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Distributions of Airborne Agricultural Contaminants Relative to Amphibian Populations in the Southern Sierra Nevada, California

Research Plan

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by

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Notice

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Abstract

The Sierra Nevada mountain range lies adjacent to one of the heaviest pesticide use areas in the USA, the Central Valley of California. Because of this proximity, concern has arisen that agricultural pesticides, in addition to other contaminants, are adversely affecting the natural resources of the Sierra Nevada. Transport and deposition of pesticides from the Central Valley to the Sierra Nevada has been documented, and several lines of evidence have implicated pesticide drift from the Central Valley as a causal factor in the dramatic population declines of four amphibian species in the Sierra Nevada.

This study focuses on contaminants in lakes at high elevation in the southern Sierra, an area where unexplained population declines of one species, the mountain yellow-legged frog, have been dramatic. The southern Sierra is of particular interest because air pollution in the Central Valley and Sierra is generally greatest in the south, watersheds in the southern Sierra differ substantially in their proximity to the Central Valley, and the region includes large areas where the mountain yellow-legged frog has completely disappeared and other areas where large numbers remain.

The goals of this study are to: (1) describe the temporal and spatial patterns of distribution of more than 30 chemical contaminants, especially agricultural pesticides (i.e., insecticides and herbicides), all of which are expected to occur in very low concentrations; (2) identify the topographic and spatial attributes of the landscape that influence contaminant distributions (e.g., upslope air flowpath distance from the Central Valley, and elevation); and (3) determine whether there is an association between contaminant distributions and unexplained population extinctions of the mountain yellow-legged frog. We will conduct a study of temporal variation of contaminant concentrations in six lakes in three major watersheds from approximately April of 2002 through autumn of 2002. Media sampled will be the snow pack, lake water, sediment, semi-permeable membrane devices suspended in lake water, and possibly dry deposition from the atmosphere. In 2003 we will conduct a spatial survey of contaminants in at least 60 lakes in four major watersheds over a 130-km segment of the southern Sierra. We will also collect tadpoles of the ubiquitous Pacific treefrog for determination of acetylcholinesterase activity. Suppression of activity of this neurological transmitter hydrolase has been used as an indicator of exposure to pesticides. Results of the spatial survey of contaminants will be used in an analysis of the current and former distributions of the mountain yellow-legged frog and Pacific treefrog based on results of ongoing biological surveys for amphibians, fish, and habitat characteristics in 3200 water bodies in Sequoia and Kings Canyon National Parks. We will also analyze lake water and other media for contaminants no longer used in the Central Valley. Some of these may be transported from other continents, and some may be selectively deposited at the higher elevations.

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Section 1

Background

1.1 Rationale for Study

The Sierra Nevada mountain range lies adjacent to one of the heaviest pesticide use areas in the USA, the Central Valley of California (Figure 1; McConnell et al. 1998). Because of this proximity, concern has arisen that agricultural pesticides, in addition to other contaminants, are adversely affecting the natural resources of the Sierra Nevada (Cahill et al. 1996). Transport and deposition of pesticides from the Central Valley to the Sierra Nevada has been going on for some time. In the 1960s, an organochlorine residue of DDT (DDE) was found in frog tissue from numerous locations throughout the Sierra Nevada (Cory et al. 1970). More recently many current-use pesticides, primarily organophosphorus compounds, have been found at both low and high elevations in rain, snow, dry fall, air, surface water, and tissues of pine trees, frogs, and fish (Zabik and Seiber 1993; Aston and Seiber 1997; Datta et al. 1998; McConnell et al. 1998; LeNoir et al. 1999; Sparling et al., in press).

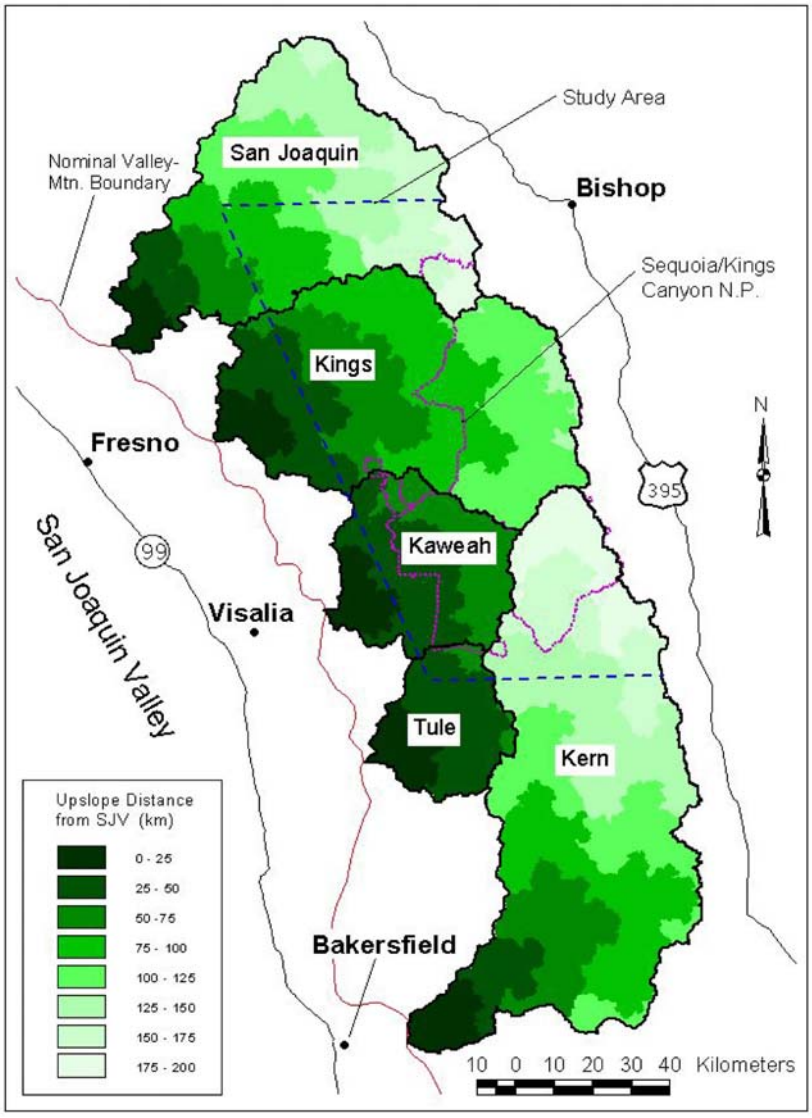

Figure 1. Study area, and upslope flowpath distances from the San Joaquin Valley. Each green shaded band indicates an increment in 25 km from the origin at the junction of the major river and the nominal boundary between the San Joaquin Valley and mountains (see Landscape and Other Metrics section for definitions and computational methods).

The impetus for the present study emanates from two types of information: action levels for contaminant concentrations, and recent dramatic population declines

of several amphibian species. At a high elevation (1920 m) site in the Kaweah River watershed, concentrations of some current-use pesticides in winter/spring rainwater were within an order of magnitude of LC_{50} values for some aquatic indicator organisms, and up to 30% of the criteria levels for protection of aquatic life (Zabik and Seiber 1993; McConnell et al. 1998). Moreover, aggregate exposure calculations for the observed mixture of pesticides in surface water near this site during summer showed that current exposure levels may be harmful to amphipods, although concentrations were well below the 96-h LC_{50} values for rainbow trout and stonefly (LeNoir et al. 1999). Given the unknowns regarding sublethal effects, synergistic effects of multiple contaminants, and toxicity of degradation products to amphibians (Bridges and Semlitsch 2000), the observed values at sites many tens of kilometers from the agricultural source are a concern.

Four species of frog inhabiting the Sierra Nevada have dramatically declined in numbers and distribution during the past several decades, and airborne agricultural contaminants have been suggested as one of several causal factors (Jennings and Hayes 1994; Drost and Fellers 1996; Sparling et al., in press). One of these species, the red-legged frog (*Rana aurora*), was declared a federally threatened species in 1996, and two others (mountain yellow-legged frog [*Rana muscosa*] and Yosemite toad [*Bufo canorus*]) are currently under review for listing as endangered (U.S. Fish and Wildlife Service 2000a, 2000b). Although there appear to be a number of factors causing the declines of the red-legged frog (a low-elevation species), proximity to upwind agriculture has been shown to be a significant correlate of the population declines (Davidson et al., in press). For two other species, the foothill yellow-legged frog (*Rana boylii*) at low elevation and the mountain yellow-legged frog at high elevation, proximity to upwind agriculture was found to be the most significant environmental factor associated with their declines (Davidson et al., in review). For the three latter species unexplained population declines in the Sierra Nevada have been most dramatic in the southern Sierra (Bradford et al. 1994b; Jennings and Hayes 1994), where exposure to agricultural contaminants is thought to be the greatest (see below).

1.2 Pesticide Transport and Deposition in the Southern Sierra

The western slopes of the Sierra Nevada are regularly bathed by surface air from the San Joaquin Valley (SJV) (Appendix A). Pesticides applied in the SJV can enter the air by drift during application, and by post application volatilization and erosion (Seiber and Woodrow 1998). Subsequently, pesticides can be transported in air as small particles, aerosols, or vapors. Downwind deposition may occur either by wet processes or by dry processes that include particle settling and vapor exchange with surface foliage, soil, and water (Seiber and Woodrow 1998). Presumably, pesticides deposited by either wet or dry processes are transported to lakes primarily by surface runoff. Agricultural pesticides are applied at all times of the year, with considerable variation in chemical use by month, and hence are available for transport to the Sierra Nevada year round (McConnell et al. 1998; LeNoir et al. 1999).

No data are available to indicate the relative deposition rates of pesticides between summer and winter, nor between wet versus dry deposition. During the warm months, however, upslope transport of pollutants from the SJV (Appendix A) dominates the air quality on the western slopes of the southern Sierra (Carroll and Baskett 1979; Cahill et al. 1996), and dry deposition of pesticides is thought to be the dominant mode of deposition (Zabik and Seiber 1993; LeNoir et al. 1999). For nitrates and sulfates, which are transported primarily as aerosols, dry deposition on the western slopes of the Sierra comprises a substantial fraction of annual deposition (Stohlgren et al. 1991). During summer thunderstorms, which occur erratically and are typically patchy in distribution, some wet deposition must occur. During late

fall and winter, when most of the annual precipitation occurs, deposition of pesticides in the Sierra Nevada is thought to occur primarily as wet deposition (Zabik and Seiber 1993; LeNoir et al. 1999). For much of the winter, air transport to the western slopes of the Sierra Nevada is largely decoupled from air within the SJV (Appendix A), and winds are dominated by northwesterly prevailing winds rather than terrain-driven winds (Cahill et al. 1996). During winter storms, which come off the Pacific Ocean, the inversion in the SJV is broken, air mixing is vigorous, and pollutants are rapidly deposited in precipitation (Cahill et al. 1996). Because of the synoptic nature of winter storms, pollutant concentrations in precipitation are relatively constant over large areas, and are generally low (Cahill et al. 1996).

1.3 Pesticide Distributions in the Southern Sierra

Two geographic patterns of distribution of pesticides and other pollutants are prominent on the western slopes of the Sierra Nevada. First, pollutant concentrations generally increase from north to south. This has been shown for a variety of pollutants, including fine sulfate and nitrate aerosols, aerosols from combustion products, fine soil particles, ozone, and several trace metals (Cahill et al. 1996). For pesticides, DDE concentrations in frogs in the 1960s were higher on the western slopes in the central and southern Sierra than in the northern and eastern Sierra (Cory et al. 1970), and current-use pesticides appear to show a similar pattern (Sparling et al., in press). This north-south pattern results largely from the greater upwind sources of pollutants for the southern Sierra than the northern Sierra, and generally stronger terrain-driven winds in the south due to steeper valley-mountain slopes (Cahill et al. 1996).

The second geographic pattern is a general decrease in pesticide concentrations as a function of distance/elevation from the SJV. Several studies have been done in the Kaweah River watershed along a distance/elevation transect extending from near the edge of the SJV (ca. 300 m elevation) up to about 2040 m elevation and 32 km from the edge of the SJV. As pesticide residues move with wind currents from the SJV into the mountains, pesticides are removed from the air by dilution, degradation, and deposition, with dilution having the largest effect (Shair 1995; Aston and Seiber 1997). Thus, pesticide concentrations have been found to decrease with distance/elevation during summer for 24-hour air samples, dry deposition, and pine needles, and during winter/spring for precipitation (Zabik and Seiber 1993, Aston and Seiber 1997; McConnell et al. 1998; LeNoir et al. 1999). Interestingly, for surface water this pattern of decrease with distance/elevation was evident only for the single sample collected at 3320 m elevation in the Kaweah watershed (about 45 km from edge of SJV) and another sample in the Kings River watershed at 3230 m and over 70 km from the SJV (LeNoir et al. 1999). Pesticide concentrations in surface water did not differ among sites at elevations $\leq$ 2040 m (LeNoir et al. 1999). Although the reduction in concentrations between 2040 and > 3200 m was striking, there is no evidence that these differences result from "different air masses." Evidence for such a separation has been observed during summer only during occasional synoptic meteorological events (Ewell et al. 1989). Moreover, tracer studies during typical summer conditions in the Kaweah watershed showed that upslope air transport operates at a relatively constant velocity up to the highest elevations sampled (3210 m), with tracer dilution occurring en route (Shair 1995).

Pesticide concentrations in the Sierra are also influenced by application rates in source areas in the SJV. In general, pesticide concentrations in air, dry deposition, and surface water in the Kaweah River watershed correspond with the seasonal pattern of pesticide application in nearby portions of the valley

(LeNoir et al. 1999). The absolute magnitude of variation in air concentration for one of the more common pesticide residues, chlorpyrifos oxon, was less than an order of magnitude from early June through mid October at the 1920-m site (Aston and Seiber 1997).

1.4 Focus on Lake Ecosystems in the Southern Sierra

This study focuses on the western slopes of the southern Sierra Nevada because pesticide exposure is expected to be greatest in this region, and because unexplained disappearances of amphibian populations have been conspicuous in this area. Moreover, several factors likely to influence terrain-driven air transport are more varied within this area than anywhere else in the Sierra. These factors include mountain-valley slopes, proximity to the Central Valley, and elevation. For example, the upslope pathway from the edge of the SJV is only about 60 km to subalpine lakes in the Kaweah River watershed, yet it is about 120 km to lakes a few kilometers away in the upper Kings River watershed, and nearly 200 km to lakes a few kilometers away in the upper Kern River watershed (Figures 1 and 2). The study focuses on lake ecosystems for sampling because the thousands of lakes in the southern Sierra comprise a major aquatic resource, and lakes constitute the primary habitat in the southern Sierra for the mountain yellow-legged frog. Lakes in this region are almost entirely confined to elevations above 2700 m, where almost no sampling has been done for current-use pesticides or contaminant transport processes.

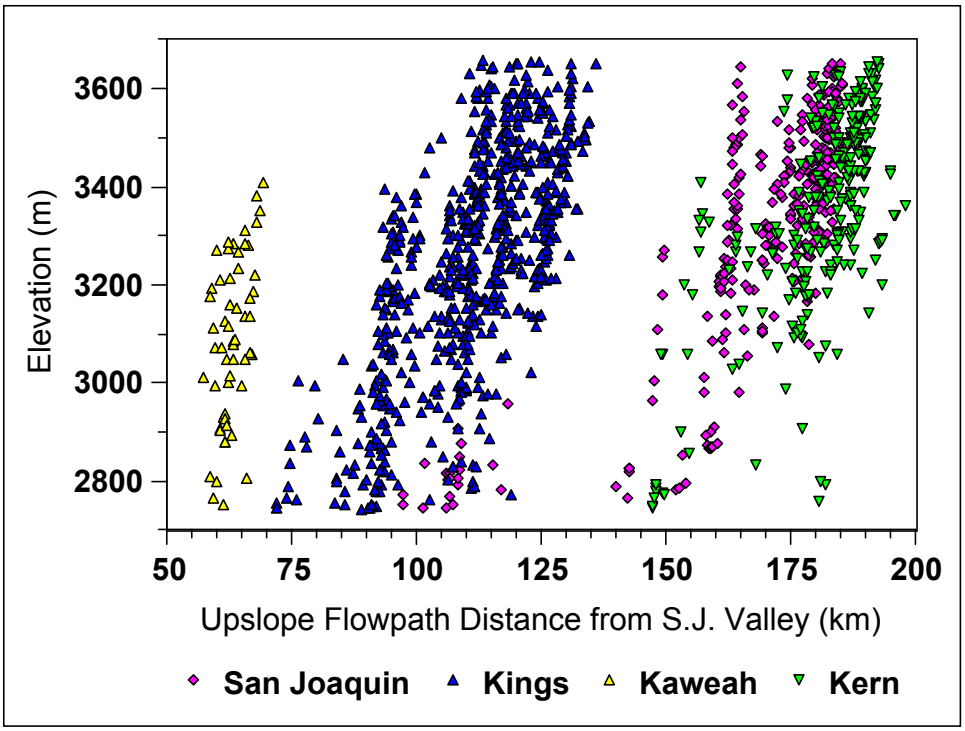

Figure 2. Lake elevation and upslope flowpath distance from the San Joaquin Valley (see Figure 1). Data are for lakes larger than 0.5 ha, and between 2740 and 3660 m elevation. Total number of lakes is 1330 (319 for San Joaquin, 57 for Kaweah, 699 for Kings, and 255 for Kern). Number of lakes is slightly overestimated primarily because the source coverages did not distinguish between lakes and marshes shown on USGS 7.5' maps.

