Adsorption of *Gamma*-BHC from Solutions on Several Selected Adsorbents

A. C. Mills[1] and J. W. Biggar

The adsorption on several selected adsorbents of *gamma*-BHC (1,2,3,4,5,6-hexachlorocyclohexane) from water, alcohol, benzene, and hexane at 20° C. was investigated. Any decomposition during adsorption was assessed by liquid scintillation counting and electron-capture gas chromatography. In general, adsorption increased in the order ethanol < benzene < hexane ≲ water. Adsorption from hexane and benzene was relatively low on peaty muck and greatest on silica gel and Venado clay. Adsorption from ethanol was significant only on peaty muck. The importance of dipole-dipole interactions in *gamma*-BHC adsorption was deduced. No decomposition occurred in aqueous and alcohol solvents, whereas some was observed in benzene and hexane solvents. Solubility and other solvent differences markedly influenced the uptake of pesticide by the different surfaces.

The mobility of pesticides resulting from the movement of water from land surfaces to water bodies holds possibilities of widespread dissipation, with inherent dangers to public health (Edwards, 1966). An important step in the movement process is adsorption, which is affected by the solvent, the surface of the solid, and the nature of the chemical.

The insecticide chosen for the present study was lindane (1,2,3,4,5,6-hexachlorocyclohexane) (99 to 100% γ-BHC), because it is relatively persistent in soils (Edwards, 1966) and presents certain health hazards to man and animals through uptake by crops in various parts of the world (Odumanov-Dunaeva and Kozlova, 1964). Of equal importance is its presence in various surface and groundwater supplies (Faust and Suffet, 1966).

Relatively few controlled laboratory experiments have been reported on the adsorptive behavior of lindane on soils and related adsorbents. Lichtenstein (1958) measured the movement of lindane from one soil layer downward through lindane-free layers in cardboard cartons under various leaching regimes. Under leaching, lindane moved most in Plainfield sand and least in a muck soil, whereas, without water application, lindane moved most in the muck soil and not at all in the sand. Press (1959) applied lindane in isohexane to columns of different African soils. From the volumes of solvent required to elute essentially all the lindane, he concluded that the finely particulate soils were relatively more adsorptive. Swanson *et al.* (1954) studied adsorption in a similar manner. Lindane was applied in petroleum ether to soil columns and leached with five aliquots of the solvent equivalent to the weight of the soil used. Exchange resins hold no lindane, and the presence of organic matter seemed to have little effect in increasing lindane adsorption. The amount of lindane adsorbed was closely correlated, however, to the per cent clay content of the soil. If these workers had used aqueous solutions of lindane, the adsorptive capacity of the organic fraction might have been significant. Nose

et al. (1964), from study of the adsorption of pentachlorophenol (PCP) from aqueous solutions, concluded that organic matter is important to PCP adsorption in soil.

The present study was made to ascertain the nature of adsorption and decomposition of γ-BHC from solutions of very low concentrations, such as those encountered in the field. Several solvents, including water, and several adsorbents were used in equilibrium studies. Since different carriers are often used for agricultural chemicals, another goal of the study was to ascertain whether the differing properties of solvents influence adsorption measurably.

EXPERIMENTAL

Crystalline γ-BHC, obtained from the J. T. Baker Co., was certified to be 99 to 100% *gamma*-isomer. The radioactive *gamma*-isomer was obtained from Nuclear-Chicago as C^{14} uniform-labeled compound supplied in benzene solution. All chemicals were reagent grade, A.C.S., Baker and Adamson; nanograde hexane was used in appropriate experiments.

Several adsorbents, including soils, clays, exchange resins, silica gel, and alumina, were utilized for the adsorption studies. The exchange resins were 100- to 200-mesh Dowex 50-W-X8 (H$^-$ form) and Dowex 1-X8 (Cl$^-$ form). Fisher certified silica gel, 100- to 200-mesh, and neutral alumina, 80- to 200-mesh, were used, as well as basic alumina. Magnesium hydroxide was prepared by combining aqueous solutions of reagent grade NaOH and MgCl$_2$.

Homoionic samples of Wyoming bentonite and kaolinite were prepared in the laboratory by leaching and sedimentation. The samples of Ca- and Na-bentonite and Ca-kaolinite ranged in particle size from 0.2 to 1.0 micron.

