UFZ Report

# Program for the prevention of diffuse pollution with phosphorus from degraded and re-wetted peat soils

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**Preface**

The cultivation of fen peat soils, carried out in Europe for about 250 years, resulted in severe degradation and oxidation of peat and loss of ecological value and functions of fenland. Currently, some of the degraded fenlands are under restoration programmes, in which re-wetting is a central measure. Soil chemical considerations and initial results in literature arose suspicion that large scale re-wetting of previously cultivated fenlands may be intensively accompanied by the mobilisation of phosphorus, its transport to adjoining aquatic systems, an accelerated eutrophication and deterioration of water quality. Therefore, the EC- project PROWATER (Program for the prevention of diffuse pollution from degraded and re-wetted peat soils) was initiated to develop scientifically based guidelines for the use and restoration of fenlands at minimised risk of phosphorus transfer to waterways.

From May 2000 until December 2003 a multidisciplinary international research team, accomplished by experienced colleagues from nature park authorities and water management worked together to succeed in the project goals. For this team the acronym PROWATER was more than simply a project acronym; it could be also an abbreviation of project and co-operation philosophy: P for power of project management, R for relationships between project partners, O for organisation of work between the partners, W for water to be protected, A for actions to reach the project goals, T for temperament of the different partners, E for energy to carry out the work packages, and R for results for practical application and knowledge development.

The whole team is very grateful to the EC for funding this project, and thus, enabling us to carry out this multidisciplinary and international research work. The project co-ordinator wishes to thank the work package managers and their teams for valuable contributions to PROWATER. Thanks also to the organisers of project meetings for hospitality and for the efforts they put into preparation and performing of scientific discussions and cultural events. The success of the project is also the result of supervision and constant support by the scientific officer of the EC at Brussels. For this reason the whole team of PROWATER particularly acknowledges Dr. Jürgen Büsing for his engagement to put forward the project. Finally we thank the UFZ Centre for Environmental

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Photo of the PROWATER team, Reading Meeting, 2001 (from left to right): Prof. I. Litaor, Tel-Hai Academic College, Upper Galilei/Israel; Dr. M. Shenker, Hebrew University of Jerusalem/Israel; Prof. R. Meissner, UFZ Centre for Environmental Research Halle-Leipzig/Germany; Prof. E. Otabbong Swedish University of Agricultural Sciences Uppsala/Sweden; Prof. P. Leinweber, University of Rostock/Germany; Albert Niedermeier, The University of Reading/UK; Dr. H. Rupp, UFZ Centre for Environmental Research Halle-Leipzig/Germany, F. Braumann, Naturparkverwaltung Drömling/Germany, Dr. A. Schlichting, University of Rostock/Germany; Dr. J. Köhn, Heiligenhagen, Germany; Prof. A. Sapek, Institute for Land Reclamation and Grassland Farming/Poland; Helmut Müller, Naturparkverwaltung Drömling/Germany; Prof. B. Sapek, Institute for Land Reclamation and Grassland Farming/Poland; Dr. S. Robinson, The University of Reading/UK.
Furthermore, the following persons – not shown on the photo – were involved in the project: Dr. J. Hacin, University of Ljubljana, Ljubljana/Slovenia; Prof. G. Nützmann, Leibniz-Institute of Freshwater Ecology and Inland Fisheries, Berlin/Germany; Dr. S. Pudenz Criteri-on - Evaluation and Information Management, Berlin/Germany; Dr. C. Hancock, Somerset Wildlife Trust, Somerset/UK; K.-H. Kaatz, Trinkwasserversorgung Magdeburg GmbH, Magdeburg/Germany.

# 1. Introduction

**Eutrophication** of freshwater, resulting from excessive N and P loads, is a global phenomenon leading to a wide range of water-related problems, including unpalatability of drinking-water, release of several toxins which are known to pose serious health hazards to livestock and humans, and a general deterioration of water quality. Phosphorus (P) is often the limiting nutrient for algae blooming, hence its control is of prime importance in reducing the accelerated eutrophication of freshwater (SHARPLEY & REKOLAINEN, 1997). The European Community has addressed this problem by starting the COST (Co-operation in Science and Technology) Action 832 „Quantifying the Agricultural Contribution to Eutrophication". Key subject areas of work included the establishment of common terminology, sampling and analytical procedures, principles of fertiliser and feed recommendations, soil organic and inorganic P release, soil erosion and leaching, incidental loss, P loss risk assessment, hydrological pathways, scaling issues, approaches to modelling and future research needs (WITHERS & CHARDON, 1998). By contrast to agricultural mineral soils, the effect of setting-aside, re-wetting and restoration measures of the P mobilization and pollution of freshwater in hydrologically sensitive areas has yet no been a important field of research on the European level, despite of its great importance.

The soils of **hydrologic sensitive regions** are often Histosols (named according to incomplete decomposition of primary organic matter). Global experience showed that intensive agricultural use of Histosols resulted in decreasing soil fertility, oxidation of peat and corresponding $CO_2$-emissions to the atmosphere, nutrient transfer to aquatic ecosystems and losses in the total area of these native wetlands. To prevent these negative environmental effects and restore some of the wetlands ecosystems, set-aside programs and re-wetting measures were promoted in several countries. There were indications in the literature that the restoration of Histosols and wetlands as a mean of environmental protection may result in an enormous P mobilization and accelerated eutrophication risk. MARTIN et al. (1997) observed relationships between ground water table and P release into soil solution and between the history of drying/re-wetting and the proportions of soluble P fractions in Histosols from the "Everglades Nutrient Removal Project" (Florida/USA). In the "Marsh Conservation Project" (Florida/USA), ROBINSON et al. (1998) measured P-concentrations up to 10 mg $l^{-1}$ soluble reactive P after re-wetting. Their modeling results suggest that the re-wetted Histosols will be a source of continuous P-release for the next 30 years. In the "Drömling", a shallow lowland peat area in Saxony-Anhalt (Germany), KALBITZ et al. (1999) observed

gradual increases in the proportions of soluble P in soil ($\approx$ 200 kg ha$^{-1}$) and the P-concentrations in near-surface groundwater ($\approx$ 0,04 mg l$^{-1}$) after re-wetting of the formerly intensive agriculturally used Histosols. In the Hula Valley (Israel) HAMBRIGHT & BAR ILAN (1995) observed elevated P concentrations following the re-wetting of peat soils, up to 0.35 mg l$^{-1}$ of total P in a newly formed lake, much higher than data reported earlier in the outlet of the Jordan River from the basin. The following **hypotheses** were formulated to explain these observations: (1) Mineralization of organically bound P during drying, aeration and oxidation of peat plus input of mineral and organic P fertilizer in periods of intensive use for pasture or arable led to large amounts of P stored in the soil, parts of which were bound to Al, Fe, and Mn oxides and hydroxides. (2) After re-wetting the increased moisture contents and lowered redox potentials resulted in dissolution of sesquioxides which released the sorbed P into the soil interstitial water. The high water table re-mobilized P, as orthophosphate ion or in dissolved organic matter (DOM).

These hypotheses were also supported by various publications: IVANOFF et al. (1998) developed a novel fractionation scheme for the investigation of organic P forms. They observed decreased proportions organic P, especially of biomass-P, after re-wetting of a Histosol. KALBITZ et al. (1999) determined a significant relationship between P concentrations in near-surface groundwater and the redox potential. Histosols in the Drömling area that were kept under wet conditions showed significantly lower P losses to the adjacent surface water. AUSBORN et al. (1997) observed basic relationships between temperature, redox potential and the contents of labile P-fractions in a few microcosm experiments. In summary, the cited publications indicated very clearly that the desired re-wetting of agriculturally used Histosols may be accompanied by an undesired P solubilisation and diffuse P losses to freshwater can cause accelerated eutrophication of downstream aquatic ecosystems. The chemical background and possible amounts of such P losses under different soil and climatic conditions were not known. The **substantial areas of Histosols** in the EC and associated countries, and **the lack of basic knowledge and conceptual models** made it difficult to predict the effects of large-scale re-wetting measures on water quality. Hence, scientifically based re-wetting strategies and a framework for political decisions (decision making system) were urgently required.

Therefore, we developed the PROWATER project to lay an improved scientific base for the sustainable management of fen peat soils in hydrologically sensitive areas. Specific objectives of the project were:

(1) to identify the chemical forms of P in native, degraded and re-wetted Histosols as one key factor for P mobilisation and P losses,

(2) to measure in some representative case studies the actual diffuse pollution with P of water that is hydrologically connected to re-wetted Histosols as a basis for modelling the P release risk in these areas,

(3) to improve or develop conceptual models of P turnover in soil by considering the special features of Histosols, and to use numerical models of fluid flow and P mass transport for predictions of P pollution from Histosols and eutrophication risk, and

(4) to develop a user-friendly decision support system (DSS) that can be used to propose re-wetting and restoration strategies for Histosols in sensitive areas that enable the prevention of freshwater resources from diffuse pollution with P and eutrophication.

The new knowledge should be generated by integrating advanced methods such as automated *in-situ* monitoring, newly developed P fractionation schemes, sophisticated spectroscopic methods, microcosm experiments and with the development and application of conceptual and numerical models, a socio-economic evaluation and the extension of research results to the end-users. Figure 1.1 illustrates the work packages and time schedule of PROWATER.

**End-users**

**WP 4**

Decision Support System, acceptance &
socio-economic consequences,
re-wetting strategies

**Researchers**

**WP 3**

Conceptual models of P transformations & modeling
of fluid flow and P mass transport, scenario calculations

**Project progress**

**WP 2**

Characterization of P-forms, transformations
and P losses by sophisticated techniques

Quantification of factors for P-mobilization in
laboratory microcosm experiments

**Research**

Soil and water sampling

Soil and water sampling

Soil and water sampling

Aquisition & statistical evaluation of field
research data: redox, pH, moisture ...

**WP 1**

Installation of automated field stations, start
& check of field measurement program

Basic characterisation of study areas
& election of experimental sites

**Research**

**Time**

**Figure** 1.1  Work packages and schedule of the PROWATER project

## 2. Study areas

### 2.1 Introduction

The experimental basis for field research of Histosol properties and P leaching were 7 study areas, in which representative experimental sites were selected, equipped with automated field stations and devices for periodic soil analyses and soil solution sampling. All study areas were fen peats and represent nationally and internationally important wetlands. They were under previous agricultural use, re-wetted in last decade or are foreseen for re-wetting. Furthermore, common are concerns about ecological effects of the re-wetting, and the quality of adjoining surface waters and the drinking water resources. The study areas represent the climatic conditions of the geographical areas in western maritime, baltic/northern lowland, subalpine and mediterranean zones as shown in Figure 2.1. Meteorological information on the sites is given in Table 2.1. In the following chapters the sit detail, including the geographical and geological setting, the hydrological and meteorological characteristics, land use and associated conflicts and concerns, and information on relevant previous research.



**Figure 2.1** Overview of the study areas

**Table 2.1** Geographical position and basic climatic characteristics of the study areas

| Study area | Latitude | Longitude | Temperature (Average °C) | Precipitation (mm year$^{-1}$) |
|---|---|---|---|---|
| Somerset Levels and Moors | 51°10′N | 3°W | 11 | 700 |
| Kristianstad Vattenrike | 57°30′N | 12°E | 7 | 700 |
| Trebel Valley | 54°05′N | 12°45′E | 7 | 600 |
| Droemling Nature Reserve | 52°50′N | 11°10′E | 8 | 600 |
| Biebrza Valley | 52°N | 21°E | 8 | 580 |
| Ljubljana Marshes | 45°58'N | 14°28'E | 10 | 1400 |
| Hula Valley | 33°N | 35°30′E | 19 | 500 |

## 2.2 Characterisation of study areas

### 2.2.1 The Somerset Levels and Moors (UK)

#### Geographical and geological setting

The Somerset Levels and Moors is a coastal floodplain marsh of 64,000 ha dissected by a largely man-made drainage system, and is the largest area of lowland wet grassland remaining in England.



**Figure 2.2** Map of the Somerset Levels and Moors.

The Levels and Moors (Figure 2.2) was an inlet of the sea about 8,000 years ago and marine clays built up (through a series of marine transgressions) a coastal barrier - the 'Levels' which lies about 6 m above mean sea level. Inland, the peat 'Moors' are at the considerably lower mean

elevation of 3 m above mean sea level.  The Levels and Moors are susceptible to fluvial floods from the rivers that flow through the low lying land towards the sea.  Houses and other properties are generally on higher ground.

### *Hydrological and meteorological characteristics*

Generally, water levels are controlled by the operation of pumps, sluices and other structures throughout the extensive ditch system wh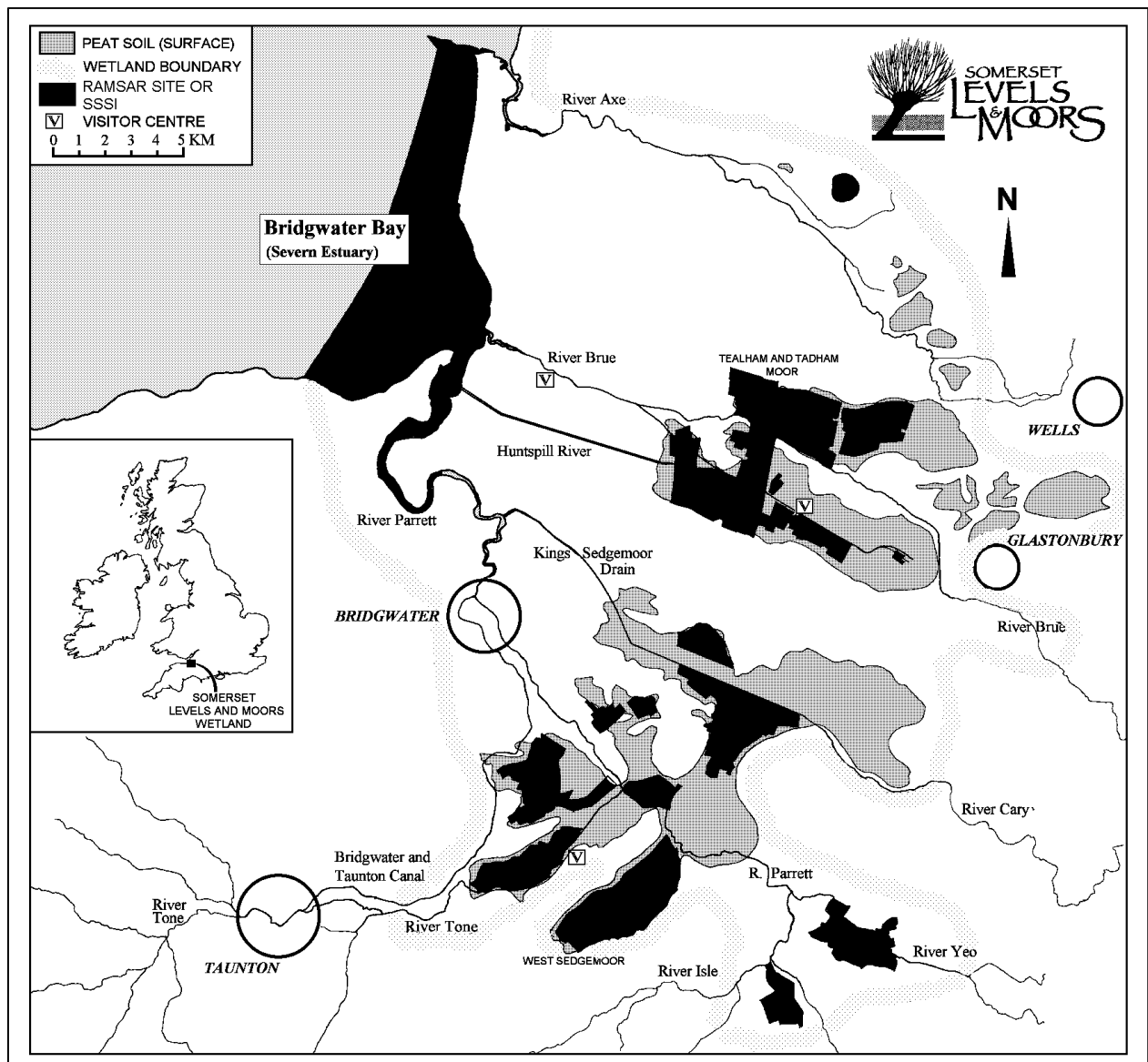ich dissects the area. Direct total annual rainfall means are about 760 mm. The estimated mean evapotranspiration load ranges from 580 mm on surrounding higher ground to at least 900 mm.  Any deficit is made up through limited flood storage in the wetland and by summer main river abstraction for irrigation, supplied through the ditches.

Peat formation began at least 6,000 years ago with a rapid increase in deposition of *Cladium*-dominated sedge peat, stimulated by climatic change leading to calcareous water flooding.  Moss peat formed on top of the sedge peat in places, creating areas of acid raised bog, and peat formation continued until about 900 AD. Today, humified and semi-fibrous peat soils are extensive. The peat is mainly between 2 m and 7 m thick.

### *Land use and associated conflicts and concerns*

The principal land use of the Levels and Moors is agriculture.  Intensive agricultural practices were adopted from 1960 onwards and are dependent upon a complex system of large scale pumped drainage.  The cumulative impacts of fertilisers, pesticides, cultivation and re-seeding with modern varieties has resulted in much increased stocking rates.  Dairy cattle, beef and sheep production now dominate the area, with a small proportion (10 - 12%) of arable crops (wheat, barley and maize).  The remainder of the land use is local industries including peat extraction.  The Somerset Levels and Moors Environmentally Sensitive Area (ESA) covers some 45% of the area.

The UK government's ESA scheme provides financial incentives for farmers to undertake management which is compatible with the conservation of landscapes and wildlife species.  Voluntary ESA agreements leading to Raised Water Level Areas (RWLAs), covering over 1200 ha, have demonstrated that carefully located higher water tables can lead to significant wetland conservation successes.  However, in spite of the RWLAs, much of the Somerset Levels and Moors no longer functions as a wetland.  The Royal Society for the Protection of Birds (RSPB) attribute the decline in numbers of breeding wader birds to low water levels in spring and early summer and a lack of winter flooding   Other changes include eutrophication of drainage

water, peat oxidation and shrinkage and other changes in soil chemistry and structure.

There is now an urgent need to restore higher water tables throughout a much wider area of the Levels and Moors. Various government and non-government organizations have agreed on a commitment to raise water levels in a number of target Sites of Special Scientific Interest (SSSIs). When a sufficient number of farmers or landowners in each SSSI agree to form a wetland block, under the ESA scheme, then the above-mentioned organizations will design a suitable scheme in which specific summer and winter water-table levels are controlled by ditch management. However, some areas will be excluded as not all farmers or landowners are prepared to enter this voluntary scheme. Furthermore, none of the existing drainage infra-structure is being dismantled; indeed, it is being improved in many areas to provide more productive agricultural land. The emerging consequence of this conflict of interests is a complex patchwork of rehydrated, drained and degraded peat throughout the Somerset Levels and Moors.

The patchwork of rehydrated and drained peat throughout the area poses a serious potential threat to water quality and major difficulties in locating the source. In both drained (agricultural) and conserved areas, pump drainage systems impose a drawdown on the peat water tables towards the field ditches. On intensively farmed land, the continuous drawdown poses a threat to both peat conservation and water quality in the ditches. In the designated wetland blocks, controlled pumping results in rapid changes in the ditch water level which produce corresponding fluctuations in the peat water table. This in turn leads to switches from aerated to waterlogged conditions in the peat. In such an environment, the potential for P mobilisation may be increased. Hence, it is suspected that continuous drawdown through peat is not the only potential contributor to P losses to the ditches, but that the water table-controlled areas may also be responsible.

### Selection of experimental sites

The experimental site is the Catcott Lows Reserve (52 ha) which is part of the Catcott, Edington and Chilten Moors SSSI. The Reserve is approximately 10 km NW of Glastonbury (see Figure 2.2), covers 52 ha and consists of five low lying fields (compartments) on badly disrupted fen peat (Altcar 1 Series). In 1990, after acquisition by the Somerset Wildlife Trust (SWT), the fields were converted from intensive arable production to a wetland nature reserve. Deep drainage and cultivation before SWT acquisition, coupled with fertiliser application, led to surface peat drying out, decomposing and the land level

falling. There were high levels of phosphate in the soil and there was a proposal to reduce it by the addition of nitrogen and potassium, sowing high cropping rye grass and repeatedly cropping for silage. Unfortunately, this scheme was not seen through to completion.

### Previous research

The vast majority of previous research in the Catcott Lows has been driven by the area's status as part of an ESA and SSSI which is a proposed SPA/Ramsar site. Consequently, since SWT acquisition, continuous records have been reported of the area's hydrology and biodiversity. More recently, SWT have conducted soil analyses across the Lows in an investigation of the reasons for the localised dominance of Soft Rush *(Juncus effusus).* This research has indicated that the available P content (as Olsen P) in the compartments is very variable (ranging from 5 to 55 mg kg$^{-1}$ soil).

### Equipment and measuring programme)

The experimental site will be equipped with an automated field research station and devices for ground water observation and soil solution sampling (see 2.3). The exact measurement and sampling depth was chosen depending on the peat profile and depth of the groundwater table. Continuous data collection from the automated field station was coupled with regular and spatially intensive soil and water sampling in the compartments and network of ditches.

## 2.2.2 The Kristianstads Vatterike Wetlands (Sweden)

### Geographical and geological setting

The land landscape surrounding the town of Kristianstad is $\leq 10$ m above sea level. Kristianstads Vattenrike (KV) wetlands (water kingdom Kristianstad) is shown in Figure 2.3. It covers 6000 ha spread over elevations of 0-100 m above sea level. Land in the county and, indeed, land in the whole of Sweden is still rising above sea level.

**Figure 2.3** Map of the rich wetlands of Kristianstad

Kristianstad Basin is standing on rockbeds deposited by the retreating Cretaceous Sea. The upper layers of the Cretaceous rocks are mainly composed of skeletal grain- and pack-stones of marine origin from the Early Campanian Age. An approximately 20 m thick sequence of strata is exposed in quarries. The distribution of the sedimentary Cretaceous rocks in the Kristianstad area is dominated by conglomerates of the Early and Late Campanian Ages and their debris, conglomerates of the Santonian Age and

crystalline rocks, boulders and remnant of encrusting epifauna of near-shore origin (ERLSTRÖM & GABRIELSON, 1992).

## *Hydrological and meteorological characteristics*

The wetlands are a net of water systems and wetlands along the lower part of the River Helge stretching 35 km from Torsebro up to the Baltic Sea Coast, Hanöbutiken. The water system includes rivers Helge, Vrams, Mjö and Vinnö and their tributaries and lakes, chief of which are Araslöv, Hammar and Yng. The Ramsar Convention on Wetlands has classified KV as Wetlands of International Importance. Within KV lie the largest reserves of groundwater system in the whole northern Europe (CRONERT, 1991; CRONERT & MAGNUSSON, 1996). Average variation of surface water level is about 1.4 m throughout the year (+1.3 m to –0.1 m over sea level; CRONERT, 1991). As a consequence of that wide amplitude, the low land along the riverbanks and some of the lakeshore are regularly flooded.

About 7000 years ago, water level of the seas rapidly started rising during melting of the Ice Age ices. In less than 1000 years the water level rose by 15 m (MAGNUSSON & VÄGREN, 1994). The sea was 1 m higher than the present Baltic Sea level, stretching 35 km up to Torsebro. Nearly all Kristianstad County was flooded. It was during that period that peat formation started. When the sea retreated, lakes and wetland emerged and considerable amounts of salts were deposited in the landscape. Drainage of the wetland for cultivation started in the 1700s and continued up to the early 1900s (MAGNUSSON, 1981). Dikes and canals were constructed, which modified the hydrology in the landscape. The landscape became drier, some lakes disappeared or even new wetlands developed where lakes had existed. In the 1900s, dams were constructed for the generation of hydro-based electricity. This created artificial lakes. Of the total area occupied by soils in Kristianstad County, 55 % sand, 25 % moraine clay (boulder clay), 10 % carbonate-rich moraine clay, and 10 % peat soils. All these soils developed from the Cretaceous sedimentary rocks. When not covered by vegetation, the sandy soils are prone to wind erosion. Wind erosion is common in Kristianstad County.

## *Land use and associated conflicts and concern*

Nearly 30% of total land in Kristianstad County (6089 km$^2$) is agricultural land. The River Helge basin is one of the most important lands for agriculture and animal husbandry in Skåne Province. About 1400 ha of the total area of KV wetlands is meadow. Of the area, 900 ha is pasture, 400 ha is mowed for hay and about 70 ha is also mowed but the grass cuts are not removed.

Permanent marsh-grasses and forest cover considerable area of KV territory. There are three categories of meadow determined by their importance: Class I meadow is given high priority and it is, hence preserved. It accommodates rare plant species and it is a roosting place for many birds. Class II is pasture in which new innovations are carried out. Class III meadow is neglected meadow. Similarly, forests are also grouped in three classes. The Class I is forest of high value, accommodating rare plant species. These forests are protected against any activities. Class II forest is also important, with management measures carried out. The Class III forest is not protected and is used by forest industry. Most of the forest, which grows in the KV territory, is a few decades old.

The major conflicts related to land use in Kristianstad Country concern extension programmes carried out on or near the KV wetland's territory. Creation of new recreational places impact negatively on biodiversity, particularly the rare plant species and roosting places for birds. Motorboats used for fishing also disturb bird population in their roosting places. Agricultural practices carried out in the landscape surrounding the KV territory cause some environmental concerns. Wind erosion is a major problem and the eroded soil is deposited into the surrounding landscape including surface waters and wetland, which must be protected against pollution. Those conflicts have significant political dimensions in the county as well as in the whole nation.

### *Selection of the experimental site*

The field station was installed about 10 km southwest of Kristianstad Town. It lies 20 m from River Vinnö's bank. The site being investigated is 1000 $m^2$, covered by marsh-grasses. The landscape is flat and no risks of runoff and soil erosion. The soil is classified by the FAO/UNESCO systems as Dystric Histosols or/and includes Eutric Histosols (TROEDSSON & WIBERG, 1986). A farmer privately owns the land. There are four types of land use in the surrounding landscape (about 1 $km^2$): 1) pastures (east); 2) ungrazed marsh-grasses harvested for hay (north); 3) permanent undisturbed marsh-grasses (west); 4) cultivated land with a patch of spruce trees (west). All are on the same side of River Vinnö. The Station is located in the land use 2 above. The wetland (1-3) is flooded during winters and early springs. In summers, groundwater level is about 1-2 m deep. The station was installed in May 2000.

### *Previous research*

Majority of soils in Kristianstad County possess low intrinsic fertility. In virgin soils, ammonium-lactate extractable (P-AL) contents are between 10 and 40 mg kg$^{-1}$ soil, the contents regarded is being inadequate for optimum growth of crops. Consequently, large amounts of P-fertilizer were applied from 1950s up 1970s. On average P recommendation was 30 kg ha$^{-1}$ yr$^{-1}$ or even more P was applied in some cases. In the middle of 1980s the high P rates were no longer cost effective. This lead to accumulation in soils of large amounts of P. Today, majority of the intensively cultivated soils contains 80-160 mg P-AL kg$^{-1}$ soil, or even more. Hence, P rates were drastically reduced to less than 10 kg ha$^{-1}$ yr$^{-1}$. About the same time, considerable agricultural reforms were introduced in Sweden. The reforms involved reduction of the acreage of cultivated land, pastures and animal density per unit area. The reforms were supposed to decrease over production and abate environmental contamination. Complying with the reforms, farmers set aside part of the cultivated land and pastures, a measure which is still going on.

Today, about 20 years ago since the reforms were introduced and fertilizer P rates were reduced, P concentrations in the groundwater and surface water are still rather high. P concentration is elevated even in the groundwater below uncultivated wet peatland, which is not impacted by adjoining cultivated land (MICHAEL DAHLMAN, 2000; personal communication). Annual discharge of P into the Baltic Sea coast in 1990 was about 8-fold higher than that e recorded in the early 1900s. P originates primarily from fertilizers, manure and sewage water. Today, about 20 % of P discharged into Kristianstad's watercourses is from sewage water. The remaining P comes from diffuse sources (agricultural land, forestland, and wetland). Of total P input, agricultural P accounts for about 52 %, deposition 16 %, forest 12 %, municipal treated sewage water 10 % and private sewage systems 9 %. Enrichment of watercourses with P is classified as low, medium, high, very high and extremely high when the concentrations (mg total P l$^{-1}$) are ≤15, 15-25, 25-50, 50-100 and >100, respectively. The values used in the classification are higher than the averages for the whole Sweden. Watercourses in Skåne Province are generally rich in nutrients compared with the other Provinces of Sweden. In Kristianstad County, majority of the KV watercourses fall into the 2$^{nd}$ - 4$^{th}$ categories of P enrichment. Tributaries of the rivers Vrams and Vinnö are in the category of extremely high P enrichment.

## Equipment and measuring programme

The experimental site was equipped with an automated field station as described in section 2.2.6. In autumn 2002, the station was severely damaged by floods, as a consequence of which it was closed and the equipment was transferred to Ljubljana where two stations were installed.


### 2.2.3 The Trebel Valley (Germany)

## Geographical and geological setting

The Trebel Valley is situated in the Northeast of Germany closely to the Baltic Sea in the state of Mecklenburg-West Pomerania. It is a river marginal wetland which occupies an area of approximately 186 km². In 1994 a region of about 3,000 ha has been evaluated by the government for re-wetting activities (Figure 2.4). Towns and villages are exclusively situated on the periphery of the fenland and the density of the settlement is on average low.

## Hydrological and meteorological characteristics

The Trebel Valley was formed during the Weichselian glacial stadium by erosion induced by the melting of the ice and the enormous water masses. So the glacial valley became extended up to a maximum of about 2 kilometres. The fenbuilding processes were initialised 8,000 years ago, when the water table was stabilised at a shallow level and the climate became warm and humid. The luxuriant growth of the vegetation and the permanent water charging from the slopes promoted peat formation.

The long-term annual mean of air temperature is 7.9°C, with January as coldest (-0.6°C) and July (16.7°C) as warmest month. The mean annual rainfall is about 588 mm, with a maximum in July (69,0 mm) and a minimum in February (29.2 mm). The evapotranspiration is 545 mm. The sun-shine-rate is about 1723 hours per year. The mean wind velocity is around 45 m s$^{-1}$. The fen areas around Langsdorf are strongly charged by groundwater. The groundwater flow is in upward direction (5.1 mm d$^{-1}$).

The thickness of the peat layer is generally more than 5 m and reaches up to 7 m. The peat soils in the Trebel Valley are predominantly classified as Fibric Histosols (FAO 1990). They are eutrophic and mostly characterised by a neutral pH. The largest losses of peat occurred between 1968 and 1996 and were 0.8 m (about 0.3 cm yr$^{-1}$). The mean elevation of the middle of the Trebel Valley is around 0.5 m above sea level.

Figure 2.4  Map of the Trebel Valley

## Land use and associated conflicts and concerns

Before the first settlement took place, the valley was mainly covered by wood. Swedish matricle maps from 1786 and 1788, respectively, show only small areas at the banks for hay production. From the beginning of the 19th century until the second half there was no agricultural activity, but after this time it began to flourish. On Prussian maps, made at the end of the 19th century, there is no wood anymore and the landscape was characterised by agriculture, and at many places shallow and later industrial peat mining was developed. Peat was excavated until the 1950s. All these forms of land use led to accelerated drainage system and construction of traffic ways. In the years of

1744 and 1800 the Phram-Channel was been built to connect the rivers Recknitz and Trebel. In the Fifties and Sixties of the 20th century the Trebel was straighten in many parts.

In the beginning of the 20th century mineral fertiliser was used to increase yields and feed more livestock from the area. The drainage system was successively improved by extension of the ditches. Until 1968 the area signed green in Figure 2.4 was used for grazing and production of hay and silage. Since 1990 the area is used for extensive pasture. Today the deep peat excavations, covering about 150000 m², are zones for fishing.

At present over 30% of the study area is nature reserve. It is nominated as a region of the Council Directive of 2 April 1979 on the conservation of wild birds (79/409/EEC) and the Directive 92/43/EEC on the conservation of natural habitats and of wild fauna and flora of the European Community.

Conflicts arise from the building of the Baltic-Sea-Highway (A20). Furthermore, the consequences of re-wetting parts of the Trebel Valley for water quality are unknown. In worst case transfer of P, eutrophication and algae blooms at the coastal zones of the Baltic Sea cannot be excluded. In this case socio-economic conflicts (natural conservation *vs.* tourism) may arise.

### *Selection of experimental sites*

Three experimental sites were selected which differ in historical and actual land use, the stage of re-wetting, chemical and physical properties, vegetation and mesoclimatic conditions.

Site Langsdorf:    Strongly degraded sedge and wood peat, extensively used for agriculture

Site Eichenthal I: Slightly degraded sedge and reed peat, natural conditions

Site Eichenthal II: Degraded and compacted sedge peat, extensively used for agriculture

At the two sites in the Eichenthal area only soil and water sampling was carried out to enable a comparison with the instrumented site Langsdorf. These three sites are representative of the Trebel Valley.

### *Previous research*

The LIFE project 1999-2003, mainly targeting on biodiversity, includes a monitoring programme total and molybdate reactive P concentrations in surface and groundwater. There is a lot of cartographic material but only one is linked with information about soil P. The evaluation of the site for the field

measuring station has mostly practical reasons. The location of the selected site is situated in the near of the meteorological station of Tribsees. A first investigation at PROWATER start has indicated that the contents of available P (ammonium-acetate-lactate extractable = AL-P) varied according to land use and peat degradation. They ranged from 20 mg kg$^{-1}$ soil at the natural site (Eichenthal I) to 68 mg kg$^{-1}$ soil at the strongly degraded site (Langsdorf). Total P concentrations in the surface water of the ditches and the river Trebel were between 0.12 and 1.47 mg l$^{-1}$.

### *Equipment and measurement programme*

The site at Langsdorf has been already equipped with an automated field research station and groundwater dip wells (see 2.3). According to soil stratification the soil sampling was be carried out at 5 different depths (0.00-0.10, 0.10-0.25, 0.25-0.50, 0.50-0.65 and 0.65-0.90 m). Water were taken from soil (suction cups), groundwater (pipe) and surface water.


## 2.2.4 The Droemling Nature Reserve (Germany)

### *Geographical and geological setting*

The Droemling is the largest fen area in Saxony-Anhalt, Germany. The Saalian glaciation pre-formed the landscape of the Droemling. The sand cover of a glacial valley was eroded and extended trenches and hollows were formed. In the Weichselian glaciation the area was also an extended river valley systems. After ice melting 10,000 to 8,000 years ago the glacial forms were filled with water. Loamy, clayey and organic sediment was deposited in the shallow lake. Today, the Droemling is a Holocene lowland landscape with a size of ca. 320 km$^2$ situated in North-east Germany (Figure 2.5). Settlements are generally situated in outlying area of the fen on higher ground (relicts of ice-age sand horst's).

**Figure 2.5** Map of Droemling Nature Reserve in Saxony-Anhalt, Germany

*Hydrological and meteorological characteristics*

The mean annual rainfall is about 600 mm. The estimated evapotranspiration ranges from 520 mm from the surrounding higher situated areas to at least 660 mm in the central parts. Thus, the fen sites of the central Droemling can have a negative water balance, because evaporation can exceed precipitation. The Droemling fens were first drained around 1750 by a system of channels and ditches for cultivation. The drainage system was continuously extended. Up to 1990 huge cultivation projects were carried out, e.g. the Weser-Elbe-waterway and several pumping stations for permanent drainage of the area. Drainage was followed by a permanent increase in land use intensity up to the early 1990s. The consequence of this intensive agricultural use was to reduce the peat thickness from 2–3 m in 1750 to 0.4–0.6 m in 1995 (ALTERMANN & REFIOR, 1997). The soils of the degraded fens contain only relict amounts of peat as a result of 200 years of agricultural use. The soil containing a peat layer are classified as Histosols. They cover about 36% of the Droemling.

Soils at stronger degraded sites surrounding the Histosols are classified as Mollic Gleysols.

### Land use and associated conflicts and concerns

The Droemling is an important agricultural, recreational, and drinking water supply area. Up to the early 1990's the Droemling was intensively farmed. Intensive livestock farming (dairy cattle and beef) with highly fertilized meadows and grassland was characteristic for the central part of the Droemling. The degraded fen sites and the surroundings were intensively tilled and used for arable crops (rye, barley, corn, oil-seed rape) with high fertilizer input.

Land use changes were initiated with the establishment of the nature park in 1990 and a nature reserve area (280 km$^2$). Intensive cultivation was converted into extensive (unimproved) forms of pasture and arable. Land use changes were accompanied by raising ground water tables according to the demands of breeding wader birds and peat conservation. In selected parts of the central Droemling intensively used grassland was converted into natural succession including the re-wetting of the remaining peats.

The German government encourages farmers to manage their fields and meadows according to the requirements of nature conservation. Financial incentives were offered for a land-management compatible with the conservation of landscapes and wildlife species. As a further action, the government of Saxony-Anhalt purchased land in sensitive areas to ensure nature protection. Traditional intensive agriculture was hindered by the measures of re-wetting and nature conservation. Furthermore, farmers were afraid because they expect deteriorating grassland quality as a result of the conservation measures. The re-wetting of selected patches was discussed controversially in the northern part of the Droemling. Some inhabitants used the argument that flooding frequently damages cellars in settlements. However, these effects are insignificant. These are several other reasons for some still existing conflicts between farmers and the nature reserve authority.

The Droemling region is one of the most important water protection areas of Saxony-Anhalt, because about 50% of the amount of water used for artificial groundwater recharge in the "Colbitz" water plant originates from the Droemling. Ground water of this region is cleaned for potable water supply of the Magdeburg urban area with its 400,000 inhabitants. Hence, aspects of surface water quality are of special interest in the Droemling.

Lacking natural precipitation especially during summer poses a potential threat to water quantity and quality. In both drained and re-wetted areas the ground water table decreases and the peat layer becomes aerated. Especially under such changeable conditions (switches from waterlogged to aerated conditions) the potential for P mobilisation may be increased. Negative effects on the surface water quality due to increased concentrations P and dissolved organic matter (DOM) must be expected.

## Selection of experimental sites

In accordance with the Droemling nature park authority, six sites representing the present day patchwork of land use were selected:

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: Change in land use 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: Natural succession of intensively used grassland with a raising groundwater table (organic soil)

Site 6: Alder forest (organic soil) (see Figure 2.5).

The first study was started immediately before initiation of the land use change at site 3 in 1996. Site 5 was left unimproved and re-wetted since 1993. According to the objectives of PROWATER the investigations were focussed on sites 4, 5 and 6 with organic soils. For comparison selected results from sites 1 to 3 will be also included and discussed in the present study.

## Previous research

Relevant investigations started in the early 1990s. They have shown the peat oxidation and other significant changes in soil structure, and the eutrophication of drainage water. It was concluded that there is an urgent need to raise ground water tables for fen conservation. On the other hand, water balance calculations have shown that there is insufficient water for the re-wetting of the whole Droemling fen area. Therefore, the re-wetting of Histosols is realistic only for selected areas with an existing water regulation system (with sluices to hold back drainage water). The effects of changes in land use and an increase in groundwater table on N, P and soil organic matter in soil, soil solution, and

groundwater at six differently used sites were investigated in the first stage of the Droemling project financed by the Ministry for Regional Planning and Environment of Saxony-Anhalt (1995 – 1998). Changes in land use from intensive crop production to unimproved pasture reduced N and P leaching from soil into groundwater. The alder forest results in much higher inorganic N and DOC contents in soil and water than grassland because of more enhanced degradation of the peat layer under this forest. Increasing groundwater tables partly decreased mineral nitrogen content of the topsoil, however peat decomposition continued due to deep water tables in summer. These deep summer water tables caused high mineralization peaks followed by temporarily high nitrate contents in groundwater at sites with an existing peat layer. Higher water tables increased P and C contents in the groundwater due to a decreased redox potential, which increased P solubility, and intensified leaching of DOM from the peat. Probably, varying moisture conditions (low water tables in summer and higher ones in winter), especially pronounced at the alder forest site, were additional reasons for high P and DOC concentrations in seepage and groundwater.

*Equipment and measuring programme*

The sites were equipped with automated field research station and dip wells (see 2.3).

