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Composite Sampling of Sediments Contaminated with White Phosphorus

Marianne E. Walsh, Charles M. Collins, Ronald N. Bailey,
and Clarence L. Grant

December 1997

Abstract: White phosphorus from exploded munitions is a difficult contaminant to characterize in the environment. Spatial heterogeneity of concentration estimates is extreme, varying over many orders of magnitude for closely spaced discrete samples. To provide cost-effective data upon which decisions may be made, two composite sampling methods were designed to aid in characterizing the site and monitoring the remedial process for an area contaminated by white phosphorus. For each method, closely spaced discrete samples were collected on a grid pattern and pooled to form composites. The composites were then divided by size fractions. Mean white phosphorus concentrations were estimated for the fine-grain-size fraction that was obtained by suspension with water. The presence of highly toxic solid white phosphorus particles, the form that may be ingested by feeding waterfowl, was determined in the coarse-grain-size fraction that was obtained by sieving.

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PREFACE

This report was prepared by Marianne E. Walsh, Chemical Engineer, Charles M. Collins, Research Physical Scientist, Ronald N. Bailey, Physical Science Technician, Geological Sciences Division, Research and Engineering Directorate, U.S. Army Cold Regions Research and Engineering Laboratory, and Clarence L. Grant, Professor Emeritus, University of New Hampshire.

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Composite Sampling of Sediments Contaminated with White Phosphorus

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INTRODUCTION

Determining how successfully a site contaminated by white phosphorus munitions can be remediated is a challenge. Because of the discrete nature of the contamination, concentration estimates can vary by several orders of magnitude among individual samples taken over a small area. Therefore, to reliably compare concentrations "before and after" remediation would require an unrealistically large number of discrete samples to be collected and analyzed. A more efficient way to characterize the contamination is to composite samples collected over a large area (greater then 100 m^2). The success of cleanup activities may be judged from the amount of white phosphorus found in the composites before and after remediation.

Background

This study was conducted at Eagle River Flats (ERF), a wetland artillery and infantry mortar range on Fort Richardson, Alaska, where dabbling ducks and swans are acutely poisoned by ingesting residues from white phosphorus munitions (Racine et al. 1992a,b; 1993). When this site was initially investigated to determine the spatial extent of the contamination, surface sediment samples were collected at approximately 25-m intervals along transects through sections of this wetland. This spacing was chosen because it is the radius of the area estimated to contain most of the fallout from the kinds of smoke projectiles that were commonly fired into ERF during training exercises (Shin et al. 1985). At each sample location, several increments of surface sediment were collected from within a 1-m-diameter area. Most of the samples from these transects contained low or undetectable concentrations of white phosphorus.

Table 1. White phosphorus concentrations found in field samples collected from Eagle River Flats. (After Racine 1995.)

Concentration range (µg/g)	*Number of samples*	*Percent of samples*
Not detected	1281	66
Detection limit to 0.00099	79	4
0.001 to 0.0099	203	11
0.01 to 0.099	185	10
0.1 to 0.99	72	4
1.0 to 9.99	43	2
10 to 99.99	38	2
100 to 999.9	16	1
1000 to 9999.9	6	0.3

Along transects where white phosphorus was detected frequently, concentrations varied widely (Table 1), with relatively few samples having high concentrations. When samples were taken at close intervals (1 to 5 m) around sample points with high white phosphorus concentrations, we again observed extreme heterogeneity, with nondetectable concentrations within a few meters of high concentration samples (over 100 µg/g). This pattern of contamination led us to believe that most of the white phosphorus was located in "hot spots" that are less then 1 m in diameter and probably are the impact points of projectiles containing white phosphorus.

Microscopic examination of high-concentration samples revealed solid pieces of white phosphorus, which were mostly 0.5 to 2 mm long; but some were up to 6 mm long, weighing over 100 mg. These particles are much larger than the fine-grained silts and clays (95% finer than 0.02 mm) (Lawson and Brockett 1993) that make up the salt marsh sediment and could easily be selected by dabbling ducks and swans searching for food or grit (Trost 1981). The very low concentrations

Table 2. Number of mallards dying from apparent white phosphorus poisoning while exposed to contaminated sediments within pens in ERF. (Data courtesy of Patty Pochop, DWRC.)

Season and year of exposure	*Hours of exposure per day*	*Total exposure (hr)*	*Number of mallards*						
			Pen 1	*Pen 2*	*Pen 3*	*Pen 4*	*Pen 5*	*Pen 6*	*Total*
Spring 1992	3	12	1	0	1	2	1	0	5
Spring 1992	3	12	0	1	2	1	3	0	7
Fall 1992	3	12	Not used	1	0	0	0	Not used	1
Fall 1992	3	12	1	0	Not used	Not used	3	0	4
Fall 1992	3	9	1	1	1	0	1	1	5
Fall 1992	24	168	Not used	2	Not used	Not used	Not used	5	7
Spring 1993	3	15	0	0	0	1	3	0	4
Summer 1993	24	264	6	4	5	6	6	3	30
Summer 1993	24	168	Not used	Not used	Not used	Not used	6	Not used	6
Fall 1993	24	168	2	5	2	5	6	2	22
Total mortality			11	14	11	15	29	11	91
No. mallards* exposed			42	54	42	42	54	48	282
Percentage mortality			26	26	26	36	54	23	32

* Six ducks per experiment.

(less then 1 µg/g) detected in most samples are probably from colloidal, dissolved, or molecular white phosphorus sorbed to sediment surfaces.

White phosphorus is a solid at environmental temperatures. It has low water solubility and a moderately high octanol–water partition coefficient. Therefore, we do not think that it would be mobile in the environment. Field and laboratory studies showed that solid pieces of white phosphorus are persistent in water and saturated sediment (Walsh et al. 1996a), but once dissolved in water or in the vapor phase, white phosphorus is not persistent. However, we have found that low concentrations (part per trillion) of white phosphorus are prevalent and persistent in field-contaminated sediments at ERF.

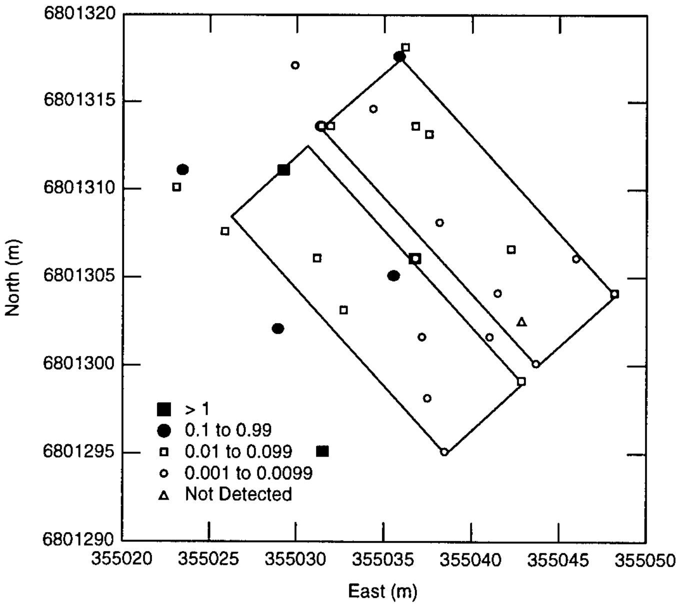


Figure 1. DWRC pens 5 and 6 showing white phosphorus concentration ranges for discrete samples taken from 1991–1994 (upper rectangle is pen 6).

During cleanup at hazardous waste sites, criteria are required to determine if a specific area requires remediation and if the area is clean afterwards. Cleanup activities are designed to eliminate risk. In the case of chemical contamination, data from toxicological studies are considered with site characteristics to determine a cleanup level that is usually expressed in soil concentration terms. If the average contaminant concentration, within a given level of confidence, in samples taken within an area falls below this level, the area is judged to be clean. This approach assumes that the spatially averaged soil concentration and sample variance may be used to estimate a long-term daily dose to receptors (USEPA 1992). However, when a contaminant is acutely toxic and heterogeneously distributed as solid particles over an area, an average concentration will not represent true exposure risk.

The problem of estimating exposure risk from white phosphorus became apparent at ERF when Denver Wildlife Research Center (DWRC) conducted studies to test the chemical bird repellent, methyl anthranilate (Clark and Cummings 1994). As a component of this study, mallards were exposed to contaminated sediment by confining them within six pens. The pens were located in an area where previous sampling had shown widespread white phosphorus contamination. For each study, six mallards were placed within these pens for various lengths of time, and feeding behavior and mortality were monitored. Over the course of the study, 282 mallards were exposed: 32% died of apparent white phosphorus poisoning. Waterfowl mortality occurred within each pen (Table 2).

