

## **Bensulfuron Methyl Dissipation in California Rice Fields, and Residue Levels in Agricultural Drains and the Sacramento River**

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Herbicides applied to rice fields in the Sacramento Valley, CA, are released into agricultural drains via runoff water. Major agricultural drains then empty into the Sacramento River where contaminants may affect the quality of drinking water and aquatic wildlife habitat. Bensulfuron methyl (BSM) (Londax®; methyl 2-[[[[(4,6-dimethoxypyrimidin-2-yl)amino]carbonyl]amino]sulfonyl]methyl]benzoate), a highly active sulfonylurea, was registered for use in California in 1989 as a rice herbicide. Although toxicity of BSM is low for mammals and fish (rat oral LD<sub>50</sub> >5000 mg/kg; rainbow trout 96-hr LC<sub>50</sub> >150 mg/L) (Beyer et al. 1988), the effect of residues on the aquatic environment, in particular plant life, is unknown.

Persistence of BSM in rice paddy water has been examined in the laboratory (Yuyama et al. 1987b) but not in the field. According to label recommendations, rice paddy water should be held on the field for at least 5 days after application of BSM. Residue levels of BSM in agricultural drains and rivers, resulting from runoff releases after this holding time, have not been determined.

This study examines dissipation of BSM from paddy water of commercial rice fields and measures residue levels in major agricultural drains and the Sacramento River.

### **MATERIALS AND METHODS**

Three commercial rice fields located in Colusa and Glenn Counties, CA, were selected to examine dissipation of BSM in paddy water. Fields 1, 2 and 3 had total areas of 24, 16 and 17 ha, respectively. Only the last paddy of each of these fields was sampled. Paddy areas were 1.3, 1.2 and 3.1 ha, for Fields 1, 2 and 3, respectively.

A 60% dry flowable formulation of BSM was aerially applied to Fields 1, 2 and 3 on May 2, 12 and 16, respectively, in 1989. Applications were made to standing water, 8 to 12 d after seeding, at the nominal rate of 0.07 kg/ha, for all three fields. Water

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was not released from the fields for at least 8 d following application.

Between May 2 and 24, 1989, daily maximum and minimum air temperatures averaged 27.8°C and 10.3°C. Daily maximum and minimum relative humidity averaged 94% and 33%, while wind speeds ranged from 1.0 to 4.2 m/s. During the study period, paddy water depths averaged 16, 7 and 11 cm, and pH averaged 7.2, 7.6 and 8.6 in Fields 1, 2 and 3, respectively.

Paddy water was sampled on 0, 1, 3, and 8 d after application (DAA) using a glass jar attached to a 4.5 m pole, which was extended into the water from the bank. Six 2-L samples were collected in polypropylene bottles on each sampling day. Each of the 6 samples was a composite of 4 subsamples. Subsamples were taken from randomly selected sites around the border of the paddy. Samples from 0 DAA were taken approximately 5 hr after application, to determine peak concentrations of BSM after full dispersion in paddy water. Background samples of paddy water were taken 1 d prior to application, and water samples were taken from irrigation supply canals on 0 and 8 DAA. BSM was detected at a low concentration (0.7 µg/L) in the background sample from Field 1, possibly due to drift. Residues of BSM were not detected in any other background or irrigation water samples (detection limit 0.5 µg/L).

Concentrations of BSM in paddy water originally determined in µg/L were normalized to kg/ha to account for variable water depths.

Water samples were collected from two major agricultural drains, the Colusa Basin Drain (CBD) and the Sacramento Slough (SS), and the Sacramento River (SR) (Fig. 1) on a weekly or biweekly schedule. Sample collection began April 24 and ended July 3, 1989. Grab samples were taken by submerging 2-L amber glass bottles 15 cm below the water surface.

Paddy, drain and river water samples were split into two 1-L samples and analyzed for BSM by the primary laboratory, California Department of Food and Agriculture (CDFA), and the quality control (QC) laboratory, Morse. Samples (in 1-L polypropylene bottles) were placed on dry ice for transport, transferred to freezers, and stored at -18°C until analyzed.