### 2.2.5 The Biebrza River Valley Basin (Poland)

*Geographical and geological setting*

The Biebrza Wetlands lie in the Northeast of Poland in an extensive ice-marginal basin, the Valley of the Biebrza River, some 195,000 ha in area (Figure 2.6). The Biebrza Valley area has a low population, lack of industry and extensive agriculture. As a consequence, these areas remained in the natural state, constituting the greatest swampy complex in the Central Europe. The wetlands occupy an area of 116,000 ha, some 60 % of the total area. The Biebrza features several types of mire. The dominant type is fen, which accounts for some 76 % of the wetland area. The waterlogged organic-mineral areas occupy 19 % and organic marshes 4 %; remaining wetlands are alluvial mineral marshes. The geological structure of the area is poorly understood. Some isolated bore-holes show mainly tertiary rocks between 80 to 100 m thick. The first water layer is built from sand with an infiltration coefficient from 1 to 20 m d$^{-1}$. Its thickness is 15 to 25 m.

### *Hydrological and meteorological characteristics*

The Histosols were formed as a result of inflow of ground- and surface water into the valley. The Biebrza peat soils are rheophilous, and do not depend directly on water from precipitation. They are fed from underground water from the adjacent uplands. Insignificant diagonal slopes cause the inflowing waters to accumulate in the depressions, creating vast wetlands. The peats in the Biebrza Valley are used in different ways. About 592 km$^2$ are now designed as the Biebrza National Park plus 668 km$^2$ of protective buffer zone around the park. A significant part of this territory was drained during the last hundred years and was used as agricultural land, almost as permanent grassland.

**Figure 2.6** Map of the Biebrza Valley

The Biebrza Valley may be distinguished into three parts:

The Upper Basin with moraine cutting through the valley floor; the dominant input of water is soligenous, associated with an intensive inflow of groundwater.

The Middle Basin, the largest of the three, is a sand-filled depression fed by ground and surface waters. The southern parts are drained by the channel of the Biebrza River.

The Lower Basin is hydrologically fed by the inflow of water from the Biebrza River, frequently resulting in surface flooding. Inflow is also influenced by groundwater input from the surrounding moraine upland.

Some hydro-technical works have been done within whole valley. Their aim was to drain the peat and enable agricultural use. The Middle Basin was most strongly drained. First drainage works were done in the middle of 19th century through building a set of drainage channels. Between 1955 and 1965 a network of channels have been constructed with distances between 100 to 300 m. The drainage of the Lower Basin was negligible. Irregular channels were built at the beginning of the 20th century to accelerate the runoff of snow-melt waters.

### Land use and associated conflicts and concerns

The farming was mostly extensive and run by families. From the 1960´s to 1990 farm were also run intensively as state-owned farms. The recession in Polish agriculture after political changes in 1989 resulted in the abandonment of the big state-owned farms with a decrease in the production in family farms. The recession in agriculture was accompanied by a lack of conservation programmes in drainage and irrigation systems. This had led to changes in groundwater levels, causing an over-drying of same parts of peat soils and the flooding of other parts.

### Selection of study sites

The study areas were located on the border between the Middle and Lower Basins. They enclose two sites Kuwasy and Bagno Lawki (Lawki Bog). **Kuwasy** comprises 6,000 ha. About 1,000 ha is a farm of Peat Experimental Station of Institute of Land Reclamation and Grassland Farming at Falenty. The site was drained in 1933-39, 1952-58 and finally in 1961-1965. The soils are mainly moorsh-peat soil (80 %) at a moderate stage and the remaining at a profound stage of moorshification. They are established mainly from moderate and high-decomposed alder swamp and reed swamp peats that are 1.5 to 7 m thick. Most soils have a mineral matter content below 25%. Soil pH ranges of 4.8 to 7.3.

In the Experimental Station is an active meteorological station of the national observation net. The mean precipitation during the vegetation period is 337 mm, and mean temperature is 13.2°C. On average the last day with

frost is May 27th, and the first frost is September 24th. A drainage and irrigation system was built on all areas of the station. At present, the water table is controlled at the highest level possible for permanent grassland, in an attempt to prevent the mineralization of peat organic matter. Since 1960´s, intensive grassland farming was adopted with P fertilizer rates of approximately 50 P kg ha$^{-1}$ yr$^{-1}$. The P rates were lowered during the last ten years. The main products are milk and hay.

Eight water-sampling points have been active since 1997. Theses points cover five parts of study area:

1. Temporary flooded with the possibility to maintain high groundwater level during vegetation season (moved meadows and pastures).

2. Long term waterlogged with possibility of feeding with irrigation water (moved meadow, possible pastures).

3. Short term waterlogged with possibility of feeding with irrigation water (moved meadow, possible pastures).

4. Short term waterlogged with no possibility of feeding with irrigation water.

5. Short term waterlogged during spring with no possibility of feeding with irrigation water (degraded moved meadow - 1-2 cuts).

**Bagno Lawki** is located within the National Park Biebrza. Up to the 1960´s, it was used by peasants as extensive, low productive meadows. Now, farming is abandoned, resulting in the development of bush and overgrown scrub over the channels. Mainly, shallow fen peat (reed swamp, tall sedge swamp, alder swamp) prevail with thickness between 0.5 and 1 m. A large part of area is flooded for 2 to 6 weeks during spring time.

Water was sampled at several points since 1997. They are located in two catenas "Grobla Honczarowska" and "Gugny.

*Previous research*

**Kuwasy,** particularly the area of Experimental Station, has been under investigations during last 50 years. There exist abundant data on changes in hydrology and associated mineralization of peat organic matter. The first investigations of available P content in soils were made in the early 1960´s, before the P fertilization on these areas was started. Therefore, the obtained data are related rather to the natural content of available P according to the Polish P-test for organic soils and to agriculturally changed fertility.

At **Bagno Lawki** another team from the Institute for Land Reclamation and Grassland Farming is investigating the water management at the site.

*Equipment and measuring program*

The Kuwasy site has been equipped with an automated field research station and devices for groundwater observation and soil solution sampling according to the description in section 2.3.

## 2.2.6 Ljubljana Marsh (Slovenia)

*Geographical and geological setting*

The Ljubljana Marsh is the most southern fen peatland in Europe covering roughly 16,000 ha (Figure 7). Today's floodplain has developed in a glacial basin of tectonic origin which was gradually filled with river sediments until the late Pleistocene. From the late Pleistocene to the Neolithic period the area was covered by a lake varying in size and depth due to fluctuations in water level. Organogenic sedimentation with peat formation began about 6000 years ago on the bottom sediment of the lake chalky clay, white in colour and rich in molusc shells, hence the name "snail marl". Today, only a few fragments of raised bogs with *Sphagnum* peat are left (Figure 2.7), whereas the rest of the Ljubljana Marsh is represented by fens with sedge peat of depth anywhere from a few cm to about 3 m. Differences in peat depth are the result of massive peat excavation, mainly for burning, throughout the 19th and the first half of the 20th century. In some areas with most extensive excavation, peat is completely degraded and the white "snail marl" is on the surface. The extent of peat excavation is also reflected in present elevational differences: from 287.5 m a.s.l. in areas with no peat left to about 292 m in isolated areas with raised bog fragments.

**Figure 2.7** Map of the Ljubljana Marsh

### Hydrological and meteorological characteristics

The majority of the ground water to the floodplain is supplied by the sometimes torrent water flows from surrounding mountainous chains (made of limestone or dolomite, altitude 400 to 1000 m) which all discharge their waters into the river Ljubljanica. Ljubljanica is a karstic river flowing through several underground passages before crossing the Ljubljana Marsh from West to East. Therefore, some of the molusc shells may originate from river sediments. Natural development of the peatland was drastically changed in 1782 when the "Gruber channel" was constructed in order to divert excess water from Ljubljanica river to protect the city of Ljubljana from regular flooding and erosion. Around 1825 systemic drainage works began with the network of open ditches (20 – 30 m apart) which has been maintained until the present time. Most of the ditches serve to drain meteorological waters and some to drain water from typical artesian wells, collectively called "Marsh windows". Today water levels are controlled locally by the depth of the ditches and generally by the flow control weirs on the river Ljubljanica and the Gruber channel. Despite the extensive drainage system, regular seasonal flooding occurs in the autumn/spring period when the river bed of Ljubljanica is overfilled with water at heavy rains. The difference elevation between the extreme west and east end of the Ljubljanica river bed (from Vrhnika to Ljubljana, Figure 2.7) is only 1 m. Therefore, the excess meteorological water

gradually spills over the lowest areas of the Ljubljana Marsh, thus creating a temporary lake, which may persist for about two weeks. On the other hand, drought periods in summer are common and the water table may drop to about 1,5 m below the surface. The minimum level of water table is imposed by the weir on the Ljubljanica river, which is, at its present construction, set to maintain the minimum water level in the river 285.6 m a.s.l., when the flow control barrier is completely closed and the water flows over the top panel. The climatic parameters for the Ljubljana Marsh (mean annual temperature 10°C, rainfall 1400 mm year$^{-1}$), are significantly different from those in other PROWATER study areas.

### *Land use and associated conflicts and concerns*

Since the establishment of the drainage system, the landscape of the Ljubljana Marsh has been shaped by peat excavation and agriculture. Apart from swampy forest and raised bog fragments, of which only two are legally protected at present, fens/grasslands cover 65% and cornfields 25% of the area. The fens of the Ljubljana Marsh can be divided into six grassland categories (SELIŠKAR 1986, HACIN ET AL. 2000), according to the prevailing botanical associations: 1. Phragmition, 2. Magnocaricion, 3. Caricion davallianae, 4. Molinion, 5. Filipendulion, and 6. Arrhenatherion. Larger complexes of the last category together represent over 50 % of all grasslands (approximately 11,000 ha), whereas other categories range from 0.5 to 20 ha in size and are scattered among the prevailing Arrhenatherion complexes. Molinion and Arrhenatherion associations are still regularly mowed with 2 to 3 cuts per year, and the hay used as feed for cattle and horses. Magnocaricion and Caricion davallianae associations are mowed irregularly – once a year or every second year; and the hay used for bedding. Filipendulion association develops on abandoned grassland and field plots and represents the first step towards shrub and tree encroachment. Tree encroachment on agricultural land is a problem associated with aging rural population throughout Slovenia.

Grassland categories 1-4 represent wetland habitats of EU community interest, as specified in the Annex 1 to the council directive 92/43/EEC (Official J. of EEC, No. L 206/7/21); whereas the entire area of Ljubljana Marsh encompasses habitats of priority bird species as specified in the Annex 2 of the council directive 79/409/EEC. Therefore, a campaign for the legal and strict protection of the entire area as an Important Bird Area (IBA) has been initiated by the BirdLife Slovenia back in 1997. In 1998 an agreement on cooperation towards the establishment of the regional park "Ljubljana Marsh" was signed between the Ministry of Agriculture, Ministry of Environment,

Municipal community of the city of Ljubljana and five local communities in the area. The entire area is also being proposed as an integral part of the European network of protected areas Natura 2000. However, the law declaring the regional park Ljubljana Marsh awaits.

Except for corn fields scattered among the grasslands, traditional low input management is still the dominant agricultural practice on the fens and thus maintains the great habitat diversity. Regular flooding in spring and autumn helps maintaining nesting bird and native plant populations. whereas summer droughts with water table as low as 1.5-2 m are not detrimental to crop and hay production. Drainage ditches are still maintained and no attempts for re-wetting have been made so far. The upper ground water layer, which is most affected by agricultural and other management practices, is supplying 30 % of all drinking water to the city of Ljubljana and surrounding settlements. Despite the extensive conservational efforts, the urbanisation pressure imposed by the close proximity of the city of Ljubljana, represents the main threat to the landscape and natural features of the Ljubljana Marsh.

*Selection and characterisation of experimental sites*

In the context of preparing background scientific information for the management plan of the future regional park, an area of approximately 1 ha was selected (Figure 2.7), in which a re-wetting field experiment was established in 1999 in order to study the effect of water table level on the productivity of field crops and grassland and on mineralization of peat. In this experiment controlled water table levels are maintained by a weir constructed on the main drainage ditch and monitored by a network of 24 piezometers positioned 25 m apart. Experimental field encompasses large plots with different cropping history: arable (A) as permanent corn field, arable converted to grassland (AG) more than 10 years ago, and permanent grassland (G), - in such a way that plots with the same cropping history could be subjected to high (HW) and low (LW) water table level. The available distribution of plots was the decisive criterion for the selection of the site. By constructing the weir a 20 – 40 cm difference in water table level was established between HW and LW plots.

The site is located on the fen area with peat depth of about 2.5 m, pH 6.5 – 7.0 and P content (CAL-method) of about 5 mg kg$^{-1}$ soil in G plots and about 30 mg kg$^{-1}$ soil in A and AG plots

*Previous research*

Despite an early recognition of the importance of the Ljubljana Marsh (KRAMER, 1905) only few studies were carried out on ecological features of the raised bog fragments (MARTINČIČ, 1987) and fens (SELIŠKAR, 1986). Over the past three years, different management regimes (cutting and fertilizing alternatives, soybean/corn crop rotation vs. corn monoculture under till and no till regime) have been studied on grassland and arable plots (ČOP et al., 2001; HACIN et al., 2000).

Microbiological studies have investigated N and C mineralization in relation to soil organic matter content and water table level in fens (HACIN et al., 2001) as well as N and C mineralization in relation to pH, soil moisture and nutrient content in bogs (ZUPANCIC & MAHNE, 1998).

*Equipment and measuring programme*

Two automated field stations (see 2.3) were installed in the existing field experiment. One on Histosol and one on Humic Gleysol, as two principal soil types on the Ljubljana Marsh. Seasonal variation in soluble P content in soil solution - sampled from ceramic suction cups, ground water, sampled from piezometers and in surface water, sampled from nearby ditches was compared with soil P content on experimental plots.

Continuous data from the two stations of soil moisture and temperature were used to determine experimental variables in short-term incubation studies for rapid assessment of the influence of environmental factors (temperature, soil moisture, pH/redox state) on microbial immobilisation/mobilisation of N and P under extreme temperature and moisture conditions, recorded in the field. The P and N immobilisation by microbial biomass under water stress conditions was assessed by the fumigation extraction method. Microbial biomass and activity under water stress (i.e. flooded/drained conditions) was assessed by substrate induced respiration (SIR) measurements. Calculation of nutrient balances and estimates of potential removal and retention of nutrients (N, P) by plant biomass in different cropping systems were based on regular soil and plant sampling.

## 2.2.7 The Hula Valley (Israel)

### *Geographical and geological setting*

The Hula Valley is the northernmost segment of the Jordan-Arava Rift Valley, and it is approximately 70 m a.s.l. The Hula valley is approximately 175 km$^2$ and it is currently drained by a system of artificial canals that empty into the Jordan River at the southern end of the Valley (Figure 8). Following the draining of the old Hula Lake and surrounding swamps in the 1950's, a surface layer of peaty soils, with an average thickness of 4 to 6 m was exposed. After four decades of intensive farming that was coupled with major deterioration of soil quality and significant subsidence of the peat soils, the least fertile plots were reflooded and a shallow lake was created.

The peaty soils of the Hula Valley are predominantly Histosols (~ 1,860 ha) that were classified into four major great groups, three of which appear in the American Soil Taxonomy; 1. Medifibrists, 2. Medihemists, and 3. Medisaprists (modified after the Israel Department of Agriculture, 1986). The role of internal combustion in Histosols pedogenesis was recognised by the Israeli classification system. Hence a great group termed *'Conflagrated Histosols'* was invoked. Using the Israeli soils taxonomy system, each of the above great groups was further divided based on the occurrence and amount of $CaCO_3$ which resulted in Medifibrists, Medihemists, Medisaprists, and 'Conflagrated Histosols' without lime, with minimal lime, and with lime. The occurrence and content of $CaCO_3$ also controlled the pH of the Histosols. Following the drainage of lake Hula and its wetlands some of the Histosols without lime exhibited highly acidic pH (< 4.0). Presently, all the Histosols exhibit pH between 5.0 and 8.0. The high organic matter content of 50-70% observed in 1945 has steadily declined after the reclamation of this area to 30-50 % in 1970 and 25-35 % in 1985. Further decline in organic matter has been currently observed.

**Figure 2.8** Map of the Hula Valley and design of the study area with observation wells and drainage canals.

The most profound transformations of the peat soils of the Hula Valley are the increase in pH, decrease in organic matter content that lead to increase in bulk density which lead to changes in hydraulic conductivity. Major cracks have developed in the Histosols following the drying up of the wetlands. Apparently, a network of macropores regulates the lateral and vertical preferential flow observed in certain areas. This phenomenon was never measured and documented. The preferential flow may have a profound effect on P fate and transport. The artesian flow mechanism that governed groundwater flow in the region was only observed intermittently in few locations. Hence, the large spatial and temporal changes in the physico-

chemical characteristics of these Histosols should be considered in studying phosphorus dynamics in the Hula wetlands.

### Hydrological and meteorological characteristics

A schematic model that describes the geohydrology of the Hula Valley is given in Figure 2.9. In general, most of the groundwater flow occurs along the fault zone in the west and the alluvial deposits in the east. An unknown amount of groundwater percolates through the peat soils of the Hula Valley.



Figure 2.9  A schematic model of the geohydrology of the Hula Valley (adapted after KAFRI & LANG, 1979)

### Land use and associated conflicts and concerns

The drainage of Lake Hula and its surrounding swamps in the 1950's was among the first major agro-engineering operations undertaken by the State of Israel. The elimination of Lake Hula and swamps provided about 6000 ha of organically-rich arable land. Following the drainage, the exposed peat soils rapidly oxidized, eventually leading to land subsidence and increased suspended material, ammonia, sulfate, and nitrate loading into Lake Kinneret through the Jordan River. The increased load of nutrients and suspended matter represented a major environmental hazard to the water quality of Lake Kinneret because 63 % of the annual recharge and 50 % of the nutrient load to the Lake flows through the Hula Basin. During the 1970's, a major restoration project was carried out that created some basic novel watershed management

practices designed to prevent nitrate leakage from the Hula Valley. Subsequent research showed that modifications in farming practices could further reduce nitrate accumulation by using certain perennial forage crops. Unfortunately, the proposed modifications were not economical for some of the area (550 ha) where the annual crop farming practice has had a deleterious effect, causing further soil degradation, erosion, and land subsidence.

The continuous decline in soil quality and fertility of these 550 ha was the main incentive for the launching a major reclamation project in the early 1990's that attempted to slow down some of the negative consequences of the drainage of valley. The project was designed to reduce nutrient flux from the Hula Valley downstream to Lake Kinneret, while creating a lake that could serve as a tourist focal point, thereby providing an alternative economical utilization of the land. The fundamental concept of the Hula Project assumed a hydrological interaction between the surface water and groundwater system and that the soil moisture content can be increased by elevating the water table and changing the irrigation system. To achieve this, a small 100 ha shallow lake, Lake Agmon, was constructed in 1994, covering the least agriculturally productive peat soils and operating as a drainage outlet for the Valley. Water discharge from Lake Agmon is diverted from the Kinneret catchment by a system of settling ponds and a holding reservoir from where water is pumped to the Eastern Galilee for use as secondary irrigation water. In addition to Lake Agmon, 90 km of new drainage canals were excavated for water supply, maintaining a higher water table, and draining excess water. The master plan for this area envisioned that the lake would become the centre of eco-tourism and enable a partial recolonization of the almost extinct wetland fauna and flora. The success of the reclamation effort may even have some global implications, especially for endangered migratory birds, which seek temporary refuge in the Hula Basin. The Hula Project was launched in 1993 before the complete acquisition of data needed for such a grand-scale eco-engineering project. Hence, the planners established a temporary research – monitoring center (1994 – 1997) that would provide all the necessary information for the management of the Hula ecosystem. Between 1993 and 1997 a concentrated research effort was made to study the chemistry, biology, and hydrology of Lake Agmon and its surroundings. In spite of this research effort (concluded in 1998), many questions have yet to be addressed and some new questions and problems have surfaced, especially concerning the hydro-bio-geochemistry of P in these altered wetlands.

### Selection of experimental sites

On the basis of current understanding of the geo-hydrology and the spatial distribution of the various Histosols two sites (10 and 12) were selected (see Figure 9) for the experimental sites and were equipped with automated field stations. The observation wells provided water table depth measurements and solutes (Na, Ca, Mg, Cl, $SO_4$, and P) distribution across the Valley. Nine soil sites across the hydrological gradient from north to south were selected for intensive P analyses (fractionation, speciation, and sorption isotherms). About 250 soil locations across the Hula Valley were sampled for the determination of the degrees of P saturation and modelling its special distribution across the Hula Valley.

### Previous research

There are more than 700 published papers and reports that describe the geology, hydrology, meteorology, agricultural issues, and socio-economical aspects of the Valley. However, there is only one short report (in Hebrew) that deals with P in the Hula Valley. This report strongly recommends various fertilization techniques to increase agricultural yield.

### Equipment and measuring programme

The experimental site was equipped with four automated field research stations and devices for groundwater observation and groundwater sampling. Two of the groundwater stations were also equipped with automated Eh and pH electrodes. Continuous data collection from the automated field stations was coupled with regular and spatially intensive soil and water sampling across the Hula Valley (see Figure 2.9).

## 2.3 Equipment and recording program

### Field equipment

All experimental sites chosen were **equipped with automated field research stations** and **devices** for ground water observation and soil solution **sampling**. Automated field research stations were running or under construction on sites of the Trebel Valley, the Droemling, and the Hula Valley at the beginning of the project. In the Hula Valley a series of automated measurement stations was operated along a hydrological gradient in a field where the water table is controlled by two parallel draining canals in which the water head can be adjusted. This enables the investigation of P mobilisation under controlled ground water levels and the setting of boundary conditions for

modelling. Figure 2.10 shows an example for the principal arrangement of measurement and sampling devices arranged to an automated field research station. The exact measurement and sampling depth can vary according to the Histosol profiles, ground water tables etc.

For matrix potential measurements the stations were equipped with electronic tensiometers at depths of 0.30 m, 0.60 m and 0.90 m. At each of these depths soil solution was collected by suction cups (in three replications) using a vacuum pump to generate approximately -50 kPa. Tensiometer measurements were recorded by a data logger. The vacuum pump was controlled by a clock timer, which enables us to collect samples according to the measuring protocol.

Groundwater table depths were measured in dip wells (gauges for the observation of surface near groundwater). They were drilled until a depths of 2 m below surface.

Soil moisture content was measured continuously by TDR soil moisture probes (IMKO, Ettlingen, Germany) at depths of 0.30 m, 0.60 m and 0.90 m.

Instrumentation was completed by the installation of redox electrodes, as redox potential is one of the key factors which influences P mobilisation. The redox potential was auto gauged by redox electrodes down to a depth of 1 m at steps of 0.1 m. Redox probes used platinum electrodes for measurement (for further details see Schmidt, 1998). The redox voltage was measured between the soil probe and a reference probe (Schott LTD, Mainz, Germany) installed in an adjoining dip well. The data measured in the field were corrected to the standard hydrogen electrode by adding 215 mV (10°C).

Tensiometer, TDR-stick probes, and redox electrodes were connected to a data logger for continuous registration and data storage.

**Figure 2.10** Principal arrangement of automated field research stations

### *Recording programme*

Each group created a **database** on the hydrologic and pedologic (and climatic) factors of P mobilisation. The Lead Contractor aggregated data measured for the whole project.

Periodic measurements of pH, and samplings of soil, soil solution (suction cups), near-surface ground water and adjoining surface water were carried out at each experimental site. The soil profiles were sampled at incremental depths from Histosol profiles down to the mineral layer on shallow and down to 1 m on deep peat. Sampling enabled direct comparison of chemical data to the measured physical and redox properties at the relevant profile depth. Despite some special aspects at each site, a unified protocol for the measurements, sampling, sample storage and pre-treatment for analyses was developed. This enabled (1) quality control, (2) assignment of field data to chemical data, (3) sample exchange for special investigations without loss in quality, relevance, and (4) the development of strictly comparable data sets that allow later statistical determination of *inter-site* differences and provide a sufficient input to modelling.

**Table 2.2** Sampling protocol for the compartments soil, soil solution, ground- and surface water

| Compartment | Measurements | Measuring time period |
|---|---|---|
| Soil | Column (only UoR) / Batch experiments; for each layer (UoR) /mixed sample over the soil profile | Once, at the beginning of the investigations |
| | Soil mosture / temperature / tension / redox | Continuously logged respectively 3 weeks |
| | Total P, sorbed P, soluble P | 3 months |
| | Oxalate and dithionite soluble Al and Fe | 3 months |
| | Fe sorbed / dissolved | 3 months |
| | Fe, Al (total digestion) | Once per year |
| Soil solution | Pt, MRP, DOC, (Al, $Fe^{3+}/Fe^{2+}$) | 3 weeks |
| Groundwater | Groundwater table | At least 3 weeks |
| | Pt, MRP, DOC, (Al, $Fe^{3+}/Fe^{2+}$) | 3 weeks |
| Surface water | Surface water table | At least 3 weeks |
| | Pt, MRP, DOC, $O_2$ (pH, Redox, Temperature) | 3 weeks |

# 3. Results and evaluation of field measurements

During the field research soil physical and chemical data were continuously recorded at the experimental sites, and soil and water samples were taken. The measurement program included soil moisture, temperature and redox potentials at different depth, as well as analyses of soil and water samples. The objectives were to understand the processes of P turnover and to lay the basis for the development of conceptual models and application of numerical modelling of P leaching and transport.

## 3.1 Redox potentials as a function of soil moisture

It was emphasised that the continuous measurement of redox potential is of central importance because redox is the driving force for P mobilisation. The redox potentials (Eh) in the soil were recorded automatically each hour against an Ag/AgCl reference electrode. The values were transformed to the standard hydrogen system according to KöLLING (2000).

Figure 3.1 shows the statistical distribution of the daily means in the upper horizons (10, 20 and 30 cm) at six experimental sites including outliers and extreme values. For all sites the evaluation period ranged from 01/01/2001 to 31/12/2002 except Ljubljana Marsh where the data acquisition started later (16/08/2002 to 23/01/2003). Within the topsoils the medians of redox potentials either significantly decreased with increasing depth (Biebrza Valley, Droemling – Alder forest, Ljubljana Marsh) or they were similar. Highest variations, expressed by the range (Min and Max) and percentiles (25 % and 75 %), were observed at sites with generally low groundwater level or conspicuous fluctuations of the water table (Biebrza Valley: 10 cm, Ljubljana Marsh: 10 and 20 cm, Droemling – Alder forest: 10 and 20 cm). Larger values and higher fluctuations confirmed the visual observations of greater aeration and peat decomposition. The effect of re-wetting was particular obvious for the Droemling sites. The Natural Succession was actively re-wetted for about 10 years, and the Alder forest was not re-wetted and aeration was relatively intensive because of a nearby big channel (see point 6 in Figure 2.5). The box plots clearly indicate that the re-wetting resulted in relatively stable low redox potentials.

**Figure 3.1** Box plot of the redox potentials in the P enriched layers of the soil profiles at the experimental sites in Europe (1-year-period of data collection, depths of redox measurements in cm)

The redox potentials measured in natural environments like soils is of **qualitative significance** because of the performance of the Pt electrode and the thermodynamic behaviour of the environment (WHITFIELD, 1969; MANSFELDT, 2003). Therefore, MANSFELDT (2003) proposed an interpretation of the numeric values on the basis of their aggregation and use of redox classes (PATRICK & MAHAPATRA, 1969; BRÜMMER, 1974; ZHI-GUANG, 1985). The redox status in soils is classified in (I) oxidising (> 400 mV, $O_2$ predominant), (II) weakly reducing (400 to 200 mV, nitrate and Mn(III,IV) reduced), (III)

moderately reducing (200 to –100 mV, Fe(III) reduced) and (IV) strongly reducing (< -100 mV, sulfate and carbon dioxide reduced). Based on this classification the bulk of the redox measurements revealed moderately reducing conditions in the investigated peat soils.

Single measurements of Eh without replicates are restricted in their potential to indicate chemical processes in soils (FIEDLER, 1997; STOLT et al., 2000; MANSFELDT, 2003), because the Pt electrodes represent redox potentials at a small scale and spatial variability is not adequately recorded. Therefore the electrodes in the present investigation were installed in small, equidistant increments of 10 cm. It has been assumed, that adjacent electrodes will provide similar Eh values. The statistical significance of the neighbourhood relationship can be proofed by Spearman´s rank correlation calculations. This is a suitable procedure, because there is no need of a normal data distribution, but is necessary to calculate with independent values, that means auto-correlation within the time series have to be eliminated by using adequate time lags.

Table 3.1 shows the rank correlation matrices for three experimental sites (Trebel Valley - Langsdorf, Droemling – Natural succession, Alder forest). Independent redox values were achieved operating with time lags from 2 (Trebel Valley - Langsdorf) to 4 (Droemling – Alder forest) days. There are significant correlations (P < 0.05) between nearly all electrodes at the three sites. The  aggregation of the redox values using rank correlation enabled identification of measurement replications of the electrodes. Additionally specific limits for the correlation coefficients were introduced for a more clearly distinction (Trebel Valley and Droemling - Alder forest:  r > 0.7; Droemling – Natural succession: r > 0.9).  With only a few exceptions these criterions led to restrictive results.

Some of the changes in redox potentials can be explained by soil moisture regime as recorded by water tension. Hence all field data (here for example of the first year) were correlated with each other, resulting in correlation matrices for each site. These correlation matrices were used to check the plausibility of the data sets and to find out general errors or problems in probe calibration, signal transmission etc. Therefore, the correlation matrices were important for quality control of data sets. Furthermore, they indicated significant and causal relationships between (1) same parameters determined at adjacent depth of soil profiles (e.g. Eh at 7 and 8 dm) and (2) different parameters indicating soil processes (soil moisture and Eh at 3 dm depth of soil profiles).

Table 3.1 Spearman rank correlation coefficients for measured redox potentials within the profile (depths in cm) at the experimental sites Langsdorf (Trebel Valley), Alder forest and Natural succession (Droemling)

| Langsdorf [1] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 |
| 10 | **0.716** | **0.803** | 0.355 | 0.585 | 0.573 | 0.415 | 0.447 | 0.581 | 0.531 |
| 20 | - | **0.782** | 0.603 | 0.429 | 0.622 | 0.474 | 0.586 | 0.668 | 0.633 |
| 30 | | - | 0.491 | 0.612 | 0.692 | 0.504 | 0.649 | 0.677 | 0.651 |
| 40 | | | - | 0.438 | **0.744** | 0.565 | **0.783** | **0.727** | **0.744** |
| 50 | | | | - | 0.664 | 0.470 | 0.599 | 0.604 | 0.500 |
| 60 | | | | | - | **0.776** | **0.925** | **0.856** | **0.861** |
| 70 | | | | | | - | **0.761** | 0.592 | **0.703** |
| 80 | | | | | | | - | **0.803** | **0.831** |
| 90 | | | | | | | | - | **0.867** |

| Alder forest [2] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 |
| 10 | **0.741** | 0.621 | **0.764** | 0.626 | **0.749** | 0.612 | -0.061* | -0.250 | 0.468 |
| 20 | - | **0.831** | 0.693 | 0.378 | 0.682 | 0.431 | -0.219* | -0.351 | 0.490 |
| 30 | | - | 0.696 | 0.468 | 0.631 | 0.432 | -0.069* | -0.105* | 0.588 |
| 40 | | | - | **0.758** | **0.901** | **0.704** | -0.260 | -0.294 | 0.576 |
| 50 | | | | - | 0.675 | **0.701** | -0.200* | -0.067* | 0.359 |
| 60 | | | | | - | **0.775** | -0.211* | -0.408 | 0.475 |
| 70 | | | | | | - | -0.096* | -0.149* | 0.204* |
| 80 | | | | | | | - | 0.666 | -0.286 |
| 90 | | | | | | | | - | -0.437 |

| Natural succession [3] | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | 20 | 30 | 40 | 50 | 60 | 70 | 80 | 90 | 100 |
| 10 | **0.930** | **0.975** | 0.766 | 0.757 | 0.813 | 0.825 | 0.771 | 0.775 | 0.558 |
| 20 | - | **0.965** | 0.880 | 0.881 | 0.873 | **0.905** | 0.878 | 0.873 | 0.405 |
| 30 | | - | 0.828 | 0.827 | 0.868 | 0.884 | 0.841 | 0.839 | 0.478 |
| 40 | | | - | **0.992** | **0.957** | **0.964** | **0.986** | **0.968** | 0.326 |
| 50 | | | | - | **0.946** | **0.961** | **0.981** | **0.963** | 0.297 |
| 60 | | | | | - | **0.954** | **0.958** | **0.953** | 0.426 |
| 70 | | | | | | - | **0.961** | **0.954** | 0.427 |
| 80 | | | | | | | - | **0.974** | 0.353 |
| 90 | | | | | | | | - | 0.353 |

[1] Daily mean values with a time-lag of 2 days (n = 307); all correlations are significant at a level of P < 0.01; bold values r > 0.7

[2] Daily mean values with a time-lag of 4 days (n = 158); correlations are significant at a level of P < 0.01 except values with *; bold values r > 0.7

The "aggregated" electrodes, combined by this procedure, can be assigned to peat layers with different chemical and hydrological behaviour. The first group in the upper horizon represents electrodes installed in the degraded and P-enriched peat with ground water fluctuation. The second group of electrodes was installed in the permanently water saturated peat layers, low in P contents. The redox electrodes in the deeper profile at the Droemling sites (Alder forest: 80 to 100 cm; Natural succession: 100 cm) were placed in the peat underlying mineral soil (sand), where oxygen was continuously supplied by the groundwater. These redox potentials were noticeable higher and hence different from those in the peat layers.

Table 3.2 shows how the data recorded at the field stations in five experimental sites were correlated with each other. For instance, number "5" (upper left) means that in all 5 experimental sites the soil moisture contents at 3 dm were significantly correlated with the soil moisture contents at 6 dm profile depth.

Table 3.2 Correlation matrix of data sets from field stations combined for 5 experimental sites at depth of soil profiles of 3, 6 and 9 dm [in italics]. Numbers indicate the frequency of highly significant ($P < 0.001$) correlations (e.g. 5 = highly significant at all sites)

| | | Moisture [θ,Ψ] | | Redox | | | | | | | | | | Temperature | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | *6* | *9* | *1* | *2* | *3* | *4* | *5* | *6* | *7* | *8* | *9* | *10* | *3* | *6* | *9* |
| Moisture | *3* | 5 | 4 | 4 | 3 | 4 | 3 | 3 | 4 | 4 | 3 | 3 | 3 | 4 | 4 | 4 |
| | *6* | | 4 | 4 | 3 | 4 | 2 | 3 | 4 | 4 | 2 | 3 | 3 | 4 | 4 | 4 |
| | *9* | | | 4 | 3 | 4 | 2 | 4 | 4 | 4 | 4 | 3 | 3 | 4 | 4 | 4 |
| Redox | *1* | | | | 3 | 5 | 3 | 5 | 5 | 5 | 4 | 4 | 5 | 4 | 4 | 4 |
| | *2* | | | | | 3 | 5 | 4 | 3 | 3 | 4 | 4 | 3 | 3 | 3 | 3 |
| | *3* | | | | | | 4 | 5 | 5 | 5 | 4 | 4 | 5 | 4 | 4 | 4 |
| | *4* | | | | | | | 5 | 5 | 5 | 3 | 4 | 4 | 3 | 3 | 3 |
| | *5* | | | | | | | | 5 | 4 | 3 | 5 | 3 | 3 | 3 | 3 |
| | *6* | | | | | | | | | 5 | 3 | 3 | 4 | 4 | 4 | 4 |
| | *7* | | | | | | | | | | 3 | 4 | 4 | 5 | 5 | 5 |
| | *8* | | | | | | | | | | | 4 | 4 | 2 | 2 | 2 |
| | *9* | | | | | | | | | | | | 5 | 3 | 4 | 4 |
| | *10* | | | | | | | | | | | | | 3 | 4 | 4 |
| Temperature | *3* | | | | | | | | | | | | | | 5 | 5 |
| | *6* | | | | | | | | | | | | | | | 5 |

The data in Table 3.2 indicate the following **basic relationships**:

(1) In some cases frequencies < 5 can be explained by outliers due to technical problems with individual probes (e.g. 2 defect tensiometers at Kristianstad) which can be identified by insignificant correlations between data sets for adjacent moisture probes and which negatively influence the correlations with other parameters such as redox and temperature.

(2) The redox potentials at adjacent depth of 4 to 7 dm and the soil temperatures were always strongly correlated. This indicates the validity of data and can be explained by slow changes of these parameters.

(3) Generally the redox potentials were influenced by the soil moisture contents. Increasing soil moisture content (decreasing matrix potential) decreased the redox potential because of interrupted diffusion of atmospheric

$O_2$. These relationships were unequivocally detected by determinations of soil moisture contents ($\theta$) or matrix potential ($\Psi$). Somewhat weaker correlation in the upper soil horizons are explained by stronger temporal fluctuations compared to deeper soil horizons.

(4) Furthermore, often the levels of groundwater table were positively correlated with the redox potentials. Decreasing redox potentials resulted from raised groundwater tables (not shown). This, together with (1) supports our working hypothesis, that re-wetting will result in decreasing redox potentials.

(5) The redox potentials were negatively influenced by soil temperature. Temperature affects transformation (organic matter, C, N and dissolved organic matter) and transport processes (water, gases, solution). These are linked with redox reactions and, therefore, may influence the redox potential. The correlation coefficients depended on the depth of soil profiles because both, soil temperature and redox potential, have distinct depth gradients.

An obvious and general relationship between the Eh values and the groundwater level was not be observed. In this respect the present data sets disagree to some reports in the literature (JENKINSON et al., 2002; KARATHANASIS et al., 2003; REUTER & BELL, 2003). SEYBOLD et al. (2002) measured low redox potentials for nearly the whole period of investigation in a wetland of Virginia and addressed this phenomenon to an all-year microbial activity in the soil. MEGONIGAL et al. (1996) defined the period of significant microbial activity as the time, where the soil temperature is > 5 °C. For our experimental sites this was valid almost for the whole year (data not shown). STOLT et al. (2000) observed very low (reductive) redox potentials in soil horizons of a wetland in Virginia, although these layers were not directly influenced by the groundwater level. They hypothesized, that this behaviour could be assigned to capillary fringe. It is well-known, that peat has a high water retention capacity due to its pore size distribution (SCHWEIKLE, 1990). The observations of our investigations confirm this. Consequently the graphs of the Eh values can be explained by microbial activity as well as permanent anaerobic conditions due to groundwater level, considering the capillary fringe.

## 3.2 Phosphorus in soil solution and adjacent surface waters

The P concentrations in soil solution, surface and ground water were acquired for a period from VI/2000 to XII/2002 (Table 3.3). Three groups of sites can be

distinguished: (1) increasing P concentration with depth of soil profiles (Somerset Levels and Droemling – Natural succession), (2) decreasing P concentrations with depth of soil profiles (Trebel Valley - Langsdorf and Droemling - Extensive grassland), (3) no obvious trend with depth of soil profiles (Biebrza Valley and Droemling - Alder forest). Group 1 sites have great fluctuations of ground water levels and group 2 sites rather constant ground water levels.

The **temporal and spatial distribution of the SRP concentrations** in soil solution in 30 and 90 cm is shown in Figure 3.2 including all sites from Table 3.3. General differences can be observed in the distribution of the concentrations > 0.01 mg $l^{-1}$ for these two profile depths (see histograms of Figure 3.2a,c). The frequency for 0.01 mg $l^{-1}$ < SRP < 0.1 mg $l^{-1}$ is much higher at 90 cm (180) than at 30 cm (128), whereas more observations in 30 cm (49) compared to 90 cm (27) for 0.01 mg $l^{-1}$ < SRP < 0.1 mg $l^{-1}$ have been made. In 30 cm SRP values > 0.1 were measured in the Biebrza and the Trebel Valley, whereas concentrations < 0.001 were only observed in the Droemling area (Figure 3.2b). For the 90 cm depth there are more sites with low concentrations (SRP < 0.001) and only at the sites Somerset Levels & Moors and Droemling – alder forest the threshold of 0.1 mg $l^{-1}$ was exceeded (Figure 3.2d). In the Ljubljana Marsh all values ranged between 0.01 and 0.1 mg $l^{-1}$ (compare Figure 3.2b and 3.2d). The guideline for water quality according to the EC policy (Council of the EC, 1998) for SRP concentration in drinking water of 0.18 mg $l^{-1}$ was exceeded by 50 % in 30 cm and 65 % in 90 cm. The critical value of 2.27 mg $l^{-1}$ has never been reached. The general reverse trends in SRP concentrations in 30 and 90 cm (linear trend function in Figure 3.2a,c) indicate a P leaching within the profile.