One of the most confounding factors in this study was being unable to quantify white phosphorus exposure of the mallards within each pen. Because of the heterogeneous distribution of white phosphorus and the wide range of concentrations found in discrete samples, average white phosphorus concentration estimates were not useful for estimating exposure. Almost all the surface samples collected from the pens had measurable amounts of white phosphorus (Racine and Brouillette 1995) (Fig. 1), but most birds exposed to these contaminated sediments were not acutely poisoned.

To see if chronic poisoning was happening, gizzard contents and fat samples were taken from those birds that did not die from acute poisoning during exposure to contaminated sediments. White phosphorus was not detected in any of the samples, suggesting that there was no chronic poisoning. Instead, acute poisoning following the ingestion of a single lethal dose of white phosphorus appeared to be the more likely scenario. Since the LD_{50} for mallards is estimated to be 3 to 4 mg/kg of body weight (Sparling et al. 1995), and the waterfowl most at risk weigh from 0.25 (teal) to 1 kg (mallards), a lethal dose is provided by the ingestion of milligram-size particles of solid white phosphorus, not the nanogram to microgram quantities associated with most of the sediment samples. The "bioavailable" form of white phosphorus must be considered when assessing remedial need or success at this site.

Objective

For this study, the contaminant of interest is a particulate dispersed in a particulate medium. Because particulate samples are inherently heterogeneous, sampling error is unavoidable; but we seek to minimize it by understanding the sources of error. In the case of white phosphorus contamination on a firing range, there is the spatial heterogeneity introduced by the mode of contamination. Then there is the heterogeneity attributable to the complex mixture of components that make up the sediment matrix (i.e., silt and clay particles, various kinds of organic matter, salts, metallic debris, water, various sizes of white phosphorus particles, etc.). In addition, the various components of the sediment matrix may be segregated or not randomly distributed. Pierre Gy (Pitard 1993, Gy 1994) calls these two properties constitution heterogeneity and distributional heterogeneity. Only the second of these may be reduced by homogenization. The error associated with constitution heterogeneity, called fundamental error, may be reduced by taking larger samples (Ramsey et al. 1989). Correct sampling, where all constitutive elements have an equal probability of being selected, requires the proper sampling tool that delineates and extracts the sample from the media. (For example, the proper sampling tool for a layer of sediment would be a cylindrical corer.) When designing a sampling plan, we must consider that these multiple sources of error place limits on achievable sampling objectives, especially because there are always time and cost constraints.

Our initial objective at ERF was not to determine average concentration. Rather, we wanted to identify the spatial bounds of white phosphorus contamination within the salt marsh. Sampling along transects at intervals corresponding to the fallout radii of the kinds of munitions used was adequate to meet this objective. Now that this site is undergoing remediation, questions arise, such as, "Has the level of white phosphorus contamination in an area declined?" or, "Are lethal quantities of white phosphorus still available to waterfowl feeding in the area?" Owing to high local spatial variability, the number of discrete samples needed for adequate coverage and resolution to answer these questions with confidence is far greater than what is affordable.

To minimize analytical costs while providing adequate resolution to characterize a contaminated area, composite sampling is typically used (Garner et al. 1988). By pooling and thoroughly mixing many samples, the concentration estimates obtained ideally represent the average concentrations in the area sampled (Gilbert 1987), and are more likely to be normally distributed than estimates obtained by discrete samples (Exner et al. 1985). However, when the contaminant is acutely toxic and located in hot spots, compositing is not generally considered desirable because the compositing dilutes the samples taken from the hot spots (Exner et al. 1985). Information on hot spot locations, however, can be obtained if the composite samples are formed from samples taken at contiguous locations (Gore and Patil 1994).

In this study, we tested two methods of compositing. The first was designed to estimate average concentration and variance to conform with current protocols where a cleanup level might be set. The second was designed to detect the presence of hot spots containing high, acutely toxic levels of white phosphorus. Details as to numbers and sizes of samples are given in the *Methods* section, and an overview of the rationale, objectives, assumptions, and approach follows.

COMPOSITE SAMPLING METHODS

Stirred composites

The traditional method of homogenizing composite soil samples uses drying, grinding, and sieving. Because of the potential hazard and loss of white phosphorus by sublimation and oxidation when soils are dried, this procedure is not applicable for sediments contaminated by white phosphorus.

We have found that white phosphorus contamination is generally confined to areas with standing water. Previous work has demonstrated that white phosphorus concentrations in the water column above contaminated sites are generally near or below detection, and are not correlated with the concentrations found in the sediment (Walsh 1995). However, if the sediments are disturbed by stirring, water column concentrations increase markedly and are correlated with the sediment concentrations. Our method for compositing white-phosphorus-contaminated samples was tested based on these features. We composited sediment samples from areas known to be contaminated, and mixed the sediment with an equal volume of water from the area. We then sampled the suspended sediment. Following analysis, concentrations were expressed on a dry weight basis.

Objective of sampling

We need to estimate mean white phosphorus concentration to rank contaminated areas by degree of contamination and to determine changes in concentration after a remedial action.

Assumptions

- Small areas (hot spots) having high concentrations and containing solid particles of white phosphorus punctuate much larger areas containing low or undetectable concentrations.
- Slow dissolution and diffusion from solid white phosphorus particles have, over the years, resulted in a partitioning that favors adsorption of molecular white phosphorus to sediment surfaces.
- White phosphorus concentrations in the fine-grain fraction of samples will be significantly higher in samples that contain solid particles than those without.
- If composite samples are formed by taking several sediment samples from designated areas and mixing each with water from those areas, the fine-grained sediment will remain suspended in the water column longer than the solid chunks of white phosphorus. The concentrations of white phosphorus found in the suspended sediment and water following thorough mixing will be correlated with the total amounts within the sample.
- To meet the above objective, composite sampling allows the analysis of fewer samples than does discrete sampling.
- The limit of quantitation of the analytical method is adequately low to accommodate possible dilution effects caused by combining some blank samples with one or more contaminated samples.

Approach

- Collect samples systematically using a two-dimensional grid with spacing designed to detect a single hot spot, if one exists, with probability of missing the hot spot no greater than 10%.
- Composite the samples by thorough mixing and take five subsamples of the composite. To sample only the fine-grained fraction, add water to the composite, mix thoroughly and sample the water and suspended sediment. Repeat with additional water to see if precision is increased.
- Determine white phosphorus in subsamples of the composite.

Sieved composites

If the objective of our sampling strategy is to determine whether solid pieces of white phosphorus are available to waterfowl, the large size difference between typical ERF sediments and milligram-size white phosphorus particles presents us with an opportunity to collect numerous point samples, which can be composited and then reduced in volume by sieving through an appropriate size mesh. White phosphorus particles, if present, are retained on the mesh and can be detected by various methods. This approach is similar to the way ducks feed and allows us to see if white phosphorus is available to dabbling ducks and swans, the receptors at most risk.

Objective of sampling

We must determine if lethal quantities of white phosphorus are available to waterfowl in a given area.

Assumptions

- Waterfowl are being acutely poisoned by the ingestion of white phosphorus.
- An acutely lethal dose of white phosphorus is in the form of at least one solid particle with a mass greater than 1 mg.
- The bulk of the solid particles resides in localized hot spots with radii on the order of 1 m.

Approach

- Collect samples systematically using a two-dimensional grid designed to detect a single hot spot, if one exists, with probabilities of missing the hot spot of 10, 20, and 40%.
- Composite the samples and isolate the fraction that potentially contains milligram particles of white phosphorus (i.e., fraction retained on 0.59-mm-mesh sieve).
- Determine if white phosphorus particles are present in the composite sample.

METHODS

Field tasks

Area sampled

We sampled an area encompassing one of the DWRC pens mentioned above because this area was known to contain white phosphorus that was available to waterfowl. These pens were located at the edge of a permanent pond in the salt marsh. The corners of pen 5 used in the DWRC studies were relocated by surveying (Fig. 1). An area of 7 × 20 m, encompassing the pen, was marked with survey lath. Prior to any activity, the area was checked for UXOs (unexploded ordnance). At the time of the sampling (May 1996) the water depth was approximately 10 cm. We visually inspected the surface before walking in the immediate vicinity to prevent suspending sediment and limiting visibility. Additionally, a hand-held magnetometer, a Heliflux Model GA52C Magnetic Locator, was used to scan the area to detect any buried ferrous metal objects. Three spots produced a signal, and these spots were marked with orange flagging and avoided.

Design of sampling grid

Samples were collected on the basis of methods described by Gilbert (1987) for locating hot spots with a chosen level of confidence that they will not be missed. These methods assume the following conditions:

- The hot spot is circular or elliptical.
- Samples are taken on a square, rectangular, or triangular grid.
- The distance between grid points is much larger than the area sampled at the grid points. (If a large portion of the area is sampled, the probability of hitting a hot spot will be greater than indicated by the model used here.)
- The definition of hot spot is clear.
- No errors are made in detecting a hot spot.

Also implied is that the area of the hot spot is small compared to the total area of interest, analogous to the proverbial needle in a haystack.

