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DEPARTMENT OF PESTICIDE REGULATION
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1020 N Street, Room 161
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August 7, 1995

To: INTERESTED PARTIES

Subject: DBCP AND BENTAZON MONITORING RESULTS SOLANO COUNTY

Enclosed, for your information, is a memorandum summarizing a year-long study (June 1993 to June 1994) in which the Department of Pesticide Regulation and the City of Vallejo analyzed surface water samples from Solano County for DBCP and bentazon residues. The data presented shows the results of the chemical analyses from several drinking water systems in Solano County that were monitored in response to reported DBCP and bentazon detections in the county's drinking water supply. In addition, potential sources of the original detections have been suggested.

If you have any questions regarding this memorandum, please contact me at (916) 324-4200.

Sincerely,

Kevin P. Bennett

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Enclosure

State of California

Memorandum

To : Don Weaver
Sr. Env. Research Scientist
Environmental Hazards Assessment Program

Date : August 1, 1995

Place : Sacramento

Phone : 324-4100

From : Department of Pesticide Regulation- Kevin P. Bennett, Env. Research Scientist
Environmental Hazards Assessment Program

Subject Dibromo-chloropropane (DBCP) and Bentazon Monitoring Results for Surface Water Samples Collected in Solano County, June 1993 to June 1994.

Scope of This Memorandum

The purpose of this memorandum is to 1) provide results from the DBCP/bentazon monitoring completed in Solano County by the City of Vallejo and the Department of Pesticide Regulation, and 2) suggest potential sources of the originally reported detections. The interpretation of data presented in this memorandum is not intended to be a formal evaluation of, or investigation into the agricultural practices in the counties mentioned.

I. Introduction

In March of 1993, the Department of Health Services (DHS), Office of Drinking Water, reported two detections of 1,2-Dibromo-3-chloropropane (DBCP) in water from the Terminal Reservoir and eight detections of bentazon in surface water samples collected at three other sites in western Solano County (Figure 1, Table 1). The samples had been collected from December 1992 to February 1993, by the City of Vallejo Water Department as part of their routine monitoring of the County's drinking water supply. After consultation with staff from the Environmental Hazards Assessment Program (EHAP) of the Department of Pesticide Regulation (DPR), the City of Vallejo conducted additional monitoring at the same sites in March 1993. DBCP was not detected in Terminal Reservoir during this re-sampling effort. However, bentazon was again detected in samples from Lake Frey and the North Bay Aqueduct but at much

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lower concentrations (Table 2). As a result, DPR and the City of Vallejo, analyzed split samples quarterly between June 1993 and June 1994, in an attempt to confirm these detections.

II. Background

DBCP Detections and Use

DBCP, a nematicide and soil fumigant for which all use was suspended in 1977, was registered in California for use on a number of vegetable crops, grapes, peaches, citrus, walnuts and almonds. DBCP was initially detected in the Terminal Reservoir in December 1992 and February 1993, at concentrations of 0.08 and 0.03 ppb, respectively. These water samples were analyzed by Analytical Laboratories (ANLAB), a City of Vallejo contract laboratory. After a careful review of ANLAB's DBCP analytical methods by quality assurance staff of the California Department of Food and Agriculture (CDFA) Laboratory Services Division, the DBCP detections appeared to be correct.[1] However, backup samples were not available for additional analyses to confirm ANLAB's findings. Since residue confirmation was not performed, analytical or laboratory error cannot be ruled out as the source of the detections. Other potential sources of the DBCP detections are further explored in the 'Results and Discussion' section below.

DBCP was not detected in water samples collected in March 1993. However, these samples were analyzed by Coast-to-Coast Analytical Services, whose detection limit was slightly higher than that of ANLAB (0.05 vs. 0.01 ppb, respectively). Therefore, the lack of confirmation between the two laboratories could have been due to the difference in detection limits.

The Terminal Reservoir is the terminus of the Putah South Canal which brings water from Lake Berryessa to both agricultural and municipal/industrial users in western Solano County (Figure 2).

