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*Environmental Pollution (Series B)* 1 (1980) 277–284

# UPTAKE OF FLUORIDE BY RYEGRASS GROWN IN SOIL TREATED WITH SEWAGE SLUDGE

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*ABSTRACT*

*Ryegrass was grown in pots of soil treated with a fluoride-rich sludge which had been implicated in an outbreak of fluorosis on a farm where it was used as a fertiliser. Results showed an approximately linear relationship between fluoride applied to soil in sludge and concentrations of fluoride in ryegrass tissue. Applications in excess of 8·7 t dry matter (dm)/ha of the sludge tested (equivalent to 290 kg/ha of fluoride) produced potentially toxic concentrations of fluoride in the first cut of ryegrass but plant tissue concentrations of fluoride decreased progressively in two later cuts. Every 100 mg/kg increase in the concentration of fluoride in soil resulting from treatment with sludge produced an increase in the concentration of fluoride in ryegrass of 18 mg/kg dm at cut 1, 8 mg/kg at cut 2 and 5 mg/kg at cut 3. In field conditions, direct ingestion of sludge and soil by grazing cattle may be as important a source of dietary fluoride as that ingested in herbage.*

## INTRODUCTION

It is well known that sewage sludge contains higher concentrations of various trace elements than do most soils and in many countries guidelines are in force which recommend monitoring of these elements, especially heavy metals, where sludge is used to fertilise agricultural land. Fluorine is not usually included in these guidelines. There are comprehensive reviews of fluoride pollution (see, for example, Smith & Hodge, 1979), but much of the literature relates to airborne fluoride which is the most common source of soil contamination. Rea (1979) draws attention to the rapid increase in demand and production of hydrofluoric acid for industry where fluorides are used in metal finishing, glass production, non-stick coatings, refrigerants and in the manufacture of propellants for aerosols. Some of this fluoride is likely to be discharged to sewerage systems. Fluoride pollution also results from aluminium smelting, brickworks and the production of phosphatic fertilisers.



*Environ. Pollut. Ser. B.* 0143-148X/80/0001-0277/$02·25 © Applied Science Publishers Ltd, England, 1980
Printed in Great Britain

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Superphosphate fertilisers contain about 1·6% fluoride (Kumpulainen & Koivistoinen, 1977) but it is a widely held view that fluoride in soil is not readily assimilated by crop plants. However, following the occurrence of fluorosis on a farm where the grass eaten by cattle had been fertilised with sewage sludge, a pot trial was undertaken to determine whether fluoride added to soil in sludge can be assimilated by grass in quantities sufficient to affect the health of animals eating it.

## MATERIALS AND METHODS

Liquid-digested sewage sludge was applied to alluvial silty loam (Milton series) in polythene pots 22 cm deep, each containing 9·5 kg of soil, at rates shown in Table 1, each treatment being replicated three times.

TABLE 1
RATES OF APPLICATION OF SLUDGE

| *Level* | 0 | 1 | 2 | 3 | 4 |
|---|---|---|---|---|---|
| Sludge ml/pot | 0 | 301 | 602 | 1204 | 2408 |
| Sludge tdm/ha | 0·0 | 2·5 | 5·0 | 10·0 | 20·0 |
| Fluoride g/pot | 0·00 | 0·36 | 0·72 | 1·44 | 2·88 |
| Fluoride kg/ha | 0 | 84 | 168 | 336 | 672 |
| Increase in soil concentration of fluoride (mg/kg dm) | 0 | 38 | 76 | 152 | 304 |

After two weeks, during which the sludge was worked into the soil, the pots were randomised and seeded with Italian ryegrass *Lolium multiflorum* Lam CV S22. Three successive cuts of ryegrass were taken when the longest leaf blades had reached about 25 cm. Table 2 presents dates of sowing and harvesting the ryegrass. Pots were re-randomised after each harvest. The cut grass was dried at 80 °C, weighed and milled to pass 1 mm. Samples of sludge, soil and grass were analysed for fluoride by the Central Veterinary Laboratory of the Ministry of Agriculture, Fisheries and Food using a potentiometric procedure following extraction with perchloric acid (0·1 M) and pH adjustment to pH 8·3 with citrate buffer (Ministry of Agriculture, Fisheries and Food, 1973).