Table 3.3 Concentrations of soluble reactive P (SRP) in soil solution, nearby surface water and ground water at the experimental sites in the project study areas (sampling period VI/2000 to XII/2002)

| No | Site | Ground water level | Profile depth | Soil solution in profiles | | | Surface water | | | Ground water | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | mean ± SD | | Mean | Median | SD | Mean | Median | SD | Mean | Median | SD |
| | | ------- cm ------ | | ---------------------------------------- mg l$^{-1}$---------------------------------- | | | | | | | | |
| 1 | Droemling, Alder forest [1] | 28 ± 20 | 30 60 90 | 0.017 0.016 0.042 | 0.015 0.017 0.035 | 0.015 0.011 0.030 | 0.193 | 0.103 | 0.252 | 0.092 | 0.076 | 0.065 |
| 2 | Droemling, Succession [1] | 19 ± 17 | 30 60 90 | 0.009 0.015 0.052 | 0.009 0.014 0.053 | 0.008 0.015 0.023 | 0.405 | 0.189 | 0.573 | 0.097 | 0.073 | 0.121 |
| 3 | Droemling, extensive Grassland [1] | 12 ± 24 | 30 60 90 | 0.009 0.006 0.005 | 0.006 0.005 0.004 | 0.010 0.006 0.005 | 0.047 | 0.030 | 0.045 | 0.033 | 0.025 | 0.027 |
| 4 | Trebel Valley, Langsdorf | 16 ± 9 | 30 60 90 | 0.299 0.023 0.022 | 0.174 0.015 0.013 | 0.373 0.029 0.027 | 0.061 | 0.061 | 0.034 | 0.092 | 0.008 | 0.168 |
| 5 | Somerset Levels & Moors | 23 ± 20 | 30 60 90 | 0.013 0.121 0.159 | 0.008 0.107 0.138 | 0.018 0.059 0.079 | 0.079 | 0.047 | 0.073 | 0.244 | 0.240 | 0.201 |
| 6 | Biebrza Valley | 54 ± 16 | 30 60 90 | 0.038 0.033 0.026 | 0.023 0.021 0.020 | 0.081 0.055 0.027 | 0.054 | 0.032 | 0.061 | 0.046 | 0.031 | 0.050 |
| 7 | Ljubljana Marsh [2] | 28 ± 12 | 30 60 90 | 0.028 0.024 0.047 | 0.027 0.023 0.045 | 0.009 0.007 0.015 | n.d.[3] | n.d. | n.d. | 0.119 | 0.120 | 0.035 |
| 8 | | 72 ± 7 | 30 60 90 | 0.049 0.047 0.036 | 0.042 0.040 0.032 | 0.025 0.015 0.010 | | | | 0.055 | 0.059 | 0.019 |

[1] period from V/2002 – III/2003; [2] period from VIII/2002 – III/2003, [3] not determined

The observed P concentrations are comparable to those cited in the previous literature. For natural and intact Histosol ecosystems in Northeast Germany BALLA & QUAST (2001) reported total P concentrations (TP) of 0.2 mg l$^{-1}$. GELBRECHT & LENGSFELD (1998) determined 0.5 mg l$^{-1}$ of SRP for growing or poorly drained Histosols. There were a few reports that a re-wetting of formerly drained and agriculturally Histosols could lead to increased P concentrations in soil solution. REDDY (1983) investigated the P mobilisation in peat soils

from Florida with different states of degradation using undisturbed soil cores. The results clearly turned out, that during increase of the water level followed by long-term saturated conditions the P mobilisation into the soil solution is 4- to 8-fold higher than under drained conditions.
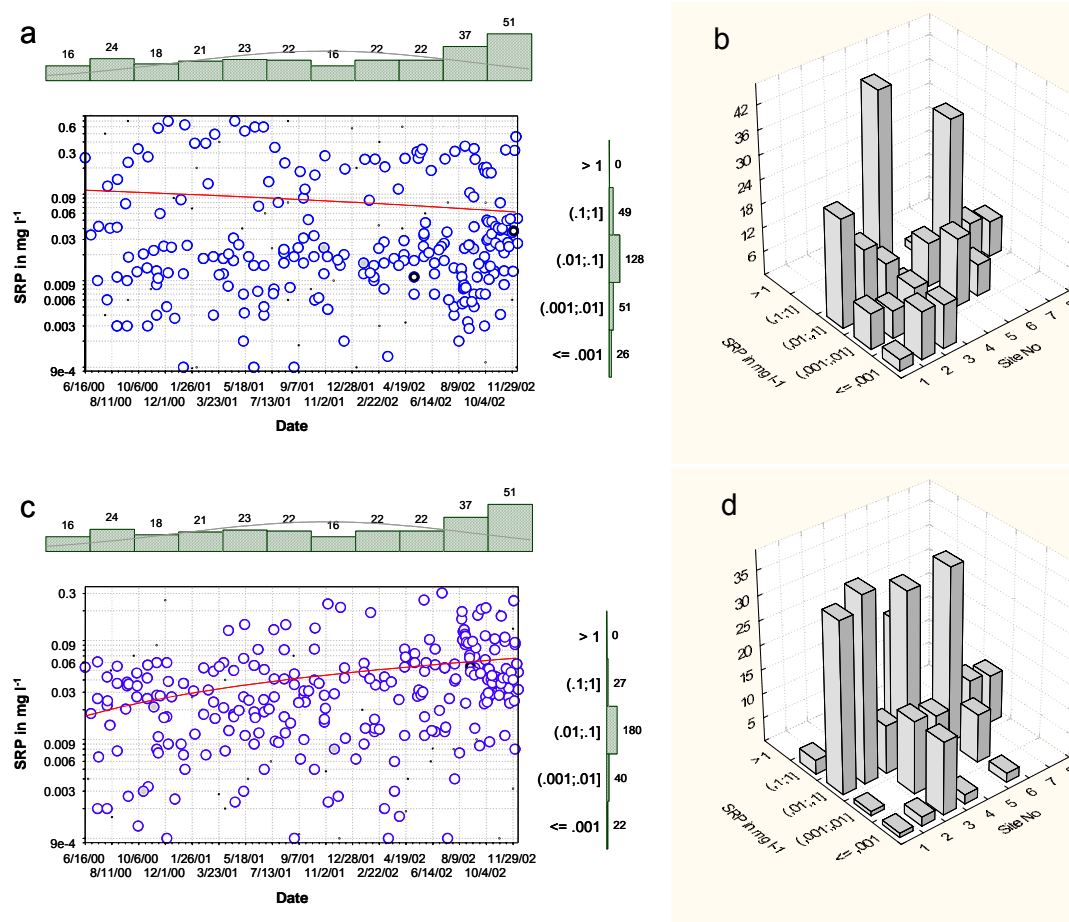


**Figure 3.2** Temporal (a and c) and spatial (b and d) distribution of SRP concentrations in soil solution in 30 (a and b) and 90 (c and d) cm depth

For alternating groundwater levels REDDY (1983) calculated P mobilisation rates of 16 to 168 kg P ha$^{-1}$ a$^{-1}$. GELBRECHT & LENGSFELD (1998) observed up to 12 mg l$^{-1}$ of SRP in the soil solution of a re-wetted peat. For a fenland in the Nuthe-Nieplitz-Valley HÖHNE (2000) reported average SRP concentrations of 0.9 mg l$^{-1}$ during uncontrolled flooding. KIECKBUSCH (2003) determined changes in maximum TP concentrations from 1.5 mg l$^{-1}$ before to 6.0 mg l$^{-1}$ after re-wetting of a fenland area in the Pohnsdorfer Stauung. Thus the

present investigations were in line with the most pertinent literature in this field of research.

## 3.3 Groundwater fluctuation – driving force for P mobilisation

The detailed evaluation of relationships between P concentrations and soil moisture for individual sites, and data comparison led to the conclusion that **groundwater level was the most suitable parameter**, common for all sites, to estimate SRP concentrations.

Two types of data sets were used for regression analysis: (1) data for the whole period of investigation and (2) data for time periods with increasing groundwater table. The calculations resulted in **two general cases of SRP concentration behaviour** in dependence on groundwater table: increasing and decreasing SRP concentrations with increasing groundwater table. The regression functions, linear and exponential, which gave the best fits (least square regression factor, $R^2$) are shown in Figure 3.3. All correlations were significant (** = P > 99.0 %; *** = P > 99.9 %). Examples are (A) Ljubljana Marsh (suction cups at soil depth of 30 cm), (B) Trebel Valley (30 cm), (C) Biebrza Valley (60 cm) and (D) Somerset Levels and Moors (60 cm). For the other sites and profile depths the correlation were weaker. The first three functions (A, B and C) were representative for only one site. A function similar to D (linear with negative coefficient of regression) was also characteristic for the sites in the Droemling. In examples A and D data for the whole period of investigation were used for calculation, and in examples B and C only data for time periods with increasing groundwater table and SRP concentrations in the relevant suction cups (sampling depth).

Environmental conditions govern the type of best-fit function. The linear function was generally applicable for the sites with high fluctuations in water table (range ≈ 50 cm). The exponential function characterised the sites with a smaller fluctuation in water table (≈ 20 cm). Positive coefficients of regression were valid for the two cases with a relatively large distance of groundwater table to the soil surface (35 - 90 cm). Negative coefficients of regression were valid for the two cases with a smaller distance of groundwater table to the soil surface (0 - 50 cm) (Figure 3.3).
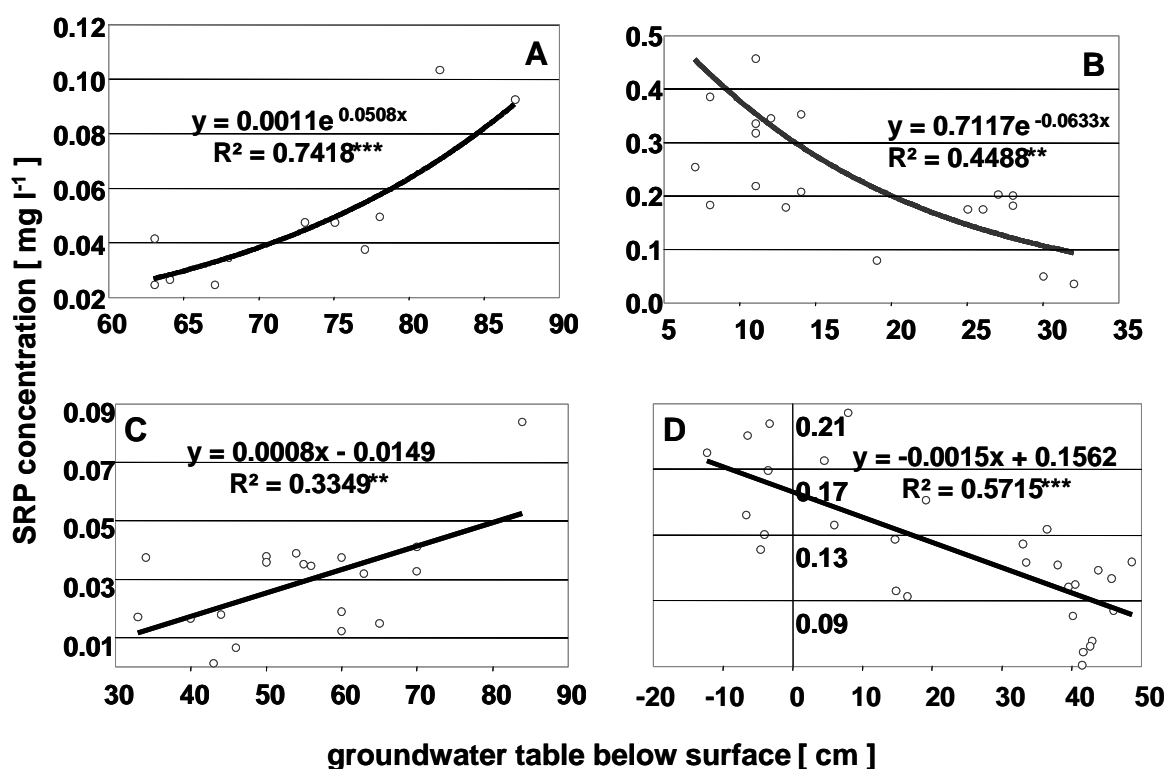
**Figure 3.3** Regression equations describing the dependence of SRP concentrations on groundwater tables: (A) Ljubljana Marsh, (B) Trebel Valley, (C) Biebrza Valley, (D) Somerset Levels & Moors

In summary, the present findings provide excellent confirmations of previous reports in the literature, which emphasised groundwater table to be the driving force for P mobilization (RUBIO et al., 1995; MARTIN et al.,1997; OLILA et al., 1997; VILLAPANDO & GRAETZ, 2001). Moreover, the broad data basis allowed to derive different types of reactions of P concentration on changes in groundwater tables.

# 4. Characterisation of soil phosphorus status

The main methods for the **characterisation of soil P status** can be grouped into (1) total P ($P_t$) determinations, agronomic and environmental soil P tests, (2) sequential P fractionations, (3) investigations by $^{31}P$ NMR spectroscopy, and (4) microbial and enzymatic P parameters. All groups of methods were applied in the PROWATER, and fundamental results are described in the following. Emphasis is placed on those project results that enable comparisons of the various sites in Europe and Israel.

## 4.1 Total P, agronomic and environmental soil P tests

Table 4.1 shows basic chemical characteristics of soils including P contents. The mean $P_t$ concentrations were in the range of 800 to 1800 mg kg$^{-1}$. At the different sites, they varied with profile depth. These variations will be discussed in the context of sequentially extracted P fractions (Figure 4.4). In topsoils and especially in subsoils, the $P_t$ concentrations were larger than in a wide range of mineral soil types (LEINWEBER et al., 2002). This is explained by P enrichment with non-decomposed organic matter in native Histosols and additional P accumulation in topsoils due to intensive agricultural use. The contents of poorly crystalline Al- and Fe-oxides, and oxalate-extractable P were investigated to calculate the P sorption capacity and degree of P saturation (DPS). The $Fe_{ox}$ concentrations were larger by an order of magnitude, and the $Al_{ox}$ concentrations by factor of about 2 to 8 than in mineral soils (LEINWEBER et al., 1999). Because of $P_{ox}$ concentrations similar to mineral soils, the resulting DPS generally were low. The DPS will be discussed in more detail below with respect to spatial variations and P leaching risk assessment.

The contents of plant-available P (Soil P tests) in topsoils and their evaluation according to national recommendation schemes mostly revealed low (l) to medium (m) values. High values were analysed only for the most intensively used soil in the Droemling (fens strongly degraded to mineral soils, not shown) and in the Hula Valley. However, it should be emphasised that this classification holds for agriculturally soils rather than for set-aside soils or fens to be restored.

World-wide, about **50 different methods** are in use for the evaluation of plant-available P ("agronomic" soil P tests). Most recently, NEYROUD & Lischer (2003) compared extraction power and agronomic consequences of the 16 most important P tests on 135 benchmark soils, which were comparatively

investigated in an European-wide inter-laboratory study. This study, however, did not include peat soils.

Table 4.1 Basic chemical characteristics and P contents of representative topsoil samples from the PROWATER study areas (Abbreviations: ox = oxalate extractable Al and Fe, eGL = extensive grassland, SU = natural succession, AL = alder forest (Histosols), Soil P test according to national recommendation schemes, l = low, m = medium, h = high, Dithionite-citrate-bicarbonate extraction for total pedogenic oxides

| Study area | pH | $C_t$ | $P_t$ | $Fe_{ox}$ | $Al_{ox}$ | $P_{ox}$ | DPS | Soil P tests |
|---|---|---|---|---|---|---|---|---|
| | | [ % ] | [mg kg$^{-1}$] | | [mmol kg$^{-1}$] | | [%] | [g kg$^{-1}$] |
| Trebel Valley (Germany) | 5.6 | 39.9 | 1024 | 299 | 28 | 18 | 11 | 12 / l |
| Warnow Valley (Germany) | 5.6 | 26.6 | 1125 | 206 | 38 | 12 | 11 | 11 / l |
| Droemling (Germany)  eGL | 5.3 | 21.8 | 776 | 146 | 47 | 11 | 11 | 21 / l |
| SU | 5.7 | 12.8 | 802 | 184 | 17 | 11 | 11 | 72 / m |
| AL | 5.2 | 39.3 | 949 | 416 | 35 | 18 | 8 | 14 / l |
| Hula Valley (Israel) | 7.3 | 13.7 | 1239 | 530 | | | | 35 / h |
| Biebrza Valley (Poland) | 6.0 | 41.2 | 1755 | 282 | 31 | 32 | 21 | 10 / l |
| Kristianstad (Sweden) | 4.8 | 13.0 | 1789 | 257 | 113 | 32 | 17 | 62 / m |
| Somerset Levels (UK) | 5.4 | 27.7 | 1171 | 279 | 64 | 16 | 9 | 29 / m |
| Ljubljana marshes, Slovenia | 6.8 | 16.4 | 1815 | 244 | 166 | 29 | 14 | 24 / l |

Therefore, a similar **methodological comparison** was carried out in PROWATER. Nationally typical agronomic soil P tests among PROWATER partners were the ammonium lactate (0.1 $M$ NH$_4$-lactate + 0.4 $M$ HOAc at pH 3.75, Sweden, P-AL), sodium bicarbonate (0.5 $M$ NaHCO$_3$ at pH 8.5, U.K., Israel, P-Olsen) and double calcium lactate (0.0195 $M$ DCaL at pH 3.6, Germany, P-DL) methods. These were compared for their extraction efficiency by using soil samples of all partners in one laboratory. For all 43 samples the extraction efficiency increased in the order P-DL < P-AL < P-Olsen. In mineral soils the order of extraction efficiency was P-Olsen < DL < P-AL (NEYROUD & LISCHER, 2003). In the PROWATER peat soils the large extraction efficiency of 0.5 $M$ NaHCO$_3$ at pH 8.5 (P-Olsen) was interpreted by its ability to extract organically bound P which neither AL nor DL were able to access (OTABBONG et al., 2004). There were linear correlations between P-Olsen and pH, and among the various P-tests. P-Al and P-DL were correlated most closely if pH was considered:

P-Al = 1.42 × P-DL + 5.35 × pH - 22.59 [mg kg$^{-1}$ d.w.]

Olsen-P was evenly distributed in the soil profiles of study areas in Germany, the UK and Slovenia. This was ascribed to previous fertilisation and P transport to deeper layers, and indicated a risk of P escaping to adjacent water bodies (OTABBONG et al., 2004).

Because of the limited value of agronomic soil P test for the prediction of P losses from soil to water, so-called **"environmental" soil P tests** have been developed. Most widely applied are the P sorption capacity (PSC) and degree of P saturation (DPS) (BREEUWSMA and SILVA, 1992). The PSC is estimated using the concentrations of $Al_{ox}$ and $Fe_{ox}$ instead of the time-consuming determination of P sorption capacity from adsorption isotherms. The DPS is expressed as:

$$DPS = [P_{ox} / 0.5 (Al_{ox} + Fe_{ox})] \times 100 [\%]$$

This relationship was applied to mineral soils and proved as an estimator for P leaching from acid sandy soils (VAN DER ZEE et al., 1990) and sandy to loamy lysimeter soils (LEINWEBER et al. 1999, GODLINSKI et al., 2004). Within PROWATER the DPS concept was applied to Histosols for the first time. The DPS was determined for all experimental sites as a general site characteristic (Table 4.1). The mean values of topsoils, ranging from 8 to 17 %, indicating no great risk of P leaching if the threshold of 25 % for mineral soils (SCHOUMANS and GROENENDIJK, 2000) is applied. In a 450-$m^2$-test plot in the Warnow Valley, the DPS was determined on a $3 \times 3$ m grid (n = 50) to investigate the small-scale spatial variability in P leaching risk. The DPS ranged from 6 to 14 %, and varied sometimes by a factor of 2 over a distance of a few meters. These variations in DPS were largely determined by variations in $Fe_{ox}$ (78 %). In the Hula Valley the DPS was recorded on a larger scale to estimate the probability of exceeding threshold values for accelerating ground water eutrophication (LITAOR et al., 2003). A strong correlation between the P sorption maxima from Langmuir isotherms and the DPS indicated that DPS can be applied to organic soils as well. The DPS values were much lower in Histosols (6.5 $\pm$ 5) than in redoximorphic marl gley soils (28 $\pm$ 18) and Vertisols (78 $\pm$ 28). Spatial analysis with a sequential Gaussian simulation technique indicated that the Histosols had a much lower risk (< 10 %) of exceeding the commonly used threshold of 25 % DPS than redoximorphic marl gley soils and Vertisols (> 60 % probability). This was visualised in a thematic map (LITAOR et al., 2003). Generally, much more detailed investigations are needed to prove if and to what extent the P leaching risk in fen peat soils depends on the DPS.

## 4.2 Sequential P fractionations

Sequential P fractionations were carried out to (1) adapt methods described in the literature to the conditions of peat samples and avoid undesired effects of sample pre-treatments, (2) point out general differences between organic and mineral soils, (3) investigate and describe the distribution of soil P forms at the experimental sites, and elucidate effects of peat degradations on the P pools, and (4) follow changes in P compounds during re-wetting in microcosms and in the field. Different sample sets were investigated to achieve these four objectives.

A brief outline of the **historical development of P fractionation schemes** is compiled in Figure 4.1. The initial proposals by CHANG & JACKSON (1957) for soils, and by PSENNER et al. (1984) for limnic and marine sediments have been improved and modified over the years. However, the vast majority of schemes have not considered the most mobile, microbially driven P fractions. HEDLEY et al. (1982) introduced the extraction of desorbable phosphate by an anion exchange resin and of labile inorganic and organic P by 0.5 M $NaHCO_3$ as first two extractions steps. Modification of this method by TIESSEN & MOIR (1993) was the basis for the final adaptation of the Hedley-fractionation to organic soil samples (SCHLICHTING & LEINWEBER, 2002). The fractionation method of IVANOFF et al. (1998), developed for peat soils, integrated the bicarbonate extraction of the original Hedley-fractionation ($NaHCO_3$-$P_i$, -$P_o$ and -$P_{mic}$ subfractions), the HCl-extraction of the BOWMAN & COLE (1978) method and the fulvic/humic-acid separations from the methods for limnic and marine sediments.
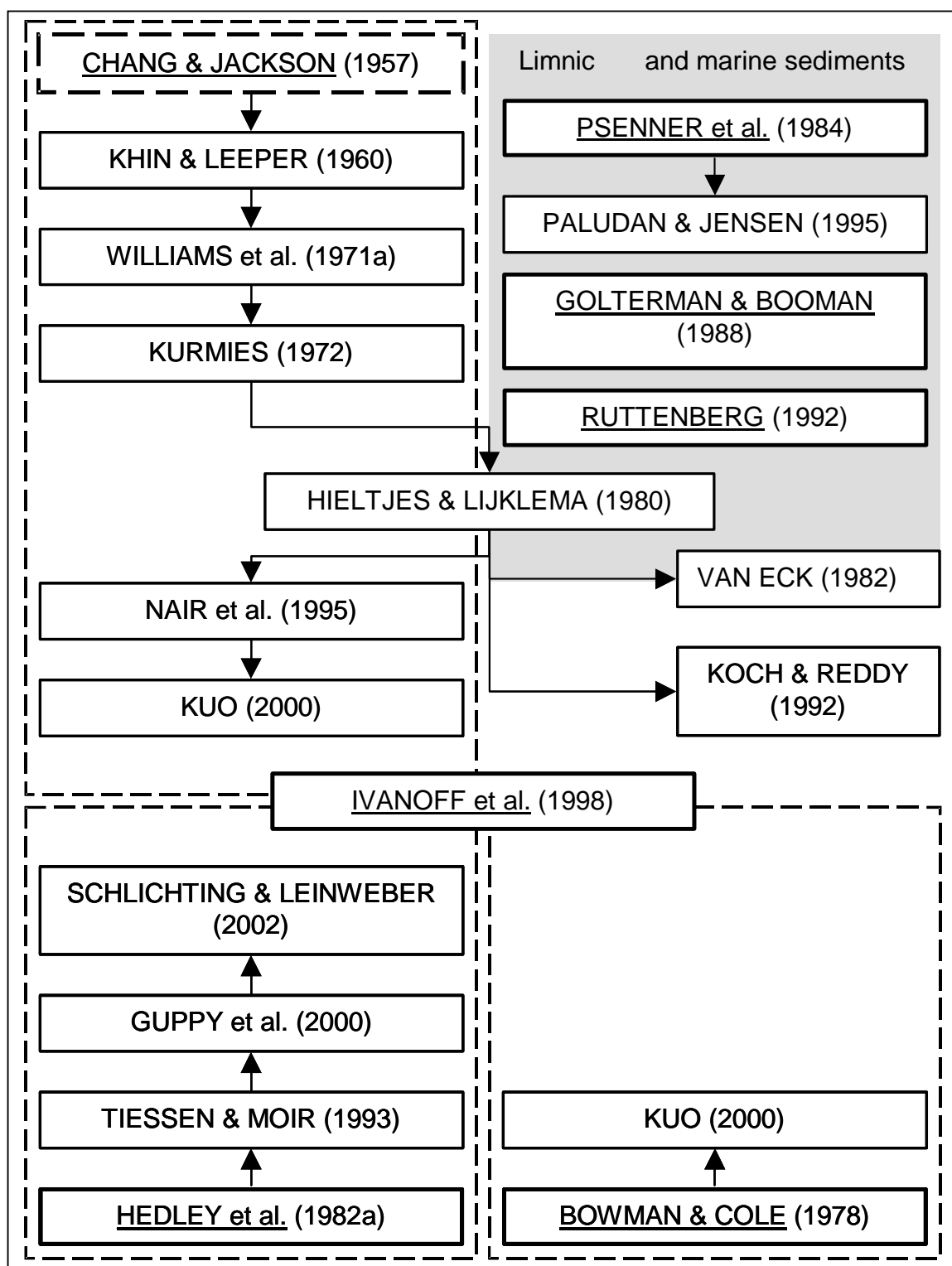
**Figure 4.1** Overview on the development of P fractionation schemes.

In the present study the method of TIESSEN et al. (1984) was slightly modified according to the organic nature of the samples. From the dried samples 0.5 g of finely milled (< 0.125 mm) material, and from the field moist samples 0.5 g on dry weight basis were weighted into a 50 ml centrifuge tube. In this tube, 0.4 g of Dowex 1x8 - 50 anion exchange resin in bicarbonate form was placed too. The resin was

weighed in a filter tube (polyethylen) with a nominal pore size of 10 μm to enable the separation from the specific light peat after shaking. After addition of 30 ml deionized water the sample was shaken for 18 hours using a reciprocal shaker at 100 rpm. Subsequently soil and soil solution, remaining in the centrifuge tube, were separated from the filter tube with the resin inside. The resin-adsorbed P, comprising of P in soil solution and labile P, was exchanged by treatment with 50 ml of 1.25 M $NaHCO_3$. The suspended peat sample was collected by centrifuging at 6000 x g for 20 minutes and decanting the supernatant and treated with 30 ml of 0.5 M $NaHCO_3$ (pH 8.5), shaken and separated as described above. It combined the labile and inorganic as well as organic and microbial P. The residue from centrifugation was shaken with 30 ml of 0.1 M NaOH, and the extract (P in humic and fulvic acids and in Al and Fe phosphates) decanted. Finally, the residual was treated with 1 M H2SO4 to extract barely soluble P (e.g. apatite P). The proportion of P that resisted even this final extraction, was calculated as the difference between total P and the sum of resin-P + $NaHCO_3$-P + NaOH-P + $H_2SO_4$-P; this is termed residual P and comprises of stable organic and inorganic P. For the extraction of total P ($P_t$), 0.2 g of finely ground (< 0.125 mm), air-dried sample was treated by a sodium hypobromite alkaline oxidation (DICK & TABATABAI, 1977). The mean coefficients of variation in triplicate fractionations were 5.3 % (resin-P), 6.2 % ($NaHCO_3$-$P_i$), 7.1 % ($NaHCO_3$-$P_o$), 2.0 % (NaOH-$P_i$), 3.7 % (NaOH-$P_o$) and 3.6 % ($H_2SO_4$-P) (n = 234 samples).

The **effects of sample pre-treatment** were investigated in detail in samples from an Eutric Histosol in the telmatic low-moor of the Warnow Valley, Mecklenburg-West Pommeria, Germany (near the city of Rostock; Latitude 54° 04' N, Longitude 12° 10' E). This fenland was drained in the last 50 years and re-wetted since 1997. The top horizon sample is a strongly decomposed amorphous sedge peat mixed with sand, characterized by muck-forming processes. Five different forms of storage or processing techniques of the peat were compared: (1) field moist, fresh (2) air-dried, (3) freeze-dried, (4) stored at 4°C in field moist form for 3 weeks, (5) frozen in field moist form at -20°C and thawed for analysis.

The different pre-treatments affected the P concentrations in various fractions and also the proportions of the P fractions as percentages of $P_t$. ANOVA results (not shown) indicated that these effects were largest for NaOH-$P_o$ and $H_2SO_4$-P. If the pre-treatments were grouped according to moist sample processing and drying, it was obvious that drying reduces the concentrations of $P_o$ in the $NaHCO_3$-extracts below detection limit and, to a lesser extent, also in the NaOH-extracts.
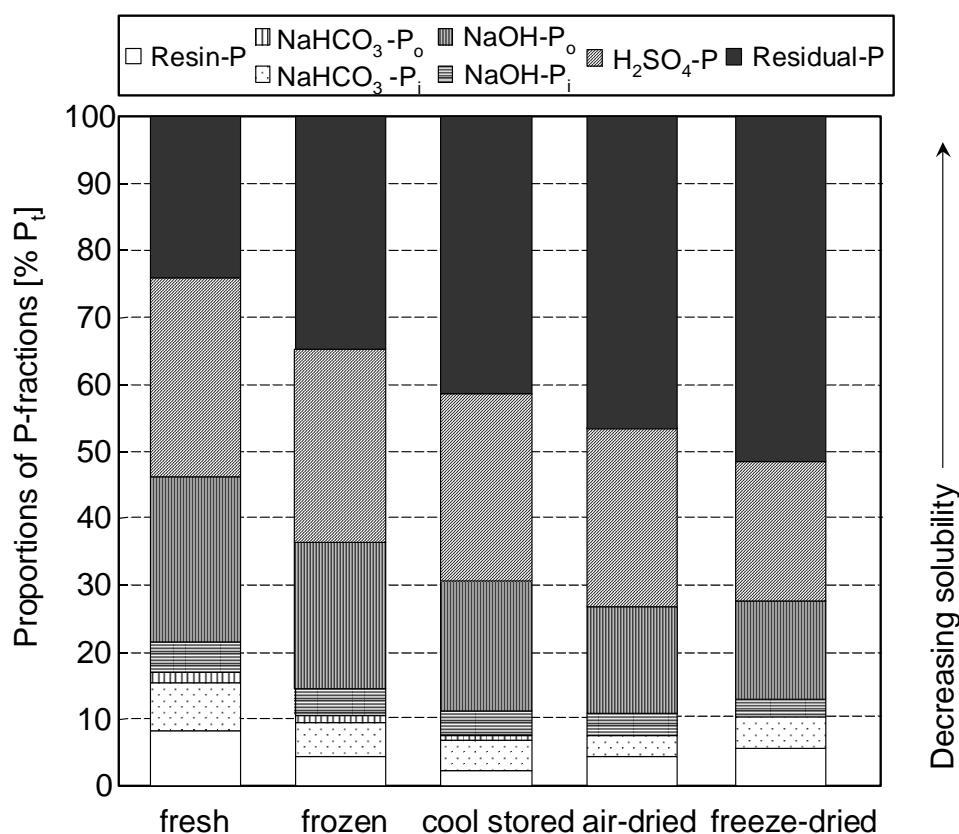
**Figure 4.2**   Proportions of sequentially extracted P fractions in an Eutric Histosol sample after different methods of pretreatment and storage. The solubility of extracted P in the fractions decreased with successive fractionation steps. (SCHLICHTING & LEINWEBER, 2002; with permission of Marcel Dekker Inc.)

Figure 4.2 shows that proportions of resin-P and $NaHCO_3$-$P_i$ decreased in the order "fresh", "frozen" and "cool stored". To a lesser extent this was also true for $NaOH$-$P_o$. The decreased proportions of these labile P-fractions resulted in corresponding increases in residual P. The proportions of residual P were largest in the air-dried and freeze-dried samples. The clearly decreased extractability of P from fresh to dried samples indicates that the residual P fraction is involved in short-term P transformations even during pretreatment and storage. The two drying methods similarly reduced the proportions of $NaHCO_3$-$P_o$ and $NaOH$-$P_o$. Corresponding reductions of organic P forms were reported from peat drying and re-wetting in laboratory experiments (OLILA et al., 1997). They stated that drying initiates autolysis and microbial cell lysis and promotes the oxidation of organic matter. Consequently, organic P was mineralized and P-binding sites were inactivated. This is assumed to enhance the P release during re-wetting and extraction as recently also reported from field studies (BRAKE et al., 1999). They observed an increase in biomass and activity of microorganisms after de-watering and aeration of raised bog peat. Promotion of microbial biomass and activity to a certain extent could explain the larger proportions of resin-P and

NaHCO$_3$-P$_i$ in the freeze-dried sample of our study. The different methods of drying especially affected the H$_2$SO$_4$-P which is often interpreted as stable Ca-bound P. The Ca content of the freeze-dried sample, extracted from the incinerated peat sample by 25 % HCl, was significantly lower (13.2 ± 0.5 g Ca kg$^{-1}$) than in the air-dried sample (15.4 ± 0.7 g Ca kg$^{-1}$). This indicated a lower solubility of Ca-phosphates in the freeze-dried sample and confirmed the smallest proportions of H$_2$SO$_4$-P and the largest proportions of residual P in the freeze-dried sample. However, the reasons for these processes are not clear at present.

The main difference between the three moist and the two dried samples was a general decreased extractability of all P fractions in the dry samples. This indicates that chemical or physical changes of the peat during drying are much more important for the P extractability than particle size or microbial processes. Binding or inclusion of P in poorly crystalline pedogenic oxides, which make up about 75 % of total Fe in these samples, could contribute to the reduced extractability after drying. Furthermore, it can be expected that drying induces a structural rearrangement of humic macromolecules and general increased hydrophobicity (WALLIS & HORNE, 1992). This means that hydrophobic surfaces are exposed to the extractants to a greater extent in dried than in fresh samples. This perhaps also contributes to the reduced extractability of P in the dried samples.

All samples had a large proportion in residual P, which in addition was strongly influenced by storing and pretreatment. The content of total organic P was about 72 % of P$_t$. The sum of NaHCO$_3$-P$_o$ and NaOH-P$_o$ was maximum 28 % of P$_t$; hence up to 44 % of P$_t$ could be organic P in the residual fraction. The residual fraction contained 48 % (air dried) and 51 % (freeze-dried) of P$_t$ (Figure 4.2). Consequently, 86 to 92 % of the residual P was in organic form, determined by the loss on ignition method of SAUNDERS & WILLIAMS (1955). These methodological studies led to the following **conclusions and recommendations**:

(1) The sequential fractionation of P forms from peat soils should be carried out with fresh samples, because of the significant influence of storage and drying on the concentrations and proportions of P fractions. The recommended protocol for P fractionation of moist peat includes crushing, separate determination of moisture content, weighing of 0.5 g soil (dry weight basis) into a filter tube which enables the subsequent separation of peat and anion exchange resin and fractionation as described above. In case samples have to be stored prior to extraction, freezing least affects P-fractions.

(2) Cool storage in the refrigerator at 4°C until fractionation and any forms of drying are not recommended for peat samples as they lead to great changes in the fractions. This makes it difficult if not impossible to compare results of sequential P fractionations from studies with different pretreatment.

(3) Further improvements of the method possibly can be achieved by purging the air outside the tubes with $N_2$ to suppress the oxidation of peat and iron oxides or by inhibition of the microbial activity prior to P fractionation.

(4) Despite great logistic efforts one set of field-moist samples was collected from the European sites and sequentially fractionated in the field-moist condition in the same laboratory to optimise data comparability.

A large set (n = 82) of samples from 17 Histosol reference profiles was investigated by sequential P fractionations to find out **general differences in P chemistry** between organic and mineral soils. The results for differently managed Histosols and Humic Gleysols in the Droemling study area were compared with 75 relevant data sets for mineral soils from the literature (Figure 4.3). The Histosols generally differed from mineral soils by (1) larger contents of $P_t$ and organic P forms, and (2) larger proportions of organic P, residual P and mobile P forms (resin-P + $NaHCO_3$-$P_i$) (compare columns for "75 mineral soils" and "Histosols"). The column for "Humic Gleysols" demonstrates that continuous intensive agricultural use of Histosols will lead to losses of P, especially of organic P forms. These Humic Gleysols were developed from the adjacent Histosols in the Droemling study area (Germany) as a result of long-term agricultural use and peat degradation. With respect to P contents and distribution of P forms they are intermediate between mineral and organic soils. Effects of land use intensity can be derived from the comparison of Histosols and Gleysols in the Droemling area, since the Gleysols result from the degradation of Histosols (SCHLICHTING et al., 2002). The following differences were observed: (1) a strong increase of the proportions of residual P in the Gleysols in connection with (2) a strong decrease in the concentrations (not shown) and proportions (Figure 4.3) of total $P_o$, and (3) slight increases in the proportions of the labile fractions (resin-P + $NaHCO_3$-$P_i$) and the $NaOH$-$P_i$ (Figure 4.3). Thus, our results confirm the view of KADLEC (1999) who reported from the Everglades that a gradual peat degradation led to the mineralization of organic P in the extractable fractions.
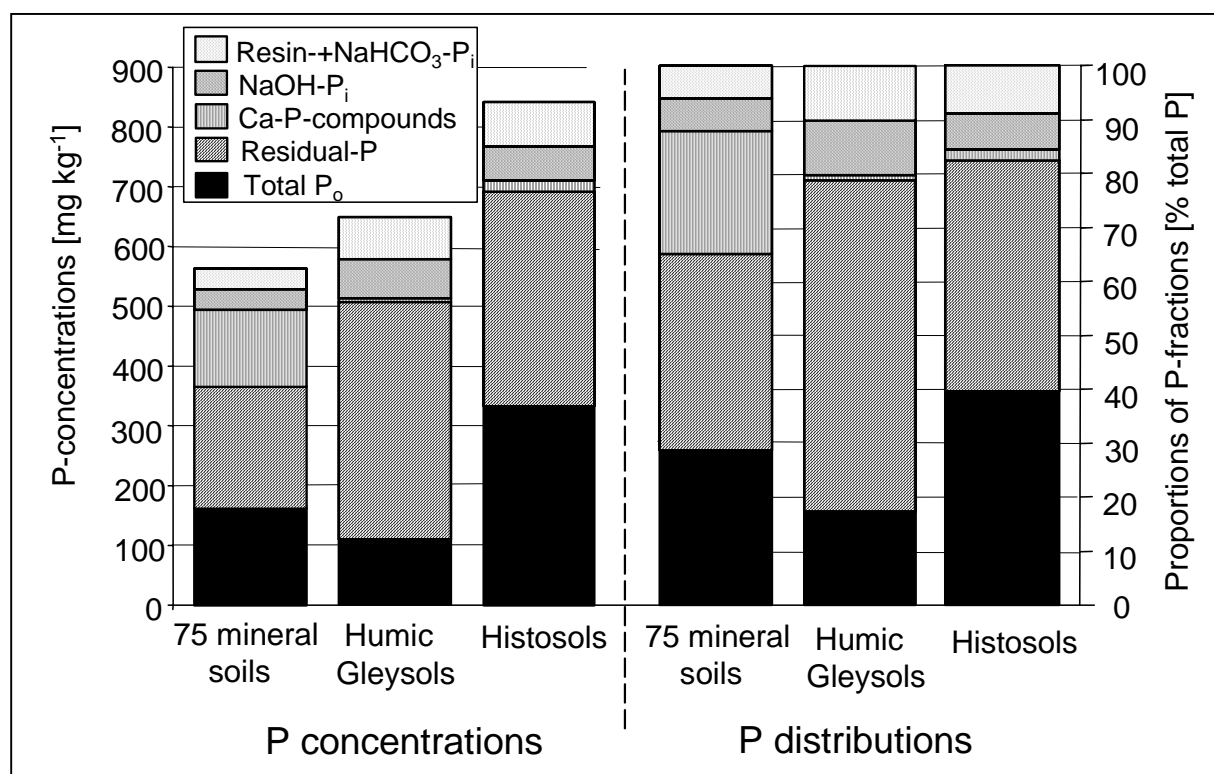
**Figure 4.3** Sequentially extracted P forms in mineral soils (literature data), Humic Gleysols and Histosols from the Droemling area (Germany).