[1]All DBCP samples were analyzed using approved U.S. EPA methods, however, they were not confirmed by mass spectrometry.

Though the Terminal Reservoir is located in a non-agricultural area, the Putah South Canal traverses areas of agricultural use. Lake Berryessa is in hilly terrain (400 to 2,200 ft.) and receives runoff from four counties, Yolo, Napa, Solano and Lake. Agricultural activity in the area primarily involves the production of grapes.

A search of the 1975 and 1976 Pesticide Use Report databases for these four counties revealed that no DBCP was commercially applied in 1975 and 454 pounds was applied to tomatoes in Yolo County only, during December 1976. DBCP was not a restricted material and there were several home garden use products registered, the amount of which cannot be quantified.

DBCP is stable to hydrolysis and has a solubility in water of 1,000 parts per million. Several of its other properties include: soil adsorption coefficient (K_{oc})=80, aerobic half-life=180 days, anaerobic half-life=740 days, (Johnson, 1991). Additionally, Steinberg et al. (1987) have found that 1,2-Dibromoethane (EDB), which has physico-chemical characteristics similar to that of DBCP, can be persistent in soils up to 13 years after application.

Bentazon Detection and **Use**

Bentazon (Basagran®, 3-isopropyl-1H-2,1,3-benzothiadiazin-4 (3H)-one 2,2-dioxide) is a selective, postemergent, contact herbicide used to control certain broadleaf weeds and sedges. In California, it is a restricted material registered for use on beans, peas, corn, soybeans, peppermint and spearmint crops as well as ornamental turf. All bentazon use for rice crops in California was prohibited in April of 1989.

Label requirements instruct that the product not be applied directly to water and that equipment wash water not be released to surface water. Effective in 1991, applications are allowed only from April 1 through July 31 of each year for all agricultural, outdoor institutional, and outdoor industrial uses

according to the modified suspension order for bentazon (CDFA Notice - Notice to registrants of economic poisons containing bentazon, dated 4/4/91).

Bentazon was initially detected in December, 1992 and February, 1993 at concentrations ranging from 2.5 ppb at Lake Madigan to 6.9 ppb at the North Bay Aqueduct (Table 1).[2] Bentazon residues were again detected in samples collected a month later, March 1993 (Table 2). As was the case for DBCP, no backup samples were available for residue confirmation, therefore, false detection due to analytical or laboratory error cannot be ruled out. The 'Results and Discussion' section below will further explore other potential sources of the bentazon detections.

All bentazon detections occurred at three sites in Solano County. Lake Madigan and Lake Frey watersheds are small and water from Lake Madigan eventually flows into Lake Frey. These watersheds, which receive surface flows solely from Solano County and Napa County, consist of hilly terrain (1000-2000 ft.) with little agriculture. However, a vineyard and an equestrian race track are located adjacent to Lake Madigan. Data for bentazon use in Solano and Napa Counties during 1991 and 1992 are presented in Table 3; there are no products registered for home use. Less than 1 pound was commercially applied in Solano County in 1992, none of which was applied in the Lake Madigan/Frey watershed. According to DPR use reports (DPR, 1991 and 1992), bentazon was not applied in Solano County in 1991, or in Napa County during either year.

The third site, the North Bay Aqueduct, carries Sacramento River water west from the Barker Slough, through urban areas, to municipal users in Solano County (Figure 3). Bentazon use data for counties with contamination potential are included in Table 4. No other counties with significant bentazon use were within reasonable distance of the Sacramento River to be a

[2]All **bentazon samples were analyzed using approved U.S. EPA methods, however, they were not confirmed by mass spectrometry.**

factor in its potential contamination.

Bentazon is stable to hydrolysis and has a solubility in water of 530 parts per million. Its other physico-chemical properties include: soil adsorption coefficient (K_{oc})=34, aerobic half-life=40 days, anaerobic half-life=365 days (Kollman and Segawa, 1995), photodegradation half-life in water=1 to 6 days (Niles and Zabik 1975; Higashi and Crosby 1987). It has the potential to contaminate surface water due to its mobility in runoff water from treated areas.