For the most part, these conditions are valid at ERF for the following reasons:

- The hot spots at ERF are most likely at the point of detonation of white-phosphorus-containing projectiles, which produce circular patterns of contamination (Walsh and Collins 1993).
- Samples were taken on square and triangular grids.
- Equal volumes of sediment were obtained at each sample point by way of a graduated coring device that had a diameter of only 2.65 cm, whereas the grid spacings used in this study varied from 0.91 to 2.44 m.
- A hot spot is defined as a localized area containing solid white phosphorus particles.
- If white phosphorus particles are abundant within each hot spot, detection errors should be minimal.

However, we do not expect the particles to be distributed evenly throughout the hot spot. Rather, the hot spots at ERF are likely to have more white phosphorus particles in their centers than towards their edges. Therefore, the number of particles found cannot be used to estimate the number of hot spots, if more than one hot spot exists.

To determine the grid spacing G, the length L of the semi-major axis (radius for a circle) of the smallest hot spot must be known. Previous studies tell us that L varies from approximately 0.5 to 1 m. Then, the acceptable probability β of not finding a single hot spot if one exists must be specified. A nomogram (Fig. 2) is then used to compute grid

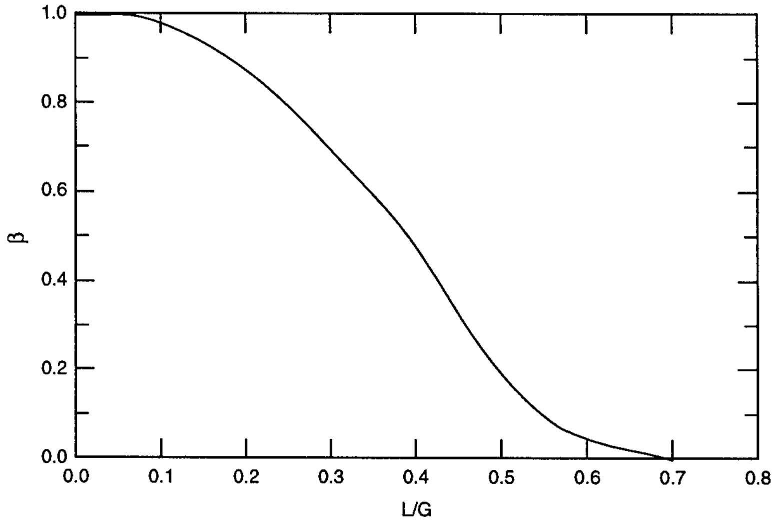


Figure 2. Curve relating L/G, *the ratio of the radius of a circular hot spot to spacing on a square grid, to risk* β *of not finding a hot spot. (After Gilbert 1987.)*

spacing (Gilbert 1987). For this study, stirred composite samples were collected to obtain a β equal to 10%, which corresponds to a grid spacing of 1.82 m for 2-m diameter hot spots. Sieved composite samples were collected for β equal to 10, 20, and 40%. Grid spacings ranged from 0.91 to 2.33 m for the square grid, and 2.00 to 2.44 m for the triangular grid (Table 3).

Also, discrete samples were collected on a 1.82-m-square grid, which corresponds to β of 10% for locating a circular hot spot with a radius of 1 m. These samples were collected to determine the location of hot spots and to compare the precision of average concentration estimates obtained by discrete and composite sampling.

Discrete samples

To relate the results of each of the field compositing protocols described below to white phosphorus concentration found by discrete sampling, we obtained individual 120-mL samples at the nodes of a 1.82-m-square grid for a total of 48 samples. In addition, we took replicate samples from five randomly chosen nodes. The top 9 cm of sediment was sampled. To maintain proper grid spacing, lath was placed at 1.82-m intervals on either side of the area sampled, and a 1.82-m quadrate constructed from $^3/_4$-in. i.d. CPVC pipe was used to determine each sampling point within the area. Samples were identified by row and column designations (Fig. 3). Rows were labeled 1 to 12 and columns 1 to 4 (Fig. 3).

Stirred composite samples

Next, we resampled the 1.82-m square grid, but this time 500-mL sediment samples were taken at each node from the top 9 cm of sediment, and four composite samples were formed, each containing 6 L of sediment. The first composite contained sediment from the first three rows (Fig. 4), the second from the next three, etc.

Each composite, having the consistency of a stiff clay, was homogenized by three mixing protocols (Fig. 4). The first protocol was simply mixing using a long handled spoon in a circular fashion. Intermittently, the composite was divided into quarters and each quarter turned over. After 10 minutes of mixing, the sample was flattened and divided into five sections. Five subsamples were obtained taken by taking a core from the total thickness of each section. We were careful to

Table 3. Grid shapes and spacings that were used to collect sieved composite samples from a 7- × 20-m area containing DWRC pen 5. Also shown are the number of samples that made up a composite sample and the total volume of sediment that was collected prior to sieving through a no. 30 mesh.

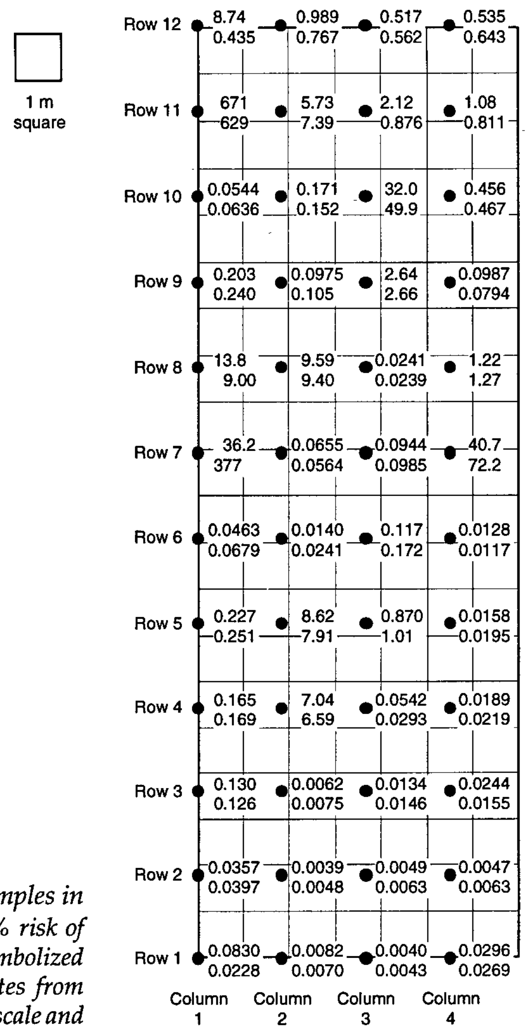
	Grid shape	β *(%)*	*Grid spacing (m)*	*No. of samples*	*Total volume (mL)*
$L = 1$	Square	10	1.82	48	2400
$L = 1$		20	1.96	44	2200
$L = 1$		40	2.33	36	1800
$L = 1$	Triangular	10	2.00	48	2400
$L = 1$		20	2.17	39	1950
$L = 1$		40	2.44	30	1500
$L = 0.5$	Square	10	0.91	184	9200

L = One-half length of long axis.
β = Risk of missing a single hot spot.

ensure that a cylindrical subsample was obtained to prevent bias. Each subsample weighed approximately 40 g (wet sediment).

Because we expected that solid white phosphorus particles were present in some of the composites, we knew that a truly homogenous sample could never be attained by mixing. We next tried sampling the smallest particle size fraction of the composite. We accomplished this by adding an equal volume of water (6 L) to the slightly less than 6 L remaining of each composite sediment sample (Fig. 4). The 1:1 sediment:water mixture was then stirred for 5 minutes. After a 5-minute settling time, during which the solid pieces of white phosphorus would fall to the bottom of the container, a glass coliwasa was used to obtain five subsamples made up of four increments from the top 11 cm of the water column containing suspended sediment. Finally, we added another 6 L of water to each composite sample to form a 1:2 sediment:water mixture, stirred, and repeated the sampling.

By sampling the suspended sediment, we discriminate against the largest white phosphorus particles, which are the cause of poor subsampling reproducibility. However, these particles



	Column 1	Column 2	Column 3	Column 4
Row 12	8.74 0.435	0.989 0.767	0.517 0.562	0.535 0.643
Row 11	671 629	5.73 7.39	2.12 0.876	1.08 0.811
Row 10	0.0544 0.0636	0.171 0.152	32.0 49.9	0.456 0.467
Row 9	0.203 0.240	0.0975 0.105	2.64 2.66	0.0987 0.0794
Row 8	13.8 9.00	9.59 9.40	0.0241 0.0239	1.22 1.27
Row 7	36.2 377	0.0655 0.0564	0.0944 0.0985	40.7 72.2
Row 6	0.0463 0.0679	0.0140 0.0241	0.117 0.172	0.0128 0.0117
Row 5	0.227 0.251	8.62 7.91	0.870 1.01	0.0158 0.0195
Row 4	0.165 0.169	7.04 6.59	0.0542 0.0293	0.0189 0.0219
Row 3	0.130 0.126	0.0062 0.0075	0.0134 0.0146	0.0244 0.0155
Row 2	0.0357 0.0397	0.0039 0.0048	0.0049 0.0063	0.0047 0.0063
Row 1	0.0830 0.0228	0.0082 0.0070	0.0040 0.0043	0.0296 0.0269

Figure 3. Square grid (1.82 m) pattern used to collect discrete samples in a 7- × 20-m area. The size of the grid was chosen based on a 10% risk of missing a 2-m-diameter hot spot. Samples were taken at the nodes symbolized by a solid circle. White phosphorus concentration (µg/g) estimates from duplicate analyses are shown at each circle. Light lines are shown for scale and represent 1 m.

