# DISTRIBUTION OF PHOSPHORUS IN SOIL AGGREGATE FRACTIONS AND ITS SIGNIFICANCE WITH REGARD TO PHOSPHORUS TRANSPORT IN AGRICULTURAL RUNOFF

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**Abstract.** Surface runoff is the major way of P transport from agricultural land to surface waters. To assess the potential of P loss in runoff in relation to soil P status, the chemical nature and distribution of soil P in different size classes of water-stable aggregates were quantified for two distinctive soil types. For both soils unfertilized areas under pasture and well-fertilized arable soils were sampled. The content of total P, organic P and microbial biomass P ($P_{mic}$) decreased in the aggregate size order < 0.1, 1–2, and 0.1–1.0 mm respectively. In contrast available P (extracted by Bray I reagent) was lowest in the < 0.1 mm aggregate size. Cultivation decreased the percentage of 1–2 mm aggregates but increased that of the < 0.1 mm aggregates. Fertilization increased markedly both total P and organic P in the < 0.1 mm fraction of arable soils compared to the corresponding samples from unfertilized grassland soils. During aggregate separation, most of P loss was in the form of particulate P and less than 1% in solution. More organic P and $P_{mic}$ were lost from the grassland soils than from the arable soils.

## 1. Introduction

The eutrophication of surface waters caused by increased nutrient loading is of growing concern. Phosphorus is often the limiting element in freshwater ecosystems and its control is of prime importance in reducing the potential for eutrophication (Sharpley and Smith, 1990). Under field conditions, the transport of P from agricultural land to the surrounding water environment occurs in solution or is associated with eroded soil materials (Johnson *et al.*, 1976; Rigler, 1979; Probst, 1985; Kronvang, 1990). Typical mean concentrations of P for the major rivers in N.E. Scotland are < 3 $\mu g\ l^{-1}$ with total annual fluxes of 10–30 tonnes ($\sim$ 0.2 kg P $ha^{-1}$). The loss of P associated with sediment is approximately double these soluble losses. For most agricultural soils the P concentration in solution is maintained at low levels (Olsen and Khasawneh, 1980) and, therefore, the P quantity lost through leaching is likely to be small. On the other hand, the P content of eroded fine soil particles (from 0.11% to over 0.88%) can be much higher than that for agricultural soils (Rigler, 1979; Probst, 1985; Kronvang, 1990). Particulate

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phosphorus (PP) in most cases accounts for at least 70–90% of the total P loss from agricultural watersheds (Johnson *et al.*, 1976; Schuman *et al.*, 1976; Sharpley and Smith, 1990). Considering that the reported total amount of soil erosion is very substantial (ranging from 0.01 to over 200 $m^3$ $ha^{-1}$ $yr^{-1}$, but mostly between 1–20 $m^3$ $ha^{-1}$ $yr^{-1}$) (Boardman, 1990), the total amounts and chemical forms of P exported from agricultural soil through erosion merits additional attention.

The assessment of P transport in surface runoff needs a good understanding of the distribution and biovailability of P in the fine soil fractions which are more readily transported. Soil particle size fractionation is routinely done in three ways:

(1) A thorough dispersion of soil followed by a sedimentation into sand, silt and clay;

(2) Separation of fresh moist soil into different aggregate size classes by dry sieving;

(3) Separation of air-dry or fresh soil into different water-stable aggregate size classes by wet sieving.

Much work has been done on the distribution of P in different soil separates, ie. sand, silt and clay fractions. However, in field situations, most of the soil particles in runoff remain as aggregates, with little dispersed clay, although the breakdown of large aggregates into small ones by rainfall and during transport may occur (Loch and Donnollan, 1983). Therefore, separation of soil into water-stable aggregate size classes by wet sieving simulates better the separation of soil aggregates in runoff under field conditions (with decreasing rate of water-flow, the larger aggregates would be deposited and the sedimented fine particles carried further away). We hypothesize that the concentration and forms of P in the fine soil fractions would be more important than that in the coarser soil fractions in relation to the transport and bioavailability of P in runoff sediment. Usually, the soluble or chemically extractable form is used as an index of P availability. But recent work has shown that microbial P could also represent an important form of potentially bioavailable P (Brookes *et al.*, 1984; Perrott and Sarathchandra, 1989; He *et al.*, 1994b) and, therefore, more attention should be paid its transport in surface runoff.

The objectives of this study were to investigate the distribution of total P, organic P, microbial P and extractable P in different classes of aggregate sizes obtained by wet sieving and to examine quantitatively their potential contribution to P transport from agricultural land.

## 2. Materials and Methods

### 2.1. Soil samples

The soils used in this study are shown in Table I. Sites were chosen where it was possible to sample arable and grassland soils from adjacent fields. All the

TABLE I

Some properties of soils used

| Soils | Soil association | Parent material | Sample no. | Land use | pH | | Organic C ($g\ C\ kg^{-1}$) |
|---|---|---|---|---|---|---|---|
| | | | | | $H_2O$ | $CaCl_2$ | |
| Brown podzolic | Insch | Basic igneous | 1 | Grassland | 4.8 | 4.3 | 57 |
| Brown podzolic | Insch | Basic igneous | 2 | Arable | 5.7 | 5.4 | 45 |
| Cultivated podzol | Foudland | Slate | 3 | Grassland | 5.3 | 4.8 | 47 |
| Cultivated podzol | Foudland | Slate | 4 | Arable | 5.3 | 4.2 | 37 |
| Grey-brown podzolic | Stonehaven | Old Red Sandstone | 5 | Grassland | 4.8 | 4.4 | 37 |
| Grey-brown podzolic | Stonehaven | Old Red Sandstone | 6 | Arable | 5.6 | 5.1 | 28 |
| Cultivated podzol | Countesswells | Granite & granitic gneiss | 7 | Grassland | 5.7 | 5.3 | 55 |
| Cultivated podzol | Countesswells | Granite & granitic gneiss | 8 | Arable | 5.3 | 5.0 | 54 |

grassland soils have never been fertilized except for the Stonehaven soil which has been unfertilized for a minimum of 25 yr. All the arable soils have been under rotational cultivation (currently barley *Hordeum vulgare*) receiving rates of fertilizers typical of north-east Scotland (100, 25 and 40 kg N, P and K $ha^{-1}$ $a^{-1}$ respectively). Soil samples (0–15 cm) were collected and gently sieved (< 2 mm) to remove stones and root material. Composite samples from each site were stored in polyethylene bags at 4 °C until analysed.

