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University of Tennessee Agricultural Experiment Station

S. Marcovitch

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STUDIES ON TOXICITY OF FLUORINE COMPOUNDS

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Bulletins of this Station will be sent, upon request, free of char to any farmer in the State.

STUDIES ON TOXICITY OF FLUORINE COMPOUNDS

By

S. Marcovitch

INTRODUCTORY

The increasing demand for arsenicals, coupled with a severe outbreak of the cotton worm (*Alabama argillacea*) and a heavy boll weevil infestation, was sufficient to deplete the available supply of arsenical poisons in 1923. Many fields of cotton were lost because of the shortage of arsenicals, for which substitutes were unavailable. The importance of the cotton crop and the increasing number of crop pests warrant further search for effective, economical stomach poisons that may be substituted for the arsenicals.

The most promising materials that possess the necessary qualifications seem to be the fluosilicates, which the writer used successfully in 1924 against the Mexican bean beetle (*Epilachna corrupta*). It is therefore imperative that further studies be made upon these fluorine compounds. There are various questions to be considered, among which are mode of action, effect on man and the higher animals, plant tolerance, comparative toxicity, effectiveness against diverse insects, and commercial availability.

This bulletin is based on 4 years' field and laboratory study, the major portion of which was carried out at the Agricultural Experiment Station, at Knoxville. The effect of fluorine compounds on higher animals was determined in the Department of Pharmacology of the University of Minnesota. The experimental work with poison baits for cutworms and grasshoppers was performed by the Assistant Entomologist, Mr. W. W. Stanley.

HISTORICAL

A careful search of scientific literature failed to disclose any reference to the use of the fluosilicates as protective agents against the ravages of phytophagous insects. In 1925 the attention of the writer was called to an obscure British patent, No. 8236, taken out by C. H. Higbee in 1896, entitled, "An Improved Composition or Material for Destroying Insects." This appears to be one of the earliest references to the insecticidal properties of the fluorine compounds. In his patent Higbee states that he considers fluorine compounds to be effective against such insects as the Colorado potato beetle (*Leptinotarsa decemlineata*) and roaches. He believed that Paris green and phosphorus were dangerous compounds to use, but that the fluorine compounds might be applied to edible plants or vegetables without risk of poisoning. The compounds employed by Higbee were fluorides of sodium and iron, the silico-fluorides of the same bases, hydrofluosilicic acid, and the borofluosilicates, either in a 1 per cent solution or a solution of 1 part in 500 parts of water. For roaches in buildings and on vessels, finely pulverized sodium fluoride and sodium silico-fluoride were advocated. Although the fluorine compounds were lost sight of as possible plant insecticides, they continued to be used as the principal ingredients in roach powders.

Marlatt (1915) recommends sodium fluoride as the most effective simple means of ridding premises of roaches.

Schafer (1915) first pointed out how sodium fluoride kills roaches. When a roach runs through sodium fluoride a little of the powder adheres to the lower part of the body and to the antennae and legs. The adhering powder irritates the antennae and legs, and the insect draws them through its mouth in the process of cleaning itself. Enough of the powder is thus taken in to cause death.

Gibson (1916) controlled the common carpenter ant (*Camponotus pennsylvanicus* and *Cremastogaster lineolata*) by dusting with sodium fluoride.

Bishopp and Wood (1917) reported that a single application of sodium fluoride was an effective insecticide for destroying poultry lice.

Cobenzl (1921) mentions sodium fluosilicate as a common ingredient of rat and roach poisons.

Sodium fluoride was successfully used by Fulton (1923) as the active ingredient in poison baits against the European earwig (*Forficula auricularia*); it was found to be as toxic as arsenious oxide, or more so, and to act more rapidly.

Hargraves (1924), working in India, reported on several fluorine compounds, including barium fluoride, calcium fluoride, sodium fluoride, and sodium fluosilicate. These materials were used as a 1 per cent emulsion against *Spilosoma lubricipeda.* The results with sodium fluosilicate were not especially favorable, and were not discussed. Attention was called, however, to the possible value of fluorspar as an insecticide, and to the high toxicity of both barium fluoride and calcium fluoride.

In South Africa, Ripley (1924) also used sodium fluoride in poison baits against locusts and cutworms.

Because of the known efficiency of fluorine in the control of certain pests, the writer, in 1923, focused his attention on the fluorine compounds as of possible control value against the Mexican bean beetle. Practical field tests with sodium fluosilicate diluted with 9 parts, by volume, of hydrated lime, gave good results. Fortunately, the bean beetle has the habit of drawing its feet through its mouth, and is therefore affected by such other fluorine compounds as calcium fluosilicate and cryolite. Cage tests made by the writer in 1924 showed that sodium fluosilicate diluted with hydrated lime was effective against the cucumber beetle (*Diabrotica vittata*), the bean leaf beetle (*Ceratoma trifurcata*), the potato beetle (*Leptinotarsa decemlineata*), the tobacco hornworm (*Protoparce quinquemaculata*), and the boll weevil (*Anthonomus grandis*), as well as chicken lice and roaches.

Tattersfield and Gimingham (1925) soon afterward showed that *Selenia tetralunaria* succumbed to both sodium and potassium fluosilicate when shoots of hazel were sprayed with 0.75 per cent and with 1 per cent suspensions of these compounds, and that there was no foliage injury. In Arkansas, Baerg (1925) found that blister beetles, which had not been successfully controlled by arsenicals, yielded to the fluosilicates without noticeable foliage injury.

Insecticidal value was claimed for various fluorides by R. C. Roark (1925), in Patent No. 1,524,884. Barium fluoride, with a solubility of 1.63 grams in 1000 cc. of water, was said to be injurious to foliage. Roark claimed, however, that calcium fluoride, lead fluoride, magnesium fluoride, nickel fluoride, and strontium fluoride—all less soluble than barium fluoride—are effective as insecticides and safe on foliage.

Ripley (1925) found that a 2 per cent solution of sodium fluoride gave excellent results against cutworms in South Africa because the fluoride was not repellent. Neither Paris green nor arsenite of soda was readily eaten.

Ninety per cent of the larvae of the sugar cane borer (*Diatrea saccharalis*) were killed with sodium fluosilicate in tests conducted in Alabama by Hinds (1925). No foliage injury is reported. Calcium arsenate failed to kill any large proportion of the borers.

Herrick (1926) obtained excellent control of the striped cucumber beetle in New York State by making 4 or 5 weekly dustings of sodium-fluosilicate-lime (1-9) at the rate of 30-35 pounds to the acre. He states that sodium fluosilicate kills and also repels the beetles.

Genter (1926) found that the mint fleabeetle (*Longitarsus menthae*) can be controlled in Michigan by the "calcium fluosilicate compound" when used at the rate of 40 pounds per acre.

In tests against the boll weevil, Mills (1926), of the Chemical Warfare Service, found that besides calcium arsenate, 3 fluorine compounds, namely, sodium fluosilicate, cryolite, and barium fluoride, were effective. Osburn (1926) found sodium fluosilicate more effective than calcium arsenate against the boll weevil in North Carolina. An average control of 80 per cent was attained in 24 hour while with calcium arsenate 48 hours were necessary for a contr of 69 per cent.

Baerg (1926) obtained good results against the striped cucumber beetle with sodium fluosilicate as well as "calcium fluosilicate compound," because, as he states, the beetles were actually killed. Marshall (1926) also reports good control in Canada.

In a series of tests by Langford (1926) in Colorado, with Paris green, white arsenic, sodium arsenite, sodium fluoride, and sodium fluosilicate, as poisons in grasshopper baits, the last was found the most effective.

Ingram (1926) reports that sodium fluosilicate at the rate of 1 pounds per acre gave practically 100 per cent control against blister beetles in southwestern Louisiana.

Lyle (1927) found Paris green more effective than sodium fluosilicate for the following species of cutworms: *Laphyma frugiperda*, *Prodenia ornithogalli,* and *A. ypsilon.*

Eyer (1927) found that as a contact spray sodium fluosilicate in Bordeaux mixture killed the nymphs of the grape leaf hopper (*Typhlocyba comes*). A dust composed of sodium fluosilicate and lime was superior to arsenicals and nicotine in reducing the percentage of wormy fruit by the oriental fruit moth (*Laspeyresia molesta*).

Eleven per cent foliage injury is reported by Jewett (1927) on beans in Kentucky when sodium fluosilicate was used with 2 parts of hydrated lime.

A progress report of the Chemical Warfare Service boll weevil investigations, by Walker and Mills (1927), points out that sodium fluosilicate on a volume basis is more toxic to the boll weevil than calcium arsenate.

In tests against the Japanese beetle (*Popillia japonica*), Fleming (1927) found that the fluosilicates of barium, potassium, and sodium were of the same order of toxicity as acid lead arsenate, and somewhat injurious to foliage.

Downes (1927) recommends, for control of the strawberry root weevil (*Brachyrinus ovatus*), the use of poisoned bait consisting of apple waste. This is the most recently advocated method. Among the various poisons tried out, such as magnesium arsenate, calcium arsenate, sodium fluoride, and sodium fluosilicate, the last named gave the most satisfactory results.

A special fluosilicate made at Edgewood arsenal, mentioned by Gehauf and Walker (1927), contains about 80 per cent sodium fluosilicate and 20 per cent silica. It proved to be at least as effective, on a pound-per-pound basis, as calcium arsenate, and with no appreciable plant injury. This light sodium fluosilicate is made by passing silicon tetrafluoride into a solution of sodium carbonate.

In Arkansas, Isley (1927) found sodium fluosilicate more effective than "calcium fluosilicate compound" against the striped cucumber beetle. The fluosilicates are reported to be more effective than the arsenicals because the beetles are actually killed rather than repelled.

Eddy (1927) also noted the high toxicity of sodium fluosilicate for the bean beetle, while barium fluosilicate was found somewhat less toxic than the sodium.

In Alabama, field tests with a special light sodium fluosilicate (80 per cent) showed a difference of 290 pounds of seed cotton per acre between the sodium fluosilicate plot and the calcium arsenate plot in favor of the former. Under conditions of heavy rainfall as in Florida, the better adhering calcium arsenate was slightly more effective than the sodium fluosilicate (Walker, 1928).

Snapp (1928) found sodium fluosilicate both as a dust and at the rate of 2 pounds to 50 gallons of water more toxic than the arsenicals to the plum curculio (*Conotrachelus nenuphar.*) The sodium fluosilicate was also toxic to peach foliage and fruit.

Howard (1928) obtained better control of the bean beetle with arsenicals than with fluosilicates, the physical properties of which he found to be poor. When the insects themselves were dusted the sodium fluosilicate killed a higher percentage than the arsenicals.

PROPERTIES AND REACTIONS OF THE FLUOSILICATES

Solubility.—The fluosilicates in general are soluble in water. Barium fluosilicate is the most difficult to dissolve; 1 gram dissolving in 3,750 cc. of water at 17°C. The fluosilicates of copper, calcium, magnesium, lead, and ammonium are very readily soluble, as indicated in table 1.

TABLE 1—*Titration of* 1 *cc. of saturated solutions of fluosilicates with* 1/10 *N NaOH and phenolpthalein, and calculated solubilities*

Fluosilicate compound	1/10 N NaOH	pH	Known solubility	Calculated solubility	Source
	cc.				
Barium	.05	3.4	1-3750	......	Grasselli
Potassium	.12	4.8	1-835	......	Eimer & Amend
Sodium	1.40	3.6	1-154	......	Grasselli
Aluminum	1.80	3.0	....	1-118	British Drug Houses
Ammonium	42.00	4.2	....	1-5	Eimer & Amend
Lead	50.00	....	....	1-4.3	Central Scientific Co.
Magnesium	56.00	2.0	....	1-3.8	Eimer & Amend
Calcium	72.00	....	....	1-2.9	Jungmann Company
Copper	88.00	....	....	1-2.4	Jungmann Company

Sodium Fluosilicate

Chemical properties. — In water, hydrolysis is thought to take place according to the following equation:

$$Na_2SiF_6+2H_2O=2NaF+4HF+SiO_2$$

One mol of sodium fluosilicate requires 4 mols of sodium hydroxide for neutralization. Twenty-one cubic centimeters of normal NaOH, or nearly 1 gram, is required to neutralize 1 gram of sodium fluosilicate according to the following equation, phenolpthalein being used as an indicator:

$$Na_2SiF_6+4NaOH=6NaF+Si(OH)_4.$$

According to the above equation, 1000 cc. of normal NaOH is equivalent to 47.07 grams of Na_2SiF_6.

With calcium carbonate, the following reaction takes place:

$$Na_2SiF_6+2CaCO_3=2NaF+2CaF_2+SiO_2+2CO_2.$$

A saturated solution of sodium fuosilicate shows a pH value of 3.6, and never goes lower than 3, indicating a buffer action, as shown in Fig. 2.

Physical properties.—Sodium fluosilicate is an acid salt, having a solubility of 1 gram in 154 cc. of water at 17.5°C., but is insoluble in alcohol. It forms hexagonal crystals, and possesses a rather high specific gravity. The particles of some of the commercial grades are large (100 microns), and not suitable for dusting. The particles of the commercial form produced by the Grasselli Chemical Company average about 10 microns, and when mixed with a suitable carrier will dust satisfactorily. In order to dust well, the particles should be from 2 to 4 microns in diameter, such as are found in a good grade of commercial calcium arsenate.

Various methods have been proposed by means of which a light, fluffy sodium fluosilicate may be produced. In 1924 the writer made a light sodium fluosilicate by using sodium silicate as a peptizing agent. Calcium silicate may also be used. This consists of fluosilicic acid with the addition of about 10 per cent of a calcium salt, such as calcium carbonate or chloride. The addition of enough sodium silicate and sodium chloride forms a mixture of calcium silicate and sodium fluosilicate, which is very much lighter than the commercial fluosilicates. Gehauf and Walker (1927) proposed a method of making a light material by passing the by-product gases of silicon tetrafluoride into a solution of sodium carbonate. This forms a gel which upon drying is said to have a specific gravity as low as .25 and contains 79.5 per cent sodium fluosilicate.

A sample of a special light sodium fluosilicate was submitted to the writer by the Bowker Chemical Company. Their product contains 80 per cent sodium fluosilicate with 20 per cent silica, and occupies 80 cubic inches to the pound. This special light sodium fluosilicate is much superior in dusting qualities to any of the commercial fluosilicates now on the market.

The J. C. Wiarda Company are marketing a light fluosilicate which contains about 65 to 70 per cent sodium fluosilicate. Their material is sold under the name "Eborex."

Calcium Fluosilicate

The properties of calcium fluosilicate have not been studied to any considerable extent. Statements may be found in the chemical literature regarding the insolubility of calcium fluosilicate. Subsequent study has shown that this compound forms monoclinic crystals and is very soluble. In water, hydrolysis proceeds rapidly, with the liberation of much free acid, and a precipitate of calcium fluoride and silica. The formation of the precipitate is apt to be misleading as to solubility. The large amount of acid liberated is indicated by the pH value, which may be as low as 1.5, or less. A gram of pure calcium fluosilicate will require 180 cc. of 1/10 N sodium hydroxide for neutralization.