1.5 Multiplicity of Factors Possibly Causing Amphibian Population Declines

A number of factors have been proposed as causal agents for amphibian population declines in the Sierra Nevada. For the mountain yellow-legged frog, these include non-native fish introductions, pesticides, acidic deposition, nitrate deposition, livestock grazing, UV-B radiation, drought, and disease (USFWS 2000a). Among these factors, strong evidence has been provided that introduced fishes have dramatically affected frog populations, and that other environmental factors are also important in determining site occupancy by the species (Knapp and Matthews 2000). Thus, it is imperative that any attempt to determine the influence of a specific factor on the distribution of this species be done in light of the effects of multiple factors, particularly introduced fishes, local environmental factors, and the other potentially adverse factors identified (Adams 1999). The potential effects of acidic deposition have been examined in several studies (Bradford et al. 1994a, 1998), two studies of UV-B relative to the mountain yellow-legged frog are ongoing (Vredenberg, Knapp, and Hansen, unpublished), and examination of individuals for evidence of disease is included in ongoing surveys for this species in the Sierra.

Section 2

Goals and Objectives

2.1 Goals

The primary goals of this study are to: (1) determine whether chemical contaminants, especially agricultural pesticides (i.e., insecticides and herbicides) currently used in the SJV, are concentrated in certain areas and at certain times within the southern Sierra Nevada at high elevation, (2) identify the topographic and spatial attributes of the landscape that influence contaminant distributions, and (3) determine whether there is an association between contaminant distributions and unexplained population extirpations of the mountain yellow-legged frog. Knowledge of contaminant distributions and associated landscape attributes will increase our understanding of the transport processes that bring contaminants to the Sierra Nevada. Such knowledge will also provide a basis to direct research or monitoring efforts at the appropriate times and places where contaminant effects are most likely to occur. Evaluation of the association between patterns of contaminant distribution and the distribution of the mountain yellow-legged frog, if any, will provide a test of the hypothesis that contaminants have been a contributing factor to the recent, dramatic population declines of this amphibian. This animal was formerly abundant throughout the Sierra Nevada and is currently undergoing review for listing as an endangered species (USFWS 2000a). Given the magnitude of the declines of this species, and the lack of long-term longitudinal studies, an evaluation of environmental correlates for changes in the species' distribution over a large area may be the most effective way to identify causes for its decline (Bridges and Semlitsch 2000; Davidson et al., in press).

A secondary goal of the project is to conduct a preliminary exploratory study of (1) both regional and long-range transport of persistent organic anthropogenic contaminants to high-elevation watersheds of the southern Sierra Nevada, and (2) elevational partitioning of semivolatile persistent contaminants. While the pesticides used in the last 20 years in the U.S. are generally not persistent, several persistent pesticides are still used in the developing countries of Asia (Li et al. 1996, Donald et al. 1999), and there is evidence that measurable concentrations of these pesticides may be deposited in western North America (Blais et al. 2000). In addition, studies in western Canada have shown that persistent chemicals preferentially condense at higher elevations (Blais et al. 1998), analogous to enhanced condensation at colder latitudes (Waina and Mackay 1993). Definitive evidence for trans-Pacific transport and deposition of persistent chemicals from Asia to the Sierra Nevada does not exist. Recent data hints at elevational partitioning in the Sierra Nevada (Landers et al. 2000), but more information is needed to conclusively demonstrate this.

2.2 Objectives and Hypotheses

The objectives and hypotheses below refer to selected chemical contaminants in lake water at high elevation in the southern Sierra Nevada, unless otherwise indicated. Following each hypothesis is a brief description of the statistical analysis for testing the hypothesis (Zar 1999 and others), or reference to more extensive discussion in the Statistical Analysis section. Statistical analyses will be done on contaminants individually and grouped in various ways:

Objective 1 *Describe the temporal variation of contaminant concentrations in aquatic media.* Hypotheses are:

H1.1. Contaminant concentrations in lake water and bed sediment are not constant over time. (ANOVA with repeated-measures for 6 sites.)

H1.2. Contaminant concentrations in lake water are directly related to concentrations in bed sediment. (Regression of concentrations in water and sediment at two times at 6 sites.)

H1.4. Temporal variation of contaminant concentrations in lake water and deposition fluxes are related to the temporal pattern of chemical application in the SJV. (Inspection of lake water concentrations and deposition flux measurements over time versus monthly application totals for five counties.)

Objective 2 *Describe the spatial distribution of contaminant concentrations in aquatic media.* Hypothesis is:

H2.1. Contaminant concentrations are not uniformly distributed across the study area. (Goodness of fit tests; also addressed by hypotheses H3.1, H3.2, and H3.3.)

Objective 3 *Current-use pesticides: Identify the topographic and spatial attributes of the landscape that influence the distribution of chemicals currently used in the SJV.* Hypotheses are:

H3.1. Concentrations in water and bed sediments are inversely related to the upslope surface air flowpath distance from the valley, and to elevation. (Stepwise regression; see Statistical Analysis section.)

H3.2. Cholinesterase activity of tadpoles is inversely related to the upslope surface air flowpath distance from the SJV, and to elevation. (Statistics same as for H3.1.)

H3.3. Contaminant concentrations differ among the four major watersheds in the southern Sierra. (Statistics same as for H3.1.)

H3.4. The composition of contaminant mixtures (i.e., relative concentrations of contaminants) differs among the four major watersheds and also varies as a function of upslope flowpath distance and elevation. (Multivariate statistics; see Statistical Analysis section.)

Objective 4 *Pesticides not currently used in SJV: Identify the topographic and spatial attributes of the landscape that influence the distribution of chemicals not currently used in the SJV.* Hypotheses are:

H4.1. Lake-water concentrations of persistent chemicals not currently used in the SJV are not correlated with upslope surface air flowpath distance from the SJV. (Statistics same as for H3.1.)

H4.2. Snow and bed sediment concentrations of persistent chemicals not currently used in the SJV with vapor pressure above 1 mPa are directly correlated with elevation. (Statistics same as for H3.1.)

Objective 5 *Determine whether the current distribution of frogs, and recent unexplained population extirpations of the mountain yellow-legged frog, are associated with the distribution of contaminants.* Hypotheses are:

H5.1. Contaminant concentrations are significant factors in determining site occupancy by the mountain yellow-legged frog and Pacific treefrog. (See Statistical Analysis section.)

H5.2. Contaminant concentrations are greatest at historic localities where the mountain yellow-legged frog has disappeared. (Logistic regression of site occupancy versus predicted contaminant concentrations.)

Section 3

General Approach

3.1 Overall Study Design

The research involves four components:

1. Contaminant temporal variation study. A study of temporal variation of contaminant concentrations in aquatic media will be conducted at six lakes beginning in spring 2002, and continuing through summer 2002. This study will provide an understanding for the magnitude of contaminant concentrations in southern Sierra lakes, temporal variation of contaminant concentrations over about half the year, and degree of correspondence between contaminant levels in different media. Pesticide application in the SJV is highly variable over the year (Appendix C). Information on the temporal variation of lake-water contaminant concentrations will be essential to planning the sampling schedule for the survey of contaminant spatial distributions.

2. Contaminant spatial distribution study. A survey of at least 60 lakes will be conducted to determine contaminant spatial distributions throughout the study area. This study will be conducted in summer 2003. We will also sample some sites remote from the study area (i.e., low elevation southern Sierra, coastal California, far northern Sierra, and eastern Sierra) for comparison with other studies at this scale.

3. Biological surveys. During 2001 (and possibly 2002) ongoing biological surveys for amphibians, fish, and habitat characteristics will be completed for all of Sequoia and Kings Canyon National Parks.

4. Data analysis. Results from the temporal study will be analyzed in 2002-2003; analysis of the spatial data and evaluation of associations between contaminant distributions and amphibian distributions will occur in 2003-2004.

3.2 Study Area and Amphibians

The study area consists of an approximately 130-km long segment of the western slopes of the southern Sierra Nevada (Figure 1). The specific area of focus is that portion above 2740 m (9000 feet) elevation, where the vast majority of lakes occur. This study area was selected because it includes the southernmost, high-elevation lakes in the Sierra, and it encompasses portions of four major watersheds, i.e., San Joaquin, Kings, Kaweah, and Kern. These watersheds vary considerably in upslope air flowpath distance from the SJV to lakes, but overlap substantially in linear distance from the SJV to lakes (Figures 2 and 3). At elevations above 2740 m, bedrock is dominated by igneous intrusive rocks rich in calcium sodium feldspars or potassium feldspar, with a few areas containing calcium carbonate-rich

sedimentary and metamorphic rocks or volcanic rocks (Melack et al. 1985). Ground cover is largely rock, soils are thin, and vegetation cover typically consists of sparse subalpine forest and alpine fell fields (Melack et al. 1985). Most lakes are glacial in origin, oligotrophic, and very low in alkalinity (Melack et al. 1985). Nearly all lakes have pH between about 6 and 8, with a few lakes with pH<6 due to natural iron pyrite deposits, and a few lakes with pH>9 due to marine meta-sedimentary sources (Melack et al. 1985.; Bradford et al. 1998). Land use is low-intensity recreation, and lakes are accessed only by trail or cross-country hiking. Precipitation occurs primarily during the winter/spring months of November to March, falling primarily as snow.

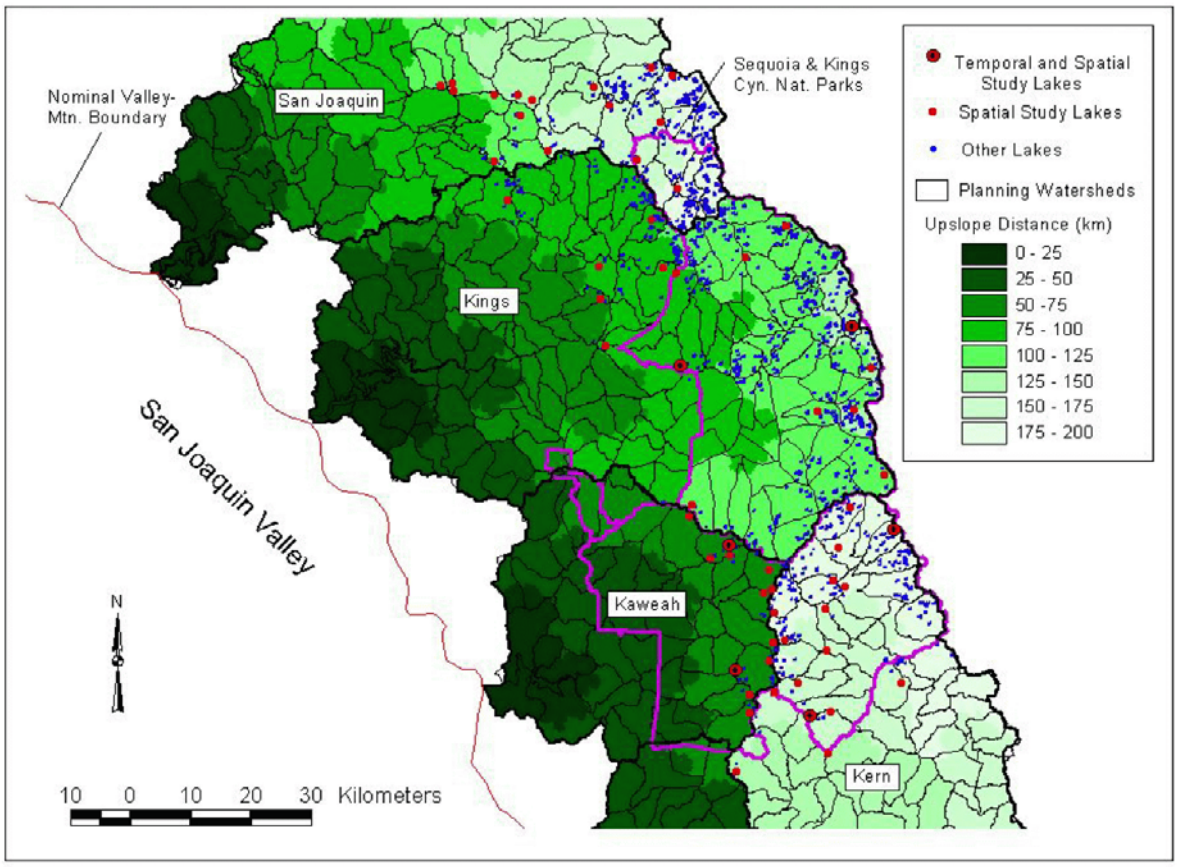

Figure 3. Distribution of lakes and sampling sites in the study area. Lakes represented are those meeting criteria described in Figure 2 (n=1330). Polygons outlined by thin black lines represent Calwater "planning watersheds" (see Landscape and Other Metrics section for definition). Green shaded bands represent upslope flowpath distance from the SJV as in Figure 1.

Four frog species inhabit the study area in lakes and ponds at elevations above 2740 m. All four species breed as soon as portions of the surface water become ice free in early spring. The mountain yellow-legged frog commonly inhabits lakes with depths greater than about 1.5 m (Bradford 1989; Knapp and Matthews 2000). Tadpoles require at least three summers to reach metamorphosis, and overwinter in water under ice (Bradford 1983; Vredenberg, unpublished). Adults remain near open water most of the time, overwintering in water or in cracks or holes near shore (Bradford 1983; Matthews and Pope 1999; Vredenberg, unpublished). The Pacific treefrog commonly inhabits shallow and often ephemeral ponds, but also may be found in deep lakes (Bradford 1989). Tadpoles reach metamorphosis during one summer. Adults remain at aquatic sites for only a few days or weeks in springtime during breeding. The

Yosemite toad is locally common in water bodies in the northern part of the study area, whereas the western toad (*Bufo boreas*) is spottily distributed in the rest of the study area (Karlstrom 1962; Bradford and Knapp, unpublished). Both of these species tend to inhabit shallow bodies of water, and tadpoles reach metamorphosis in one summer. Adults generally remain at the aquatic breeding site for only a few days or weeks at the time of breeding (Karlstrom 1962; Kagarise Sherman 1980).

3.3 Target Media

Lake water will be the primary sampling medium for assessing the temporal and spatial characteristics of contaminant distributions. This choice is dictated by the large number of lakes to be sampled in a limited time frame. The field and laboratory logistics of such a study with the resources available require the sampling medium to be easy to sample reproducibly, and the analytical cleanup and analysis to be rapid. Lake water meets these criteria better than other potential aquatic media. Concentrations in water are likely to be lower for some compounds than those in bed sediment and possibly in aquatic organisms, but previous studies have detected chlorothalonil, chlorpyrifos, diazinon, endosulfan I, endosulfan II, malathion, and trifluralin in lake water in the study area (LeNoir 1999). The triazine herbicide, atrazine, was detected in lake water in Isle Royale Michigan (Thurman and Cromwell 2000), which is much farther removed from areas of heavy use than the current study area (U.S. Geological Survey 1998). The principal approach for measuring the contaminant concentrations in lake water will be active sampling, using field filtration and extraction, during discrete sampling events. Semi-permeable membrane devices (SPMDs) will also be evaluated as a passive method of estimating lake-water contaminant concentrations integrated over time (Prest et al. 1995). Because SPMDs have not been used for sampling relatively polar compounds that are the focus of this study, a new type of passive sampler possibly better suited for these contaminants, the polar organic chemical integrative sampler (POCIS; Alvarez et al. 2000), will also be evaluated.

