APPENDIX

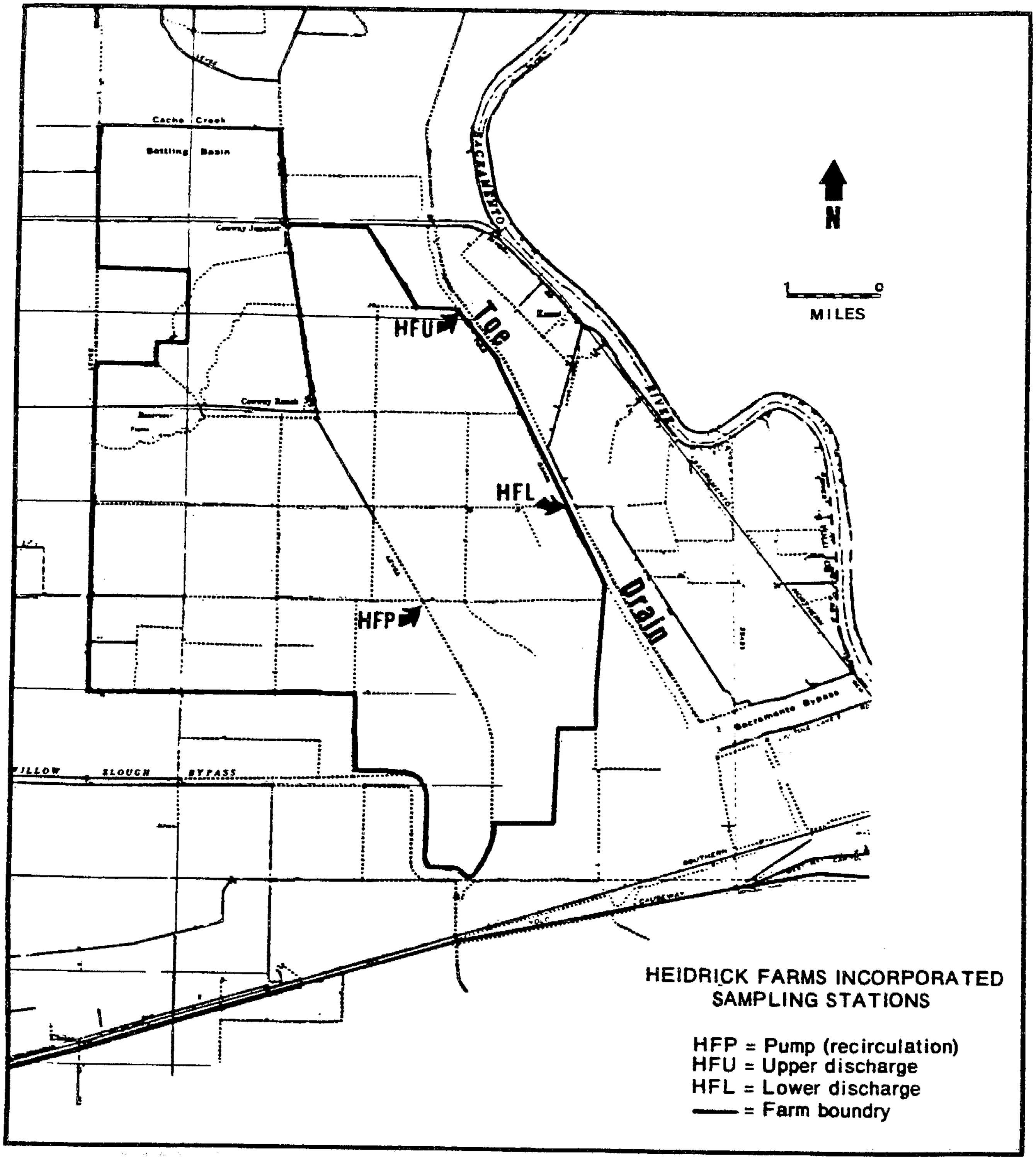

Figure A-1. OUTLINE OF HEIDRICK FARMS INC. (RD2035) RECIRCULATION SYSTEM AND RICE HERBICIDE MONITORING LOCATIONS. DRAIN DISCHARGES WERE SAMPLED AT STATIONS HFU (UPPER) AND HFL (LOWER). SOURCE: USGS TOPOGRAPHIC 15 MINUTE, DAVIS QUAD.

Table A-2. ORDRAM 8E AND 10G APPLIED TO HEIDRICK FARMS INC. RECIRCULATION AREA (RD2035). 1/

DATE OF APPLICATION		FORMULATION E = EMULSIFIABLE G = GRANULES	POUNDS A.I. APPLIED (CUMULATIVE %)	POUNDS ACRE
April	15	8E	757 (8.3)	3
	16	"	1148 (21)	"
	23	"	1395 (36)	"
	26	"	287 (38)	"
	27	"	207 (42)	"
	28	"	502 (47)	"
May	2	"	797 (56)	"
	5	"	598 (62)	"
	21	10G	675 (70)	4
	22	"	1670 (88)	"
	23	"	80 (89)	0.4
	24	"	1000 (100)	4

FORMULATION		TOTAL POUNDS	TOTAL ACRES
8E		5691	1947
10G		3425	1068
	TOTAL	9116	3015

1/CDFA, 1984 (PUR)

Table A-3. POUNDS OF BOLERO 10G APPLIED TO HEIDRICK FARMS INC. RECIRCULATION AREA (RD 2035). 1/

DATE OF APPLICATION	POUNDS A.I. APPLIED 2/	CUMULATIVE PERCENT
May 10	160	0.93
12	2295	14
13	1550	23
14	2405	37
15	1870	48
16	890	53
17	1885	64
18	1010	70
19	1165	77
21	850	81
23	660	85
24	770	90
26	1216	97
29	560	100

TOTAL POUNDS = 17,286
TOTAL ACRES = 4,353

1/ CDFA, 1984 (PUR)
2/ Applied at 4 pounds/acre

Table A-4. MOLINATE AND THOBENCARB CONCENTRATIONS MEASURED IN HEIDRICKS FARMS INC (RD2035) DURING 1984.

					UG/L	
LOCATION	DATE	LAB	TEMP(C)	EC	MOLINATE	THIOBENCARB
RECYCLING PUMP (HFP)	5- 2	CAL	9.4		22	[1.0
	2r				22	[1.0
	7	"	18.8		46	[1.0
	7r				46	[1.0
	21	SCC			16	67
	21	CCC				57
	24	SCC			43	130
	24	CCC				120
	28	SCC			58	63
	28	CCC				58
	31	SCC			28	31
	31	CCC				28
	6- 1	CAL	22.7		9.9	55
	1r				10	54
	4	SCC			24	34
	4	CCC				33
	7	SCC			7	5
	7	CCC				4.2
	11	SCC			6	26
	11	CCC				27
	12	CAL	21.6	800	3.5	17
	14	SCC			6	18
	14	CCC				14
	18	SCC			4	13
	18	CCC				15
	19	CAL	23.8	700	2.4	9.1
	21	SCC			3	10
	21	CCC				10
	29	CAL	23.3	700	1.3	3.8
NORTHERN DISCHARGE (HFU)	6- 6	CAL	17.7	800	1.8	24
	7	SCC			2	41
	8	CAL	17.7	750	1.6	22
	11	SCC			1	24
	12	CAL	22.7	800	1.0	16
	12r				1.1	18
	14	SCC			2	21
	18	"			1	15
	19	CAL	26.1	700	[1.0	7.2
	21	SCC			1	11
	29	CAL	25.5	600	[1.0	5.8
MIDDLE DISCHARGE (HFL)	6- 6	CAL	18.3	760	8.9	51
	7	SCC			17	69
	8	CAL	19.9	1000	14	23
	11	SCC			18	23
	12	CAL	22.2	950	8.8	11

12r				9.6	13
14	SCC			18	17
18	"			9	13
19	CAL	24.9	800	4.3	6.0
21	SCC			6	8
29	CAL	24.9	700	2.2	3.8

1/ r=replicate.

2/ Laboratories: CAL=California Analytical Laboratories, SCC=Stauffer Chemical Company, CCC=Chevron Chemical Company.

3/ Electrical Conductivity in microsiemens/cm.

Table A-5. POUNDS OF ORDRAM 10G APPLIED TO RECLAMATION DISTRICT 108. 1/

DATE OF APPLICATION		POUNDS A.I. APPLIED	POUNDS/ACRE	CUMULATIVE PERCENT
April	20	160	4	0.5
	29	940	4	3
May	2	1328	4	7
	3	1340	4	12
	5	708	4	14
	7	174	3	14
	8	845	4	17
	9	4925	5	33
	10	1765	4	38
	11	1692	4	44
	12	2025	4	55
	13	3075	4	60
	14	3840	5	72
	15	300	5	73
	16	2360	3	81
	17	1935	5	87
	19	665	4	89
	23	486	3	91
	24	450	4	92
	28	10	5	92
June	2	920	4	95
	4	720	3	97
	5	560	3	99
	7	120	4	100

TOTAL POUNDS = 31,343
TOTAL ACRES = 7,804

1/ CDFA, 1984.

Table A-6. POUNDS OF BOLERO 10G APPLIED TO RECLAMATION DISTRICT 108.[1]

DATE OF APPLICATION		POUNDS A.I. [2] APPLIED	CUMULATIVE PERCENT
May	7	1,065	6
	8	665	9
	11	4,116	31
	12	1,775	40
	13	1,620	49
	14	430	51
	15	2,260	63
	16	540	66
	17	900	70
	18	1,555	79
	20	775	83
	21	1,266	89
	24	284	91
	25	720	94
	27	140	95
	28	8	95
June	3	905	100

TOTAL POUNDS = 19,004 TOTAL ACRES = 4,969

---

[1] CDFA, 1984.

[2] Applied at ~4 lbs/acre.

Table A-7. MOLINATE AND THIOBENCARB CONCENTRATIONS WITHIN RECLAMATION DISTRICT 108.

				CONCENTRATION (UG/L)	
				MOLINATE	THIOBENCARB
DATE 1/	TIME	TEMP(C)	EC 2/	(SEM,N) 3/	
MAY 2	1315	16.1		<1.0	<1.0
2r				<1.0	<1.0
7	1115	18.8		<1.0	<1.0
7r				<1.0	<1.0
9	1330	21.6		<1.0	<1.0
9r				<1.0	<1.0
11	0910	21.6		1.4	<1.0
11r				1.4	<1.0
14	1045	22.7	550(L)	43	1.2
14r				15	1.0
16	1917	21.6	480(L)	52.0(1.27,5)	2.4(0.08,5)
17	0100	19.9		37.8(0.97,5)	2.4(0.31,5)
17	0700	19.9		41.6(0.93,5)	3.0(0.17,5)
17	1300	21.1		31.3(0.95,4)	2.7(0.35,4)
17	1900	21.1		31.2(0.97,5)	3.2(0.54,5)
20	1535	28.3		90	11
20r				95	13
23	1310	26.1		58	17
23r				56	18
24	2000	24.4		79.6(1.72,5)	15.0(0.84,5)
25	0230	23.3		78.0(1.10,5)	13.4(0.60,5)
25	0830	23.3		68.8(2.00,5)	12.0(0.32,5)
25	1430	24.4		61.6(0.93,5)	10.6(0.26,5)
25	2030	24.4		56.4(1.08,5)	10.0(0.04,5)
30	1730	30.5	480	36	6.2
30r				35	6.9
JUNE 1	1250	24.4		30	6.6
1r				33	7.6
5	1135	25.2	500	24	3.4
5r				26	3.8
12	1040	22.2	440	8.7	3.9
12r				12	5.8
19	1210	26.6	480	2.2	1.3
19r				3.6	1.9
29	1100	24.9	380	1.3	<1.0
29r				1.4	<1.0

1/ r=replicate.

2/ Electrical conductivity in dS/m (L=sample EC measured in the laboratory).

3/ SEM=Standard Error of Means.
N=Number of water samples.

Table A-8. REPLICATE SAMPLE CONCENTRATIONS FOR TWO 24-HOUR PERIODS WITHIN RECLAMATION DISTRICT 108.

			UG/L	
DATE	RUN	TIME	MOLINATE	THIOBENCARB
May 16	I	1917	53	2.5
			52	2.4
			56	2.5
			49	2.4
			50	2.1
17	II	0130	36	2.0
			41	2.4
			37	3.6
			39	2.2
			36	1.9
17	III	0700	40	3.7
			39	2.7
			43	2.9
			42	3.0
			44	2.9
17	IV	1300	30	2.7
			34	1.9
			30	2.7
			31	3.6
17	V	1900	28	4.2
			31	2.2
			31	4.7
			32	2.6
			34	2.1
May 24	I	2000	76	14
			86	18
			80	15
			78	13
			78	15
25	II	0230	77	12
			75	12
			77	15
			81	14
			80	14
25	III	0830	75	13
			71	12
			68	12
			63	11
			67	12
25	IV	1430	65	11
			61	11
			60	9.9
			60	10
			62	11
25	V	2030	53	9.8
			59	10
			57	10
			58	10
			55	10

Table A-9. MASS EMISSION OF RICE HERBICIDES FROM RD 108 USING THREE METHODS OF ESTIMATION[1].

Herbicide	Year	Method[2]	Total Pounds Discharged
Molinate	1982	1	3,768
	1984	1	721
	1984	2	643
	1984	3	646
Thiobencarb	1982	1	3,008
	1984	1	125
	1984	2	114
	1984	3	152

[1] See methods section for explanation of calculations.

[2] Methods 1, 2, and 3 utilized 16-17, 29-32, and 59 concentration points, respectively, to graph the discharge curves.

Table A-10. RICE HERBICIDE CONCENTRATIONS IN THE EAST NATOMAS DRAINAGE CANAL (RD1000).

			UG/L	
DATE[1]	TEMPERATURE (°C)	EC[2]	MOLINATE	THIOBENCARB
5-24			74	16
24r			77	18
30	23.8	400	40	38
6-12	19.7	375	4.6	8.9
12r			5.3	10.0
19	23.3	500	1.7	11
19r			1.9	13
29	23.3	450	<1.0	2.5
29r			<1.0	2.3

1/ r = replicate
2/ Electrical Conductivity, dS/m.

Table A-11. RICE HERBICIDE CONCENTRATIONS IN THE LOWER SACRAMENTO RIVER AND SACRAMENTO-SAN JOAQUIN DELTA-ESTUARY (1984).

LOCATION	DATE[1]		TIME	TEMP. (°C)	ug/L	
					MOLINATE	THIOBENCARB
SACRAMENTO RIVER						
Freeport	May	21	1531	19.9	14	<1.0
		21r			14	<1.0
		29	1445	21.0	8.9	1.4
		29r			8.8	1.0
Walnut Grove	May	21	1405	19.4	14	<1.0
		21r			13	<1.0
		29	1335	21.5	10	<1.0
		29r			9.6	1.1
Rio Vista	May	21	1230	18.8	9.9	<1.0
		21r			9.2	<1.0
		29	1000	22.0	10	<1.0
		29r			9.4	1.0
Collinsville	May	26	1010	19.4	2.2	<1.0
		26r			6.7	<1.0
		30	1040	20.5	7.4	1.6
		30r			8.0	<1.0
NORTHERN DELTA						
Toe Drain	May	21	1037	19.9	1.1	<1.0
		21r			1.1	<1.0
		29	1030	23.0	2.4	<1.0
		29r			2.0	<1.0
Prospect Sl.	May	21	1100	19.9	3.3	<1.0
		21r			3.9	<1.0
		29	1044	22.0	4.5	<1.0
		29r			4.8	<1.0
Cache Sl.	May	21	1152	19.9	<1.0	<1.0
		21r			<1.0	<1.0
		29	1110	23.0	<1.0	<1.0
		29r			<1.0	<1.0
Cache Sl.	May	21	1118	18.8	5.7	<1.0
		21r			N.M.[2]	N.M.
		29	1057	21.5	6.4	<1.0
		29r			7.0	<1.0
CENTRAL DELTA						
Delta Cross Channel	May	21	1045	19.9	13	<1.0
		21r			14	<1.0
		29	1325	- -	8.0	<1.0
		29r		- -	11	<1.0

---

[1] r = replicate sample.

[2] not measured.

TABLE A-11 (Continued)

LOCATION	DATE [1]		TIME	TEMP. (°C)	ug/L MOLINATE	ug/L THIOBENCARB
CENTRAL DELTA (continued)						
Mokelumne River, South Fork (Little Potato Sl.)	May	21	1115	19.4	7.9	<1.0
		21r			9.3	<1.0
		29	1400	- -	6.8	<1.0
		29r		- -	6.2	<1.0
SUISUN BAY						
Chipps Island	May	26	0830	18.8	4.3	<1.0
		26r			8.3	<1.0
		30	0830	19.9	2.3	<1.0
		30r			2.5	<1.0

---

[1] r = replicate sample.

