THE DISTRIBUTION OF SOLUTE BETWEEN WATER AND SOIL¹

F. K. CAMERON AND H. E. PATTEN

In studying the distribution of an added solute between an absorbent and solvent there is difficulty in obtaining accurate data when the absorbent already contains the solute in question. There is no method of determining absolutely the quantity of any soluble material in a soil, which has already been absorbed on the soil grains, and the total amount present as absorbent material cannot be ascertained, although the amount of solute present in the water added to the soil be measured exactly.

To determine the character of this distribution readily, water-soluble bodies have been used which are not contained in the soil naturally, and which are not appreciably changed by contact with the soil. Thus, there is known the quantity of solute, that of the soil and of the water; and there are obtained a series of systems in equilibrium in which the distribution of solute between water and soil can be examined quantitatively.

Soil, Gentian Violet, Water

The dye gentian violet has been found particularly well adapted to studying distribution, because it is very slightly changed, if at all, by contact with the soils used or with quartz flour, and because it can be readily estimated colorimetrically to within a fraction of a part in a million of solution. It is a basic dye (gentianin), represented by the formula $(\text{CH}_3)_2\text{N} \cdot \text{C}_6\text{H}_3 : \text{SCIN} : \text{C}_6\text{H}_3 \cdot \text{NH}_2$, analogous to ammonia bases in general. The solubility of the dye in water at 25° is approximately 6.8 percent by weight.

One hundred gram portions of each soil were placed in strong glass bottles of some 300 cc capacity, with 150 cc of dye solution, agitated in a shaker for several days, placed in a

¹ Published by permission of the Secretary of Agriculture.

centrifuge and whirled for several hours, and a small portion of the liquid withdrawn from each and the dye content estimated colorimetrically. The bottles were then replaced in the shaker, again centrifuged, and the dye in solution again determined. This was repeated till equilibrium had been reached, which usually required about a week's time.

It was found that the necessity of centrifuging these bottles at room temperature for hours to insure settlement after complete mingling of soil and solution had finally been secured, rendered a thermostat useless for the present purpose. The experiments presented here were accordingly carried out at room temperature, which varied but little from 25°.

By a separate experiment it was found that 100 grams of Marshall silt loam¹ absorb 4 cc of water from a saturated atmosphere at 29°. This was taken as representing the volume of water which is extracted from the solution when brought into contact with this soil. So, in effect, the volume of solution for which the concentration of dye is determined is not 150 cc—the volume of the liquid added—but 146 cc.

Similarly 100 grams of Hagerstown loam¹ absorb 4.5 cc of water from a saturated atmosphere at 29°, and accordingly this value was used in calculating the concentration of the solutions after absorption. The quartz flour used absorbed 0.8 cc water under the same conditions, but as this correction affects the distribution curve by less than 1 percent, it is neglected.

Table I gives the experimental data for the distribution of gentian violet between soil and water. The first column shows the concentration of dye solution added; the weight of dye withdrawn from solution per kilo of soil is shown in the second column for Marshall silt loam, a representative fertile soil; and the grams of dye remaining in a liter of solution, in the third column. The distribution for Hagerstown loam, another fertile soil, is given similarly in the fourth and fifth

¹ For a description of these soils see, Soil Survey Field Book, Bureau of Soils, U. S. Dept. Agr., Field Season, 1906, pp. 48, 126, 144.

columns; and for fine quartz flour in the sixth and seventh columns.

TABLE I
Soils and gentian violet

Distribution						
Dye added per liter	Marshall silt loam		Hagerstown loam		Quartz flour	
	Dye per kilo soil	Dye per liter solution	Dye per kilo soil	Dye per liter solution	Dye per kilo quartz	Dye per liter solution
Grams	Grams	Grams	Grams	Grams	Grams	Grams
0.04	—	—	—	—	0.06	trace
0.10	—	—	—	—	0.14	0.0001
0.5	—	—	—	—	0.743	0.0040
0.67	—	—	—	—	1.984	0.0108
1.33	—	—	1.9996	0.00023	1.901	0.066
2.00	3.00	trace	—	—	2.66	0.224
2.66	—	—	3.9998	0.00140	2.89	0.740
3.33	4.999	0.0001	4.9996	0.00250	2.95	1.370
4.66	—	—	—	—	2.97	2.668
6.67	9.999	0.00083	9.9825	0.0120	2.93	4.710
10.00	—	—	14.95	0.0325	—	—
13.33	19.99	0.006	19.817	0.1250	—	—
16.66	24.97	0.020	—	—	2.90	14.75
20.00	29.91	0.060	20.45	6.525	—	—
21.33	31.89	0.070	—	—	—	—
26.67	37.00	2.050	20.25	13.500	—	—

