Phosphorus losses from agricultural soils: Processes at the field scale

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COST Action 832

Quantifying the Agricultural Contribution to Eutrophication

Selected papers from the Meetings of Working Group 2

Phosphorus losses at the field scale

May 13th to 5th 1999, Cordoba, Spain

September 21st to 23rd 2000, Gumpenstein, Irdning, Austria

ALTERRA, Wageningen, The Netherlands

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Notes:

Please refer to a paper in this report as in the following example:

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Pages 4 and 6 were intendedly left blank; blank pages 94 and 118 were left out.

Introduction

Founded in 1971, COST is an intergovernmental framework for European Co-operation in the field of Scientific and Technical Research, allowing the co-ordination of nationally funded research on a European level.

In July 1997 COST action 832, entitled "Quantifying the Agricultural Contribution to Eutrophication" was started, focussing on phosphorus (P). The aims of this actions are to:
(I) develop a common technical understanding of the processes, forms and pathways of P loss in land run-off, and
(ii) develop a methodological framework for identifying the relative contribution of different diffuse P sources at the farm and catchment level.
These aims will be achieved through definition of conceptual models of P cycling in EU agricultural systems, P transfer in surface and sub-surface run-off at a range of scales and impacts of diffuse P on surface water quality.
Chairman of the Action is P.J.A. Withers (UK), vice-chairman W.J. Chardon (Nl).

In March 1998, 16 countries had joined the Action, which will finish in July 2003. Working groups will develop four major themes:

	Theme	Co-ordinator
WG1	Phosphorus cycling in agriculture	J.P. Destain, Belgium
WG2	Phosphorus losses at the field scale	O.F. Schoumans, Netherlands
WG3	Phosphorus losses at the catchment scale	B. Kronvang, Denmark
WG4	Impacts of diffuse phosphorus on water quality	S. Orfanidis, Greece

This volume contains selected papers presented at two meetings organised by WG2, Phosphorus losses at the field scale. The first meeting was on May 13th to May 15th 1999 in Cordoba, Spain (local organiser J. Torrent). The second meeting was on September 21st and 23rd 2000, in Gumpenstein, Irdning, Austria (local organiser G. Eder).

The topic of the first meeting was to identify the processes in soils which are relevant for the loss of P from fields. For the second meeting an inventory was made of (European) data of P losses on the local (field) scale, and of models that are used in Europe for the description of surface and subsurface transport of P. Also, the role of hydrology in P transport was discussed.

The final meeting of WG2 was held together with WG1 in October 2002, in Zürich, Switzerland, and focussed on the possibilities of known and new P risk indicators that can be used at the field scale. Selected papers of that meeting will be published in the Journal of Plant Nutrition and Soil Science. Cost Action 832 will end in July 2003.

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The role of soil processes: Synthesis of actions

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1. Preface

In the autumn of 1998 this document was developed in order to co-ordinate the activities of one of the research topics of Working Group 2 of COST action 832 “Methodologies for estimation the agricultural contribution of eutrophication”. The major purpose of WG2 is to develop a methodology to estimate phosphorus (P) losses at field scale. At the first COST 832 meeting in Greenmount College, Antrim, N. Ireland, June 16-17, 1998, it was decided to group the WG2 activities into 4 topics:

- Topic 1 Soil Processes
- Topic 2 Erosion and surface runoff
- Topic 3 Leaching and subsurface flow
- Topic 4 Critical loads and Risk assessment

2. Concepts and definitions

2.1 Role of soil processes within the overall WG 2 framework

The objective of WG 2 is to develop a methodology to estimate P losses from agricultural soils at the field scale based on current scientific knowledge. Simplified, P loss or P transfer from agricultural soils to receiving waters can be seen as a two step process: first, the transfer of any P-containing compound from the immobile phase (bulk soil) to the mobile phase (water) by e.g. desorption or detachment, followed by net movement of the carrying water phase. It was agreed that topic 1 ‘soil processes’ would only deal with the study of *P transfer mechanisms* between the mobile and immobile phase, irrespective of hydrological pathway. Once P is ‘loaded’ into a mobile water phase, several *hydrological pathways* can be followed. The most general subdivision differentiates between *subsurface pathways* (e.g. leaching and ‘vertical’ erosion/migration) and *surface pathways* (e.g. runoff and ‘horizontal' erosion). According to this framework, the different WG 2 topics could be (re)defined as follows:

- Topic 1 P transfer mechanisms between bulk soil and a mobile water phase
- Topic 2 P loss by surface pathways at field scale
- Topic 3 P loss by subsurface pathways at field scale
- Topic 4 critical load and risk assessment at field scale

2.2 P transfer between bulk soil and a mobile water phase

In the first version of this document, it was attempted to subdivide P release and retention mechanisms into two broad categories. On one side, a wide range of *P-specific soil chemical, physico-chemical and biochemical reactions* can be identified controlling solution P intensities. On the other hand, a series of *non P-specific soil physical mechanisms* controls the concentration of P-containing particles in the passing water flow.
However, it was felt that this approach ‘masks’ or ‘ignores’ the grey zone of colloidal P release mechanisms. The scheme below presents an attempt to organise P release and

retention mechanisms according to (classical) dissolved-colloidal-particulate continuum. Two general terms, solubilisation and erosion have been introduced to describe the release of ‘dissolved’ and ‘particulate’ compounds respectively. Again, the use of two terms is not fully able to reflect colloidal behaviour.

Process / mechanism	**General release-term**
Sorption / desorption of orthophosphate	solubilisation
Sorption / desorption of organic and condensed P forms	solubilisation
Mineralisation / enzymatic hydrolysis of organic and condensed P forms	solubilisation
P release and uptake by soil micro-organisms, plants	solubilisation
Detachment / retention of P-containing inorganic and organic colloidal particles	detachment
Physical destruction of P-containing organic materials	detachment
Detachment / sedimentation of soil particles	detachment

It is important to realise that any of these release mechanisms can occur irrespective of the hydrological pathway considered. Thus, this scheme can be used to tackle ‘subsurface transport of eroded particles’ and ‘surface transport of solubilised P compounds’.

2.3 Some additional comments

It should be noted that e.g. the term ‘*erosion’* is defined above purely as the transfer of soil colloids and particles to a carrying water flow. Usually, the term ‘erosion’ is linked to a hydrological pathway, i.c. surface transport (overland flow, etc.). Similarly, it was felt that the widely used term *‘leaching’* did not fit well in the above picture, as it combines solubilisation and (subsurface) transport processes. Furthermore, the term leaching usually does not include subsurface transport of particles. For this combination of process and pathway the term ‘*migration*’ is used sometimes.

Field-scale variability of the P release/retention mechanisms is governed by the spatial variability of the resp. controlling soil parameters (e.g. texture, organic matter, P sorption capacity, pH, temperature, etc.). Some of these parameters are time-constant, others like pH, Eh and soil solution ionic strength are more temporally variable. Within topic 1, it is likely that this aspect ‘at field scale’ will not receive that much attention. On the other hand, the temporal and spatial variability at the field scale becomes important when release mechanisms are combined with hydrological pathways and P loss from field scale is considered (activities of topics 2 and 3 within WG2).

An overview of nomenclature regarding hydrological pathways and P loss mechanisms can be found in Haygarth & Sharpley (2001).

2.4 Suggested terminology for P lost in runoff and drainage water

Comparisons between soil P mobility studies are severely hampered by differences in analytical methodology and terminology for solution P fractions. On the Antrim WG 2 meeting the need for a standardised analytical methodology and nomenclature was formulated. Reviews of operationally defined P fractions can be found in Broberg and Persson (1988) and Robards *et al.* (1994). During the P Workshop in Wexford (september 1995), Sharpley and Pionke also proposed a list of "unified" P terminology (see Johnston *et* *al*., 1997). Here, we briefly summarise fractionation procedures for solution P and propose a scheme for fraction terminology.

P fractionation procedures for natural water samples are built up along two fractionation axes: a *size* fractionation axis and a *chemical* fractionation axis.

Physical or size fractionation reflects the particulate - colloidal - dissolved concept. As a standard procedure in both limnology, oceanography and soil science, 0.45-µm membrane filtration is used to distinguish between particulate and dissolved material. If colloid-sized material is present, part of it will in general pass 0.45-µm filters and be present in the "dissolved" phase. The occurrence of P containing colloids in soil solutions and soil leachates was demonstrated by a.o. Gerke (1992), Haygarth *et al*. (1997) and Sinaj *et al*. (1998).

Chemical fractionation reflects the different P-bonds occurring in solution. As a standard procedure, molybdate reactive phosphorus and total phosphorus are determined on (filtered) soil waters. Further chemical fractionation may involve the use of UV photo-oxidation or acid hydrolysis to distinguish between on the one hand organic phosphates: P-O-C (esther bond) and P-C or P-N bond (both direct bond), and on the other hand condensed phosphates (P-O-P bonds). For an extensive discussion of organic P forms see the paper by Gil-Sotres *et al.* in this volume.

The terminology given below is based on "conventional" size fractionation with 0.45 µm filters, followed by chemical fractionation. Hence, a terminology for the truly "dissolved" species (e.g. determined after ultrafiltration at 10 kD) is not included.

	- - - - -	**Physical fractions**	**- - - - -**
Chemical fractions	**Unfiltered sample**	**Filtered sample (0.45 µm)**	**By difference unfiltered - filtered**
Molybdate reactive	TRP Total Reactive P	DRP Dissolved Reactive P	PRP = TRP - DRP Particulate Reactive P
Total	TP Total P	TDP Total Dissolved P	TPP = TP - TDP Total Particulate P
By difference	TUP = TP - TRP Total Unreactive P	DUP = TDP - DRP Dissolved Unreactive P	PUP = TUP -DUP Particulate Unreactive P

Therefore, it would be more appropriate to mention explicitly the size fractionation used, rather than to keep the letter D(issolved) open for interpretation. In such a scheme, MRP (molybdate reactive P) is a general term used to indicate a chemical fraction only, without size specification. One would refer to the MRP content of a 0.45-µm filtrate simply as MRP (<0.45µm).

The difference between total P and molybdate reactive P is often termed "organic P" instead of "unreactive" P. The term organic neglects the potential presence of condensed or colloid bound P species in solution. "True" organic phosphorus can be determined after UV photo-oxidation of the sample as the difference of MRP before and after UV-photooxidation.

3. Soil processes and P losses: state-of-the-art

Simplified, P loss rates are P concentration (mass volume^{-1}) × flow (volume time^{-1}). Our topic "Soil processes", as defined in the previous chapter, only deals with prediction of concentrations which can be mobilised and transported by a given hydrological flow. The terms 'solubilisation' and 'erosion' were introduced to cover the wide range of P release mechanisms.

3.1 Review of P mobility studies

In general, prediction of solution P concentrations should take into account the entire soil P cycle. For recent reviews of the soil P cycle, see e.g. Frossard *et al*. (1995), Magid *et al*. (1995). Studies of subsurface transport of P have mainly focussed on orthophosphate or MRP losses from soil, while studies looking at surface transfer of P mainly deal with the total and bio-available amounts of P exported from a given area. The mobilisation of other P compounds, such as organic P and P containing colloids is much less understood. However, both types of P species may be much more mobile than free orthophosphate, since the negatively charged orthophosphate ion is protected from sorption by covalent and/or electrostatic bonding to carbon or metal ions in the resp. molecules / colloids. Current knowledge gaps include:

- Relative importance of non-orthophosphate forms in soil waters? Relation with soil type and land use? Is it restricted to pasture soils, or do arable soils also “suffer” from important non-ortho-P losses?
- Can colloidal inorganic and organic matter act as a carrier / a sink in the solution phase for orthophosphate, thereby enhancing orthophosphate mobility?

Therefore, reviews should:

- Assess the relative importance of non-orthophosphate forms for P losses. For erosion mechanisms, dissimilarities in P composition between bulk soil and eroded particles/colloids are of central interest.
- Evaluate differences in mobilised P forms and amounts for different combinations of soil type and land-use (cropping vs. pasture).

3.2 Conceptual and deterministic model descriptions

Much effort has been put on developing simplified relationships between soil solution P concentrations and soil P status (see also "environmental soil P tests"). In general, these models (only) deal with sorption and desorption of orthophosphate in a soil-water system. A good example of this approach is the Dutch protocol on P-saturated soils (Van der Zee *et al*. 1987), in which the concepts "P sorption capacity" and "degree of P saturation" were defined for acid sandy soils. This protocol has been used extensively in a.o. the Netherlands, Belgium, Northern Germany to map the P saturation parameters from field to regional scales.

Mechanisms of both organic P and colloidal P release are not well understood. Most authors stress the role of microbial activity, while other papers have focussed on sorption/desorption behaviour of natural organic matter and/or selected organic P compounds. Reviews should summarise current concepts and process descriptions of soil chemical, physico-chemical and biochemical reactions ('solubilisation') as well (P-related?) mechanisms for erosion of (colloidal) soil particles. Moreover, given the knowledge gaps with regard to mobilisation/erosion of non-orthophosphate P-forms, they should also address the questions:

- Which processes control concentrations of organic and condensed P forms in solution, and what is their relative importance? (e.g. microbial turnover).

- Mobilisation of colloids by detachment / retention: pH, ionic strength and ratio divalent/ monovalent cations in the soil environment are important determining factors.

3.3 Soil testing for environmental risk

The need for an environmental soil P test is intimately linked with the establishment of upper critical limits for P in soils. These limits should take into account the soil P concentration for optimal crop production and the soil P concentration which "produces" environmentally sound (sustainable) P losses. Sibbesen and Sharpley (1997) give a good overview of the philosophy behind environmental soil P testing.

An environmental soil P test only looks at the soil compartment. It should be kept in mind that the risk for P loss is a combination of the soil P risk and the hydrological risk (topic 4 of WG 2; risk assessment).

In agreement with the plant availability concept (available P = all P that can be taken up by plant roots in one growing season), one can attempt to define mobile P as all P that can be lost from the soil. The environmental impact will be determined by the loss rate, (combination of P concentration and composition of mobile phase and water flow leaving the soil or field compartment by different pathways). The usefulness of this concept is clear for leaching, but much less clear for erosion.

Environmental soil P test values can be derived from (generalised) *intensity-quantity relationships*. The intensity corresponds to the activity of P in soil solution and is often determined by a water or $CaCl_2$ solution extract. The quantity factor refers to the plant-available P reserve and is determined by chemical extraction methods, by anion exchange resin extractions, or by isotopic dilution (^{32}P) techniques. The capacity factor is generally related to the phosphate buffering power and phosphate fixing capacity of the soil. The mechanism by which the intensity, quantity , and capacity factors are regulated is particularly influenced by soil properties such as amorphous Al and Fe oxides, soil pH, clay or organic matter contents, and by the prevailing form of soil P.

The most straightforward way of establishing environmental soil P test values is to study quantity - intensity relationships on individual soil samples. However, the P intensity (P concentration and composition in the mobile phase) of a topsoil is not directly related to the concentrations and/or amounts of P lost from the pedon or field (cfr. sorption in subsoil). Therefore, attempts have been made to correlate "conventional" soil P quantities (e.g. Olsen-P, Mehlich-P) of the topsoil to P concentrations in runoff and leachate waters (e.g. Sibbesen and Sharpley, 1997).

Again, most of the work done only considers sorption/desorption of orthophosphate and "neglects" other P forms and release mechanisms. The above description reflects some of the conceptual problems with environmental soil P testing:

- Should we include organic and colloidal P forms in the intensity measurements?
- Should we use a point-approach (mechanistic - relating intensity and quantity for individual soil samples) or a spatial approach (correlation - relating intensities in water flows leaving the system to an averaged soil P quantity)
- Does a similar concept exists for erosion? Are environmental soil P tests useful anyway?

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Terminology of transport phenomena and erosion at the field scale

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Introduction

A special definition for same terms is often very helpful for mutual understanding. It is important to use the same or similar sources. In this chapter published terminologies from the publications: *"Terminology for Soil Erosion and Conservation", Bergsma, E. (coord.), ISSS (1996),* and the *"Glossary of Soil Science Terms", SSSA (1997)* are given, partly completed to give this summary of relevant terms of transport phenomena and erosion processes at the field scale.

Accelerated erosion - See **erosion**, *accelerated erosion*

bank/ terrace - A constructed earth embankment, incorporating a channel on the upslope side, typically traversing a slope to control and/or prevent the erosion of that slope, by intercepting, diverting or storing runoff instead of permitting it to floe uninterruptedly down the slope (B)

bypass flow - See **preferential flow**.

catchment - The area which supplies water by surface and subsurface flow from rain to a given point in the drainage system.

colluvium - Unconsolidated, unsorted material being transported or deposited on side slopes and/or on the basis of slopes by mass movement and by local, unconcentrated runoff

compaction - The result of various natural and man-made processes in the soil causing a high density in some layer, with lower permeability for water and air (B)

concentrated flow - A relatively large water flow over or through a relatively narrow course.

cover crop - Close-growing crop, that provides soil protection, seeding protection, and soil improvement between periods of normal crop production, or between trees in orchards and vines in vineyards. When ploughed under and incorporated into the soil, cover crops may be referred to as green manure crops.

crust - A transient soil-surface layer, ranging in thickness from a few millimetres to a few centimetres, that is either denser, structurally different or more cemented than the material immediately beneath it, resulting in greater soil strength when dry as measured by **penetration resistance** or other indices of soil strength

cumulative infiltration - Total volume of water infiltrated per unit area of soil surface during a specified time period. Contrast with infiltration flux (or rate).

depression - Any relatively sunken part of the surface, especially a low-lying area surrounded by higher ground.

depression storage - The amount of water stored by depressions in the land surface (B)

drain tile - Concrete, ceramic, plastic, or other rigid pipe or similar buried structure used to collect and conduct profile drain-water from the soil in a field.

drain, to - (i) To provide channels, such as open ditches or drain tile, so that excess water can be removed by surface or by internal flow. (ii) To lose water (from the soil) by percolation.

drainage basin - A general term for a region or area bounded by a drainage divide and occupied by a drainage system.

drainage, surface - Used to refer to surface movement of excess water - includes such terms as ponded, flooded, slow, and rapid.

eluviation - The removal of soil material in suspension (or in solution) from a layer or layers of a soil. Usually, the loss of material in solution is described by the term "leaching." See also **leaching**

enrichment ratio (ER) - See **erosion**, *enrichment ratio (ER)*.

erodible - See **erosion**, *erodible*

EROSION

erosion - (i) The wearing away of the land surface by rain or irrigation water, wind, ice, or other natural or anthropogenic agents that abrade, detach and remove geologic parent material or soil from one point on the earth's surface and deposit it elsewhere, including such processes as gravitational creep and so-called tillage erosion; (ii) The detachment and movement of soil or rock by water, wind, ice, or gravity. The following terms are used to describe different erosion types, processes, and mechanisms:

- *accelerated erosion* - Erosion in excess of natural rates, usually as a result of anthropogenic activities.

- *bed load* - The sediment that moves by sliding, rolling, or salting on or very near the streambed; sediment moved mainly by tractive or gravitational forces or both but at velocities less than the surrounding flow. *(not important in the field scale)*

- *deposit* Material left in a new position by a natural transporting agent such as water, wind, ice, or gravity, or by the activity of man

- *detachment* - The removal of transportable fragments of soil material from a soil mass by an eroding agent, usually falling raindrops, running water, or wind; through detachment, soil particles or aggregates are made ready for transport.

- *enrichment ratio (ER)* - The ratio of a compound's concentration in the eroded soil to the noneroded soil; the same for eroded water flow to the normal water flow.

- *ephemeral gully* - Small channels eroded by concentrated flow that can be easily filled by normal tillage, only to reform again in the same location by additional runoff events.

- *erodibility* - (i)The degree or intensity of a soil's state or condition of, or susceptibility to, being erodible. (ii) The K factor in the Universal Soil Loss Equation. See also **erosion** USLE.

- *erodible* - Susceptible to erosion.

- *erosion classes* - A grouping of erosion conditions based on the degree of erosion or on characteristic patterns. (Applied to accelerated erosion; not to normal, natural, or geological erosion.) Four erosion classes are recognised for water erosion and three for wind erosion.

- *erosion potential (EI)* - A numerical value expressing the inherent erodibility of a soil or maximum potential erosion. In the Universal Soil Loss Equation (under clean tillage, up and down slope) EI = $RKLS/T$.

- *erosional surface* - A land surface shaped by the erosive action of ice, wind, or water; but usually as the result of running water.

- *erosive velocity* - Velocity of the erosive agent necessary to cause erosion.

- *erosivity* - The measured or predicted ability of water, wind, gravity, or any other erosion agent, to cause erosion.

- *furrow erosion* - The erosion that occurs with the process of furrow irrigation.

- *furrow mulching* - The practice of placing straw or other mulch materials in irrigation furrows to increase infiltration and reduce erosion.

- *geological erosion* - The normal or natural erosion caused by natural weathering or other geological processes. Synonymous with natural erosion over a geologic time frame or large geographic area.

- *grassed waterway* - A natural or constructed waterway, usually broad and shallow, covered with grasses, used to conduct surface water from or through cropland.

- *gully* - A channel resulting from erosion and caused by the concentrated but intermittent flow of water usually during and immediately following heavy rains. Deep enough (usually >0.5 m) to interfere with, and not to be obliterated by, normal tillage operations.

- *gully erosion* - The erosion process whereby water accumulates and often recurs in narrow channels and, over short periods, removes the soil from this narrow area to considerable depths, often defined for agricultural land in terms of channels too deep to easily ameliorate with ordinary farm tillage equipment, typically ranging from 0.5m to as much as 25 to 30m.

- ***headcut*** - Small abrupt elevation drops (1-5 cm) on the floor of rills or irrigation furrows that result in accelerated erosion as they undercut the rill floor and migrate upstream.
- ***hydroseeding*** - The technique of spraying a slurry of seeds, tackifier, mulch and fertiliser on bare ground (often steeply sloping) to hold soil in place while awaiting germination of a ground cover.
- ***interrill erosion*** - The removal of a fairly uniform layer of soil on a multitude of relatively small areas by splash due to raindrop impact and by sheet flow.
- ***irrigation-induced erosion*** - Erosion caused by irrigation, in which water quality, decreasing downslope runoff and rapid hydration in the furrow runoff stream affect the expression of erosion processes.
- ***natural erosion*** - Wearing away of the earth's surface by water, ice, or other natural agents. under natural environmental conditions of climate, vegetation, etc., undisturbed by man. See also **erosion**, *geological erosion*.
- ***rainfall erosivity index*** - A measure of the erosive potential of a specific rainfall event. In the Universal Soil Loss Equation it is defined as the product of two rainstorm characteristics: total kinetic energy of the storm times its maximum 30-minute intensity.
- ***rill*** - A small, intermittent water course with steep sides; usually only several centimetres deep
- ***rill erosion*** - An erosion process on sloping fields in which numerous and randomly occurring small channels of only several centimetres in depth are formed; occurs mainly on recently cultivated soils. See also **erosion**, *rill*.
- ***saltation*** - A particular type of momentum-dependent transport involving: (i) The rolling, bouncing or jumping action of soil particles 0.1 to 0.5 mm in diameter by wind, usually at a height <15 cm above the soil surface, for relatively short distances. (ii) The rolling, bouncing or jumping action of mineral grains, gravel, stones, or soil aggregates effected by the energy of flowing water. (iii) The bouncing or jumping movement of material downslope in response to gravity.
- ***saltation flux*** - The rate of saltation per unit area.
- ***sheet erosion*** - The removal of a relatively uniform thin layer of soil from the land surface by rainfall and largely unchanneled surface runoff (sheet flow).
- ***shelter belt*** - See **erosion**, *windbreak*.
- ***slope length*** The distance along a slope subject to interrupted overland flow, from the beginning of overland flow to where deposition starts, or where flow enters well defined channels, such as gullies. (B)
- ***soil loss tolerance (T value)*** - (i) The maximum average annual soil loss that will allow continuous cropping and maintain soil productivity without requiring additional management inputs. (ii) The maximum soil erosion loss that is offset by the theoretical maximum rate of soil development which will maintain an equilibrium between soil losses and gains.
- ***splash erosion*** - The detachment and airborne movement of small soil particles caused by the impact of raindrops on soils.
- ***suspension*** - The containment or support in fluid media (usually air or water) of soil particles or aggregates, allowing their transport in the fluid when it is flowing. In fluids at rest, suspension follows Stoke's Law. In wind this usually refers to particles or aggregates <0.1 mm diameter through the air, usually at a height of >15 cm above the soil surface, for relatively long distances.
- ***tillage erosion*** - The down slope displacement of soil through the action of tillage operations.
- ***transport*** the part of the erosion process that involves movement of soil particles away from the point of detachment
- ***tunnel erosion*** - The formation of natural pipes in soil or other unconsolidated deposits by eluviation or other processes of differential subsurface flow.
- ***universal soil loss equation (USLE)*** - An equation for predicting, A, the average annual soil loss in mass per unit area per year, and is defined as, $A = RKLSCP$, where R is the

rainfall factor, *K* is the soil erodibility factor, *L* is the length of slope, *S* is the percent slope, *C* is the cropping and management factor, and *P* is the conservation practice factor.

- *wind erosion equation* - An equation for predicting E, the average annual soil loss due to wind in mass per unit area per year, and is defined as *E=IKCLV*, where *I* is the soil erodibility factor, *K* is the soil ridge roughness factor, *C* is the local climatic factor, *L* is the field width, and *V* is the vegetative factor.

- *windbreak* - A planting of trees, shrubs, or other vegetation, usually perpendicular or nearly so to the principal wind direction, to protect soil, crops, homesteads, roads, etc., against the effects of winds, such as wind erosion and the drifting of soil and snow.

field capacity - The water content of a soil after it has drained a few days following complete saturation

filter strip - A strip or area of vegetation for removing sediment, organisms, nutrients and chemicals from runoff (B)

flooding - Accumulation of large amounts of runoff on the landscape as a result of rainfall in excess of the soil's ability to drain water from the landscape before extensive inundation and ponding occurs

flow velocity (of water in soil) - The volume of water transported per unit of time and per unit of cross-sectional area normal to the direction of water flow.

geological erosion - See **erosion**, *geological erosion*.

ground water - Subsurface water in the zone of saturation

hydraulic conductivity - See soil water

hydraulic gradient (soil water) - A vector (macroscopic) point function that is equal to the decrease in the hydraulic head per unit distance through the soil in the direction of the greatest rate of decrease. In isotropic soils, this will be in the direction of the water flux.

hydraulic roughness - The roughness of a channel bed or banks (including vegetation) causing retardance of flow, or flow resistance (B)

infiltrability - The flux (or rate) of water infiltration into soil when water at atmospheric pressure is maintained on the atmosphere-soil boundary, with the flow direction being one-dimensionally downward.

infiltration - The entry of water into soil.

infiltration capacity - See **infiltration flux**.

infiltration flux (or rate) - The volume of water entering a specified cross-sectional area of soil per unit time [$L\ t^{-1}$].

infiltration, cumulative - See **cumulative infiltration**.

interception - See **precipitation interception**

irrigation-induced erosion - See **erosion**, *irrigation-induced erosion*.

LAI - A canopy parameter defined as leaf surface area per unit of ground area

laminar erosion - The removal of a more or less horizontal layer of soil material from the surface of land by erosion (it is similar to surface erosion) (B)

lateral erosion - Erosion of the sides of a channel by streamflow (B)

leaching - The removal of soluble material from soils by percolating waters

linear erosion - Erosion in the lines of concentrated flow, such as in master rills, gullies (B)

litter - Loose organic materials at the surface layer is not in an advanced stage of decomposition, usually freshly fallen leaves and needles.

macro pore flow - The tendency for water applied to the soil surface at rates exceeding the upper limit of unsaturated hydraulic conductivity, to move into the soil profile mainly via saturated flow through macro pores, thereby bypassing micro pores and rapidly transporting any solutes to the lower soil profile. See also **preferential flow**.

MAP

- *large-scale* - A map having a scale of 1:10.000 or larger.

- *medium-scale* - A map having a scale from 1:10.000, exclusive, to 1:100.000, inclusive.

- *small-scale* - A map having a scale smaller than 1: 100.000.

map unit, soil - (i) A conceptual group of one to many delineations identified by the same name in a soil survey that represent similar landscape areas comprised of either: (1) the same kind of component soil, plus inclusions, or (2) two or more kinds of component soils, plus inclusions, or (3) component soils and miscellaneous area, plus inclusions, or (4) two or more kinds of component soils that may or may not occur together in various delineations but all have similar, special use and management, plus inclusions, or (5) a miscellaneous area and included soils. (ii) A loose synonym for a delineation.

mass flow (nutrient) - The movement of solutes associated with net movement of water.

mass movement - Dislodgement and down slope transport of soil and rock material as a unit under direct gravitational stress. The process includes slow displacements such as creep and solifluction, and rapid movements such as landslides, rock slides, and falls, earth flows, debris flows, and avalanches. Agents of fluid transport (water, ice, air) may play an important, if subordinate role in the process.

micro-depression - A small deepening in the surface to store water

offsite effects - All damages and influences by loads caused by erosion outside the field

onsite effects - All erosion damages on the field

overland flow - The part of rainfall that flows off at the surface of land in non-concentrated flow or in temporary very shallow channels, including rills (B)

partial area - The part of a catchment which produces runoff

pediment - A gently sloping, erosional surface developed at the foot of a receding hill or mountain slope. The surface can be bare or it may be thinly mantled with alluvium and colluvium in transport to the adjacent valley

pedisediment- A layer of sediment, eroded from the shoulder and back slope of an erosional slope, that lies on and is, or was, being transported across a pediment.

penetration resistance - The force per unit area on a standard cone necessary for penetration by the cone

percolation, soil water - The downward movement of water through soil. Especially, the downward flow of water in saturated or nearly saturated soil at hydraulic gradients of the order of 1.0 or less.

preferential flow - The process whereby free water and its constituents move by preferred pathways through a porous medium. Also called bypass flow.

precipitation interception - The stopping, interrupting, or temporary holding of descending precipitation in any form by mulch, a vegetative canopy, vegetation residue or any other physical barrier.

prerill - Very shallow rills or shallow microchannels, up to about 3 cm deep (often formed by harrows)

rainfall erosivity index - See **erosion**, *rainfall erosivity index*.

rainfall interception - See **precipitation interception**.

relief - The relative difference in elevation between the upland summits and the lowlands or valley of a given region.

runoff - That portion of precipitation or irrigation on an area which does not infiltrate, but instead is discharged from the area. That which is lost without entering the soil is called *surface runoff*. That which enters the soil before reaching a stream channel is called *ground water runoff or seepage flow* from ground water. (In soil science *runoff* usually refers to the water lost by surface flow; in geology and hydraulics *runoff* usually includes both surface and subsurface flow.)

SDR - A measure of the sediment actually reaching a stream or lake expressed as the quantity of material reaching a specific point in a drainage system divided by the quantity actually eroded in the catchment above the same point. (B)

sediment - Transported and deposited particles or aggregates derived from rocks, soil, or biological material

sedimentation - The process of sediment deposition.

sealing - See **surface sealing**

sheet erosion - See **erosion**.

slope aspect or exposition - The direction of slope
slope steepness – The inclination of a slope

SLOPE

back slope - The hill slope position that forms the steepest, and generally linear, middle portion of the slope. In profile, back slopes are bounded by a convex shoulder above and concave foot slope below.
foot slope - The hill slope position that forms the inner, gently inclined surface at the base of a slope. In profile, foot slope s are commonly concave and are situated between back slope and a toeslope.
nose slope - The projecting end of an interfluve , where contour lines connecting the opposing side slopes form a convex curves around the projecting end and lines perpendicular to the contours diverge downward. Overland flow of water is divergent.
shoulder - The hill slope position that forms the uppermost inclined surface near the top of a slope. If present, it comprises the transition zone from back slope to summit. This position is dominantly convex in profile and erosional in origin.
toe slope - The hill slope position that forms a gently inclined surface at the base of a slope. Toeslopes in profile are commonly gentle and linear.

soil detachment - The removal of transportable fragments of soil material from a soil mass by an erosive agent (rain, flowing water, wind)

SOIL MAP

soil map - A map showing the distribution of soils or other soil map units in relation to the prominent physical and cultural features of the earth's surface. The following kinds of soil maps are recognised: **soil map, detailed** - A soil map on which the boundaries are shown between all soils that are significant to potential use as field management systems. The scale of the map will depend upon the purpose to be served, the intensity of land use, the pattern of soils, and the scale of the other cartographic materials available.
- *detailed reconnaissance* - A reconnaissance map on which some areas or features are shown in greater detail than usual, or than others.
- *generalised* - A small-scale soil map which shows the general distribution of soils within a large area and thus in less detail than on a detailed soil map. Generalised soil maps may vary from soil association maps of a county, on a scale of 1 cm = 633 m, to maps of larger regions showing associations dominated by one or more great soil groups.
- *reconnaissance* - A map showing the distribution of soils over a large area as determined by traversing the area at intervals varying from about 1000 m to several kilometres. The units shown are soil associations. Such a map is usually made only for exploratory purposes to outline areas of soil suitable for more intensive development. The scale is usually much smaller than for detailed soil maps.
- *schematic* - A soil map compiled from scant knowledge of the soils of new and undeveloped regions by the application of available information about the soil-formation factors of the area. Usually on a small scale (1:1.000.000 or smaller).

soil compaction - Increasing the soil bulk density, and concomitantly decreasing the soil porosity, by the application of mechanical forces to the soil.
soil hydrophobicity - The tendency for a soil particle or soil mass to resist hydration, usually quantified using the water drop penetration time test.
soil piping or tunneling - Accelerated erosion which results in subterranean voids and tunnels.
soil roughness - The degree of uneveness of the soil surface, related to surface depression storage and resistance to splash and overland flow (B)

soil structure - The combination or arrangement of primary soil particles into secondary units or peds. The secondary units are characterised on the basis of size, shape, and grade (degree of distinctness).

soil water - ***hydraulic conductivity*** - The proportionality factor in Darcy's law as applied to the viscous flow of water in soil, i.e., the flux of water per unit gradient of hydraulic potential. If conditions require that the viscosity of the fluid be divorced from the conductivity of the medium, it is convenient to define the permeability (intrinsic permeability has been used in some publications) of the soil as the conductivity divided by the fluidity of the fluid. For the purpose of solving the partial differential equation of the non steady-state flow in unsaturated soil it is often convenient to introduce a variable termed the soil water diffusivity.

spatial variability - The variation in soil properties (i) laterally across the landscape, or (ii) vertically downward through the soil. splash erosion - See erosion, *splash erosion*.

subsurface flow - Water flow through the soil , usually close to and approximately parallel to the land surface.

surface runoff - See **runoff**.

surface sealing - The deposition by water, orientation and/or packing of a thin layer of fine soil particles on the immediate surface of the soil, greatly reducing its water permeability.

thalwege, pathway – Preferred runoff and erosion path which recognised by land surface morphology (see linear erosion)

through fall - That portion of precipitation that falls through or drips off of a plant canopy.

tile drain - Concrete, ceramic, plastic etc. pipe, or related structure, placed at suitable depths and spacings in the soil or subsoil to enhance and/or accelerate drainage of water from the soil profile.

tillage erosion - See **erosion**, *tillage erosion*.

TILLAGE

- *clean tillage (clean culture, clean cultivation)* - A process of ploughing and cultivation which incorporates all residues and prevents growth of all vegetation except the particular crop desired during the growing season.

- *combined tillage operations* - The simultaneous operation of two or more different types of tillage tools (on the same implement frame) or implements (subsoiler-lister, lister planter, or plough planter) to simplify control or reduce the number of trips over the field.