APPENDIX K

```
* Program . . . MASTMENU.PRG
* Author  . . . WENDY WYELS
* Date  . . . . MAY 1, 1986  Updated 14 July 1988

* Master menu for Sacramento River pesticide dilution model

* Set working environment
CLEAR ALL
SET HEADING OFF
SET ESCAPE OFF
SET DEFAULT TO A
SET HELP OFF
SET MENU OFF
SET SCOREBOARD OFF
SET BELL OFF
SET STATUS OFF
SET SAFETY OFF
SET TALK OFF

* Initialize memory variables
  runmenu = .T.
  menu = .T.
  PUBLIC hold,half,redn,bmass,mmass,pest
  PUBLIC nonmol,exmol,nonthio,exthio,water,dshift
  STORE 0.00 TO exmol,nonmol,exthio,nonthio
  STORE 0.00 TO lbnonbol,lbexbol,lbnonmol,lbexmol
  STORE 0.00 TO m1,m2,b1,b2,c
  STORE 0.00 TO moldis,boldis,moldisk,boldisk
  pest = 'molinate'
  water = '1985'
  COPY FILE flow85.dbf TO flow.dbf
  half = 4.8
  mredn = 1
  tredn = 1
  hold = 8.0
  bmass = .85
  mmass = 2.00
  dshift = 0
  var = SPACE(1)
  choice = SPACE(1)


@ 1,0
TEXT
             SACRAMENTO RIVER PESTICIDE DILUTION MODEL
             -----------------------------------------
     Two rice herbicides, Ordram (molinate) and Bolero
(thiobencarb)
are applied to rice fields in the Central Valley above
Sacramento.
As part of the tillage practices, the fields are flooded prior to
application, and are then drained from April through June.  The
herbicide-laden tailwater is either recycled to another field or
released into the Sacramento River.  High levels of molinate in
```

```
the
river cause fish kills, while high thiobencarb concentrations
create
a bad taste in the City of Sacramento's drinking water.

     This model calculates the dilution effect of the Sacramento
River on the two herbicides; the concentration of each at Verona
(the confluence of the Feather and Sacramento Rivers) and the
City
of Sacramento is displayed or printed out.

     A third herbicide, Basagran (active ingredient bentazon),
was
detected in the River and the City's treated drinking water in
1986.
Because there is no accepted half-life for this chemical in the
literature, it is not a part of the model.

ENDTEXT
@ 23,1 SAY ' Press any key to continue . . . '
SET CONSOLE OFF
WAIT
SET CONSOLE ON

DO WHILE runmenu
   CLEAR
   @ 1,0
   TEXT
      MASTER MENU FOR SACRAMENTO RIVER PESTICIDE DILUTION MODEL
      ---------------------------------------------------------
                   1. Choose water year

                   2. Choose pesticide used

                   3. Shift date of max pesticide application

                   4. Choose dissipation values

                   5. View default and/or current values

                   6. Run simulation; tabulate or graph results

                   7. Exit this program

   ENDTEXT
   @ 18,5 SAY 'CHOOSE A NUMBER ! ' GET choice
   @ 20, 5 SAY '(PS: you do not have to hit the RETURN key)'
   READ

* Select the appropriate file

   DO CASE
      CASE choice='1'
         STORE .T. TO menu
```

```
         DO water
      CASE choice='2'
         STORE .T. TO menu
         DO pest
      CASE choice='3'
         STORE .T. TO menu
         DO shift
      CASE choice='4'
         STORE .T. TO menu
         DO dissip
      CASE choice='5'
         DO default
      CASE choice='6'
         STORE .T. TO menu
         DO run
      CASE choice='7'
         STORE .F. to runmenu

   OTHERWISE
      @ 21,11 SAY 'YOU BLEW IT !'
      @ 22,11 SAY 'PRESS ANY KEY TO CONTINUE  '
      SET CONSOLE OFF
      WAIT
      SET CONSOLE ON

   ENDCASE

ENDDO
CLEAR
CLOSE DATABASES
SET SAFETY ON
SET STATUS ON
RETURN

* End of master menu file
```

```
* Program . . . WATER
* Author  . . . WENDY WYELS
* Date  . . . . MAY 1, 1986

* Subprogram of Sacramento River pesticide dilution model;
* determines which water year file to use.

DO WHILE menu
   CLEAR
   @ 1,0
   TEXT

                         WATER YEAR MENU
                         ---------------

        Choose a historical water year with characteristics
        similar to the year you are interested in.

               1.  1977  (low flow)
               2.  1978  (low-normal flow)
               3.  1980  (normal flow)
               4.  1982  (high-normal flow)
               5.  1985  (low flow)
               6.  View current value
               7.  Return to master menu

   ENDTEXT
   @ 18,5 SAY 'Enter the number you want . . . ' GET var
   READ


* Select the appropriate file
   DO CASE
      CASE var = '1'
        water = '1977'
        COPY FILE flow77.dbf TO flow.dbf
        RETURN
      CASE var = '2'
        water = '1978'
        COPY FILE flow78.dbf TO flow.dbf
        RETURN
      CASE var = '3'
        water = '1980'
        COPY FILE flow80.dbf TO flow.dbf
        RETURN
      CASE var = '4'
        water = '1982'
        COPY FILE flow82.dbf TO flow.dbf
        RETURN
      CASE var = '5'
        water = '1985'
        COPY FILE flow85.dbf TO flow.dbf
        RETURN
      CASE var = '6'
```

```
        CLEAR
        @ 5,11 SAY 'The water year currently in use is: ';
          + water
        @ 15,11 SAY 'Press any key to continue'
        SET CONSOLE OFF
        WAIT
        SET CONSOLE ON
      CASE var = '7'
         STORE .F. TO menu

   OTHERWISE
      @ 20,11  SAY  'OOPS !  TRY AGAIN !'
      @ 21,11  SAY  'PRESS ANY KEY TO CONTINUE'
      SET CONSOLE OFF
      WAIT
      SET CONSOLE ON

   ENDCASE

ENDDO
CLEAR
CLOSE DATABASE
RETURN
```

```
* Program . . . PEST
* Author  . . . WENDY WYELS
* Date  . . . . MAY 2, 1986  UPDATE: 14 JULY 1988

* Subprogram of Sacramento River pesticide dilution model;
*  determines which pesticide is used and how many total pounds
*  are applied.

DO WHILE menu
   CLEAR
   @ 1,0
   TEXT

                       PESTICIDE USE MENU
                       ------------------

            1.  Molinate is the only pesticide applied
            2.  Thiobencarb is the only pesticide applied
            3.  Both molinate and thiobencarb are applied
            4.  View current values
            5.  Return to the master menu

       Note: Non-exempt acreage (usually on the west side of the
       Sacramento River) discharges tailwater directly from the
       fields to the river.
       Exempt acres (usually on the east side of the Sacramento)
       are those which reuse or recycle the tailwater to other
       fields before discharging into the river or do not
       discharge to the river at all.  Herbicide concentrations
       from these acres are substantially lower since time
       has been allowed for degredation.


   ENDTEXT
   @ 23, 5 SAY 'Which do you choose ?  ' GET var
   READ

* Select the appropriate file; enter the pounds applied

   CLEAR
   DO CASE
      CASE var = '1'
        STORE 0.00 TO nonthio,exthio
        @ 5,5 SAY 'How many pounds of molinate was '
        INPUT '     applied on non-exempt acreage ?   ' TO nonmol
        @ 10,5 SAY 'How many pounds of molinate was '
        INPUT '     applied on exempt acreage ? ' TO exmol
        pest = 'molinate'
      CASE var = '2'
        STORE 0.00 TO nonmol,exmol
        @ 5,5 SAY 'How many pounds of thiobencarb was '
        INPUT '     applied on non-exempt acreage ?   ' TO
nonthio
        @ 10,5 SAY 'How many pounds of thiobencarb was '
```

```
          INPUT '      applied on exempt acreage ?  ' TO exthio
          pest = 'thiobencarb'
        CASE var = '3'
          @ 5,5 SAY 'How many pounds of molinate was '
          INPUT '      applied to non-exempt acreage ?  ' TO nonmol
          @ 8,5 SAY 'How many pounds of molinate was '
          INPUT '      applied to exempt acreage ?  ' TO exmol
          @ 12,5 SAY 'How many pounds of thiobencarb was '
          INPUT '      applied to non-exempt acreage ?  ' TO nonthio
          @ 15,5 SAY 'How many pounds of thiobencarb was '
          INPUT '      applied to exempt acreage ?  ' TO exthio
          pest = 'molinate and thiobencarb'
        CASE var = '4'
          CLEAR
          @ 5,1 SAY 'The pesticide used is: ' + pest
          @ 9,1 SAY 'Total pounds molinate applied;
 (non-exempt): '+ STR (nonmol,10,2)
          @ 11,1 SAY 'Total pounds molinate applied (exempt): ';
+ STR (exmol,10,2)
          @ 15,1 SAY 'Total pounds thiobencarb applied;
 (non-exempt): ' + STR (nonthio,10,2)
          @ 17,1 SAY 'Total pounds thiobencarb applied;
 (exempt): '+ STR (exthio,10,2)
          @ 22,11 SAY 'Press any key to continue'
          SET CONSOLE OFF
          WAIT
          SET CONSOLE ON
        CASE var = '5'
          STORE .F. TO menu

        OTHERWISE
          @ 20,11 SAY 'You hit the wrong key ! '
          @ 21,11 SAY 'Press any key to continue'
          SET CONSOLE OFF
          WAIT
          SET CONSOLE ON

   ENDCASE
ENDDO
CLEAR
CLOSE DATABASES
RETURN
```

```
* Program . . . DISSIP
* Author  . . . WENDY WYELS
* Date  . . . . MAY 2, 1986   Update: 14 July 1988

* Subprogram of Sacramento River pesticide dilution model;
*  allows user to change pesticide dissipation values

DO WHILE menu
   CLEAR
   @ 1,0
   TEXT
                                DISSIPATION VALUES
                              ----------------------

                        1. Molinate holding period
                        2. Molinate half-life
                        3. Weighted av. mass discharge of thiobencarb
                        4. Weighted av. mass discharge of molinate
                        5. Molinate reduction due to recycling
                        6. Thiobencarb reduction due to recycling
                        7. View current values
                        8. Return to master menu


   ENDTEXT
   @ 18,5 SAY 'Select a number . . . ' GET var
   READ

   CLEAR
   DO CASE
      CASE var = '1'
        @ 2,0
        TEXT
           The holding period is the amount of time the
        water must be held on the field after molinate is
        applied, and is set by regulatory agencies.  A
        longer holding period provides more time for evaporation,
        photolysis, and adsorption to the soil.  Hence, less
        molinate is released to the river.  The current (1985)
        holding time is 8 days.  Enter the holding period you
        want to use in this simulation . . .  (and hit return).

        ENDTEXT

        INPUT  '           ' TO hold
          DO WHILE hold < 8
             @ 15,0 CLEAR
             @ 17,1 SAY 'The holding period must be at least 8 !'
             INPUT 'Enter a new holding period . . ' TO hold
          ENDDO
      CASE var = '2'
        @ 5,1 SAY 'The half-life of molinate has been'
        @ 6,1 SAY 'determined through field experiments,'
        @ 7,1 SAY 'and is approximately 4.8 days.'
```

```
        INPUT 'Enter the half-life you want . .  (return)' TO
half
      CASE var = '3'
        @ 5,1 SAY 'The measured (1985) weighted average mass'
        @ 6,1 SAY 'discharge of thiobencarb from the Colusa'
        @ 7,1 SAY 'Basin Drain, Sacramento Slough, and RD108'
        @ 8,1 SAY 'is 7.9 %.  Enter the value you wish to use.'
        INPUT 'Enter a percent; hit return . . .    ' TO bmass
      CASE var = '4'
        @ 5,1 SAY 'The measured (1985) weighted average mass'
        @ 6,1 SAY 'discharge of molinate from the Colusa'
        @ 7,1 SAY 'Basin Drain, Sacramento Slough, and RD108'
        @ 8,1 SAY 'is 8.5 %.  Enter the value you wish to use.'
        INPUT 'Enter a percent; hit return . . .   ' TO mmass
      CASE var = '5'
        @ 2,0
        TEXT
          Exempt acres are those which practice conservation
        measures such as tail-water recycling.  This leads to
        a reduction in the amount of pesticide in the water when
        it is finally released to the river (if it is released
        at all).  What % reduction in molinate discharge do
        you expect as a result of conservation measures?
          Use a number between 0 and 100; 0 means the full
        amount of pesticide is released, while 100 indicates
        that no pesticide is in the tail-water (or that tail
        water is never released to the river).
        ENDTEXT
        INPUT 'Enter a number; hit return . . . ' TO mredn
      CASE var = '6'
        @ 2,0
        TEXT
          Exempt acres are those which practice conservation
        measures such as tail-water recycling.  This leads to
        a reduction in the amount of pesticide in the water when
        it is finally released to the river (if it is released
        at all).  What % reduction in thiobencarb discharge do
        you expect as a result of conservation measures?
          Use a number between 0 and 100; 0 means the full
        amount of pesticide is released, while  100 indicates
        that no pesticide is in the tail-water (or that tail
        water is never released to the river).
        ENDTEXT
        INPUT 'Enter a number; hit return . . . ' to tredn
      CASE var = '7'
        CLEAR
        @ 2,1 SAY 'Holding period (days): ';
            + STR (hold,4,1)
        @ 4,1 SAY 'Molinate half-life (days): ';
            + STR (half,5,2)
        @ 6,1 SAY 'Weighted av. mass discharge of thiobencarb: ';
            + STR (bmass,5,2)
        @ 8,1 SAY 'Weighted av. mass discharge of molinate: ';
            + STR (mmass,5,2)
```

```
        @ 10,1 SAY '% reduction in molinate discharges due to
recycling: ';
            + STR (mredn,6,2)
        @ 12,1 SAY '% reduction in thiobencarb discharges due
            to recycling: '; + STR (tredn,6,2)
        @ 18,10 SAY 'PRESS ANY KEY TO CONTINUE'
        SET CONSOLE OFF
        WAIT
        SET CONSOLE ON
      CASE var = '8'
        STORE .F. TO menu

      OTHERWISE
        @ 20,10 SAY 'YOU DID NOT FOLLOW DIRECTIONS !'
        @ 21,10 SAY 'PRESS ANY KEY TO CONTINUE'
        SET CONSOLE OFF
        WAIT
        SET CONSOLE ON

   ENDCASE
ENDDO
CLEAR
CLOSE DATABASE
RETURN
```

```
* Program . . . SHIFT
* Author  . . . WENDY WYELS
* Date  . . . . JULY 28, 1986

* Subprogram of Sacramento River pesticide dilution model;
* shifts the date of maximum pesticide application

DO WHILE menu
   CLEAR
   @ 1,0
   TEXT

            SHIFT DATE OF MAXIMUM PESTICIDE APPLICATION
            -------------------------------------------

       The pounds applied/day of both molinate and thiobencarb
    has been averaged for the 1980, 1981, and 1982 rice-growing
    seasons.  (Statistice were used from the four major rice
    growing counties: Colusa, Glenn, Sutter, and Yolo).  A
    statistical program was then used to smooth the curves
    into two generalized herbicide application curves.

       The data shows that 50% of the molinate is applied by
    May 17 and 50% of the thiobencarb by May 24.  It is possible
    to change the date of 50% application by two weeks, either
    earlier or later.

       If you wish to change the 50% date, enter a number from
    -14 (ie, an earlier growing season) to 14 (a later growing
    season).  Entering "0" will keep the 50% dates the same as
    the 1980-82 average.

    (Enter a number and hit return)
   ENDTEXT
   @ 23,5 SAY 'Date change: ' GET dshift
   READ

USE perapply.dbf
  GO TOP
  DO WHILE .NOT. EOF ()
    REPLACE day WITH (day + dshift)
    SKIP
  ENDDO

CLOSE DATABASES
RETURN
```

```
* Program . . . DEFAULT
* Author  . . . WENDY WYELS
* Date   . . . . MAY 2, 1986  UPDATE: 14 JULY 1988

* Subprogram of Sacramento River pesticide dilution model;
*   lists the current/default values of all variables

CLEAR

   @ 1,7 SAY 'CURRENT VALUES FOR ALL VARIABLES'
   @ 2,7 SAY '--------------------------------'
   @ 3,1 SAY 'The water year is: '+ water
   @ 4,1 SAY 'The pesticide in use is: '+ pest
   @ 6,1 SAY 'Pounds molinate applied (non-exempt): ';
       + STR (nonmol,10,2)
   @ 7,1 SAY 'Pounds molinate applied (exempt): ';
       + STR (exmol,10,2)
   @ 8,1 SAY 'Pounds thiobencarb applied (non-exempt): ';
       + STR (nonthio,10,2)
   @ 9,1 SAY 'Pounds thiobencarb applied (exempt): ';
       + STR (exthio,10,2)
   @ 11,1 SAY 'Molinate holding period (days): ';
       + STR (mhold,4,1)
   @ 12,1 SAY 'Molinate half-life (days): ';
       + STR (mhalf,6,2)
   @ 14,1 SAY 'Weighted av. mass discharge of thiobencarb: ';
       + STR (bmass,5,2)
   @ 15,1 SAY 'Weighted av. mass discharge of molinate: ';
       + STR (mmass,5,2)
   @ 16,1 SAY '% reduction in discharge of molinate '
   @ 17,5 SAY 'from exempt areas: ' + STR (mredn,6,2)
   @ 19,1 SAY '% reduction in discharge of thiobencarb '
   @ 20,5 SAY 'from exempt areas: ' + STR (tredn,6,2)
   @ 21,1 SAY 'Shift in date of 50% pesticide application (days):
';
        + STR (dshift,3)
   @ 23,10 SAY 'TO CHANGE ANY VALUE, RETURN TO THE MASTER MENU'
   @ 24,10 SAY 'PRESS ANY KEY TO CONTINUE'

SET CONSOLE OFF
WAIT
SET CONSOLE ON
RETURN
```

```
* Program . . . RUN
* Author  . . . WENDY WYELS
* Date  . . . . MAY 14, 1986  UPDATE 14 JULY 1988

* Subprogram of Sacramento River pesticide dilution model;
* makes actual calculations and tabulates data.

* Clear the menu off the screen
  CLEAR

* Speed up program execution
  @ 15,4 SAY 'WORKING . . .'
  @ 17,4 SAY 'DO NOT DISTURB ME ! '

* Set up work areas
  SELECT 1
   USE flow.dbf
  SELECT 2
   USE perapply.dbf
  SELECT 3
   USE calc.dbf

* First order decay equation for molinate (determines %
remaining)
  k = .693/half
  lnc = 4.605-(hold*k)
  c = EXP(lnc)

* Convert % reduction (from exempt acres) to a decimal (% left)
  mrednn = (100-mredn)*.01
  trednn = (100-tredn)*.01

* Total lb applied * % applied/day = lb applied/day.
* Separate calculations for nonexempt and exempt acerage.
  SELECT 2
  GO TOP
  DO WHILE .NOT. EOF ()
    REPLACE lbnonbol WITH (bolero * nonthio *.01)
    REPLACE lbexbol WITH (bolero * exthio *.01)
    REPLACE lbnonmol WITH (molinate * nonmol *.01)
    REPLACE lbexmol WITH (molinate * exmol *.01)
    SKIP
  ENDDO

* Calculate pounds discharged/day from both
* exempt and nonexempt acreage
* (m1,m2,b1,b2,moldis,boldis are memory variables)
  GO TOP
  DO WHILE .NOT. EOF ()
      m1 = lbnonmol * mmass * .01 * c * .01
      m2 = lbexmol * (mmass * .01 * mrednn) * c *.01
      b1 = lbnonbol * bmass * .01
      b2 = lbexbol * (bmass * .01 * trednn)
* Total pounds discharged for each chemical
```

```
   moldis = m1 + m2
   boldis = b1 + b2
* Convert discharge from pounds to kilograms
   REPLACE moldisk WITH (moldis * .454)
   REPLACE boldisk WITH (boldis * .454)
   SKIP
 ENDDO
 USE

* Shift date to take 6 day lag time into account (between end
* of holding time and appearance into the river).
 SELECT 1
 GO TOP
 DO WHILE .NOT. EOF ()
    REPLACE day WITH (day + hold + 6)
 SKIP
 ENDDO

* Shift flow and discharge fields into a new file
 SELECT 3
   APPEND FROM perapply
   INDEX ON day TO calc
   UPDATE ON day FROM flow REPLACE sac WITH flow->srsac, ì
verona WITH flow->srfr

* Divide chemical discharged (kg) by river flow (cfs)
* Multiply by 408.56 to convert to ppb
*   (Constants: 86400 sec/day, .0357 ft3/l, 1,000,000,000 ug/kg)
 GO TOP
 DO WHILE .NOT. EOF ()
   REPLACE molsac WITH ((moldisk/sac) * 413.19)
   REPLACE molver WITH ((moldisk/verona) * 413.19)
   REPLACE bolsac WITH ((boldisk/sac) * 413.19)
   REPLACE bolver WITH ((boldisk/verona) * 413.19)
   SKIP
 ENDDO

* Determine format of printout
 CLEAR
 @ 7,1 SAY 'The results can either be scrolled across'
 @ 8,1 SAY 'the screen, or sent to the printer.  If'
 @ 9,1 SAY 'you use the printer, make sure that it is'
 @ 10,1 SAY 'on-line and the paper is at the top of the page.'
 @ 11,1 SAY 'Also, turn the printer off and then on to set'
 @ 12,1 SAY 'the report form at the top of the page.'
 @ 14,1 SAY 'Enter P (printer output) or S (screen output)' GET
var
 READ
   IF UPPER (var) = 'P'
     SET DEVICE TO PRINT
     REPORT FORM results.frm TO PRINT
       * print variable values
         @ 47,12 SAY 'VARIABLE VALUES FOR THIS RUN'
         @ 48,12 SAY '----------------------------'
```

```
     @ 49,5 SAY 'Water year: '+ water
     @ 50,5 SAY 'Pounds molinate applied (non-exempt): ';
       + STR (nonmol,10,2)
     @ 51,5 SAY 'Pounds molinate applied (exempt): ';
       + STR (exmol,10,2)
     @ 52,5 SAY 'Pounds thiobencarb applied (non-exempt): ';
       + STR (nonthio,10,2)
     @ 53,5 SAY 'Pounds thiobencarb applied (exempt): ';
       + STR (exthio,10,2)
     @ 54,5 SAY 'Molinate holding period (days): ';
       + STR (hold,4,1)
     @ 55,5 SAY 'Molinate half-life (days): ';
       + STR (half,6,2)
     @ 56,5 SAY 'Weighted av. mass discharge of thiobencarb:
';

       + STR (bmass,5,2)
     @ 57,5 SAY 'Weighted av. mass discharge of molinate: ';
       + STR (mmass,5,2)
     @ 58,5 SAY '% redn in chem discharge from exempt areas:
';

       + STR (redn,6,2)
     @ 59,5 SAY 'Shift (in days) of 50% pesticide
application: ';
       + STR (dshift,3,0)

     * Housekeeping (clear all working files)
      SELECT 3
      ZAP
      COPY FILE perptrn.dbf TO perapply.dbf

    SET DEVICE TO SCREEN

  ELSE
   * Display results on console
    CLEAR
    SET CONSOLE ON
    @ 1,15 SAY 'SACRAMENTO RIVER PESTICIDE DILUTION MODEL'
    @ 3,26 SAY '--- ALL VALUES IN PPB ---'
    @ 4,3 SAY 'DATE'
    @ 4,15 SAY 'MOLINATE'
    @ 4,29 SAY 'MOLINATE'
    @ 4,43 SAY 'THIOBENCARB'
    @ 4,60 SAY 'THIOBENCARB'
    @ 5,13 SAY 'SAC R-VERONA'
    @ 5,28 SAY 'SAC R-SAC'
    @ 5,42 SAY 'SAC R-VERONA'
    @ 5,61 SAY 'SAC R-SAC'
    STORE 7 TO ln
     GO TOP
     DO WHILE .NOT. EOF ()
      @ ln,1  SAY date
      @ ln,14 SAY molver
      @ ln,29 SAY molsac
      @ ln,43 SAY bolver
```

```
              @ ln,61 SAY bolsac
                STORE ln+1 TO ln
                  IF ln > 23
                  WAIT
                  CLEAR
                     @ 2,26 SAY '--- ALL VALUES IN PPB ---'
                     @ 4,3 SAY 'DATE'
                     @ 4,15 SAY 'MOLINATE'
                     @ 4,29 SAY 'MOLINATE'
                     @ 4,43 SAY 'THIOBENCARB'
                     @ 4,60 SAY 'THIOBENCARB'
                     @ 5,13 SAY 'SAC R-VERONA'
                     @ 5,28 SAY 'SAC R-SAC'
                     @ 5,42 SAY 'SAC R-VERONA'
                     @ 5,61 SAY 'SAC R-SAC'
                     STORE 7 TO ln
                  ENDIF
                  SKIP
             ENDDO
           WAIT
           CLEAR
          ENDIF

* Housekeeping (clear all working files)
  SELECT 3
  ZAP
  CLOSE DATABASES
  COPY FILE perptrn.dbf TO perapply.dbf

CLOSE DATABASES
RETURN
```

DATABASE: FLOW85
Sacramento River flow at Colusa, Knights Landing,
Feather River, and Sacramento.

date	day	SRC	SRKL	SRFR	SRSAC
03/20/00	-11	0	0	11000	12500
03/21/00	-10	0	0	10600	12100
03/22/00	-9	0	0	10100	11600
03/23/00	-8	0	0	10100	11300
03/24/00	-7	0	0	10100	11300
03/25/00	-6	0	0	10200	11500
03/26/00	-5	0	0	9970	10800
03/27/00	-4	0	0	11300	12600
03/28/00	-3	0	0	13400	14900
03/29/00	-2	0	0	14800	16300
03/30/00	-1	0	0	15100	16600
03/31/00	0	0	0	15000	16300
04/01/00	1	0	0	14100	15700
04/02/00	2	0	0	13400	14800
04/03/00	3	0	0	13400	14200
04/04/00	4	0	0	13100	14200
04/05/00	5	0	0	13000	13900
04/06/00	6	0	0	12900	13300
04/07/00	7	0	0	12400	13300
04/08/00	8	0	0	11900	12900
04/09/00	9	0	0	11800	12700
04/10/00	10	0	0	12000	12800
04/11/00	11	0	0	11700	12400
04/12/00	12	0	0	10600	11700
04/13/00	13	0	0	9900	11600
04/14/00	14	0	0	9680	11300
04/15/00	15	0	0	9670	11000
04/16/00	16	0	0	10100	12700
04/17/00	17	0	0	11000	13900
04/18/00	18	0	0	11400	13300
04/19/00	19	0	0	11300	13800
04/20/00	20	0	0	11300	13600
04/21/00	21	0	0	11100	13100
04/22/00	22	0	0	10800	13300
04/23/00	23	0	0	10800	13200
04/24/00	24	0	0	10800	12100
04/25/00	25	0	0	10200	11100
04/26/00	26	0	0	9470	10500
04/27/00	27	0	0	9050	9800
04/28/00	28	0	0	8520	9170
04/29/00	29	0	0	8050	9610
04/30/00	30	0	0	7870	9880
05/01/00	31	0	0	7940	10200
05/02/00	32	0	0	8300	10700
05/03/00	33	0	0	8570	11600
05/04/00	34	0	0	9050	12200
05/05/00	35	0	0	9620	12000
05/06/00	36	0	0	9800	12000
05/07/00	37	0	0	9940	12300
05/08/00	38	0	0	9670	12600
05/09/00	39	0	0	9720	13100
05/10/00	40	0	0	10000	13500
05/11/00	41	0	0	10200	14000
05/12/00	42	0	0	10500	14100
05/13/00	43	0	0	10600	14200
05/14/00	44	0	0	10800	13800
05/15/00	45	0	0	11000	13300
05/16/00	46	0	0	11100	12900
05/17/00	47	0	0	12700	15100
05/18/00	48	0	0	14000	15000
05/19/00	49	0	0	14200	14600
05/20/00	50	0	0	13000	13200
05/21/00	51	0	0	11700	13200
05/22/00	52	0	0	11700	12900
05/23/00	53	0	0	11800	12800
05/24/00	54	0	0	11800	12900
05/25/00	55	0	0	12400	13800
05/26/00	56	0	0	12500	14600
05/27/00	57	0	0	12800	14700
05/28/00	58	0	0	13200	14900
05/29/00	59	0	0	13500	15200
05/30/00	60	0	0	14000	15400
05/31/00	61	0	0	14200	15600
06/01/00	62	0	0	14200	16200
06/02/00	63	0	0	14100	16200
06/03/00	64	0	0	14100	15600
06/04/00	65	0	0	13700	15700
06/05/00	66	0	0	13000	15100
06/06/00	67	0	0	12500	14900
06/07/00	68	0	0	11500	13500
06/08/00	69	0	0	10600	12600
06/09/00	70	0	0	10200	11700
06/10/00	71	0	0	10700	12100
06/11/00	72	0	0	11000	12300
06/12/00	73	0	0	11200	12400
06/13/00	74	0	0	10900	13400
06/14/00	75	0	0	10200	12600
06/15/00	76	0	0	9790	12000
06/16/00	77	0	0	9520	11400
06/17/00	78	0	0	9670	11600
06/18/00	79	0	0	9840	12700
06/19/00	80	0	0	10100	12900
06/20/00	81	0	0	10100	13100
06/21/00	82	0	0	10400	12700
06/22/00	83	0	0	10600	12900
06/23/00	84	0	0	10700	13300
06/24/00	85	0	0	11100	13400
06/25/00	86	0	0	11500	14200
06/26/00	87	0	0	10900	13500
06/27/00	88	0	0	10600	12700
06/28/00	89	0	0	10400	12100
06/29/00	90	0	0	10800	12500
06/30/00	91	0	0	11600	14400

