# IMPLEMENTATION OF
# SPECIAL MONITORING WITH MACRORETICULAR RESINS
# IN THE RUSSIAN RIVER BASIN,
# SONOMA COUNTY, CALIFORNIA

[Prepared in partial fulfillment of the workplan,
"Toxic Substance Detection and Early Warning
for the Russian River", May 14, 1985.]

by

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# TERMINOLOGY

This section defines some of the terms used in this report. Some are technical, others are working definitions.

Analyte - the element or compound of interest in an analysis

Anion - a negatively-charged ion

Bed Volume - the amount of resin in a column

Blank - a resin sample not exposed to water, but analyzed the same as any other resin sample

> Method blank - a resin sample not exposed to water, nor any other environmental factors and anaylzed the same as an environmental resin sample (provides information on background contamination from laboratory procedures)
>
> Field blank - a resin sample not exposed to water, but taken into the field with a resin sampler, un-capped and re-capped, left with the resin columns in the sampler, and analyzed the same as the environmental resin samples (provides information on background contamination from laboratory and field procedures)

Breakdown - as applies to the organics testing, the separation of a compound into various smaller compounds

Cation - a positively-charged ion

Chelation - causing a metal ion to bond to another compound; forming a ligand (chelate)

Complexing agent - a compound capable of binding a metal ion or molecule into a chelate (ligand)

Elute - wash a metal ion or compound from a resin with an acid solution

Eluate - concentrated acid solution resulting from an elution (elutriate)

Extract - similar to elution, except a solvent treatment of a resin to remove an organic compound from the resin; the resultant concentrated solvent solution

## TERMINOLOGY (CONT'D)

Frit - a fine screen or filter used to keep resins in a column

Fractionation - the splitting of an extract into additional extracts based on molecular weight or polarity

Hydration - exposing the resin to water, thus rinsing the methanol from the resin

Hydrolysis - reaction of a compound with the ions of water ($H^+$, $OH^-$_

Ligand - a metal bound to an organic compound (chelate)

Method detection level - the level at which a chemical is reliably quantitated (MDL); for metals work in this study the MDL was twice the appropriate blank value.

Percent recovery - the amount of an analyte extracted or eluted from a resin (recovered) with respect to the quantity added (spiked); i.e., the efficiency of the resin

Quantitate - to measure or determine the quantity of a substance

Replicate - repeat a procedure, e.g., replicate sampling; the repeated procedure, e.g., replicate samples

Rinsate - solution resulting from rinsing a spiked resin with water, i.e., the rinsings that contain the spiked compound not adsorbed by the resin

Speciation - as regards metals in solution, the separation of a metal's presence into various forms such as anionic, cationic, ligand

Spike - add a known quantity of a compound to a resin or solution; the resultant solution.

### ABBREVIATIONS

AC = alternating current
cm = centimeter
DC = direct current
g = gram
ID = inside diameter
L = liter
M = molar
mg = milligram
mL = milliliter
mm = millimeter
ng = nanogram
OD = outside diameter
ug = microgram

# EXECUTIVE SUMMARY

As part of a two-year, Federally-funded water quality management and planning program [Section 205(j) of the Federal Clean Water Act], the Regional Water Quality Control Board (Regional Board) and the Sonoma County Water Agency (SCWA) tested special resins for use in sampling surface waters for heavy metals and organic compounds. The resins have high affinities for various ions and compounds and result in highly concentrated extracts. This allowed us to measure metals in water as low as one-fortieth of the conventional lower detection limit.

The testing involved construction of resin columns and sampling apparatus, construction of a special laboratory by the SCWA, laboratory testing of resin efficiencies, fine-tuning of previously developed methods, and actual sampling of the Russian River and tributaries.

The sampler we designed allowed us to sample water at various repetitive intervals, and route the sample to any of three sets of columns. Our investigations began with a 110-volt sampler, however we found supplies to construct a fully portable sampler that will run on a 12-volt deep-cycle battery.

We used three resins for heavy metals sampling: Chelex-100 for positively charged ions (cations), AG 1X-8 for negatively charged ions (anions), and Duolite S-587 for organo-metallic complexes. We were able to account for most or all of the various ionic forms of the metals in water that we tested by using the three resins in series.

We tested Amberlite XAD-4 and XAD-8 resins for sampling organic compounds, primarily pesticides and herbicides. We were unable to achieve consistently good results with either resin, i.e., some compounds went unaccounted in laboratory testing.

The Russian River sampling revealed nothing unusual. Metals concentrations were all below existing and/or recommended criteria and standards.

The Regional Board intends to continue its use of the resins for metals sampling, however will not pursue the use of resins for organic compounds in the near future.

# INTRODUCTION

## Background

The project, "Toxic Substance Detection and Early Warning for the Russian River", (NCRWQCB, 1985) was a cooperative effort among the Regional Board, the Sonoma County Water Agency (SCWA), and N.E.T. Pacific, Inc. (formerly Anatec Laboratories, Inc.) (NET). Seventy-five percent of its funds came from a Section 205(j) grant provided by the Environmental Protection Agency (EPA), while the remaining twenty-five percent was provided in materials and services by the contributors. The Regional Board administrated the project, using a contract with Sonoma State University to provide student help for most of the experimentation. The SCWA and NET provided laboratory space, a field site, equipment, expertise, and additional manpower as needed.

One task in a previous 205(j) project to identify potential discharge sources within the basin (NCRWQCB, 1983) was to look at the possibility of using accumulating resins for surface water monitoring of heavy metals and organic chemicals. Upon completion of that program the findings indicated the concept of using resins to accumulate ions and compounds from environmental water samples was viable and would require minimal development to implement. The current project was developed in response to those findings. This report fulfills Task 3 to the Section 205(j) project, "Toxic Substance Detection and Early Warning for the Russian River". The primary objective of Task 3 was: "...to transfer the resin column prototype from University of California development to Regional Board implementation" (NCRWQCB, 1985).

## Resin Monitoring Theory

Resin column monitoring involves the principle of accumulation of ions or chemicals on a resin, thus concentrating the ions or chemicals of interest. It has the advantage of continuous sampling of water over a specific time period with the ability to measure chemicals at very low levels. Short-term peaks in concentration are attentuated, however, by inclusion with many days of relatively low concentrations. Two types of resins were investigated for use in monitoring dissolved metals and organic compounds in surface waters:

1) Chelating ion exchange resins: These resins accumulate dissolved or weakly-complexed metals. The metal ions replace existing $Cl^-$, $Na^+$, $NH4^+$, or $H^+$ ions in the resin, due to the stronger affinity for the resin molecules.

2) Adsorbent resins: These resins accumulate metal-organic complexes and other organic molecules. The organic molecules are relatively inert with regard to the resins and do not undergo ion exchange, rather they are sorbed to the resins. The adsorbent resins vary in polarity, the more polar ones attracting the more polar molecules; adsorbent resins with varying polarities used in series theoretically can accumulate a wide variety of molecules.

The resins were first exposed to a water sample then treated to extract the dissolved metal and/or organic compounds. The extraction techniques differed depending on the compounds being monitored. The resultant extracts were analyzed by atomic absorption spectrometry, high performance liquid chromatography, and/or gas chromatography.

Under the previous project, researchers at the University of California, Santa Cruz (UCSC) reported on the use of resin columns to measure ultra-trace metals in solution and to determine their speciation in fresh waters (Bruland, et.al. 1985). Their experiments used an exchange resin to accumulate ions in series with an adsorbent resin to accumulate metal complexes. Four ion exchange resins were studied: CHELEX-100, HQ-8, AG 1-X8, and UCSC HQ-8 (the latter developed by UCSC and not available for commercial use). The adsorbent resin was DUOLITE S-587. Additional information on these resins appears in Appendix A. The resins were characterized in the laboratory with respect to their efficiency and specificity in relation to pH, flow rate through the resins, and the presence of various dissolved organic substances. The resins were packed into Teflon columns and tested for precision and accuracy under field conditions on the Russian and Sacramento Rivers.

Researchers at the University of California, Davis (UCD) reported on the use of resin columns to measure trace organic compounds in water (Seiber, et.al. 1985). Amberlite XAD-4 resin was studied and compared in efficiency to liquid-liquid partitioning and polyurethane foam sampling. Chlorinated hydrocarbons, PCBs, and selected esters were studied as special cases in addition to other organic compounds. A survey of the resin column literature is included in the UCD report as well as detailed methodologies for resin extraction and recovery problems. UCD tested the XAD-4 resin in Teflon columns with a portable pumping unit on the Russian River, Sacramento Valley streams and agricultural drains, and from a well at Davis, California.

The UCSC studies for recovery of metals using radiotracers in the laboratory showed that the Chelex cation exchange resin removed all of the studied metals in the presence of non-chelating organic molecules except for $Fe^{+3}$, which was recovered on Duolite. At varying pH levels, no more than 20% of the $Fe^{+3}$ was lost. Complexing molecules, on the other hand, held substantial fractions of the metals in solution and caused a low collection by the Chelex. However, metal/organic complexes which passed through the Chelex column were nearly entirely retained by the Duolite resin. The UCSC report concluded that using Chelex-100 in series with Duolite S-587 should retain nearly quantitative amounts of dissolved metals in fresh water systems (Bruland, et.al. 1985).

The UCD organics tests with XAD-4 resin used a series of pesticides at 10 ug/liter (L) and 0.1 ug/L concentrations. At the higher concentration, resin recovery efficiencies were determined for a number of water samples containing mixtures of a few compounds that could be quantitated together using the same analytical techniques. At the lower level, recovery efficiencies were determined for water samples containing a mixture of compounds from widely differing classes. After compound quantitation this complex mixture was fractionated into compound classes using high performance liquid chromatography. The separate fractions were re-analyzed to determine the extent of clean-up and any effects of that fractionation on recoveries.

Recovery efficiencies averaged 66.4% ± 8.9 standard deviations (SD) for the 0.1 ug/L level and 75.6% ± 3.1 SD for the 10 ug/L level. Recovery efficiency was better for resin extraction at the lower concentration (0.1 ug/L) than for liquid/liquid solvent extraction. The UCD report concluded that by using both a methylene chloride and an acidified acetone extraction in series on a resin sample, most compounds could be quantitatively extracted (Seiber, et.al. 1985).

Some compounds require special extraction methods. Inter-resin reactions, hydrolysis, volatility, and high dissociation constants may necessitate some special techniques for: Captan (hydrolysis), 1,2-dichloropropane, trichloroethylene, some esters (volatility), picloram (inter-resin reactions), 2,4-dichlorophenoxyacetic acid, pentachlorophenol (high dissociation constants), and formaldehyde.

## Basic program

Embarking on the implementation of actual surface water monitoring using resin column methodology in the Russian River basin necessarily required the testing and subsequent modification of those methods developed by UCD and UCSC. We relied heavily on the reports provided by each of the institutions for our work with the resins, but also entered into a period of research involving literature reviews and telephone conversations with the manufacturers of the resins and others working with the resins.

Our laboratory work and discussions with manufacturers, chemists, university scientists, and other scientists resulted in a resin guide, upon which we based our remaining monitoring and laboratory investigations, titled "A Guide to the Preparation and Use of Selected Macroreticular Resins for Environmental Monitoring: North Coast Region" (Fairchild and Klamt, 1988). That guide is attached as Appendix A.

Field testing of the resin sampling apparatus was conducted in accordance with the resin guide to test the field methodology and laboratory procedures as a combined effort. Those field tests necessitated further modifications to our methods and the resin guide and resulted in the implementation of actual monitoring of the Russian River and selected tributaries.

It is the sequence of methods modification, field testing and surface water monitoring that is the subject of this report. We present the results of each of those phases of the process with the final analysis being the discussion of monitoring results from the Russian River basin and recommendations for further work with the resins. Prior reports providing a basis for this effort are directly referenced to reduce the size of the main body of this report.