Snow melt is the dominant source of water for the lakes in the study area. Therefore, it is important to evaluate the relative significance of snow melt as a source of pesticide loads. Analysis of snow-pack samples will be conducted during the temporal variation study, and if snow melt appears to be an important source of contaminants in the lakes, an approach to measure this input will be included in the spatial distribution study.

Contaminant loads in bed sediment will also be examined. Analysis of lake bed sediments is complementary to water analysis in assessing the significance of pesticide contamination of lakes. Though many of the primary target analytes have relatively low K_{ow} values (Appendix B), there is evidence that some extensively bind to sediment particles. In addition, more hydrophobic organic contaminants are preferentially adsorbed onto fine particles (Kralik, 1999; Shelton and Capel, 1994). These chemicals might also have significant impacts on aquatic organisms, and several will be determined as part of the suite of secondary target analytes (see Target Analytes section).

Total dry deposition and wet deposition fluxes of contaminants will be measured during the contaminant temporal variation study, if a suitable sampler can be developed (see Sampling and Measurement Methods section). Total dry deposition includes particle-bound and vapor-phase pesticide deposited on surfaces by wind currents. Deposition fluxes at the study sites should be directly related to pesticide use patterns in the SJV.

Tadpoles will be analyzed for acetylcholinesterase activity, which can be suppressed by exposure to pesticides, and has been used as an indicator of exposure to both organochlorine and organophosphate pesticides in birds and amphibians (Rosenbaum et al. 1988; Sparling et al., in press).

3.4 Target Analytes

The principal criterion for selecting primary target analytes for the contaminant study was substantial use in the SJV near the study area (specifically, Fresno, Kern, Kings, Madera, and Tulare Counties). It was assumed that consistent substantial use over the three years 1996-1998 would predict continued substantial use during the study. Of course, ongoing regulatory actions, such as the recent restrictions on chlorpyrifos use may affect future use patterns. The 31 proposed primary target chemicals in Table 1 were nearly all used in the SJV at a median annual application rate of at least 5000 kg. The exception is lindane, which had a median annual use of less than 500 kg. Lindane (γ-hexachlorocyclohexane) was included in the target list because it is a persistent organochlorine pesticide, and its detection limit by the planned analytical method should be low enough to detect even with relatively low use. Target analytes in Table 1 represent a range of agricultural chemicals, including organophosphorus pesticides, organochlorine insecticides and fungicides, herbicides of various types, and three pesticides of miscellaneous natures. The peak use periods of the 31 chemicals span an entire year.

Other criteria that contributed to the selection of the compounds in Table 1 were (1) appropriate vapor pressure, (2) reasonable persistence in the water column, and (3) probable detectability using the proposed sampling and analytical procedures. A detailed description of these other selection criteria is provided in Appendix B. Principal transformation products of several of the primary target analytes (e.g., the oxygen analogs of the organophosphates) will also be determined.

In addition to the primary target analytes that represent current-use pesticides in the Central Valley, the aquatic organisms in the study area are also potentially exposed to parent compounds and derivatives of persistent pesticides no longer used in the U.S. This exposure could be from compounds persisting in sediments many years after their use in the U.S. was terminated, and it could be from compounds deposited after long-range transport from developing countries where they are still used. Other potential stressors include a host of anthropogenic chemicals that are not agricultural pesticides. Many of these compounds will be determined in the samples, especially sediments, collected to determine the primary target analytes. Tentatively, this suite of secondary target analytes includes the pesticides DDT, DDE, dieldrin, heptachlor, heptachlor epoxide, hexachlorobenzene, α-HCH, and cis- and trans-nonachlor, as well as selected polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs), dibenzo-p-dioxins (PCDDs), and dibenzofurans (PCDFs). The final list of secondary target analytes will depend on their detectability with a reasonable level of additional effort using the sampling and extraction protocols that will be optimized for the target analytes.

Table 1. Tentative list of 31 primary target analytes.[a] Transformation products that will also be determined are not listed.

Compound	Class	Annual Use (kg)	Season of Peak Use
alachlor	aniline herbicide	7,259	spring
azinphos methyl	organophosphorus pesticide (OP)	78,543	summer
butylate	thiocarbamate herbicide	20,549	spring
carbaryl	carbamate pesticide	208,877	summer
chlorothalonil	organochlorine (OC) fungicide	211,521	spring/summer
chlorpyrifos	OP	650,598	summer
cyanazine	triazine herbicide	183,568	summer
DCPA (chlorthal dimethyl)	phthalate herbicide	10,185	spring/summer
diazinon	OP	145,766	winter
dicofol	OC pesticide	164,026	summer
disulfoton	OP	10,309	spring/summer
endosulfan (both I and II)	OC pesticide	54,430	summer
EPTC	thiocarbamate herbicide	96,144	spring
ethalfluralin	aniline herbicide	5,070	spring
lindane (γ-HCH)	OC pesticide	463	spring
linuron	substituted urea herbicide	18,836	fall/spring
malathion	OP	65,331	summer/spring
methidathion	OP	92,307	winter/summer
methyl parathion	OP	24,892	spring
metolachlor	aniline herbicide	22,914	spring
napropamide	amide herbicide	18,372	winter/spring
pebulate	thiocarbamate herbicide	25,926	spring
pendimethalin	aniline herbicide	131,569	spring
permethrin	synthetic pyrethroid pesticide	23,574	summer
phorate	OP	36,546	spring
phosmet	OP	135,764	summer/spring
propargite	sulfonic acid pesticide	550,508	summer
simazine	triazine herbicide	216,616	winter
trifluralin	aniline herbicide	232,891	spring
tribufos	OP	250,774	fall

[a] Information extracted from State of California (1999) for the period 1996-1998. Annual use data are active ingredient applied in Fresno, Kern, Kings, Madera, and Tulare Counties in the year of median use of individual chemical during that three-year period.

Section 4

Contaminant Temporal Variation Study

4.1 Study Sites

We selected six lakes from the set of 60 to be included in the contaminant spatial study (Figure 3). The six were chosen with the expectation that they would reflect a diversity of contaminant conditions, but not necessarily represent the study area as a whole. Criteria for selection were: (1) location in Sequoia and Kings Canyon National Parks because helicopter support is available, (2) equal representation in Kings, Kaweah, and Kern watersheds, (3) proximity to the SJV (i.e., a "near" and a "far" site in each watershed), and (4) ease of access by foot for at least one site to be used for frequent sampling and ancillary studies. The six lakes selected range in elevation from 2930 m (9610 feet) to 3643 m (11,950 feet), and range in size from 0.5 to 17.2 ha.

4.2 Study Design

This study will involve sampling from approximately April 2002 through October 2002. The six lakes will be sampled by two field crews, accessing each site by helicopter. The timing of sampling is determined largely by the requirement for about 20 hours of water sampling at a site. The study includes the following sampling elements.

Snow pack: In 2002, the snow column will be sampled once at four of the lakes near the time of peak snow accumulation and prior to snowmelt (approximately early April).

Monthly scale variability: Lake water (and suspended particulate matter) will be collected at four-week intervals from the six lakes to follow temporal variation on a monthly scale. These measurements will be conducted from May through October, 2002. After ice-off, lake water will be collected from near the outlet. While lakes are ice covered (i.e., May, and possibly through July for the higher lakes, depending on the snowpack and weather), lake water will be collected from immediately beneath the ice at a location over deep water. These samples are expected to represent recent snowmelt because meltwater at this time is typically at 0ºC and tends to flow over the warmer lake water (Bradford 1983).

Weekly scale variability: Weekly lake-water samples will be collected at one of the six lakes during June, August, and October 2002. This will provide a total of 12 week-long intervals to assess temporal variability on a weekly scale over the ice-free period.

Optional sampling design for weekly scale variability. If method development establishes that a commercially available programmable, submersible water-sampling device is suitable for the study (see Field Sampling Approach in Sampling and Measurement Methods section below), it will be tethered underwater to automatically collect 200-300 L, integrated over each of the 12 weekly intervals.

Short-term intensive sampling events: The lake that will be sampled weekly will also be the subject of three eight-day intensive sampling events. These will be scheduled during June, August, and October. Eight daily lake-water samples will be collected during each of these sampling periods to provide integrated concentration measurements for comparison with passive sampling (see below), and to test our expectation that day-to-day variability of pesticide concentrations is small.

Sediment sampling: Sediments will be collected in June and October 2002 from all six lakes to determine loadings of chemicals that tend to partition to this medium.

Passive sampling of lake water: SPMDs and POCISs will be deployed during the short-term intensive sampling events. Comparison of the sums of the eight daily active sampling measurements and the passive sampler concentrations will provide an estimate of the sensitivity and variability of the passive sampling method for the target analytes in a lake-water medium. This will complement laboratory calibration of SPMDs and POCISs for selected target analytes that will be performed at the USGS laboratory in Columbia, MO. To assess the performance of SPMDs and POCISs in measuring lake-to-lake differences in pesticide concentrations integrated over longer periods, the devices will be deployed at three lakes during each of the monthly sampling periods from June through October 2002, and the results compared with active sampling measurements from the monthly and weekly sampling events.

Deposition measurements: If a suitable sampler can be developed for total dry deposition and wet deposition (see Sampling and Measurement Methods section), they will be installed at three lakes in early summer, 2002. Deposition samples will be collected every two weeks from mid July through until October 2002. This will provide three sets of nine measurements at each site.

Tadpole cholinesterase activity: Tadpoles of the Pacific treefrog will be collected in August of 2001, and July and August of 2002, from two bodies of water near each lake, including the lake itself if tadpoles are present. If tadpoles of the mountain yellow-legged frog are available in suitable numbers, specimens of this species will also be taken.

Ancillary environmental data: Data will be collected for a number of environmental parameters including lake pH, electrical conductivity, dissolved oxygen, temperature, maximum lake depth, and precipitation. See Sampling and Measurement Methods section for these and other parameters.

Section 5

Contaminant Spatial Distribution Survey

5.1 Study Sites

We selected lakes for sampling in a stratified random manner designed to test the hypotheses listed above, and to provide a representative sample of habitat for the mountain yellow-legged frog. We selected 60 lakes for sampling in the spatial survey in the following manner:

1. Elevation > 2740 m (~9000') and < 3660 m (~12,000'). The minimum elevation is set because relatively few lakes occur below 2740 m. The maximum elevation represents the approximate upper elevation limit for the mountain yellow-legged frog (Jennings and Hayes 1994).

2. Lake area > 0.5 ha. Lakes of this minimum size are likely to be of sufficient depth (i.e., > 1.5 m) to comprise potential habitat for the mountain yellow-legged frog, and they are accurately represented on USGS 7.5' maps.

3. Twelve lakes were selected from the Kaweah watershed, and 16 from each of the other three watersheds. The Kaweah watershed is under-represented because its lakes vary relatively little in upslope and linear distance from the SJV, and its lakes are distributed over a much smaller area than the other watersheds (Figures 2 and 3).

4. Within each watershed, lakes were stratified by upslope air flowpath distance from the SJV and elevation (Figure 3). For both flowpath distance and elevation, the range in values (max-min) was divided into 4 equal-sized intervals (except we used only three distance categories for the Kaweah watershed), and one lake was randomly selected from each distance/elevation category per watershed. One lake was excepted from this process, and was included because of its accessibility and history in previous studies.

5. A further restriction was placed upon lake selection in order to maximize the number of Calwater "planning watershed" units represented, thus spreading the lakes out spatially within each watershed (Figure 3). That is, if a lake being selected was in a Calwater unit that was already represented among selected lakes, it was excluded from the selection process unless there were no alternatives. The order of selection of distance/elevation categories was randomized.

6. Finally, we rejected a selected lake if it was within 1.0 km of an already-selected lake, if it drained into or from an already-selected lake, or if the lake was dammed.

Of the resulting 60 lakes, 36 are within Sequoia and Kings Canyon National Parks and 24 are in the three adjacent national forests (Figure 3). All lie within designated wilderness areas. The lakes range in elevation from 2744 m (9000 feet) to 3643 m (11,950 feet), and range in size from 0.5 to 32.0 ha.

5.2 Study Design

Results of the temporal variation study will be used to finalize the design of the contaminant spatial distribution survey. Some spatial variation in contaminant levels must be evident from the temporal variation study to warrant proceeding with the spatial distribution survey. Assuming this is the case, we will choose a sampling period when the temporal variation study indicates contaminant levels in lake water are likely to be measurable and relatively stable, presumably after ice-off. We expect to conduct the spatial distribution study in summer, 2003. If the snow-pack samples collected in the temporal variation study indicate that snow melt is an important source of pesticide contamination, the spatial distribution of loadings from snow melt will be incorporated in this phase of the project. The approach for evaluating loading from snow melt (e.g., the number of sites to be included, and whether to measure contaminants in snow pack or intensively monitor lake water during spring melt) would be decided in 2002, with sampling occurring in 2003.

Lake-water sampling will be by the active sampling (i.e., field filtration and extraction) method, unless the evaluation of SPMDs and POCISs during the temporal variation study indicates that passive sampling can be reliably substituted. Each site will be sampled over approximately a 20-hour period for water and Pacific treefrog tadpoles as described for the temporal study. Sediment will be included in the sampling if the temporal variation study indicates concentrations of some contaminants in sediment are higher or more stable than concentrations in lake water. Sampling will be done by two crews of two individuals each, accessing each site by helicopter. Because the survey of all 60 lakes (plus some duplicates) will take place over about 8 weeks, we will sample the lakes in blocks of 8 (i.e., a randomly selected “near” and “far” lake relative to the SJV from each of the 4 watersheds) over a 5-day period. We may also add additional sites if our cost estimates become more optimistic based on results of the temporal variation study. We may also incorporate snow sampling at some sites if warranted based on the results of the temporal variation study.

We will also sample a few sites remote from the study area (specifically, low elevation southern Sierra, coastal California, far northern Sierra, and eastern Sierra) for comparison with previous and ongoing studies at this scale. These sites will be selected to coordinate with the ongoing study by USGS-Biological Resources Division of pesticides and amphibians throughout central California and the Sierra Nevada. The present study is complementary to the USGS study by focusing more intensively on one portion of the Sierra and one amphibian species. In particular, our sampling will be more intensive temporally and spatially than the USGS study, and at higher elevation. Moreover, multiple factors will be included in our analysis of association between contaminants and amphibian distribution.

Section 6

Biological Surveys

Hypotheses concerning frog distributions will be addressed for the two widespread species in the study area: the mountain yellow-legged frog and Pacific treefrog. Several factors are known to be important determinants for the occurrence of these species. Consequently, such factors must be included in the analyses in order to detect relationships between frog occurrence and contaminant variables. Chief among these is the presence/absence of introduced fishes and lake depth (Bradford 1989; Knapp and Matthews 2000).

Analysis of amphibian distributions will be done for Sequoia and Kings Canyon National Parks only (Figures 1 and 3). This is because fish stocking has been much less intensive in the parks than in the neighboring national forests, and consequently fish density is much lower (Knapp and Matthews 2000). Thus, analysis of frog distributions in the parks affords the best opportunity to detect relationships between the distributions of frogs and contaminants.

In 1997, 1059 water bodies were surveyed in a consistent manner for frog populations, fish presence/absence, and habitat characteristics (Knapp and Matthews 2000). In 2000, further surveys were conducted in the same manner for over 900 water bodies in the parks under the supervision of Roland Knapp. These surveys also include examination of individuals for evidence of chytrid fungus infection, which has been implicated as a factor in the amphibian declines in the Sierra Nevada and elsewhere (Carey et al. 1999). In 2001, surveys will continue in unsurveyed areas, and a portion of the areas previously surveyed in 1997 will be re-surveyed. By the end of summer of 2001 (or possibly 2002), all of the 3200 mapped water bodies in the parks will have been surveyed.

Section 7

Sampling and Measurement Methods

7.1 Methods for Active Field Sampling and Determination of Contaminants in Lake Water

7.1.1 Data Quality Objectives

The lake water contaminant concentrations found by LeNoir et al. (1999) at two sub-alpine lakes (3,231 and 3,322 m elevation) can be used to estimate the detection limits needed to reliably determine a substantial number of the target analytes. Contaminant levels in the lakes were below detection limits for four of eight analytes in that study, and the measurable concentrations were generally less than 1 ng/L. The chemicals measured in that study (chlorothalonil, chlorpyrifos and its oxon, diazinon, endosulfan I and II, malathion, and trifluralin) are more widely used in the adjacent Central Valley than many of the target analytes of this project (Table 1). To detect differences in contaminant levels across space and time, detection limits should be at least a factor of 50 below the measured concentrations. Therefore, method detection limits below 5 pg/L will be sought for most of the target analytes. This will require collection of large volumes of lake water, gas chromatography/mass spectrometry (GC/MS) analysis of a substantial fraction of the extracted analytes, low instrumental detection limits, and low method blanks. Because concentrations of some of the secondary analytes (i.e., those not currently used in the SJV) are expected to be even lower than those of the target analytes (Donald et al. 1999), method detection limits on the order of 50 fg/L will be sought for these. Instrument detection limits for these compounds in the negative chemical ionization (NCI) mode should be substantially lower than those of most of the target compounds in the electron impact (EI) mode, facilitating lower method detection limits if blank levels can be minimized.