In Fig. 1 are charted the distribution curves for the three soils given in Table I. Since the purpose is to compare the *form* of the curves at greatest curvature, the curves are given on the same chart but necessarily to widely different scales. The concentration of dye in solution is taken as abscissa, and the concentration of the soil as ordinate. The curves thus obtained appear to be parabolic in form. By extrapolating the curve in Fig. 1, when drawn to scale, the maximum absorptive capacity of the soil for gentian violet is found to be approximately 38 grams of dye per kilogram of soil for Marshall silt loam, when the solution is saturated with respect to the dye. For Hagerstown loam the maximum absorptive capacity is 20.45 grams dye per kilogram of soil; and for quartz flour,

2.97 grams dye per kilogram quartz. These absorptive capacities are in the ratio of 113:61:1, and show that each soil has its own specific absorptive power. The soil grain area of Marshall silt loam is probably about the same as that of Hagerstown loam, as a comparison of their mechanical analyses shows, and yet the Marshall soil absorbs nearly twice the amount of dye taken up by the Hagerstown soil. Again, both of these soils have an area presented by their grains probably twice as great as the surface offered by the same weight of the quartz flour used, and yet the quartz has by no

Fig. 1

means half the absorptive capacity of either of the soils. The presence of organic matter is undoubtedly a very important factor in determining the magnitude of the absorption. But it is certain that the mineral constituents of a soil, as well as the organic matter it contains, are a factor in determining its absorptive capacity, and that mineral constituents other than gelatinized products of hydrolysis are capable of absorbing soluble bodies from the soil solution to a marked extent.

Considering the concentrations of dye when the soil has

nearly reached its maximum absorption capacity a computation from the data in Table I shows that Marshall silt loam abstracted from solution 92.5 percent of the total dye added; the Hagerstown loam, 51.1 percent; and the quartz flour, 59 percent. At lower concentrations of dye in solution the soils absorb relatively more dye, and although the dye is truly distributed between soil and solution, the soil holds so large a portion of dye that for practical purposes the dye is all absorbed. Thus, for 0.5 gram dye added, the Marshall silt loam absorbed 97 percent, the Hagerstown loam 99.99 percent, and the quartz flour 59 percent of dye. When only 0.075 gram dye was added the quartz flour absorbed 99 percent, leaving but 1 percent in solution. Consequently, it is clear that absorption experiments carried on over a limited range of concentrations may lead to false conclusions regarding the distribution. Further, these experiments emphasize the fact that a soil may hold a relatively large quantity of water-soluble material even in contact with a very dilute aqueous solution.

Quartz Flour, Eosine, Water

Table II gives the data for the distribution of sodium eosine between quartz flour and water. Here the absorptive capacity of the quartz for eosine does not tend to a limiting value, as it does for gentian violet, but the absorption of eosine increases almost proportionally with the quantity of

TABLE II
Quartz Flour and Eosine

Dye added per liter solution	Distribution	
	Dye absorbed per kilo quartz	Dye per liter solu- tion
Grams	Grams	Grams
0.0331	0.009	0.027
0.1000	0.0135	0.091
0.3351	0.084	0.274
1.0000	0.348	0.768
10.0000	4.200	7.200

eosine in solution. The distribution is therefore represented by a rather flat parabolic curve, which bends rather toward the axis of concentration in quartz than toward the axis of concentration in solution as in the cases considered above.

Manure Extract, Soil, Water

Several concentrations of a well fermented and matured manure extract were allowed to stand in contact with soils, with frequent shaking, for two weeks at room temperature. Then the supernatant liquid was poured off, centrifuged, evaporated to dryness, and the organic matter determined by weighing before and after ignition. The quantity of organic matter in the original manure extract solution was determined similarly.

TABLE III
Soil and manure extract

Organic matter in added extract per liter	Distribution					
	Hagerstown loam		Marshall silt loam		Norfolk sand	
	Organic matter per kilo soil	Organic matter per liter solution	Organic matter per kilo soil	Organic matter per liter solution	Organic matter per kilo soil	Organic matter per liter solution
Grams	Grams	Gram	Gram	Gram	Gram	Grams
0.147	0.056	0.133	—	—	(—)0.129	0.179
0.294	0.364	0.203	—0.109	0.321	(—)0.100	0.319
0.588	0.740	0.403	0.354	0.500	0.077	0.569
1.175	1.180	0.880	0.885	0.954	0.440	1.065

Table III contains data for Hagerstown loam, Marshall silt loam, and Norfolk sand. A correction for the volume of water absorbed on the soil grains was not applied here as it amounts to less than 1 percent, and the data serve to show merely the general trend of the distribution. As there is some organic matter already present in the soil, the absorption appears negative for low concentrations of manure extract, since the organic matter comes out of the soil and increases the total amount present in solution. For Hagerstown loam the maximum absorptive capacity was found, by ex-

trapolation of the distribution curve, to be approximately 1,700 parts per million. This means that with very great concentration of manure in solution, one kilo of this soil would absorb 1.7 grams of this soluble manure from the extract and no more. The data do not admit of calculating the maximum absorptive capacity for the other two soils, but a comparison of the soils on the basis of the highest quantity of manure absorbed by each gives a ratio of 2.7 : 2 : 1, in the order, Hagerstown loam, Marshall silt loam, and Norfolk sand respectively. Here the order of the absorption capacities is the reverse of that found for gentian violet as shown in Table I, where Marshall silt loam had nearly twice the absorptive power found for the Hagerstown loam.