Figure 4.4 shows the results of Pt determinations and sequential P fractionations from all PROWATER sites. The Pt concentrations ranged from 1100 to 1789 mg kg$^{-1}$ in the 0-20 cm soil layer, from 430 to 1442 cm in the 20-50 cm soil layer and from 319 to 1242 mg kg$^{-1}$ in the 50-70 cm layer (Figure 4.4). The Histosol at Kristianstad had the largest Pt concentrations throughout the profile. This is explained by P inputs from intensive agriculture and flooding with P-enriched surface water. At all sites, the Pt decreased with increased soil depth. Since the subsoils contained less decomposed peat, Pt was relatively enriched in topsoils due to organic matter oxidation (= peat loss) and P fertiliser input.

Except for Hula Valley, where the most dominant fraction was $H_2SO_4$-P, **NaOH-P$_o$** was the **most abundant** P-fraction in topsoils (mean: 32 % of P$_t$). At sites Biebrza, Ljubljana and Kristianstad this fraction remained large or even increased in proportion at greater soil depth. At sites Trebel and Somerset, residual P became quantitatively more important with increasing soil depth. The NaOH-P$_o$ represents moderately labile fulvic acids and relatively stable humic acids. Specifically, NaOH-P$_o$ in the fractionation sequence is purported to comprise low molecular weight monoester P forms that are strongly

chemisorbed to amorphous and crystalline oxyhydroxide and oxide surfaces (HEDLEY et al. 1982). Consequently, the very high proportion of NaOH-$P_o$ (17 – 44 %) in the soils can be attributed to high contents of monoester inositol hexaphosphates (IHP). Through $^{31}$P-NMR spectroscopic analysis, it is well known that IHP accumulates in Histosols that have been flooded for several (> 3) years (ROBINSON et al., 1998). However, larger proportions of NaOH-$P_o$ in subsoils were not reflected by increases in $NaHCO_3$-$P_o$. Therefore, it is hypothesized that NaOH-$P_o$ in these soils represents P in association with relatively stable humic acids rather than P in moderately labile fulvic acids.

**Residual P** accounted for 13 to 56 % of $P_t$. Generally, the proportions of residual P increased with increasing soil depth although not for all sites and soil depth. Sites could be separated into Somerset, Trebel and Ljubljana, and Kristianstad, Hula and Biebrza. The mean residual P proportions followed the order 30 % (0-20 cm) < 47 % (20-50 cm) $\approx$ 46 % (50-70 cm) in the first group and 17 % (0-20 cm) < 21 % (20-50 cm) = 21 % (50-70 cm) in the second group. Residual-P in mineral soils as well as in Histosols represents P in stabile organic compounds such as lignin- and organo-metal-complexes (SYERS et al., 1973; HSU, 1977; TIESSEN et al., 1984). Progressive peat degradation was found to decrease the proportions of residual P in organic soils (KOCH & REDDY, 1992; THOMAS et al., 1999; SCHLICHTING et al., 2002). Subsoils of native peat had about 75 % of $P_t$ in the residual fraction according to the fractionation scheme of HIELTJES & LIKLEMA (1980) and OLILA et al. (1995). This general view was supported by the depth distribution of residual P in the current study. Furthermore, the profiles at Kristianstad, Hula and Biebrza were throughout the profile more strongly degraded than Somerset, Trebel and Ljubljana which had largely preserved peat below 20 cm soil depth. It was shown unequivocally that residual P in Histosols is organic P ($\approx$ 90 % of residual P; SCHLICHTING et al., 2002). Therefore, **relatively stable and non-extractable organic P forms** were quantitatively most important in these soils, and **accounted for approximately half of the $P_t$** in these profiles.

The **$H_2SO_4$-soluble $P_i$** pool represents the P associated with Ca and Mg minerals. The largest proportions at Hula Valley reflect the occurrence of carbonate (7-17 %) and pedogenic gypsum in these soils (LITAOR et al., 2004). Among the other sites, the proportions of $H_2SO_4$-P varied from 7 to 28 % of $P_t$ but did not differ markedly for each site as a function of depth. Under most natural conditions, Ca and Mg bound P is essentially unavailable to biological assimilation and is considered not important in controlling the leaching potential of P.

The **$P_i$ extracted with NaOH** represents the P associated with crystalline Fe and Al oxides and amorphous oxyhydroxide surfaces. Compared with waterlogged mineral soils, which often contain as much as 50 % of $P_t$ in the Fe (and Al)–bound form, the Histosols used in the current study contained on average only 8 % (0-20 cm), 9 % (20-50 cm) and 4 % of $P_t$ (20-50 cm) in this fraction. In topsoils the order of sites was Hula (17 %) > Biebrza (12 %) > Trebel (6 %) > Ljubljana, Somerset (5 %) > Kristianstad (2 %). Except for continuing large proportions at Hula (23 and 15 %), at the other sites the proportions of NaOH-$P_i$ were rather similar; around 5 % at 20-50 cm and 50-70 cm profile depth. The similarity in depth distribution between NaOH-$P_i$ and $H_2SO_4$-P at Hula suggests that NaOH also perhaps extracts some of the Ca-P-compounds. Furthermore, large concentrations of crystalline and amorphous pedogenic Fe- and Al-oxides throughout the profile may be another reason for the relatively large proportions of NaOH-$P_i$ at this site. The large value at Biebrza topsoil is explained by severe degradation, residual P enrichment in Al/Fe-oxide-bonds and previous mineral P fertilization. Since the stability of Al/Fe-oxides strongly depends on the redox potential, the topsoils of these sites seem to be more vulnerably to re-wetting induced P-mobilisation from dissolved Al/Fe-oxides than the other sites.
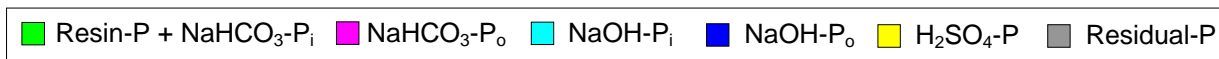
The remaining **labile fractions**, resin-P and NaHCO$_3$-$P_{i,o}$, on average accounted for 10 % (0-22 cm), 14 % (20-50 cm) and 10 % of $P_t$ (50-70 cm). The increase in proportions of labile P between 0-20 and 20-50 cm soil depth was observed at all sites. In topsoils, the summed $P_t$-proportions followed the order Trebel (15 %) > Biebrza (14 %) > Somerset (9 %) $\approx$ Kristianstad (8 %) > Hula and Ljubljana (6 %). In the subsoils (20-70 cm) site Trebel always had the largest (22-20 %) and Hula and Ljubljana the smallest proportions (9 %) of labile P.

Under forest the resin-P and NaHCO$_3$-P fractions accounted for larger proportions at 0-10 cm than at 10-40 cm (THOMAS et al., 1999), indicating relative enrichments with peat degradation. Similarly, KOCH & REDDY (1992) found increased proportions of the most labile P fraction (NH$_4$Cl-$P_i$) with increasing land use intensity. By contrast, QUALLS & RICHARDSON (1995) and SCHLICHTING et al. (2002) found larger proportions of labile P in native than in intensively used peat soils.
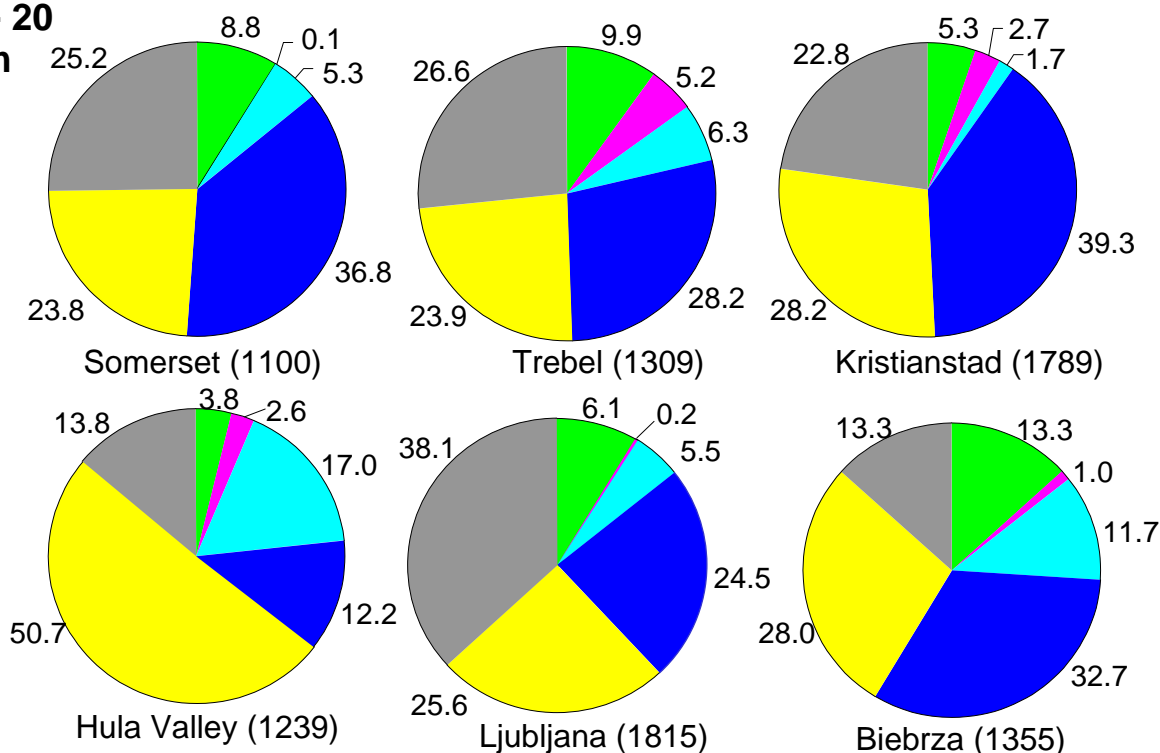
Among the three labile P fractions, inorganic P (resin-P + NaHCO$_3$-$P_i$) was more abundant (about 8-11 %) than the NaHCO$_3$-$P_o$ (mean: 2 %). The proportions of **resin-P + NaHCO$_3$-$P_i$** throughout the soil profile were largest at Biebrza and Trebel. Large contents were also analysed in the subsoil of

Somerset. These fractions contain P in soil solution and $P_i$ weakly held by reactive surface which exchanges into soil solution (HINGSTON et al. 1974; WALKER & SYERS, 1976). These $P_i$ forms can originate from direct inputs of fertiliser, and from the mineralisation of organic matter. Previous fertiliser inputs explain the large proportions at Biebrza. This reason can be excluded at Trebel site. Intensive microbial decomposition and downward movement in soil profile, and small proportions of sorptive pedogenic oxides in subsoils, are hypothesized to be the reason for the relatively large proportions of resin-P + $NaHCO_3$-Pi in the profile at the Trebel site. Similar processes supported by the periodic pump drainage, perhaps explain the relative enrichments of labile inorganic P in the subsoil at Somerset.
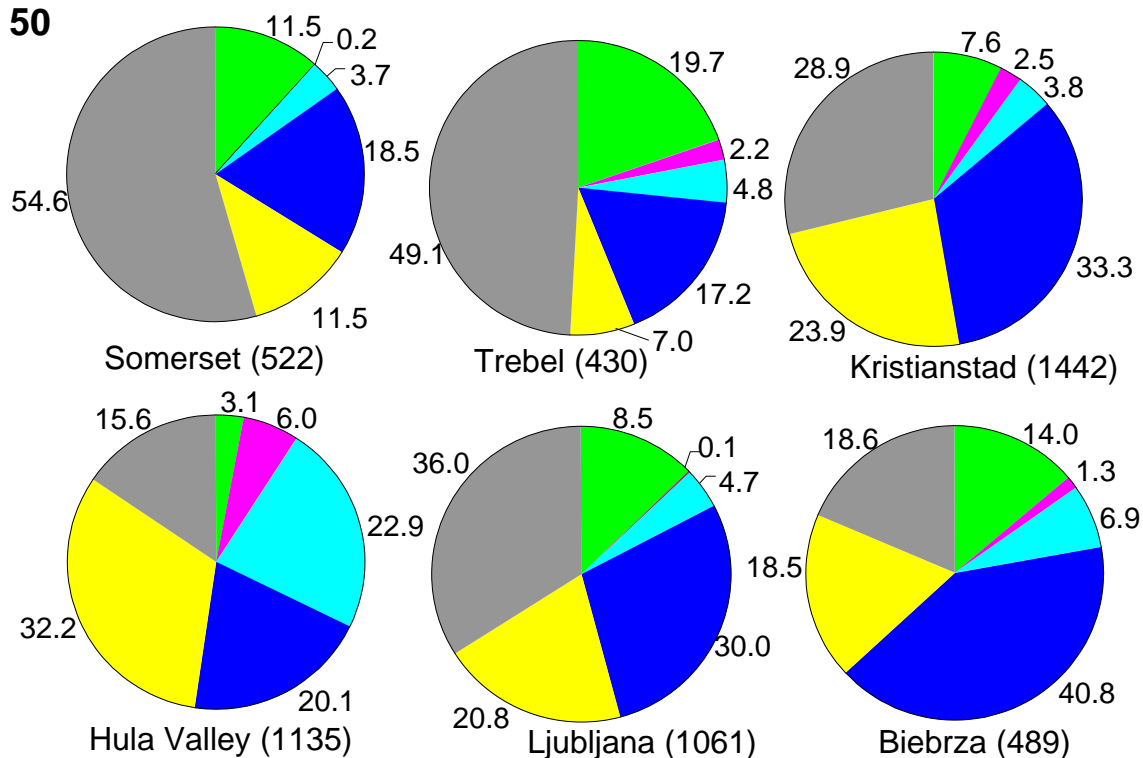
The depth distribution of **$NaHCO_3$-$P_o$** indicated clear differences between sites. The largest proportion was found at Trebel topsoil (5 %), but it decreased to < 1 % towards the 50-70 cm soil depth. Large $NaHCO_3$-P proportions throughout the profiles were observed for Hula and Kristianstad (3-6 %). Somerset and Ljubljana had < 1 % of $P_t$ in the $NaHCO_3$-$P_o$ fraction at all soil depths. Labile $P_o$ forms (e.g., nucleic acids and phospholipids) were positively correlated with biomass C (TATE & NEWMAN, 1982). Therefore, the profile differences are explained by differences in aeration and microbially driven mineralisation of this fraction, which probably were comparably strong at Somerset and Ljubljana sites during sampling. Generally, the small proportions of $NaHCO_3$-$P_o$ to a certain extent can be explained by chemical hydrolysis of $P_o$ to $P_i$ during alkaline extractions, as observed previously by other workers (IVANOFF et al., 1998). This can represent a serious limitation to the chemical extraction of $P_o$. For example, during 16 h extractions of selected, reagent-grade organic compounds, IVANOFF et al. (1998) reported 6% hydrolysis of glycerophosphate in 0.5 M $NaHCO_3$ and 41% hydrolysis of D-glucose-6-phosphate in 0.5 M NaOH.

Legend: Resin-P + NaHCO$_3$-P$_i$ | NaHCO$_3$-P$_o$ | NaOH-P$_i$ | NaOH-P$_o$ | H$_2$SO$_4$-P | Residual-P

**0 - 20 cm**

Somerset (1100): 8.8, 0.1, 5.3, 36.8, 23.8, 25.2

Trebel (1309): 9.9, 5.2, 6.3, 28.2, 23.9, 26.6

Kristianstad (1789): 5.3, 2.7, 1.7, 39.3, 28.2, 22.8

Hula Valley (1239): 3.8, 2.6, 17.0, 12.2, 50.7, 13.8

Ljubljana (1815): 6.1, 0.2, 5.5, 24.5, 25.6, 38.1

Biebrza (1355): 13.3, 1.0, 11.7, 32.7, 28.0, 13.3

**20 - 50 cm**

Somerset (522): 11.5, 0.2, 3.7, 18.5, 11.5, 54.6

Trebel (430): 19.7, 2.2, 4.8, 17.2, 7.0, 49.1

Kristianstad (1442): 7.6, 2.5, 3.8, 33.3, 23.9, 28.9

Hula Valley (1135): 3.1, 6.0, 22.9, 20.1, 32.2, 15.6

Ljubljana (1061): 8.5, 0.1, 4.7, 30.0, 20.8, 36.0

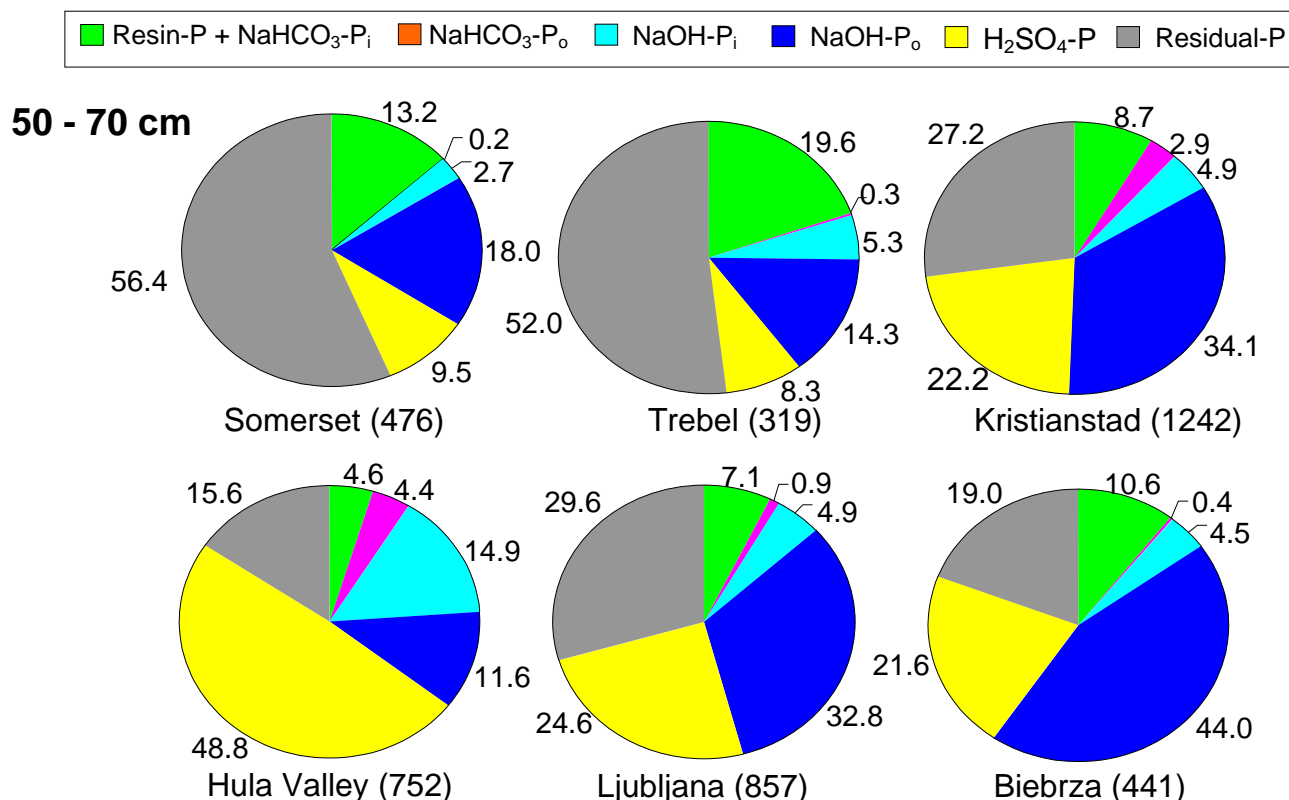Biebrza (489): 14.0, 1.3, 6.9, 40.8, 18.5, 18.6

**Figure 4.4** Labile and non-labile pools of P in the 0-20, 20-50 and 50-70 cm soil depths for the different sites (% of $P_t$; values in parentheses are soil $P_t$, mg kg$^{-1}$).

Correlations were calculated to explain the concentrations of **sequentially extracted P fractions as a function** of total elemental composition, extractable metals and P, organic matter contents and pH (Table 4.2). The total contents of metals were significantly correlated with all P fractions (except $Mn_t$ with resin-$P_i$). Correlations were particularly good for NaOH-$P_o$ and $H_2SO_4$-P. According to HEDLEY et al. (1982), the NaOH-$P_o$ fraction comprises low molecular weight monoester P forms that are strongly chemisorbed to amorphous and crystalline oxyhydroxide and oxide surfaces. The general binding mechanisms are confirmed by these correlations. The relationships closer for total concentrations of Fe, Al and Mn than for the oxalate-extracted concentrations of these elements indicate that in addition to amorphous minerals also crystalline pedogenic oxides may be involved in the binding of NaOH-$P_o$.

In mineral soils, $H_2SO_4$-P is interpreted as chemically stable Ca-phosphate (WALKER & SYERS, 1976; TIESSEN et al., 1984; WAGAR et al., 1986). The absence of a significant correlation between the concentrations of $H_2SO_4$-P and $Ca_t$ along with the relationships between $H_2SO_4$-P and total and oxalate-extracted Fe, Al and Mn, very similar to the relationships for NaOH-$P_o$, indicates that the $H_2SO_4$-P fraction also contains organically bound P in association with pedogenic oxides. The low solubility perhaps originates from the diffusion of the P into, or occlusion in, crystalline Fe-, Al- and Mn-oxides. With a few exceptions, the contents of oxalate-extracted metals were most closely correlated with NaOH-$P_o$ and $H_2SO_4$-P (Table 4.2). The present data to a certain extent confirm the findings of VANCE et al. (1996) who emphasized the importance of organo-aluminum-complexes in the NaOH-$P_o$ fraction of organic soils. The weaker, mostly insignificant correlations for the labile fractions (resin-$P_i$ to $NaHCO_3$-$P_o$) suggest that poorly crystalline pedogenic oxides in these soils contribute to the more stable, less labile or exchangeable P fractions. This seems to be a significant difference to mineral soils, in which poorly crystalline pedogenic oxides are important binding sites for P (PARFITT, 1978). The relationships between stable P fractions and concentrations of both, total and extractable metals, indicate parallel residual enrichments of P and metals upon peat degradation and oxidation. This is supported by the negative correlation between P fractions and $C_t$ contents. Progressive peat oxidation, resulting in decreased $C_t$ contents, led to residual P enrichments in the more stable fractions dominated by pedogenic oxides as binding partners. On the other hand, this relationship also could originate from the interference of peat degradation and parallel organic C loss and P inputs along with agricultural land use.

The concentrations of $P_{ox}$ and $P_{dl}$ were significantly correlated with the concentrations of all sequentially extracted P fractions, similar to the relation-ships found for $Fe_t$ and $Al_t$. The $P_{ox}$ accounted for 33-56 % of $P_t$ in these soils. The oxalate extraction was proved to solubilise poorly crystalline pedogenic oxyhydroxides (SCHWERTMANN, 1964) as well as proportions of Fe bound in organic complexes (BASCOMB, 1968). The large proportions of $P_{ox}$ as a percen-tage of $P_t$, and the correlations with all sequentially extracted P fractions and the total contents of metals indicate that P-metal interactions occur in all P fractions. In other words, there is no sharp distinction between fractions with respect to the involvement of metals in P binding. In conclusion, this suggests that environmental changes altering the binding capacity of the pedogenic metal oxyhydroxides have an influence on mobilisation of phosphate.

The relationship between the $P_{dl}$ fraction and all sequentially extracted P fractions indicates that in addition to the labile P fractions (resin-P, $NaHCO_3$-P) the relatively stable P fractions (NaOH-P, $H_2SO_4$-P and residual P) may contribute to plant-available P. Root exudate effects on pedogenic oxides and hydrolysis of organic P-compounds could be possible mechanisms for P mobilisation and transfer into the plant-available pool. However, the chemical identity of $P_{dl}$, and the validity of interpretations derived for mineral soils need to be checked for organic soils.

Table 4.2 Matrix of the Pearson correlation coefficients for linear relationships between chemical properties and the concentrations of sequentially extracted P-fractions (mg kg$^{-1}$) (n = 31). Significance level of correlations: ** $P < 0.01$ and * $P < 0.05$ (2-sided test)

| | Resin-$P_i$ | $NaHCO_3$-$P_i$ | $NaHCO_3$-$P_o$ | NaOH-$P_i$ | NaOH-$P_o$ | $H_2SO_4$-P | Residual-P |
|---|---|---|---|---|---|---|---|
| $Fe_t$ | 0.425* | 0.588** | 0.565** | 0.604** | 0.820** | 0.774** | 0.552** |
| $Al_t$ | 0.405* | 0.567** | 0.569** | 0.593** | 0.817** | 0.770** | 0.591** |
| $Mn_t$ | n.s. | 0.520** | 0.584** | 0.459** | 0.848** | 0.774** | 0.471** |
| $Ca_t$ | n.s. | - n.s. | - 0.483** | - n.s. | - 0.471** | - n.s. | - 0.490** |
| $C_t$ | - n.s. | - n.s. | - 0.413* | - n.s. | - 0.703** | - 0.668** | - 0.593** |
| $N_t$ | 0.419* | n.s. | n.s. | n.s. | - n.s. | - n.s. | - 0.551** |
| $S_t$ | - n.s. | n.s. | n.s. | - n.s. | n.s. | - n.s. | n.s. |
| $Fe_{ox}$ | n.s. | n.s. | 0.389* | 0.459** | 0.493** | 0.497** | - n.s. |
| $Al_{ox}$ | - n.s. | n.s. | n.s. | n.s. | 0.571** | 0.566** | 0.631** |
| $Mn_{ox}$ | n.s. | n.s. | 0.524** | n.s. | 0.774** | 0.704** | n.s. |
| $P_{ox}$ | 0.646** | 0.673** | 0.625** | 0.800** | 0.961** | 0.974** | 0.371* |
| $P_{dl}$ | 0.486** | 0.506** | 0.378* | 0.698** | 0.791** | 0.800** | 0.454* |
| pH | n.s. | - n.s. | - 0.449* | n.s. | - n.s. | - n.s. | - n.s. |

## 4.3 $^{31}$P NMR Spectroscopy

Samples from 5 Histosol profiles were prepared for liquid-state **$^{31}$P-NMR spectroscopy**. In these studies a newly developed, improved extraction procedure including pre-treatment with 1 $M$ KCl to remove labile $P_i$, extraction with NaOH/EDTA mixture and passing through a Chelex-100 column to remove paramagnetic species (ROBINSON et al., 1998) was applied.

The concentrations of labile P in the 1 $M$ KCl-extracts always were < 5 mg kg$^{-1}$, equivalent to < 1 % of $P_t$ (not shown). These values were smaller than KCl-P found in previous investigations of peat soils (REDDY et al., 1995; KOCH

& REDDY, 1992; ROBINSON et al., 1998). Much more P was extracted by NaOH/EDTA. Concentrations of 96 to 1134 mg P kg$^{-1}$ corresponded to 40 to 76 % of soil $P_t$ (Table 4.3). The contents of soil-$P_t$ and NaOH/EDTA-$P_t$ were largest in topsoils and decreased with profile depth. This is an indicator of peat degradation and intensive land-use. The relative proportions of NaOH/EDTA-$P_t$ as a percentage of soil-$P_t$ did not show clear trends with profile depth which can be interpreted by differences in peat forming vegetation and mineral admixtures.

The **$^{31}$P NMR spectra** recorded had quite different signal/noise ratios. The signal/noise ratios decreased with increasing profile depth. This is explained by the $mR_{Fe/P}$, and partly $mR_{Mn/P}$, which increased with profile depth and reflected the influence of paramagnetic materials on the NMR spectra (Table 4.3). This effect could not be substituted for by an increased scan number. Good spectra quality was achieved at $mR_{Fe/P} < 5$ and 25.000 to 50.000 Scans. Furthermore, the $mR_{Ca/P}$ was > 10 in some samples. Large concentrations of $Ca^{2+}$ can compete with $Fe^{2+}$ for adsorption by Chelex 100 (SIGMA$^{®}$) and reduce the efficiency of Fe-removal from samples. The $^{31}$P-NMR spectra from the Ljubljana samples had the best signal/noise ratios (Figure 4.5).

About 19 different peaks were observed in the spectra which were assigned to **three groups of P-compounds**: ortho-$P_i$, ortho-P-monoester ($\delta$ = 4,22 ppm) and P-diesters ($\delta$ = 0,68 and –0,88 ppm). Since internal standards are not used in $^{31}$P-NMR spectroscopy the chemical shift of the ortho-$P_i$-peak is the basis for spectra interpretation. This peak is usually observed at chemical shifts of 5.7 ppm (MAKAROV et al. 2002) or 5.98 bis 6.09 ppm (TURNER et al. 2003a). In the present investigations the ortho-$P_i$ peak was observed between 5.44 ppm (minimum) and 5.57 ppm (maximum). Difference from the literature data can be explained by differences in solution pH (CROUSE et al. 2000).
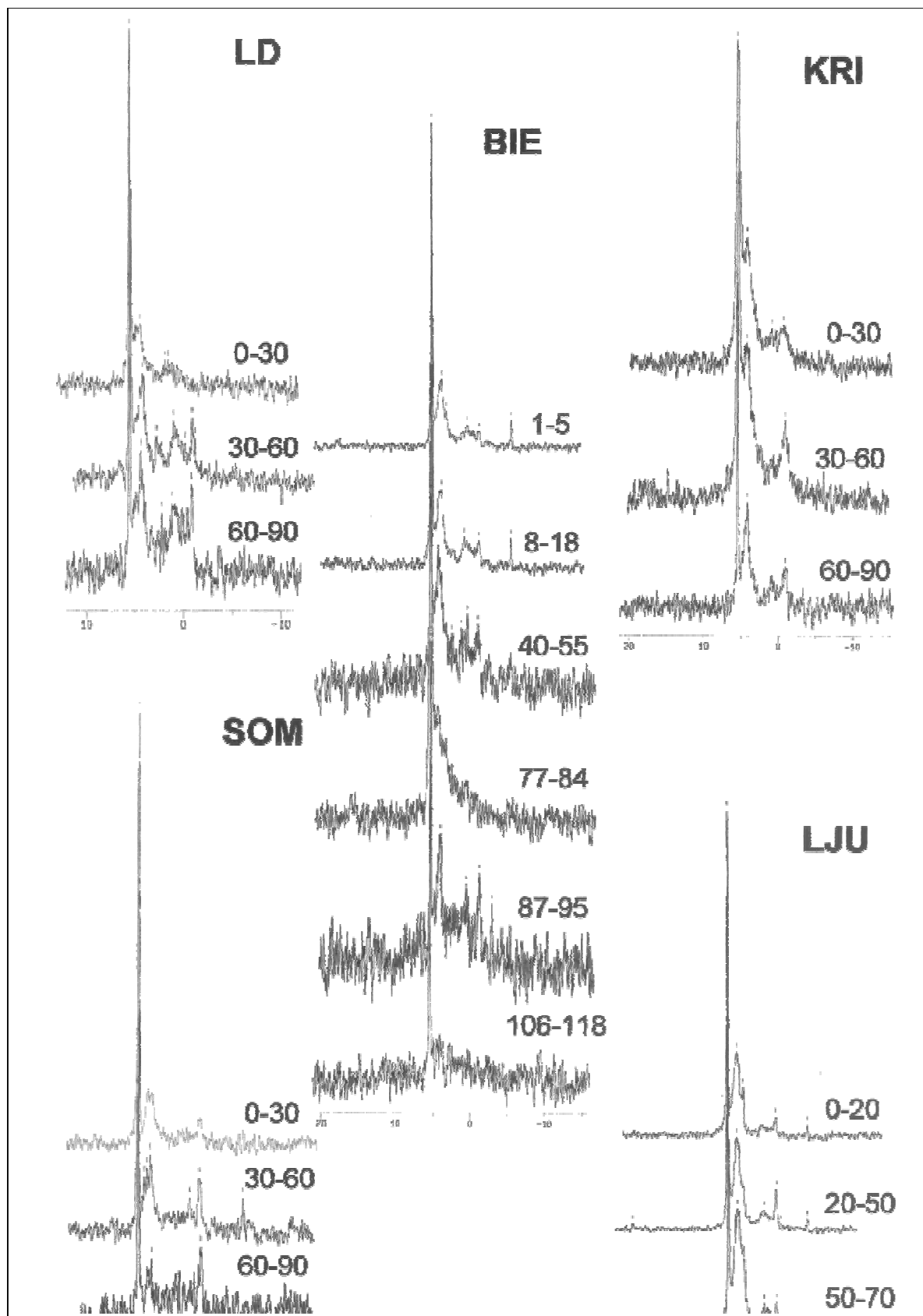
**Figure 4.5** 31P NMR spectra of samples from most European sites of the PROWATER project: LD = Langsdorf, Trebel Valley; BIE = Biebrza; KRI = Kristianstad; SOM = Somerset Levels and Moors,  LJU = Ljubljana;

**Table 4.3** Contents of soil-$P_t$, extractability of P by NaOH/EDTA and molar Fe/P-, Mn-P and Ca-P ratios in the NaOH/EDTA-extracts. SOM = Somerset Levels and Moors, LD = Langsdorf in the Trebel Valley, BIE = Biebrza, KRI = Kristianstad, LJU = Ljubljana

| Site | Profile depth | Soil-$P_t$ | $P_t$ | Proportion of $P_t$ | $mR_{Fe/P}$ | $mR_{Mn/P}$ | $mR_{Ca/P}$ |
|------|------|------|------|------|------|------|------|
| | [ cm ] | [ mg kg$^{-1}$ ] | | [%] | [mol mol$^{-1}$] | | |
| SOM | 0-30 | 1050 | 619 | 59 | 6.23 | 3.55 | 7.69 |
| | 30-60 | 253 | 153 | 61 | 9.54 | 2.02 | 8.66 |
| | 60-90 | 234 | 96 | 41 | 12.79 | 6.89 | 57.83 |
| LD | 0-30 | 1237 | 942 | 76 | 13.51 | 0.55 | 40.28 |
| | 30-60 | 457 | 286 | 63 | 11.57 | 2.30 | 28.06 |
| | 60-90 | 396 | 183 | 46 | 12.07 | 12.11 | 51.01 |
| BIE | 0-5 | 2128 | 1115 | 52 | 2.88 | 0.84 | 5.11 |
| | 5-18 | 1383 | 905 | 65 | 3.55 | 0.66 | 7.39 |
| | 40-55 | 841 | 333 | 40 | 16.03 | 3.04 | 34.53 |
| | 77-84 | 778 | 584 | 75 | 8.14 | 3.56 | 22.28 |
| | 87-95 | 204 | 123 | 60 | 27.75 | 25.79 | 71.96 |
| | 106-118 | 192 | 128 | 67 | 8.90 | 14.42 | 35.44 |
| KRI | 0-30 | 1099 | 800 | 73 | 9.41 | 0.64 | 1.15 |
| | 30-60 | 1284 | 558 | 43 | 7.74 | 0.65 | 0.98 |
| | 60-90 | 732 | 403 | 55 | 7.22 | 4.63 | 1.18 |
| LJU | 0-20 | 1815 | 1210 | 67 | 3.52 | 1.05 | 7.71 |
| | 20-50 | 1061 | 713 | 67 | 4.18 | 1.13 | 10.37 |
| | 50-70 | 857 | 622 | 73 | 4.98 | 1.07 | 14.98 |

Evidence for the validity of ortho-$P_i$-peak assignments is provided by the significant correlation with the photometrically determined ortho-$P_i$ (Figure 4.6). The increased deviations from the regression line, (in proportion with increased ortho-$P_i$ in topsoils) is explained by signal overlap in the $^{31}$P-NMR spectra.
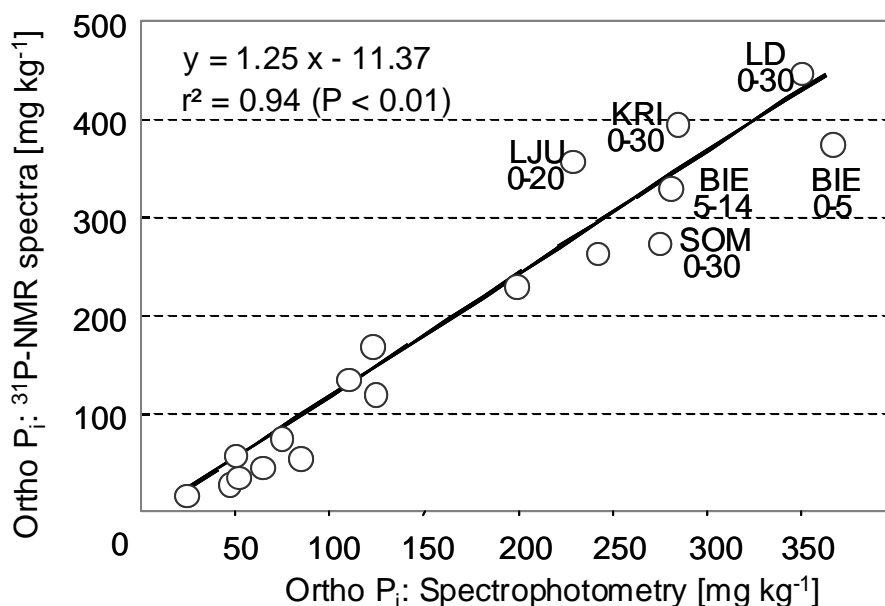
**Figure 4.6** Correlation between ortho-$P_i$ as determined by ^{31}P-NMR spectroscopy and ortho-$P_i$ as determined by spectrophotometry.

The peak area integration in the ^{31}P-NMR spectra revealed differences in the P pools among sites and within soil profiles (Table 4.4). The topsoils always had large proportions of ortho-$P_i$ (32 to 50 %) and of ortho-P-monoesters (31 to 51 % of NaOH/EDTA-$P_t$). P-diesters were less abundant (12 to 27 % of NaOH/EDTA-$P_t$). These ranges generally confirm data for peat soils by ROBINSON et al. (1998) who found 28 to 49 % of ortho-$P_i$, and by MAKAROV (1998) who found 33 % of ortho-P-monoester and 16 % of P-diesters.

At all sites, except Biebrza, the proportions of ortho-$P_i$ decreased with increasing soil depth. The gradients decreased in the order LD > KRI > LJU > SOM. The proportions of P-diesters increased with soil depth in the order LD > SOM > KRI. There was no consistent trend for the proportions of ortho-P-monoesters. The exception of Biebrza is explained by the very specific sequence of peat humification, composition of peat, mineral mud layers and admixtures which interfere with profile-dependent processes. Minor proportions of pyrophosphate (< 3 %) were observed in topsoils of the Biebrza and Ljubljana sites. Pyrophosphates are hydrolysis products of polyphosphates, which can originate from mineral P fertilizer (SUBBARAO et al., 1977). The abundance of pyrophosphate can be an indicator of recent applications (within months) of mineral P fertiliser (BLANCHAR & HOSSNER, 1969; SAVANT & RACZ, 1973).

**Table 4.4** Proportions of P-compounds in NaOH/EDTA-extracts as determined by $^{31}$P-NMR spectroscopy

| Site | Profile depth | Ortho-$P_i$ | Ortho-P-monoester | P-diester | Ratio mono-/diester |
|------|---------------|-------------|-------------------|-----------|---------------------|
| | [ cm ] | | [ % ] | | |
| SOM | 0-30 | 45 | 33 | 22 | 1.50 |
| | 30-60 | 33 | 33 | 33 | 1.00 |
| | 60-90 | 34 | 22 | 44 | 0.50 |
| LD | 0-30 | 48 | 31 | 21 | 1.48 |
| | 30-60 | 21 | 33 | 45 | 0.73 |
| | 60-90 | 22 | 28 | 49 | 0.57 |
| BIE | 0-5 | 34 | 37 | 26 | 1.42 |
| | 5-18 | 37 | 33 | 27 | 1.22 |
| | 40-55 | 24 | 36 | 30 | 0.95 |
| | 77-84 | 43 | 47 | 10 | 4.70 |
| | 87-95 | 17 | 27 | 56 | 0.48 |
| | 106-118 | 40 | 28 | 30 | 0.88 |
| KRI | 0-30 | 50 | 30 | 20 | 1.50 |
| | 30-60 | 42 | 28 | 29 | 0.93 |
| | 60-90 | 31 | 40 | 29 | 1.38 |
| LJU | 0-20 | 32 | 51 | 12 | 4.15 |
| | 20-50 | 26 | 48 | 22 | 2.22 |
| | 50-70 | 24 | 58 | 14 | 3.69 |

Ortho-P-monoesters originate from sugar phosphates and mono-nucleotides, and the peak at 4.22 ppm is one of the characteristic signals of *myo*-inositolhexaphosphate (TURNER et al., 2003a,b). P-diesters can originate from plant- and microbial-derived DNA and phospholipids. The relative enrichments of ortho-$P_i$ in topsoils, mostly at the expense of P-diesters, is explained by the mineralisation of plant- and microbes-derived diester-P-compounds (HAWKES et al., 1984; HINEDI et al., 1988). On the other hand, larger proportions of P-diesters in subsoils can result from a reduced mineralization rate due to restricted microbial populations and activity under anaerobic conditions. Furthermore, various enzymes are necessary for the mineralisation of P-diesters, which are inactive in subsoils. Additionally, the P-diesters possibly are more stable in subsoils if they contain lipopoly-saccharides which originate from external membranes of gram-negative bacteria (LIBBERT, 1991). Finally, the occurrence of free $Fe^{3+}$ in soil can reduce the degradation of esters in soil (MÖLLER et al., 2000).