TABLE 2
DATES OF SOWING AND HARVESTING THE POT-TRIAL

| *Event* | *Date* |
|---|---|
| Sludge applied to pots | 20 July 1978 |
| Seed sown | 4 August 1978 |
| Cut 1 (21 days) | 25 August 1978 |
| Cut 2 (26 days) | 20 September 1978 |
| Cut 3 (37 days) | 27 October 1978 |

## RESULTS

Results of the analyses of sludge and untreated soil are presented in Table 3.

Table 4 shows details of the yield of three successive cuts of grass from the pot trial. Increases in yield of ryegrass as a result of sludge application were observed in all three cuts and were most marked at the second cut. Tissue concentrations and uptake of fluoride (Figs. 1 and 2 respectively) also increased as a result of sludge application. The highest tissue concentrations and the greatest uptake occurred in the first cut and decreased successively in the second and third cuts. Thus for cut 1, the highest rate of application of sludge (Level 4) produced an increase in tissue concentration of fluoride in ryegrass of 51·7 mg/kg and an increase in uptake of 746 μg/pot, but at cut 3 the same rate of application produced increases of only 16 mg/kg and 182·2 μg/pot, respectively. The relationships between both tissue concentration and uptake of fluoride, with fluoride applied in sludge (Figs. 1 and 2), were approximately linear. Every 100 mg/kg increase in the concentration of fluoride in soil resulting from sludge addition produced an increase in the

TABLE 3
ANALYSIS OF SOIL AND SLUDGE

| | *Soil* | *Sludge* |
|---|---|---|
| Total fluoride mg/kg dry matter | 150 | 33500 |
| Dry solids % | | 3·6 |
| pH in water (1:2·5 w/v) | 7·0 | [a] |

[a] At the end of the experiment pH values in soil-sludge mixtures were in the range 6·8–7·1.

TABLE 4
YIELDS OF RYEGRASS (g DRY MATTER/POT) IN SUCCESSIVE CUTS FROM THE POT TRIAL

| | *Rate of application of sludge* | | | | |
|---|---|---|---|---|---|
| | 0 | 1 | 2 | 3 | 4 |
| Cut 1 | 9·92 | 12·34 | 15·61 | 14·58 | 13·62 |
| | 8·97 | 12·66 | 14·53 | 12·31 | 15·21 |
| | 10·72 | 13·08 | 13·50 | 14·93 | 12·48 |
| mean (LSD, $p = 0·05$, 1·98) | 9·87 | 12·69 | 14·55 | 13·94 | 13·77 |
| Cut 2 | 4·68 | 6·23 | 11·39 | 16·22 | 17·93 |
| | 5·02 | 9·56 | 11·86 | 13·96 | 16·47 |
| | 4·15 | 7·25 | 9·24 | 15·90 | 19·83 |
| mean (LSD 2·50) | 4·62 | 7·68 | 10·83 | 15·36 | 18·08 |
| Cut 3 | 6·68 | 6·65 | 7·83 | 7·97 | 10·95 |
| | 5·63 | 6·26 | 9·92 | 9·68 | 8·22 |
| | 5·76 | 6·27 | 8·66 | 11·78 | 10·74 |
| mean (LSD 2·22) | 6·02 | 6·39 | 8·80 | 9·81 | 9·97 |