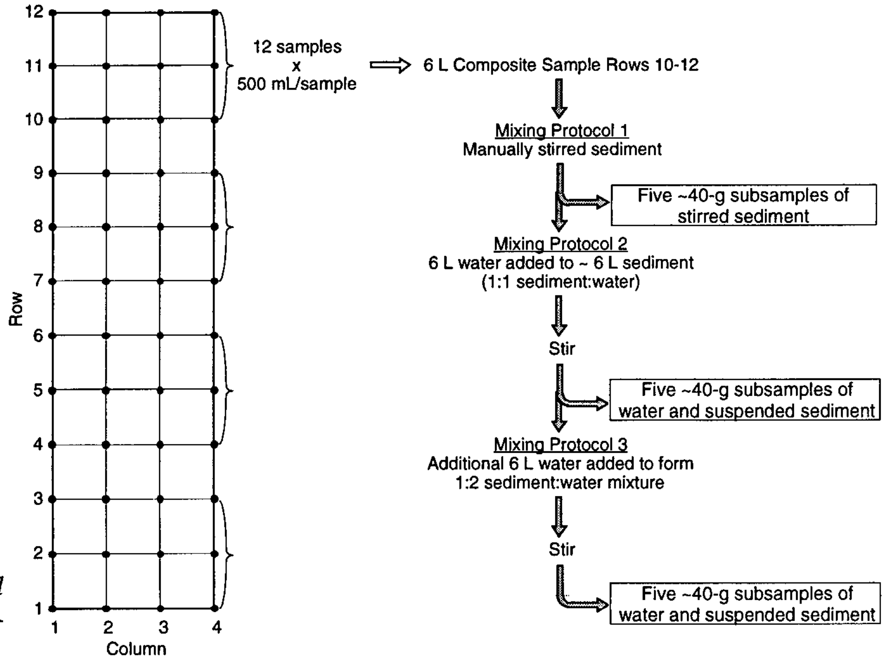


Figure 4. Mixing protocols and subsampling of stirred composite samples

are also the cause of acute poisoning of waterfowl; thus, we designed and tested a second compositing approach to detect the presence of these particles.

Sieved composite samples

The tight grid spacing required to detect a hot spot results in numerous samples, adding up to a large volume of sediment. If the objective of sampling is to detect milligram-size white phosphorus particles, and the sediment is fine silt and clay, samples can be pooled and white phosphorus particles isolated from the bulk of the sediment by passing the samples through a 30-mesh (0.59-mm) sieve. The material remaining on the mesh can then be examined for white phosphorus particles.

We collected samples on square and triangular grid patterns, based on the assumptions that the contaminated hot spots are circular with radii of 1.0 m. Additional samples were collected based on the assumption that the hot spot radius was 0.5 m and β equals 10%. To maintain proper grid spacing, quadrates and triangles were constructed from $^{3}/_{4}$-in. i.d. CPVC pipe and fittings.

At the grid nodes, a measured volume (50 mL) of sediment was collected using a syringe corer (2.65-cm i.d., 9-cm length) and samples were combined in a wash bucket equipped with a 30-mesh sieve (Forestry Supply, Jackson, Mississippi, Part No. 77255) to produce one composite sample for the 7- × 20-m area. The wash bucket was held underwater, and the sediment stirred to wash away its fine-grained part and reduce the volume of the sample. Previously, when ERF sediments were sieved in this way, the volume was reduced by a factor of about 100, depending on the amount of organic matter present. Each composite sample was placed in a glass jar equipped with a septa cap and refrigerated in the dark until analysis. Duplicate samples were taken for each grid shape and spacing.

Laboratory tasks

Discrete samples

The 53 discrete samples from the 1.82-m-square grid were analyzed in duplicate using the standard method of analysis for white phosphorus in sediment (USEPA 1995). For this method, white phosphorus is solvent-extracted from 40-g wet subsamples, and the solvent is analyzed by gas chromatography (GC). This method determines the total mass of white phosphorus present in a sample, and the results are expressed in concentration units (µg/g). Following removal of the isooctane from each sample, the dry weight of each sediment subsample was measured and white phosphorus concentrations were calculated using dry sediment mass.

Following subsampling for the GC analysis, approximately 80 mL or 120 g of sample remained, and we examined this sediment for white phosphorus particles by spreading each sample on an aluminum plate and heating until all water evaporated. If white phosphorus particles were present, we detected them by observing a localized area of intense smoke and flame, and the formation of a bright orange residue. Particles greater than 0.3 mm in diameter (26 µg) can be detected using this method (Walsh et al. 1995). These samples were not sieved because the amount of sediment was small.

Stirred composite samples

The stirred compositing method produced 15 subsamples from each of the four composites taken, for a total of 60 subsamples. To each of the subsamples, we added 40 mL of isooctane to extract the white phosphorus. After shaking the samples for 18 hours, we collected the isooctane extract and a 1-µL aliquot was analyzed by GC-NPD. Each subsample was allowed to dry in a fume hood, and the air dry weight determined. Concentrations were expressed as mass of white phosphorus (µg) per dry sediment mass (g).

Sieved composite samples

To detect the presence of white phosphorus, the sieved composite samples were warmed to room temperature, and headspace Solid-Phase Micro Extraction (SPME) followed by gas chromatography was performed (Walsh et al. 1996b). When the SPME method indicated that white phosphorus was present, we examined the sample using a dissecting microscope, picking out white phosphorus particles and measuring them with a micrometer. When we observed no more particles under the microscope, the sample was spread in a thin layer on an aluminum pan and heated to ignite any remaining white phosphorus particles, as described above.

Data analysis

Discrete samples. All descriptors of populations, such a mean, standard deviation, and variance, as well as statistical tests such as ANOVA, assume that data are normally distributed. So, concentration estimates obtained from the duplicate analyses for the discrete samples were plotted on normal probability paper to determine if the assumption of a normal distribution was reasonable. The data transformed by taking the natural logs were also plotted. Sampling variance, defined as the spatial heterogeneity, and analytical variance, ascribable to mixing, subsampling, extraction, dilution, and measurement in the laboratory, were calculated using ANOVA on the untransformed or transformed data.

Stirred composite samples. Concentration estimates obtained for the stirred composite samples were also plotted on normal probability paper to determine if compositing and mixing normalized the data. Both ANOVA and the Kruskal-Wallis test (the nonparametric equivalent of ANOVA) were used to compare the means obtained by the three mixing protocols.

Sieved composite samples. The numbers of particles detected using each grid spacing and shape were tabulated.

Table 4. White phosphorus concentrations and numbers of particles found in discrete samples taken from the nodes of a 1.82-m-square grid in a 7- × 20-m area. Two subsamples of each discrete sample were extracted and analyzed.