Venado clay was determined by x-ray diffraction analysis to contain approximately 40% montmorillonite. The soil samples were prepared by saturating with solutions of calcium or magnesium acetate, leaching with distilled water, and drying. They were then ground with a porcelain mortar and pestle to a sieve size less than 1.0 mm. and oven-dried for 24 hours at 110° C.

Table I shows carbon and surface-area determinations made on a few of the adsorbents. Per cent carbon

Department of Water Science and Engineering, University of California, Davis, Calif. 95616

[1] Present address, C-52 N.D. South, % AFPRO Extension II. New Delhi 16, India

content was determined by total combustion (American Society of Agronomy, 1965) and surface area measurements were made by the method of Bower and Gschwend (1952). The organic-matter content of individual samples of Venado clay was reduced by hydrogen peroxide treatment.

The surface area of silica gel appears excessively high, compared with reported values of 710 ± 60 sq. meters per gram (Dyne and Sagert, 1966) calculated by the B.E.T. equation, using N_2 as the adsorbent. However, the present silica gel had a particle size of 100- to 200-mesh, compared with 50- to 60-mesh used by the cited investigators. Consequently, 890 sq. meters per gram may not be an unreasonable value. The surface area reported for Ca-bentonite compares closely with those obtained by Bower and Gschwend (1952).

When a factor of 1.9 (ratio of the weight of total organic matter to the weight of carbon) is applied to the per cent carbon obtained for Staten peaty muck, the organic matter content of this soil is 22.7%. The per cent carbon content of untreated and H_2O_2-treated Venado clay indicate that the H_2O_2 treatment removed nearly two-thirds of the organic matter present in this soil.

Solutions of *gamma*-isomer BHC were made up in liter quantities to contain 5 or 100 μg. per ml. of lindane for the benzene studies, 5 μg. per ml. for the ethanol and aqueous studies, and 100 μg. per ml. for the hexane studies. Each of these solutions contained 5 μc. per liter of radiochemical isomer, allowing 10,000 to 14,000 c.p.m. for 2 ml. of solution by liquid scintillation counting.

Benzene solutions were made up directly from the radioactive solution obtained from the supplier. The others were made by evaporating benzene aliquots containing the proper number of microcuries to dryness under a gentle nitrogen stream and taking up in the appropriate solvent. In the case of aqueous solutions, 5 ml. of 200-proof ethanol was used to take up the precipitate, so that aqueous solutions contained 0.5% ethanol. Although this procedure might allow some loss by volatilization, the actual concentrations used in the adsorption studies were known by analysis and the proper concentrations used in the calculations, thus eliminating errors from this source. However, losses

due to volatilization could not be detected within the limits of experimental error. The stock solutions were stored for a short time in glass-stoppered bottles in the dark.

Five grams of oven-dried absorbent were weighed into a 125-ml. glass-stoppered Erlenmeyer flask. (Ten grams of adsorbent were employed for some of the materials, as indicated). To ensure a low uniform moisture content in the adsorbents, in most cases the flasks were placed in an oven for 36 hours at 110° C. before organic solutions were added, and for 15 hours at 60° C. before aqueous solutions were added. Following the heat treatment, 25 ml. of the appropriate solution were added to each flask. Duplicates were included for each adsorbent and each solvent. Adsorbent blanks and standard blanks in duplicate were also included, allowing for a check on losses during equilibration. The flasks were glass-stoppered, covered with polyethylene bags, and placed in a constant-temperature water bath at 20° ± 0.05° C. The flasks were shaken at a rate of 60 shakes per minute for 20 hours and sampled after standing for 50 hours, by which time adsorption equilibrium had been established in all systems employed. Time studies on adsorption equilibria indicated that all systems had reached equilibrium after 70 hours of contact. Benzene systems were near equilibrium after 5 hours and showed no change between 70 hours and 120 hours. Hexane systems showed some decomposition between 70 hours and 240 hours. Aqueous systems showed some decomposition between 112 and 160 hours, as measured by gas chromatography and liquid scintillation. The 70-hour period assured equilibrium in all the systems and was a convenient period for completing other steps in the equilibrium studies.