In the making of calcium fluosilicate, precaution has to be taken to keep the compound from going over to calcium fluoride. The latter material will usually be formed unless one is careful to use neutral salts for the calcium base, and to dry the compound at room temperature. Most of the calcium fluosilicate samples submitted have been found to be principally calcium fluoride as shown in table 2.

TABLE 2—*Titration of 1 gram of salts of fluosilicic acid with 1/10 N NaOH*

Compound	1/10 N NaOH with methyl orange	1/10 N NaOH with phenolphthalein	Source
	cc.	cc.	
Sodium fluosilicate, C. P.	15	218	Baker
Calcium fluosilicate	65	180	Jungmann
” ”	25	45	Eimer & Amend
” ”	......	5	Smith
” ”	5	7	British Drug Houses
Calcium fluosilicate compound	......	8	Victor
Magnesium fluosilicate, C. P.	20	188	Eimer & Amend
Barium fluosilicate, C. P.	......	110	Eimer & Amend

“Calcium Fluosilicate Compound”

This material is a by-product residue obtained in the manufacture of phosphoric acid from phosphate rock by the volatilization method. As phosphate rock contains calcium fluoride, there is reason to believe that the fluorine in the “compound” exists in the form of calcium fluoride, and not in the form of a fluosilicate, which is readily decomposed by heat. Its measure of toxicity is low, and more like that of calcium fluoride, so that the name “calcium fluosilicate compound” is misleading. Pure calcium fluosilicate is very soluble and very toxic.

COMMERCIAL AVAILABILITY

Phosphate rock contains about 3 per cent calcium fluoride. The large amount of this rock used in the making of acid phosphate for fertilizer purposes insures an adequate supply of by-product fluorine compounds.

The manufacture of acid phosphate is one of the largest chemical industries. More than 2,000,000 tons of phosphate rock are annually mined in the United States. It is thus possible to recover enough fluorine to make over 50,000 tons of sodium fluosilicate—more than enough to supply our domestic needs for years to come. Large amounts of sodium fluosilicate are also imported from Europe.

When sulphuric acid is added to phosphate rock for the production of acid phosphate, fumes are liberated. Formerly these fumes were allowed to escape, but as they were very injurious to vegetation, laws were enacted requiring that the gases be confined.

The gases are now conducted into towers, where silicon tetrafluoride reacts with dripping water to form a weak solution of fluosilicic acid. In most cases this acid is not saved but is allowed to drain away. In the production of sodium fluosilicate, sodium chloride is added to the fluosilicic acid, and sodium fluosilicate precipitates out. The commercial material is fairly pure, containing about 98 per cent sodium fluosilicate. An analysis submitted by the Virginia-Carolina Chemical Company of their product is as follows:

	Per cent
Sodium fluosilicate	98.55
Sodium chloride	.60
Moisture	.10
Free silica and undetermined	.75
Sodium Carbonate	None

The presence of silica and flourine in phosphate rock, together with the great affinity they have for each other, insures the extensive and cheap production of fluosilicates. Sodium fluosilicate may now be purchased in bulk for 4½ cents per pound. The fluorides are made from the by-product sodium fluosilicate, and are therefore relatively more expensive.

The reaction which takes place in the manufacture of acid phosphate may be represented thus:

$$CaF_2+H_2SO_4=2HF+CaSO_4$$

$$4HF+SiO_2=SiF_4+2H_2O$$

$$3SiF_4+2H_2O=2H_2SiF_6+SiO_2$$

$$H_2SiF_6+2NaCl=Na_2SiF_6+2HCl$$

NATURE OF POISONING BY FLUORINE COMPOUNDS

Effect on insects.—Marlatt (1915) states that it is not definitely known whether sodium fluoride acts through the breathing pores or as a stomach poison. Shafer (1915), in his bulletin, "How Contact Insecticides Kill," reports that sodium fluoride is primarily a stomach poison, and, being non-volatile, does not act through the spiracles. As sodium fluoride is soluble, it produces an irritation which causes a roach to draw its feet and antennae through its mouth. Shafer observed that sodium fluoride may kill roaches in from 5 to 22 hours, even when none of the material is swallowed, and that "some of the powder is moistened or dissolved in the exudation about the bases of the legs and on the thinner portions of the outer integument." Sodium fluoride is more rapid as a stomach poison than as a contact insecticide. The *irritation*, as the result of some sort of chemical reaction caused by fluorides, is distinguished by Mote, Wilcox and Davis (1926) from *cleanliness* as a natural tendency on the part of insects to clean any powdered material from the body. These authors consider that because of the natural "cleaning-up" habit of certain insects, dusts are more effective than sprays.

Dew in its relation to the effect of dusts.—The importance of taking advantage of the "cleaning-up" habit of the Mexican bean beetle was strikingly shown in cage tests where the beetles could be observed. Some of the plants were waterd to simulate dew, and the upper side of the foliage was dusted with sodium fluosilicate mixed with 3 parts of sulphur. Other plants were dusted without being watered.

Where the plants were not watered the beetles became uneasy and attempted to fly away. After 48 hours, no feeding was observed, and 50 per cent of the beetles succumbed. In the cage simulating dew the beetles began to feed at once, and within 40 hours destroyed large areas of the leaves and showed 25 per cent mortality.

In our field tests the dusts were always applied after the dew was off the plants, and good control was obtained. Prior to dusting, 95 beetles to the row were counted in one of the plots. Four hours after the dust was applied only 5 beetles to the row were present.

By taking advantage of the "cleaning-up" habit of the adult Mexican bean beetle, it is possible to drive them away or destroy them. Since they crawl over the tops of the plants, the dust may be directed to the sides of the plants so that the tops of the leaves as well as parts of the lower surfaces will be covered. This results in a great economy of time, as the operation of applying the dusts to the underside of the leaves is very laborious, and discourages many farmers in their fight against the bean beetle.

Further confirmation of the value of dusts is given by Walker and Mills (1927) in the report of their work with the boll weevil. They observed that a weevil ingests the poison by accidentally picking up particles of the dust on its moist snout. Walker and Mills state that a dust "must not stick so tightly to the plant that it can not be readily picked up by the weevil."

Effects of fluorine compounds on vertebrates.—The manner of action of fluorine compounds on vertebrates and other organisms has been studied by various investigators. In the pharmacological literature, fluorides are classed as protoplasmic poisons, and often referred to as calcium precipitants, because they remove calcium from the tissues. Wieland and Kurtzahn (1923), in their study of the action of fluorine, came to the conclusion that sodium fluosilicate liberates fluorine ions, and toxic effects are manifest because these ions combine with the calcium in the tissues. The poisonous character of hydrofluoric acid is due to the "intact hydrofluoric acid molecules" which penetrate cells readily.

Importance of calcium.—The importance of calcium, as well as of other salts, was investigated by Ringer (1880), who noted that the contractions of the excised heart were not normal in pure sodium chloride solution isotonic with blood serum. This solution was unsatisfactory, for after a few minutes the heart stopped beating. When traces of calcium and potassium were added, the heart beat became normal. This phenomenon was also investigated by Loeb (1889), who found that a pure sodium chloride solution is a strong poison for many marine organisms. The poisonons quality may be neutralized or antagonized by a trace of calcium choride, in the ratio of one mol of calcium to 200 mols of sodium. Other bivalent ions, such as barium, cobalt, zinc, magnesium, and lead, may be substituted for the calcium. Similarly, the importance of magnesium and calcium in a certain ratio was determined for the larvae of the barnacle. Having ascertained the significance of the ratio of $\frac{Na}{Ca}$ and $\frac{Na+K}{Mg+Ca}$ Loeb concluded that the "salts with univalent ions are injurious if their concentration exceeds a certain limit, and this injurious action is diminished by a trace of a salt with a bivalent cation." By "physiologically balanced salt solutions" we mean that in the ocean (and in the blood or lymph) the salts exist in such ratio that they mutually antagonize the injurious action which one or several of them would have if they were alone in solution.

The same law of mutual antagonism, according to Osterhout (1914), seems to hold in the plant kingdom as well.

Loeb (1901) also investigated a number of salts whose anions are liable to form insoluble calcium salts, as sodium fluoride, sodium carbonate, sodium phosphate, sodium oxalate, sodium citrate, and sodium tartrate. Fresh frog muscle that was placed in solutions of the above salts (1 gram molecule in 10 liters of water) performed a series of powerful contractions when removed into the air. This phenomenon, Loeb termed "contact reaction." Addition of calcium chloride to the solutions stopped the contact reaction. When the nerve alone was placed in the salt solutions, the muscle began to twitch in 5 minutes and finally went into tetanus. These salts therefore increase the irritability of the nerve as well, through the withdrawal of calcium.

Many of the salts mentioned are used as saline cathartics. MacCallum (1903) showed that 10-cc. doses of sodium citrate, sulphate, or tartrate produced pronounced purgation with copious secretion in the intestine when injected subcutaneously in rabbits. The intensity of the action followed this order: Barium chloride, sodium citrate, sodium fluoride, sodium sulphate, sodium tartrate, sodium oxalate, and sodium phosphate. Applications of calcium chloride or magnesium chloride inhibited these effects. It seems that the stimulating action of the purgative salts is due to displacement of calcium and consequent irritability. This does not appear to be the case with barium, which, however, may displace calcium in a way unknown at present.

The exact relationship of magnesium and calcium in the animal body is obscure, but the question has recently been illuminated by the work of Mathews and Austin (1927). These authors have shown that the fatal dose of magnesium sulphate for intravenous injections in dogs is 0.23 to 0.28 gram per kilo. Dogs with hypercalcemia tolerated 0.30 gram, whereas hypocalcemic dogs were killed by 0.14 to 0.19 gram. It is evident that the toxicity of magnesium sulphate is closely related to the calcium content of the blood.

Relation of calcium to permeability.—The total amount of blood calcium in a rabbit weighing 2 kilos is probably around 10 mg. Since 200 mg. per kilo of sodium fluoride injected intravenously is fatal, it is evident that all of the calcium might be precipitated out. The lack of calcium is considered to increase the permeability for sodium chloride and water, which then act as a poison. Loeb (1905) believed that calcium in some way forms a precipitate whereby the membrane becomes less readily permeable.

In order to account for the change in permeability, Clowes (1916) suggested the emulsion structure of the superficial layer in cells. The sodium salts tend to produce an emulsion of oil in water. Under normal conditions both types of emulsions exist in the surface membranes. A lack of calcium would shift the emulsion structure to one of oil in water and thus alter the permeability for water-soluble substances.

Hirschfelder and Serles (1926) have used Clowes' hypothesis to account for the antagonistic action of magnesium and calcium. They found that in olive oil emulsions, magnesium salts tend to increase the water-in-oil phase more than do calcium salts, owing to the much greater solubility of magnesium oleate in oil. The injection of magnesium salts into the body should therefore tend to diminish the oil-in-water phase of a balanced emulsion; and the injection of calcium salts tends to restore it to the normal physiological balance.

Although Clowes' view of the emulsion structure of the cell membrane is useful, it is not adequate to account for all the facts. Weiser (1926) proposes that the cell membrane be considered as a more or less rigid semi-permeable pellicle, comparable in certain respects to a copper ferrocyanide membrane consisting of myriads of minute particles analogous to a colloidal sol. The space between the particles is more or less occupied by adsorbed water and the film capable of reversible coagulation. Below a certain concentration the salts will pass through a copper ferrocyanide membrane and sugar will not, while at higher salt concentrations both will pass through; the salts being soluble in the water layer and passing through the membrane. Sugar molecules can not pass through because of the strong negative adsorption. When the salt concentration reaches the critical coagulation value, the result is an agglomeration of the particles, which carry with them their film of adsorbed water, leaving cracks through which the sugar can pass. Reversing the coagulation by adding a peptizing agent re-forms the semi-permeable film, and the sugar will no longer pass through. The membrane of the living cell is therefore likened to a colloidal sol that can undergo reversible coagulation, thus altering the permeability with reference to the action of salt pairs.

Fisher (1921) suggests that calcium and magnesium globulinates when robbed of their bases, tend to precipitate "globulinic" acid with an increased hydration capacity and diffusibility of the albumin type of proteins.

Influence of calcium on electrical conductivity.—The property of semi-permeability is associated with a high degree of electrical resistance. All conditions that increase general permeability, such as the action of cytolytic substances, unbalanced salt solutions, or poisons, high temperature, or other lethal agents, also increase electrical conductivity (Osterhaut, 1922; Lillie, 1923). When two salts are present in appropriate proportions ($20NaCl+1CaCl_2$) conductivity is unaltered.

Calcium appears to be necessary for the intimate union between the nerve end-plate and muscle cell or for the normal properties of the synaptic junctions. In pure isotonic solution, calcium salts render muscle resistant to stimulation, while magnesium salts have a strong anti-stimulating, or narcotic, action. The semi-permeable partitions, or surface films, of cells seem to be intimately connected with electrical sensitivity of living protoplasm.

Fluorides as enzyme poisons.—Loevenhart and Pierce (1906) have shown that sodium fluoride has a marked inhibiting action on lipase. Pancreatic esterase is injured by sodium fluoride in dilutions less than 1-80,000. Waksman and Davison (1926) found that pepsin and trypsin are apparently not affected. In the insects, Shafer (1915) found sodium fluoride detrimental to the catalases.

Symptoms of poisoning by fluorides in animals.—According to Robertson (1911, 1924), small doses of such calcium precipitants as citrates, oxalates, fluorides, tartrates, oleates, and other soaps, act as cathartics on mammals. Larger doses produce peripheral twitchings, succeeded by convulsive movements and marked disturbances of equilibrium. The forelegs are extended and the head is thrown back. Convulsive effects may be produced by the injection of minute doses to the white matter of the cerebellum, but not to the gray matter above.

Tappeiner (1889) noted the systemic effects of sodium fluoride on mammals to be salivation, gastroenteritis, dyspnea, muscular weakness, and tremors, with fall of arterial pressure and stoppage of respiration and heart.

Siegfried (1901) observed that the intestinal epithelium is destroyed, even though the poison may be introduced through other channels.

Schultz (1889) found that subcutaneous injections of sodium fluoride produced a paralysis of the brain and spinal cord, profuse flow of saliva, and hemorrhage from the gastric mucosa.

Dose of fluorine compounds fatal to higher animals.—It is generally believed that fluorides are not as toxic as the arsenicals to man and the higher animals, but the available data are meager. The lethal dose of sodium fluoride by mouth for mammals is considered by Tappeiner (1889) to be 0.5 gram per kilo. Wieland and Kurtzahn (1923) give between 0.1 and 0.2 gram per kilo for rabbits. Ripley (1924) says that 1 gram of sodium fluoride is reported to have killed a 20-pound dog in 4 days. For intravenous injections, Schultz (1889) gives 0.2 to 0.4 gram for rabbits, and 0.3 gram for dogs. Blaizot (1883) obtained a lethal effect intravenously against rabbits with only 0.1 gram per kilo.