DATABASE: FLOW77
Sacramento River flow at Colusa, Knights Landing,
Feather River, and Sacramento.

date	day	SRC	SRKL	SRFR	SRSAC
03/20/00	-11	0	0	8220	8120
03/21/00	-10	0	0	7750	7750
03/22/00	-9	0	0	6960	6900
03/23/00	-8	0	0	6720	6870
03/24/00	-7	0	0	6600	6600
03/25/00	-6	0	0	6760	6400
03/26/00	-5	0	0	6790	6650
03/27/00	-4	0	0	6770	6650
03/28/00	-3	0	0	6730	6500
03/29/00	-2	0	0	6310	6200
03/30/00	-1	0	0	6000	5950
03/31/00	0	0	0	5880	5610
04/01/00	1	5560	5120	6070	5760
04/02/00	2	5840	5350	6280	5850
04/03/00	3	5870	5580	6390	6100
04/04/00	4	5830	5550	6410	6150
04/05/00	5	5640	5480	6240	6010
04/06/00	6	5410	5160	6020	5700
04/07/00	7	5190	4810	5680	5630
04/08/00	8	4990	4560	5640	5600
04/09/00	9	5080	4350	5510	5500
04/10/00	10	5450	4210	5810	5400
04/11/00	11	5660	4560	6280	5800
04/12/00	12	5400	4840	6410	6100
04/13/00	13	5050	4580	6120	6150
04/14/00	14	5040	4360	5560	5250
04/15/00	15	5180	4060	5490	5200
04/16/00	16	5400	3640	6120	5700
04/17/00	17	5570	3670	6270	6120
04/18/00	18	5990	3680	6250	6150
04/19/00	19	6170	3830	6570	6200
04/20/00	20	6280	4250	6430	6350
04/21/00	21	5950	5200	6180	6100
04/22/00	22	5920	4100	5870	5800
04/23/00	23	5980	3840	5870	5280
04/24/00	24	6280	3620	6180	5750
04/25/00	25	6310	3510	6550	6340
04/26/00	26	6310	3700	6490	6190
04/27/00	27	6350	4130	6710	6460
04/28/00	28	6420	4250	6740	6620
04/29/00	29	6400	4310	6690	6700
04/30/00	30	6480	4380	6800	6870
05/01/00	31	6770	4810	7540	7700
05/02/00	32	7180	5350	8480	8610
05/03/00	33	7490	6630	8880	8690
05/04/00	34	7630	7420	9160	8910
05/05/00	35	7780	7510	8910	8640
05/06/00	36	7530	6810	8200	8250
05/07/00	37	6970	6520	7480	7480
05/08/00	38	6570	6370	7310	7330
05/09/00	39	6970	6280	7210	7460
05/10/00	40	7610	6820	7560	8000
05/11/00	41	7650	7400	8230	8490
05/12/00	42	8200	7440	8570	8670
05/13/00	43	8930	8310	9290	9200
05/14/00	44	7630	8170	9300	9900
05/15/00	45	6900	7090	8620	8540
05/16/00	46	6460	6410	7910	8090
05/17/00	47	6190	5910	7230	7440
05/18/00	48	5950	5530	6690	7000
05/19/00	49	5740	5440	6520	6610
05/20/00	50	5650	5460	6690	6950
05/21/00	51	5630	5420	6670	6990
05/22/00	52	5620	5510	6690	7370
05/23/00	53	5540	5170	6500	7100
05/24/00	54	5660	4840	6170	6570
05/25/00	55	5530	4850	6070	6760
05/26/00	56	5500	4960	6200	6670
05/27/00	57	5580	5070	6500	6680
05/28/00	58	5760	5230	6640	6700
05/29/00	59	5790	5210	6640	6500
05/30/00	60	5600	5120	6600	6200
05/31/00	61	5350	4530	5950	6000
06/01/00	62	5060	4390	5040	5800
06/02/00	63	4610	3990	4780	5800
06/03/00	64	4420	3540	4760	5810
06/04/00	65	4510	3360	4700	5730
06/05/00	66	4830	3410	4730	5730
06/06/00	67	5130	3640	4880	6100
06/07/00	68	5200	3830	5140	6310
06/08/00	69	5110	3930	4950	6410
06/09/00	70	5170	3840	4760	6590
06/10/00	71	5490	4010	4510	6060
06/11/00	72	5580	4160	4820	6140
06/12/00	73	5770	4350	5070	6460
06/13/00	74	5930	4620	5510	6900
06/14/00	75	5970	4650	5580	6940
06/15/00	76	6350	4670	5370	6510
06/16/00	77	6410	5000	5580	6870
06/17/00	78	6520	5110	5850	7440
06/18/00	79	6740	5390	6070	7290
06/19/00	80	6990	5790	6550	7560
06/20/00	81	7210	5890	6630	7540
06/21/00	82	7260	5990	6420	7260
06/22/00	83	7230	5910	6420	7300
06/23/00	84	7130	5790	6210	7310
06/24/00	85	7110	5650	6140	7180
06/25/00	86	7300	5620	6070	7230
06/26/00	87	7640	5950	6700	7780
06/27/00	88	7770	6020	7190	8170
06/28/00	89	7650	6120	6910	8030
06/29/00	90	7590	5970	6910	7970
06/30/00	91	7630	5880	6910	7740

DATABASE: FLOW80

Sacramento River flow at Colusa, Knights Landing,
Feather River, and Sacramento.

date	day	SRC	SRKL	SRFR	SRSAC
03/20/00	-11	0	0	45800	51600
03/21/00	-10	0	0	42800	49400
03/22/00	-9	0	0	39300	46300
03/23/00	-8	0	0	36300	43400
03/24/00	-7	0	0	32800	40400
03/25/00	-6	0	0	29500	37700
03/26/00	-5	0	0	26900	35100
03/27/00	-4	0	0	25300	33000
03/28/00	-3	0	0	24600	32200
03/29/00	-2	0	0	23700	31200
03/30/00	-1	0	0	23000	30600
03/31/00	0	0	0	22500	29800
04/01/00	1	10900	11600	21900	29400
04/02/00	2	11100	11700	21400	27900
04/03/00	3	10800	11600	20800	26100
04/04/00	4	10800	11500	20700	25900
04/05/00	5	10900	11800	21400	26800
04/06/00	6	12000	12000	22000	27400
04/07/00	7	12000	13000	22600	27800
04/08/00	8	11200	12500	22400	27900
04/09/00	9	10700	11800	21600	27100
04/10/00	10	10400	11200	20500	25900
04/11/00	11	10100	11000	19400	24900
04/12/00	12	9710	10500	18700	24000
04/13/30	13	9340	10100	18000	23100
04/14/00	14	9020	9540	17300	22500
04/15/00	15	8490	8670	16700	21900
04/16/00	16	7900	8450	15700	21100
04/17/00	17	7350	7830	14900	20600
04/18/00	18	6960	7040	14200	21000
04/19/00	19	6680	6550	13800	20200
04/20/00	20	6660	5950	12800	19400
04/21/00	21	7350	6110	12700	19500
04/22/00	22	8140	6890	13000	19600
04/23/00	23	7990	7330	13600	20000
04/24/00	24	7660	6840	13500	20000
04/25/00	25	7050	6660	13000	19400
04/26/00	26	6870	6060	12300	18700
04/27/00	27	6830	5990	11900	18000
04/28/00	28	6520	5810	11600	17100
04/29/00	29	6290	5460	11200	17800
04/30/00	30	6200	5240	10600	16600
05/01/00	31	6220	5100	10500	16200
05/02/00	32	6150	4760	10400	16500
05/03/00	33	6090	4510	9930	15200
05/04/00	34	6300	4570	9570	13900
05/05/00	35	6520	4930	9440	13700
05/06/00	36	6600	5300	8880	13700
05/07/00	37	6670	5500	8920	13400
05/08/00	38	6600	5700	8960	13100
05/09/00	39	6580	6240	9450	14200
05/10/00	40	7160	6950	10800	15200
05/11/00	41	8240	8320	12800	16900
05/12/00	42	8080	9160	14300	18600
05/13/00	43	7700	8860	14300	18800
05/14/00	44	7380	8540	13900	19100
05/15/00	45	7270	8320	13800	18300
05/16/00	46	7010	8010	13300	18100
05/17/00	47	6330	7560	12800	17400
05/18/00	48	5980	7070	12300	16900
05/19/00	49	5820	6660	11900	16700
05/20/00	50	5660	6420	11600	15800
05/21/00	51	5670	6290	11700	15600
05/22/00	52	5750	6270	12300	16200
05/23/00	53	5950	6440	12800	16300
05/24/00	54	5950	6770	13100	15900
05/25/00	55	5990	7200	13200	16000
05/26/00	56	6090	7470	12500	15400
05/27/00	57	6120	7460	12900	14900
05/28/00	58	6060	7420	13900	16300
05/29/00	59	5910	7310	13100	15600
05/30/00	60	5740	6970	12200	14600
05/31/00	61	5580	6570	11500	14200
06/01/00	62	5600	6380	11000	13500
06/02/00	63	5620	6090	10800	13800
06/03/00	64	5820	6010	10500	13000
06/04/00	65	5860	6000	10400	13300
06/05/00	66	6060	6400	10700	13400
06/06/00	67	6220	6970	11300	14100
06/07/00	68	6340	7230	12000	14700
06/08/00	69	6760	7220	13000	15300
06/09/00	70	7330	7130	13800	16100
06/10/00	71	7670	7340	14300	16200
06/11/00	72	7540	6980	14700	16600
06/12/00	73	7480	6400	15200	17600
06/13/00	74	7740	6350	15700	18000
06/14/00	75	8030	6670	16300	18600
06/15/00	76	8720	7300	16300	18700
06/16/00	77	9240	7890	16800	19000
06/17/00	78	9300	8150	17500	19600
06/18/00	79	9480	8040	17800	19900
06/19/00	80	9980	8180	17800	20000
06/20/00	81	0	8400	17900	20300
06/21/00	82	0	8420	17500	20700
06/22/00	83	0	8650	17300	20500
06/23/00	84	0	7720	16700	20400
06/24/00	85	0	7030	16400	20300
06/25/00	86	0	7280	16800	21000
06/26/00	87	0	7130	16800	21000
06/27/00	88	0	7030	16100	20100
06/28/00	89	0	6960	15800	19700
06/29/00	90	0	7030	15800	19700
06/30/00	91	0	6730	15000	19300

DATABASE: FLOW78

Sacramento River flow at Colusa, Knights Landing, Feather River, and Sacramento.

date	day	SRC	SRKL	SRFR	SRSAC
03/20/00	-11	0	0	52400	63400
03/21/00	-10	0	0	47400	57800
03/22/00	-9	0	0	42400	51100
03/23/00	-8	0	0	38000	45500
03/24/00	-7	0	0	34800	41400
03/25/00	-6	0	0	33000	39100
03/26/00	-5	0	0	31600	37200
03/27/00	-4	0	0	30300	35600
03/28/00	-3	0	0	29200	34400
03/29/00	-2	0	0	28300	33700
03/30/00	-1	0	0	27700	32800
03/31/00	0	0	0	27300	32600
04/01/00	1	14400	13700	27300	32600
04/02/00	2	19500	14600	28200	33000
04/03/00	3	22000	22200	31800	36500
04/04/00	4	18300	20200	33200	38900
04/05/00	5	20800	19100	32400	37900
04/06/00	6	19500	21000	33700	39600
04/07/00	7	27800	20000	36200	42000
04/08/00	8	30900	26600	40000	46000
04/09/00	9	25700	29500	41100	47600
04/10/00	10	23500	29300	40600	47600
04/11/00	11	22000	28500	39300	46100
04/12/00	12	21000	27100	37600	44100
04/13/00	13	20000	25600	36100	42500
04/14/00	14	18800	23900	34500	40600
04/15/00	15	18900	22500	33200	39200
04/16/00	16	20200	21400	32900	38700
04/17/00	17	23000	23100	34600	39300
04/18/00	18	20800	24700	35000	39600
04/19/00	19	19300	23500	33500	38000
04/20/00	20	17800	21900	31900	36200
04/21/00	21	18800	20200	30600	34500
04/22/00	22	16700	19700	30200	35000
04/23/00	23	14700	18300	28600	34900
04/24/00	24	13700	16600	26800	33100
04/25/00	25	12300	14700	25900	32600
04/26/00	26	16800	15200	29100	35100
04/27/00	27	21800	17900	33200	39300
04/28/00	28	17500	21900	34200	40900
04/29/00	29	15200	19500	31300	38500
04/30/00	30	16500	17300	29800	36600
05/01/00	31	16200	15900	29900	36800
05/02/00	32	15700	15800	29600	36500
05/03/00	33	14900	15000	29100	37400
05/04/00	34	14400	14300	27900	36300
05/05/00	35	13900	13800	27200	35800
05/06/00	36	13500	13500	26700	35000
05/07/00	37	13200	13000	25800	34100
05/08/00	38	12900	12400	23900	32300
05/09/00	39	12200	11800	22500	30900
05/10/00	40	11700	11200	20800	29200
05/11/00	41	11300	10600	19200	27700
05/12/00	42	10800	9950	16500	24900
05/13/00	43	10500	9800	16100	23700
05/14/00	44	10400	9680	15900	23400
05/15/00	45	10500	9800	16000	23500
05/16/00	46	10600	10200	16300	22900
05/17/00	47	9960	9980	16300	22900
05/18/00	48	9390	9400	15800	23200
05/19/00	49	9090	8750	15000	21400
05/20/00	50	8960	8420	14300	20800
05/21/00	51	8810	8240	13800	20100
05/22/00	52	8710	8200	13700	19200
05/23/00	53	8580	8400	14100	19100
05/24/00	54	8270	8650	14300	19400
05/25/00	55	8140	8840	13800	19400
05/26/00	56	8050	8660	12600	17900
05/27/00	57	7950	8340	12900	18200
05/28/00	58	7740	8180	12500	17800
05/29/00	59	7690	7980	11800	17000
05/30/00	60	7580	7800	11900	17000
05/31/00	61	7460	7710	12100	17200
06/01/00	62	7410	7480	11400	16400
06/02/00	63	7190	6890	10500	14700
06/03/00	64	6860	6380	9770	13900
06/04/00	65	6530	6030	9330	13500
06/05/00	66	6380	6150	9240	13200
06/06/00	67	6270	5630	9520	13400
06/07/00	68	6540	5440	9670	13600
06/08/00	69	6720	5480	9830	13700
06/09/00	70	6710	5440	9470	12400
06/10/00	71	6740	5160	9360	12200
06/11/00	72	6930	5120	9420	12300
06/12/00	73	6730	5190	9510	12400
06/13/00	74	6700	4970	9210	12100
06/14/00	75	6750	4840	8950	11900
06/15/00	76	6920	4640	8820	11800
06/16/00	77	7160	4910	9120	12100
06/17/00	78	7250	5210	9330	12300
06/18/00	79	7250	5520	9650	12700
06/19/00	80	7230	5800	9800	12800
06/20/00	81	7250	5860	9540	12600
06/21/00	82	7160	5610	9220	12100
06/22/00	83	7140	5290	8910	11800
06/23/00	84	7100	5580	8870	11700
06/24/00	85	7080	5510	8850	11600
06/25/00	86	7270	5500	8850	11600
06/26/00	87	7530	5750	9070	11700
06/27/00	88	7530	5920	9330	12000
06/28/00	89	7570	6040	9530	12300
06/29/00	90	7590	6160	9620	12400
06/30/00	91	7650	6460	9890	12600

DATABASE: FLOW82
Sacramento River flow at Colusa, Knights Landing,
Feather River, and Sacramento.

date	day	SRKL	SRFR	SRSAC
03/20/00	-11	0	57500	69500
03/21/00	-10	0	56100	68300
03/22/00	-9	0	54500	67100
03/23/00	-8	0	52600	63000
03/24/00	-7	0	49600	59300
03/25/00	-6	0	46000	55800
03/26/00	-5	0	42200	52300
03/27/00	-4	0	38500	48300
03/28/00	-3	0	35400	45000
03/29/00	-2	0	33400	43000
03/30/00	-1	0	32900	42600
03/31/00	0	0	36900	47900
04/01/00	1	35900	55300	72800
04/02/00	2	36300	63100	83000
04/03/00	3	35500	65100	87500
04/04/00	4	36300	67400	88000
04/05/00	5	35500	66700	87100
04/06/00	6	33800	65200	85100
04/07/00	7	32900	63500	79100
04/08/00	8	31600	62200	75900
04/09/00	9	29900	61000	72000
04/10/00	10	27000	59900	69400
04/11/00	11	28000	62000	73900
04/12/00	12	38100	68000	93700
04/13/00	13	39000	69800	92900
04/14/00	14	39200	70300	87100
04/15/00	15	39600	69800	81100
04/16/00	16	40400	69600	83500
04/17/00	17	40100	69100	79800
04/18/00	18	39500	68500	82400
04/19/00	19	38100	67400	81500
04/20/00	20	35800	65600	79900
04/21/00	21	32800	64000	77400
04/22/00	22	27800	62400	74200
04/23/00	23	22400	60300	70800
04/24/00	24	19900	57900	68200
04/25/00	25	19000	55300	65700
04/26/00	26	18200	52800	63300
04/27/00	27	20000	50500	61000
04/28/00	28	24900	49900	59700
04/29/00	29	24600	50900	60500
04/30/00	30	22500	50800	60900
05/01/00	31	0	49600	60100
05/02/00	32	0	48600	59000
05/03/00	33	0	47700	57900
05/04/00	34	0	47100	57000
05/05/00	35	0	45700	55900
05/06/00	36	0	44300	54000
05/07/00	37	0	43100	53000
05/08/00	38	0	41600	51200
05/09/00	39	0	39200	49000
05/10/00	40	0	36900	47000
05/11/00	41	0	35000	45200
05/12/00	42	0	33400	43800
05/13/00	43	0	30900	41500
05/14/00	44	0	27600	38100
05/15/00	45	0	25200	36000
05/16/00	46	0	23300	34000
05/17/00	47	0	22300	33000
05/18/00	48	0	22700	32800
05/19/00	49	0	23300	33300
05/20/00	50	0	24800	34500
05/21/00	51	0	25100	33700
05/22/00	52	0	24700	32500
05/23/00	53	0	25000	31700
05/24/00	54	0	25300	32600
05/25/00	55	0	25700	33000
05/26/00	56	0	27800	35400
05/27/00	57	0	29700	39400
05/28/00	58	0	30600	41400
05/29/00	59	0	30300	41000
05/30/00	60	0	29300	39000
05/31/00	61	0	28400	37100
06/01/00	62	0	27600	36400
06/02/00	63	0	27500	36000
06/03/00	64	0	25900	34900
06/04/00	65	0	23400	32400
06/05/00	66	0	21200	30800
06/06/00	67	0	19700	28100
06/07/00	68	0	19000	27000
06/08/00	69	0	19900	28100
06/09/00	70	0	20400	28400
06/10/00	71	0	18900	26100
06/11/00	72	0	18500	26400
06/12/00	73	0	18600	26100
06/13/00	74	0	18800	26200
06/14/00	75	0	18700	25900
06/15/00	76	0	18900	26000
06/16/00	77	0	19200	26000
06/17/00	78	0	18700	25200
06/18/00	79	0	18300	24900
06/19/00	80	0	17700	24400
06/20/00	81	0	17100	23500
06/21/00	82	0	17000	23300
06/22/00	83	0	16800	22600
06/23/00	84	0	16500	22700
06/24/00	85	0	16200	22400
06/25/00	86	0	15500	21400
06/26/00	87	0	14800	19800
06/27/00	88	0	14800	19400
06/28/00	89	0	15000	19600
06/29/00	90	0	15000	20100
06/30/00	91	0	15500	20200
*** Total ***				
	4120	944600	******	******

```
Structure for database: B:CALC.dbf
Number of data records:        0
Date of last update   : 07/12/88
Field  Field Name  Type       Width    Dec
    1  DAY         Numeric        3
    2  DATE        Date           8
    3  MOLDISK     Numeric       15      2
    4  BOLDISK     Numeric       15      2
    5  SAC         Numeric        6
    6  VERONA      Numeric        6
    7  MOLSAC      Numeric        5      2
    8  MOLVER      Numeric        5      2
    9  BOLSAC      Numeric        5      2
   10  BOLVER      Numeric        5      2
** Total **                      74
```

```
Structure for database: B:FLOW.dbf
Number of data records:      103
Date of last update   : 07/12/88
Field  Field Name  Type       Width    Dec
    1  DATE        Date           8
    2  DAY         Numeric        3
    3  SRC         Numeric        6
    4  SRKL        Numeric        6
    5  SRFR        Numeric        6
    6  SRSAC       Numeric        6
** Total **                      36
```

DATABASE: PERAPPLY
Percent of each chemical applied per day.

