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Landscape factors in material transport from rural catchments in Estonia



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ORIGINAL PUBLICATIONS

- I Pärn J & Ü Mander (2007) Landscape factors of nutrient transport in temperate agricultural catchments. WIT Transactions on Ecology and the Environment 104:411–423
- II Pärn J, L Randmaa & Ü Mander (2009) Dynamics of concentrations of total organic carbon in Estonian streams, 1992–2007. WIT Transactions on Ecology and the Environment 124:47–53
- III Pärn J, K Remm & Ü Mander (2010) Correspondence of vegetation boundaries to redox barriers in a Northern European moraine plain. Basic and Applied Ecology 11:54–64
- **IV Pärn J** & Ü Mander (20XX) Increased organic carbon concentrations in Estonian rivers in the period 1992–2007 as affected by deepening droughts. Biogeochemistry (under review)
- V Pärn J & Ü Mander (20XX) Rise of nutrient runoff following reintensification of land use and increasing water discharge in a small northern rural catchment. Journal of Hydrology (submitted)

The contribution of the author in the listed publications is as follows:

Publication I: The author was responsible for half of the design of the study and is entirely accountable for the data collection, analysis and

writing.

Publication II: The author performed part of the design and data collection,

most of the analysis and all of the writing.

Publication III: The author was the chief designer and the sole collector of the

data, the main analyst and writer.

Publication IV: The author was partly responsible for the design and the data

collection, and was the chief analyst and writer.

Publication V: The author was a minor co-designer of the study, was

responsible for most of the data collection and the analysis,

and was the principal writer.

ABSTRACT

The flow of chemical materials along spatial elements is a fundamental aspect of landscape ecology. Currently special attention is dedicated to the identification and mitigation of the environmental impacts of chemical loadings using freshwater wetlands and riparian buffers. Little effort has been made to investigate the formation and functioning of ecotones at the interfaces between the upland and riparian zones. The margins of riparian mires act as redox geochemical barriers. Such biogeochemical hot spots retain elements that have leached from upland soils. The impacts of landscape features on nutrient transport are especially relevant in Estonian rural catchments which experienced the collapse of collectivised agriculture followed by a drop in nutrient losses and subsequent stabilisation at low flow. Simultaneously, human activities may have intensified the role of northern European peatlands as sources of organic carbon. There are 10.091 km² of peatlands in Estonia, 60–70% of which are artificially drained. An increasing frequency of droughts has been observed during the last half-century, and this constitutes a threat of increased decomposition of peat and further export of organic carbon, especially from manmade drainage sites.

The present work was an effort towards a better understanding of the ecosystem processes that drive the transport of nitrogen, phosphorus and organic carbon in Estonian agricultural landscapes. The specific objectives of this work were as follows:

- a) To review the literature on the role of landscape factors on nitrogen and phosphorus fluxes from source areas to surface water;
- b) To analyse the correspondence of ecotones to horizontal redox barriers in a till plain in Estonia;
- c) To clarify the influence of land use intensification on nutrient and organic matter losses from the Porijõgi agricultural catchment in Estonia during the period 1997–2009 and to test a simple empirical model of nitrogen and phosphorus runoff;
- d) To explain the changes in organic carbon concentrations from Estonian rivers in the period 1992–2007.

The main sources for the literature review were works indexed by Mander & Mauring (1994) for the sources published until 1993 and by the Institute of Scientific Information Web of Science for 1994–2007. Data was collected for the purpose of three analyses: a) a conceptual diagram of nitrogen and phosphorus transportation, b) a display of determination coefficients between nutrient losses and landscape (complex spatial) factors and c) an analysis of the relationship between nutrient losses and catchment size in the agricultural catchments in temperate climate.

In order to investigate the ecotones, twenty-four random transects were surveyed on the till plain, and sampled across sharp soil moisture boundaries as proxies of redox barriers. The shifts in vegetation perpendicular to the boundaries were investigated by comparing the herbaceous plant cover in two

adjacent 10 metre wide plots. Curves of dissimilarity were computed by moving the 20 m split-window along the transects.

N and P runoffs were both calculated and simulated for the Porijõgi and its sub-catchments. To calculate organic carbon trends in Estonia, direct TOC (total organic carbon) measurements and COD_{KMnO4} (permanganate oxygen consumed) from 11 catchments were used. The trends were correlated with an index of hydrological droughts and with trends in sulphate concentrations.

The results of the literature review led to the conclusion that in catchments with varying inputs, soil qualities, the proportion of certain land uses, proximity to the water body and runoff factors are the determinants. When the inputs are constant in time, chemical and physical conduits and barriers determine the flows, and the factors of the landscape pattern explain the differences in nutrient losses. Nitrogen is often determined by factors of agriculture and soil characteristics, especially moisture, controlling denitrification. The greatest variance among N losses is in small catchments. Phosphorus transport is stronger in connection with physical factors, especially flow conduits and barriers. The link with the amount of riparian buffers and landscape pattern is therefore even clearer for P.

The riparian mire – upland redox barriers in the soil were found to be marked by corresponding vegetation boundaries in the studied Estonian till plain. Such ecotones can be observed in aerial and satellite imagery at the footslopes, revealing redox barriers and related hot spots in agricultural landscapes. The barriers and corresponding ecotones occur below cultivation terraces in field margins. Man-made drainage removes redox barriers and corresponding ecotones, making the landscape uniform and therefore vulnerable to disturbances, such as floods and droughts. The ecotones may represent functional boundaries for delineating wetlands and planning the sustainable use of agricultural landscapes.

The accretion of nutrient runoff from the Porijõgi and its sub-catchments during the 1997–2009 period was caused by the magnification of water discharges in the last two years and the re-intensification of agricultural landuse, although the recovery of nutrient flows fell remarkably short of expectations, probably owing to catchment retention. Export of organic carbon compounds in Estonian streams increased in the years 1992–2007, in spite of a general decrease in water discharges during that period. The main drivers of the increased dissolution of peat were the extremely low water tables deepened by man-made drainage, as revealed by close correlations with rising trends in droughts.

Conclusively, this thesis provided insight into chemical cycling in the northern rural catchments, especially presenting a landscape geochemical approach towards ecotones and supporting the linkage between the increase in organic carbon export and climate change. Furthermore, the present work is the first to analyse the rise in nutrient runoff due to the recovery of agriculture in Estonia.

I. INTRODUCTION

1.1. Landscape as the facilitator of nutrient cycling

The flow of chemical materials along spatial elements is a central topic in land-scape ecology (Forman & Godron 1986). The cycling of nutrients in rural catchments has been recorded in depth (Vitousek et al 1997; Neal & Heathwaite 2005), with the major focus on human impact such as overall land use intensification (White et al 1979), increased fertilisation (Miller 1979), afforestation (Bormann & Likens 1979) and stream channelization (Yarbro et al 1984). The consequences of land use change are especially relevant in Central and Eastern European rural catchments, which experienced the collapse of collectivised agriculture followed by substantial ecological and socio-economic impacts. More and more attention is dedicated to the identification and mitigation of the environmental impacts of chemical loading using freshwater wetlands and riparian buffers (Karr & Schlosser 1978; Whigham et al 1988; Verhoeven et al 2008).

In nutrient cycling, the basic landscape unit is catchment. In this thesis, landscape is considered to be a geo-system or geo-complex, a comprehensive complex of natural (physical, chemical, biological) and anthropogenic factors distinguished at various hierarchical levels (i.e micro-, meso- and macro-chores; Solntsev 1949; Neef 1961). Depending on the degree of human interaction, landscape characteristics can be dominated by either natural aspects or human management. The main natural factors in such a complex landscape system are water, topography, soil, geology and climate conditions, as well as plants (vegetation cover) and animals (fauna). Likewise, the ecosystem approach deals with the same factors as ecosystem components, but in contrast to ecosystems, where all of the relations are considered via biota, the geo-system/landscape concept considers all relationships (Leser 1978). Different factors at different temporal and spatial scales do, however, play different roles in determining landscape character. Climatic and geological conditions give rise to the basic natural character of a landscape, whereas topography, soil and vegetation cover are important in the formation of the detailed character of a landscape, and are influenced by human management (Forman & Godron 1986).

The two basic preconditions for a chemical element to be transported in catchment are: a) the availability of material and b) the availability of energy. Both, and especially the latter, are directly or indirectly controlled by landscape (complex spatial) factors. These are generally accepted and addressed as controls over biogeochemical fluxes (Gergel et al 2002). According to the geochemical concept of elementary landscapes (Perelman 1975), landscape is a centralised system. The association of soil cover and vegetation serves as its centre (Uuemaa et al 2008). In investigating material flows, elementary landscapes are identified as the largest possible areas of uniform soil cover and vegetation. The elements are typically aligned along hillslopes as mesotopographic sequences.