## METHODS

### Quality Assurance/control

An essential part of any investigation of methodology and resulting monitoring program is a set of procedures to define the precision and accuracy of the results. Our quality assurance/control program was patterned after the generally-accepted methods outlined by the EPA in 1972 (EPA, 1979). The program originally developed is detailed in "Quality Assurance Program for Toxic Substance Detection and Early Warning for the Russian River" (NCRWQCB, 1987), however, modifications to the program were necessary as the project proceeded. Protocols were modified as we began to work with the real-world situations of resin preparation, surface water sampling, and resin extractions.

As a general rule we analyzed replicate environmental samples on a frequency of at least one duplicate analysis per every ten samplings. Additionally, we analyzed method blanks and field blanks on a routine basis. Method blanks were columns that were prepared and extracted in the laboratory. Field blanks were method blanks that were taken into the field during environmental sampling and exposed to the same conditions as the sampling columns with the exception of not having water pumped through them. The minimum detection level (MDL) was defined as twice the appropriate blank, i.e., the MDL was based on background levels and changed with changes in technique, contamination, etc.

Although we relied heavily on work by others regarding resin recovery efficiencies, we also performed spike/recovery experiments with the resins, i.e., we pumped solutions containing known quantities of compounds through the columns, extracted the columns, and compared what was extracted with what was in the original solution. The percent recovery was the percentage of the compound of interest in the extract, e.g., 100% recovery meant that all of the compound pumped through the column was found in the extract. These three basic tests (duplicate analyses, analysis of blanks, and spike/recovery tests) provided us with information on the precision of the methods, background contamination levels, and efficiency of the methods in accumulating and recovering the compounds.

### Materials and Lab Procedures

All handling of the resins prior to sampling and during extraction were performed in a clean room in the SCWA laboratory to reduce contamination from airborne particulates (Adelojou and Bond, 1985; see Mitchell, 1973 and Murphy, 1976 for descriptions of clean rooms). All air entering the room was supplied under positive pressure through a high efficiency particulate filter. Approximately half of the laboratory bench was surrounded by heavy PVC sheeting; that area was designated as the cleanest portion of the clean room and all raw resins work was performed within its confines.

The Teflon resin columns are made of 1 cm ID X 1.4 cm OD Teflon PFA tubing fitted with end pieces milled from Teflon TFE rod. Each end piece is fitted with Teflon connectors to accommodate 3 mm OD Teflon tubing (Figure 1). The columns are 13 cm long and contain a bed volume of approximately 5 mL (5 grams) of resin. Polyethylene frits (70 micron mesh) were used to contain the Chelex and Ag resins due to their small size (100-200 mesh). Teflon screen (105 micron mesh) was used for the Duolite and organics resins.

The automatic sampler/pump system, as originally designed at UCSC and modified for use by the Regional Board, draws water through a 3 mm OD (1.5 mm ID) Teflon tube to an AC peristaltic pump fitted with 25 cm of silicone pump tubing (Figure 2). The sample passes from the pump head to a series of 3-way Teflon solenoid valves controlled by a 4-channel timer/actuator. The valves are actuated (opened) by the timer/actuator and the sample stream passes through a filter cartridge packed with glass wool, then into the resin column set connected to the appropriate valve. The filter is purged prior to each sampling event, bypassing water as illustrated in Figure 2. The outlet from each resin column set enters a separate collection vessel used to measure the actual volume pumped through each resin column set. The timer/actuator is capable of 10 separate programs, and in this way, can run continuously and unattended, collecting subsamples with any of three sets of resin columns over pre-selected time intervals. Several column arrangements are possible and include: (1) a single column, (2) columns in series to determine saturation of the resins and subsequent "breakthrough", (3) a split stream leading to two parallel sets of columns in series, and (4) sequential columns in series with different resins to partition chemicals by polarity or activity (Table 1).

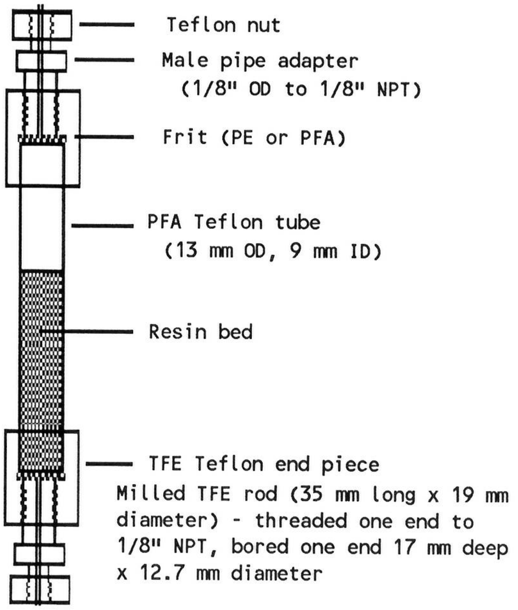


Figure 1. The Teflon resin column design used to sample heavy metals and complex organic chemicals.

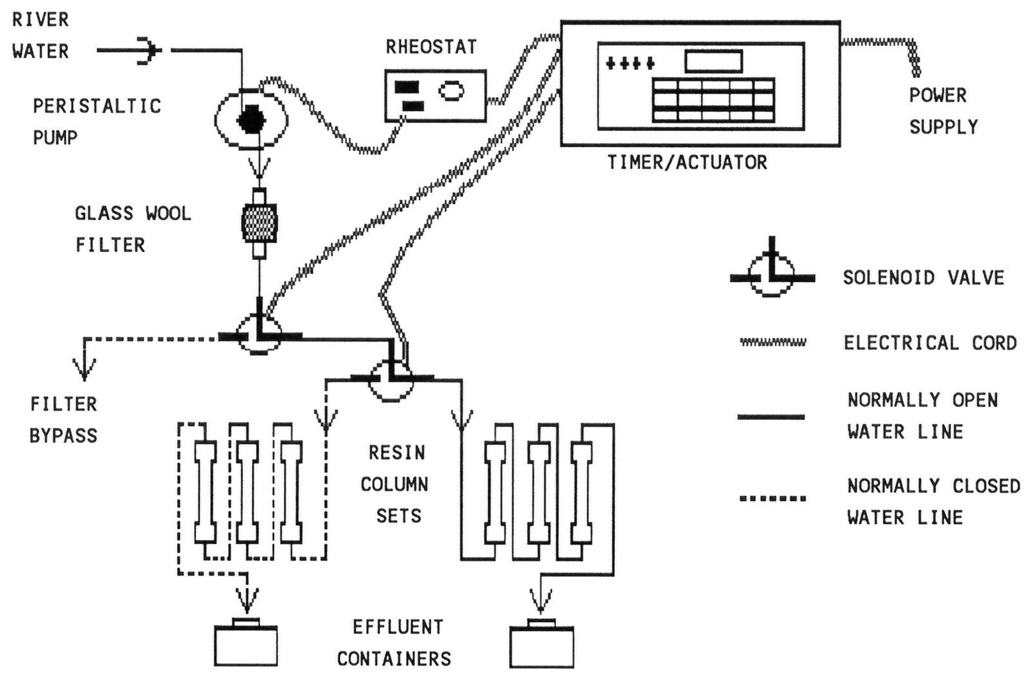


Figure 2. Basic resin column sampler design used for Russian River monitoring. Duplicate column setup is depicted.

Early in 1988 we discovered a 12-volt, DC operated timer/actuator that was not available for this study. Now we are able to sample virtually anywhere a 12-volt battery can be carried. An equipment list for both the AC and DC samplers is presented in Appendix B.

When possible, the sampler set-up was performed in a clean laboratory, otherwise in a field location out of the wind and free from dust. Disposable polyethylene gloves were worn during the handling of the sampler components that contacted sample water or the resins. Care was taken at all times to minimize contact with the resin columns themselves and any portion of the set up that would contact the sample and/or resin. When field blanks were used, they were exposed to the environment similarly, then recapped and left in the sampler.

For a fresh set-up or new location, the Teflon tubing and solenoids were joined as though the columns were installed and the system was flushed. As the sample water was pumped through the system, the delivery rate of the pump was set between two (2) and three (3) mL/minute. The rate was checked three times to assure stability. All pertinent information was recorded in a resin sampler log book.

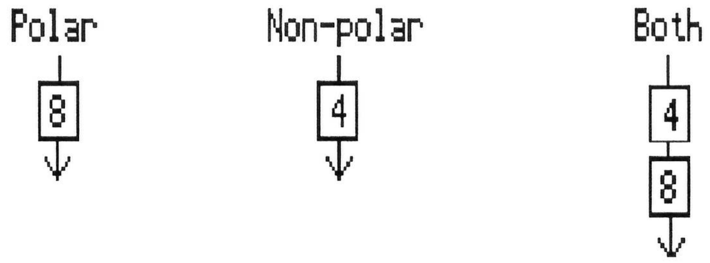
Table 1. Resin column configurations for partitioning chemicals, obtaining duplicate samples, and determining resin saturation (breakthrough).

## LEGEND

4 XAD-4 8 XAD-8 ☒ Chelex-100 ▒ AG 1X-8 ■ Duolite S-587

### Organic Chemicals

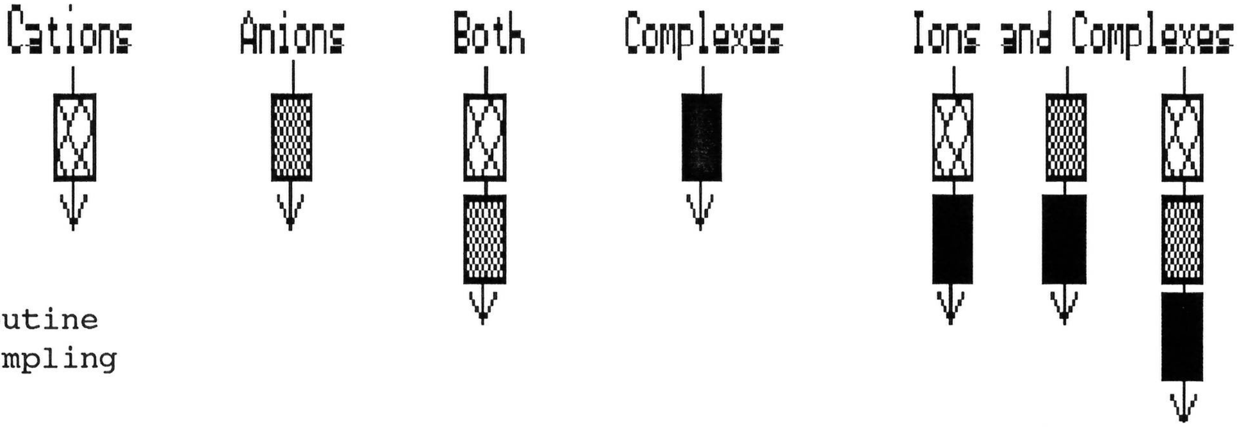
Routine Sampling



Duplicates Any of the above sets in parallel.

Saturation Above sets in series, like resins grouped.
(e.g. for 'Both' use XAD-4 in series followed by XAD-8)

### Metals



Routine Sampling

Duplicates Any of the above sets in parallel.

Saturation Above sets in series, like resins grouped.
(e.g. for 'Both' use XAD-4 in series followed by XAD-8)

## Organics Resins Methods

We chose the adsorbent resins Amberlite XAD-4 and XAD-8, Rohm and Haas Company, Philadelphia, PA, based on a previous 205(j) project (NCRWQCB, 1983 and Sieber, 1985) and the work of others (Junk, et.al., 1974, Dressler, 1979, Richard and Junk, 1986). We began our organics resins work with the UCD methods (Sieber, 1985), and through a series of experiments ended with a modified method. Both methods are presented in detail in Appendix A.

Resin recovery efficiencies were tested with two types of experiments: 1) field sampling simulation, and 2) direct resin spikes. The field sampling simulation involved pumping an aqueous solution of compound or compounds of interest (spike) through a column setup in the laboratory under simulated field conditions. Analysis of the spike solution, the resins, and the effluent (solution that passed through the column), and subsequent mass-balancing provided us with information of the ability of the resins to accumulate the compounds and recovery efficiencies of the methods.