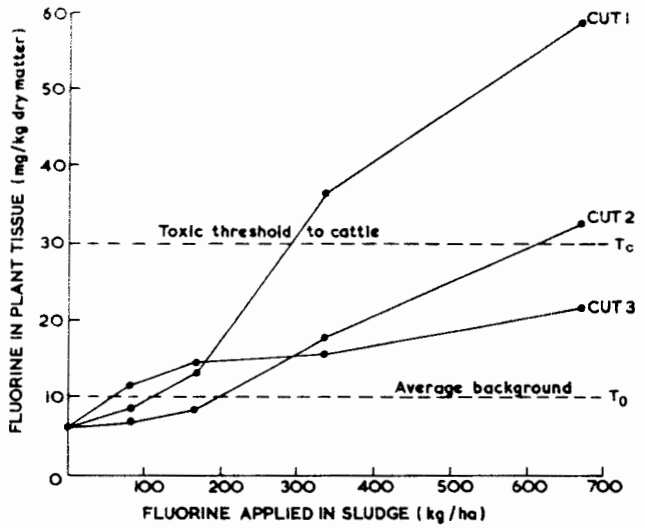


Fig. 1. The relation between fluoride in ryegrass tissue from three successive cuts and fluoride added to soil in sewage sludge. $T_0$ is the maximum value likely to be found in uncontaminated herbage; $T_c$ is the zootoxic threshold. Each point is a mean of three replicates. LSD = Least Significant Difference between means, $p = 0{\cdot}05$.

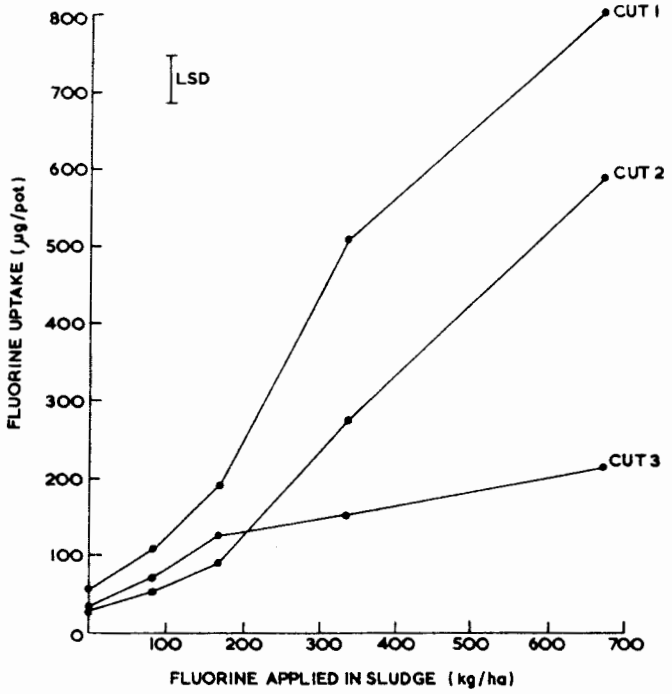


Fig. 2. Uptake of fluoride by three successive cuts of ryegrass plotted against fluoride added to soil in sewage sludge. Each point is a mean of three replicates. LSD = Least Significant Difference between means, $p = 0{\cdot}05$.

concentration of fluoride in grass of 18 mg/kg at cut 1, 8 mg/kg at cut 2 and 5 mg/kg at cut 3. Mean fluoride availability, expressed as fluoride uptake/fluoride applied, declined from 0·03% at cut 1 to 0·017% at cut 2, and 0·013% at cut 3.

## DISCUSSION

Robinson & Edgington (1946) reported that most soils contain 20–500 mg/kg of fluoride derived from minerals such as fluorapatite ($Ca_{10}F_2(PO_4)_6$), fluorspar ($CaF_2$) and cryolite ($Na_3AlF_6$), but some micaceous clays contain several thousands of mg/kg. Bowen (1966) quotes a common value for fluoride in soil of 200 mg/kg which agrees with the concentration of 150 mg/kg found in the soil used in the pot trial (Table 3). Uncontaminated herbage normally contains $<10$ mg/kg fluoride (Rose & Marier, 1977) and ryegrass from the control pots which had received no sludge contained about 6 mg/kg (Fig. 1).