The sampling and analysis methods must also be reproducible. An overall recovery precision (RSD) of $\leq$30% will be the goal of the study. Overall recovery precision will be affected by variations in lake chemistry and between-sampling-team variance. Between-sampling-team variance will be assessed in a field trial before the temporal variation study begins. Surrogate recoveries will be used to estimate the overall recovery precision.

7.1.2 General Sampling and Analysis Approach

The sampling and analysis approach for the target analytes in lake water can be summarized as field filtering and extraction of 200-300 L of lake water onto a glass fiber filter and appropriate extraction resin, extraction of the filter and resin with organic solvent, appropriate extract cleanup and volume reduction, and analysis by GC/MS in the EI and NCI modes, using selective ion monitoring (SIM). The

methods of LeNoir et al. (1999), Shelton and Capel (1994), and Jarman (Walter Jarman, University of Utah, unpublished) will be used as starting points. Extensive method development and testing will be conducted prior to April 2002 to finalize the approach. Method development will focus on field sampling (water extraction), sample processing (back extraction of resin), cleanup, volume reduction, and analysis (GC/MS methods). Our first priority will be to have a working method in time for pilot field work in late fall 2001. This will allow us to evaluate the entirety of field and laboratory protocols and associated logistics and make modifications in time for the 2002 sampling season. It may necessitate using an existing analytical method for a limited number of pesticides (e.g., those measured by Lenoir et al. [1999]) for the 2001 effort and introducing improved methods for the entire suite of primary and secondary target analytes in 2002.

7.1.3 Method Development for GC/MS Analysis

Adaptation of the methods referenced in Table B.1 (Appendix B) will be used as a starting point for two composite methods, one EI(SIM) for all the analytes and one NCI(SIM) for the chlorinated analytes that are amenable to that ionization method. Emphasis will be given to high-volume injection approaches (Engewald et al. 1999), where 100 μL or more of sample can be analyzed. This will allow analysis of a large portion of the total extract (30% or more) without complicated solvent evaporation schemes and micro-sample handling, both of which introduce additional analytical uncertainty. Two qualifying ions, in addition to the major ion for quantification, will be used for compound identification. In addition to the parent compounds, major environmental transformation products, such as the oxygen analogs of the phosphorothioate pesticides, will be measured.

7.1.4 Method Development for Sampling and Sample Processing

These two aspects of the methodology will be developed concurrently. Throughout, contamination will be minimized. Whenever possible, materials contacting water sample, resin, or extracts will be cleaned by baking at 550°C. Otherwise, solvent rinsing procedures will be developed.

The first decision to be made is the type of extraction resin to be used. XAD-2 (Datta et al. 1998), and C18 (LeNoir et al. 1999, Thurman and Cromwell 2000) have been used to extract organic contaminants from water, although XAD-4 can also be used for water analysis (Rohm and Haas 1999) and it has been used to collect some of the target contaminants from air (Zabik and Seiber 1993, Aston and Seiber 1997, LeNoir et al. 1999). Recently, a mixed styrene-divinylbenzene/methylmethacrylate resin has provided good recovery for polar solutes from water (Osemwengie, unpublished). Each of these resins will be evaluated for analyte recoveries, maximum practical sampling rate, and analyte breakthrough volume (300 L sample volume being the goal).

Once the optimal resin and water extraction conditions have been determined, the resin cleanup and back extraction (removing analytes to an organic solvent for GC/MS) methods will be optimized. If acceptable blanks are not attainable with reasonable cleanup effort, the resin selection process will resume. Resin drying will be performed with a purifed nitrogen stream. Glass fiber filters containing suspended particulate matter will be batch extracted with solvents (e.g., Soxhlet). In-column elution will be developed and evaluated for the resin. If performance is inadequate, batch extraction (e.g., Soxhlet) will be pursued. Extraction may need to be effected with chlorinated solvents (LeNoir et al. 1999). Although methylene chloride has been used as a solvent for the determination of chlorinated pesticides by NCI GC/MS with large-volume sample injection (Staniewski et al. 1993), it may be more practical to perform solvent exchange prior to analysis. Separation on floracil and/or silica will be used to isolate the

various primary and secondary target compound classes. With the large-volume injection method, extract volumes will only have to be reduced to about 200-300 μL. This will be effected by either Kuderna Danish or TurboVap (Zymark Corporation, Hopkinton, MA) evaporation.

7.1.5 Field Sampling Approach

Once water extraction and lab processing procedures are successfully applied on spiked reagent water in the laboratory, a series of field experiments will be performed to develop and validate the field extraction methods and the overall sampling/processing/analysis method. The following describes the initial approach for the field extraction methods:

Water samples will be collected using a field-portable extraction system capable of extracting at least 200 L of water in less than 20 hours. Initial method development will be with the Infiltrex 100 instrument (Axys Group, Sidney, British Columbia). This instrument comprises a glass-fiber (45 μm) filter to collect suspended particulate matter, an extraction column containing approximately 50-g resin, a positive-displacement pump to draw the water sample through the filter and extraction column, a flow-measuring sensor, a microprocessor for instrument control, and internal power through two 6-V alkaline batteries (an external battery for additional power will be used to sample the required volume of water). The pump follows the extraction column, and all sample-contacting components upstream of the pump are Teflon to minimize contamination and analyte sorption loss.

Before ice-off a hole will be drilled in the ice with an ice auger at a location over relatively deep water. Before use, the sampling apparatus will be thoroughly rinsed with lake water before the glass fiber filter and resin column are installed. The sampling apparatus will be placed adjacent to the hole, and the sample will be drawn through tubing described below from a point 5-10 cm below the ice level and about 1 m lateral to the hole.

After ice-off, the sampling apparatus will be deployed on the shore of each lake near the outlet. A sampling boom constructed of 3/4" aluminum channel, approximately 9 m in length, supported by high-density polyethylene floats will be used to deploy PTFE Teflon tubing (3/8" I.D.) from the sampling device to a point approximately 5-7 m from shore, and 20 cm depth. The depth of the lake at the sampling position will be determined to be at least 1 m before sampling.

After about 18 hours of sampling (300 L water sample), the resin column and glass fiber filter will be removed, wrapped in aluminum and sealed in glass jars. The rest of the sampling apparatus will be cleaned with detergent and water and a small amount of deionized water prior to transport from the site. Resin and filter will be cooled to 4°C within 2 hours and transported back to the Environmental Sciences Division (ESD) laboratory within 3 days of collection.

An alternate sampling procedure will be followed for the weekly scale variability sampling if the Infiltrex 100 is used in the programmed mode. The Infiltrex will be programmed to collect 42 samples, one every four hours, during the week. Total sample volume will be determined during method development. Before initiating programmed sampling, surrogate compounds will be injected on-site while sampling a small volume of lake water. The sampling program will be activated (with a delay to allow site disturbance to subside) and tethered 30 cm below the surface at the sampling position with a float and anchor. The float will be below water surface to minimize the chance of disturbance during sampling.

7.2 Passive Sampling Methods

Two SPMD and two POCIS devices will be deployed at a depth of 50 cm near the lake outlet. They will be tethered to the lake bottom with a screw anchor and steel cable.

7.3 Contaminants in Snow

A pit will be dug with a snow shovel to the base of the snow pack. Snow will be removed from the pit wall with a cleaned aluminum or stainless-steel shovel to expose a clean surface; then snow sample will be collected from four equal-length segments spanning the entire depth of snow pack. Approximately 40 kg of snow will be collected from each segment. A duplicate sample will be collected at one of the sites. The general sample-processing approach used in Canadian studies (Blais et al. 1998) will be used. Snow from each segment will be placed in a separate pre-rinsed aluminum can, sealed, and transported back to the laboratory. Snow will be melted slowly in the laboratory, then extracted, processed, and analyzed the same as the lake water.

7.4 Contaminants in Bed Sediment

Bed sediment will be collected from the deepest portion of the lake from a float tube. The sampling device will be a gravity corer similar to those used by Hongve (1972) and Rose et al. (2001). The corer will be dropped or pushed into the sediment depending on the depth of the lake, and retrieved by a connected line. A plunger will be used to extrude the sediment, and 8-12 0.5-cm slices will be collected, to a maximum depth of 4 to 6 cm. If necessary, replicate cores will be taken to collect a sample of at least 20 g in each slice. At some lakes, a separate core will be taken for ^{210}Pb dating (Turner 1998). All samples will be stored in contaminant-free Teflon jars, protected from light, cooled to 4°C within 2 hours, and transported to the ESD laboratory within 3 days of collection. Samples will be extracted, processed, and analyzed using published approaches (Muir et al.1995, Okumura and Nishikawa 1995, Pearson et al. 1997, Fernandez et al. 1999, Rose et al. 2001) as starting points.

7.5 Contaminants in Deposition

Development of a suitable sampling system will be pursued in 2001. We expect to collaborate in this work with experts in deposition monitoring. We have discussed possible approaches with Dr. Thomas Holsen of the Civil and Environmental Engineering Department of Clarkson University. Design considerations will include ability to sample unattended, stabilization of at least a limited suite of analytes for two-week periods, operation on small batteries (or without power), and a relatively small footprint and unobtrusive appearance. Optimally, a sampler for both total dry deposition and wet deposition will be developed. However, if such a system proves unfeasible, a simple dry-deposition sampler can provide useful data. For the latter, either greased mylar strips (Franz et al. 1998, Odabasi et al. 1999) mounted on an aluminum sheet, or an ungreased collector (LeNoir et al. 1999) could be deployed under a cover to protect the sampler from rain (Ferm and Holtberg 1999). The sampling system will be evaluated in the Las Vegas Valley prior to deployment at the study sites. Samplers will be deployed at three contaminant temporal variation study sites in 2002. Deposition samples will be placed in Teflon jars, cooled to 4°C, and transported to the ESD laboratory within 3 days of collection. Extraction and cleanup procedures will depend on the collection medium, but will probably be based on published methods (Franz et al. 1998, Odabasi et al. 1999, LeNoir et al. 1999).

7.6 Tadpole Cholinesterase Activity

It is unlikely that any amphibians will inhabit more than two or three of the six lakes, largely because of the ubiquity of fish in the larger lakes. However, we anticipate being able to locate other water bodies near each of the six sample sites that will contain tadpoles of the Pacific treefrog and, in a few cases, tadpoles and adults of the mountain yellow-legged frog. We will collect whole tadpoles of the Pacific treefrog near all six sites at two times, July and August. Sample size will be 5-10 individuals at each site (one individual per cryovial). We will collect individuals from two ponds if possible because of family level variation in toxic effects (Bridges and Semlitsch 2000). Collection will be done by dip net, and animals will be killed by freezing in liquid nitrogen, carried in a 5-liter dewar. If tadpoles of the mountain yellow-legged frog are abundant (i.e., > 40 individuals in their second or later summer), we will also collect specimens in the same manner as for the treefrog. We estimate that no more than 3 individuals (second year or older) of this species would be collected per site. We also anticipate Pacific treefrog tadpoles to occur near nearly all of the 60 lakes in the spatial survey. Assuming the spatial survey takes place during mid summer, when tadpoles are available, we will collect individuals during the spatial survey in the manner described above. To reduce the possibility of transmitting amphibian pathogens between sites, particularly chytrid fungus, all equipment used in collecting amphibian specimens or contacting the lake benthos or vegetation (e.g, nets, tevas, waders, sediment corer) will be thoroughly dried between sites or decontaminated with a solution of bleach or the veterinary disinfectant, Quat-128.

Tissue samples will be sent to the Dr. Don Sparling at Patuxent Wildlife Research Center, Laurel, MD, for analysis of acetylcholinesterase activity according to established methods (Ellman et al. 1961), and in the same manner as current USGS projects. Samples will be temporarily stored at -80ºC. Transport will be in containers with liquid nitrogen or dry ice.

7.7 Ancillary On-site Environmental Data

pH will be measured with a pH meter and quick-responding electrode suitable for waters with extremely low ionic strength. Electrical conductivity will be measured with a portable meter. Both pH and conductivity will be measured in the field, using standards to calibrate before and after each measurement. Water temperature will be measured with a calibrated liquid-filled maximum-minimum thermometer suspended in the water column near the water sampling intake. For the six lakes in the temporal study, lake depth will be taken at 9 approximately evenly spaced points, and at the point of maximum depth, once with a plumb line from a float tube. Water level will be monitored monthly for these lakes by measuring the water level relative to a plastic stake imbedded in the lake bottom. Prior to ice-off, dissolved oxygen and temperature profiles for the water column will be measured using a Yellow Springs Instruments oxygen meter. Precipitation will be measured continuously for the six lakes in the temporal study using a battery-powered rain gage and data logger placed near each lake. For the 60 lakes in the spatial survey, maximum lake depth will be measured during the biological survey. Weather records for both the temporal study and spatial survey will be obtained from Lodgepole and Huntington Lake, both at approximately 2150 m (7,000 feet) elevation.

7.8 Landscape Metrics and Other Variables

The nominal boundary between the SJV and Sierra Nevada was defined as the approximate line where the mountain-valley slope changes substantially. In the Kaweah River area, this boundary corresponds approximately with the edge of the air mass that moves up slope each morning in summer (Shair 1995). This boundary was delineated from raised relief and contour maps as a general NW-SE line following certain contour levels, but the line was smoothed to eliminate prominent lateral deviations. Contour levels comprising the basis for this delineation are the 150-m contour for slopes near the San Joaquin, Kings, and Kaweah Rivers, increasing to 180 m near the Kern River.

Upslope air flowpath distance from the SJV is approximated by assuming that the air flowpath is the opposite of the downslope water flowpath. The latter is calculated from a 100-m digital elevation model (DEM) and the Grid module of Arc/Info (version 7; ESRI, Redlands, CA; Watershed, Flowdirection, Flowaccumulation, and Sink commands) and the Flowlength commands in ArcView (version 3.2, ESRI, Redlands, CA). For computation, the origin for each watershed was the point where the respective river crosses the nominal boundary between the SJV and the Sierra Nevada (Figures 1 and 3).

Calwater "planning watersheds," which range in size from about 1200 to 4000 ha, are obtained from the California Watershed Map (CALWATER version 2.2; California Resources Agency, Sacramento). Lake surface area is obtained from digital line graphs (USGS) derived from USGS 7.5' topographic maps. Elevation is also taken from these maps. Lake volume will be computed for the 6 lakes in the temporal study from lake surface area and bathymetry using a float tube and plumb line. Volume of each lake in the spatial survey will be estimated assuming that lake shape is an inverted conical polygon, i.e., estimated volume = lake surface area * maximum lake depth/3. Watershed area for each lake will be derived from 30-m DEM using ArcView. Pesticide application data will be obtained for Madera, Fresno, Kings, Tulare, and Kern Counties on a monthly basis from the California Department of Pesticide Regulation. Data for pesticide use are available at the township spatial scale.

7.9 Field Logistics and Training

We plan to reach sites using a helicopter on contract to the Sequoia and Kings Canyon National Parks, based at the Park Headquarters at Ash Mountain. Justification for helicopter use is provided separately. During the monthly sampling in the contaminant temporal study, and during the contaminant distribution survey, two crews of two individuals will be transported from one site to another each day, over a period of 4 to 5 days. A single crew of two will conduct the weekly and short-term intensive sampling events. For the latter, an additional helicopter trip will transport the supplies needed for the extended stay. Crews will be prepared to be picked up within a fairly wide time window (e.g., 3 hours), and remain in place or hike out as necessary if the helicopter is co-opted for emergencies. Except during the short-term intensive sampling events, field samples of extracts from lake water, sediment, SPMD/POCISs, dry deposition, and tadpoles will be transported from the field site by helicopter each day to Park Headquarters. An individual will receive the samples there and place them in a refrigerator (or liquid nitrogen for tadpole samples) until transport to the ESD laboratory at Las Vegas. Field samples collected during the short-term intensive sampling events will be held at the sampling site in a cooler at 4°C at the sampling site until the end of the sampling event. Individuals participating in field sampling will receive helicopter training in coordination with the Sequoia and Kings Canyon National Parks, and safety training through EPA. Field crews will be composed of individuals from EPA identified below, and National Park Service employees or cooperators. All individuals participating in the field sampling will undergo training to ensure standard operating procedures are followed.