The direct resin spikes simply involved adding a known amount of the compound of interest to approximately 2.5 grams of resin in a solvent cleaned beaker in the laboratory. The resin and a solvent rinse from the beaker were both extracted and analyzed by gas chromatograph (GC) or GC/mass spectroscopy. Those experiments provided data on the abilities of the resins to adsorb a compound, and the efficiency of our methods in removing and accounting for the compound. The direct resin spikes represented the least variable of the experiments because of the absence of water and most other variables.

All experiments were performed with solvent-cleaned glassware and tubing. Method blanks for each compound accompanied each test. The contract laboratory performed the direct resin spikes and all extractions and analysis; we performed the field sampling simulations.

The resins were prepared by rinsing with water, basifying, acidifying and extracting. The originial method (Seiber, 1985) involved 24-hour stepwise extractions in a Soxhlet extractor containing a fabric sock (Nylon or Dacron) with acetone, methylene chloride, and methanol. The method used for the final tests involved 24-hour extraction with methanol, methylene chloride, ethyl acetate, and a final extraction with methanol. Resins from both procedures were stored in methanol under refrigeration until used.

Two extraction methods were employed, both of which were modified as test results became available. For neutral compounds (DDD, Lindane, Diazinon, Malathion) the method involved methylene chloride extraction, removal of water, and replacement with hexane (Seiber, 1985). This extraction was modified for the last set of experiments by substituting a 1:1 binary mixture of methylene chloride and ethyl acetate for the extraction solvent. Care was taken to dry the resin almost completely prior to extraction and to use generous portions of sodium sulfate in the reduction and de-watering phases. However, if the resin was too dry, the resins developed a static charge and resin beads could be lost.

For acidic compounds and those that undergo hydrolysis or have high dissociation constants in water (2,4-D, penta- and tetrachlorophenol) an acidified acetone extraction was originally used as presented by Seiber (1985). The resin was extracted with acetone acidified to 5% (volume-to-volume) with 6.0 M HCl, then reduced in volume. The resulting extract was combined with 100 mL of organic-free distilled, deionized water containing 5% (volume-to-volume) 6.0 M HCl, and extracted twice in a separatory funnel with 30 mL methylene chloride. The extract was de-watered with sodium sulfate and dried before methylation and hexane replacement. The method was modified for the final experiments by substituting methanol acidified to 0.5% (volume-to-volume) with 6.0 M HCl for the acidified acetone. The acidified water in the following step was 0.5% 6.0 M HCl instead of the original 5%. Again care was taken to dry the resins and use sodium sulfate during de-watering steps.

Columns were packed by removing the top fitting from a clean, Teflon column rinsed with organic-free distilled, deionized water, pouring the resin slurry into the column to a gravity packed volume of approximately 5 mL, and replacing the top fitting.

The columns were wrapped in foil and stored in zip-lock bags. The containerized resin column sets were then labeled with resin type, date, and technician's name and refrigerated. The appropriate information was recorded in the log book. Prior to testing, the resins were hydrated with sequential flushing of 15 bed volumes (approximately 45 mL) using organic-free distilled, deionized water.

## Metals Resins Methods

The final methods for monitoring heavy metals are detailed in the resins guide, Appendix A. The resins are outlined in the introduction: Chelex 100 (cation exchange resin, BioRad), AG 1X-8, (oxy-anionic exchange resin, BioRad), and Duolite S-587 (adsorbent resin, Rohm and Haas). A summary of our experimental methods to arrive at those final techniques follows.

The basis for our investigations was the methodology presented by Bruland, et. al. (1985). We relied heavily on their work for our methods, both in terms of actual techniques and the efficacy of the methodology. Our initial work produced some disparate results and many questions regarding the chemistry of the resins and their relative activities emerged. Numerous conversations with the UCSC researchers, other researchers, and the resin manufacturers themselves resulted in additional experiments comparing the various methods in use in an attempt to resolve the problems.

We tested the resins with respect to the various methods of resin preparation and elution for a number of heavy metals. The results of those experiments and the experience of others using the resins (Paulson, 1985, Kingston, et.al, 1978, Greenberg and Kingston, 1983) were the methods we finally used.

As mentioned above, the final methods are detailed in another report (Appendix A) and are only outlined here. Our approach was to first clean and/or condition the resins, pack the columns (also meticulously cleaned), and store the resin columns under refrigeration until use. All materials that contacted the resins or resin column parts were meticulously cleaned and stored in a dilute nitric acid solution. We used the previously described sampler for the environmental sampling. This allowed us to have many sets of columns at each site and to sample at pre-set intervals. After sampling, the columns were returned to the laboratory and the metals eluted by successive elution with acid solutions in the clean room. The eluates were delivered to a contract laboratory for analysis by atomic adsorption spectrophotometry. The resins then were re-conditioned for re-use. Method blanks provided information on background levels of contamination for each batch of resins.

The metal concentration in a sample was calculated by a simple sample to eluate volume, i.e. the sample was concentrated into a small eluate volume. For example, if 2.0 L was pumped through the resin and the resulting eluate volume was 100 mL (0.100 L), the concentration factor was 2.0 L/0.100L, or 20. Thus an eluate concentration of 50 ug/L, translates to a sample concentration of 50/20, or 2.5 ug/L.

## Monitoring Effort

Resin column sampling was initiated in September of 1986. Since then, heavy metals were sampled at Wohler Bridge 15 times, in the Ukiah and Cloverdale areas once, in Big Sulphur Creek once, and in the Mark West Creek system on eight occasions. The Russian River basin and the sampling sites are illustrated in Figure 3.

Since the samplers operated on 110 volt AC, sampling was limited to locations with appropriate electrical services (standard house current), which obviously limited our selection of sampling sites. The development of a DC-operated sampler will allow us much more flexibility in the future.

The length of sampling varied from 2 to 24 days, but generally lasted about seven days. The volume of water passed through the columns was usually about 2 liters (L), and ranged from 1.5 to 6.8 liters. Sampling frequency was generally five (5) minutes in every 30 minutes, i.e. the pump pushed water through the columns at the rate of 2-3 mL/minute for five (5) minutes every half hour for the duration of the sampling period. A contact period, a time when water was static in a column in contact with the resin, of 10-15 minutes was provided during each sampling event (30 minutes).

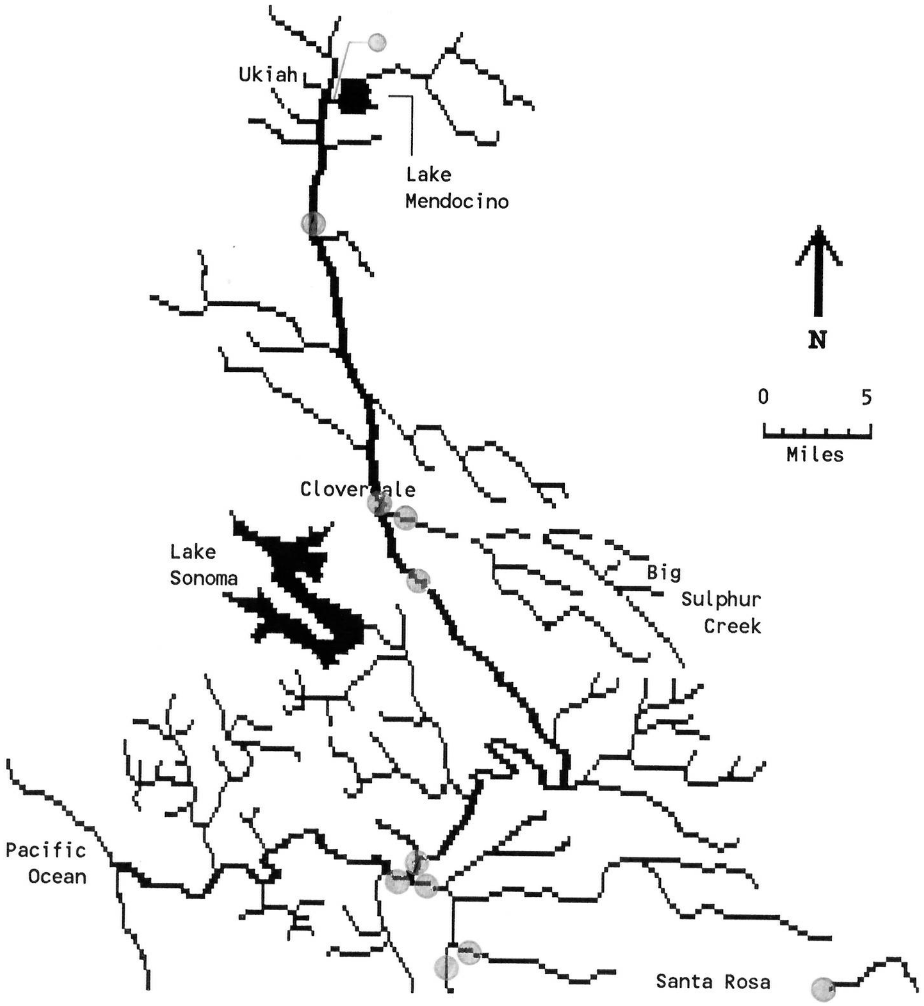


Figure 3. The Russian River basin and resin column sampling stations for 1986, 1987, and 1988.

# RESULTS

## Organics Resins

The investigation of the technique to use Amberlite XAD resins (Rohm and Haas, Philadelphia, PA) involved five separate tests, the results of which follow.

The first test was a simple spike/recovery test in duplicate using seven compounds in water. The solutions were pumped through XAD-4 resin in a simulated field situation. Extraction of the resins was performed with the methods originally presented in Seiber (1985) and Appendix A, Method 1, with the exception that fluorisil cleanup was used instead of high performance liquid chromatography. Analysis was by gas chromatograph. Overall, recoveries were low and variable. Very small amounts of analyte passed to the second column, with the exception of 2,4-D (Table 2). In the case of 2,4-D, some analyte was found in the second column and in the water that passed through both columns (effluent).

The chromatograms showed more compounds in the extract than the analyte of interest. Since the blanks were free of such compounds, we suspected hydrolysis of some compounds and interaction or reactions amongst compounds had created the additional chemicals. Knowing that approximately 48 hours was required to pump the spike solution through the columns, we attempted to look at breakdown and interactive compounds.

Table 2. Spike/recovery summary for duplicate aqueous spikes of p,p-DDD, Lindane, Diazinon, Malathion, 2,4-D, pentachlorophenol, and tetrachlorophenol in combination. Columns A and B were in series, duplicate results are separated by "/".

| | micrograms of analyte from: | | | | Total %[+] |
|---|---|---|---|---|---|
| Compound | spike | column A | column B | effluent | recovery |
| p,p-DDD | 75/89 | 23/11 | 0.63/0.91 | 0/0 | 13/31 |
| Lindane | 140/108 | 60/38 | 3.0/4.2 | 0/0 | 39/45 |
| Diazinon | 200/378 | 227/188 | 1.6/2.4 | 0/0 | 114/50 |
| Malathion | 38/54 | 68/41 | 0.47/0.73 | 0/0 | 183/77 |
| 2,4-D | 90/97 | 41/17 | 41/71 | 18/11 | 141/141 |
| PCP * | 78/78 | 21/0.94 | 1.9/2.4 | 0/0 | 29/4.2 |
| TCP * | 75/76 | 13/0.31 | 6.6/6.7 | 0/0 | 26/9.3 |

[+] amount from columns and effluent divided by amount spiked

* PCP = pentachlorophenol, TCP=tetrachlorophenol

To investigate the possibility of interaction with the water (hydrolysis) and/or breakdown producing compounds different from the parent compound, we instructed the laboratory to spike the resins directly. The spiking was performed with a chlorinated pesticides solution (p,p-DDD, Lindane, Diazinon, Malathion), an herbicide (2,4-D), and fungicides (penta- and tetrachlorophenol), each separately into separate resin samples. In addition, we performed field simulations using two aqueous solutions separately (same groups as above). The extraction and analysis methodology was unchanged for this test.

