From the preceding data, it seems probable that large amounts of silica are being and have been deposited in marine sediments, especially shales. If conditions are suitable, there could be a segregation of silica, either during weathering or during transport and deposition, whereby relatively pure siliceous deposits could be precipitated.

Much of the segregation could take place upon weathering. From a study on the weathering of a granite gneiss, Goldich (13) has indicated that the residual products contain much more alumina and less silica than the original rock. Mason (10) states, "From pH 5-9 the solubility of silica increases considerably, but alumina is practically insoluble. Under these conditions, removal of silica can take place, leaving alumina behind, as has been inferred during the formation of laterites and bauxites."

The pH of 5-9 is a common pH of present-day streams and silica would, therefore, be predominant over alumina. This is borne out from the data by Clarke on analyses of river water which were given before in this discussion.

In order to obtain a clean separation of silica, the land in all probability must be in a state of low relief. Under conditions of low relief it would be possible to have a mantle of residual material which would retain the alumina and iron and contribute relatively large quantities of silica to fluviatile waters. It is believed that relief is a very important factor in the formation of siliceous deposits. This is not a new idea. Moore and Maynard (14) stated, "At the present time the greater portion of the silica entering sea water is being deposited with the clays and silts, but at times of peneplanation, when chemical denudation is at its maximum, the silica as well as other chemical precipitates might form pure deposits."

When the silica, which is weathered under the conditions outlined above, is carried to the sea, it is in all probability precipitated or flocculated. The mechanism must be that the silica is precipitated by the presence of large amounts of electrolytes or ions in sea water. If Fe+++, Al+++, or some other highly charged cation or positive colloid were present, it is possible that it would be attracted to the SiO₃ ion or to the negatively charged colloidal silica and cause precipitation or flocculation to form clay minerals. A small amount of a highly charged cation could precipitate a large quantity of silica. During diagenesis the excess silica could be released from the complex to form colloidal-size quartz.

References

- 1. ROY, C. K. Am. J. Sci., 243, 393 (1945).

- RUI, C. R. Am. J. SOL, 253, 393 (1945).
 CLARKE, F. W. U. S. Geol. Survey Bull. 770 (1924).
 SVERDRUP, H. V., JOHNSON, M. W., and FLEMING, R. H. The Oceans. New York: Prentice Hall (1942).
 RANKAMA, K., and SAHAMA, TH. G. Geochemistry. Chi-cago: Univ. of Chicago Press (1950).
 PROMPRY H. H. G. Geochemistry New York, New Yo
- 5. BUCKLEY, H. H. Crystal Growth. New York: Wiley (1951).
- REVELLE, R. J. Sedimentary Pet., 5, 37 (1935).
 CORRENS, C. W. "Die Sedimente des äquatorialen atlantis-chen Ozeans." Deutsche atlantische Exped. Meteor., 1925-27, Wiss. Erg. Bd. III, Teil III.

8. GRIM, R. E., DIETZ, R. S., and BRADLEY, W. F. Bull. Geol. Soc. Amer., 60, 1785 (1949). 9. JOHNSON, F. W. "Non-Carbonate Minerals in some In-

- diana Limestones and Dolomites." Unpublished M.S. thesis, Indiana Univ.
- 10. MASON, B. H. Principles of Geochemistry. New York: Wiley (1952).
 11. STEIGER, G. J. Wash. Acad. Sci., 4, 59 (1914).
 12. PETTIJOHN, F. J. Sedimentary Rocks. New York: Harper
- (1949).
- 13. GOLDICH, S. S. J. Geol., 46, 17 (1938).
- 14. MOORE, E. S., and MAYNARD, J. E. Econ. Geol., 24, 272 (1929).

Manuscript received November 24, 1952.

Diethyl 2-chlorovinyl Phosphate and Dimethyl 1-carbomethoxy-1-propen-2-yl Phosphate—Two New Systemic **Phosphorus Pesticides**

R. A. Corey, S. C. Dorman, W. E. Hall, L. C. Glover, and R. R. Whetstone

Sbell Agricultural Laboratory, Modesto, and Shell Development Company, Emeryville, California

The use of organic phosphates as pesticides has increased rapidly since their discovery by Gerhard Schrader (1) in Germany immediately prior to World War II. Following this, Schrader proceeded to demonstrate the activity of certain of these as systemic poisons: poisons taken into and transported through the plant. Much additional work has been done by other workers since Schrader's discovery.

During an investigation of certain new organic phosphorus compounds at the Shell Agricultural Laboratory, 2 have given outstanding results when used as systemic poisons and as fumigants. The 2 organic phosphorus compounds are diethyl 2-chlorovinyl phosphate (distils at 116° C at 10 mm) and dimethyl 1-carbomethoxy-1-propen-2-yl phosphate (distils at 106-7.5° C at 1 mm).