The landscape type, this research especially concentrates on, is the till plain dissected by glacial valleys, which is a predominant landscape type of Northern European landscapes. In these, soil wetness and moisture conditions in the plains are mainly determined by topography. A corresponding topographic pattern is observed in the spatial distribution of plant communities. The high and dry parts of the Northern European till plains are xeromorphic Scots pine and Norway spruce forests on Albeluvisols. The Stagnic Luvisols and Planosols of midslope mesomorphic conditions are mainly agricultural fields intersected by patches of mixed forest (spruce, birch, aspen, linden, oak, ash, maple). Moving downslope, moist birch forests occur on Gleysols, and eventually riparian mires with seminatural grassland prevail on Histosols (Granö et al 1952; Varep 1964; Arold 2001).

Particularly sensitive landscape elements (e.g. hill slope hollows) serve as conduits for nutrient fluxes, whereas resistant elements act as barriers or sinks (e.g., riparian strips for down slope flow). In resistant landscape elements, where nutrients are held for a substantial time, transformations of material occur, and these are controlled by the complex of qualities of the area (e.g., transformation of nitrogen, controlled by tree species and the availability of oxygen; Burt & Pinay 2005). In addition, uptake of nitrate is related to ecosystem photosynthesis and denitrification is related to ecosystem respiration (Mulholland et al 2008) wherefore vegetation pattern is of primary importance in the processes.

1.2. Riparian-upland ecotones as redox barriers

While the riparian buffer zones have been extensively investigated, little attention has been devoted to ecotones at the riparian-upland interface (Knauer & Mander 1989; Mitchell & Branfireun 2005). These are defined as transition zones from upland automorphic to riparian hydromorphic habitats. Descriptive criteria generally incorporate ecological characteristics such as local geomorphology, sediment and nutrient transportation pattern and the spatial extent of hydrophile communities (US Army Corps of Engineers Waterways Experiment Station 1987). For decades, the coincidence of physical and vegetation boundaries was the basic assumption for the German-Russian school of landscape systematics (Passarge 1919), and was supported by ample case studies (e.g Wierenga et al 1987). The presence of ecotones may be unrelated to physical features, but other things being equal, the edaphic conditions determine their position (Wiens et al 1985). Fluctuating climate, water, nutrient conditions, forestry and agriculture add stochasticity to their formation (Forman & Godron 1986; Kleyer et al 2007). Vegetation boundaries may be blurred by an ecological mass effect, as vegetation units with sufficient area spread their species over their boundaries to sites where a self-maintaining population cannot exist (Grytnes et al 2007). About 80% of changes in landscapes are smooth, and a relatively small number of boundaries are sharp (or hard; Forman & Godron 1986; Sebastiá 2004; Schaetzl & Anderson 2005). It is therefore

important to explain in which conditions hard ecotones are present in the landscape and where the same amount of change is spread over a greater distance as a continuum (Forman & Godron 1986). Growing attention is paid to soil boundaries as landscape abiotic edges or landscape elements in their own right (Mander & Murka 2003; Sommer 2006) and soil structure as a landscape indicator (Uuemaa et al 2008).

Regarding N and P flows and ecotones, the concept of horizontal geochemical barriers is relevant. The marginal zones of riparian mires act both as redox and sorptional barriers. These collect a large number of elements that have leached from upland soils. The humic and peaty soils of the footslopes are enriched with calcium, phosphorus, magnesium and other elements (Perelman 1975; 1986). The barriers may be only a few metres wide (Hill et al 2000). In such biogeochemical hot spots, the turnover of elements is more intense than in normal organic soils (McClain et al 2003). About 30 m of groundwater flow under the riparian wood is sufficient to remove all nitrate (Pinay et al 1993; Pinay & Decamps 2006). Also in regard of other elements, redox barriers are controls of nutrient and heavy metal transport to riparian zones and water bodies, effecting hypoxia, eutrophication, and toxic algal blooms in the water (McClain et al 2003; Szpakowska et al 2003). These marginal soils are more favourable to plant growth, and the zones are relatively abundant in plant species (Perelman 1975; 1986).

Deluvial sands and loamy sands accumulate in the margins of downslope fields. When a field is ploughed in the same direction for dozens of years, field terraces build up as contour banks of humus-rich soil. Due to their convex shape and the fact that they were mostly covered with perennial grass or bushes, cultivation terraces act as mechanical barriers against downhill fluxes of phosphorus and carbon. With the low water retention capacity of the deluvial sands, the lower parts of the field terraces act as natural sinks for water. The resulting oxic conditions of the soil in cultivation terraces facilitate nitrification, oxidizing ammonia to nitrites. These are ready-to-use substances for denitrification in the anaerobic conditions of the mire, strengthening the role of ecotones as effective biogeochemical barriers to nitrates (Kruk 2003).

The width and location of the ecotone is subject to great spatial variance, depending on the local land forms (especially the flood-prone area), the size and the position of the stream in the drainage network, the hydrologic regime and the water holding capacity of the soil (Granö et al 1952; Johnston & Naiman 1987; Mitchell & Branfireun 2005).

1.3. Land use change in Estonian rural catchments in 1987–1997

An enormously rapid change in land use and, furthermore, a great reduction in fertiliser use has been reported for Estonia in the early 1990s (Mander & Palang 1994; Löfgren et al 1999). In comparison with the level at the end of 1980s,

only 5-30% of the N and P mineral fertilisers and 30% of the manure were applied in the agricultural lands of the catchment in 1995 (Löfgren et al 1999; Mander et al 2000). In the thoroughly investigated case of the Porijogi River (Mander et al 2000), a significant change in the land use pattern of the catchment took place during 1987–1997. The share of abandoned land expanded from 1.7 to 10.5%, while arable lands have decreased from 41.8 to 23.9%. Forested areas, natural and cultivated grasslands increased from 40.0 to 44.8%, from 6.7 to 10.3% and from 6.4 to 6.8% respectively. In abandoned grasslands, young forest ecosystems began to develop. For instance, on automorphic soils grey alders (Alnus incana) and silver birches (Betula pendula) were the predominating pioneer species, while wet meadows were covered by willow bush (Salix spp) or birch (Betula pubescens) stands. Due mainly to the deterioration of drainage systems, wetlands increased in area from 3.4 to 3.7%. In subcatchments, land use change differed notably. The wooded upper course subcatchment experienced no significant change, whereas the agricultural Sipe and Vända showed a remarkable transition similar to the entire catchment. In the Sipe sub-catchment, arable land fell from 58.5 to 19.1%, and the amount of abandoned land increased from 1.2 to 27.2%, whereas forested areas, wetlands, and grasslands showed a slight increase. In the Vända sub-catchment, about 90% of the arable land became seminatural and cultivated grassland (a rise from 0.5 to 49.5% and from 0.9 to 24.6% respectively; Mander et al 2000). In 1997– 2001, the land-use in the Porijõgi stabilised at low intensity (Kull et al 2005). Such dynamics are typical of the transition economy of the early 1990s (Mander & Palang 1994; Löfgren et al 1999).

1.4. Nutrient dynamics in Estonian rural catchments in the period 1987–2005

The downgrade of agricultural land-use did not bring about an immediate response by nutrient flows in the early 1990s (Stålnacke 1996; Löfgren et al 1999). However, towards the middle of the decade, a reduction of nutrient runoff and a subsequent stabilisation at low flow followed (Stålnacke et al 2002, Mourad et al 2006, Iital et al 2010, Nõges et al 2010). In the case of the Porijõgi, the nutrient losses decreased noticeably from both the entire catchment and agriculturally used sub-catchments (Mander et al 1998). At the same time, the wooded upper course sub-catchment showed no significant change in mean annual nutrient and organic matter runoff (Kull et al 2005). The main reason for the reduction was the land-use change followed by the drop in fertiliser use (Mander & Palang 1994). Likewise, there are similar trends of nutrient runoff from mosaic catchments described in analogous studies (Larsen et al 1998; Grimyall et al 1999).

