# Some Changes in Pond Chemistry and Photosynthetic Activity Following Treatment With Increasing Concentrations of Chlorpyrifos

J. E. Butcher, M. G. Boyer, and C. D. Fowle

*Department of Biology and Centre for Research on Environmental Quality York University Downsview, Ontario, M3J 1P3 Canada*

The recent review by HURLBERT (1975) on secondary effects of aquatic pesticides clearly establishes that enhanced photosynthetic activity by algae in ponds is a consequence of pesticide treatment. In our work on the effects of treatment of standing ponds with Abate and chlorpyrifos (BUTCHER 1975; BUTCHER et al. 1975) we have observed in many experiments, post treatment development of green algae in excess of that in control ponds, concomitant with chemical changes associated with this phenomenon. In this report a representative series of chemical data from ponds treated with increasing concentrations of chlorpyrifos are presented to illustrate the scope, magnitude and duration of the response and some evidence for its underlying causes.

## METHODS AND MATERIALS

We used a series of artificial ponds approximately 2.5 x 1.8 x 0.6 m in depth, lined with polyethylene and inoculated with 48kg dry weight of leaf litter from temporary woodland pools containing a diverse fauna. One year later, three ponds were treated in the late spring with a single dose each of chlorpyrifos* at 1.0, 0.01 and 0.004 ppm. Two untreated ponds were used for controls. Data were collected daily over a period in excess of 80 days. Dissolved oxygen (DO) and temperature were assessed with a EIL Model 15A dissolved oxygen meter and total $CO_2$ ($CO_2$) by the methods given in GOLTERMAN (1969). Total organic carbon (TOC) total phosphorus (TP) and total Kjeldahl nitrogen (N) were determined by standard methods. Other common parameters; pH, soluble $CO_2$ and conductivity were also measured routinely (BUTCHER 1975) but are not discussed here. All daily measurements were made at approximately 2:00 p.m.

Records of the extent and duration of algal blooms were maintained. Bloom periods were recognized by the presence of visible actively-growing algae.

---

* Dursban $^{R}$M-3633 (active ingredient chlorpyrifos) [0,0-diethyl 0-(3,5,6-trichloro-2-pyridyl) phosphorothioate], a product of the Dow Chemical Company.



Bulletin of Environmental Contamination & Toxicology, Vol. 17, No. 6 © 1977 by Springer-Verlag New York Inc.

## RESULTS

Since the two control ponds developed synchronously, both chemically and biologically, their data have been combined for purposes of discussion (Fig.1, A). As would be expected, visible blooms in all ponds (Fig.1, A-D) were associated with DO levels in excess of those found between blooms. The quantitative differences during bloom periods among control and treated ponds were crude but reliable indicators of the apparent size and photosynthetic activity of the algal blooms. Considerable fluctuations in DO were evident even during peak bloom periods (Fig.1, A-D). These would appear to have their cause in either a temporary decline in photosynthesis as a result of lower light intensities, or in temperature and barometric changes. For example, from day 50-55 (Fig.1, A-D) the synchronized declines in DO in all ponds correlated with a decline in those environmental factors listed in Figure 2.

While bloom periods within any treatment were associated with declining or generally lower $CO_2$ values there were no obvious differences among the concentrations of $CO_2$ in treated and control ponds when presented in this manner (Fig.1, A-D). However, treated ponds differed from the two control ponds in some conspicuous, quantitative characteristics. Mean levels of DO were clearly at variance. Control ponds had a mean DO of 7.3 ppm over the experimental period, while treated ponds in order of decreasing pesticide concentrations, exceeded this value at 10.7, 7.9 and 7.6 ppm. Blooms were visibly larger and in total time more persistent than those in control ponds. The 12-day bloom period (Fig.1, A) was the only time visible algae accumulated in control ponds. In treated ponds, however, blooms lasted 45, 28 and 22 days respectively (Fig.1, B-D). Species of algae varied also. In control ponds the predominant form was a species of *Mougeotia*. While other species; *Chlorella*, *Spirogyra*, blue-green algae such as *Oscillatoria* and *Anabaena*, as well as diatoms, were present they did not form a significant component of the total biomass. The species of algae appeared to be virtually identical in the two lower treatments. In the 1.0 ppm treatment however, the predominant species was *Chlorella*. That the high pesticide treatment selectively promoted the growth of *Chlorella* instead of *Mougeotia* seems possible.