In regard to sodium fluosilicate, comparatively little information is available. For rabbits, Wieland and Kurtzahn (1923) state that the lethal dose by mouth is between 74 and 149 mg. per kilo. When subcutaneously injected, Siegfried (1901) states, the fatal dose for hedgehog is between 1.43 and 2.14 grams per kilo. A cat given 0.98 gram per kilo did not die. It is evident, from the high doses given, that impure compounds were used by Siegfried, as well as by many of the other early workers.

Experiments with rabbits.—In order to arrive at more exact information as to lethal doses, the writer used chemically pure fluorine compounds in a series of experiments with rabbits. The lethal dose of sodium fluoride by mouth seems to be between 192 and 475 mg. per kilo. Of sodium fluosilicate, 125 mg. per kilo is fatal, but 100 mg. is not (table 3). The lethal dose of potassium arsenite, as given by Sollman (1924), is from 5 to 15 mg. per kilo. The soluble arsenicals seem to be, therefore, considerably more toxic than sodium fluosilicate when given by mouth (Fig. 1). Even the insoluble calcium arsenate is reported to be more toxic than sodium fluosilicate. The lethal dose of sodium fluosilicate is 2½ for rabbits and 4 for dogs when calcium arsenate is 1. Of barium fluoride, the lethal dose is 4 for rabbits and 14 for dogs (Walker and Mills, 1927).

TABLE 3—*Lethal doses of fluorine compounds for rabbits*

No.	Weight	Compound	Dose per kilo	Effect on life
	Grams		mg.	
1	2,100	Sodium fluoride per Os	125	Not fatal
2	2,600	” ” ” ”	192	Not fatal
3	2,100	” ” ” ”	475	Lived 1 hour
4	2,000	Sodium fluosilicate per Os	100	Not fatal
5	2,000	” ” ” ”	125	Lived 5 days
6	1,550	” ” ” ”	250	Lived 30 minutes
7	1,800	” ” ” ”	275	Lived 1 hour
8	2,500	” ” ” ”	400	Lived 45 minutes
9	1,200	” ” (intravenously)	10	Lived 2 minutes

Intravenously, 10 mg. per kilo of sodium fluosilicate was fatal in 2 minutes. One rabbit was given 5 mg. per kilo, which was not fatal. The same animal was given 2.5 mg. at intervals of 15 minutes, a total of 12.5 mg. in all, and did not succumb. The lethal dose of potassium arsenite is given as 7 mg. per kilo within 2 days. At this rate, sodium fluosilicate is almost as toxic as the arsenite, and very much more rapid in its action, when injected intravenously.

Continued feeding of small amounts of arsenic and fluorine.—The question of safety in the eating of fruits and vegetables that have been sprayed or dusted with poisonous materials, such as the arsenicals, is assuming widespread significance. American apples are being barred from England because of the high arsenical residues. The quantity allowed by the Royal Commission on Arsenical Poisoning in 1903 was 1.429 mg. per kg. of foodstuffs.

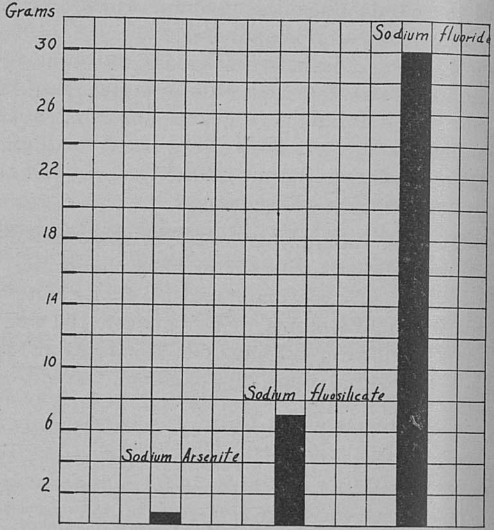

Fig. 1. The relative toxicities of arsenicals and fluorine compounds to man

Recently Hartzell and Wilcoxon (1927) analyzed 47 apples from sprayed trees, and found an average of 0.173 mg. of arsenic trioxide per kilo of fruit, with a maximum of 0.704 mg. per kilo. This is considerably below the British tolerance, but indicates that small amounts of arsenic are present on sprayed fruit. As many people are accustomed to eating an apple a day, the question arises as to the effect on the public health of the continued ingestion of small doses of arsenic. The meager evidence available has been obtained through experiment with rabbits, guinea pigs, and rats.

O'Kane (1917) fed guinea pigs with various amounts of lead arsenate. Daily doses of from 1.7 mg. to 11.9 mg. were not fatal over a period of 30 days. A daily dose of 13.6 mg. was fatal within 22 days. Since the therapeutic dose of arsenic to humans is 2 mg., O'Kane concludes that sprayed apples "offer very slight danger, provided rains have intervened after spraying." Reeves (1925) records that horses and cattle fed from 20 to 30 grams of arsenic trioxide for a period of 18 months showed no evidence of injury. Sheep are mentioned as requiring only 4 to 8 grams daily.

Sollman (1921) continued his feeding experiments for long periods of time (9 to 24 weeks) with albino rats, and obtained some remarkable results. Daily doses of as little as .00005 to .0005 mg. of arsenic trioxide per kilo produced a distinct retardation of growth. A marked loss of weight occurred when doses of .0015 to .005 mg. per kilo were given. These daily doses are only 1/800 to ¼ of the U. S. P. therapeutic dose of 2 mg. The evidence from these experiments would indicate that extremely small amounts of arsenic, such as are found on sprayed fruit, may impair the health of the individual if administered over a period of about six months. More data on the cumulative action of arsenic over extended periods of time are necessary if safe conclusions are to be drawn.

On the other hand, as far as fluorides are concerned, Sollman (1924) found that when sodium fluoride doses of 8 mg. per kilo are administered daily to rats no deleterious effect on growth or food consumption occurred within 9 weeks. When 15 to 150 mg. per kilo were fed, a progressive impairment of growth and food consumption resulted, but with little mortality and no histological lesions.

Christiani and Chausse (1927) continued their experiments over a period of several years. They found that daily doses of 50 mg. of sodium fluoride were fatal to guinea pigs within 2 or 3 months. Doses of 10 mg. were followed by apparent good health for 10 months, yet impairment of health may appear after 2 or 3 years. With sodium fluosilicate, daily doses of 50 mg. per kilo caused death in 18 days. Fourteen mg. per kilo caused death in 51 days; 8 to 10 mg. per kilo was harmless to one of the animals, but the other died in 233 days.

From the above data on the continued administration of arsenic and fluorine compounds in small quantities, sodium fluoride seems very much safer than arsenic. Sodium fluosilicate, although much more toxic than sodium fluoride, seems to be safer than arsenic. Under practical conditions sodium fluosilicate, because of its soluble nature, would readily dissolve in the dews or be washed away by rains so that the residue left on sprayed fruit or foliage would tend to be insignificant. The soluble nature of most fluorides and fluosilicates, on the other hand, renders the problem of obtaining a compatible mixture with fungicides extremely difficult.

Preliminary tests with a copper fluoride complex indicate that this material gives promise of being a good fungicide as well as insecticide for spraying purposes.

Effect of fluorine compounds on man.—Baldwin (1889) summarized the literature up to 1889, and experimented upon himself. He records a case in which 26 grams of the sodium fluoride were used instead of baking powder in making 26 wheat cakes. Assuming the material to have been thoroughly mixed, the amount taken by several different persons was 9, 6, and 5 grams each, respectively. Severe symptoms of nausea, cramps, and vomiting were experienced, but all recovered. One of the persons required 4 weeks for total recovery. Baldwin himself swallowed 0.03 gram of sodium fluoride with no effect; 0.09 gram produced a little salivation, and 0.25 gram produced nausea in 2 minutes. This gradually increased in severity for 20 minutes. The nausea continued the following day, but disappeared the second day.

Vallee (1920) reports that 0.228 to 0.456 gram of sodium fluoride were taken by different individuals when the material was used in pastry through mistake for sodium bicarbonate. Considerable nausea and vomiting was experienced for 36 hours, but all recovered. McNally (1923) records 4 deaths from sodium fluoride. One woman took 4.5 to 5 grams as a laxative, through mistake, and died 4 hours later.

A fatal case of poisoning by sodium fluosilicate was recently reported in the Journal of Industrial and Engineering Chemistry, Vol. 3, No. 22, 1925 (news edition). Sodium fluosilicate was taken instead of sodium bicarbonate for a mild stomach ailment, and death ensued after 10 hours. The poisonous properties of the soluble fluorine compounds are evidently greater than are generally recognized. They are sufficiently dangerous to warrant the use of poison labels, especially in view of their increasing use as insecticides and the frequent cases of death reported from fluorides being taken through mistake.

ATTRACTIVENESS OF FLUORINE COMPOUNDS TO INSECTS

Evidence is accumulating that certain insects are repelled by the arsenicals and will not consume a lethal dose. Ripley (1925) calls attention to the fact that in South Africa cutworms are repelled by arsenicals in poison baits, and are not readily poisoned. In his experimental work with individual cutworms under laboratory conditions, he found that sodium fluoride, although not as toxic as the arsenites, gave much better control because the bait was more readily consumed.

Since Mr. W. W. Stanley, the Assistant Entomologist at the Tennessee Station, is engaged in a study of cutworms, an attempt has been made to repeat Ripley's findings by using the more toxic sodium fluosilicate rather than sodium fluoride.

For the sake of uniformity in feeding, the larvae of *Feltia ducens* were starved about 24 hours and individual specimens placed in small tin boxes, together with poisoned bait and chopped lettuce. The green food was used with the bait in order to give the worms a choice of food. Any repellent effect, it was thought, would thus be revealed. The baits were made up and used according to the methods given in the section describing the tests of baits against *Melanoplus femur-rubrum*. Sodium arsenite is of the same order of toxicity to insects as sodium fluosilicate and should give, theoretically, about the same kill. The tests with over 100 individual cutworms showed a mortality, at the end of 72 hours, of 88 per cent for the sodium fluosilicate, at the rate of 1-56, while the sodium arsenite gave 57 per cent kill. In one experiment with 10 larvae, white arsenic gave a mortality of 40 per cent, at the same strength. Sodium fluoride showed about the same order of toxicity as sodium fluosilicate.

Our preliminary work thus confirms the findings of Ripley, and indicates that the arsenites are strongly repellent to cutworms such as *Feltia ducens*, whereas fluorine compounds are more readily eaten and give much better control. In another season it is hoped that these experiments may be repeated with other species of cutworms.

Ingram (1926) also noted that calcium arsenate and Paris green, because of their repellent action, would not control blister beetles, whereas sodium fluosilicate gave practically 100 per cent control.

Lyle (1927) working with *Laphyma frugiperda, Prodenia ornithogalli,* and *A. ypsilon*, obtained better control with Paris green than with sodium fluosilicate. In our tests we used the sodium fluosilicate in solution in order to get a more uniform bait. This may explain the superiority of the sodium fluosilicate in the tests with *Feltia ducens.*

ATTRACTIVENESS OF FLUORINE COMPOUNDS TO VERTEBRATES

To higher animals, Higbee (1926) found that fluorine compounds seem to be distinctly distasteful. In experiments by the writer, chickens refused to eat bran containing sodium fluosilicate in the proportion of 10 parts of bran to 1 of the fluosilicate. Small chicks, a few weeks old, ate the mixture and died after 3 days of continuous feeding. It is well known that chickens will eat cutworm baits containing Paris green. Guinea pigs also refused to eat meal containing sodium fluosilicate. In an experiment with a wild mouse, the mixture was not eaten, although Cobenzyl (1921) states that rats and mice readily eat sodium or potassium fluosilicate mixed in the proprotion of 1 part to 10 parts of meal. When the mouse was placed in a cage with sodium fluosilicate dusted over the floor, considerable uneasiness was manifested. Within 36 hours the animal succumbed.

PLANT TOLERANCE OF FLUOSILICATES

Character of foliage injury.—During several years of dusting or spraying beans or apples, defoliation has never been observed as a result of the use of sodium fluosilicate. In the presence of moisture, the burning that results is usually local in character. The injury is frequently seen at the edges of the leaves, which at first lose their turgidity, then become limp, and after a few days turn brownish and shrivel. Most commonly, injured spots become translucent and thinner than the surrounding areas.

In an attempt to estimate the degree of injury the following scale was used:

Very slight—Smallest amount of injury visible
Slight—Up to ⅛ of the area of the leaf killed
Moderate—⅛ to ¼ of the leaf killed
Severe—¼ to nearly the whole of the leaf killed

Of all the plants tested, cotton tolerates sodium fluosilicate best, being but very slightly injured, if at all, by the pure material. Walker and Mills (1927) applied 13 dustings of 80 per cent sodium fluosilicate on cotton, over a period of 25 days, without foliage injury. Used as a dust, the fluosilicates of barium or sodium do not injure the foliage of apple, bean, and peach to any marked extent. The Solanaceae, especially tobacco, are more or less readily injured. Fleming (1927) found that smartweed is very readily injured, and therefore used it as a test plant for studying foliage injury by fluosilicates.

In order to study the tolerance of plants to arsenicals and fluorine compounds, the writer dusted potato plants with sodium arsenite and sodium fluosilicate—both being soluble compounds. Those plants that were dusted with sodium arsenite were killed, whereas the plants dusted with sodium fluosilicate received only slight to moderate injury. Swingle, Morris, and Burke (1923) obtained severe injury on apple with potassium arsenite at the rate of 1 gram to 2000 cc. of water. In Tennessee, sodium fluosilicate at the rate of 1 pound to 200 pounds of water showed but very slight injury. In Illinois, Anderson (1927) applied on peach 6 sprays of sodium fluosilicate at the rate of 2 pounds to 50 gallons of water, with no foliage injury. Some of the fruit, however, had an insipid taste.

One of the principal factors causing foliage injury was found to be moisture, as was also noted by Fleming (1927). Humidity by itself does not seem to be important, as shown in several tests. Bean plants were kept in an atmosphere of 95 to 98 per cent humidity, and yet were not injured by dusts of sodium fluosilicate. As soon as free moisture was applied, foliage injury usually followed. The practice of applying fluosilicates in the early morning hours, when dew is present, may, therefore, be the cause of injury to foliage.

Effect of various carriers on foliage injury.—Hydrated lime was used in 1924 as a carrier for sodium fluosilicate, in order to insure better distribution of the material. At the rate of 1 part, by volume, of commercial sodium fluosilicate to 9 parts of hydrated lime, no injury was noted. The dusts were applied about nine o'clock in the morning, after the dew had disappeared. The dry summers of 1924 and 1925 also aided in preventing foliage injury.

