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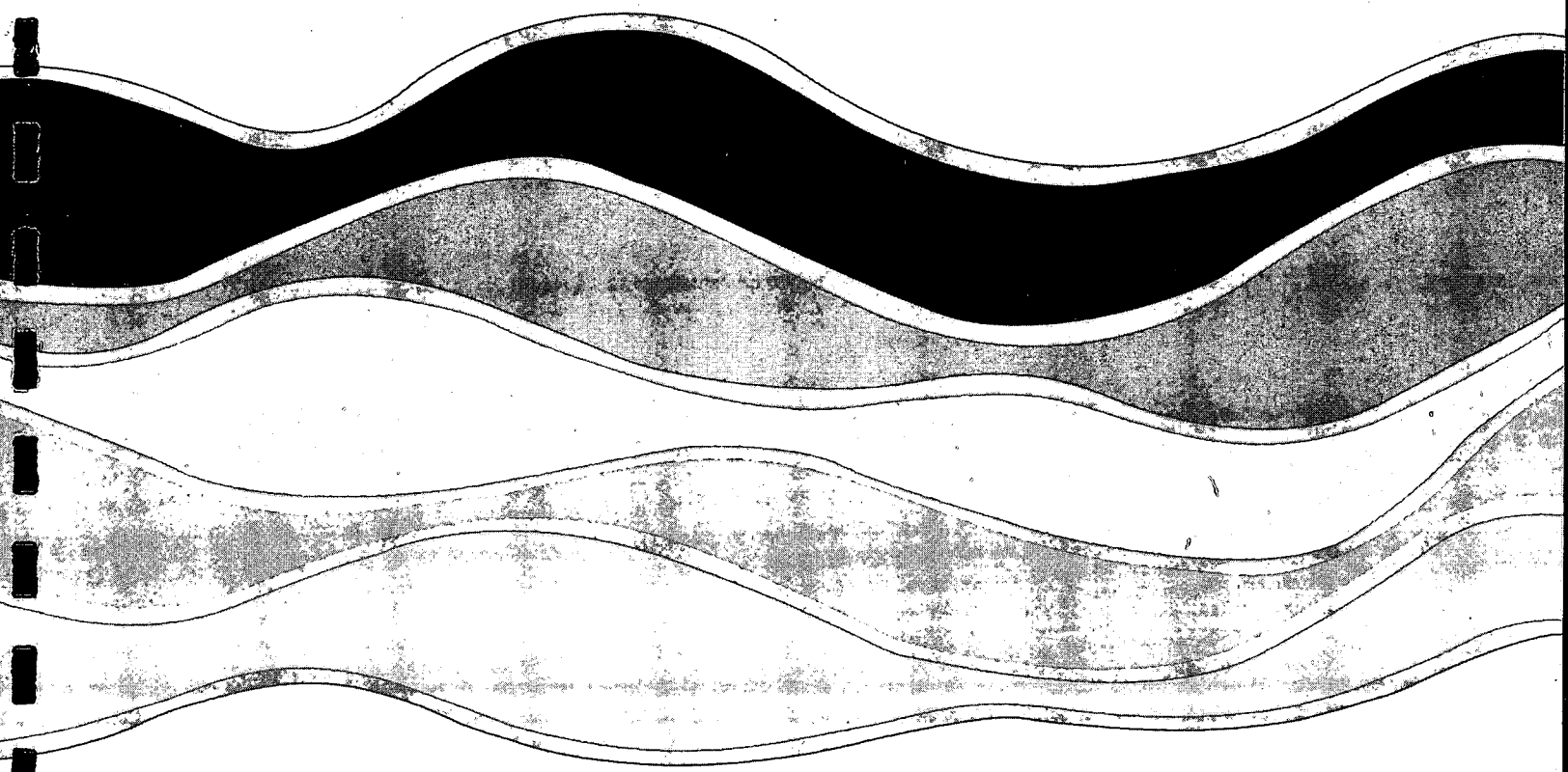