This experiment is important in showing that absorption is dependent as much on the nature of the solute as on that of the absorbent. It further indicates the probable futility of attempting to select empirically a dye with which quantitative measurements might be made to determine the absorptive power of a soil for manures or fertilizers, or to determine its relative crop-producing power.

Selective Absorption

The effect of fine powder or other absorbing media in selectively absorbing the base and leaving the solution acid has been considered in a previous paper,¹ but the distribution of the solute is particularly interesting in this connection. For this purpose Peters'² results on the absorption of potassium chloride by a soil have been recalculated for Table IV and Fig. 2, so that they might be compared with the data given above.

The similarity between this curve and the previous curves in Fig. 1 shows that selective absorption proceeds in the same manner as absorption which is not accompanied by a marked chemical reaction.

---

¹ Bull. No. 30, p. 60, Bureau of Soils, U. S. Dept. Agr., 1905; see also, Bell and Cameron: Jour. Phys. Chem., 10, 658 (1906).

² Landw. Vers.-Stat., 2, 129 (1860).

TABLE IV

The distribution of potassium between soil and solution of potassium chloride, according to Peters

Potassium per kilo soil	Potassium per liter solution
Grams	Grams
1.011	0.0648
1.096	0.0628
1.168	0.0677
1.238	0.0797
1.328	0.089
1.390	0.127
1.453	0.203
1.511	0.361
1.579	0.679
1.610	1.310

Fig. 2

The magnitude of the absorption effect by which a soil withdraws a salt from solution is well illustrated by these measurements of Peters'. With his most dilute solution, 67 percent of the total potassium added was absorbed; and in the case of his most concentrated solution (originally 16 times as concentrated as the most dilute one), 20 percent of the base was absorbed. But it should also be kept in mind that the *percentage* of solute absorbed is dependent upon the relative mass of solution and solvent, and in the case of a soil in the field the proportion of soil to soil solution is so large

that the percentage of solute absorbed must be very great indeed at such concentrations of the soil solution as normally exist in humid areas.

Peters determined also the calcium extracted from the soil by these same solutions which were being studied mainly with respect to the absorption of potassium. He found that the calcium is distributed in a manner entirely analogous to potassium, and that the curve for the distribution of the calcium between soil and water has apparently the same form as that for potassium. This observation indicates that the selective absorption of two solutes or of two radicles may proceed simultaneously but in a very nearly independent manner at least when the concentrations of both are low.

But little of the extant work on absorption is available for such considerations. For example, Lagergren¹ has pointed out that van Bemmelen's work involves such striking chemical changes in many cases that it is out of the question to consider the systems of which he treats as types of "adsorption" phenomenon, and equally of course as typical absorption effects. Nevertheless, some of van Bemmelen's data furnish most important and interesting cases, as, for instance, his results for the distribution of hydrochloric acid (HCl), and potassium chloride (KCl), between stannic oxide and water,² which are plotted in Figs. 3 and 4. In Fig. 3 only his values calculated for stannic oxide ($\text{SnO}_2 \cdot 2.2\text{H}_2\text{O}$) are used. Ordinates are in milligram molecules of hydrogen chloride in 1 gram molecule of water, and abscissas in milligram molecules of hydrogen chloride in 1 gram molecule of stannic oxide. The dotted portion of the curve indicates the probable direction if no solution of stannic oxide in hydrochloric acid had taken place. The curve in reality changes its trend entirely owing to this solution of tin oxide in hydrochloric acid solution, and to the change in the composition of the solution as well as to the consequent decrease in effective absorbent material and surface.

¹ Bihang till K. Sv. Vet.-Akad. Handl., 24, Afd. II, No. 5 (1898).

² Zeit. anorg. Chem., 23, 112 (1900).

Comparing the curves in Figs. 3 and 4, it is seen that the distribution of potassium chloride between hydrated stannic oxide and water is a linear function, but this same absorbing material shows an entirely different distribution curve when hydrochloric acid is used. Thus it will be seen that the same

Fig. 3

Fig. 4

several types of distribution curves are obtained whether the solute be absorbed as a whole or whether there be a selective absorption of some constituent of the solute or mixture of solutes.