- *conservation tillage* - Any tillage sequence, the object of which is to minimise or reduce loss of soil and water; operationally, a tillage or tillage and planting combination which leaves a 30% or greater cover of crop residue on the surface.

- *contour tillage* - Performing the tillage operations and planting on the contour within a given tolerance.

- *controlled traffic* - A farming system, including tillage in which the wheel tracks of all operations are confined to fixed paths so that recompaction of soil by traffic (traction or transport) does not occur outside the selected paths.

- *conventional tillage* - Primary and secondary tillage operations normally performed in preparing a seedbed and/or cultivating for a given crop grown in a given geographical area, usually resulting in <30% cover of crop residues remaining on the surface after completion of the tillage sequence.

- *crop residue management* - Disposition of stubble, stalks, and other crop residues by tillage operations. (i) To remove residues from the soil surface (burying); (ii) To anchor residues partially in the surface soil while leaving the residues partially exposed at the surface (mulch tillage); (iii) To leave residues entirely at the soil surface intact or cut into smaller pieces. (Residues may be removed by non tillage methods, i.e., harvesting, burning, grazing, etc.)

- *crop residue management system* - The operation and management of crop land to maintain stubble, stalks, and other crop residue on the surface to prevent wind and water erosion, to conserve water, and to decrease evaporation.

- ***land forming*** - Tillage operations which move soil to create desired soil configurations. Forming may be done on a large scale such as gully filling or terracing, or on a small scale such as contouring, ridging, or bedding.
- ***land planing*** - A tillage operation which redistributes small quantities of soil across the soil surface to provide a more nearly level or uniformly sloped surface.
- ***loosening*** - Decreasing soil bulk density and increasing porosity due to the application of mechanical forces to the soil via tillage.
- ***minimum tillage*** - The minimum use of primary and/or secondary tillage necessary for meeting crop production requirements under the existing soil and climatic conditions, usually resulting in fewer tillage operations than for conventional tillage.
- ***mulch*** - (i) Any material such as straw, sawdust, leaves, plastic film, loose soil, etc., that is spread or formed upon the surface of the soil to protect the soil and/or plant roots from the effects of raindrops, soil crusting, freezing, evaporation, etc. (ii) To apply mulch to the soil surface.
- ***mulch farming*** - A system of tillage and planting operations which maintains a substantial amount of plant residues or other mulch on the soil surface.
- ***mulch tillage*** - Tillage or preparation of the soil in such a way that plant residues or other materials are left to cover the surface; also, mulch farming, trash farming, stubble mulch tillage, plough less farming; operationally, a full-width tillage or tillage and planting combination that leaves >30% of the surface covered with crop residue.

- ***no-tillage (zero tillage) system*** **-** A procedure whereby a crop is planted directly into the soil with no primary or secondary tillage since harvest of the previous crop; usually a special planter is necessary to prepare a narrow, shallow seedbed immediately surrounding the seed being planted. No-till is sometimes practised in combination with subsoiling to facilitate seeding and early root growth, whereby the surface residue is left virtually undisturbed except for a small slot in the path of the subsoil shank.
- ***stubble mulch*** - The stubble of crops or crop residues left essentially in place on the land as a surface cover before and during the preparation of the seedbed and at least partly during the growing of a succeeding crop.
- ***stubble mulch tillage*** - See **tillage**, *mulch tillage*; **tillage**, *plough less farming*.

tile drain - Concrete, ceramic, plastic etc. pipe, or related structure, placed at suitable depths and spacings in the soil or subsoil to enhance and/or accelerate drainage of water from the soil profile.

transport capacity - The ability of runoff to carry soil materials from one point to another

tunnel erosion- see **erosion,** *tunnel erosion*

underground runoff (seepage) - Water that seeps toward stream channels after infiltration into the ground.

unsaturated flow - The movement of water in soil in which the pores are not filled to capacity with water.

vadose or unsaturated **zone** - The aerated region of soil above the permanent water table.

vapour flow - The gaseous flow of water vapour in soils from a moist or warm zone of higher potential to a drier or colder zone of lower potential.

water repellent soil - See soil hydrophobicity, water drop penetration time.

water table - The upper surface of ground water or that level in the ground where the water is at atmospheric pressure.

Water flow at the field scale

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Abstract

In this introductory paper, I try to summarize some major features of water flow at the field scale relevant for the subsequent discussion of P losses. After the definition of the field scale as a hydrologically arbitrary but agronomically essential scale between the plot and the hillslope scale the flow mechanisms at that scale are discussed. It is emphasized that it is crucial to understand the interplay between the spatial patterns of flow paths and the pools of mobile solutes in the soil. The differences between surface and subsurface flow are discussed as well as the main factors enhancing surface runoff. Despite the substantial differences between flow in the soil and on the soil surface I argue that it is important to treat the two processes together because they are mutually dependent and the flow path out of a field may well be a sequence of subsurface and surface flow. In the last part, the spatial and the temporal heterogeneity are discussed. The paper concludes with the proposition to compare the P-losses in different areas of Europe based on conceptual models containing the most important processes and controlling factors for different regions.

Key words: heterogeneity, subsurface flow, overland flow, drainage systems

1. Introduction

Water is the main agent of transport of all P-forms from fields into waters. To understand P-losses a proper knowledge of the water fluxes is needed. In the following I try to summarize some major features of water flow at the field scale relevant for the subsequent discussion of P losses. The focus is on experimental field-work and the conceptual model that follow from this kind of research. This shall be a background for evaluating the actual state-of-the-art in assessing and modeling P losses at the field scale.
Modeling is an essential part of scientific work. However, the notion of a model is not always unambiguously used. In the following I use "model" for a well-defined mental representation of a natural phenomenon. We can distinguish between different levels of models:

- conceptual models
- mathematical models
- simulation models.

Conceptual models represent the phenomenon of interest by the structures of the entire system, the main processes occurring and the relevant boundary and initial conditions (Tsang, 1991). All mathematical and numerical models rely on an underlying conceptual model (even if this model is not formulated explicitly). In a mathematical model the quantities contained in the conceptual model, their relationships and the processes are written down in a mathematical form (e.g., partial differential equations). In soil physics or hydrology these mathematical models are generally far too complex to be solved analytically. Therefore, they are often translated into numerical approximations that can be solved as a numerical algorithm.
Models can be looked at as (complex) scientific hypotheses. Applying a simulation model implies therefore that one accepts the underlying hypotheses to be true or to come close enough to reality to be useful. However, as scientific hypotheses models never can be proven to be correct, at most they can be validated properly. This means that a model could not be rejected against a null-hypothesis for many different situations. If the conditions for which the models are used are within the range used for validation it is reasonable to accept

the model. If a model fails in a validation process, there are two basically different possibilities:

- parameterization problems: The model may be right, but its output is wrong due to erroneous parameters. In soil physics and hydrology it is often a major problem to obtain correct parameters;
- the underlying conceptual model is wrong.

If the model is wrong, the model results will in general not be in accordance with independent measurements. However, the effects of erroneous parameters and model errors may compensate each another. If one uses inverse parameter estimation procedures, it may be possible to fit a wrong model to a measured output with wrong parameters. Instructive examples are given by Jury and Roth (1990, p. 43) and by Grayson and Moore (1992). It may also turn out during an inverse parameter estimation that no parameter set can describe the observed field results. This is strong evidence for the underlying model to be false or incomplete (Schmied *et al*., 2000).

In our context it will be of special importance to test whether the conceptual models underlying existing simulation models are in agreement with the findings of experimental field work. Therefore, this article concentrates on demonstrating the complexity involved in water and solute transport at the field scale. This shall be used as a background against which one may judge:

- the agreement between the conceptual models of existing simulation models and those resulting from field studies
- for which conditions the simulation models may be applied successfully
- the main scientific problems related to measure and model P losses at the field scale.

2. The European context

Within this COST action 832, it should be kept in mind that there exists a large variability within Europe concerning the factors influencing water flow and P losses. The area of agricultural production covers an area of almost 30° of latitude (Crete, 35°N to about 63°N at the northern end of the Gulf of Bothnia) with climatic conditions varying from Mediterranean to almost arctic and a large variability in soil conditions (see Table 1). The agricultural practice is also highly differentiated according to the natural and the socio-economic situations. For example, we can distinguish regions of intensive dairy farming like Denmark with predominant grassland cultivation and regions dominated by arable land. Subsurface drainage systems as important management tools are found mainly in the northern parts of the continent according to the soil and climatic conditions (Robinson and Rycroft, 1999), whereas the risk of soil erosion is in general much higher in the Mediterranean region due to more intense rainfall, often sparse vegetation and steep terrain.

3. Characterization of the field scale

Because transport is dominated by different factors at different scales it is useful to start with a description how the field differs from the (generally) larger hillslope (or subcatchment) and catchment scale as well as from the smaller plot scale. From a hydrological point of view hillslopes and catchments are natural units in the sense that they are delimited by non-arbitrary boundaries (even if there may be uncertainty in locating them always precisely in space (and time)) for some cases (Baveye and Boast, 1999). They are separated by no-flow boundaries and the flow processes within a single unit are independent of the processes in the neighboring ones. In contrast, fields and plots are arbitrarily delineated (from a hydrological point of view), and the fluxes within a field or plot are generally influenced by the surrounding areas. From an agronomic perspective however, the field scale is a logic one since it is at this scale that a certain portion of the landscape is managed in a homogenous way.

Table 1. Soil types in Europe. After FAO (1993).

Soil type	Area [km^2]	[%]
Podzols	2136240	21.5
Podzoluvisols	1616840	16.2
Cambisols	1572880	15.8
Luvisols	1426580	14.3
Leptosols	648360	6.5
Calcisols	566570	5.7
Kastanozems	555980	5.6
Fluvisols	402500	4.0
Regosols	268480	2.7
Gleysols	176410	1.8
Chernozems	98551	1.0
Histosols	32824	0.3
other	456710	4.6

Plots are the most arbitrary units in our context. They are delineated and located in the landscape mainly based on practical aspects related to the experimental goals and methodological possibilities. Nevertheless, scientifically the plot scale is a very important scale allowing to study processes inaccessible at larger scales but relevant for entire fields, hillslopes or catchments. One of the large problems pertinent to this scale is the question how to relate results to fields or even larger units.

This scaling problem is closely linked to the spatial variability of soil properties and water fluxes. The heterogeneity at the plot scale is due to small-scale variability in the pore structure. At the field scale, additional factors may dominate the spatial variability. Apart from a natural random heterogeneity there may exist deterministic trends (e.g., due to topography) of soil properties within fields that are not relevant at the plot scale. Technical installations like subsurface drains also contribute to the artificial, deterministic variability that has to be considered at the field scale but can often be neglected at the plot scale.

Going from the field to the hillslope or catchment scale new factors get relevant. The position in the landscape may strongly influence the runoff behavior due to the differences in soil moisture status or due to changes of the soil type along a catena. This effect may also exist for fields but is much more important for hillslopes covering the entire continuum from the hill-crest to the lower parts along the river. The human impact causes also spatial variability not existing at the field scale by fields managed by different farmers. To understand the response of entire hillslopes or catchments one has to consider also that the out-flowing water from single fields may be affected by artificial channelisation or remediation measures like buffer belts (Haycock *et al*., 1997). Such factors only come into play at scales larger than fields. In erosion research this aspect is well known as the problem of the delivery ratio linking the on-site erosion rates to the sediment yields at the catchment scale (Walling, 1990). Recent publications show that the problems still remains to be settled (Trimble and Crosson, 2000).

To conclude this section, I would like to mention another important difference between the plot and field scale: their ratios between the lateral, horizontal extension and depth. For the plot scale this ratio is in many cases in the order of about one and the main flow direction is vertical. In contrast, for the field-scale this ratio is in the order of about 10 to 100 or even larger. For transport into surface waters lateral transport is the dominant flow direction.

4. Flow mechanisms at the field scale

The classical scheme of flow processes at the field and hillslope scale differentiates between surface and subsurface runoff. They differ in many important aspects like in the travel times or the different parts of the soil getting into contact with the flowing water. The physics of transport is also quite different. Subsurface flow is mainly laminar due to the restricted size of most pores and can be described by Darcy's law (Darcy, 1856) except for very large pores like soil pipes. In contrast, surface runoff may cover the entire range from laminar sheet flow to fully turbulent rill flow (Gerits *et al*., 1990) and is described by the Saint Venants equation (Moore and Foster, 1990). Due to these differences between surface and subsurface processes it is often necessary to use different theoretical and experimental approaches. This may create problems of compatibility for experimental and modeling purposes. The adequate temporal and spatial resolution for measuring and model calculations may be quite different. Despite the physical differences between surface and subsurface flow processes a comprehensive analysis of the transport phenomena at the field scale shows that they are closely linked. In the following I try to give an overview on the dominant flow paths at the field scale and to show how surface and subsurface flow may be coupled.

As mentioned above, lateral transport is the main flow direction at the field scale if we are concerned with surface waters. Therefore I focus on saturated water flow, which dominates lateral transport. We may group different flow systems according to the temporal scale of the lateral flow process and according to the depth of the lateral flow paths into two broad categories: continuous and event-based lateral transport. For continuous lateral flow to exist a persistent ground water table has to be present. Precipitation can infiltrate completely through the vadose zone feeding the groundwater. As well in the vadose (or unsaturated) soil as in the saturated subsoil the hydraulic conductivity has to be sufficiently large to convey all precipitation water downwards and laterally towards the open channel. In general, continuous lateral transport occurs in permeable subsoils.

Event-based lateral transport occurs when the hydraulic conductivity for vertical infiltration and or lateral saturated transport in the subsoil is limited. If the vertical hydraulic conductivity at a given depth of the unsaturated zone is too small a perched water table builds up causing lateral transport. Sometimes the thin compacted plow pan is sufficient to cause saturated lateral flow in the topsoil (e.g., Fleige and Horn, 2000).

If infiltration is limited right at the soil surface overland flow occurs. There are several causes limiting infiltration and inducing surface runoff:

- *High intensity rainstorms*. If the rain intensity exceeds the infiltration capacity of the soil surface runoff occurs. This process was the basic mechanism Horton proposed in the early 30's to explain storm flow (Horton, 1933). Under European conditions this is probably not the main factor causing surface runoff in undisturbed soils.
- *Saturated soil conditions*. If the soil is already saturated prior to a rain event all the additional water has to flow on the surface. This mechanism causes surface runoff to occur mainly in the wet, lower parts of a field.
- *Surface sealing*. Especially on arable land with poor soil cover the plash effect of rain-drops may destroy the soil structure causing a sealing of the soil surface. With its dense structure (e.g., Römkens *et al*., 1990) the infiltration rates decreases strongly enhancing surface runoff. Sealing may also be caused by manuring or by the crop residues left on the fields (e.g., Bischoff and Herrmann, 1984).
- *(Temporal) Hydrophobicity*. If soil dries out strongly its physico-chemical surface properties change and it may get water-repellent. This is observed on many different soils (Wallis and Horne, 1992). It can induce finger flow in the soil and reduce the infiltration capacity to only about one percent of the capacity under wettable conditions. Therefore hydrophobicity may also cause surface runoff and severe erosion (Osborn *et al*., 1964). In Europe, it has been intensively studied for sandy soils under Dutch conditions (Dekker and Ritsema, 1996) but it is also known from other regions (e.g., Scherrer, 1997).

- *Frozen soil*. Soils freeze regularly in many agricultural areas of Europe reducing the infiltration capacity of a soil substantially. Hence, melting snow or rain will often flow on the surface. This can cause erosion or transport of solutes that were applied on the frozen soil or stem from a tiny layer of unfrozen soil above the frozen bulk soil. An example of the relevance of freezing on the hydrological regime is given in Øygarden (1997).
- *Soil compaction*. Grazing animals or management of machinery may cause surface compaction (Fleige and Horn, 2000).

The quantitative importance of surface and subsurface flow depends on soil conditions, climate, topography but also on soil cover and management practices. The relative importance of the two main flow paths varies within broad boundaries. Table 2 summarizes some results from the literature. It gives an idea about the range of the relative flow volumes without pretending to be a representative overview.

The depth at which lateral transport occurs, determines to a certain degree the travel time of the water and the solutes from the soil surface to the outflow from the field. Overland flow seems to interact with only the topmost mm to cm of the soil (Ahuja, 1986; Zhang *et al*., 1997), and the travel times are very short. With increasing depth of the vadose zone where transport is mainly vertical the mean travel time increases. However, it is not only the depth of the unsaturated zone that determines the travel time for the vertical transport. In many field soils it has been observed that the flow paths are highly variable in space often causing fast transport of water and solutes through a very limited portion of the soil volume. Under such preferential flow conditions, the travel time distributions typically show a double peak behavior. There is mostly a small first and a second large peak. A smaller portion of the water passes through the profile in a very short time of minutes to few hours. Most of the water flows through the soil matrix with much longer residence times of weeks to even years. Preferential flow has been shown to be widespread in very different soils under various climatic conditions (e.g., Flury *et al*., 1994). It may be caused by biopores or cracks (Beven and Germann, 1982), wetting front instabilities causing fingering (Raats, 1973) or by textural changes causing funneled flow (Kung, 1990a; Kung, 1990b).

Many of the physical structures like worm-holes or cracks extend mainly in vertical direction and cannot cause preferential flow in lateral direction. However, there are also examples reported in the literature, where fast lateral transport was observed (Steenhuis *et al*., 1988). One may distinguish between two relevant soil structures: networks of laterally connected cracks extending into the depths of groundwater and so-called soil pipes. In heavy clay soils, it has been observed that cracks may extend to considerable depths and well below the groundwater table. At least in some cases these cracks are sufficiently connected in lateral directions to allow for substantial water flow (Inoue, 1993; Ruland *et al*., 1991). Soil pipes are products of subsurface erosion (Bryan and Jones, 1997). They are especially important in organic soils of humid uplands, dry badlands and degraded rangelands. In Europe, evidence for soil piping in agricultural areas is reported for Spain (García-Ruiz *et al*., 1997).

Whereas vertical preferential flow has been investigated very intensively over the last 20 years lateral preferential flow received much less attention. One obvious reason for this is the relative ease to study vertical preferential flow at the plot scale compared to the experimental difficulties encountered by research on lateral transport at the field scale. However, it should be kept in mind that the observation of vertical preferential flow at a given site does not imply the occurrence of lateral preferential flow. Further, one should notice that a fast hydrological response does not imply fast water and solute transport neither (Sinaj *et al*., 2002). Many studies have shown that even during peak flow conditions most of the water discharged by subsurface drainage systems or open streams is so-called old or pre-event water. Preferential flow may be involved in this context as the transport mechanisms conveying substantial amounts of water quickly through the unsaturated soil increasing the water table, forcing the old water to be pushed out downstream by a steeper hydraulic gradient.

Table 2. Flow partitioning between subsurface and surface runoff

Land use (country)	Texture	Slope [%]	Drainage [% precipitation]	Surface runoff [% precipitation]	Special observations	Reference
Arable land (Finland)	Clay	0 - 1.5	5 - 54 (total flow yr^{-1})	6 - 53 (total flow yr^{-1})	large variability due to changes in the drainage system	Turtola & Paajanen (1995)
Grassland (Switzerland)	Loam	10 - 18	-	3.0 - 4.7	flow weighted average for 16 events, no drainage	von Albertini *et al.* *(1993)*
Arable land (Norway)	Silty clay loam	4 - 8.5	7 - 39 (total flow yr^{-1}) median: 18	14 - 31 (total flow yr^{-1}) median: 25	influence of frozen soil	Øygarden *et al.* (1997)
Arable land (Germany)	Loamy sand to sandy loam	7 - 17	-	0.6 - 1.3	undisturbed field soil	Fleige & Horn (2000)
				43.2 - 49.9	traffic rut	
Arable land (Finland)	silty / heavy clay	4	10 - 18	10 - 12	surface runoff incl. snow melt	Paasonen-Kivekäs *et al.* (1999)
Arable land (USA)	Loam	0 - 4	-	0 - 3.4	rainfall surface runoff	Ginting *et al.* (2000)
			-	0.9 - 3.1	snow melt surface runoff	
Arable land (Japan)	Heavy clay	-	51.5 - 53.5	5.4	annual values	Inoue (1993)
			11.4 - 90.0	0 - 40.7	event values	
Arable land	Heavy clay	0.6 - 1.5	21 - 26	17 - 42	annual values	Turtola & Jaakola (1995)
Grassland (Finland)			15 - 19	22 - 35	annual values	

By the mechanism of preferential flow most of the sorbing soil matrix is by-passed. This is one of the mechanisms explaining how strongly sorbing solutes like P or pesticides may get transported from the soil surface to the groundwater. Based on the assumption of well-mixed flow conditions as expressed by the convection-dispersion equation this is almost excluded under most conditions.

The flow paths within a field are not just influenced by the hydraulic conductivities of different horizons or the connectivity of macropores. In many agricultural soils the hydraulic conditions are substantially influenced by artificial drainage systems. They may change the hydraulic response of a field and the relevant flow paths to a large degree. Due to the lowered water table they may reduce surface runoff (Robinson and Rycroft, 1999). But drainage systems are not only large preferential pathways in lateral directions. Due to their field installation and often artificial backfill they are also large vertical preferred flow paths and may redirect surface runoff or lateral flow in the plough layer into subsurface drains. The most obvious example is the draining of ponded depression into tile-drains (Moore and Larson, 1980). But mole drains and the trench above deeper drainage systems may have similar effects (Addiscott *et al*., 2000; Øygarden *et al*., 1997; Stamm, 1997; Stamm *et al.*, 2002). The relevance of the drainage system on the hydrology of a field is also demonstrated by the changes in the ratio of surface runoff to tile flow as observed by Turtola and Paajanen (1995) after changing the drainage system (Fig. 1).

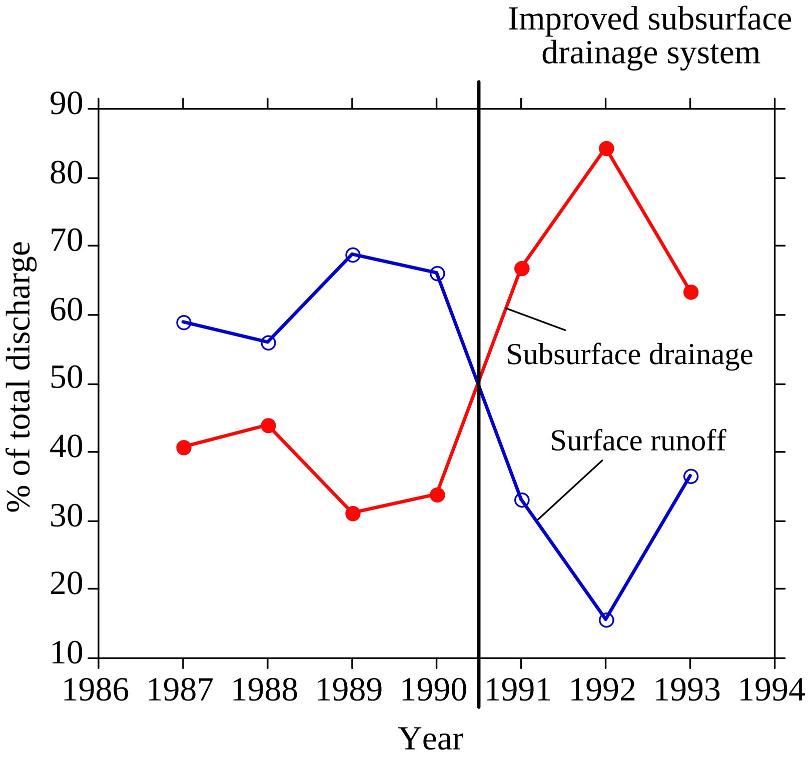

Figure 1. Effect of an improved drainage system on discharge partitioning between surface and drainage runoff (data from Turtola and Paajanen (1995)).

In order to understand the solute losses from fields it is not sufficient to have a proper knowledge on the relevant flow paths and transport processes. The crucial point to understand is how the relevant flow paths are coupled in space and time to the pools of mobile solutes, colloids or particles. Two examples shall demonstrate how the water quality is determined by the interplay between flow paths and pools of mobile nutrients.

In a field study on drainage water in grassland soils we have observed that the P concentrations increased always with discharge during flow events (Stamm *et al*., 1998) whereas the nitrate concentration normally decreased (Stamm *et al*., 1995). This result can be explained by the different position of the pools of mobile P and nitrate in the profile. Due to the high sorption capacity of the loamy soil matrix high concentrations of mobile P were limited to the topsoil receiving substantial amounts of surplus P in the form of slurry and manure. Hence, an increase in P concentration occurred during high flow periods due to fast transport of P-enriched water from the topsoil down to the tile drain. In contrast, nitrate as a mobile, non-sorbing anion was leached through the entire profile and normally, the topsoil is not the main pool of nitrate. Hence, along the fast flow paths, the water normally did not get into contact with pools of high nitrate concentrations and preferential flow caused a decrease of the nitrate concentration during high flow periods.

However, the relationship between flow rate and solute concentration is not specific for a given solute but depends on site-specific bio-geochemical conditions. In wet soils where nitrate gets denitrified in the lower parts of the profile and where the nitrate pool is mainly in the vicinity of the macropores of the topsoil due to atmospheric deposition, fertilization or mineralisation, the nitrate losses may be strongly connected to preferential flow (Hagedorn *et al*., 1999).

Based on this overview on the flow paths at the field scale I would like to draw some conclusions.

- Although often investigated separately in field experiments and often not included in the same simulation models subsurface and surface flow are closely coupled and can hardly be understood one without the other. For example, it has been demonstrated that the flow volume of surface and subsurface runoff may be dependent on each another (Robinson and Rycroft, 1999). Furthermore, the traditional separation between the two flow mechanisms can be quite arbitrary. In certain occasions, water leaving a field as subsurface flow was transported at or at least close to surface within the field. Hence, instead of having two alternative flow-paths there may be a sequence of both.

- One should recognize that drainage systems impose special, spatially defined boundary conditions to the flow processes in the undisturbed soil in-between. The often expressed belief subsurface drains were ideal measuring devices for transport into shallow groundwater (e.g.,Lennartz *et al*., 1999; Villholth *et al*., 1998) neglects that the transport behavior observed at the drainage outlet is the combined effect of the soil properties and the characteristics of the drains. In this context it should be remembered that there are different drainage systems like shallow mole or deep pipe drains that may influence the hydrology of a soil quite differently (see below). Therefore, for modeling purposes it is not sufficient to parameterize the soil properties properly but one has to consider the site specific drainage properties as well.

- To understand the export behavior of a field it is not sufficient to know the flow paths of water. It is essential to understand the spatial and temporal coupling of flow paths and the solute pools.

5. Influence of heterogeneity on flow processes

Precipitation falling on a given field encounters mostly a very heterogeneous flow system. Spatial heterogeneity is an important aspect but variability is even more complex in that important soil properties may change over time scales relevant for practical or experimental purposes.

5.1 Spatial heterogeneity

It is useful to separate spatial heterogeneity into a deterministic and random part. The deterministic heterogeneity can be explained by factors like topography, texture or management practices. In contrast, the random part of heterogeneity cannot be inferred from other quantities. Furthermore, it should be recognized that part of the heterogeneity is due to natural variability, but human impact may also contribute substantially.

The deterministic variability may be due to natural factors like topography or soil type. For surface runoff or erosion topography is the major controlling factor since it directly determines the flow direction on the surface. Often, the same holds for subsurface flow, causing depressions to be especially wet. Since soil-forming processes are strongly influenced by the water regime soil properties vary frequently according to the topographical position. In a classical way this is expressed by the catena principle. A less obvious relationship between topography and soil properties was found by Zehe and Flühler (2001) for earthworms in a German loess area. The worm abundance was correlated with the position within the hillslope. Higher densities were observed in the wetter colluvium areas enhancing the tendency for preferential flow.

Agricultural management causes also spatial variability in a deterministic way. As mentioned in the previous section, subsurface drainage systems may have a large influence on preferential flow by intersecting and draining macropores in a restricted area. This has been recently demonstrated by Shipitalo and Gibbs (2000) by injecting smoke into a drainage system. The soil surface connected by preferred flow paths to the tile drain was only a narrow band of about one meter width. We have found similar results in a grassland soil (Stamm, 1997; Stamm *et al.*, 2002). This means that the hydrological role of preferred flow paths depend on their connectivity to subsurface drains. A few studies have also demonstrated that the backfill material may be an important flow path for water and solutes into the subsurface drainage systems (Øygarden *et al*., 1997). Chow *et al*. (1993) have reported that with natural soil used as backfill material the hydraulic properties were persistently altered above the drains. For mole drains it is reported that the neighboring soil is changed as well (Schroeder, 1968. p. 286).

Wheel traffic due to agricultural management is a second important factor causing spatial heterogeneity. On arable land, the hydraulic properties often vary according to their position as traffic lines, row or interrow areas. Compaction affects the infiltration behavior into soils (Kulli *et al*., 2000) and may enhance surface runoff or interflow on the plough pan (Fleige and Horn, 2000).

Apart from the deterministic variability many soil properties exhibit a strong random spatial heterogeneity. The hydraulic properties belong to the quantities varying most and the variability at the field scale can be enormous. As can be seen from Tab. 3, a mean value may be almost meaningless given the large coefficients of variation.

In contrast to classical statistical problems the data are not independent but normally show spatial autocorrelation. Therefore, special methods, mostly taken from geostatistics, are needed to deal with this kind of data (e.g., Cressie, 1991). The correlation length for different soil properties may differ substantially. For soil hydraulic properties they may be correlated over fairly short distances of few meters only, whereas chemical properties like organic matter content tend to have longer spatial dependences of up to several hundred meters (Mulla and McBratney, 2000).

Table 3. Spatial variability of some soil properties.

Properties	Coeff. of variation (%)	Sample size	Study area (ha)	References
Physical properties				
Sand content	55	0.34 dm^3	150	Nielsen *et al*. (1973)
	7	-	0.19	Wagenet (1981)
	49	-	-	Coelho (1974)
Silt content	27	0.34 dm^3	150	Nielsen *et al*. (1973)
	12	-	0.19	Wagenet (1981)
	22	-	-	Coelho (1974)
Clay content	23	0.34 dm^3	150	Nielsen *et al*. (1973)
	7	-	0.19	Wagenet (1981)
	18	-	-	Coelho (1974)
Bulk density	7	-	0.19	Wagenet (1981)
	11	-	-	Coelho (1974)
Saturated hydraulic conductivity	60 - 106	6.5 m^2	150	Nielsen *et al*. (1973)
	52	0.09 m^2	0.19	Wagenet (1981)
	147	0.11 m^2	-	Coelho (1974)
Unsaturated hydraulic conductivity	106 - 452	6.5 m^2	150	Nielsen *et al*. (1973)
Transport				
Drainflow	33 - 55	0.24 ha	5	Addiscott *et al*. (2000)
TP losses	36 - 85	0.24 ha	5	Addiscott *et al*. (2000)
MRP losses	50 - 60	0.24 ha	5	Addiscott *et al*. (2000)
Cumulative infiltration	25	0.09 m^2	-	Starr (1990)
Chemical properties			-	
pH	2 - 15	-	-	Mulla & Bratney (2000)
Organic matter content	21 - 41	-	-	Mulla & Bratney (2000)
Soil available P	39 - 157	-	-	Mulla & Bratney (2000)
Agricultural properties				
Crop yield	8 - 29	-	-	Mulla & Bratney (2000)

5.2 Temporal heterogeneity

Many soil properties change over time scales relevant for practical applications. However, the relevant time scales differ considerably. There are fast processes like the crust formation at the soil surface occurring during single storms. Soil freezing changes soil properties also very rapidly once it occurs. Other processes governed by climatic conditions induce changes more slowly exhibiting an obvious seasonality. The vegetation cover is a well-known example influencing the risk of erosion, the amount of intercepted water by the vegetation or the flow resistance to overland flow. However, weather conditions may influence soil properties also in a more erratic way. It has been shown for Danish conditions that during a single vegetation period the soil surface may switch from wettable to water repellent and back (de Jonge *et al*., 1999).

There are also changes to be observed on the time scale of several months or years. The type of management for example (e.g., plowing against tining), may influence the drainage behavior over several months after the treatment (Dougherty *et al*., 1995). During a crop rotation of several years including grassland cultivation it has been observed that the infiltration pattern of a field changed considerably (von Albertini *et al*., 1995). These changes can be caused by abiotic processes like drying or by activities of organisms like earthworms. For a drainage system, it has been shown that its effect on water flow is not stable over time (Turtola and Paajanen, 1995) but may change over several years.

Many of these temporal changes affect the soil surface, which is exposed to the most extreme natural and anthropogenic influences. However, shrinking and swelling in heavy clay soils affect larger depths and the structural changes are not confined to the topsoil (Hillel, 1998).

5.3 Combined effects of spatial and temporal heterogeneity

The impacts of temporal and spatial variability have not to be independent. An instructive example relates to the influence of frozen soil on the infiltration behavior. It has been shown experimentally (Baker and Spaans, 1997; Derby and Knighton, 1997) that local topographic depressions may act as hot spots for infiltration as long as infiltration is inhibited by a frozen soil surface. Same effects may occur under heavy rainfall when surface runoff occurs that is retained by depressions.

Agricultural practice has also a strong influence on soil properties. Several studies have shown that the hydraulic conductivities of arable land change substantially during the season. Furthermore, it seems that the spatial correlation structure of the heterogeneity also varies in time (e.g., Logsdon and Jaynes, 1996).

Drainage systems often consist of different types of drains within a single field. Installed at different depths and directions lateral and the main or collection drains may influence the transport behavior very differently. An example is given by Schmied and Kohler (1999) for a 7 ha field. The lateral drains at 70 to 100 cm depth were almost non-effective for most of the time. The majority of the water was drained by main drains at 150 cm depth. Only during periods of very high water table the lateral drains lowered the water table. Hence, depending on the hydraulic conditions the spacing of the active drains changed from 100 to 20 m only. Furthermore, the flow direction switched for 90°(F ig. 2).

6. Conclusions for assessing or modeling P losses at the field scale

It has been shown above that water flow and solute transport at the field scale is governed by a considerable number of different factors. Some of them are time invariant, like topography or soil type, others like the surface conditions, change in time due to natural processes and human impact. Furthermore, the relevant factors like soil hydraulic properties are often spatially very heterogeneous.

For the assessment of water and solute fluxes this means that it is important to measure the soil properties and the solute and water fluxes at the right time and the right locations. A sufficient understanding of the flow regimes, that is an apriori conceptual model, is required therefore prior to field measurements or modeling. Such an apriori model should contain the most important factors relevant at a given site. In the framework of a European-wide COST action it might be worthwhile to establish conceptual models for P losses for different regions in order to compare the processes contributing to P-losses over whole Europe. This could be a basis to decide which existing simulation models can be applied for what kind of problems or what kind of measurements are needed to compare the risk situation of different areas.