Row	*Column*	x (*m*)	y (*m*)	*WP conc.* (*µg/g dry weight*)		*Mean*	*Field replicates* *Separate samples*		*Particles found by hot plate*	*Mass of sediment examined for particles* (*g*)
1	1	0	0	0.0830	0.0228	0.0529			0	125
1	2	1.82	0	0.0082	0.0070	0.0076			0	115
1	3	3.64	0	0.0040	0.0043	0.0042			0	119
1	4	5.46	0	0.0296	0.0269	0.0282			0	115
2	1	0	1.82	0.0357	0.0397	0.0377			0	126
2	2	1.82	1.82	0.0039	0.0048	0.0043			0	122
2	3	3.64	1.82	0.0049	0.0063	0.0056	0.0059	0.013	0	108
2	4	5.46	1.82	0.0047	0.0063	0.0055			0	122
3	1	0	3.64	0.0130	0.0126	0.0128			0	131
3	2	1.82	3.64	0.0062	0.0075	0.0068			0	123
3	3	3.64	3.64	0.0134	0.0146	0.0140			0	129
3	4	5.46	3.64	0.0244	0.0155	0.0200			0	127
4	1	0	5.46	0.165	0.169	0.167			0	134
4	2	1.82	5.46	7.04	6.59	6.82			0	105
4	3	3.64	5.46	0.0542	0.0293	0.0417	0.0636	0.0601	0	104
4	4	5.46	5.46	0.0189	0.0219	0.0204			0	123
5	1	0	7.28	0.227	0.251	0.239			0	117
5	2	1.82	7.28	8.62	7.91	8.26			0	118
5	3	3.64	7.28	0.870	1.01	0.939			0	132
5	4	5.46	7.28	0.0158	0.0195	0.0176			0	116
6	1	0	9.1	0.0463	0.0679	0.0571			0	128
6	2	1.82	9.1	0.0140	0.0241	0.0190			0	130
6	3	3.64	9.1	0.117	0.172	0.145			0	134
6	4	5.46	9.1	0.0128	0.0117	0.0122	0.0571	0.0541	0	115
7	1	0	10.9	36.2	377	206			9	137
7	2	1.82	10.9	0.0655	0.0564	0.0610			0	127
7	3	3.64	10.9	0.0944	0.0985	0.0965	0.169	0.186	0	111
7	4	5.46	10.9	40.7	72.2	56.4			6	126
8	1	0	12.7	13.84	9.00	11.42			0	117
8	2	1.82	12.7	9.59	9.40	9.50			0	120
8	3	3.64	12.7	0.0241	0.0239	0.0240			0	125
8	4	5.46	12.7	1.22	1.27	1.24	0.671	0.818	0	125
9	1	0	14.6	0.203	0.240	0.222			0	129
9	2	1.82	14.6	0.0975	0.105	0.101			0	130
9	3	3.64	14.6	2.64	2.66	2.65			0	121
9	4	5.46	14.6	0.0987	0.0794	0.0890			0	127
10	1	0	16.4	0.0544	0.0636	0.0590			0	110
10	2	1.82	16.4	0.171	0.152	0.161			0	108
10	3	3.64	16.4	32.0	49.9	40.9			0	104
10	4	5.46	16.4	0.456	0.467	0.461			0	107
11	1	0	18.2	671	629	650			102	117
11	2	1.82	18.2	5.73	7.39	6.56			5	105
11	3	3.64	18.2	2.12	0.876	1.50			0	108
11	4	5.46	18.2	1.08	0.811	0.947			0	101
12	1	0	20	8.74	0.435	4.59			0	112
12	2	1.82	20	0.989	0.767	0.878			0	121
12	3	3.64	20	0.517	0.562	0.540			0	104
12	4	5.46	20	0.535	0.643	0.589			0	118

RESULTS

Discrete samples

White phosphorus was detectable by solvent extraction and gas chromatography in every discrete sample taken on the 1.82-m-square grid; concentrations ranged from 0.0039 to 671 μg/g (Tables 4 and 5, Fig. 3). The lowest concentration found was approximately ten times the method detection limit.

The data were not normally distributed (Fig. 5), as is common with environmental data for low-concentration contaminants, and especially when the dominant form is particulate. Even the log-transformed data were skewed (Fig. 6a,b), but much closer to normal distribution than the untransformed data.

Keeping in mind that the assumption a normal distribution is violated by this data set, even when log transforms were used, sampling variance overwhelmed analytical variance (Table 6). Even when the data were partitioned by proximity into four subdivisions (i.e., rows 1 to 3, rows 4 to 6, etc.), analytical variance was always less than sampling variance for the log-transformed data.

The degree of spatial heterogeneity in this relatively small area (7 × 20 m) is evident when we consider that the ratio of the highest concentration found to the lowest is over 172,000 (Table 6). In contrast, heterogeneity within subsamples of the same discrete sample was much less, with 44 of the 48 pairs within a factor of two. Again, grouping the data by proximity into four subdivi-

Table 5. Means, maximums, minimums, medians, and geometric means for duplicate analyses of discrete samples collected on 1.82-m-square grid grouped by rows to form four subdivisions.

	White phosphorus conc. (μg/g)		
	Subsample 1	*Subsample 2*	*Mean of subsamples*
All rows (n = 48)			
Mean	17.6	24.6	21.1
Max.	671	629	650
Min.	0.0039	0.0043	0.0042
Median	0.108	0.129	0.123
Geometric mean	0.227	0.223	0.234
Rows 1 to 3 (n = 12)			
Mean	0.0193	0.0140	0.0166
Max.	0.0830	0.0397	0.0529
Min.	0.0039	0.0043	0.0042
Median	0.0106	0.0100	0.0102
Geometric mean	0.0117	0.0109	0.0116
Rows 4 to 6 (n = 12)			
Mean	1.43	1.36	1.39
Max.	8.62	7.91	8.26
Min.	0.0128	0.0117	0.0122
Median	0.0856	0.119	0.101
Geometric mean	0.133	0.146	0.141
Rows 7 to 9 (n = 12)			
Mean	8.74	39.3	24.0
Max.	40.7	377	206
Min.	0.0241	0.0239	0.0240
Median	0.712	0.755	0.733
Geometric mean	0.868	1.06	1.01
Rows 10 to 12 (n = 12)			
Mean	60.3	57.6	58.9
Max.	671	629	650
Min.	0.0544	0.0636	0.0590
Median	1.04	0.705	0.913
Geometric mean	1.94	1.45	1.83

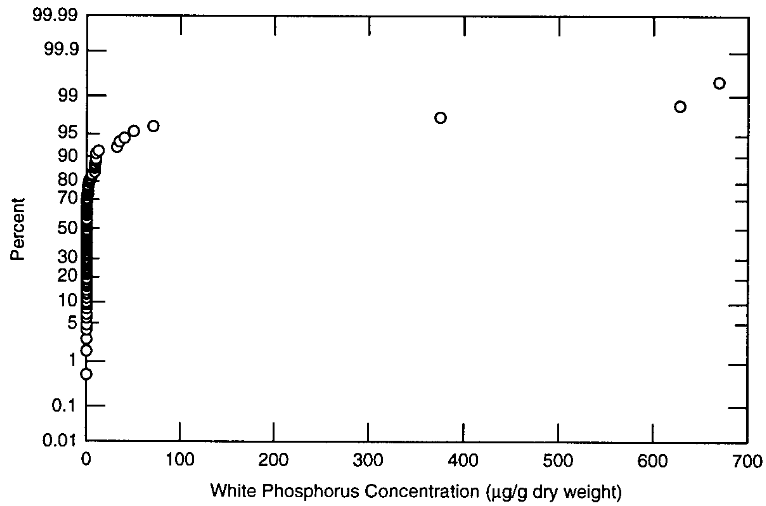


Figure 5. Probability plot of white phosphorus concentration data obtained on 1.82-m-square grid. Because the data are not normally distributed, they do not fall on a straight line.

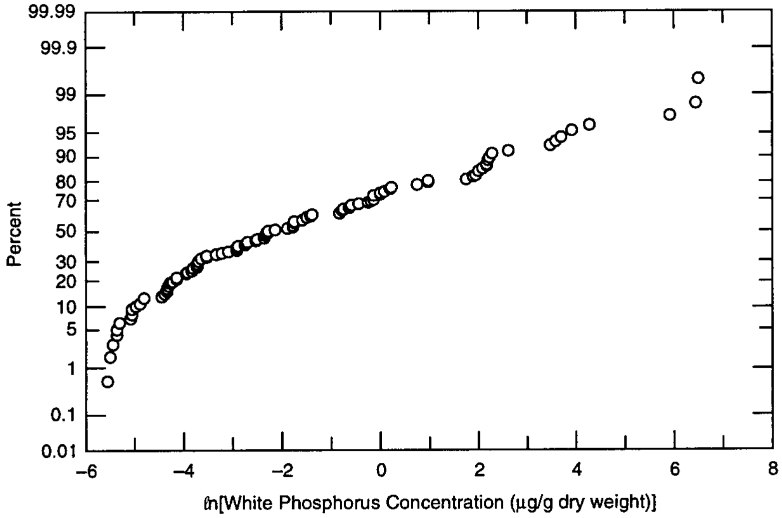
Table 6. Comparison of sampling and analytical variance in untransformed and transformed data for discrete samples.

	All rows	*Rows 1 to 3*	*Rows 4 to 6*	*Rows 7 to 9*	*Rows 10 to 12*
Untransformed					
Ratio of highest conc. to lowest for discrete samples	172,000	21.2	737	15,800	12,300
Largest conc. ratio for duplicates	20.1	3.65	1.85	10.4	20.1
Transformed					
Mean of natural logs	–1.45	–4.46	–1.960	0.013	0.603
Sampling variance of natural logs	17.4	1.42	10.2	16.6	12.5
Analytical variance of natural logs	0.204	0.090	0.046	0.254	0.428
F Ratio	85	16	220	65	29

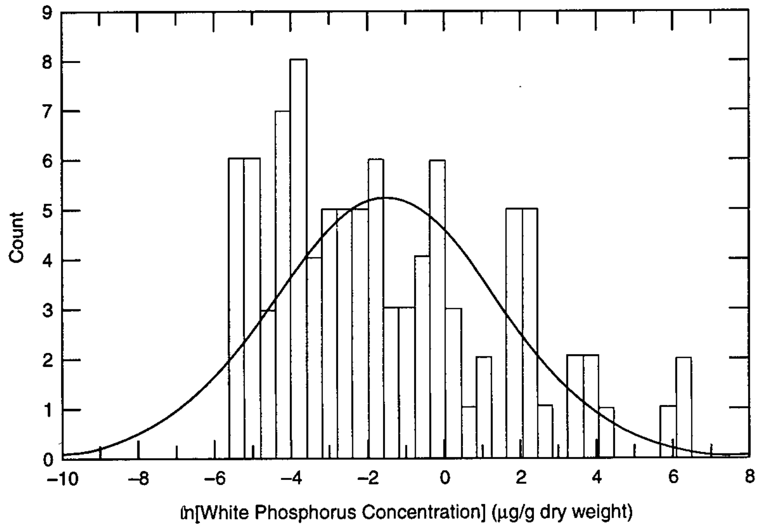
sions, spatial heterogeneity was always much greater than that observed in subsamples of each discrete sample (Table 6).