In systems with benzene or hexane as the solvent, aliquots of the equilibrated solution were removed directly from the flasks, which were kept in place in the bath. The flasks containing ethanol or water as the solvent were removed from the bath, swirled, and the contents poured into 50-ml. stainless-steel centrifuge tubes. These were immediately centrifuged for 20 minutes at 10,000 r.p.m. (15,000 G). This procedure ensured sedimentation of the clay in the ethanol and aqueous media. Ten milliliters of the supernatant were transferred to a glass-stoppered test tube. The aqueous solutions were extracted by adding 10 ml. of nanograde hexane and inverting the glass-stoppered test tube back and forth for 1.5 minutes. Longer mixing times did not improve extraction.

The equilibrium solutions were analyzed both by liquid scintillation counting (LS) in a Packard Tri-Carb spectrometer and by electron-capture gas chromatography (GC) with an Aerograph Hy-Fi chromatograph Model 600-B equipped with a recorder and a disk integrator.

Matched vials were used in the LS analysis and two channels were used to check on quenching, which did not occur. Five 10-minute counts were made on all samples, resulting in a per cent deviation between replicates of less than 1.5%, and usually less than 0.8%. Liquid scintillation solution consisted of 865 ml. of ethanol, 1370 ml. of 1,4-dioxane, 1370 ml. of toluene, 180 grams of naphthalene, 18 grams of PPO, and 0.36 gram of POPOP. Two-milliliter aliquots of the hexane-

Table I. Some Characteristics of Selected Adsorbents

Adsorbent	pH	Cation Exchange Capacity, Meq./100 Grams	% C, Oven-Dry Wt.	Surface Area, Sq. M./Gram
Ca-Staten peaty muck	6.6	54	11.9	2.3×10^2
Ca-Venado clay	8.5	48	3.1	4.2×10^2
H_2O_2-treated Ca-Venado clay	a	a	1.2	4.1×10^2
Ca-Columbia silt loam	7.5	14	1.1	a
Ca-bentonite	8.3	80	0.08	8.1×10^2
Silica gel	4.4	a	a	8.9×10^2

a Undetermined.

extracted aqueous solutions or aliquots of samples taken from experiments not receiving the extraction were put into the scintillation solution, shaken, brought to the temperature of the spectrometer, and counted as previously noted.

Because the response of the electron-capture detector of the GC is not linear over a wide concentration range, it was necessary to dilute the samples to a concentration which would fall within the linear range of the detector. Dilutions were performed using nanograde hexane, followed by injection into the GC. The column used was a 5-foot by 1/8-inch borosilicate glass column packed with 60/80 Chromosorb W, having as the liquid phase 5% Dow II. Oven temperatures were kept at 180° C. and the pressure of the nitrogen carrier gas was maintained at 25 p.s.i. Appropriate standard solutions were injected between every four to six experimental samples.

Dual analysis was used to determine whether the BHC-isomer had decomposed in the adsorption flasks, and the extent of any decomposition. When decomposition was concluded to be nil (concentration of the equilibrium solution by GC greater than 90% of the concentration by LS analysis), the LS concentration values were used for calculation of the amounts adsorbed. The latter were used, since the GC analysis was concluded to be only half as precise as the LS analysis.

The solubility of γ-BHC in aqueous medium was determined at 20° and 30° C., and 10° and 20° C. for hexane. To correspond to the aqueous systems used in the adsorption experiments, the solutions contained 0.5% ethanol by volume. Powdered isomer crystals were added to 400 ml. of solvent in excess of the solubility by stirring in glass-stoppered 1-liter bottles. The bottles were placed in a constant-temperature bath and shaken intermittently for 68 hours. After this period, aliquots were removed and filtered through a 5-micron fritted glass filter into glass-stoppered test tubes. Aqueous solutions were then extracted with nanograde hexane as previously described, diluted, and analyzed by both liquid scintillation and gas chromatography. Table II shows the solubility determinations. The solubility in water is somewhat higher than that reported by Robeck *et al.* (1965) because of the 0.5% alcohol present in the aqueous solvent. Since the concentration of lindane used in the adsorption experiments is well below the saturation values, no difficulty of precipitation was experienced in these experiments.

RESULTS AND DISCUSSION

The influence of heat pretreatment of soil on adsorption of lindane from benzene solutions on Ca-Venado clay was studied. Table III indicates the influence of heating 10 grams of soil for 72 hours before the addition of 25 ml. of benzene solution containing 5 μg. of lindane per ml. Positive adsorption on Venado clay of lindane from benzene solutions is possible apparently only if the adsorbent has been preheated above room temperature. The reason may be the loss of interlayer water at higher temperatures. This water may be adsorbed on sites which have more affinity for the lindane molecules than for benzene molecules.