Distribution Formula

A number of investigators have advanced formulas to express the distribution of a solute between a solvent and an absorbing medium. These expressions have been generally suggested by the apparent analogy to the distribution of the solute between two non-consolute solvents, for which two general equations have been proposed.

If C be the concentration of the solute in one solvent and C_1 the concentration in the other, then, when there is no association of solute in either solvent, the distribution is described by the formula $C/C_1 = K$, but if there be association of solute in either solvent the formula becomes $C^n/C_1 = K$; K is a constant for any standard conditions.

Examples of linear distribution between a solid and liquid are known. For instance Gaubert¹ observed it for the absorption of methylene blue by crystals of phthalic acid deposited from solution in the dye, when the solution is cooled; and for the absorption of the same dye by crystals of nitrate of urea. And van Bemmelen² has studied an interesting case in the absorption of potassium chloride by stannic oxide, as shown in Fig. 3.

The exponential formula has been found to hold more or less well for a number of cases of absorption of which a few will be cited. Thus Schmidt³ found it held for the absorption of iodine and several acids by charcoal, but it did not hold for the absorption of picric acid by cellulose or of eosine or malachite green by silk. Küster⁴ found such a relation held for the absorption of iodine by starch. Walker and Appleyard⁵ studied a case of unusual interest, finding that the distribution of picric acid between water and silk was described by the formula, $-\frac{S}{W^{2.7}} = 35.5$, where S represented concentration

¹ *Comptes rendus*, **142**, 936 (1906).

² *Zeit. anorg. Chem.*, **23**, 113 (1900).

³ *Zeit. phys. Chem.*, **15**, 60 (1894).

⁴ *Liebig's Ann.*, **283**, 360 (1894).

⁵ *Jour. Chem. Soc.*, **69**, 1334 (1896).

of the dye in the silk, and W the concentration in water. This would indicate that, in the concentration studied, the molecule of picric acid in the water solution is 2.7 times as large as that represented by the formula $C_6H_2(NO_2)_3OH$, but this is negated by the cryoscopic measurements of the osmotic pressure, and of the conductivities of aqueous solutions of picric acid.

Biltz¹ has studied several similar cases. An especially interesting one is the absorption of alizarin by ferric oxide, the distribution being described by an exponential formula. But the curve representing it does not go through the origin. That is, the concentration of the solution must be above a certain value before any absorption on the solid could take place. Similar cases, as for instance, in the absorption of phosphates from solution by soils, have been observed in this laboratory.

The data given above for the distribution of a solute between water and soil do not accord well with the equation $C''/C_1 = K$, but with equations of a more complex form. As these complex equations are different for each particular case and are purely empirical they are not given here. A reason for the deviations from the simpler form of the distribution equation was apparent in the marked changes in the state of aggregation or "flocculation"² of the soil particles induced by different concentrations of the solute in the aqueous solutions. In the absorption of eosine by quartz, where the distribution curve was very flat and approached a straight line there was no flocculation of the absorbing grains which could be observed readily. But the same quartz flour was decidedly flocculated when absorbing gentian violet and very differently at different concentrations of dye. Moreover, the extent of the flocculation, with increasing amount of dye,

¹ Ber. d. chem. Ges. Berlin, **37**, 1766, 3138 (1904); **38**, 2963, 2973, 4143 (1905); Biltz und Utescher: Nachr. K. Ges. Wiss. Göttingen, Math.-Physik. Klasse, **18** (1904); **46**, 271 (1905).

² Patten: Trans. Am. Electrochem. Soc., **10**, 66 (1906).

went through a maximum, so that no simple formula could be expected to hold for the distribution curve.¹ The soils studied showed similar flocculation phenomena.

Conclusions

The foregoing data and considerations lead to the following conclusions:

(1) The distribution of solute between solvent and absorbent, presents, in general, the same characteristics with soils as with other absorbents.

(2) For any series of soils or other absorbents, the order of the absorptive capacities for one solute may be entirely different from the order for another solute.

(3) The distribution of a solute between solvent and absorbent appears to be represented by the formula $C^n/C_1 = K$, where n may be less than, equal to, or greater than unity. Generally, when soils are the absorbents, the change of surface or "flocculation" introduces a modifying factor and the form of the distribution equation becomes more complex.

*Bureau of Soils,
U. S. Department of Agriculture,
Washington, D. C.*

---

¹ In an article which has come to our attention since writing the above, Pelet and Grand (Rev. Gen. Mat. Col., 11, 255 (1907) abstract Jour. Soc. Chem. Ind., 26, 1920 (1907)) describe a curve for silica, methylene blue and water for which they give the formula $\frac{x}{m} = \beta C^{1/p}$, where x is the quantity of dye absorbed, m the weight of silica, C the end concentration of the dye solution, and β and p are constants.