1.5. Landscape models of nutrient runoff

Spatial computer models have been developed to meet the need to evaluate land management effects on soil erosion and nutrient losses. The emphasis of the research has shifted from empirical models such as USLE (Wischmeier and Smith 1978), its modifications MUSLE and RUSLE (EPA 1992) to distributed parameter simulation models, such as ANSWERS (Beasley et al 1980), HSPF (Bicknell et al 1984), AGNPS (Young et al 1985), PULSE (Bergström et al 1987), SWAT (Arnold et al 1993), HBV-N (Arheimer & Brandt 1998), MONERIS (Behrendt et al 2000) and PolFlow (de Wit 2001). Nevertheless, the empirical models provide satisfactory results for the description of the longterm trends of nutrient losses from agricultural catchments (Sandner et al 1993; Ripl 1995; Andersen et al 1998; Joelsson and Hoffmann 1998; Delgado et al 2006). Such predictions may lack precision because the variability in export coefficients is great and there is no theoretically generalised information about which ecosystem processes contribute to nutrient transport (Garten & Ashwood 2003). Empirical associations only varyingly succeed in implicating actual relations (Allan 2004). This is the case for a number of landscape-specific reasons, including (a) covariation of factors, (b) the existence of multiple, scaledependent mechanisms (e.g Jones et al 2001; Allan 2004), (c) the autocorrelation (self-dependence) between spatial elements (Legendre & Fortin 1989), (d) the predictive power is low in very small watersheds (less than 1– 10 km²) because the spatial arrangement of landscape patches is critical at these small scales (Strayer et al 2003). It is probably due to these problems that most nutrient transport correlation analyses use only the simplest of spatial factors (for example, the percentage of certain land use). More sophisticated and abstract factors such as FRAGSTATS metrics (McGarigal et al 2000) or catchment area (Burt & Pinay 2005) are addressed considerably less often.

1.6. Landscape factors of organic carbon fluxes

In northern river basins, peatlands are the most important source of organic carbon (TOC; Pettersson et al 1997; Gordeev & Kravchishina 2009), with 4–13 t C km⁻² annually lost from mires to the waters of the Baltic Sea (Eriksson 1991). Northern peatlands comprise a third of the global soil carbon pool (Gorham 1991). This accounts for an equivalent of 60% of the atmospheric carbon pool (Oechel et al 1993), with the net annual carbon sequestration rate in Baltic mires estimated at 8–55 t C km⁻² (Eriksson 1991; Smith et al 2008). Global warming may have begun to destabilise the sinks, gradually turning them into sources of DOC (dissolved organic carbon), with potentially serious implications for global warming (Freeman et al 2001).

There are 10,091 km² of peatlands in Estonia, constituting 22.3% of the country's total area. These are situated under various moisture regimes and

management practices, ranging from bogs and swamps to artificially drained forests and agricultural fields on peatlands (Allikvee & Ilomets 1995). Of these, 60–70% are artificially drained (Ilomets & Kallas 1995). Aerobic conditions caused by man-made drainage intensify the decomposition of peat into organic acids (Perelman 1975), commonly referred to as "browning the waters" (Roulet & Moore 2006).

In mires, the anaerobic conditions prevent the enzyme phenol oxidase from removing phenolic compounds that inhibit biological decomposition. Freeman et al have suggested that oxygen limitation on a single mire enzyme may be all that prevents the release of the northern peatland carbon stock into the atmosphere (and is thus an enzymic 'latch'). Most of the carbon is released directly as CO₂, while a significant proportion is exported as DOC (dissolved organic carbon). These processes are especially prone to take place when droughts occur (Freeman et al 2001). A semi-empirical model based on the enzymic 'latch' concept captured the approximate trend in DOC fluxes (Worrall & Burt 2005). Other studies provide diverse results (Evans et al 2006), with some proposing that lowered water tables increase peat-dissolved organic carbon production (e.g Tipping et al 1999), while others suggest a decrease (e.g Freeman et al 2004) or no significant change (e.g Blodau et al 2004).

The number of extremely dry or rainy days has increased greatly in Estonia between 1957 and 2006. The annual variation in droughts and wet spells has risen simultaneously (Tammets 2007). In the neighbouring climatic conditions of southern Sweden, a slight trend towards prolonged hydrological droughts has been observed since the 1960s (Hisdal et al 2003). Models of the Estonian climate simulate a rising trend in drought risk and gradually drier soils in summer between now and the 2070s (Lehner & Döll 2001; Järvet 2004). One major reason for an accretion of organic carbon in northern European catchments may be a depletion of SO_4^{2-} (sulphate ion), causing a greater dissolution of soil organic carbon. Specifically, the reduction of the SO_4^{2-} deposition resulting from lower atmospheric pollution prohibits methane-producing archaea (Gauci et al 2002; Monteith et al 2007). It has been suggested that this mechanism caused a boost in organic carbon export from the water bodies of Great Britain from the mid-1990s to the mid-2000s (Evans et al 2005). The reduction in the atmospheric deposition of nitrogen compounds can also affect soil chemistry in a manner that amplifies the export (Findlay 2005). Furthermore, Roulet & Moore (2006) argue that the export of organic carbon is probably determined by multiple related geochemical factors.

In Estonia, the post-Soviet re-organisation of industry that took place in the 1990s led to a great reduction in the atmospheric deposition of SO_4^{2-} and nitrogen compounds (Treier et al 2008), while nitrate fluxes from agriculture plummeted as well (Mander et al 1998; Iital et al 2010).

1.7. Objectives

The present work was an effort towards a better understanding of the ecosystem processes that drive the transport of nitrogen, phosphorus and organic carbon in Estonian agricultural landscapes. The specific objectives of this work were as follows:

- a) To review the literature on the influence of landscape factors (geomorphology, hydrology, soil, vegetation, land-use) on nitrogen and phosphorus fluxes from source areas to surface water regarding the magnitudes of fluxes that constitute nitrogen and phosphorus transport, spatial factors that have been reported as significant as determinants of nutrient transport and the relationship between catchment size and the amount of nutrients lost in the agricultural catchments in temperate climate (Publication I);
- b) To analyze the correspondence of ecotones to horizontal redox barriers in a till plain in Estonia, with the existence of vegetation boundaries within a 20m vicinity of the barriers as the main hypothesis (Publication III).
- c) To clarify the influence of land use intensification on nutrient and organic matter losses from the Porijogi agricultural catchment in Estonia during the period 1997–2009 and to test a simple empirical model of nitrogen and phosphorus runoff that integrated land use, fertilisation, soil, and water discharge characteristics (Publication V).
- d) To explain the changes in organic carbon concentrations from Estonian rivers in the period 1992–2007 through the land use composition of the catchments and long-term changes in hydrological droughts, water discharge and chemistry (Publications II; IV).

2. MATERIALS AND METHODS

2.1. Literature review methods

The main sources of literature for this thesis were works indexed by Mander & Mauring (1994) for the sources published before 1995 and by the Institute of Scientific Information Web of Science for 1995–2007 (Publication I; Pärn & Mander 2007). Data was collected for the purpose of three analyses: a) a conceptual diagram of nitrogen and phosphorus transportation, b) a display of determination coefficients between nutrient losses and landscape (complex spatial) factors and c) an analysis of the relationship between nutrient losses and catchment size in the agricultural catchments in a temperate climate. The following are some relevant comments on the methods:

- a) The subject of the conceptual diagram was the nitrogen and phosphorus lost from the root zone of source areas and transported towards the surface water. The inputs to source areas (fertilisers, deposition, nitrogen fixation) and nutrients moved from source areas as crops were not taken into consideration. The transport and transformation of nutrients in surface water bodies was also not considered. This study was performed at the catchment scale. This means that figures from studies performed at field scale were avoided. Therefore the ranges presented may differ from average field scale records, as there are relatively few nutrient studies at catchment scale. The range of flux magnitudes on the diagram was defined as the quartile values (the recorded values between ½ and ½ of the median value). In most cases the extreme values were also presented in the text. In other words, no averaging or recalculation of the previously recorded figures was done. All flux magnitudes are cited as they were in the literature.
- b) Only statistically significant determination coefficients (p<0.05) were collected as the data for the analysis.
- c) It was difficult to find the data for the analysis at catchment size, as catchment area is mostly not correctly reported or it is unclear at which scale the magnitude of nutrient flux has been estimated (catchment or field). Only figures were included from works where these problems did not occur.

Table 1. Characteristics of studied catchments. Percentages concerning lakes provided by Järvekülg (2001), other data by Iital et al (2010).