The systemic activity of the two new compounds was measured by a root absorption technique. In this test the materials are diluted to the desired ppm of toxicant in water from a 1% by weight acetone solution. This dilute solution is placed in a 250-ml Erlenmeyer flask and a pinto bean plant with 2 primary leaves and with roots washed free of soil is placed in the flask. A gas barrier of nonabsorbent cotton is placed in the neck of the flask around the stem of the pinto bean plant to prevent fumigation effects from volatile compounds. The pinto bean plant has been infested previously with 2-spotted mites, Tetranychus bimaculatus, Harvey. Mortality counts are made 48 hr after introduction into the flask. Two compounds that have systemic activity and are in commercial use were used as reference materials, i.e., Systox¹ (diethyl 2-mercaptoethyl thionophosphate) and OMPA² (octamethylpyrophosphoramide).

¹Chemagro Corporation, 350 Fifth Avenue, New York 1, N. Y. ² Monsanto Chemical Company, St. Louis 4, Mo.

TABLE 1 CONTACT SPRAY AND SYSTEMIC ROOT ABSORPTION ACTIVITY OF ORGANIC PHOSPHORUS COMPOUNDS

Compound	Contact Approx. LD ₅₀ g/100 ml			Systemic	Mammalian, acute oral LD ₅₀ mg/kilo	
	Pea aphid	2-Spotted mite	Housefly	ĽĎ₅₀ ppm*	Mice	Rats
Diethyl 2-chlorovinyl phosphate Dimethyl 1-carbomethoxy-1-	0.09	0.05	0.02	0.75	30.5	7.0
propen-2-yl phosphate	0.002	0.008	0.008	0.75	9.0	4.0
Systox	0.001	0.006	0.1	1.5		8.0
о́мра	0.07	0.1	> 5.0	25.0		13.5

* Parts toxicant per million parts water.

Laboratory contact spray tests with these compounds have been run using pea aphids, Macrosiphum pisi (Kalt.), and adult houseflies, Musca domestica L., in addition to 2-spotted mites. The mammalian toxicity for diethyl 2-chlorovinyl phosphate and dimethyl 1-carbomethoxy-1-propen-2-yl phosphate was determined by Kodama, Morse, and Hine (2). A figure for OMPA was taken from Lehman (3) and that for Systox was supplied by the manufacturer.

Contact, systemic, and mammalian toxicity data are given in Table 1. It may be seen that the new compounds showed extremely high systemic activity, moderate to high contact activity, and mammalian toxicities approximately equal to those of Systox and OMPA.

TABLE 2

FUMIGATION ACTIVITY TO RED FLOUR BEETLE, Tribolium castaneum, AT 25.5° C

ı	Space fumigation		Grain fumigation	
	Dose	Re- sults	Dose	Re- sults
Compounds	ml/500-ml flask	% mortality, 24 hr	ml/2-qt jar	% mortality, 24 hr
Diethyl 2-chlorovinyl phosphate	0.0001	100	$0.0012 \\ 0.005$	88 100
Dimethyl 1-carbo-	0.0004	35	0.0012	5 2
methoxy-1-propen- 2-yl phosphate	0.0015	90	0.005	100
Chloropierin			0.004	0
-			0.015	100
Methyl bromide			0.004	2
			0.015	100

The space fumigation effects of these compounds were determined in 500-ml glass flasks against the red flour beetle, Tribolium castaneum (Herbst). To determine the effects in grain, the same species was used in 2-qt jars filled with barley. Results are summarized in Table 2. These data indicate high activity of the compounds as space fumigants and a greater activity for the compounds as grain fumigants than is obtained with either chloropicrin or methyl bromide.

References

1. SCHRADER, G. The Development of New Insecticides. B.I.O.S.

- Final Report No. 714 (revised), London : H.M.S.O. (1947). 2. KODAMA, J., MORSE, M., and HINE, C. H. Federation Proc., in press.
- 3. LEHMAN, A. J. Assoc. Food & Drug Officials U. S., Quart, Bull., 15, 122 (1951).

Manuscript received November 26, 1952.

The Hydrogen Ion Concentration of Human Fetal Blood in Utero at Term

Irwin H. Kaiser¹

Department of Obstetrics and Gynecology, University of Minnesota Medical School, Minneapolis

Recent studies of the acid-base and electrolyte status of newly born infants have reinforced the impression that these infants maintain equilibria substantially different from those of the adult (1). The outstanding differences are a lower pH in the blood and a lower CO_2 content in the plasma.

The investigations of Noguchi (2) concerning the pH of the infant's blood at birth make it clear that acidosis is present at that time. They do not, however. demonstrate whether this acidosis is a consequence of labor or maintenance of in utero conditions. pH data are at present available on only 5 infants in utero (3, 4). The values on 4 of these (4) vary widely, include contradictory differences and are based on calculation rather than direct mensuration. It, therefore, appeared desirable to measure the pH of the blood of the human fetus in utero at term.

Blood samples were obtained at the time of elective Cesarean section at term. The mothers received a variety of preanesthetic medications, followed by local infiltration anesthesia. Maternal blood samples were procured from a peripheral and from a uterine vein. The uterine incision was made and the umbilical cord only delivered. Fetal blood samples were then taken simultaneously from umbilical artery and vein. Oiled, heparinized syringes were employed, and after filling were capped and placed in ice.

pH determinations were made by means of a glass electrode as soon as possible after sampling. Samples

¹ pH determinations were done through the cooperation of E. B. Brown of the Department of Physiology and J. D. MacCarthy of the Department of Laboratory Medicine.