bolero	molinate	date	lbnonbol	lbexbol	lbnonmol	lbexmol	moldisk	boldisk	day
0.000	0.000	04/15/00	0.00	0.00	0.00	0.00	0.00	0.00	15
0.000	0.004	04/16/00	0.00	0.00	0.00	0.00	0.00	0.00	16
0.000	0.021	04/17/00	0.00	0.00	0.00	0.00	0.00	0.00	17
0.000	0.062	04/18/00	0.00	0.00	0.00	0.00	0.00	0.00	18
0.000	0.028	04/19/00	0.00	0.00	0.00	0.00	0.00	0.00	19
0.000	0.012	04/20/00	0.00	0.00	0.00	0.00	0.00	0.00	20
0.000	0.014	04/21/00	0.00	0.00	0.00	0.00	0.00	0.00	21
0.000	0.081	04/22/00	0.00	0.00	0.00	0.00	0.00	0.00	22
0.000	0.071	04/23/00	0.00	0.00	0.00	0.00	0.00	0.00	23
0.000	0.045	04/24/00	0.00	0.00	0.00	0.00	0.00	0.00	24
0.000	0.129	04/25/00	0.00	0.00	0.00	0.00	0.00	0.00	25
0.000	0.266	04/26/00	0.00	0.00	0.00	0.00	0.00	0.00	26
0.000	0.466	04/27/00	0.00	0.00	0.00	0.00	0.00	0.00	27
0.000	0.249	04/28/00	0.00	0.00	0.00	0.00	0.00	0.00	28
0.000	0.881	04/29/00	0.00	0.00	0.00	0.00	0.00	0.00	29
0.000	0.897	04/30/00	0.00	0.00	0.00	0.00	0.00	0.00	30
0.185	1.801	05/01/00	0.00	0.00	0.00	0.00	0.00	0.00	31
1.295	2.494	05/02/00	0.00	0.00	0.00	0.00	0.00	0.00	32
0.294	2.273	05/03/00	0.00	0.00	0.00	0.00	0.00	0.00	33
1.647	2.433	05/04/00	0.00	0.00	0.00	0.00	0.00	0.00	34
1.525	3.430	05/05/00	0.00	0.00	0.00	0.00	0.00	0.00	35
1.482	3.895	05/06/00	0.00	0.00	0.00	0.00	0.00	0.00	36
0.706	3.976	05/07/00	0.00	0.00	0.00	0.00	0.00	0.00	37
1.957	3.972	05/08/00	0.00	0.00	0.00	0.00	0.00	0.00	38
1.015	3.130	05/09/00	0.00	0.00	0.00	0.00	0.00	0.00	39
2.006	3.776	05/10/00	0.00	0.00	0.00	0.00	0.00	0.00	40
0.663	1.998	05/11/00	0.00	0.00	0.00	0.00	0.00	0.00	41
3.334	4.792	05/12/00	0.00	0.00	0.00	0.00	0.00	0.00	42
0.875	4.060	05/13/00	0.00	0.00	0.00	0.00	0.00	0.00	43
0.518	3.661	05/14/00	0.00	0.00	0.00	0.00	0.00	0.00	44
1.224	3.917	05/15/00	0.00	0.00	0.00	0.00	0.00	0.00	45
3.230	3.287	05/16/00	0.00	0.00	0.00	0.00	0.00	0.00	46
3.895	3.270	05/17/00	0.00	0.00	0.00	0.00	0.00	0.00	47
2.446	1.373	05/18/00	0.00	0.00	0.00	0.00	0.00	0.00	48
5.012	5.136	05/19/00	0.00	0.00	0.00	0.00	0.00	0.00	49
3.802	4.151	05/20/00	0.00	0.00	0.00	0.00	0.00	0.00	50
1.716	4.833	05/21/00	0.00	0.00	0.00	0.00	0.00	0.00	51

DATABASE: PERAPPLY
Percent of each chemical applied per day.

bolero	molinate	date	lbnonbol	lbexbol	lbnonmol	lbexmol	moldisk	boldisk	day
2.979	3.087	05/22/00	0.00	0.00	0.00	0.00	0.00	0.00	52
7.024	2.553	05/23/00	0.00	0.00	0.00	0.00	0.00	0.00	53
1.768	3.444	05/24/00	0.00	0.00	0.00	0.00	0.00	0.00	54
3.418	1.253	05/25/00	0.00	0.00	0.00	0.00	0.00	0.00	55
2.667	2.159	05/26/00	0.00	0.00	0.00	0.00	0.00	0.00	56
4.858	2.831	05/27/00	0.00	0.00	0.00	0.00	0.00	0.00	57
5.327	1.807	05/28/00	0.00	0.00	0.00	0.00	0.00	0.00	58
5.794	2.162	05/29/00	0.00	0.00	0.00	0.00	0.00	0.00	59
11.144	1.451	05/30/00	0.00	0.00	0.00	0.00	0.00	0.00	60
1.819	0.080	05/31/00	0.00	0.00	0.00	0.00	0.00	0.00	61
3.430	1.176	06/01/00	0.00	0.00	0.00	0.00	0.00	0.00	62
3.127	0.660	06/02/00	0.00	0.00	0.00	0.00	0.00	0.00	63
1.549	0.433	06/03/00	0.00	0.00	0.00	0.00	0.00	0.00	64
1.039	0.604	06/04/00	0.00	0.00	0.00	0.00	0.00	0.00	65
0.809	0.319	06/05/00	0.00	0.00	0.00	0.00	0.00	0.00	66
0.475	0.172	06/06/00	0.00	0.00	0.00	0.00	0.00	0.00	67
0.053	0.208	06/07/00	0.00	0.00	0.00	0.00	0.00	0.00	68
0.198	0.024	06/08/00	0.00	0.00	0.00	0.00	0.00	0.00	69
1.380	0.343	06/09/00	0.00	0.00	0.00	0.00	0.00	0.00	70
0.356	0.092	06/10/00	0.00	0.00	0.00	0.00	0.00	0.00	71
0.389	0.065	06/11/00	0.00	0.00	0.00	0.00	0.00	0.00	72
0.779	0.090	06/12/00	0.00	0.00	0.00	0.00	0.00	0.00	73
0.792	0.057	06/13/00	0.00	0.00	0.00	0.00	0.00	0.00	74
0.000	0.013	06/14/00	0.00	0.00	0.00	0.00	0.00	0.00	75
0.000	0.029	06/15/00	0.00	0.00	0.00	0.00	0.00	0.00	76
0.000	0.000	06/16/00	0.00	0.00	0.00	0.00	0.00	0.00	77
0.000	0.000	06/17/00	0.00	0.00	0.00	0.00	0.00	0.00	78
0.000	0.000	06/18/00	0.00	0.00	0.00	0.00	0.00	0.00	79
0.000	0.000	06/19/00	0.00	0.00	0.00	0.00	0.00	0.00	80
0.000	0.000	06/20/00	0.00	0.00	0.00	0.00	0.00	0.00	81
0.000	0.000	06/21/00	0.00	0.00	0.00	0.00	0.00	0.00	82
0.000	0.000	06/22/00	0.00	0.00	0.00	0.00	0.00	0.00	83
0.000	0.000	06/23/00	0.00	0.00	0.00	0.00	0.00	0.00	84
0.000	0.000	06/24/00	0.00	0.00	0.00	0.00	0.00	0.00	85
0.000	0.000	06/25/00	0.00	0.00	0.00	0.00	0.00	0.00	86
0.000	0.000	06/26/00	0.00	0.00	0.00	0.00	0.00	0.00	87
0.000	0.000	06/27/00	0.00	0.00	0.00	0.00	0.00	0.00	88

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                                   DATABASE: PERAPPLY
                          Percent of each chemical applied per day.

 bolero   molinate  date        lbnonbol     lbexbol     lbnonmol     lbexmol      moldisk       boldisk   day

  0.000     0.000 06/28/00          0.00        0.00         0.00        0.00         0.00          0.00    89
  0.000     0.000 06/29/00          0.00        0.00         0.00        0.00         0.00          0.00    90
  0.000     0.000 06/30/00          0.00        0.00         0.00        0.00         0.00          0.00    91
  0.000     0.000   /  /            0.00        0.00         0.00        0.00         0.00          0.00    92
*** Total ***
100.001    99.996                   0.00        0.00         0.00        0.00         0.00          0.00  4173
```

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Structure for database: A:perapply.dbf
Number of data records:      78
Date of last update   : 07/02/86
Field  Field Name  Type       Width    Dec
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    2  MOLINATE    Numeric        6      3
    3  DATE        Date           8
    4  LBNONBOL    Numeric       14      2
    5  LBEXBOL     Numeric       14      2
    6  LBNONMOL    Numeric       14      2
    7  LBEXMOL     Numeric       14      2
    8  MOLDISK     Numeric       15      2
    9  BOLDISK     Numeric       15      2
   10  DAY         Numeric        3
** Total **                     110
```

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Structure for database: A:perptrn.dbf
Number of data records:      78
Date of last update   : 07/02/86
Field  Field Name  Type       Width    Dec
    1  BOLERO      Numeric        6      3
    2  MOLINATE    Numeric        6      3
    3  DATE        Date           8
    4  LBNONBOL    Numeric       14      2
    5  LBEXBOL     Numeric       14      2
    6  LBNONMOL    Numeric       14      2
    7  LBEXMOL     Numeric       14      2
    8  MOLDISK     Numeric       15      2
    9  BOLDISK     Numeric       15      2
   10  DAY         Numeric        3
** Total **                     110
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APPENDIX L

DRAFT

JUN 1985

THE DESIGN AND USE OF A CONCENTRATING/SAMPLING SYSTEM FOR THE DETERMINATION OF DISSOLVED TRACE ELEMENT CONCENTRATIONS AND SPECIATION IN NATURAL WATERS

W. M. Landing, G.A. Gill, and K. W. Bruland
University of California
Santa Cruz, CA 95064

Submitted to:
State of California Water Resources Control Board
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INTRODUCTION

There is a significant need, from the standpoint of "water quality", to develop accurate and non-contaminating sampling and analytical procedures for the determination of trace element concentrations and speciation in natural waters. Such procedures must be rigorously defined or characterized to reliably and adequately distinguish between the many possible chemical forms in which trace elements occur in aqueous systems. In response to the needs of the State of California Water Resources Control Board, this report describes our continuing research in the development and application of such procedures for the determination of potentially hazardous trace element species in rivers and other natural water resources.

To achieve this goal, a sampling system has been designed and constructed which provides time-integrated concentration (from ultra-trace levels) of many dissolved trace transition metals and metalloid species from natural waters. The sampling system employs filtration and ion-exchange chromatographic methods, for the separation and concentration of various dissolved trace elements from solution. Uncomplexed as well as kinetically "labile" complexed transition metal cations, strongly bound or "inert" metal-organic complexes, and oxyanionic metal and metalloid species can be isolated by this system. The ion-exchange resins have been characterized for their metal specificity and collection efficiency with respect to variations in pH, flow rate, and with and without the presence of several model organic substances known to form dissolved metal-organic complexes.

By modifying a previously published method, a technique has been developed for the production of a silica-immobilized 8-hydroxyquinoline cation exchange material (UCSC 8-HQ) which offers higher exchange capacity and stronger metal binding characteristics than other commercially available resins. In addition, a polystyrenedivinylbenzene-immobilized 8-hydroxyquinoline resin, soon to be commercially available (Sea-Chem), was tested under conditions found optimal for the other resins.

Finally, an integral part of the successful development of this methodology was the adoption of "clean" sampling and analytical techniques taken from our experiences in the precise and accurate measurement of dissolved trace elements in seawater (Bruland, et al. 1978; Bruland, et al., 1979; Bruland, 1980; Landing and Bruland, 1980; Bruland and Franks, 1983).

STUDY AREAS

Several field sampling experiments were undertaken to test and evaluate prototype systems. The sampling system was used to collect samples from the pristine Merced River in Yosemite National Park, the Russian River, and the more heavily impacted Sacramento River. A summary of collection sites and sampling details are given in Table 1.

Three sites were sampled on the Russian River. The northern-most site, Turula Vinyard (TV), lies a few miles downstream of the City of Ukiah, which is downstream of the input from the cities waste water treatment facility. The Wohler Dam (WD) site represents the source of water for the City of Santa Rosa and the surrounding area. The River Bend (RB) site lies downstream of the tributary input from the waste water treatment facilities for the City of Santa Rosa and a few miles upstream of Guerneville.

Five collection sites were occupied along the Sacramento River and adjacent local watersheds. The Ord Bend (OB) site is along a relatively unimpacted section of the river, upstream of the major agricultural and urban discharge sources. Within the City of Sacramento, the river was sampled at Bryte Station (BS) to the north of the city and at Freeport Marina (FM) to the south. To investigate the impact from agricultural sources, samples were obtained from a well mixed, rapidly flowing, agricultural drainage slough within the Colusa Wildlife Refuge (CWR). Finally, samples of drinking water were collected from the No. 12 tap at the City of Sacramento Water Plant (SWP).

MATERIALS AND METHODS

Preparation of Silica-immobilized 8-hydroxyquinoline Cation Exchange Resin

A procedure was developed at the University of California at Santa Cruz (UCSC) for the preparation of an silica-immobilized 8-hydroxyquinoline cation exchange resin (8-HQ). Preparation of the UCSC 8-HQ resin followed a modified version of the synthesis technique reported by Marshall and Mottola (1983). A variety of silica supports with varying pore-sizes and surface areas were used. In addition, to produce a large yield of final product, without using large solution volumes, a scaled-up synthesis was developed.

The modified silica-immobilization synthesis procedure was as follows. One hundred grams of an oven-dried (120° C, 12 hours) silica support (see Table 2) was placed in a clean, dry reflux apparatus with a solution consisting of 20 mL of aminophenyltrimethoxysilane (Petrarch Systems Inc.) and 180 mL of dry toluene (HPLC grade, stored over molecular sieves). After five hours of reflux with constant stirring, the arylamine product was filtered, rinsed with dry toluene and dried (75° C, 12 hours). This product was diazotized for 60 minutes at 0° C in a 1.0 L solution of 1.5 M $NaNO_2$ in 2 M HCl. The diazonium salt-silica product was filtered, rinsed three times with 50 mL of ice cold distilled and de-ionized water (DDW), and added to a 1.0 L solution of 0.7 M 8-hydroxyquinoline in 95% ethanol. This mixture was allowed to react for 60 minutes at 20 °C, until visible effervescence had ceased. The silica-immobilized 8-

hydroxyquinoline product (UCSC 8-HQ) was filtered, sequentially washed with 95% ethanol, a 1.0 M HCl/0.1 M HNO_3 acid mixture and DDW, and then air dried.

Because of the relatively low cost and ready availability of the K-60 silica support, this material was used to develop the scaled-up synthesis procedure. In three parallel experiments, 20 g of K-60 was refluxed for 5 hours in 200 mL of 10% aminophenyltrimethoxy silane in toluene. The arylamine silica products were then reacted with three different concentrations of the initial reaction materials:

(1) a 1000 mL solution of 0.3 M $NaNO_2$ in 2 M HCl;
(2) a 500 mL solution of 0.6 M $NaNO_2$ in 2 M HCl;
(3) a 200 mL solution of 1.5 M $NaNO_2$ in 2 M HCl;

The resulting diazotized products were subsequently reacted with stoichiometrically equivalent amounts of 8-HQ in solvent:

(1) a 1000 mL solution of 0.14 M 8-HQ in 95% ethanol;
(2) a 500 mL solution of 0.28 M 8-HQ in 95% ethanol;
(3) a 200 mL solution of 0.7 M 8-HQ in 95% ethanol.

Preparation of Resin Columns

Sampling columns were constructed of 9 mm (ID) X 12 mm (OD) Teflon tubing cut to 200 mm lengths. Top and bottom fittings were machined at UCSC to accommodate 1/8" MIPT X 3 mm (OD) Teflon tube connectors (Chemplast). The resins were supported in the columns with a porous polyethylene disc. Prior to assembly, all plastic parts were sequentially washed with acetone, dilute Micro detergent (Cole-Parmer), and DDW, soaked 24 hours in 6 M HCl and rinsed thoroughly with DDW. After assembly, the sampling system was further washed with 95% ethanol, DDW, a 2 M HCl/0.1 M HNO_3 mixture, and rinsed again with DDW.

Before packing in columns, the ion exchange resins were batch cleaned using acid solutions found most effective for eluting metals. Thus, AG1 X-8 was washed with 4 M HCl, the polystyrene 8-HQ and Chelex-100 resins were washed with 2.5 N HNO_3, while the UCSC 8-HQ and Duolite resins were washed with a 2 M HCl/0.1 M HNO_3 acid mixture. All reagents used for washing and eluting the resins were purified in a quartz sub-boiling distillation apparatus (Q-reagents)(Kuehner et al., 1972).

After batch rinsing with quartz-distilled water (QDW), the columns were filled from a resin slurry to a gravity packed volume of approximately 5 cm x 1 cm^2 (5 mL). The packed columns were then further cleaned by eluting with 25 one mL aliquots of the appropriate Q-acid mixture and rinsed with QDW until neutral effluent was obtained. The AG1 X-8 and Duolite S-587 were prepared in the Cl^- form, while Chelex-100, UCSC 8-HQ and polystyrene 8-HQ were prepared in the $(NH_4)^+$ form with dilute NH_4OH (pH = 9). All resin washing, Q-reagent and water preparations, and column manipulations were performed in the UCSC clean laboratory in class-100 laminar flow clean air benches.

Characterization of Ion Exchange Resins

The ion-exchange resins, described below, were characterized for uptake capacity, extraction efficiency, and metal binding specificity using several trace elements as functions of pH and flow rate, with various types of model dissolved organic substances in a simulated freshwater solution matrix.

(1) **AG1 X-8 (strong base) anion exchange resin (100-200 mesh, Bio-Rad).** AG1 X-8 is a cross-linked styrenedivinyl benzene polymer with 3.2 mmole/g of quaternary amine functional groups. In a typical anion exchange reaction the chromate anion, $Cr(VI)O_4^{2-}$ displaces two chloride ions on the resin.

(2) **Chelex-100 cation exchange resin (100-200 mesh, Bio-Rad).** Chelex-100 is a cross-linked styrenedivinylbenzene polymer with 2.9 mmole/g of imidodiacetate functional groups. In a characteristic exchange reaction, Cu^{2+} would displace two Na^+, NH_4^+ or H^+ ions, depending upon the cationic resin form prepared for use.

(3) **Silica-immobilized 8-hydroxyquinoline; 35-70 mesh, prepared in our laboratory (UCSC 8-HQ).** The UCSC 8-HQ cation exchange resin contains approximately 200 umole/g Cu^{2+} complexing capacity. In a typical exchange reaction, Cu^{2+} would displace either two Na^+, NH_4^+ or H^+ ions, depending on the resin form prepared.

(4) **Polystyrenedivinylbenzene-immobilized 8-hydroxyquinoline; 20-50 mesh (Sea-Chem, Canada).** This resin is similar to the UCSC 8-HQ resin, except that the substrate to which the active functional groups are attached is an organic polymer resin rather than silica.

(5) **Duolite S-587 anion exchange resin; 16-50 mesh (Diamond Shamrock/Rohm and Haas).** Duolite S-587 resin is a cross-linked

phenolic-formaldehyde polymer containing 1.9 mmole/g of secondary and tertiary amino functional groups. This resin is recommended (by the manufacturer) for the collection of high molecular weight Fulvic and Humic acids (FA/HA) from neutral solutions. Thus, it has bifunctional binding characteristics. That is, it has the potential to collect both anionic macromolecules and non-labile metal-organic complexes which do not interact with the cation exchange resins. Recent tests have also suggested that this resin has some cation exchange capacity (J. Donat, personal communication).

To simulate a freshwater solution matrix, free of dissolved organic materials, tap water was treated as follows. After adjustment to approximately pH 2, it was sequentially passed through (5 cm X 1 cm^2) columns of Amberlite XAD-8 (Rohm & Haas), Amberlite XAD-2 (Rohm & Haas) and silica immobilized C-18 (Waters Associates) adsorbent resins at 15 mL/min. These resin columns were pre-cleaned by washing with 250 mL of methanol and 500 mL of a 2 M HCl/0.1 M HNO_3 acid mixture.

The cation exchange resins were characterized in columns using carrier-free, radiotracers including: Mn(II)-54, Fe(III)-59, Co(II)-57, Cu(II)-64, Zn(II)-65 and Cd(II)-109 (New England Nuclear and Amersham). Due to the high specific activity of the radiotracers, it was possible to conduct experiments at environmentally natural sub-micromolar concentrations. The model organic compounds added to organic-free tap water for these experiments were nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA) and commercially available aquatic Fulvic and Humic acids (FA/HA, USGS Denver Water Resources Division).

The experiments were conducted as follows. Test solutions were forced through the resin using a 10-channel peristaltic pump. Initially, 100 mL of the organic-free tap water (pH 6.5) was passed through to condition the columns. This step was necessary to avoid large pH changes when test solutions are introduced. Next, from 500 to 1000 mL of test solution was pumped through the columns at flow rates of 2, 5 and 8.5 mL/min. The test solutions consisted of organic-free tap water, adjusted to pH 6.5 with concentrated NH_4Ac, a small volume of the radiotracers of interest, and (5 mg/L) of one of the organic chelators (NTA, EDTA, FA, or HA). The pH was adjusted using 6 M HCl and 1 M NaOH, monitoring the changes with a pH meter. The test solutions were allowed to equilibrate with the radiotracer for 10 to 12 hours before use. After passage of the test solutions, the resin in the columns was resuspended with DDW, and placed in 30 mL conventional polyethylene (CPE) vials.

Radiotracer activities were determined using a fixed-geometry Ge(Li) detector with electronic amplification. The decay events were recorded with a (Canberra) multichannel, pulse-height analyzer and compared to the original tap water solution containing radiotracer spikes in 5 mL of solution.

The anion exchange resin, AG1 X-8, was tested using spikes of stable Cr(VI), As(V) and Se(VI) which were added to neutral tap water at part per million concentration levels and pumped through 5 cm x 1 cm^2 columns of pre-cleaned AG1 X-8 prepared in the Cl$^-$ form. Due to the collection of HCO_3^- and CO_3^{2-} by this resin, degassing occurs upon acidification. Thus, the resin was first resuspended and placed in a Teflon beaker for several hours with 10 mL of 4 M HCl. This resin slurry was then poured back into the column and eluted with an additional 15 one mL aliquots of 4 M HCl.

Field Sampling Methods

The trace element sampling/concentrating system uses a peristaltic pump to continuously draw water through Teflon tubing from the sample source. The sample passes through a short length of silicon tubing (used in the pump-head), through a 0.20 um cartridge filter, a series of Teflon solenoid valves or three/four way connector fittings, the resin columns, and finally to collection containers (to measure sample volume concentrated).

The sampling system was developed for use with either an AC or DC power supply. The system designed to run on a 12 Volt battery is shown schematically in Figure 1. The sample is pulled through approximately 15 meters of 1.5 mm (ID) Teflon tubing encased in a protective sheath of Bevaline-IV flexible polyvinyl chloride/polyethylene tubing (Cole-Parmer). The Masterflex DC peristaltic pump (Cole-Parmer) uses a pump head containing stainless-steel rollers and a 25 cm length of 2 mm (ID) silicone tubing. The pump forces sample through a 0.20 um pore-size Flourex filter cartridge (Millipore), it is then split using Teflon fittings, and is passed through the resin columns, where effluent water is collected in 4 or 10 L Cubitainers (Cole-Parmer). The system will run continuously for 100 hours using a class-27 deep-cycle marine battery. Illustrated in Figure 1 is one possible column arrangement. Here, the sample stream is split to allow simultaneous collection using two different resins.