TABLE 4—*Effect on foliage of various carriers when used with sodium fluosilicate at the rate of 2 to 1. Foliage sprinkled with water before dusts applied*

Material	Carrier	Foliage injury		Notes
		Cucumbers	Beans	
Sodium fluosilicate...	Hydrated lime....	Moderate......	Moderate......	
" " ...	Hydrated lime....	Slight.........	Slight.........	Foliage not wetted
" " ...	Calcium carbonate	Moderate......	Slight.........	
" " ...	Talc............	Slight.........	Very slight....	
" " ...	Barium carbonate	Slight.........	Slight.........	
" " ...	Flour...........	....	None.........	
" " ...	Sulphur.........	....	Very slight....	
Hydrated lime, C. P...	None...........	Severe........	None.........	
Hydrated lime, Comm.	None...........	Moderate......	None.........	
Sodium fluosilicate...	Hydrated lime....	Slight.........	Very slight....	Humidity 96%, but no free moisture

Subsequent study has revealed the fact that in the presence of moisture, when lime is not used to excess, severe foliage injury may result. As shown in table 4, when potted bean plants were first watered to simulate dew, and then dusted with sodium fluosilicate mixed with 2 parts of lime, the plants were burned. This was strikingly shown with chemically pure lime (plate 1). A small amount of lime with sodium fluosilicate will probably react as follows:

$$Na_2SiF_6+Ca(OH)_2=CaSiF_6+NaF+SiO_2+H_2O$$

A 1-to-1 mixture in the presence of water will give the following reaction:

$$Na_2SiF_6+2Ca(OH)_2=2CaF_2+2NaF+SiO_2+2H_2O$$

With an excess of lime:

$$Na_2SiF_6+3Ca(OH)_2=3CaF_2+2NaOH+SiO_2+2H_2O$$

According to the above equation, the formation of the soluble calcium fluosilicate and sodium fluoride may explain the cause of the foliage injury when hydrated lime is not used to excess, and in the presence of moisture, as when dew is present. Theoretically, 2 parts of hydrated lime should completely convert the sodium fluosilicate to calcium fluoride, but in poorly mixed dust it is probable that only enough lime may be present to give the undesirable soluble products. Hydrated lime is one of the few carriers that are everywhere available, and was used on that account. It is possible, however, to avoid foliage injury on beans with sodium fluosilicate when used 1-9, by volume, and to make the application after the dew has disappeared.

Other carriers, such as talc, sulphur, calcium carbonate, barium carbonate, and flour, were also tried out. In the presence of moisture, calcium carbonate and barium carbonate produced only slight injury on beans when used at the rate of 2 parts to 1 of sodium fluosilicate (table 4). The sulphur and talc mixtures produced very little or no injury, while flour seemed to be the best (plate 2). A dust composed of sulphur—about 3 parts by weight or 6 parts by volume—should be satisfactory from the standpoint of preventing foliage injury on beans. The sulphur has also the advantage of being repellent to the bean beetle, and may aid in the control of the bean leaf hopper (*Empoasca mali*).

During the course of the investigations on foliage injury, hydrated lime only was used on cucumbers. In the presence of moisture, moderate foliage injury resulted. With chemically pure lime, severe foliage injury was produced, as shown in plate 1. It seems that hydrated lime when first applied, and in the presence of moisture such as dew, is caustic to cucumber foliage. If lime is applied after the dew is off the plants, a coating of the insoluble carbonate will be formed after a few hours, with no apparent injury. This is but another example of the harmful effects of certain dust insecticides applied when dew or moisture is present on the foliage.

Buffer action of sodium fluosilicate.—It is possible that the comparatively high degree of tolerance shown by plants for sodium fluosilicate can be explained by its buffer action. A saturated solution of sodium fluosilicate (1-200) has a pH value of 3.6, whereas the same equivalent of hydrofluosilicic acid has a pH of 1.6. The sodium, therefore, increases the pH value (decreases the intensity of acidity) and, together with the silica, seems to act as a buffer (tables 5, 6, 7). This is better shown by the dilution and titration curves in Figs. 2 and 3. The pH falls to 3 when the solution is diluted to 1-2000, and remains at this value even when the dilution is as high as 1-20,000. Considerable acidity is indicated at 1-80,000*, with a pH value of 3.8. In

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*1-80,000 is equal to .00037 N.

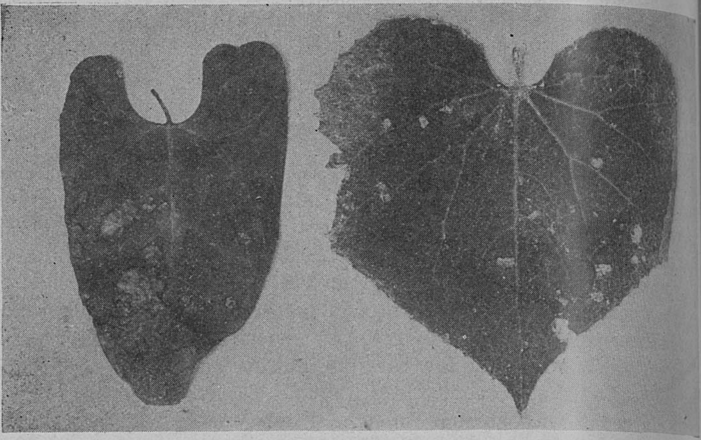

Plate 1. Left—Cucumber leaf injured by hydrated lime alone, in the presence of moisture. Right—Bean leaf injured by sodium fluosilicate plus 2 parts of hydrated lime, in the presence of moisture.

tests with acids and acid salts, a pH of 1.9 or less appears injurious to foliage. A tenth normal solution of sulphuric acid or sodium bisulphate (pH 1.5) gave considerable injury to bean and potato foliage (table 8). The fact that the pH of sodium fluosilicate never goes below 3 may account for its comparative safety on plants.

The more readily soluble sodium fluoride, magnesium fluosilicate, and pure calcium fluosilicate, espcially the last, are injurious to foliage. "Calcium fluosilicate compound," being insoluble, is quite safe

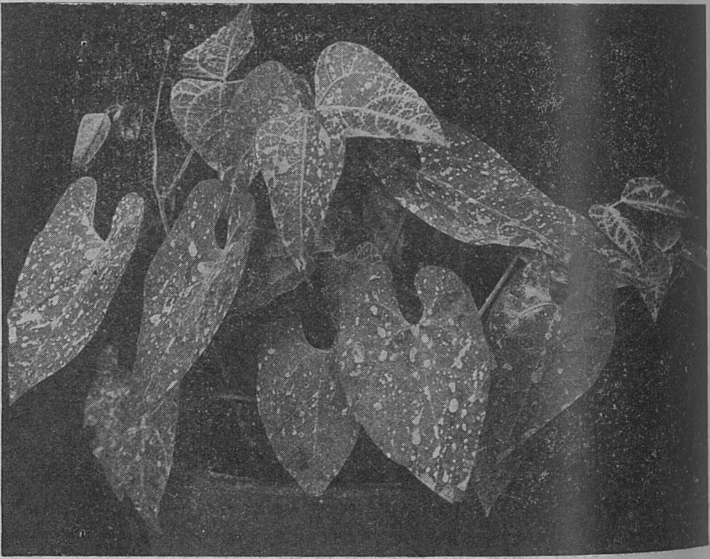

Plate 2—Potted bean plant dusted when wet, with sodium fluosilicate and 2 parts of talc, showing no foliage injury

TABLE 5—*The pH values of various fluosilicates as affected by dilution*

Dilution	Na_2SiF_6	$CaSiF_6$	$MgSiF_6$	$BaSiF_6$	$NaHSO_4$
1- 100	....	1.6	2.9	....	1.5
1- 200	3.6	2.2	2.9	....	1.7
1- 1000	3.2	3.0	3.0	....	2.2
1- 2000	3.0	3.0	3.0	....	....
1- 4000	3.0	3.2	3.0	3.5	2.9
1- 6000	3.0	3.2	3.0	3.4	3.0
1- 10,000	3.0	3.2	3.2	3.4	3.1
1- 20,000	3.0	3.3	3.5	3.4	3.4
1- 30,000	3.2	3.5	3.6	3.4	3.8
1- 40,000	3.4	3.6	3.8	3.5	4.0
1- 50,000	....	....	....	3.6	....
1- 60,000	....	3.7	4.1	....	4.6
1- 80,000	3.8	....	....	....	....
1-100,000	4.1	....	....	....	....
1-200,000	4.7	....	....	....	....

TABLE 6—*The pH values of 10 cc. (1-200) of various fluosilicates as affected by titration with 1/10 N sodium hydroxide*

1/10 N NaOH	Na_2SiF_6	$CaSiF_6$	$MgSiF_6$	$BaSiF_6$	$NaHSO_4$	HCl (1-180)
None	3.6	2.2	2.9	3.5	1.7	1.0
4 drops	....	2.4	....	....	1.8	....
6 "	4.0	2.5	3.4	4.0	....	....
9 "	4.1	2.6	3.7	....	1.9	....
12 "	4.2	....	3.8	4.3	....	1.2
15 "	4.4	2.7	....	....	1.9	....
18 "	4.4	....	4.0	5.8	....	....
24 "	4.6	2.8	4.2	7+	1.9	1.3
30 "	4.7	....	....	....	....	....
36 "	4.8	2.9	4.5	....	2.1	....
48 "	4.9	3.0	4.7	....	2.2	1.4
3 cc.	4.9	3.8	4.9	....	2.7	1.5
4 cc.	5.1	4.4	5.0	....	5.6+	1.5
5 cc.	5.2	4.8	5.1	....	....	1.6
6 cc.	5.3	5.0	5.3	....	....	1.7
7 cc.	5.4	5.2	7+	....	....	1.8
8 cc.	5.5	5.4	....	....	....	1.9
9 cc.	5.6	5.6	....	....	....	2.3
10 cc.	6.1	7+	....	....	....	6+
11 cc.	7+	....	....	....	....	....

TABLE 7—*The pH values of 10 cc. of a 1-200 solution of sodium fluosilicate as affected by titration with 1/30 N* $Ca(OH)_2$

1/30 N CaOH	pH	1/30 N CaOH	pH	Notes
None	3.5	10 cc.	4.3	
4 drops	3.5	12 cc.	4.3	
12 drops	3.6	14 cc.	4.3	
24 drops	3.7	16 cc.	4.4	
2 cc.	3.9	20 cc.	4.5	Solution becoming turbid
3 cc.	3.9	25 cc.	4.5	
4 cc.	4.0	28 cc.	5.9	Turbidity more pronounced
5 cc.	4.1	29 cc.	6.0	
6 cc.	4.1	30 cc.	6.0	
7 cc.	4.1	31 cc.	6.0	
8 cc.	4.1	40 cc.	7.4	Calcium fluosilicate neutralized to calcium fluoride.

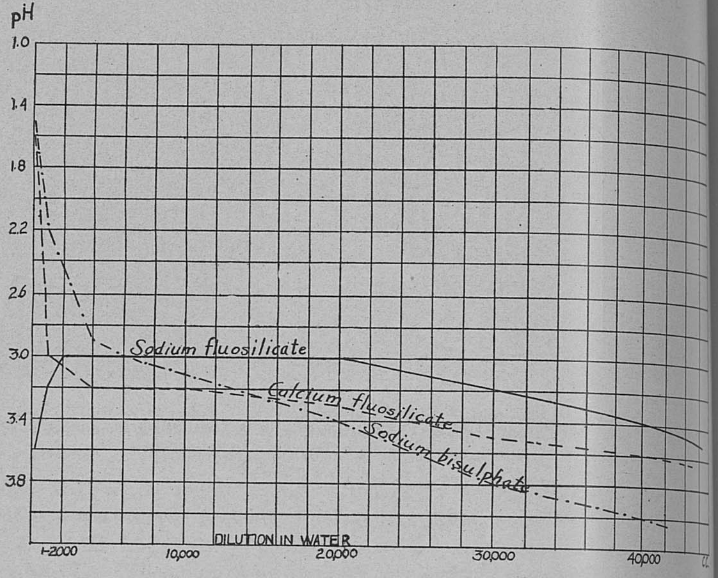

Fig. 2. Relation between dilution and hydrogen-ion concentration of fluosilicates

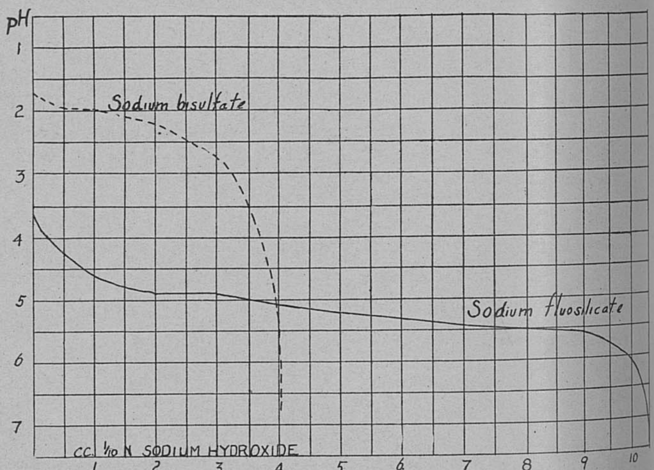

Fig. 3. Titration curve of 10 cc. of a 1-200 solution

TABLE 8—*Foliage tests with solutions of known pH, and per cent of injury*

Material	Normality	pH	Per cent foliage injury on beans	Per cent foliage injury on potatoes
Sulphuric acid................	1.	....	Severe........	Severe
" "	.1	1.30	Moderate.....	Moderate
" "	.01	2.07	Slight........	Slight
" "	.005	3.33	None.........	None
" "	.001	3.28	None.........	None
Sodium bisulphate..............	.1	1.51	Moderate.....	Moderate
" "	.02	1.97	None.........	None
" "	.01	2.15	None.........	None
" "	.005	2.41	None.........	None
Sodium fluosilicate (1-200)......	.08	3.60	Very slight...	Very slight
Magnesium fluosilicate (1-200)..	.08	2.90	Very slight...	Very slight
Fluosilicic acid	.1	1.60	Moderate.....	Moderate
Fluosilicic acid	.05	1.90	None.........	Very slight

on various types of foliage. Barium fluosilicate with a solubility of 1-3,750 also seems to be safe on foliage. When the latter was used as a spray with fish-oil soap or Kayso, slight injury was seen. This may have been due to the formation of calcium fluosilicate.

Fluorine as a stimulant for plants.—Gautier and Clausman (1915, 1919) studied the effect of calcium fluoride as a fertilizer or stimulant. These investigators report a stimulating action on wheat, oats, carrots, potatoes, peas, beans, cabbage, poppy, and hemp. No influence could be demonstrated with rye, barley, buckwheat, or mustard, while beets and turnips grew to a less extent.

Voelcker (1921) applied fluorine in small amounts to wheat grown in pots. The yield of untreated wheat is given as 100. Calcium fluoride and calcium fluosilicate were applied at the rate of 500 pounds to the acre, and gave yields of 43 and 191, respectively. The yields from the fluorides of potassium and sodium, applied at the rate of 0.05 per cent fluorine, are given as 340 and 460, respectively. When sodium fluoride was applied to the extent of 0.1 per cent fluorine, it prevented germination and produced a caking effect on the soil. This did not take place with the potassium fluoride, which at the same rate showed a yield of 453. These results indicate a moderate stimulation from calcium fluosilicate and a fourfold increase from potassium fluoride.