Another experiment indicated the influence of the

Table II. Solubility of γ-BHC in Aqueous and Hexane Solutions at 10°, 20°, or 30° C.

Solvent	Temp., ° C.	Conc. of Sat. Soln.
Distilled water with 0.5% ethanol	20	8.5 μg./ml.
	30	13.1 μg./ml.
Nanograde	10	9.8 mg./ml.
hexane	20	14.0 mg./ml.

Table III. Effect of Heat Pretreatment of Ca-Venado Clay on Adsorption of γ-BHC from Benzene Solution at 25° C.

Temp. of Pretreatment, ° C.	Equilibrium Concn., μg./Ml.	% Deviation between Duplicates	x/m, μg. Adsorbed per Gram of Adsorbent
25	5.05	0.2	−0.12
111	4.60	0.5	1.00
224	4.49	0.8	1.27

Table IV. Effect of Saturating Cation and H_2O_2 Treatment upon Adsorption of γ-BHC on Ca-Venado Clay from a 5-μg./Ml. Aqueous Solution at 20° C.

Adsorbent	Equilibrium Concn., μg./Ml.	% Deviation between Duplicates	x/m, μg./Gm.
Ca-Venado clay	0.373	0.2	18.5
Mg-Venado clay	0.372	0.1	18.5
Ca-Venado clay (H_2O_2-treated)	0.745	0.2	17.0

cation on the exchange complex, and of the soil organic matter upon the adsorption of lindane on Venado clay from an aqueous solution of 5.0 μg. per ml. Solution volume added in this case was 20 ml. The results are shown in Table IV. Changing the saturating cation from Ca^{2+} to Mg^{2+} had no apparent effect on adsorption from aqueous solutions. The x/m value, however, was definitely reduced by the H_2O_2 treatment of Venado clay. This reduction is due undoubtedly to the partial loss of organic matter. Table I showed that the H_2O_2-treated Venado clay still contained 1.2% carbon, slightly more than one-third of the carbon content of the untreated soil. We have noted that Venado clay contains approximately 40% montmorillonite. The x/m value for the adsorption of γ-BHC on Ca-bentonite from a 5.0-μg.-per-ml. aqueous solution is about 10 μg. per gram, as shown in Table VIII. Consequently, comparing 10 with 17 μg. per gram, one must conclude that the adsorption of γ-BHC from aqueous solutions is influenced considerably by the portion of organic matter which is quite resistant to the H_2O_2 treatment and is probably, in effect, adsorbed strongly on the clay surface.

The adsorption differences of γ-BHC are assumed due in part to the differing solubilities of γ-BHC in the different solvents, and in part to the structure and affinity of the solvent molecule for the particular adsorbent. Making allowance for the differences in initial concentration between different adsorbent-solvent systems, lindane competes for adsorption sites most effectively with water and least effectively with ethanol. To generalize for the adsorbents employed, the adsorp-

Table V. Adsorption of γ-BHC from 100-μg./Ml. Benzene Solution at 20° C.

Adsorbent	x/m, μg./Gm.
Na-nontronite	−2.3
Ca-bentonite [a]	−2.2
Na-bentonite	−1.9
Cation exch. resin	−1.6
Anion exch. resin	−1.6
Na-kaolinite	−1.3
Ca-Staten peaty muck [a]	−1.2
Alumina (basic) [a]	2.7
Ca-Columbia silt loam [a]	2.8
Mg(OH)$_2$	6.4
Ca-Venado clay [a]	12.1
Silica gel [a]	13.5

[a] 10.0 grams rather than 5.0 grams of adsorbent employed. Negative values in the table arise in part from differential evaporation losses and exclusion of the adsorbate relative to solvent uptake by the adsorbent.

Table VI. Adsorption of γ-BHC from 100-μg./Ml. Nanograde Hexane Solution at 20° C.

Adsorbent	x/m, μg./Gm.
Cation exch. resin	−1.8
Anion exch. resin	1.4
Ca-Staten peaty muck [a]	38.8
Na-kaolinite	50.7
Mg(OH)$_2$	66.4
Alumina (neutral)	68.6
Na-bentonite	72.5
Alumina (basic) [a]	80.6
Ca-Columbia silt loam [a]	94.1
Ca-bentonite [a]	97.2
Ca-Venado clay [a]	166.0
Silica gel [a]	245.0

[a] 10.0 grams rather than 5.0 grams of adsorbent employed. Negative values in the table arise in part from differential evaporation losses and exclusion of the adsorbate relative to solvent uptake by the adsorbent.