The recoveries for direct resins spikes were good, ranging from 78% for p,p-DDD to 117% for Diazinon (Table 3). The results for the aqueous solutions were varied with low recoveries. With the exception of 2,4-D, very little of the compounds passed the first or second column. In all cases, however, the amount of compound measured in the aqueous spike solution was considerably lower than originally calculated from the actual amount of compound added to the water.

These results plus those from the first test led us to believe that the extractions were reasonably good, as can be seen from the direct resin spikes. The compounds were undergoing some type of interaction or breakdown in the aqueous solutions, as evidenced by the large difference between the amounts added and the amounts actually measured in the aqueous spiking solutions. The recoveries from the field simulation using aqueous solutions were similar to those from the first test with the exception of Diazinon, Malathion, and 2,4-D, which were much better in the first test (Tables 2 & 3).

The next experiment investigated the recovery of selected chemicals in water that had been allowed to sit at room temperature the same period as was required to perform a field simulation. Simply, we added known amounts of p,p-DDD, Lindane, Diazinon, Malathion, 2,4-D, and pentachlorophenol separately to water and allowed the solutions to sit at room temperature for 48 hours. Numerous unidentified compounds appeared in the chromatograms from each solution. The original compounds (parent compound) were measured at 0 to 91% of the original concentrations. Recoveries were similar to the previous test (spike solutions analyzed after the test, 2nd column of simulation, Table 3) with the exception of Diazinon and pentachlorophenol, which were lower in this test (Tables 3 & 4). It appeared that the parent compounds had transformed into other compounds to varying degrees just while on the shelf (Table 4).

The sequence of results led us to believe that the answer to the low recoveries lay in dividing the presence of those breakdown/hydrolysis products, the sum of which would add up to the spiked amount. We decided to spike the XAD-4 and XAD-8 resins directly with p,p-DDD, Lindane,

Table 3. Spike/recovery summary for XAD-4 resins spiked directly and with aqueous solutions. Duplicate results are separated by "/".

Direct spikes in duplicate

| | Micrograms analyte: | | Percent |
|---|---|---|---|
| Compound | spiked | recovered | recovered |
| p,p-DDD | 4/4 | 3.6/3.1 | 90/78 |
| Lindane | 4/4 | 3.4/3.5 | 85/88 |
| Diazinon | 10/10 | 11.7/9.4 | 117/94 |
| Malathion | 10/10 | 11.4/10 | 114/100 |
| 2,4-D | 25/25 | 24.9/27 | 100/108 |
| PCP * | 25/25 | 26/23 | 104/109 |
| TCP * | 25/25 | 22/20 | 88/80 |

Simulation with aqueous spikes (Columns A and B in series)

| | Micrograms in spike: | | Micrograms measured in: | | | Total + |
|---|---|---|---|---|---|---|
| Compound | prepared | measured | Col A* | Col B | effl.* | recovery |
| p,p-DDD | 40.4/39.4 | 29/56 | 4.7/6.3 | 0.1/0 | 0/0 | 17/11 |
| Lindane | 40.4/39.4 | 32/28 | 7.6/9.8 | 1.0/1.0 | 0/0 | 27/39 |
| Diazinon | 40.4/39.4 | 14/45 | 5.9/8.4 | 0/0 | 0/0 | 42/19 |
| Malathion | 40.4/39.4 | 2.9/8.4 | 1.5/0 | 0/0 | 0/0 | 52/0 |
| 2,4-D | 404/394 | 259/281 | 38/38 | 8.3/8.3 | 5.8/6.8 | 20/19 |
| PCP * | 404/394 | 262/338 | 56/56 | 0.6/3.9 | 0/0 | 22/18 |
| TCP * | 404/394 | 268/239 | 32/41 | 1.4/5.3 | 0/0 | 12/19 |

+ amount from columns and effluent divided by amount measured in spike
* PCP=pentachlorophenol, TCP=tetrachlorophenol
Col A & Col B = columns A and B, effl. = column effluent

Diazinon, Malathion, 2,4-D, and pentachorophenol separately, eliminating the possibilities of hydrolysis and/or chemical interactions. The experiments consisted of dosing 5-gram portions of each resin, in duplicate, with 500 micrograms of each compound. The compound, in methanol solution, was mixed thoroughly with the resin and allowed to remain undisturbed and at room temperature for a period of twelve minutes. The resin (with some portion of dosed compound sorbed) was then rinsed serially with water and the rinsate collected for later analysis. Rinsed resin was then extracted and the extracts analyzed by combined gas chromatography-mass spectroscopy (GC/MS). The rinsate was also extracted and analyzed by GC/MS.

Table 4. Recoveries and numbers of apparent breakdown products for aqueous solutions allowed to stand at room temperature for 48 hours. Initial concentrations were 10 micrograms/liter for all compounds. Duplicate results separated by "/".

| Compound | % Recovered | Number of apparent breakdown products |
|---|---|---|
| p,p-DDD | 87/91 | 11/9 |
| Lindane | 41/73 | 0/0 |
| Diazinon | 0/0 | 9/10 |
| Malathion | 4.8/3.7 | 10/10 |
| 2,4-D | 84/72 | 7/7 |
| Pentachlorophenol | 15/18 | 0/0 |

This experiment resulted in very low recoveries of the parent compounds from the resins except for Malathion, and the existence of few suspect compounds, none of which were likely breakdown/hydrolysis products (Table 5). Comparing the two resins, XAD-4 appeared to perform better than XAD-8 with the exception of Malathion, which was equivalent for both resins. It appeared that the poor recoveries from the first test might be due to three factors: 1 - chemical changes in the structure of the compounds in water with and without other compounds, 2 - the inability of the XAD resin to accumulate some compounds, and 3 - the inability to fully extract some compounds from the resin.

Discussions with researchers at UCD (Keydel and Woodrow, 1988) resulted in a change in methodology and another experiment. This final test involved simulation of environmental sampling (as in the first tests) and controlled direct spiking of the resin by the contract laboratory. We wished to once more compare the efficiency of the methods on just the resins (direct spikes) and with aqueous solutions (field simulations).

We tested p,p-DDD, Lindane, and 2,4-D in the field simulation experiment. Duplicate aqueous spiking solutions were prepared separately for each compound. The contract laboratory retained a 1.0 L sample of the spike for analysis. After completion of the simulation, we returned the empty spike solution bottles, the resins, and the effluent samples to the laboratory for analysis. In this way we could account for any compound that stayed on the spike bottle (i.e. did not pass through the columns), the amount of compound recovered from the resin columns, and any compound that passed through the columns into the effluent bottle. Recoveries were calculated using the spike amount minus that found in the empty spike bottle (if any) as the amount of compound that actually passed through the column.

Table 5. Summarized results for duplicate Amberlite XAD-4 and XAD-8 resin spike/recovery experiment for six pesticides dosed at 500 micrograms (ug). Duplicate results are separated by "/".

XAD-4 Resin

| Compound | Micrograms from: | | Percent Recovery: | |
|---|---|---|---|---|
| | Rinsate | Resin | Resin | Total |
| p,p-DDD | 50.5/45.3 | 214/275 | 43/55 | 53/64 |
| Lindane | 45.0/51.0 | 120/100 | 24/20 | 33/30 |
| Diazinon | 99.0/107 | 33.0/329 | 6.6/66 | 26/87 |
| Malathion | 73.5/74.5 | 321/366 | 64/73 | 79/88 |
| 2,4-D | 0/0 | 0/0 | 0/0 | 0/0 |
| Penta-chlorophenol | 0/0 | 157/0 | 31/0 | 31/0 |

XAD-8 Resin

| Compound | Micrograms from: | | Percent Recovery: | |
|---|---|---|---|---|
| | Rinsate | Resin | Resin | Total |
| p,p-DDD | 42.0/42.6 | 29.5/452 | 5.9/90 | 14/99 |
| Lindane | 109/101 | 15.0/18.5 | 3.0/3.7 | 25/24 |
| Diazinon | 191/254 | 25.5/59.0 | 5.1/11.8 | 43/63 |
| Malathion | 66.5/55.0 | 412/370 | 82/74 | 96/85 |
| 2,4-D | 0/0 | 0/0 | 0/0 | 0/0 |
| Penta-chlorophenol | 0/0 | 0/80.2 | 0/16 | 0/16 |

In the direct resin spikes, the contract laboratory spiked individual hydrated resin samples directly. The resin was extracted and analyzed as well as the rinsate from the beaker used for the spike. In the case of p,p-DDD and 2,4-D, a laboratory accident resulted in no data for this experiment. Time and budget constraints prevented a repeat experiment.

In the aqueous spike p,p-DDD was found in both the empty spike bottle and the resin samples. Resin recoveries were low: 22% and 16% (Table 6). Those recoveries were comparable to previous aqueous spikes (Tables 2 and 3), indicating the methods were inefficient in collecting adsorbed p,p-DDD from the resins. The direct resin spike data are not available due to the laboratory accident.

Lindane was found in nearly equal amounts in both the resin and effluent, i.e., nearly 50% of the compound passed through the resin. Percent recovery from the resin was 35 and 40 (Table 6), comparable to the previous aqueous spikes (Tables 2 and 3). The direct resin spikes unexpectedly yielded very low recoveries, both 7.4%. The previous direct resin spikes ranged from 30 to 88 percent (Tables 3 and 5).

Table 6. Spike recovery summaries for XAD-4 resin subjected to duplicate aqueous spikes and direct resin spikes with p,p-DDD, Lindane, and 2,4-D. Duplicate results separated by "/".

Aqueous spikes

| | micrograms from: | | | | |
|---|---|---|---|---|---|
| Compound | spike | spike bottle | resin | effluent | Resin % recovery |
| p,p-DDD | 261/280 | 22/21 | 58/45 | 20* | 22/16 |
| Lindane | 28.0/24.9 | ND/ND+ | 9.7/9.9 | 7.3/5.0 | 35/40 |
| 2,4-D | 15/19 | ND/ND | 11/11 | 4/3 | 73/58 |

Direct spikes

| | micrograms: | | |
|---|---|---|---|
| | spiked ++ | recovered | Percent recovery |
| p,p-DDD | ------------ lab accident --------------- | | |
| Lindane | 175/175 | 13/13 | 7.4/7.4 |
| 2,4-D | ------------ lab accident --------------- | | |

* two effluent samples combined
\+ ND = not detected
++ amount spiked is amount of compound added minus that left behind in the beaker

The 2,4-D aqueous spikes showed some compound passing the columns into the effluent, although 73% and 58% of the spike was recovered from the resin duplicates (Table 6). The resin recoveries for aqueous 2,4-D spikes were generally variable amongst the three tests (Tables 2, 3, and 6), probably due to instrument and analyst variability and slightly different test conditions. The direct resin spikes for 2,4-D are not available due to a laboratory accident.

## Metals Resins

### Background contamination

Twelve method blanks were analyzed for each of seven heavy metals (Figure 4a). The most common contaminant was zinc occurring in the Chelex and Duolite columns. Chromium, copper, and lead were found in the Chelex and AG 1X-8 resin eluates to lesser degrees.

The analyses of the acids, bases, and water used in our procedures identified zinc as the most common acid contaminant. Chromium, copper, and lead were found at lower concentrations in some of the acids and the distilled water we used in our preparation and elutions.

