SYNTHETIC DETERGENTS IN SEWAGE SLUDGE[1])

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SUMMARY

Synthetic detergents may get into the soil if sewage sludge is used as a fertilizer and if, in market gardening, waste water or water infected with waste water, is used. Investigations were made as to the effects of this on the growth of plants. It appeared that, when the soil was poor in adsorbing matter (clay and humus), damage was already done when only small quantities were used. If, however, the soil was rich in adsorbing matter, the damage was not great. The cause of the damage may be a disturbance of the water management in the soil. The experiment may therefore have given a somewhat coloured representation: in practice, water will be applied at far more irregular periods than in the experiment. Besides, there may be a cumulation of detergents in practice so that we shall have to be more careful than the data obtained by the experiment require. Efforts to get at a prohibition of the use of microbiologically resistent detergents should, from the part of horticulture, be encouraged.

Synthetic detergents have been used to an ever greater extent the last few years. Great quantities are daily discharged and find their way into the purification plants. Part of these detergents get into the sludge obtained in these plants, the sludge mostly being used as a fertilizer. The question therefore arises whether these detergents have not a harmful effect on the quality of the sludge.

Besides using the sludge as a fertilizer, these detergents can also get into the soil in another way. First when waste water is used for irrigation of arable or horticultural land. Secondly when ditch water polluted with waste water is used for sprinkling, watering or infiltration. No data are available on the quantities of detergents which thus penetrate into the soil. It is expected to be of only little importance, however.

PROPERTIES OF DETERGENTS

HAMMERTON (4) gives the following average composition of a synthetic detergent:

Sodium alkylaryl sulphonate	20%
Sodium phosphates	38%
Sodium sulphate	23%
Sodium silicate (as solids)	8%
Sodium carboxymethyl cellulose	1%
Fatty alcohol amide	3%
Balance – mainly water	7%

According to ir. K. J. NIEUWENHUIS (Laundry Experiment Station, Delft) a small quantity of perborate should be added to this list.

Looking at the list we come to the conclusion that the greater part of the raw materials will do hardly any damage, the alkylarylsulphonates and the perborates possibly forming an exception. The latter, however, are used in small quantities and because of their great solubility they will almost com-

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pletely be carried off with the effluents, whereas the former is adsorbed by the sludge. The degree of adsorption depends on the kind of sludge. LOCKETT (9) says about this: "When the sludge is in a well oxidized state, and consequently of high density, and present in reasonable amount, the harmful effect (LOCKETT means the harmful effect on the purification itself, so not when sludge is used as a fertilizer) of syndets resistent to oxydation is minimized as a consequence of the greater adsorption of the syndet by the sludge and the lower concentration of free detergent in the mixed liquor".

The condition which he considers the most favourable for purification gives sludge with the highest content, however, so sludge which, when used as a fertilizer, will most easily lead to difficulties. According to Dr. H. VAN DER ZEE, chemist-bacteriologist of the purification plant Amsterdam-West, the sludge of this plant sometimes consists for 2% (calculated on dry matter) of these sulphonates.

The following data on the properties of detergents are taken from AINSWORTH (1). These detergents consist of molecules which can be divided into two atomic groups: a "hydrophile", or water attracting group, which makes the detergent soluble, and a "hydrophobe" or water repelling group which makes the detergent concentrate at the border layer of the water. The molecules so arrange themselves that the hydrophile group is turned towards the water side, the other to the reverse. Under border layer is not only understood the surface, but also the layer of contact between water and solid matter or some liquid or other. Particles of matter and the like are surrounded by a moleculair layer of these substances, as a result of which they are separated from other bodies and consequently come loose very easily to be emulsified at that. Besides, the reduction of the border layer tension of the water has an increase of the penetrative power of the water as a result.

The detergents used in washing preparations are alkylarylsulphonates. The hydrophile group consists of a sulphonate benzene ring, the hydrophobe group of a long paraffin chain. The hydrophobe group reacts as an anion, contrary to all other detergents in which this group reacts as a cation or has no-ion properties.