	Narva	Suur Emajõgi	Pärnu	Kasari	Vihterpalu	Keila	Vääna	Pudisoo	Valgejõgi	Võhandu	Väike Emajõgi
Area [km ²]	47,815	7,828	5,154	2,640	474	635	316	132	453	1,130	1,050
Pop. density											
[inh/km ²]	6.9	9.4	17.7	12.1	3	34.1	57.7	10.1	27.3	29.8	24.1
Agricultural [%]	39	43	38	34	17	46	44	20	29	47	46
Arable [%]	16	20	23	22	10	24	25	7	13	10	13
Forest [%]	45	41	47	49	57	38	35	60	47	42	46
Mires [%]	12	11	13	16	26	12	10	18	21	7	6
Lakes [%]	8	3	<1	<1	<1	<1	<1	<1	<1	1	<1

2.2. Study areas

Water chemistry and river discharge data were obtained from 16 Estonian rivers with a total catchment area of 67,627 km² (Figure 1; Table 1; Publications II; IV; V; Pärn et al 2009; Pärn & Mander 20XXa; b). The largest investigated catchments were those of the Narva (measured in Vasknarva; 47,815 km²), Suur Emajõgi (in Tartu; 7,828 km²) and Pärnu (in Oore; 5,154 km²) rivers. The rest of the rivers can be grouped as follows: (1) small rivers in northern Estonia (Kasari, Vihterpalu, Keila, Vääna, Pudisoo, Valgejõgi) and (2) small rivers in southern Estonia (Porijõgi, Väike Emajõgi, Võhandu). The Rannapungerja, Kunda and Jägala measurements were eliminated, as the discharges were considered to be heavily influenced by the industrial hydroelectric power plants that began operation in the years 1999–2002. The Purtse River was also left out because its discharge and chemistry were largely controlled by mine water input (Rätsep & Liblik 2001). There were no TOC data available for the Porijõgi. This left a total of 11 rivers in the organic carbon analysis (Publications II; IV), whereas only the nutrients were investigated in the Porijõgi (Publication V).

The northern catchments lie on Ordovician and Silurian limestones, whereas the southern ones are on sandy-silty and clayey Devonian sandstones. The rocks are overlaid by Quaternary deposits that are mostly less than 5 m thick. The most abundant of the sediments (>100 m) are found in the southern Estonian uplands. The limestone plateaus of northern Estonia are characterised by karst phenomena. The topography is fairly low and flat, with maximum elevations of mostly about 30–100 m above sea level.

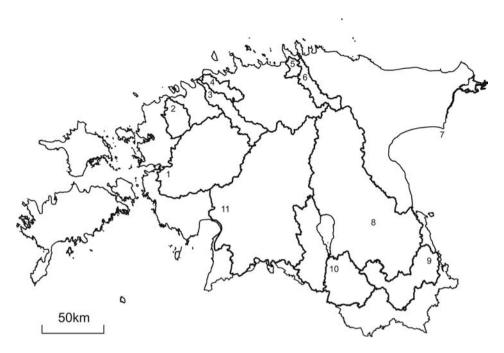


Figure 1. Studied catchments in Estonia: (1) Kasari, (2) Vihterpalu, (3) Keila, (4) Vääna, (5) Pudisoo, (6) Valgejõgi, (7) Narva, (8) Suur Emajõgi, (9) Võhandu, (10) Väike Emajõgi, (11) Pärnu. See Table 1 for the sizes and land use composition parameters of the catchments.

About 48% of the investigated catchments are covered by coniferous and mixed types of forests, the rest being mires (12%) and agricultural land that formed roughly 40% of the drainage area (Iital et al 2010). The main forest tree species in Estonia are pine (35%), birch (30%) and spruce (17%; Adermann 2008). The mires mainly include open fens and peat bogs, but also inland and coastal marshes. The investigated catchments are highly variable in terms of the proportion of mires, ranging between 6–26% in 2009 (Iital et al 2010; Table 1). Detailed information on the land use composition of the individual catchments is presented by Iital et al (2010; Table 1). The Narva, Suur Emajõgi and Võhandu rivers mainly originate from lakes. The Väike Emajõgi is also strongly influenced by the water level of its sink Lake Võrtsjärv, while the Pärnu River and the small streams of northern Estonia are not significantly influenced by standing freshwater bodies (Järvekülg 2001; percentages of lakes in Table 1; Publications II; IV).

2.3. The Porijõgi catchment and Rõngu-Palupera study area

The Porijõgi River drainage basin (258 km²) is one of the tributaries of the Emajõgi River that flows into Lake Peipsi (Figure 2; Publication V). The Rõngu-Palupera area is a typical lodgement till plain between Lake Võrtsjärv and Otepää Heights (Publication III; Pärn et al 2010). The landscapes of these territories are representative of the whole of southern Estonia. The catchment is located on the border of two landscape regions: the Southeast Estonian Till Plain and the Otepää Heights (Varep 1964). The central and northern parts of the catchment lie within a ground till plain 5–10 km south of Tartu (58°23' N; 26°44' E). The absolute altitude of the plateau is from 30 to 60 m with undulated relief (slopes normally achieve 5-6%) and intersected by primeval valleys (0.5-3 km wide and up to 40 m deep) formed by streams during the Pleistocene and transformed by glaciers during the last glaciation. Portions of these valleys are filled with glaciofluvial sands and gravel. The southern part of the drainage basin (10–13 km) south of Tartu lies on the northern slope of the Otepää Heights, which are composed of kames with a great variety of glacial deposits. The altitude of this region is up to 120 m; the relative heights reach 30–35 m (Varep 1964; Mander et al 1998; Arold 2001; Publications III; V).



Figure 2. The Porijõgi catchment and Rõngu – Palupera study area on a Landsat image in 2005. See the bright patches of cultivated fields and dark forests.

The bedrock of the catchment is formed by red Devonian sandstone (compact sandstone with clay and aleurolite layers from the Aruküla and Burtnieki times) overlain by loamy sand-till of the Weichselian glaciation or glaciofluvial and glaciolacustrine sands and gravel. The Devonian sandstone lies at a depth of 2 m (in the lower course) to 60 m (on the hills of Otepää Heights). The depth of the groundwater table varies (0.5–20 m) depending on relief and geomorphologic conditions. The main part of the Porijogi River and some of its tributaries (most impressively the Tatra stream) flow in primeval valleys. The upland soils are predominantly podzoluvisols, planosols and podzols on loamy sand and fine sandy loam with a surface soil organic matter content of 1.6–1.9%. The soil pH is 5.6-6.5 with a declining trend during recent decades, due to the intensive fertilisation that was practiced up to the end of the 1980s (150 kg N, 70 kg P and 100 kg K ha⁻¹ y⁻¹ on arable lands and cultivated grasslands; Mander et al 1989) which resulted in the leaching of Ca and other cations. On the other hand, the Ca content in podzoluvisols and podzols is normally low (0.1–1.0% CaO) and is enriched in agricultural fields by liming. Long-term leaching has resulted in elevated Ca content in groundwater (80–160 mg L⁻¹) and the accumulation of spring tufa deposits in valleys where the seeping groundwater is well buffered by riparian and hyporheic zones (Publications III; V).

About 45% of the catchment has the potential to be used as arable land. However, during the 1990s arable land decreased from 41 to 24% (Mander et al 1998). In wooded areas (about 45% of the territory), coniferous and mixed forests are most common. In valleys and other depressions, mixed forests, alder stands, willow bushes and various meadows predominate on gleysols and peatlands. Bogs overgrown by pine or birch forests occur on the borders of watersheds. The northern part of the catchment usually has larger patches of fields, grasslands and forests, while a very mosaic landscape predominates in the hilly southern part. During the period 1950–1997, winters were considerably milder (increase of air temperature in February from -7.9 to -5.5° C) and a change in the precipitation pattern (less rain in the warmer period and more in winter; average annual 520 mm y⁻¹) influenced the mean annual water discharge (Mander et al 1998; Publications III; V).

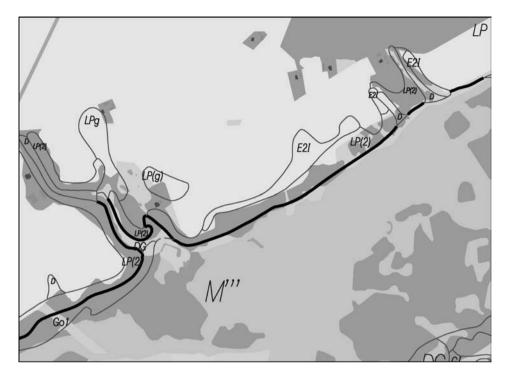


Figure 3. An example of the identification of sharp soil boundaries in the soil map (bold lines).

2.4. Cartographic identification of redox barriers

Sharp soil moisture boundaries on the Estonian 1:10,000 Soil Map were used as the proxy of redox barriers, as these described the abrupt change in redox conditions required for the formation and functioning of the barriers (Publication III; Pärn et al 2010). Originally the map was produced by the national soil survey in 1954–1990, which used field measurements of redoximorphic mottling in the horizons and the thickness of the organic layer as the basis for the interpretation of soil moisture regime. For the delineation of soil boundaries, the original survey used the network of sampling sites, while the visual interpretation of the terrain (soil colour, topography and vegetation) provided supporting data.