EXPERIMENTAL

Determination of comparative toxic values.—For the determination of comparative toxicities of various inorganic chemicals, the larvae of the Culicidae proved especially well adapted, since they are abundant, easily obtained or bred, and live in a medium that lends itself readily to chemical changes of any desired concentration. Campbell (1926) recently succeeded in making quantitative toxicological tests by feeding known quantities of soluble arsenicals to caterpillars. While his work appears to be exact, his investigations are limited to a few chemicals. Comparative values of a large number of chemicals can be determined better and in a shorter time by the use of mosquito larvae. It is thus possible to obtain comparative data which seem significant, especially when compared with results of work on other insects.

Methods.—The mosquito larvae were collected from rain barrels and brought to the laboratory. The most common species during the greater part of the summer is *Culex quinquefasciatus*. Occasionally other species of Culex were present in the same receptacle. Although there seems to be little difference in resistance among the different species of Culex, the following method was later adopted to insure a pure culture of a single species: A single egg mass was placed in a jar, to which was added dried blood, a well-known fertilizer. This material proved satisfactory for raising the larvae to maturity. The larvae grew very well, also, on a diet of yeast, but frequently the water became contaminated with dense growths, which proved detrimental. Dried blood was therefore adopted.

Ten or more larvae were placed in 50-cc. tumblers containing the chemical in solution or suspension. Observations were made at hourly intervals, when possible; and in many cases were continued for 72 hours. The time when cessation of movement was observed was taken as the measure of toxicity. The percentage of the larvae that succumbed was calculated according to the number present. Due to the variation in resistance among the individuals of the same species, the time in which 50 per cent mortality occurred was later adopted. In the discussion that follows, the word "toxic" is used synonomously with the word "lethal."

The acids and bases tested were of corresponding normality, whereas molar solutions were used for the salts. In a few cases 1 gram of the material was used with varying amounts of distilled water. Conductivity water, free from carbon dioxide, was used for testing bases. LaMotte standards were adopted in making hydrogen-ion determinations.

Manner in which mosquito larvae succumb.—It is evident that mortality of mosquito larvae in solutions may occur by penetration of the lethal agent through the chitinous membranes covering the exterior of the body, or through the stomach walls after ingestion of the material by mouth. With inorganic chemicals, the oral method seems to be the principal one in which poisoning takes place, for it is possible to kill Culex larvae readily by insoluble stomach poisons, such as lead arsenate in suspension. Bodine (1923) also points out that pupae, which are known not to eat, are very much more resistant to acids than larvae. According to Chidester (1916), the pupae of *Culex pipiens* can withstand a concentration of 40 per cent of sea water. On the other hand, many organic chemicals, and especially those that are volatile, kill rapidly. This is presumed to be because they enter through the thinner portions of the body wall and breathing tube.

Species studied.—The common rain-barrel mosquitoes—*Culex quinquefasciatus*, *C. salinarius*, and *C. restuans*—were used in the tests.

There seem to be but slight differences in susceptibility among the three species. Tests were also made with *Orthopodomia signifer,* the tree-hole mosquito. This species was found to be very much more resistant than the larvae of Culex. A few tests were also conducted with *Anopheles punctipennis.* The larvae of Anopheles seem to be as susceptible as Culex to non-volatile chemicals, and, being surface feeders, least resistant to volatile chemicals floating on the surface of the water.

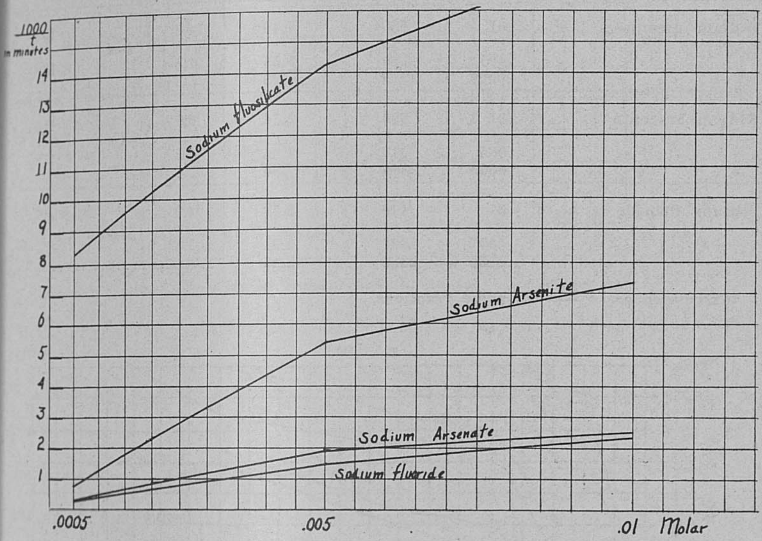

Fig. 4. Velocity of fatality. *Culex quinquefasciatus*

Discussion.—Since sodium fluosilicate acts as a stomach poison, a comparison with the arsenicals would be desirable. At 0.02 molar, or 1 part in 266 parts of water, it killed the larvae of *O. signifer* in 8½ hours. With sodium arsenite, 0.02 molar, about the same time was required to produce a lethal effect (table 10).

Sodium fluosilicate at 0.01 molar (1-532) concentration produced 50 per cent mortality of the larvae of *Culex quinquefasciatus* within 55 minutes, whereas at the same concentration sodium arsenite required 135 minutes, sodium arsenate 390 minutes, and sodium fluoride 420 minutes. A parallel series of survival times was secured with concentrations of 0.005 molar, as indicated in table 9. An inspection of Fig. 4, where the concentration is plotted against the reciprocal of the survival time (the velocity of fatality), reveals a curve similar to the action of lead nitrate on *Leuciscus phoxinus* as worked out by Carpenter (2). This curve appears to correspond to the equation $K=\frac{1}{t}\log\frac{1}{\text{conc.}}$ where t=survival time and K a constant expressing a numerical value of toxicity. With such an equation we get a value of K for sodium fluosilicate of 34.5, sodium arsenite 13.1, sodium arsenate 4.8, and sodium fluoride 4. Sodium fluosilicate is therefore 8

TABLE 9—*Toxicity studies on Culex quinquefasciatus, showing survival of 50 per cent mortality.* $K=\frac{1}{t}\log\frac{1}{\text{conc.}}$. *Temperature* 75°F.

Compound	Molar Conc.	Survival time Minutes	Reciprocal $\frac{1000}{t}$	Value of K.*	Average value of K.	Calcul valu of t
Sodium fluosilicate	.01	55	18.10	36.2	34.5	58
	.005	70	14.30	32.9		65
	.0005	120	8.33	....	....	....
Sodium arsenite	.01	135	7.40	14.8	13.1	152
	.005	180	5.55	11.5		175
	.0005	1260	.79	....	....	....
Sodium arsenate	.01	390	2.56	5.1	4.8	416
	.005	510	1.96	4.5		479
	.0005	2880	.34	....	....	....
Sodium fluoride	.01	420	2.38	4.7	4.0	500
	.005	660	1.51	3.4		575
	.0005	2880	3.40	....	....	....

*Calculated as $\frac{1000}{t}$ to avoid fractions.

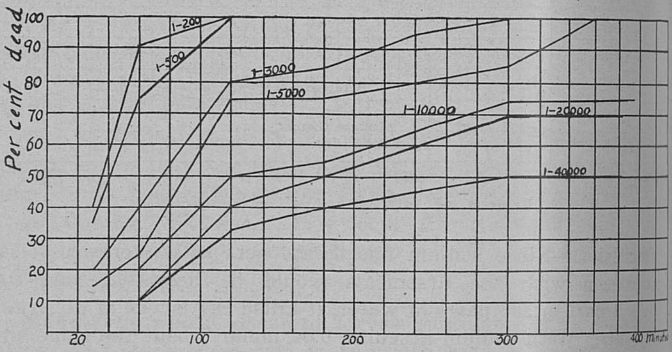

Fig. 5. Velocity of fatality. *Culex salinarius* in sodium fluosilicate solutions

times more toxic than sodium fluoride. Other curves showing survival time and velocity of fatality are given in figures 5, 6, and 7.

Of the organc acids at 0.02 N, salicylic was the most toxic to *C. quinquefasciatus,* followed by oxalic, formic, and acetic acids, respectively (table 13). Similar results were obtained by Bodine (1923). Salicylic and oxalic acids appear even more toxic than hydrofluoric of corresponding normality. Similar results were obtained against *O. signifer*. With the latter, benzoic acid showed some toxicity at 0.02 N, but tartaric, citric, lactic, acetic, gallic, and boric acids were practically inert.

In a comparison of a series of metals, mercury was found to be the most toxic to *O. signifer*, which succumbed to 0.02 molar mercuric bichloride in 1 hour. The larvae of Culex were more sensitive to

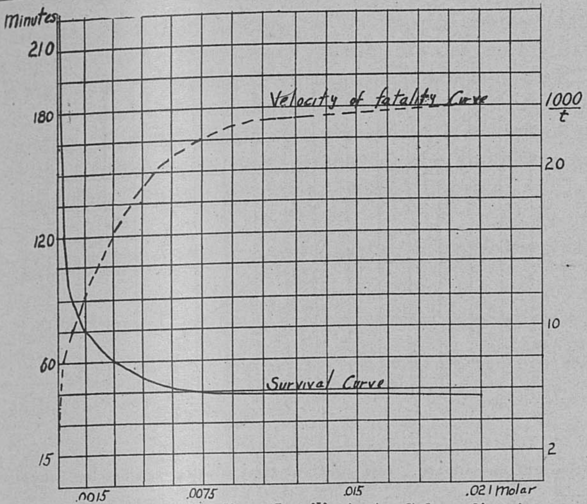

Fig. 6. Toxicity of sodium fluosilicate to *Culex salinarius*

TABLE 10—*Toxicity studies with Orthopodomia signifer. Temperature 70°F.*

.0002 M.

Per cent dead

Compound	½ hr.	1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	6 hrs.	7 hrs.	8 hrs.	24 hrs.	48 hrs.	72 hrs.
Sodium fluosilicate	....	....	....	....	....	....	....	....	....	55	100	....
.002 M.												
Sodium fluosilicate	....	....	....	....	....	....	....	....	....	65	100	....
Mercuric chloride	....	....	....	75	90	100	....	....	....	....	....	....
Salicylic acid	....	....	....	....	....	....	....	....	....	100	....	....
Oxalic acid	....	....	....	....	....	....	....	....	....	100	....	....
Formic acid	....	....	....	....	....	....	....	....	....	25	50	75
.02 M.												
Sodium fluosilicate	....	....	....	....	....	45	65	90	....	....	....	....
Calcium fluosilicate	....	50	100	....	....	....	....	....	....	....	....	....
Lead fluosilicate	....	....	....	....	....	....	....	....	20	100	....	....
Magnesium fluosilicate	....	....	....	....	....	....	....	....	20	75	....	....
Sodium arsenite	....	....	....	....	....	50	65	90	....	....	....	....
Sodium arsenate	....	....	....	....	....	....	....	0	0	100	....	....
Sodium cyanide	....	....	....	50	....	....	100	....	....	....	....	....
Sodium bisulphate	....	....	....	....	....	....	....	....	....	85	100	....
Sodium bisulphite	....	....	....	....	....	....	....	30	50	90	100	....
Sodium fluoride	....	....	....	....	....	....	....	....	....	0	0	0
Sodium silicate	....	....	....	....	....	....	....	....	....	0	0	0
Sodium chloride	....	....	....	....	....	....	....	....	....	0	0	0
Sodium oxalate	....	....	....	....	....	....	....	....	....	0	0	....
Sodium hydroxide	....	....	....	....	....	....	....	....	....	0	0	....
Mercuric chloride	75	100	....	....	....	....	....	....	....	....	....	....
Chromium fluoride	....	....	....	....	....	....	....	....	10	55	100	....
Antimony acid	....	....	....	....	....	....	....	....	10	55	100	....
Arsenious acid	....	....	....	....	....	....	100	....	....	....	....	....
Hydrofluoric acid	....	....	....	20	30	40	60	80	100	....	....	....
Salicylic acid	50	75	100	....	....	....	....	....	....	....	....	....
Oxalic acid	....	....	75	100	....	....	....	....	....	....	....	....
Formic acid	....	....	....	80	100	....	....	....	....	....	....	....
Benzoic acid	....	....	....	....	....	85	100	....	....	....	....	....
Phosphoric acid	....	....	....	....	....	....	....	....	0	0	0	....
Tartaric acid	....	....	....	....	....	....	....	....	0	0	0	....
Citric acid	....	....	....	....	....	....	....	....	0	0	0	....
Lactic acid	....	....	....	....	....	....	....	....	0	0	0	....
Acetic acid	....	....	....	....	....	....	....	....	0	0	0	....
Gallic acid	....	....	....	....	....	....	....	....	0	0	0	....
Boric acid	....	....	....	....	....	....	....	....	0	0	0	....
Hydrochloric acid	....	....	....	....	....	....	....	15	....	50	65	90

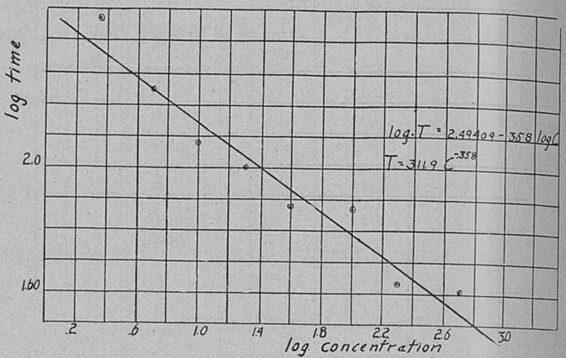

Fig. 7. Sodium fluosilicate. Log survival time plotted against log concentration

TABLE 11—*Toxicity studies with Orthopodomia signifer. Temperature 70°F.*

.2 M.