The distinctions between treatments and controls implied from the data (Fig.1) are more clearly revealed when the differences between the mean of the controls and the corresponding values of the treated ponds were compared (Fig.3, A-F). When plotted, the excess of DO and $CO_2$ in treated ponds compared to the control ponds was closely associated with the periods of bloom. During the 12-day bloom period in control ponds (Fig.1, A), an inter-bloom period for the two lowest treatment ponds, $CO_2$ was considerably higher (Fig.3, D, F).

As with the duration of the algal blooms, the number of days

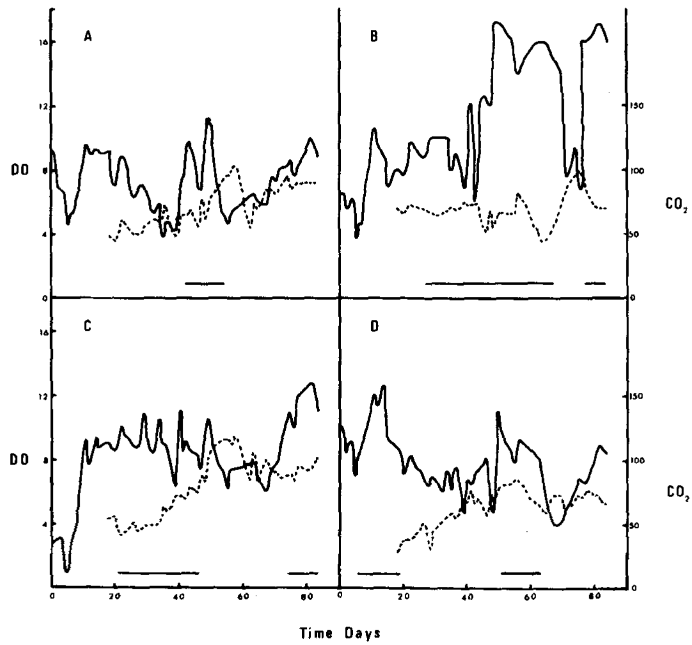


Figure 1

Dissolved oxygen (DO) and total carbon dioxide ($CO_2$) in control and chlorpyrifos-treated ponds. A - mean of control ponds; B - 1.0 ppm; C - 0.1 ppm; D - 0.004 ppm. (DO——; $CO_2$---). Horizontal bars indicate algal blooms.

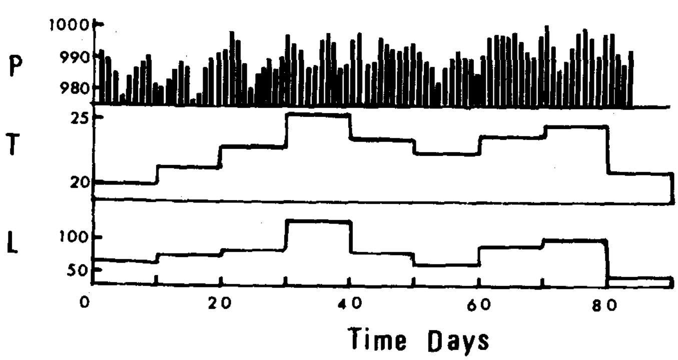


Figure 2

Some environmental parameters. P - atmospheric pressure; T - 10-day means of water temperature (c); L - 10-day totals, hours of sunlight.

in which the DO of treated ponds exceeded the controls were positively correlated with the dose. At the 1.0 ppm chlorpyrifos treatment DO values exceeded those of the controls for 57 days or 69 percent of the time. The 0.1 and 0.004 ppm treatments exceeded the control values for 54 days and 38 days or 65 and 46 percent respectively.

Data from other chemical parameters were assessed for their interpretive value. At the highest treatment level, (1.0 ppm), TOC, TP and N, each expressed as a difference from the control mean (Fig.4, A-C) were correlated with the onset of the algal bloom. This could be expected since the unicellular alga, Chlorella, the major component of the bloom, was not filtered prior to analysis.