## 2.2. AGGREGATE-SIZE FRACTIONATION

Four of the eight experimental soils (samples 1, 2, 5 and 6) were selected for aggregate-size fractionation. Fresh soil (250 g) from each composite sample was mixed with 1 L of distilled water in a 2 L plastic bottle (20 cm in height and 12 cm in diameter) and shaken end-over-end by hand for one min. The resulting suspension was passed through a series of four stainless steel sieves with decreasing mesh sizes, 1, 0.5, 0.25 and 0.1 mm on a mechanical sieve shaker (Williams, 1983). Each size fraction (No. 1–4) was washed with distilled water using a fine-tip water bottle and by gently agitating the sieve contents to avoid additional disruption of the aggregates until the wash water was free of smaller particles. The washing was passed through the remaining sieves in the same manner. The suspension which passed through the 0.1 mm sieve was centrifuged (3660 g for 10 min) and the soil residue (< 0.1 mm fraction) in the centrifuge tube was resuspended in distilled water. The supernatant solution which still contained particulates was collected and stored at 4 °C for later use. The sieving procedure was repeated until sufficient quantities of each fraction had been obtained for chemical and microbial analysis. All the fractions thus obtained were dried to about 50% moisture content at 25 °C. For the 1–2, 0.5–1, 0.25–0.5 and 0.1–0.25 mm fractions, 2–3 hr drying was enough but for the < 0.1 mm suspension up to two days was required. The suspension samples were stirred and mixed from time to time during the drying period to ensure a uniform sample was obtained. The aggregate samples as well as the whole soil were incubated in plastic bags with sealed ends at 25 °C in a constant room temperature for a 10 day equilibration period prior to the measurement of microbial C and microbial P. During the incubation, the bags were opened for air change each day. Soil moisture content was measured at the same time as microbial analysis. Subsamples of soil and aggregates were air-dried and ground by ball mill for chemical analysis.

The final suspension (about 10 L after separating one kg field moist soil) for each soil was reduced in volume to one L by rotary evaporation at < 30 °C under reduced pressure. Aliquots of this concentrated suspension were used to estimate $P_{mic}$, and sub-samples of the remaining suspension were passed through a 0.1 $\mu$m membrane filter and the filtrate used for determining inorganic P by Murphy and Riley's method (1962) and total P by ICP-OES (ARL Model 3580).

## 2.3. CHEMICAL ANALYSIS

The pH of the soil sample was measured using both distilled water and 10 mM $CaCl_2$ at 1:1 solution/soil ratio. Total organic C of soil and aggregates was determined using an Elemental Analyzer (Model 1106), and total P and organic P by a sequential extraction procedure (Bowman, 1989). Available P of both air-dried soil and moist soil was estimated using the Bray I method (Bray and Kurtz, 1945) and P concentration in the extracts determined by ICP-OES.

## 2.4. MEASUREMENT OF $P_{mic}$ AND $C_{mic}$

In the basic procedure (Jenkinson and Powlson 1976; Wu *et al.*, 1990 and Brookes *et al.*, 1982) soil samples were exposed to alcohol-free $CHl_3$ vapour in a vacuum desiccator at room temperature for 24 h. The fumigated soils were then put in a clean empty desiccator and residual $CHCl_3$ removed from the fumigated soil by repeated evacuation. The measurement of $C_{mic}$ in soil and aggregate samples is done by extracting the fumigated soil immediately following $CHCl_3$ removal by shaking 25 g of soil for 30 min with 100 $cm^3$ 0.5 M $K_2SO_4$. After filtering through a Whatman No. 42 filter paper, we analyzed the filtrate for organic C by an automated u.v. – persulphate procedure, and the biomass C ($C_{mic}$) was calculated as follows: $C_{mic} = E_c/K_c$ where $E_c$ (the flush of extractable organic C) = (0.5 M $K_2SO_4$ extractable organic C in the fumigated soil) minus (0.5 M $K_2SO_4$ extractable organic C in the unfumigated control soil). $K_c$ is the conversion factor, for which a value of 0.45 was assigned (Jenkinson and Powlson, 1976).

$P_{mic}$ in soil and aggregate samples was extracted using 0.03 M $NH_4F$-0.025 M HCl or 0.5 M $NaHCO_3$ for 30 min at solution/solid ratio of four, centrifuged (3660 g for 10 min) and filtered through Whatman No. 42 filter paper. Activated charcoal (pretreated with HCl and $NaHCO_3$) was added to remove the dissolved organic materials when necessary. The P concentration in the filtrate was determined by the method of Murphy and Riley (1962). The biomass P ($P_{mic}$) in soil is calculated from the formula: $P_{mic} = E_p/K_p$ where $E_p$ = (the extractable P in the fumigated soil) minus (the extractable P in the unfumigated control soil) and $K_p$ = the conversion factor (a value of 0.35 was assigned for the $NH_4F$-HCl extraction (He *et al.*, 1994a) and 0.40 for the $NaHCO_3$ extraction (Brookes *et al.*, 1992)). Correction for phosphate adsorption in the estimation of biomass P was made using a recovery curve of added phosphate at rates, 10, 25 and 40 mg P $kg^{-1}$.