The contents of ortho-P-monoesters ($y$ [mg kg$^{-1}$]) were correlated with the mean annual values of climatic factors:

$y = 0.037 \times$ precipitation [mm] $- 4.56 \times$ temperature [°C] $+ 46.0$; $r^2 = 0.992^{**}$ (topsoils)

$y = 0.037 \times$ precipitation [mm] $- 4.30 \times$ temperature [°C] $+ 44.1$; $r^2 = 0.963^*$ (subsoils)

Similar relationships between $P_o$ and climatic factors were reported for mineral soils (TATE & NEWMAN, 1982; SUMANN et al., 1998; AMELUNG et al., 2001). This indicates, that wetter and cooler climatic conditions favour the enrichment of ortho-P-monoesters. This agreement suggests that the reactions leading to the stabilisation of P-monoesters may be the same in mineral and organic soils.

In summary, peat aeration and Histosol use led to enrichments of exchangeable $P_i$, most probably bound to pedogenic oxides, and of rather stable ortho-P-monoesters in topsoils. Inositolphosphates, the main group among ortho-P-monoesters, as well as ortho-$P_i$ are stabilised in soil by interactions with Al-, Fe- and Ca-compounds. The field measurement indicated that the Fe-compounds will be reduced and become soluble under the conditions of re-wetting. Hence, the NMR-data showed that P compounds were enriched in topsoils that are susceptible to mobilisation under anaerobic conditions.

## 4.4 New evidence for the P pools in fen peat soils

This chapter aims to integrate the previous results on the chemistry of P compounds in the fen peat soils obtained by different complementary methods. Inorganic forms of P were extracted (1) sequentially by anion exchange resin, $NaHCO_3$ and NaOH, and (2) by NaOH/EDTA according to ROBINSON et al. (1998) and quantified in the $^{31}$P NMR spectra. The sums of $P_i$ in the sequential fractionation (158 $\pm$ 32 mg kg$^{-1}$) were smaller than ortho-$P_i$ from NaOH/EDTA-extraction and $^{31}$P NMR (193 $\pm$ 34 mg kg$^{-1}$). Accordingly, more $P_o$ (372 $\pm$ 242 mg kg$^{-1}$) was extracted by NaOH/EDTA than by $NaHCO_3$ and NaOH-$P_o$ (313 $\pm$ 231 mg kg$^{-1}$). This confirms the suitability of the NaOH/EDTA extraction for the as pre-treatment for $^{31}$P NMR spectroscopy of organic soils. Thus, in the present sample set we achieved a better recovery of $P_o$ than in sample sets from organic soils in the Everglades (ROBINSON et al. 1998). Despite these slight differences the results of the two analyses were correlated and complemented each other. Ortho-$P_i$ from $^{31}$P-NMR was

significantly correlated with resin-Pi ($r^2 = 0.273$; $P < 0.05$) and NaOH-$P_i$ ($r^2 = 0.382$; $P < 0.01$).

Table 4.5 shows relationships between P compounds determined by $^{31}$P NMR spectroscopy and sequentially extracted organic P forms. NaHCO$_3$-$P_o$ as the most labile organic P form was correlated with the contents of ortho-P-diesters. The rather stable P forms were correlated with the contents of ortho-P-monoesters. This difference confirms that ortho-P-monoesters are more stable than diesters, which was previously reported for humic acids and soils (NEWMAN & TATE, 1980; HINEDI et al., 1988; BEDROCK et al., 1994; MAKAROV et al., 1996; MÖLLER et al., 2000). The ortho-P-monoesters are stabilised in soil by reactions with pedogenic oxyhydroxides (STEWART & TIESSEN, 1987). ANDERSON (1980) showed that the high charge density in inositol phosphates favours the formation of relatively insoluble complexes with Fe and Al which protect the inositol phosphates from further degradation.

Table 4.5 Matrix of the Pearson correlation coefficients for linear relationships between the concentrations of sequentially extracted organic P-fractions (mg kg$^{-1}$) and organic P-compounds as determined by $^{31}$P-NMR-spectroscopy (mg kg$^{-1}$) (n = 20). Significance level of correlations: ** $P < 0.01$ and * $P < 0.05$ (2-sided test) [1] $P_{o,s}$ = NaHCO$_3$-$P_o$ + NaOH-$P_o$

| | NaHCO$_3$-$P_o$ | NaOH-$P_o$ | $P_{o,s}$[1] | Residual-P | $P_{o,s}$ + Residual-P |
|---|---|---|---|---|---|
| Ortho-P-monoesters | 0.282 | 0.640** | 0.625** | 0.520* | 0.725** |
| Ortho-P-diesters | 0.650** | 0.724** | 0.736** | 0.118 | 0.601** |
| Sum ortho-P-esters | 0.433 | 0.732** | 0.724** | 0.438 | 0.756** |

## 5. Peat transformations and P release in microcosm studies

Three sets of microcosms studies were designed to follow different pathways of P release: (1) In the Trebel Valley soils we intended to disclose relationships between redox potential, release of soluble reactive P and changes in sequentially<extracted P fractions. (2) In the Hula Valley we hypothesized predominance of microbial-driven geochemical transformations that lead to release of adsorbed P. (3) In the Ljubljana marsh, based on temperature dependence of P release rate, we hypothesized the predominance of P mineralization from the degraded soil organic matter.

Therefore, the general **objective of microcosm studies** was to follow processes of P release from soils of various wetland sites that differed much in their climatic conditions and soil properties. Understanding these processes is of great importance both for giving the basic information to draw guidelines for soil and water-table management, and for establishing a conceptual model, that will serve as a basis on which kinetic terms for each of its components will be added to form a quantitative model, that in combination with an hydrological model will allow reliable prediction of P loss from the studied sites

### 5.1 Histosols from the Trebel Valley

The microcosm experiments with Histosols from the Trebel Valley were aimed to disclose the dependence of soluble reactive P (SRP) concentration on redox potentials and to find out changes in the amounts and proportions of sequentially extractable P-forms during re-wetting.

Investigations were carried out for two diagnostic horizons (5-20 and 20-40 cm profile depth) which were expected to be flooded due to re-wetting. Furthermore, the samples were selected according to their distinct physical and chemical soil properties (Table 5.1).

Homogenised samples were incubated in dark chambers at different temperatures (6°C and 20°C) under conditions comparable to those in field (original bulk density). The SRP concentrations varied strongly among different peat samples and temperature regimes. For LD05-20 mean values of $0.077 \pm 0.072$ mg $l^{-1}$ (6°C) and $0.253 \pm 0.307$ mg $l^{-1}$ (20°C) were observed. For LD20-40 the concentrations were much lower (6°C: $0.024 \pm 0.017$ mg $l^{-1}$; 20 °C: $0.069 \pm 0.058$ mg $l^{-1}$). The t-test for independent sample sets resulted in significant differences between the single values (n = 30) of measured SRP concentrations (6°C: P < 0.001; 20°C: P < 0.005) and an uniformity of variance (Levene-test; P < 0.001). Figure 5.1a shows the temporal variation of the SRP

concentrations (mean values in mg $l^{-1}$) and the redox potentials (minimum and maximum values in mV) during the incubation at 20°C for the two peat samples. Highest variations within the 5 replicate redox measurements were observed for LD20-40. In the two both peat samples the redox potentials decreased continuously within the first 90 days, meanwhile the SRP concentrations gradually increased. After this period fluctuations of the Eh values led to equivalent changes in SRP concentrations, which are visualised by values of mean and standard deviation and significant correlations ($P <$ 0.05) in Figure 5.1b.

Table 5.1  Chemical properties of the peat soil (profile depths 0-20 and 20-40 cm) from the Langsdorf site (LD, Trebel Valley) used for microcosm experiments; means ± standard deviation (SD) of replicated analyses (* SD < 0.01)

|  |  | LD05-20: 5–20 cm | LD20-40: 20–40 cm |
|---|---|---|---|
| pH | - | $5.65 \pm 0.20$ | $5.74 \pm 0.11$ |
| LOI | % | $80.1 \pm 0.1$ | $83.8 \pm 0.1$ |
| $C_t$ | % | 37.9* | 41.0* |
| $N_t$ | % | 2.77* | 2.73* |
| $P_t$ | mg kg$^{-1}$ | $1276 \pm 12$ | $692 \pm 8$ |
| $P_{dl}$ | mg kg$^{-1}$ | $30.7 \pm 0.9$ | $11.6 \pm 1.3$ |
| $P_{ox}$ | mg kg$^{-1}$ | $607 \pm 5.1$ | $226 \pm 8.2$ |
| $Fe_{ox}$ | mg kg$^{-1}$ | $18862 \pm 307$ | $14255 \pm 273$ |
| $Al_{ox}$ | mg kg$^{-1}$ | $808 \pm 5.1$ | $521 \pm 14.6$ |
| $Mn_{ox}$ | mg kg$^{-1}$ | $247 \pm 3.0$ | $133 \pm 0.8$ |

In addition to the acquisition of the redox potentials and the SRP concentrations, P forms in the soil were analysed. Before and after the experiments the peat samples were subjected to double-lactate extraction (RIEHM, 1948) and sequential P fractionation according to HEDLEY et al. (1982). The $P_{dl}$ concentrations increased by 36 to 44 % during the incubation compared to the initial concentrations shown in Table 5.1: The greatest changes occurred in the sampled incubated at 6°C.
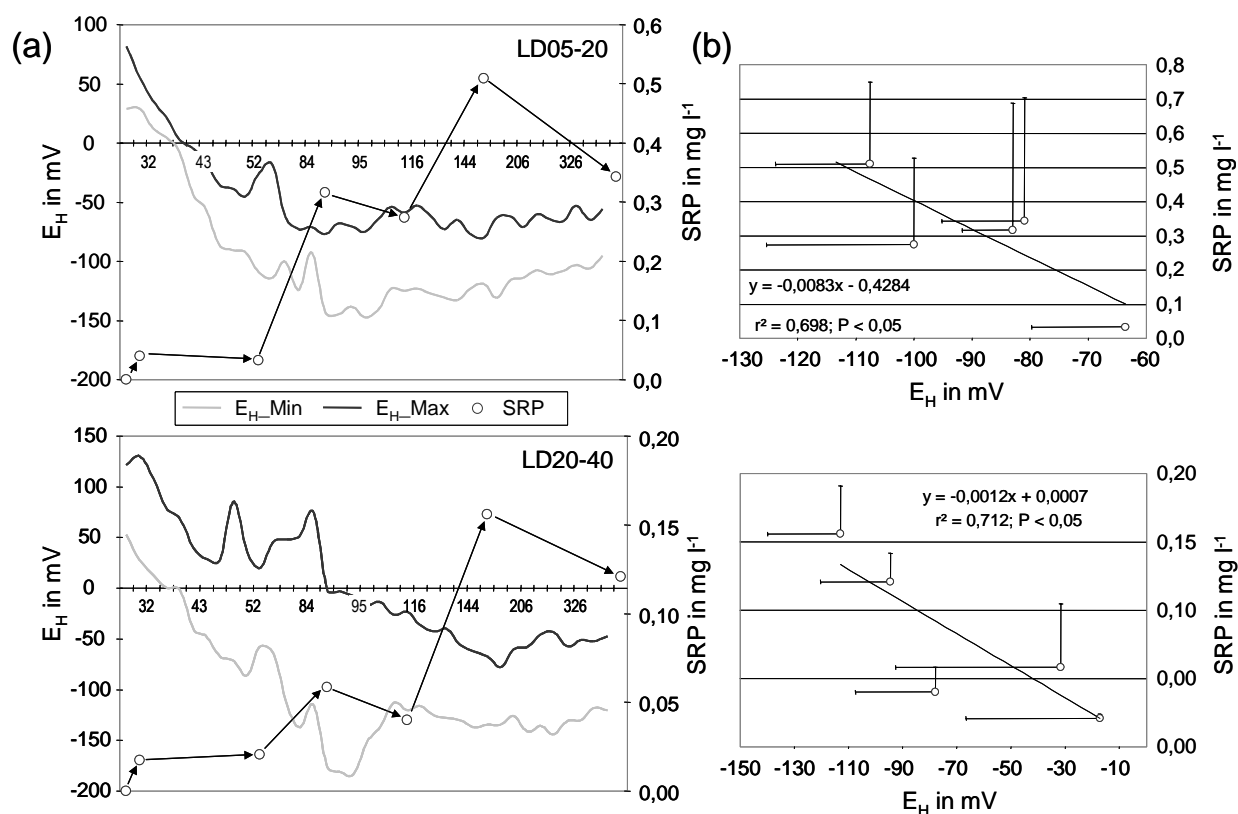
**Figure** 5.1  Redox potential and SRP concentrations in the microcosm experiments with Trebel Valley peat at 20°C: (a) time dependence and (b) their relationships
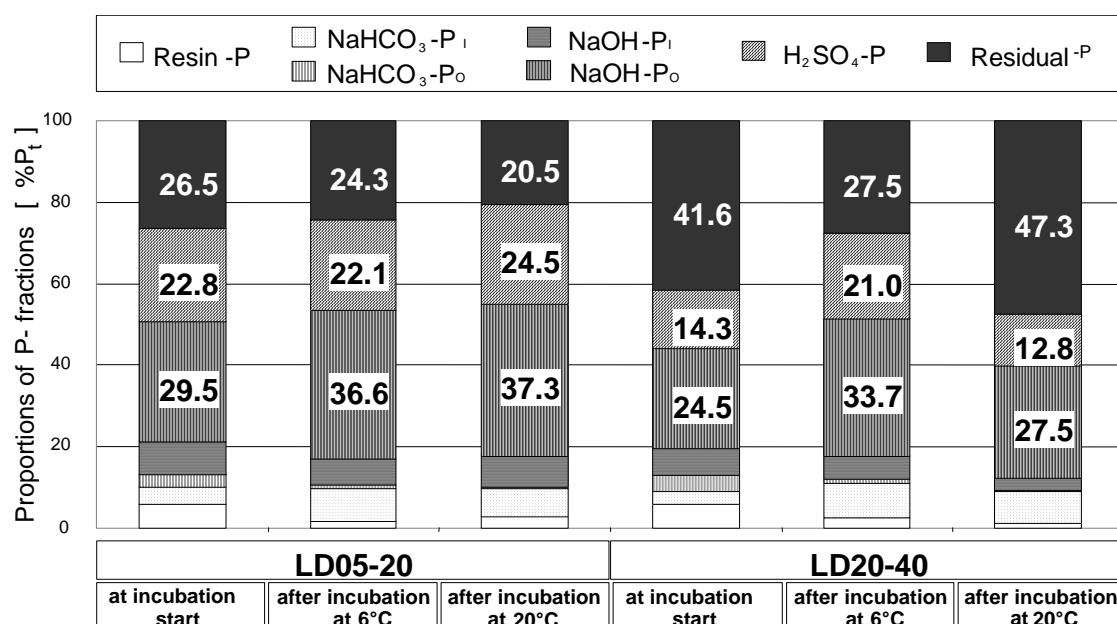


**Figure** 5.2  Proportions of the sequentially extracted P fractions before and after Incubation of two peat horizons at 6 and 20°C

The **sequential P extraction** (Figure 5.2) pointed to a relative mobilisation of P as indicated by the increase in the sum of all extractable P-fractions during re-wetting in all variants, except for sample LD20-40 at 20°C. This high temperature, however, is clearly above the temperatures under field conditions. On the other hand, there was a decrease of labile-P (resin-P + $NaHCO_3$-$P_i$ + $NaHCO_3$-$P_o$ = -2.6 ± 1.0 %) in all experiments. While resin-P clearly decreased and the proportion of $NaHCO_3$-$P_o$ was reduced to a minimum, proportions of $NaHCO_3$-$P_i$ increased up to factor 3.

The incubation of the deeper horizon at 6°C resulted in the highest increase in sum of all extractable P-fractions (+14.1 %), but in the smallest decrease of labile-P (-1.1 %). The temperature affected the P-fractions in the deeper horizon much more than in the upper horizon. The proportions of all fractions for LD20-40 at 6°C and 20°C where significantly different and showed considerable increases especially for $NaOH$-$P_o$ (9.2 %) and for $H_2SO_4$-P (6.7 %) at 6°C. For the upper horizon there was only a significant difference in resin-P and $NaHCO_3$-$P_o$.

Figure 5.3 shows how the sequential P fractions from anaerobic incubation in the laboratory compare to the P fractions from the field study (Langsdorf, Trebel Valley) at project start and after 18 months of re-wetting.
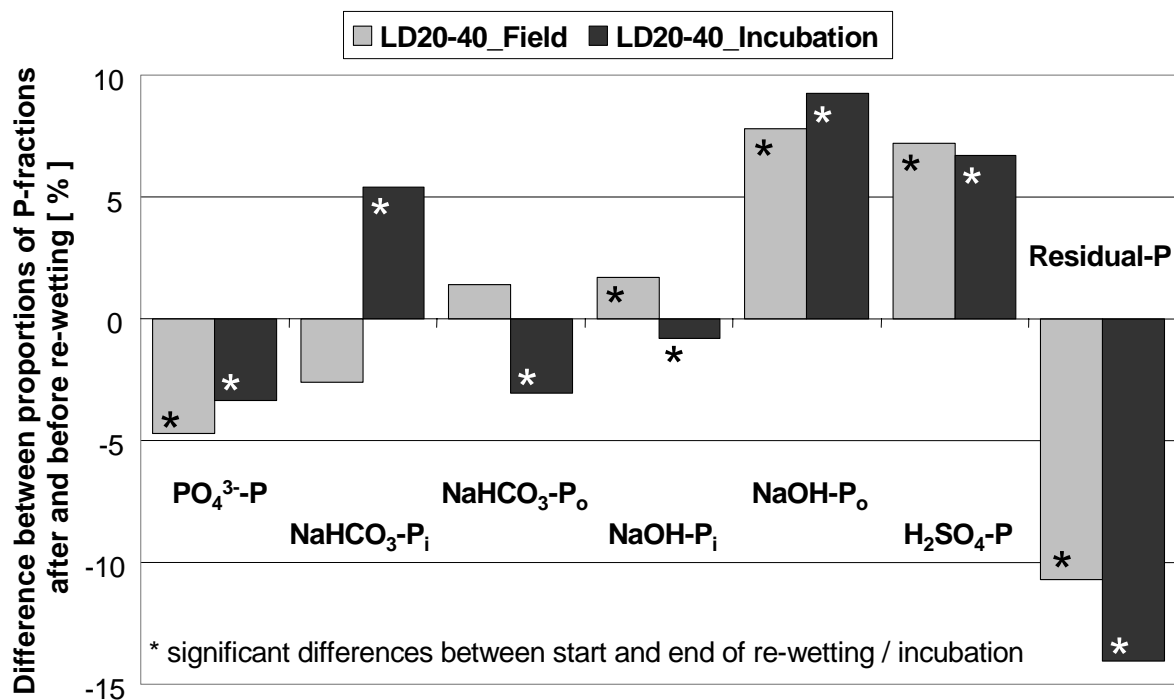


Figure 5.3 Influence of re-wetting on distribution of P-fractions: comparison between field observations and results from incubation at 6°C in microcosms

The only significant changes observed for field samples were decreased proportions of resin-P ($PO_4^{3-}$-P) and of $NaHCO_3$-$P_o$ in the upper layer (5-20 cm) following re-wetting. For the underlying horizon (20-40 cm) the proportions of resin-P, $NaOH$-$P_o$ and $H_2SO_4$-P increased, while residual-P significantly decreased. Compared with the results from microcosm experiments the significant changes in P-fractions from the deeper horizon (20-40 cm) and the incubation at 6°C were general agreement. This is explained by the similar environmental conditions. The soil temperature in field was on average 10.4 °C in the relevant time period. The mean water table was 17.6 cm below surface and the time of total flooding of this horizon was more than 2/3 of the whole period.

The significant correlations revealed from the microcosm experiments confirmed the predominant influence of the redox potential on P mobilisation and therefore for P concentration in soil solution. The redox potential depends on temperature regime. No significant differences in Eh values were found for the two types of peat substrates. Comparable results were reported by KOERSELMAN et al. (1993) during anaerobic incubation of sedge and moss peat. On the other hand SAH et al. (1989) and PHILLIPS (1998) illustrated, that a decrease of redox potential depends on the amount of organic matter.

The stabilisation of the Eh values within approximately 5 weeks (Figure 5.1a) during incubation experiments took much more time than previously reported (MARTIN et al., 1997; PONNAMPERUMA, 1972). Possibly, the slow reaction can related to a reduced access of easily available C for microbial activity and/or the redox buffer capacity of nitrate. The deviations between the replicates of redox measurement were relatively high during all experiments as also reported elsewhere (VEPRASKAS & WILDING, 1983). Such a wide variability among electrodes could be considered explained by different microsite environments in the soil (COGGER et al., 1992). Furthermore, there are several reports in the literature about factors, which can be possibly cause electrode failures, like poisoning (BAILEY & BEAUCHAMP; 1971; BOHN, 1971), leakage (MANN & STOLZY, 1972) and epoxy breakdown (MUELLER et al., 1985). Therefore, redox buffer was used to check the electrodes for such malfunctions before and after their use in the experiments. The redox buffer consisted of hexacyanoferrat (II) and hexacyanoferrat(III) according to FUNK & SCHÄR (1998). Measurements were done under stepwise dilution (down to 5 % of the concentrated solution) with largest deviations of 5 mV before and 21 mV after incubation. Hence, the variation of the Eh values can not be explained by electrode malfunctions, but by microscale soil heterogeneity. Similar observation were reported for the field measurements.

Besides the redox potential, the P mobilisation under anaerobic conditions was also strongly influenced by the temperature. Similar to the results of BARROW & SHAW (1975) higher temperatures led to increased P concentrations in soil solution. Furthermore, the concentrations of $P_{dl}$ in the P-enriched peat significantly increased during the microcosm experiment. Corresponding to this results KOERSELMAN et al. (1993) observed higher concentrations of plant-available P (extraction with ammonium-lactate) in sedge peat after incubation due to higher temperature. According to MEHADI & TAYLOR (1988), BARROW (1975) and SAH et al. (1989) higher temperature can lead to an increased P sorption in the soil as observed for LD20-40.

In summary, the microcosm experiments confirmed the hypothesis, that long-term stable environmental conditions will have generally positive effects on the availability of P. However, these conditions are not valid for the experimental sites, where seasonal fluctuations occur and a maintenance of the water table is either not feasible (due to the absence of water) or unwanted (due to management strategies like grazing).

## 5.2 Histosols from the Hula Valley

To study the geochemistry and the P transformation processes in the peat soils of the re-wetted peat soils of the Hula Valley, an experimental setup was designed to follow the processes in controlled microcosms that simulate biological and geo-chemical conditions of the re-wetted soils. The evolved changes as measured in 4 representative soils of the valley incubated in the biogeochemical microcosms were compared to data collected in the field to approve similarity of the conditions and processes between the two systems. While soil profiles in the study area (Fig. 5.4) were composed of distinguished horizons that varied in their organic matter and $CaCO_3$ content, as well as in pH and other major soil characteristics, we used a uniform 120-cm soil column in the microcosms study. Thus, while in the field many interactions conceal the underlying processes and correlations between measured variables, we could relate the processes measured in the microcosms to the change of water table as a single major factor.

In the **laboratory**, a bottom-sealed 128-cm PVC column with internal diameter of 103 mm was used as a frame in which the following components were installed: (1) Three redox and three pH electrodes in depths of 30, 70, and 100 cm; (2) All electrodes were connected through electric resistor adaptors to a data logger, and pH and Eh were measured and recorded each 10 minutes; (3) Three water sampling tubes in the same three depths, each

connected inside the column to a porous cup and in the outer end to a 35-mL sampling syringe; (4) A water level control tube connected to the bottom of the column through a porous cup and to a 300-mL reservoir fixed at adjustable height. Four soils representing four soil types of the Hula Valley were used in the study: (1) a deep un-drained and un-degraded peat soil that was permanently below water table; (2) a calcareous soil developed in the outskirts of the swamps; (3) a shallow (50-60 cm) intensively cultivated decayed peat soil overlying organic-mineral material developed along the margins between the former Hula swamps and the Hula Lake (soil #9); and (iv) similar to soil #9 but left fallow for about 5 years (soil #10). The first soil was taken from the bottom of a deep (ca. 300 cm) fresh ditch while the later three were taken from the upper 5-20 cm layer at each site. The soils were thoroughly mixed with 0.1% (w/w) ground wheat straw, serving as an electron donor, and packed in the column to form a bulk density of ca. 1.3 kg $l^{-1}$. Water table was set in depth of 50 cm below soil surface. Soil solution samples were collected periodically from the saturated zone. Soils were sampled before packing in the microcosms and after 200 days of incubation.

In the **field sites**, automated stations measuring pH and redox at three depths (above and below water-table) were constructed at two sites in the Hula Valley: (1) site #10 with a profile composed of shallow degraded peat soil overlying marl layer; and (2) site #12 with a deep peat profile. All electrodes were connected through electric resistor adaptors to data loggers, and pH and Eh were recorded each 30 minutes. Shallow ground water from the saturated zone was sampled periodically through shallow wells. Water table was monitored periodically. Soil samples were collected by auger and stored at –20°C till analysis.

The following analyses were carried out: common soil tests (following SPARKS et al., 1996) were carried in triplicates for pH and organic matter and $CaCO_3$ content. Total P content was determined after $HClO_4$ digestion. Fe, Mn, and Al were determined in the same digest for total content; after ammonium oxalate extraction, for non-crystalline hydroxides content; and after citrate-bicarbonate-dithionite extraction, for total free hydroxides content. Water samples from microcosms and field were filtered through 0.45 μm filters immediately after sampling, pH and EC were measured and then samples were acidified for further analyses. Sub-samples were analysed immediately after sampling for $Fe^{2+}$ content using ferrozine and measuring absorbance of the Fe-(ferrozine)3 complex at 562 nm. All water samples and extracts were analysed colormetrically for dissolved inorganic P by the method of MURPHY & RILEY (1962). Total P in solutions was determined after digestion with $H_2SO_4$

and ammonium persulfate at 121°C. The dissolved organic P was calculated as the difference (total-P minus inorganic-P). Total dissolved Fe, Ca, Mn, and Al were measured by inductively coupled plasma-atomic emission spectroscopy (ICP-AES; Spectro, Germany) in the filtered and acidified samples. Phosphorus fractionation in the soil samples before and after incubation was carried by a modification of the Hedley procedure.

Table 5.2 Soil properties prior to incubation. Organic matter, weight loose in dry combustion; $CaCO_3$ by volumetric $CO_2$ measurement; pH in water extract; Total content of P, Fe, Al, and Mn by soil wet combustion with $HClO_4$. Presented data are averages ± standard deviations of 3 replicates.

| Soil | Organic matter / | $CaCO_3$ | pH | Fe (total) | Al (total) | Mn (total) | P (total) |
|------|------|------|------|------|------|------|------|
| | % | % | | % | % | g kg$^{-1}$ | g kg$^{-1}$ |
| #9 | 34.3±0.4 | 14.2±0.7 | 7.50±0.05 | 4.45±0.03 | 4.65±0.12 | 0.30±0.00 | 1.58±0.02 |
| #10 | 29.1±0.7 | 2.9±0.2 | 7.26±0.03 | 5.02±0.04 | 4.26±0.03 | 0.31±0.01 | 1.22±0.01 |
| Calc | 8.7±0.2 | 25.9±5.8 | 8.28±0.03 | 4.36±0.01 | 5.36±0.02 | 0.54±0.01 | 1.45±0.01 |
| Deep | 38.3±1.4 | 37.7±2.4 | 7.59±0.02 | 1.63±0.01 | 1.01±0.01 | 0.56±0.01 | 0.62±0.01 |

The **soil properties** of the Hula Valley samples prior to incubation are summarised in Table 5.2. Extractable Fe, Al, Mn, and P by CBD and ammonium oxalate are detailed in Table 5.3. The P content in peat soils from various locations and depths (data not shown) were found to negatively correlate with organic matter content and positively correlate with Fe-hydroxide content.

Table 5.3 Content of soil extractable Fe, Al, Mn, and P by citrate-bicarbonate-dithionite extraction (CBD) and ammonium oxalate at pH 3 in the dark (oxal). Presented data are averages ± standard deviations of 3 replicates.

| Soil | Fe (CBD) | Al (CBD) | Mn (CBD) | | P (CBD) | |
|------|----------|----------|----------|--|---------|--|
| | % | % | g kg⁻¹ | | g kg⁻¹ | |
| #9 | 2.68 ± 0.05 | 0.: ± 0.03 | 0.20 | ± 0.01 | 0.61 | ± 0.03 |
| #10 | 3.34 ± 0.06 | 0.∕ ± 0.01 | 0.23 | ± 0.01 | 0.48 | ± 0.02 |
| Calc | 1.95 ± 0.02 | 0.17 ± 0.00 | 0.34 | ± 0.00 | 0.30 | ± 0.00 |
| Deep | 0.41 ± 0.03 | 0.04 ± 0.00 | 0.14 | ± 0.01 | 0.08 | ± 0.01 |

| Soil | Fe (oxal) | Al (oxal) | Mn (CBD) | P (oxal) |
|------|-----------|-----------|----------|----------|
| | % | % | g kg⁻¹ | g kg⁻¹ |
| #9 | 2.39 ± 0.01 | 0.57 ± 0.01 | 0.17 ± 0.00 | 1.15 ± 0.02 |
| #10 | 3.19 ± 0.08 | 0.74 ± 0.01 | 0.18 ± 0.01 | 0.86 ± 0.01 |
| Calc | 0.55 ± 0.02 | 0.30 ± 0.02 | 0.18 ± 0.00 | 0.84 ± 0.01 |
| Deep | 0.51 ± 0.01 | 0.13 ± 0.00 | 0.09 ± 0.00 | 0.42 ± 0.00 |

Figure 5.4. shows the course of **pe+pH drop and concentrations of dissolved mineral Ca, Fe²⁺, P, Al, and Mn** after aerated peat top soil from site was submerged 50 cm below water table in the microcosm. The Eh above water table increased from +250 to +700 mV within 30 days and remained quite stable at this value for the next 8 months (data not shown). At depth of 50 cm below water table Eh dropped after submerging from +250 mV to -200 mV within 9 days in the deep peat and in the calcareous soils, 40 days in soil #10, and 53 days in soil #9. Reduction of $Fe^{3+}$ to $Fe^{2+}$ was found to start with pe+pH drop below 7 and increased sharply with pe+pH fall below 4. Phosphorus release coincides with Fe reduction and was shown to correlate with Fe and Mn, but not with Ca, Al, Zn, or Cu dissolution. Similar trends were found in Soil #10. In the calcareous soil redox had dropped faster and reached lower values than in the peat soils, indicating lower redox buffer capacity.
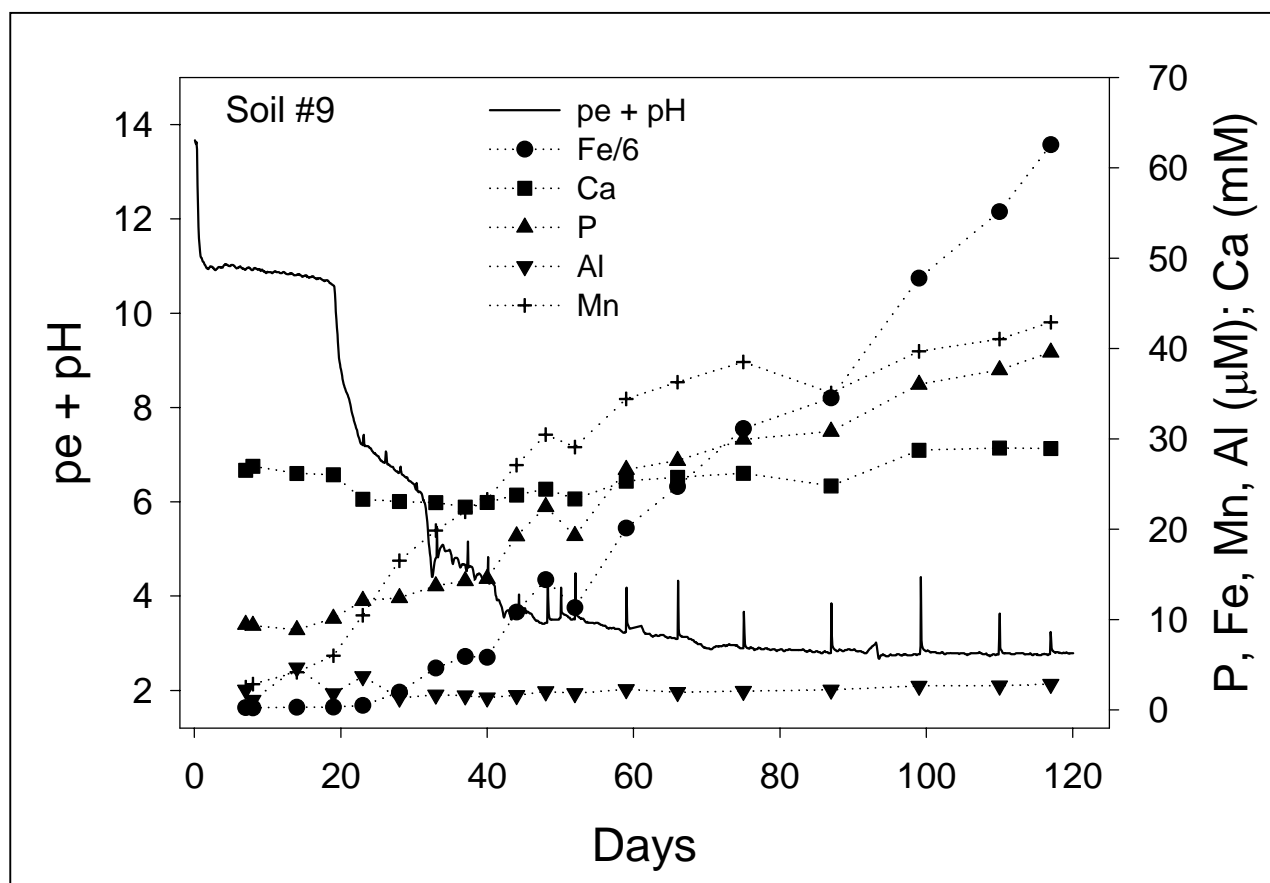
**Figure** 5.4 Content of soil extractable Fe, Al, Mn, and P by citrate-bicarbonate-dithionite extraction (CBD) and ammonium oxalate at pH 3 in the dark (oxal). Presented data are averages ± standard deviations of 3 replicates.

## Field redox and pH measurement in the Hula Valley

A six-month course of Eh measurements at 3 depths (30, 60, and 100 cm) in a station located in site #10 is shown in Figure 5.5. Water table was in depth of 37-58 cm below surface. The Eh above water level (at 30 cm depth) was stabilized after about 30 days in the range of +340 to +480 mV, while at and below water level it fell to the range of -180 to -200 mV. Similarly, a 78-day course of pe+pH at 3 depths (90, 150, and 190 cm below surface) was recorded at site #12. Water table during this period was in depth of 104-175 cm (not shown).
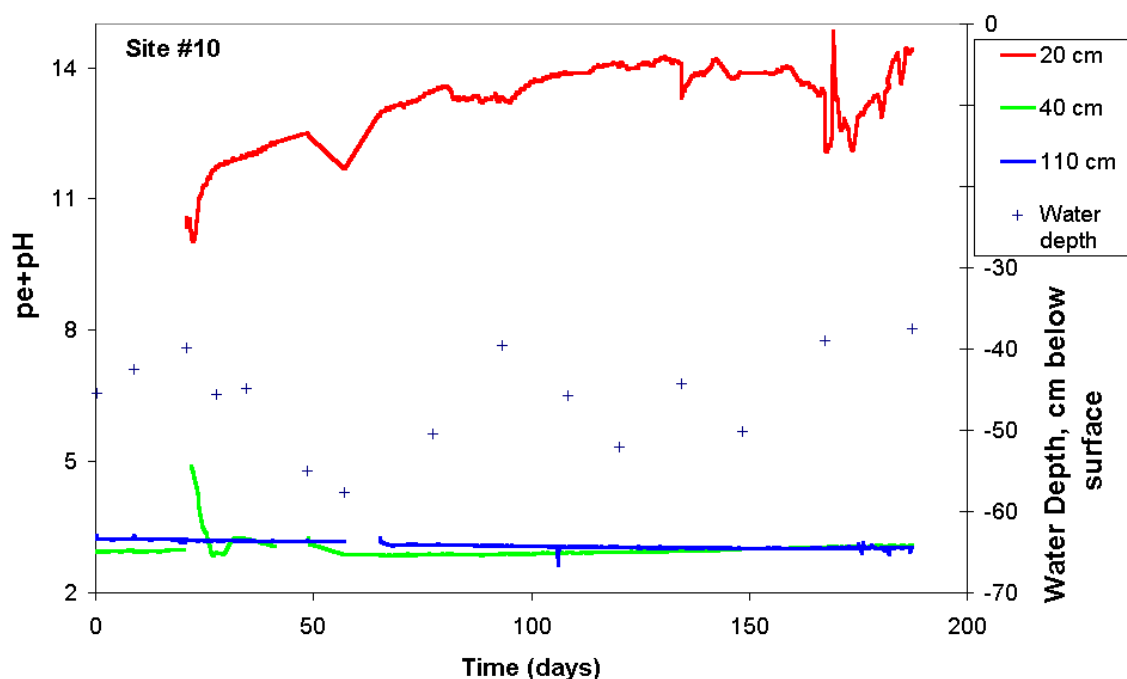
Figure 5.5 Redox potentials and water table depth in monitoring station #10 in the Hula Valley, shallow degraded peat soil overlying marl layer. Redox measurements taken every 30 minutes, June to December, 2002. Water table depth measurements taken manually.

The **similarity of Eh patterns in the biogeochemical microcosms to those measured in the field** indicates that the microcosms well simulated processes that take place in the field. Shallow groundwater samples exhibited high levels of up to 3 mg $l^{-1}$ dissolved P and high concentration of up to 900 µM $Fe^{2+}$. Concentrations of dissolved P and $Fe^{2+}$ were positively correlated in some shallow groundwater samples when correlation was tested for each site separately, however no such correlation was found among shallow groundwater sampled in a transect of a field along a hydrological gradient. We attributed the lack of spatial correlation to the complexity of P solubility in the study area, which is a product of myriad of processes such as adsorption-desorption, co-precipitation, and chemical equilibria of several chemical systems (Ca-P, Fe-P, Fe-$CO_2$-P, and Fe-S-P).

**Geo-chemical calculations: saturation indices and stability diagrams**

Geo-chemical calculations were carried out to indicate solid phases that might control the processes in the studied environments. For these calculations data were compiled from microcosm incubations and from field data of the Hula

Valley. Field data from Somerset (England, provided by Steve Robinson), Trebel Valley (Germany, provided by Andre Schlichting), and Droemling (Germany, provided by Holger Rupp) were included for comparison.

While solutions became **over-saturated for pyrite** as pe+pH fall below 4.5, actual precipitation is shown to begin only when pe+pH fall below 3.5 (Fig. 5.6A). Such low values were found in the calcareous soil in the microcosms study and in several field measurements. Indeed, stability diagrams indicate that down to pe+pH values of 4.4, Fe concentrations were controlled by ferric and ferric-ferrous hydroxides, while below pe+pH values of 3.5 most of the soil solutions were unsaturated in regard to these minerals. The low Fe activities in this low redox range are attributed to precipitation of pyrite (or other Fe-S minerals).