Section 8

Data Management and Analyses

8.1 Data Management

Field data will be collected on data sheets, and entered into a *SAS* (*SAS* Institute Inc., Cary, NC) database in our laboratory. For each sample collected, sampling, processing, and analysis log sheets and final analytical data sheets will be maintained in a single folder. Raw analytical data will be maintained on the GC/MS data system. Final data and associated metadata will be maintained on EPA's National Exposure Research Laboratory Database for Ecochemistry Studies (NDES), an Oracle®-based database linked to the EPA Environmental Information Management System. Reports from NDES will be generated to directly enter into *SAS* for statistical analysis. Data and metadata on NDES will also be available outside EPA via the internet.

8.2 Statistical Analyses

Statistical analyses will be done using *SAS* except where stated otherwise. Several hypotheses will be tested using common techniques listed in Goals and Objectives. For hypotheses concerning contaminant concentrations as a function of landscape features (H3.1 H3.3, H4.1, H4.2), stepwise regression (n=60) will be used. The dependent variable will be contaminant concentration (for individual analytes or groups of analytes) and independent variables will be upslope air flowpath distance from the SJV, elevation, watershed designation, maximum lake depth, estimated lake volume, and lake watershed area. We will also test whether linear distance to the SJV is a better predictor of contaminant concentration than upslope air flowpath length. Hypothesis H3.2 (cholinesterase activity) will be tested in a similar fashion. To detect meaningful correspondence between the composition of contaminant mixtures and environmental variables (H3.4), we will use multivariate analyses (e.g., canonical correspondence and redundancy analyses using CANOCO 4; ter Braak and Šmilauer 1998).

We will develop a model predicting contaminant concentrations for the study area based on results from the above multivariate analyses, or based on spatial interpolation models (e.g., Kriging). Validation of the model will be evaluated using jackknife or cross-validation procedures (Journel and Huijbregts 1978; Sheskin 2000).

Possible associations between contaminant concentrations and the distribution of frogs (H4.1) will be examined at three spatial scales. (1) At the scale of the major river watersheds (n=4), we will evaluate associations by inspection of plots of % of lakes occupied by the two frog species and plots of either the means of measured contaminant concentrations in the watersheds or the means of contaminant concentrations predicted by the above model. (2) At the scale of Calwater planning watersheds (n~55), stepwise regression will be used. The dependent variable will be % occupancy of lakes by the frog species, and the independent variables will be mean predicted contaminant concentration, % lake occupancy by fish, and means for several other habitat and isolation variables known or suspected to be

important in determining site occupancy (Knapp and Matthews 2000). Some of these independent variables reflect other hypotheses for amphibian population declines, e.g., pH and EC may reflect vulnerability to acidification (Bradford et al. 1994a), and elevation may reflect vulnerability to UV-B and climate change (Davidson et al., in press). (3) At the scale of individual lakes (n ~ 3200), we will use Generalized Additive Models using the GAM function in SPlus to fit additive models (Cleveland and Devlin 1988; Hastie and Tibshirani 1991). GAM will be used rather than linear models because GAM relaxes the assumption that the relationships between the dependent and independent variables are linear (Cleveland and Devlin 1988; Hastie and Tibshirani 1991). The dependent variable will be frog presence/absence and/or abundance, and independent variables will be predicted contaminant concentrations, fish presence/absence, and several other habitat and isolation variables known or suspected to be important in determining site occupancy as described above (Knapp and Matthews 2000). Because the sample size is large, we can include concentrations for a number of contaminants to test for combinations that most influence frog distribution. We will test for spatial autocorrelation of variables using semivariograms (Englund and Sparks 1991), and adjust for autocorrelation by eliminating sites within the zone of dependency of other sites (i.e., thinning of data; Davis 1973, Thompson 1992) or adjusting degrees of freedom (Pinel-Alloul et al. 1999).

Section 9

Permits and Approvals

9.1 Permits and Permissions

All lakes selected for sampling occur in wilderness areas managed by either the National Park Service (Sequoia and Kings Canyon National Parks) or USDA National Forest Service (Sierra, Sequoia, and Inyo National Forests). Research approval permits and permissions will be obtained from these agencies prior to commencement of field activities. Collecting permits for amphibian specimens will be obtained from the California Department of Fish and Game and the National Park Service.

9.2 Justification for Helicopter Support

Permission to use helicopter support in wilderness areas will be sought prior to the 2001 field season for National Park lands, and prior to the 2002 field season for National Forest lands. Helicopters will be used to transport field crew and equipment among sample sites, and bring samples out from the backcountry, as described in the Contaminant Temporal Study and Contaminant Spatial Survey. Helicopter support is needed because of the timing and sample-handling requirements of the study. To minimize the influence of temporal variation in contaminant concentrations, sampling must be done within a short time frame (e.g., six lakes in three days in the contaminant temporal variation study). To ensure sample integrity, samples will be extracted at the ESD laboratory within seven days of collection, reflecting the holding times of the target analytes (Zaugg et al. 1995) and samples must be cooled (4 ºC) within two hours of collection. None of these criteria can be met using over-land access.

Section 10

Quality Assurance

A detailed Quality Assurance Project Plan (QAPP) will be developed and approved by the EPA QA officer at the Las Vegas laboratory prior to initiation of field work. Some elements that will be included in this plan have been described above in individual sections. The QAPP will require standard operating procedures for all activities. All individuals participating in sampling will receive training to ensure consistency of sampling.

Section 11

Schedule

Year # (From - To)	Description	Date(s)
Year 1 (11/2000 - 10/2001)	Project planning.	11-12/00
	Methods development.	12/00-7/01
	Field testing, final SOPs compiled, field training.	8/01
	Biological surveys continued and possibly completed.	6-10/01
	Pilot study for contaminant temporal variation study (Seq./Kings Cyn. Nat. Parks [SEKI]). (See Table 2 for details of the schedule.)	8-10/01
Year 2 (11/2001 - 10/2002)	Contaminant temporal variation study (Seq./Kings Cyn. Nat. Parks [SEKI]).	4-10/02
Year 3 (11/2002 - 10/2003)	Preliminary analysis of contaminant temporal variation study.[1]	11-12/02
	Contaminant spatial distribution survey (SEKI and national forests).	6-10/03
	Data analysis of contaminant temporal study.	
	Data analysis of contaminant spatial distributions relative to environmental factors and amphibian distributions.	
	Manuscript preparation.	

[1] Preliminary analysis focuses on appropriate time frame for spatial study.

Sampling Frequency
D = Daily
W = Weekly
M = Monthly
Numerals indicate number of lakes sampled for each event.

Table 2. Schedule for contaminant temporal variation study, 2002.

	April			May			June			July			August			Sept.			October		
Sample Description	D	W	M	D	W	M	D	W	M	D	W	M	D	W	M	D	W	M	D	W	M
Snow			4																		
Water						6	1	1	6			6	1	1	6			6	1	1	6
Passive samplers								1	3			3		1	3			3		1	3
Sediments									6												6
Deposition[1]									3		3	3		3	3		3	3		3	3
Tadpole cholinesterase activity[2]												6			6						

[1] Deposition will be collected every two weeks.

[2] Tadpole sampling will also occur in August 2001.

Section 12

Personnel and Responsibilities

Personnel and their general responsibilities are provided in Table 3. See Appendix D for résumés.

Table 3. Personnel and responsibilities.

Name	Affiliation	Primary Responsibilities
David Bradford, Ph.D.	2	Co-Principal Investigator (biology); field sampling
Ed Heithmar, Ph.D.	1	Co-Principal Investigator (chemistry); field sampling, data management
Chad Cross, Ph.D.	2	Statistical design and analysis
Elizabeth Gentry	1, 3	Methods for field sampling and chemical analysis
Roland Knapp, Ph.D.	4	Biological surveys and related data analysis
Georges-Marie Momplaisir, Ph.D.	1	Analytical methods development; field sampling, data management
Maliha Nash, Ph.D.	2	Statistical design and analysis
Lee Riddick	1	Analytical methods development; sample analysis
Charlita Rosal	1	Sediment sampling methods
Nita Tallent-Halsell	2	Project coordinator; logistics; field sampling
Katrina Varner	1	Methods development for water sampling and processing; field sampling

[1] U.S. EPA, National Exposure Research Laboratory, Environmental Sciences Division, Environmental Chemistry Branch, Las Vegas, NV

[2] U.S. EPA, National Exposure Research Laboratory, Environmental Sciences Division, Landscape Ecology Branch, Las Vegas, NV

[3] Tulane University, School of Public Health, New Orleans, LA

[4] University of California, Sierra Nevada Aquatic Research Laboratory, Mammoth Lakes, CA

Section 13

Facilities, Equipment, and Other Resources

The Environmental Sciences Division of the National Exposure Research Laboratory at Las Vegas has extensive facilities for chemical analyses, statistical analyses, and field logistics. The analytical chemistry facilities and equipment available in the Environmental Chemistry Branch are described in Appendix E. The Laboratory has obtained a GC/MS to be dedicated to this project. We have a laboratory that can be used as a field staging area, vehicles, and all software for statistical analysis, spatial analysis, and data base management described above. An Infiltrex 100 water sampling device is currently on loan for method development from the Axys Group, Sidney, British Columbia. Additional sampling devices for sampling water and other media will be purchased. The National Park Service (NPS) will provide laboratory space at the Southern Sierra Research Center at Ash Mountain to process samples received from the field. NPS will also provide helicopter support on a cost reimbursable basis. Funding for the ongoing biological survey has been provided primarily by NPS and the joint EPA/NPS Park Research and Intensive Monitoring of Ecosystems Network (PRIMENet).

Section 14

Anticipated Products

1. Journal article on temporal variation in pesticide levels in lakes in the southern Sierra Nevada.

2. Journal article on comparison of active sampling methods for current-use pesticides in lake water.

3. Journal article on comparison of active sampling methods, SPMDs, and POCISs for current-use pesticides in lake water.

4. Journal article on pesticide distributions and associated environmental variables in the southern Sierra Nevada.

5. Journal article evaluating the role of pesticides in determining the current distribution and population changes of the Mountain Yellow-legged Frog and Pacific treefrog in southern Sierra Nevada.

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Appendix A

Patterns of Surface Air Movement in the San Joaquin Valley and Southern Sierra Nevada

A.1 Surface Air Movements in the San Joaquin Valley

During all seasons except late fall and winter, air is transported into the San Joaquin Valley (SJV) primarily through the Carquinez Straits to the vicinity of Stockton, and thence southeast to the southern end of the SJV (Smith et al. 1981; Hayes et al. 1984; Blumenthal et al. 1985). During summer and early fall, this northeast-to-southeast transport is effected by surface layer winds and a low-level (100 to 1000 m) nocturnal jet (Smith et al. 1981; Blumenthal et al. 1985). Another characteristic feature during summer in the SJV is the early morning development of the Fresno Eddy, a counterclockwise circulation of the lower 500-700 m of the atmosphere (Smith et al. 1981; Blumenthal et al. 1985; Roberts et al. 1990). The eddy is typically centered west of Visalia near Highway 99 and extends from about Delano to Fresno. Together, the nocturnal jet and Fresno Eddy effectively distribute pollutants throughout the southern part of the SJV (Smith et al. 1981; Blumenthal et al. 1985). However, a consequence of the eddy is that pollutants on the east side of the SJV are often less dispersed and can accumulate more in stagnant or recirculating air masses than those on the west side of the valley (Blumenthal et al. 1985). During the afternoon in summer and early fall, mixing depths in the SJV generally increase to about 1000 m above ground level (Smith et al. 1981). Most of the air exiting the SJV goes over Tehachapi Pass and adjacent slopes at the southern end of the valley (Smith et al. 1981; Blumenthal et al. 1985; Roberts et al. 1990). About 15% of the air exiting the SJV goes up the Sierra slopes (Roberts et al. 1990). Residence times for pollutants are estimated to be one to two days, depending mainly on release location (Smith et al. 1981; Tracer Technologies 1992).

During late fall and winter, the SJV is characterized by near-stagnant conditions that are interrupted by occasional scouring events resulting from the passage of frontal systems (Smith et al. 1981; Blanchard et al . 1999). During an 11-year period, such intervals of poor ventilation lasted up to 19 days (Smith et al. 1981). Maximum mixing heights during these times are often in the range of 200 to 500 m (Smith and Lehrman 1996; Lehrman et al. 1998).

A.2 Surface Air Movements in the Southern Sierra Nevada

During summer the dominant wind regime consists of a very regular oscillation of upslope and downslope winds controlled by the diurnal variation of solar heating of the Sierra slopes (Ewell et al. 1989; Cahill et al. 1996). This pattern is remarkably consistent from day to day except when disrupted by synoptic-scale meteorological events. Upslope velocities generally exceed downslope velocities, resulting in a net upslope transport. At the latitude of Sequoia National Park, depth of this terrain-driven

wind system decreases from about 1000 m at the edge of the SJV to about 350 m at Emerald Lake, approximately 42 km away at 2720 m elevation (Ewell et al. 1989).

Tracer studies show that the major transport pathways from the SJV into the Sierra are the larger river valleys (Tracer Technologies 1992). However, few data are available to describe how closely air follows the upslope/downslope topography at the upper reaches of the major river watersheds. Tracer studies in the Kaweah River area show that surface air moves upslope to the highest elevations sampled (Tablelands at 3210 m elevation, 60 km from release point) by mid afternoon following tracer release near the edge of the SJV between 2 and 8 AM (Shair 1995). Shair (1995) suggested that air converging at major ridges from opposing upslope flows, such as the Great Western Divide separating the Kaweah and Kern River watersheds, likely experiences considerable vertical mixing, resulting in rapid dilution by an order of magnitude, and at least partial removal by upper level winds.

During winter air at elevations above 500 to1000 m in the Sierra are frequently above the mixed layer in the SJV, and thus are effectively decoupled from the air circulation in the valley (Blanchard et al. 1999; Cahill et al. 1996). Prevailing northwesterly winds dominate at these times, rather than terrain-driven winds, and levels of pollutants in air are extremely low (Cahill et al. 1996). During winter storms, the inversion in the SJV is broken, air motion and mixing are vigorous, and mixed air is transported to the Sierra Nevada (Cahill et al. 1996).

Appendix B

Additional Selection Criteria for Target Analytes

There were many more than 31 pesticides, herbicides, and fungicides used in excess of 5000 kg annually in the Central Valley near the study area. The list in Table 1 was derived using additional criteria that would likely affect the probability of analyte detection. Those additional criteria are summarized in Table B.1. First, the vapor pressure of target analytes must be low enough to allow deposition and minimize subsequent volatilization. This criterion eliminated a number of fumigants that are used in enormous quantities in the Central Valley. All 31 primary target analytes have equilibrium vapor pressures less than 5000 mPa ($<5x10^{-7}$ atm). No minimum volatility was set for the target analytes, since dry deposition of analyte on wind-blown particles could be a significant loading mechanism.

Second, persistence in the water column, either dissolved or sorbed on suspended particulates, must be long enough to allow detection for at least a few weeks after deposition. Rate constants for hydrolysis at two pH values (5 and 7) (U.S. Department of Agriculture 1989) were used to estimate half-lives for hydrolysis. Table B.1 shows that nearly all the target analytes have half-lives of at least 30 days in the pH range 5 to 7. The exceptions are phorate and phosmet, which have maximum predicted half-lives of 3 and 9 days, respectively. However, the octanol-water partition coefficient, K_{ow} for each of these compounds is at least 10^3 (Table B.1). This indicates an affinity for organic matter in suspended and bed sediment that may prolong persistence of these compounds. The other mechanisms of chemical degradation, photolysis and microbial metabolism, were not considered as selection criteria, because environmental factors affecting each are unpredictable. For information purposes, possible photolysis is indicated in Table B.1 when available data indicate photolysis half-lives of less than 7 days in distilled water. It should be noted that although both diazinon and trifluralin are predicted to be rapidly photolyzed, both have been detected in lakes in the study area (LeNoir et al. 1999). Irrespective of whether degradation is likely, major degradation products, such as the oxygen analogs of the phosphorothioate pesticides, will also be measured whenever possible.