The $P_{mic}$ in the supernatant suspension was measured using a method similar to that used by Hasebe *et al.* (1985). Briefly, 2.0 $cm^3$ $CHCl_3$ was added to 20 $cm^3$ suspension in a 50 $cm^3$ plastic centrifuge tube and the contents were then shaken overnight. Following fumigation the residual $CHCl_3$ was removed by repeated evacuation. Both the control and the fumigated samples were then treated with a small amount of activated charcoal to remove dissolved organic material and passed through a 0.1 $\mu$m membrane filter. The P concentration in the filtrate was

TABLE II
Distribution of aggregate sizes (mm) in soils

| Sample no. | Land use | Distribution of aggregate size (%) | | | | | Recovery (%) |
|---|---|---|---|---|---|---|---|
| | | 1–2 | 0.5–1 | 0.25–0.5 | 0.1–0.25 | < 0.1 | |
| 1 Insch | Grassland | 44.0 | 14.2 | 9.4 | 6.5 | 21.6 | 95.7 |
| 2 | Arable | 26.2 | 13.9 | 6.1 | 10.8 | 39.6 | 96.6 |
| 5 Stonehaven | Grassland | 23.5 | 13.9 | 11.5 | 13.6 | 34.4 | 96.9 |
| 6 | Arable | 21.5 | 12.0 | 11.8 | 11.7 | 38.5 | 95.5 |

TABLE III
Total organic and available P in experiment soils

| Sample no. | Total P | Organic P ($mg\ P\ kg^{-1}$) | Available P (Bray-1) | |
|---|---|---|---|---|
| | | | Air-dry soil | Moist soil |
| 1 | 1075 ± 4 | 514.9 ± 2.7 (47.9)[a] | 20.9 ± 0.1 | 4.3 ± 0.2 |
| 2 | 1702 ± 5 | 717.5 ± 2.9 (42.2) | 48.1 ± 0.3 | 6.1 ± 0.3 |
| 3 | 1346 ± 2 | 693.2 ± 1.4 (51.1) | 37.0 ± 0.3 | 11.5 ± 0.2 |
| 4 | 1447 ± 2 | 754.5 ± 2.5 (52.1) | 132.3 ± 0.5 | 30.4 ± 0.7 |
| 5 | 1087 ± 3 | 526.4 ± 2.7 (48.4) | 50.3 ± 1.0 | 12.2 ± 0.2 |
| 6 | 1110 ± 3 | 551.7 ± 1.7 (49.7) | 117.1 ± 2.1 | 16.7 ± 0.4 |
| 7 | 1075 ± 1 | 541.6 ± 0.9 (50.3) | 16.5 ± 0 | 5.0 ± 0.2 |
| 8 | 1388 ± 2 | 622.2 ± 2.1 (44.8) | 79.8 ± 0.2 | 16.8 ± 0.2 |

[a] Value inside bracket is the percentage of organic P of the total P.

determined as stated previously. $P_{mic}$ was calculated using $K_p = 0.35$ and no sorption correction was made.

## 3. Results and Discussion

### 3.1. General Soil Characteristics

In general, the grassland soils contained higher amounts of organic carbon than the corresponding arable soils with mean values of 40 g C $kg^{-1}$ (grassland) compared with 41 g C $kg^{-1}$ (arable) (Table I). The distribution pattern of water-stable aggregates was also different for the grassland and arable soils (Table II). Cultivation decreased the percentage of microaggregates (0.5–2.0 mm) and increased that of the < 0.1 mm fraction, which is in agreement with the observations of Gupta and Gerida (1988) and is probably related to the organic matter content in soils (Table I). The Insch soil displayed a much greater variation between arable and

TABLE IV

Microbial biomass C ($C_{mic}$) and microbial biomass P ($P_{mic}$) in soils

| Sample no. | $C_{mic}$ | $P_{mic}$ | | C/P ratio in microbial biomass | |
|---|---|---|---|---|---|
| | | $NH_4F$-HCl | $NaHCO_3$ | $NH_4F$-HCl | $NaHCO_3$ |
| | (mg C $kg^{-1}$) | (mg P $kg^{-1}$) | | | |
| 1 | 1050.3 ± 26.7 | 58.5 ± 2.7 | 35.3 ± 5.2 | 18.0 | 29.8 |
| 2 | 464.2 ± 25.7 | 37.1 ± 3.5 | 70.5 ± 8.2 | 12.5 | 6.6 |
| 3 | 529.0 ± 11.1 | 44.4 ± 0 | 29.3 ± 0 | 11.9 | 18.1 |
| 4 | 397.1 ± 23.2 | 25.6 ± 1.1 | 16.9 ± 4.9 | 15.5 | 23.5 |
| 5 | 585.7 ± 30.8 | 45.2 ± 1.8 | 52.9 ± 3.9 | 13.0 | 11.1 |
| 6 | 330.5 ± 9.1 | 10.5 ± 0.9 | 18.8 ± 2.4 | 31.5 | 17.6 |
| 7 | 581.4 ± 25.0 | 55.3 ± 6.1 | 12.5 ± 0 | 10.5 | 46.5 |
| 8 | 565.6 ± 20.8 | 37.5 ± 1.5 | 33.3 ± 3.6 | 15.1 | 17.0 |
| Mean | | | | 16.0 | 21.3 |

[a] Extractable P determined by ICP.

grassland soils than the Stonehaven soil (Table II). Fertilization increased total P in the arable soils (Table III) which contained a mean value of 1412 mg P $kg^{-1}$ as opposed to 1146 mg P $kg^{-1}$ in grassland soils. Similarly, the arable soils contained higher organic P (Table III) with a mean value of 661 mg P $kg^{-1}$ compared with 569 mg P $kg^{-1}$ for the grassland soils. However, the largest difference was found for available P (Table III) which was on average three times greater in the arable soils than the grassland soils, 94 mg P $kg^{-1}$ compared with 31 mg P $kg^{-1}$. According to the index of soil available P, 20 mg P $kg^{-1}$ of Bray I – P is considered to be high so that the arable soils have very high available P levels (Table III). In the majority of cases the percentage of organic P was approximately 50% of the total P. No consistent trend with cultivation type was apparent.

