples were analyzed by solvent extraction followed by gas chromatography (Walsh and Taylor 1993). The sediment surrounding the residual particle was obtained using a 26.5-mm-diameter polypropylene corer (produced by cutting off the tapered end of a 50-cm^3 syringe). The corer was centered over the area where the P_4 particle was placed and pushed to the bottom of the container. The sediment was transferred to a 120-mL glass jar equipped with a Teflon-lined cap, and the P_4 was extracted with isooctane and analyzed by gas chromatography using the procedure outlined in the analytical method. Fifteen additional samples were prepared (three replicates at each moisture content) and extracted immediately to establish the day 0 mass of P_4.

DETERMINATION OF SAMPLING INTERVALS

A rigid sampling interval was not set initially. Because the vapor pressure of P_4 is an exponential function of temperature, the rate of loss of P_4 was expected to be significantly higher at 20°C then at 4°C, so the sampling intervals were shorter for the higher temperatures. In addition, sublimation of P_4 depends on the diffusion coefficient of P_4 vapor. The diffusion coefficient of P_4 in sediment is unknown but can be assumed to be less than in air. In sediment the effective diffusion coefficient decreases as moisture content increases. Thus the sampling interval for the high-moisture-content samples was longer than the lower-moisture-content samples.

Based on a previous experiment in which ERF sediments were air-dried at 20°C, samples below saturation at or above 20°C were sampled intensively within the first two weeks of incubation.

ANALYSIS OF DATA

Moisture content was expressed as degree of saturation. Residual particle masses were normalized to the day 0 mass (*M/Mo*) and plotted vs. time. Regression analyses were performed if appropriate to see if significant changes in mass occurred as a function of time.

APPENDIX B: METHODS FOR FIELD INVESTIGATIONS
Monitoring Sediment Moisture and Temperature in Eagle River Flats and Resampling of Field-Contaminated Sites

FIELD STUDY TO MONITOR SEDIMENT MOISTURE AND TEMPERATURE

Selection of sites

Sites were selected along an east–west transect through Area C, extending from a permanently flooded zone to the east through the intermittent ponded area to the west, across the mudflat zone to the levee adjacent to the Eagle River (Fig. 15). Sites were selected based on elevation. The elevation change along this transect was on the order of 50 cm, and sites were chosen to represent this gradient. Sites were not be located in gullies. First, a survey of the elevation change between the permanently flooded site and the river levee was conducted by measuring the elevation at 16 points along the transect. Then study sites were selected such that one site (site 1) was permanently flooded, four sites (sites 2–5) were in the intermittent pond, three sites were on mudflat (sites 6–8), and two sites were on the river levee (sites 9–10) (Fig. 16).

Surveying was performed using a Leitz SET4C electronic total station and a triple reflective prism mounted on a 1.45-m-tall prism rod. One person ran the total station, while two people occupied each site to be surveyed with the prism rod.

A control point located on the platform of an observation tower in Area C pond was surveyed in from "BM Crane," one of the four permanent survey benchmarks with known coordinates and elevations located on high points around the perimeter of ERF. The surveyed-in control point on the tower platform was then used as a temporary benchmark (TBM). Universal Transverse Mercator (UTM) coordinates and the elevation were calculated for the TBM. This TBM was then used to provide horizontal and elevation control for the survey of the transect through Area C.

The electronic total station was set up on the tower platform, over the control point, and the instrument was back-sighted to a reference azimuth mark. The two-person party moved to each location to be surveyed, and the triple prism on the prism rod was placed on the ground at each site. To achieve uniformity in surveying elevations, the tip of the prism rod was placed inside a bucket, which was in a tub placed on the ground surface. This provided a uniform bearing surface for the rod tip, keeping it from sinking down into the soft mud. The horizontal angle and vertical distance from the total station to the prism were then measured and recorded. Based on the horizontal angle and vertical distance from the control point, the height of the total station above the control point, and the height of the prism above the survey point, a set of UTM coordinates and an elevation for the survey point were calculated.

Only uncontaminated sites were selected. The sediment at each site was tested for the presence of P_4 particles using a field screening procedure (Walsh et al., in prep). This method involves spreading a thin layer of sediment across the bottom of an 8-in.-diameter aluminum pie pan and heating the pan on a propane camp stove. The presence of P_4 particles is detected by localized areas of intense flame, which leaves a bright orange residue. To confirm that sites were free of contamination, samples of the surface sediment were analyzed using the laboratory method.

Conditions at each site, such as water depth, vegetation, water conductivity, pH and redox potential, were recorded. Water depth was measured using a tape measure, vegetation was identified by Dr. Charles Racine, and water conductivity, pH and redox potential were measured with a YSI Model 3500 water quality meter.