ALGAL BIOAVAILABILITY STUDY OF PHOSPHORUS IN DI-2-ETHYLHEXYL-PHOSPHORIC ACID AND TRIBUTYL PHOSPHATE: FEASIBILITY TESTS

M.N. Charlton and J.E. Milne

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Algal Bioavailability Study of Phosphorus in Di-2-ethylhexyl-phosphoric Acid and Tributyl Phosphate: Feasibility Tests

Management perspective

The use of di-2-ethylhexyl-phosphoric acid (DEHPA) and tributyl phosphate (TBP) in some proprietary mineral processing plants is causing eutrophication problems. At the request of Environmental Protection, Ontario Region, Environment Canada an experiment was conducted to test the feasibility of finding which chemical might be most responsible for undesirable algal growths. Sufficient DEHPA-P was extracted under laboratory conditions to stimulate growth. TBP-P was not extracted efficiently enough. It was pointed out that this type of experiment will depend largely on the P extraction efficiency and that this can be measured more easily than biological responses.

Perspectives de gestion

L'utilisation d'acide di-2-éthylhexyl-phosphorique (DEHPA) et de phosphate de tributyle (PTB) dans certaines usines de traitement exclusif de minéraux entraîne des problèmes d'eutrophisation. À la demande de la Protection de l'environnement, Région de l'Ontario, d'Environnement Canada, on a procédé à une expérience pour voir s'il est possible de déterminer quel est le produit chimique le plus incriminable pour la croissance indésirable d'algues. On a pu extraire assez de P provenant du DEHPA dans les conditions du laboratoire pour stimuler la croissance. Par contre, l'extraction de P du PTB n'a pas été assez importante. On estime que ce type d'expérience dépend largement de l'efficacité de l'extraction de P, processus beaucoup plus facilement mesurable que les réactions biologiques.

Introduction

Chemicals containing phosphorus are used in some mineral processing industries. Di-2-ethylhexyl phosphoric acid (DEHPA) and tributyl phosphate (TBP) are phosphorus containing chemicals thought to be potential sources of phosphorus causing eutrophication problems. At the request of (EP/OR) an experiment was set up to examine the feasibility of testing algal response to these chemicals to help determine which one would best be reduced in mineral processing.

Methods

Each chemical was digested in 30% H_2SO_4 for 30 min in glass beakers to simulate conditions in mineral processing. One mL of chemical was added to 5 mL of acid and gently swirled during the digestion time. Neither chemical dissolved. The entire beaker contents were transferred to 1 L volumetric flasks and made up to volume with distilled water. Aliquots from these stock flasks were then used to make different concentrations in 200 mL of tapwater in 250 mL erlenmeyer flasks which were used for algae cultures. Two flasks used as controls contained tapwater only.

Assuming 100% purity and density of one in the chemicals supplied and a digestion efficiency of P = 100%, the concentrations in the experiment would have been:

DEHPA 9%P, 1 mL = 90 mgP
stock is 1 mL of chemical in 1000 mL water = 90 mg/L

mL stock in 200 mL erlenmeyers:	0.2	0.5	1.0	2.0	4.0
[P]ug/L	72	180	360	720	1440

TBP 11% P, 1 mL = 110 mgP
stock is 1 mL of chemical in 1000 mL water = 110 mg/L

mL stock in 200mL erlenmeyers:	0.2	0.5	1.0	2.0	4.0
[P]ug/L	88	220	440	880	1760

Actual concentrations in the stock solutions were however much different than ideal expectations (analyses by Mr. J. Fraser, Wastwater Technology Centre , Burlington). Total P in the water phase of the stock DEHPA was 5.00 mg/L and was only 0.165 mg/L in the stock TBP. The concentrations in the experimental flasks were then:

DEHPA

mL stock in 200 mL erlenmeyers:	0.2	0.5	1.0	2.0	4.0
[P]ug/L	5.0	12.5	25	50	100

TBP

mL stock in 200 mL erlenmeyers:	0.2	0.5	1.0	2.0	4.0
[P]ug/L	0.165	0.41	0.82	1.64	3.28

Each flask, including controls, was inoculated with 1 mL of Hamilton Harbour water on July 9, 1990.