The sampling system designed for use with 110 - 130 Volt AC power is illustrated in Figure 2. In this design a Masterflex AC pump is used, while the other components are the same as for the DC system described above. After passage through the Fluorex filter cartridge, the sample enters a series of 3-way Teflon AC solenoid valves controlled by a programmable 4-channel timer/actuator (Chrontrol). When the valve is not actuated, the sample stream by-passes the attached resin column(s) and continues on to the next valve in series. When a valve is opened, the sample stream is diverted through the resin column(s) connected in-line. In this way, the sampler can operate continuously and unattended, collecting integrated subsamples over pre-selected time intervals. Sample contamination is effectively eliminated since the sample contacts only Teflon surfaces prior to interaction with the resins, with the exception of the short piece of silicone pump tubing and the polypropylene housing of the filter cartridge.

Also illustrated in Figure 2 are several possible column arrangements, including: A single column (line #1), two columns in series (line #2), a split stream arrangement, leading to two sets of columns in series (lines #3a and b), and two columns in series with different resins (line #4). This figure clearly illustrates the sampling versatility available with the system.

At the field sampling sites, the inlet tubing of the sampling system is placed approximately 0.3 meters below the river surface in well mixed water (2 to 3 meters from shore). Prior to sample collection, at least 2 L of river water is pumped through the system to fill the filter cartridge and thoroughly rinse wash solutions from the system. The resin columns were then attached and sampling was conducted using pre-determined sampling intervals (see Table 1). Typically, sampling is conducted at flow rates ranging from 2.5 to 5 mL/min until 1-5 liters of sample have been passed through each resin column.

Sample Analysis

After sampling, the columns are returned to the clean laboratory, resuspended to remove air pockets, and eluted with 25 one mL portions of the appropriate acid mixture. The AG1 X-8 was first degassed for at least 4 hours in 10 mL of 4 M HCl in Teflon beakers, then poured back into the columns, and further eluted with 15 one mL aliquots of 4 M HCl.

All samples were analyzed using a Perkin/Elmer, 5000 Atomic Absorption Spectrophotometer equipped with an HGA-500 graphite furnace atomizer, background correction lamps, and an AS-40 auto sampler. The analytical technique of standard additions was used to compensate for suppressed signals arising from matrix differences among the various column eluates. Optimized ashing and atomization conditions similar to those recommended by the manufacturer were used, including addition of 500 ppm Ni (II) for the determination of As and Se.

RESULTS AND DISCUSSION

Characterization of Si-Immobilized 8-Hydroxyquinoline Resin.

The total Cu exchange capacities of the UCSC 8-HQ cation exchange resins, prepared using four different silica support materials (see Table 2), was determined. For the test, 0.2 g of each oven-dried (70 °C, 12 hours) resin was placed in a 20 mL CPE vial with 20 mL of a 24 uM Cu^{2+} solution (buffered at pH 5 with 0.02 M NH_4Ac). The solutions were allowed to equilibrate for 30 to 120 minutes with periodic shaking. After the resin settled, the Cu concentrations in the supernatant solutions were measured by flame atomic absorption spectrometry (FAAS). The exchange capacity (umole/g) was calculated from the difference between the initial and final equilibrated Cu concentrations. The results are shown in Table 2.

The total Cu exchange capacity for ICN silica gel resin, prepared by exact duplication of the reported procedure (192 umole/g), was similar to that reported by Marshall and Mottola (1983, 1984) (between 191 and 260 umole/g). With the other silica supports, Cu exchange capacities ranged from 115 to 186 umole/g. The lowest values are believed due to inefficient heating and stirring during the initial silylation step of the synthesis. To test for possible interference effects due to Cu complexation effects by the ammonium acetate, the exchange capacity of the K-60 product was determined in 0.2, 0.02 and 0.002 M NH_4Ac solutions. Identical results were obtained at all three concentrations indicating that complexation by acetate did not significantly effect the exchange capacity determinations.

It is important to note that a significant time dependence of the Cu^{2+} exchange capacity was observed at pH 5 for all but the ICN product. The results in Table 2 illustrate that shaking times of 120 minutes were sufficient to approach the maximum exchange capacity.

All three products, prepared in the scaled-up synthesis procedure, had identical Cu^{2+} exchange capacities (Table 2). This indicates that solution volumes and reactant concentrations could be altered as long as stoichiometric quantities of reactants are maintained.

This modified synthesis has a number of useful features. It can be successfully conducted on large quantities of relatively inexpensive and readily available silica supports in a short period of time (48 hours or less). By using a silica support with a high surface area, a Cu^{2+} exchange capacity from 3 to 4 fold greater than the capacity of a commercially available silica-immobilized 8-HQ resin (60 umole/g, CPG-500, Pierce Chemical Co.) is obtained. The large particle size also permits higher flow rates at lower pressures for pumped system applications.

The total metal exchange capacity of the K-60 product was further determined using ten different trace metal cations as a function of pH in batch equilibrium experiments. Metal solutions of approximately 10 uM in 0.02 M NH_4Ac were prepared. Twenty milliliters of this solution was added to 0.2 g of resin, the pH adjusted with microliter quantities of HCl and NaOH, and the vials were shaken overnight (10 to 12 hours). The supernatant metal concentrations were measured by FAAS and compared to standards prepared in the same matrix. Blank experiments run on unreacted K-60 silica showed no significant exchange capacity for any of the metals tested over the pH range investigated.

The exchange capacities for Mn(II), Fe(III), and Co(II), are shown in Figure 3(a). For these metals, exchange capacity increased with pH. The exchange capacities for Ni(II), Cu(II) and Zn(II) were more constant with pH (Figure 3b), although the Zn capacity increased sharply at pH 8. Figure 3(c) shows that the exchange capacities for Cd(II) and Pb(II) increased slightly with pH, while the exchange capacity for Ag(I) decreased slightly above pH 7. The exchange capacity for Hg(II) was nearly constant between pH 5.5 and 8.5.

Some of the increased exchange capacities at higher pH may be attributed to the dissociation of a phenolic proton, which has an acid dissociation constant (pKa) between 7 and 7.5 (Marshall and Mottola, 1983). Metal cations can also form insoluble oxyhydroxides at high pH, although this should only be marginally important for $Fe(III)(OH)_3^o$, $Cu(II)O^o$, and $Hg(II)(OH)_2^o$ over the pH and concentration ranges used in these experiments (Stumm and Morgan, 1980; Turner et al., 1981). The 0.02 M NH_4Ac may also keep metals in solution (with respect to oxyhydroxide precipitation) without influencing their response to the resin, as found for Cu^{2+}.

These results show that the UCSC 8-HQ cation exchange resin has a high exchange capacity for the ten cations tested over the pH range examined. Thus, the resin should perform quite well in concentrating inorganic metal species and (kinetically) labile organic-metal complexes from natural waters. It has been shown previously that similarly prepared resins, containing this functional group, will effectively concentrate several cationic trace metals from solutions where high concentrations of Mg(II) and Ca(II), such as seawater, are present (Sturgeon et al., 1981).

Laboratory Studies of Resin Efficiency and Specificity

Modelling of Metal Complexation and Resin Interaction

As described earlier, a series of experiments were conducted investigating the collection efficiency and specificity of the various resins used in this work. In order to interpret the results from these experiments it is important to clearly understand the types of interactions occurring between the various dissolved solution species and the resin. One useful approach is with thermodynamic equilibrium modelling. Using the metal complex formation constants available in Martell and Smith (1974), and the iterative computer program HALTAFALL (Dyrssen et al., 1968), the equilibrium distributions of metal species in the radiotracer experiment solutions can be predicted.

Table 3 illustrates that at pH 6.5, in organic-free solutions, trace metals are distributed among free ion, acetate, ammonia, and hydroxide complexes. Hydroxide complex formation is extremely important in the aqueous chemistry of Fe(III) which forms a neutral $Fe(III)(OH)_3^0$ species (61%) and should be approaching some equilibrium with an amorphous oxyhydroxide precipitate (Stumm and Morgan, 1980). The remaining acetate, ammonia, and hydroxide complexes should behave as labile metals in solution. That is, the metal complex dissociation rates for these species are relatively rapid (Marcus and Kertes, 1969), allowing the resin to successfully compete for (the majority) of the metal ion in solution.

With the addition of the metal complexing ligand NTA, the solution equilibria shifts, and anionic metal(NTA) complexes become dominant solution forms, with the exception of $Mn(NTA)^{1-}$. Iron (III) is prevented from forming a precipitate by being held in solution, principally by Fe(NTA) complexes.

In the presence of EDTA the solution equilibria shifts again, and anionic metal-EDTA complexes dominate the solution speciation. These strong metal-organic complexes are considered particularly non-labile or inert, due to the "chelate-effect" induced by the multidentate complexing nature of the EDTA ligand.

The metal-organic complexation constants for Fulvic and Humic Acids are not well known. Because of the complexity of these high molecular weight, amphoteric organics, in many cases even the acid dissociation constants have only been reported as average values. These uncertainties will introduce some error into the equilibrium distributions presented in Table 3. To crudely account for these limitations, equilibrium calculations were conducted using metal-FA and metal-HA complexation constants which varied an order of magnitude above and below average values taken from Mantoura et al. (1978) and Christman and Gjessing (1983).

In the case of Mn(II), a value for the FA/HA conditional complexation constant of 5×10^4 yielded the equilibrium distribution at pH 6.5 given in Table 3. Using pKa values from

10^4 to 10^5 illustrated that the Mn(Ac) complex accounted for 5 to 12% of the total Mn in solution, while the free Mn(II) ion decreased in importance from 70 to 25% and the Mn(FA/HA) complex increased in importance from 20 to 70%, as the equilibrium value increased.

With Fe(III), changes in the metal/organic complexation constant simply shifted the pH at which $Fe(III)(OH)_3^0$ became the dominant species in "solution" (at the expense of Fe(FA/HA) complexes). Varying the equilibrium constant from 10^{12} to 10^{14} caused the transition pH to shift from 6.5 to 7.1.

For the remaining metals studied, Table 3 shows that the equilibrium distributions were divided among free metal ions, acetate complexes, and metal (FA/HA) complexes (using average metal (FA/HA) complexation constants). Distributions are also given for Hg(II) and Pb(II) which were not included in laboratory studies.

In a typical field sampling situation or laboratory study, sample solutions pass through cation exchange columns of Chelex-100 or UCSC 8-HQ followed in sequence by the Duolite S-587 anio exchange resin. Because of the relatively small solution volume within the resin bed, the solution is exposed to an extremely high effective concentration of resin binding sites. For Chelex-100, this site concentration is estimated at 1 M, using data provided by the manufacturer (2.9 milliequivalents per gram dry resin and 0.7 meq./mL wet resin). An effective site concentration of 0.2 M is estimated for UCSC 8-HQ (200 ueq./g dry resin and 100 ueq./mL wet resin). Thus, the total number of resin exchange sites in a 5 cm x 1 cm^2 (5 mL) column greatly exceeds the total amount of trace metal cations in solution. Thus, the effective concentration of binding sites remains constant.

As solution enters the resin bed, cationic metal species come in close contact with complexation sites on the resin occupied by other cations (eg. NH_4^+, Na^+, or H^+). When there is a higher affinity for the metal to complex with the resin rather than solution species there will be an exchange transfer between the metal and an chelated cation on the resin. In this manner, all labile complexes will dissassociate and the metal cations produced will exchange to the resin.

The degree to which the two cation exchange resins complex various trace metal species can also be predicted using the HALTAFALL computer program. Metal-resin and proton-resin association constants were chosen from the values presented by Martell and Smith (1974) for imidodiacetate ligands (primarily N-benzylimidodiacetate) and free 8-hydroxyquinoline. The total ligand binding site concentrations were as described above. For this calculation, it is necessary to assume that the solution reach equilibrium with the resin while in the column.

Table 4 shows that only EDTA is predicted to hold substantial fractions of the metals in solution. With NTA or FA/HA present, the resins should effectively outcompete solution ligands and sequester metals from solution. However, since the solution spends only a short time in contact with the resin, typically 20 to 90 seconds, we must consider that slowly dissassociating (less labile) organic complexes may not reach equilibrium within the resin bed. Under such conditions, anionic metal/organic complexes may pass through the cation exchange resins, especially at high flow rates. Ideally, these species will then be collected on the next column containing Duolite S-587 resin.

Cation/Duolite Resin Radiotracer Experiments

Metal Radiotracer collection efficiency and specificity results for Chelex-100 obtained at pH 6.5, flow rates from 2 to 8.5 mL/min, and with model organic complexing ligands present are shown in Figure 4. With few exceptions, Chelex-100 efficiently collected all of the metals studied in organic-free solution and with NTA and FA/HA added. Metals complexed by EDTA were poorly collected by the cation exchange resin. However, anionic metal/organic complexes which passed through the Chelex column were nearly quantitatively retained by the Duolite S-587 resin.

Only Fe(III) exhibited any significant decrease in retention by the Chelex-100 column with FA/HA added to solution. Again, nearly quantitative recovery (presumably of anionic metal fulvic and humic acid complexes) was observed with Duolite S-587 resin in series. These experimental results agree, in general, with the thermodynamic modelling predictions. This is especially significant considering the uncertainties in estimating complexation constants for fulvic and humic acids and the paucity of information available regarding the lability (or kinetic dissociation rates) of metal organic complexes.

The information obtained from repeating the collection efficiency experiments using the UCSC 8-HQ cation exchange resin are shown in Figure 5. The results are quite similar to that obtained using Chelex-100 and illustrate that EDTA and FA/HA can prevent quantitative recovery of Fe(III) on the cation exchange resin. Once again, anionic metal/organic complexes which passed the UCSC 8-HQ resin were quantitatively retained by the Duolite S-587 adsorbent resin at low flow rates. These results are also in good agreement with the equilibrium modelling predictions.

For both Chelex-100 and UCSC 8-HQ, Fe(III) recovery efficiencies were reduced in the presence of EDTA and FA/HA, particularly at higher flow rates. This could indicate that there is a rate-limiting effect associated with the dissociation of some metal/organic complexes. Moreover, this illustrates the utility of employing Duolite S-587 in-line in order to obtaining a measure of total dissolved metal concentrations. Significant losses of metal(EDTA) complexes were observed at the highest flow rate (8.5 mL/min, or about 3 column volumes per minute), indicating that Duolite S-587 interactions with some anionic metal/organic complexes may also be kinetically slow.

The trace metal recovery efficiency and specificity of these resin combinations were also tested as a function of pH (range 5.5 to 8.5) at a flow rate of 5 mL/min (Figure 6). Experimental conditions were as described previously. Recoveries using Chelex-100 were essentially quantitative for all metals except Fe(III) over the pH range tested. The Duolite S-587 resin collected a major fraction, but not all, of the Fe(III) not collected by the Chelex-100 column. In all cases, the amount of Fe(III) not recovered by both columns was ≤ 20 % . Similar results were obtained using the UCSC 8-HQ resin (Figure 7), except that the

Fe(III) recovery losses in organic-free solution were more significant (30 to 40% at pH greater than 6.5). Precipitation and non-quantitative collection of $Fe(III)(OH)_3^o$ may be responsible for this poor recovery. However, Chelex-100 in combination with Duolite S-587 collected Fe(III) with good efficiency over the entire pH range.

These experiments demonstrate 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. These results also illustrate that the dissociation kinetics of dissolved metal-organic complexes can influence the efficiency of the cation exchange resins, especially at higher flow rates (greater than 5 mL/minute). Apparently, interaction kinetics between Duolite S-587 and dissolved metal-organic complexes can also limit the collection efficiency at high flow rates, although this was only significant in the case of metal-EDTA complexes.

Preliminary results for the commercially available polystyrenedivinylbenzene 8-hydroxyquinoline (PSDB 8-HQ) resin are presented in Figure 8. The PSDB 8-HQ resin was tested for the uptake and release of Cd, Mn, and Zn only, at pH 6.0, and a flow rate of 2 mL/min. In organic-free solution, the PSDB 8-HQ resin effectively concentrated these trace metals. With NTA and EDTA present, however, the PSDB 8-HQ resin proved to have a somewhat weaker chelating ability than the UCSC 8-HQ resin. EDTA was able to successfully outcompete the resin for the majority of the Cd and Zn, as was the case for the Chelex-100 resin. As before, the Duolite S-587 resin quantitatively retained the remaining organic-metal fraction.

Our interest in the PSDB 8-HQ resin is three-fold. First, it is scheduled to be commercially available. Second, the low metal content of the organic matrix avoids contamination problems often associated with silica supports. Third, the PSDB based 8-HQ resin is much more stable to basic and acidic conditions than the silica-immobilized resin. Consequently, this resin can be more rigorously cleaned and repeatedly eluted.

We were only able to acquire 20 grams of Sea Chem's prototype resin for our preliminary studies. Sea Chem is currently attempting to manufacture kilogram quantities of resin. When this is accomplished, the PSDB 8-HQ resin, together with Chelex-100 and Duolite S-587, are likely to be resin combinations of choice.

Anion Resin

The AG1 X-8 anion exchange resin was tested for uptake and release efficiencies using stable oxyanions spikes in organic-free tap water solutions at pH 6.5. Metal concentrations in acid eluates were measured using FAAS. The Agl X-8 resin exhibited very good overall removal and elution efficiency (greater than 95%) for chromate, arsenate and selenate. We are continuing our studies with this resin to determine its suitability for use with other oxyanionic metallic and metalloid species.

FIELD SAMPLING PROGRAM

Russian River

Trace metal analytical results for Cu, Zn, Cd, and Pb from samples collected at three sites on the Russian River during early May, 1984 are presented in Table 5. Total dissolved metal (TD "metal") concentrations, were obtained by summing the amount of metal retained on the cation exchange column and the Duolite S-587 resin.

Total Dissolved Cu and TD Pb show the best concentration agreement among the simultaneously collected resin pairs. This good agreement for Cu most likely resulted because of the amount of Cu collected. In all cases, the analytical Cu signal was well above the blank detection limit (see Table 10). Moreover, these results suggest that a substantial fraction of the TD Cu, and perhaps TD Zn, was associated with dissolved organic matter (30 to 70% and 4 to 79%, respectively).

The results for TD Zn exhibited significantly poorer agreement among the resin column pairs. In part, this was due to the small amount of Zn isolated and the high Zn blank, which lowers the analytical detection limit (see Table 10). Note that the UCSC 8-HQ/Duolite pair consistently gave higher values for TD Zn. At the Turula Vineyard site, where the highest TD Zn concentrations were observed (200 to 500 ppt), only 4 to 7% of the TD Zn was complexed with dissolved organic matter. Total dissolved Zn concentrations were uniformly lower at the downstream Wohler Dam and River Bend sites (14 to 92 ppt), and a higher fraction of TD Zn was organically complexed (up to 80%).

For both Cu and Zn, Chelex-100 retained a smaller fraction of the TD metal compared to the UCSC 8-HQ resin. Consequently, larger amounts of metals were typically retained on the Duolite

S-587 column used in series with the Chelex-100 resin. Because the total amount of metal collected is in good agreement for both resin pairs, this suggests that the Duolite resin collects any metal not retained by the cation chelating resin. This result is consistent with the information from the laboratory studies using radiotracers and model organic ligands.

Cadmium concentrations were also close to the detection limit, but still showed relatively consistent agreement for TD Cd among the resin column pairs. In agreement with Cu and Zn, TD Cd was higher at the Turula Vineyard site (2.5 to 4.1 ppt) than at either downstream location (0.2 to 1.2 ppt). No organically complexed Cd was observed on the Duolite resin.

Total dissolved Pb concentrations also show reasonable concentration agreement for both resin pairs. It is important to note that the collection efficiencies of the cation exchange resins for cationic Pb^{2+} and Pb species were not tested. Total dissolved Pb concentrations were low, less than 40 ppt at all sites, with a minimum value of 14 ppt. An organically complexed Pb fraction was not detected.

Oxyanion concentrations for Cr, As and Se, collected using AG1 X-8, are shown in Table 9. Dissolved Cr concentrations ranged from 0.2 to 0.7 ppb, dissolved As from 0.3 to 0.9 ppb, and dissolved Se from 27 to 87 ppt (which was near the detection limit). No obvious upstream versus downstream trend was observed for these elements.

Sacramento River

Samples were collected from three locations along the

Sacramento River and at an agricultural drain in the Colusa Wildlife Refuge (a local watershed) during late May, 1984. In addition, a more detailed study, where triplicate resin column pair collections were obtained, was conducted in April 1985. Labile, organically associated, and total dissolved metal concentrations for Cu, Zn, Cd, and Pb for the May 1984 study are given in Table 6. The results for Cu, Zn, Cd, and Fe for the April 1985 study are given in Table 7.

Total dissolved Cu concentrations showed excellent concentration agreement between the two resin pair systems at all five sites. Higher TD Cu concentration were observed in the Colusa Wildlife Refuge agricultural drain (4.8 ppb) and at the water treatment facility (2.9 ppb) compared to the river stations (range 1.1 to 1.6 ppb). From 56 to 75% of the TD Cu was organically complexed with respect to Chelex-100. As expected, organic Cu complexation was less significant (6 to 59%) based on the UCSC 8-HQ/Duolite resin pair. There was no obvious difference in the percentage of Cu organically complexed between the river stations and the Colusa Wildlife Refuge agricultural drain. At the water treatment facility, however, the fraction of organically complexed Cu was slightly lower (21%) than at the other study sites. Excellent replication was obtained for all Cu fractions isolated using the Chelex/Duolite and UCSC 8-HQ/Duolite resin pairs during the more detailed study in April 1985 (Table 7). Moreover, the TD Cu concentrations for this latter study agree very well with previous observations. These consistencies lend considerable support to the reliability of the system.

In contrast, TD Cd concentrations were lowest in the agricultural drain (2.8 to 2.9 ppt) and showed some variability at the river sites (4.6 to 13 ppt) and in the Water Treatment Plant (3.6 to 6.4 ppt). It is important to note that for the 1984 collections, concentrations were all near the detection limit (see Table 10). This most likely accounts for much of the reported variability. No significant amounts ($\leq$ 5%) of organically complexed Cd were detected. Total dissolved Cd concentrations obtained in the 1985 study (6.7 to 8.9 ppt) fell within the range of previous observations (2.8 to 13 ppt). Total dissolved Cd concentrations collected by the UCSC 8-HQ Duolite resin pair were slightly lower than that for the Chelex/Duolite resin pair (6.8 ± 0.2 vs. 8.4 ± 0.4 ppt, respectively).

Total dissolved Zn concentrations were highest at the Ord Bend and Bryte Station sites (300 to 600 ppt and 550 to 590 ppt, respectively) and were similar to TD Zn concentrations observed at the Water Treatment Plant (350 to 370 ppt). At Freeport Marina in 1985, TD Zn concentrations (220 to 250 ppt) were almost half that found at the 1984 river stations described above. Good agreement was observed between the resin pair systems in the 1985 study for TD Zn (219 ± 8 vs. 249 ± 11 ppt). In general, no significant amounts ($\leq$ 5%) of organically complexed Zn were found, with the exception of the Colusa Wildlife Refuge site, where 30 to 50% of the TD Zn was organically complexed.