Storage stability for BSM in water was examined, and intra- as well as inter-laboratory analyses were conducted as part of a QC program. Water samples were spiked with 5 µg/L BSM and stored frozen, in polypropylene bottles, for 112 d. No loss of BSM occurred over this time period. Field samples were extracted within 14 d after collection. Blind water spikes were prepared at three levels (2, 30 and 62 µg/L) and submitted to each laboratory for analysis. Results from each laboratory were analyzed by linear regression for the relationship between the true spike concentration and the measured concentration. The resulting intercepts and slopes of the regression lines were not significantly different from 0 and 1, respectively, indicating that the measured and true values were approximately equal (Table 1).

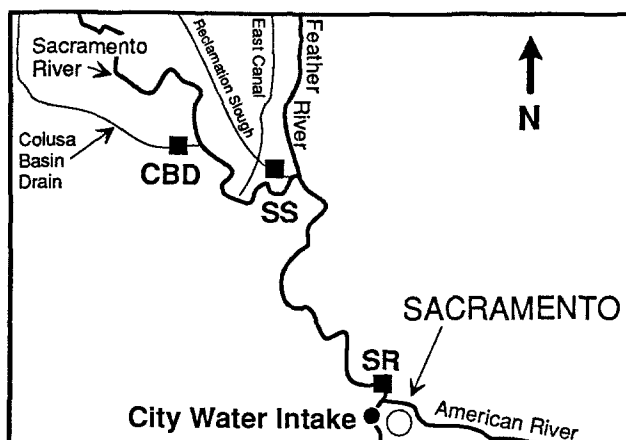


Figure 1. Locations of i) sampling sites (■) on agricultural drains, Colusa Basin Drain (CBD) and Sacramento Slough (SS), and the Sacramento River (SR) and ii) Sacramento City Water Intake (●).

Table 1. Intercept and slope for linear regression models comparing CDFA and Morse Laboratory results for blind spikes and field split samples.

|                                       | Intercept | Prob> F | Slope | Prob> F |
|---------------------------------------|-----------|---------|-------|---------|
| Blind Spikes vs CDFA                  | 0.76      | 0.55    | 1.03  | 0.41    |
| Blind Spikes vs Morse                 | -0.14     | 0.88    | 1.04  | 0.15    |
| Field Split Samples-<br>CDFA vs Morse | 0.31      | 0.12    | 1.01  | 0.05*   |

\* Slope significantly different from 1.0 ( $\alpha=0.05$ )

A similar comparison was made for BSM field (paddy, drain and river) split sample results from the primary and QC laboratories. Field split results were analyzed by linear regression for the relationship between BSM concentrations determined by the CDFA laboratory and by Morse laboratory. The intercept was not significantly different from 0; however, the slope was significantly different from 1 (Table 1). This indicates that, in general, results from CDFA were slightly higher than results from Morse. Actual absolute differences in measured values between the two labs were small (0 to 8  $\mu\text{g/L}$ , over a range of concentrations from <0.5 to 112  $\mu\text{g/L}$ ). The significant F value was due to the large sample size ( $n = 131$ ) which increased the power of the test to detect small differences not considered to be meaningful by the authors.

Solvent extraction procedures and high-performance liquid chromatography analyses for BSM in water were similar to those previously described for experiments conducted in Japan (Yuyama et al. 1987b). The detection limit was 0.5 µg/L. Mean recoveries of BSM from water were  $102 \pm 5.1\%$  ( $n = 36$ ).

## RESULTS AND DISCUSSION

On application day, average water depths in the paddies were 18.8, 9.1 and 10.8 cm in Fields 1, 2 and 3, respectively. Based on these water depths and the nominal application rate of 0.07 kg/ha, expected initial concentrations of BSM were 37, 77 and 65 µg/L. Approximately 5 hr after application, average measured concentrations of BSM in paddy water were 29 µg/L in Field 1, 96 µg/L in Field 2, and 71 µg/L in Field 3. Concentrations in Fields 2 and 3 were higher than expected based on the nominal application rate, and the concentration in Field 1 was lower. Calculated application rates based on measured concentrations were 0.05 kg/ha in Field 1, 0.09 kg/ha in Field 2 and 0.08 kg/ha in Field 3. Since tank samples were not taken, it was unknown whether discrepancies between nominal and calculated application rates were due to mixing and loading, or to other factors (e.g. drift, measurement error). The following data analyses of BSM in paddy water are based on the calculated application rates and are discussed in terms of % of applied BSM to facilitate comparisons among the fields.