TOXIC PROPERTIES

There are various publications on the toxic properties of detergents for micro-organisms and some on those for fish. Only one detail could be found on the effect on higher plants.

As for the properties of micro-organisms two groups of detergents can be distinguished viz. those which can be decomposed microbiologically and those which are not affected by this decomposition (HURLEY, 8, SAWYER, 13). SAWYER (13) calls the first group biologically soft, the second biologically hard. The latter group has a strong restricting effect on the decomposition processes.

As regards the toxicity for fish, HERBERT and all. (6) say that, in a period of 12 weeks the death percentage of rainbow trout was 50%, with a concentration of 3 ppm alkylarylsulphonate. According to HENDERSON and all. (5) the toxicity in hard water is much greater than in soft. In soft water the toxicity would be about equal to that of soap, in hard water it would be about 40 times as much as in soft water.

DEGENS and all. (2) have investigated the effect of toxic properties on various kinds of fish. Some of the tested fish (*Rhodeus amarus* and *Carassius vulgaris*) died at a concentration of 40 ppm after 5 hours.

As regards the toxicity for higher plants, we have only data from DEGENS and all. (2) at our disposal, who tested various water plants (*Valisneria spiralis, Helodea canadensis, Riccia fluitans, Calomba carolinisana* and *Ludwgiia Murlettii*). With a concentration of 40 ppm in the water in which they were growing, the plants were not affected at all.

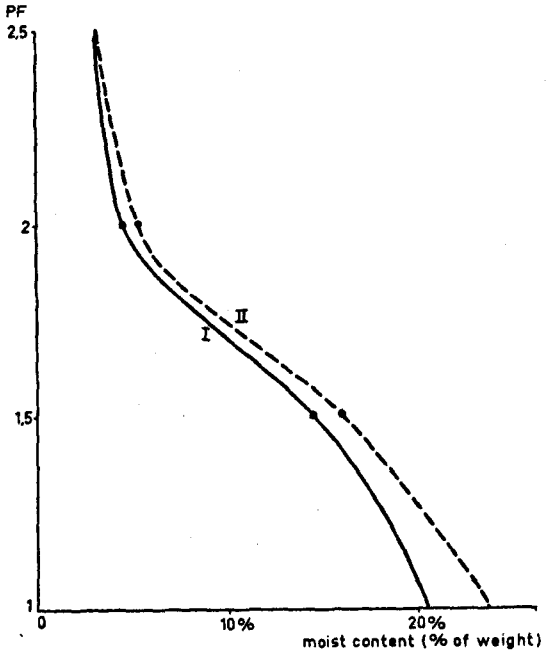
POSSIBLE EFFECTS WHEN APPLIED AS A FERTILIZER

Though we have but few data at our disposal on the effect on agricultural and horticultural crops, we can form an idea of what difficulties may be expected. These difficulties can be classified into three groups.

1. Difficulties in the plant. It is not excluded that these detergents, if they penetrate into the plant, will, from a physiological point of view, have highly serious effects. The change of the surface tension of the cell saps might have a harmful effect. The substances need therefore be adsorbed by the plant, which has not yet been proved. Besides, the effects obtained by DEGENS and all. (2) are such that we cannot take it that detergents will cause much damage in this way.

2. Difficulties in the system soil - plant. We may take it that, in a soil saturated with detergents, the root of a plant is surrounded with a monomoleculair layer of these detergents. It is not impossible that the respiration and the water take up will be affected by this.

3. Difficulties in the soil. The research revealed that, when detergents were



GRAPH 1 INFLUENCE OF DETERGENTS ON THE pF OF THE SANDY SOIL.
I sand without detergents.
II sand with 18 mg alkylarylsulphonates in a liter.

applied, the water-air condition greatly changed. The soil, when treated with a much smaller quantity of water, was soon too wet and quite different from non-treated soil. The superfluous water leaked out very easily. The total water capacity of the soil seemed to recede very quickly. This again made the soil dry up more quickly. The difference between treated and non-treated soil was that, at times, the treated soil was too wet and too dry. It also appeared that the structure of soil, treated with detergents, soon became worse in quality.