Measurement of sediment temperature and moisture

Sediment temperature and moisture were measured every 10 minutes and averaged hourly from May 25 to August 26 using sensors interfaced with

Campbell Scientific (Logan, Utah) CR10 dataloggers. The average hourly measurements were stored on Campbell Scientific SM716 storage modules. Each datalogger was installed on an instrument tripod with a 3-m center mast to keep the datalogger above flooding tide levels (Fig. 17). These tripods were self supporting and did not require any stakes to be driven into the ground for anchoring. The dataloggers were powered with 12-V rechargeable batteries, which were trickle charged with a MSX5 5-W solar panel attached to the top of the center mast.

Soil temperatures were monitored using Model 107B soil–water temperature probes, which utilized the Fenwal Electronics UUT51J1 thermistor probe, which has an accuracy of ±0.4°C over the range –33°C to +48°C. Probes were placed 5, 10, 20 and 30 cm deep at each site.

Sediment moisture was monitored at 5, 10, 20 and 30 cm deep at each site using Model 257 (Watermark 200) soil moisture sensors, which estimate the soil water potential in the range of 0–2 bar. The output from the sensors is the ratio of excitation voltage to signal voltage, from which resistance is calculated. Resistance is functionally related to soil water potential. A sensor in saturated sediment will give a resistance near zero; as sediment dries, resistance increases. These sensors have internal gypsum tablets, which reduce the error associated with changing salinity.

Periodically samples were collected for determination of the gravimetric moisture content. Samples were collected down to 30 cm using an Oakfield Model B 2-cm-diameter soil sampling tube. Recovered soil cores were split into subsamples, placed into plastic bags, labeled with site number, depth and date, and returned to the field laboratory for determination of gravimetric water content.

The gravimetric water content θ_g of a sample of moist soil was measured by weighing the moist soil sample, drying it at 105°C for 24 hours to remove the water, and reweighing it.

$$\theta_g = (\text{mass}_{\text{wet soil}} - \text{mass}_{\text{dry soil}})/\text{mass}_{\text{dry soil}}.$$

Bulk density measurements

Sediment samples were collected from each site to determine the bulk density. A 35-cm-deep pit was dug at each site; then brass cylinders (i.d. = 5.39 cm, length = 3.0 cm) were pressed into the undisturbed sediment of the side wall of the pit at 5, 10, 20 and 30 cm deep. The sediment was dug out around the outside of each cylinder, and the cylinders were capped and returned to the lab. The total volume of sediment was weighed, dried for 24 hours at 105°C and reweighed, and the dry bulk density of the sediment ρ_b was estimated:

$$\rho_b = \text{mass}_{\text{dry soil}}/\text{volume}_{\text{cylinder}}.$$

This method slightly underestimated the bulk density since the cores shrank slightly upon drying.

Tensiometers

A series of SoilMoisture (SoilMoisture Equipment Corp., Santa Barbara, California) Series 2725 tensiometers were installed at six sites to provide another measure of near-surface sediment moisture. Tensiometers provide a direct analog readout of soil suction in centibars. The tensiometers consist of a sealed hollow plastic tube filled with water with a porous ceramic tip at the bottom. As the sediment surrounding the buried ceramic tip dries out, water is drawn out through the ceramic tip, creating a suction within the hollow tube. The resulting suction is read by an attached dial gauge, which is graduated from 0 to 100 centibars (kPa) of soil suction. The tensiometers were installed at 25 and 10 cm deep (the minimum depth for the model of tensiometer) at three sites within the intermittent ponded area, two sites on the mudflat and one site on the river levee.

Air-entry value

Using a standard Tempe pressure cell (SoilMoisture Equipment Corp., Santa Barbara, California), a moisture retention curve (Hillel 1982) was determined for a sediment sample collected south of the transect between sites 3 and 4 (Fig. 16) in the intermittent ponded area (at site 883 discussed in the next section). This curve was used to estimate the air-entry value, which gives an indication of how far the water table must drop before surface sediments become unsaturated. It also gives an estimate of the tensiometer reading corresponding to the onset of unsaturated conditions as sediments dry. To generate the curve, air pressure was applied to a core of saturated sediment placed on a porous ceramic plate in the Tempe pressure cell. Air pressure was incrementally increased, and the amount of water forced out of the sediment was recorded. The air-entry value corresponds to the pressure at which capillary forces are overcome and air begins to penetrate the sediment matrix.

Water surface elevations

Piezometers were used to measure the water surface elevation along the transect. Each piezometer was constructed from 1.9-cm-i.d. CPVC pipe. Slots were cut at one end of the tube to allow water to enter. Slots (1 mm wide) were spaced at 1-cm intervals on either side of the first 10 cm of each 1.52-m-long pipe. A nylon mesh was pulled over the slotted end and secured with duct tape. On May 20, piezometers were inserted to a depth of approximately 80 cm at sites 1–9. A 2-cm-diameter placement tool was gently inserted into the ground to form a pilot hole slightly smaller than the o.d. of the CPVC pipe. The piezometer pipe was then inserted into the hole. The turf at site 10 (river levee) was too thick to allow gentle insertion of the placement tool, so no piezometer was placed at this site. The water level inside each pipe was read on a periodic basis using a thin wooden dowel. Water levels were measured on May 24, June 20 and August 19.