At 5 of the 48 grid nodes, we took a second 120-mL sample. Based on the results of a paired *t*-test comparing the means of the analytical replicates, no significant difference was found between the first and second sample taken at each node. In general, the ratio of the high to the low mean concentration estimate was less then a factor of two (Table 7).

White phosphorus particles were observed at only four sample points (Table 4), all of which had concentrations over 5 µg/g. The largest num-



a. Probability plot of data transformed by taking the natural logarithm of each value.



b. Histogram of log-transformed values with Gaussian curve superimposed.

Figure 6. Log-transformed data.

Table 7. Ratio of high to low analytical replicates and ratio of high to low means for field replicates taken at five nodes of a 1.82-m-square grid.

Analytical replicate	*First field sample*	*Second field sample*	*Ratio of high:low means*
Row 2, column 3			
1	0.0049	0.0059	
2	0.0063	0.013	
Mean	0.0056	0.00945	1.69
Ratio of high:low rep.	1.29	2.20	
Row 4, column 3			
1	0.0542	0.0636	
2	0.0293	0.0601	
Mean	0.04175	0.0619	1.48
Ratio of high:low rep	1.85	1.06	
Row 6, column 4			
1	0.0128	0.0571	
2	0.0117	0.0541	
Mean	0.01225	0.0556	4.54
Ratio of high:low rep	1.09	1.06	
Row 7, column 3			
1	0.0944	0.169	
2	0.0985	0.186	
Mean	0.09645	0.1775	1.84
Ratio of high:low rep.	1.04	1.10	
Row 8, column 4			
1	1.22	0.671	
2	1.27	0.818	
Mean	1.25	0.745	1.67
Ratio of high:low rep	1.04	1.22	

ber of particles (102 particles in 117 g of sediment) was found at the sample site with the highest concentrations, which were 671 and 629 µg/g for the duplicate analyses.

Stirred composite samples

The extreme sampling heterogeneity observed in the discrete sampling was reduced by compositing (Tables 8 and 9). Relative standard deviations (%RSD) for each of the three mixing protocols were all much less than those observed for the discrete samples. However, none of the mixing protocols consistently produced what might be considered low %RSDs. These results emphasize the extreme difficulty in sampling for this heterogeneously distributed contaminant.

The %RSDs are a reflection of the degree of normality, and the mean %RSDs are 58.2, 32.6, and 29.9% for mixing protocols 1, 2, and 3, respectively. Both of the mixing protocols that called for water being added to the composites had lower variability, and subsamples from the 1:1 sediment:water mixtures (mixing protocol 2) yielded mean concentrations that were in fairly close agreement to the stirred sediment (mixing protocol 1) means. By plotting on probability paper the concentration estimates obtained by the analysis of discrete samples and those obtained by compositing, we see graphically that compositing aided in normalizing the data (Fig. 7). As a result, estimates of the mean concentrations obtained from composites may be used for statistical comparisons that assume Gaussian distribution. Mixing protocol 3 (1:2 sediment:water) did not appear to yield any added benefits over mixing protocol 2.

Estimates of mean concentration obtained by the three mixing protocols were compared within

Table 8. White phosphorus concentration estimates for subsamples of stirred composites taken from four subdivisions of a 7- × 20-m area, and comparisons of means within each subdivision for composites with and without water added.

Concentrations (µg/g)			*Comparison of means*	
Sediment	*1:1 sed:water*	*1:2 sed:water*	*ANOVA F ratio*	*Kruskal-Wallis H value*
Rows 1 to 3				
0.0242	0.0263	0.0191		
0.0357	0.0229	0.0228		
0.0259	0.0248	0.0264		
0.0250	0.0238	0.0206		
0.0247	0.0274	0.0239		
Mean				
0.0271	0.0250	0.0226	2.2 ($p = 0.15$)	3.62 ($p = 0.16$)
Rows 4 to 6				
0.892	1.16	0.895		
0.813	1.53	0.627		
2.22	0.701	0.671		
4.97	0.717	0.737		
0.865	0.741	0.822		
Mean				
1.95	0.970	0.750	1.8 ($p = 0.20$)	3.98 ($p = 0.14$)
Rows 7 to 9				
4.49	6.41	7.02		
2.18	2.73	1.93		
4.35	4.75	1.84		
6.88	1.96	2.14		
19.2	2.27	1.84		
Mean				
7.43	3.62	2.95	1.6 ($p = 0.24$)	3.98 ($p = 0.14$)
Rows 10 to 12				
38.3	19.2	18.2		
42.7	21.7	14.5		
30.8	37.8	16.9		
24.4	36.3	16.5		
18.9	42.3	12.0		
Mean				
31.0	31.5	15.6	5.89 ($p = 0.0165$)	9.38 ($p = 0.0092$)

Table 9. Statistics for discrete and stirred composite samples for the four subdivisions.

	White phosphorus conc. (μg/g dry weight)			
	*Discrete**	*Stirred composite*		
	samples (n = 12 *means of dups)*	*Sediment* (n = 5)	*1:1 Sed:water* (n = 5)	*1:2 Sed:water* (n = 5)
Rows 1 to 3				
Mean	0.0166	0.0271	0.0250	0.0226
Variance	2.41×10^{-4}	2.37×10^{-5}	3.39×10^{-6}	8.02×10^{-6}
Standard deviation	0.0155	0.00487	0.00184	0.00283
RSD (%)	93.0%	18.0%	7.35%	12.5%
Range	0.0042 to 0.0529	0.0242 to 0.0357	0.0229 to 0.0274	0.0191 to 0.0264
Median	0.0102	0.0250	0.0248	0.0228
Geometric mean	0.0116	0.0268	0.0250	0.0224
Rows 4 to 6				
Mean	1.39	1.95	0.970	0.750
Variance	8.40	3.20	0.135	0.012
Standard deviation	2.90	1.79	0.367	0.109
RSD (%)	208%	91.6%	37.9%	14.5%
Range	0.0122 to 8.26	0.814 to 4.97	0.701 to 1.53	0.627 to 0.895
Median	0.101	0.892	0.741	0.737
Geometric mean	0.141	1.47	0.920	0.744
Rows 7 to 9				
Mean	24.0	7.43	3.62	2.95
Variance	3555	46.4	3.61	5.19
Standard deviation	59.6	6.81	1.90	2.28
RSD (%)	248%	91.7%	52.4%	77.1%
Range	0.0240 to 206	2.18 to 19.2	1.96 to 6.41	1.84 to 7.02
Median	0.773	4.49	2.73	1.93
Geometric mean	1.01	5.63	3.26	2.5
Rows 10 to 12				
Mean	58.9	31.0	31.5	15.6
Variance	34740	95.4	106	5.77
Standard deviation	186	9.77	10.3	2.40
RSD (%)	316%	31.5%	32.8%	15.4%
Range	0.0590 to 650	18.8 to 42.7	19.2 to 42.3	12.0 to 18.2
Median	0.913	30.8	36.3	16.5
Geometric mean	1.83	29.7	30.0	15.5

* The variances and the RSDs (%) are not strictly valid because of non-normality of the distribution, but they are useful for comparison.