At our request ir. F. K. KOENIGS made a research into the pF of soil which had and had not been treated with detergents. The results have been given in graph 1. It appeared that the pF of the soil had indeed somewhat been disturbed by the addition of these substances, though the effect was much smaller than had been expected.

ORIENTATING RESEARCH

The data given on the toxic effect in other organisms led to a small experiment in 1957 to investigate the harmful effect of hese detergents. A quantity of 75 mg detergent per liter was added to a few pots in which spinach was grown on sand. This quantity appeared to have a harmful effect on the crop. As it had not been proved that this was caused by alkylarylsulphonates, a more extensive test was made the next year, now with alkylarylsulphonates alone.

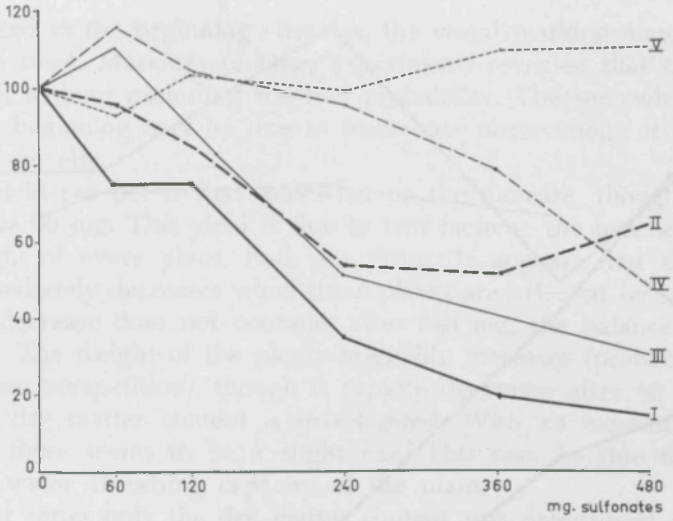
EXPERIMENT, 1958

This experiment consisted of 4 series I, II, III and IV, each series consisting of 6 Mitscherlich pots. The pots were filled with coarse pleistocene sand, found on the spot, but so deep away that it could be said to be entirely without humus. 7 kilos of sand were taken for every pot. 100 grammes of sewage sludge were added to series II, and 100 grammes of sewage sludge and 100 grammes of town waste compost to series IV. These dressings were (with a supposed top soil of 20 cm) equal to 25 tons/ha, so a relatively small dressing. It proved to be impossible to mix the sludge in this relatively wet condition homogeneously through the soil and clod formation therefore took place. The sewage sludge itself also contained alkylarylsulphonates, viz. 2.7 mg per gramme of dry matter.

To every pot of these series, 0, 60, 120, 240, 360 and 480 mg of sulphonate were added; to series I, III and IV of the same composition, tetra propyleen benzene sulphonate was added and to series II of another composition dodecylbenzene sulphonate.

All these objects were in duplicate. (Owing to a misunderstanding the pots with 240 mg in series II fell out).

The effect of the sulphonates already became clear when the pots were filled. The quantity of water, which, normally, was sufficient to bring the soil on field capacity, was, when sulphonates were used, far too great. The soil was soaked and consisted of slimy clay, part of the water passing off quickly. This confirms the impression that a harmful effect, at least partly, may be the result of periodically too wet soil (after water supply) and too dry soil (if the superfluous water has passed off). The pots were watered every other day. Because of this the results of the experiment could not entirely be