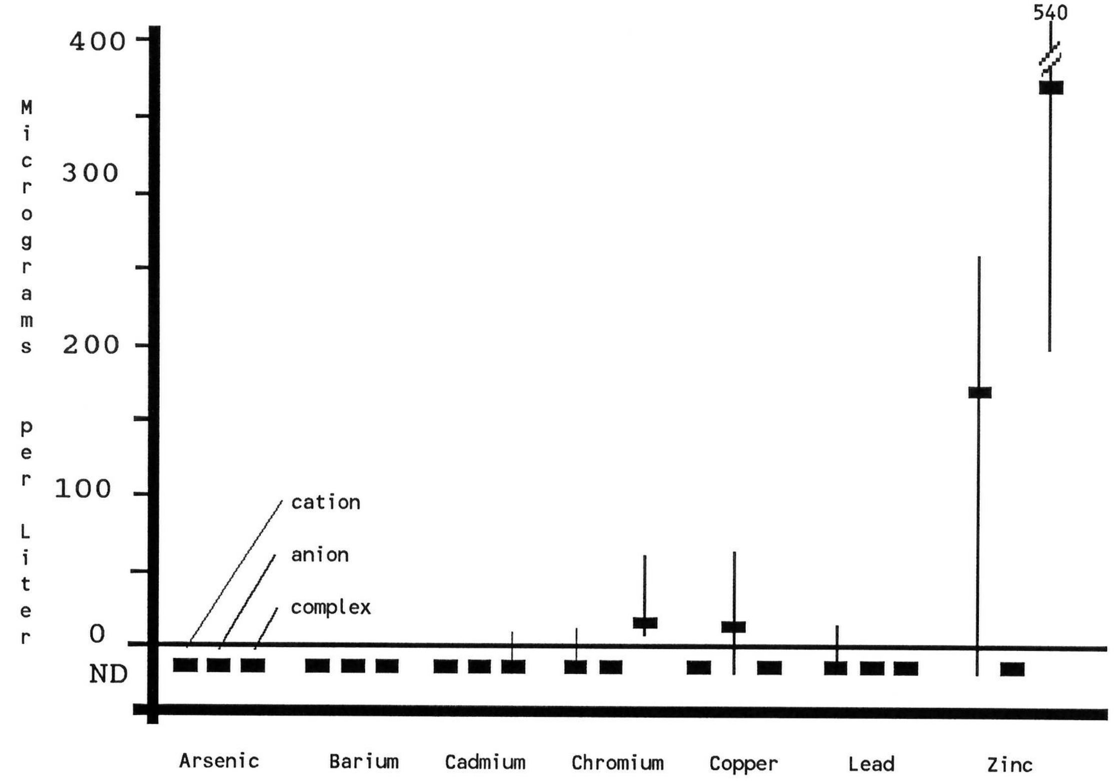


Figure 4a. Laboratory method blanks for seven metals, cationic, anionic, and complexed forms. Bars represent median value, lines are ranges, ND is non-detectable.

Twenty-five field blanks were analyzed during the project, with boron and zinc found at the highest levels in the Duolite resin. Chromium, copper and lead were the next most common contaminants in all three resins (Figure 4b). Very low levels of arsenic were found in all three resins.

The higher variability in background contamination levels in the field likely was due to variations in analytical techniques at the contract laboratory, minor variations in the chemicals used to prepare the columns and resins, and differences in contamination while in the field. As stated in the quality assurance/control section of the methods section of this report, the MDL changed with changes in background contamination levels, varying with the conditions of each sampling or test. In this way changes in the sampling conditions were reflected in the concentrations we considered above background.

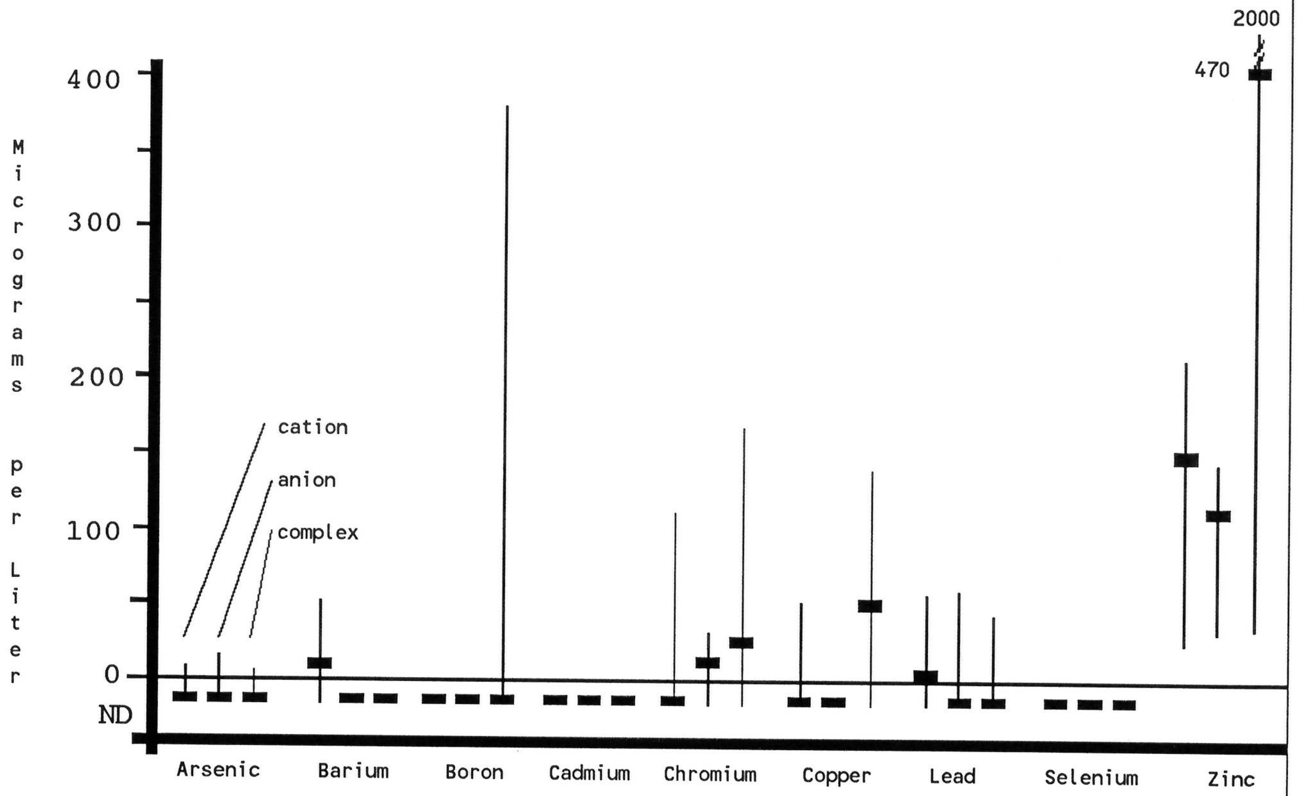


Figure 4b. Field method blanks for nine metals, cationic, anionic, and complexed forms. Bars represent median value, lines are ranges, ND is non-detectable.

## Precision

The precision of duplicate analyses as the relative percent difference (RPD)[1] is summarized in Figures 5a and 5b. For this analysis, an eluate concentration of less than detectable by the analytical instrument was treated as that value, e.g. for selenium, the detection limit was 5 ug/L, so the value used for a reported result of <5 ug/L was 5 (see McBean and Rovers, 1984 for a discussion using "less than" values).

Precision as determined from duplicate analyses varied among metals and ionic state. The most variation was seen from the adsorbent resin, Duolite, followed by the oxy-anionic resin, AG 1X-8 for field duplicates (Figure 5a). The precision of laboratory duplicates was generally better than for the field, with the highest variation from the AG 1X-8 resin (Figure 5b). Better precision, (low RPD) was observed from duplicates with high concentrations; those with low concentrations were more variable.

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[1] $$\text{RPD} = \frac{\text{(high value-low value)}}{\text{(high value+low value)/2}} \times 100$$

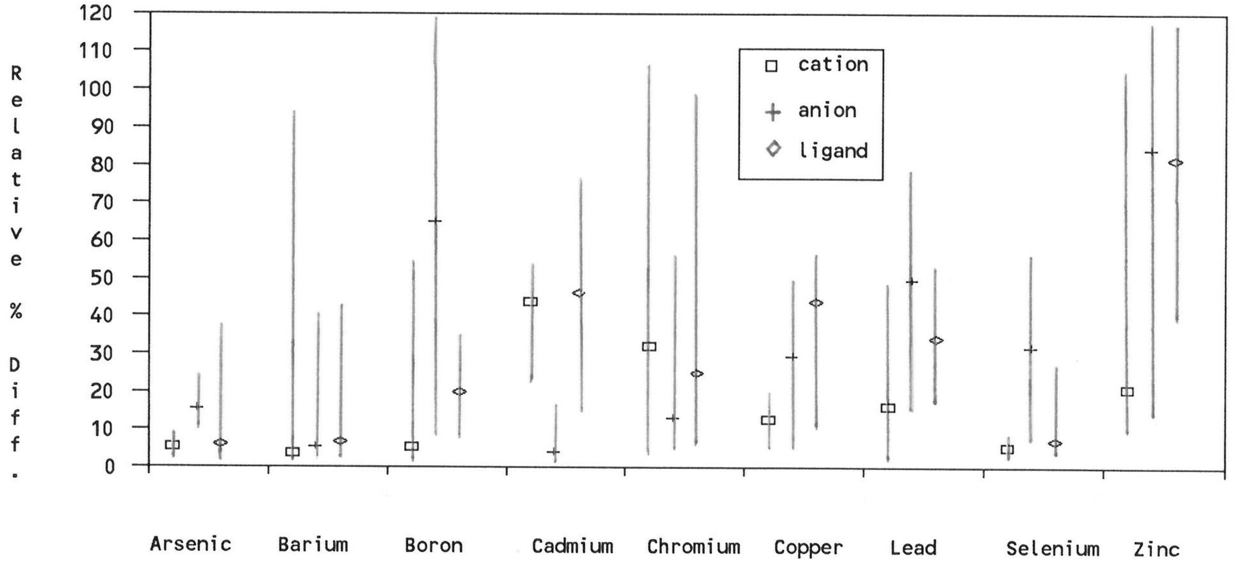

Figure 5a. Relative precision of field replicates for cationic, anionic, and complexed forms of nine metals. Symbol is median RPD and line indicates bounds of 25th and 75th percentiles.

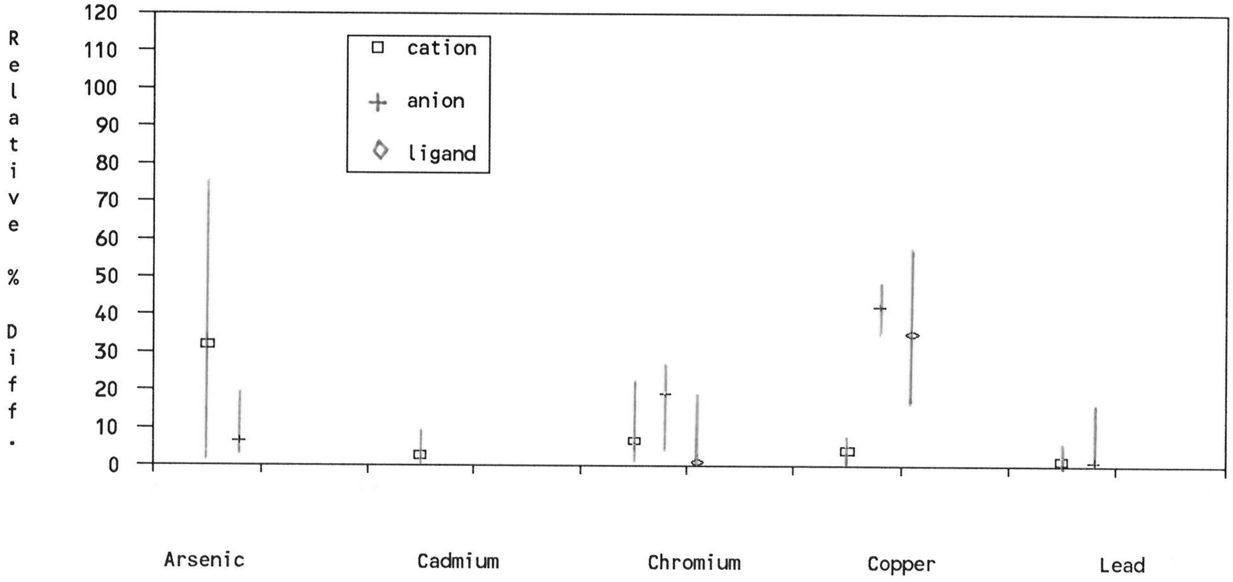

Figure 5b. Relative precision of laboratory replicates for cationic, anionic, and complexed forms of five metals. Symbol is median RPD and line indicates bounds of 25th and 75th percentiles.