The culture flasks were arranged between two banks of 2 continuously illuminated fluorescent tubes 24 inches long. Flasks were agitated several times each day. This apparatus was set up on a laboratory bench at room temperature.

Results

The pH of tapwater and flasks containing 4 mL of each stock solution was 6.2. Since there did not seem to be a pH effect due to the acid used in extraction no attempt was made to further adjust the pH. The insolubility of the chemicals was a factor in the degree of P extraction since the conditions such as degree of mixing etc. may have an effect on the extraction efficiency. Clearly, the extraction was very inefficient.

By July 13 there was noticeable growth in some of the DEHPA cultures. None of the flasks exhibited sufficient growth to cause a green colour. By eye, algal filaments were visible but some of the growth could have been bacterial.

Growth of algae was monitored with a spectrophotometer at 663 nm on July 17, 23 and 30. Spectrophotometric scans were relatively flat from 400 to 750 nm. Absorbance of the water in the flasks is shown in Table 1 and Fig. 1. Most of the DEHPA additions seemed to stimulate growth except for the flask containing 4 mL of the stock. Results for TBP are probably unusable since only the 0.5 mL addition resulted in more growth than either of the controls. This is an unfortunate result of the low extraction efficiency during the acidification period.

The aliquots withdrawn for the culture flasks were taken from below the layer of floating chemical in the stock flasks. Nevertheless, some of the chemical may have been directly introduced. The culture results are consistent with the total P analyses of the water phase in the stocks and this means that biological tests on the extracts themselves are not necessary. Within the dilution series for DEHPA the growth response in terms of slope and ultimate absorbance did not always follow the projected concentration differences. This may be due to some individual responses of particular flasks and may have not occurred if the experiment had more replication. If mild acidification is able to extract the phosphorus from these chemicals the

main variable is the extraction efficiency. Thus, more needs to be known about the conditions in the industry to properly simulate the fate of the P in the chemicals.

There are therefore two issues in the problem: (1) the degree of breakdown and release of P in the processing and (2) the amount of P release from partially broken or intact molecules once these materials are released in wastewater.

Only a rudimentary experiment was attempted for this report. A more thorough investigation would require knowledge of the fate of DEHPA and TBP during the industrial process and the likelihood of biological degradation and P release in the polluted water. The fate of the residual organic fragments may also be interesting.

Conclusions

Under the laboratory conditions of gentle contact between acid and DEHPA sufficient P was extracted to stimulate algal growth. Insufficient P was extracted from TBP to stimulate growth.

The results of this type of experiment are strongly affected by the acidic extraction conditions and may be predictable from orthophosphate tests on extracts.

Additional testing may include the residual organic molecules which may have the potential to act as bacterial substrate.

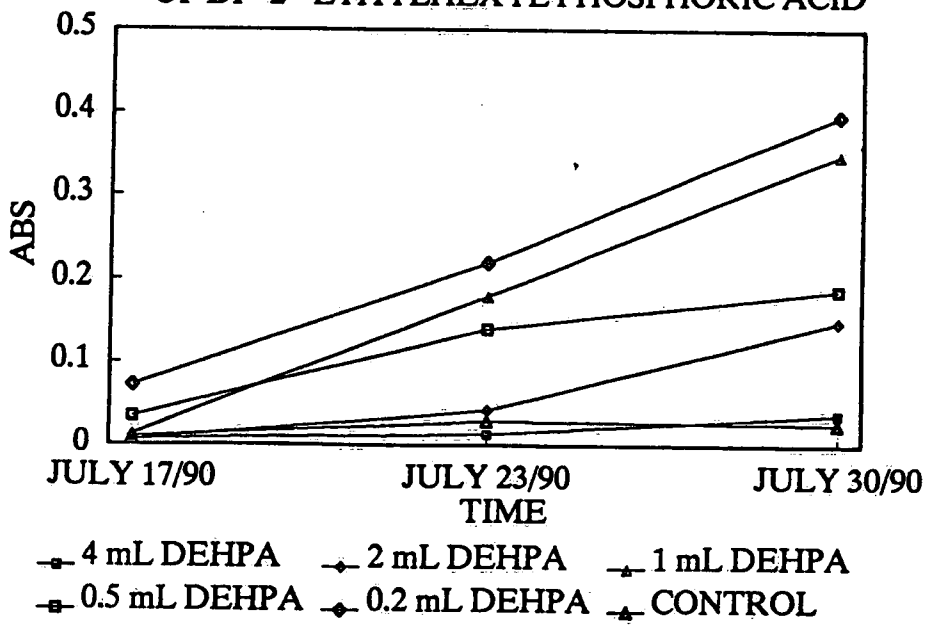
Table 1. ALGAE GROWTH (ABSORBANCE) IN VARIOUS CONCENTRATIONS OF TRIBUTYL PHOSPHATE (TBP) AND DI-2-ETHYLHEXYL PHOSPHORIC ACID (DEHPA)