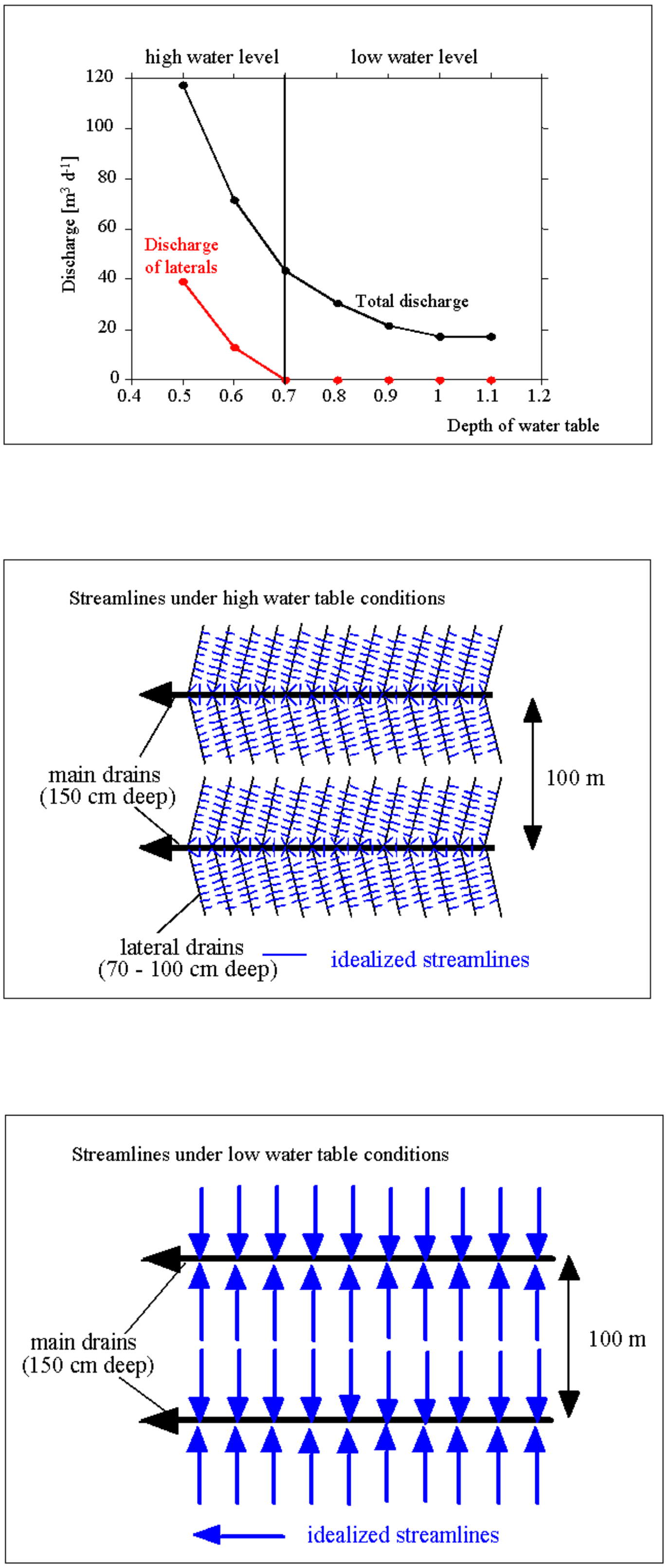

Figure 2. Water table level and idealized stream lines towards a tile-drain system of the study site described by Schmied and Kohler (1999) and Abbaspour et al. (2001).

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Review of concepts and process description on biological mechanisms

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1. Soil organic phosphorus

Walker and Syers (1976) have provided a basic model of P cycling, on a pedogenic time-scale, which describes the relation between P transformations and soil formation, and that has been verified for other ecosystems (Gressel and McColl, 1997). According to this model, in a young soil the main source of P is from weathering of primary minerals, mostly apatites, which account for about 95% of the total P in igneous rocks. Mineral weathering releases P into soil solution, where P can be taken up by plants and micro-organisms, sorbed onto solid surfaces, form secondary minerals or be lost through erosion or leaching. Subsequently, litterfall, root decay and exudation, and death of organisms return biologically held P creating a complex balance between geochemical and biochemical processes. Thus, in mature soils, organic P (Po) constitutes between 20 and 80% of total P in the surface layers of soils.

Soil Po content is related with soil genesis. Thus, Harrison (1987) showed that Histosols (570 ± 52 µg g^{-1}), Mollisols (329 ± 15 µg g^{-1}) and Ultisols (320 ± 48 µg g^{-1}) are, in absolute values, the soil orders with the highest levels of organic P and, if Po is considered as a percentage of the total P content, the soil orders with the highest figures are Histosols (59 ± 5 %), Vertisols (56 ± 4 %) and Mollisols (50 ± 2 %). Oxisols is the soil order showing the lowest levels of organic P, both in absolute values (84 ± 11 µg g^{-1}) and as a percentage of the total P (25 ± 3 %). Not only soil genesis and development influences the organic P content but it also depends on soil management. For example, Harrison (1987) indicated that, in the winter-cold zone of the world, the highest levels of Po are found in native grassland soils (525 ± 26 µg g^{-1}; n = 147 soil samples) and the lowest in cultivated soils (330 ± 14 µg g^{-1}; n = 300 soil samples), and this difference suggests the strong influence of P mineralisation on the available P content in arable ecosystems.

Soil organic P exists in many complex chemical forms, which differ markedly in their behaviour, mobility and resistance to hydrolysis (bio-availability) in the soils (Magid *et al.* 1996). One way of characterising the different Po forms present in soils is to consider their role in the soil P cycle and to differentiate these forms in relation with their turnover rate, which is usually carried out by sequential fractionation procedures. One of the most widely used fractionations is that of Hedley *et al*. (1982), which differentiates the following fractions: biologically-assimilable inorganic P (resin P), labile Pi and Po adsorbed on soil colloidal surfaces (HCO_3^- Pi and Po), organic and inorganic P compounds bound strongly by chemical sorption to the iron and aluminium oxides of the soil surfaces (NaOH Pi and Po), P bound strongly to internal soil surfaces (P extracted with NaOH after sonication, ultra sound NaOH Pi and Po) and, finally, inorganic phosphates such as apatites (HCl Pi). The ecological meaning of these fractions varies according to the different authors (Cross and Schlesinger, 1995), but in general Po bicarbonate is considered a relatively labile fraction (rapid turnover Po) and Po hydroxide and ultra sound are stable Po fractions (slow turnover Po). In the majority of soils, and independently of the degree of soil development, NaOH extractable Po is the predominant fraction, both as absolute values and as a percentage of total extracted Po, which suggests that a high proportion of organic P (between 60-75%) is in stable forms (Cross and Schlesinger, 1995; Trasar-Cepeda *et al*., 1990; Sharpley *et al*., 1985)

Another way to characterise soil organic Po is to use structural methods in order to differentiate the several Po compounds identified in soils. Most soil Po can be broadly classified by the P bonds to the organic part of the compound (Dalal, 1977). There are three types of P bonds: ester bonds (C-O-P), direct bonds to carbon or nitrogen (C-P or N-P) and condensed bonds (P-O-P). Ester bonds can be subdivided into monoester (sugar phosphates, mononucleotides and inositol phosphates) and diester (mainly nucleic acids and phospholipids). The ^{31}P NMR (Newman and Tate, 1980) is one of the structural methods most used because it differentiates among polyphosphates, pyrophosphates (both compounds with P-O-P bonds), diester and monoester phosphates, inorganic orthophosphate and phosphonates (compounds with a C-P bond). According to this technique monoester phosphates constitute the majority of the known Po in soils (between the 33 and the 100 % of the extracted Po) whereas diesters constitute between 0 and 44% of the Po in NaOH extracts (Condron *et al*., 1985; Gil-Sotres *et al*., 1990; Guggenberger *et al*., 1996). This distribution in soils is the opposite to that found in plants and animal debris where the diester phosphates are the predominant compounds.

2. Biological control on phosphorus release to soil solution

The soil microbial biomass mainly consists of bacteria and fungi and has been defined as the living part of the soil organic matter excluding plant roots and soil animals larger than 5×10^3 μm^3 (Sparling, 1985). The soil microbial biomass controls soil solution phosphorus in three ways:

- Removal of inorganic and organic P from solution by uptake and/or mineralisation, and subsequent immobilisation of the obtained P into cell structures.
- Release of organic P to soil solution on cell death and lysis.
- Release of inorganic P through excretion by microbial grazers.

The growth and death of the soil micro-organisms can have significant impacts on the solution P. Growing cells takes up inorganic P and immobilise it in their cell structures. Although uptake is dominantly as inorganic P, there is some evidences of direct uptake in organic forms (Anderson, 1980).The absorbed inorganic P is converted to organic forms so that on cell death the P is released to the soil as predominantly organic P. The balance between these two factors controls the forms and concentration of P in the soil solution.

Due to the low availability of inorganic P in soil, the organic P mainly contributes to plant nutrition and to microbial uptake through its mineralisation and subsequent release of inorganic P. P mineralisation rate depends on microbial activity and on the activity of phosphatases (Dalal, 1977). Consequently, the release of inorganic P through the destruction of the organic matter is usually divided in biological mineralisation and biochemical mineralisation. Biological mineralisation involves the release of inorganic P as a consequence of the carbon oxidation and the microbial growth and turnover, while in biochemical mineralisation the release of inorganic P, independent of microbial respiration, is controlled by the supply and need for P and involves the hydrolysis of ester-phosphates by extra-cellular hydrolytic enzymes (phosphatases) both free in solution and stabilised by sorption to the colloidal fraction (McGill and Cole, 1981).

There are several soil phosphatases (Malcolm, 1983, Bishop *et al*., 1994) and the most commonly determined are: phosphomonoesterases, phosphodiesterases and phytases. Phosphomonoesterases act on phosphate monoesters and according to their optimum pH they are divided in acid and alkaline phosphomonoesterases. Both are adaptive enzymes: acid phosphomonoesterase predominates in acid soils while alkaline phosphomonoesterase predominates in neutral and basic soils (Speir and Ross, 1978). It is very important to note that the data for kinetic and thermodynamic parameters vary widely following different authors (Dick and Tabatabai, 1984; Pang and Kolenko, 1986; Trasar-Cepeda and Gil-Sotres, 1988) and are dependent on soil properties suggesting that these enzymes are stabilised on soil colloids (Burns, 1982). Phosphodiesterase acts on the diesterphosphates and despite the fact that it provides the substrate for phosphomonoesterase activity, it is a less studied enzyme. Both phosphomonoesterase and phosphodiesterase show seasonal fluctuation but in any case both activities are highly correlated with a large number of soil properties (Baligar *et al*., 1988; Rastin *et al*., 1988; Trasar and Gil-Sotres, 1987; Trasar-Cepeda *et al*., 1999).

The importance of extracellular phosphomonoesterases for the Pi supply is controversial. Several authors consider that phosphomonoesterases are unable to hydrolyse the phosphomonoesters in soils due to the high stabilisation of these compounds on humic and inorganic soil colloids (Bishop *et al*., 1994; Brannon and Sommers, 1985). However, other authors (Tarafdar and Claasen, 1988) clearly showed the existence of a narrow relation between the decrease of organic P in the rhizosphere and the increase of enzyme activity level.

Because it is impossible to separately quantify the contribution to the overall Po mineralisation of biological and biochemical processes the estimation of organic P mineralisation is usually carried out using different approaches.

One approach is to look for the long term net organic P mineralisation, which is estimated from changes in total organic P content over years of cultivation. Following this approach the organic P mineralisation rates varies between 2 and 48 kg ha^{-1} y^{-1} and these rates are clearly dependent of the geographical location (Adeptu and Corey, 1977; Chater and Mattingly, 1980; Nyami, 1991; Sharpley and Smith, 1983; Tiessen *et al*., 1983). Several authors have stressed the importance of Po mineralisation in providing adequate Pi surplus in temperate soils.

Another approach is to study the short-term net organic P mineralisation deduced from changes during the year in selected organic P fractions. Po-HCO_3^- is usually considered as the fraction most sensitive to these changes. In agreement with published results, the organic P mineralisation rate oscillates between 10 and 100 kg ha^{-1}, and woodland and pasture soils are the soils with the highest rates of net Po mineralisation, while artic soils are those showing the minimum values (Perrott *et al*., 1990; Sharpley and Smith, 1985; Sparrow *et al*., 1990; Trasar-Cepeda, 1987).

Other published methodologies to estimate the Po mineralisation rate are determination of the gross P mineralisation by using labelled phosphorus or by differentiating in the P solution pool the contribution of the mineralisation of the organic P and the solubilisation of the inorganic soil phosphorus (Zou *et al*., 1992), the mineralisation rate of labelled ATP (Frossard *et al*., 1996) and the quantification of the net release of ^{32}P from plant residues labelled before their addition to the soil (Friesen and Blair, 1988).

In addition to mediating the turnover of Po, soil micr-organisms may also constitute a significant reservoir of P (Brookes *et al*., 1984; Tiessen *et al*., 1994). Soil microbial biomass shows a strong seasonal variation and these variations are obviously related to the quantity of labile carbon in soil and to soil moisture and temperature (Dalal, 1998). The influence of these later two variables on the activity of soil micro-organisms can be modelled by complex equations, which include not only the influence of temperature and moisture but also the interaction between the two variables (Leirós *et al*., 1999; McDonald *et al*., 1995).

The estimation of the size of microbial biomass is a routinely used method in soil biochemistry (Anderson and Domsch, 1978; Jenkinson and Powlson, 1976; Vance *et al*., 1987). Generally biomass-C and -N are clearly dependent on biochemical, chemical and physical soil properties and can be easily modelled (Díaz-Raviña *et al*., 1993; Joergensen *et al*., 1995; Trasar-Cepeda *et al*., 1999). Microbial P varies between 6 and 183 kg ka^{-1} (Díaz-Raviña *et al*., 1993; Joergensen *et al*., 1995; Stewart *et al*., 1980) showing the highest values in woodland and grassland soils and the lowest in cultivated soils (Brookes *et al*., 1984). The soil management has a great influence on the level of P held in microbial biomass and in biological or organic farming system, the microbially mediated turnover of organic P may be more important that in conventional farming (Oberson *et al*., 1996).

Management of bio-dynamic and bio-organic farming systems aims towards a stimulation of biological soil activity and thus to a higher turnover of organic substrates.

It is important to note that the percentage distribution of organic P forms in microbial biomass is totally different to that of the soil organic matter. The majority of the total P in micro-organisms is in the form of phosphodiesters such as nucleic acids (DNA, RNA, polynucleotides) and phospholipids. Nucleic acids dominate microbial organic P constituting around 60% of the intracellular P in fungi, bacteria and mycorrhizal mycelium (Webley and Jones, 1971). Phospholipids only account for circa 5-30% of the organic P in micro-organisms (Magid *et al*., 1996), and are dominated by phosphatidyl ethanolamine (Stewart and Tiessen, 1987). Phosphomonoesters constitute only 10-25% of the organic P in a range of micro-organisms. They are dominantly sugar phosphates, such as glucose-6-phosphate and only a minor fraction of inositol phosphates. The fact that phosphodiesters constitute the majority of the microbial P inputs in the soils yet are only measured in small amounts in the soils suggests that they must be rapidly hydrolysed to other forms. In addition, the apparent lack of adsorption by phosphodiesters to soil particles means that they are mobile in the soil and have the potential to be readily transferred to surface waters (Turner and Haygarth, 2001).

Under changing environmental conditions, a portion of the soil microbial biomass will always be killed. The dead cells provide a carbon substrate for the remaining organisms and release nutrients to the plant available pool (Anderson and Domsch, 1980). Thus, release and immobilisation of nutrients are generally closely related to changes in environmental factors such as moisture, temperature, wetting-drying cycles, or freezing-thawing cycles.

Soil fauna which grazes on the microbial populations include bacterial grazers, protozoa, nematodes and fungal grazers such as micro-arthropods and protozoa. Grazers show seasonal patterns, which appear to correspond to the soil microbial biomass. The results on the influence of grazers on P cycling and release to soil solution are contradictory.

3. Leaching of organic phosphorus

Soil organic phosphorus can contribute to environmental pollution through two main processes:

- Release of inorganic P as a consequence of mineralisation of organic phosphorus, and subsequent leaching of this Pi.
- Solubilisation and leaching of organic P compounds.

The leaching of Pi is the topic of another working group and in this paper only the possibility of organic P leaching will be discussed.

Though substantial transfer of Po can occur through both surface and subsurface pathways, Po is particularly vulnerable to transfer through subsurface pathways because of its mobility in the soil compared to the Pi forms: while inorganic P is readily fixed in the soil and prevented from leaching by precipitation with Ca, Fe and Al or sorption to clays and other soil particles (Frossard *et al*., 1995), some Po is not strongly sorbed and can move easily through the soil to surface waters (Chardon *et al*., 1997). Moreover, it is now recognised that when Po reach surface waters it can contribute to algal growth after the release of Pi by phosphatase enzymes. Therefore, if the contribution of agricultural P pollution to eutrophication is to be comprehensively understood, it is essential to consider the Po fraction being transferred in runoff from the land (Turner and Haygarth, 2001).

The possibility of transfer to surface waters of soil phosphorus depends both on the solubility and the lability of the organic P compounds and on the affinity of the organic phosphorus by soil colloids.

Although monoester phosphates like inositol-hexa-phosphate (IHP) are strongly adsorbed to soil particles (Cosgrove, 1977; Dalal, 1977), the large amounts accumulated in the soil suggest that transfer to surface waters is likely to occur. Therefore, because of the strong binding of IHP to clays and metals in the soil, the probable mechanisms for IHP transfer in runoff is through IHP adsorbed to colloidal sized metal or clay-humic complexes. Taking in account the strong stabilisation of monoester phosphates, IHP would remain resistant to breakdown in aquatic environments where it probably constitutes a relatively unavailable Po fraction.

In contrast to monoester phosphates the apparent lack of adsorption by diester phosphates to soil particles means that they are mobile in the soil (Cosgrove, 1967) and have the potential to be readily transferred to surface waters. Although their labile nature means that they may be hydrolysed before they have chance to escape from the soil, the 18 day hydrolysis time for RNA in soil showed by Harrison (1982) or the 28 days for diester phosphates in sludges (Hinedi *et al*., 1988) indicates that released diester phosphates would have ample time to escape intact to surface waters.

In native soils, the mobility of organic P compounds is limited because the P cycle is practically a closed system and the majority of the organic P is monoester. In other words, the most labile and mobile organic P forms are transient and only the stabilised Po forms are able to accumulate (Cosgrove, 1977; Dalal, 1977).

The picture is different in agricultural soils when organic wastes are used as fertilisers, because in the majority of these products the main components of organic phosphorus are diesters (Hinedi *et al*., 1988). Diesters have relatively high mobility in spite of their rapid degradation rate and although there is not direct evidence for diester phosphates transfer from soils to surface waters, the high phosphodiesterase activity detected in upland stream waters provides indirect evidence that it occurs (Christmas and Whitton, 1998).

In heavily manured soils, there is a great increase in soil organic phosphorus content not only on the soil surface but also in the whole profile, suggesting the possibility of a downward Po movement (Sharpley *et al*., 1984). Furthermore, it has recently been indicated (Chardon *et al*., 1997) that in soil leachates dissolved Po concentration is higher than molybdate reactive P, which clearly confirms the mobility of some organic P compounds. These high Po concentrations may result from lysis of bacterial cells, flushing of the soil by rainfall and removal of the released Po compounds in leached water.

The risk of soluble P losses when organic wastes are used as fertilisers is very important from an environmental point of view because in many areas of Europe a high proportion of applied P comes from animal excreta (Sibbesen and Runge-Metzger, 1995). Thinking on the possibility of quantifying these Po losses it is important to note that the release of microbial Po is potentially greatest in springtime, when lysis of microbial cells coincides with periods of high biological activity and, therefore, of a large microbial pool (Magid and Nielsen, 1992). Furthermore, the concentration of dissolved organic P in solution is dependent not only on fertilisation levels, but also on pH values (Ron Vaz *et al*., 1993; Rydin and Otabbong, 1997), and according to Gerke (1992) organic P concentration increases with soil pH due to the increasing solubility of organic matter when the pH rises.

4. Modelling phosphorus transfer

Numerous comprehensive mathematical models have been developed to simulate the fate of agricultural chemicals in soil and their transport to surface waters, with the purpose of aiding the selection of management practices capable of minimising water quality problems (Sharpley *et al*., 1995). There are several comprehensive models available simulating soil P cycling, transfer between agricultural systems and loss in runoff that facilitate identification of alternative management strategies and basic research needs. However, a major limitation to model use is often the lack of detailed parameterisation data on soil physical, chemical and biological properties as well as climate, crop and tillage information. Consequently, the use of these models to provide quantitative estimate of P loss under specific environmental conditions is limited and the use of many models is recommended only for comparison of relative effects of management strategies on P transfer. Among the described models only a few of them consider the possibility of the estimation of Po losses trough leaching, some of these are the following:

- The model from Smith (1979) focused on soil organic matter decomposition.
- The model developed by de Jong and Klinkhamer (1983) that consider the downward movement of P in humus.
- The Century model (Parton *et al.*, 1988).
- The ANIMO 3.5 model (Groenendijk and Kroes, 1999).

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Solubilization of phosphorus:
Concepts and process description of chemical mechanisms

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1. Introduction

Phosphorus (P) is an essential element for living organisms, both in terrestrial and aquatic ecosystems. Within ‘normal’ agriculture, P is added to soils in order to maintain or ameliorate crop production. In regions with confined animal production often more P containing manure is produced than is necessary for maintaining soil fertility, and manure is considered as a waste product. Application of excessive amounts of manure to soils has led to an increased movement of P from soils to surface waters, on many places leading to eutrophication. This paper deals with the chemical mechanisms by which P can be released from the solid matrix of a soil to the liquid phase: the soil solution or ground water. After this release P can move with the liquid to surface water, either across the soil surface or through the subsoil.

Biological processes by which organic matter is mineralized, releasing inorganic P, is the subject of another paper in this volume, by Gil-Sotres *et al*. Some overlap may occur with the papers by Barberis & Withers, and by Quinton on particle bound P.

In the following (i) the pools of P in the soil and the fate of P that is added to the soil are briefly discussed; (ii) chemical factors are discussed which can influence the different pools; (iii) experimental or environmental conditions are mentioned where the chemical factors occur, and may thus have implications for leaching of P. Finally, mathematical descriptions of sorption reactions of P in soils are summarized.

2. Pools of phosphorus in soil and flows between pools

In the following (simplified) scheme a number of pools are shown in which P can be found, both in the solid phase of the soil and within the soil solution. In the solid phase a distinction is made between organic (left) and inorganic forms (right), in the soil solution between ortho-P and dispersed colloidal P. The last fraction can be either adsorbed on inorganic colloids (clay particles, Fe/Al-hydroxides), or is bound to dissolved organic matter (DOC).

solid phase	**'solution'**	**solid phase**
organic forms		inorganic forms
living biota		precipitated
fresh organic material stable organic matter ('humus')	ortho-P	adsorbed absorbed (in aggregates)
	dispersed colloidal/organic P	attached colloids

In the solid phase the precipitated pool mainly consists of Ca-P in calcareous soils, and in heavily manured neutral soils besides Ca-P also struvite can be expected when the sorption capacity of the soil is exceeded (de Haan & van Riemsdijk 1986, Bril & Salomons, 1990).

Sorbed P can be distinguished into adsorbed P, on the surface of aggregates, and P sorbed inside aggregates (fixed, 'absorbed'). Also, P can be associated with colloids which are (a metastable) part of the soil matrix.

The flows of P between the pools can be summarized as follows. Living biota can die, and P becomes part of fresh organic material. From this pool, P can be released by biological breakdown (mineralization), forming more stable organic matter and/or inorganic P in solution. Especially on calcareous soils, soluble ortho-P can precipitate (as a separate phase or on the surface of e.g. carbonates) or adsorb on the surface of Fe/Al-hydroxides. Adsorption is a fast process, which can be followed by diffusion into aggregates and sorption on internal surfaces; this process is mainly important with amorphous hydroxides. Also, P can be associated with colloidal material; depending on soil conditions, this material can be attached to the soil matrix or be dispersed in the soil liquid.

Directly relevant for loss of P to the environment are ortho-P in solution and P associated with suspended particles. Recent research indicates that in soil solution particle bound P can represent the majority of total P (Lookman, 1995; Chardon *et al*., 1997; Haygarth *et al*., 1997; Hens and Merckx, 2001). It was shown that the particle size forms a continuum, which makes the distinction between soluble P and particle bound P questionable.

Flows that can bring P in solution (solubilize) are: mineralization of organic material, dissolution of precipitated P; desorption of adsorbed P; diffusion of P from the interior of aggregates, followed by desorption; breaking of the association between P and dispersed colloids, and detachment of P containing colloids from the soil matrix.

3. Input of phosphorus to soils

The main forms of P input to soils are:

- superphosphate and other mineral fertilizers
- solid or liquid animal manure
- sewage sludge or (drinking) water treatment sludge

Superphosphate readily dissolves in soil and will enter, in first instance, the pool of dissolved ortho-P, followed by adsorption or precipitation. After application of superphosphate to a soil, the conversion of MCP (monocalciumphosphate) into DCPD (dicalciumphosphate dihydrate) can cause temporal and local acidification of the soil:

$$Ca(H_2PO_4)_2.H_2O + H_2O \rightarrow CaHPO_4.2H_2O + H_2PO_4^- + H^+$$

The pH of the solution around fertilizer granules can reach values below 1.5, which causes dissolution of both Fe and Al hydroxides (Lindsay, 1979; par. 12.13). Reprecipitation of the Fe and Al, with co-precipitation of P, can produce colloidal material. However, overall effects of addition of superphosphate will be local and concentrated in the top soil.

Both animal manure and sewage sludge contain P in organic form, which can be released through mineralization. The process of mineralization can locally cause anaerobic conditions. Animal manure also contains precipitates of P (with Ca, NH_4, K, Mg; Bril & Salomons, 1990), which will easily dissolve. Sludges can contain insoluble Fe- or Al-P precipitates due to secondary treatment with Fe or Al salts. In general, these precipitates have a large sorption capacity for P, and can thus be responsible for a reduction of plant available P (Elliot & Dempsey, 1991).

Through conversion of urea, liquid manure is often oversaturated with bicarbonate. After field application, volatilization of CO_2 causes a (temporal) increase in soil pH:

$$HCO_3^- + H^+ \rightarrow H_2CO_3{}^0 \rightarrow CO_2\uparrow$$

Comparable reactions were found in soils after application of urea fertilizers (Hartikainen & Yli-Halla, 1996), and under urine patches on grassland soils (Williams *et al*., 1999).

Summarizing: the application of P containing compounds may have a varying local and (in most cases) temporal influence on soil chemistry, which can change the behaviour of P forms that were already present in the soil.

4. Chemical conditions which can influence phosphorus behaviour in soils

The processes that cause retention or release of P are summarized in the following scheme, including the main soil types for which the processes are relevant. The left column shows processes leading to the retention of P by the solid phase; the middle shows corresponding processes that release P, and the right column shows the soil types were these processes are important.

retention	release	soil types
fast adsorption	fast desorption	all soils
slow 'absorption' on amorphous Fe/Al-oxides	slow desorption	non-arid soils
precipitation (mainly Ca-P and NH_4-P)	dissolution	calcareous soils over-fertilized soils
particle settling, sedimentation	detachment	all soils

The main factors influencing reactions of P in soils are:

- pH
- ionic strength / cations
- organic acids
- redox potential
- temperature

In the following, these factors will be briefly discussed.

pH. Changes in pH have a large influence on the solid phase of the soil, since pH determines the surface charge of Fe/Al-hydroxides, the main sorption medium of P. An increase of the pH reduces the positive charge of hydroxides, and mobilizes anionic P-forms like ortho-P and P bound to dissolved organic carbon (DOC). However, at a higher ionic strength the effect of pH on P sorption is less pronounced than at a low ionic strength (Barrow, 1989). Examples of mobilization of P at elevated pH are:

- the application of lime, a normal agricultural practice for maintaining soil fertility after application of urea (Hartikainen & Yli-Halla, 1996);
- below animal urine spots (Williams *et al*., 1999) or after application of mixed manure slurry (see above; van Faassen *et al*., 1990);
- from particulate P in surface water, due to e.g. sewage effluent with a higher pH than the soil from which the particles originate (Fox, 1991).

In calcareous soils where precipitates with Ca determine P solubility, a decrease of pH causes dissolution of the precipitates, and thus causes P release.

Ionic strength / cations. The effect of ionic strength can be separated in the influence on (1) P sorption and (2) colloids with which P is associated. However, if mobile soil colloids are a continuum, (see above), it will be hard to distinguish experimentally between desorption of ortho-P and detachment of reactive P on small colloids.

Cations have an influence on P sorption via the neutralization of the negative charge of the sorbed P. Small cations that can reach the soil surface more closely have a larger influence than large ions. Barrow & Shaw (1979) found that desorption of P varied in the presence of different monovalent cations as follows: Li > Na > NH_4 > K,Rb > Cs. They also found that desorption in $MgCl_2$ was faster than in $CaCl_2$. The influence of a decrease in the concentration of $CaCl_2$ from 0.1 to 0.001 was relatively small: in 96 hr P desorption doubled.

The following examples show that a decrease in ionic strength can be important for mobilizing P, through its influence on the detachment of colloidal particles.

- During 7 years the effluent of maize grown, outdoor lysimeters was sampled on MRP, total P, NO_3 and Cl. Results showed that P was mobilized during periods with a low NO_3 and Cl-content of the effluent, indicating a low ionic strength (Fig. 1). Binding of P to colloidal material, mobilized at low ionic strength, was given as an explanation of these results (Chardon *et al*., 1997).
- Shaking soil with Na-solution can cause mobilization of DOC, by removing divalent (Ca^{2+}) bridges between organic anions and clay mineral surfaces (Greenland, 1971).
- The stability of soil aggregates can be increased both by Ca and by microbial activity, which is ascribed to bridging between Ca, humic acids and clay particles (Muneer & Oades, 1989). Thus, reducing Ca-content will increase dispersion.
- At low concentrations of bivalent cations, the mobility of humic substances (Tipping & Ohnstad, 1984) and of colloidal forms of iron phosphate (Cameron & Liss, 1984) is greatly enhanced.

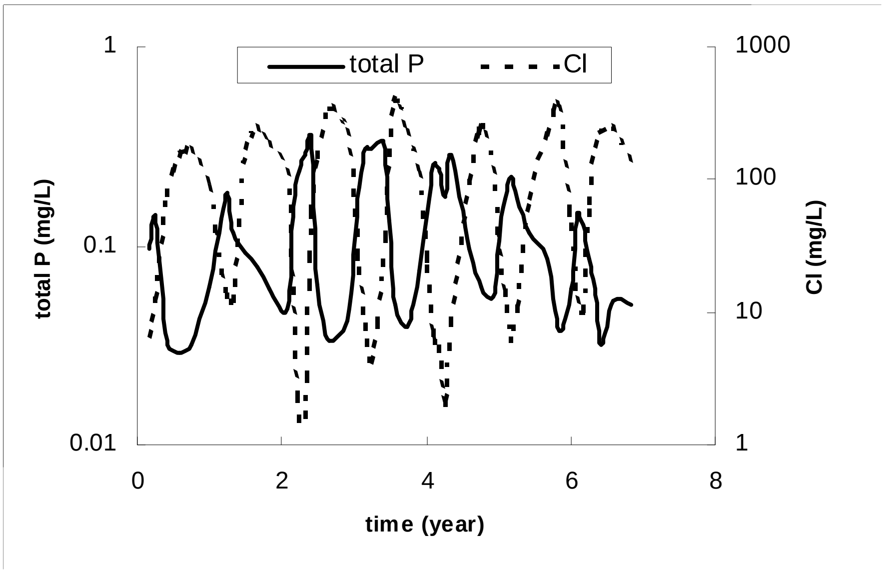

Figure 1. Inverse relation between total P and chloride in lysimeter effluents (data Chardon et al., 1997).

The influence of several factors on the behaviour of colloid bound P is further discussed in the paper by Barberis and Withers in this volume. Recently, Kretzschmar *et al*. (1999) extensively reviewed the role of colloids in transport of contaminants.

A low ionic strength in the soil solution can be expected in case of preferential flow, the transport mechanism by which relative high volumes of water flow through a small portion of the soil volume (Simard *et al*., 2000). Preferential flow makes it possible that rain water, with a much lower ionic strength than the average soil solution, passes through the soil profile without equilibrating with the soil solution. It can thus mobilize colloidal material from the soil. Preferential flow can either be caused by (1) a local low hydraulic conductivity, forcing the water to soil parts with a normal conductivity, or (2) by soil parts that have a high hydraulic conductivity, attracting water from the surrounding soil.

- A *low* hydraulic conductivity can be caused by soil material with a low porosity, e.g. clayey material, or by organic matter causing water repellency of a soil (Dekker and Ritsema, 2000). Water repellency occurs in natural and agricultural soils all over the world, but its influence on transport of agrichemicals (like P) is poorly understood due to insufficient knowledge about the water flow and transport processes (Ritsema and Dekker, 2000).
- A *high* hydraulic conductivity can be found in macropores (> 100 μM), originating from e.g. soil cracks, root channels, and earthworm borings (Edwards *et al*., 1993). Preferential flow through these pores only occurs when the rainfall intensity exceeds the infiltration capacity of the bulk soil (Simard *et al*., 2000).

***Organic acids**.* Organic acids compete with P for sorption sites when they are in anionic form, thus enhancing P mobilization. The source of acids can be e.g. plant roots, animal manure, and sewage sludge.

Citric acids, as produced by plant roots in P-deficient soils, dissolve Fe, Al and the P adsorbed to it (Gerke, 1992). However, the impact will be concentrated around plant roots, thus an environmental effect is probably not to be expected. High molecular weight material from animal manure and the high pH of liquid manure both influence P leaching (Gerritse, 1981; Chardon *et al*., 1997).

Redox potential. Reducing conditions in a soil can be responsible for reducing iron compounds. If P is adsorbed on the Fe-oxides it will be mobilized. When conditions become oxic again re-precitation of the Fe will occur, and P will re-adsorb. This leads to mobile forms of colloidal Fe-P-compounds (Mayer & Jarrell, 1995). Extensive research on the influence of redox on P mobility was done in rice fields, where flooding induces anaerobic situations; this research was reviewed by Ponnamperuna (1972). Other causes of a low redox potential are the application of manure, which will only have a temporal and local effect, and an increase in water table of a soil. This will have an effect if P, leached from the topsoil, has enriched the subsoil; in this case an increase in P loss can be expected. However, at present no research on this specific topic is known to the authors. In The Netherlands, increasing the water table is studied with the aim of reducing the 'drying out' of nature reserves.

***Temperature**.* An increase in temperature enhances a number of soil processes:

- kinetics of movement of ions within aggregates (slow reactions), both absorption and desorption / mobilization;
- mineralization of organic matter (e.g. increasing P availability in spring);
- dissolution of precipitated P.

The adsorption of P itself decreases by an increase in temperature (Barrow, 1992), the sum of adsorption and absorption will increase in most cases. Overall, temperature has more influence on the transport of P between pools than on the distribution of total P over the different pools, and is probably less relevant for P solubilization.

5. Modelling sorption and desorption of P

In the past, a number of models have been developed that describe sorption processes of P in soils. Models that describe sorption of inorganic P forms are summarized in the appendix. These models are able to predict the behaviour of inorganic P both in the laboratory and under field conditions (Schoumans & Groenendijk, 2000). However, untill now no models that describe sorption (kinetics) of specific organic or particular forms of P were developed. At present there is thus an unbalance in modeling skills between inorganic forms of P on the one hand and organic/particular forms on the other hand.

6. Summary and conclusions

From the chemical factors mentioned above than can solubilize P in soils, the following are probably most important, and thus should receive more attention:

- preferential flow, which creates a flow of water with a low ionic strength through the soil, which can mobilize colloidal P forms;
- application of liquid manure, which increases soil pH and adds high molecular weight organic acids;
- increasing the soil water table, in situations where the subsoil is enriched with P.