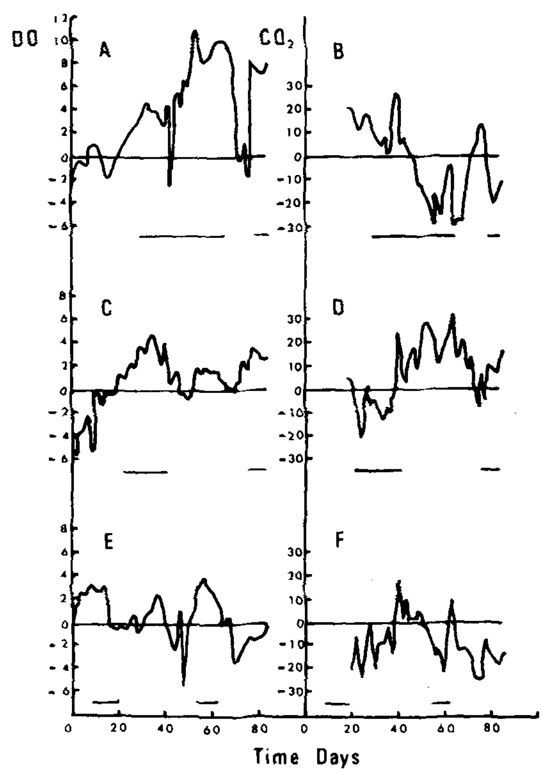


Figure 3

Dissolved oxygen (DO) and total carbon dioxide ($CO_2$) in chlorpyrifos-treated ponds relative to means of controls. A, B - 1.0 ppm; C, D - 0.1 ppm; E, F - 0.004 ppm. Horizontal bars indicate algal blooms.

At lower treatment levels (Fig.4, D-I) filamentous algal blooms, because they existed as aggregated mats, were excluded from the analyses. Values of TOC, N and P, each tended to be equal to or fall below those of the controls perhaps reflecting incorporation of the nutrients by Mougeotia. One further aspect of the data seems of interest. In all cases, treatments were followed by a small but measurable increase in TP (Fig.4, B,E,H), approximately 7 - 11 days after treatment. That this is indicative of phosphorus recirculated on decomposition of zooplankton and benthic fauna would seem plausible.

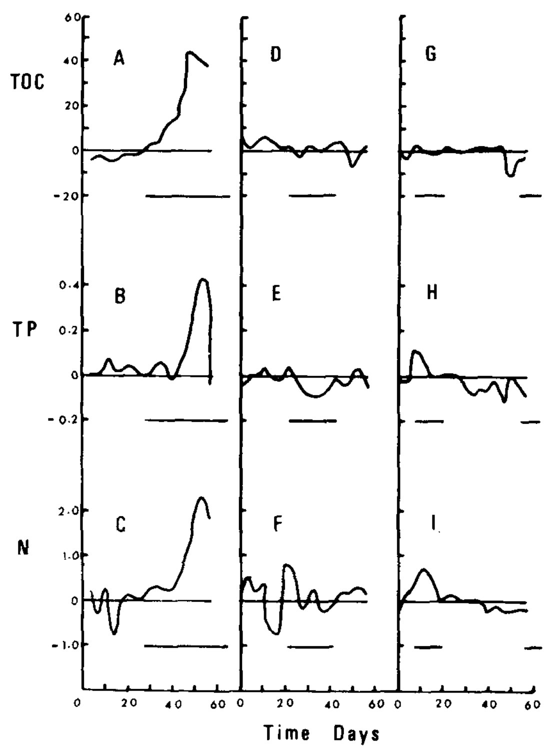


Figure 4

Total organic carbon (TOC), total phosphate (TP) and Kjeldahl nitrogen (N) in chlorpyrifos-treated ponds as differences from the controls. A, B, C - 1.0 ppm; D, E, F - 0.1 ppm; G, H, I - 0.004 ppm. Horizontal bars indicate algal blooms.

## DISCUSSION

The results obtained in these experiments support those of HURLBERT et al. (1975) and SIVASITHAMPARAM (1969) in establishing that the organophosphorus pesticide chlorpyrifos brings about, either directly or indirectly, an enhancement of algal growth in aquatic environments. The diversity of algae involved in their studies, primarily green and blue-green, would suggest a non-selective process depending at least in part on the species prevalent at the time the application is made. The presence of *Mougeotia* sp., the same genus as observed in the controls, in two of the three treatments in our experiments would also support this conclusion. However, in one treatment, the highest, an entirely different alga, *Chlorella*, was present suggesting that the concentration of the pesticide may be important in determining which algae become prevalent.