Water level measurements at the permanently flooded site

Pond water levels were monitored at the permanently flooded site (site 1) using a Campbell Scientific UDG01 ultrasonic depth gauge. The depth gauge was attached to the end of a bracket arm, which was in turn attached to the center mast of the tripod. The sensor was suspended on the bracket arm approximately 2.5 m above the water surface. The primary components of the depth gauge sensor are the Polaroid ultrasonic transducer and the Polaroid 6500 sonar ranging module (CSI 1993). The sensor measures the distance from the bottom of the sensor to a surface by bouncing an ultrasonic pulse off of the surface and listening for the return echo. The distance to the surface is determined from the elapsed time. The speed of sound in air depends on the air temperature, so that is also measured by the datalogger at the same time. The signal from the depth gauge sensor is processed by the datalogger, corrected for the air temperature, and stored. Readings were taken by the datalogger every ten minutes and averaged every hour. The accuracy of the depth gauge sensor for the setup we used is ±1 cm. The elevation for the bottom of the depth gauge sensor was established by surveying from a known control point. Water surface elevations were determined from the difference between the water surface and the elevation of the bottom of the sensor.

Placement of P_4 particles

In mid-May, before the series of flooding tides beginning May 23, P_4 particles were planted at each site. Ten >5-cm-deep cores were obtained at each site using an Oakfield Model B 2-cm-diameter soil sampling tube. Cores were obtained within a 0.25-m^2 area and were approximately 20 cm apart. Within the 0.25-m^2 area, cores were obtained from areas with similar conditions (i.e. similar water depth, vegetation cover). A P_4 particle produced in the laboratory was placed at a depth of 3–5 cm within each core, and each core was placed within a nylon mesh bag. The bag was tied off, and survey tape and string were attached. Each site was surrounded by survey lath, and strings from the nylon bags were tied around the lath. The cores were left undisturbed until August.

Retrieval of P_4 particles

In August the nylon bags containing the cores were retrieved. On August 22–23 five cores were recovered for visual examination. These cores were placed in plastic bags in a cooler, returned to our field lab, and, on the same day as collection from the field, examined. If a P_4 particle was found, its diameter was measured using a micrometer, and the appearance of the particle and the surrounding sediment was noted.

The rest of the cores were recovered on August 30 and prepared for analysis of P_4 residues by gas chromatography. The cores were removed from the nylon bags and placed in preweighed jars containing 10 mL of reagent-grade water. These samples were cooled to 4°C and returned to CRREL, where isooctane was added and the samples were shaken overnight. The residual P_4 in the isooctane extracts was determined by gas chromatography.

Analysis of data

The mass of P_4 remaining for each of five replicate particles at each location was determined following solvent extraction using the standard laboratory method for P_4 residue in sediment. Residual particle masses were normalized to the Day 0 mass (M/Mo) and plotted vs. location.

RESAMPLING OF PREVIOUSLY CHARACTERIZED CONTAMINATED SITE

Collection of samples

Site 883 was relocated based on UTM coordinates and the presence of the stubs of some lath that had been used to mark the site in 1992. The

UTM coordinates for site 883, the center point of the close-interval sampling, are 354,981.6E, 6,801,183.8N. The site was located 160 m west of the observation tower in Area C and was marked with survey lath. Surface samples were collected at the center point and at 1-m intervals from the center point out to 5 m, for a total of 41 samples. Eight duplicates were taken also. Samples were shipped to Waterways Experiment Station (Vicksburg, Mississippi) for analysis of P_4 using the gas chromatographic procedure developed at CRREL. Samples taken from the smoke round crater were shipped to CRREL for analysis of P_4.

Analysis of data

Nonparametric statistics (sign test for paired observations) (Natrella 1963) were used to compare the concentrations found in 1992 and 1994 around site 883. Nonparametric statistics were used since the data are not normally distributed.

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Remediation of sediments at Eagle River Flats, a salt marsh contaminated with particles of white phosphorus (P_4), may require severe alterations of the wetland by dredging, draining or covering. However, some sediments may undergo decontamination naturally in areas that are seasonally exposed to air. To predict the persistence of white phosphorus particles in sediments, a literature review was conducted for the physical and chemical properties of white phosphorus. The persistence of millimeter-size white phosphorus particles was studied by laboratory and field experiments. White phosphorus particles were found to be persistent indefinitely in saturated sediments. In unsaturated sediments, loss was rapid (within 24 hours) at 20°C and retarded by low temperatures.

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