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APPENDIX

1. Fast adsorption

An extensive equation that describes adsorption of different ions on varying components (e.g. clay, org. matter, hydroxides, lime) is given by Barrow (1987, p.86).

$$\theta = \frac{K.\ \alpha.\gamma.C.e^{(-zF\psi/RT)}}{1 + K.\ \alpha.\gamma.C.e^{(-zF\psi/RT)}} \qquad (1)$$

where: θ is the proportion of the component occupied by the adsorbed ion
K is the binding constant for the ion
z is the valence of the adsorbing ion
ψ is the electrostatic potential of the component
α is the fraction of the adsorbate present as the ion
γ is the activity coefficient
C is the total concentration of the adsorbate
F,R Faraday and gas constant, respectively
T is absolute temperature

The Langmuir equation describes adsorption of a component at equilibrium, for given values of T, pH, surface potential:

$$Q = Q_{max} \frac{K.C}{1 + K.C} \qquad (2)$$

where Q is concentration of adsorbate on the surface and Q_{max} is the sorption maximum.

For non calcareous sandy soils ($5 < pH < 6$; salt conc. = 10^{-2}N) it was found that K varies from 10 to 100 $m^3\ mol^{-1}$ (van der Zee *et al*., 1988). Also, Q_{max} was estimated from oxalate extractable Al and Fe-content according to (van der Zee *et al*., 1990):

$$Q_{max} = \beta\ (Al+Fe)_{ox} \quad \text{and} \quad \beta \approx 0.5/3 \qquad (3)$$

2. Slow sorption

For the slow process of sorption (S), also called 'absorption', empirical functions are used most of the time. As an example, Van der Zee and Van Riemsdijk (1986) used the polynomial:

$$S(c,t) = \sum a_i \{\ln (I)\}^i \qquad \text{with} \qquad I = \gamma \int (c-c_e)\ dt \qquad (4)$$

The symbol *I* is called exposure integral. C_e corresponds with a threshold value below which no slow sorption is assumed to occur. The value of C_e is almost zero if the slow reaction is ascribed to the slow penetration of an adsorption front into a porous reactive particle. Since Eqn. (4) has no maximum, Eqn. (5) was presented as an alternative by Freese *et al*. (1995):

$$S(c,t) = S_{max} \frac{(kI)^{\omega}}{1 + (kI)^{\omega}} \qquad (5)$$

with k and ω as parameters, and S_{max} as the maximum that S will reach after prolonged exposure of a soil to P.

For non-calcareous sandy soils the following estimation was made (Van der Zee *et al*., 1990):

$$S_{max} = \tau(Al+Fe)_{ox} \quad \text{and } \tau \approx 1/3 \qquad (6)$$

Schoumans (1995) used the following equation for the long term sorption:

$$dS/dt = \sum \omega (KC^N - S) \qquad (7)$$

3. Total Sorption

In many studies total sorption (F) was measured, and described with an extended Freundlich equation (Kuo and Lotse, 1974; Barrow and Shaw, 1975):

$$F = k\, c^n\, t^m \qquad (8)$$

Total sorption can also be calculated as the sum of fast adsorption and slow sorption, which depends both of exposure time and of the concentration to which the soil is exposed:

$$F(c,t) = Q(c) + S(c,t) \qquad (9)$$

Combining Eqns. (3) and (6) gives the estimation of the maximum of F, used for non calcareous sandy soils (Van der Zee *et al*., 1990):

$$F_{max} = 0.5\ (Al+Fe)_{ox} \qquad (10)$$

However, in a number of studies also more crystalline oxides (e.g. dithionite extractable fractions) were included in the estimation of F_{max}. (Borggaard, 1986; Torrent *et al*., 1992; Werner & Pihl, 1998). These studies led to the conclusion that in soils relatively poor in oxalate extractable Fe and Al, and thus more rich in crystalline forms, the approach of Eqn. (10) may lead to underestimation of the sorption maximum of a soil for P.

Influence of soil processes on detachment of P forms: A review of experimental data

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1. Introduction

Loss rates of phosphorus (P), for erosion as for leaching, can be expressed as:

$$\text{P loss} = \text{P concentration (mass} \bullet \text{volume}^{-1}) \bullet \text{flow (volume} \bullet \text{time}^{-1})$$

P concentration (P_{conc}), in this case, can be seen as formed by two terms:

$$P_{conc} = (\text{mass of P} \bullet \text{mass of erodible soils}^{-1}) \bullet (\text{mass of erodible soil} \bullet \text{volume}^{-1})$$

The first term represents the amount of P retained by erodible soil particles and is controlled by P-specific soil chemical, physico-chemical and biochemical reactions. The second term is regulated by dispersion/flocculation behaviour of soil colloids, these depend on size and surface properties of erodible particles and are, at least in part, P-dependent.

This report will review results concerning:

1. dissimilarities in P composition between bulk soil and eroded particles/colloids evaluating differences in mobilised P forms and amounts from different combinations of soil type and land use;
2. mobilisation of colloids by detachment/retention: effect of ionic strength, pH, presence of monovalent/divalent cations in soil environment;

From a practical point of view particles with diameters < 2µm may constitute the most mobile size fraction in porous media, beyond 1 µm particle removal from the suspension through sedimentation or/and interception increase rapidly. So most of the attention will be devoted to behaviour of particles < 2µm. These particles in the soil can be aggregated in more or less stable forms. Agricultural practices can influence the partitioning of P between soil aggregates directly through the preferential sorption of fertiliser P by smaller aggregates or indirectly by modifying the size distribution and the stability of aggregates.

2. P concentration in erodible soil particles

The existence of P in association with different particle-size fractions (*separates*) is affected by pedogenetic processes and by anthropogenic factors.

Early investigations were generally aimed to investigate the effects of pedogenetic processes or soil management practices on P distribution among the separates. Only in the recent years published papers aimed to evaluate the anthropogenic aspects and to estimate the potential contribution of different separates to P transport from agricultural land.

The comparison between the reported results is not always easy as, according to the different purposes of the papers:

- soil particles size fractionation is done in different ways, obtaining different sizes, and often, in the oldest papers, are not given enough details about the size of the obtained particles;
- the depth of sampling is various;
- the forms of P analysed are different and obtained with different methodology;
- the chemical and physical characteristics of the soil are not fully described.

Nevertheless, some generalisations are possible not distinguishing between ways of fractionations and type of soil and recalculating, when possible, the data according to the classification clay (<2μ) silt (2-20 or 50μ) sand (20 or 50 -2000μ).

The main results are: total P increases with a decrease of particle size (Williams and Saunders 1956a; Bates and Baker, 1960; Syers *et al*., 1969; Hanley and Murphy, 1970; Tiessen *et al*., 1983; Zhu *et al*., 1983; Day *et al*., 1987; Choudhry, 1988; Guzel and Ibrikci 1994; Agbenin and Tiessen, 1995; (Oggard, 1996); Sinaj *et al*., 1997). The concentration of total P in the sand is relatively low (Williams and Saunders, 1956a; Bates and Baker, 1960; Syers *et al*., 1969; Juo and Ellis, 1968; Choudhry, 1988) and a fairly high proportion is inorganic, mainly Ca-P, and of primary origin. The P in the clay fractions is largely of secondary origin, mainly Fe-bound, and is the result of accumulation of both organic and inorganic P (Williams and Saunders, 1956a, b; Bates and Baker, 1960; Juo and Ellis, 1968; Tiessen *et al*., 1983; Sinaj *et al*., 1997) that can be ascribed to the greater surface area and retention capacity (Syers *et al*., 1969; Tiessen *et al*., 1983; Guzel and Ibrikci, 1994; Sinaj *et al*., 1997) of the clay. Data of enrichment ratios, calculated as the ratio of the total P content of separates to that of soil (P_{tot}-ER) (Sharpley, 1985) show an inverse trend with clay content (Figure 1).

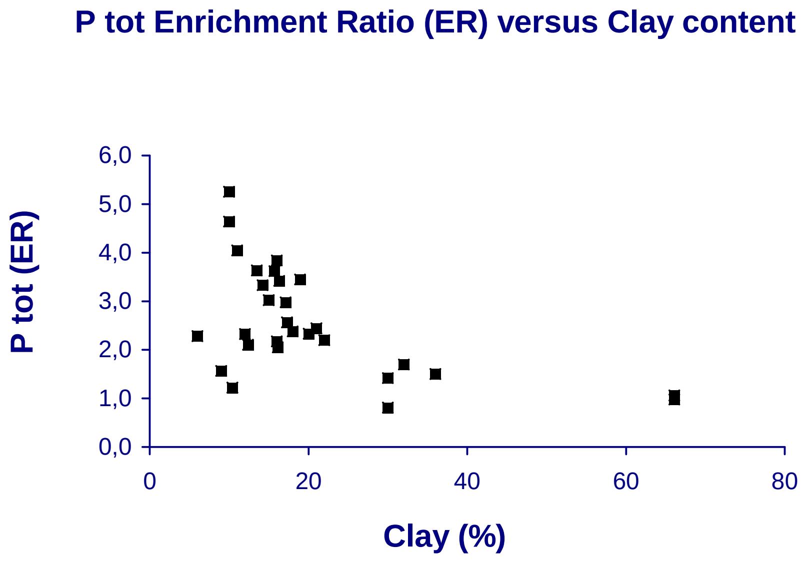

Fig. 1 Relationship between enrichment ratio (ER) of total P and clay content

Organic P is also concentrated in the finest separates (clay>silt) (Williams and Saunders, 1956a; Bates and Baker, 1960; Syers *et al*., 1969; Hanley and Murphy, 1970; Tiessen *et al*., 1983; Zhu *et al*., 1983; Choudhry, 1988; Guzel and Ibrikci 1994) and represent from 6 to 83 % of total P in the clay (mean 42% n=27) while in the soil it represented from 2 to 73% of total P in the soil (mean 33% n=27). Agbenin and Tiessen (1995), studying soils from a toposequence in Northeast Brazil, demonstrated that even when organic P constitutes an insignificant portion of total P the lowest amounts are associated with the sand and the highest with the clay showing the role of surface stabilisation. Also for organic P the inverse trend P_{org}-ER versus clay content exist (Figure 2).

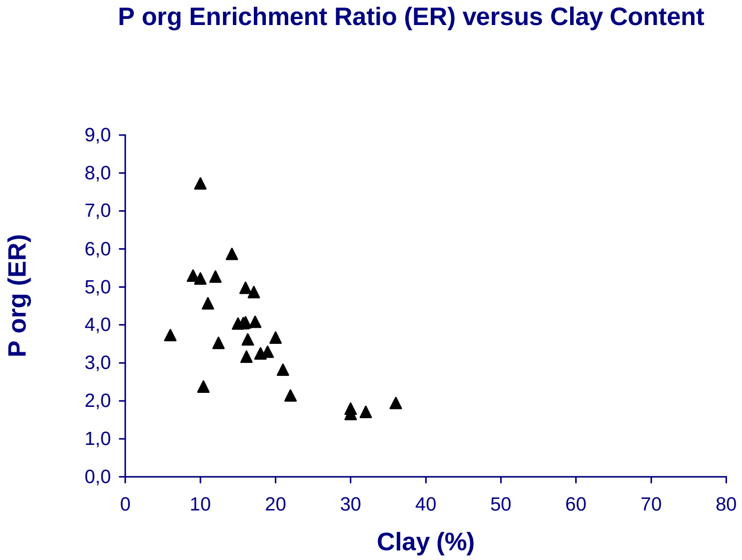

Fig. 2 Relationship between enrichment ratio (ER) of organic P and clay content

A significant proportion of soil P could be transported as microbial biomass phosphorus as the content of P in the biomass (He *et al*., 1995) is highest in the < 0.1 mm fraction that would be more readily lost to runoff.

The total P and the organic P contents of the clay decreases down the profile (Williams and Saunders, 1956a, b; Bates and Baker, 1960; Syers *et al*., 1969; Guzel and Ibrikci, 1994) this can due both to biocycling and to anthropogenic reasons.

Total P is higher in the clays and silts of the well drained soils (Williams and Saunders, 1956a; Hanley and Murphy, 1970), whereas the sand fractions of the poorly drained soils are higher in the total P and have a higher proportion of organic P than the sands of well drained soils. Mc Donnell (1957) suggested that the higher organic P level in the clay of well drained soil may have been caused by a higher P level in herbage or that the higher level of Al and Fe oxides may have led to the formation of soils with high content of organic P. The higher proportion of organic P in the sands of poorly drained soils could also result from under-composed organic material separated with the sand fraction.

Cultivation always increases the amount in clay separates: not only, as expected when fertilisation is done (Maguire *et al*., 1999) but also when no phosphate fertiliser is added (Tiessen *et al*., 1983;). That is probably due to the P biocycling that lead to accumulate P in fine fractions.

Available P has been evaluated in separates with a number of methods:
- acetic acid (Williams and Saunders, 1956b; Bates and Baker, 1960);
- Truog (Williams and Saunders, 1956b; Bates and Baker, 1960);
- lactate (Williams and Saunders, 1956b);
- Bray (Bates and Baker, 1960; He *et al*., 1995; Takahashi, 1996);
- Olsen (Zhu *et al*., 1983);
- resin (Agbenin and Tiessen, 1995; Maguire *et al*., 1999);
- isotopically exchangeable (Sinaj *et al*., 1997);
- water (Maguire *et al*., 1999);
- algae-available (Oggard, 1996).

However, contrasting results were obtained: Agbenin and Tiessen (1995), Takahashi (1996) and Sinaj *et al*. (1997) found an increase of available P with decreasing separates sizes, while Bates and Baker (1960) and He *et al*. (1995) found an inverse trend.

Maguire *et al*. (1998) showed that resin P increases with decreasing separate size while water extractable P decreased. Takahashi (1996) pointed out that Bray-2P concentrated in the separates <0.1 μm but grinding the separates <0.25 μm the amount of Bray-2P decreased, and Yoshida (1992) obtained similar results grinding Andosols. Sinaj *et al*. (1997) indicated that in the smallest separates (< 2μm) accumulated was P available for plants, probably located on Fe oxides, clay, and organic matter.

These methods are based on different mechanism: Kamprath and Watson (1980) proposed four general reactions contributing to P release from soil: a) anion exchange, b) acid dissolution, c) cation complexation, and d) cation hydrolysis. Acetic acid, Truog and lactate release P from soils through one or more of these mechanisms, for example for Bray-1P method reactions a) and b) are probably dominant. Resin method instead, uses a so-called ‘infinite sink’ in which the extraction reaction is moved on the right side by the removal of phosphate from the solution by the resin. The isotopic exchange is based on an exchange between the P on soil surfaces and the P in the solution. So, probably resins and isotopic exchange are less influenced than Truog, lactate and acetic acid by the modification in solid:solution ratio and by the presence of a different number of adsorption sites on the solid surfaces. In fact, Barrow and Shaw, (1976) demonstrated that the quantity of extracted P, by Olsen method, depends partly on the amount displaced from soils and partly on the extent of secondary adsorption that is regulated by the soil:solution ratio and by the composition of extracting solution. (particularly by the capacity of the present anions to compete with phosphate for adsorption sites).

Determining available P from separates with the same solid: solution ratio used for the soils the number of sorption sites available for re-adsorption is strongly changed, especially for clays separates. These can explain why some authors found a decreasing in available P in smallest separates. When P is extracted by an infinite sink (resin) or determined by isotopic dilution the ratio solid:solution and the re-adsorption are less important and an increase with decreasing particle size was found.

Tentative conclusions

Clays are particularly enriched in total P in soils poor in clay content. P on clays is organic or bound to iron and aluminium oxides. So ER is higher than 1 for total P, organic P and resin P. But clays are rich in available sorption sites so often these particles can act both as a sink or as source of P.

There are some lacks:

- for erosion purposes it should be better to analyse the first 2-5 cm of soil and not A horizon or ploughing depth;
- different methods of obtaining separates can simulate various degrees of erosive events, should be useful to have information of the P content of separates obtained with different methods;
- nobody, as long as we know, evaluated the P sorption saturation of clay separates. This parameter should be the key factor in regulating sorption/desorption behaviour of clays in waters;
- for evaluating available P should be useful to have more information based on methodologies using an 'infinite sink', to evaluate the quantity factors and water or dilute $CaCl_2$ to estimate Intensity factor.

3. Modification in dispersion/flocculation phenomena of soil colloids due to the presence of P

As seen from the previous results, due to their high specific surface area and reactivity, mobile inorganic particles consist mainly of clay minerals and hydrous iron and aluminium oxides that may accumulate P on their surface and thus contribute to P losses. But to significantly influence P transport mechanisms, in addition to high reactivity, these colloids must be present in relatively high concentrations in soils solution and that is regulated by dispersion /flocculation phenomena.

While numerous evidences have been gathered to support the occurrence and environmental significance of colloid mobility, there has been little work investigating the specific geochemical controls on colloid stability and transport in natural systems.

In soils there are fixed-charge constituents, mostly crystalline clay minerals that develop a negative charge as a result of lattice substitutions, and variable-charge constituents, mainly iron and aluminium oxides. The net surface charge of these particles is dependent on pH, ionic strength and ionic composition of the soil solution that greatly influence dispersion /flocculation behaviour of these particles and thus their mobility in the soil system. In addition the net surface charge of these particles can be modified by their reaction with anions as phosphate. In fact although the adsorption of phosphate on soil surfaces involves specific chemical bonding of phosphate ions with Fe oxides (Parfitt *et al*., 1976; Goldberg and Sposito, 1985; Torrent *et al*., 1990), the charge and the electrical potential of the surface can affect the adsorption extent. When ions react with charged surfaces, the electrical potential plays a role closely analogous to that played by energy of adsorption for reaction between molecules and uncharged surfaces (Barrow, 1993). The electric potential of the reacting surface and the speciation of adsorbate ions are controlled by pH suspension and by the nature and concentration of electrolytes (Barrow *et al*., 1980).

Cations near the negatively charged clay surfaces are subject to an electrostatic attraction towards the surface as well as a tendency to diffuse into bulk solution. As a result, the concentration of cations diminishes exponentially as a function of distance from the clay surfaces forming the 'electrical double layer'. The formation of the double layer leads to mutual repulsion of opposing clay surfaces in dilute electrolyte solutions. The repulsive forces decrease when the double layer is compressed, this happens as the valence of the cation and/or the ionic strength of the solution increases.

Attractive forces as well exist between clay particles, mainly Van der Waals forces. These forces can be active only when the distance between particles is small; so as the double layer is compressed attractive forces become more important. When the net force is attractive the clay particles remain close together and they flocculate, conversely if the net force is repulsive the particles may exist as separate entities in a dispersed state.

The Point of Zero Charge (PZC), i.e. the pH at which the net surface charge of a solid equals zero, is an important parameter affecting both the colloidal stability and the interactions of the colloids with the larger, and thus immobile, soils particles. Above the PZC, minerals possess a net negative charge, while below this pH, the net charge is positive. Silica, layer silicates and the manganese oxides have PZC <4 so they would exhibit a net negative surface charge under most environmentally relevant pH conditions. On the other hand, iron and aluminium oxy-hydroxides have PZC ≈ 7-8 so they can have positive, neutral or negative charge depending on the soil pH.

So we can look at the soil solid phase as a system formed by an immobile phase (having mainly negative charge and formed by silt, sand and aggregates of clay minerals-organic materials-oxides) and a potential mobile phase. Iron and aluminium oxides and clay minerals constitute this potential mobile phase that can be enriched of P.

It is well known that in presence of KCl or $NaClO_4$ the charge of goethite changes from positive to negative value increasing the pH and the differences in the entities of the charge decrease with increasing ionic strength of the solution (Barrow, 1985). In the presence of $CaCl_2$ the goethite never showed a negative value of zeta potential (ζ), neither to the highest pH values (Celi *et al*. 1998). The ζ decrease, from +50 to +18 mV was followed by a particle size increase from 0.8 to 1.6 μm. The presence of Ca^{2+} caused a surface excess of positive charge at all pH values. This can be attributed to the fact that Ca^{2+} is adsorbed on the surface by specific bonding and the bond strength increases with increasing pH (Kinniburgh *et al*., 1975). Thus, Ca^{2+} balances the surface excess negative charge caused by pH increasing.

Barrow (1985) demonstrated that, in presence of monovalent cations (K^+ or Na^+) surface charge of goethite is influenced by phosphate adsorption moving PZC towards more acidic pH values.

The adsorption of inositolphosphate (IHP) caused a higher change of the surface that became negative (-45 mV) even at pH 4 (Celi *et al*. 1999). After IHP adsorption goethite was dispersed at all pH values while after adsorption of inorganic P it was dispersed only at pH higher than 5.

In presence of $CaCl_2$ after IHP adsorption, ξ of the surface changed from -16 to -5 mV following the increasing pH, while after Pi adsorption it showed values ranging between +2 and -4 mV; both adsorbates caused flocculation.

Liang and Morgan (1990) observed that relatively high concentrations of phosphate enhance colloidal stability through charge reversal on positively charged particles resulting in surfaces exhibiting an effective net negative charge at pH<<ZPC.

Puls and Powell (1992), studying the behaviour of spherical, monodisperse Fe_2O_3 colloids, (100-300 nm) showed that at pH < or > than PZC the particles are dispersed while at pH $\approx$ PZC iron oxides particles are flocculated. But when suspended in NaH_2PO_4 0.010 M the Fe_2O_3 particles were dispersed from pH 4 to 11. In addition to increase stability region where the particles are net negatively charged, the magnitude of that charge is increased at a given pH by these charged anions, thus contributing to enhanced stability of the iron oxide particles over the pH range. The presence of phosphate dramatically affected the transport of colloidal particles trough a column packed with aquifer solids (mainly quartz and albite): no colloidal transport occurred for iron oxides at pH<PZC indicating electrostatic interaction between the positively charged iron oxides and the net negatively charged matrix material. But, in presence of NaH_2PO_4 the iron oxide particles could pass almost completely through the column tests indicating that the increased negative surface charge on the particles resulted in increased repulsion between the Fe_2O_3 particles and the aquifer solids.

The charge-reversal effect could have significant implications in the subsurface if sufficient amounts of specifically sorbed anions are present and capable of increasing the repulsion between individual colloidal particles (increased stability) as well as between the mobile particles and the immobile matrix minerals, thus promoting their transport.

The specific adsorption of the predominantly divalent phosphate anion onto iron oxides surface causes a charge reversal of the initially net positively charged surface and an increase in inter-particles separation due to increased particle-particle repulsive forces. The effect is a lowering of the PZC and an increase in net negative charge near the particle surface over a wide pH range. This also increased the repulsion between the mobile, negatively charged particles and the immobile, net negatively charged matrix of the soils. As a result, the particles remain at a greater distance from the pore walls where the fluid velocity is higher. This charge exclusion, in addition to size-exclusion phenomena, may explain the faster transport of the P containing iron oxide particles.

Recently, Haynes and Naidu (1998) reviewed the effects of applications of phosphate fertilisers on soil physical conditions. They pointed out that applying high rates of fertiliser phosphate on acid soils containing high levels of soluble and exchangeable Al can be favoured flocculation of soil colloids and increased the water holding capacity of the soils through the precipitation of Al as insoluble Al phosphate that can act as flocculating and cementing agent in a similar way to hydroxy-Al compounds.

Addition of phosphoric acid can increase aggregate stability of soils as its addition lowers the pH and solubilises Al compounds or $CaCO_3$ with subsequent aggregating effects (Robbins *et al*., 1972; Yeoh and Oades, 1981).

Tentative conclusions

Mobilisation of colloids, phyllo-silicates and iron and aluminium oxides in soil-waters systems depends on the dispersion/flocculation phenomena.

From the point of view of colloids enriched with P the key factor should be the charge of iron and aluminium oxides. When neutral they can aggregate (oxide/oxide) and flocculate, when positive they can interact with negatively charged clay minerals and flocculate, when negative they disperse. In absence of phosphate sorbed on them the charge is positive at pH< PZC, neutral at pH=PZC and negative for pH >PZC. When inorganic phosphate is sorbed on it, in presence of solution containing monovalent cations, a charge reversal of the initially net positively charged surface happens, this charge reversal is even more important when IHP is sorbed on it. This increases the repulsion between the mobile, negatively charged particles and the immobile, net negatively charged matrix of the soils. The presence of bivalent cations produces surfaces more positive in absence of P and less negative in presence of P, so the overall effect is aggregating.

Soil conditions that can promote dispersion of iron (and aluminium?) oxides are thus:

- presence of P sorbed on the oxides, (even more if IHP is sorbed)
- pH not acidic
- presence of monovalent cations (saline soils?)
- dilute solutions.

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Detachment and transport of particle-bound P: Processes and prospects for modelling

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1. Introduction

Given that much of the soil phosphorus is associated with soil surfaces, it is reasonable to presume that soil erosion is likely to be an important mechanism for transporting phosphorus from agricultural fields to the aquatic environment. The work of Catt et al. (1998) supports this. In a comparative study of phosphorus transport routes they showed that in the Brimstone field experiment, located on a clay soil, losses of phosphorus in soil drainage were between 0.37 and 0.91 kg ha^{-1}, compared with phosphorus losses of between 0.03 and 1.22 kg ha^{-1} in surface runoff. Losses in surface runoff reported from the Woburn Erosion Reference Experiment by the same authors are somewhat higher, at between 0.8 and 18.7 kg ha^{-1} for a four-year arable rotation.

In this short paper I will give a brief review of soil detachment and transport processes (the term soil erosion is not used to avoid confusion). Then discuss how these processes will influence the transport of P and finally consider the prospects for modelling in this area.

2. Soil detachment and transport processes

Soil detachment and transport processes are well described in the literature, and reviews can be found in a number of standard texts on the subject e.g. Morgan (1995) and Hudson (1995).

Soil detachment can be viewed as a number of interacting processes occurring within a landscape. These processes are linked spatially, by flows of energy and material and vary temporally due to changes in rainfall and soil topographical, hydrological and chemical properties. Figure 1 attempts to illustrate these relationships. The key detachment processes of splash (raindrop) detachment and flow detachment are identified and those parameters and variables that influence them are indicated. Figure 1 could be viewed as representing a soil erosion model at a point in the landscape, however, such points will be linked to others which they will also influence.

The processes of soil detachment and transport have been described in terms of mathematical equations by a number of authors (e.g. Styczen. and Nielsen, 1989; Poesen, 1985). For splash detachment the most common approach is to relate the amount of splashed material to the kinetic energy of the rainfall. One such relationship is that used by the European Soil Erosion Model (EUROSEM) (Morgan et al., 1998).

In EUROSEM raindrop or splash detachment (DR; m^3 s^{-1} m^{-1}) is described using the relationship:

$$DR = \frac{k}{\rho} KE\, e^{-zh} \qquad (1)$$

where k is an index of the detachability of the soil (g J^{-1}) for which values must be obtained experimentally, ρ_s is the particle density (kg m^{-3}), KE is the total kinetic energy of the net rainfall at the ground surface (J m^{-2}), z is an exponent varying between 0.9 and 3.1, depending on soil, and h is the mean depth of the surface water layer (mm).

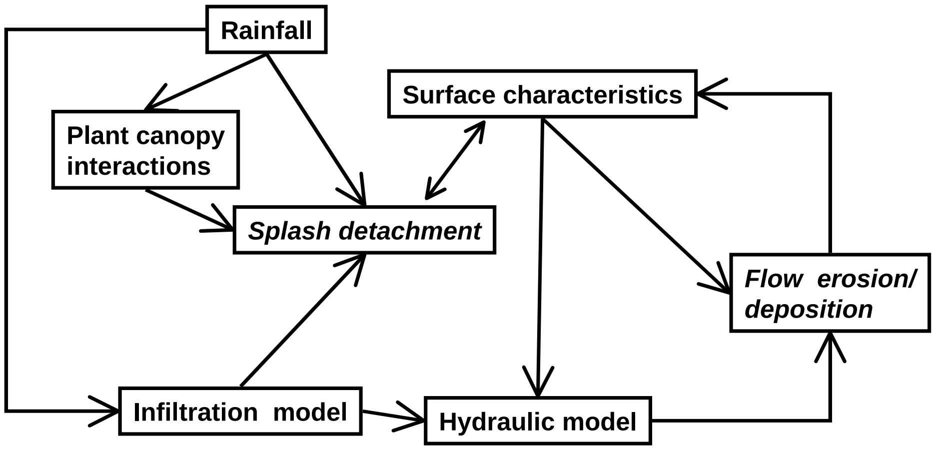

Figure 1, Flow chart demonstrating the influence of key factors on detachment and transport processes.

Equation 1 illustrates the importance of interactions with other components of the erosion process. The kinetic energy of the rainfall is influenced by the rainfall characteristics: larger drops have larger kinetic energies, whilst smaller drops have lower energies. Rainfall characteristics are altered when raindrops hit the plant canopy: some will shatter producing smaller drops, while some will coaless on leaves before falling to the ground as large drops. Brandt (1989) has shown that, in forests, large drops from leaves may be significant sources of splash detachment. Splash detachment is also affected by the depth of water on the soil surface, which is linked to the soil's infiltration properties and surface microtopography.
The description of flow detachment and deposition in current process based soil erosion models is more variable. Some models such as WEPP (Nearing et al., 1989) describe both detachment and deposition separately. Others such as EUROSEM (Morgan et al., 1998) and GUEST (Rose et al., 1983) describe detachment and deposition of material as a continuous interchange of material with the current position of balance giving the ambient sediment concentration. According to the theory used in EUROSEM the flow detachment rate (DF: m^3 s^{-1} m^{-1}) is given by:

$$DF = \beta\, w\, v_s\, (C_m - C) \qquad (2)$$

where β is a flow detachment efficiency coefficient, which becomes equal to unity when material is being deposited, V_s the settling velocity of particles m s^{-1}, C the actual sediment concentration, w is the width of flow (m) and C_m the equilibrium sediment concentration.

Detachment by flow will be highly dependent upon the velocity of the overland flow, this is in turn dependent upon the roughness of the soil surface over which the water flows, which is affected by the splash detachment. The surface characteristics also influence the amount of flow detachment through influencing the resistance to the shear forces imparted on it by the overland flow. Feed backs also exist here due to changes in the surface properties caused by both splash and flow detachment.

It is worth noting that at present no process-based soil erosion model takes the effect of soil chemical properties into account when describing soil detachment.

3. Interaction between erosion processes and P transport

Current soil erosion models have concentrated on simulating bulk soil losses. However, it is well known that amounts of phosphorus transported by surface runoff are often greater then the concentration of P in the bulk soil, because phosphorus is associated primarily with the finer fractions of the soil (Syers & Walker, 1969) and water erosion is a selective process. It is also generally accepted that the selectivity decreases as the magnitude of an erosion event increases (Massey and Jackson, 1952; Quinton et al., 2001). This is illustrated in figure 2, which, using data from the Woburn Erosion Reference Experiment (Catt et al., 1994), shows P concentrations declining as soil loss increases.

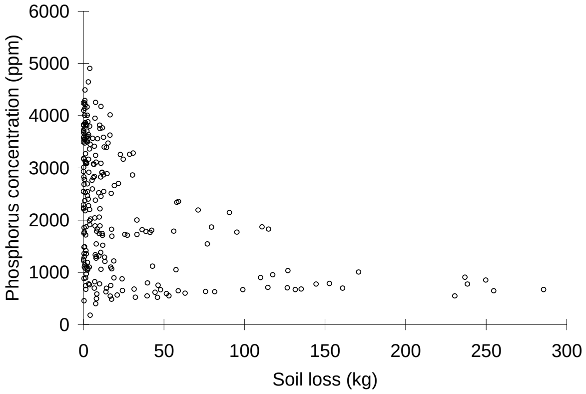

Figure 2: Effect of event magnitude on P concentration.

Interestingly, the variability of P concentrations found in the sediment also decreases with increasing P loss. It is hypothesized that this is due to the variability in the intensity of the erosion events for smaller magnitude soil losses: an event may be short duration and intense, or long duration and of low intensity, and give the same soil loss.

Due to their higher selectivity small erosion events contribute a disproportionate amount of P to the total P lost form an area. This is illustrated in figure 3, which shows that, when ranked in order of magnitude, events contributing 50% of the soil loss through relatively small amounts of sediment contribute over 75% of the total P loss.

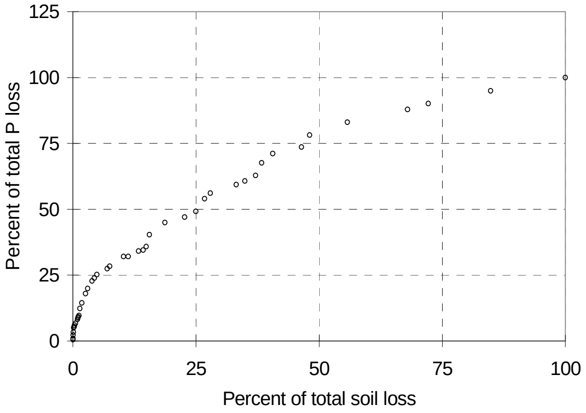

Figure 3: Relationship between ranked soil loss and the percent of total P lost from plot 7 of the Woburn Erosion Reference Experiment.

4. Prospects for modelling

Theoretically, selectivity will operate in two components: detachment and transport. There is little doubt that the finer fractions of the soil, once in suspension, will travel the greatest distances. The clay-sized fractions remain in suspension even in standing water due to their colloidal nature. This leads to the enrichment of finer materials as the flow's distance of travel increases. However, whilst in theory selective detachment also seems likely, there has been little experimental work done on the selectivity erosion of different size classes from soils. Work has instead tended to concentrate on the selective detachment and transport of sediments from non-cohesive sources with a narrow particle size range, for example Poesen and Savat's (1980) study of particle size separation by splash and runoff, Govers' (1990) work on shallow flow transport capacities and Poesen's (1985) study of splash detachment. There are some exceptions, notably the work of Torri and Sfalanga (1986) who considered the selective detachment of material from clay aggregates and found enrichment in the 0.063 to 0.5mm size range.

Present models which simulate P loss by erosion fall into two categories: those which use and empirical equation to calculate a P enrichment ratio or those which attempt to model the selectivity process explicitly.

The empirical approach utilises equations based on the early work of Massey and Jackson (1952). In their equation P enrichment ratio is related to soil loss:

$$\ln(ER) = a + b \ln(sed) \qquad (3)$$

in which ER is the sediment discharge (kg ha^{-1}) and a and b are constants which depend upon soil type and cropping practices. Equation 3 is easy to apply, but given the data presented in figure 2, there will be obvious problems for lower magnitude events.

The process-based approach, which is based on theory proposed by Foster et al (1980) has relied on modelling deposition. It is based on three simple rules:

1. If the energy of the flow is greater than that require to transport all the entrained material then all size classes are transported;
2. If the energy of the flow is lower than that required to transport the smallest material, then all size classes are deposited;
3. If the energy is enough to transport some size classes, but not others then is distributed amongst the particle size classes.

This approach, although operational in CREAMS (Knisel et al., 1980) and Opus (Smith, 1990) is based on limited experimental data, and virtually no validation work has been attempted.

5. Conclusion

This paper has briefly reviewed the relationship between detachment and transport processes and the loss of P associated with sediment in overland flow. However, at present we are still learning how to model these processes. If we are to better describe the processes of selectivity then experimental and field studies will be required to test existing theory and develop new ones.