Total dissolved Pb concentrations were highest at the upstream Ord Bend site (48 to 59 ppt) and in the agricultural drain (47 to 53 ppt). Lower TD Pb concentrations were found at the Bryte site (10 to 15 ppt) and in the Water Treatment Plant (9 to 25 ppt). Organically complexed Pb was barely detectable (3 to 11% of the TD Pb) in a few samples.

For the 1985 study, TD Fe measurements were conducted to test the resin column system on an element for which modelling predictions and laboratory studies show significant interactions with model organic ligands. As shown in Table 7, Fe concentrations did not replicate as well as for other trace metals and the UCSC 8-HQ/Duolite resin pair yielded slightly higher values for TD Fe (1.3 vs. 1.9 ppb). Much of this variability can be explained by the high Fe blanks associated with the Duolite and UCSC 8-HQ resins (see Table 10). It is also possible that some of the variability was due to failure of the resin to successfully outcompete organically complexed Fe forms, particularly for Chelex-100 (see the radiotracer experiments). Thus, it is possible that the dissolved Fe results reported are only minimum estimates. Nevertheless, the resin column pairs suggest, as previous studies predicted, that substantial fractions of TD Fe are organically complexed (between 29 and 88%).

The concentrations of dissolved anionic Cr, As and Se in the Sacramento River samples are reported in Table 9. Dissolved Cr concentrations were highest and similar at the upstream Ord Bend site and in the Water Treatment Plant (0.32 and 0.33 ppb, respectively). In contrast, dissolved As was highest in the agricultural drain (2.5 ppb) compared to the Water Treatment Plant (0.5 ppb). Dissolved As concentrations at the other two river sites were similar (between 1.8 and 1.9 ppb). Dissolved Se concentrations were also high in the agricultural drain (102 ppt) compared to the other sites (range: 31 to 43 ppt).

To summarize, in the 1984 study total dissolved concentrations of Cu, Zn, Cd, As and Se were similar between the upstream Ord Bend and downstream Bryte Station locations, while Pb and Cr concentrations were elevated at the upstream stations. Total dissolved Cu concentrations were slightly higher in the Water Treatment Plant than in the river, while this trend was reversed for dissolved As. In addition, higher concentrations of dissolved As and Se, and TD Cu were found in the Colusa Wildlife Refuge agricultural drain. In the 1985 study, concentrations of Cu and Cd at Freeport Marina were similar to values obtained at nearby Bryte Station in 1984. Significantly lower concentrations were observed for Zn in the 1985 study between these study sites. Whether this reflects changes in Zn concentrations or improvements in maintaining contamination is not clear. Finally, evidence for metal-organic complexation was most significant for Cu and Fe. In most cases, only small fractions (generally $\leq$ 5%) of organically complexed Cd, Zn, and Pb were observed.

Merced River

A sampling site on the Merced River was occupied in April 1985 to critically evaluate the performance of the resin column sampling system. In contrast to the other rivers studied, the Merced River is relatively pristine. At the sampling site, it has a much lower total dissolved solid (mean = 25 mg/L) and suspended load (range: 5 to 23 mg/liter), and typically has a much lower pH (between 5.9 and 6.9) (Sorensen, 1982; USGS, 1982). These factors suggest that the Merced may have markedly lower dissolved metal concentrations and perhaps significantly different metal speciation. Labile, organically associated, and total dissolved metal results for Cu, Zn, Cd, and Fe obtained for three simultaneously collected resin pair samples are given in Table 8.

The Chelex/Duolite and UCSC/Duolite resin pair systems gave metal concentrations that replicated well and yielded TD concentrations that were in good agreement for the metals studied, given the extremely small amounts of metals concentrated. In many cases, the total amount of metal isolated was less than or slightly higher than the analytical blank value. This arose, in part, from the small volumes ($\leq$1.2 liters) of solution preconcentrated. Also, TD Cu in the Merced River were 10 to 30 times lower than in the Russian or Sacramento Rivers. Total dissolved Cd and Zn concentrations were comparable to Russian River values (see Table 11). In contrast, TD Fe concentrations were 2 to 7 times higher than in the Sacramento River.

Large fractions of Cu and Fe were organically complexed (57-83% and 6-71%, respectively) based on the Chelex-100/Duolite resin pairs. Only small amounts (3-6%) of TD Zn were organically complexed. Suprisingly, there appears to be a significant amount of organically complexed Cd (29 to 87%), although this feature may be fortuitous and simply due to the small amount of Cd collected in relation to blank levels. In general, the fractionation of metals into labile and organically associated forms is consistent with that observed at the other study sites, with the possible exception of Cd.

CONCLUSIONS

Total dissolved concentrations of Zn, and Cd were generally higher in the Sacramento River than in the Russian or Merced Rivers. Substantially lower TD Cu concentrations were observed at the Merced River compared to the Russian and Sacramento Rivers. In contrast, TD Fe concentrations were slightly elevated in the Merced compared to the Sacramento River. There was no substantial difference for Pb concentrations between the Sacramento and Russian Rivers. To a first approximation, the degree of organic complexation was quite similar between the three river systems. However, the dissolved metal-organic complexes collected from these two rivers appear to be less labile than those formed in the laboratory studies using commercially available reference Fulvic and Humic Acids.

The two cation exchange resins used in this work provide different measures of the lability of dissolved metals. This results from the strength of the metal-organic complex relative to the strength of the metal-resin interaction. Our findings suggest that most metals tend to form stronger bonds with the UCSC 8-HQ resin relative to Chelex-100. Thus, the UCSC 8-HQ resin was capable of sequestering more metals from organically associated metal complexes than was Chelex 100. By placing a cation exchange resin in series with the Duolite S-587 resin column, it is possible to provide a reasonable measure of both the labile cationic and the kinetically inert or organically associated dissolved metals in solution. By summing these two fractions an estimate of total dissolved metal concentrations is obtained. That it is possible to perform such a fractionation at such extremely low trace (and ultra trace) levels is noteworthy.

In many cases, the field observations were hindered by detection limits (e.g. Zn, Cd, and Pb). In the most recent field tests (April 1985) it was possible to substantially lower analytical blanks (see Table 10) and thereby markedly lower detection limits. Because of such improvements it is now possible to conduct trace element studies in relatively pristine waters, such as the Merced River. The measurements reported here also illustrate the range of metal concentrations, and clearly demonstrate that metal contents are substantially lower than previously reported by another independent laboratory. The disparity between our results and previous reports resides in detection limits, which for the other laboratory were high and precluded them from obtaining accurate determinations (Table 10).

Table 11 contains a brief comparison between our results and the average dissolved trace element concentrations reported recently by Martin and Whitfield (1983) for the world's rivers. The only large difference between the world average values and our results is for dissolved Zn. Our results for TD Zn are two orders of magnitude lower than reported for World average river water. This result is not suprising in light of recent investigations. For example, Shiller and Boyle (personal communication) have data, from a number of major rivers, which suggest that most literature values for dissolved Zn are <u>at least</u> an order of magnitude too high. This discrepancy most likely reflects the extreme sampling and analytical precautions necessary to collect uncontaminated samples for dissolved Zn and, by analogy, many other dissolved metals in uncontaminated natural water systems.

The sampling system has proven to be reasonably simple to operate and quite successful at collecting uncontaminated trace metal samples. The analytical results obtained have provided a good first estimate of total dissolved trace metal and metalloid concentrations of a number of trace elements in several California rivers. This report provides the preliminary background material necessary to devise more detailed sampling schemes regarding site location and sampling procedures in order to more fully characterize the aqueous geochemistry of several trace transition elements in river systems.

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Table 1

Sites Occupied and Sample Types Collected

Sampling Site	Resin[1]	Collection Date	Volume (liters)
<u>Russian River</u>			
Turula Vineyards	Chelex/Duolite	5-5-84	3.80
	UCSC 8-HQ/Duolite	to	5.69
	Agl X-8	5-9-84	3.41
Wholer Dam	Chelex/Duolite	5-8-84	7.20
	UCSC 8-HQ/Duolite	to	12.9
	AGl X-8	5-9-84	3.52
	Chelex/Duolite	5-9-84	6.24
	UCSC 8-HQ/Duolite	to	4.52
	AGl X-8	5-10-84	4.43
	Chelex/Duolite	5-10-84	8.13
	UCSC 8-HQ/Duolite	to	5.43
	AGl X-8	5-11-84	4.75
River Bend	Chelex/Duolite	5-9-84	4.39
	UCSC 8-HQ/Duolite	to	8.67
	AGl X-8	5-10-84	4.82
	Chelex/Duolite	5-10-84	6.12
	UCSC 8-HQ/Duolite	to	8.49
	AGl X-8	5-11-84	6.88
<u>Sacramento River</u>			
Ord Bend	Chelex/Duolite	5-29-84	6.97
	UCSC 8-HQ/Duolite	to	5.40
	AGl X-8	5-30-84	5.26
Bryte	Chelex/Duolite	5-31-84	6.84
	UCSC 8-HQ/Duolite	to	7.52
	AGl X-8	6-1-84	4.04
Colusa Wildlife Refuge	Chelex/Duolite	5-30-84	5.90
	UCSC 8-HQ/Duolite	to	3.34
	AGl X-8	5-31-84	2.57
City of Sacramento, Water Treatment Facility	Chelex/Duolite	5-31-84	6.76
	UCSC 8-HQ/Duolite	to	9.32
	AGl X-8	6-1-84	4.44

Table 1 (cont.)

Sampling Site	Resin[1]	Collection Date	Volume (liters)
Freeport Marina[2]	Chelex/Duolite	4-5-85 to 4-7-85	2.03, 2.20, 2.37
	UCSC 8-HQ/Duolite		2.08, 2.70, 1.57
<u>Merced River</u>			
Yosemite National[2] Park-Happy Isles	Chelex/Duolite	3-16-85 to 3-17-85	0.942, 0.808 0.407
	UCSC 8-HQ/Duolite		0.898, 1.23 0.361

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[1] Chelex: Chelex-100, cation exchange resin; 100-200 mesh, (Bio-Rad)

Duolite: Duolite S-587, anion exchange resin; 16-50 mesh, (Diamond Shamrock/Rohm and Haas)

UCSC 8-HQ: Silica-immobilized 8-hydroxyquinoline; 35-70 mesh, prepared at the University of California at Santa Cruz

AG1-X8: AG1-X8, a strong base anion exchange resin; 100-200 mesh (Bio-Rad).

[2] Three simultaneous resin pair collections were obtained.

Table 2

Properties and Cu(II) Exchange Capacities of the Silica Supports used in the Synthesis of Silica-immobilized 8-hydroxyquinoline

Resin Property/ Exchange Capacity	Kieselgel 60 (K-60)[1]	MN-Kieselgel (MNK)[2]	TLC Si-gel (ICN)[3]	Porasil A (P-A)[4]
Particle Size (um)	210-500	105-210	5-15	75-125
Mean Pore Diameter (nm)	6	-	6	10
Mean Surface Area (m^2/g)	550	500	550	350-500
Exchange Capacity (umol/g) (pH=5; 0.02 M NH_4Ac)	116-158	120-162	192	124-186
Normal Reagent Conc.	145			
2X " "	145			
5X " "	145			
Time Dependence of Exchange Capacity (umol/g)				
30 min.	24	36	187	63
60 min.	102	148	189	176
120 min.	116	162	192	186

[1] K-60: E. Merck

[2] MNK: Brinkmann Instrument Co.

[3] ICN: ICN Pharmaceuticals

[4] P-A: Waters Associates

Table 3

Predicted Trace Metal Thermodynamic Speciation Equilibrium using the HALTAFALL Computer Modelling Program

Metal	organic-free		NTA[1]		EDTA[2]		FA/HA[3]	
	Species	%	Species	%	Species	%	Species	%
Mn(II)	Mn^{2+}	84	Mn^{2+}	58	Mn^{2+}	<1	Mn^{2+}	38
	$Mn(Ac)^0$	16	$Mn(Ac)^0$	11	$Mn(EDTA)^{2-}$	99	$Mn(Ac)^0$	7
			$Mn(NTA)^{1-}$	31			$Mn(L)^{n-}$	55
Fe(III)	Fe^{3+}	<1	Fe^{3+}	<1	Fe^{3+}	<1	Fe^{3+}	<1
	$Fe(OH)_2^{2+}$	39	$Fe(NTA)^0$	1	$Fe(EDTA)^{1-}$	91	$Fe(OH)_3$	9
	$Fe(OH)_3$	61	$Fe(NTA)_2^{3-}$	4	$Fe(OH)(EDTA)^{2-}$	9	$Fe(OH)_3^0$	9
			$Fe(OH)(NTA)^{1-}$	90			$Fe(L)^{n-}$	85
			$Fe(OH)_2(NTA)^{2-}$	5				
Co(II)	Co^{2+}	73	Co^{2+}	<1	Co^{2+}	<1	Co^{2+}	43
	$Co(Ac)^0$	27	$Co(NTA)^{1-}$	99	$Co(EDTA)^{2-}$	99	$Co(Ac)^0$	16
							$Co(L)^{n-}$	40
Cu(II)	Cu^{2+}	21	Cu^{2+}	<1	Cu^{2+}	<1	Cu^{2+}	<1
	$Cu(NH_3)_2$	11	$Cu(NTA)^{1-}$	99	$Cu(OH)(EDTA)^{2-}$	99	$Cu(L)^{n-}$	99
	$Cu(Ac)^o$	42						
	$Cu(Ac)_2^{2-}$	23						
Zn(II)	Zn^{2+}	69	Zn^{2+}	<1	Zn^{2+}	<1	Zn^{2+}	9
	$Zn(Ac)^o$	26	$Zn(NTA)^{2-}$	99	$Zn(EDTA)^{2-}$	99	$Zn(Ac)^o$	4
	$Zn(Ac)_2^{2-}$	5					$Zn(L)^{n-}$	86
Cd(II)	Cd^{2+}	40	Cd^{2+}	<1	Cd^{2+}	<1	Cd^{2+}	18
	$Cd(Ac)^o$	43	$Cd(NTA)^{1-}$	98	$Cd(EDTA)^{2-}$	99	$Cd(Ac)^o$	20
	$Cd(Ac)_2^{2-}$	17					$Cd(Ac)_2^{2-}$	8
							$Cd(L)^{n-}$	54

Table 3 (cont.)

Metal	organic-free		NTA[1]		EDTA[2]		FA/HA[3]	
	Species	%	Species	%	Species	%	Species	%
Hg(II)	Hg^{2+}	2					Hg^{2+}	<1
	$Hg(Ac)_4^{6-}$	98					$Hg(L)^{n-}$	99
Pb(II)	Pb^{2+}	12					Pb^{2+}	9
	$Pb(Ac)^{o}$	51					$Pb(Ac)^{o}$	37
	$Pb(Ac)_2^{2-}$	34					$Pb(Ac)_2^{2-}$	25
	$Pb(OH)^{1+}$	3					$Pb(OH)^{1+}$	2
							$Pb(L)^{n-}$	26

[1] NTA= nitrilotriacetic acid

[2] EDTA = ethylenediaminetetraacetic acid

[3] FA/HA = Fulvic and Humic Acids

Table 4

Thermodynamic Speciation of Trace Metal Solutions in Equilibrium With Chelating Resins Using the HALTFALL Computer Program

Metal	Resin	NTA[a]		EDTA[b]		FA/HA[c]	
		Species	%	Species	%	Species	%
Mn(II)	Chelex	$Mn(R)_1$	>99	$Mn(EDTA)_1$	>99	$Mn(R)_1$	>99
	8-HQ	$Mn(R)_1$	>99	$Mn(EDTA)_1$	>99	$Mn(R)_1$	>99
Fe(III)	Chelex	Fe(OH)(R)	15	Fe(EDTA)	90	Fe(OH)(R)	15
		$Fe(OH)_2(R)$	85	Fe(OH)(EDTA)	9	$Fe(OH)_2(R)$	85
	8-HQ	$Fe(OH)_2(R)$	>99	Fe(EDTA)	91	$Fe(OH)_2(R)$	>99
				Fe(OH)(EDTA)	9		
Co(II)	Chelex	$Co(R)_2$	>99	Co(EDTA)	51	$Co(R)_2$	>99
				$Co(R)_2$	49		
	8-HQ	Co(R)	>99	Co(EDTA)	>99	Co(R)	>99
Cu(II)	Chelex	$Cu(R)_2$	>99	Cu(OH)(EDTA)	>99	$Cu(R)_2$	>99
	8-HQ	Cu(R)	>99	Cu(OH)(EDTA)	>99	Cu(R)	>99
Zn(II)	Chelex	$Zn(R)_2$	>99	Zn(EDTA)	56	$Zn(R)_2$	>99
				$Zn(R)_2$	44		
	8-HQ	Zn(R)	98	Zn(EDTA)	>99	Zn(R)	>99
		Zn(NTA)	2				
Cd(II)	Chelex	Cd(R)	3	Cd(EDTA)	98	Cd(R)	2
		$Cd(R)_2$	97	$Cd(R)_2$	2	$Cd(R)_2$	98
	8-HQ	Cd(NTA)	1	Cd(EDTA)	>99	Cd(R)	>99
		Cd(R)	99				

[a] NTA= nitrilotriacetic acid (26 uM)

[b] EDTA = ethylenediaminetetraacetic acid (17 uM)

[c] FA/HA = Fulvic and Humic Acids (30 ueq/L)

(R) = resin binding ligand

Conditions: pH = 6.5; NH_4Ac = 0.03 M; Chelex-100 = 1 M;
UCSC 8-HQ = 0.2 M

Table 5

Labile, Organically-Associated, and Total Dissolved Metal Concentrations for the Russian River, May 1984.

Sampling Site/ Resin Column	Copper (ppb)	Zinc (ppt)	Cadmium (ppt)	Lead (ppt)
Turula Vineyard				
Chelex	0.37 (32%)	200 (93%)	4.1 (28%)	28 (97%)
Duolite	0.78 (68%)	15 (7%)	*[a]	1 (3%)
Total	1.15	215	4.1	29
UCSC 8-HQ	0.62 (76%)	470 (96%)	2.5	23
Duolite	0.20 (24%)	21 (4%)	*	*
Total	0.82	491	2.5	23
Wohler Dam (1)				
Chelex	0.13 (21%)	11 (69%	1.2	24
Duolite	0.50 (79%)	5 (31%)	*	*
Total	0.63	16	1.2	24
UCSC 8-HQ	0.45 (79%)	31 (42%)	0.88	19
Duolite	0.12 (21%)	43 (58%)	*	*
Total	0.57	74	0.88	19
Wholer Dam (2)				
Chelex	0.13 (36%)	30 (61%)	0.67	28
Duolite	0.23 (64%)	19 (39%)	*	*
Total	0.36	49	0.67	28
UCSC 8-HQ	0.70 (52%)	87 (95%)	1.0	40
Duolite	0.64 (48%)	5 (5%)	*	*
Total	1.34	92	1.0	40
Wholer Dam (3)				
Chelex	0.10 (20%)	20 (51%)	0.40	22
Duolite	0.41 (80%)	19 (49%)	*	*
Total	0.51	39	0.40	22
UCSC 8-HQ	0.66 (86%)	53 (91%)	0.29	33
Duolite	0.11 (14%)	5 (9%)	*	*
Total	0.77	58	0.29	33
River Bend (1)				
Chelex	0.17 (36%)	3 (21%)	0.20	39
Duolite	0.30 (64%)	11 (79%)	*	*
Total	0.47	14	0.2	39
UCSC 8-HQ	0.23 (66%)	34 (87%)	0.62	14
Duolite	0.12 (34%)	5 (13%)	*	*
Total	0.35	39	0.62	14

Table 5 (Cont.)

Sampling Site/ Resin Column	Copper (ppb)	Zinc (ppt)	Cadmium (ppt)	Lead (ppt)
River Bend (2)				
Chelex	0.16 (29%)	30 (57%)	0.82	31
Duolite	0.56 (71%)	23 (43%)	*	*
Total	0.72	53	0.82	31
UCSC 8-HQ	0.33 (69%)	87 (95%)	0.40	24
Duolite	0.15 (31%)	5 (5%)	*	*
Total	0.48	92	0.40	24

* Below Detection Limit

ppb Parts-Per-Billion (ug/liter)

ppt Parts-Per Trillion (ng/liter)

Table 6

Labile, Organically-Associated, and Total Dissolved Metal Concentrations for the Sacramento River, May 1984.