Per cent dead

Compound	½ hr.	1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	6 hrs.	7 hrs.	8 hrs.	24 hrs.	48 hrs.	72 hrs.
Hydrofluosilicic acid	....	....	....	100	....	....	....	....	....	....	....	....
Hydrofluoric acid	....	....	100	....	....	....	....	....	....	....	....	....
Hydrochloric acid	....	....	50	55	100	....	....	....	....	....	....	....
Sodium hydroxide	....	....	....	....	50	75	85	100	....	....	....	....
Sodium silicate	....	....	....	....	....	....	....	25	....	75	100	....
Sodium bisulphate	....	....	....	....	100	....	....	....	....	....	....	....
Sodium bicarbonate	....	....	....	....	....	....	....	....	....	0	10	20
Sodium chloride	....	....	....	....	....	....	....	....	....	0	0	10
Sodium fluoride	....	....	....	....	....	10	15	30	50	100	....	....
Chromium fluoride	....	....	....	....	....	80	100	....	....	....	....	....
Potassium iodide	....	....	....	....	....	....	....	....	....	60	90	....
Potassium chlorate	....	....	....	....	....	....	....	....	....	0	0	0
Sodium bromide	....	....	....	....	....	....	....	....	....	0	0	0
.5 M.												
Sodium fluoride	....	....	....	....	40	80	95	100	....	....	....	....
Sodium silicate	....	....	....	....	....	....	20	25	....	60	80	100
Sodium chloride	....	....	....	....	....	....	....	....	....	35	60	80
Potassium chloride	....	....	....	....	....	....	....	10	....	40	90	100
Sodium bicarbonate	....	....	....	....	....	....	....	....	....	15	50	85
Ferrous sulphate	....	....	....	....	....	....	15	25	....	75	100	....
.1 M.												
Sodium chloride	....	....	....	20	....	....	100	....	....	....	....	....
Sodium fluoride	....	....	....	80	80	85	95	100	....	....	....	....
Sodium silicate	....	....	....	15	....	....	80	80	....	95	....	....
Ferrous sulphate	....	....	....	....	75	85	100	....	....	....	....	....

salts of zinc and lead than to those of barium or copper (table 14). Considering the known properties of barium, its degree of toxicity to insects is very small. Judging from the concentrations used, sodium fluosilicate is several hundred times more toxic to *C. salinarius* than barium chloride. Sodium silicate also showed little toxicity.

When the halogen salts were compared, the following order of toxicity was noted: Chloride<bromide<iodide<fluoride.

TABLE 12—*Toxicity studies with Culex salinarius. Temperature 82°F. June 16, 1926*

Per cent dead

Compound	½ hr.	1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	6 hrs.	7 hrs.	8 hrs.	16 hrs.	24 hrs.	48 hrs.	72 hrs.
Sodium fluosilicate													
(1-200)	40	90	100	....	....	....	....	....	....	....	....	....	....
(1-500)	35	75	100	....	....	....	....	....	....	....	....	....	....
(1-1000)	35	40	80	95	100	....	....	....	....	....	....	....	....
(1-3000)	20	40	80	85	95	100	....	....	....	....	....	....	....
(1-5000)	15	25	75	75	80	85	100	....	....	....	....	....	....
(1-10,000)	....	20	50	55	65	75	75	75	....	90	100	....	....
(1-20,000)	....	10	40	50	60	70	70	70	....	80	100	....	....
(1-40,000)	....	10	33	40	45	50	50	50	....	70	100	....	....
(1-80,000)	....	....	....	....	10	10	15	20	....	....	45	55	65
(1-150,000)	....	....	....	....	....	....	....	....	....	....	30	50	60
(1-300,000)	....	....	....	....	....	....	....	....	....	....	0	15	15
Barium fluosilicate													
(1-3750)	25	50	60	65	75	90	90	95	....	....	....	....	....
Sodium arsenite													
(1-200)	15	80	100	....	....	....	....	....	....	....	....	....	....
(1-40,000)	....	....	....	....	....	....	....	....	....	....	90	90	90
Sodium fluoride													
(1-200)	....	....	100	....	....	....	....	....	....	....	....	....	....
(1-1000)	....	....	....	80	100	....	....	....	....	....	....	....	....
(1-5000)	....	....	....	....	15	....	25	....	45	45	50	90	100
Acid phosphate (commercial)													
(17-2000)	....	....	....	....	....	50	....	65	....	....	95	100	....
(17-10,000)	....	....	....	....	....	....	....	....	....	....	50	80	92
(17-100,000)	....	....	....	....	....	....	....	....	....	....	0	30	45

TABLE 13—*Toxicity studies with Culex quinquefasciatus. Temperature 75°F. September 24, 1926*

.01 N

Per cent dead

Compound	½ hr.	1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	6 hrs.	7 hrs.	8 hrs.	24 hrs.	48 hrs.	72 hrs.
Sulphuric acid	....	5	10	15	....	70	....	85	90	100	....	....
Hydrochloric acid	....	0	0	15	....	60	....	70	85	100	....	....
Nitric acid	....	0	0	10	....	30	....	50	55	100	....	....
Hydrofluosilicic acid	....	40	80	90	100	....	....	....	....	....	....	....
Hydrofluoric acid	....	25	60	100	....	....	....	....	....	....	....	....
Sodium hydroxide	....	....	....	0	....	0	....	5	5	85	95	95
Calcium hydroxide	....	....	....	0	....	0	....	0	5	85	100	....
Ammonium hydroxide	....	....	....	0	....	0	....	30	40	85	95	95
Barium hydroxide	....	....	....	0	....	0	....	15	15	95	100	....
.02 N												
Oxalic acid	....	....	100	....	....	....	....	....	....	....	....	....
Formic acid	....	20	50	50	....	80	100	....	....	....	....	....
Salicylic acid	100	....	....	....	....	....	....	....	....	....	....	....
Acetic acid	....	....	....	0	....	0	....	0	20	45	60	65
Phosphoric acid	....	....	....	....	....	....	....	....	0	45	90	95
Hydrofluoric acid	40	60	90	100	....	....	....	....	....	....	....	....

TABLE 14—*Toxicity studies with Culex salinarius. Temperature* 80°F. *J*
6, 1926

.05 M.
Per cent dead

Compound	½ hr.	1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	6 hrs.	7 hrs.	8 hrs.	16 hrs.	24 hrs.	48 hrs.	72 hrs.	Not
Sodium acetate	....	....	....	....	....	....	....	....	....	....	15	20	25	....
Sodium chloride	....	....	....	....	....	....	....	....	....	....	0	0	20	....
Barium chloride	....	....	....	....	....	....	....	....	....	....	75	100	....	....
Barium acetate	....	....	....	....	....	....	....	....	....	100	....	....	....	....
Zinc acetate	....	....	....	....	30	50	75	....	....	....	95	....	....	....
Lead acetate	....	....	....	....	25	50	65	....	....	....	100	....	....	....
Potassium iodide	....	....	....	....	....	....	....	....	....	....	65	100	....	....

.5 M.

Compound	½ hr.	1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	6 hrs.	7 hrs.	8 hrs.	16 hrs.	24 hrs.	48 hrs.	72 hrs.	Not
Sodium chloride	....	....	....	85	....	....	....	....	....	....	....	....	....	....
Barium chloride	....	50	100	....	....	....	....	....	....	....	....	....	....	....
Barium acetate	....	....	90	100	....	....	....	....	....	....	....	....	....	....
Zinc chloride	....	....	80	80	....	....	....	....	....	....	....	....	....	....
Copper acetate	....	....	....	85	....	....	....	....	....	....	....	....	....	....
Lead acetate	....	....	100	....	....	....	....	....	....	....	....	....	....	....

.001 N.

Compound	½ hr.	1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	6 hrs.	7 hrs.	8 hrs.	16 hrs.	24 hrs.	48 hrs.	72 hrs.	Not
Hydrochloric acid	....	....	....	....	....	....	....	....	....	....	....	15	25	....
Sodium hydroxide	....	....	....	....	....	....	....	....	....	....	....	0	20	....

.002 N.

Compound	½ hr.	1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	6 hrs.	7 hrs.	8 hrs.	16 hrs.	24 hrs.	48 hrs.	72 hrs.	Not
Hydrochloric acid	....	....	....	....	....	....	....	....	....	....	40	70	....	65% in 30 hour
Sodium hydroxide	....	....	....	....	....	....	....	....	....	....	0	20	....	....

.005 N.

Compound	½ hr.	1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	6 hrs.	7 hrs.	8 hrs.	16 hrs.	24 hrs.	48 hrs.	72 hrs.	Not
Hydrochloric acid	....	....	....	....	....	....	....	....	....	100	....	....	....	....
Sodium hydroxide	....	....	....	....	....	....	....	....	....	30	60	....	....	....

TABLE 15—*Toxicity studies with Culex quinquefasciatus. Temperature* 70°F.
July 15, 1926

.002 M.
Per cent dead

Compound	½ hr.	1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	6 hrs.	7 hrs.	8 hrs.	16 hrs.	24 hrs.	48 hrs.	72 hrs.
Sodium fluoride	....	....	....	....	....	....	....	....	....	10	40	70	[illegible]
Sodium oxalate	....	....	....	....	....	....	....	....	....	0	0	30	[illegible]
Sodium silicate	....	....	....	....	....	....	....	....	....	20	45	95	[illegible]
Chromium fluoride	....	....	....	....	....	....	....	....	....	55	60	75	[illegible]
Control (distilled water)	....	....	....	....	....	....	....	....	....	20	30	60	[illegible]
Oxalic acid	....	....	....	....	....	....	....	....	....	40	45	75	[illegible]
Formic acid	....	....	....	....	....	....	....	....	....	25	40	80	[illegible]
Salicylic acid	....	....	....	....	....	....	....	....	....	100	....	....	....

.02 M.

Compound	½ hr.	1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	6 hrs.	7 hrs.	8 hrs.	16 hrs.	24 hrs.	48 hrs.	72 hrs.
Sodium fluoride	....	....	10	10	....	....	20	....	35	....	100	....	....
Sodium acid fluoride	....	....	50	85	....	95	....	....	95	....	100	....	....
Sodium oxalate	....	....	....	....	....	....	....	....	....	....	40	90	[illegible]
Sodium silicate	....	....	....	....	....	....	....	....	....	....	20	50	[illegible]
Sodium bisulphate	....	....	....	....	....	30	50	....	65	....	100	....	....

It is of interest to note that the toxicity studies confirmed, in many cases, the Hoffmeister series: $SO_4 > Cl > B' > NO_3 > I > ScN$ for the anions and $Mg > Li > Na > K$ for the cations. Potassium fluoride is more toxic than sodium fluoride, while the latter is more toxic than barium fluoride. Ammonium sulphate is much less toxic than ammonium sulphocyanide (table 16).

Culex larvae are in the habit of feeding on organic matter from the bottom of containers. It is therefore possible to use insoluble materials for toxicity studies. The fluorides and other insoluble chemicals were used at the rate of 1 gram to 100 cc. of water. Calcium, magnesium, and strontium fluoride showed low toxic values, as did also calcium fluosilicate compound (table 16). The fluorides of copper and barium killed in 6 and 3 hours, respectively, while lead

TABLE 16—*Toxicity studies with Culex quinquefasciatus. Time in which 50 per cent mortality occurred. Temperature 80°F. July 27, 1927*

Compound	Strength	Hours	Notes
Copper fluoride	1-100	6	Washed
Lead fluoride	1-100	1¼	pH 4.4
Lead fluoride	Saturated Sol	6	Strength about 1-2000
Aluminum fluosilicate	1-100	6	
Cryolite (synthetic)	1-100	2½	pH 4.5
Calcium fluoride	1-100	84	
Magnesium fluoride	1-100	54	
Strontium fluoride	1-100	55	
"Calcium fluosilicate compound"	1-100	29	
Barium fluoride	1-100	3	pH 5.2
Barium fluoride	Saturated Sol	6	Strength about 1-600
Lead arsenate	1-100	4	Washed
Calcium arsenate	1-100	11	
Calcium arsenate	1-100	5	Remained in water 3 days before testing
Calcium arsenate	1-100	3	Remained in water 10 days before testing
Paris green	1-100	3	Washed
Paris green	1-100	1¾	Not washed
Paris green	1-100	5	Filtrate only tested
Calcium arsenate	1-100	7	Filtrate tested after 24 hrs.
Sodium fluoride	1-1000	5½	pH 7.4
Sodium fluoride plus Hydrochloric acid	1-1000 .01 N	3	pH 3.5
Sodium fluoride plus Sodium hydroxide	1-1000 .01 N	8½	pH 10.7
Potassium fluoride	.02 M	3⅓	
Sodium fluoride	.02 M	5	
Ammonium fluoride	.02 M	4	
Sodium phosphate (primary)	.02 M	37	pH 5.6
Sodium phosphate (secondary)	.02 M	35	pH 8.3
Sodium phosphate (Tertiary)	.02 M	10	
Sodium fluoride plus Sodium carbonate	.02 M .1 M	3 1/6	
Sodium carbonate	.1 M	9	
Sodium phosphate (Meta)	.02 M	....	Non-toxic
Sodium pyrophosphate	.02 M	....	" "
Sodium hypophosphite	.02 M	....	" "
Sodium phosphite	.02 M	....	" "
Ammonium sulphate	.05 M	....	" "
Ammonium sulphocyanide	.05 M	5	
Barium fluoride	1-1000	6½	
Sodium fluoride	1-1000	2	
Sodium fluosilicate	1-200	2/3	
Sodium fluosilicate plus Calcium hydroxide	1-200 1-100	7	

fluoride required only 1¼ hours for a lethal effect. Among the insoluble arsenicals, Paris green, lead arsenate, and calcium arsenate killed in 1¾, 4, and 11 hours, respectively. The interesting point here is that lead arsenate proved more toxic than calcium, while under field conditions the reverse is true. If the calcium arsenate is allowed to remain in the water 3 days, a greater toxicity is manifested. It is probable that the carbon dioxide in the water partially decomposes the calcium arsenate into a more soluble form. Further evidence on this point is furnished by Walker and Mills (1927). They also found that a coating of calcium carbonate may appear on the outer surface of each particle after 5 days or more, thus rendering the arsenic more or less inaccessible and ineffective. Calcium arsenate, therefore, is comparatively less toxic when first dusted on plants; becomes more toxic under the action of carbon dioxide; and finally, when coated over with calcium carbonate, is again less toxic.

The role of acidity.—A series of 0.01 N acids were compared with a series of 0.01 N bases. Hydrofluoric acid was most toxic, the larvae of Culex having succumbed in 3 hours. Hydrofluosilicic was almost as toxic, followed by sulphuric, hydrochloric and nitric. With the last, only 55 per cent of the larvae were dead at the end of 8 hours. On the other hand, the bases exhibited comparatively little toxic action. At the end of 8 hours, 5 per cent of the Culex larvae had succumbed to the sodium hydroxide, 15 per cent to barium hydroxide, and 40 per cent to ammonium hydroxide; while a few still lived even after 2 or 3 days.