The highest variability was observed in cationic arsenic, anionic copper, and complexed copper for the laboratory samples (Figure 5b). The data for those metal species contained a large number of low concentrations, at times not larger than two times the background or blank values. The highest variability in the field samples was observed for cationic cadmium and chromium, anionic boron, lead, and zinc, and complexed cadmium, copper and zinc. Again low concentrations were responsible for some of the variability, especially for boron, cadmium, chromium, and lead. Murphy (1976) presents the relationship of increased variability of results with lowered concentration for a given method. Additionally, cadmium, copper, chromium, lead, and zinc were occasional contaminants (produced higher background values) in our supplies, as previously noted.

## Resin recovery efficiencies

Resin recovery efficiencies, the percentage of metal recovered from a resin after a solution is passed through it, was tested by UCSC using radioactive tracers for cadmium, cobalt, copper, iron, manganese, and zinc in cationic form and in the presence of various complexing agents. Resin recovery efficiencies for the cationic exchange resin, Chelex-100, and the adsorbent resin, Duolite S-587, in series ranged from about 50 to 115% (Bruland, et.al., 1985).

When no organic complexing agent was present, the metals were recovered from the cation exchange resin almost without exception. In the presence of complexing agents, the adsorbent resin played a larger role in accumulating the metallo-organics, dependent on the strength of the complexing agent as regards individual metals. The researchers concluded that "...nearly quantitative recovery (for the trace metal cations tested) would be expected from natural fresh water samples using column combinations of Chelex-100 or UCSC 8-HQ resin followed by Duolite S-587 resin" (Bruland, et.al. 1985).

As previously mentioned, we relied heavily on the work by the UCSC researchers for our methods, both in actual technique and as regards the efficacy of the methods. Of the six metals they tested, we also tested recovery efficiencies for two: cadmium and copper. We tested resin recovery efficiencies for arsenic, cadmium, chromium, copper, and lead. Overall recoveries for those five metals ranged from 67% (cadmium at 80 ug/L) to 121% (lead at 340 ug/L). Variations in recovery were noted by metals, ionic state, and concentrations of the spiking solutions. For example, as illustrated in Figure 6, copper in the presence of a complexing agent was retained to the greatest degree on the Duolite resin. Without the complexing agent, copper was retained primarily by the Chelex-100 and, to a lesser degree, the AG 1X-8 resin. Arsenic in water primarily as an oxy-anion and not in the presence of a complexing agent was retained on the AG 1X-8 resin. Chromium was retained on both the Chelex-100 and AG 1X-8 resins as a cation and anion. However, with some complexing agent present, chromium was retained by the AG 1X-8 and Duolite as an oxy-anion and ligand, respectively (Figure 6).

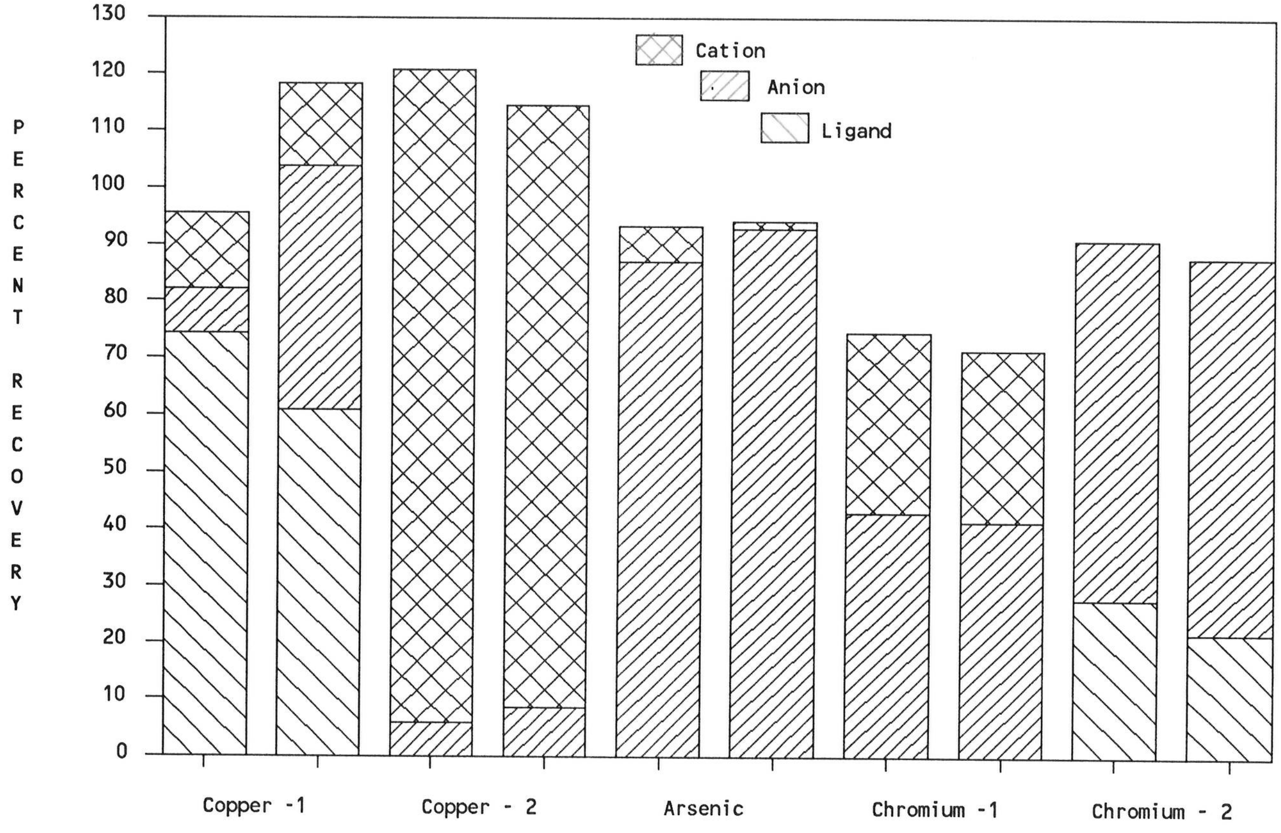

Figure 6. Resin recovery efficiencies for Chelex-100 (cationic), AG 1X-8 (anionic) and Duolite S-587 (ligand) resins for copper with complexing agent (#1) and without complexing agent (#2), arsenic without complexing agent, and chromium without complexing agent (#1) and with a small amount of complexing agent (#2).

In summary, for the metals we tested, we attained good recoveries using the three resins in series. The expected ionic forms were found on the appropriate resins, and little of the analytes of interest went unaccounted. The Russian River sampling (environmental monitoring) was reliable in terms of accounting for the majority (if not all) of each metal in solution in the river water. The precision of the methods was within a median of 50% relative percent difference for all duplicate analyses and for all the metals except boron and zinc.

## Environmental monitoring

Heavy metals sampling in the Russian River basin was limited in scope by the dependence on 110 volt AC electrical supply. Our main focus was the SCWA site below Wohler Bridge, although we did sample the river in the Ukiah and Cloverdale areas during 1987, and the Mark West Creek system in 1987 and 1988. (Please refer to Figure 3, page 12).

Metals concentrations were generally very low with respect to State and recommended Federal criteria (Table 7). For example, the drinking water standards for arsenic, chromium, and lead are 50 ug/L. The EPA draft drinking water criterion for arsenic is 2.2 ng/L, but is based on the consumption of fish as well as water, not water only. Our monitoring detected these metals at less than one-fourth the current standards in all cases (Tables 8 - 13). Those measurements that appear in the data tables as a trace (i.e., marked with "*") do no appear in any of the graphs presented below.

Table 7. State and Federal criteria, standards, and proposed criteria for selected heavy metals in water,nanograms per liter.

| | Drinking Water: | | Protection of F-water life:[1] | |
|---|---|---|---|---|
| | State | EPA | 4-day Average | Maximum |
| Arsenic | 50,000 | 2.2[2] | 190,000<br>(+3 valence state) | 440,000 |
| Barium | -- | $1 \times 10^6$ | | |
| Boron | -- | --- | | |
| Cadmium | 10,000 | 10,000 | 2,000 | 8,600 |
| Chromium | 50,000 | 50,000 | | |
| +6 valence | | | 11,000 | 16,000 |
| +3 valence | | | 370,000 | $3.1 \times 10^6$ |
| Copper | -- | $1 \times 10^6$ | 21,000 | 34,000 |
| Lead | 50,000 | -- | 7,700 | 200,000 |
| Selenium | -- | 10,000 | 35,000[3] | 260,000 |
| Zinc | -- | $5 \times 10^6$ | 47,000[3] | 570,000 |

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[1] criteria for protection of freshwater life calculated at 200 mg/L hardness; criteria not to be exceeded more than once in 3 years

[2] draft recommended criterion for arsenic assumes consumption of fish and a risk level of $10^{-6}$

[3] 1-hr average

(SWRCB, 1981; EPA, 1980, 1985a,b,c,d)

For the most part, the metals we sampled were observed in terms of their speciation (ionic state) as follows:

| Metal | Ligand | Anion | Cation |
|---|---|---|---|
| Arsenic | t | ++ | t |
| Barium | t | t | ++ |
| Boron | ++ | + | + |
| Cadmium | + | + | ++ |
| Chromium | + | ++ | t |
| Copper | t | + | ++ |
| Lead | t | t | t |
| Zinc | t | t | ++ |

t = trace, not ≥ twice field blanks
+ = occasionally measureable
++ = predominant species

At the Wohler site we observed some increases in concentrations of chromium and copper during the late winter and spring of 1988 (Tables 8, 9, and 10, Figure 7) The higher concentrations (with the exception of September) were observed when the Russian River flow rates measured a few miles downstream exhibited a definite storm-event hydrograph.

The sampling in the Ukiah area included the East Fork of the Russian River and the river downstream of Ukiah. No differences were observed in the metals concentrations or speciation. In comparison to the Russian River at Wohler Bridge, the Ukiah samples showed elevated chromium and lead concentrations (Table 11).

The Cloverdale area sampling included three sites: the Russian River upstream of Cloverdale and Big Sulphur Creek, Big Sulphur Creek, and the river downstream of both Big Sulphur Creek and Cloverdale. The Big Sulphur Creek site had higher concentrations of boron (about three times that of the river) and mercury (about twice that of the river). Copper and lead were slightly lower in Big Sulphur Creek than the river (Table 11). The river monitoring did not show an increase in boron or mercury from the upstream to downstream of Big Sulphur Creek. The sampling of metals in the river indicated higher concentrations of barium, copper and lead at the Cloverdale Sites compared to the Wohler site, 10 times in the case of lead (Table 11).