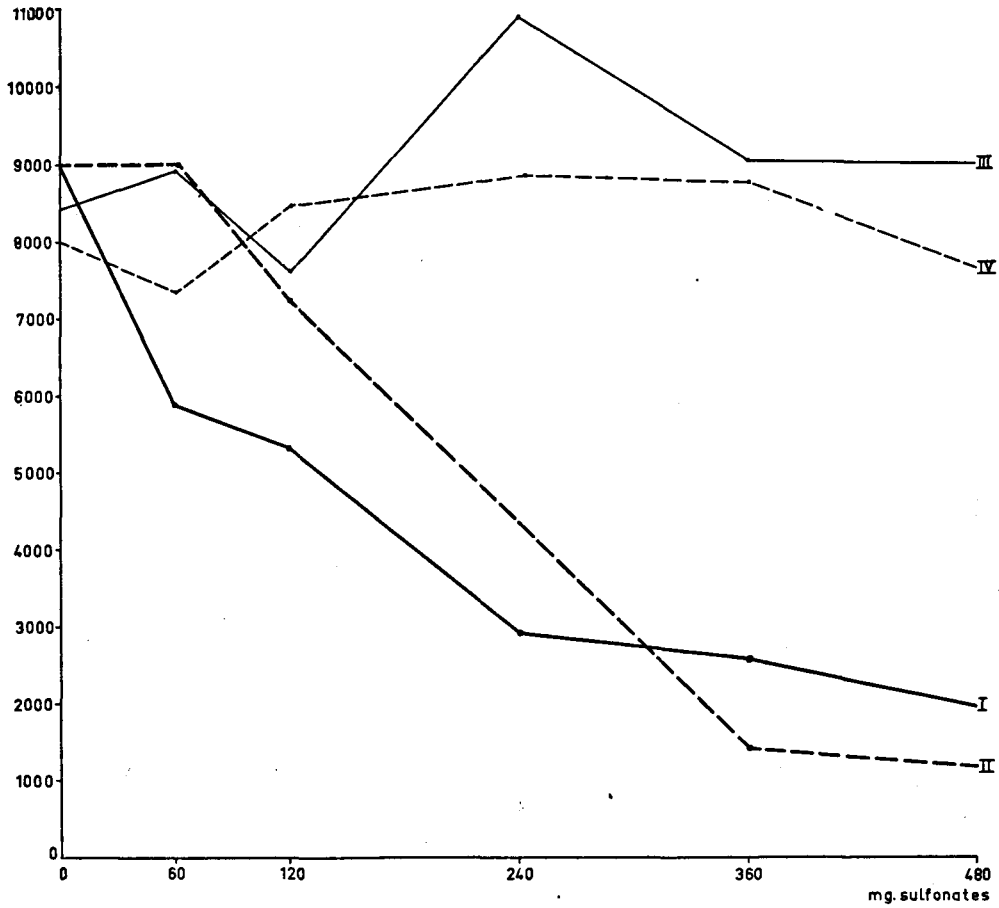
GRAPH 2 INFLUENCE OF DETERGENTS ON SOME QUANTITIES. THE SCALES OF THE CURVES ARE IN SUCH A WAY THEY ALL START AT THE SAME POINT.

I taxation marks of the spinach in the first week of december.
II number of developed plants in a pot (100 = 67 plants).
III total weight of all plants in a pot (100 = 46 gram).
IV main weight of one plant (100 = 686 mg).
V dry matter content of the plants (100 = 6.3 %).

compared with the results obtained in practice: the plants did not completely dry out, they often were too wet. Whether this has created more or less favourable conditions than are found in practice, cannot without more be ascertained; we have got the impression that conditions were somewhat too favourable.

Spinach was used as an experiment crop in these series. The pots stood in an unheated glasshouse on a slowly rotating disc, as a result of which the difference in place could not in any way affect the result.

FIG. 1 REACTION OF SPINACH TO SULFONATES. FROM THE LEFT TO RIGHT: 0, 120, 240, 480 MG. SULPHONATES A POT OF 7 LITERS.



GRAPH 3 PRODUCTION OF SPINACH IN POTS WITH OR WITHOUT SULPHONATES. POTS FILLED AS FOLLOWED.

I sand with sulphonate a.
II sand with sulphonate b.
III sand with sewage sludge and sulphonate a.
IV sand with a mixture of sewage sludge and town waste compost and sulphonate a.

The plants were sown at the end of September, a mark was given early in December and they were harvested at the end of January with the exception of series I which was harvested two weeks earlier. The mild winter made it possible for the plants to continue growing without being in danger of frost damage. The entire plant, including the roots, were harvested. The sand was carefully removed by washing on a sieve. Any particles of sludge and gravel were removed with a pair of tweezers. Then the plants were dried in a drying stove at 105° C.