III. Monitoring Plan

Although the Maximum Contaminant Levels of 0.20 ppb for DBCP and 18 ppb for bentazon in drinking water (California, 1993) were not exceeded, the DHS Office of Drinking Water requested EHAP's assistance in determining possible causes for the DBCP and bentazon detections. After consultation, staff from the City of Vallejo, DHS, and DPR agreed that DPR and the City of Vallejo would analyze split samples from Terminal Reservoir, Lake Frey, Lake Madison and the North Bay Aqueduct quarterly between June 1993 and June 1994, in an attempt to confirm the presence of these two chemicals. City of Vallejo personnel were to collect and split surface water samples from the original four detection sites, one-half of each split sample would be analyzed by their laboratory and one-half by DPR's laboratory. Samples from Terminal Reservoir were to be analyzed for DBCP while samples from Lake Madigan, Lake Frey and the North Bay Aqueduct were to be analyzed for bentazon.

Surface water samples were collected on June 10, 1993 (North Bay Aqueduct was sampled on June 30, 1993 due to a scheduling conflict), September 10, 1993, December 10, 1993, March 10, 1994, and June 16, 1994. For the March 10, 1994 sampling, DPR did not deliver sample bottles to City of Vallejo personnel on time and thus did not receive split samples for analysis. DBCP and bentazon analyses for the City of Vallejo were performed by Coast-to-Coast Analytical Services for the 1993 sampling dates and FGL Environmental for the 1994 sampling dates; both laboratories had a method detection level (MDL) of

0.01 for DBCP and 2.0 ppb for bentazon. Split samples for DPR were analyzed by Enseco Laboratories for DBCP (MDL = 0.02 ppb) and by the CDFA Laboratory Services for bentazon (MDL = 0.1 ppb).

IV. Results and Discussion

DBCP

Monitoring conducted through the cooperative efforts of the City of Vallejo and DPR showed that DBCP was not present in any of the surface water samples analyzed by any of the analytical laboratories for the period of June 1993 to June 1994.

As stated previously, all DBCP use was suspended in 1977, however, a total of 454 pounds of DBCP was applied to tomatoes in the pertinent counties during the two years immediately preceding prohibition of the product. The Lake Berryessa region and the Putah South Canal are the most likely areas to contribute DBCP residues to the Terminal Reservoir. However, the transport mechanism for this potential contamination is surface water. Given DBCP has a 180 day aerobic half-life and 15 years since the last legal application, its seems that the contamination of the Terminal Reservoir, due to legal use, was unlikely. A possible source of the DBCP contamination may have been illegal use or dumping of remaining stock.

Alternately, the source of the contamination at Terminal Reservoir may have been due to the diffusion of DBCP (aerobic $t_{1/2}$=180 days) from micropores, in previously treated soil, into the soil water. In comparison, EDB, which has an aerobic half-life of 44 days, has been found in soil up to 20 years after application (Sawhney, 1986). Rainfall during the period from November 1992 through January 1993 totaled 33 inches, an increase of 76% over the previous year and 70% over the previous three year average. Areas which were not normally saturated may have experienced extended periods of saturation, thus providing a mechanism for diffusion of DBCP into soil water. Subsequent runoff during the winter of 1992/93 may have transported DBCP residues into Lake Berryessa and/or

the Putah South Canal. Little is known about the entrapment of DBCP in micropores. Its suggestion as a possible source of contamination of the Terminal Reservoir is made in the absence of any substantial data on historical DBCP use in the regions affected.

Additionally, though the analytical method used by the initial laboratory for detecting DBCP **was** reviewed by CDFA Laboratory Services and appeared to be correct, no backup sample was analyzed to confirm its presence. Also, mass spectrometry was not used to confirm any of the DBCP detections. Quality assurance procedures (e.g.-rinse blanks, field blanks) were not in place either, therefore, the possibility of laboratory contamination or analytical error cannot be disproved as potential sources of the detections.