### 3.2. Measurement of $P_{mic}$ in soils and its distribution in aggregates

$P_{mic}$ is usually measured by the $CHCl_3$ fumigation – 0.5 M $NaHCO_3$ extraction method (Brookes *et al.*, 1982; Hedley and Stewart, 1982). However, for soils with low pH (below 6.0), high organic matter and high available P, the $NaHCO_3$ extraction was less effective in detecting the P flush from the microbial biomass following fumigation, compared to 0.03 M $NH_4F$-0.025 M HCl extraction (He *et al.*, 1993a). In this study, $P_{mic}$ was measured using both methods for the eight test soils. The results are shown in Table IV. For soil 3, 4, 5, 6 and 8, both methods gave similar values but for the other three soils (No. 1, 2 and 7), the results were very different. Based on $C_{mic}$ measurements, the C/P ratio in microbial biomass with $P_{mic}$ determined by the $NH_4F$-HCl procedure (from 11.9 to 31.5, mean 16.0)

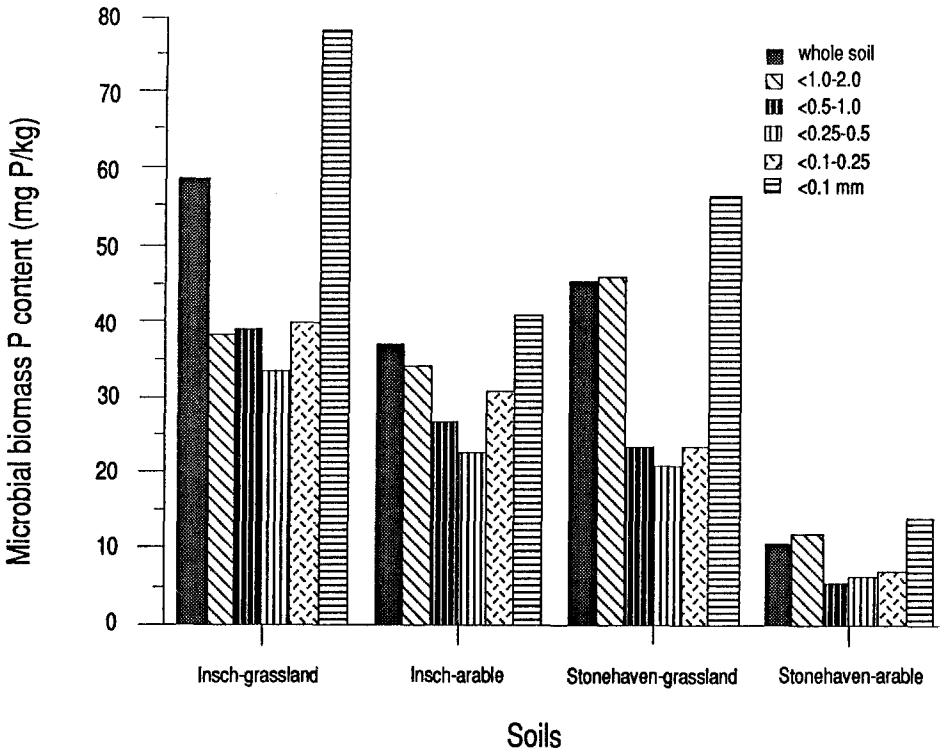


Fig. 1. Distribution of microbial P in soils and soil aggregate sizes (mm).

was more comparable with the reported values of soil microbial biomass (Brookes *et al.*, 1984; Perrott and Sarathchandra, 1989; He *et al.*, 1994a) and cultured microorganisms (Anderson and Domsch, 1980) compared to that obtained using the $NaHCO_3$ method (from 6.6 to 46.5, mean 21.3). Moreover, $P_{mic}$ determined by the $NH_4F$-HCl method was well correlated positively with organic C and $C_{mic}$ ($r$ = 0.829 and 0.790, respectively) whilst for the $NaHCO_3$ method there was poor correlation ($r$ = 0.024 and 0.039, respectively). These results indicate that the $NaHCO_3$ extraction procedure is not suitable for measuring $P_{mic}$ in these soils and therefore, the $NH_4F$-HCl method was selected for the determination of $P_{mic}$ in the soil aggregates.

From Table IV it can be seen that the grassland soil contained a larger amount of $P_{mic}$ than the corresponding arable soil, which complies with the general rule: soil microbial biomass decreases in the order, grassland > forest > arable as reviewed by Smith and Paul (1990). In quantity, $P_{mic}$ was much greater than available P determined using fresh moist sample and greater than available P obtained with air-dried samples for all of the test grassland soils except for sample No. 5 (Tables III and IV). The marked increase in available P in soil after air-drying has been partly attributed to the contribution from microbial P (Sparling *et al.*, 1987; 1989).