Most observations were made in series I (photo 1). These are all reflected in graph 2. The scales for all the quantities have so been chosen that at 0 sulphonate they all come to the same point.

The marks given early in December showed the greatest decline. This may be due to two reasons: the plants had the greatest difficulties in the early stage of their development, though, later they somewhat made up for the

damage suffered in the beginning; besides, the visual marking may have been somewhat too strict. Markings of other experiments revealed that the latter is probably true, without excluding the first probability. The somewhat irregular course in the beginning may be due to inaccurate observation: it is not confirmed anywhere else.

The total yield per pot is first somewhat on the increase, though it rapidly decrease above 60 mg. This yield is due to two factors: the number of plants and the weight of every plant. Both are given. It appears that the number of plants immediately decreases when these plants are affected by sulphonates, but that the decrease does not continue after 240 mg, the balance remaining at about 60%. The weight of the plants originally increases (probably because of the less keen competition), though it rapidly decreases after 60 mg.

Finally the dry matter content is investigated. With an increasing content of detergents there seems to be a slight rise. This may be due to a disturbance of the water absorbing capacity of the plant.

Of the other series only the dry matter content was determined. These are, together with series I, reflected in graph 2. First of all this graph reveals that both kinds of sulphonates have the same effect. It further became clear that the addition of an adsorbtion material (in this case sewage sludge) has compensated the damage, in spite of the fact that 2.7% of the dry matter in the sludge still consisted of sulphonates. This means that every pot is given an extra dressing of:

$$\frac{2.7}{100} \times \frac{25.6}{100} \times 80 \text{ gr} = 553 \text{ mg.}$$

(The dry matter content was 25.6%, the quantity of sludge per pot 80 gr).

This is more than the highest dressing of the sulphonate level!

Some effect was still noticeable on the first date, but this was entirely gone later. When town waste compost was added, which brought still more adsorbing material into the soil, no effect was noticeable on the first date either (see graph 3).

The entire yield of the pots with sludge, and that of the pots with sludge and compost was a little lower than that of the others. Considering the almost horizontal lines in the graph 3 it is excluded that this effect must be attributed to the quantity of sulphonates in the sludge.

Finally a few pots were filled with clay, with and without the addition of alkylaryl sulphonate. There was hardly any difference between these pots.

Other crops

In order to investigate whether spinach is representative the reaction of a number of crops on a dressing of 240 mg sulphonate was ascertained. The reactions were as follows: (all the plants were sown on the spot, with the exception of cyclamen. The latter variety has been set out as plants of approx. 3 cm long).

Andive. Great reaction. Plants in the sulphonate pots about $^1/_3$ to $^1/_4$ in extent in relation to others. No necrose symptoms.

Tomato. Keen reaction, though less than in andive. No necrose elther.

Cauliflower. Reaction comparable with that of tomatoes.

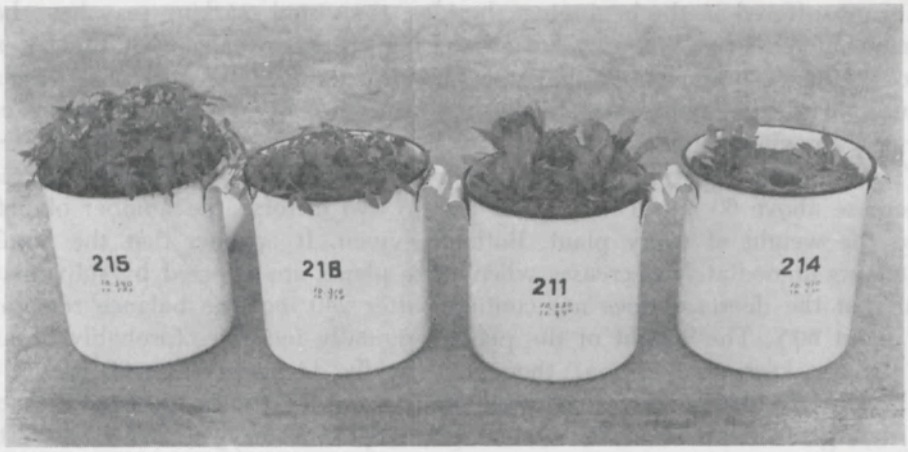


FIG. 2 REACTION OF TOMATO AND ENDIVE TO SULPHONATES. POTS 215 AND 211 WITHOUT, 218 AND 214 WITH 240 MG SULPHONATES A POT.