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Influence of soil processes on solubilisation of P forms: A review of experimental data

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1. Introduction

Understanding solubilisation of phosphorus (P) from solid soil to waterways is complex, but holds the key to controlling leaching and therefore eutrophication. Reviewing the processes of P solubilisation is further complicated by the variety of techniques for sampling combined with the range of analytically defined forms that are available for defining 'soluble P'. Since studies have focussed on a variety of P *forms* in a range of sampling *scales* and *circumstances*, it is often difficult to isolate the key parameters, particularly when attempting cross comparisons of databases (Haygarth and Sharpley, 1999). Before proceeding with a review it is, therefore, necessary to be aware of these variances, which can be classified into (1) P forms and (2) sampling and scale.

2. Phosphorus forms in solution: operational and chemical definitions

(see also paper by Hens & Schoumans, this volume).

Operational definitions: Filtration is used to define the difference between 'soluble' or 'dissolved' and 'particulate' forms of P. However, these classifications are problematic because different laboratories can use different filter sizes, and studies have shown that P can be associated with a continuum of <0.45 μm sized particles or colloids (De Haan *et al*., 1984; Haygarth *et al*., 1997). This attaches considerable ambiguity to the definition of 'soluble', 'solubilisation' and 'solution' and due caution must be applied when interpreting published information. There are similar problems with chemical definitions such as inorganic P, organic P and orthophosphate P in water. The most common method for P determination is by the molybdate (Mo) blue reaction (Murphy and Riley, 1962) and the main misinterpretation is that the procedure *exclusively represents* inorganic orthophosphate. Although the original Murphy-Riley Mo-blue reaction *per se* is a reaction specific to orthophosphate-P, the sample preparation procedure which precedes the colour reading can readily transform P, resulting in over estimations (Edwards and Withers, 1998). The Murphy-Riley procedure can also determine loosely bound inorganic and organic forms of P, reflecting either Mo enhanced hydrolysis, hydrous ferric oxide-orthophosphate reactions, or interferences with silica (Ciavatta *et al*., 1990). Thus, it is technically incorrect to refer to Murphy-Riley determined fractions which are Mo-reactive as 'orthophosphate' or 'phosphate'. Classification of operationally defined P in water is defined at greater length in Haygarth and Sharpley (1999).

Chemical definitions: Analytical difficulties and challenges have meant that chemical definitions of P have been used less than operational definitions, but there are some published papers. In general, information is limited to studies employing enzymatic techniques to soil water extracts and soil solutions obtained by centrifugation (Pant *et al*., 1994; Shand and Smith, 1997). Shand and Smith (1997) used soil solution from an acid peaty podzol in north-east Scotland under improved grassland to determine acid phosphatase and phytase hydrolysable P forms. Both enzymes released 54 - 67% of the dissolved organic P present in the solution, indicating the presence of monoester P forms, although *ca* 40% of the dissolved condensed P was also hydrolysed. Pant *et al*. (1994) obtained soil water extracts of four acid soils and showed that whilst phosphatase hydrolysed between 20 - 28% of the organic P, indicating the presence of monoester P in the samples, phytase hydrolysed an additional 27-35%, indicating the presence of inositol hexaphosphate in solution. Recently, Espinosa *et al*. (1999) used strong anion exchange HPLC to show the presence of a range of organic P compounds in soil leachate water. Orthophosphate constituted *ca* 70% of the total dissolved P in the sample, whilst the remaining 30% was comprised of inositol hexaphosphate and glucose phosphate in approximately equal proportions, plus traces of ATP, phosphonates and other unidentified compounds.

3. Sampling and scale

Solubilisation of P is studied using a variety of field and laboratory techniques, which we call experimental scales, and all have a strong bearing on the interpretation of the data. At the smallest scale, samples of soil are removed from the field and solution can be extracted in the laboratory. These may employ a variety of extractants, mostly water, at varying solid/solution ratios, but may also use centrifugation techniques for displacement of *in situ* soil water. At the next largest scale, samples are taken *in situ* and may involve taking soil water from suction cups under tension, or passively drained water from lysimeters, at the soil profile (m^2) or slope/field (ha) scale. Considerable difficulties arise when comparing waters at these various experimental scales. For example, Chapman *et al*. (1997) studied free drainage lysimeters in the laboratory to compare the P composition of drainage waters with those obtained from measurements of P in solutions and extracts of the same soil. Their results showed major differences between the various experimental measurements. Firstly, concentrations of total P in the soil solution were twice as large as those in the leachate water. In addition, leachate water from the lysimeters contained *ca* 70% dissolved reactive P and 30% dissolved organic and condensed P. However, soil solution obtained after destructive sampling of the lysimeters contained only *ca* 54% DRP, whilst DOP represented a much larger proportion of the total soil solution P. In terms of soil water extracts, the choice of extract ratio is critical in determining the composition and concentrations of P determined. Low extract ratios compared more favourably to the composition of leachate P, with a 1:1.2 extract ratio providing the most accurate estimate. This is far lower than the extract ratios used in the most common water extract methods, where a much wider ratio is more common. A particularly notable example is called the Pw method, as described by Van der Paauw (1971), which uses a ratio of 60:1 water to soil both on a volume basis, preceded by 22 hour 'moistening' of the soil sample. The moistening process may represent a useful 'equilibration' step and, indeed, a high correlation between Pw value and soil P status was found, although this did not reflect differences between soil factors, such as $CaCO_3$ content, pH and other factors relating to the soil. This is an important point as it implies that soil solution P is mostly related to P status and that variations is soil properties and hence land use are of less importance.

In a field study, Magid *et al*. (1992) used free draining lysimeters and suction cups installed at 90 cm depth in a sandy arable soil to compare the two methods of soil solution sampling. Soil solution contained relatively similar proportions of organic and inorganic P (*ca.* 2.2 µM). However, the P composition and concentrations from the lysimeters were significantly different. Inorganic P concentrations were *ca* 2.5 times greater than those of organic P, whilst concentrations of both forms were greater (10 µM and 4 µM for inorganic and organic P, respectively) than in the suction cups. The lower P concentrations in the suction cups than the lysimeter drainage may have been a function of the depth of sampling in the soil. Problems associated with the used of suction cups have been noted by other authors (Hansen and Harris, 1975; Hatch *et al*., 1997).

Preliminary conclusion about the approach

The differences in P composition and concentrations determined in drainage waters and soil solutions, therefore, appear to relate strongly to the type of water being sampled. Suction cups and centrifugation both measure relatively immobile pore water, whilst lysimeters additionally measure the mobile water moving through preferential flow pathways. Therefore lysimeters, perhaps, provide more accurate measures of the P forms and concentrations in drainage water and the ability of suction cups/soil solution to indicate P transfer depends on the mobility of the water being measured. This is important, because it is drainage water that will reach surface waters and impact on water quality. The implication is that it is only possible to compare differences in P forms and concentrations between soil types/land-uses/managements within an experimental scale (e.g. soil solution extract), but misleading to compare differences between scales (e.g. soil solution extract compared to lysimeter water). This review, therefore, splits experimental studies into three sections: soil solution extracts in the laboratory, lysimeter studies (m^2) and slope/field scale (ha). We conclude by making a provisional recommendation of a standardised European method for assessing soil potential P solubilisation (PPS), to form a basis of the discussion during the workshop.

4. Review of experimental studies

4.1 Soil solution extracts

Organic P frequently forms the dominant fraction (up to 90%) of the total P in soil solution under a range of soil types, land-uses and management conditions, from P-deficient upland soils to high input lowland agricultural soils (Chapman *et al*., 1997; Helal and Dressler, 1989; Magid *et al*., 1992; Ron Vaz *et al*., 1993; Shand *et al*., 1994). This phenomenon is not restricted to upland soils, but also occurs in soils under arable cropping (Magid and Nielson, 1992). Therefore, at the soil solution scale, it is clear that organic P forms are an important component of P release from the soil.

Ron Vaz *et al*. (1993) used centrifugation at low speeds to obtain soil solution from lowland soils (typic fragiothod) that had been under various cropping (arable and cut grassland) and fertilisation regimes. The relative importance of inorganic, organic and condensed P forms showed considerable variation between treatments. DRP ranged between 12% for the zero-P fertiliser treatment to 56% at the highest input site. Condensed P forms ranged between 11 - 39% of the total, displaying a rapid decline with increasing soil P status. However, dissolved organic P, measured by UV oxidation, remained relatively large and constant across treatments at between 42 - 62% of the total dissolved P. Concentrations of DRP and DOP increased as soil pH increased. Dissolved reactive P concentrations decreased down the profile, whilst organic and condensed P concentrations remained relatively constant, suggesting the mobility of these compounds and their importance in P transfer.

Shand *et al*. (1994) found that soil solution from P-deficient upland grazed pastures contained average total P concentrations between 51 - 119 $\mu g\ L^{-1}$, which were similar across three different soils. Organic P dominated the soil solution P and exceeded inorganic P concentrations by 5-20 times: for the three soils over two years , inorganic P ranged between 4 - 9 $\mu g\ L^{-1}$ and organic P between 23 - 76 $\mu g\ L^{-1}$. Maximum concentrations of inorganic, organic and total P were in August-October during the two years, which coincided with the minimum soil water contents. Fertilisation with P had little impact on the proportions or concentrations of P forms in solution. Centrifugation was also used by Chardon *et al*. (1997) to investigate the P composition of soil solution under heavy manure application. They found that the proportion of the total P as organic P increased significantly with depth, implying the mobility of manure-derived organic P in the soil.

Magid and Nielson (1992) and Magid *et al*. (1992) used suction cups to determine P forms and concentrations in soil solution at different depths under freely-draining pasture and arable soils with low organic carbon contents (<1%). Pasture soils contained higher concentrations of inorganic and organic P in solution at 30 cm depth than the arable soils. Inorganic P concentrations were greater than organic P concentrations at 30 cm under both land-uses, whilst at 90 cm depth in the arable soil, organic and inorganic P made up similar proportions of the total. Temporally, inorganic P was found to display autumn minima, with winter minima in organic P. Dils & Heathwaite (1996) used piezometers to determine the DRP: DOP ratio of soil solution at depth under pasture to be *ca* 0.02 - 0.3, indicating the dominance of organic P at depth in this soil, whilst Helal & Dressler (1989) found that centrifuged top-soil solution contained up to 90% organic P.

The most likely mechanisms involved in the maintenance of high organic P and low inorganic P in soil solutions appear to be microbially determined. Seeling and Zasocki (1993) used sterile and non-sterile soils to determine that organic P in soil solution declined to zero in the absence of a microbial population, whilst inorganic P concentrations increased substantially. The processes of immobilisation of solution inorganic P by the biomass and release in organic forms on cell death maintain a low inorganic, but high organic P concentration (see paper by Gil-Sotres *et al.* in this volume).

Soil water extracts are used to infer the pool of potentially mobile P in the soil and to predict the P concentrations that might be found in soil leachate. However, these types of studies can be potentially misleading (see earlier). Chapman *et al*. (1997) showed that the choice of soil:water ratio can strongly influence the concentrations and proportions of P fractions in the extracts. By comparing P in extracts at different ratios with soil solution and leachate water concentrations, they were able to determine that the optimal extract ratio for prediction of the relative proportions of inorganic and organic P in leachate water was *ca* 1:1.2. They found that the proportion of inorganic P in the extract increased from 71 - 92% as the extract ratio increased from 1:1.5 - 1:15.4, whilst the dissolved organic P component decreased from 26 - 6% for the same ratios.

4.2 Lysimeters

In general, the forms and concentrations of P determined in drainage from lysimeters do not resemble those in soil solution. This indicates the importance of preferential flow pathways in the soil, providing rapid movement of drainage water to depth (Turner and Haygarth, 2000). At the laboratory scale, several studies have examined P forms in leachate from small-scale lysimeters. Chapman *et al*. (1997) compared P forms and concentrations in leachate from laboratory columns sown with grass, with those obtained from soil solution after destructive sampling of the cores at the end of the experiment. They found that dissolved inorganic P in leachate from the lysimeters represented *ca* 70% of the total P. However, in soil solutions, dissolved inorganic P represented only 54% of the total P at the expense of an increase in organic P, which represented a much larger proportion of the total P in the soil solution. Chardon *et al*. (1997) used heavy manure applications to unpacked, unvegetated topsoil overlying sand. They determined very high concentrations of total P in leachate, which was dominated by organic P forms. This finding is consistent with the studies of Hannapel *et al*. (1963a; 1963b) and Turner *et al* (1998) who found that under organic carbon amendment, soil leachate was increasingly dominated by organic P at the expense of inorganic P. This appears to correspond to elevated biological activity in the soil, increasing P turnover through the solution.

Turner and Haygarth (1999) used large-scale monolith lysimeters (80 cm in diameter, 130 cm deep) to monitor P forms and concentrations under a range of contrasting permanent grassland soil types. Despite a wide range of soil P contents, total P concentrations in solution were remarkably similar at *ca* 100 µg L^{-1} over several years. Maximum concentrations >200 µg L^{-1} were detected in the springtime, reaching more than 4 mg L^{-1} in one drainage year (Simard *et al*., 1998). The leachate was dominated by inorganic P from all soil types (60-70% of the total P), that occurred mainly in the dissolved (<0.45 µm) form. Dissolved organic P represented only 6-16% of the total P on average, although large amounts were measured in the springtime, possibly released as a result of increased microbial turnover (concentration (see paper by Gil-Sotres *et al.*). Interestingly, unreactive P forms >0.45 µm constituted a large proportion of the total P transferred, which might possibly consist of microbial cells and cell debris (Hannapel *et al*., 1963b).

Chardon *et al*. (1997) used field lysimeters of 40 cm depth under heavy manure application, sown with maize. Unlike soil solutions and laboratory columns, where organic P represented the majority of the solution/leachate P, organic P represented only 75% on average of the leachate P from the field lysimeters. Magid *et al*. (1992) used field lysimeters in an arable soil to compare the P forms with soil solution obtained from suction cups. Leachate from the free-draining lysimeters contained more inorganic than organic P and greater concentrations of both forms than suction cups (10 µM and 4 µM for inorganic and organic P, respectively), averaging *ca* 70% for inorganic P and *ca* 30% for organic P. Soil solution sampled using suction cups averaged 50% for each fraction.

4.3 Slope field (ha) scale – beyond the soil profile

Most studies on the slope/field scale relate to artificial drainage. Dissolved reactive P is the dominant form reported at these scales. For example, in artificially drained clay soils in south-west England, Haygarth et al. (1998) reported that total dissolved P concentrations were dominated by reactive P. However, of the total P (including particulates), reactive and unreactive P forms contributed 50% each. Similarly, Turtola and Jaakola (1995) found that artificial drainage from heavy clay soils under arable and pasture in Finland were dominated by dissolved reactive P and that particulate P was a large fraction of the total. Jordan and Smith (1985) found that dissolved reactive P dominated the drain outflow from a small pasture catchment in Northern Ireland, but that dissolved unreactive P forms accounted for ca 30% of the total P transferred. Heckrath et al. (1995) studied P in pipe drainage from low carbon arable soils under heavy P fertilisation in the UK. They found that dissolved reactive P accounted for 78 - 86% of the total P determined, with dissolved organic P representing only 4.5% on average, although up to 40% under certain conditions.

5. Summary of the literature review

- There are significant difficulties associated with defining soluble P and P released by solubilisation mechanisms, because of problems describing P forms and the varied experimental circumstances that describe ‘solubilisation’.
- It is only possible to compare data for soils sampled and analysed in a similar manner. For example, it is not possible to compare data from suction cups to data from monolith lysimeters. This means that the amount of useful published data available is small.
- Most studies to date have focused on methodology, rather than on comparisons between agronomic/soil variables. The variation between solution sampling methods is very high and makes differences in agronomic treatments difficult to untangle. There is, therefore, the need for further studies using the same sampling technique, to compare agronomic treatments, systematically.
- We need to agree a simple protocol for determining potential solubilisation of P forms in the soil profile, which can be subsequently tested and applied around Europe.

6. Provisional protocol, meant for discussion

Methodology for testing European soils for potential for P solubilisation (PPS).

We decided that displacement of *in situ* soil water is not a satisfactory approach to PPS, because in dry conditions, soils may contain little or no water. We therefore prefer an extract method, outlined below:

- *Sample depth*: This is to be discussed fully elsewhere in the WG2, but is particularly relevant to a PPS test. Sample depths for PPS are strongly related to the effective depth of interaction (EDI) of runoff water: For example, a shallow sample depth, such at 0-2 cm or 0-5 cm may be most appropriate. Alternatively, two sample depths may provide a better insight, with the second one comprising a bulk of 0-10 or even 0-20 cm.
- *Sample preparation*: This is to be discussed fully elsewhere in the WG2, but is also particularly relevant to PPS. Length and means of sample storage are important. Size of soil sieve (eg. < 2 mm or < 4 mm), if any, is also a consideration. We advocate minimal sample storage time and minimal soil disturbance. *In situ* (antecedent) soil moisture conditions also warrant consideration, as they will vary spatially and temporally, and will have a high impact on the PPS value determined.
- *Extract ratios:* Since there is much controversy over soil to water extraction ratios, we suggest that both a high and a low ratio should be used. The low ratio may be 1:1.2 (soil to water, by volume) and the suggested high ratio will be 1:15 (soil to water, by volume). PPS values can be quoted for both ratios.
- *Equilibration:* Once soils are in bottles we suggest that static equilibration period of 24 hours is essential. This should be conducted at 20^{o}C.
- *Extraction:* Gentle shaking should be undertaken for 1 hour at 20^{o}C.
- *Primary Filtration:* Should occur immediately after extraction with Whatman No. 2 paper.
- *Secondary Filtration:* Should occur immediately after primary filtration with CNA membranes <0.45 µm.
- *PPS determination:* Total P (after persulphate digestion or similar) is the primary determinant to be applied to both filtrates. PPS after primary filtration will be 'Total P' and PPS after secondary filtration will be 'Total P <0.45'. Additional P forms can be determined using the protocol outlined earlier, to derive 'unreactive', 'reactive', '<0.45' and '>0.45' forms (according to the method described above).

A PPS method such as this could provide a particularly effective risk assessment for P transfer in rapid flows, such as overland or preferential, associated with all forms of P. Alternative, more traditional chemical agronomic soil P tests, may provide a more refined means of assessing 'leaching' potential, which will occur during the slower water flows (discussed elsewhere in WG2).

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Environmental soil P-test in relation to solubilisation

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1. Introduction

Starting with Dyer, already in 1894, an attempt was made on measuring the available P in soils and relating the results to the need for phosphate fertilisers . He theorised that an ideal extracting solution would be one that had a pH similar to that of root sap. Since 1945 there has been a number of significant developments in the area of soil chemistry and soil fertility which have had a marked impact on our understanding and interpretation of soil tests for P. The objectives of these tests are listed as follows: (i) grouping of soils into classes for the purpose of making fertiliser recommendations, (ii) prediction of the probability of getting a profitable response to application of fertiliser P, and (iii) providing an index of the P amount a soil can supply. (Kamprath and Watson, 1980). Considering the different chemical methods which have been proposed, the following groups can be identified (Sibbesen, 1983; Houba *et al*., 1992; Sims, 1993):

- methods employing hydrochloric acid and ammonium fluoride. This group includes two related methods published by Bray and Bray and Kurtz. The stronger acid extractant removes more of the phosphorus from the less soluble forms. In both solutions the fluoride ion is included for the replacement of sorbed phosphate;
- methods involving stronger acid extractants. These refer to various strengths of HCl in soil solution at various ratios;
- methods involving weaker or very weak extractants: one is a simple water extraction;
- methods employing acetic acid buffered with sodium acetate: the original method, buffered at pH = 4, known as the Morgan method;
- methods using a strong complexing agent (lactic acid).

An overview of the extractants currently used is presented in Table 1. It is obvious that in accordance with the specific complexation or solubilisation strength, the P amount recovered will differ.

A good soil test should meet the following three criteria:

- the extractant used should extract all or a proportionate part of the available form or forms of the nutrient from soils with variable properties;
- the amount of nutrient extracted should be measured with reasonable accuracy and speed;
- the amount extracted should be correlated with the growth and response of each crop to that nutrient under various conditions (Kamprath and Watson, 1980).

It has been found that the methodologies of some P-test methods have sometimes been dictated by practical rather than by theoretical considerations. Selected extraction conditions are not necessarily the most efficient (van der Paauw, 1971).

Considering the results it has been clearly established that the soil P-tests developed do not have a clear relation with the mass balance for P in soil. Neither is there a direct relation between soil P content and the P transfer to surface waters or eutrophic response of P-sensitive waters. Neither do they provide information on the various reactions in which the soil P is involved, such as mineralisation, release, fixation, leaching, surface run-off or erosion. From an agronomic point of view, Aslying stated already in 1964 that the total amount of available P in the soil is not of direct importance in the P supply to plants.

An excellent overview of the conventional soil tests for assessing the phosphorus status of soils was made by Kamprath and Watson (1980), based upon the criteria for a good soil test, the soil factors affecting P uptake and the mechanisms of P removal by extractants.

Quite often soil testing procedures were inspired by fertilizer trials, which were subsequently correlated by hit or missing chemical extractions.

As a concluding remark with regard to the foregoing general considerations, it should be emphasised that severe doubts remain on the use and efficiency in predicting the behaviour of strongly adsorbing solutes such as phosphate in an aqueous medium with regard to the extractants as compiled in Table 1. Whether the methods which will only rely on quantity rather than on intensity parameters are more useful in order to assess the phosphate status in the soil solution is still questionable, and should be evaluated thoroughly and carefully.

2. Literature review on soil P-test in relation to environmental purposes

As a result of the post-1945 agricultural intensification over Western Europe a gradual increase in the P-status of agricultural soils has occurred. It clearly appeared that all countries currently operate at an annual surplus of 10 to 20 kg P per ha. This long-term accumulation of P in soil will result in greater losses of P from diffuse agriculturally derived sources into aquatic ecosystems. The size of the P surplus is not the only factor that determines potential P losses, although significant relationships between P content of drain flow and soil accumulation have been observed for both arable land and grassland (Heckrath *et al*., 1995, Smith *et al*.,1995). Facing the increasing concern of eutrophication problems, especially in Western European countries, one should be aware of the fact that this problem is quite young, and thus very little information is expected to be available so far. Losses occur through a combination of leaching and an association with eroded soil material, and agricultural practices influence both the amount and chemical forms of P present in soil.

Conceptual models describing P export from non-point sources in agricultural soils are useful in developing an understanding of the key processes which control P losses, namely soil P sorption kinetics, soil physical properties, management history and practices which together influence the transport route through the soil profile.

Due to the extensive number of significant references in the sixties and seventies in relation to the mechanisms of P retention, both in calcareous and non-calcareous soils, one should actually be able to understand and to predict the various pathways in which phosphate interacts with soil colloids. In non-calcareous soils, ligand exchange on sesqui-(hydr)oxide surfaces is assumed to be the main mechanism controlling the fate of P in soils through sorption and desorption phenomena, at least on the short-term. It follows that this type of P will also respond to influx changes due to varying environmental conditions.

Irrespective of the source of P sorbed, an increase of the P saturation of sesqui(hydr-) oxides will also be reflected by a gradually increasing desorption rate into the dispersing soil solution. It follows that eroded soil may act as a sink for P (Hartikainen, 1979; Sharpley *et al*., 1981). This leads to the assumption that two important properties of a soil/solution dispersion are on the one hand its equilibrium P concentration and on the other hand the ability to maintain this concentration in response to changing conditions (House *et al*., 1998). Of course this statement is not very new and has been stressed already 40 years ago, reflecting the well known and very popular concepts for people involved in phosphate chemistry on *intensity* and *quantity*. These have been thoroughly elaborated in the framework of the phosphate status in soils monitoring the readily available phosphate in soils towards crops.

It is generally assumed that both drainage waters and to a larger extent also surface runoff is responsible for the P load of water bodies. The latter may contain very large amounts of suspended solids and so this particulate P is expected to exceed usually the molybdate reactive P (MRP), which is measured using the conventional method of Murphy and Riley (1962).

The composition of freshwater is highly variable: while average stream waters are about 1 mM in ionic strength, being essentially dominated by calcium bicarbonate, the ionic strength of seawater can go up to 500 mM, essentially dominated by sodium chloride

(Andrews *et al*., 1996). Changes from a fresh water to a marine chemical environment will cause a sudden change in ionic strength with concomitant flocculation of colloidal particles, a well known phenomenon in colloid chemistry, which has been clearly evidenced in soil conditions by Sholkovitz (1978). In addition, changes in ionic strength will also play an important role in the extent of phosphate desorption (Caraco *et al*., 1990). It clearly follows from these observations that a suitable extractant to monitor the level of soluble P in the soil solution should explicitly take care of ionic strength properties of the solution. In that framework it has been evidenced by Zwolsman (1994) that also the soluble P, as molybdate reactive phosphate, shows an almost linear decreasing relationship with an increasing salinity of the environmental medium.

In an attempt to measure the profile distribution of soil P and P leaching at seven sites in lowland England on freely draining soils with a history of organic manure applications, Smith *et al*.(1998) sampled soil water using suction cups at different depths. A curvilinear relationship was obtained between the topsoil extractable Olsen P in the 0-30 cm zone and the mean molybdate reactive phosphate concentration in the leachate at 30 cm depth. Concentrations of the latter in water draining below 30 cm appeared to increase sharply at Olsen extractable P concentrations in the soil $>$ 70 mg per litre. This seems to be in perfect agreement with the observations of Heckrath *et al*. (1995), who defined a “change point” for Olsen P at 60 mg kg^{-1} in the plough layer.

Different authors suggest that the P loss in surface runoff might be greater than via leaching because of the sorption of phosphate from infiltrating water, where movement occurs slowly through the soil profile. This has been confirmed in reviewing a number of studies where losses from applied P fertiliser were monitored. Fertiliser P losses via subsurface leaching, both soluble and particulate, were generally less than 1% of applied P, whereas losses ranged up to 9% in runoff. A principal aim remains to relate P-release characteristics to dominant soil properties and determine the significance of selective erosion of finer soil material on the desorption of P in the aquatic environment.

Using a comparative study including 12 soils from 4 different countries, Barberis *et al*. (1996) found a significant difference in the amount extracted by specific methods. Mean values increased in the order: Olsen P (60 mg kg^{-1}), CAL-P (98), strip-P (106), and resin P (118 mg kg^{-1}). These values represented less than 15% of total P. A comparative value for water extractable P is limited to 2.15 mg kg^{-1}. For agronomic purposes, correlation is often considered sufficient and actual quantities of P extracted are seldom compared. It is important to compare the efficiency of individual chemical extractants and use this information to provide an insight into the chemical forms of P present. It is suggested that generally (NaOH + citrate-bicarbonate) P is believed to encompass much of the forms related to over-fertilisation such as:

- stoichiometric complex Fe- and Al-containing phosphates, which are hydrolysed by NaOH;
- phosphate sorbed by hydroxylated surfaces and released by ligand exchange with OH^- and citrate ions;
- phosphate adsorbed on $CaCO_3$ which is desorbed by citrate;
- labile Ca-phosphates dissolved by the Ca-complexing action of citrate and the Ca-precipitating effect of bicarbonate.

While the P-amounts as recovered by most extractants in Table 1 refer to *quantity* estimations of the phosphate pool of the soil, the *intensity* parameter is usually measured in water or in 0.01 M $CaCl_2$ solution. Different authors, of which Gunary and Sutton (1967) are among the pioneers, suggest that the intensity parameter, which stands for the concentration of P in the soil solution, is more important for P uptake by plants than the quantity. The intensity can also be estimated using a reference method such as the labile P by isotopic dilution or by any suitable chemical extraction, as shown in Table 1. Relating chemical tests to solubilisable P, one should refer to the well known P sink methods such as iron-coated paper strips, (Sharpley,1993) or the anion-exchange resin method mentioned above. These techniques are adopted from soil analysis and may become very useful in water analysis, although their applicability seems to be hampered by practical limitations (Uusitalo and Yli-Halla, 1999).

In a review on soil P-tests for assessment of environmental P losses of dissolved reactive phosphorus (DPR) in Finland, Yli-Halla *et al*. (1995) used a water extraction during a very short time. This method seems to provide an excellent agreement with the measured DPR concentrations in surface runoff on the field, which appeared to be clearly superior over more complicated analyses, such as Quantity-Intensity plots. With regard to that problem, it should be emphasised that, according to Hartikainen (1982), the amount of desorbed P correlates very well with the ratio NH_4F-extractable P/oxalate extractable Al. Moreover it is known that a water extraction has proved to be more sensitive than extractions with dilute salt solutions, such as 0.01 M $CaCl_2$, because the ionic strength of the runoff waters is generally much lower than that of soil solutions.

In relation to water extraction, the very straightforward study of Self-Davis *et al*. (2000) should be mentioned here. In opposition to other authors, according to van der Paauw (1971) the effect of pre-moistening seems to be very important.

3. Motivation for the proposed methods

In analogy to the extraction procedures for identification of the P-status with regard to nutrient purposes to crops, it is clearly established that the amount recovered will be affected by the procedure adopted. This applies in essence also for one of the simplest extraction method so far, namely the water extraction or a dilute electrolyte solution. A thorough evaluation of this solvent to recover the phosphate from soils in order to obtain an effective availability index was undertaken by van der Paauw (1971). Each part of the procedure was improved step by step by observing the correlation of index with the phosphate content in the plants in standard pot trials. The merits of the final procedure, expressed as the P_w method, were then tested by varying the extraction procedure. The method was clearly tested against methods of reference such as isotopic exchangeable soil phosphate and appeared to provide results which were in the same order of magnitude. It is concluded that in these conditions water will mobilise the same P fractions from the soil, and these fractions should be identified as labile P fractions which are able to exchange permanently with phosphate in the soil solution.

The following observations were made by van der Paauw (1971):

- using a wide extraction ratio between water and soil the interpretation of the P-values was the same for different soil types;
- dried soils clearly created artefacts. It was shown that better results were obtained following pre-moistening, thus restoring the original properties of the soil.

Considering the very recent and highly relevant references aiming to assess the status of P in the soil solution from an environmental point of view, we are inclined to strongly support the use of water or a dilute electrolyte solution, for both conceptual and experimental reasons. The ultimate choice will be affected by the difference in ionic strength of the media targeted. While a dilute electrolyte solution such as 0.01 M $CaCl_2$ seems to correspond with the concentration in the soil solution, a much lower ionic strength is expected to occur in the liquid phase of surface runoff, due to dilution effects.

4. Description of the methods proposed

4.1 Determination of $CaCl_2$-extractable P for soils and sediments

Weigh out 1g dry soil from the top 0-30 cm layer into a centrifuge tube. Add 25 ml of 0.01 M $CaCl_2$ and shake for 24 hours. Centrifuge at 4000 rpm for 10 minutes. Filter through filter paper and measure P concentration using the colorimetric method Murphy and Riley (1962).

4.2 Determination of dissolved reactive phosphorus (DRP) using water extraction

A 1:100 soil to solution ratio on weight – volume basis is shaken for 1 hour in a centrifuge tube, followed by an equilibration for 17 hours and finally the suspension is shaken for 10 minutes. After filtration through a 0.2 µm filter, dissolved P is measured using the Murphy and Riley (1962) method.

4.3 Determination of phosphate saturation degree in non-calcareous soils

In order to quantify the eutrophication risk of agricultural land in non-calcareous areas with intensive livestock, the phosphate saturation degree (DPS) has been introduced as a simple index (Breeuwsma and Schoumans, 1987, Breeuwsma *et al*., 1995). This degree is defined as the ratio between the amount of phosphate accumulated in soils to a critical depth (P_{act}) and the maximum phosphate sorption capacity (PSC) of the soil to that depth. The relation is expressed by :

$$\mathrm{DPS} = \frac{P_{act}}{\mathrm{PSC}} \times 100\%$$

where : DPS = degree of phosphate saturation (%)
P_{act} = actual amount of sorbed phosphate (kg P_2O_5 ha^{-1})
PSC = phosphate sorption capacity (kg P_2O_5 ha^{-1})

The phosphate sorption capacity of non-calcareous soils can be assessed by the equation (Schoumans *et al*., 1986; van der Zee, 1988):

$$\mathrm{PSC} = \sum_{i=1}^{n} 0.5\left(\mathrm{Al}_{ox} + \mathrm{Fe}_{ox}\right)_i * \rho_{d,i} * L_i * 0.71$$

where Al_{ox} = oxalate extractable aluminium of soil layer i (mmol kg^{-1})
Fe_{ox} = oxalate extractable iron of soil layer i (mmol kg^{-1})
ρ = dry bulk density of soil layer i (kg m^{-3})
L = thickness of soil layer i (m)
N = amount of observed layers
0.71 = factor converting mmol P m^{-2} to kg P_2O_5 ha^{-1}

Phosphorus bound to reactive aluminium and iron will dissolve during the oxalate extraction. Therefore, the actual amount of sorbed phosphorus can be calculated as follows:

$$P_{act} = \sum_{i=1}^{n} P_{ox} * \rho_d * L * 0.71$$

P_{ox} = oxalate extractable phosphorus of soil layer i (mmol kg^{-1})

The phosphate saturation degree of a soil profile can be calculated by the mean contents of P_{ox}, Al_{ox}, and Fe_{ox} over the observed depth :

$$DPS = \frac{P_{ox}}{0.5\left(Al_{ox} + Fe_{ox}\right)} * 100\%$$

Weigh 5 g of air-dried soil in a dry polyethylene bottle of 250 ml. Add 100 ml of the oxalate extraction solution and close the bottle. Include blank samples as well. Shake mechanically for 2 hours in a darkened conditioned room at a constant temperature of 20 ℃. Filter the extracts through a paper filter. Discard the first 10 ml of the filtrate and collect the remainder in a polyethylene bottle, after which 10 ml of the filtrate is transferred into a beaker to which 1 ml of concentrated sulphuric acid is added. The mixture is heated to 200 to 250 ℃ till a dark mixture is obtained. After cooling, 2 ml H_2O_2 is added and heated again to destroy the excess of H_2O_2. The solution is transferred into a 50 ml flask and made up to volume with distilled water. The P content is measured according to Scheel (1936), and the content of Al and Fe is determined using AAS. Also, P, Fe and Al can be determined simultaneously in the extract by ICP-AES (Novozamsky *et al*., 1986).

Extracting solution: oxalate-oxalic acid
Dissolve 17.56 g oxalic acid $(COOH)_2.2H_2O$ and 28.40 g $(COONH_4)_2$ in 1 litre flask with distilled water.