Sampling Site/ Resin Column	Copper (ppb)	Zinc (ppt)	Cadmium (ppt)	Lead (ppt)
Ord Bend				
Chelex	0.71 (44%)	590 (97%)	9.5	57 (97%)
Duolite	0.92 (56%)	18 (3%)	*	2 (3%)
Total	1.63	608	9.5	59
UCSC 8-HQ	1.42 (87%)	298 (97%)	13	46 (96%)
Duolite	0.21 (13%)	9 (3%)	*	2 (4%)
Total	1.63	307	13	48
Bryte Station				
Chelex	0.36 (25%)	543 (92%)	4.6	14 (93%)
Duolite	1.08 (75%)	48 (8%)	*	1 (7%)
Total	1.44	591	4.6	15
UCSC 8-HQ	1.07 (76%)	542 (98%)	7.90 (100%)	9 (90%)
Duolite	0.34 (24%)	10 (2%)	0.04 (<1%)	1 (10%)
Total	1.41	552	7.94	10
Water Treatment Facility				
Chelex	2.28 (79%)	332 (83%)	3.60 (99%)	8 (89%)
Duolite	0.59 (21%)	70 (17%)	0.04 (1%)	1 (11%)
Total	2.87	402	3.64	9
UCSC 8-HQ	2.25 (94%)	325 (93%)	6.3 (98%)	24 (96%)
Duolite	0.14 (6%)	24 (7%)	0.1 (2%)	1 (4%)
Total	2.39	349	6.4	25
Colusa Wildlife Refuge				
Chelex	1.59 (41%)	158 (52%)	2.7 (96%)	47
Duolite	2.31 (59%)	148 (48%)	0.1 (4%)	*
Total	3.90	306	2.8	47
UCSC 8-HQ	4.38 (90%)	254 (68%)	2.9	49 (92%)
Duolite	0.46 (10%)	120 (32%)	*	4 (8%)
Total	4.84	374	2.9	53

*Below Detection

ppb Parts-Per-Billion (ug/liter)

ppt Parts-Per Trillion (ng/liter)

Table 7

Labile, Organically-Associated, and Total Dissolved Metal Concentrations for the Sacramento River, April 1985

Sampling Site/ Resin Column	Copper (ppb)	Zinc (ppt)	Cadmium (ppt)	Iron (ppb)
<u>Chelex/Duolite</u>				
Chelex	0.43 (40%)	217 (96%)	6.90 (99%)	0.30 (28%)
Duolite	0.64 (60%)	9 (4%)	0.06 (1%)	0.77 (72%)
Total	1.07	226	6.96	1.07
Chelex	0.46 (41%)	200 (95%)	6.64 (100%)	0.21 (12%)
Duolite	0.65 (59%)	11 (5%)	0.03 (<1%)	1.58 (88%)
Total	1.11	211	6.67	1.79
Chelex	0.48 (43%)	214 (97%)	6.71 (98%)	0.27 (29%)
Duolite	0.63 (57%)	6 (3%)	0.14 (2%)	0.66 (71%)
Total	1.11	220	6.85	0.93
<u>Mean and Standard Deviation</u>				
Chelex	0.44 ± 0.22	210 ± 9	6.75 ± 0.13	0.26 ± 0.05
Duolite	0.64 ± 0.01	9 ± 3	0.08 ± 0.06	1.0 ± 0.5
Total	1.10 ± 0.02	219 ± 8	6.83 ± 0.15	1.26 ± 0.46
<u>UCSC 8-HQ/Duolite</u>				
UCSC 8-HQ	1.24 (89%)	225 (95%)	8.03 (99%)	1.40 (69%)
Duolite	0.16 (11%)	11 (5%)	0.07 (1%)	0.62 (31%)
Total	1.40	236	8.10	2.02
UCSC 8-HQ	0.95 (85%)	250 (98%)	8.11 (100%)	1.20 (71%)
Duolite	0.17 (15%)	4 (2%)	0.01 (<1%)	0.50 (29%)
Total	1.12	254	8.12	1.70
UCSC 8-HQ	1.11 (88%)	252 (98%)	8.85 (100%)	*
Duolite	0.15 (12%)	4 (2%)	0.03 (<1%)	0.76
Total	1.26	256	8.88	
<u>Mean and Standard Deviation</u>				
UCSC 8-HQ	1.10 ± 0.15	242 ± 15	8.33 ± 0.45	1.3
Duolite	0.16 ± 0.01	6 ± 4	0.04 ± 0.03	0.63 ± 0.13
Total	1.26 ± 0.14	249 ± 11	8.37 ± 0.44	1.86

* Below Detection limit
All resin pair combinations were obtained simultaneously.
Collection Site: Freeport Marina
ppb Parts-Per-Billion (ug/liter)
ppt Parts-Per Trillion (ng/liter)

Table 8

Labile, Organically-Associated, and Total Dissolved Metal Concentrations for the Merced River, April 1985

Sampling Site/ Resin Column^a	Copper (ppb)	Zinc (ppt)	Cadmium (ppt)	Iron (ppb)
Chelex/Duolite				
Chelex	0.006 (17%)	118 (97%)	0.5	2.1 (29%)
Duolite	0.030 (87%)	4 (3%)	*	5.1 (71%)
Total	0.036	122	0.5	7.2
Chelex	0.006 (21%)	112 (95%)	0.2 (71%)	1.8 (38%)
Duolite	0.022 (79%)	6 (5%)	0.5 (29%)	3.0 (62%)
Total	0.028	118	0.7	4.8
Chelex	0.013 (43%)	130 (94%)	0.3 (13%)	2.6 (40%)
Duolite	0.017 (57%)	9 (6%)	2.0 (87%)	3.9 (60%)
Total	0.030	139	2.3	6.5
Mean and Standard Deviation				
Chelex	0.008 ± 4	120 ± 9	0.3 ± 0.2	2.2 ± 0.4
Duolite	0.023 ± 7	6 ± 3	12	4.0 ± 1.1
Total	0.031 ± 4	121 ± 9		6.2 ± 1.2
UCSC 8-HQ/Duolite				
UCSC 8-HQ	*	88 (95%)	1.9 (95%)	4.8 (47%)
Duolite	31	5 (5%)	0.1 (5%)	5.4 (53%)
Total		93	2.0	10.2
UCSC 8-HQ	*	106 (90%)	2.2	5.6 (57%)
Duolite	32	12 (10%)	*	4.2 (43%)
Total		118	2.2	9.8
UCSC 8-HQ	*	149	–	5.0 (34%)
Duolite	88	*	–	9.6 (66%)
Total	–	149	–	14.6
Mean and Standard Deviation				
UCSC 8-HQ	–	114 ± 31	2.0	5.1 ± 0.4
Duolite	50 ± 33	8	–	6.4 ± 2.8
Total	–	120 ± 28	2.1	11.5 ± 3.6

*Below Detection

[a] All resin pair samples were obtained simultaneously.

ppb Parts-Per-Billion (ug/liter)

ppt Parts-Per Trillion (ng/liter)

Table 9

Chromium, Arsenic, and Selenium Concentrations for the Russian and Sacramento Rivers, May 1984

Site	Cr(VI) (ppb)	As(V) (ppb)	Se(VI) (ppt)
Russian River			
Turula Vinyard	0.20	0.29	87
Wholer Dam (1)	0.70	0.87	64
Wholer Dam (2)	0.28	0.44	47
Wholer Dam (3)	0.32	0.45	44
River Bend (1)	0.29	0.50	65
River Bend (2)	0.24	0.53	27
Sacramento River			
Ord Bend	0.32	1.82	31
Bryte Station	0.15	1.88	43
Water Treat. Facil.	0.33	0.47	43
Colusa Wild. Ref.	0.13	2.48	102

Samples collected using AG1 X-8 anion exchange resin

ppb Parts-Per-Billion (ug/liter)

ppt Parts-Per Trillion (ng/liter)

Table 10

Analytical Blanks, Detection Limits, and Comparative Detection Limits with the Anatech Laboratory for Copper, Zinc, Cadmium, and Lead

Resin Type/ Sampling Site	Cu (ng)	Zn (ng)	Cd (ng)	Pb (ng)	Fe (ng)
Chelex-100					
Russian River	27±4	200±100	3±2	12 ±10	N.D.[c]
Sacramento River[a]	24±3	34±19	0.4±0.2	1±1	N.D.
Sacramento River[b]	1.9±0.4	3.2±6	≤0.07	N.D.	4.2±1.7
Merced River	2.9±0.9	6.8±1.6	≤0.07	N.D.	5.3±2.6
UCSC 8-HQ					
Russian River	35±3	53±26	18±3	56±11	N.D.
Sacramento River[a]	170±150	150±30	20±3	37±7	N.D.
Sacramento River[b]	197±21	16.7±1.2	0.13±0.14	N.D.	3120±90
Merced River	214±11	18±2	≤0.04	N.D.	3150±370
Duolite S-587					
Russian River	36±4	40±13	0.4±0.5	2±2	N.D.
Sacramento River[a]	49±4	25±10	0.2±0.3	3±1	N.D.
Sacramento River[b]	8.6±1.5	7.4±2.0	≤0.05	N.D.	666±32
Merced River	2.5±1.7	12.4±3.1	0.19±0.13	N.D.	1010±150
Detection Limits[d]					
Chelex-100 (ppt)	0.98	5.7	0.11	1.5	3.2
UCSC 8-HQ (ppt)	24	2.4	0.14	1.0	410
Duolite (ppt)	2.4	3.8	0.14	1.5	140
Anatech[e] (ppt)	10,000	10,000	10,000	-	-

[a] May 1984

[b] April 1985

[c] Not Determined

[d] Detection Limit is defined as three times the standard deviation associated with replicate determinations of blanks. For this comparison, a mean sample volume of two liters is assumed.

[e] Data provided from report to State Water Resources Control Board.

ppb Parts-Per-Billion (ug/liter)

ppt Parts-Per Trillion (ng/liter)

Table 11

Average Total Dissolved Trace Element Concentrations for the World's Rivers, Compared to the Range of Values Obtained From the Russian, Sacramento, and Merced Rivers

Element	World Average[a]	Russian River	Sacramento River	Merced River
Cu (ppb)	1.5	0.35 - 1.3	0.75 - 4.8	0.028 - 0 .036
Zn (ppt)	30,000	14 - 491	211 - 608	93 - 149
Cd (ppt)	20	0.2 - 4.1	2.9 - 12.6	0.5 - 21
Pb (ppt)	100	14 - 40	9 - 59	N.D.[b]
Cr (ppb)	1	0.21 - 0.70	0.13 - 0.33	N.D.
As (ppb)	1.7	0.29 - 0.87	0.47 - 2.5[c]	N.D.
Se (ppt)	-	27 - 87	31 - 102[c]	N.D.
Fe (ppb)	40	N.D.	1.1 - 2.0	4.8 - 14.6

[a] Average river water values taken from Martin and Whitfield, 1983.

[b] Not Determined

[c] The highest value was observed in the agricultural drainage slough in the Colusa Wildlife Refuge.

ppb Parts-Per-Billion (ug/liter)

ppt Parts-Per Trillion (ng/liter)

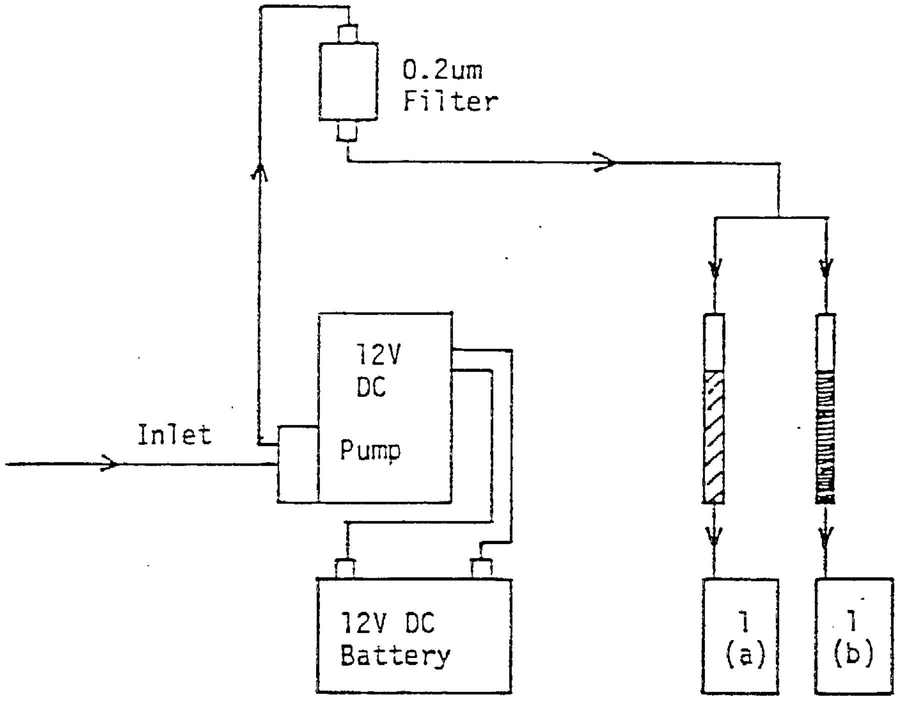

Figure 1: Schematic illustration of the 12 V DC-powered sampling system, showing a sampling scheme consisting of a split stream arrangement and two resin pair columns in series.

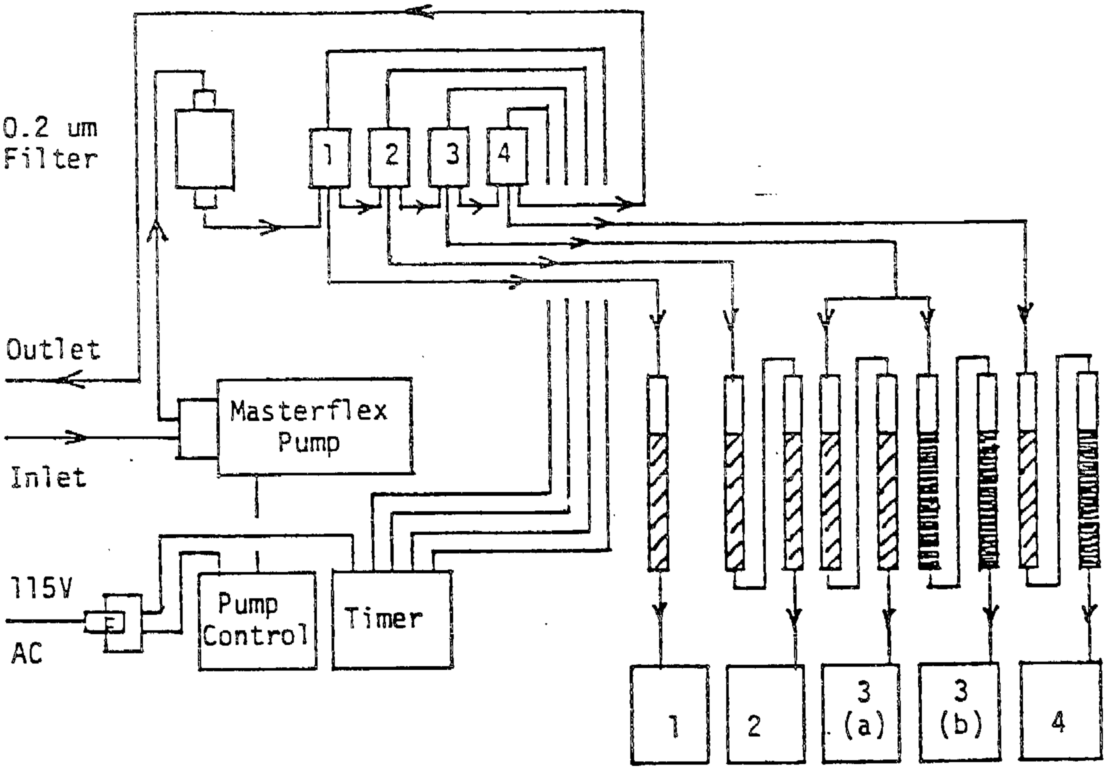

Figure 2: Schematic illustration of the 110-130 V AC-powered sampling system. The column arrangements shown are: A single column (line 1), two columns in series (line 2), a split stream configuration leading to two parallel sets of resin columns in series (lines 3a and 3b), and two columns in series with different resins (line 4).

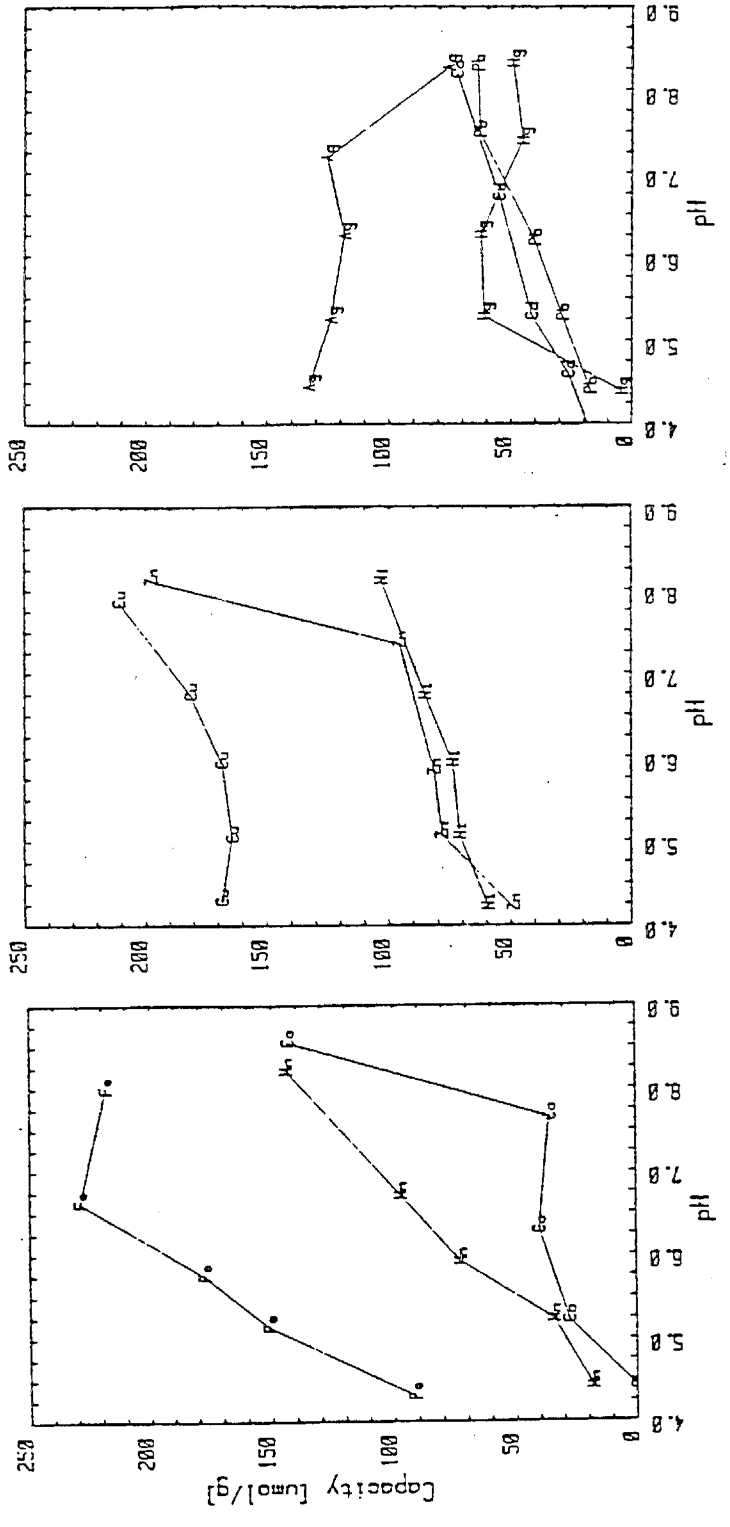

Figure 3: Metal exchange capacities of the UCSC 8-HQ cation exchange resin as a function of pH for: (a) Mn(II), Fe(III), and Co(II); (b) Ni(II), Cu(II), and Zn(II); (c) Ag(I), Cd(II), Hg(II), and Pb(II).

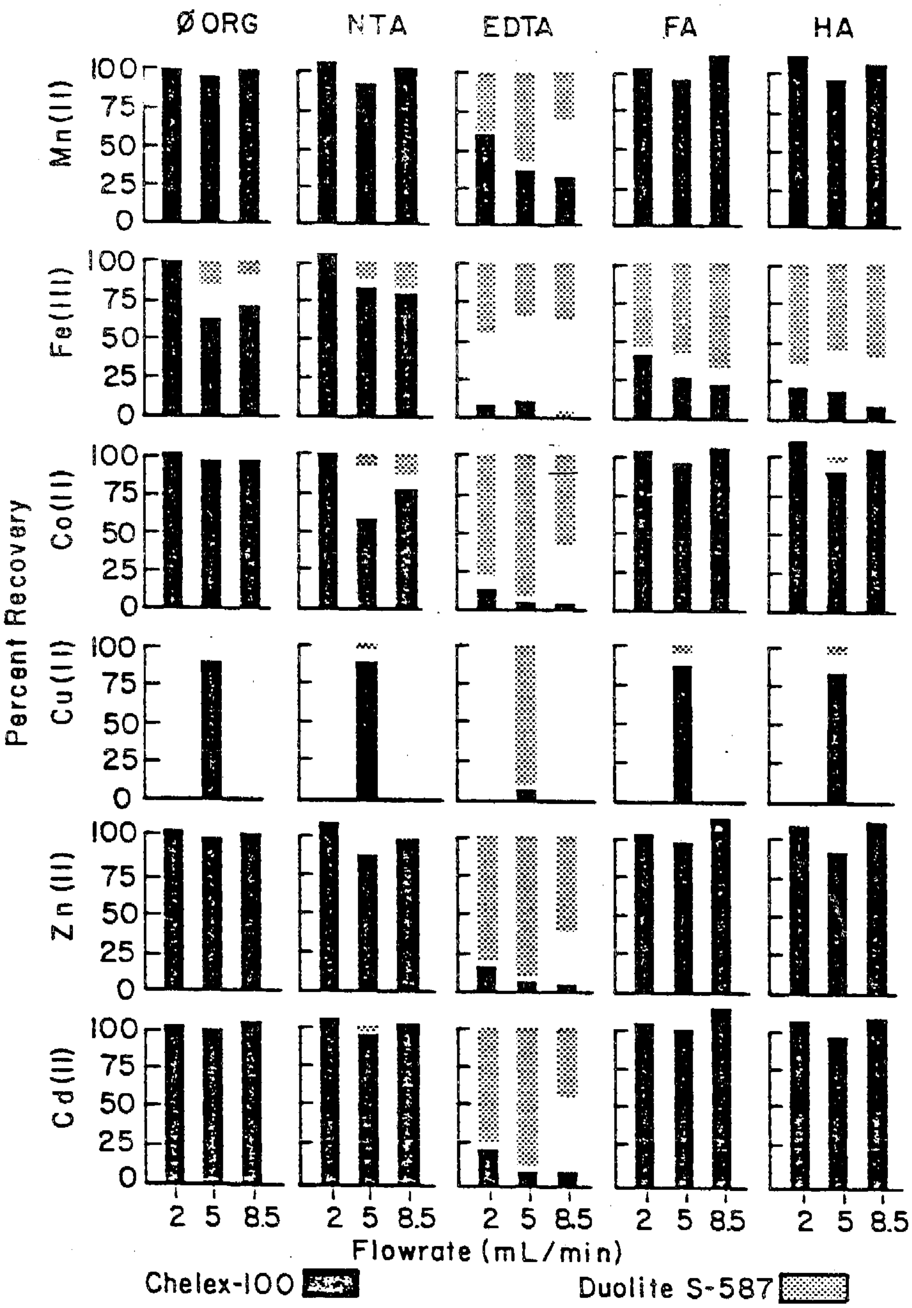

Figure 4: Radiotracer recovery efficiencies (%) for test solutions passed sequentially through columns of Chelex-100 and Duolite S-587 resins as a function of flow-rate. Test solutions were prepared with organic-free tap water (ø) adjusted to pH 6.5 with ammonium acetate to which were added 5 mg/L quantities of nitriloacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), or riverine fulvic and humic acids (FA/HA).