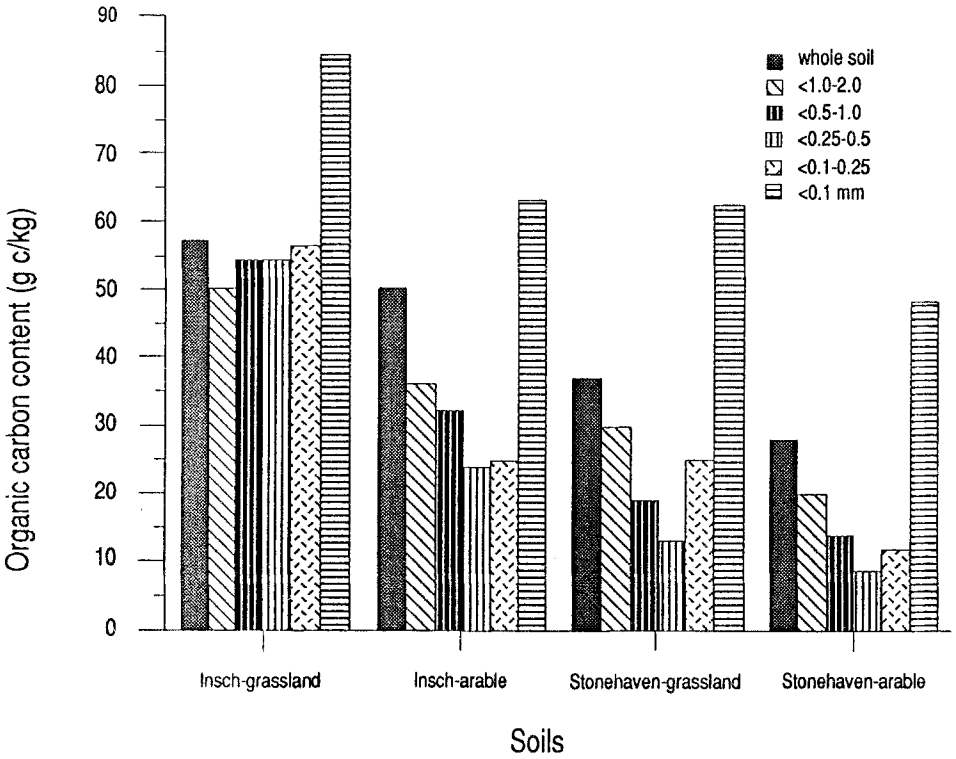


Fig. 2. Distribution of organic C in soils and soil aggregate sizes (mm).

The distribution of $P_{mic}$ in different aggregate size fractions is shown in Figure 1. In general, $P_{mic}$ was greatest in the finest fractions (< 0.1 mm) and the largest aggregates (1.0–2.0 mm), and tended to be lower in the intermediate aggregate sizes. This difference seemed more marked in the grassland soils. The distribution of organic C and $C_{mic}$ in different aggregate size classes (Figures 2 and 3) was generally comparable with that of $P_{mic}$ (Figure 1). There was a significant correlation between $C_{mic}$ and organic C ($r = 0.867$), and $P_{mic}$ was closely related with $C_{mic}$ and organic C in aggregates ($r = 0.841$ and 0.788, respectively). These results indicate that both organic matter and microbial biomass tend to concentrate in the finer soil material. Organic matter is the main agency of aggregate stabilization, and microorganisms are involved in the formation of stable aggregates, fungi tending to bind together larger soil particles and bacteria stabilizing clay particles (Lynch and Bragg, 1985). Many factors appear to influence this relationship. Gupta and Germida (1988), for example, reported that macroaggregates in a Canadian prairie soil contained higher organic C and $C_{mic}$ than microaggregates (< 0.25 mm), which differs from the findings of this study. A possible reason is that a dry-sieving method was used to obtain aggregate size classes in their study. Dry aggregate stability is important in arid soils, but in most cases, the stability of aggregates when they are wet is more relevant. Water, either directly as rainfall or as surface runoff, is the

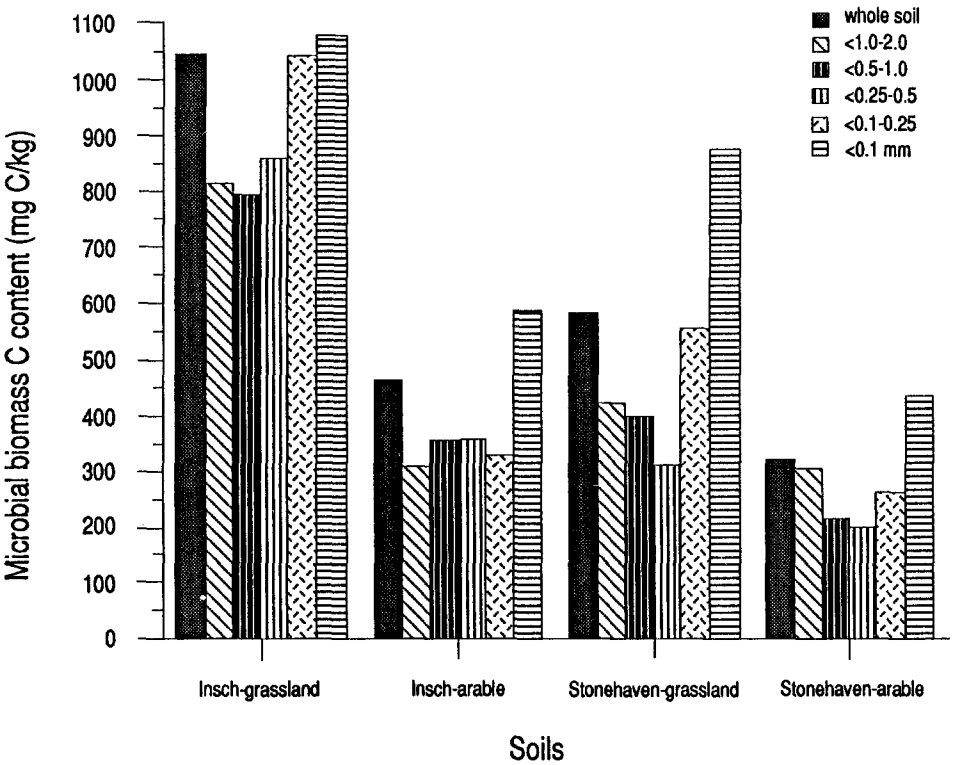


Fig. 3. Distribution of microbial biomass C in soils and soil aggregate sizes (mm).