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APPENDIX

Table 1. Soil P-test methods used in European countries

P-test	Method	pH	Country	Reference
Pw	1:60 (v/v), extraction with water 22 h incubation, 1 h shaking	soil	Netherlands	Sissingh (1971) Van der Paauw (1971)
Pw modified	1:50 (v/v), extraction with water 2 h shaking	soil	Germany	Schachtschabel & Koster (1985)
P-Al	1:20 (w/v), 0.1 M ammonium lactate + 0.4 acetic acid, 2 h shaking	3.75	Belgium	Egnér *et al.* (1960)
DL	1:50 (w/v), 0.02 M calcium lactate +0.02 M HCl, 1.5 h shaking	3.7	Germany	Egnér & Riehm (1955)
CAL	1:20 (w/v), 0.05 M calcium lactate + 0.05 M calcium acetate + 0.3 M acetic acid, 2 h shaking	4.1	Austria, Germany	Schüller (1969)
NH_4Ac	1:5 (w/v), ammonium acetate	4.65	Belgium, Finland	van den Hende & Cottenie (1960)
EUF	Electro Ultra Filtration		Germany, Austria	Nemeth (1979)
Dyer	1:5, citric acid 2%, 4 h shaking	≈3	France	Dyer (1894)
Joret-Hebert	1:25, ammonium oxalate 0.2 M 2 h shaking	neutral	France	Joret & Hebert (1955)
Olsen	1:20 (w/v), 0.5 M sodium bicarbonate 1 h shaking	8.5	Denmark, England Australia, New Zealand	Olsen *et al.* (1954)
Morgan	6:30 (v/v), 10% sodium acetate 0.5 h shaking	4.8	Ireland	Morgan (1941)
Bray-1	1:10 (w/v) 0.03 M NH_4F + 0.025 M HCl, 5 min shaking	3.0	Tropical countries	Bray & Kurtz (1945)
Mehlich-1	1:5 (w/w) 0.05 M HCl+ 0.0125 M H_2SO_4, 5 min shaking	1.2	USA	Nelson *et al.* (1953)
Mehlich-3	0.2 M acetic acid +0;25M NH_4NO_3 +0.015 M NH_4F + 0.013 M HNO_3 +0.001 M EDTA, 5 min shaking	2.5	USA	Mehlich (1984)

Influence of re-wetting soils on phosphorus behaviour

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1. Introduction

The majority of fenland soils in Northeast Germany has been drained since the late 18th century. Peat drainage allowed an increasing intensity of agricultural land use until the early 1990s but regular cultivation also resulted in a severe peat degradation. Nowadays considerable efforts have been made to restore such degraded wetland sites (Pfadenhauer and Klötzli 1996). One representative example of restoration is the "Droemling" fen area (Fig. 1), which has experienced rising groundwater tables and significant land use change from intensive agriculture (crop and grassland farming) to unimproved pasture since the early 1990s. However, detailed investigations of the impact of Histosol (FAO classification system: synonyms: peat soils, fens) use and degradation on the nutrient cycle, and of re-wetting on the pollution of freshwater with phosphorus (P) have been mostly reported from projects in the U.S.. Re-wetted Histosols were shown to be a source of continuous P-release for the next 30 years.

Today, only 36 % of the Droemling area is covered by organic soils (Histosols). Other significant soil types are mollic Gleysols, which lie adjacent to Histosols, and dry sandy soils (Cambisols).

Changing land use is often combined with an elevated nutrient export from soil to groundwater in the first month after implementation of the new land use system (Meissner et al. 1998). Especially P is a problem for ground- and surface waters in the "Droemling" fen area because of the increasing risk of surface water euthrophication. Simultaneously, the quality of groundwater recharge, which is necessary to ensure the drinking water supply for more than 400,000 people, is declining. Currently, the high P loadings in the Droemling catchment, and partly elevated concentrations in ground and surface waters of specific sites under restoration, demand research covering the unknown effects of fen restoration on nutrient dynamics. By contrast, other pollutants do not play an important role in this wetland area (Kalbitz et al. 1998). Therefore, the objectives of our study were:

- to identify and quantify the effects of differences in land use intensity and land use change towards fen restoration on phosphorus in the soil solution and groundwater;
- to determinate the effects of raising the groundwater table on the form and mobility of nutrients in the soil solution and groundwater.

2. Materials and methods

In accordance with the Droemling nature park authority, 6 representative sites with different land uses were selected (Fig. 1):

Site 1: long-term intensive crop farming with high fertilizer input (mineral soil)
Site 2: long-term intensive grassland farming with high fertilizer input (mineral soil)
Site 3: changing land use pattern from long-term intensive crop farming to an unimproved grassland (mineral soil)
Site 4: unimproved grassland (extensive grassland farming with low input; organic soil)
Site 5: formerly intensively used grassland in natural succession with a raised groundwater table (organic soil)
Site 6: alder swamp forest (organic soil)

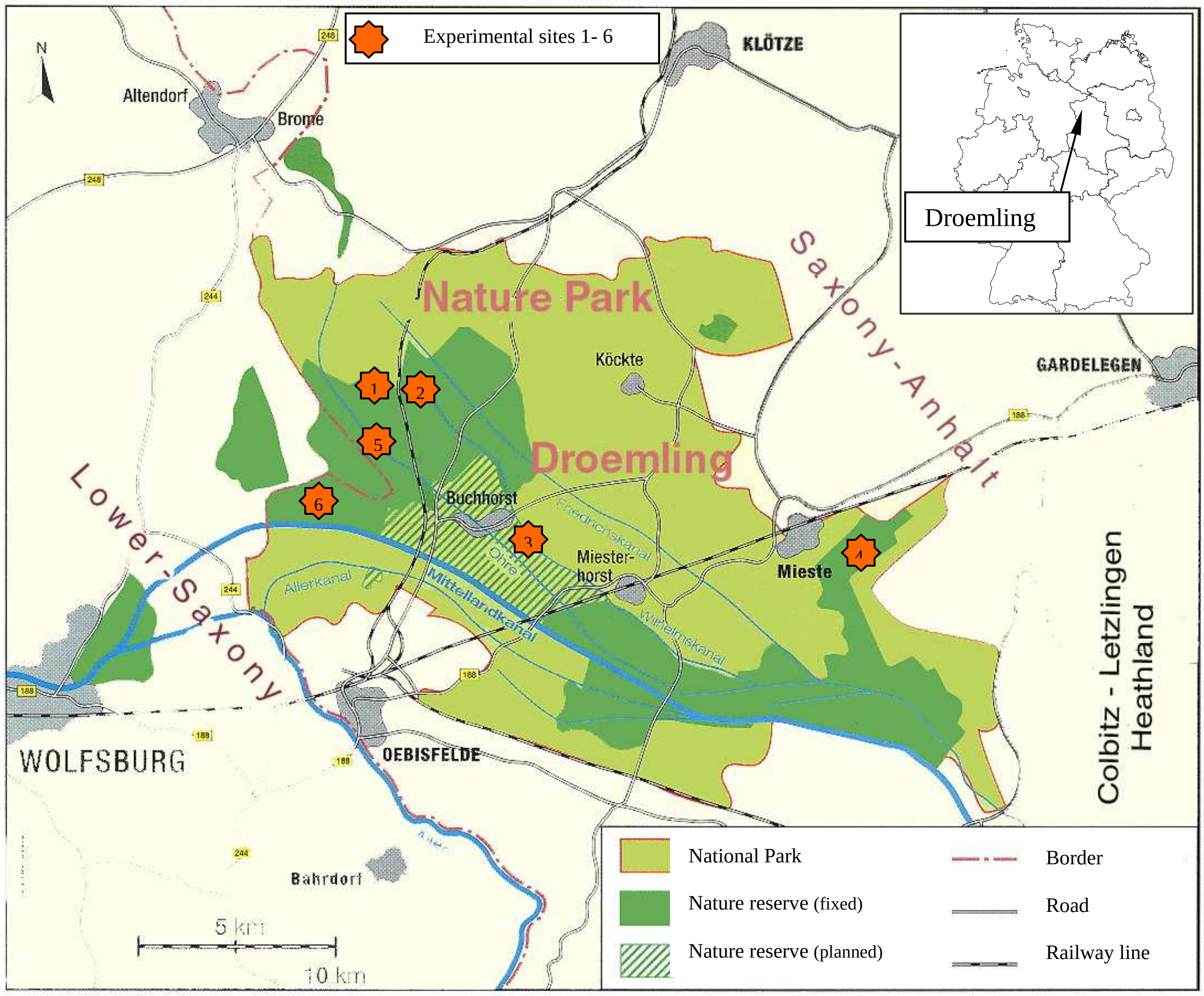

Fig. 1. The Droemling Nature Reserve in Saxony-Anhalt, Germany

Since Spring 1996, we sampled topsoil (0 - 25 cm), soil solution at 3 depths (25 cm, 55 cm, 95 cm) by ceramic suction cups (3 replicates) and groundwater at intervals of 3 weeks over a period of 2.5 years. The studies were started immediately before initiation of the land use change at site 3. We analysed plant available phosphorus (P_{CAL}, extraction with calcium lactate; VDLUFA 1991) in topsoil samples. Furthermore, total phosphorus (TP) and soluble reactive phosphorus (SRP) were analysed in all water samples according to German standard methods (DIN 38405, DIN 38406, DIN 38409). Additionally, the redox potential of the groundwater was measured in the field using a platinum electrode. The measured values were converted to the hydrogen electrode.

3. Results and discussion

The plant available phosphorus content of the soil determined by a standard method (P_{CAL}) was used to characterize a mobile (plant available) P fraction as a possible source for P in the soil solution and groundwater. The highest amounts of P_{CAL} were found in the topsoil of site 3 where maize was planted over a period of several years (Fig. 2). Annual P fertilization exceeded the plant uptake so that the soil was enriched with P. After the land use change to unimproved grassland, there is no opportunity to decrease this P content by plant uptake. In contrast, the other intensively used sites (site 1, 2) show P_{CAL} amounts in the soil were more representative of this land use pattern. By comparison, the amounts of P_{CAL} in the soil are low at the extensively or unused sites with an existing peat layer (site 4 - 6). However, the succession site (site 5) shows significantly higher amounts of P_{CAL} in the topsoil compared to the other two sites (4, 6) containing a peat layer. This is the result of the previous high P-input grassland farming with at site 5 up to the early nineties, whereas site 4 and 6 have never been used for high intensity agriculture.

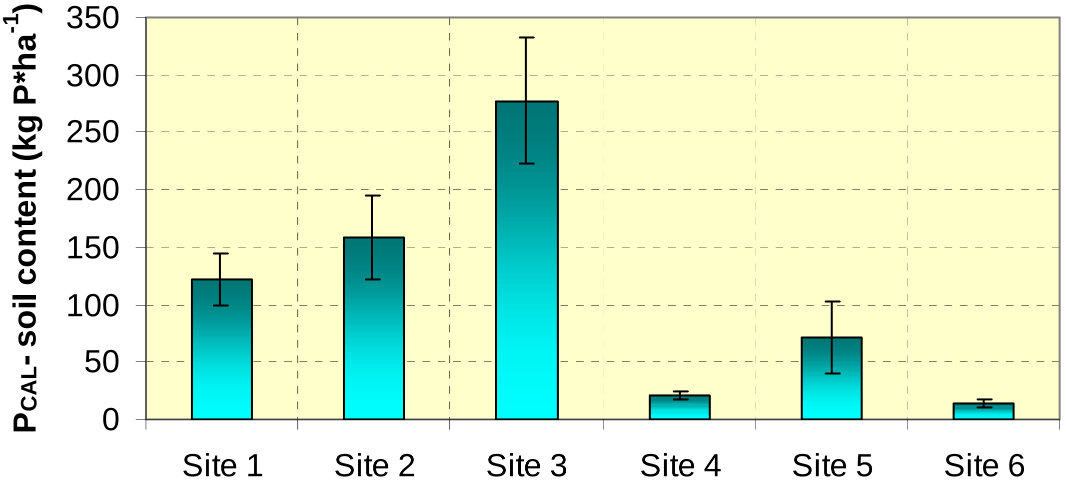

Fig. 2 Content of plant available phosphorus (P_{CAL}) in the Droemling fen area

We did not find any direct effect of the different P_{CAL} amounts in the topsoil on P contents (both TP and SRP) in soil either the solution or the groundwater. Only in the soil solution at 25 cm depth of site 1 (intensive crop farming) were there significantly higher P concentrations than at the other sites. This corresponds to results of Heckrath et al. (1995) showing that P-leaching is more likely to occur where continuously more P fertilizer is used than the crops require. The P contents of the soil solution at site decreased with soil depth up to 55 cm with no further effects of land use and fen restoration.

Peaks in the TP contents of soil solution occurred after P fertilization. This hints at a possible P leaching mechanism at the intensively used sites getting periodical P amendments (site 1 and 2). At the intensively used grassland site, P concentration increased to 60 and 62 µg L^{-1} at 55 and 95 cm depths, respectively after P fertilization in spring 1996. Also, at the site with intensive crop farming, the TP concentration increased after P fertilization in spring 1997 and 1998. Maximum values of 175, 64 , and 48 µg L^{-1} at 25, 55 and 95 cm depths, respectively were measured (Fig. 3).

TP and SRP concentrations in the groundwater are significantly higher than those of the soil solution at 95 cm depth at all sites (Fig. 3). Increasing P concentrations were observed in soil solution in 95 cm depth compared with 55 cm depth at the site being restored (site 5) and the alder swamp forest (site 6), both with an existing peat layer. This increase was caused by ascending SRP contents. Therefore, the increase in the proportion of SRP in TP is highest at these two sites. Measured redox potentials are lowest at the alder swamp forest site followed by site 5 and site 2, whilst, the soils of site 5 and site 6 had the highest contents of iron oxides (Fig. 4). These results correspond to the higher proportion of SRP at 95 cm depth at site 5 and 6 as described above. The increases in P content and in the SRP portion could be caused by an improved solubility of phosphate at low redox potentials. Fe^{3+} is converted to Fe^{2+} at the measured potentials (100 to 200 mV) which results in a greater dissolving of iron oxides and consequently in a mobilization of phosphate bound by these oxides. Sims et al. (1998) show that leaching losses from organic soil depend on sesquioxide content.

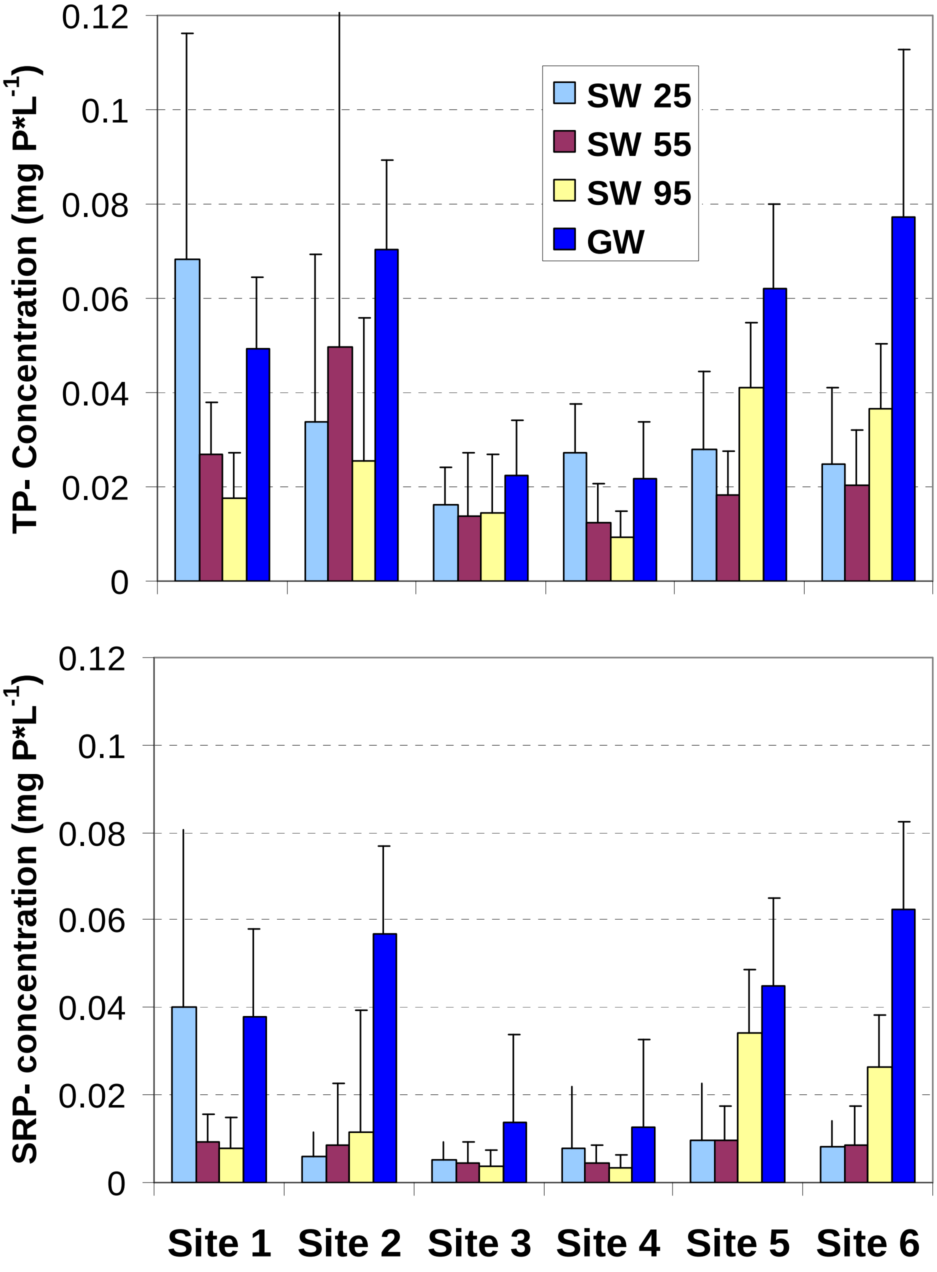

Fig. 3 TP and SRP concentration (average value and standard deviation) in seepage and groundwater

Significant correlations between redox potentials and SRP concentrations (and TP) support this hypothesis (Fig. 5). Also, high amounts of carbon available for microbes favour large reduction in the redox potential.

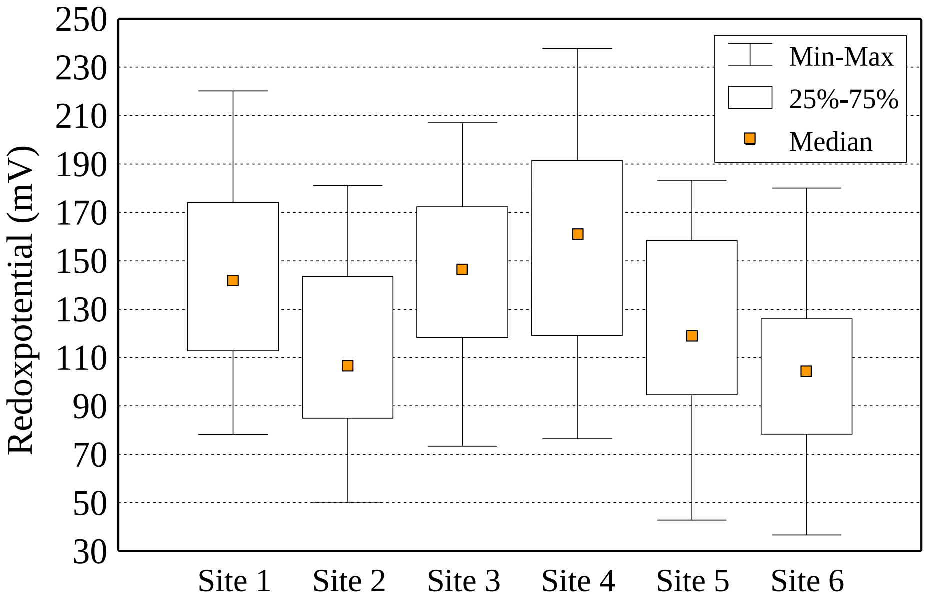

Fig. 4 Redoxpotential in the groundwater of the Droemling sites

Groundwater P concentrations are significantly lower at site 3 and site 4 compared with our other sites. The proportion of SRP to TP are also lower at site 3 and site 4, whereas the redox potentials are a little higher (site 3: 137 mV, site 4: 149 mV, site 5: 115 mV, site 6: 97 mV). Therefore, the dissolution of phosphate bound by iron oxides should be less pronounced at site 3 and site 4 than at the other sites.

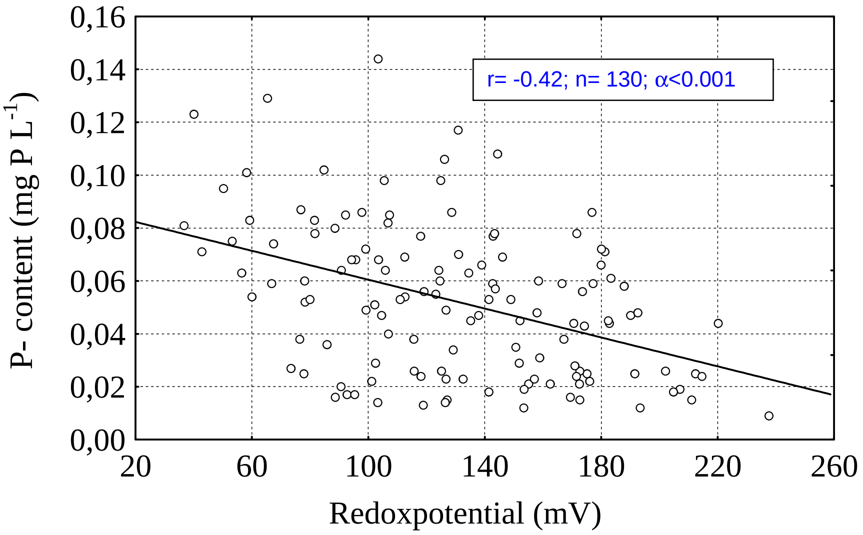

Fig. 5 Relation between Redoxpotential and P concentration in the groundwater of the Droemling sites

The decisive influence of the redox potential on P concentration in the groundwater has to be considered when assessing the effects of raising the water table which will result in decreasing redox potentials and hence in increasing P contents. P mobilization will be especially high in soils with high contents of iron oxides and mobile P causing increased euthrophication risk. Mainly soils with an existing peat layer show high contents of oxides, but these soils have to be restored first. Therefore, before restoration can be started, the mobile P content should be decreased by a plant uptake to limit P mobilization. However, it is not known whether decreasing the amount of potentially mobile P is possible. Benke and Hermanspahn (1998) reported that effects of management activities to decrease plant available potassium contents of soils are only successful after 4 to 5 years. Whether this finding is also true for phosphorus needs to be investigated. Restoration of the succession site (site 5) was started with high plant available P contents of the soil. We have to conclude that the already high P contents of soil solution and groundwater at this site will grow if water tables are raised still further. The increase in the water table is necessary to ensure a successful restoration, i. e. to stop peat mineralisation (see previous section).

Martin et al. (1997) showed that varying moisture conditions (change of drying and water-logging) favor high P contents in the groundwater. In the “Droemling” fen area such varying moisture conditions are especially pronounced at the alder swamp forest site and constitute an additional reason for high P concentrations in soil solution and groundwater. Furthermore, a potential risk of eutrophication increases if a movement of P into surface waters occurs.

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The use of simulation models describing surface transport of phosphorus

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1. Introduction

A questionnaire about modelling the surface transport of phosphorus was sent by the Finnish Environment Institute to countries participating the COST 832 program. The aim of the questionnaire was to get a qualitative and quantitative overview about available models dealing with *surface transport* of phosphorus in COST 832 countries. The questionnaire consisted of 12 questions (Appendix 1) and was sent to all 18 countries participating in the COST programme. Six countries responded to the questionnaire and 7 different erosion and/or phosphorus transport models were received (Table 1.)

Table 1. Erosion and phosphorus transport models used in the COST 832 countries

Model	*Country*
National Soil-P loss model	Ireland
Erosion 2D (single slopes) 3D (small watersheds), PEPP	Germany
ICECREAM	Finland, Sweden
EUROSEM	United Kingdom
Sharpley	United Kingdom

2. Data requirements

The meteorological data requirements of these models vary according to the model complexity. Physically based models, such as EUROSEM, require typically event oriented rainfall data in detailed resolution while models such as the National Soil-P model uses mean annual rainfall values. Deterministic models, such as the ICECREAM model, uses daily air temperature, precipitation and radiation data. EROSION 2D/3D and PEPP models assume DEM in best resolution, as well as land use and soil data in the same scale. EUROSEM requires data on daily crop status (%canopy cover and height, % basal area). ICECREAM needs information on slope steepness, data on crop identification, on tillage implement and on cultivation practices.

Soil data needed for EROSION 2D/3D and PEPP models consist of data such as roughness, erosion resistivity, canopy cover, texture, bulk density, initial moisture and organic contents. ICECREAM needs information on soil specific gravity, fraction of clay, sand and organic matter, soil moisture content at field capacity and wilting point, soil porosity, soil pH and available P in the soil (determined by the NH_4-acetate method used in Finland). EUROSEM combined with SHARPLEY models requires topsoil data on particle size distribution, stonyness, roughness, cohesion/stability, bulk density, saturated hydraulic conductivity, bicarbonate extractable and total P status (temporal resolution dependent on timing of manure/fertiliser additions). Data on rill dimensions would be advantageous. In the National Soil-P model soil types in the catchments are divided into four broad categories and weighted according to the risk of P-loss due to soil P desorption.

3. Erosion equations

Erosion equations in EROSION 2D/3D and PEPP models are predominantly based on physical processes occurring in soil. The basic idea of the model is the assumption that the erosive impact of overland flow and droplets is proportional to the momemtum fluxes exerted and the falling droplets respectively. Erosion is limited either by the amount of sediment that can be detached from the soil surface or by the transport capacity of the flow. For detachment, the erosive impact of overland flow and falling droplets must exceed the shear strength of the soil. In order to transport detached particles the vertical flow component within the flow must counteract the settling of the particles for deposition. The ICECREAM erosion regression equations are based on empirical data. The erosion submodel computes soil loss along a given slope and the sediment yield at the end of a hillslope in accordance with the modified USLE. EUROSEM computes soil loss as a sediment discharge, defined as a the product of the rate of runoff and the sediment concentration in the flow, to give a volume of sediment passing a given point in a given time. The computation is based on the dynamic mass balance equation.

4. Surface runoff equations

In the National Soil-P model surface runoff (MRP) is based on empirical equation:

$$MRP = 0.1 - 0.04(-1.2 \cdot High\ grassland - 1.9 \cdot Soil\ type + 2.8 \cdot Seminatural\ areas + 4)$$

Modified infiltration equation of Green and Ampt is used to calculate rainfall excess in EROSION 2D/3D and PEPP models. EUROSEM is linked to the KINEROS model, which is a physically based distributed model that solves dynamic mass balance equation for water using a kinematic wave assumption. KINEROS generates runoff as infiltration-excess using the infiltration model of Smith and Parlange. ICECREAM simulates daily runoff using a modification of the SCS curve number method. The SCS equation relates runoff to soil type, land use and management practices.

5. Output of P in the models

The National Soil-P model predicts the *molybdate reactive* P for 35 river subcatchments in Ireland. EUROSEM combined with Sharpley simulates total P and speciation in terms of dissolved and particulate fractions. ICECREAM simulates P in surface runoff and the particle bound P. EUROSEM 2D/3D and PEPP models are so far lacking P equations, but the Sharpley-equation or measurements on P in runoff and particulates will be exploited in thefuture.

6. Limitations in the use of the models

Because the National Soil-P model describes diffuse P losses on a national scale, the limitations of this model lie in the scale of the work. According to the authors, the better approach would probably be to predict P losses from a single catchment and then scale up to include larger areas. EROSION 2D/3D and PEPP models are not valid for cold climate frozen soils. Requirements for sub-hourly rainfall data restricts the use of EUROSEM application due to limited data availability. EUROSEM is most appropriate for tilled land on sloping topography. Difficulties may be encountered elsewhere. ICECREAM is not valid for soils where organic matter content > 12 %.

Due to erosion equations based on US erosion data, the ICECREAM model should be locally tested and calibrated. ICECREAM is most appropriate to assess relative changes in erosion and P variations for different soil and land-use classes.

7. Discussion on calibration, testing and sensitivity analysis

Calibration and/or testing of models is an essential part in a modelling procedure. All models described in this study have been calibrated or tested against field data. The problem is that data on erosion, surface runoff and P are rather scarce, and more data should be gathered for further model testing.

Sensitivity analysis gives answers for model users on the sensitivity and uncertainty of the modelled erosion and P output. For most of the above mentioned erosion models, soil water content, soil stability/cohesion, saturated hydraulic conductivity and Manning n roughness are sensitive parameters and have a great influence on erosion amounts. In general, sensitivity analysis can give guidelines to the question, which variables should be measured more accurately.

Recently the GCTE (Soil Erosion Network launched by the Global Change and Terrestrial Ecosystems:
http://mwnta.nmw.ac.uk/GCTEFocus3/Publications/reports/report6/report6web.htm
has organised a series of model comparisons, the results of which showed that the predictive quality of many models is rather poor. In contrast, individual model developers and users report good results. Thus, one may wonder if the good results are an outcome of calibration? It has also been argued that regression equations are not used in physically based models. That is true, but even in these models, some of the processes have to be parameterised and this produces empirical equations or coefficients into the model code. Are these equations valid in all situations?

How accurate can erosion and P output simulations be achieved? Processes in nature tend to be rather complicated. Process descriptions are not necessarily valid for complex, spatially heterogeneous soils where information such as rill formation areas or the fraction of preferential flow is difficult to get. The input parameters are seldom known in detail and the spatial variability of, for instance soil parameters, is huge even inside a field plot.

8. Model references and/or contact persons:

National Soil-P model:

Contact person: Karen Daly, research officer, Teagasc, Johnstown Castle, Co. Wexford, Ireland

EROSION 2D (single slopes) /3D (small watersheds), PEPP

Contact person: Kai Gerlinger, Dr. Ludwig Consultants, Herrenstr. 14, D-76133, Karlsruhe, Germany (PEPP)
Prof. Jurgen Schmidt TU Bergakademie Freiberg, Germany, email: schmidt@bohrl.tbt.tu-freiberg.de (EROSION 2D/3D),

ICECREAM:

Contact person: Sirkka Tattari, Finnish Environment Institute, P.O. Box 140, FIN-00251 Helsinki, Finland. E-mail: sirkka.tattari@vyh.fi.

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Contact person: Dr. John Quinton, Email: j.quinton@cranfield.ac.uk

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APPENDIX

QUESTIONNAIRE (Part II): The use of simulation models describing surface transport of phosphorus.

1. Name of the model and the main reference?

2a. Requirements for meteorological input parameters: which input parameters are necessary and at which temporal resolution (hourly, daily, monthly, annual, single value)

2b. Requirements for land use input parameters (slope, crop data, tillage data): which input parameters are necessary and at which temporal resolution (daily, monthly, annual, single value)

2c. Requirements for soil input parameters: which input parameters are necessary and at which temporal resolution (daily, monthly, annual, single value)

3. Description of the erosion equations used in the model.

4. Description of the surface runoff equations used in the model.

5. What kind of output in terms of P is delivered (total P, dissolved P or whatever kind of P-form)

6. Description of P transport (particle P and dissolved P) and enrichment of P.

7. Limitations in the use of the model? (for example, equations are not valid for organic soils, or for frozen soils)

8. If equations (runoff, erosion and P transport) involve regression coefficients, has it been calibrated for local conditions?

9. How much "parameter tuning" was needed and which parameters were modified?

10. Has the model been validated, tested with independent data? Describe for which data: soil texture, crop, hydrological conditions.

11. Have you performed a sensitivity analysis, leading to priority list of factors? What were the most important parameters?

12. Is the model freely available? Contact person?

Phosphorus losses as a result of surface runoff: Field data

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Introduction

Being part of a bigger exercise on amounts and pathways of P transfer from land to water, this questionnaire dealt with the flow path „soil erosion“. The questionnaire was distributed to all members of WG 2 of COST Action 832. In general, the return of filled questionnaires was quite small. Nevertheless, it contains valuable information which should not be discarded. Results will be presented question by question in the format of tables. Additionally, a short summary/conclusion will be provided for questions with more responses. For questions 3 to 6 no conclusion is given as the number of responses was too small.

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1) What are amounts of P loss via surface runoff and erosion at plot scale reported in your country?

1 A) Conclusion/Summary

Reported losses of total P ranged from 0.1 kg P/ha/y to 20 kg P/ha/y. In addition to this variation between the different experiments, total soil losses also differed remarkably with consecutive years of the same experiment. With higher rates of soil erosion, losses of total P clearly increased. With lower amounts of total P, the contribution of dissolved P to the total load increased. For experiments with low soil erosion rates (for some references this was not declared explicitly but is a conclusion from applied management practices), the dissolved P load contributed considerably to the total amount of P lost at a particular site.

1 B) Results in detail

Country	***Objective***	**Plot Description**	**Total P (kg/ha/y)**	**Dissolved P (kg/ha/y)**	**Reference**
Ireland	P loss from grassland to water	4 different levels of P fertilization, gleys and brown earth	0.5->4.0	80 % of TP, MRP 75 % of TP	10
Ireland	P loss from grassland to water	Isolated field plots with sub-surface drainage systems, plot size 0.2 ha, receiving 0,10, 20, 40, 80 kg P/ha/y	No results yet	No results yet	
Sweden	P loss for different treatments during winter	South-Western Sweden, plot size 22x10m, late autumn ploughed, no catch crop, 1993-1995	1.5-11.9	0.2-1.3	11
Sweden	P loss for different treatments during winter	South-Western Sweden, plot size 22x10m, late autumn ploughed, english ryegrass as catch crop, 1993-1995	1.5-12.5	0.2-1.4	11
Sweden	P loss for different treatments during winter	South-Western Sweden, plot size 22x10m, spring ploughed, no catch crop, 1993-1995	1.4-14.6	0.6-3.6	11
Sweden	P loss for different treatments during winter	South-Western Sweden, plot size 22x10m, spring ploughed, english ryegrass as catch crop, 1993-1995	1.2-18.2	0.5-3.2	11
Sweden	P loss for different treatments during winter	South-Western Sweden, plot size 22x10m, early autumn ploughed, winter wheat, 1993-1995	2.3-13.3	0.3-2.6	11
Danmark	P loss for different management treatments	Foulum, fine loamy sand, plot size 22.1x3m, 1989-1992 (means), grass	0.183	0.135	8
Danmark	P loss for different management treatments	Foulum, fine loamy sand, plot size 22.1x3m, 1989-1992 (means), spring ploughed, catch crop	1.29	0.152	8

Danmark	P loss for different management treatments	Foulum, fine loamy sand, plot size 22.1x3m, 1989-1992 (means), spring ploughed, catch crop	1.29	0.152	8
Danmark	P loss for different management treatments	Foulum, fine loamy sand, plot size 22.1x3m, 1989-1992 (means), autumn ploughed, no catch crop, soil loss 2.7 t/ha	3.2	0.11	8
Danmark	P loss for different management treatments	Foulum, fine loamy sand, plot size 22.1x3m, 1989-1992 (means), autumn ploughed, winter wheat tilled up and down, soil loss 12.8 t/ha	17.3	0.32	8
Danmark	P loss for different management treatments	Foulum, fine loamy sand, plot size 22.1x3m, 1989-1992 (means), autumn ploughed, winter wheat tilled across slope, soil loss 11.1 t/ha	15.2	0.28	8
Danmark	P loss for different management treatments	Foulum, fine loamy sand, plot size 22.1x3m, 1989-1992 (means), black fallow, soil loss 10.9 t/ha	20.0	0.39	8
Danmark	P loss for different management treatments	Ødum, fine sandy loam, plot size 22.1x3m, 1989-1992 (means), grass	0.10	0.06	8
Danmark	P loss for different management treatments	Ødum, fine sandy loam, plot size 22.1x3m, 1989-1992 (means), spring ploughed, catch crop	0.18	0.05	8
Danmark	P loss for different management treatments	Ødum, fine sandy loam, plot size 22.1x3m, 1989-1992 (means), spring ploughed, catch crop	0.5	0.05	8
Danmark	P loss for different management treatments	Ødum, fine sandy loam, plot size 22.1x3m, 1989-1992 (means), autumn ploughed, no catch crop, soil loss 1.2 t/ha	1.9	0.12	8
Danmark	P loss for different management treatments	Ødum, fine sandy loam, plot size 22.1x3m, 1989-1992 (means), autumn ploughed, winter wheat tilled across slope, soil loss 0.5 t/ha	0.8	0.12	8
Danmark	P loss for different management treatments	Ødum, fine sandy loam, plot size 22.1x3m, 1989-1992 (means), black fallow, soil loss 5.9t/ha	6.7	0.18	8
UK	Nutrient losses and crop yields for different management practices	Woburn – standard treatment (6 years mean), 0.1 ha plots, cultivation up and down slope, standard treatment, sandy loam	2.43	MRP 0.09	2, 12

UK	Effect of drainage on runoff and nutrient loss	Brimstone, 0.24 ha plots, clay soil, direct drilled, winter cereals, undrained plot	3.1	MRP 0.98	2, 12
UK	Application of various P fertilisers	Rosemaund, 30m^2 plots, silty soil, 33kg inorganic P in spring, 1995-1996	0.05	MRP 0.01	2, 12
UK	Application of various P fertilisers	Rosemaund, 38 m^3 slurry in autumn and spring	0.1	MRP 0.05	2, 12
UK	Application of various P fertilisers	Rosemaund, 27 t FYM in autumn	0.08	MRP 0.03	2, 12
UK	Application of various P fertilisers	Rosemaund, 76 m^3 slurry in autumn	1.55	MRP 0.75	2, 12
UK	Effect of drainage on surface runoff and nutrient loss	Rowden, grassland undrained (surface = 0-30cm), 1994	3.15	MRP 1.28	2, 12
UK	Effect of drainage on surface runoff and nutrient loss	Rowden, grassland drained (surface = 0-30cm), 1994	0.38	MRP 0.16	2, 12
UK	Maize and Slurry application effect on nutrient loss	South-West England, 15x2.2m plots, 12/98-5/99, no P amendment	1.27	MRP 0.38	13
UK	Maize and Slurry application effect on nutrient loss	South-West England, 15x2.2m plots, 12/98-5/99, slurry single application	3.13	MRP 1.99	13
UK	Maize and Slurry application effect on nutrient loss	South-West England, 15x2.2m plots, 12/98-5/99, slurry single application+plough	1.62	MRP 0.77	13
UK	Maize and Slurry application effect on nutrient loss	South-West England, 15x2.2m plots, 12/98-5/99, slurry single application+tyne	1.13	MRP0.48	13
UK	Maize and Slurry application effect on nutrient loss	South-West England, 15x2.2m plots, 12/98-5/99, slurry triple application	4.28	MRP 2.56	13
Austria	General effects of conservation management practices for sugar beets	Upper Austria, plot size 2x8 m, 1993-95, conventional treatment (plough, no catch crop), soil loss 8.8-25 t/ha	3.9-13.6	-	15
Austria	General effects of conservation management practices for sugar beets	Upper Austria, plot size 2x8 m, 1993-95, plough, catch crop, soil loss 0.9-1.6 t/ha	0.5-1.0	-	15
Austria	General effects of conservation management practices for sugar beets	Upper Austria, plot size 2x8 m, 1993-95, chisel, catch crop, soil loss t/ha	0-0.7	0-0.5	15

2) What are the most critical times during a year and for what form of P?