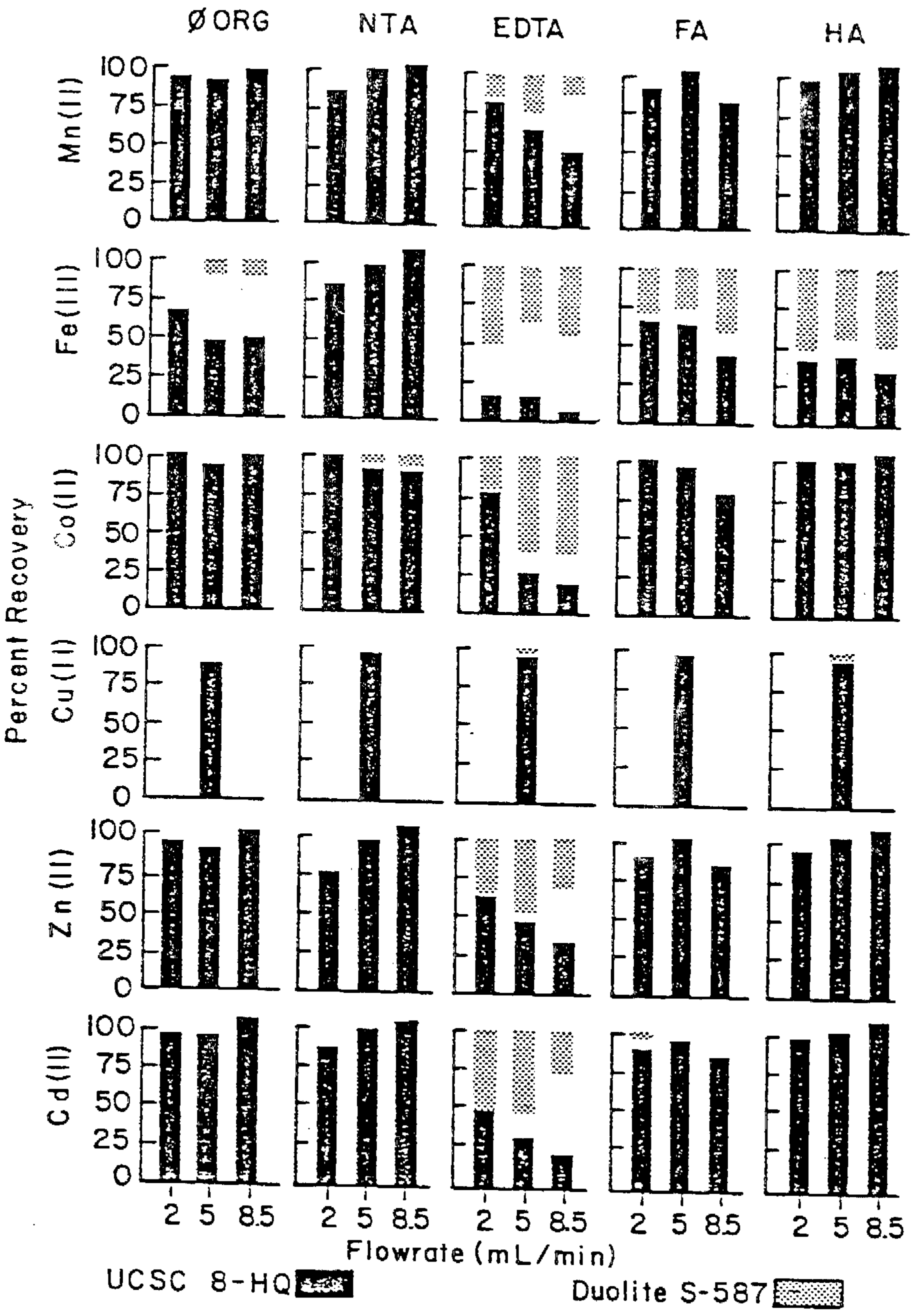

Figure 5: Radiotracer recovery efficiencies (%) for test solutions passed sequentially through columns of UCSC 8-HQ and Duolite S-587 resins as a function of flow-rate. Test solutions are as in figure 4.

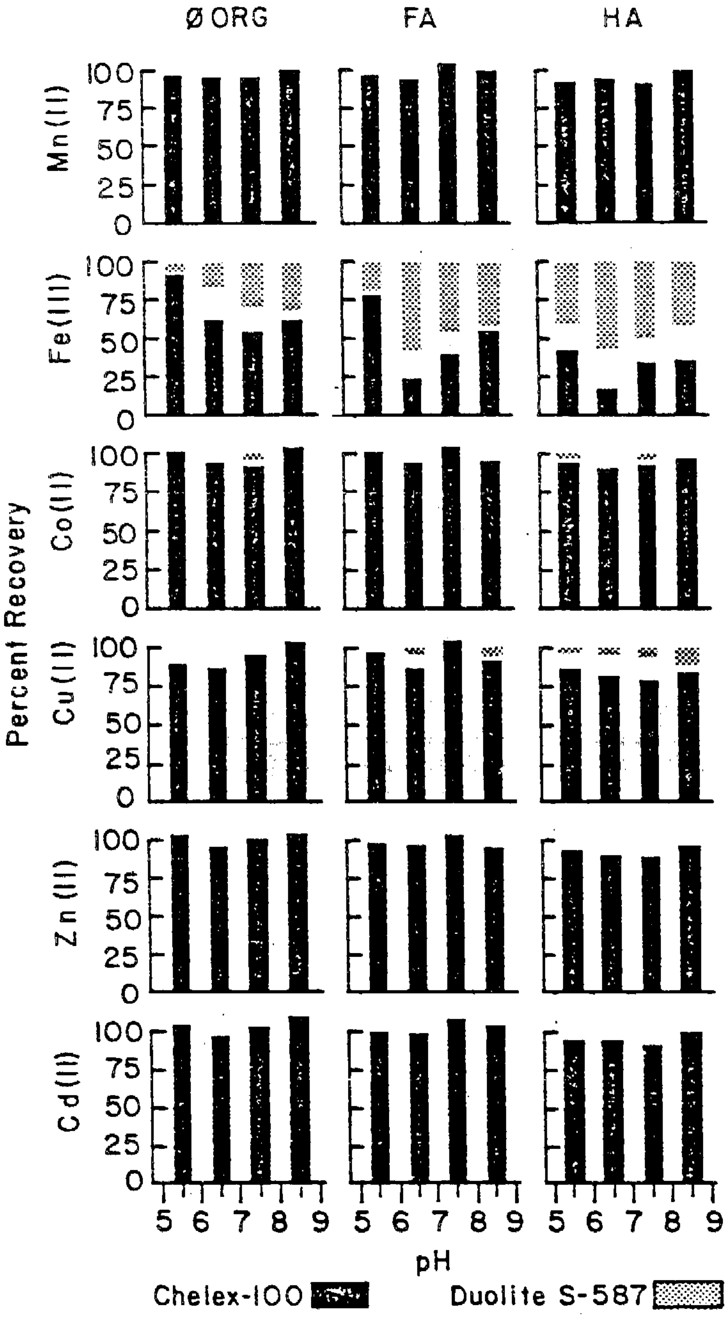

Figure 6: Radiotracer recovery efficiencies (%) for test solutions passed sequentially through columns of Chelex-100 and Duolite S-587 resins as a function pH at a flow-rate of 5 mL/min. Test solutions are as in figure 4.

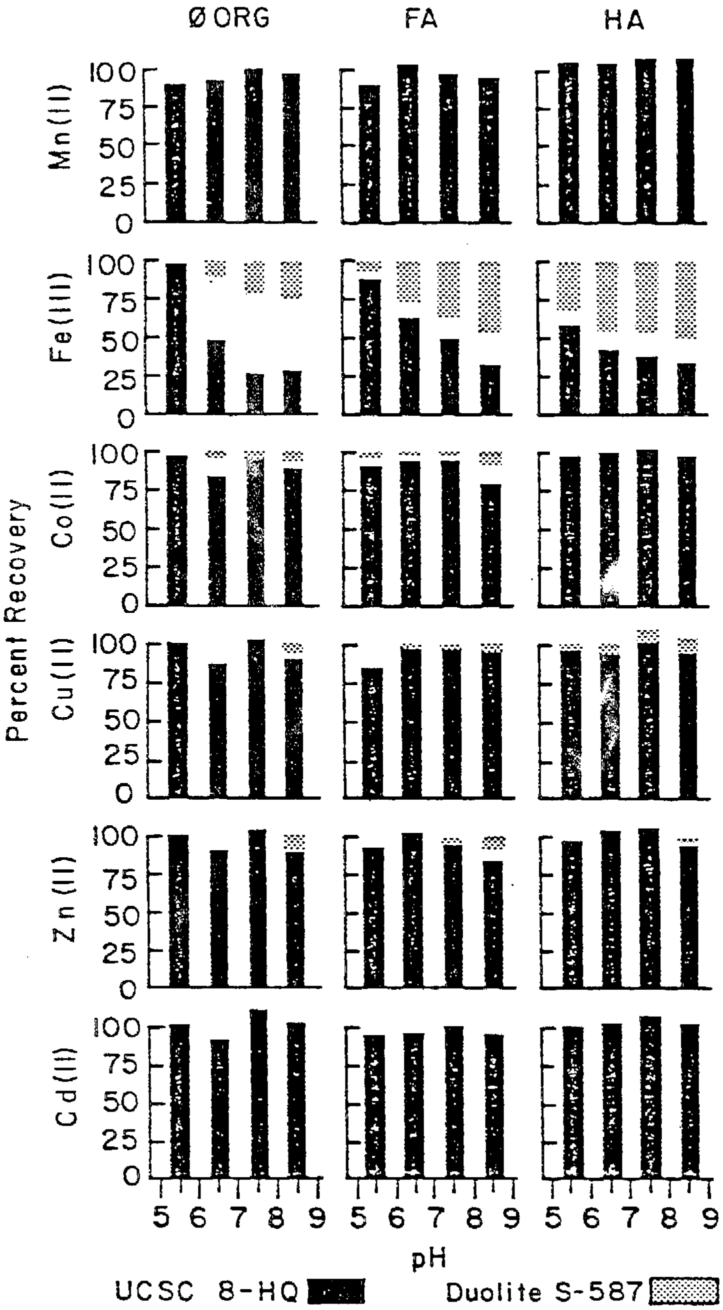

Figure 7: Radiotracer recovery efficiencies (%) for test solutions passed sequentially through columns of UCSC 8-HQ and Duolite S-587 resins as a function pH at a flow-rate of 5 mL/min. Test solutions are as in figure 4.

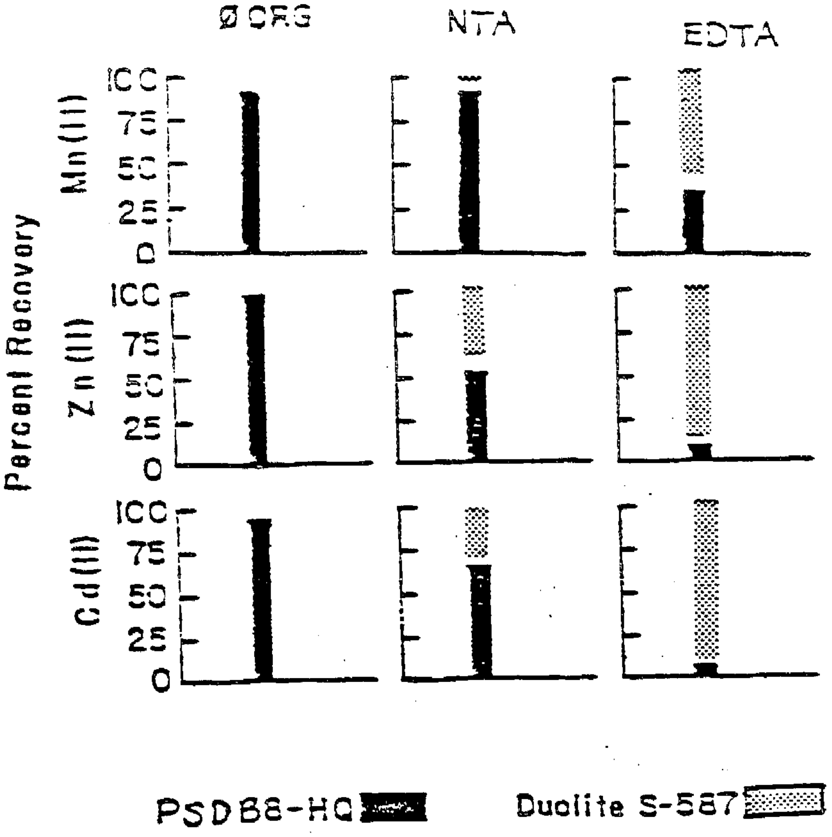

Figure 8: Radiotracer recovery efficiencies (%) for test solutions passed sequentially through columns of PDSB 8-HQ and Duolite S-587 resins at a pH of 6.0 and a flow-rate of 2 mL/min. Test solutions are as in figure 4.

APPENDIX M

SUMMARY AG. EXTENSION REPORT

To obtain a better understanding of the cropping patterns and pesticide usage in the Sacramento Valley, Farm Advisors from the University of California's Cooperative Extension were contacted. Information relating pesticide use to major drainage areas, as well as timing of applications, was obtained. This report summarizes acquired data and recommends areas of further study.

Contacts

Between February and March 1984, County Agricultural Cooperative Extension offices responsible for areas with possible drainage impact on the Sacramento River were contacted. The eleven offices approached included those in Shasta, Tehama, Glenn, Butte, Colusa, Sutter, Yolo, Sacramento, Glenn, Placer, and Solano Counties. Most discussions with the farm advisors were held over the phone. However, with Sutter, Yolo, Solano, and Butte County offices, time was provided during the Agency's normal staff meetings to discuss drainage flows and pesticide use. All counties contacted have been very responsive with the exception of Glenn County which is still waiting for advice from their toxicologist. Glenn and Butte County Cooperative Extensions strongly recommend contacting the Agricultural Commissioner for each county to obtain more exact data on agricultural patterns.

Cropping Patterns

Orchards border the rivers and grow in the "better soils" at the fringes of valleys. Field crops of wheat, corn, tomatoes, and rice predominate in the Colusa, Sutter, and American Basins. Although pesticide application is unique by crop, some general patterns are followed.

Orchards

The major tree crop in the Valley is the walnut - closely followed by almonds, prunes, peaches, and apricots. Most practices are similar to those associated with walnuts. During the dormant season, December thru February, herbicides are applied to combat annual weeds and grasses. Roundup and Paraquat are applied in large amounts, however, many other copper solutions, organophosphates, or organophosphate and oil mixtures can be and are used. (Almond growers apply Simazine in December and may apply Parathion, Diazinon, Lorsban or Supracide in January). Applications involve ground crews, with either strip spraying or discing.

During February and March, carbamates such as Benomyl and Ziram or organics such as Captan and Bravo may be applied to control brown rot and shot hole. These fungicides are applied to almond orchards and may also be used on peaches and prunes.

Insecticide applications begin in April during early flower development and may continue through summer depending on the tree crop. To combat insects such as coddling moth, aphids, and scale insects, copper sprays may be applied up to 8 times in April, with organophosphates or organophosphates plus oil usually applied during May and July - frequency being dependent upon insect population density.

Guthion is a main summer organophosphate used to control peach twig borer. Omite (propargite), Plictran, and Vendex, all organic compounds, are major miticides used during the summer. Diazinon is another organophosphate insecticide used on orchards and may be applied between early winter and late summer depending upon the crop and individual grower.

To summarize, in orchards, herbicides are applied during the dormant period (Dec-Feb), fungicides are applied in spring, and insecticides may be applied spring and/or summer. The irrigation period may last from the end of April thru August.

Grains and Alfalfa

Wheat and barley are the major grains grown in the Sacramento Valley. Phenoxy herbicides are applied to most fields between December and February, timing is a dependent on the growth stage. Chemicals used include 2,4-D, MCPA, Bromoxynil, Avenge, and Hoelon.

In Tehama County, pre-emergent application is accomplished by aerial applications to wet soils, with irrigation held off until the first part of May. Grass kills have never been noted off field after rain runoff so the chemicals are assumed to remain on-site.

Similar patterns are followed with alfalfa. The pesticides such as Toxaphene, Xylene, Methomyl, and Velpar are applied between December and February. After the first cutting of alfalfa, Eptam, a thiocarbamate, may be applied with the irrigation water for weed control. Alfatox, a diazinon/methoxychlor mixture, could be applied from the middle to end of March.

Insecticide applications are similar for both grains and alfalfa. Spraying of miticides and worm killers, may occur between May and August if there is a problem.

Row Crops

Corn, tomatoes, sugar beets, and dry beans make up the major row crops in the Sacramento Valley. Pesticide use depends on the crop. Major chemicals applied include Propargite, Dicofol, Carbaryl, and, until 1983, D-D mixture. Applications are normally by ground crews, usually from late spring through summer. What is applied and when is up to each individual grower. About 90% of the planted seeds are first treated with a fungicide. Most growers go through "moist" planting where the fields are pre-irrigated, allowed to dry, and then crews go in to plant. Movement of the treatment fungicide is not likely.

Tomatoes are grown spring through fall. In the Clarksburg area in Yolo County, tomatoes are rotated with wheat. Paraquat may be applied in January to control annual weeds and grasses. During February and March, Enide (an acetamide compound) is used against more persistent weeds such as barnyard grass, chickweed, and foxtail. After March, Devrinol (a propionamide compound) is used against other grasses while insecticides are employed against mites. Peak application occurs in June and July with Methyl Parathion most comonly used. However, no applications occur unless there is a problem. Sulfur is also used in mite and disease control.

Corn undergoes most of its pesticide applications during May and June. Propargite (Omite) and Dicofol (Kelthane) are the major insecticides used to control mites.

Dry Beans are found in Colusa and Sutter Counties. (15 and 25 thousand acres respectively in 1982). Pesticides used include Ethylene Dibromide, Acephate, Dicofol, and Propargite.

Sugar beets, grown to some extent in all the Sacramento Valley Counties although mainly in Solano County, use the pesticides Methomyl, and Phorate.

Rice

Of all crops in the Sacramento Valley, rice shows the greatest possibility of off-site transportation of applied pesticides since chemicals are applied directly to the water surface in flooded fields. Pesticides applied to this crop include:

Molinate
Thiobencarb
Blue Vitriol
MCPA
Bentazon
Carbofuran
Methyl Parathion
Propanil
Carbaryl
Xylene
Silvex
Sodium Chlorate
Parathion
Captan

A detailed study on the impacts of molinate and thiobencarb in the aquatic system can be fouind in the SWRCB "Rice Herbicides. A Water Quality Assessment" publication. (Cornacchia et al., 1984).

Summary

General consensus from the farm advisors is that agricultural practices pose no immediate threat to the Sacramento River or major water ways. Concern was expressed over rice pesticides (which are applied directly to water), irrigation tail water (excess water draining from farmland during irrigation), and the herbicide Eptam which is applied in the irrigation water after the first cutting of alfalfa.

Herbicides are persistent but fix tightly to the soil. The only expected movement would be combined with soil erosion, as may have occurred during the floods of 1982 and 1983. Some herbicides may leach with heavy rains, though the only suspected case is the possibility of solicam migrating from orchard to orchard (Solano County).

Organophosphates have a short half life with detectable residues lasting less than one month and usually less than one week. Residue on fruit averages a 2-3 week life span, so normally no washing occurs after harvest. Guthion is the most persistent with a residue life of about 25 days.

Major drainages into the Sacramento River occurs at the following locations:

Colusa Basin Drain

Reclamation District 108

Sutter By-Pass and Reclamation Slough, Sacramento Slough

Feather River

American River

Pumping Plant at Clarksburg (During Dec-Jan) Possible drainage out of Bryte

Yolo By-Pass (Toe Drain) into Cache Slough

Some farms may discharge directly to the River or smaller sloughs into the River, but the overall impact should be small when compared to the major drains. The pumping plant at Clarksburg is of particular interest since its discharges to the River may at times correspond to 2,4-D and MCPA applications to wheat in the area.

According to most offices in the Ag Extension, the 1984 irrigation season should be fairly representative of "normal" irrigation and growing seasons - especially when compared to the unusually wet winters of 1982 and 1983. The only notable change would be irrigation practices moving up one month to begin in April instead of May.

The farm advisors also pointed out that many pesticides can be bought over the counter for private use. No restrictions can be placed on the private home owner so chemical concentrations making their way into storm drains may present a greater threat to aquatic life than those found in agricultural drains. Suggestions were made to contact all retailers to obtain a more realistic view of the amounts of chemicals used. Time and funding will dictate the amount of effort which can be devoted to such a project.

JK:ljl

April 1984

APPENDIX N

[illegible] 25 1989

State of California

The Resources Agency

Memorandum

To : Ed Anton, Chief
Planning and Standards Development Branch
Division of Water Quality
State Water Resources Control Board
901 P Street
Sacramento, CA 95814

Date : January 23, 1989

From : **Department of Fish and Game**

Subject : Environmental Services Division (ESD) Administrative Report 87-2

This memorandum is in response to your questions regarding ESD Administrative Report 87-2, entitled "Hazard Assessment of Rice Herbicides Molinate and Thiobencarb to Larval and Juvenile Striped Bass." I have listed your specific questions below, along with our response:

1. What is the meaning of the term "guideline" as used in Administrative Report 87-2?

Response: The guidelines recommended by the Department of Fish and Game in Administrative Report 87-2 were meant to be specific concentrations of molinate and thiobencarb that the Department viewed as the maximum acceptable levels in agricultural drains that would minimize hazards to opossum shrimp until water quality criteria or objectives could be formally developed and adopted. The guidelines were not intended to be used as water quality criteria, water quality standards, or water quality objectives; these terms were not used in Administrative Report 87-2.

2. Were the Department's recommended guidelines intended to be permanent?

Response: No. The recommended guidelines were intended as interim guidance pending development of new information or formal establishment of water quality objectives.

3. What were the recommended guidelines based upon, and what was their intended application?

Response: The guidelines of 54 ug/l molinate and 12 ug/l thiobencarb were based on toxicity studies using opossum shrimp that were performed by Stanford Research International. The guidelines were intended to be applied to agricultural drains for the protection of opossum shrimp in the downstream Sacramento - San Joaquin River Estuary and Delta (Delta).

4. Were the recommended guidelines intended to be applied directly to the Sacramento River and Sacramento-San Joaquin Delta Estuary?

Response: No. The guidelines were intended to be applied directly to the agricultural drains, with the expectation that dilution would reduce concentrations of herbicides in the Sacramento River and Delta to levels well below those found in the drains. This is described on pages 47-61 of Administrative Report 87-2.

5. What was the nature of the data that the hazard assessment and recommended guidelines were based upon? Were the recommended guidelines intended to be fully protective of all aquatic life in the Sacramento River and Delta?

Response: The hazard assessment and guidelines were developed using existing toxicological data, and using data from toxicity tests on striped bass performed by the Department. When the Department first began toxicity tests using striped bass, standard protocols for this species did not exist, and working with early life stages proved difficult. The Department's initial bioassay work was therefore in part developmental in nature. Testing procedures were modified as work progressed, and recent work has confirmed our earlier findings. However, even with the addition of these Department study results, a limited data base of toxicological data existed for rice herbicides. Administrative Report 87-2 reflects this, concluding on page 60 that ". . . not all aquatic species have been tested under all conditions."

In the Department's view, water quality objectives for waters of the State should fully protect all aquatic life at all times. However, as described earlier, our recommendations were forwarded as suggested guidelines, not as suggested water quality objectives. They were developed to minimize the hazards to opossum shrimp, the most sensitive species that had been tested at that time. They were not developed or intended to fully protect all aquatic life in the Sacramento River system, as would water quality objectives.

6. Does the Department support development of water quality criteria and water quality objectives for rice herbicides in the Sacramento River and Delta?

Response: Yes. The Department fully supports development of water quality criteria and water quality objectives for materials that are toxic to fish and wildlife, including molinate and thiobencarb. As stated earlier, we believe water quality objectives should fully protect all aquatic species.

In conclusion, I trust these answers to your inquiries provide the needed clarification of Administrative Report 87-2.

Don Lollock

Donald L. Lollock, Chief
Environmental Services Division