main agent of aggregate breakdown as observed by Loch and Donnollan (1983) for two different soil types in Australia. During the disintegration of macroaggregates when submerged in water, microorganisms and small pieces of plant debris are likely to be detached and enter smaller aggregate size fractions. Moreover, organic matter such as humic materials and polysaccharides tend to associate more strongly with clay than with silt or sand. In this study, obvious breakdown of larger aggregates in water was observed, particularly for arable soils, and the 0.1-0.5 mm aggregates contained many more discrete mineral particles than either the 1–2 mm or the 1–2 mm or the < 0.1 mm fractions. Therefore, information obtained from soil aggregates separated using wet sieving could be more meaningful in understanding the transport of P from agricultural land compared to that obtained using a dry-sieving method. These results indicate that a significant proportion of soil P could be transported as microbial biomass phosphorus as the content of $P_{mic}$ is highest in the < 0.1 mm fraction which would be most readily lost to runoff.

### 3.3. Distribution of total P, organic P and available P

The distribution of total P in soil aggregates showed a somewhat similar pattern to that of organic C, $P_{mic}$ and $C_{mic}$ (Figure 4), with total P tending to be higher in

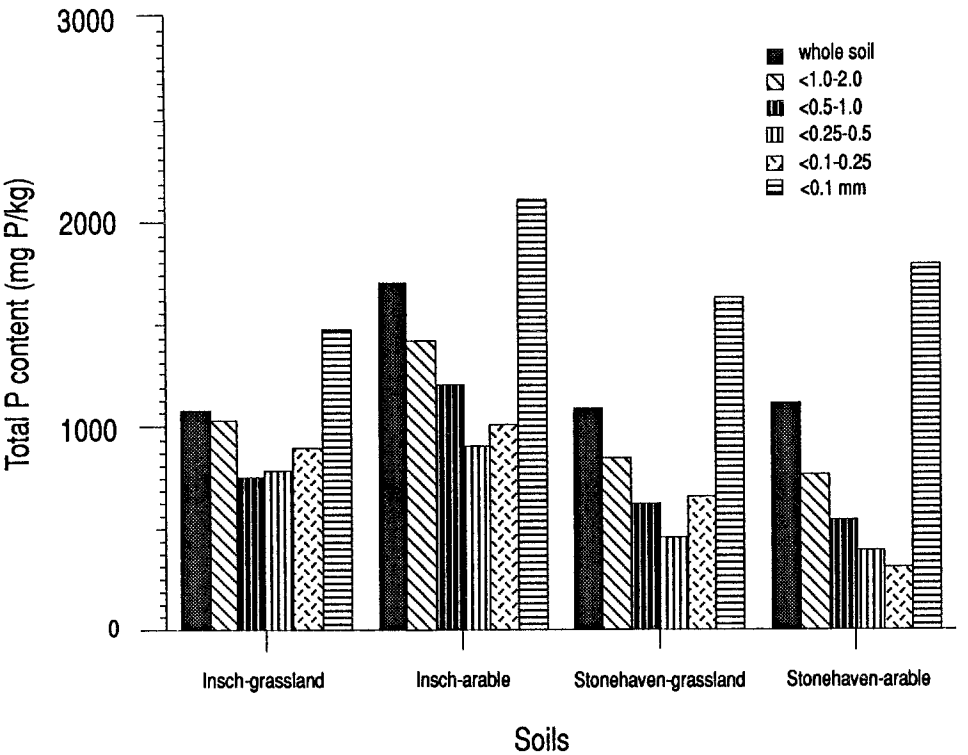


Fig. 4. Distribution of total P in soils and soil aggregate sizes (mm).

the < 0.1 mm fraction. However, there were no obvious differences between the grassland and arable soils, nor between the different soil associations.

The distribution of organic P in different classes of agregate sizes (Figure 5) was in good agreement with that of total P (Figure 4) and with total C (Figure 2). The content of organic P in the large aggregates (1–2 mm) was generally higher than that in the 0.1 to 0.5 mm aggregate sizes for all of the soils tested. Organic P in each size fraction was possitively correlated with the total P ($r = 0.827$). Organic P accounts for approximately half the total P in all soil samples (Table III). The proportion of organic P is slightly higher in the 1–2 mm aggregates compared with those of finer size.