	JULY 17/90	JULY 23/90	JULY 30/90
	ABS	ABS	ABS
TBP 4 mL	0.007	0.007	0.010
TBP 2 mL	0.005	0.009	0.010
TBP 1 mL	0.010	0.011	0.012
TBP 0.5 mL	0.019	0.141	0.150
TBP 0.2 mL	0.004	0.010	0.022
CONTROL	0.036	0.053	0.043
DEHPA 4 mL	0.007	0.014	0.038
DEHPA 2 mL	0.006	0.043	0.149
DEHPA 1 mL	0.013	0.180	0.349
DEHPA 0.5 mL	0.035	0.140	0.187
DEHPA 0.2 mL	0.072	0.220	0.396
CONTROL	0.010	0.029	0.026

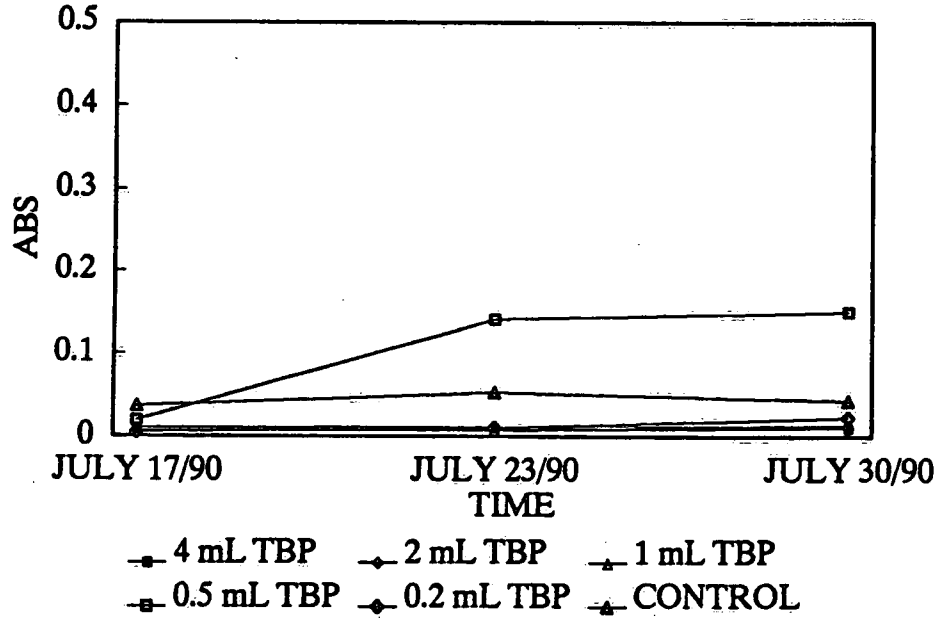
JULY 23/90 average pH - 6.0
JULY 30/90 average pH - 6.5