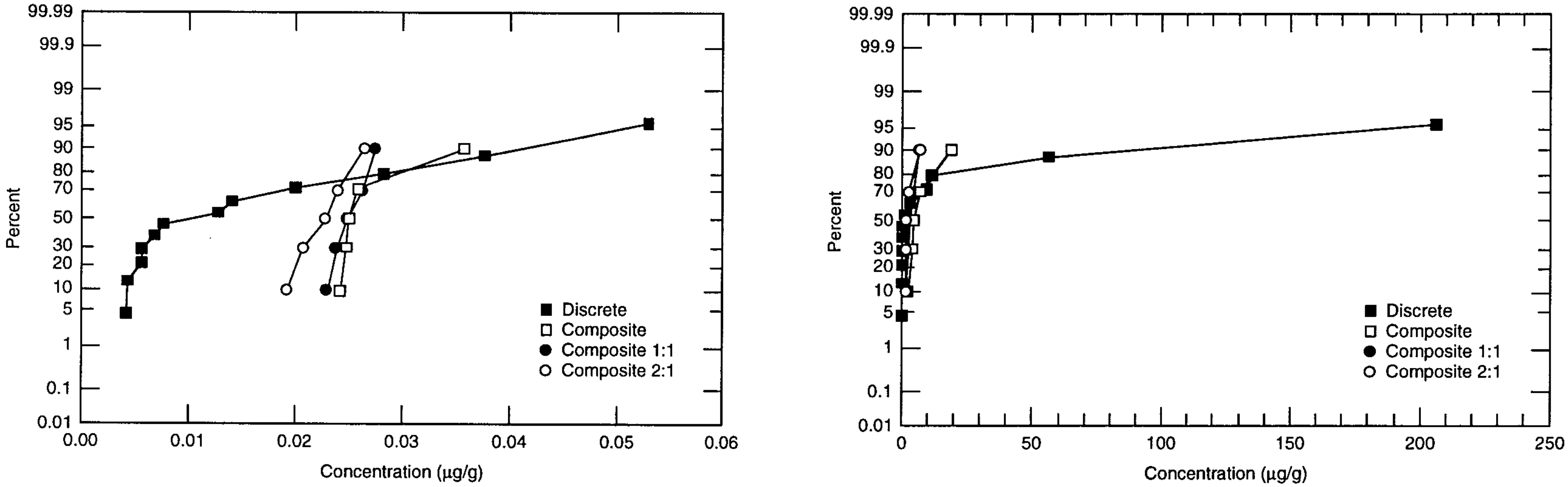
each subdivision sampled. Both ANOVA and the Krusal-Wallis test indicated that the means were not significantly different within three of the four subdivisions ($p > 0.05$) (Table 8). The significant difference was observed for the composite formed from rows 10 to 12, where the white phosphorus particles were most numerous and the highest concentrations found.

In terms of ranking the four subdivisions of the area sampled by level of contamination, the discrete sampling showed that the level of contamination increased sequentially with the first subdivision (i.e., rows 1 to 3) having the least contamination and the last subdivision (rows 10 to 12) having the most contamination. The mean composite concentrations ranked the subdivisions in this same order with fewer analyses (Table 9).

Sieved composite samples

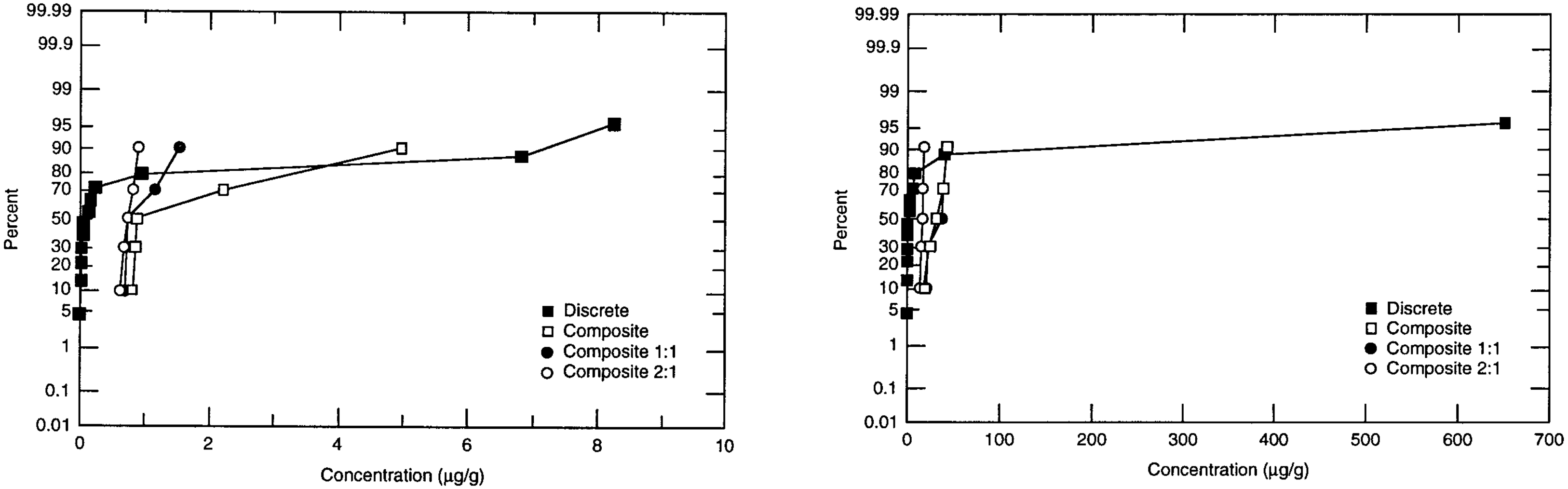
The ponded area we sampled was sparsely vegetated. Despite the large amount of sediment collected to form the composite samples (Table 3), once they were sieved, the volume in all cases was reduced to less than 100 mL. This volume of sediment can be analyzed without subsampling in the laboratory using headspace SPME. The SPME analysis detected a large amount of white phosphorus in each of the sieved composite samples collected.

Originally, we planned to count white phosphorus particles by spreading the sieved composite sample on a pan, heating, and counting flames. This approach was used for the first sample examined (2.33-m-square grid, rep. 1) (Table 10); however, so many particles were present in



a. Rows 1 to 3.

c. Rows 7 to 9.



b. Rows 4 to 6.

d. Rows 10 to 12.

Figure 7. Probability plots of discrete and composite samples taken within each subdivision. (Composite—mixing protocol 1; composite 1:1—mixing protocol 2; composite 2:1—mixing protocol 3.)

Table 10. Numbers of white phosphorus particles retained on a 0.59-mm mesh from sieved composite samples.*

Grid size (m)	*Grid shape*	*Number sample sites*	*Number of particles*		
			Rep 1	*Rep 2*	*Total*
0.91	Square	184	75	50	125
1.82	Square	48	21	34	55
1.96	Square	44	14	12	26
2.33	Square	36	28	43	71
2.00	Triangle	48	7	8	15
2.17	Triangle	39	29	9	38
2.44	Triangle	30	6	3	9

* 50-mL sediment samples collected at the nodes of regular two-dimensional grids within a 7- × 20-m area.

this sample that, once heated, it resembled the grand finale of a fireworks display. With so many particles simultaneously igniting and the residue of adjacent particles merging, accurate counting of the particles was difficult. For the remaining samples, we used microscopic examination first as described above in *Methods*.

White phosphorus particles were detected using each of the grid sizes and shapes we tested (Table 10). The greatest number of particles was found using the smallest (0.91 m) grid where the most samples were composited; however, number of samples in each composite was not related to the numbers of particles detected.

The particle sizes were typical of what we had observed previously in samples collected from permanently flooded areas. Of the 208 particles that were found by microscopic examination, most were between 0.59 mm (the size of the mesh used for sieving) and 2 mm in their longest dimension (Fig. 8), which is equivalent in mass to 0.2 to 7.6 mg for spherical particles. The largest particle found measured 7.4 × 3.7 × 3.0 mm and weighed approximately 150 mg.

DISCUSSION

The source of the white phosphorus contamination (i.e., point detonating projectiles) makes representative sampling a formidable task at Eagle River Flats and other wetland artillery and infantry mortar ranges. Some time ago, we examined the distribution of white phosphorus from point detonating smoke rounds fired from an 81-mm mortar at an upland site. We found that most of the residual white phosphorus was located within 2 m of the point of impact and that white phosphorus concentrations decreased exponentially out to 22.5 m away (Walsh and Collins 1993). Extrapolating these results to the pattern of contamination at ERF, any detection of white phosphorus at a sampling point, no matter how low the concentration, told us that white phosphorus munitions had been fired nearby. Thus, there was potentially at least one hot spot within a 20-m radius around the point of detonation of a round. The environmental conditions on this particular range lead to the unfortunate situation where acutely toxic white phosphorus residues are ingested by waterfowl. Because of the severity of the contamination and associated waterfowl mortality, Eagle River Flats is being remediated. The goal is to reduce waterfowl mortality by reducing their exposure to the white phosphorus residues.

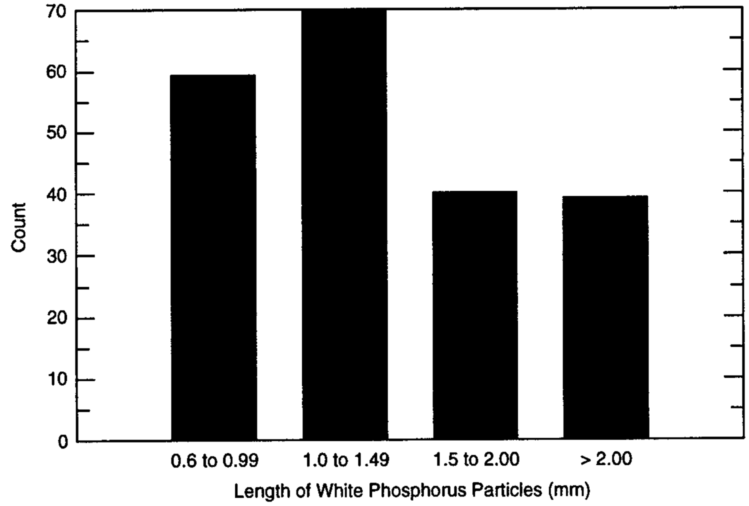


Figure 8. Size distribution of white phosphorus particles retained on a 0.59-mm mesh from composite samples taken from DWRC pen 5.