Microcosms and field data from the Hula Valley (Israel), and from field data from Somerset (England), Trebel Valley (Germany), and Droemling (Germany) were plotted on the **stability diagrams of Ca-P minerals** (Fig. 5.6B) and **Fe(III)-P minerals** (Fig. 5.6C). These diagrams indicate that P concentration in most soil solutions was controlled by quite stable minerals. The Hula soils (and those of Somerset, England) were controlled by the Ca-P system, however upon reductive P release from the degraded peat soils (#9 and #10) this system could not effectively retain the released P and keep its original saturation for the Ca-P minerals. Thus Ca-P minerals of lower stability had become over-saturated upon reduction (Fig. 5.6B) and may be formed in the soils. Indeed the Ca-P minerals were found to dominate soil P (by Hedley fractionation, data not shown) in the four Hula soils.
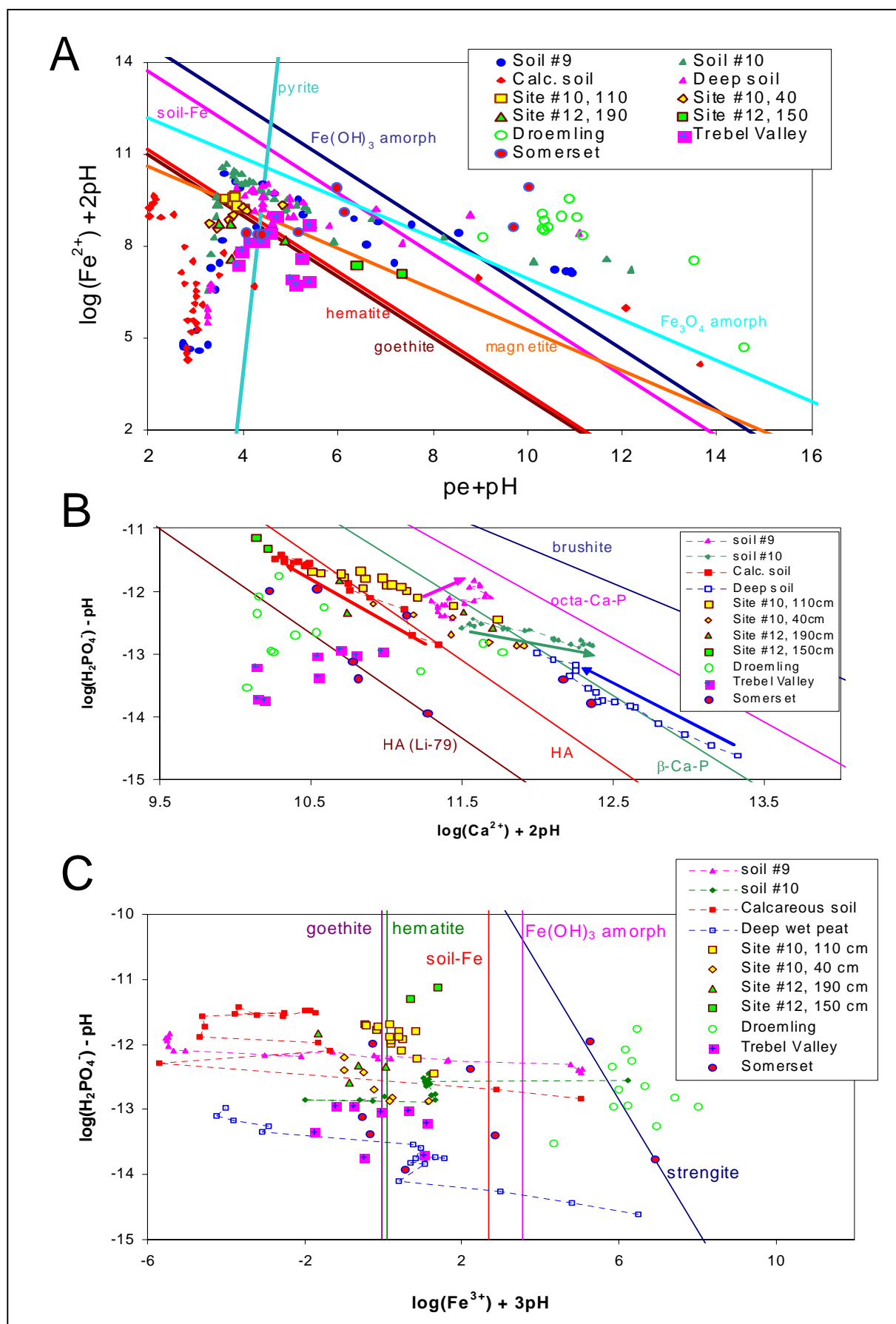
**Figure** 5.6 Soil solution data and stability diagram for various mineral phases from PROWATER experimental sites (for detailed description see next page).

A) Stability diagrams of selected Fe minerals and experimental data from the microcosms incubations and from field data from the Hula Valley (Israel), and from field data from Somerset (England), Trebel Valley (Germany), and Droemling (Germany).

B) Double-function chemical potentials of $H_2PO_4^-$ and $Ca^{2+}$ of experimental data from the microcosms incubations and from field data from the Hula Valley (Israel), and from field data from Somerset (England), Trebel Valley (Germany), and Droemling (Germany). Stability lines of brushite, octa-Ca-P, and β-Ca-P are plotted according to stability constants from VIEILLARD & TARDY (1984) with additional line (the lowest) for HA according to LINDSAY (1979). Data from the microcosms are connected by chronological dashed lines and arrows are drawn to indicate time sequence.

C) Double-function chemical potentials of $H_2PO_4^-$ and $Fe^{3+}$ in microcosms (100-cm depth) and in field soil solutions from the Hula Valley (Israel), and from field data from Somerset (England), Trebel Valley (Germany), and Droemling (Germany). Stability lines of strengite and Fe-hydroxides are plotted according to VIEILLARD & TARDY (1984). Data from the microcosms are connected by chronological dashed lines, all beginning from the right-hand side.


## 5.3 Wetland soils from the Ljubljana marsh

For wetland soils in the Ljubljana marsh (Slovenia) we hypothesized a predominance of P mineralization from the degraded soil organic matter. In this process the P release rate depends on temperature. This was investigated in the two principal soil types found in the Ljubljana marsh (Slovenia) such as Histosols and Humic Gleysols.  The Histosols contained approximately twice as much soil organic matter (SOM) as the Humic Gleysols. In a field experiment in the Ljubljana marsh high (HW) or low (LW) water table levels were maintained over 3 years on plots with high (HC) or low (LC) SOM content and cropping history of arable converted to grassland (AG) or permanent grassland (G) (Fig. 5.7). Soils from these sites were selected based on soil P analyses for incubation studies to assess the effect of  SOM content and soil moisture on N and P mobilization / immobilisation by soil micro-organisms.


**P status of soils and method of incubation experiments**

Tests for total and plant available P (CAL-P, determined by the calcium–acetate-lactate extraction), indicated that total P contents in the upper layer (0-30 cm) were similar in all plots, and were not related to cropping history, SOM content or water table level. Concentrations of soluble CAL-P, however, were higher in AG plots, and were associated with higher water table (HW) and higher carbon content (HC). Based on these results fresh samples were collected from 0-30 cm depth on AG-HC-HW and AG-LC-LW plots, homogenized and incubated at room temperature at moisture content close to those recorded in the field, about 50 % of water holding capacity (WHC), and at two higher soil moisture conditions of 70 and 90 % of WHC. The WHC was

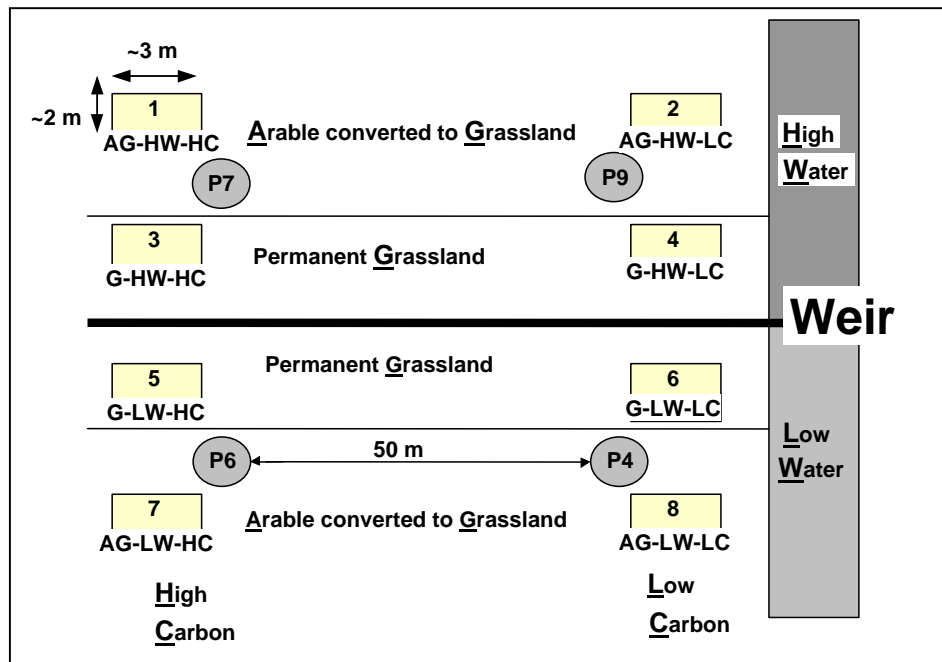maintained throughout the incubation by replenishing gravimetric water loss every 3 days.



Figure 5.7 Schematic presentation of the experimental field in the Ljubljana marsh

N and P in the microbial biomass ($N_{mic}$ and $P_{mic}$) were measured by the fumigation-extraction method. Net P mineralization was greater in HC soil than in LC soil (Fig 5.8 – left 2 panels), and in both it was greater at 90% WHC than at 70 or 50 % WHC (Fig 5.9, left 2 panels). The same trend was observed in net N mineralization (data not shown) and the ratio of $N_{min} : P_{min}$ was 5 : 1.

Net P mineralization was paralleled by a decrease in P immobilized in microbial biomass. The data on microbial biomass P ($P_{mic}$) suggest that HC soil contains (per $cm^3$) about twice as much microbial biomass as LC soil. In both soils, $P_{mic}$ decreased with increasing soil moisture (Fig 5.9, right 2 panels). Microbial biomass N (MBN) was also measured (data not shown). The mean ratio $N_{mic} : P_{mic}$ was 11 : 1, which corresponds well to the N : P ratio in the microbial cell. These findings may support the hypothesis that microbial mineralization is the major P release mechanisms in these soils.
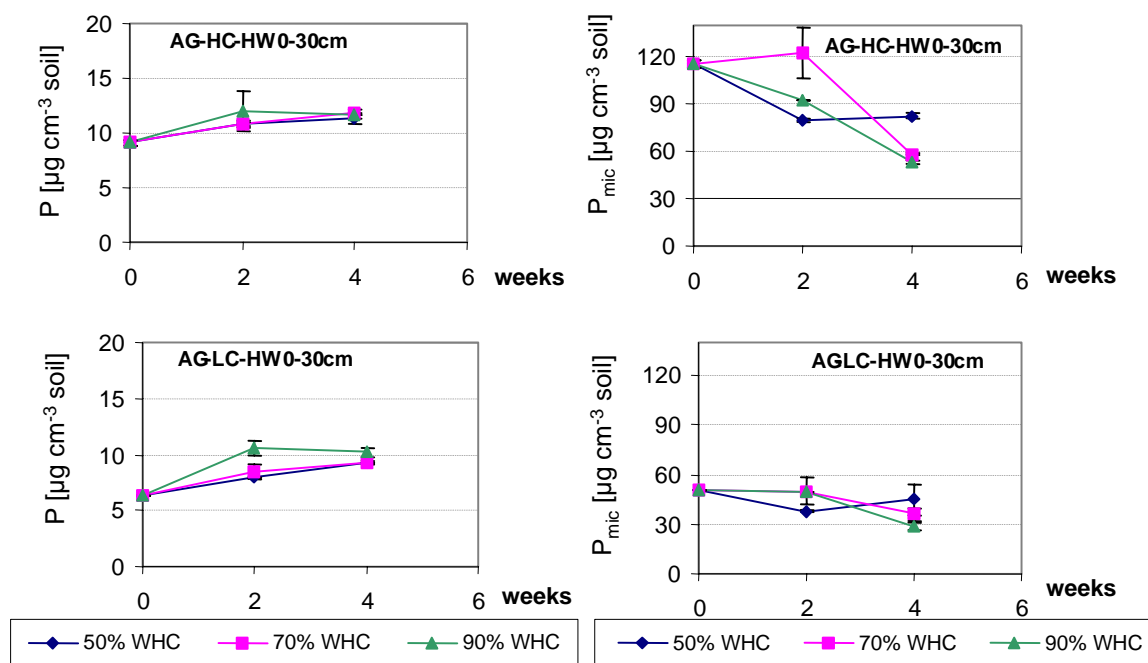
.

**Figure** 5.8 Net P mineralization and immobilization (represented as microbial biomass P, $P_{mic}$) during 4-week incubation period of fresh homogenized samples from the four plots in Slovenia, at 20ºC and different levels of water holding capacity (WHC); data points represent means ($\pm$ SD) of 2 replicates.

Microbial biomass/activity measurements by the substrate induced respiration (SIR) also indicated 1.2 to 2.3 times higher microbial biomass/activity in HC soil than in LC soil (Fig. 5.9). It should be noted, however, that SIR method measures the response to glucose of only the active part of soil microbial population. According to Fig. 5.9, activity of microbial population, present in soil samples at the start of incubation, is significantly lower when exposed to extreme soil moisture content (50 % or 90 % WHC). Similar response at the end of incubation (Fig. 5.9, lower panel) may thus indicate selective proliferation during incubation of microbial groups adapted to extreme soil moisture conditions. This view is supported by a non significant change in response at optimum (i.e. 70 % WHC) soil moisture content. The difference in response at 50 % WHC in HC and LC soil may be attributed to significant difference in water potential at the same % WHC (Fig. 5.9)
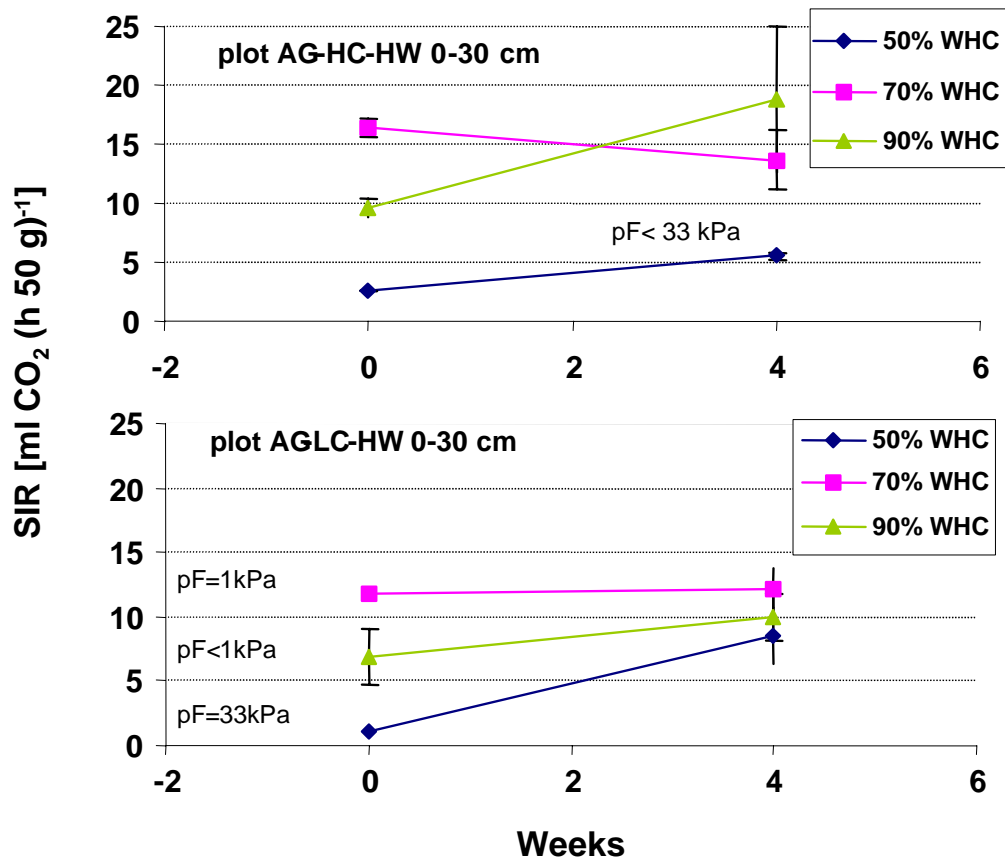
**Figure 5.9** Microbial biomass/activity measured as substrate induced respiration (SIR) at the start and end of incubation; data points represent means ($\pm$ SD) of 2 replicates.

The higher P mineralization rates in topsoil and lower P retention capacity in subsoil of high carbon (HC) soil compared to low carbon (LC) soil were also reflected in higher concentrations of soluble reactive P in ground water sampled from piezometers on respective plots (see chapter 3).

**Conclusions**

Each of these experimental setups was shown to successfully represent field conditions, and each enabled us to study the target processes. The microcosm experiments with soils from the Trebel Valley showed that besides the redox potential, the P mobilisation was also strongly influenced by the temperature. Higher soil temperatures resulted in a larger P mobilization. This may explain, why in Histosols from the Hula Valley under mediterranian climatic conditions not only the peat mineralizations was much stronger than at the other experimental sites but also the P mobilization under re-wetting conditions was more intensively. The microcosms used to study the soils of the Hula Valley were designed to allow reconstruction of the biogeochemical conditions in the studied soils. They were found to successfully reflect the processes that take

place once the water-table is raised and soil layers are flooded. While soil profiles in the study area were composed of distinct horizons that varied in their OM and $CaCO_3$ contents, as well as in their pH and other major soil characteristics, the uniform 120 cm-soil columns used in the microcosms study enabled us to follow the effect of water-table depth as a single variable factor. Thus, while in the field many interactions may influence the underlying processes and correlations between measured variables, we could relate the processes measured in the microcosms study to the change in the water-table as a single major factor. Similarities in ranges of redox, pH, and concentrations of solutes, and trends of changes indicate that the processes that were characterized in the microcosms were applicable to similar soils in the field.

The four studied soils from the Hula Valley were similar in their major mechanisms of P release upon submergence; in all cases, P was released mainly due to reductive dissolution of Fe-hydroxides. However, the soils seemed to differ with respect to the retention mechanisms of the released P. In the more calcareous soils, the Ca-P system controlled P concentrations, probably indicating that much of the released P was fixed by precipitation of Ca-P minerals. In the two degraded peat soils, rich in OM and Fe-hydroxides and lower in $CaCO_3$, this mechanism was not sufficient to retain the soils' original Ca-P saturation which increased with time of submergence. Unfortunately, in the case of the studied area, the re-flooding program and the construction of the new lake were located in the midst of the area governed by degraded peat soils. This may be the reason for the sharp increase in P concentrations measured in Lake Agmon in the first few years following its construction. The ratio of Fe : P was shown to be small in all soils at the beginning of the process and to increase to high values as the process progressed. Thus it is suggested that the first pulse of P release is the most risky for the environment; later on the solutions contain enough Fe to effectively retain the released P by means of co-precipitation or adsorption onto newly formed Fe-hydroxides as the solution encounters oxidized conditions. Nevertheless, alternate reduction-oxidation conditions within the soil profile caused by fluctuating water-table depth may easily release the re-fixed P in each cycle of reduction.

Finally, the microcosms used to study the soils of the Ljubljana marsh soils, Histosols and Humic Gleysols, were designed to assess microbial activity. Histosol (HC soil) contained approximately twice as much SOM as Humic gleysol (LC soil). The studies of N mineralization (elsewhere), and P mineralization and immobilization into microbial biomass (this study) indicated that microbial biomass and activity in the two soils were proportional to SOM

content. These results suggest that SOM content was the principal factor governing the extent of general microbial transformations of C, N and P in peat soils. Mineralization and immobilization of these three major nutrients was carried out by diverse microbial groups and is therefore not indicative of specific microbial activity. The effect of SOM content became much more pronounced when the activity of specific group of microorganisms is studied as indicated in our studies of denitrification (data not presented). Up to 100 % conversion of $NO_3$ to $N_2O$ could be observed in HC soil compared to less than 5 % in LC soil. Concomitant respiration ($CO_2$ evolution) in the two soils is roughly proportional to SOM or microbial biomass content.

# 6. Phosphate adsorption

The phosphate adsorption was studied in soils from all experimental sites. Two different types of **batch experiments** were carried out to determine (1) the static P adsorption and (2) the time dependent P ad-/desorption. Static P adsorption were determined for all sites except the Droemling area. For these samples the time dependency of P ad-/desorption was determined according to BARROW & SHAW (1975) to obtain input parameters for P transport modelling with MORPHO (PUDENZ, 1998).

The results of the static P adsorption batch experiments according to NAIR et al. (1984) are summarised in Table 6.1. The fitting parameters were derived from the Langmuir equation (Equation 6.1, LANGMUIR, 1918) and from the Langmuir equation in the linearised form (Equation 6.2, BACHE & WILLIAMS, 1971). The equation is based on the assumption of a limited number of equivalent sorption sites and neglects interactions between sorbed atoms, molecules or ions (RICHTER, 1986; MOORE & HUMMEL, 1986; SCHULTHESS & SPARKS, 1991).

*Langmuir:*

$$S = S_{max} \times \frac{k \times C_{eq}}{1 + k \times C_{eq}}$$

6.1

*Langmuir, linearised form:*

$$\frac{C_{eq}}{S} = \frac{C_{eq}}{S_{max}} + \frac{1}{k \times S_{max}}$$

6.2

For the linearised form (equation 6.2) a plot of $C_{eq}/S$ against $C_{eq}$ should give a straight line with the slope $1/S_{max}$ from which an adsorption maximum $S_{max}$, and a constant k relating to the bonding energy can be calculated (BACHE & WILLIAMS, 1971). The quality of the fits, expressed by r², ranged from 0.70 to 0.99. The parameters for the linear Langmuir equation of static isotherms indicated decreasing sorption maxima ($S_{max}$) with increasing depth of soil profiles. This is explained by a stronger alteration of peat in the topsoils compared to subsoils. The $S_{max}$ in the topsoils ranged from 629 to 3523 mg kg$^{-1}$, whereas in the subsoils they were only between 217 and 2122 mg kg$^{-1}$. Similar differences were observed for the constant k, which was larger in topsoils that in subsoils at most of the sites. The exceptions Hula Valley and Biebrza Valley can be explained by the influence of limnic or anthropogenic mineral compounds on the sorption behaviour.

**Table 6.1** Fitting parameters for the linear Langmuir equation of the static P adsorption isotherms

| | Profile depth | $S_{max}$ | k | $r^2$ |
|---|---|---|---|---|
| | cm | mg kg$^{-1}$ | | |
| Hula Valley | 0-20 | 1699 | 0.770 | 0.93 |
| | 20-40 | 2032 | 34.120 | 0.98 |
| | 40-60 | 2122 | 4.080 | 0.94 |
| | 60-70 | 735 | 3.190 | 0.92 |
| | 70-110 | 719 | 0.930 | 0.96 |
| Biebrza Valley | 1-5 | 1202 | 0.070 | 0.92 |
| | 8-18 | 649 | 0.371 | 0.92 |
| | 19-23 | 708 | 0.593 | 0.93 |
| | 24-36 | 610 | 0.705 | 0.92 |
| | 40-55 | 662 | 1.294 | 0.93 |
| | 58-75 | 716 | 2.927 | 0.95 |
| | 77-84 | 763 | 4.575 | 0.97 |
| | 87-95 | 724 | 2.408 | 0.92 |
| Somerset Levels & Moors | 0-30 | 2032 | 1.217 | 0.99 |
| | 30-60 | 568 | 0.150 | 0.70 |
| | 60-90 | 217 | 0.145 | 0.98 |
| Trebel Valley   Langsdorf | 0-30 | 3523 | 0.452 | 0.99 |
| | 30-60 | 861 | 0.141 | 0.97 |
| | 60-90 | 805 | 0.117 | 0.98 |
| Kristianstad Vattenrike | 0-30 | 1082 | 0.216 | 0.81 |
| | 30-60 | 835 | 0.042 | 0.90 |
| | 60-90 | 317 | 0.035 | 0.87 |
| Ljubljana Marsh   Station 1 | 0-30 | 667 | 9.867 | 0.93 |
| Station 2 | 0-30 | 629 | 5.034 | 0.94 |

For some sites **better fits** were obtained by other equations, like Freundlich and Tempkin or modified (corrected) versions of the original forms. This will be shown with results from the Trebel Valley because of the best data basis, and because the influence of peat degradation and humification on P adsorption became obvious. Top soil samples from different degradation stages and a complete soil profile were studied. The unfitted sorption iso-therms, drawn from the results of the batch experiments, are visualised in Figure 6.1. The isotherm points represent mean values of triplicate determina-tions. The standard deviations were summarised for the samples compared and accounted for 3 and 6 %. For the topsoils (0-30 cm, Figure 6.1a) there was an obvious trend according to peat decomposition. The stronger the degradation the higher were the sorption maximum and the buffer capacity.

This resulted in the order LD > ETII > ETI. The P sorption within the profile of the Langsdorf site (Figure 6.1b) was differentiated by the strongly decomposed topsoil (0-30 cm) and the less decomposed and well preserved underlying peat (30-60 and 60-90 cm).
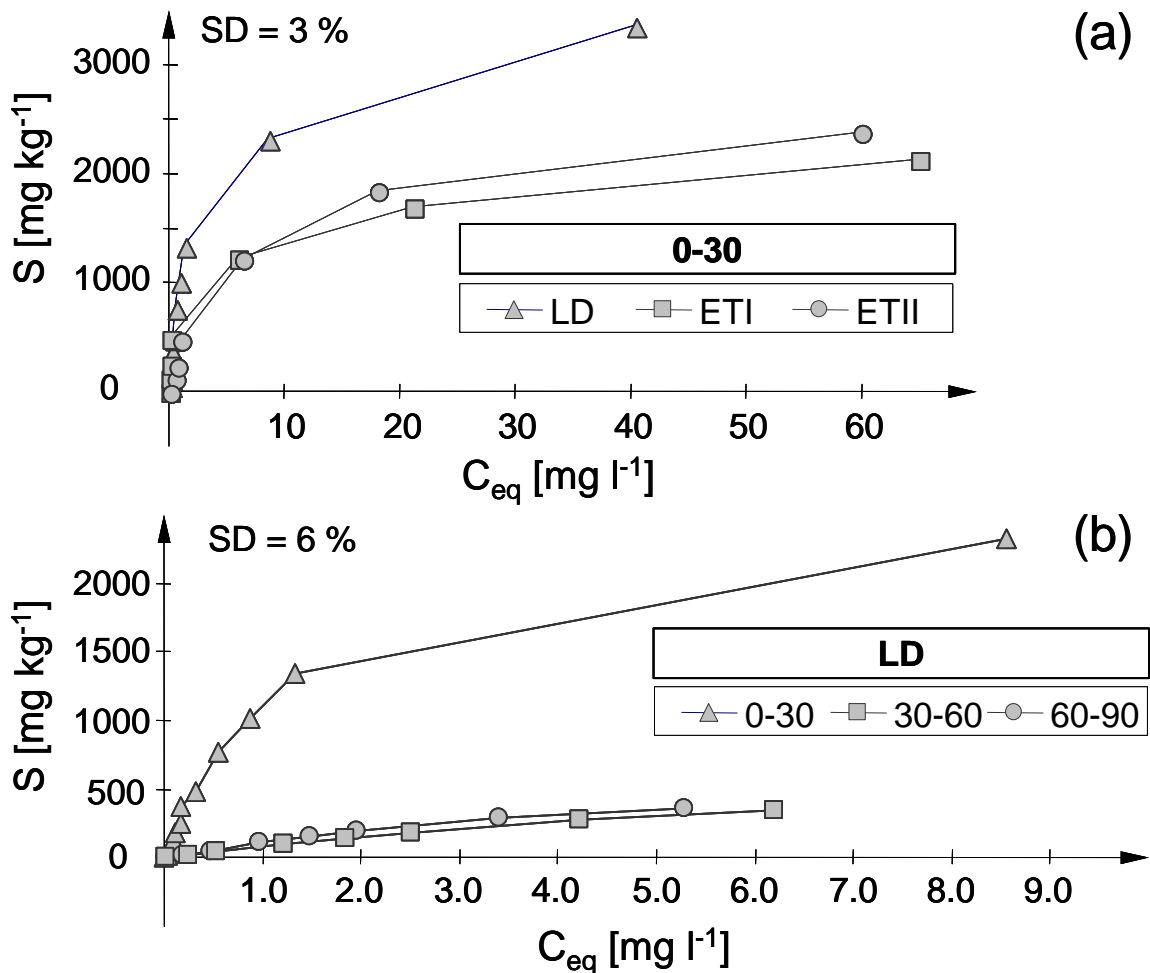


**Figure 6.1** Unfitted sorption isotherms for (a) the topsoils in the Trebel Valley (LD = Langsdorf, ET = Eichenthal, and (b) the peat horizons at the Langsdorf site.

Additionally to the linear Langmuir equation the experimental isotherms for the peat soils of the Trebel Valley were fitted to other models, which were suitable to describe P adsorption with a moderate number of parameters (Equations 6.3 to 6.6). The Freundlich equation (6.4), first applied by RUSSELL & PRESCOTT (1916), is the oldest model for the description of P adsorption. The equation is based on the assumption, that the affinity term decreases exponentially with increasing adsorption (BARROW, 1978), and $k_F$ and $b$ are coefficients. The Tempkin equation is based on a model of linear decreasing binding energy with increasing adsorption (HAYWARD & TRAPNELL, 1964). It can

be derived from the Langmuir equation (BERKHEISER et al., 1980). The simplified equation (6.6) is valid if extreme values of sorbed P (S) are excluded.

*Langmuir, corrected:*

6.3
$$S = S_{max} \times \frac{k_L \times C_{eq}}{1 + k_L \times C_{eq}} - S_0$$

*Freundlich:*                                                         *Freundlich, corrected:*

6.4 $\quad S = k_F \times C_{eq}^b$            6.5 $\quad S = k_F \times C_{eq}^b - S_0$

*Tempkin:*

6.6
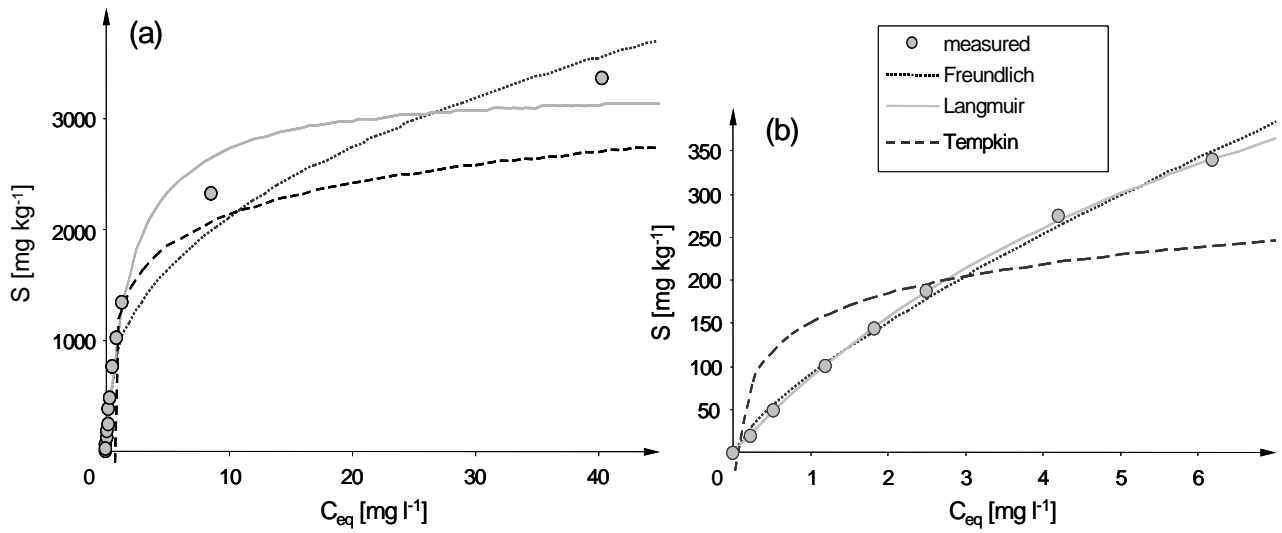$$S = k_{T1} \times \ln\left(k_{T2} \times C_{eq}\right)$$



Figure 6.2 Comparison of the fitting quality for the sorption models applied to (a) the topsoil (0-30 cm) and (b) the subsoil (60-90 cm) of the Langsdorf site (LD)

**Table 6.2** Fitting qualities (r²) of the Freundlich, Langmuir and Tempkin isotherms for the experimental sites of the Trebel Valley (topsoils n = 3, subsoils n = 6)

| | | Langmuir | | Freundlich | | Tempkin |
|---|---|---|---|---|---|---|
| | | Normal | Corrected | normal | Corrected | |
| Topsoil | Mean | 0.982 | 0.983 | 0.965 | 0.984 | 0.918 |
| | Median | 0.985 | 0.985 | 0.958 | 0.984 | 0.911 |
| | SD | 0.011 | 0.010 | 0.012 | 0.006 | 0.031 |
| | Min | 0.967 | 0.970 | 0.954 | 0.977 | 0.883 |
| | Max | 0.994 | 0.994 | 0.981 | 0.991 | 0.958 |
| Subsoil | Mean | 0.998 | 0.998 | 0.996 | 0.998 | 0.797 |
| | Median | 0.998 | 0.998 | 0.997 | 0.999 | 0.800 |
| | SD | 0.002 | 0.002 | 0.003 | 0.003 | 0.060 |
| | Min | 0.994 | 0.994 | 0.990 | 0.993 | 0.693 |
| | Max | 1.000 | 1.000 | 1.000 | 1.000 | 0.891 |

The three original models describe the P adsorption for soils that have no P already adsorbed. However, under field conditions a discrete amount of P is initially sorbed ($S_0$), which has to be considered by a correction of the functions (Equations 6.3 and 6.5).

The coefficients of the model parameters are presented in Table 6.3. During the stepwise approximation of the initially sorbed P ($S_0$), using the corrected Langmuir equation, negative values were calculated sometimes. In such implausible cases the parameters were substituted by the values from the original Langmuir equation.

**Table 6.3** Calculated model parameters for the equations of Langmuir, Freundlich and Tempkin[1]

| Site | Profile Depth | Langmuir | | | Freundlich | | | Tempkin | |
|---|---|---|---|---|---|---|---|---|---|
| | | $S_{max}$ | $k_L$ | $S_0$ | $k_F$ | b | $S_0$ | $k_{T1}$ | $k_{T2}$ |
| | | mg kg$^{-1}$ | l kg$^{-1}$ | mg kg$^{-1}$ | l kg$^{-1}$ | - | Mg kg$^{-1}$ | l kg$^{-1}$ | - |
| LD | 0-30 | 3289 | 0.491 | 0.0[2] | 1822 | 0.230 | 808.8 | 409.0 | 22.8 |
| | 30-60 | 737 | 0.195 | 7.0 | 144 | 0.613 | 25.8 | 65.3 | 13.0 |
| | 60-90 | 770 | 0.131 | 2.5 | 103 | 0.687 | 12.2 | 49.1 | 21.1 |
| ET I | 0-30 | 2187 | 0.220 | 0.0[2] | 1296 | 0.170 | 506.5 | 219.9 | 99.3 |
| | 30-60 | 567 | 0.298 | 0.0[2] | 148 | 0.540 | 6.0 | 40.5 | 174.6 |
| | 60-90 | 436 | 0.339 | 0.3 | 151 | 0.417 | 32.0 | 49.9 | 27.6 |
| ET II | 0-30 | 2625 | 0.140 | 0.0[2] | 1224 | 0.238 | 763.2 | 373.6 | 5.4 |
| | 30-60 | 491 | 0.163 | 1.4 | 88 | 0.565 | 9.8 | 38.9 | 37.2 |
| | 60-90 | 456 | 0.144 | 0.0[2] | 77 | 0.564 | 8.8 | 36.5 | 32.0 |

The **$S_{max}$** of the Langmuir equation and the corresponding parameters for the intensity of P sorption from the equations of Freundlich ($k_F$) and Tempkin ($k_{T1}$) showed obviously higher values for the topsoil horizons. The $S_{max}$ were larger by factors up to 7 (2187 to 3289 mg $kg^{-1}$) for topsoils than for subsoils (436 and 770 mg $kg^{-1}$). The values of $k_F$ (up to factor 25) and $k_{T1}$ (up to factor 20) showed similar differences between topsoils and subsoils. The $S_0$ of the Freundlich equation were also strongly different (topsoils: 763.2 to 808.8 mg $kg^{-1}$; subsoils: 6.0 to 32.0 mg $kg^{-1}$). On the other hand the affinity term $k_L$ as well as the parameters b and $k_{T2}$ showed no uniform trend within the profiles. The values of the initially sorbed P ($S_0$) derived from the Langmuir equation were all approximated to zero.

Beside the model parameters **additional information** can be derived from the isotherm equations. These are (1) the equilibrium P concentration, where the processes of ad- and desorption neutralise each other (WOLF et al., 1985; $EPC_0$ = equilibrium P concentration at zero sorption point), and (2) the P sorption capacity (PSC) and degree of P saturation (DPS). These parameters are practically relevant because they are estimators of the of the P retention (NIEMIENEN & JARVA, 1996; AXT & WALBRIGDE, 1999; BEHRENDT & PÖTHIG, 1999) and the diffuse P pollution from catchment areas (LOOKMAN et al., 1995; REDDY et al., 1995; RICHARDSON & VAITHIYANATHAN, 1995; LEINWEBER et al., 1997b; YOUNG & ROSS, 2001; ZHOU & LI, 2001).

The **$EPC_0$ values** were calculated under approximation to $S_0 \rightarrow 0$ using the corrected Freundlich equation and the Tempkin equation. The $EPC_0$ values calculated from the Tempkin equation were generally larger than those derived from the corrected Freundlich equation. The concentrations showed no uniform trend within the profiles. For the natural site (ETI) the concentrations ranged from 0.003 to 0.036 mg $l^{-1}$ and were much lower than those calculated for the strongly degraded sites (LD and ETII) with values between 0.021 to 0.186 mg $l^{-1}$. These concentrations are critical because they indicate a mesotrophic to eutrophic status of the peat water body. If we assume that the peat is hydraulically connected to the adjacent ditches (BAUR, 1998) there is a potential risk of eutrophication.

The calculation of the **total P sorption capacities ($PSC_t$)** were based on the $S_{max}$ values derived from the Langmuir isotherms (NIEMIENEN & JARVA,

1996; AXT & WALBRIGDE, 1999; BEHRENDT & PÖTHIG, 1999). The **degree of P saturation (DPS)** was calculated according to BEHRENDT & PÖTHIG (1999).

6.7 $\qquad$ $PSC_t \text{ [kg ha}^{-1}\text{]} = 3 \times (S_{max} + \text{soil-}P_t) \text{ [mg kg}^{-1}\text{]} \times \rho_d \text{ [g cm}^{-3}\text{]}$

6.8 $\qquad$ $DPS \text{ [%]} = \text{soil } P_t \ / \ (S_{max} + \text{soil-}P_t) \times 100$

Table **6.4** P sorption capacity (PSC) and degree of P saturation (DPS) for the sites in the Trebel Valley

| Site | Profile depth | $PSC_t$ | DPS |
|------|------|------|------|
| | cm | kg ha$^{-1}$ | % |
| | 0-30 | 3530 | 27.3 |
| LD | 30-60 | 573 | 38.3 |
| | 60-90 | 455 | 34.0 |
| | 0-30 | 1969 | 46.7 |
| ET I | 30-60 | 562 | 57.7 |
| | 60-90 | 314 | 54.2 |
| | 0-30 | 3258 | 39.6 |
| ET II | 30-60 | 406 | 52.8 |
| | 60-90 | 288 | 47.8 |

At all sites the PSC was largest in the topsoil and decreased with increasing profile depth (Table 6.4). According to the degree of degradation the PSC values followed the order LD > ETII > ETI. The DPS showed a reverse trend within the profile with lower values of 27.2 to 46.7 % in the topsoils and higher values (34.0 to 82.1 %) in the subsoils

General conclusions for the applied models can be drawn from the quality of fit and the DPS of the soils. The Langmuir and Freundlich equations were suitable to describe the P sorption for the topsoils as well as for the subsoils. The Tempkin equation was applicable only for the topsoils of the present study. This disagrees to POLYZOPOULOS & PAVLATOU (1992) who described the Langmuir model to be useful only for soils with high DPS values. However, there are some restrictions for the models concerning the concentration range. Whereas the Langmuir equation is well suited for high equilibrium P concentrations and therefore for the calculation of P sorption maximum, the Tempkin equation gives a more precise prediction for the lower concentration range and can be used for $EPC_0$ determination. As already cited in the literature (RICHARDSON & VAITHIYANATHAN,1995) the Freundlich equation fits the whole concentration range for organic soils.