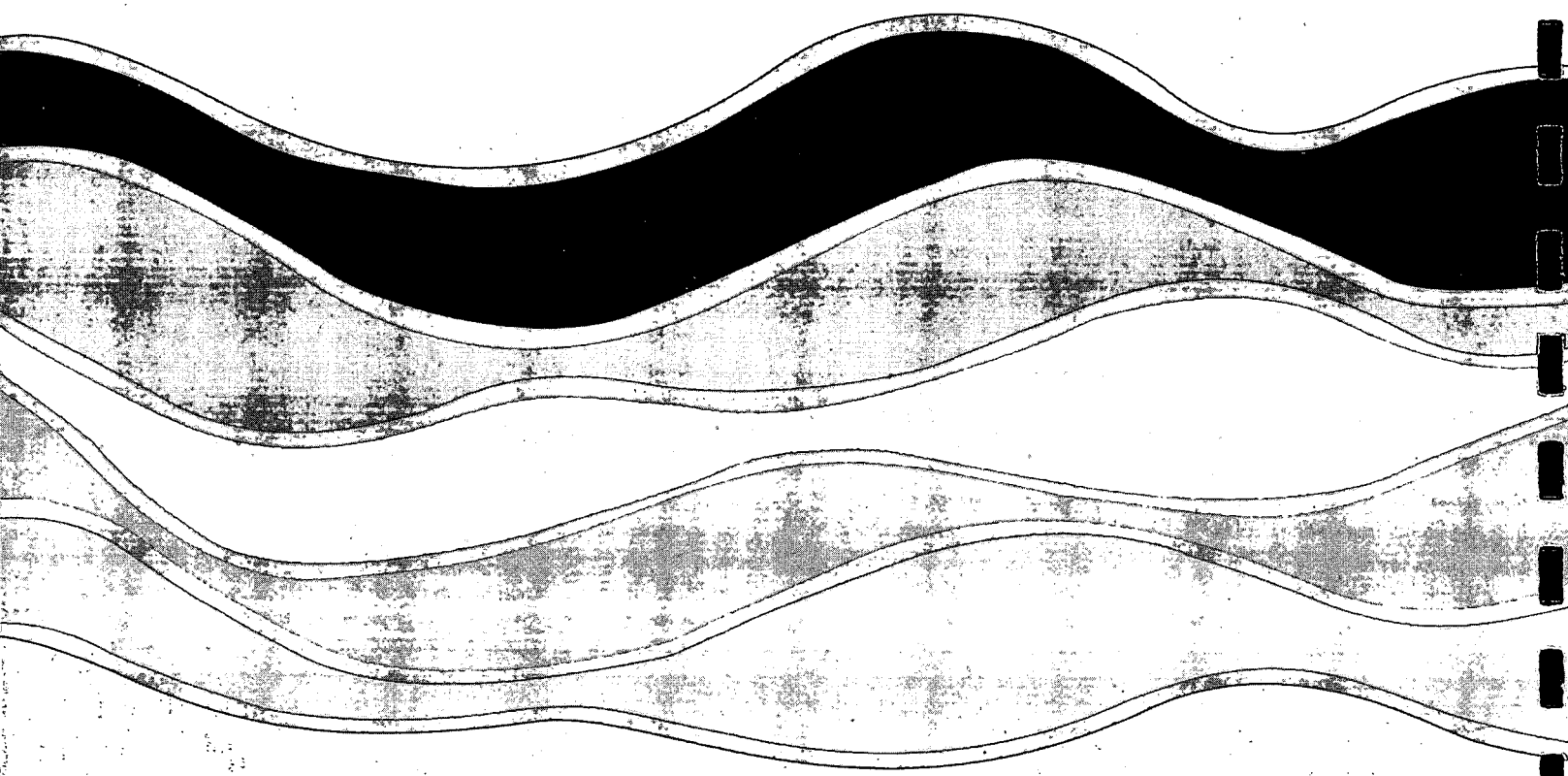
ALL VALUES ARE MEASURED IN ABS ON A VARIAN DMS 100 UV SPECTROPHOTOMETER

ALGAE GROWTH IN VARIOUS CONCENTRATIONS
OF DI–2–ETHYLHEXYL PHOSPHORIC ACID



ALGAE GROWTH IN VARIOUS CONCENTRATIONS
OF TRIBUTYL PHOSPHATE





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