Mark West Creek drains the mountains to the east of Santa Rosa and the Santa Rosa plains area, entering the Russian River just downstream of the Wohler site. During the spring of 1988 we sampled Mark West Creek six times for two-week intervals each time (Table 12). Copper concentrations were higher than the river at the beginning of the

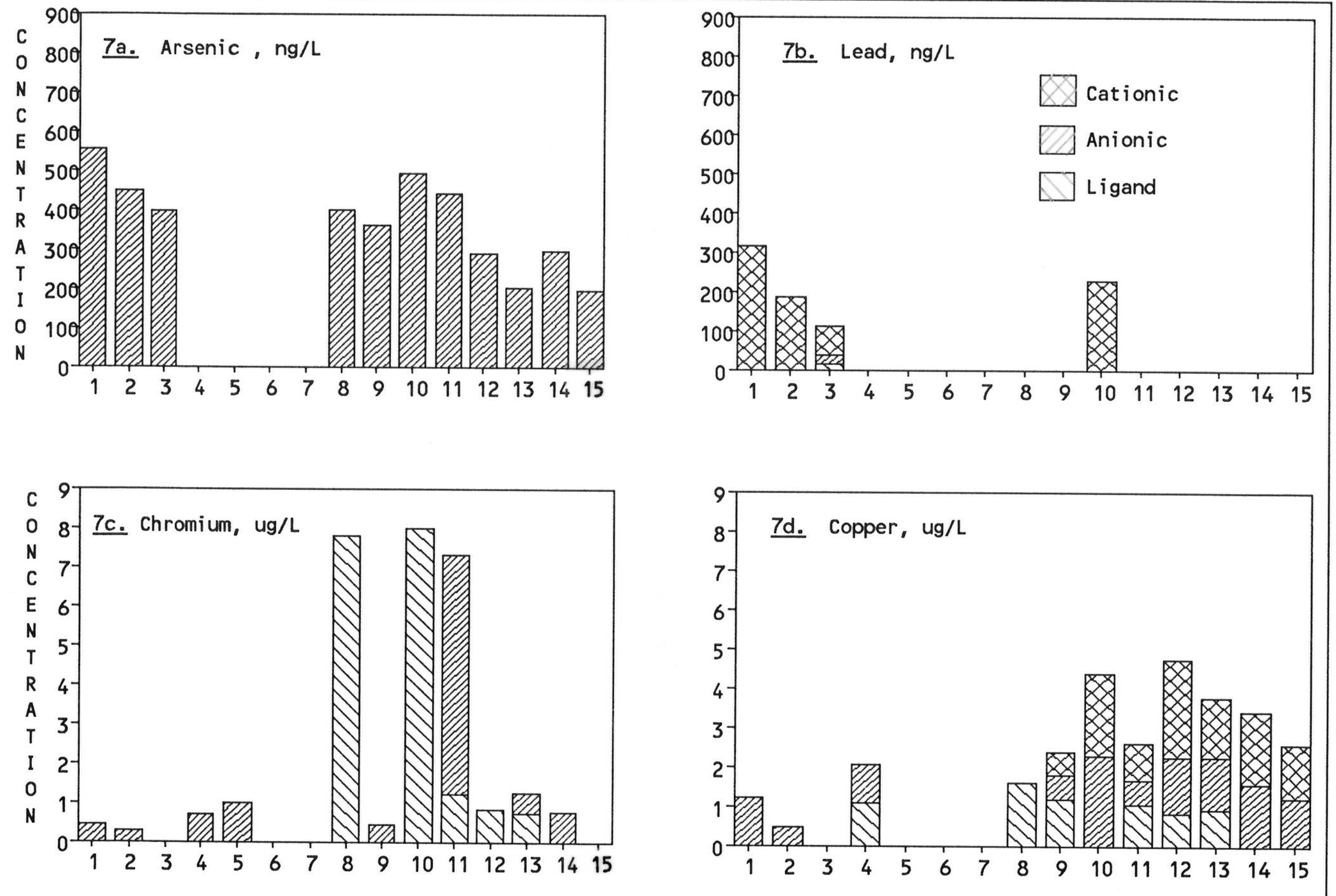

Figure 7. Concentrations of arsenic, lead, chromium, and copper at the Wohler site in the Russian River from September of 1986 through April of 1988. Numbers on the horizontal axes refer to the sampling dates as listed chronologically on Tables 8, 9, and 10 on the following pages.

sampling, but decreased through the period to concentrations similar to the Russian River at Wohler. A discharge of copper sulphate into the upper Laguna de Santa Rosa, tributary to Mark West Creek, on April 22, 1988 was likely the source of another slight rise in copper levels during the May 5-19 sampling. With the general decreasing trend in copper came a shift from cationic to anionic as the predominant form (Table 12). Arsenic fluctuated in concentration and was considerably higher than the Russian River. Barium and lead were found at close to the levels in the river during the same period.

We also sampled the Mark West Creek system at the confluence of Santa Rosa Creek and the Laguna de Santa Rosa, upstream of the confluence with Mark West Creek on April 16-20 and June 16-19, 1987 (Table 13). Overall, the Laguna de Santa Rosa had higher levels of most metals, though not appreciably different from the samples obtained during the spring of 1988. Arsenic and lead were not detected in Santa Rosa Creek upstream of Santa Rosa, were measured as a trace in Santa Rosa Creek downstream of Santa Rosa, and were measured at higher concentrations in the Laguna de Santa Rosa than in Santa Rosa Creek.

Table 8. Results of 1986 metals resin column monitoring on the Russian River at the Sonoma County Water Agency Wohler diversion dam, Sept. 9-14, Oct. 1-9, Nov. 19-29, 1986.

| Element/ Chemical class | Average concentration, ng/L: Sept | Oct | Nov |
|---|---|---|---|
| Arsenic | | | |
| cationic | ND[1] | ND | 15* |
| anionic | 555 | 447 | 398 |
| ligand + | ND | ND | 15* |
| Cadmium | ND | ND | NA |
| Chromium | | | |
| cationic | 192* | 173* | ND |
| anionic | 459 | 298 | ND |
| ligand | ND | 141* | ND |
| Copper | | | |
| cationic | 322* | 440* | ND |
| anionic | 1219 | 487 | ND |
| ligand | 301* | 408* | ND |
| Lead | | | |
| cationic | 315 | 188 | 74 |
| anionic | ND | 47* | 25 |
| ligand | 1055* | 204* | 15 |
| Mercury | NA | NA | NA |
| Selenium | | | |
| cationic | NA | NA | 15* |
| anionic | NA | NA | 25* |
| ligand | NA | NA | 15* |
| Zinc | | | |
| cationic | NA | 1295 | 438 |
| anionic | NA | 997* | 716 |
| ligand | NA | 19876 | 517 |
| Sampling duration (days) | 6.85 | 7.85 | 9.95 |

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[1] ND = not detected, NA = not analyzed

* trace (i.e. ≤ 2x of blank)

Table 9. Results of 1987 metals resin column monitoring on the Russian River at the Sonoma County Water Agency Wohler diversion dam, Dec. 30, 1986-Jan 7, 1987, Mar. 6-14, June 10-15, June 23-26, Sept 28-Oct 2, Nov 19-Dec 1, Dec 1-7, and Dec 10-24, 1987.

| Element/ ionic state | Average concentration for the period, ng/L: | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Jan | Mar | June 15 | June 26 | Sept | Nov | Dec 1 | Dec 10 |
| Arsenic | | | | | | | | |
| cationic | 33* | ND[1] | ND | ND | ND | ND | ND | ND |
| anionic | 556* | 302* | 377* | 380* | 400 | 360 | 492 | 443 |
| ligand + | 27* | ND | 3100* | ND | ND | ND | ND | ND |
| Barium | | | | | | | | |
| cationic | NA[1] | 17000 | 30600 | 39100 | 9810 | 4800* | 27540 | 5800 |
| anionic | NA | 2340 | 945* | ND | 400 | ND | ND | ND |
| ligand | NA | 1000* | ND | ND | 400 | ND | ND | ND |
| Boron | | | | | | | | |
| cationic | NA | 12700 | ND | ND | ND | 1560 | 13016 | 6560 |
| anionic | NA | ND | 2320* | 1270* | 3400 | 6110 | 6739* | 3200 |
| ligand | NA | 7350* | 10800* | 28600 | 13400 | 8730 | 211468 | 12800 |
| Cadmium | | | | | | | | |
| cationic | NA | NA | ND | NA | ND | ND | 885 | 305 |
| anionic | NA | NA | ND | NA | ND | ND | ND | 305 |
| ligand | NA | NA | 3520 | NA | ND | ND | ND | ND |
| Chromium | | | | | | | | |
| cationic | ND | ND | 2440* | 1620* | ND | ND | ND | 1220 |
| anionic | 703 | 1000 | ND | 1580* | ND | 440 | 3120 | 6100 |
| ligand | ND | ND | NA | 2920* | 7810 | 980 | 8000 | 1220 |
| Copper | | | | | | | | |
| cationic | ND | 333* | 1160* | 1060* | 1000 | 600 | 2080 | 915 |
| anionic | 949 | 1000* | 1050* | 1390* | 600 | 600 | 2300 | 610 |
| ligand | 1100 | ND | ND | 683* | 1600 | 1200 | 6900 | 1070 |
| Lead | | | | | | | | |
| cationic | 50* | ND | 202* | 62* | ND | 24* | 230 | 15 |
| anionic | 114* | ND | 116* | 62* | ND | 24* | 208 | 61 |
| ligand | 278* | ND | 1370* | 124* | ND | 24* | 258 | 76 |
| Mercury | NA | NA | NA | ND | NA | NA | NA | NA |
| Selenium | NA | NA | NA | ND | NA | NA | NA | NA |
| Zinc | | | | | | | | |
| cationic | 1630* | NA | 6190* | 16200* | 3200 | 2280 | 9700 | 3360 |
| anionic | 556 | NA | 6890* | 3680* | ND | 1090 | 16700 | 1520 |
| ligand | 8660* | NA | NA | 43500* | 2000 | 873 | 11300 | 1520 |
| Sampling duration (days) | 8.18 | 7.75 | 5.04 | 3.09 | 2.19 | 12.85 | 6.04 | 13.98 |

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[1] ND = not detected, NA = not analyzed

* trace (i.e. ≤ 2x of blank)

Table 10. Results of 1988 metals resin column monitoring on the Russian River at the Sonoma County Water Agency Wohler diversion dam, Feb 5- 19, Feb 19-Mar 14, Mar 14-28, Mar 30-Apr 16, 1988.

| Element/ ionic state | Average concentration for the period, ng/L: | | | |
|---|---|---|---|---|
| | Feb 5 | Feb 19 | Mar 14 | Mar 30 |
| Arsenic | | | | |
| cationic | ND | ND | ND | ND |
| anionic | 289 | 204 | 297 | 197 |
| ligand | ND | ND | ND | ND |
| Barium | | | | |
| cationic | 9293 | 4686 | ND | 4692 |
| anionic | ND | ND | 1398* | ND |
| ligand | ND | ND | 16928 | ND |
| Boron | | | | |
| cationic | NA | NA | NA | ND |
| anionic | NA | NA | NA | 2573 |
| ligand | NA | NA | NA | 12713 |
| Cadmium | | | | |
| cationic | ND | 192 | ND | ND |
| anionic | ND | ND | ND | ND |
| ligand | ND | 133* | ND | ND |
| Chromium | | | | |
| cationic | ND | ND | 526* | ND |
| anionic | ND | 528 | 790 | ND |
| ligand | 826 | 726 | 526* | ND |
| Copper | | | | |
| cationic | 2478 | 1519 | 1842 | 1362 |
| anionic | 1446 | 1332 | 1579 | 1211 |
| ligand | 826 | 925 | 526* | ND |
| Lead | | | | |
| cationic | ND | ND | ND | 15* |
| anionic | ND | ND | ND | 15* |
| ligand | ND | ND | ND | 15* |
| Sampling duration (days) | 14 | 23.7 | 14 | 17.1 |

[1] ND = not detected, NA = not analyzed

* trace (i.e. ≤ 2x of blank)

Table 11. Results of metals resin column monitoring on the Russian River in the Cloverdale and Ukiah areas, July 20-27 and August 17-21, 1987, respectively.