Table VII. Adsorption of γ-BHC from 5.0-μg./Ml. Ethanol Solution at 20° C.

Adsorbent	x/m, μg./Gm.
Silica gel	−1.10 [a]
Ca-bentonite	−0.60
Ca-Venado clay	−0.30
Ca-kaolinite	0.15
Ca-Columbia silt loam	0.35
Ca-Staten peaty muck	3.70

[a] Negative values in the table arise in part from differential evaporation losses and exclusion of the adsorbate relative to solvent uptake by the adsorbent.

Table VIII. Adsorption of γ-BHC from 5.0-μg./Ml. Aqueous Solution at 20° C.

Adsorbent	x/m, μg./Gm.
Ca-kaolinite	2.70
Ca-Oakley sand	9.40
Silica gel	9.70
Ca-bentonite	10.3
Ca-Columbia silt loam	16.3
Anion exch. resin	20.6
Ca-Venado clay	22.5
Cation exch. resin	24.6
Ca-Staten peaty muck	24.6

tion of γ-BHC from the solvents increases in the following order: ethanol < benzene < hexane ≳ water. Aside from ethanol, the solvents are arranged in the order of decreasing solubility of γ-BHC. One can hypothesize, then, that the combination of ethanol's polarity and organophilic character is important in making it most effective in competing with γ-BHC for adsorption sites.

With a few exceptions, the order of adsorbents is the same in Table V as in Table VI. Since the solubility of γ-BHC in benzene is about 14 times that in nanograde hexane, it is understandable why x/m values were lower for the benzene system. But the competitive effectiveness of the benzene molecule may be greater than that of hexane also because of the differing molecular shape and electrical properties. The benzene molecule is more "compact" than that of hexane, possibly improving adsorption in spaces between the exchangeable ions on the oxygen surfaces of the kaolinite. Also, the cross-sectional area of benzene corresponds closely with that of lindane, although the benzene molecule is planar, in contrast to the lindane molecule. Thus, lindane has little advantage over benzene in terms of size and shape, whereas it is more compact than hexane.

Since the adsorption of γ-BHC, particularly in hexane, is greater on silica gel, clays, and alumina than on Staten peaty muck, it would seem that the polarity of lindane may be important in its adsorption on polar inorganic surfaces.

Table VII indicates no significant adsorption of γ-BHC from ethanol except on Ca-Staten peaty muck. This gives us another indication that the polar character of this compound is important in its adsorption on silica gel, clay minerals, and Venado clay. Apparently the strong polar nature of ethanol, together with its tendency to form hydrogen bonds, allows it to compete effectively against γ-BHC on these adsorbents. The positive adsorption of the compound from ethanol on Staten peaty muck leads one to conclude that the nonpolar organic constituents of this soil may have more affinity for lindane than for ethanol.

Referring to Table VIII, the order of adsorption with water is considerably different from the order with benzene or hexane systems. The exchange resins and the muck, as well as Venado clay, exhibit the highest affinity for γ-BHC. Water molecules would not be attracted to the nonpolar organic constituents which make up the matrix of the exchange resins, as well as a considerable part of the muck soil. With such solvent competition eliminated, it is understandable why the x/m values were highest for these materials. This should also explain why adsorption was significantly higher on Ca-Venado clay than on Ca-bentonite.

The fact that the water molecule, as a dipole, can offer some competition for adsorption sites on crystal surfaces of clays, silica gel, and sand accounts for the lower adsorption values for γ-BHC on these adsorbents than on the organic-type (or organic matter–containing) absorbents. Although the dipole moment of water is less than that of γ-BHC (1.84 debye units, compared with 2.84 for γ-BHC), water tends to form hydrogen bonds with crystal surfaces. Probably, the type of hydrogen bond formed by water (O—H————O) with

Table IX. Decomposition of γ-BHC in Benzene and Hexane at 20° C.

| Adsorbent | pH (Measured in Distilled Water) | Amount of γ-BHC Decomposed, μg. | |
		In benzene solution[a]	In hexane solution[a]
Silica gel	4.4	145	0
Ca-Staten peaty muck	6.6	169	0
Ca-Columbia silt loam	7.5	234	0
Ca-bentonite	8.3	96	0
Ca-Venado clay	8.5	166	165
Alumina (neutral)[b]	8.15	—	2150
Alumina (basic)	10.0	2450	1690

[a] Initial solution concentration, 100 μg. per ml.
[b] Only 5.0 grams of adsorbent used in the experiment.

oxygen surfaces is of greater energy than that possibly formed by γ-BHC (C—H————O)). This is because of the greater polarity of the O—H group than of C—H. The C—H bond moment has been estimated as 0.4D. and that for O—H has been calculated as 1:52D (Barrow, 1961).