BSM declined exponentially in paddy water of the three fields. Data were fitted to an exponential model using a least-squares method for the three fields combined (Fig. 2). Variance among the fields was approximately constant over time; therefore, data were not transformed to fit a log-normal model. The dissipation half-life for the three fields combined was 2 d. Yuyama et al. (1987b) also reported a rapid decline in water concentrations, within 3 to 4 d, for both technical and granular formulations of BSM applied in the laboratory to a simulated rice paddy.

When dissipation data from each of the fields were fitted individually to exponential models, the resulting half-lives ranged from 1 to 4 d. Variation in half-lives among these fields was small, indicating that in general, BSM will not persist in the water component of the aquatic environment. It should be noted, however, that results from the Yuyama et al. (1987a, 1987b) studies indicated that dissipation of BSM from paddy water may be due to adsorption onto paddy soil. If this is the case, BSM may persist in the aquatic environment for longer periods than indicated by dissipation from water alone.

Residues of BSM were first detected in late May in the CBD and they continued to be detected at low levels through June (Fig. 3). In the SS, BSM was detected for a shorter period of time, during the first half of June, at levels below 1 µg/L. Applications of BSM were made from May 1 to July 18, 1990 in the area draining

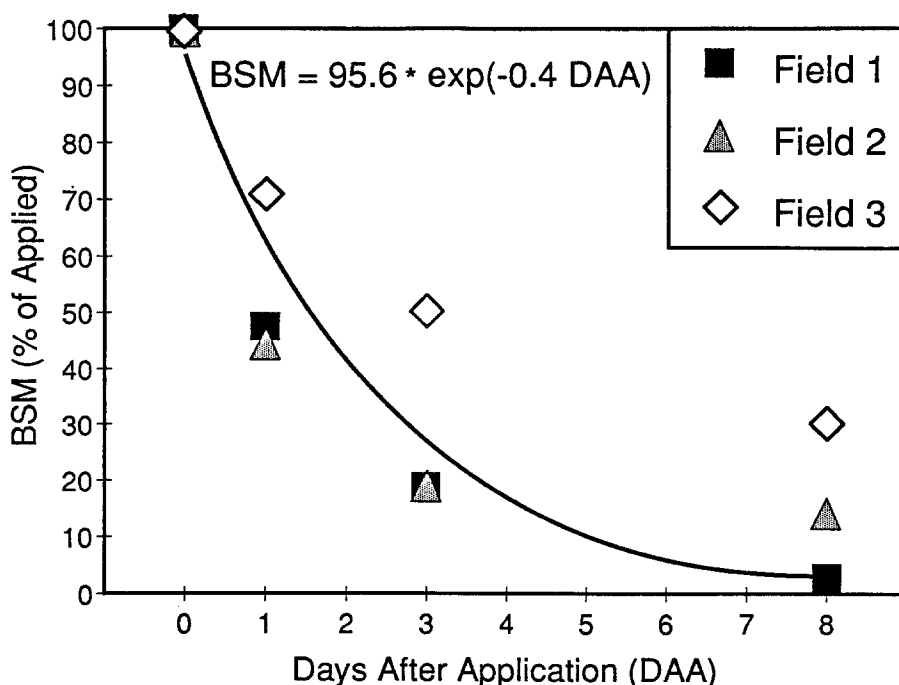


Figure 2. Fit of exponential model to bensulfuron methyl (BSM) dissipation in paddy water over days after application. Each data point is an average of six samples.

into the CBD and the SS. The appearance of these residues reflected the period of water release from rice fields which follows an enforced holding period after application of the rice herbicide, molinate, as well as the recommended holding period for BSM. Higher concentrations and the longer detection period of BSM in the CBD vs the SS may have been due to the larger area treated in counties draining into the CBD (ca 66,483 vs ca 53,684 ha) (CDFA, 1989). Water management practices, i.e., closed drainage systems and water recycling, may also have reduced the residue load going into the SS. These practices are not generally used in the area draining into the CBD.