In contrast to the total P and organic P, the distribution of available P (Bray I-P) between soil aggregate sizes followed a different pattern (Figure 6). The content of available P in the < 0.1 mm fraction was markedly lower than that in the other larger size classes and whole soil. The amount of available P in the 0.1-2.0 mm fractions were remarkably similar to the whole soil sample. Possible reasons for the decrease in available P in the finest fraction could be: (1). They have a higher P-sorption capacity and therefore P is bound more tightly in this fraction compared to the other fractions. (2) Being air-dried from a suspension, the P extractability is decreased as a consequence of the drying process. The index of available P

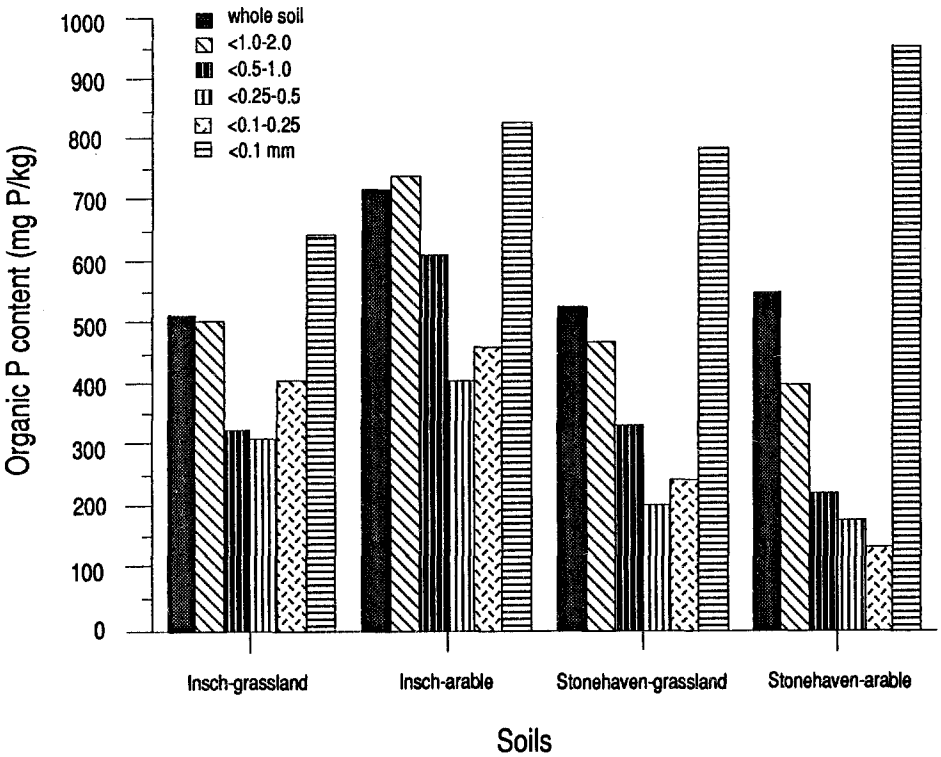


Fig. 5. Distribution of organic P in soils and soil aggregate sizes (mm).

is conventionally used to indicate P status in soil, but such an index may be not enough to reflect P status in runoff sediment as shown in this study. A possible reason for the lower amounts of available P in the Insch soil compared with the Stonehaven soil is that the clay fraction of the former contains significant amounts of halloysite whereas the clay fraction of the latter is dominated by 2:1 silicate clays (Wilson *et al.*, 1984). Typically, kaolin minerals and halloysite in particular because of its fine particle size, have a higher P adsorption capacity than the 2:1 clays.

### 3.4. The quantity and forms of soil P not recovered during aggregate separation and its significance in the P transport by runoff

The balance of P not recovered during aggregate separation (Table V) was calculated using the data of total P, organic P, available P and $P_{mic}$ content in soil and aggregates (Figures 1, 4, 5 and 6), the percentage of each aggregate size to the whole soil (Table II), and the P concentration in the final solution. From Table V it can be seen that during the aggregate separation (submergence of soil in water, sieving and washing with distilled water with gentle shaking, the leachate/soil ratio being about 10), the amount of total P which was not recovered ranged from 86.5 to 164.9 mg

TABLE V

The quantities and forms of P not recovered during aggregate separation

| Sample no. | Total P ($P_t$) | Organic P ($P_o$) | | Available P ($P_a$) | | $P_{mic}$[b] | | | Solution P | | pp[c] |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Soil | | Suspension | $P_t$ | $P_i$ | |
| | mg P $kg^{-1}$ | | | | | | | | | | |
| | | | $P_o/P_t$ | | $P_a/P_t$ | | $P_{mic}/P_t$ | | | | |
| 1. | 86.5 (8.0)[a] | 49.7 (9.7) | 0.57 | 4.1 (19.4) | 0.05 | 13.6 (23.3) | 0.16 | 1.12 | 0.53 | 0.43 | 2000.6 |
| 2. | 164.9 (9.7) | 36.0 (5.0) | 0.22 | 11.2 (23.3) | 0.07 | 3.5 (9.5) | 0.02 | 0.18 | 0.26 | 0.23 | 4851.0 |
| 3. | 98.8 (9.1)[a] | 42.1 (8.0) | 0.43 | 5.2 (10.5) | 0.05 | 6.2 (13.7) | 0.06 | nd[d] | 0.42 | 0.25 | 3996.1 |
| 4. | 109.7 (9.9) | 35.7 (6.5) | 0.33 | 29.6 (25.3) | 0.23 | 0.4 (4.1) | 0.003 | nd | 0.74 | 0.68 | 2442.4 |

[a] Value inside bracket is the percentage of lost P in their total P of the soil.

[b] $P_{mic}$-soil means soil microbial biomass P lost during aggregate separation and $P_{mic}$-suspension is the $P_{mic}$ detected in the suspension after centrifugation to separate the < 0.1 mm aggregate.

[c] PP is the P content of particulate left in the supernatant solution after centrifugation to separate the < 0.1 mm aggregate calculated using the data of total P lost and the percentage of soil material unrecovered.

[d] nd = not detected.