The adsorption values for γ-BHC from water on Ca-kaolinite and Ca-bentonite can be compared in terms of total specific surface area rather than the mass of clay. On this basis, the adsorption is far greater on Ca-kaolinite than on Ca-bentonite—0.18 vs. 0.0127 μg. per (meter)^2. Assuming that an interlayer adsorption of γ-BHC on bentonite does occur, this molecule apparently can compete with the water molecule much more effectively on the hydroxyl surfaces of kaolinite than on the oxygen surfaces of bentonite. The above data indicate the importance of dipole-dipole interactions in the adsorption of γ-BHC from solution. Dispersion forces may also be important. According to an equation given by Verwey and Overbeek (1948), the energy of adsorption due to dispersion forces is a function of the distance from the center of the adsorbed particle to the clay surface, the polarizabilities of the clay ions and the adsorbed molecule, and the ionization potentials of the clay ions and the adsorbed molecule. No values were available for ionization potentials, but the polarizabilities of γ-BHC and of each of the four solvents were calculated from published values for refraction indices. On the basis of the calculated polarizabilities alone. one would expect adsorption of γ-BHC on crystalline surfaces from the following solvents to increase according to the scheme hexane < benzene <

ethanol < water. But the true order with respect to the organic solvents is reversed. One can only conclude that, given the limited information about the solvents and adsorbate involved, the contribution of dispersion forces to adsorption may be important, but remains unclear.

In the initial studies, γ-BHC was concluded to decompose on certain adsorbents in hexane and in benzene, but to decompose little or not at all in the ethanol and aqueous systems. This was evident when GC analysis was compared with LS analysis. The equilibrium experiments were all conducted at 20° C. and 70 hours of contact. Whenever decomposition was evident, the GC analysis was used in calculating the amount adsorbed, such as in Tables V and VI. Thus, decomposition products would not be taken as lindane adsorption, although it cannot be concluded that these products would not interfere with lindane adsorption.

Table IX indicates a positive relation between the pH of an adsorbent in distilled water and the extent of decomposition of γ-BHC in hexane or benzene solutions, though several inconsistencies are evident. For example, in benzene solution, the clays are out of place. For hexane, alumina and Ca-Venado clay are reversed, suggesting that such a relation between pH as measured in aqueous solvents and decomposition in organic solvents may have limited value.

LITERATURE CITED

American Society of Agronomy. Methods of Soil Analysis. No. 9, Madison, Wis., 1965.
Barrow, M., "Physical Chemistry," McGraw-Hill, New York. 1961.
Bower, C., Gschwend, F., Soil Sci. Soc. Am. Proc. 16, 342–5 (1952).
Dyne, P., Sagert, N., Nature 210, 1153–4 (1966).
Edwards, C. A., Res. Revs. 13, 83–112 (1966).
Faust, S. D., Suffet, I. H., Res. Revs. 15, 44–113 (1966).
Lichtenstein, E. P., J. Econ. Entomol. 51, 380–3 (1958).
Lind, E. L., Hobbs, M. E., Gross, P. M., J. Am. Chem. Soc. 72, 4474–7 (1950).
Nose, K., Suzuki, T., Fakunaga, K., Soil Sci. Plant Nutr. 10(2), 45 (1964).
Odumanov-Dunaeva, G. A., Kozlova, K. I., Botan. Zh. 49(9), 1272–8 (1964).
Press, J. M., Bull. World Health Organ. 20, 153–62 (1959).
Robeck, G. C., Dostal, K. A., Cohen, J. M., Kreissal, J. F., J. Am. Water Works Assoc. 57, 181 (1965).
Swanson, C. L. W., Thorp, F. C., Friend, R. B., Soil Sci. 78, 379–88 (1954).
Verwey, E. J. W., Overbeek, J. Th. G., "Theory of the Stability of Lyophobic Colloids," Amsterdam, 1948.