There are several investigations about the P sorption capacity in wetlands. NIEMINEN & JARVA (1996) observed PSC values of 82 to 673 kg ha$^{-1}$ for topsoils of drained fens in Finland. LOPEZ-HERNANDEZ & BURNHAM (1974) reported PSC´s of 0 to 58.7 kg ha$^{-1}$ for organic soils in Great Britain. For wetland soils (mineral and organic) in North America the PSC´s ranged from 8 to 3300 kg ha$^{-1}$ (RICHARDSON, 1985; AXT & WALBRIDGE, 1999). In a study for peat soils in Northeast Germany BEHRENDT & PÖTHIG (1999) reported mean PSC values of 1550 mg kg$^{-1}$ (topsoils, 0-30 cm), 750 mg kg$^{-1}$ (subsoils, 60-90 cm) and 850 mg kg$^{-1}$ (subsoils, 60-90 cm). Furthermore, only about 10 % of the investigated peat had a DPS < 50 % and 32 % of had a DPS > 80 %. Compared to these results most of the peat soils of the Trebel Valley (66 %) had DPS below 50 %. BEHRENDT & PÖTHIG (1999) defined DPS  75 % as a critical threshold for P mobilisation, because above this value the EPC$_0$ concentrations strongly increased (> 0.25 mg l$^{-1}$). For the samples from the Trebel Valley this threshold value was never exceeded. Regression analysis revealed no significant correlation between DPS and EPC$_0$.

In most cases the calculated EPC$_0$ values were conspicuously different from the determined SRP concentrations of soil solutions in the field. For the topsoils the calculated EPC$_0$ values of 0.029 (Freundlich) and 0.044 mg l$^{-1}$ (Tempkin) were below the average concentrations from the field research (0.299 mg l$^{-1}$). In samples from subsoils the EPC$_0$ values were larger than mean soil solution concentrations by factor 2. These differences can be explained at least partly by the use of dry peat samples for batch experiments. Under anaerobic conditions the P sorption is much higher than under aerobic environment (KHALID et al., 1977), which may possibly explain EPC$_0$ (batch) < SRP (field). On the other hand the water movement in peat soils under field conditions, controlled by soil pores, is slow and the contact of SRP to the soil matrix only marginal (RICHARDSON & VAITHIYANATHAN, 1995).

# 7. Modelling of P transport at the catchment scale (Hula Valley)

## 7.1    Objectives

The **main goal of this modelling approach** was to compute water and P budgets for the altered wetland of the Hula Valley, Israel. The methodologies tested could be used in other wetlands in Europe and elsewhere. Specific objectives were (1) to establish a conceptual flow model of the hydrological system in the study area and (2) to build a numerical water balance model that computes water budget. The establishment of a reliable water budget allowed us to compute P budget using several assumptions.

## 7.2    Methods

The conceptual flow model in a given wetland was ascertained through the use of various hydrological tools. In the Hula Valley, Israel, we installed 80 **observation wells** across the study area to a depth of 5 meter. We also installed three clusters of observation wells to a depth of 5-, 10- and 15 meters, so the vertical hydraulic gradient can be assessed. The site selection was based on field observations, colour air photographs interpretation, local expert knowledge, and existing hydro-geological information. The first site located west of Lake Agmon (Fig. 7.1) exhibited large number of cracks, fissures, and holes especially in the shallow depth of 1 to 3.5 meters below surface. The next site located south of plastic barrier installed to a depth of 4-6 meter below surface to dam the groundwater flow and create Lake Agmon. The third site located near the confluence of the Eastern and Western drainage canals of the Jordan River and is highly affected by previous agricultural practices such as old drainage canals that were refilled but potentially could serve as a conduit to groundwater flow.
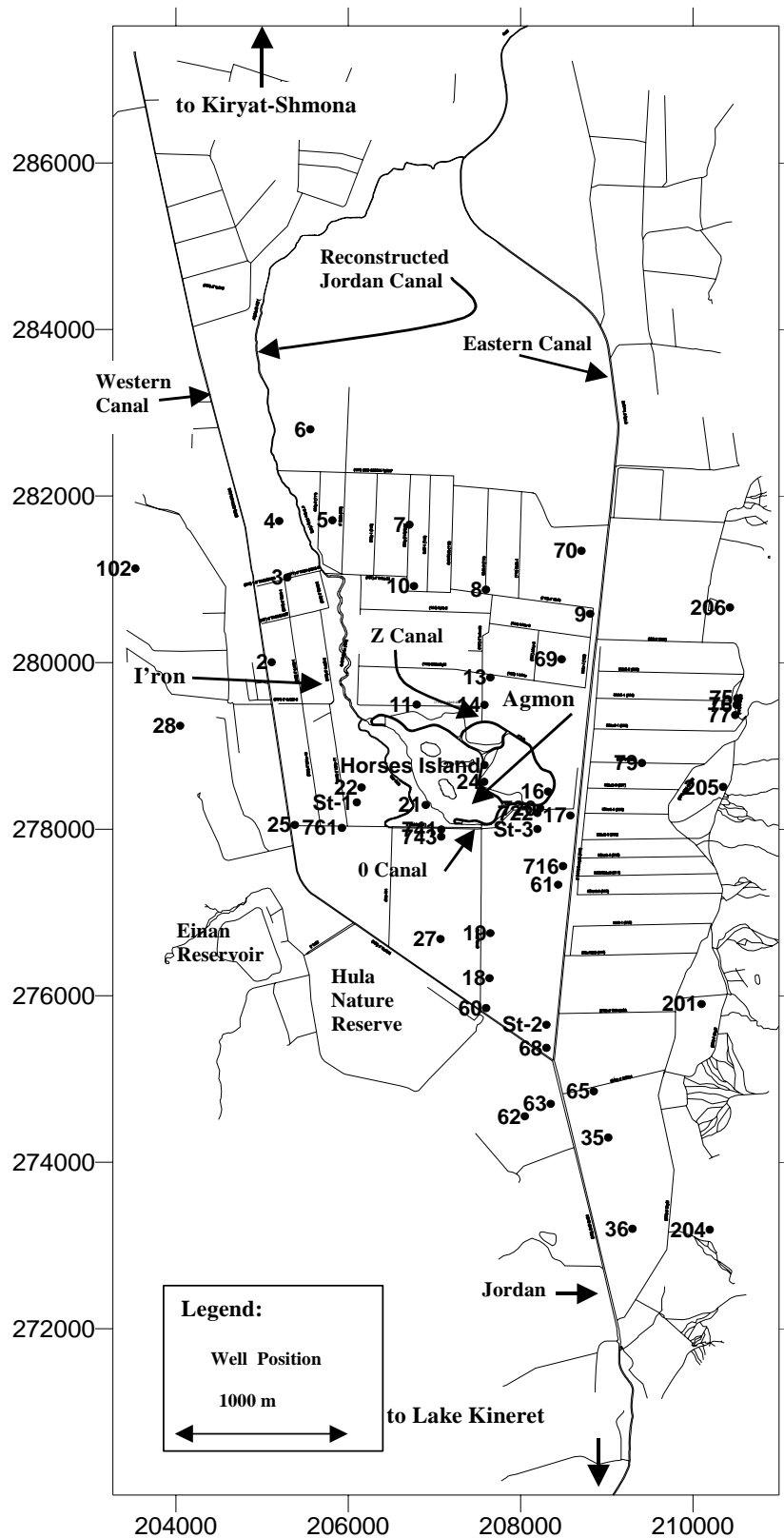
**Figure 7.1** The location of observation wells, drainage canals and the three clusters of observation wells (st-1, 2 - & 3) in the Hula Valley, Israel.

The hydraulic head (h), temperature and electrical conductivity at each of the nine observation wells have been monitored since July 2001 using an automated monitoring system. In addition to the real time measurements of hydraulic heads in the 3 selected clusters we measured the monthly fluctuation of hydraulic head in 80 observation wells scattered throughout the valley.

We used **point dilution techniques and slug tests** to measure the hydraulic conductivity (K) of the soil in the three clusters at depths of 2-5 m, 8-10 m and 12-15 m. The water stage in the reconstructed Jordan River (R-JR) and adjacent drainage canals were monitored continuously since the summer of 2002. The water stage was measured using an automated gauge connected to a data logger.

**Water samples** from the 80 observation wells were taken seasonally during 2001 and 2002. More than 500 water samples were collected and analysed for major cations (Ca, Mg, K, Na) metals (Fe, $H_4SiO_4$, Al), anions (Cl, $SO_4$), alkalinity, dissolved organic carbon, and dissolved phosphorus, pH, and electrical conductivity. The molar ratios of Ca/Mg, Ca/$SO_4$, Ca/$HCO_3$, Na/Cl, Mg/Cl, and $SO_4$/Cl were computed for further multivariate and geostatistical interpretation.

The **groundwater flow and water budget** were calculated using numerical water balance modelling. The observed head distribution from the 80 observation wells was used to specify the initial head conditions and the model calculates fluxes to and from the specified head nodes using Darcy's law. We used the USGS Modular Groundwater Flow Model coupled with graphical user interface of GMS 3.1 which provide versatile data entry, numerous output options and various statistical and geostatistical tools. The boundary conditions of the problem were examined using pattern recognition analysis that ascertained the spatial distribution of hydraulic heads coupled with the chemical parameters. The spatial distribution of all the hydro-chemical parameters was assessed using the geostatistical software library and user's guide GSLIB (DEUTSCH & JOURNEL, 1994). Next, we analysed the spatial distribution of the combined parameter of all the 19 hydro-chemical variables using the discriminant scores which are the linear combination of the 19 variables at each observation wells using the discriminant analysis routine of SPSS. Discriminant analysis computes the canonical discriminant functions (DSF) which are the linear combination of the measured variables that maximised the differences between the means of *k* groups in *n* dimensions. We applied the Mahalanobis distance with conditional probability for entering and removing hydro-chemical parameters.

## 7.3 Methodology and scientific achievements

### *Real-time in-situ monitoring of groundwater, EC and temperature*

The **hydraulic head** distribution in the 3 clusters of observation wells along with **their EC and temperature pattern** is depicted in Figures 7.2 to 7.4. The hydraulic head in Station # 1 located west of Lake Agmon has been in its minima in September of each year. During the autumn months the hydraulic head began to rise even before the rainy season began because of a rise in the water stage in the Reconstructed Jordan River. The water level fluctuation in the Reconstructed Jordan River stemmed from the ecological management of Lake Agmon. The groundwater recharge following rain events in all monitoring stations were extremely fast followed by quick decrease in groundwater level as the storm ceased. The hydraulic head distribution in the 3 measuring depths of station # 1 was remarkably similar. The groundwater level fluctuated by less than 60 cm during most of the monitoring season except during the extremely wet winter of 2002-2003 that elevated the groundwater to above surface creating prolonged flooding of the study area.

The averaged EC (4 mS cm$^{-1}$) of groundwater at depth of 15 meter in Station # 1 was significantly higher than shallower depths of 10- and 5 meter depths (3.2 mS cm$^{-1}$ and 2.5 m cm$^{-1}$ respectively). The EC distribution at 10- and 15 meter depth were fairly constant throughout the monitoring period, while the EC values measured at 5 meter fluctuated greatly in response to aerial recharge following rain events. Similarly, the temperature of the groundwater showed constant profile at 10- and 15 meter depths and strong seasonal pattern of groundwater temperature at shallower depth (Fig. 7.2).

The hydraulic head distribution in Station # 2 located near the confluence of the major canals of the Jordan River in the Hula Valley (see Fig. 7.1) varied greatly with time and depth (Fig. 7.3). During the autumn months the hydraulic head at 10 meter depth is significantly higher than the hydraulic head at shallower depth suggesting a persistent vertical flow component. This pattern has been reversed following an aerial recharge by rain. The groundwater level at this local fluctuated by more than 1.8 meter during the first monitoring year and by more than 2.2 meter during the second monitoring period. The EC values registered at 10 meter depth remained fairly constant (~ 3.7 m cm$^{-1}$) while the EC values at 5 meter depth fluctuated in response to aerial recharge by rain. Similarly, the temperature of the groundwater showed constant profile at 10 meter depth and strong seasonal pattern of groundwater temperature at shallower depth (Fig. 7.3).
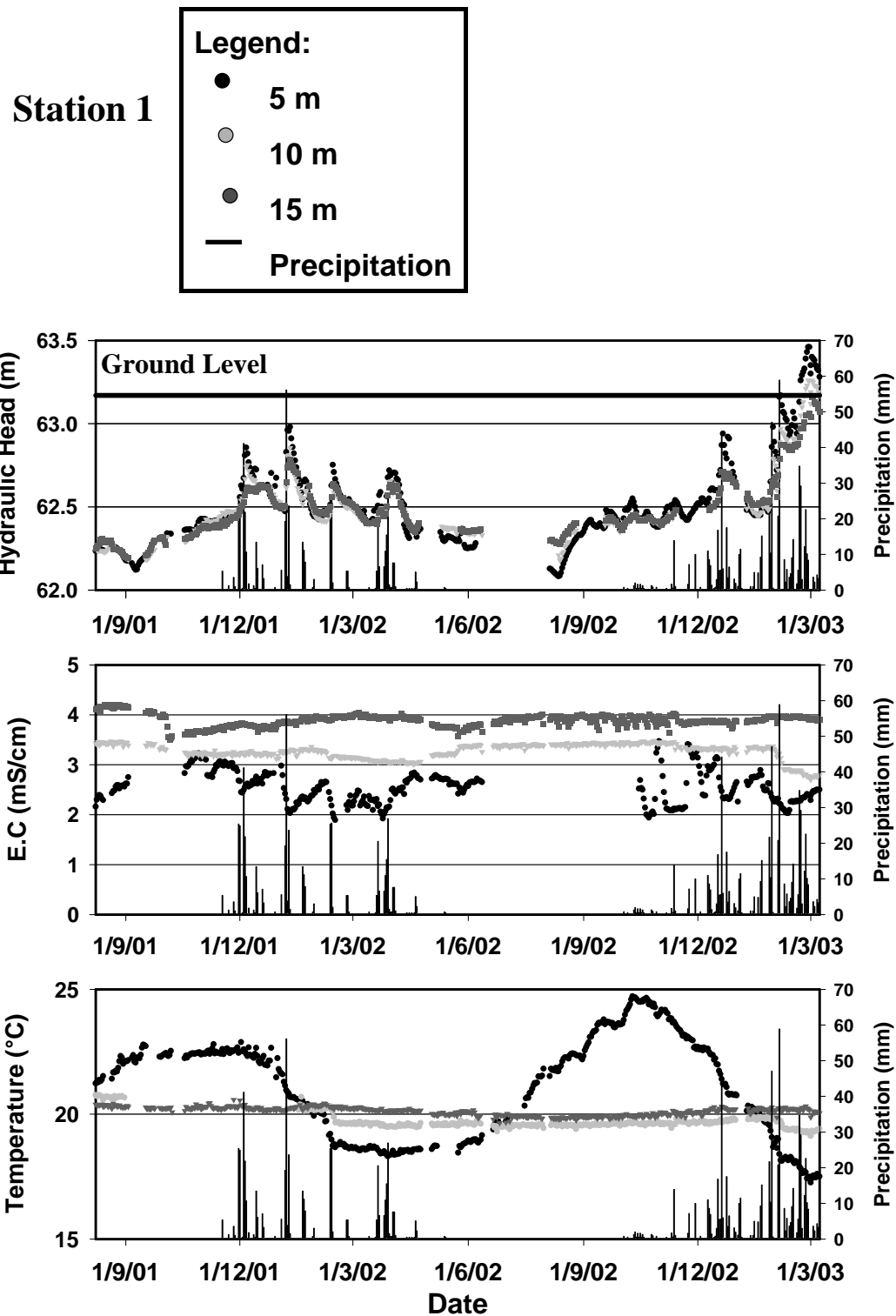
**Figure 7.2** The hydraulic head, EC and temperature distribution measured in Station # 1.
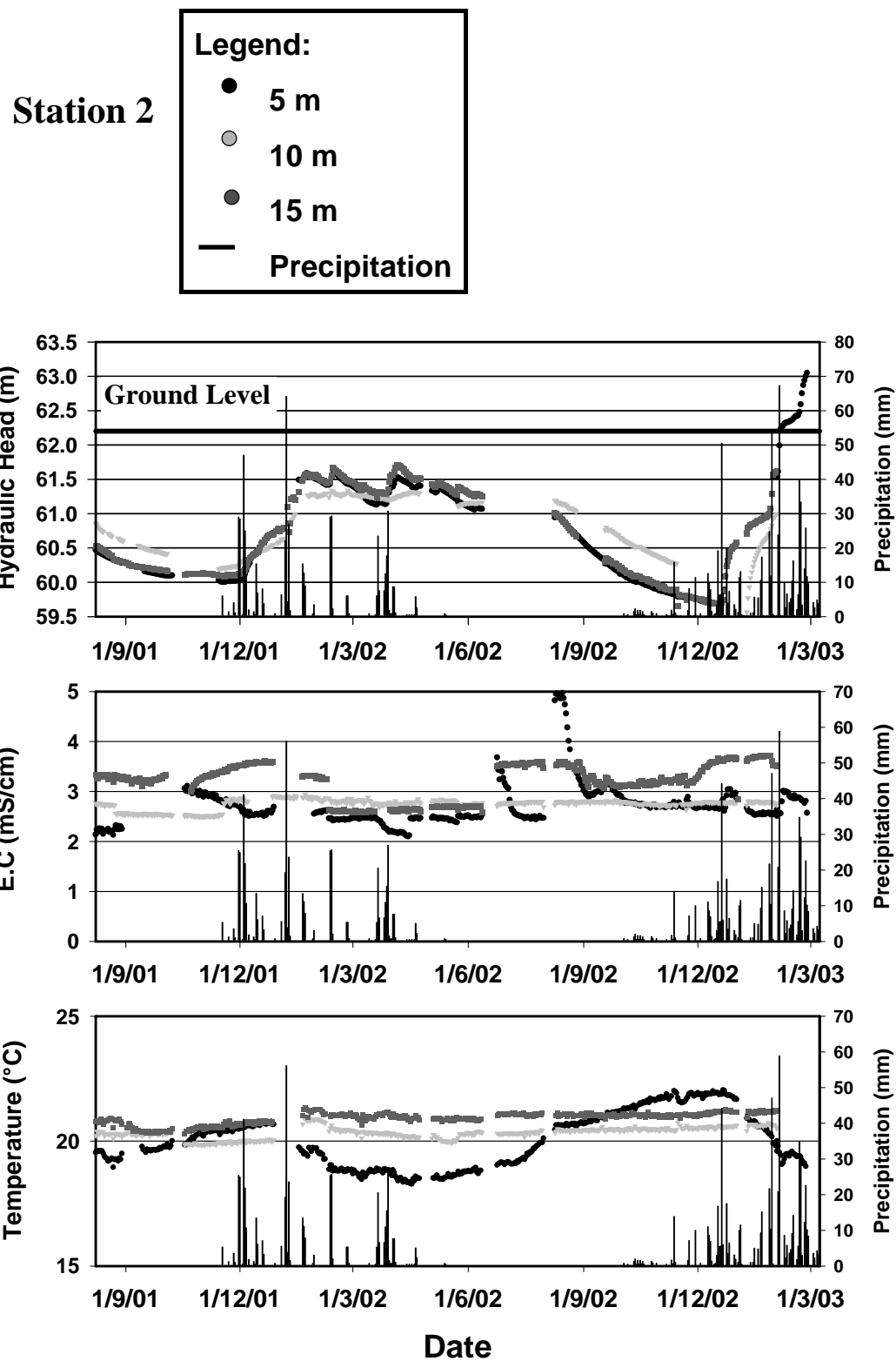
**Figure 7.3** The hydraulic head, EC and temperature distribution measured in Station # 2.

The hydraulic head distribution in Station # 3 located just south of the plastic barrier that prevents groundwater seepage from Lake Agmon (see Fig. 7.1) also showed a higher hydraulic head values at depths of 10 and 15 meter below surface compared with shallower depth during the beginning of the monitoring period (Fig. 7.4).

This pattern has been reversed following an aerial recharge by rain. The vertical flow component did not return in the following summer due to heavy irrigation in this location. The groundwater level south of the plastic barrier fluctuated by more than 3.4 meter during the monitoring period. The EC values registered at 10- and 15 meter depths remained fairly constant (~ 3.2 mS cm$^{-1}$) while the EC values at 5 meter depth fluctuated in response to aerial recharge by rain. Similarly, the temperature of the groundwater showed constant distribution at greater depths and a typical seasonal pattern of groundwater temperature at shallower depth (Fig. 7.4) but the temperature record is incomplete and truncated at times due to malfunctioning and electrical problems with the data logger and the sensors.

The results of the **monitoring program at the 3 stations** suggest that groundwater flow in this altered wetland environs is influenced by several mechanisms. In the summer and autumn months the vertical flow component is quite pronounced especially in the southern end of the valley where the impact of re-flooding and the creation of Lake Agmon is negligible. The source of the observed vertical flow component is probably from deeper recharge generated from the Eastern Galilee Mountains to the west of the valley as suggested by NEUMAN & DASEBERG (1977) and GILAD (1987). In the area near the reconstructed Jordan River the recharge mechanism is largely dominated by leakage from the R-JR and other drainage canals that mask the vertical flow component. The horizontal flow mechanism is also important in replenishment of evapotranspiration loss (~ 57 mm month$^{-1}$ during the winter and more than 210 mm month$^{-1}$ during the summer), thus the hydraulic head in this local does not varied significantly with time. Winter storms generated considerable aerial recharge in the study area that quickly affected the hydraulic head distributions and reversing the vertical head gradient across the study area. In the past, the reversal of the vertical head distribution was short lived (NEUMAN & DASBERG, 1977) but the major land use change in the area such as the creation of Lake Agmon, and increased groundwater pumping in the foothills along the valley have reduced this vertical flux component. The groundwater hydrograph exhibited short duration because of quick discharge from the shallow depth (5 meter) to the drainage canals. This strong and quick response to aerial re-

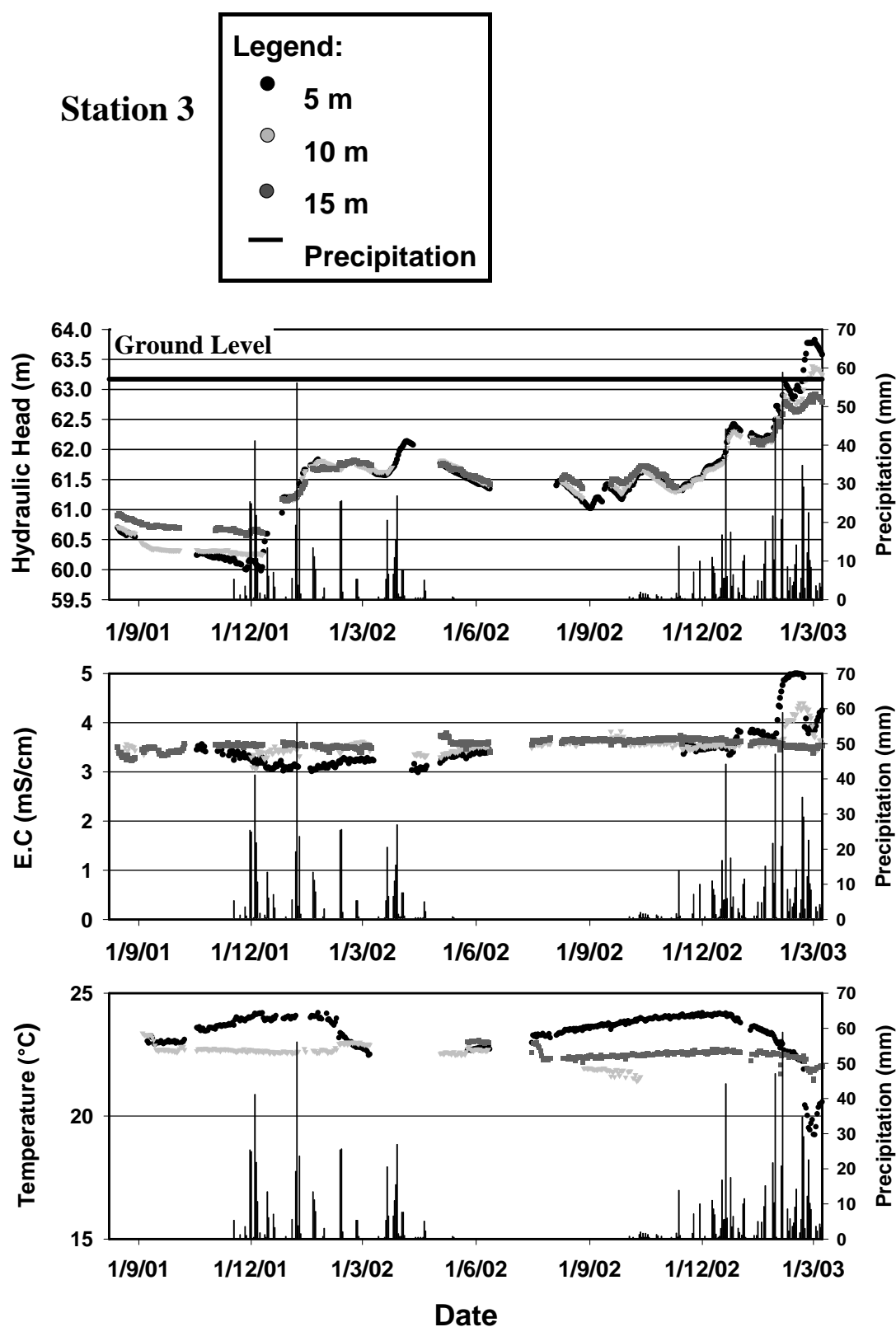charge either by precipitation and/or irrigation suggests high transmissivity in the shallow depths.



**Figure 7.4** The hydraulic head, EC and temperature distribution measured in Station # 3.

## Flow Parameters

The **hydraulic conductivity (K) values** varied greatly with depth and location (Fig. 7.5). In layers deeper than 5 meters the K values did not exceed 0.1 m d$^{-1}$ and in some instances the K values were significantly lower than 0.01 m d$^{-1}$. In the shallower depth of the altered peat soils we measured extremely high values of K (> 100 m d$^{-1}$) that are similar to K values measured in coarse sand.
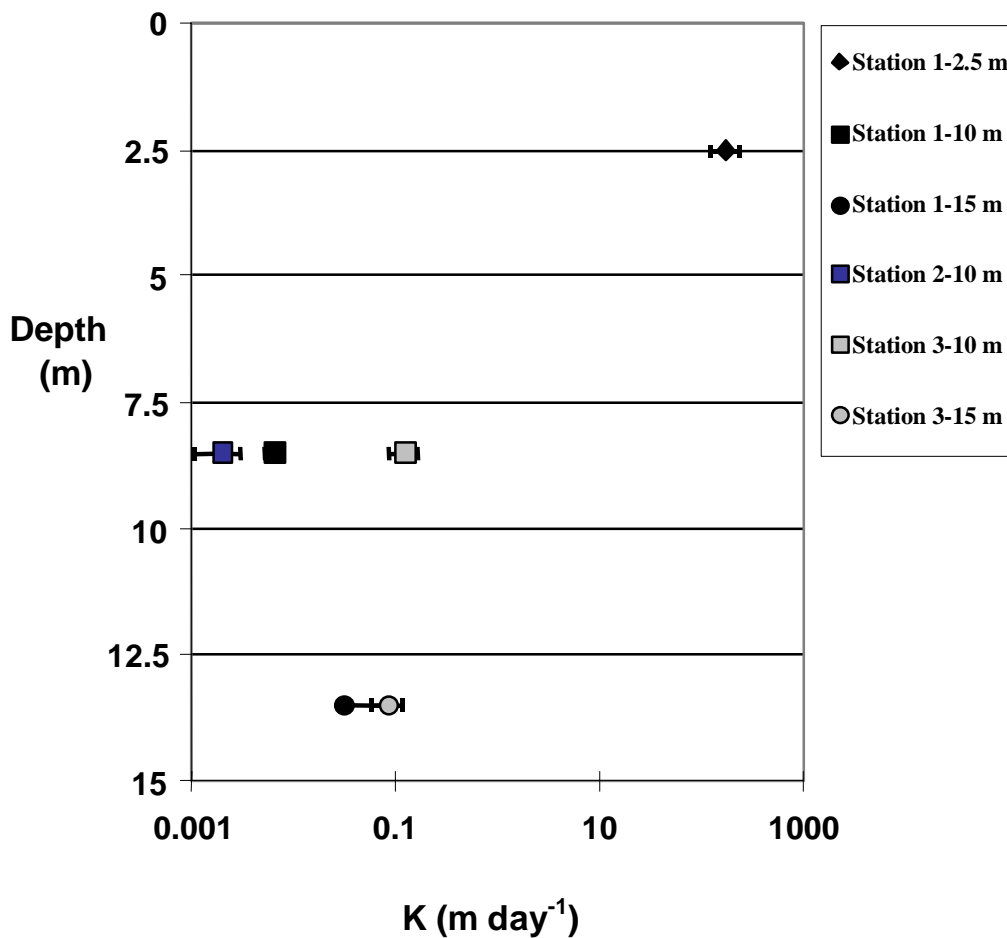
**Figure 7.5**   Hydraulic conductivity measurements at 5 selected locations.

## Hydro-chemical constituents

The results of the canonical discriminant analysis are depicted in Table 7.1. The first computed canonical discriminant function represents 15 of the 19 measured variables and explained up to 99 percent of the variance. The basic premise of groundwater flow along the regional hydrological gradient is the

interconnectivity of the flow that should influence the chemistry of the groundwater along its flow path. The groundwater samples collected from the observation wells located in the deep peat section north of Lake Agmon was successfully grouped on the basis of its chemistry with less than 4 percent of the cases wrongly classified (Table 7.1). On the other hand, the groundwater samples collected from the transitional layers as well as the limnic marl were successfully classified on the basis of their chemistry in only 70 to 78 percent of the cases. The discriminant analysis results suggest that groundwater chemistry collected from the deep peat area has no similarity to groundwater collected just south of the deep peat area and may have little hydrological connection between these two areas.

Table 7.1 Classification and cross-validation results of the discriminant analysis using the 19 hydro-chemical parameters.

| | | | Classification results[b,c] | | | |
|---|---|---|---|---|---|---|
| | | | Predicted group membership | | | |
| | | GRP | 1.00 | 2.00 | 3.00 | Total |
| Original | Count | 1.00 | 78 | 1 | 1 | 80 |
| | | 2.00 | 3 | 51 | 16 | 70 |
| | | 3.00 | 1 | 6 | 40 | 47 |
| | % | 1.00 | 97.6 | 1.3 | 1.3 | 100.0 |
| | | 2.00 | 4.3 | 72.9 | 22.9 | 100.0 |
| | | 3.00 | 2.1 | 12.8 | 85.1 | 100.0 |
| Cross validated[a] | Count | 1.00 | 77 | 2 | 1 | 80 |
| | | 2.00 | 4 | 50 | 16 | 70 |
| | | 3.00 | 1 | 9 | 37 | 47 |
| | % | 1.00 | 96.3 | 2.5 | 1.3 | 100.0 |
| | | 2.00 | 5.7 | 71.4 | 22.9 | 100.0 |
| | | 3.00 | 2.1 | 19.1 | 78.7 | 100.0 |

[a] Cross validation is done only for those cases in the analysis. IN cross validation each case is classified by the functions derived from all cases other than that case.

[b] 85.8 % of original grouped cases correctly classified

[c] 83.2 % of cross-validated grouped cases correctly classified

The **chemistry of the groundwater samples** collected from the transitional peat area show high similarity to the chemistry of the purely limnic marl environs thus indicating that these two areas are better hydrologically connected. Additional analysis of conservative ions such as Cl showed that the deep peat soils exhibited the highest concentrations of Cl (averaged > 400 mg l$^{-1}$) compared with averaged Cl concentrations of 250 mg l$^{-1}$ and 300 mg l$^{-1}$ in the transitional soils and limnic marl areas respectively. The pattern of hydrochemical parameters as emerged from the discriminant analysis suggest that groundwater from the deep peat soils may have limited connectivity to the area west of Lake Agmon and that most of the groundwater north of the Agmon is flowing to drainage canals that empty directly into Lake Agmon. On the other hand, the chemical similarity between groundwater of the transitional soils and the limnic marl area indicates of hydrological connectivity between these two areas that most likely is driven from the flow conductance of the reconstructed Jordan River. These results provide the required information for setting up the boundary conditions of the numerical model simulation.


### *Numerical water balance simulation*

On the basis of the above results which include monthly measurements of hydraulic heads in 80 observation wells, real-time in-situ measurements of hydraulic heads, temperature and EC, parameterisation of hydraulic conductivity, and pattern recognition analysis of the interconnectivity of the groundwater flow in the study area we established a numerical model using the following attributes:

1. The model consists of two layers. The upper layer (the top 5 meter) was assigned a K value of 100 m d$^{-1}$, whereas the lower layer (5 to 15 meter) was assigned a K value of 0.01 m d$^{-1}$,

2. The grid size of the numerical modelling was derived from the measured local gradient used to compute the K value from the point dilution experiment,

3. The reconstructed JR is important boundary condition that impact inflow to the area and minimise the influence of evapotranspiration,

4. Because of the low K values of the second layer and the small differences in hydraulic heads between 10 meter and 5 meter depth during most of the monitoring period, the vertical water flux is insignificant for total water budget calculation,

5. Groundwater flow into the main drainage canals of the Jordan River except where decoupling of the western canal from groundwater was observed (Tizpris & Miron, 1998),

6. The plastic barrier south of Lake Agmon was assigned no flow boundary on the basis of isotopic data, hydro-chemical parameters and hydraulic head analysis,

7. All the major drainage canals within the area of interest can be a source of water into the shallow aquifer or can serve as drainage pathways, thus were assign the 'river boundary' of MODFLOW to accommodate water flow in and out of these canals

8. The modelling of the groundwater assumes quasi steady state condition.

The numerical simulation of the study area is depicted in Figure 3.3-6. Groundwater flow was generated from the reconstructed JR into the area bounded by the plastic lining barrier and the western canal. Groundwater flow was heavily influenced by water flow from canal 404 and canal 312. Canal 404 is a continuation of the reconstructed JR south of Lake Agmon whereas canal 312 is the southern outlet of Lake Agmon into the Western Canal. Discharge calculations in both canals have shown that in most cases the canals were contributors to groundwater flow rather than draining the area. The model was calibrated using key observation wells located across the simulated area. The model was considered calibrated when the estimated parameter uncertainty and associated 95 % confidence intervals were less than 30 cm for the entire simulated area. No improvements were achieved in the mean absolute error with further parameterisation of the K or boundary conditions.

The numerical simulation with the conditions outlined above suggested that water flux from groundwater to the western and eastern drainage canals is approximately 7,400 $m^3$ $d^{-1}$ or about 220,000 $m^3$ month$^{-1}$. These water budget calculations are reasonable estimation of water flux from the Hula Valley to the JR during the period where the hydraulic head in the study area is relatively stable (see Figs 7.2 to 7.4). These calculations are erroneous during the winter months (underestimation) because of considerable aerial influx or during prolong draught without irrigation like in the fall of 2002 (overestimation).

The **P budget calculations** were based on additional assumptions related to P physico-chemistry behaviour in this altered wetland environs. We assumed that the P concentrations measured in more than 200 groundwater samples analysed during the monitoring period is in quasi steady state with the

flow conditions and no significant sorption/desorption or precipitation/dissolution have occurred along the flow path. The sorption/desorption assumption was based on the construction of numerous sorption isotherms that showed that the limnic marl material exhibited low to moderate sorption maxima and high $EPC_0$. In addition, we saw no distinct spatial pattern of P that could suggest increase or decrease in P concentrations along the flow path. Using these assumptions along with the flow assumptions outlined above we found that the P flux from the groundwater to the drainage system is approximately $10.3 \pm 7.4$ kg d$^{-1}$ or $310 \pm 220$ kg month$^{-1}$ or $3.7 \pm 2.6$ t yr$^{-1}$.
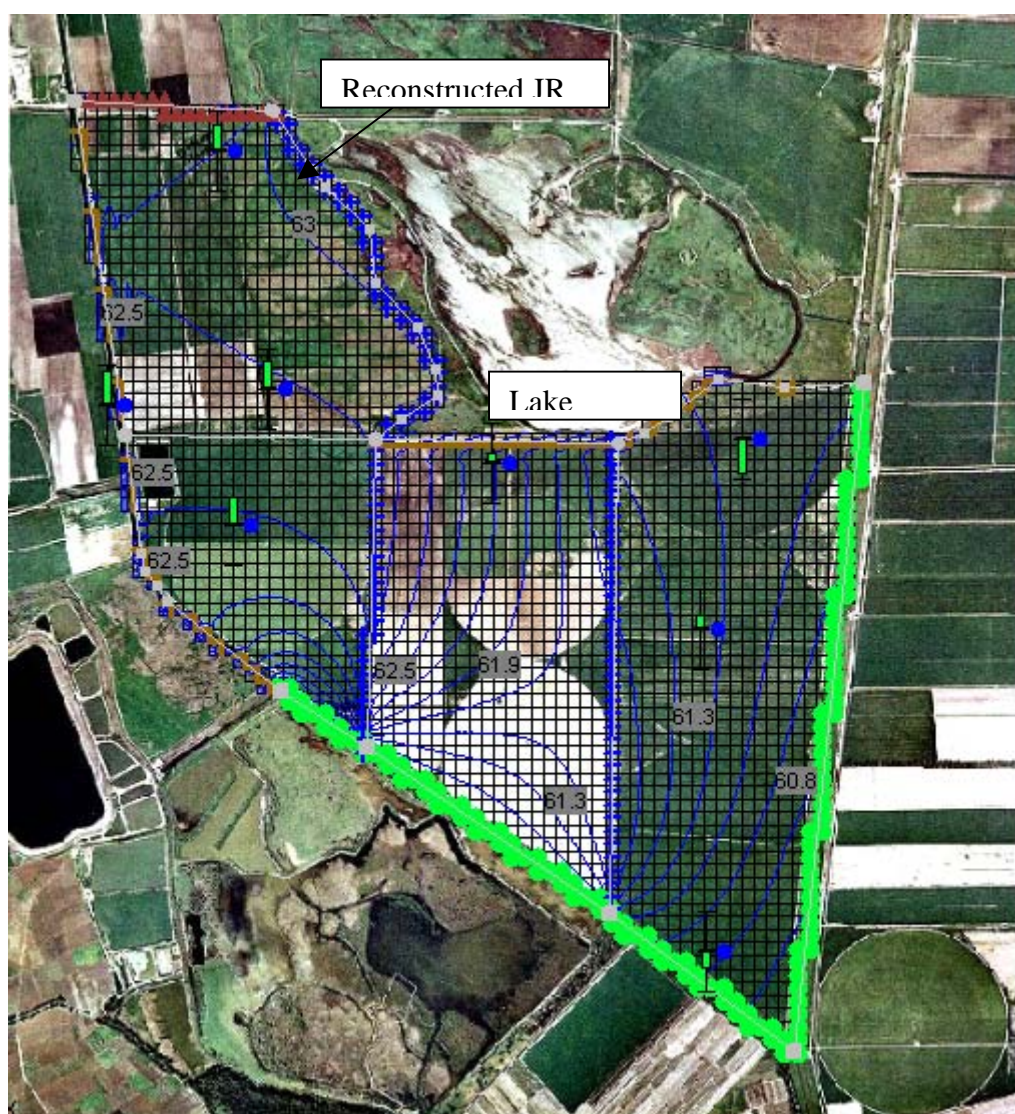


**Figure 7.6** Numerical simulation of water budget in the study area

ROM (1999) calculated that the relative contribution from the Hula Valley to P loading in the Jordan River is approximately 10.4 t yr$^{-1}$ of soluble P. This calculation was based on comparing the P loading in the Jordan River at the valley inlet with the P loading in the valley outlet where Mekorot, the Israeli Water Company installed hydrometric and water sampling stations. ROM (1999) could not differentiate between groundwater influx and water that could have come from unmonitored drainage canals and ditches located between the two measuring points. Hence, the present calculations suggest that P loading to the Jordan River from groundwater flow is at least 35 percent of the total soluble P reaching the outlet of the Hula Valley.