Finally, all target analytes will have to be detectable by the sampling and analytical methods to be used in the study. The methods generally require sufficient sorption on an extraction resin to effect extraction from a large volume of water. For the resins being considered for this study, this attribute can be roughly predicted by a high K_{ow}. For comparison, malathion, with a K_{ow} of about 500, was detected in lake water in the study area using methods analogous to those planned (LeNoir et al. 1999), although the volume of water extracted in that study was substantially less than the volumes that will be extracted in this study. A careful evaluation of extraction efficiencies is part of the experimental design. Another requirement for the target analytes is that they be determinable by gas chromatography/mass spectrometry (GC/MS) using either electron-impact ionization (EI) or negative chemical ionization (NCI) with selective ion monitoring. The literature contains appropriate methods for all of the target analytes (see references in Table B.1). Method development will determine if all of the target analytes can be determined in a single GC/MS run using each ionization method.

Table B.1. Factors affecting probable detection of primary target compounds listed in Table 1.[a]

Compound	Vapor Pressure (mPa)	$t_{1/2}$ pH 7[b]	$t_{1/2}$ pH 5[b]	log(K_{ow})[c]	Photolysis Likely[d]
alachlor	4.1	no data	no data	2.9	no
azinphos methyl	0.027	26	43	2.7	yes
butylate	1730	700	700	4.1	no
carbaryl	0.2	11	no data	2.3	no
chlorothalonil[e]	0.076	stable	stable	2.9	no
chlorpyrifos	2.3	29	77	5.0	no
cyanazine	0.0002	stable	151	2.1	no
DCPA (chlorthal dimethyl)	0.33	stable	stable	>5[g]	no
diazinon	8	139	12	3.1	yes
dicofol	1.3	4	87	4.3	no
disulfoton	24	23 (40°C)	no data	4.0	yes
endosulfan (I and II)[e]	0.8	35[f]	150[f]	3.1	no
EPTC	3200	stable	stable	3.3	no
ethalfluralin	12	>30	>30	5.1	yes
lindane (γ-HCH)	4.4	stable[f]	stable[f]	3-3.8[g]	no
linuron	1.5	1100	1100	3.0	no
malathion	0.7	6	116	2.7	no
methidathion[h]	190	no data	no data	4.7	no data
methyl parathion	0.2	41	69	3.5-3.8[f]	no data
metolachlor	1.7	stable	stable	3.0	no
napropamide	0.27	stable	stable	3.3	yes[f]
pebulate	1180	no data	no data	4.0	no
pendimethalin	1.2	stable	stable	5.2	yes[f]
permethrin	0.02	stable	stable	6.1	no
phorate	85	3	3	3.9	no
phosmet[i]	0.06	<1	9	3.0	yes
propargite	0.006	77	122	3.7	no
simazine	0.0008	stable	stable	2.1	no
trifluralin	6.7	>30	>30	5.1	yes
tribufos[j]	0.213	stable	stable	5.5	no

[a] All data taken from U.S. Department of Agriculture (1989), except where noted. All values are for 20 or 25°C (20°C, if available, unless noted). All compounds are included in the GC/MS method of Zaugg et al. (1995), except where noted. Major degradation products that will be determined are not listed.

[b] Hydrolysis half-life in days at the pH indicated.

[c] Logarithm of the octanol-water partition coefficient (K_{ow}, no units).

[d] "yes": photolysis rate constant indicates a half-life to photolysis of less than 6 days, except where noted.

[e] Included in GC/MS method of LeNoir et al. (1999).

[f] From Oregon State University (1996).

[g] Calculated from solubilities in water and a variety of organic solvents (data in U.S. Dept. of Agriculture 1989).

[h] Included in GC/MS method of Aston and Seiber (1997).

[i] Included in GC/MS method of Okumura and Nishikawa (1995).

[j] Included in GC method of U.S. Environmental Protection Agency (1993).

Appendix C

Use Patterns of Six Organophosphorus Pesticides in the San Joaquin Valley Near the Study Area

The temporal, as well as spatial, pattern of pesticide application in the SJV is highly variable. The data provided by the Department of Pesticide Regulation (State of California 1999) for the years 1996-1998 has been analyzed for approximate temporal (monthly time scale) and spatial (on a county basis) characteristics. This Appendix describes some results for six organophosphorus (OP) pesticides for the year of median use of each. Inspection of this data, combined with the relatively short persistence of some of the target contaminants in surface waters (Appendix B), indicates that pesticide concentrations in lake water may exhibit significant temporal variability.

Figures C.1 through C.6 show the use, by month and by county, of six organophosphate (OP) pesticides for the year of median use of each in five counties in the SJV. Many OPs follow the general temporal trend shown for chlorpyrifos (Figure C.1) and azinphos methyl (Figure C.2), i.e., much heavier use in the summer months than the remainder of the year. However, diazinon (Figure C.3) and methidathion (Figure C.4) were used mostly in the winter, with substantial summer use. Tribufos (Figure C.5) was used exclusively in the fall, and phorate (Figure C.6) in the spring. Even for the OPs of predominantly summertime use, application can vary considerably on a shorter time scale. Chlorpyrifos use increased gradually beginning in May and peaking in August, while azinphos methyl use abruptly began in June and declined monotonically through August.

Figure C.1. Chlorpyrifos use by month and county

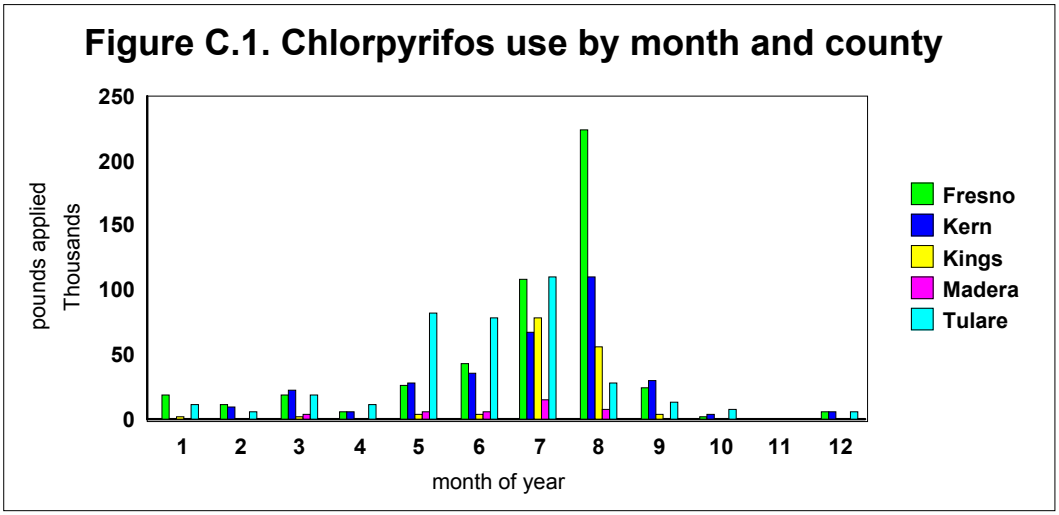


Figure C.2. Azinphos methyl use by month and county

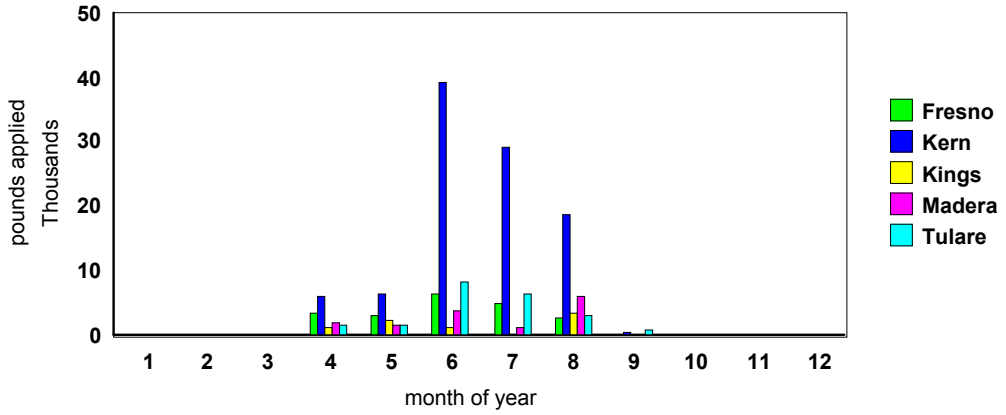


Figure C.3. Diazinon use by month and county

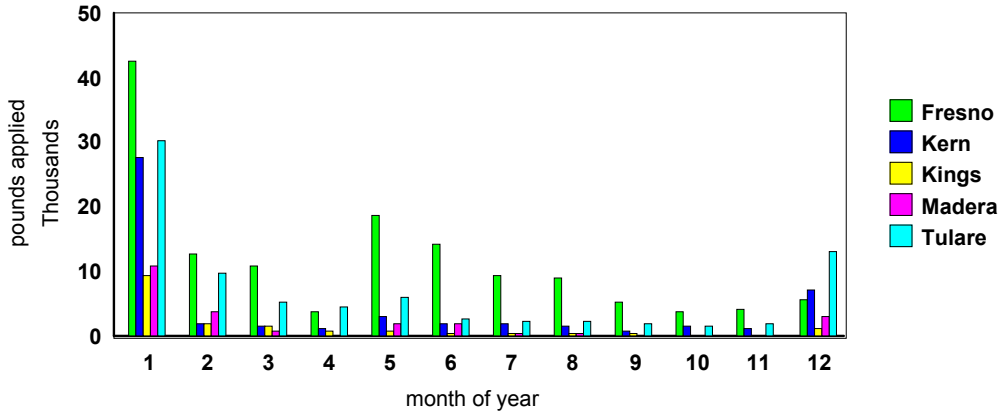
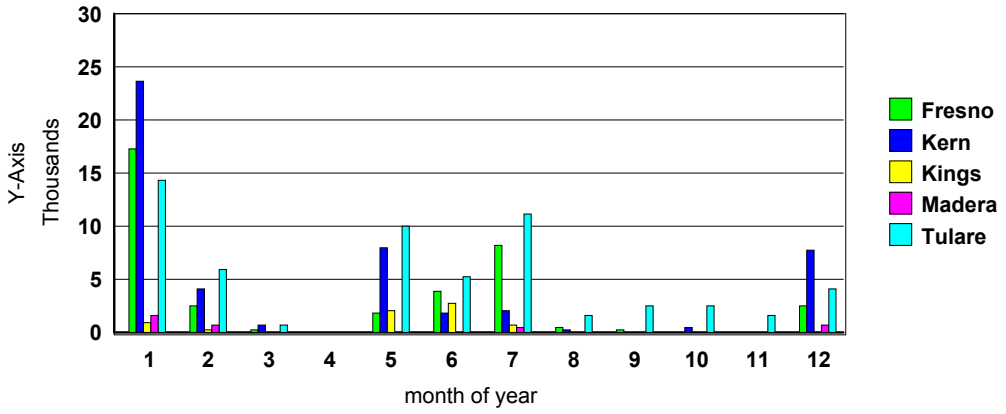
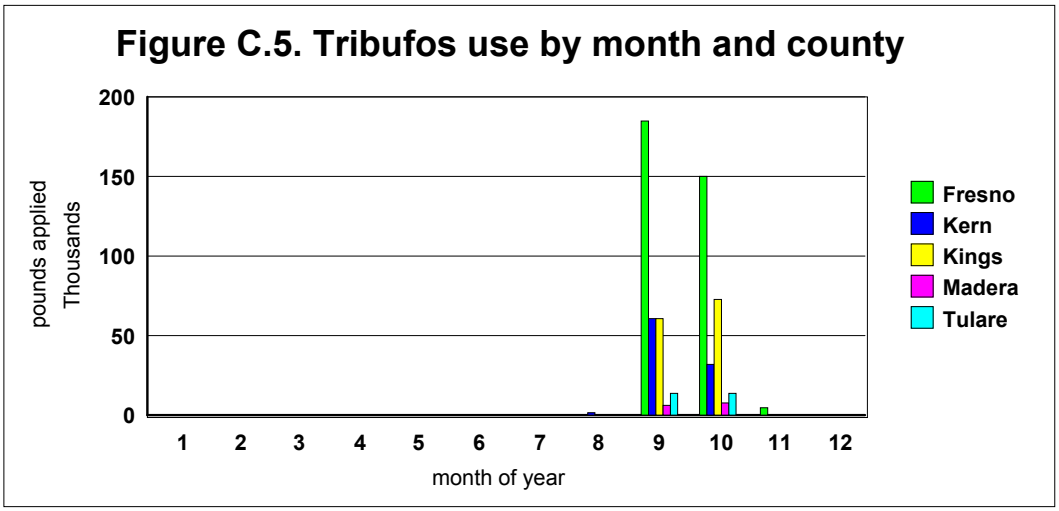
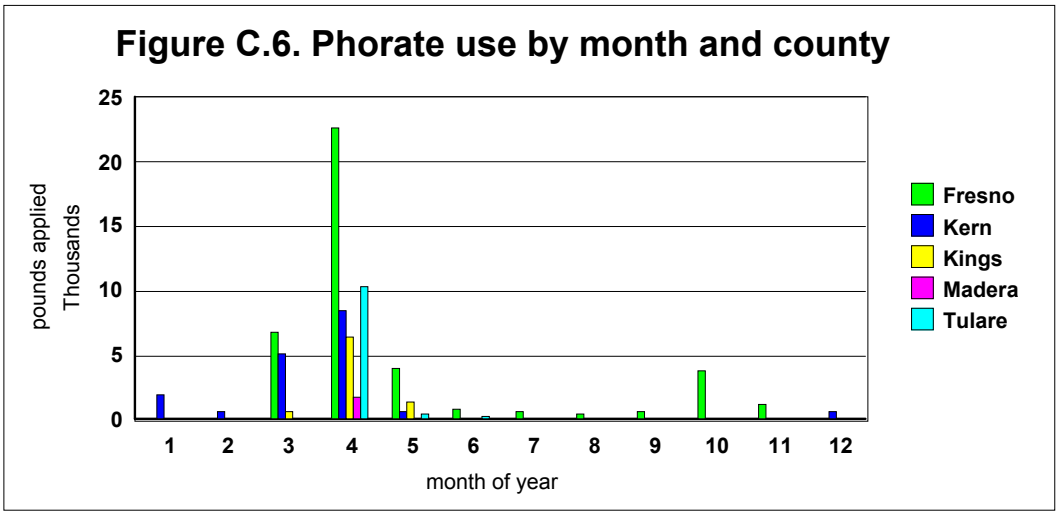


Figure C.4. Methidathion use by month and county







There are also significant differences in pesticide use by county, overall as well as by season. For example, azinphos methyl (Figure C.2) is distinguished from other OPs in that its use was dominated by Kern County, which lies at the southern end of the SJV, presumably where the upslope winds in the Kern River watershed originate. In the early summer, chlorpyrifos (Figure C.1) was used predominantly in Tulare County; in the late summer, it was used mainly in Fresno County. These differences indicate that analysis of the data from the temporal variation study, combined with simultaneous township-scale pesticide use data from the State of California Department of Pesticide Regulation, may be sufficient to provide some evidence of the importance of upslope surface-air transport of pesticides.

Appendix D

Résumés of Participants

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Education

Ph.D. in Biology, University of California, Los Angeles, 1982

M.A. in Zoology, University of California, Berkeley, 1972

B.A. in Biology, California State University, Fresno, 1968

Experience

Research Ecologist: U.S. Environmental Protection Agency, National Exposure Research Laboratory, Las Vegas, 1992 - present.

Adjunct Faculty: Department of Biological Sciences, Univ. of Nevada, Las Vegas, NV, 1995 - present.

Visiting Assistant Professor and Research Scientist: Environmental Science and Engineering Program, School of Public Health, University of California, Los Angeles, 1988 - 1992.

Senior Biologist: Envirosphere Company, Santa Ana and Sacramento, California, 1986 -1988.

Assistant Professor: Biological Sciences Department, Northern Illinois University, 1985 - 1986.

Postdoctoral Research Associate: Zoology Department, University of Adelaide, Australia, 1983 - 1985.

Recent Publications

Bradford, D.F., S.E. Franson, G.R. Miller, A.C. Neale, G.E. Canterbury, and D.T. Heggem. 1998. Bird species assemblages as indicators of biological integrity in Great Basin rangeland. Environmental Monitoring and Assessment, 49: 1-22.

Wade, T., B. Schultz, J.D. Wickham, and D.F. Bradford. 1998. Modeling the potential spatial distribution of beef cattle grazing using a geographic information system. Journal of Arid Environments, 38: 325-334.