| Element/ ionic state | Average concentrations for the period, ng/L: | | | | |
|---|---|---|---|---|---|
| | Cloverdale area: | | | Ukiah area: | |
| | Upstrm. | Sulphur | Dnstrm. | Upstrm. | Dnstrm. |
| Arsenic | | | | | |
| cationic | ND[1] | ND | ND | ND | ND |
| anionic | 314* | 351* | 385* | 720 | 635 |
| ligand + | ND | ND | ND | ND | 265* |
| Barium | | | | | |
| cationic | 39079 | 35672 | 26401* | 30856 | 29100 |
| anionic | 829 | ND | ND | ND | ND |
| ligand | 889 | ND | ND | ND | ND |
| Boron | | | | | |
| cationic | ND | ND | ND | ND | ND |
| anionic | 3197 | 4561* | ND | ND | ND |
| ligand | 27235 | 25731 | 71468 | ND | ND |
| Chromium | | | | | |
| cationic | 884 | 1111 | ND | ND | ND |
| anionic | ND | 1696* | ND | 15600 | 13757 |
| ligand | 3234* | 2924* | 2183* | 4571 | 4339* |
| Copper | | | | | |
| cationic | ND | ND | ND | 571 | 635 |
| anionic | ND | 1404 | 1206 | 780 | 741 |
| ligand | 17682 | 5848* | 6533* | 6857* | 6878* |
| Lead | | | | | |
| cationic | 2252* | 4854* | 3100* | 5714 | ND |
| anionic | 1184* | 6433* | 1433* | ND | ND |
| ligand | 1908 | 2222* | 2475 | ND | ND |
| Mercury | | | | | |
| cationic | ND | ND | ND | ND | ND |
| anionic | 37* | ND | 112 | ND | ND |
| ligand | 63* | 64 | ND | ND | ND |
| Selenium | | | | | |
| cationic | ND | ND | ND | NA[1] | NA |
| anionic | ND | ND | ND | NA | NA |
| ligand | ND | ND | ND | NA | NA |
| Sampling duration (days) | 3.50 | 3.75 | 2.17 | 3.65 | 3.89 |

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[1] ND = not detected, NA = not analyzed

* trace (i.e. ≤ 2x of blank)

Table 12. Results of metals resin column monitoring in Mark West Creek at the confluence of Mark West Creek with the Russian River, June 23-26, 1987 and Mar 3-17, Mar 17-31, Mar 31-Apr 16, Apr 16-22, Apr 22- May 5, and May 5-19, 1988. River downstream values are for June 23-26, 1987 period.

| | Average concentration for the period, ng/L: | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | River | Mark West Creek on: | | | | | | |
| Element/ ionic state | downstream Mark West | Jun 23 | Mar 3 | Mar 17 | Mar 31 | Apr 16 | Apr 22 | May 5 |
| Arsenic | | | | | | | | |
| cationic | ND[1] | ND | ND | ND | ND | ND | ND | ND |
| anionic | ND | 4462 | 487 | 1632 | 923 | 4095 | 995 | 1940 |
| ligand + | ND | ND | ND | 158* | 175 | 91* | ND | ND |
| Barium | | | | | | | | |
| cationic | 33333 | 25203 | 3601 | 4738 | 3025 | 24570 | 4266 | NA |
| anionic | ND | ND | ND | ND | ND | ND | ND | NA |
| ligand | ND | ND | ND | ND | ND | ND | ND | NA |
| Boron | | | | | | | | |
| cationic | ND | ND | ND | NA | NA | 5460* | NA | NA |
| anionic | 2439 | 14980 | 1271* | NA | NA | 16380 | NA | NA |
| ligand | 50406 | 33260 | 8896 | NA | NA | 48230 | NA | NA |
| Cadmium | | | | | | | | |
| cationic | NA | NA | 126* | ND | ND | ND | ND | NA |
| anionic | NA | NA | ND | ND | ND | ND | ND | NA |
| ligand | NA | NA | ND | ND | ND | ND | ND | NA |
| Chromium | | | | | | | | |
| cationic | 976* | 1626* | 424* | 526* | ND | ND | ND | 245* |
| anionic | 2114* | 730* | 847* | 790* | ND | ND | 474* | ND |
| ligand | 6585* | 3802* | 2542 | 526* | ND | ND | ND | ND |
| Copper | | | | | | | | |
| cationic | ND | ND | 4236 | 1842 | 478* | ND | 711* | 872* |
| anionic | ND | 1324 | 1906 | 1579 | 796 | 1820* | 948* | 1410 |
| ligand | 10569* | 8074* | 2330 | 526* | 318* | ND | ND | 518* |
| Lead | | | | | | | | |
| cationic | 1138 | 244* | ND | ND | 48* | 91* | 47* | 54* |
| anionic | 163* | 282* | ND | ND | 33* | 182* | 119 | 251 |
| ligand | 325* | 214* | ND | ND | ND | ND | 24* | ND |
| Mercury | ND | ND | NA | NA | NA | NA | NA | NA |
| Selenium | ND | ND | NA | NA | NA | NA | NA | NA |
| Zinc | | | | | | | | |
| cationic | 12195* | 21138* | 1483* | 790* | 2866* | 9100* | 1659* | 5450* |
| anionic | 68292* | 13303* | ND | ND | 3343 | 6370 | 1422* | 4070 |
| ligand | 26829* | 27280* | 1694* | 10528* | 6368* | 27300* | 8058* | 12300* |
| Sampling duration (days) | 2.4 | 2.4 | 14 | 14 | 15.9 | 6.1 | 13 | 13 |

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[1] ND = not detected

* trace (i.e. ≤ 2x of blank)

Table 13. Results of metals resin column monitoring in the Mark West Creek system on April 16-20 and June 16-19, 1987.

| | Average concentration for the period, ng/L: | | | | |
|---|---|---|---|---|---|
| Element/ ionic state | Upstrm S.R. Creek | | Dnstrm S.R. Creek | | Laguna de Santa Rosa |
| | April | June | April | June | |
| **Arsenic** | | | | | |
| cationic | ND[1] | 726* | ND | ND | ND |
| anionic | ND | ND | 1736 | 2256 | 4548 |
| ligand + | ND | ND | 3595 | ND | 2630 |
| **Barium** | | | | | |
| cationic | 25242 | 50847 | 22802 | 36778 | 30832 |
| anionic | 1262* | ND | 1158* | ND | 882* |
| ligand | 971* | ND | ND | ND | ND |
| **Boron** | | | | | |
| cationic | ND | 13317* | 576* | ND | ND |
| anionic | 11650* | ND | 2315 | ND | ND |
| ligand | 30097* | 41162* | 23959* | 30354* | 18550* |
| **Cadmium** | ND | ND | NA[1] | ND | NA |
| **Chromium** | | | | | |
| cationic | 1359* | ND | 17673 | ND | ND |
| anionic | 4951* | 1210* | 577* | 2528 | 5234* |
| ligand | ND | ND | 4532* | 5263 | 4975* |
| **Copper** | | | | | |
| cationic | 1359* | 2421 | 731* | ND | ND |
| anionic | ND | 2421 | 926* | ND | 490* |
| ligand | ND | 2421 | 8136* | 19221* | 10962* |
| **Lead** | | | | | |
| cationic | ND | ND | 118* | ND | 250* |
| anionic | ND | ND | 290 | ND | 151* |
| ligand | ND | 605 | 908* | 840 | 724* |
| Sampling duration (days) | 3.00 | 1.98 | 2.17 | 2.26 | 2.47 |

[1] ND = not detected, NA = not analyzed

* trace (i.e. ≤ 2x of blank)

## DISCUSSION

### Organics Resins

Initial organics resins investigations including various spiking procedures, resulted in significant changes in experimental methodology. This revised methodology was presented herein, not as a recommended procedure, but as an historical chronology of our efforts to utilize the XAD resins to sample a broad spectrum of organic pesticides and herbicides in the aqueous environment.

Initially it appeared that some compounds could be recovered at acceptable levels, however further testing resulted in a large variability in results. Consistent recovery of compounds from the resin exposed to an aqueous solution was not achieved, except for DDD and Lindane. Recoveries for both of those compounds were very low, but not as variable as for other compounds.

Usually significant amounts of 2,4-D passed the first column in a series and occasionally the second. Chlorinated phenolics usually passed through only the first column.

The direct resin spikes were performed to eliminate the variables of hydrolysis and breakdown from aqueous solutions and chemical interactions from mixtures of compounds in a spike solution. Adding a compound directly to a resin sample was the least complicated manner in which to test the ability of the resin to absorb the compound. Attempts to account for the apparent loss of compound by direct resin spikes yielded variable results, but indicated either our techniques were not duplicable and/or the resins bound the compounds to varying degrees through the process. Perhaps other variables such as stability of the analytical instruments, slight variations in technicians' handling of the resins and extracts, pH, amount of hydration of the resins, temperature, chemistry of the diluted spike solution, and concentration of the spike are controlling factors that we cannot effectively evaluate from the data we have collected.

Commercial "set packs" (Analytichem and Millipore) are available consisting of a resin column loaded with a resin specifically designed for a class of compounds (e.g. neutrals of low polarity). Those columns are designed for laboratory use where a water sample is poured through the column. The column is then extracted with a single solvent, and the resultant extract analyzed. It may be possible to use a set of those columns in a field sampler in lieu of the XAD resins. Such a procedure would be desirable from the standpoints of commercial availability (no preparation necessary), ease of use, and ease of extraction (solvent is poured through the column instead of the resin being removed from the column and taken through a rigorous extraction process.

## Metals Resins

We have developed accurate and precise methods for preparing, sampling, and eluting the three heavy metals resins for monitoring water. The questions of precision within field replicates have been adequately researched for a study of this type. The resin recovery efficiency tests were realistic and indicate accurate measurement of those metals tested using Chelex-100, AG 1X-8, and Duolite S-587 in series. We intend to continue to use the resins in spike/recovery testing of metals in addition to those already tested, in background contamination testing, and in environmental monitoring.

Background contamination was highest in the Chelex and Duolite resins. Additional steps in the preparation of those resins is recommended (Zief and Horvath, 1976). Since all the resins are exposed to distilled, deionized water during their preparation, quartz sub-boiling point distillation is indicated (Mitchell, 1973, Murphy, 1976). Although our preparation solutions had very low to non-detectable levels of contaminating metals, the resins may accumulate those contaminants at various steps in the preparation techniques. The concentrated acids prior to dilution were of high purity, thus no additional treatment of the acid solutions is specifically indicated.

The two bases used to prepare Chelex and Duolite should be treated to remove contaminant metals by filtering through acid-cleaned Chelex. The contaminated Chelex could then be regenerated with clean acid and clean ammonium hydroxide. Kingston, et.al. (1978) employed such a method in measuring trace metals in seawater.

The elution of the resins with acid to strip the accumulated metals was quite efficient in our resin recovery tests. Kingston, et. al. (1978) indicated that ten mL of eluting acid was sufficient to strip Chelex-100 of transition metals after pre-treatment for high alkaline earth metals in seawater samples. On the other hand, we found that 50 separate one mL elutions was a more quantitative procedure than the 25 originally used, and incorporated that into our methods early on. Additionally, one may wish to follow the procedure of Kingston, et. al. (1978) and pre-elute the Chelex, after sampling, with ammonium acetate to strip the alkaline earth metals that may interfere with typical AA spectroscopy. This may be indicated only in estuarine or seawater sampling where alkaline earth metals are found in high concentrations.

The presence of chromium and copper at higher levels in the field blanks than in the lab blanks indicates the need for more stringent field procedures. One improvement may be to assemble and exchange/service the columns in the laboratory instead of the field.

For the most part, nothing unusual was discovered in the environmental monitoring. Our findings regarding the ionic states of various metals in water were consistent with others (Manahan, 1972, EPA, 1980, 1985a,b,c,d), with the possible exception of boron. Manahan (1972) states that boron in water is generally undissociated. We found it primarily in the adsorbent resin (presumably undissociated), and also in the ionic resins in both cationic and anionic states.

The higher chromium and copper values at the Wohler site during the winter of 1987-88 were correlated with high stream flow events, likely from an upstream source that is activated during high-flow storm events, and may be either geogenic or anthropogenic. The Regional Board intends to monitor the river in 1988 to determine if the relationship reappears. Additional monitoring to locate sources will be attempted as appropriate.

The Regional Board also intends to use the heavy metal monitoring techniques in other watersheds and (possibly) in groundwater investigations. To those ends, we will be refining our techniques and gathering additional data on background contamination, precision, and recovery efficiencies, as well as collecting data on heavy metals levels and speciation (ionic states) in other waters in the region.

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