The CBD and the SS waters, ca 18 to 24 km upstream from the SR sampling site, are diluted as they flow into the Sacramento River (Fig. 1). Residues are further diluted at the confluence of the Feather River with the Sacramento River 16 km upstream of the SR site. Consequently, BSM residues were not detected at the SR sampling site, which is located approximately 0.8 km above the city water intake. The United States Environmental Protection Agency's (USEPA) acceptable daily intake level is set at 0.2 mg/kg/day (USEPA, 1989). Using USEPA's method of calculation (USEPA, 1987) this translates into a drinking water equivalent level of 7000 µg/L. Residues in the CBD and the SS (Fig. 3) were three orders of magnitude below that level. Other water quality standards have not been set for BSM.

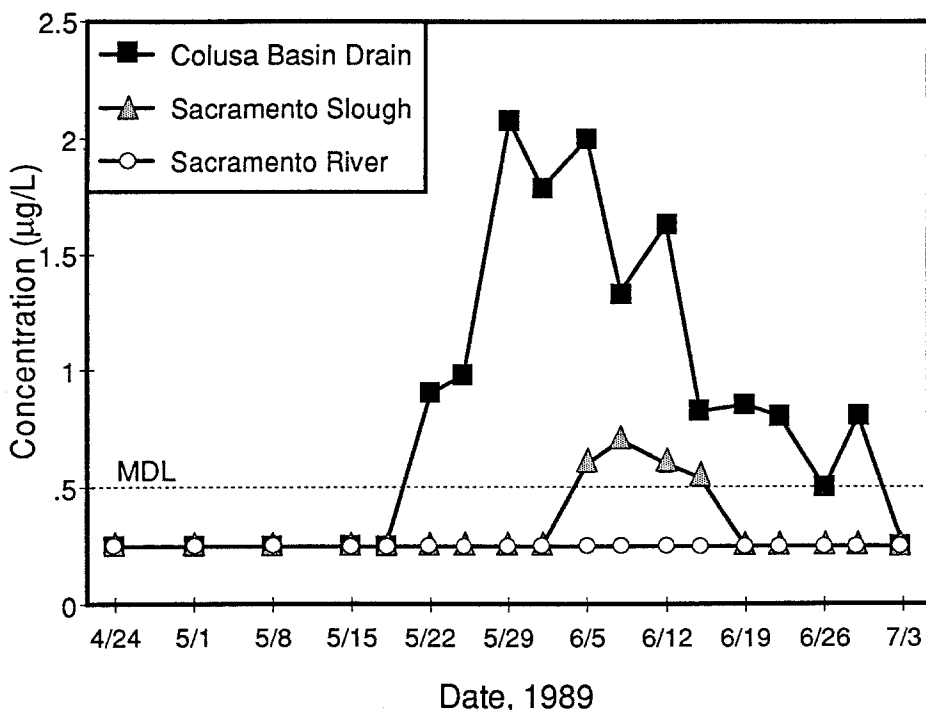


Figure 3. Bensulfuron methyl concentrations in agricultural drain and river water. Concentrations below the minimum detection limit (MDL) are shown as values between 0 and 0.5 µg/L.

Although BSM was applied at low rates and has a short dissipation half-life in paddy water, low-level residues were still detected in major agricultural drains for as long as a month. The presence of residues in agricultural drains for this length of time indicates the potential of rice runoff water to affect the quality of the aquatic environment.

**Acknowledgments.** Mention of trade names or commercial products does not constitute endorsement or recommendation for use by the California Department of Food and Agriculture. The authors thank E. I. Du Pont de Nemours & Co., DE and Morse Laboratories, CA for assistance in analytical methods and analysis of quality control samples. Special thanks to the California Department of Fish and Game for collection of drain and river samples and the Environmental Monitoring staff for their support.

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