Much higher concentrations of fluoride occur in soils near areas of fluorspar mining. Concentrations of fluoride of 2–17% in fluorspar mine wastes in the Peak District and Weardale have been reported (Cooke *et al.*, 1976). These workers found very high concentrations of fluoride in the leaves of grasses growing naturally on these sites, and the foliage of perennial ryegrass *Lolium perenne* L. CV. S23 grown in fluorspar waste containing 17·42% fluoride, assimilated 2745 mg/kg fluoride without displaying any symptoms of phytotoxicity. Thus it is not surprising that no symptoms of toxicity were apparent in the ryegrass from the pot trial where the highest foliar concentration of fluoride recorded was 60 mg/kg (Fig. 1). Atmospheric fluoride is much more toxic to plants (Weinstein, 1977).

Of more concern is the possible zootoxicity of foliage containing enhanced concentrations of fluoride. The toxicity described as fluorosis is essentially a skeletal disorder resulting from ingestion of increased dietary fluoride over a prolonged period. The extent of exposure can be monitored by measuring the concentration of fluoride in the bones of animals, where it accumulates (Underwood, 1971). For cattle, 4500 mg/kg fluoride in the bones is said to be the toxic threshold (Underwood, 1971). Among domestic species, cattle are the most sensitive to fluorosis, followed by sheep and pigs, and poultry which are comparatively resistant (Rose & Marier, 1977). Suttie (1977) lists fluoride tolerances for domestic animals. Various US State regulations make it unlawful for an industry to emit fluoride at a level that will cause the fluoride content of nearby forage to exceed 30–40 mg/kg. Underwood (1971) suggests that intakes greater than 30 mg/kg and 70 mg/kg in the diet can be toxic to cattle and sheep respectively. In the UK there are statutory constraints on levels of fluoride in the whole feed for various animals (Fertilizer & Feeding Stuffs Amendment 1976): 30 mg/kg for cattle in milk, 50 mg/kg for other cattle, 100 mg/kg for pigs and 350 mg/kg for poultry. Overall it seems that the zootoxic threshold ($T_c$) is 30 mg/kg while the maximum concentration likely to occur in uncontaminated herbage ($T_0$) is 10 mg/kg (Fig. 1).

Figure 1 suggests that in the present trial the background value ($T_0$) may be exceeded (i.e. contamination may be detected) in ryegrass grown on soil which has received 60 kg/ha fluoride in sludge, and that the threshold value ($T_c$) may be achieved by a dressing of 290 kg/ha fluoride in sludge. These results agree with other evidence (Kumpulainen & Koivistoinen, 1977), that an addition to soil of 200–250 kg fluoride/ha, as a mixture of phosphate fertiliser and sodium fluoride, was required to produce a definite increase in the fluoride content of spinach, lettuce and carrot. A recent review (Weinstein, 1977) suggests that soil and plant concentrations of fluoride correlate poorly, but Fig. 1 shows an approximately linear relationship between fluoride in soil and fluoride in plant tissues.

The threshold value of 290 kg fluoride/ha applied to cut 1; at cut 2, 610 kg/ha of fluoride was required to achieve the critical value ($T_c$), whilst at the third cut even the highest rate of application of sludge (equivalent to 672 kg/ha fluoride) produced concentrations of fluoride in herbage of only 21·7 mg/kg, which is less than the critical value. The reason for this decline in availability of soil fluoride over the three cuts may be associated either with equilibration of sludge and soil or, conceivably, with differences in growing conditions between the three crops. Depletion of soil fluoride seems unlikely to be of importance, since after three cuts only 0·06 % of the fluoride added to soil as sludge (at the highest level) had been removed in the cut herbage. There was no leaching from pots beyond the capillary mat upon which each stood. Other workers have observed a similar decline in availability of heavy metals in successive crops after applications of sludge to soil (Viitasalo, 1978; Hinesly *et al.*, 1979).