2 A) Conclusion/Summary

Response for this question differed from country to country. Nevertheless one critical period for P losses pointed out by various responses seems to be winter and the snowmelt period. Results on associated forms of P are too few to draw conclusions.

2 B) Results in detail

Country	Time	P form	Reference
Ireland	summer, autumn	PO_4-P	
Ireland	High rainfall intensity following a dry period and P fertilisation	DRP	
UK	Winter cereal fields in autumn with little ground cover and tramlines, erosion losses also from grassland around gateways and poached areas		4
Sweden	December-January	Part-P, PO_4-P	11
Austria	Intensively used areas – May to June, Extensively used areas- Snowmelt period	Part-P, PO_4-P	
Germany	End of winter on thawing soils, high rainfall events at critical times for SRP/MRP		
Norway	Melt water in spring	-	5

3) What do you deem the most important factors for P loss via surface runoff/erosion with respect to soil properties?

3 A) Conclusion/Summary

See results in detail

3 B) Results in detail

Country	**Factor**
Ireland	heavy soil with surface layer saturated or near saturated with P
Ireland	Soil permeability and soil P status
UK	Texture, drainage, dispersibility, Soil hydraulic properties, more runoff = more erosion (normally)
Austria	Soil hydraulic properties

4) What do you deem the most important factors for P loss via surface runoff/erosion with respect to landscape properties?

4 A) Conclusion/Summary

See results in detail

4 B) Results in detail

Country	**Factor**
UK	Keeping the soil on the field and preventing it from moving is probably better than trying to stop it once it is on the move
Austria	Concentrated flow paths in connection with steep slopes

5) What do you deem the most important factors for P loss via surface runoff/erosion with respect to climatic conditions?

5 A) Conclusion/Summary

See results in detail

5 B) Results in detail

Country	**Factor**
Ireland	High rainfall gives increased P concentration and therefore very high P load (example: 40% of annual P loss occurred in a rainstorm of 150mm of rain over 4 days)
UK	Don’t forget the selective nature of erosion and the disproportionately large amount of P moved by small events
Ireland	Most important events are high rainfall rates at critical times
Austria	Heavy storms (rainfall amount bigger than 10mm) occurring in spring time

6) What do you deem the most important factors for P loss via surface runoff/erosion with respect to land use?

6 A) Conclusion/Summary

See results in detail

6 B) Results in detail

Country	**Factor**
Ireland	At grassland sites high losses occur after applying slurry and P fertiliser
UK	Land use is most important, with sufficient ground cover for soil protection P losses are minimal, slurry application is a major source of soluble P loss rather than particulate ‚organic‘ P loss although the latter may occur in heavy storms where manure is left on the surface, if you have more P in the soil you will get more P in the sediment
Germany	Time of fertiliser application
Austria	Low soil cover at the most critical time in the year (spring for agricultural used areas)

7) Please rank the most critical factors

7 A) Conclusion/Summary

Soil cover was one factor named by 4 out of 5 countries to be a critical one. Priorities are clearly different for countries with a high percentage of grassland like Ireland. This demonstrates the shift of problems in different countries depending on types of prevailing land use. Livestock density seems to be another issue of high importance for P loss risk (4 countries out of 5).

7 B) Results in detail

Country	**Factor**
Ireland	1. High soil P or high surplus P input that leads to saturation or near saturation of the surface layer of soil, each year fertiliser and manure are added to the soil surface and this surface layer interacts with rainfall 2. Intensive grazing of animals on high P soils, particularly in wet weather 3. Spreading manure and fertiliser on wet soil or before rain, particularly is soil is already high in P 4. Peat soils at risk from high P loss if surplus is applied
UK	1. Good ground cover 2. Incorporation of manure (contradictory)
Sweden	1. Heavy rain on just frozen soil 2. Runoff intensity 3. Soil texture 4. Aggregate stability 5. P-storage in soil 6. No grass crop 7. Livestock density
Germany	1. High rainfall events at critical times 2. Bare soils with high P contents especially of SRP/MRP due to long lasting P surpluses 3. Too high animal densities (more than 1 LFU/ha)
Germany	1. Soil cover can be influenced by the farmer 2. All other parameters are to consider in their complex under actual conditions 3. Site specific things (local influences)

Models describing phosphorus losses by subsurface transport used in Europe

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Abstract
Within Europe only a few models are available which are able to quantify the diffuse phosphorus (P) losses by leaching to groundwater and surface waters at the field scale. In this article the P cycle of each model and the process description of P interactions are described and compared. Finally, the impact of these interactions on the organic, inorganic and particulate phosphorus mobilisation and losses are evaluated.

1. Introduction

In most (European) countries subsurface P flow is assumed to be a minor problem and thus, most work has been done on transport of P by erosion (Sharpley and Rekolainen, 1997). Only in flat European countries most attention is paid to model subsurface losses of phosphorus. However, recently P transfer through the soil becomes more popular because many countries are aware that P losses can occur by subsurface transport, especially in cracked clay soils with drains (Sims *et al*. 1998). Within the COST 832 action an inventory was made of the models which can describe the P losses by subsurface flow, often denoted as leaching. In Table 2 these models are summarised.

Table 1. Phosphorus subsurface transport models used at the field scale within Europe (based on a questionnaire)

Country	Model	description
Belgium	WAVE	Water and Agrochemicals in the Vadose Environment
Denmark	-	
England	-	
Ireland	-	
France	no response	
Finland	-	only ICECREAM is used: erosion model
Germany	MORPHO	Modelling of Regional Phosphorus Transport
Hungary	no response	
Netherlands	ANIMO	Agricultural Nutrient Model
Norway	-	
Sweden	GLEAMS/PARTLE	Groundwater Loading Effects of Agricultural Management systems, including a subroutine for Particle Leaching
Switzerland	-	CENTURY is used for modelling dynamics in the root zone

In this chapter the following models will be discussed: WAVE (Ducheyne et al., 1998), MORPHO (Pudenz and Nützmann, 1997; Pudenz et al., 1999), ANIMO (Groenendijk and Kroes, 1999) and GLEAMS/PARTLE (Knisel, 1993; Shirmohammadi et al., 1998).

2. Visualisation of the P cycle as used in the models

In Fig. 1a – 1c an overall presentation is given of the P cycle in soils as assumed in the models. No such figure is available of the MORPHO model.

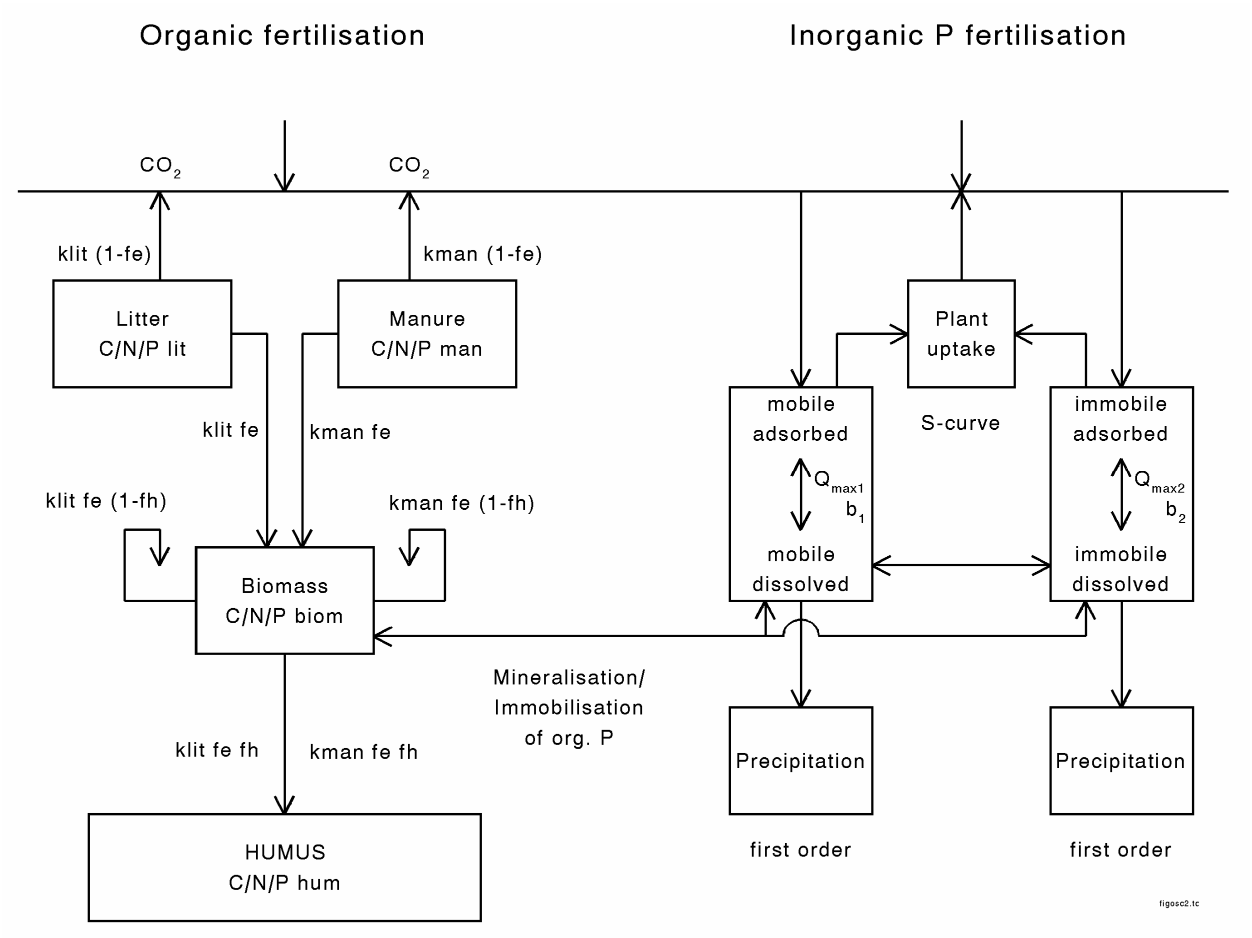

Fig. 1a P cycle of the WAVE model

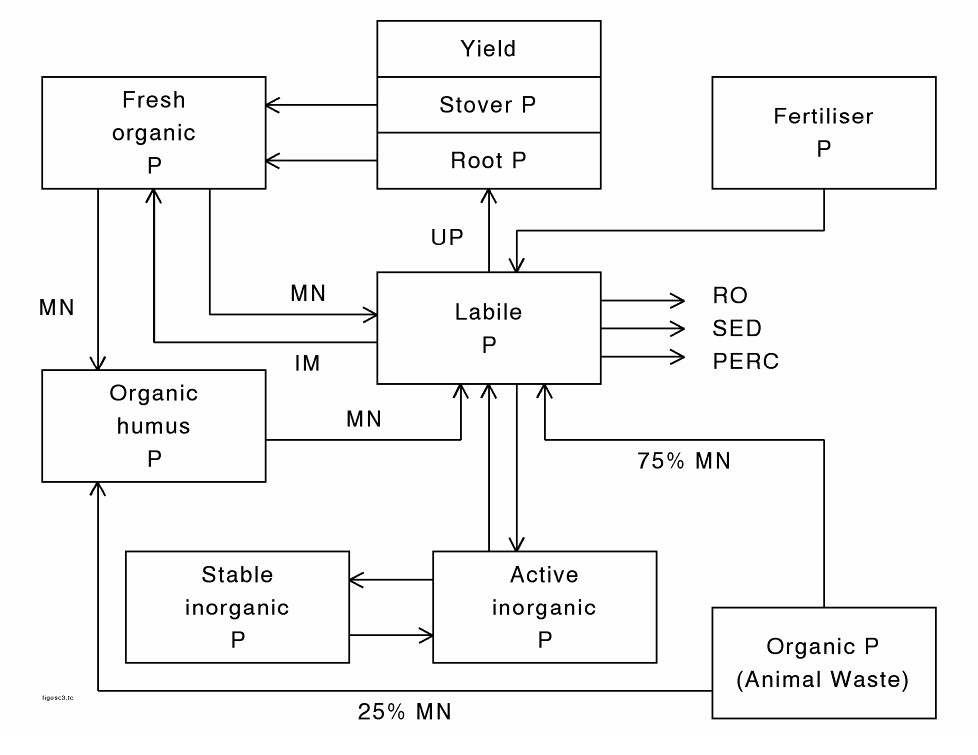

Fig. 1b P cycle of the GLEAMS model

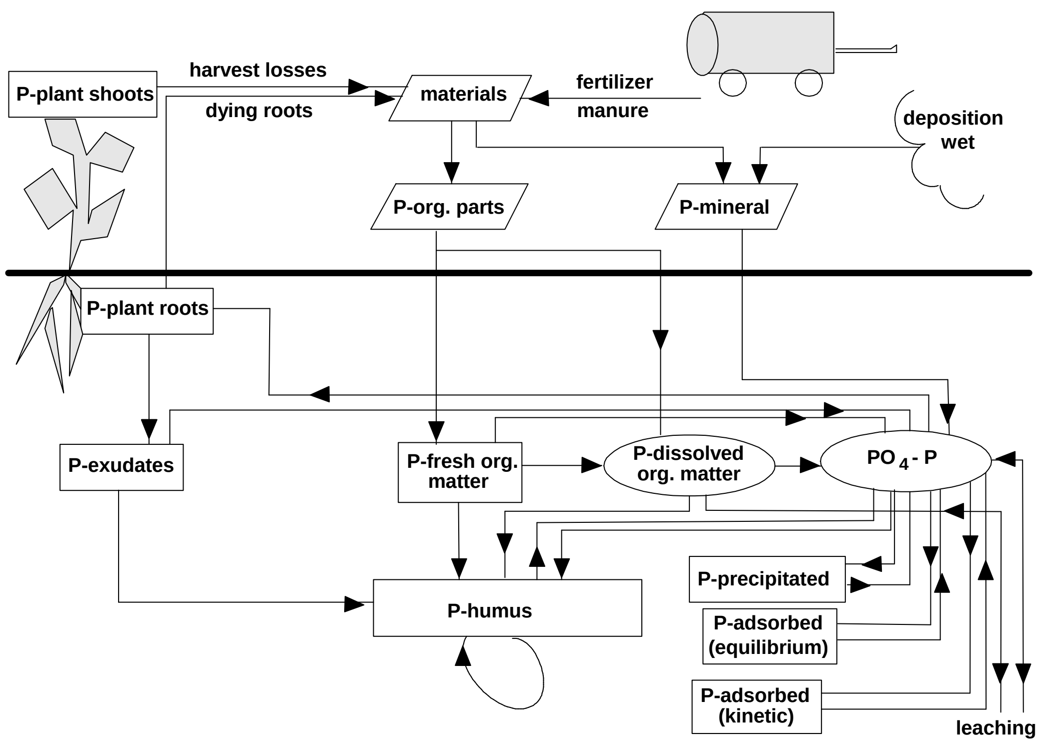

Fig. 1c P cycle of the ANIMO model

3. Process description

3.1 Addition of P materials

Inorganic P forms

In all models fertiliser P is assumed to be 100% soluble, which means that the inorganic P forms are directly added to the labile pool. Only ANIMO has the possibility to include a solubilisation rate of the inorganic P form added.

Organic P forms

In the MORPHO model the organic P-cycle is not modelled. The assumption is made that all organic material is easily mineralised.

In the GLEAMS and WAVE model two forms of organic P can be added:
- Fresh Organic P of crop residues/roots (FOP or LIT)
- Organic P of animal waste (ORGP of MAN)

The same approach is used in the erosion models CREAMS/ICECREAM

In ANIMO three forms of organic P forms can be distinguished
- Fresh organic P of crop residues/roots
- Root exudates during growing season
- Organic P of animal waste (different forms of material)
  Each organic P material is defined by a distribution of typical organic P fractions each which is own decomposition rate.

3.2 Organic P dynamics: transformations of pools

In the GLEAMS (and [ICE]CREAM model) the Residue Mineralisation of Fresh Organic P (FOP) called RMP is described by

RPM = decomposition rate of crop residues * FOP

About 75% of RMP becomes labile (inorganic) P (PLAB) and 25% becomes Stable Organic humus pool (SORGP). Furthermore the mineralisation of Stable Organic humus P (SORGP; humus P) is defined by

PMN = decomposition rate of carbon mineralisation * SORPP * $\text{Factor}_{\text{Temp, N, }\theta}$

Figure 2 shows the overall transformation of organic P dynamics in the GLEAMS model.

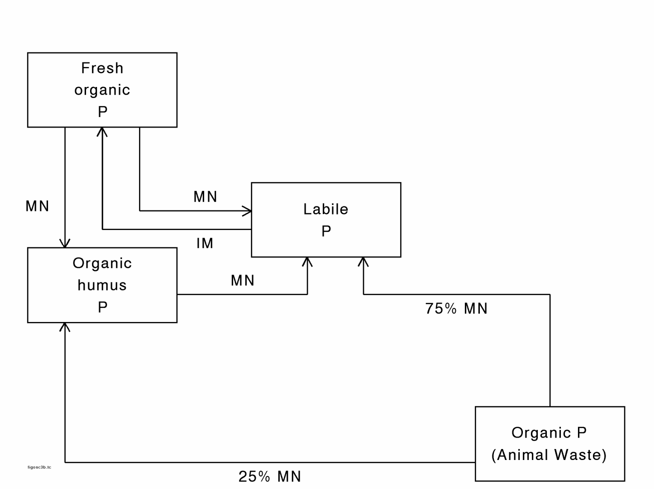

Fig. 2 Transformation of organic P in GLEAMS

In the WAVE model the fraction of fresh organic material and manure is effectively transformed in biomass when a part of the fresh material is respired (see Fig. 3)

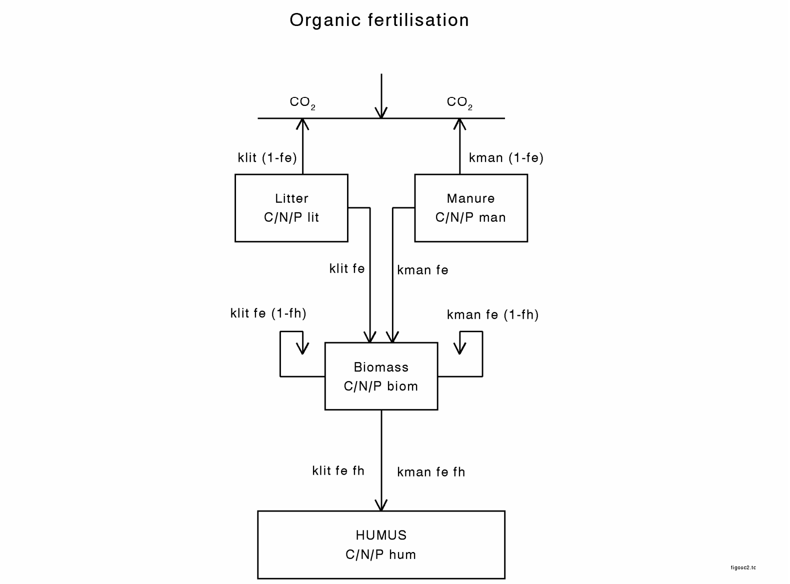

Fig. 3 Transformation of organic P in WAVE

In the WAVE model, the pool of biomass is decomposed into humus and, finally, humus is mineralised into inorganic P. These processes are described by:

Humification = decomposition rate of biomass * biomass
Mineralisation = decomposition rate of humus * humus

In ANIMO the mineralisation of organic P material is based on a uniform description of the decomposition of all organic P pools (see also fig 1c):

$$\begin{aligned}\text{Mineralisation} = {} & \text{decomp. rate}_{OM,\,i} * \text{Organic Matter fraction i } (OM_i) * \text{Factor}_{Temp,\,pH,\,\theta} \\ & + \text{decomp. rate}_{DOC} * \text{Dissolved Org. Carbon (DOC)} * \text{Factor}_{Temp,\,pH,\,\theta} \\ & + \text{decomp. rate}_{EX} * \text{Exudates (EX)} * \text{Factor}_{Temp,\,pH,\,\theta} \\ & + \text{decomp. rate}_{HUM} * \text{Humus (HUM)} * \text{Factor}_{Temp,\,pH,\,\theta}\end{aligned}$$

In GLEAMS, WAVE and ANIMO model the total amount of organic P in soils is about 20-30% of total amount of P in soils. In Table 2 all the organic P pools that can occur in these three models are summarised.

Table 2. Names of soil organic P pools used in models

Pool	GLEAMS	WAVE	ANIMO
Organic P pool of animal manure	ORG	MAN	-
Fresh organic matter	FOP	LIT	OM1, OM2
Dissolved organic matter	-	-	DOM
Exudates	-	-	EX
Biomass pool	-	BIOM	-
Stable organic humus pool	-	HUM	-
Stable organic/biomass pool	SORGP	-	HUM

From Table 2 it is clear that in practice the differences between the models in the way the organic P pools are handled are quite small. With respect to the addition of material all three models use two solid forms for fresh organic material (ORG/FOP, MAN/LIT and OM1/OM2). Only ANIMO uses an additional solid form as exudates (EX), formed during the growing season. Furthermore, in ANIMO a part of the added organic matter goes directly into solution as dissolved organic matter (DOM). Furthermore, all models distinguish a stable organic matter/biomass pool (SORGP, HUM). Only the WAVE model separates this lumped pool into two parts (BIOM and HUM). Finally, based on the process description, it seems that all models use first order rates for the decomposition or transformation of these pools. Sometimes the rate is corrected for the influence of temperature, pH or water content.

3.3 Inorganic P dynamics: transformation of pools

In the GLEAMS model three (theoretical) pools are defined:

- Labile P (PLAB or P_L) which can be seen as the amount of P that is available for plants.
- Active inorganic P (PMIN or P_A).
- Stable inorganic P (SOILP or P_s).

The formation of these three pools (see fig 1b) is determined by:

PLAB = P_L = fertiliser P + 75% of mineralised FOP + 75% of mineralised SORGP + movement
from the active pool to the labile pool
PMIN = P_A = formed by the transformation/movement of labile pool to active pool (fast)

SOILP = P_S = formed by the transformation/movement of active pool to the stable pool (slow)

The rate of fast (from labile to active) and slow (from active to stable) movement is described by:

$$\text{FAST} = \text{rate}_{L \rightarrow A} * (P_L - P_A * psp/(1-psp))$$

where rate $_{L \rightarrow A}$ is a constant and psp = function of base saturation, pH, clay, $CaCO_3$.

$$\text{SLOW} = \text{rate}_{A \rightarrow S} * (4 * P_A - P_S)$$

where rate $_{A \rightarrow S}$ is a constant or also a function of psp

Also in the ANIMO, MORPHO and WAVE model three pools are used. In these models the behaviour of inorganic P is based on the same (Dutch) deterministic approach, namely a soil physical/chemical description of the inorganic P forms in soils and their transformations. The inorganic P pools are:

- Adsorbed P at the surface of aggregates like Al and Fe (hydr)oxides (directly available mineral P) called Q
- Diffused ('absorbed') P in aggregates and adsorbed or precipitated in the amorphous/micro crystalline aggregates (slowly available mineral P) called S
- Precipitated P (directly or slowly available mineral P) called PREC

The adsorption reaction (Q) is described by the Langmuir equation:

$$Q = K\, c\, Q_m / (1 + K\, c)$$

The diffusion/precipitation reaction is based on the Unreacted Shrinking Core Model (Van der Zee, 1988):

$$S = F(I) = \sum a_j \ln^j (I) \text{ and } I = \gamma \int (C - C_e)\, dt$$

The MORPHO model can handle this equation in order to describe this diffusion/precipitation process, but also a simplified equation can be used, like ANIMO and WAVE both do:

MORPHO: $dS/dt = \sum a_j \ln^j (I)$ or $S = K\, C^n\, t^m$
ANIMO: $dS/dt = \sum \alpha_i (K_{Fi}\, C^n - S_I)$
WAVE: $dS/dt = \Gamma (C_{mob} - C_{immob})$
and C_{immob} at equilibrium $S_{im} = K\, C_{immob}\, S_m / (1+K\, C_{immob})$

In MORPHO the assumption is made that all precipitated P is going into solution within the time step. So in fact, no precipitated pool is modelled. Only ANIMO and WAVE have the option of a first order reaction for precipitation and going into solution of precipitated P.

Schoumans and Groenendijk (2000) showed that, based on this soil chemical/physical approach, it is possible to model also soil P test values that are commonly used for fertilisation recommendations. Thus, labile P, as a value for plant available P, can also be modelled based on these kinetics.

In Table 3 the inorganic P pools of the models are summarised.

Table 3. Inorganic P pools in soils

	GLEAMS	ANIMO / MORPHO / WAVE
Labile P	PLAB	-
Active P	PMIN	-
Stable P	SOILP	-
Adsorbed P		Q

Diffused P	S
Precipitated P	PREC

Conclusion: Although there are differences in the definitions in inorganic P pools and the description of transformation of inorganic P pools, the differences in modelling of inorganic P forms are quite small. All models describe a fast reaction of easily available P. The major differences can be assigned in the way the slow soil phosphate reaction in soils are modelled. All models use different equations to simulate this pool. Most of the time the parameters of these equations are calibrated on field data.

4 Phosphorus losses

4.1 Organic P losses

In the MORPHO and WAVE model organic P losses can not be modelled. Also in the GLEAMS model organic P is not directly modelled, but related to the amount of labile pool. In ANIMO organic P loss is modelled by:

Formation: $d\theta c_{om} / dt = (1 - f_h) \int \sum k_i \, OM_i \, dt$

Decomposition: $- d\theta c_{om} / dt = k_s \, \theta \, c_{om} \, dt$

P-loss organic: $= flux * c_{om}$

4.2 Inorganic P losses

In ANIMO, MORPHO and WAVE the inorganic P concentration in soil solution is determined by the amount of P adsorbed on the surface of aggregates and can be solved from the Langmuir equation:

$$Q = K\, c\, Q_m / (1 + K\, c) \quad \Rightarrow \quad c_p = 1 / (K (Q_m/Q - 1))$$

thus, P-loss inorganic equals: $flux * c_p$

In GLEAMS the following equation is used:

$$CPLABW = C_{av} * \beta / (1 + \beta * K_D)$$

where:

C_{av} = PLAB ∗ EXP [–(F – ABST) / (SSG ∗ K_D (1 – POR) + POR)] (mg kg^{-1})

K_D = partitioning coefficient = C_s / C_w = 100 + 2.5 ∗ percentage clay (–)

β = extraction coefficient = soil mass per unit of volume flow (g cm^{-3})

F = Precipitation depth (mm)

ABST = abstraction = amount of water to fill up layer to saturation (mm)

POR = soil porosity (g cm^{-3})

SSG = soil specific gravity (g cm^{-3})

4.3 Particulate P losses

In ANIMO, MORPHO and WAVE the particulate P concentration in soil solution is not modelled.

The GLEAMS model extended with the PARTLE-module (used for clay soils) describes the amount of particulate P transported. In fact the average annual sediment concentration in drain (input parameter) determines the amount of daily particulated P transported based on the P content of the top layer daily percolation (fraction). In formula:

$$PP = SC * PERC * PC_1 * (K_{mac}/K_{mat}) / (1 - R) * f_{conversion}$$

PP	= particulate-P lost through subsurface drains	(kg ha^{-1})
SC	= average annual sediment concentration in the subsurface drain	(mg l^{-1})
PERC	= daily percolation	(cm)
PC_1	= ortho-P content in top layer	($\mu g\ g^{-1}$)
K_{mac}, K_{mat}	= macropore resp. matrix hydraulic conductivity	(cm h^{-1})
R	= percolation fraction = annual percolation /annual precipitation	(-)

A very important input parameter is the average annual sediment concentration in de subsurface drain.

With respect to the (overall) modelling of P losses only the description of inorganic P losses can be compared between the models. The ANIMO, MORPHO and WAVE approach is quite simply based on the Langmuir equation of the fast reversible adsorption reaction in each soil layer, which determines the inorganic P concentration in that layer. In the GLEAMS model the pool of easily available P (labile pool) determines the inorganic P concentration; however, in that case some transformations are made.

5. Conclusions

Within Europe only a few models are used to estimate P losses by leaching. These models are GLEAMS, ANIMO, MORPHO and WAVE. In these models a part of the transformations of P forms or pools which are found in soils are modelled (chemical, physical, biological transformations together with the water flow). No model is able to describe all P forms that can be transported through the soil profile to groundwater and surface waters. Inorganic P transport is modelled by all models. The differences between the GLEAMS model and the other models are quite large, since the definitions of the inorganic P pools in the soil are quite different. However, also within the GLEAMS model, the inorganic P concentration in the soil solution is strongly determined by the labile pool, more or less similar to the other models (ANIMO, MORPHO and WAVE). In these three models the inorganic P concentration in the soil solution is related to the amount of reversible adsorbed P. The ANIMO model is able to describe the leaching of organic P, and the GLEAMS model, extended with the PARTLE module, is able to assess particulate P transport in clays soils.

The major differences in the P pools are found in the organic pools and in the description of the inorganic pools. With respect to the organic P pools differences are found between the modelling of biomass and humus and the dissolved organic P pool. In the WAVE model, biomass and humus are separated; in GLEAMS and ANIMO these two pools are lumped, and MORPHO does not describe the organic P pool at all. Finally, only ANIMO distinguishes a dissolved organic pool. As regards to inorganic P the approaches between GLEAMS and the other models are quite different. ANIMO, WAVE and MORPHO use a chemical/physical deterministic approach and GLEAMS a more practical empirical approach. However, in both types of model the slow reaction of phosphate in soils (diffusion/precipitation reaction) is described by different functions with seem to fit the available (field) data quite well. Only the MORPHO model is able to use the theoretical function based on the unreacted shrinking core model for the diffusion/precipitation reaction.

Finally, although models may differ, they probably are complementary!

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Phosphorus losses as a result of subsurface runoff: Field data

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1. Introduction

This chapter contains a general evaluation of the participation and the new knowledge regarding the questionnaire on the review of available data on the amount of phosphorus losses at field scale as a result of subsurface runoff (lysimeter/plot/field). During the evaluation support was received from Ruth Grant (Denmark), Barbro Ulen (Sweden), Oscar Schoumans (Netherlands), Gerfried Eder (Austria) and all the other participants of this questionnaire action.

The questionnaire was developed from the steering group "subsurface runoff" of the WG2 "Phosphorus losses at field scale" and at the beginning of March 2000 distributed via e-mail to all members of the COST 832 management committee and all members of WG 2. Furthermore, our colleague Gerfried Eder from Austria distributed the questionnaire amongst the 200 members of the Austrian Lysimeter Group. In this group are participants from 17 European and 2 Non-European countries involved.

We received a reply from 17 colleagues from 12 countries. Because 18 countries are signed the COST action 832 the reply rate was about 67%. The quality of answering the questionnaire was different. Not all participants gave answers to all questions. But in the whole we got an adequate overview about investigations and available data regarding the quantity and sources of P losses at field scale as a result of subsurface runoff.

Because of the wide variation in the answers of the different questions we tried to collect all information and select it in a set of comparable tables. In the following a short evaluation of the results will be given as a basis for further discussion with the panel. Based on this discussion it is recommended to prepare joint conclusions and a schedule for future work to tackle the problems regarding subsurface P losses. In the last chapter of this book answers to the questions are given.

Question 4: There is a tendency in Europe to investigate and estimate the different P sources. P from diffuse sources is often >50% of the total P loss which comes into the water resources. The knowledge about the quantity of the diffuse P sources is different in the countries. The classification of the sources is not equal and makes a comparison difficult. But the available information show that the pathways Erosion > Agricultural production > Drainage are dominant within the diffuse sources.

Question 5: Since the variation of average amounts of subsurface P loss is so large many participants preferred to give ranges instead of average values. The range of TP subsurface loss varies between 0.0 kg TP ha^{-1} y^{-1} in Finland (fine soils) to > 5kg TP ha^{-1} y^{-1} in the Netherlands (calcareous sandy soils with high nutrient input). Most of the countries tried to make distinctions between different impact factors as animal density, hydrology, soil condition and type of land use. The comparison between the countries is more difficult because of the different natural climatical - pedological and hydrological conditions and the measuring of various chemical P forms (for example: most countries TP, but DK only DP and FIN - TP and part.-P and (DRP)-$P0_4$-P)

Question 6: The ranking of pathways for subsurface P loss at field scale was very different and showed the urgent need for further research. According to the available information the following temporary ranking of pathways is possible:
1. vertical/lateral flow to field drains
2. vertical flow in the profile
3. lateral flow in the soil layers
4. transport of accumulated P in soil after rewetting (answers only from 4 countries).