Table 2. Sharp soil boundaries (×) as proxies of redox barriers. Sharpness is defined as a distinctive taxonomic difference between adjacent soil units. H – hydromorphic (Histosols), G – semihydromorphic (Gleysols), g – hygromorphic (gleyic soils), M – mesomorphic, X – xeromorphic.

	Н	G	g	M	X
Н			×	×	×
G				×	×
g					×

The soil taxa represented in Estonian till plains were ordered along the gradient of the moisture regime (Table 2) following the Estonian soil survey manual (Publication III). The axis was divided into five moisture regime classes (Glazovskaya 1981): 1) xeromorphic (dry for most of the vegetation period), 2) mesomorphic (moist for most of the vegetation period), 3) hygromorphic (seasonally wet), 4) semihydromorphic (wet for most of the vegetation period, and 5) hydromorphic (constantly wet). The sharpness of boundary was defined as the taxonomic distance between two bordering delineations (Table 2). The Rõngu-Palupera region, a typical Northern European till plain in Southern Estonia (Figure 2; see Varep 1964 and Arold 2005 for the description of the landscape region), was selected as the study area. In the area, a classification of the soil boundaries was implemented using two sharpness classes: sharp (rank-order distance 2 or more) and diffuse (consecutive classes; Table 2; see Figure 3 for an example of the classification).

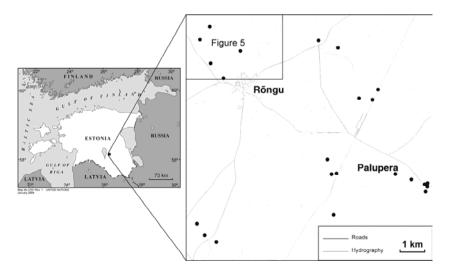


Figure 4. Location of the Rõngu-Palupera study area in Northern Europe. Study sites shown as dots.

2.5. Field investigation of ecotones

Twenty-four random transects across sharp soil boundaries were selected for investigation (Figures 4: 5: Publication III). In the field, the soil boundaries were located by a network of soil samples measuring the depth and characteristics of soil horizons. In order to detect redox barriers, the depth of the upper limit of the g horizon (the upper limit of redoximorphic mottling) and the depth of the organic or sapric horizon was recorded. The vegetation was sampled in 24 continuous belt transects along the topographic sequence. The data were collected from at least 50 m in both directions from the soil boundary in arbitrary topographic vegetation belts of 1 m along the transects and 20 m perpendicular to them along the contours. The cover of herbaceous plant and sub-shrub (<50 cm height) species in the belts was determined by visual estimates of the share of the ground covered by any part of the plants. The arbitrary boundaries of the belts (isohypses with an interval of 1 m along the transect) were determined and checked using a tachymeter. This method provided readily interpretable data fields of defined spatial extent (1×20 m). It also served the purpose of studying ecotones not as points along transects, but as vegetation belts along physical features. Depending on visibility and the clearness of the transition, the length of transects varied from 125 to 195 m. For the purpose of vegetation dissimilarity analysis, the data were generalised in 5 m belts.



Figure 5. An example of the location of transects in the landscape northeast of Rongu.

2.6. Redox barrier location

Redox barriers were detected in a univariate moving split-window soil boundary location analysis, using the depth of the upper limit of the g horizon as the variable indicating long-term soil moisture conditions (Publication III). In the presence of a sapric or histic upper horizon, the depth of g horizon was recorded as 0. In the absence of gleyic features in the 1 m soil cross-section, the depth was recorded as 1 m. A 20 m moving split window (corresponding to the minimum width of delineations on the 1:10,000 soil map) was used at an interval of 2.5 m. For each window mid-point position, average depths of the g horizon in both window halves were calculated. Dissimilarity was calculated as the difference between the two depths and the window that moved along the transects. The peaks in the resulting dissimilarity curves were interpreted as indicating the location of the barriers. In the transects where no peaks occurred in the depth of gleyic horizons, the depth of the organic horizon was used as the scalar.

2.7. Vegetation boundary detection

The dissimilarity of species coverage between window halves was calculated for each window-midpoint position as Euclidean distances (Publication III). The step of window positions was 5 m and the extent of the window was 20 m, i.e 10 m in both directions along the transect. The window positions were coarsened to reduce the amount of calculations and because a 1 meter shift had no real meaning when the window extended to 20 m. Vegetation plots within the window half were averaged. The transects were analyzed in groups according to vegetation type and an ecologically distinct presence of artificial drainage. Based on soil moisture regime, the transects were divided into two classes: 1) natural (transects across areas with natural moisture regime) and 2) artificially drained (transects that cross an ecologically and spatially distinct portion of artificially drained areas). Ecological distinction was defined as a lack of coherence between the vegetation type and the soil moisture regime class at a given site (Mander & Murka 2003), e.g an Oxalis type forest or an agricultural field on a histic soil. Spatial distinction was defined as a minimum extent of 20 m of ecologically incoherent belts across the transect.

In describing the ecotones, it proved impossible to apply the standard method presented in Cornelius & Reynolds (1991) and Hennenberg et al (2005), as the distribution of dissimilarities calculated both from the actual transects and from the 1000 randomised transects corresponded to no common parametric distribution. The distribution of the Euclidean distances can never absolutely match normality because the probability density function of this indicator is pruned from the side of smaller values, as the Euclidean distance cannot have a negative value. The expected frequency of values within given limits calculated from a theoretical distribution cannot be applied to an empirical distribution

when the empirical distribution significantly differs from the theoretical distribution.

The following characteristics were determined for each group: 1) the border between the two adjacent types of vegetation, defined as a statistically significant peak in the dissimilarity curve and 2) the two ecotone limits to the left and right of the border, marking the beginning and the end of the shift from one type of vegetation to another. The ecotone limits were defined as the maximum extent of indicator species of a vegetation type into the adjacent vegetation type separated by the border. The samples of dissimilarity values were placed on a common horizontal axis, using two kinds of reference points: 1) the true positions of the redox barriers (as defined above) and 2) the talus of the slope. The talus was defined as the lowest end of the slope segments that exceeded 1° of inclination. Transects that did not feature such inclinations in any part were removed from the analysis of slope position but not from the analysis of their relative position to redox barriers (Publication III).

2.8. Statistical significance tests of vegetation dissimilarity curves

The statistical test proceeded from a separate null model of spatial randomness of vegetation plots on transects to test the existence of a reliable transition zone (Publication III). The relative location of vegetation plots was iteratively randomised on the transects, which maintained the variance pattern of vegetation descriptions on transects. The 95% confidence limit of the null model was defined as the 950th value of the Euclidean distances in increasing order calculated from the 1000 randomisations. The one-tailed confidence limit was applied, since only the upper side of the distribution was of interest. The dissimilarities from the 1000 randomisations of plots were calculated within a moving window of the same size, as in the case of actual transects. That is, the window always covered four random plots from a transect.

2.9. Water chemistry data

The Estonian national environmental monitoring programme initiated the measurements of total N and P, COD_{KMnO4} (permanganate oxygen consumption), SO_4^{2-} and phenolics in Estonian rivers in 1992 (Publications II; IV; Pärn et al 2009; Pärn & Mander 20XXa). TOC measurements (total organic carbon) began in 1998 at 21 gauges. The gauges were selected in order to determine the transport of pollutants through the main rivers of Estonia to the Baltic Sea, Lake Peipus and Lake Võrtsjärv. Water samples were subsequently collected and analysed by the Department of Environmental Engineering of Tallinn University of Technology (northern Estonia), the affiliate laboratory of the Estonian

Environmental Research Centre in Viru County (north-eastern Estonia), Tartu Environmental Research Ltd (southern Estonia) and the affiliate laboratory of the Estonian Environmental Research Centre in Pärnu County (south-western Estonia). The analysis of the water samples was carried out following the standard international methods for examination of water and wastewater quality (APHA 1981). Water was sampled from 6 to 12 times a year, resulting in 40–50 TOC measurements for most of the streams in the years 1998–2007. Exceptionally, there were only a total of 8 TOC measurements from the Vihterpalu and Pudisoo gauges from February 1998 to April 1999. Little data was available on phenolics, as only three investigated gauges had more than 10 phenolics measurements (Keila, Suur Emajõgi and Narva). The investigated data can be freely downloaded from the directory http://loodus.keskkonnainfo.ee (Publications II; IV).