Before cut 1 the grass grew fastest, as indicated by the short period (21 days, Table 2), for the crop to achieve cutting length. The conditions of light and temperature which generated this growth would also cause rapid transpiration and this might enhance fluoride uptake, which is regarded as a passive process (Cooke *et al.*, 1976). Such fast growth and rapid transpiration would be unlikely to occur in the field, and the results may overestimate the fluoride uptake which would occur in normal field conditions. DeVries & Tiller (1978) have shown that uptake of elements by crops from soil treated with sludge tends to be greater in glasshouse conditions than in field conditions. In the second and third cuts growth was progressively slower, as evidenced by the longer growing period required to reach cutting length (26 and 37 days respectively, Table 2).

Figure 1 suggests a limit of 290 kg fluoride/ha (i.e. an increase in the concentration of soil fluorine of 133 mg/kg) which can be added as a single dressing of sludge to a neutral soil without exceeding the zootoxic threshold in herbage of 30 mg/kg. This limit is dependent on the pH value of the soil, and might be lower in strongly acid soils where fluoride is more soluble and more readily assimilated by plants (US National Academy of Sciences, 1971). Whilst the threshold concentration for fluoride toxicity in cattle is about 30 mg/kg, advisory experience shows that a toxic concentration is about 100 mg/kg in the diet for a year, which is equivalent to

1000 mg fluoride/day for an adult cow consuming 10 kg dry matter daily (M. K. Lloyd, pers. comm.). The maximum concentration of fluoride observed in grass from the pot trial was 58·7 mg/kg (Fig. 1). Even in the unlikely event of field conditions maintaining this concentration throughout the year and the cow eating nothing but grass, the fluoride content of its diet would still be only 587 mg/day. But direct ingestion of sludge or sludge and soil could supply additional fluoride to the diet sufficient to cause fluorosis. Ingested soil has been shown to account for 1·1–10·9 % of the dry matter intake of cattle grazing between November and March (Thornton, 1974). Soil ingestion would be maximal in cattle left to overwinter outside when grass is short and soil soft, conditions which would enhance the intake of fluoride by direct ingestion especially where the sludge was applied directly to grassland and not ploughed in. For instance, a normal application of 2 tdm/ha of the sludge used in the pot trial, which contained 33500 mg fluoride/kg, would supply 6700 mg fluoride/$m^2$.

The results suggest that uptake of fluoride from soil by ryegrass does occur and would contribute some fluoride to the diet of cattle. A more important source may be direct ingestion of fluorine-rich sludge and contaminated soil which some farm management practices inadvertently encourage. Thus conventional application rates of fluorine-rich sludge to permanent grassland could result in fluorosis amongst grazing cattle. Risk is clearly dependent on the concentration of fluoride in the sludge. It is now evident that the sludge used in this study was exceptionally contaminated. A recent survey of 87 sludges found a range of fluoride concentrations of 80–1950 mg/kg dry solids (Rea, 1979). The results of the pot trial suggest that sludges with fluoride levels in this range would present no problem when utilised as a fertiliser for agricultural land. The fluoride content of the sludge tested in this study (33500 mg/kg dry solids) was about 16 times higher than the normal maximum value. Such fluoride-rich sludges occur only at sewage-treatment works with industrial users of fluoride in their catchments; Rea's (1979) results suggest that fluoridation of the water supply has little effect on the fluoride content of sewage sludges. Industrial demand for fluoride is increasing and stricter controls on aerial emissions could result in more being discharged to sewers. Monitoring of fluoride levels in sludges from such works is clearly advisable if the sludges are to be disposed of by utilisation on agricultural land, since their application to permanent grassland could cause excessive fluoride levels in the diet of grazing cattle.

## ACKNOWLEDGEMENTS

The help of Mr M. Lloyd, Ministry of Agriculture, Fisheries and Food, Central Veterinary Laboratory in supplying advice and arranging for analysis of samples of sludge, soil and plant material is gratefully acknowledged. This paper is published by permission of the Director of the Stevenage Laboratory, Water Research Centre.

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