Question 7: The ranking of importance of factors which influence subsurface P loss was different in the countries. Based on the answers the following temporary ranking is possible:

- input of P (P-surplus > P-fertilisation rate > Form of P input)
- soil conditions (inorg. P content > pedological conditions > TP content = org. P content)
- hydrological conditions (high ground water level > storm flow conditions > base flow conditions > temporary ponding)
- meteorological conditions (precipitation surplus > precipitation rate)

Question 8: The origin of P loss by subsurface runoff results mostly from slurry or manure application. In Norway from grassland areas with high animal density most P-subsurface P loss is organic-P, while in clay areas macropore flow of particulate-P is dominating. The distribution of P fractions is often not known and varies from country to country. The results show that usually the amount of inorganic P fractions > organic P fractions. Organic P in soil and drainage water is generally low but autumn applied slurry can cause movement of organic P. Especially in Ireland the TDP and DRP amounts are very high and 80% of the TP. It may be explained by much grassland compared to arable land.

Question 9: The survey shows that in most of the European countries national research programs about P losses from soil to water are running or scheduled. In Denmark, Norway and Poland this research programs are supported by national monitoring programs about P-losses. In Spain a specific national research program was not mentioned but there also some projects about this topic at work. The analysis shows that the research programs are complex, sometimes linked with Nitrogen (Austria, Germany, Netherlands) and focused especially to important tasks of every country. But the importance of subsurface P loss is clearly visible and underline our activities in the COST action 832.

Question 10: The kind of investigations about subsurface P loss is also different in the countries. The most popular method are investigations in plot and field scale (all 12 countries). In 6 of them this investigations are connected with catchment studies. Laboratory, lysimeter and model studies are carried out in 4 countries and pot studies only in The Netherlands have been done. In Germany, England, The Netherlands and Sweden the investigation about subsurface P loss are carried out in different scales - this procedure is very important for the reliability of the results and it's using under practical conditions.

Question 11: The measuring methodology for estimating subsurface P-loss fits to the different kind of investigations. A using of automatic sampling devices is usual and this measurement is often completed by additional manual measuring of specific parameters. Beside measuring of important parameters under natural conditions in situ (as discharge, drainage flow, soil parameters) in Switzerland dye and tracer experiments to study infiltration pattern and travel time of solutes are carried out. In Spain the effect of soil amendments (which type not described) on P losses in marsh soils is under investigation. In Germany microcosm experiments for studying P mobilisation in soils under different conditions (as pH changes, redox, temperature etc.) are carried out. The used techniques are modern but fully new high sophisticated techniques for measuring subsurface P loss have not been represented during this survey.

Question 12: Essential contents of measuring programs for estimation P subsurface losses are focused to the following relations:

- soil P status and subsurface leaching losses;
- pathways of P leaching and temporal distribution of P;
- seasonal and short time variation of P leaching losses and P losses during the year in surface and subsurface water;
- P leaching losses in dependence from soil and agricultural management (arable land, grassland, tillage, crop rotation, inorganic and organic fertilisation, ground water table, drainage system);
- One of the most important goals is to make the P balance complete at the field scale (including uptake, fixation and leaching).

Question 13: Most of the countries carry out meteorological (precipitation, temperature, evapo-transpiration), hydrological (drainage flow, ground water level, seepage water, surface flow), agricultural (registration of agricultural practice, fertilisation, crop type, irrigation water, yield crop production, tillage), chemical (TP, DRP, TRP, TPP, organic P etc) and pedological (soil profile, P in soil, soil properties, organic matter etc) investigations. Conspicuous is the different indication of the different P forms (although a table with the different P forms was given in the questionnaire) in the answers of the participants which makes the comparison between the countries difficult. Furthermore surprising was the little investigation about soil physics.

In order to have more information about the chemical analysis of soil and water P an additional survey was started at the begin of September 2000 between the participants of this questionnaire action. The results which are essential for modelling of subsurface P loss will presented from our colleague Oscar Schoumans (NL).

Question 14: Beside Denmark (?) all countries will offering data from special experiments for a common data bank, if the projects are finished. But also at this time from some countries data sets available for testing of subsurface P loss models. The representatives from this countries will bring the data sets to Gumpenstein or will prepare available data sets in the near future and give them to Oscar Schoumans (NL).

Question 15: Beside Switzerland and Poland (no information) all other countries are interested in future co-operation on subsurface P loss. The main tasks of interests are:

- amount of subsurface P loss under different agricultural and pedological conditions;
- release and subsurface transport of P during re-wetting of fen soil;
- transport of bacteria (microbiology) after slurry application including colloid chemistry;
- subsurface P loss via subsurface drainage systems (including backfill and filter material);
- prediction of conditions for variability of P leaching losses;
- estimation of subsurface P leaching losses in different scales (plot, field to catchment);
- importance of geological origin of the soils for the subsurface P loss (why differ P loss so much from different areas).

Question 16: The answers regarding the recommendations of methodologies to carry out subsurface P measurements showed also a large variation. Four countries do not have any recommendations for a preferred measuring methodology. Other countries prefer drainage measurement > experimental fields > lysimeter and suction (tensio) cups. To give adequate recommendations is difficult because the variability under natural conditions is wide and the design of the measuring facilities depends mostly from the task. Important is that most of the countries agree that measuring is also necessary in the future and with modelling only we will not solve our problems; a combination of measuring and modelling makes sense and may be an effective way for further research on this topic.

Question 17: The answers regarding the proposals for important topics of future work to investigate P loss by subsurface runoff showed that most of the participants are interested on further applied and basic research. The most important topics mentioned are:

- to find relations between the intensity of farming and fertilisation on subsurface P loss and give recommendations to reduce the P loss;
- to find relations between soil P test and P loss (interaction between soil hydrological properties and P loss);
- to develop realistic and reliable models for modelling P loss from soil to water;
- to develop technical measures to prevent P losses and their impact on nitrogen losses;
- to solve problems of P-adsorption and P-sorption in connection with Fe-adsorption and Fe-sorption (Fe-oxidation) in drainage pipes;
- to carry out soil erodibility studies to understand the origin of particulate P in subsurface flow and thus to prevent the losses;
- to explain the fate of subsurface P after re-wetting of histosols.

Question 18: We got supports from several colleagues for this questionnaire (especially literature from Finland, Switzerland, Netherlands, and Germany). On this way the evaluation team of the answers of the questionnaire will say Thanks to all colleagues for participation.

Provisional conclusions regarding the goals of the questionnaire:

Goals of the questionnaire	Evaluation of the goals
a review of data about P loss within subsurface runoff	data reviewed and available
recommendations for carrying out subsurface P losses measurements at different scales	a lot of ideas have been presented, a common evaluation is necessary
to identify gaps in current knowledge	a lot of proposals have been presented, a common evaluation is necessary

Question 1,2,3: Participation of countries and institutes for answering the questionnaire on the review of available data on the amount of Phosphorus losses at field scale as a result of subsurface runoff

Nr.	Country	Code	Institute / Authority	Remarks
1	Austria	A	▪ Federal Research Institute for Agriculture in Alpine Regions – BAL Gumpenstein	focused to alpine part of Austria
2	Switzerland	Ch	▪ Swiss Federal Research Station for Agroecology and Agriculture ▪ Swiss Federal Institute of Technology, Zurich (ETH)	
3	Germany	D	▪ UFZ – Centre for Environmental Research Leipzig – Halle ▪ Bavarian State Authority of Soil Science and Plant Production, Freising ▪ Dr. K. Isermann, Consulting office for sustainable agriculture, Hanhofen	
4	Denmark	DK	▪ National Environmental Research Institute of Soil Science	
5	Spain	E	▪ University of Sevilla Institute of Soil Science	focused to Andalucia
6	Finland	FIN	▪ Agricultural Research Centre of Finland ▪ Helsinki University of Technology, Lab of Water Resources	focused to south – western part of the country
7	United Kingdom	GB	▪ Agricultural and Environmental Science Division, Department of Agriculture and Rural Development, Belfast	focused to Northern Ireland
8	Ireland	IRL	▪ TEAGASC, Wexford	
9	Norway	N	▪ Centre for Soil and Environmental Research, Jordforsk	
10	Netherlands	NL	▪ Alterra Wageningen	
11	Poland	P	▪ Institute of Soil Science and Plant Cultivation, Pulawy	focused to the region Lubelskie
12	Sweden	S	▪ Swedish University of Agricultural Sciences, Division of Water Quality Management, Uppsala	

Question 4: Estimation of P sources for different countries in Europe

Code	P from point sources [%]	P from diffuse sources [%]
A	no data	no data
CH [1)]	72 (12..72)	28 (28..96)
D	34	66
DK	43	57
E	no data	no data
FIN	35	65
GB [2)]	25	75
IRL [3)]	50	50
N	no data	no data
NL	53	47
P	no data	no data
S	27	73

[1)] Information in () for different catchments
[2)] L.Neagh drainage area 4450 km², Northern Ireland
[3)] Estimation, because of limited information

Question 4: Origin of P from point, agricultural and other diffuse sources for different countries

Country	P from point sources [%]	P from diffuse sources [%]				
		Erosion (a)	Drainage (b)	Agricultural production (c)	□ (a+b+c)	Other
Austria						
Switzerland						
a) river Rhine	72	8	3	15	26	2[1]
b) lake Constanz	12	63	1	13	77	11[1]
c) Kanton Zurich	65	10	3	11	24	11[1]
d) Kanton Bern Midland	68	12	2	10	24	8[1]
e) Kanton Bern Pre-Alps	16	35	3	29	67	17[1]
f) Kanton Bern Alps	4	85	1	6	92	4[1]
g) Kanton Bern Jura	45	15	4	18	37	18[1]
Germany	34	22	9	9	40	26[2]
Denmark	43				31	26
Spain						
Finland	35				60	5
United Kingdom						
a) L. Neagh	25				63	12[3]
Ireland[4]	50				50	
Norway						
Netherlands	53		20	27	47	
Poland						
Sweden	27	20[5]	45	8	73	

[1] Σ ground water + atmospheric deposition – precipitation + direct diffuse input

[2] Σ ground water + atmospheric deposition – precipitation + urban areas

[3] Septic tanks

[4] Estimation, because of limited information

[5] upward seepage

Question 5: Average amount of subsurface P-losses and background information about the influence of different circumstances on this process

Code	Average amount of subsurface loss $[kg\ ha^{-1}\ yr^{-1}]$	Specific information about P subsurface loss $[kg*ha^{-1}*yr^{-1}]$				
		Animal density	Hydrology	Soil	Arable Land	Grassland
A	TP <0.5 (grassland)					0.3-0.6
CH	TP 0.07-0.21				TP in different basins: river Rhine: 0.02 lake Constanz: 0.13 Kanton Zurich: 0.19 Kanton Bern Midland: 0.16 Kanton Bern Pre-Alps: 0.14 Kanton Bern Alps: 0.14 Kanton Bern Jura: 0.21	TP in different basins: river Rhine: 0.18 lake Constanz: 0.15 Kanton Zurich: 0.17 Kanton Bern Midland: 0.09 Kanton Bern Pre-Alps: 0.07 Kanton Bern Alps: 0.07 Kanton Bern Jura: 0.11
D	TP 1.15 see table below					
DK	DP <0.1		high groundwater table, application of slurry or grazed areas TP 0.5-1.0	high P level or slurry application DP 0.5-2.0		
E	TP 0.02-0.2			drained marsh soils in SW Spain TP 0.02-0.2		

FIN	TP 0.0-1.42			**clay soils** drainage water low/moderate P status part. P 0.1-1.3 (DRP)-PO_4-P 0.0-0.012 **fine soils** part. P 0.0001-0.02 (DRP)-PO_4-P 0.0-0.01		
GB					TP 4.9	TP 0.8
IRL	no load information (only overland flow DRP: 0,5-4)					
N	TP <1 – 4.5			silty clay: < 1 peat soil: 4.5		
NL	TP 1->5 (NL divided into 3634 plots; unique combination of land use, soil type, drainage and hydrological conditions, P input, P saturation degree)			TP from -peat soils: 1.5-4 -marine areas: >1.5 -non calcareous sandy areas with shallow groundwater level: 1-2 -calcareous sandy soils with high nutrient input (bulb flowers): >5		
P	no data					
S	TP 0.4	zero to few TP 0.3 max. TP 0.6	low discharge, short duration TP 0.3; high discharge, low duration TP 0.5	coarse texture TP 0.3; fine texture TP 0.4		

Question 5: For the hydrological and meteorological conditions of Germany typical P-measurement data in soil solution, drainage water, ground water and springs

(According to Driescher, E.; Gelbrecht, J. (1988); Scheffer, F.; Schachtschabel, P. (1989))

Medium		Unit	Concentration
Soil solution	optimal plant growth	mg TP*L^{-1}	0.2 ... 0.4
	below the root zone	mg TP*L^{-1}	0.003 ... 0.2
	seepage water (1m) below arable land with waste water irrigation	mg TP*L^{-1}	< 77
Ground water	not polluted (average)	mg DRP*L^{-1}	0 ... 0.023
	not polluted below forested areas	mg TP*L^{-1}	< 0.005
	below not agricultural used land (ground water depth >5 m)	mg TP*L^{-1}	0.005 ... 0.1
	below arable land (ground water depth >5 m)	mg TP*L^{-1}	0.02 .. 0.2
	below eutrophic peatlands (fen soils)	mg TP*L^{-1}	3 ...8
Drainage water	below intensive used arable land (former GDR- East Germany)	mg TP*L^{-1}	3.6
Springs	bank filtration of the river RUHR (infiltration length 50 m)	mg TP*L^{-1}	0.03 ... 0.3
	meadow spring	mg TP*L^{-1}	0.207
	natural forest spring	mg TP*L^{-1}	0.091

Question 6: Ranking of pathways for subsurface P-loss at field scale

Code	Country	Specific conditions	Vertical flow in the profile	Lateral flow in the soil layers	Vertical/lateral flow to field drains	Transport of accumulated P in soils after rewetting 1)
A	Austria	grassland	1 (earthworm holes)	2		
CH	Switzer-land	alluvial soils organic soils	2 1 (accumulated P in soils during precipitation)		1 2	
D	Germany		4	3	1	2
DK	Denmark		1	3	2	not known in detail
E	Spain				1	
FIN	Finland		2	3	1	
GB	United Kingdom (Northern Ireland)	one catchment (4450 km^2)	3	2	1	
IRL	Ireland	free drainage hill slope hydrology	1	 1		
N	Norway		2	3	1	1 or 4 depending on soil type
NL	Netherlands		3/4	1	2	4/3
P	Poland		no data			
S	Sweden	diss. P (DRP/TRP) part.P (TP/TUP)	1		2 2	 1

1) Especially fen soils or histosols

Ranking factors

1	most important
2	important
3	moderate important
4	less important

Question 7: Importance of factors for subsurface P-loss

Factor	A	CH	D	DK	E	FIN			GB (North.Irl.)	IRL	N	NL	P	S
						TP	PO_4-P	part.P						
Input of P	**I**	**I**	**I**		**II**								no	
▪ P-surplus			1	1			2			1	2	1	infor-	
▪ P-fertilisation rate	2		3	2						2	1	2/3	mation	1
▪ Forms of P input	1		2	3						2	3	3/2		
Soil conditions	**II**	**II**	**II**		**I**		**III**	**I**						
▪ Total P content			3	3						4	1	4		
▪ Inorganic P content			2	1			1			1	2	1		1
▪ Organic P content			4	3						3	3	2		
▪ Pedological conditions	3		1	2		1				2	4	3		
Meteorological conditions	**III**		**IV**											
▪ Precipitation rate	4		1	1						2	2	2		
▪ Precipitation surplus			2	2		2				1	1	1		
Hydrological conditions		**II**	**III**				**III**	**II**						
▪ High groundwater level			1	1								1		
▪ Base flow conditions			4	2								2		
▪ Storm flow conditions			2	3		3				1	1	3		
▪ Temporary ponding			3	4								4		1

Ranking factors **I-IV main groups** **1-4 specific factors**

I most important III moderate important 1 most important 3 moderate important

II important IV less important 2 important 4 less important

Question 8: Origin of P-loss by subsurface runoff and information about distribution of P fractions

Code	Origin of P-loss	Distribution of P Fraction		Ratio
		inorganic	organic	organic P / inorganic P
A	no results			
CH	slurry / manure			
D	slurry / manure			
DK	top soil or slurry / manure application	from TP in drainage water: 50% part.P, 50% DRP	in soil and drainage water generally low	
E				0-0.5 in depending on the flow rate
FIN	slurry	most P inorganic	autumn applied slurry can cause movement of org. P	
GB		DRP: 46.2% DDP: 18.7% PP: 35.1 %		
IRL		from TP: 80% TDP and DRP (DRP predominate)		
N	from grassland with high animal density: organic-P in clay areas: particulate-P (macropore flow)			
NL		inorganic forms 40-70%, depends on soil type (peat soils versus other) and meteorological conditions, percentage DUP increases with the depth		
P	no information			
S	from surface	from TP: 40% PO_4-P		

Question 9: Kind of research programs running or scheduled regarding subsurface P-loss

Code	Research Programmes
A	▪ National research programme with the following topic: N and P losses by leaching under - arable land and grassland - fertilised with cattle slurry, farm yard manure, composed farm yard manure and mineral P fertiliser
CH	▪ National research programme (no specific information)
D	▪ National research programme (UBA-Umweltbundesamt) „Nutrient emissions into river basins of Germany“ (finished 1999) ▪ National research programme: „Causes of P contamination of lakes in agricultural used catchments and measures for improving the situation“ (Bavaria) ▪ National statement of the VDLUFA: “High P-contents in Soils – Ecological Risks – Solutions for Reduction“ (in preparation 2000) ▪ International research programme (EC):“PROWATER“; this programme is aimed to develop scientifically based guidelines for the use and restoration of histosols that reduce the diffuse pollution of water with P
DK	▪ National monitoring programme „Action Plan of the Aquatic environment Nation wide Monitoring Programme: Agricultural catchment areas“; main topic: Quantifying and explain the amount of P losses from agriculture to water ▪ Research programme: „Loss of dissolved and particulate phosphorus from arable catchment by subsurface drainage“; main topics: Describing and quantifying the contribution of dissolved P, particulate P to P transport in drainage water. Developing strategies for obtaining reliable estimates of P losses
E	▪ No specific research programme, but some research projects about this topic are involved in the national Plan of R + D
FIN	▪ Scheduled joint national research programme with following topics: - P transport via surface and subsurface flow in clay soils- under reduced tillage, quantifying P losses through subsurface runoff and drainage water compared with autumn ploughing - Role of soil matrix, macropores and back-filled drainage trench in subsurface P transport - Sources of the suspended solids in the subsurface drainage waters - Influence of different drainage systems (conventional / controlled drainage on P load)

	▪ National research programme on nutrient losses from organic farming, quantifying P losses through surface runoff and drainage water from fine sandy soil under cereal/grass cultivation ▪ National research programme on characteristics of eroded soil material (and part. P) compared with the source soil
GB	▪ National R and D projects: - Northern Ireland change network – freshwater - Controlling P losses from agriculture - Factors controlling the P leaching potential of grassland soils - Causes of variation in nutrient concentrations in Northern Ireland surface waters (grazed plot experiments)
IRL	▪ International ERDF-EPA contract study on quantification of P loss from soil (finished 2000) ▪ Possibility for future work in a National Programme 2000-2006 (no decision at this time)
N	▪ National Agricultural Environmental Monitoring Program; quantifying amounts of P-loss from agricultural land
NL	▪ National Nutrient programme “Dynamics and management of nutrients on local and regional scale” with the following major general objectives: - Determine the nutrient losses for different types of farm systems (which N and P surpluses are necessary for good food production, what are the nutrient losses to groundwater and surface water, how big is the cap between ‘agricultural inevitable losses’ and ‘environmental acceptable losses’) - Which managing approaches can be used to reduce this cap (source-oriented measures, isolation of ‘hot spots’, hydrological measures in a watershed, chemical measures, eg. Adding natural P binding materials) - Developing simple indicators, which can be used for monitoring purposes - Advisement
P	▪ National research programme for monitoring the status of macro- (including P) and microelements in ground water
S	▪ Parts of FOOD 21 (national programme about sustainability of agriculture)

1) Vereinigung Deutscher Landwirtschaftlicher Untersuchungs- und Forschungsanstalten

2) Programme for the prevention of diffuse pollution with phosphorus from degraded and rewetted peat soils

Question 10: Kind of investigations about subsurface P loss

Code	Type of investigation	Labo-ratory	Pot	Lysi-meter	Plot / Field	Catch-ment	Model
A	▪ Lysimeter and field experiments about P leaching			X	X		
CH	▪ Monitoring of P-concentration on drained grassland and tracer experiments to study the fast P-transport into a well established tile drain (1994-1996)				X		
D	▪ Microcosm experiments to explain P mobilisation in soils ▪ Laboratory, lysimeter, field and catchment investigations on P leaching and modelling of P subsurface transport (MORPHO) ▪ Irrigation experiments on plots / fields for measuring P leaching ▪ Water sampling of brooks (quantity and quality) in catchments with different land use intensities	X		X	X	X	X
DK	▪ Water sampling from suction cups, drained areas, Olsen-P at field level: 6 catchments since 1989 (one catchment from 1993 – 1996 – finished)				X	X	
E	▪ Drainage flow and water composition in marsh soils ▪ Effect of soil amendments on P losses in marsh soils ▪ Laboratory experiments to study the effect of the soil solution composition on P release from soils and the effect of reduction processes on P release from marsh soils	X			X		
FIN	▪ Field scale measurements on surface runoff, subsurface drainage flow and P concentration of the waters (1995-1999) in a representative agricultural area in southern Finland (at present time modelling)				X		X
GB	▪ Catchment studies of P loss, laboratory extraction for relationships between Morgan and Olsen soil P tests, water soluble P and degree of P saturation, grazed plot / field monitoring to examine impact of raising soil P on P loss	X			X	X	

IRL	▪ 4 field sites (TEAGASC) and a number of river catchment studies for measuring P leaching				X	X	
N	▪ field measurements on farmers field				X		
NL	▪ Laboratory (relation between soil P test values and ortho-P concentration, sorption and desorption characteristics of different soil types – in order to get parameters for modelling purposes on local and regional scale ▪ Pot (P mining experiments which plants and addition natural soil chemical additions) ▪ Pot (4 fields – 2 sandy, 1 peat, 1 clay; in each field 6 plots with different combinations of N/P inputs ▪ Field (1 field – clay – investigate the influence of nutrient transport in cracked soils – just started) ▪ Catchment (validation of modelling P-losses – mostly subsurface – to surface water in a catchment of about 5000 ha sandy area) ▪ Model (about 10 P-modelling studies have been carried out in different regions of the NL)	X	X		X	X	X
P	▪ Lysimeter and field investigations; P in ground water at 3500 measuring points			X	X		
S	▪ Lysimeter under free drainage; drained experimental plots and fields for measuring P leaching			X	X	X	X

Question 11: Kind of measuring methodology for estimating subsurface P-loss

Code	Measuring Methodology
A	▪ Different types of lysimeters: - gravitation lysimeters (1m x 1m x 1m) - leaching water collectors / seepage water collectors (type UMS in Munich) - monolithic field lysimeters ▪ Field trials
CH	▪ Discharge measurements in tile drains (comparison between organic and mineral soil) ▪ High resolution sampling with automatic sampling devices ▪ Dye experiments to study infiltration pattern ▪ Tracer experiments to study travel time of different solutes
D	▪ Microcosm experiments for studying P mobilisation in soils under different conditions (as pH changes, redox, temperature etc.) ▪ 20 non weighable lysimeters with free drainage ($1m^2$, 1.25 m depth), filled with sand, loamy sand, loess and loam; different forms of land management ▪ 6 soil hydrological measuring stations, field investigations equip with TDR probes, tensiometers, suction cups, located in a re-wetting fen soil area (different stages of re-wetting) ▪ Field and catchment investigations of subsurface P pathways from surrounding fields to ditches (using ground water observation pipes and seepage measuring devices) ▪ Automatic water sampling devices, combined with outflow measurements in catchments with different land use intensities and artificial rain on drained fields and grassland in order to determine subsurface P loss under several conditions
DK	▪ Soil water sampling from suction cups (teflon type) each week, drainage water and stream water sampling by discrete sampling technique ▪ Drainage water and stream water sampling by intensive (continuous) sampling technique
E	▪ Laboratory experiments to study the effect of soil solution composition on P release from soils and the effect of reduction process on P release from marsh soils ▪ Drainage flow and water quality (marsh soils) ▪ Effect of soil amendments on P losses in marsh soils
FIN	▪ Field investigations (1.8/3.1 ha), drained with tile drains, measuring subsurface drainage flow with a V-notch weir in the main collector pipe, measuring water level using a sensor every 15-30 minutes collecting water samples manually and using an automatic sampler to study detailed variation
GB	▪ Plots (each 0.2 ha) receiving 0, 10, 20, 40 and 80 kg P $ha^{-1}yr^{-1}$ ▪ Separate flow measurements for drainage (1 m) and surface runoff ▪ Daily measurement of all P fractions
IRL	▪ Subsurface flow measured in one drain and in one field drain where 80 % of water in the drain came from subsurface flow and 20 % from overland flow
N	▪ Field measurements of surface and drainage losses, measuring continuous discharge volume and taking discharge proportional water samples
NL	▪ Laboratory, pot, plots, fields, models (compare question 10)
P	▪ 70 lysimeter with free drainage ($1m^2$, 1.4 m depth) filled with sandy, loamy and loess soils and used with different crops and 3 levels of P fertilisation

	▪ Field investigations, water samples from ditches, outlet of drain pipes, wells, piezometers – two times per year (spring and autumn)
S	▪ Soil monoliths under free drainage (lysimeter) ▪ Drained experimental plots and fields

(Question 12): Essential contents of measuring programmes for estimation P subsurface loss

Code	
A	▪ N and P-leaching losses
CH	▪ P leaching losses in dependence from fertilisation, precipitation, ground water table and drainage runoff
D	▪ P-leaching losses in dependence from fertilisation practices, P-balance, land use intensity and different stages of re-wetting ▪ Relations between P stages in soils and P subsurface leaching losses
DK	▪ General monitoring by weekly discrete sampling ▪ Seasonal and short time variation in losses of diffuse P-losses (base flow and storm flow conditions)
E	▪ Study and modelling at P losses and P movement in drained soils
FIN	▪ Pathways and temporal distribution of P and N transport in field scale ▪ P leaching losses in surface runoff and drainage water
GB	▪ Soil P status, soil and water P fraction, continuous monitoring of P
IRL	▪ No information
N	▪ TP-loss during the year in surface and subsurface water
NL	▪ Make the P balance complete at field scale (or plots within a field) including uptake, fixation (inorganic / organic) and leaching
P	▪ No information
S	▪ Different soil P status, different tillage, different manure application, different winter green crops and grasslands

Question 13: Comparison of measuring parameters to estimate subsurface P-loss

Code	Meteorological	Hydrological	Agricultural	Chemical	Pedological
A	precipitation, temperature, transpiration (daily)	seepage water from lysimeter once a week	amount of fertilisation and it‘s P content		
CH	precipitation (automatic)	drainage flow and groundwater level (automatic), flow proportional sampling and additional manual sampling		dissolved P; suspended P; adsorbed P	soil profile
D	precipitation (irrigation), global radiation, air humidity, air temperature, evapotranspiration (automatic and manual, daily)	amount of seepage water from lysimeters (once per month) seepage water from suction cups (3 week cycle), groundwater level (daily and monthly)	registration of agricultural practice (yearly interview)	TP and DTP weekly samples in brooks and drains; drain water at irrigation experiments TP seepage water from lysimeter (every month) TP, molybdate reactive P (every 3 weeks)	soil profile total, sorbed and soluble P (every 3 month) soil moisture, matrix potential, soil temperature
DK	climatic data (daily)	percolation obtained by modelling drainage water and stream water continuous logging of discharge	registration of agricultural practice (yearly interview)	P fractions in water: TP, DRP, DP (weekly)	Olsen-P in soils (once during study period)
E	precipitation	drainage flow and flow composition	amount of irrigation water amount of fertiliser amendment loss, yield crop production	particulate P, dissolved TP, dissolved organic P dissolved inorganic P dissolved molybdate reactive P	Initial soil properties and soil P forms
FIN	precipitation, temperature, humidity, (automatic measurement daily),	surface and subsurface flow, groundwater level (automatic measurement and also	agricultural practice: crop type, fertiliser type and rate (N, P), tillage, crop yield and	TP and PO_4-P in 1-3 times per week depending on storm events and every 4 hr from	soil properties: bulk density, porosity, particle size distribution, organic

	further-more snow and frost depths, snow water content (manual)	manual) continuous flow measurement (data logger on clay soils, manual recording on the fine sandy soil)	N content	automatic sampling Total N, NO_3-N and NH_4-N (manual and automatic sampling) Suspended solids (manual and automatic sampling) Water analysis about 20 times per year from flow proportional samplers Remark: TP-DRP = Part P	matter content, properties of two back filled drainage trenches NO_3-N and NH_4-N in 0-120 cm soil profiles (30 cm layers)about 3-6 times per year
GB	precipitation and temperature (daily)			P-fractions measured daily: DRP, TRP, TPP	
IRL	precipitation, temperature, evapotranspiration and other meteorological data (daily)	depth of water table, flow proportional sampling with automatic flow recorders and samplers		DRP all samples, TDP and TP on some samples TON (total oxidised N) NH_4 and K in water samples	soil and site description
N	precipitation and temperature (continuously)	water discharge	input, output, soil tillage	TP in volume proportional samples every 2. week	P in soil (P-AL)
NL		inert tension cups (20, 30, 60 and 100 cm below surface, measuring TDP and DRP once per week		TDP, DRP in the soil solution after centrifugation and filtering (0.45 µm) TDP, DRP in the seepage water (tension cups)	measuring the P concentration in the solution (TDP, DRP) 3 times per year (early spring before manure application, 1 or 2 weeks after manure application, autumn) mixed samples from different depth (0-30 cm)
P	no information				
S	precipitation and temperature (daily)	continuously flow	soil use, amounts of mineral and organic fertilisation	TP, DRP and PP depending on flow	

Question 14: Offering of data for a common data bank

Code	Kind of Data			
	Laboratory	Lysimeter	Plot / Field	Catchment
A		long time lysimeter data about P loss under grassland fertilised with four different amounts of cattles slurry		
CH	No data available at the moment, because project at this time is not finished.			
D		long time lysimeter data about TP leaching under different soils and different forms of land use		No data available because projects at this time are not finished
DK	No data available			
E			hydrogram from drainage water, climatic and crop data, composition of drainage water	
FIN			long term plot / field data on TP and DRP loss from clay and sandy soil, (15-25 measurement / year) under cereal and grass cultivation with different amounts of P fertilisation and different tillage system	
GB			filed plot: 10 years of measurement of drainage P loss (5x0.2ha plots) field drain: 20 years (not continuous) of measurements of drainage P losses (5 ha of fields)	
IRL			4 field sites (results for 1997)	
N	Losses of P from surface and subsurface in 2 field studies in south eastern Norway			
NL	All data available in the near future for model validation, when completed			
P		long time lysimeter data about subsurface P loss	long time data about amount of P in ground water under different forms of agricultural land use and soil types	
S		precipitation, temperature, daily flow TP, DRP and PP	precipitation, temperature, daily flow TP, DRP and PP	

Question 15: Main tasks of interests for co-operation on subsurface P loss

Code	
A	▪ subsurface P loss, measured with lysimeters
CH	▪ no interest
D	▪ joint projects about release and subsurface transport of P during re-wetting of fen soils (histosols) ▪ joint projects about transport of bacteria (microbiology) after slurry application and about colloid chemistry
DK	▪ interested, but not specified
E	▪ interested, but not specified
FIN	▪ joint projects about subsurface P loss via subsurface drainage systems; subsurface drainage techniques e.g. backfill and filter material and controlled drainage to prevent P losses ▪ joint projects about subsurface P loss, based on field scale plot experiments (in lysimeters there was no P movement in through flow)
GB	▪ prediction of conditions which promote short term high P loss ▪ reasons for high year on year variability (cx5) in P loss under controlled conditions ▪ build up of soil P fractions under grazed conditions
IRL	▪ P loss from agriculture to water which special interest in losses from small fields (about 1 ha) and small catchments (20 to 1000 ha) in both surface and subsurface flow
N	▪ Subsurface P-losses on field scale
NL	▪ measuring P losses by leaching at field scale (pasture, maize land)
P	no information
S	▪ joint projects about the importance of geological origin of the soils for the subsurface P loss (why differ P loss so much from different areas?)

Question 16: Recommendation of methodologies to carry out subsurface P loss measurements

Code	
A	• gravitation lysimeters
CH	• difficult to give recommendations, because variability under natural conditions diverse, but essential for progress are model trials and field trials
D	• combination of investigations in different scales (laboratory – lysimeter – field – catchment) • measurement in drains or other suction free methods
DK	• intensive drainage water measurements
E	• no recommendation
FIN	• no recommendation
GB	• drain flow-continuous monitoring – use of remote sensing (via internet) to access flow record to enable intensive sampling of short term storm events
IRL	• measurement in drains and in streams
N	• no recommendation
NL	• measuring during the year the P-pools in soil solution (tensio cups) • measuring the P-pools in surface water (edge of the field with a ditch starting in the field) in an area without upward seepage • measuring the P-balance and water balance of the field including the surface water • modelling the groundwater fluctuation and the water fluxes in different directions • compare modelled nutrient concentration in the soil solution and nutrient flows to surface water with the measured values
P	• no recommendation
S	• experimental fields

Question 17: Most important topics for future work in studying P loss by subsurface runoff

Code	
A	• Intensity of farming and fertilisation
CH	• Problems of P-adsorption and P sorption in connection with Fe-adsorption and Fe-sorption (Fe oxidation) in drainage pipes
D	• Reduction of P losses in dependence from farming practices (P-contents, application techniques, tillage) • Fate of subsurface P after re-wetting of histosols • Reliable modelling of subsurface P transport from catchment to water courses
DK	• Establishing a relationship between P losses versus agricultural conditions, soil conditions, climate • Modelling P losses from soil
E	• No answer
FIN	• Impact of soil properties and subsurface drainage system on water flow and nutrient transport in field scale • Sources of suspended solids in subsurface drainage waters • Technical measures to prevent P losses and their impact on nitrogen losses • Soil erodibility studies to understand the origin of particulate P in subsurface flow and thus to prevent the losses
GB	• Relationships between soil P test and P loss – interaction between soil hydrological properties and P loss • Contribution of slurry (farm wastes) application to P losses • What is the relative contribution of surface runoff to P losses?
IRL	• Quantifying P losses to water under different soil and farming conditions and how it can be reduced to acceptable levels (recommended boarder value for sustainable agriculture: P loss < 0.5 $kg*ha^{-1}* yr^{-1}$)
N	• Modelling
NL	• Data collecting on P pathways and P forms to surface waters under different circumstances • Use models during the data collection and / or add more data collection if necessary
P	• No answer
S	• To be able to advice steps (tilling, manure handling etc.) to reduce the P losses

Queation 18: Further comments and remarks

Code	
A	Supporting this action and distribute the questionnaire amongst the 200 national and international members of the Austrian Lysimeter Study Group.
FIN	Literature (Ph D from EILA TURTOLA) on the research sites and on P losses in subsurface flow in Finland
IRL	„This is a big challenge to the agricultural industry. Good luck!“
NL	With respect to P: unfortunately, the more we measure the less we know!