Similar results were secured with *O. signifer*. At 0.02 N hydrochloric acid showed a toxicity of 50 per cent in 24 hours, whereas sodium hydroxide was entirely ineffective even after 3 days (table 10). A concentration of 0.2 N sodium hydroxide was necessary before a

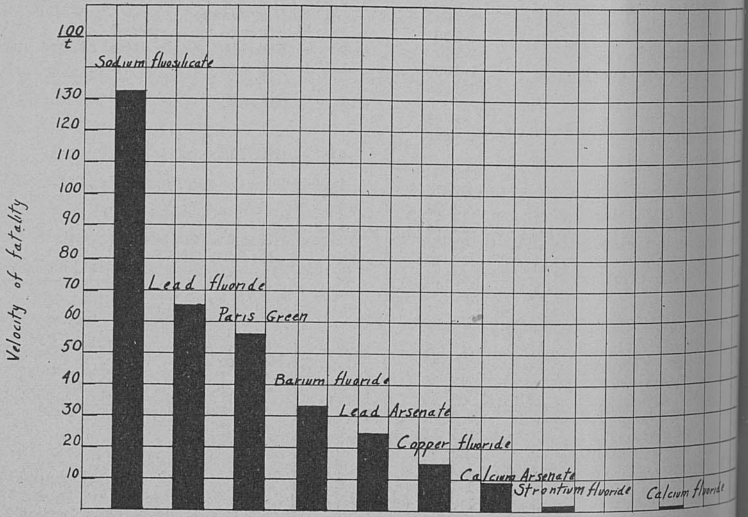

Fig. 8. The relative toxicities of arsenicals and fluorine compounds to *Culex quinquefasciatus*

lethal effect was obtained. In New Jersey, Headlee (1921) had to use 20 grams of sodium hydroxide in 1000 cc. of tap water, equivalent to the amount necessary for a 0.5 N solution, in order to get a killing dose against *A. cantor* and *A. sollicitans* in 2 days. These preliminary observations indicate that the hydrogen ion is more toxic than the hydroxyl ion, or that acidity is a factor in toxicity.

The influence of acidity was studied from another angle. Sodium fluoride is neutral or slightly alkaline with a pH of 7.5 at a concentration of 0.5 molar. With a 1-1000 solution, 50 per cent mortality occurred within 5½ hours. The addition of 0.01 N hydrochloric acid caused the larvae to succumb in 3 hours, whereas the same amount of 0.01 N sodium hydroxide added to the sodium fluoride prolonged the life of the larvae to 7 hours. In the same way acidified sodium arsenite was found more toxic than when made alkaline. Sodium fluosilicate also has an acid reaction, and proved to be about 8 times more toxic than sodium fluoride (table 9). Pure calcium fluosilicate has a greater hydrogen-ion concentration than sodium fluosilicate, and was correspondingly more toxic.

Patterson (1925) found the hydrogen-ion concentration to be an important factor in the development of the larvae. She found calcium superphosphate in concentrations of 17-2000 and 17-10,000, having, respectively, pH values of 3 and 3.4, toxic to *Culex fatigans* and *Theobaldia longiareolata* within 72 hours. These results were duplicated at Knoxville with *C. quinquefasciatus*. Patterson claims even relatively weak solutions of superphosphate of lime (17-1,000,000) to be toxic. The writer, however, was unable to get any killing with such low concentrations. No effects on the larvae were observed when these chemicals were added to the natural breeding waters at the rate of 17-1,000,000.

Although Culex larvae are intolerant of slightly acid waters, relatively large amounts of acid-producing chemicals must be employed under practical conditions. A 1-10,000 solution of sodium fluosilicate is toxic to larvae in distilled water. Little effect, however, was observed when the powder was added at the same rate to natural breeding waters charged with large amounts of organic matter. At the rate of 1-2000, sodium fluosilicate killed all the larvae within 16 hours, while at 1-4000 some killing was evident after 1 day and all were dead in 2 days. Sodium bisulphate, or nitre cake, was ineffective when added at the rate of 1-1000. At this rate Headlee (1921) was barely able to kill *C. pipiens*, in New Jersey, within 2 days, and he recommends that for best control the nitre cake be used at the rate of 1-100. Sodium fluosilicate is thus much more toxic than nitre cake when applied to water heavily contaminated with organic matter and dust.

The effect of changes in the hydrogen-ion concentration was also studied by MacGregor (1921). He observed that *Finlaya geniculata*, a European tree-hole mosquito, inhabits waters with a pH value of 4.4. When these larvae were transferred to alkaline water, with a pH of 8.2 to 8.4, they failed to develop. On the other hand, *A. maculipennis*, *A. bifurcatus*, and *Ochleretatus nemorosus*, which inhabit alkaline water, failed to develop in water made acid with acetic acid and wi a pH of 4.4. The larvae developed, however, in water made alkali with sodium hydroxide showing a pH of 9.6.

Larvae of *O. signifer,* which is classed as a tree-hole mosqui were found at Knoxville to breed in a concrete basin designed for manure pit. The water was alkaline and showed a pH value of 7.

Laboratory experiments with Anopheles punctipennis.—Par green is now being used as a larvicide against various species of An opheles (King, 1926). Among some of the chemicals tested at Knox ville, crude naphthalene gave very good results against Anopheles bu not against Culex. When crude naphthalene was dusted lightly ov water in battery jars, the larvae succumbed in from 1 to 6 hou (table 17). Paris green, under similar conditions, acted much mo slowly. Considering cost, and the fact that it may be dusted, cru naphthalene is worthy of further trials under practical conditions.

Field tests against the Colorado potato beetle and other insects.— The larvae of the potato beetle easily succumb to sodium fluosilicate

TABLE 17—*Toxicity studies with Anopheles punctipennis. Temperature 8 June* 25, 1926

Per cent dead

Compound	½ hr.	1 hr.	2 hrs.	3 hrs.	4 hrs.	5 hrs.	6 hrs.	7 hrs.	8 hrs.	24 hrs.	48 hrs.	
Crude naphthalene	50	90	....	....	....	....	100	....	....	....	....	....
Dinitrobenzene	....	....	....	....	....	....	50	....	....	100	....	....
Paris green	....	....	....	....	....	....	0	....	....	100	....	....
Sodium fluosilicate (1-200)	....	25	100	....	....	....	....	....	....	....	....	....
Crude naphthalene	....	50	100	....	....	....	....	....	....	....	....	....
Dinitrobenzene	....	....	....	0	....	30	30	30	....	100	....	....
Paris green	....	....	50	....	....	50	....	50	....	100	....	....
Paris green	....	....	....	80	....	100	....	....	....	....	....	....

TABLE 18—*Cage tests of insecticides, used as dusts at the rate of 25 pound per acre, against the Colorado potato beetle. Larvae nearly full-grow*

Material or compound	Date of application	Per cent dead								Inju to folia
		2 hrs.	4 hrs.	8 hrs.	24 hrs.	32 hrs.	48 hrs.	56 hrs.	72 hrs.	
Barium chloride 2%	May 20	....	....	....	0	0	0	....	....	None
Barium chloride plus 4 parts lime	"	....	....	....	0	0	0	....	....	"
Arsenic sulphide	"	....	....	....	0	0	0	....	....	"
Copper oxalate	"	....	....	....	0	0	....	....	....	"
Barium hydrate	"	....	....	0	0	....	....	....	....	
Sodium fluosilicate 85% plus 2 parts of lime	"	....	25	85	95	....	....	....	....	" "
Magnesium fluoride	May 24	....	0	0	0	0	0	....	0	"
Strontium fluoride	"	....	0	10	25	25	25	....	30	"
Lead fluoride*	"	....	75	100	....	....	....	....	....	Sligh
Zinc fluoride	"	....	60	90	95	100	....	....	....	None
Lithium fluoride	"	....	50	90	95	100	....	....	....	Sligh
Sodium oxalate	May 25	....	....	0	0	....	0	....	....	None
Iron oxalate	"	....	....	0	0	....	....	....	....	"
Magnesium oxalate	"	....	....	0	0	....	....	....	....	"
Aluminum fluosilicate	"	....	50	90	95	....	....	....	....	Sever
Sodium bisulphate	"	....	....	0	0	....	0	....	....	None
Barium carbonate	"	....	....	....	0	0	0	....	....	"
Barium oxalate	"	....	....	....	0	0	0	....	....	"
Calcium arsenate	"	....	....	90	100	....	....	....	....	

*Sticks well.

Even full-grown larvae may be killed in from 2 to 4 hours. This may be attributed to the fact that the sodium fluosilicate is slightly soluble. When the insoluble arsenate of lead was used the large larvae were often observed to enter the ground before a lethal dose was consumed. Cook and McIndoo (1923) state that 90 per cent of the arsenic eaten had been voided by the silkworm before death ensued. A material which kills rapidly is valuable during showery weather, when dusts are washed off the plants before a toxic dose is consumed.

The larvae of the potato beetle may be readily killed by sodium fluosilicate diluted with 9 parts, by volume, of hydrated lime. Magnesium fluoride, with a solubility of 1-11,500, was not toxic against the larvae of the potato beetle. Strontium fluoride, being almost as soluble (1-8547), gave a kill of 25 per cent in 24 hours, with little better results after 72 hours (table 18). Lead fluoride killed the larvae in 8 hours.

Chemically pure arsenious acid, or white arsenic, gave no kill and no foliage injury. A commercial white arsenic gave a kill of only 25 per cent in 24 hours, and showed foliage injury (table 19). Swingle, Morris, and Burke (1923) state that one of the most striking facts brought out in their work is that arsenic trioxide may be applied with very little foliage injury. White arsenic is known to be very slowly soluble, and exists in several forms, which may account for its variable

TABLE 19—*Cage tests of insecticides, used as dusts at the rate of 20 pounds per acre, against the Colorado potato beetle. Larvae nearly full-grown*

Material or compound	Date of application	Per cent dead								Injury to foliage	Notes
		2 hrs.	4 hrs.	8 hrs.	24 hrs.	32 hrs.	48 hrs.	56 hrs.	72 hrs.		
Iron formate	May 25	....	....	0	0	....	....	....	....	None	
Chromium fluoride	”	....	50	....	60	....	....	....	....	”	
Iron fluoride	”	....	60	....	75	....	....	....	....	”	Shower after 8 hours
Lead fluosilicate	”	....	65	....	85	....	....	....	....	Severe	
Picric acid	”	....	0	....	0	....	....	....	....	None	
“Calcium fluosilicate compound”	May 20	....	15	50	80	....	....	....	....	”	
Barium chloride	May 26	....	....	0	40	....	....	....	....	”	
Oxalic acid	”	....	....	0	25	....	....	....	....	Severe	
Salicylic acid	”	....	....	0	0	....	....	....	....	Slight	
Barium fluosilicate	”	40	60	75	95	....	....	....	....	....	
Arsenious acid C.P.	June 3	....	....	0	15	....	....	....	....	None	
Arsenious acid (Globe)	”	....	....	....	25	....	....	....	....	15%	
[illegible] (50% Wiarda)	”	....	....	85	....	....	....	....	....	5%	
Barium fluosilicate, 2 lbs. to 50 gals.	”	....	50	75	90	....	....	....	....	None	
Sodium fluosilicate	”	90	100	....	....	....	....	....	....	10%	80% in 1½ hr.
Sodium fluoride	”	60	75	100	....	....	....	....	....	20%	40% in 1½ hr.
“Calcium fluosilicate compound”	”	....	....	15	20	....	....	....	....	None	
Paris green	”	....	90	95	98	....	....	....	....	Slight	
Sodium arsenite	”	60	90	95	98	....	....	....	....	Very severe	
Arsenic acid	”	80	90	95	100	....	....	....	....	Very severe	
Dinitrobenzene	”	....	0	0	0	....	....	....	....	Slight	Acts as a repellent
Paranitrochlorobenzene	”	....	0	0	0	....	....	....	....	”	
Copper cyanide	”	....	....	....	15	....	....	....	....	”	

action. Schwartze (1922) showed that a finely divided form of arsenious oxide was 5 times more toxic to rats than a coarsely divided form.

With Culicid larvae, oxalic acid and the oxalates showed high toxicity, but against the potato beetle the oxalates were inert (table 18). Theoretically, the soluble oxalates should be very toxic because of the highly insoluble nature of calcium oxalate, but it is probable that the oxalates are burned to CO_2 before a fatal dose is consumed. Oxalic acid was very effective against adult bean beetles, but gave a kill of only 25 per cent in 24 hours against potato beetles, and burned foliage severely.

The barium compounds—barium carbonate and barium hydrate—were inert. A 2 per cent solution of barium chloride had no effect, but pure barium chloride dusted on the vines gave a kill of 40 per cent in 24 hours (table 19).

The fluosilicates are not only effective as stomach poisons but are also very useful against certain mandibulate insects heretofore not controlled by arsenicals.

Epicauta sp. and *Macrobasis unicolor.*—Through the use of fluosilicates Baerg (1925), in Arkansas, and Ingram (1926), successfully controlled blister beetles, which are not susceptible to control by arsenicals. Sodium fluosilicate, diluted with an equal quantity of hydrated lime, was used with safety on soybeans.

Diabrotica vittata.—In the past the control of this well-known pest has been far from perfect, because of the repellent effect of arsenic on the species. However, as a result of its habit of drawing its feet through its mouth, the adult beetle readily succumbs to the fluosilicates. Excellent control has been obtained, therefore, in Tennessee; by Baerg (1926) and Isely (1927) in Arkansas; by Marshall (1926) in Canada; and by Herrick (1926) in New York.

Menopon biseriatum.—Bishopp and Wood (1917) have used sodium fluoride successfully against poultry lice. Sodium fluosilicate was found by the writer to be superior to sodium fluoride in that it prevents reinfestation. Better control was also obtained against the wing louse (*Lipeurus variabilis*).

Ectobia germanica and Blatta orientalis.—These pests are now commonly controlled by sodium fluoride. Equally good results have been obtained in Knoxville with sodium fluosilicate.

Tinea pellionella.—A very severe infestation of the clothes moth upon rugs was observed in a home during the summer of 1927. The rugs were thoroughly wetted on both sides with a ½ per cent solution of sodium fluosilicate, and within a week or two the larvae disappeared. Upholstered furniture infested with the tow bug (*Lasioderma serricorne*) was also treated with a solution of sodium fluosilicate, and equally good results were obtained.

Laboratory experiments with clothes moth larvae showed that they readily succumbed when fed on raw wool which had been dipped in a 1-200 solution of sodium fluosilicate. Larvae allowed to crawl over the powder were not affected. To produce mortality the powder must be eaten.

A proprietary clothes-moth remedy known as "Larvex" is sold on the market at five dollars per gallon. Larvex is simply a solution of sodium fluosilicate. A gallon of it contains about 1 ounce of sodium fluosilicate, worth less than 1 cent. An effective home-made "larvex" may be produced by dissolving 1 ounce of sodium fluosilicate in 1 gallon of water.

Melanoplus femur-rubrum.—Grasshoppers were selected in the toxicity studies because the materials they feed upon can be subjected to experimental control. The difficulties in the way of obtaining exact data with most chewing insects may be largely overcome by the use of poison baits. In order to eliminate the factor of variability resulting from the feeding of some grasshoppers and the apparent indifference to food of other individuals, they were starved 24 hours, after which time they showed considerable uniformity in their desire to eat. Soluble compounds were prepared in definite proportions to moisten the bran. Enough of the solution was used to saturate the bran thoroughly, thus making sure that all the bran flakes were equally moistened. The results were surprisingly uniform, and substantiated those obtained with mosquito larvae.

All the experiments were performed in an outdoor insectary, at temperatures ranging from 70°F. to 80°F. For cages, large glass cylinders, 10 inches in diameter, were placed over garden soil in benches. The bran mixed with the insecticide was scattered over the damp soil in the cages, and 10 hoppers were released at 8:30 a. m. The bait was removed at 4:30 p. m. and the hoppers were placed in cages with grass. The baits consisted of 28 grams of bran and 75 cc. of insecticide.