In addition to the data provided by the national environmental monitoring programme, independent water samples were collected in the Porijõgi and its subcatchments (Publication V; Pärn & Mander 20XXb). The drainage basin was divided into 8 sub-catchments, each of which had different land use structure (Mander et al 1989). Water discharge was measured and water samples were taken monthly from the closing weirs of each sub-catchment. Eleven sampling rounds were made in 2007, seven in 2008 and one in March 2009. The samples were analyzed for BOD₇, NH₄-N, NO₂-N, NO₃-N, total-N, PO₄-P, total-P, and SO₄, also following APHA standards. In order to extrapolate the estimates of the sub-catchments in the period 1998–2006 and in 2009, regression equations were calculated between the concentrations at the Reola gauge and the sub-catchments with the threshold of R²>0.8.

Three sub-catchments were studied: (1) the upper course of the Porijõgi (12.3 km²) on the slope of the Otepää Heights, which is relatively undisturbed and dominated by forests (>75%), (2) the Sipe stream (9 km²) with medium intensity of agriculture and a well developed riparian wetland zone along the stream and (3) the Vända ditch (2.2 km²) with intensive agricultural use and more than 65% arable land at the end of the 1980s (Mander et al 2000). In the Vända, intensive agriculture is not associated with any significant measures to control non-point pollution (Mander et al 1996; Mourad et al 2006). The entire 258 km² catchment of the Porijõgi River behind the Reola gauge of the Estonian Meteorology and Hydrology Institute (EMHI) is used in the model analysis (Publication V).

2.10. Concentrations trend analysis

The statistical properties of chemical concentrations in fresh water are usually not normally distributed (Gilliom & Helsel 1986). Therefore a modified version of the seasonal Mann–Kendall test was used (Grimvall & Libiseller 2002; see von Brömssen 2004 for the software package), referred to as the partial Mann–Kendall (PMK) test. The PMK test also makes it possible to account for missing

data in data sets. The univariate Mann–Kendall statistic for a time series $\{Zk, k = 1,2,n\}$ of data is defined as

$$T = \sum_{j < i} \operatorname{sgn}(Z_i - Z_j),$$
 [1]

where

$$sgn(x) = \begin{cases} 1, & if \ x > 0 \\ 0, & if \ x = 0 \\ -1, & if \ x < 0 \end{cases}$$

If there are no ties between the observations, and there is no trend in the time series, the test statistic is asymptotically normally distributed with

$$E(T) = 0$$
 and $Var(T) = n(n-1)(2n+5)/18$ [2]

Both non-seasonal and seasonal PMK tests were run (using four seasons: March–May, June–August, September–November, December–February) on the COD_{KMnO4}, SO₄²⁻ concentrations, annual average discharges and annual numbers of drought days for each river (Publications II; IV).

2.11. Organic carbon correlation analyses

In order to test the relationships between the magnitudes of trends of ${\rm COD_{KMnO^4}}$ and the trend slopes in water discharges, the numbers of drought days and ${\rm SO_4^{2-}}$ concentrations, Spearman's correlation analyses were performed. Trends with land use percentages were also correlated. In the analysis, each individual trend slope of a river constituted a data point (n=11). In order to test the power of ${\rm COD_{KMnO^4}}$ as the proxy of organic carbon (Kopáček et al 1995; Cheng et al 2005), a Spearman's correlation was calculated between the concentrations of ${\rm COD_{KMnO^4}}$ and ${\rm TOC}$ for each river (Publications II; IV).

2.12. Hydrological analysis

Daily discharge data [m³ s⁻¹] were collected by EMHI (the Estonian Meteorological and Hydrological Institute), determined in Parshall flumes (Publications II; IV; V). The discharges were calculated from the water level measurements in the river gauges performed by the trained staff of EMHI. Independent field gauging was performed at the Vända ditch, the Sipe ditch and the Porijõgi upper course sub-catchments alongside the water sampling in the years 2007–2009. Regression equations were calculated with the threshold of R²>0.8 to extrapolate data for 2009 based on the above-mentioned measurements. Runoff of N and P (kg ha⁻¹ d⁻¹) was calculated daily using the flow-weighted values and sub-

sequently calculated as monthly and annual means (see Rekolainen et al 1991). Potential evapotranspiration was determined following the Monteith method with modifications by Allen et al (1989). Actual evapotranspiration was calculated according to the Oldekop (1911) method modified by Tamm (1994). During the growing season actual evapotranspiration was the weighted average of land use classes over the catchment. For winter, potential evapotranspiration measurements were used. In order to obtain an annual parameter for the amount of hydrological droughts, days were counted with a discharge below 10% of the summer half-year average (April–September) for each year (Publications II; IV; V).

2.13. Land use data

Land use was analysed using the 1:10,000 Estonian Basic Map (2005) as the groundwork. The actual pattern, especially the location of abandoned lands, was investigated during fieldwork in May 2008 (Publication V). The following land use categories were determined: arable land, forested areas (forests, shrub), cultivated grasslands (fertilised, with sod to be tilled after each 5–8 years), (semi)natural grasslands (without fertilisation, extensively mowed or non-mowed), wetlands (swamps, fens, bogs, wet meadows), and abandoned land (former arable land and cultivated grasslands that had not been used for at least the last two years). In the nitrogen and phosphorus runoff model the following groups of land use classifications were used: (1) arable land, (2) grasslands and fallow land, and (3) forests and wetlands.

2.14. Nutrient runoff model

A simple empirical model developed by Sandner et al (1993) and modified by Mander et al (2000) was used was used for the analysis of N losses:

$$Q_{N} = F_{1} \times F_{2} \times F_{3N} \times F_{4} \times 20, \qquad [3]$$

where:

Q_N was the nitrogen runoff,

 F_1 was the integrated land use factor characterizing the dominant land use pattern in the catchment,

F₂ was the integrated soil factor,

 F_{3N} was the fertilisation factor for nitrogen,

F₄ was the hydrology factor characterising the variation of annual water discharge compared to the long-term average,

20 was the coefficient that characterizes the average nitrogen runoff from the catchment in relation to intensive agriculture (kg N ha⁻¹ y⁻¹; Mander et al 1998). For phosphorus runoff the model structure as for nitrogen was used:

$$Q_P = F_1 \times F_2 \times F_{3P} \times F_4 \times 0.5,$$
 [4]

where:

 Q_{P} was the phosphorus runoff

 F_{3P} was the fertilisation factor for phosphorus; 0.5 was the coefficient that characterised the potential average phosphorus runoff from the catchment regarding intensive agriculture (kg P ha⁻¹ y⁻¹; see Mander et al 1989; Publication V).

3. RESULTS AND DISCUSSION

3.1. Literature review of landscape factors of nitrogen transport

Common topological scores of elementary landscapes in temperate agricultural catchments are presented in Figure 6 (Publication I; Pärn & Mander 2007). The leaching of nitrogen into surface water occurs mainly in the case of permeable (sandy) or acidic soil and the absence of slope. Depending on these conditions, the rate of leaching is usually 8.8–29.0 kg N ha⁻¹ y⁻¹ (Peterjohn & Correll 1984; Kronvang et al 1995; Figure 6A). Leaching is typical for autonomous landscape elements (Perelman 1975). In the presence of slope and impermeable soil or artificial ground cover, surface flow predominates in the transportation of excess nitrogen. Depending on the conditions, average surface flow is 3.4–15.9 kg N ha⁻¹ y⁻¹ (Peterjohn & Correll 1984; Kronvang et al 1995). Surface flow is typical for transit landscape elements (Perelman 1975).

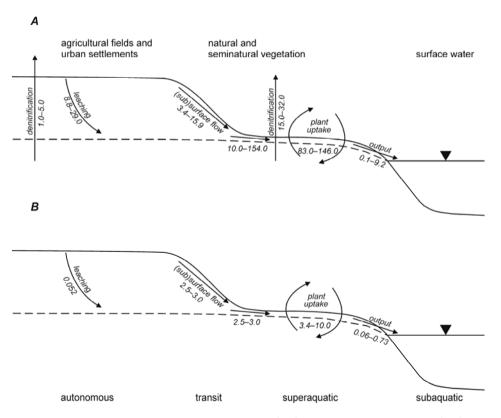


Figure 6. Median fluxes of a) nitrogen [kg N ha⁻¹ y⁻¹]; b) phosphorus [kg P ha⁻¹ y⁻¹] on a common topological score of geochemical landscape elements.