Bradford, D.F., S.D. Cooper, T.M. Jenkins, Jr., K. Kratz, O. Sarnelle, and A.D. Brown. 1998. Influences of natural acidity and introduced fish on faunal assemblages in California alpine lakes. Canadian Journal of Fisheries and Aquatic Sciences, 55: 2478-2491.

Wade, T.G., J.D. Wickham, and D.F. Bradford. 1999. Accuracy of road density estimates derived from USGS DLG data for use in environmental applications. Photogrammetric Engineering & Remote Sensing 65: 1419-142.

Ultsch, G.R., D.F. Bradford, and J. Freda. 1999. Physiology: coping with the environment. Pp. 189-214 *in* R.W. McDiarmid and R. Altig (eds.), Tadpoles: The Biology of Anuran Larvae. University of Chicago Press, Chicago.

Canterbury, G.E., T.E. Martin, D.R. Petit, L.J. Petit, and D.F. Bradford. 2000. Bird communities and habitat as ecological indicators of forest condition in regional monitoring. Conservation Biology 14: 544-558.

Bradford, D.F., R.D. Jennings, and J.R. Jaeger. *Rana onca* Cope 1875, relict leopard frog. Pp. 000-000 *in* M.J. Lannoo (ed.), Status and Conservation of U.S. Amphibians, University of California Press. In Press.

Jaeger, J.R., B.R. Riddle, R.D. Jennings, and D.F. Bradford. Evidence for phylogenetically distinct leopard frogs (*Rana onca*) from the border region of Nevada, Utah, and Arizona. Copeia. In Press.

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Education

B.S. (1993; Purdue University): Biology (Ecology, Evolutionary, and Population Biology)

B.S. (1994; Purdue University): Forestry and Natural Resources (Wildlife Science)

M.S. (1997; Old Dominion University): Computational and Applied Mathematics (Statistics)

Ph.D. (1998; Old Dominion University): Ecological Sciences (Quantitative Ecology)

Academic & Professional Positions

Purdue University, West Lafayette, Indiana. 1994. Teaching Assistant, Department of Biological Sciences.

U. S. Fish and Wildlife Service, Back Bay National Wildlife Refuge, Virginia Beach, Virginia. 1997. Biological Research Intern.

Old Dominion University, Norfolk, Virginia. 1998. Teaching Assistant, Department of Biological Sciences.

Old Dominion University, Norfolk, Virginia. 1998. Lecturer, Department of Biological Sciences/Department of Mathematics and Statistics.

Ivy Tech State College, Lafayette, Indiana. 1999 Instructor, Department of Mathematics and Biology.

U.S. Environmental Protection Agency, Environmental Sciences Division, Landscape Ecology Branch, Las Vegas, Nevada. 1999-present. Postdoctoral Research Scientist.

University of Nevada–Las Vegas, Las Vegas, Nevada. 2000-present. Associate Graduate Faculty, Environmental Studies Department.

Expertise

Statistical sampling design and analysis

Animal-Habitat modeling

Quantitative ecological theory and application

Herpetological conservation and population biology

Recent Publications

1998 Cross, C. L., and C. Marshall. *Agkistrodon piscivorus piscivorus*. Predation. Herpetological Review 29(1):43.

1998 Cross, C. L., J. B. Gallegos, F. G. James, and S. T. Williams. A new technique for artificially incubating loggerhead sea turtle eggs. Herpetological Review 29(4):228-229.

2000 Cross, C. L. Behavioral Ecology of the eastern cottonmouth (*Agkistrodon p. piscivorus*) in a natural and an anthropogenic marsh habitat in southeastern Virginia. Program Book and Abstracts of the 80th Annual Meeting of the American Society of Ichthyologists and Herpetologists, La Paz, B.C.S., Mexico.

2000 Cross, C. L. A new design for a lightweight squeeze box for snake field studies. Herpetological Review 31(1):34.

2000 Cross, C. L., and P. M. Waser. Estimating population sizes of banner-tailed kangaroo rats. Southwestern Naturalist 45(2):176-183.

Beth Gentry

Education

BS in Chemical Engineering (October 1998)

Worcester Polytechnic Institute (Worcester, Massachusetts)

MPH (Masters in Public Health) in Environmental Health Science (May 2001)

Tulane University School of Public Health (New Orleans, Louisiana)

Work Experience

National Network of Environmental Management Systems (NNEMS) Fellowship
Environmental Protection Agency Las Vegas, NV (June 2000 - June 2001)

- Developing methods using the GC/MS to detect trace levels of pesticides
  - Negative Electron Capture
  - Electron Ionization
- Evaluating Solid Phase Extraction (SPE) Sampling Methods
- Procedure, and GC/MS
- Authoring Quality Assurance/Control Project Plan

Intevac: Santa Clara (January -August 1997)
Jr. Engineer (8 month internship)

- Pending Patent - infrared calibrator
- Tested methods of infrared temperature measurement
- Designed fittings
- Worked with infrared camera
- Utilized Computer Skills: Autocad R13, Excel, Word, LabTech, & System Software

Allied Technology Group: Fremont (October-January 1999)
Jr. Engineer (3 month position)

- Set Up Sampling Schedules for Waste Disposal
- Aided in Editing Closure Reports
- Set Up Cost Tracking Systems
- Certified: 40 Hour OSHA Hazardous Waste Training (29 CFR 1910.120 e)

Independent Research

Estrogenic/Androgenic Effects of Methyl Tert-Butyl Ether (MTBE) January 2000 - June 2000

- Responsible for Growing Health Cells
- Evaluated Level of Estrogenic/Androgenic Activity in cells using a Luminometer
- Analyzed Results

Laboratory Assistant November 1999 - March 2000

- Collected Water Samples•Prepared Samples Used to Evaluated an Optimal Indicator Bacteria Test

International Project Costa Rica **May 1996 - August 1996**

- Created Proposal to Increase Foreign Profit by Improving Service
- Worked for 3 months at Atlas Electrica's Headquarters in Costa Rica
- Communicated with Distributors in El Salvador, Nicaragua, Panama, and Guatemala

Membrane Filtration **August 1997 - May 1997**

- Designed and Performed Experiments to Purify Water Using Membrane Filtration
- Evaluated Membraned Filtration in Terms of a Final Cleaning Step in a Residence

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Education

B.A. Mathematics and Chemistry, Biscayne College, Miami, FL

Ph.D. Analytical Chemistry, University of Pittsburgh
Thesis: "Application of the Hydride Generation Techniques to Continuum Source Atomic Fluorescence Spectrometry"

Experience

Research Chemist **1997 - Present**
Environmental Chemistry Branch
ESD/NERL
U. S. Environmental Protection Agency

Acting Manager **1996 - 1997**
Analytical Chemistry Research Program
CRD/NERL
U. S. Environmental Protection Agency

Research Chemist **1985 - present**
Analytical Chemistry Research Program
CRD/NERL
U. S. Environmental Protection Agency

Assistant Professor **1978 - 1985**
Department of Chemistry
University of New Orleans

Research Interests

Environmental analytical chemistry, trace element speciation, inductively coupled plasma mass spectrometry, hyphenated analysis techniques, sample introduction approaches for atomic spectrometry, atomic fluorescence spectrometry, gas-phase molecular luminescence spectrometry, environmental transport and fate of contaminants.

Professional Societies

American Chemical Society

Society for Applied Spectroscopy

Selected Publications

"Investigation of arsine-generating reactions using deuterium-labeled reagents and mass spectrometry" Pergantis, S. A.; Winnik, W.; Heithmar, E. M.; Cullen, W. R. *Talanta* **1997**, 44, 1941-1947.

"Microscale flow injection and microbore high-performance liquid chromatography coupled with inductively coupled plasma mass spectrometry via a high-efficiency nebulizer" Pergantis, S. A.; Heithmar, E. M.; Hinners, T. A. *Anal. Chem.* **1995**, 67, 4530-4535.

"Determination of metals in solid samples by complexation-supercritical fluid extraction and gas chromatography-atomic emission detection" Liu, Y.; Lopez-Avila, V.; Alcaraz, M.; Beckert, W. F.; Heithmar, E. M. *J. Chromatogr. Sci.* **1993**, 31, 310-316.

"Minimization of interferences in inductively coupled plasma-mass spectrometry using on-line preconcentration" Heithmar, E. M.; Hinners, T. A.; Rowan, J. T.; Riviello, J. M. *Anal. Chem.* **1990**, 62, 857-864.

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Current Position

Research Scientist: University of California, Santa Barbara / Marine Science Institute

Education

1986 B.A. in Aquatic Biology. University of California, Santa Barbara.

1992 Ph.D. in Biology. University of California, Santa Barbara.

Extramural Grants (Last Two Years Only)

U.S. Department of Agriculture: $83,612 **July 1998 - June 1999**
Introduced trout in the Sierra Nevada, California: A proposal to study their distribution and impacts on aquatic ecosystems.

Environmental Protection Agency and National Park Service: $208,316 **July 1999 - June 2002**
Analysis of natural and anthropogenic factors in controlling the distribution of amphibians in the alpine Sierra Nevada.

Yosemite Fund: $256,250 **May 2000 - April 2002**
Faunal surveys of Yosemite National Park's lentic habitats and their use in understanding impacts of nonnative fish and designing aquatic restoration measures.

National Science Foundation: $303,000 **June 2000 - June 2003**
Collaborative research: Recovery of ecosystem structure and function following exotic species eradication.

Publications (Last Five Years Only)

1996 Knapp, R. A., and V. T. Vredenburg. Spawning by California golden trout: characteristics of spawning fish, seasonal and daily timing, redd characteristics, and microhabitat preferences. Transactions of the American Fisheries Society 125: 519-531.

1996 Knapp, R. A., and V. T. Vredenburg. A field comparison of the substrate composition of California golden trout redds sampled with two devices. No. Amer. J. Fish. Mgmt. 16: 674-681.

1996 Knapp, R. A., and K. M. Matthews. Livestock grazing, golden trout, and streams in the Golden Trout Wilderness, California: impacts and management implications. No. Amer. J. Fish. Mgmt. 16: 805-820.

1998 Knapp, R. A., and K. M. Matthews. Eradication of non-native fish by gill netting from a small mountain lake in California. Restoration Ecology 6: 207-213.

1998 Knapp, R. A., V. T. Vredenburg, and K. M. Matthews. The effect of stream channel morphology on golden trout spawning habitat and recruitment. Ecological Applications 8: 1104-1117.

1999 Matthews, K. R., and R. A. Knapp. A study of high mountain lake fish stocking effects in the U.S. Sierra Nevada wilderness. International Journal of Wilderness 5: 24-26.

1999 Knapp, R. A., and H. K. Preisler. Is it possible to predict habitat use by spawning salmonids? A test using the California golden trout (*Oncorhynchus mykiss aguabonita*). Canadian Journal of Fisheries and Aquatic Sciences 56: 1576-1584.

2000 Knapp, R. A. and K. R. Matthews. Nonnative fish introductions and the decline of the mountain yellow-legged frog (*Rana muscosa*) from within protected areas. Conservation Biology 14: 428-438.

2000 Knapp, R. A., J. A. Garton, and O. Sarnelle. The use of egg shells to infer the historical presence of copepods in alpine lakes. Journal of Paleolimnology, in press.

2000 Knapp, R. A., K. R. Matthews, and O. Sarnelle. Resistance and resilience of alpine lake faunal assemblages to fish introductions. Ecological Monographs, in press.

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Educational Background

1995 Ph.D. Chemistry, McGill University, Department of Food Science and Agricultural Chemistry
Thesis title: *Development of Analytical Methods for the Speciation of Arsenic in the Marine Environment.*

1989 B.Sc. Chemistry, Montreal University, Department of Chemistry

Professional Experience

Research Chemist **April 1999 to Present**
U.S. Environmental Protection Agency, NERL/ORD. Trace element speciation in environmental samples, using on-line coupled techniques.

Research Chemist /Laboratory Coordinator **December 1998 - April 1999**
University of Nevada Las Vegas, Harry Reid Center for Environmental Studies, Las Vegas NV. The research work involved the development of analytical methods based on Hydride Generation coupled with atomic absorption spectrometry for the identification and quantification of naturally occurring inorganic arsenic, selenium and antimony species in groundwaters collected in the Southern Nevada region. Such information was necessary in order to determine the oxidizing/reducing properties of the groundwaters. The total concentrations of the elements in the water samples were corroborated by Inductively Coupled Plasma Mass Spectrometry analyses. I also act as laboratory coordinator for the groundwater geochemistry group.

Post-Doctorate Fellowship of the National Research Council **1995-1998**
U.S. Environmental Protection Agency (EPA), at the National Exposure Research Laboratory, Characterization Division in Las Vegas, NV. Research in the area of Trace Element Speciation Using High-Performance Liquid Chromatography-Inductively Coupled Plasma/Mass Spectrometry (HPLC-ICPMS), HPLC-Electrospray-MS/MS, HPLC-AAS and GC-MS.

Research Associate **1993-1994**
McGill University, Department of Food Science & Agricultural Chemistry. Speciation of Arsenic and Selenium in Sediments, Sediments Porewaters and seafoods by High Performance Liquid Chromatography-Atomic Absorption Spectrometry.

Field Experience

Survey Cruise along the Saguenay River from Rimousky to Chicoutimy, sponsored by Fisheries and Ocean Canada *(May 1991 and May 1992)*. Collection and preservation of samples of sediments and sediment porewaters for arsenic speciation.

Selected Publications and Presentation

Marshall, W.D. and Momplaisir, G.M., "Chromatographic Approaches to Trace Element Speciation*" in Metal Speciation and Bioavailability in Aquatic Systems*, Tessier, A., and Turner, D. Eds., John Wiley and Sons LTD 1995, Chap. 7.

Momplaisir, G.M., Lei, T. and Marshall, W.D., "Performance of a Novel Silica T-tube Interface for the AAS Detection of Arsenic and Selenium Compounds in HPLC Column Eluate," *Anal. Chem*. 1994, 66, pp 3533-3539.

Tan, Y., Momplaisir, G.M., Wang, J. and Marshall, W.D., "Performance of a Silica T-tube Interface for the AAS Detection of Cadmium, Copper, Lead, Zinc and Mercury in Flowing Liquid Streams," *J. Anal. At. Spectrom*. 1994, 9, pp. 1153-1159.

Momplaisir, G.M., Betowski, L.D. and Winnick, W., "Determination of Nine Organoselenium Compounds Using High-Performance Liquid Chromatography Coupled with Electrospray Mass Spectrometry" 46th ASMS Conference on Mass Spectrometry and Allied Topics, Orlando, Florida, June 1-5, 1998.

Pergantis, S.A., Momplaisir, G.M., Heithmar, E.M. and Hinners, T.A., "Speciation of Arsenic in References Materials by Using Micro-HPLC/ICPMS, 44th ASMS Conference on Mass Spectrometry & Allied Topics, Portland, Oregon, May 12-16, 1996.

Momplaisir, G.M., Lei, T. and Marshall, W.D. "Speciation of Arsenic and Selenium by HPLC-AAS," 24th International Symposium on Environmental Analytical Chemistry, Ottawa, Canada, May 1994.

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Landscape Ecology Branch
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Education

Soil Physics / Geostatistics and Experimental Statistics (Ph.D.), New Mexico State University

Soil Physics / Geostatistics and Experimental Statistics (M.S.), New Mexico State University

Agricultural Engineering / Soil Science (B.S.)

Research Interest

Developing space-time models to characterize responses of biological variables to environmental change.

Developing indicators and indices for biotic and abiotic variables based on geostatistical techniques.

Using parametric and nonparametric multivariate analyses (CART, GAM, MARS) to analyze binary (present/absence) data as related to environmental variables.

Work History

July 1998 - present, US EPA, Physical Scientist (3-year post doctoral position), U.S. EPA, ORD, NERL, LEB, Las Vegas Nevada. Developing GIS and remote sensing, watershed-based modeling and statistics for interpolating the consequences of landscape changes on aquatic and terrestrial resources.

May 1998 - June 1998, New Mexico State University, Research Specialist, based at U.S. EPA, ORD, NERL, CRD, Las Vegas Nevada. Geostatistical analysis on mammal, vegetation and ant data for the multiple stressor project.

May 1995 - April 1998, National Research Council, Research Associate, U.S. EPA, ORD, NERL, CRD, Las Vegas Nevada. Research focused on evaluating ecosystem properties and processes that may change in a predictable pattern along gradients of disturbance, particularly those associated with livestock grazing.

March 1992 - May 1995, Hydrogeologist, Foothill Engineering Co. / U. S. Geological Survey, Nuclear Hydrology Program, Nevada Test Site, Mercury, Nevada. Study of water movement, distribution and status in relation with geological formations at Yucca Mountain, Nevada.