French beans. Part of the plants had died in the pots with sulphonate. The plants which survived were originally far behind the others. Later, this difference was less, however.

Carrots. About half the number of plants had died. The others looked bad. It appeared that carrots showed the greatest reaction.

Lettuce. Reaction about the same as endive.

Cyclamen. Poor reaction. Superficially there were hardly any difference. There was a slight difference when the number of leaves of 5 plants were counted (without sulphonate 13 and 13, with sulphonate 12 and 9). This difference is such, however, that hardly any importance must be attached to it.

The sequence is intensity of reaction was:

1. carrots
2. andive, lettuce and spinach
3. tomato
4. cyclamen.

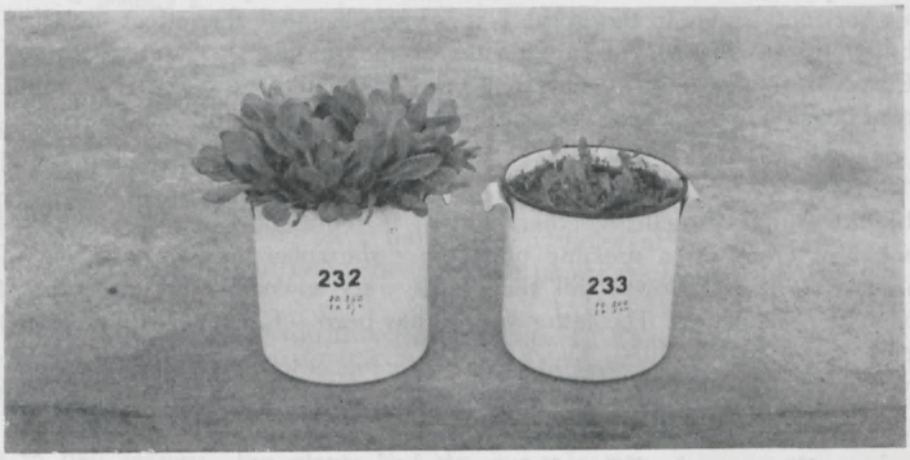


FIG. 3 REACTION OF LETTUCE TO SULPHONATES. AT THE LEFT SIDE WITHOUT, AT THE RIGHT SIDE WITH 240 MG SULPHONATES A POT.

Beans are out of place in this list. If we consider the number of plants which died down, beans would have to be ranked between 1 and 2. If the quality is considered between 3 and 4.

Conclusions

1. It appeared that sulphonates had a very harmful effect on the development of most horticultural crops. Of all the crops tested, the cyclamen alone formed an exception.
2. It seems that the harmful effect is, in fact, the disturbance of the balance of humidity. Soil which contains sulphonates is too wet already, when only little water is added; it loses this water in a very short time.
3. The harmful effect is greatly reduced if the soil contains sufficient adsorbtion material in the form of clay or organic matter.
4. Consequently the experiment has not led to the conclusion that, when sewage sludge is applied, the detergents in it have an immediate harmful effect. No decicive answer was given, however, as to what is the effect if sulphonates cumulate by repeated usage and what, if the water supply is more irregular than in this experiment.
5. On the part of horticulture, the efforts which are being made by various quarters to get a prohibition of the use of micro-biologically non-decomposed detergents, are underlined.

Final remark

I now want to express my thanks to those, who, during my experiments, have given me their assistance: Prof. dr. A. C. Schuffelen, for the hospitality I received at his laboratory and his careful perusal of this article; Dr. F. F. R. Koenigs for his pF research, the other members of the laboratory staff for their assistance during the experiment and Ir. K. J. Nieuwenhuis, Dr. H. van der Zee, Dr. Stoorvogel and Dr. Frissel for the information they gave me. Finally I want to thank the concern which supplied me with the necessary detergents.

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