Leaching and surface flow are mostly addressed together as the flow from autonomous landscape units (agricultural fields and urban areas) through transit units (slopes, adjacent to water bodies) to superaquatic landscape elements (riparian forest and grassland; Perelman 1975). The flow has been much more extensively studied and therefore greater variance can be reported. Most of the estimated or measured fluxes are within 10–154 kg N ha⁻¹ y⁻¹ Kronvang et al 1995; Hall et al 2001; Hefting et al 2004; Koo & O'Connell 2006; Teimeyer et al 2006), but fluxes of from 1.8 (Koo & O'Connell 2006) to 3110 and 6270 kg N ha⁻¹ y⁻¹ Hefting et al 2004) have been reported from Western European autonomous landscape units to the superaquatic (riparian buffer) zone.

Superaquatic landscape units differ substantially from autonomous and transit landscape units in terms of their flat topography, hydromorphic soils (Histic and Histosols), anaerobic condition and natural and seminatural vegetation (forest, shrub and grass). Such areas act as barriers for the fluxes from geochemical transit zones. Due to this specific set of conditions, denitrification and plant uptake occur as the main outward fluxes. Depending on the availability of nitrogen and the anaerobic conditions, the rate of denitrification at catchment scale has mostly been reported to be 15–32 kg N ha⁻¹ y⁻¹ (Addy et al 1999; Lilly et al 2003; Hefting et al 2004; Jordan & Smith 2005), but fluxes of 400 kg N ha⁻¹ y⁻¹ (Brüsch & Nilssen 1991) and more have also been recorded. Denitrification in exceptionally aerobic parts of the subaquatic zone is 5 kg N ha⁻¹ y⁻¹ and less (Johnston 1991; Wendland 1992; Hefting et al 2004), which is similar to autonomous landscape units (Garten & Ashwood 2003). Plant uptake in superaquatic landscape units varies considerably depending on human disturbance (harvesting), natural disturbances (flooding), the aerobic conditions and present plant species. Riparian vegetation is most commonly reported to be able to take up 83–146 kg N ha⁻¹ y⁻¹ (Hefting et al 2001; Silvan et al 2004), although significantly smaller fluxes have been recorded (Peterjohn & Correll 1984; Bischoff et al 2001; Silvan et al 2004). Vegetation uptake will act as an actual nitrogen flux only to the extent that grass or wood are removed by human activities.

Denitrification, plant uptake and the remaining nitrogen retention capacity of a superaquatic riparian buffer is never able to remove all excess nitrogen. Even in sites with a natural or seminatural buffer zone between a nitrogen source area and a surface water body, a range of 0.01–142 kg N ha⁻¹ y⁻¹ is reported to enter the water (Kadlec & Tilton 1977; Fetter Jr et al 1978; Prentkti et al 1978; Young et al 1980; Bingham et al 1980; Yates & Sheridan 1983; Peterjohn & Correll 1984; Lowrance et al 1984; Jacobs & Gilliam 1985; Abernathy et al 1985; Pinay & Decamps 1988; Dillaha et al 1988; Schwer & Clausen 1989; Knauer & Mander 1989; Magette et al 1989; Cooper 1990; Brüsch & Nilsson 1991; Hoffmann 1991; Werner 1994; Prasuhn & Braun 1995; Prasuhn et al 1996; Mander et al 2000). The uppermost extreme values of more than 20 kg N ha⁻¹ y⁻¹ (Abernathy et al 1985; Dillaha et al 1988; Magette et al 1989; Kronvang et al 1995) are probably fluxes from adjacent slopes without superaquatic buffer zones. In most median cases, the flux is 0.1–9.2 kg N ha⁻¹ y⁻¹ (Young et al

1980; Bingham et al 1980; Yates & Sheridan 1983; Peterjohn & Correll 1984; Lowrance et al 1984; Pinay & Decamps 1988; Schwer & Clausen 1989; Knauer & Mander 1989; Cooper 1990; Brüsch & Nilsson 1991; Hoffmann 1991; Mander et al 2000).

The following paragraph presents the results of the analysis of relationships between catchment scale factors and measured nutrient losses. A complex index of topography, soil water conductivity and soil depth has been reported to have exclusively high explanatory power (95%) over nitrogen loss (Uuemaa et al 2005). In certain conditions soil moisture regime can explain a very large degree of variance in nitrogen transport (Young & Briggs 2005). This is probably because soil moisture depends greatly on topography and soil water conductivity in determining denitrification and vegetation. A good example of an abstract but sophisticated landscape factor is the Stream Proximity index by Agnew et al (2006), defined as the shortest distance to a stream. The precondition for the factor to determine nitrogen fluxes is a small variance in land use and vegetation. In catchments where nitrogen fluxes are controlled more by inputs than by retention in barriers, the proportion of urban or agricultural land use and road density will explain a significant proportion of nitrogen loss (Jones et al 2001; Uuemaa et al 2005). The same probably goes for the factor of the proportion of natural areas, as a linearly negative function of agricultural and urban areas. Meanwhile factors of landscape pattern such as Edge Density and Mean Nearest Neighbour are more likely to influence nitrogen fluxes in a more mosaic catchment (Uuemaa et al 2005).

The influence of landscape structure is confined by factors of composition, illustrated by a complex factor of edge density and agricultural land use being a good predictor of nitrogen loss (Uuemaa et al 2007). A combination, including edge density, Mean Shape index, contagion, proportion of natural area, the proportion of agricultural land use, the proportion of bogs and mires and the proportion of urban land use, was recorded as the best determinant function of nitrogen transport (Table 1). A recent study by Burt & Pinay (2005) had suggested watershed size to be a complex control of nitrogen transport. The evidence provided by them shows great variability in nitrogen loss from small watersheds with an area of less than 5000ha, but little variability from the river systems as a whole. In other words, the signal-to-noise ratio is low in large basins (i.e subtle changes in land-management practices cannot be detected at the basin outlet), but high in smaller tributaries. Similar data were presented in this work. Although it did not include basins larger than 11,000 ha, a slight decrease in variability was noticed from 5000 ha upwards (Publication I).

3.2. Landscape factors of phosphorus transport

The main sources of excess phosphorus are fertilisers, manure and human waste (Publication I). There is a well established link between available phosphorus and agricultural/urban land use. The intensity of leaching depends on soil acidi-

ty and permeability (sandiness). It is, however, a minor pathway of transport (0.052 kg P ha⁻¹ y⁻¹; Peterjohn & Correll 1984), as a median of 2.5–3.0 kg P ha⁻¹ y⁻¹ flows from source areas in surface flow and subsurface flow (Peterjohn & Correll 1984; Mander et al 1997; Tunney et al 2000; Figure 6B). In the presence of slope and pathways and a lack of vegetation, the flow can be 3.15 kg P ha⁻¹ y⁻¹ (Haygarth et al 1998) and more. In superaquatic conditions (even ground and the presence of natural and seminatural vegetation), plants take up a mean of 3.4–10.0 kg P ha⁻¹ y⁻¹ (Peterjohn & Correll; Silvan et al 2004). Depending on these conditions, plant uptake can be up to 13.1 kg P ha⁻¹ y⁻¹ (Silvan et al 2004). In most cases only 0.06–0.73 kg P ha⁻¹ y⁻¹ escapes from superaquatic landscape units and contaminates surface water (Fetter et al 1977, Peterjohn & Correll 1984; Schwer & Clausen 1989, Knauer & Mander 1989; Kronvang et al 1995; Mander et al 2000). Depending on topography, soil and vegetation, riparian fields and slopes can emit up to 0.8–11.3kg P ha⁻¹ y⁻¹ (Young et al 1980; Dillaha et al 1988; Magette et al 1989, Brazier et al 2004).

Phosphorus flux is determined by flow path length as a complex factor of topography, distance (Agnew et al 2006) and runoff (Kronvang et al 1995; Table 1). This link is explained by the importance of surface flow in phosphorus movement. Another good predictor is the proportion of urban land use in catchment (Uuemaa et al 2007). This may be because human waste (detergents) and industry are great sources of phosphate. The amount (length) of riparian vegetation strips is obviously one of the landscape controls over nutrient fluxes (Jones et al 2001). Landscape pattern, expressed as contagion and Shannon's diversity, can also determine a large proportion of phosphorus fluxes (Uuemaa et al 2005). The reason for this is the amount of physical and chemical barriers present in a heterogeneous landscape.

No conclusion about the effect of catchment size on phosphorus losses could be drawn from the data collected in this thesis. The results instead present two subsets of data: higher values from the intensively managed Slapton catchment in Devon, which has steep riverside grasslands (Johnes & Heathwaite 1997; Heathwaite et al 2003; Brazier et al 2004) and lower values from the less intensively managed Porijõgi in Estonia (Mander et al 2000) and the Demnitzer Mühlenfließ in Brandenburg (Gelbrecht et al 2005), which has superaquatic seminatural floodplains (Publication I).