For the insecticides, a strength of 1 gram in 150 cc. was employed. Thus 75 cc. of a solution of the insecticide gave a final strength of 1 gram of poison to 55 grams of bran. Insoluble materials were mixed according to the dry method.

The bulk of the experiments were carried out with the two soluble materials, sodium fluosilicate and sodium arsenite. In a 48-hour period 100 per cent mortality was produced by the sodium fluo-

TABLE 20—*Summary of tests of insecticides used as poison baits against Melanoplus femur-rubrum*

Material	Strength of solution	Strength of bait	No. of Experiment	Temperature	Per cent dead 7 hrs.	24 hrs.	31 hrs.	48 hrs.	55 hrs.
Sodium fluosilicate	1-150	1-56	4	70°-75°F.	13	41	83	100	....
Sodium arsenite	1-150	1-56	3	70°-75°F.	12	38	73	89	100
Paris green	......	1-150	1	70°-75°F.	32	50	84	84	....
White arsenic	......	1-50	1	70°-75°F.	20	40	80	100	....
Sodium bisulphate	1-50	1-18	1	70°-75°F.	10	10	10	20	20
Sodium fluosilicate .... plus Sodium arsenite	1-150 1-150	1-56 1-56	1	70°-75°F.	10	60	80	100	....
Sodium fluosilicate .... plus Sodium fluoride........	1-150 1-150	1-56 1-56	1	70°-75°F.	20	100	....	....	....
Check	......	......	7	70°-75°F.	0	0	0	0	0
Sodium fluosilicate ...	1-150	1-56	2	92°F.	40	100	....	....	....
Sodium arsenite	1-150	1-56	2	92°F.	30	100	....	....	....
Sodium fluoride	1-150	1-56	1	92°F.	40	90	....	....	....

silicate, while sodium arsenite showed but 89 per cent (table 20). Only one experiment was performed with Paris green and white arsenic, and these showed a toxicity similar to that of sodium arsenite. Langford (1926), in Colorado, also found sodium fluosilicate more toxic than sodium fluoride, sodium arsenite, Paris green, and white arsenic. The repellent effect which might be obtained with the arsenicals in the presence of food was not studied as with the cutworms, but it is hoped that this point may be taken up at another time, for evidence is accumulating that the arsenites are repellent to locusts.

Temperature and toxicity of fluosilicates.—The fluosilicates were first tried out in cages under field conditions in the summer of 1925. An unusually rapid kill was obtained in several instances with "calcium fluosilicate compound." Similar results were obtained during the hot months of 1926, but could not be duplicated in the insectary. The influence of temperature was suspected. For further study of this factor, a series of experiments were initiated in constant-temperature cabinets in the summer of 1927. Bean plants were dusted with sodium fluosilicate mixed with 3 parts of sulphur. At 80°F. 40 per cent of the beetles succumbed in 24 hours. Very little difference could be noted at 91°F., but at 108°F. 100 per cent mortality occurred overnight (table 21). Even sulphur alone caused the same mortality at 108°F. During the hot summer months of 1925 air temperatures of 90°F. to 102°F. were common, while soil temperatures often reached 120°F. In cages the bean beetles frequently attempted to fly away, and landed on the ground, which was dusted. Under such conditions, it is easily possible to obtain a much more rapid kill during hot sunshine than in cool and cloudy weather. Corresponding results were secured with sodium arsenite, and sodium fluosilicate for Culex larvae. A 1-5000 solution of sodium fluosilicate caused no mortality in 1 hour at temperatures of 47°F. to 82°F. At 91°F. 20 per cent succumbed, while at 107°F. there was a mortality of 50 per cent (table 22).

These experiments indicate that temperature is an important factor in toxicity, especially above 100°F.

TABLE 21—*Effect of temperature and moisture on toxicity of sodium fluosilicate against the adult Mexican bean beetle. Ten beetles used in each cage*

Material	Temperature	Moisture	Per cent dead 6 hrs.	Per cent dead 24 hrs.	Per cent dead 48 hrs.	Notes
Sodium fluosilicate with 3 parts sulphur	108°F.	Dry	30	100	....	
Control	108°F.	"	0	0	0	
Sulphur	108°F.	"	0	100	....	
Sodium fluosilicate with 3 parts sulphur	80°F.	"	20	40	50	Beetles not feeding
Sodium fluosilicate with 3 parts sulphur	80°F.	Wet	0	12	25	Beetles feeding
Control	80°F.	"	0	0	0	Plant destroyed

TABLE 22—*Effect of temperature on toxicity to the larvae of Culex quinquefasciatus*

Material	Temperature °F.	Per cent dead 1 hr.	1½ hrs.	2 hrs.	2½ hrs.	4 hrs.	6 hrs.
Sodium fluosilicate (1-5000)................	47	0	0	15	....	35	60
" " "	60	0	40	60	....	....	....
" " "	82	0	60	....	....	....	....
" " "	91	20	60	....	....	....	....
" " "	100	40	60	....	....	....	....
" " "	107	50	80	....	....	....	....
Control	107	0	0	0	0	75	100
Sodium arsenite (1-5000)......................	47	0	0	0	0	0	0
" " "	82	0	20	....	....	....	....
" " "	91	0	20	....	....	....	....
" " "	100	0	20	....	....	....	....
" " "	107	50	90	....	....	....	....

EFFECT OF FLUORINE COMPOUNDS ON DIFFERENT TYPES OF ORGANISMS

Bacteria.—The fluosilicates possess marked antiseptic properties, and are considered superior to either the fluorides or corrosive sublimate in certain medical practices. A 23 per cent solution of ammonium bifluoride is considered useful for the treatment of pyorrhea alveolaris, and for the disintegration of the tartar.

Anderson (1927) found that sprays of sodium fluosilicate (2 pounds to 50 gallons of water) on peach gave excellent control against bacterial spot (*Bacterium pruni*). This disease, considered the most serious disease of the peach in Illinois, is not controlled by the ordinary fungicides, nor by arsenicals now in use. Dr. Anderson noted that sodium fluosilicate in dilutions ranging from 1-4000 to 1-4500 would always produce sterility when the solutions were inoculated with *Bacterium pruni*.

Protozoa.—Several tests performed by the writer with protozoa indicate that fluorine compounds are highly toxic. A solution of sodium fluosilicate (1-10,000) is fatal to full-grown *Paramoecium caudatum* almost instantaneously. At the same strength, quinine sulphate required 18 minutes to stop movement; sodium fluoride (1-1000) required 60 minutes; and sodium arsenite seemed to be non-toxic. Sodium fluoride (1-200) required about 20 minutes to kill, whereas sodium arsenite (1-200) required 35 minutes. Somewhat similar results were secured with *Euglena* sp. The high toxicity of fluorine compounds for protozoa suggests their usefulness against pathogenic protozoa. For this purpose, one would have to use organic fluorides, the chemistry of which is but little understood.

Annelida.—The common earthworm (*Lumbricus terrestris*) was used to determine the effect of fluorine compounds on the annelidae in general. In strengths of 1-10,000, both sodium fluosilicate and mercuric chloride required 25 minutes to produce a lethal effect (table 23). Thymol required 55 minutes, while with potassium cyanide more than 5 hours were necessary. In a comparison of sodium

TABLE 23—*Toxicity studies with Lumbricus terrestris, showing time in minutes when movements ceased. Temperature 70°F.*

Material	1-200	1-1000	1-10,000	1-50,00
Sodium fluosilicate	15	20	35	100
Sodium fluoride	25	40	180	....
Sodium arsenite	80	240	....	....
Potassium cyanide	....	30	300+	....
Mercuric chloride	....	10	25	....
Thymol	....	7	55	240+
Oil of chenopodium	....	80	....	....
Quinine sulphate	....	120	....	....
Magnesium fluosilicate	....	25	....	....

fluosilicate, sodium fluoride, oil of chenopodium, quinine sulphate, and sodium arsenite (1-1000), 20, 40, 80, 120, and 240 minutes, respectively, were required to obtain a kill.

Ascaris lumbricoides.—Thymol (1-1000) killed Ascaris in 7 minutes, while from 8 to 40 minutes were necessary with sodium fluosilicate. In strengths of 1-10,000, mercuric chloride, thymol, and sodium fluosilicate required 1½, 5, and 2 to 6 hours, respectively, for a lethal effect. With "calcium fluosilicate compound" (1-500) in a 1 per cent salt solution, the worms lived about 24 hours.

Pisces.—The toxicity studies with fish were made on the common shiner *Notropis antherinoides.* Potassium cyanide (1-200) was the most toxic, requiring but 3 minutes to stop movement. At the same strength, bichloride of mercury required 10 minutes, sodium fluosilicate 15 minutes, and sodium arsenate 36 minutes. With sodium fluosilicate, 1 part in 1,000,000 was fatal within 10 hours.

CONCLUSION

As the white rat is a standard for pharmacological studies, so the mosquito may be employed for insect toxicology. For insects and lower organisms, sodium fluosilicate is more toxic than sodium arsenite. Since fluorine seems to affect the precipitation of essential calcium from the tissues, the meager calcium content of the lower organisms may account for their susceptibility to fluorine compounds. By the aid of the formula $K = \frac{1}{t} \log \frac{1}{\text{conc.}}$, a numerical toxicity value of 34.5 was obtained for sodium fluosilicate, 13.1 for sodium arsenite, 4.8 for sodium arsenate, and 4 for sodium fluoride. On the other hand, to man and the higher animals the arsenicals are at least 9 times more toxic than sodium fluosilicate, and 30 times more toxic than sodium fluoride.

Data as to the consequences of the continued daily administration of minute quantities of arsenic are too fragmentary and conflicting to furnish dependable conclusions. As the basis for an estimate of the effects of small daily doses of arsenic on man, more reliable results may be obtained with the omnivorous rat than with herbivorous animals. Sollman's work with the rat shows that daily doses of arsenic trioxide of only 1/800 to ¼ of the U. S. P. therapeutic dose of 2 mg. did produce a distinct retardation in growth within 9 to 24 weeks.

SUMMARY

The fluosilicates appear to be the best available substitutes for the arsenicals as agents for the protection of plants against phytophagous insects. Although sodium fluosilicate was described in a patent as early as 1896, its insecticidal value remained in obscurity until 1924.

The fluosilicates have been effective against the following insects: Mexican bean beetle (*Epilachna corrupta*), cucumber beetle (*Diabrotica vittata*), potato beetle (*Leptinotarsa decemlineata*), boll weevil (*Anthonomus grandis*), blister beetles (*Epicauta sp.*), sugar cane borer (*Diaetrea saccharalis*), cutworms (*Feltia ducens*), various flea beetles, biting lice, and grasshoppers.

Many insects, when they come into contact with powdered fluorides, clean themselves by drawing their antennae or feet through the mouth. In this way a lethal dose of poison may be consumed. Dusts also stimulate the "cleaning-up" habit of insects.

Dry dusts of sodium fluosilicate and sulphur were found to be more effective than dusts in the presence of moisture against adult bean beetles. Dew seems to interfere with the efficiency of dusts for the bean beetle, by causing the powder to stick to the plants.

The fluorine compounds are protoplasmic poisons, and their systemic action seems to be produced by the withdrawal from the tissues of calcium—the element that is essential for proper permeability—and its precipitation as calcium fluoride.

Minimum fatal doses of various substances by mouth for mammals are about as follows: Sodium fluoride, 0.5 gram per kilo; sodium fluosilicate, 0.12 gram; and potassium arsenite, only 14 mg. At these rates the following amounts would be lethal to man: Sodium fluoride, 30 grams; sodium fluosilicate, 7.2 grams; potassium arsenite, 0.84 gram. As little as 4.5 grams of sodium fluoride has been fatal.

Intravenously, 10 mg. per kilo of sodium fluosilicate was fatal to rabbits in 2 minutes.

Sollman (1921) found that the continued daily administration for 24 weeks of .0005-.0015 mg. of arsenic trioxide to albino rats produced a marked loss of weight. Christiani and Chausse (1927) reported that 2 mg. of sodium fluosilicate fed daily to guinea pigs caused death in 233 days, although 10 mg. of sodium fluoride fed 10 months caused no apparent harm.

Fluorine compounds do not seem to be repellent to insects, and are therefore, in many cases, more effective than arsenicals, especially with the cutworm (*Feltia ducens*). On the other hand, for higher animals, such as birds and mammals, fluorine compounds are distasteful in poison baits.

Plants tolerate soluble fluosilicates better than soluble arsenicals. Free moisture seems to be the principal agency responsible for foliage injury by fluosilicates. Dusting when dew is on plants' should avoided.

In the presence of moisture, hydrated lime, when used as a carr for sodium fluosilicate, may be the cause of foliage injury. Sulp or flour was found to be safer than lime as a carrier, when used the rate of 2 parts to 1 of sodium fluosilicate. In the presence moisture, hydrated lime alone is capable of causing foliage injury cucumbers.

For quantitative toxicological tests, mosquito larvae were fo to be well suited. Sodium fluosilicate, 0.01 molar, is more toxic th sodium arsenite, and much more toxic than sodium arsenate. T insoluble fluorides of calcium, magnesium, and strontium show a l order of toxicity.

Of the organic acids, salicylic was the most toxic, followed b oxalic, formic, benzoic, and acetic.

Of the metals, mercury was the most toxic. Barium, lead, zi and copper showed some toxicity, although small in comparison wi that of fluorine.

Against *Orthopodomia signifer* 0.02 N hydrochloric acid had lethal effect, though none was observed with 0.02 N sodium hydroxi

Sodium fluosilicate is at least 8 times more toxic than sodi fluoride to mosquito larvae. Two acid fluorides, chromium and a timony, were found more toxic than the slightly alkaline sodi fluoride.

A solution of sodium fluosilicate (1-10,000) is toxic to *Culex qui-quefasciatus* in distilled water. Under practical conditions, in natur breeding waters, heavily charged with organic matter, it requir enough of the powder to equal 1-4000 to produce a lethal effect in days. Sodium fluosilicate proved to be much more toxic than "nit cake".

Crude naphthalene, when used as a dust on the surface of th water, was capable of destroying *Anopheles punctipennis* within a fe hours.

Oxalates, barium carbonate, and a 2 per cent solution of bari chloride, in field tests, were ineffective against the Colorado pota beetle.

Grasshoppers also proved to be well adapted for toxicity studie Sodium fluosilicate in poison baits is slightly more toxic than sodi arsenite.

The arsenicals and fluorine compounds are much more effecti under high temperatures, especially above 100°F.

The fluosilicates possess marked antiseptic properties, and ar highly toxic to protozoa. A 1-10,000 solution of sodium fluosilica is almost instantaneously fatal to *Paramoecium caudatum.* Sodi fluoride (1-1000) required 60 minutes for a lethal effect, while th same strength of sodium arsenite was harmless.

Against the earthworm (*Lumbricus terrestris*) a 1-10,000 soluti of sodium fluosilicate was fatal within 25 minutes; thymol, 55 minutes potassium cyanide, 5 hours.

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