## *Summary*

The quantity and quality of groundwater flowing through altered wetland of the former Hula swamps and lake may influence the water quality of Lake Kineret, which provides up to 30 % of the potable water to the state of Israel. Recent land use change transformed the least fertile peat soils to a new shallow lake (1.1 km$^2$) which introduced significant changes in groundwater flow characteristics of these soils. A water balance was calculated using numerical model that was based on pedological evaluation of the shallow hydro-stratigraphic units, monthly and real-time measurements of hydraulic heads, seasonal analyses of chemical constituents and determination of hydraulic conductivity. The boundary conditions of the numerical modelling were determined using a pattern recognition analysis that employed kriging routine coupled with discriminant analysis of 19 hydro-chemical parameters. The numerical water balance modelling suggested that water flux from groundwater to the drainage system during the rainy season amounted to approximately 7,400 m$^3$ d$^{-1}$ or 220,000 m$^3$ month$^{-1}$. The P budget calculations were based on several assumptions related to the physico-chemical attributes of P in this altered wetland environs. For example, we assumed that the P concentrations in groundwater is in quasi steady state with the flow conditions and no significant sorption/desorption or precipitation/dissolution have occurred along the flow path. Using these assumptions we found that the P flux from the groundwater to the drainage system is approximately 3.7 ± 2.6 t yr$^{-1}$ which is about 35 percent of the soluble P reaching the outlet of the Hula Valley.

# 8. Decision support systems, assessment of acceptance, socio-economic consequences, and implementation strategies

*How to match stakeholders interests in processes of ecosystem renewal and how assist decision making with decision support systems?*

## 8.1 Introduction

Re-wetting peat swamps belongs to a set of measures for ecosystem restoration and renewal that becomes popular in the late 20th century and will still be a task for the first half of the 21st century. The paradigm regarding the use and use value for peat swamps had changed from draining swamps for the purpose of use as agricultural land towards protecting and assessing total environmental values that include values such as water regime, cleaning-up surface water, climate regulation, bird sanctuary, tourism and recreation etc. to allow for economic valuation and decisions.

The key parameter for this study is phosphorus (P). The main question of this study was: Does re-wetting affect the water quality within the ecosystem and downstream by P release and subsequent eutrophication? And if yes, how decisions have to be made to prevent this pollution and how can the environmentalist target of preventing open space ecosystem be achieved?

We applied different methodological approaches of socio-economic, environmental and ecological economics research, decision theory and management practice.

This chapter will mainly explore the findings of natural science and will translate the results into decision support system that may allow for better understanding and management.

## 8.2 Sustainability and decision making processes

Sustainability approaches related to decision-making and management (options) base on quantitative (1), or semi-quantitative (2), or qualitative (normative) (3) aspects of valuation / ethics. Tools for strong decision-making (a), or decision-making with involved risk (b), or uncertainty (c) vary significantly. Whereas (1) and (a) goes along with quantitative data which have been measured or observed in reality and allow for predictable response, (2) and (b) respectively require data sets translated into each other. The one way or the other, responses or outcomes of decisions or applied management

strategies may be assessed. They will appear with a probability of 0 to 100 per cent (probabilities between 0 and 1). In case of lacking quantitative data (3, c) a mix of parameter data and/or contextual "data" are usually used to narrow down the probability paths or space for unwanted and wanted outcomes.

BINGHAM et al. (1995) distinguish between **information needs** for decision-making in general and **decisive information**. Decision support in the ecological – economic context requires joint modelling including:

- "review what information existing ecological model(s) accept and in what form predictive information is generated,

- begin to explore ways the ecological model(s) need to be adapted to serve policy or valuation purposes and /or what economists could do with the information generated, and then

- organise a valuation study given previous work on linkages with the ecological model."


To design a decision-making process or a decision support system the following sets of data are required:

- Specific causes of the wetland degradation – data and parameter for the subsequent states the system passed through in history and may respond to the re-wetting process (data and parameter must base on the same methodology for comparison and valuation).

- A methodological framework that allows for both ecological and (socio)economic analysis – characteristics and parameters that allow to compare functional and structural data as well as context data (environmental such as climate, societal such as political regulation).

- Valuation tools as

- monetary valuation and cost-benefit analysis

- multi-criteria analysis and evaluation or contingent ranking

- tools that bases on key processes and assuring resilience of the specific system and the contextual impacts and responses

- tools that simply avoid systems cross-border impacts and preserve the specific system.

We do still face the lack of building integrated models for natural and social Science. The aim for interdisciplinary studies mainly is to reach agreement on:

- "terminology and typology appropriate to valuation,

- the scale of effects to be analysed and possible associated thresholds,

- valuation methodologies,

- links between valuation and systems and scenario analysis,

- the transferability of information and results in both scientific and economic realm,

- the focus of analytical approach, whether thematic or by site,

- consideration of valuation within its context, i.e. the prevailing political and social framework"

(TURNER et al., 2000).

In the project the focus is on strategic decisions and long-term sustainability (agreed in almost all site specific management plans). In such strategies decision support system have to assure (HILDÉN, 1997):

- completeness

- parsimony (absence of redundancy)

- logical consistency (not given because of strong differences between the sites, site specific experiences and stakeholders interests)

- accuracy
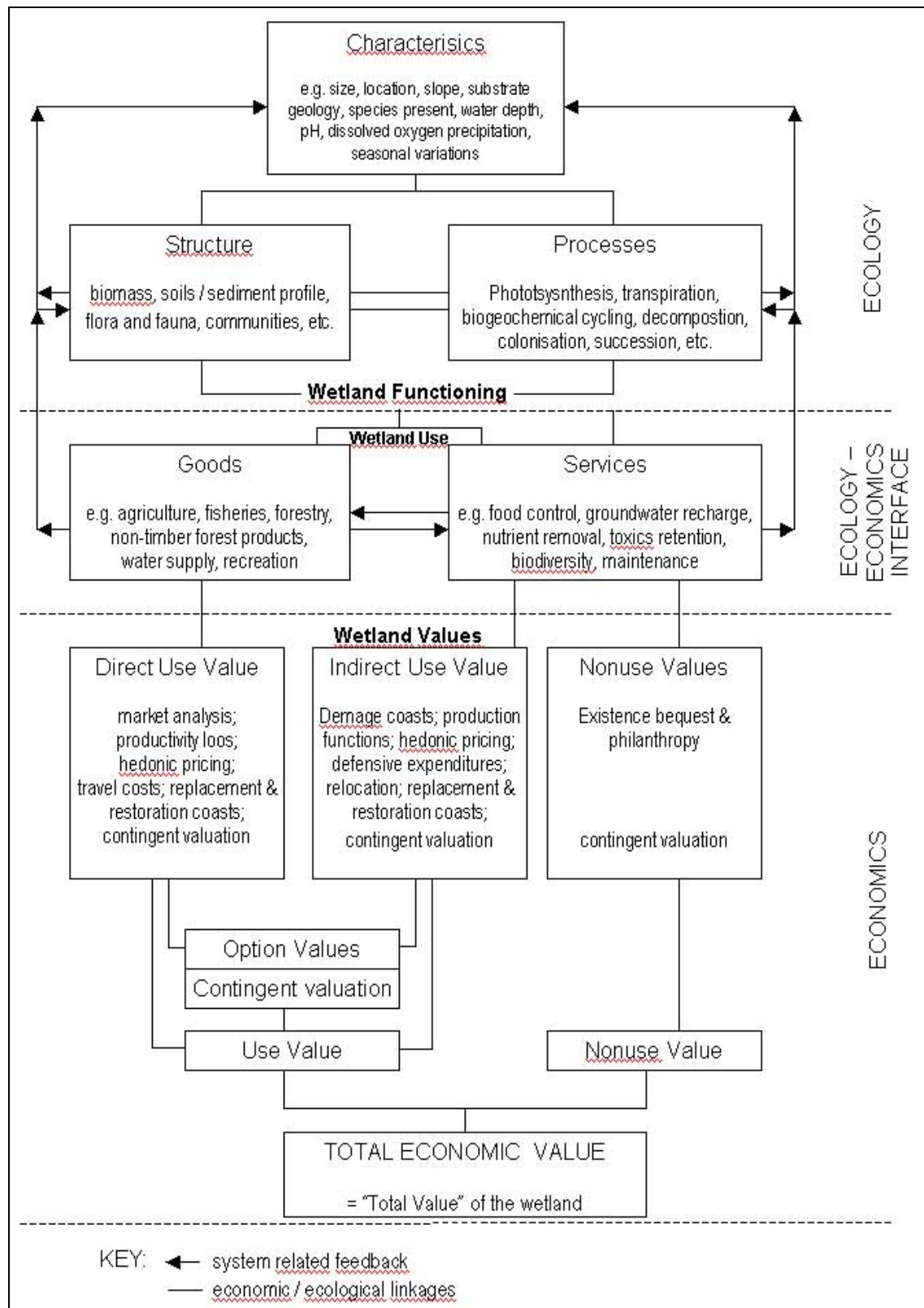
- practicality

- transparency

- neutrality.

**Figure 8.1** Connections among wetland functions, uses and values (TURNER et al., 2000)

In almost all cases evaluated in this study the management plans are already in place and addressing the P problem in these plans is a late-comer and has to be integrated in a process that already had settled and

administered. In addition, we had to learn in the project that the "system" itself had passed through many ecological, economic and social thresholds.

## 8.3 Results from natural science

Natural science answered the question of emerging risk for P pollution during and after re-wetting processes yes for almost all locations. The results are exploited in detail in chapters 3 to 7. However, the time scales, natural, economic or political factors and drivers may differ from site to site. Obviously, this result demands that different and individual decision support systems for each ecosystem have to be designed. In addition, specific key parameters have to be implemented in the site specific decision support model. Finally, the comparison of different sites also made clear that the stage of development or degradation of the individual ecological system is important to the overall management regime.

However, a general model (Fig. 8.2) that one may apply for all sites is a very simple matrix but it takes into account that all systems & sites have passed through a four step cycle. Re-wetting in this model presumes that a system as a whole should (political will) be brought back into a "pristine" stage.

| P / Ground water table | Low | high |
|---|---|---|
| low | · | ● ↑ |
| high | · | ● |

Figure 8.2 General model to assess the state-of-the-art of the individual wetland systems.

However, one aspect of the irreversibility of the preceding process is that due to fertilisation P has accumulated depending from the site parameters in different concentrations in different horizons of the soil and therefore different time paths of removal or to a long-term potential for P pollution on-site or off-site (downstream) may occur.

## 8.4 Results from social science

History of land use and land use intensity, especially P application to increase short-term agricultural productivity, ploughing and degradation of organic content of the soil and therefore changing the physico-chemical processes within the soil functioning have been indicated the main drivers for change.

Five options have been designed for fen area management throughout this project. They all base on some experience but lack large scale application.

1. Avoiding further P input.

2. Water table management (water authorities or farmers as main stakeholders), avoiding fluctuation of the water table but loosing the opportunity of (extensive) agricultural management (highly subsidised at present) but risking bushing and changes in fauna and flora with uncertain outcomes and experiencing serious water deficits during summer (when evaporation is larger than precipitation), requires changes in land-use practices but may allow for P export by plant cropping at times when the fenland is able to carry machinery, technologies and opportunities for using biomass required.

3. Redox potential and ion (Fe, Al, Ca) management (science as the main stakeholder), small scale test field management to monitor and to reduce process uncertainties and apply later for larger scales (regional differentiation to acknowledge).

4. Experimental management; removing degraded peat layer (with P, surface layers of 30 to 50 cm) and starting a process of peat / reed growing by water table management to built up reed-peat with high organic content and capacity to bind P (suitable for large areas ?).

5. Risk management by re-wetting anyway (while usually lacking water for doing so) and buffer with an artificial wetland downstream to rebound released P in newly established organic soils (large-scale landscape management where altitude allows for this).

The first management rule is obvious and should be strengthen by all economic and political means. There is no doubt that this is essential for all other management regimes in wetlands. Every other single management scheme (2-5) bases on the overall assumption and proof that P release occurs through re-wetting and may endanger downstream uses of water for different purposes. P causes eutrophication that reduces overall environmental quality and quality of life. Eutrophication may also cause under certain circumstances harm to human and animal health by supporting the production of neuro-toxins

(reducing regional opportunities for bathing, tourism or agriculture). In addition, re-wetting has a negative impact on climate protection because of the release of greenhouse gases.

From the comparative study we identified four stages of development of each individual ecosystem,

- "natural",

- drainage and agricultural use without fertilisers,

- exhaustion of fertilisers, degradation of soils and artificial fertilisation,

- re-wetting.

Each stage follows different constitutional parameters both in the physical and in the socio-economic system. We therefore tried to apply the **Pressure – State – Impact – Response (PSIR)** model (TURNER, 1997) to understand the processes and time paths of response. It became obvious that the socio-economic and technological, in some cases also political, drivers are very similar but the time of impact start (drainage and later fertilisation) and the technological opportunities at that time matters a lot. As rule of thumb the later the impact, e.g. drainage, started but the better the technological options the more sever the impact and the shorter the time until (negative) response of the ecosystem occur (Hula Valley and Somerset Levels and Moors). Again, this lead to the conclusion that each site needs to be treated individually for developing decision support systems (DSS).

We therefore decided to concentrate on the Droemling area where the users conflict is obvious and the data base by the end of the project allowed for building up a DSS on the basis of scenarios derived from the field and laboratory experiments and measurements (Fig. 8.3).
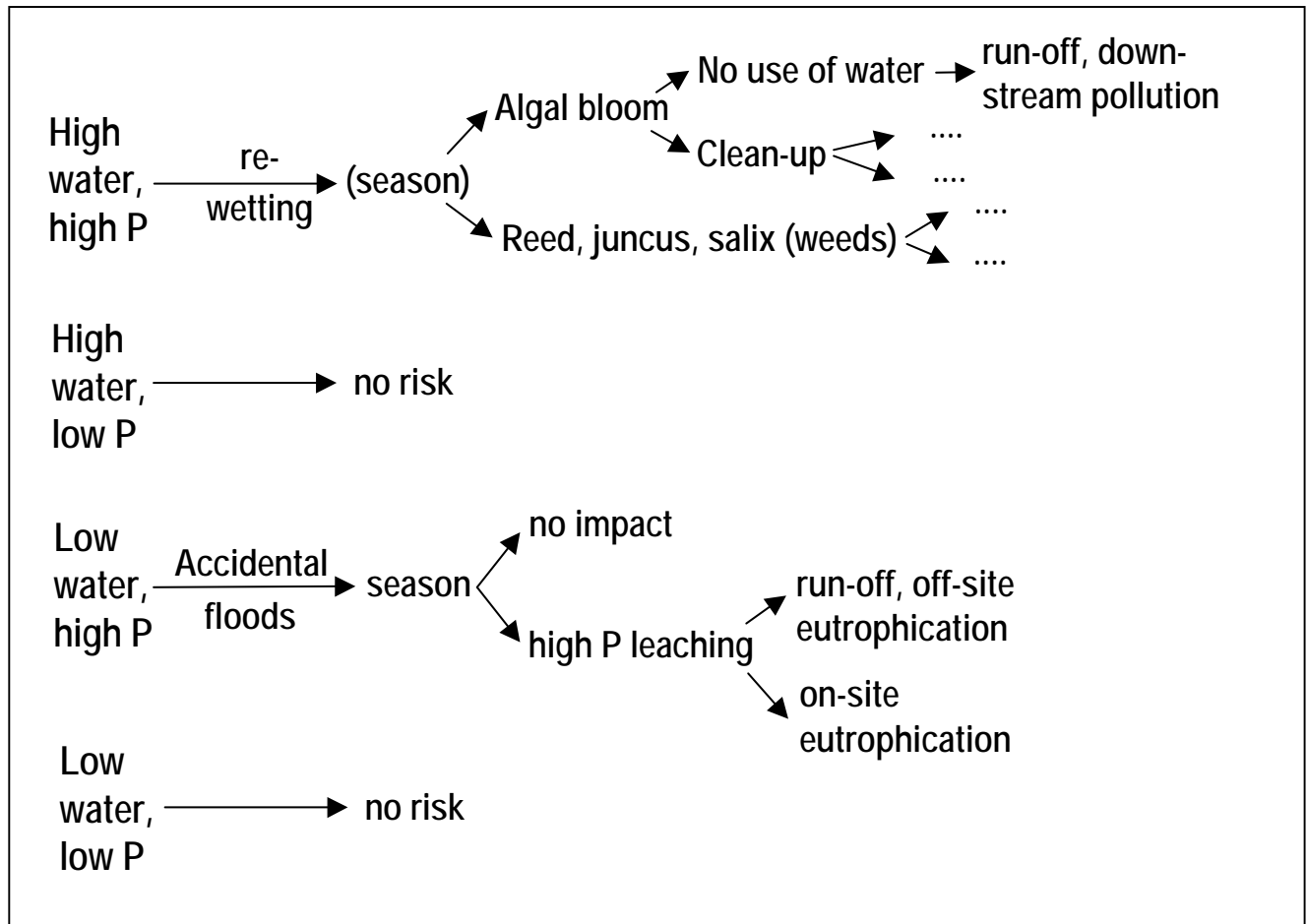


**Figure 8.3** A pre-preliminary decision support model for P management in re-wetting processes.

## 8.5 The Droemling case study

The Droemling area is a shallow peat swamp fed by water from the Ohre river. The water of the river is used upstream in Lower Saxonia (cross border issue) mainly for watering fields. Water is short in the region in summer. Evaporation is higher than water supply during summer. The Ohre river has provided raw water for groundwater infiltration in the Colbitz – Letzlinger Heide since the 1960s. This management regime is a stable source for drinking water for

600.000 inhabitants in the Magdeburg region. Infiltration takes place annually between September and May / early June. It amounts about 5 per cent of the annual water flow of the river. The this way enriched groundwater potential is a long-term storage basin.

The Droemling is a natural reservoir for the raw water supply for the region. The management scheme of infiltration (enrichment of groundwater stocks) has been proofed being successful for decades. The Droemling area was used by agriculture and should be renewed as a nature sanctuary in line with the FFH guidelines of the EU as a wetland.

Peat swamps were sinks for nutrients since they accumulated during their evolution degraded biomass and the upstream material. The wetland formed a kind of natural filter and therefore also accumulated nutrients. The peat swamps grew until they reached the surface of the water basins in which they have been formed. The wetlands and the water level were almost in a steady-state condition. Depending on the main plants *(Alnus, Juncu*s, reed, and others) forming the peat at the site over hundreds of years the soil structure and properties may differ. Fertilisers such as N, and P were used by the plants that naturally grew on this soils. While the nutrient stocks steadily but in an almost steady-state situation grew slowly, the flows remain more or less constant over time. Organic soil like peat remained in a constitution that one may describe as "living soil".

After land was transformed into agricultural land **(A)** grazing or harvest of field crops took biomaterial and nutrients away from the sites. The flows got out of balance, the stocks delivered nutrients to the demand. Consequently the productivity for agricultural production decreased. A lack of nutrients was identified as the main reason. To avoid shortage in nutrients artificial fertilisation with N, P and K was introduced to compensate for the diminishing rates of harvest. This worked for some years but after this time in relation to ongoing degradation of peat soils the imbalance of stock and flows increased as well as the vulnerability of these soils.

Water levels were reduced by draining the area **(B)** for the reason that mechanisation of agricultural production required that the soil could carry machinery for tillage, harvest and later fertilisation. Draining the soils led to a "dying" organic soil (peat degradation). "Dying" was caused by two main reasons (1) decreasing the water table, and (2) interrupting the soil structure by tillage and increasing the physical pressure on the soil surface by using machinery. Ever increasing rates of fertilisation exceeded the harvest output and the stocks of fertilisers steadily grew. Both (A and B) lead to a response of

the system of the living soil. A pre-condition for production is that this soil was alive. A and B caused damage in the systems structure and functioning and the degraded soil could not longer regulate the relations between stocks and flows as the proportions of P fractions indicate (e.g. Fig. 5.2). This in consequence lead to an accumulation of nutrient stocks and an uncontrolled release when the then "dead" soils were re-wetted or flooded. The desorbability is clearly indicated in Figure 6.1.

P release through re-wetting processes may harm the quality of drinking water supply because of higher DOM loads because of eutrophication of the raw water. With regard to higher P remobilization rates it is expected that higher costs for drinking water processing or limits to infiltration rates or lower water quality may appear.

With regard to all sites studied in this research a stakeholder conflict of re-wetting at this site is the most expected. The main target therefore is to avoid any possible harm to the raw water what is used for infiltration and providing drinking water to 600.000 people. This environmental use function therefore is prior. At the same time and at the same place a Natural Development Plan set the target of re-wetting for a Nature Park Sanctuary that belongs to the FFH list of the state Lower Saxony – Anhalt.

At least two stakeholder conflicts override all other possible conflicts in this region

- protection of the raw water quality and assuring the quantity of raw water that is needed for a sustainable supply of drinking water to a region with 600,000 inhabitants (in line with the EU Water Guideline that does not allow for diminishing water quality),

- re-wetting of the Droemling area for ecosystem renewal and nature protection.

A set of other targets is of minor importance.

The results of the soil and water observation show that there is a risk of pollution. These results are due to measurements in the field, in-situ and in-vitro experiments but also from simulation models (Fig. 8.4). The P concentration in the Ohre river is slightly increasing, the trends are significant (Fig. 8.5).
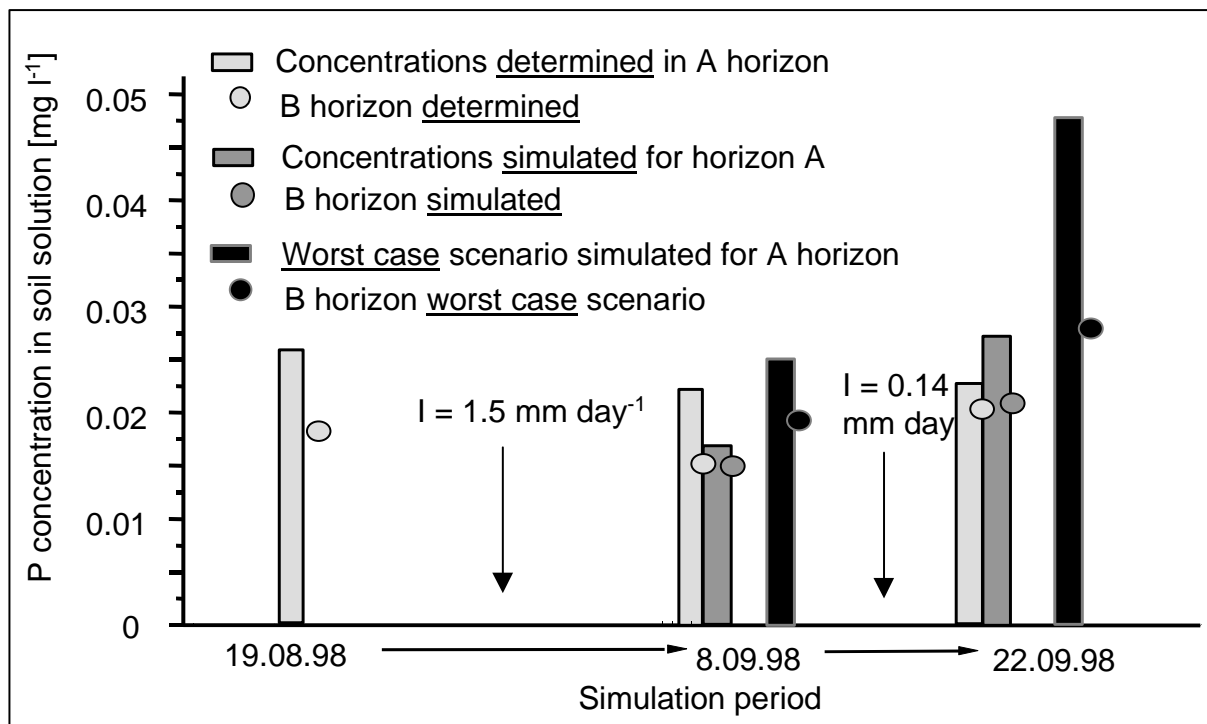
**Figure 8.4**  Simulation of P mobilisation in the Succession plot of the Droemling area

The basic assumption that re-wetting causes P remobilization is evident. Since there is a risk of P pollution and therefore a risk to uses of other stakeholders a decision support system makes sense. Consequently some questions seek answers, e.g. there are questions for quantities and scales of the processes affected by re-wetting. Other questions are, for instance, do risks occur continuously, or temporarily, and if yes, in what intervals and in which spatial magnitude do they occur, and then, what are the options to react or to manage at the interface of the environmental and the socio-economic system.

The following result from the **microcosm experiments** is very important for the decision support model: P release increases after two weeks of flooding and there is a strong relation between water table and redox-potential with the risk of P release shown in microcosm experiments (see Figs. 5.1 and 5.4). That means that the decision support model has include **a monitoring of two week intervals**. This implies in turn that a pre-condition for the management as well as the decision-making process is a strong monitoring program to prevent a decrease of raw water quality or to have options to interact with the environmental system of the Droemling.
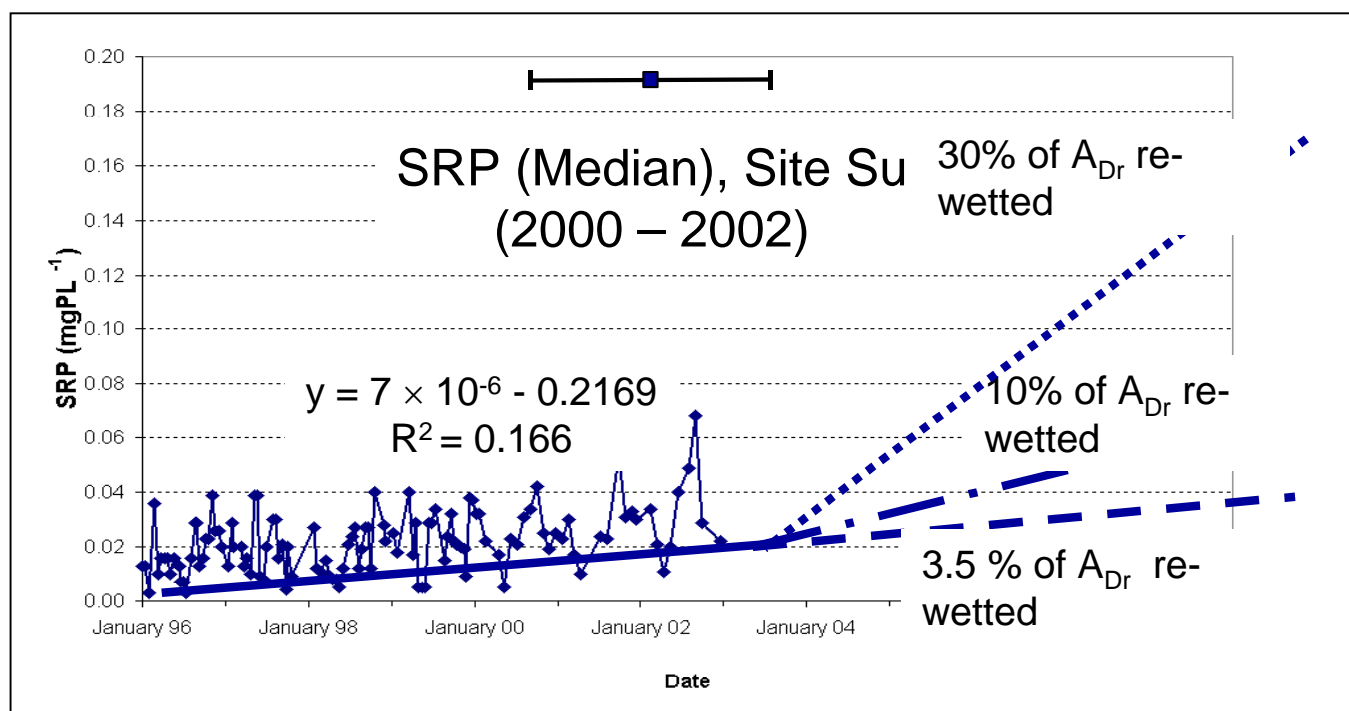
**Figure 8.5** Long-term trend in the concentrations of soluble reactive P (SRP) in the Ohre river, and forecast of SRP concentrations if the re-wetted area is increased from 3.5 % (present situation) to 10 % and 30 %.

When comparing graphical presentations of **P fractions** before and during re-wetting (e.g. Figs. 5.2 and 5.3) we do see that the P remobilization affects only part of the P stock but probably is a long-term problem since other fractions may go through processes of remobilization later because of balances between fractions under natural conditions. On the other hand, the results show that the impact of P remobilization is mainly restricted to the top horizons were the largest water table fluctuations occur. This leads us to another consequence to the decision support model. Long-term monitoring or re-wetting on additional areas within a site should only be done after monitoring of the P stocks and the fractions within the stock at the site that was already re-wetted before and further risk from this first re-wetted area is no longer to expect.

Further, we do assume for the decision support model that we do not have to expect threshold effects. Such effects would override the risk statements and would lead to real uncertainty for the whole process. "True uncertainty" can be excluded when looking on spatial dimensions of the problem. The spatial extension of the re-wetting process matters a lot for mitigating the stakeholder conflict or to prevent for higher costs of management. We therefore return to the findings of the physical and soil

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science at the Droemling site. The simulation model and the forecast of P in the Ohre river (Figs. 8.4 and 8.5) show that the risk of P release due to the re-wetting process can be managed. However, re-wetting of the whole site at once is to prevent.

We do propose, further, to apply the **EU Cost Action 832 recommendations** to monitor the SRP and phytoplankton values in the surface water, the sum of both should not exceed 50 µg l$^{-1}$. This is seen in limnology as a value that does not lead to eutrophication of surface water and consequently an increase in DOM values is not to presume.

It is important to acknowledge and to accept by the involved stakeholders that at first only 3.5 % of the area designed for re-wetting are due to this management scheme. Only later, the re-wetted area can be expanded. Expansion of re-wetting requires monitoring of surface water in two week intervals and observation of P stocks at least in the A horizon twice a year or before expanding the re-wetted area.

Re-wetting on 10 % of the area will increase the risk of eutrophication and the risk for raw water supply as well as the risk of losses in the infiltration area in quantity and quality substantially. A re-wetting of 10 % of the area should be postponed as a mid-term management option.

A 30 % re-wetting will exceed the systems capacity and resilience at present. The management plan may only take this as an option for a long-term management plan.

The risk of higher costs to the drinking water supply and the risk of the loss of the infiltration area by higher impacts of DOM to prevent in the first rank of targets in the management regime in this region. This recommendation or demand is in line with the EU Water Guideline. The project therefore has provided a good example for best practice, conflict solution strategies and assistance to decision-making processes by transdisziplinary science approaches.

It also has to be acknowledged that the shortage of water and the seasonal aspects of water supply and evaporation calls for a larger management regime that also takes intro account the upstream use of water for watering fields. The cross boarder management plan (with Lower Saxony) has to set quantitative targets of decreasing water demand for the purpose of watering fields since the targets of drinking water supply and preventing changes of water table in the re-wetted areas have to be ranked higher for

their risk potentials than all the other used by stakeholders in the same drainage basin.

Finally, the conflict of targets between water supply for drinking water purposes and re-wetting for nature protection and ecosystem renewal processes may increase due to global climate change and high rate of evaporation and therefore increasing water deficits in the re-wetted parts of the Droemling. The monitoring scheme in unity with the decision support model will provide a basis to mitigate this risk.

The re-wetted area should not exceed 3 % of the total area of the Droemling. The re-wetting process is limited to the reservation area of the nature park at present. All other areas are used extensively by agriculture. Although the sole option at present only a minor part of the peat swamps can be protected by this strategy. A renewal of the peat swamp demands a greater area for flooding that only could be an option for later times and demands also cross border regulations for a sustainable drainage basin management and wise water management.

## 8.6 The Droemling decision support and management model

The basic assumptions for the **decision support system (DSS)** have been explained in the pervious chapter. The results have been discussed and analysed with stakeholders from the Trinkwasserversorgung Magdeburg and the Droemling Nature Reserve Agency. The following preconditions are to meet for the DSS:

- protecting raw water quality and assuring quantity for drinking water supply (see also EDWARDS et al., 2000)

    - keep SRP and phytoplankton values in surface water lower than 50 µg l$^{-1}$

    - keep DOM values low or decrease them

    - monitor every other week the P and DOM values

    - secure the infiltration period from September until May / early June in quantity and quality

    - avoid expansive technical solutions

- state-of-the-art (high water / high P)

- target function

    - high water / low P

- low P in the A horizon
- process
  - 3 % re-wetting, SRP in surface water will slightly increase, limits to eutrophication may temporarily achieved
  - 10 % re-wetting, SRP in surface water will steadily increase, limits to eutrophication will often be achieved
  - 30 % re-wetting, SRP in surface water will strongly increase, limits to eutrophication will exceeded permanently
- management options
  - no further fertilisation that will only add to the nutrient stock and therefore to risk
  - limit re-wetting to 3 per cent of the area in the first period
  - low use intensity of agriculture
  - P extraction where possible or add to economic value of stakeholders
- monitoring
  - SRP and phytoplankton, every other week
  - P stocks in A horizons in re-wetted areas for long-term monitoring and expanding of re-wetting areas in future

The decision support system for the Droemling is attached as a separate file.

## 8.7 Summary

The analysis of all study sites shows that two expectations drove the transformation of peat swamps into "dry" land for agricultural uses

1. to increase the area of arable land to respond on increasing numbers of population or increasing demand for food, fodder or pastures

2. to increase the crop yields by application of NPK – fertilisers.

The process accelerated, however, very recently and was accompanied by the factor of mechanisation and the use of machinery in these very sensitive habitats. This process started in all locations almost at the same time, in the 1950s and 1960s. The use of machinery or the lack of appropriate machinery to these sites requires lowering the water table considerably for the use of the machinery, that cannot be substituted by rainfall or other sources of

water supply immediately. The soil structures and functions changed. Many added values of wetlands got lost in a very short time. Agrarians, ecologists, soil scientists and even economists observed the negative impacts of this strategy on-site and in some locations also off-site.

However, in all locations the situation was reverted in the 1980s or the 1990s because of the

- better knowledge and bad experience

- low economic competitiveness of degraded peat soils compared to other arable land

- set-aside strategies of the EU or the increasing value of secure water quality

- increasing environmental awareness

- international studies on environmental values (environmental valuation) and added value of wetlands

- policy regulation and integrated environmental strategies for drainage basins.

Hence, the responses to re-wetting differ among the sites mainly due to management practise for water, the thickness of peat layers and the loads of P accumulated in the layers.

The overall conclusions of the studies evaluated here, is that the added value of wetlands in the landscape consists of three fundamental parts

1. wetlands assure the resilience of landscapes since they regulate or participate in the regulation of the water balance in a region

2. wetlands are filters and storage reservoirs or water (carbon and other substances)

3. wetlands are destinations for ecological tourism and may provide alternative sources of income to the local population.

The resilience of the regional ecosystem is supported by wetlands, however, it depends on other actors or the "co-operation" between factors, too.

Wetlands need appropriate technological – economic strategies for use and management. It is important to acknowledge that wetlands evolved or have been formed over very long periods of time, at least 5.000 years. The most important factor during the genesis of wetlands is the fact, that the annual water supply to the landscape in all study sites on average was much higher in these times as it is nowadays.

An individual decision support system has been developed for the Droemling area. The decision support system may assist conflict mitigation strategies and provides a long-term perspective for the re-wetting process in this region.

Decision support systems demand a continuous monitoring of physical data and may give support to stakeholders to iterate the management plans and options to avoid costs and at the same time to steer the process for ecosystem renewal. However the processes are long-term ones and depend on interdisciplinary of stakeholders, scientists and policy makers.

Decision support systems also may assist finding critical or trigging points for understanding and process steering. Hence "translating" data from one scientific discipline into another and to invite stakeholders in this process is a long-term challenge but worth to try.

# 9. The stakeholders view: guidelines for best management practices

## 9.1 The Droemling Nature Reserve

The investigations in the Droemling fen area, which were part of PROWATER, have shown that the redox potential is a crucial parameter for the assessment of P mobilisation. Redox dynamics is an important regulator of the binding and mobilisation of P in Histosols. Therefore, it is of key importance in risk assessment regarding the diffuse pollution and the eutrophication of surface waters. It was demonstrated that water table fluctuations determine redox potentials and, thus, the probability of P mass transport from the re-wetted sites to watercourses. Thus, the site-specific management of water table may enable both, fen peat conservation and preventing an accelerated P off-site transport.

The following guidelines can be established:

- Ground water table between 0 and approximately 0.3 m below surface level; water table oscillations between water logging and drying (seasonal ground water levels below 1 m) should be avoided.

- Management regime: extensively managed as unimproved pasture or grassland with biomass removal.

A strong monitoring system should be established before and during the re-wetting of Histosols including P in soil (P content and P fractions), soil solution, ground water and surface water. The DSS developed was found as a suitable tool for short-term monitoring and decisions on the establishment of new re-wetting areas. In addition to the data worked out in PROWATER, the suitability of relatively simple element ratios in soil solution and ground water (Fe : P, and Fe : S) for evaluating the risk potential needs to be further examined. Currently, the greatest gaps in knowledge, and thus the most important research needs, are related with the **persistence of diffuse P pollution from re-wetted areas**. Therefore, the stakeholders concerned about the development of Droemling area strongly vote for <u>long-term investigations</u> of re-wetting effects at degraded fen areas.

## 9.2 The Ljubljana Marsh case

Taking into account the extreme habitat diversity in the area, general and local measures for regulation of water table levels are recommended. In order to

ensure adequate water supply during drought periods in summer, the reconstruction of the dams on the Ljubljanica river and on the Gruber Channel is being proposed as to rise the minimum water table for at least 1 m, without increasing the risk of flooding in winter. A system of weirs on the main drainage ditches is being proposed to control water table levels locally, in such a way that about 30 cm of unsaturated zone is ensured throughout the year. Due to past fertilisation, arable land and arable land converted to grassland are the richest in soluble mineral P and, therefore, the major sources of diffuse pollution with phosphorus of ground water. According to the results of our field experiment, frequent removal of plant biomass as well as nitrogen fertilisation, which enhances the P uptake by plants may considerably reduce the pool of soluble P in the soil and hence the subsequent losses to ground water. Furthermore, the uptake of P by the riparian vegetation and aquatic macrophytes along the drainage ditches contribute to the reduction of soluble P in surface waters. Therefore, the regular cleaning of ditches by heavy machinery, which has been practised so far, is not recommended. Alternative uses of plant biomass (biomass for fuel, composting) are being explored in locally funded projects and should be recommended to complement agricultural interest.

## 10. Summary of main PROWATER results

Most project results were described and discussed in detail in the previous chapters. In the following, a final overview on main POWATER achievements and conclusions will be given. This is the result of intensive discussions at the Ljubljana Meeting, June 2003, and agreement among all project partners.

*What did we achieve and deliver to the scientific community and to the stakeholders ?*

(1) Developed and implementation of an automatic field measurement station for degraded and restored wetlands.

(2) Sets of field measurement data on important soil physical properties and evaluation protocol.

(3) Inventory of the relevant properties of sites and Histosols according a geographical gradient.

(4) Experimental system for the prediction of P solubilisation in Histosols based on fundamental principles in soil chemistry.

(5) Construction of thematic maps of degree of phosphorus sorption capacity in an altered wetland.

(6) The geochemistry of phosphorus in peat soils of a semiarid altered wetland.

(7) Improved methods for the characterisation of P in Histosols based on $^{31}$P NMR and sequential P fractionation.

(8) Scenarios for site-specific P mobilisation based on an adapted model of P leaching.

(9) Decision support tools for the restoration of Droemling fenland and prevention of diffuse P pollution of freshwater systems.

(10) Proposals for best management practices of fenlands.

*The main joint conclusions are:*

PROWATER was highly relevant for temperate and xeric peat wetlands, and the selected study areas were well suited to investigate the chemistry of P turnover in anthropogenically influenced and re-wetted Histosols.

We confirmed the hypothesis that redox dynamics is an important regulator of the binding/mobilisation of P in Histosols. We also demonstrated the importance of water table fluctuations in the mass transport of P from the re-wetted sites. Therefore, the site-specific management of the water table is of crucial importance for preventing the increased solubilisation and transport of soil P from the site.

In specific cases, modelling has proved to be well suited to estimate P inputs to surface waters and should be used for scenario calculations as a basis for the development of a Decision Support Systems (DSS).

***The following important research needs were identified:***

- Development and evaluation of site-specific management regimes in connection with an adapted DSS.

- Process studies about P-transport mechanisms in different scales, especially the phenomenon of lateral flow from the re-wetted area into the surface water.

- Evaluation the impact of climate change on Histosol restoration.

The project publication list in the following indicates who of the partners owns which result, and which results were obtained and published in teamwork. Finally, we emphasise that the process of result delivery to the scientific community through scientific publications as well as to the stakeholders is still going on and proofs the great practical impact of PROWATER.

## 11. Project publications: peer reviewed articles, PhD thesis and patents

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