Recent Publications

Nash, M.S., W.G. Whitford, A.G. de Soyza, J. Vanzee, and K. Havstad. 1999. Livestock activity and Chihuahuan Desert annual plant communities: Boundary analysis of disturbance gradients. Ecological Applications 9: 814-823.

Nash, M.S., W.G. Whitford, J. Vanzee, and K. Havstad. 2000. Ant (Homoptera, Formicidae) response to environmental stressors in the northern Chihuahuan Desert. Environmental Entomology 29: 200-206.

Jones K.B., A.C. Neale, M.S. Nash, K.H. Riitters, J.D. Wickham, R.V. O'Neill and R.D. Van Remortel. 2000. Landscape correlates of breeding bird richness across the United State Mid-Atlantic region. Environmental Monitoring and Assessment 63:159-174.

Jones KB, Heggem DT, Wade TG, Neale AC, Nash MS, Mehaffey MH, Hermann KA, Selle AR, Augustine S, Goodman IA. Pedersen J, Bolgrien D, Viger JM, Chaing D, Lin CJ, Zhong Y, Baker J, and Van Remortel R. 2000. Assessing landscape condition relative to water resources in the western United States: Strategic approach. Environmental Monitoring and Assessment 64:227-245.

Pitchford A., J.M. Denver, A.R. Olsen, S.W. Ator, S. Cormier, M.S. Nash, and M. Mehaffey. 2000. Testing landscape indicators for stream condition related to pesticides and nutrients: Landscape indicators for pesticides study for mid-Atlantic coastal streams (LIPS-MACS). EPA/600/R-00/87. USEPA, ORD, Washington DC 20460.

Nash, M.S., and W.G. Whitford. *In Press.* Ants as biological indicators for monitoring changes in arid environments: lessons for monitoring protected areas. Proceedings of 1st International Symposium and Workshop on Arid Zone Environment Research and Management Options for Protected Areas. Jan 23-25, 2000, Abu Dhabi, UAE.

Nita Tallent-Halsell

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Education

Master of Arts in Science, Biology/Statistics, University of Nevada, Las Vegas, 1998

Bachelor of Science, University of Nevada, Las Vegas, 1989

Experience

Ecosystem Restoration Research

LEB Remote Sensing, GIS and Landscape Ecology Training Coordinator

LEB Global Positioning Systems Lead

ESD-LV Health and Safety Committee Chairperson

EMAP - Forest Health Monitoring, National Logistics Coordinator (1993-1995)

EMAP - Surface Waters Logistics Coordinator (1991)

EMAP - Arid Lands Logistics Coordinator (1992-93)

Publications

Tallent-Halsell, N. and L. R. Walker. (in prep). Lake Mohave Riparian Ecology and Restoration.

Tallent-Halsell, N. and L. R. Walker. (in prep). Response of Salix gooddingii and Tamarix ramosissima to flooding and substrate types.

Tallent-Halsell, N. and L.R. Walker. (in prep). Management recommendations for Lake Mohave riparian sustainability and restoration.

de Soyza, A. G., J. W. Van Zee, W. G. Whitford, A. Neale, N. Tallent-Halsell, J. E. Herrick and K. M. Havastad. (2000) Indicators of Great Basin rangeland health. Journal of Arid Environments. 45:289-304.

Tallent-Halsell, N. 1995. Training Strategies for Ecological Monitoring Programs: The Forest Health Monitoring Experience. p. 398-408. In: Power, J.M., M. Strome and T.C. Daniel (editors). 1995. Proceedings of Decision Support - 2001 Vol. I, Toronto, Canada September, 12-16, 1994. American Society of Photogrammetry and Remote Sensing, Bethesda, Maryland, USA.

Tallent-Halsell, N. (ed). 1994. Forest Health Monitoring Field Methods Guide. EPA/620/R-94/027. U.S. Environmental Protection Agency, Washington, D.C.

Kepner, W.G., R.O. Kuehl, R.P. Brechenridge, J.M. Lancaster, S.G. Leonard, D.A. Mouat, T.G. Reinsch, K.B. Jones, A.C. Neale, T.B. Minor, and N. Tallent-Halsell. 1994. Environmental Monitoring and Assessment Program: Arid Ecosystems 1992 Pilot Report. EPA/620/R-94/015. U. S. Environmental Protection Agency, Washington, DC.

Tallent-Halsell, N. 1993. Logistics *In*: Franson, S. 1993. Environmental Monitoring and Assessment Program: EMAP-Arid Colorado Plateau Pilot Study - 1992 Implementation Plan. EPA/600/7-93. U.S. Environmental Protection Agency, Washington, DC.

Presentations, Posters and Published Abstracts

Tallent-Halsell, N. and L.R. Walker. 1999. Southwestern Sustainability along a Lower Colorado River Impoundment. Mojave Desert Science Symposium, February 25-26, 1999, Las Vegas, Nevada.

Tallent-Halsell, N. 1998. Developing a conceptual model of landscape and ecosystem dynamics for riparian restoration on a lower Colorado River Impoundment. Society of Ecological Restoration Conference, September 27-30, 1998. Austin, Texas.

Tallent-Halsell, N. and L. R. Walker. 1998. Riparian species response to inundation and drought: a greenhouse experiment on *Salix gooddingii* and *Tamarix ramosissima* cuttings. Ecological Society of America-83rd Annual Meeting, August 2-6, 1998, Baltimore, Maryland.

Tallent-Halsell, N. 1998. Southwestern Riparian Sustainability and Restoration in a Man-made Ecosystem. National Symposium on Ecosystem Restoration, July 29-31, 1998, Baltimore, Maryland.

Tallent-Halsell, N. and L.R. Walker. 1997. Goodding Willow Ecology in a man-made southwestern riparian ecosystem. Presented at 1997 Ecological Society of America Meeting, August 10-14, 1997. Albuquerque, New Mexico.

Tallent-Halsell, N. 1997. Goodding Willow Ecology on the Shoreline of Lake Mohave. Presented at Forty First Annual Meeting of the Arizona - Nevada Academy of Science, April 19, 1997. University of Nevada, LV.

Lee Riddick

Education

- 1984-1987, Louisiana State University: *Microbiology*
- 1996, B.S. University of Nevada, Las Vegas: *Chemistry*

Experience

- Research Chemist, Environmental Chemistry Branch, ESD, NERL, U.S. EPA, 1996-present
- NNEMS Fellow, U.S. EPA, Las Vegas, NV 1993-1996
- Biochemistry Technician, University of Nevada, Las Vegas 1992-1993

Expertise/Research

Method development using Capillary Electrophoresis (CE) and GC-MS for detection of environmental pollutants.

Charlita Rosal

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Educational Background

M.S. Environmental Chemistry, **1991**
University of Nevada Las Vegas
Thesis title: *Polonium-210 Radioactivity in Lake Mead Fish*

M.S. (ABT) Chemical/Environmental Engineering, 1980-82
University of the Philippines, Diliman, Quezon City, Philippines

B.S. Chemical Engineering, 1979
Mindanao State University, Marawi, Philippines

Professional Experience

Research Environmental Scientist **June 1990 to Present**
U.S. Environmental Protection Agency, NERL/ORD

Current research involves method development for speciation of arsenic from environmental samples using capillary electrophoresis/UV (CE/UV) and CE/inductively coupled plasma mass spectrometry (CE/ICPMS). Performs multielement inorganic analyses on PRIMENet and other environmental samples. First 5 years of Agency work involved in research, development, and evaluation of new and improved methods for environmental monitoring and characterization of waste sites. Served as a Project Officer for research related to underground storage tanks, ground-water/surface water, and saturated zone monitoring and characterization of surface/subsurface environmental conditions and contaminants.

Nuclear Research Scientist **1979 - 1982**
Philippine Atomic Energy Commission, Diliman, Quezon City, Philippines

Performed routine processing of radioisotopes consisting of target preparation, irradiation of samples, chemical processing and/or purifying of irradiated materials and activity assaying of the products. Prepared soil samples for irradiation for uranium analysis using delayed neutron activation analysis. Involved in tests and experiments in radioimmunoassay. Performed routine dispensing and quality assurance/quality control of radioisotopes for human use.

Katrina E. Varner

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Education

B.S., Developmental and Cellular Biology, minor in Social Services, University of Nevada, Reno, 1987

Experience

1990-Present	Environmental Research Scientist, U.S. Environmental Protection Agency, Las Vegas
1989-1990	Organic Chemist, FiberChem, Inc.
1987-1989	Chemist I, Las Vegas Valley Water District

Publications

Amick, E.N., Pollard, J.E., and Varner, K.E., "An Evaluation of Four Field Screening Techniques for Measurement of BTEX," EPA/600/R-94/181, U.S. Environmental Protection Agency. September 1994.

Portnoff, M.A. and Varner, K.E., "Measurement and Analysis of Vapor Sensors Used at Underground Storage Tank Sites," EPA/600/R-95/181, U.S. Environmental Protection Agency. May 1995.

Kreamer, D.K., James, D.E., and Varner, K.E., "Determination of Pollutant Distribution and Movement by Controlled Laboratory Experiments," EPA/600/R-96, U.S. Environmental Protection Agency. November 1996.

Hampton, D.R. and Varner, K.E., "Improving Free Product Monitoring and Recovery," EPA/600/R-97, U.S. Environmental Protection Agency.

Amick, E.N. and Varner, K.E., "Field Analysis of Soil and Water Samples for Petroleum Hydrocarbons at Sites in Las Vegas, Nevada Utilizing Quick Turnaround Methods," EPA/600/R-97, U.S. Environmental Protection Agency.

Eskes, C., Honegger, P., Jones-Lepp, T., Varner, K., Mattheiu, J.M., and Monnet-Tschudi, F. "Neurotoxicity of Dibutyltin in Aggregating Brain Cell Cultures," *Toxicology in Vitro*, 13 (1999), 555-560.

Lepp-Jones, T., Varner, K., McDaniel, M. and Riddick, L. "Determination of Organotins in Water by Micro-Liquid Chromatography-Electrospray Ion Trap Mass Spectrometry," *Applied Organometallic Chemistry*, 1999.

Jones-Lepp, T. and Varner, K. "Speciation and Detection of Organotins from PVC pipe by Micro-Liquid Chromatography-Electrospray Ion Trap Mass Spectrometry" *Analytical Chemistry*, under review, 1999.

Varner, K. and Jones-Lepp, T. "Development and application of a micro-liquid chromatography-electrospray/ion trap mass spectrometry method for the detection of two suspected endocrine disruptors: Dibutyltin and triphenyltin, in natural waters and fish tissue" National ACS Proceedings 1999.

Jones-Lepp, T. and Varner, K. "Development and Application of a Solid Phase Extraction and Micro-liquid Chromatography-electrospray/ion trap Mass Spectrometry Method for Detecting Three Pharmaceuticals in Natural Waters: Prozac, Prilosec, and Claritan" American Water Works Association, American Research Foundation Conference, 1999.

Presentations

Varner, K.E. 1994. Monitoring Hydrocarbons at UST Sites. USEPA Region 9All-States Meeting. Lake Tahoe, CA.

Varner, K.E. 1995. Field Screening Methods for BTEX. USEPA Technical Support Project Meeting/Engineering and Ground Water Forum. Las Vegas, Nevada.

Varner, K.E. 1996. Expedited Site Assessment Methods for Underground Storage Tank Facilities Workshop. Martinsburg, West Virginia and Kansas City, Missouri.

Jones, T.L., Varner, K.E., and Riddick, L.A. 1997. Using µ-Liquid Chromatography Electrospray-Ion Trap Mass Spectrometry to Measure Organotins in an Ambient Environment. 45th American Society for Mass Spectrometry and Allied Topics Conference. Palm Springs, California.

Eskes, C., Honegger, P., Monnet-Tschudi, F., Jones-Lepp, T., and Varner, K. 1998. Toxicity of Dibutyltin in Aggregating Brain Cell Culture: Comparison with Trimethyltin and Triethyltin. Environmental Toxocolgy Conference, 1998. London, England.

Varner, K.E. and Jones, T.L. 1998. "Organotins, They're Everywhere. Are They Coming to You?" NERL-LV Research Expo. Las Vegas, NV.

Varner, K.E. 1999. "Dibutyltin Measured in Brain using µ-Liquid Chromatography Electrospray/Mass Spectrometry" Western Regional ACS Pacific Conference on Chemistry and Spectroscopy, Ontario, CA.

Appendix E

Environmental Chemistry Branch Facilities/Instrumentation

The Environmental Chemistry Branch (ECB), ESD, NERL-Las Vegas, comprises 4000 ft^2 of laboratory space. The labs contain a dozen fume hoods, as well as glove boxes, clean benches, and a HEPA-filtered instrument room for low-level analyses. The branch maintains a wide array of in-house state-of-the-art analytical instruments for preparation, separation, and detection of organic, inorganic, and organometallic stressors and indicators of exposure.

Organics: ECB possesses several mass spectrometers. A Finnigan-MAT 900S-Trap with position- and time-resolved ion-counting focal-plane detector can perform high-resolution MS and MS^n experiments at ultra-low concentrations. A VG 70-250SE is also available for high-resolution MS. Other mass spectrometers include a Finnigan TSQ 700, three Agilent 6890 GC/5973 MSDs (one with PCI/NCI), Hewlett-Packard 5890 GC/5972 MSD, Varian Saturn II Ion Trap GC/MS, Finnigan GCQ Ion Trap GC/MS, Finnigan 4000, and two ThermoQuest LCQs. In addition to gas chromatography and liquid chromatography (through electrospray interface) sample introduction, some of these mass spectrometers can be configured with fast atom bombardment and solid probes.

Three Beckman capillary electrophoresis instruments have variable UV detectors, diode array detector, and Ar ion laser (488 nm) detector. A stand-alone optical bench with laser sources is available (located at UNLV). A 5W medium scale Ar ion laser allows access to all of the Ar ion lines including the deep UV from frequency doubling; a 2.5W Ar/Kr mixed-gas laser W increases the number of lines available, including the near IR region; also available are Liconix HeCd 354 nm and 325 nm lasers, and HeNe 595 nm 633 nm lasers. A Beckman CE/MS interface for quadrupole mass spectrometers is also available.

Other instrumentation includes an Hewlett-Packard 5890 Series II GC with electronic pressure programming and autosampler with FID and ECD and a 5890 GC with autosampler and NPD. Hewlett-Packard 5890 Series II Plus GC with 5921A He-plasma atomic emission detector (AED) and electronic pressure programming is used for selective gas chromatographic determination of compounds containing heteroatoms. A Spex Fluorolog 2 spectrofluorimeter, a Perkin-Elmer Lambda 9 spectrometer, Spectra-Physics liquid chromatograph with diode array and fluorescence detectors, and CAMAG instrumental thin-layer chromatography system (consisting of TLC spotter, automated multiple development instrument, and computer-controlled densitometer with UV, visible, and fluorescence detection) are also in-house. Other instrumentation includes two HP 1090 HPLCs with DAD and programmable fluorescence detectors, and a custom made vacuum distillation apparatus with HP GC/MSD.

For sample preparation and cleanup, the following equipment is available: a Hewlett-Packard supercritical fluid extraction instrument and supercritical fluid chromatograph, a Suprex Prepmaster SFE,

a Waters Millenium HPLCS for high performance gel permeation chromatography, a Danaus ASE 200 thermally assisted solvent extraction instrument, a Savant ISS110 Integrated SpeedVac system for concentration of DNA samples, a Forma Scientific 4520 incubator shaker, and Zymark TurboVap 500 and TurboVap II evaporators.

Inorganics: Element-specific detection systems include a VG PlasmaQuad II STE ICPMS, which can be equipped with a Mistral desolvation unit (VG Elemental) for ultra-high sensitivity, and Thermo Jarrell Ash AA Scan 4 atomic absorption spectrometer equipped with a Model 188 graphite furnace atomizer. The VG ICPMS is installed in a room supplied with HEPA-filtered air. Syringe pumps (ISCO model 100DM) and reciprocating pumps (Dionex microscale gradient pumps) are available for delivery of liquid flows required for different modes of microscale high-performance liquid chromatography. Milestone automatic mercury analyzer for fluids and tissues/solids (requiring no liquid reagents). Various extraction and digestion systems (heating block, steam distillation, etc.) are available.

Computers: One Silicon Graphics Indigo 2 workstation and three SGI Octanes are in-house, with access to UNLV or Bay City Cray supercomputers.