Bentazon

Monitoring also showed that bentazon was not present in any of the surface water samples analyzed by any of the analytical laboratories for the period of June 1993 to June 1994.

Bentazon is stable to hydrolysis, highly soluble, has an aerobic half-life of 40 days, and can be applied from April to July only. Detectable residues in surface water 5 months after a legal application of bentazon may be possible under turbid water conditions, where bentazon use is high. Since photodecomposition is a dominant degradation pathway for bentazon (Niles and Zabik, 1975), turbid systems where light penetration is poor, will have a slower rate of dissipation than in well lit systems. However, Lakes Madigan and Frey have little turbidity. Additionally and more importantly, less than 1 pound of bentazon was applied to Solano and Napa Counties in the two years prior to the initial detections, and there were no bentazon products registered for home use (Table 3). Given a l-6 day photodegradation half-life, pesticide use reports and application restrictions, the bentazon contamination in Lakes Frey and Madison may have been the result of applications outside the prescribed window of application or improper disposal of the product.

The North Bay Aqueduct's source water is the Sacramento River, near Barker Slough (Figure 3) and thus, bentazon contamination in the aqueduct may have resulted from normal agricultural practices in counties in addition to Yolo (e.g. Solano, Sacramento, Sutter and Glenn). In turbid waters such as the Sacramento River near Barker Slough, bentazon dissipation is reduced and detectable residues may have been present. However, tables 3 and 4 show the relatively small totalamount of bentazon that was applied in 1991 and 1992 in the above counties, contributing flows to the Sacramento River. The bentazon contamination of the North Bay Aqueduct may have resulted from the cumulative runoff of legal applications in counties upstream of the aqueduct's intake; based on bentazon's photodegradation rate, application window, and primarily on the pesticide use report, this seems unlikely. As was the case for the detections at Lakes Madigan and Frey, the bentazon contamination in the North Bay Aqueduct may have been the result of applications outside the prescribed window of application or improper disposal of the product.

Information on the entrapment of bentazon in the interstitial soil matrix is lacking. However, bentazon has a small soil adsorption coefficient (K_{oc}=34) and high water solubility and thus, readily tends to partition into soil water. More importantly, the mechanism for the transport of bentazon through the soil profile is limited to soil-water as compared to that of DBCP which is both soil-water and gaseous transport. Bentazon is therefore, not expected to be locked into soil micropores. Consequently, its diffusion from micropores in previously treated soils is unlikely.

As mentioned previously, there were no backup samples available for analysis of the original bentazon detections, and mass spectrometry was not involved in the chemical analysis. Also, rinse blanks and/or field blanks were not in place, and thus the possibility of false detections resulting from laboratory contamination or analytical error cannot be ruled out as potential sources of the bentazon detections.

V. Conclusion

The initial reports of DBCP and bentazon contamination in Solano County surface drinking water supplies from December 1992 through February 1993, showed very low concentrations that spanned a relatively short period of time. Additionally, the measured concentrations did not exceed the maximum contaminant levels for DBCP and bentazon of 0.20 and 18 ppb, respectively. Follow up sampling in March of 1993 by the City of Vallejo found no DBCP; bentazon was detected, but at concentrations an order of magnitude lower than in prior months.

A joint City of Vallejo/DPR study from June 1993 to June 1994 did not detect residues of DBCP or bentazon at any sampling locations. Given the limited scope of this study, some speculation on potential contamination sources was required to supplement scientific data, and no conclusive evidence of illegal contamination or chemistry laboratory error could be confirmed. Therefore, since analytical results from the joint monitoring program were all negative, further investigation into the source(s) of prior detections is not recommended at this time. The City of Vallejo will continue 'to sample these sites as part of their routine monitoring program and will report the results to DHS. DHS will contact DPR if additional detections are found.

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