One of the more significant questions arising relates to the cause of the algal blooms. HURLBERT (1975), while citing the possibility of alternatives, makes a strong case for release from grazing pressure as a cause of the increase in algae. In support of this, the depressive effects of organophosphorus pesticides on potential or actual invertebrate grazers is well established (HURLBERT et al. 1970; HURLBERT et al. 1972; BUTCHER 1975). What seems more controversial is the extent to which grazers suppress algae, particularly filamentous algae. In fact, zooplankton, as one component of the grazing chain, might be cited not only as herbivores but as efficient contributors to the phosphorus cycle important for algal survival and growth (MARTIN 1965, 1968; HARGRAVE and GREEN 1968).

Among alternative or additional explanations, the role of phosphorus should not be ignored since it may be derived both as a component of the pesticide as well as through the decomposition of the invertebrates killed. The quantities added in the insecticide as elemental phosphorus; 0.09, 0.009 and 0.00036 ppm for the high, medium and low treatments used in this study, might seem relatively insignificant in the light of some known requirements (VOLLENWEIDER 1968). However, such values need not be insignificant at a bloom threshold.

In summary, the virtual complete elimination of zooplankton by 48 hours followed by the development of algal blooms, supports the concept of reduced grazing pressure as an explanation for the initiation of blooms by the pesticide. While the delay in initiation of visible algal blooms (6 - 20 days) might be interpreted adversely the rapid post treatment increase in $O_2$ relative to the controls (Fig.3, A,C and E) reflects early initiation of photosynthetic activity.

However, some evidence outlined here would also support at least a partial role for other factors. The correlation between the size and persistence of the algal blooms and the concentration of the pesticide leads to a suggestion that a required element such as phosphorus may be a major factor in the total magnitude of the response and in the variation in species. In all three applications there was an obvious post-treatment increase in TP in absolute terms (BUTCHER 1975) as well as relative terms (Fig. 4, B, E and H). These always greatly exceeded the elemental phosphorus added in the pesticide and were thus not entirely attributable to it. That these phosphorus levels could influence the size, duration and magnitude of the blooms is suggested by correlations between the rather abrupt termination of blooms and the times at which TP declines sharply in treated ponds (Fig.4, E,H).

## ACKNOWLEDGEMENTS

We wish to thank the Pesticide Advisory Committee, Ontario Ministry of the Environment for a grant in support of this research and also representatives of the Water Quality Laboratory of the Ministry for advice and assistance in water analysis.

## REFERENCES

BUTCHER, J. E.: The Effects of two Organosphosphorus Insecticides on some Chemical and Biological Properties of Standing Ponds. M.Sc. Thesis. York University, Downsview, Canada, 1975.

BUTCHER, J., M. G. BOYER, and C. D. FOWLE: Water Pollution Research in Canada 10, 33 (1975).

GOLTERMAN, H. L.: Chemical analysis of Fresh Water. IBP Handbook No. 8. Oxford: Blackwell Scientific 1969.

HARGRAVE, B. T., and G. H. GREEN: Limnol. Oceanogr. 13, 332 (1968).

HURLBERT, S. H.: Residue Reviews 57, 81 (1975).

HURLBERT, S. H., M. S. MULLA, J. O. KEITH, W. E. WESTLAKE, and M. E. DÜSCH: J. Econ. Entomol. 63, 43 (1970).

HURLBERT, S. H., M. S. MULLA, and H. R. WILLSON: Ecol. Monogr. 42, 269 (1972).

MARTIN, J. H.: Limnol. Oceanogr. 10, 185 (1965).

MARTIN, J. H.: Linol. Oceanogr. 13, 63 (1968).

SIVASITHAMPARAM, K.: Proc. Ceylon Ass. Advmt. Sci. 25, 1 (1969).

VOLLENWEIDER, R. A.: Paris, Rep. Organization for Economic Cooperation and Development, DAS/SCI/68. 27, (1968).