Even though ERF is an estuarine salt marsh, large areas undergo prolonged seasonal drying. We have found that white phosphorus particles are not persistent in these areas, and natural attenuation is one remedial process under investigation. Secondly, some ponds within the marsh have been temporarily drained to promote drying of contaminated sediments. Remediation will be considered successful if the amount of white phosphorus in the sediments declines to a level that is no longer hazardous to waterfowl. The need to evaluate remedial success led to this study.

For this study we chose to sample an area that was known to contain white phosphorus that was available to feeding waterfowl: the DWRC pen 5 that was used for chemical bird repellent studies. This pen is located near the edge of a permanently flooded pond, and, since 1990, when we began our studies, has always been covered with water. In the DWRC study, within this 7- × 20-m area, a total of 54 mallards, in groups of six, were penned for various lengths of time. Of these 54 mallards, 29 died of apparent white phosphorus poisoning. In the studies where the mallards were confined continuously for one week or more, all the birds died (Table 2). This pattern of mortality says that, if the mallards took enough "samples" from the sediments within the pen, they eventually would hit a hot spot. Modeling our sampling approach after the behavior of the ducks, we also took numerous samples; however, we chose the sample points systematically so that we would have some idea of our risk of missing a hot spot.

The results from the discrete samples taken on a 1.82-m-square grid indicated that the white phosphorus particles within this 7- × 20-m area were indeed localized in "hot spots" (Fig. 3). Spatial heterogeneity was enormous, with concentrations varying over six orders of magnitude. Recall the 25-m sampling interval originally used at ERF; only one discrete sample would have been taken from an area this size. Given the range of concentrations detected in this study, discrete samples taken at 25-m intervals will help to roughly define the bounds of the contamination but cannot be used to draw conclusions about the level of spot contamination unless blank samples predominate.

The assumption that the radii of the hot spots are around 1 m appears to be valid. For example, two hot spots were located in row 7 (Fig. 3), and the samples adjacent to each had relatively low concentrations of white phosphorus.

The two compositing methods tested were found to meet the specific objectives for which they were designed. The stirred compositing method permitted us to rank areas by average concentrations. Three mixing protocols were tested, all of which yielded data that approached a normal distribution (unlike the data from discrete samples). Of the three protocols, mixing a volume of sediment with an equal volume of water enhanced mixing and consequently reduced variability between subsamples. In addition, when white phosphorus concentrations were based on dry sediment mass, there were no significant differences between the mean concentrations found by manually stirring sediment and those found by sampling the suspended sediment in a 1:1 sediment:water mixture.

The sieved compositing method enabled us to determine the presence of solid white phosphorus particles.

For future applications of these compositing methods, what size grid would we recommend? The size of the grid depends on the acceptable risk of missing a single hot spot (β), if one exists. In all likelihood, more than one hot spot exists in highly contaminated areas of ERF or other impact areas, as we found in the 7- × 20-m area sampled for this study. If more than one hot spot exists, and we are still interested in finding only a single hot spot with a probability of 90%, how might the grid size be changed? If we know the number of hot spots (*H*), we may use a binomial distribution to compute the grid spacing needed to find a certain number (*h*) of these spots at an acceptable risk (Gilbert 1982):

$$\text{Probability of hitting exactly } h \text{ of } H \text{ hot spots} = \left(\frac{H!}{h!(H-h)!}\right)(1-\beta)^{h}\beta^{(H-h)}.$$

Unfortunately, we have no idea of how many hot spots exist in ERF. Gilbert (1982) presents two options when this knowledge is unavailable. The first is to guess a likely number of hot spots, based on historical information, and use the binomial distribution as shown above. The second is more complicated, and involves choosing an a priori Poisson distribution and using a compound binomial distribution. We lack sufficient information for either approach. However, we can determine the extremes of grid spacing by systematically increasing the number of hot spots in our calculation and seeing how grid size may increase while maintaining an acceptable risk of missing hot spots. For example, we set the probability of hitting zero of H hot spots to 10% (or some other acceptable risk) and the binomial distribution simplifies to

Probability of hitting exactly 0 of H hot spots

$$= 0.1 = \beta^H \text{ for } H = 1, 2, 3 \ldots$$

Then, solving for β, we see that

$$\beta = (0.1)^{(1/H)} .$$

Going back to the operating curve relating *L/G* to risk β (Fig. 2), we can calculate G, the grid spacing needed to maintain a 90% chance of hitting *at least* one hot spot. Results of this calculation for $H = 1, 2, 3, \ldots 15$ (Fig. 9) shows that the grid spacing needs to be on the order of a few meters to find at least one hot spot with a radius (L) of 1 m, unless the number of hot spots is large. Even if 100 hot spots exist, the grid spacing can be no larger than 10 m to find at least one hot spot 90% of the time.

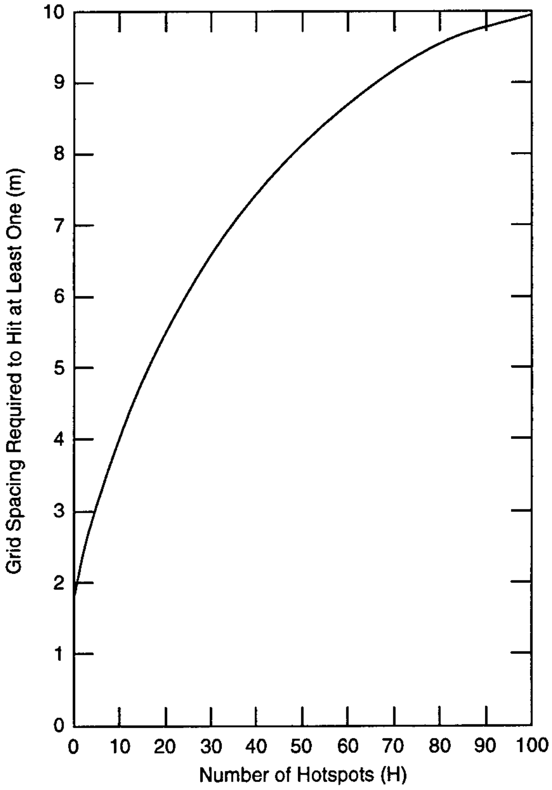


Figure 9. Effect of the number of hot spots on the grid size designed to detect at least one hot spot with a radius of 1 m while maintaining a 10% risk of not hitting any hot spots.

This requirement for such tight grid spacing emphasizes the importance of compositing samples to reduce the total number of samples submitted for analysis. Because a single hot spot can contain enough white phosphorus to poison hundreds of ducks, the prudent approach would be to keep the grid spacing small (approximately 2 m). However, for a large area, a compromise would still be necessary between a low risk of missing hot spots and the number of samples that is affordable.

For a large pond that is known to be contaminated and is being subjected to a remedial treatment, the area could be divided into sections. Composite samples representing each section could be formed by collecting discrete samples at 2-m intervals along transects through each section. Ideally, the same sampling approach would be conducted before the start of remediation and used iteratively to monitor it. The assumption used would be that if the remedial process worked along the transect, it also worked for the rest of the section.

CONCLUSIONS

When the need arises to determine the level of white phosphorus contamination in an area, composite sampling as described in this report is a cost-effective alternative to exhaustive discrete sampling and analysis. The stirred compositing approach provides concentration estimates with greater precision than discrete samples. It may be used to rank areas in terms of contamination level and permit monitoring of the decline in contamination after a remedial action. The sieved compositing approach may be used to determine if waterfowl-available white phosphorus is present in an area.

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13. ABSTRACT (*Maximum 200 words*)

White phosphorus from exploded munitions is a difficult contaminant to characterize in the environment. Spatial heterogeneity of concentration estimates is extreme, varying over many orders of magnitude for closely spaced discrete samples. To provide cost-effective data upon which decisions may be made, two composite sampling methods were designed to aid in characterizing the site and monitoring the remedial process for an area contaminated by white phosphorus. For each method, closely spaced discrete samples were collected on a grid pattern and pooled to form composites. The composites were then divided by size fractions. Mean white phosphorus concentrations were estimated for the fine-grain-size fraction that was obtained by suspension with water. The presence of highly toxic solid white phosphorus particles, the form that may be ingested by feeding waterfowl, was determined in the coarse-grain-size fraction that was obtained by sieving.

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