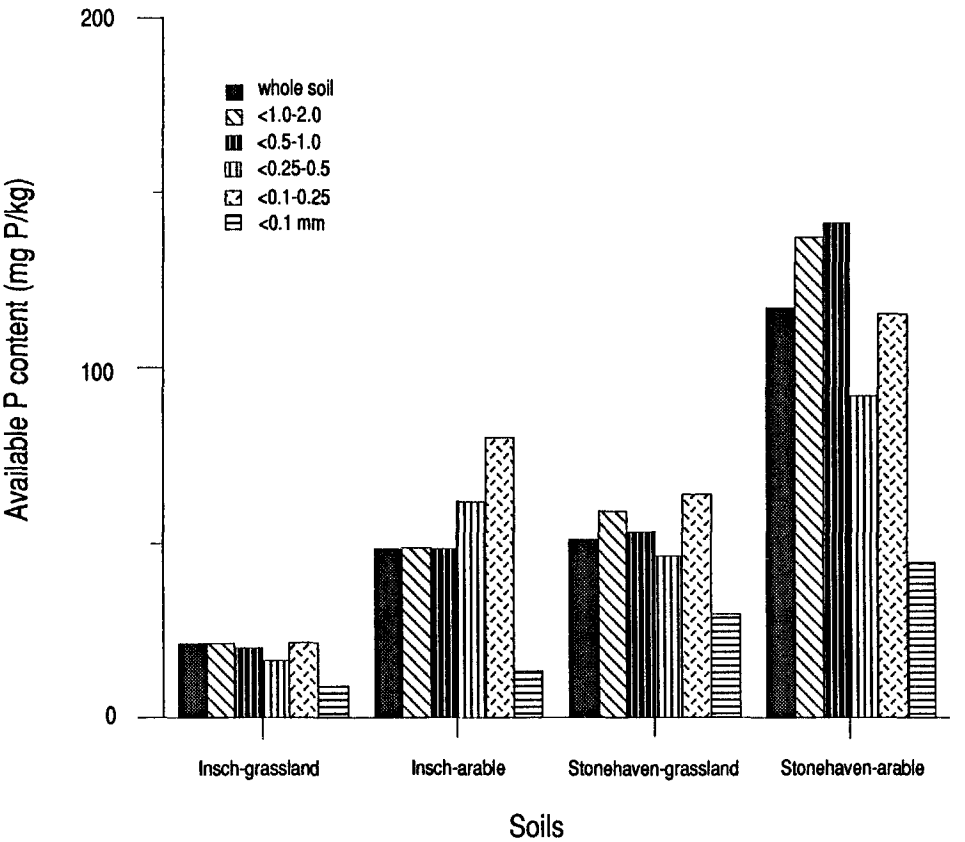


Fig. 6. Distribution of available P in soils and soil aggregate sizes (mm).

P $kg^{-1}$, accounting for about 8–10% of the total P content in the experimental soils. More P was lost from the arable soils than from the corresponding grassland soils. Unrecovered organic P varied from 35.7 mg P $kg^{-1}$ to 49.7 mg P $kg^{-1}$, accounting for 5.0–9.7% of soil organic P or 22–58% of the total unrecovered P (mean 39.5%). In contrast to total P, more organic P was lost from the grassland soils than from the arable soils. For instance, organic P accounted for 57.5% of total unrecovered P for the Insch grassland soil but only 21.8 for the Insch arable soil (Table V). Compared to total P and organic P, the amount of unrecovered available P and $P_{mic}$ lost was small but they accounted for a higher percentage of their total content in soil, the former being 10.5 to 25.3 (mean 19.6%) and the latter 4.1 to 23.3% (mean 12.7%), with more available P lost from arable soil but more $P_{mic}$ from grassland. These results could imply that available P and $P_{mic}$ might decrease more rapidly than total P or organic P after the soil is subjected to erosion. The loss of available P was partly due to the release of soil P into solution during aggregate separation, but in addition, leaching and wetting-drying processes may also change the extractability of soil P. As for $P_{mic}$, only a small amount (1.12 and 0.18 mg

P $kg^{-1}$) was recovered from the final suspension of Insch grassland and arable soil and no $P_{mic}$ was detected in the suspension for Stonehaven soil series. The amount of P recovered in solution was less than 1% of total unrecovered P although it accounted for 2.6 to 5.5% of the unrecovered available P (Table V). Of the solution P 60–90% was in a molybdate reactive form. As the soil materials were carefully collected during separation, except for particulates left in the supernatant solution after centrifugation which accounted for 3.1 to 4.5% of the whole soil according to the recovery of soil during separation (Table II), it can be calculated that P content of the particulate fraction was 2001 mg P $kg^{-1}$ to 4851 mg P $kg^{-1}$, about 1.9 to 2.9 times higher than that of the corresponding soil (Table V). These results, though not directly obtained from field experiments are very comparable with previous findings by Johnson *et al.* (1976), Rigler (1979), Kronvang (1990) and Sharpley and Smith (1990), showing that the transport of P to runoff from agricultural land is mainly in the form of solid-P with little in solution and is related with soil P status and land use.

## 4. Conclusions

The results presented here enable some inferences to be drawn regarding the physical and chemical nature of P transported to surface waters and to its potential availability within the aquatic ecosystem. Very little P, less than 1% of the total unrecovered P, is found in solution, and 60–90% of this dissolved P is in a molybdate reactive form. The results support the view that the major form in which P is transported from soils to waters is as suspended particulates. The finest aggregate size (< 0.1 mm) contains a disproportionate amount of both the total P and the organic P and $P_{mic}$ also tends to be concentrated in these aggregates. However, very little of the P associated with the fine aggregates is available, as assessed by the Bray I method, and it may be concluded that such P-rich aggregates carried into surface waters should not immediately give rise to eutrophication problems. This does mean to say, however, that this will continue to be the situation after these particulates have been deposited in river or lake sediments and where a change in environment, particularly redox conditions, might be expected to occur. So far as the effect of land use is concerned, more organic P is lost from grassland soils compared with arable soils, and also more $P_{mic}$, but very little of this P is available.

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