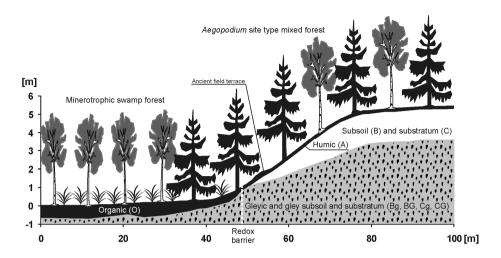


Figure 7. A schematic view of a topographic soil-vegetation sequence in the studied Estonian moraine plain

3.3. Redox barriers and vegetation boundaries in an Estonian till plain

The field investigation of redox barriers in the landscape yielded the following results (Publication III; Pärn et al 2010). Of the 24 sampled dissimilarity curves of the depth of the gleyic horizon, 22 showed a peak, which was interpreted as a redox barrier (see Figure 7 for an example of a transect and Figure 8 for the data on the depth of the gleyic horizon and the dissimilarity curves). In transects No 16 and 23, no peak in the dissimilarity curve of the depth of the gleyic horizon occurred, while a peak of more than 20 cm of difference occurred in the dissimilarity curve of the depth of the organic horizon. In the transects with a significant proportion of gleyic soil (transects No 3, 7, 9, 13, and 18), the peaks were below 30 cm, while each of the transects with a mesomorphic soil showed a peak of more than 30 cm of difference.

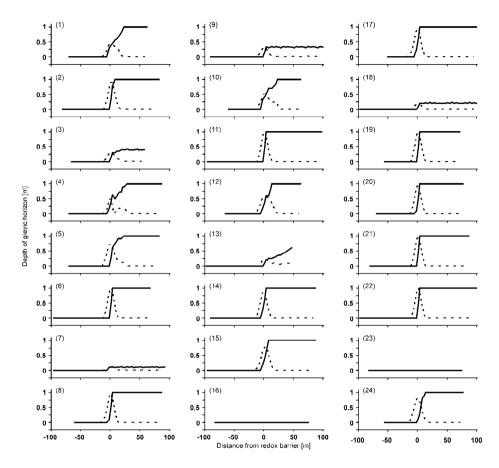


Figure 8. Depth of gleyic horizon (solid line) and dissimilarity curve (dashed line). The number of transect is presented in parenthesis. The dissimilarity in a split-window midpoint position was calculated as the difference in the average depths of gleyic horizon between two 10 m window halves. The window was moved across the transects and the peaks in the dissimilarity curves were interpreted as present or relict redox barriers

In most of the studied sites situated at natural moisture conditions, a complete shift in vegetation composition occurred below the horizontal redox barrier and above the talus, having a transition zone less than 20 m wide (Figures 9; 10). Each of the 24 calculated vegetation dissimilarity curves exceeded the 95% confidence limit of the null model in some region. A single significant peak in dissimilarity with ecotone limits less than 20 m apart occurred in 15 curves – 11 sites with natural soil moisture regime and 4 artificially drained sites. A peak or a series of peaks within 20–40 m occurred in 7 transects, with 3 drained sites among them. Transect No 15 showed two peaks more than 20 m away from their neighbouring peaks. The drained forest / forest transects No 16 and 23 showed more than three significant but extremely low (0–12.25) peaks, which were less than 20 m from their neighbouring peaks (Publication III).

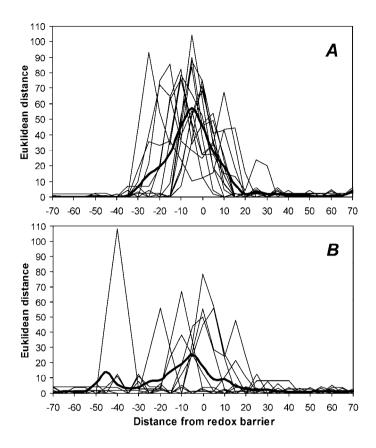


Figure 9. Vegetation dissimilarity between 20 m window halves on transects (thin curves) and the mean of all transects (bold curve). A — transects across soils with natural moisture regime (n=14), B — transects that cross artificially drained areas (n=10).

3.4. Position of vegetation boundaries relative to redox barriers

In general, the vegetation boundaries were found to be a few metres below the estimated redox barrier, as expected by Perelman (1975; 1986 Publication III). Here is the detailed account. A total of 14 transects ran entirely across soils with natural moisture regimes (Figure 9A), while 10 transects crossed a distinct portion of artificially drained area (Figure 9B). Note that the average dissimilarity curve calculated across natural soils was symmetrical with the peak a few metres below the redox barrier (mean=-3.49, SD=16.43). The average curve calculated across the artificially drained sites was asymmetrical with multiple peaks (mean=-9.65, SD=25.63).

The transects in natural moisture conditions that cross from swamp forest or grass mire to dry forest or agricultural field showed vegetation borders in the vicinity of the soil redox barriers, ranging from 25 m below the barriers (towards the wet soil) to 12.5 meters above it (towards the dry soil; Figure 10). The lower ecotone limits lay from 30 m below the redox barrier to 5 m above it. The higher ecotone limit lay from 12.5 m into the wet section to 15 m into the dry soil.

Between different types of vegetation transitions (swamp forest or grass mire as the wet section and dry forest or agricultural field as the dry part), no fundamental differences were observed. The median positions of the vegetation border between the four types ranged from 0 to 10 m below the redox barriers. In the vicinity of the drained forest / forest redox barriers, multiple significant but extremely small vegetation borders were detected along the entire length of the transects (Figure 9B; 10). The drained forest / forest site featured a single high peak in vegetation dissimilarity but did not correspond to the soil boundary, as the vegetation border lay 40 m below the soil boundary. The drained forest / agricultural field vegetation borders were placed at 10–20 m towards the histic soil. The vegetation borders of the drained agricultural field / agricultural field sites ranged from 5 m towards the histic soil to 15 m towards the mesomorphic soil. The difference in vegetation was mainly caused by a greater share of *Urtica dioica* and *Phalaris arundinacea* on the histic soil, which is not ecologically significant in terms of site types.

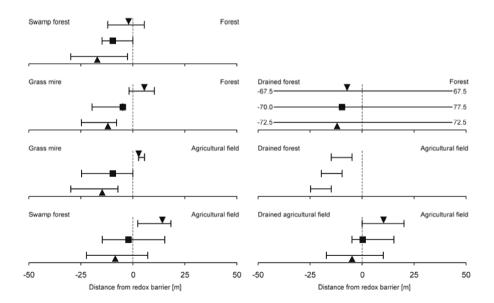


Figure 10. Medians of the positions of vegetation borders (blocks), lower ecotone limits (lower triangles) and upper ecotone limits (upper triangles) with ranges (whiskers) relative to soil redox barriers. The transects were grouped by vegetation type and the presence of artificial drainage.

In the transects that cross artificially drained soils, some vegetation borders were observed in the vicinity of the redox barriers and slope taluses (Figure 10). However, there was little spatial consistency in the position of the borders, as the generalised curve obtained by averaging the individual curves was asymmetrical (Figure 9B). Most of the vegetation borders involved extremely small changes in vegetation, which do not separate vegetation site types (classification according to Paal 1997), e.g boundaries between adjacent agricultural fields or between forest patches of the same site type. Some ecologically relevant borders were observed in the case of the transition from drained forests to agricultural fields, where the vegetation border lay 10-20 m towards the histic soil (Figure 10). In artificially drained sites, the correspondence of the soil boundaries to vegetation borders was generally poor. This leads to the conclusion that the soil redox barriers were relict. Man-made drainage removes actual redox barriers from the soil and corresponding boundaries from the vegetation, making the landscape more uniform. In a natural soil moisture regime, ecotones are easily detected by sharp moisture boundaries of large-scale soil maps. When the strips of forest or seminatural grassland are displaced from the slopes and utilised as cultivated fields, the slopes will be vulnerable to water and wind erosion. By the removal of these biogeochemically active riparian margins, an access transportation of nutrients into water bodies will become much more likely. In the forests, the ecotones act as barriers against the spread of wildfires and the migration of pests. The removal of the ecotones will make the landscape vulnerable to these disturbances. Hence the relative amount of relict soil boundaries is a measure of human impact (Mander & Murka 2003).

The actual soil moisture conditions are usually not presented in the available databases at either regional or national scale. Plans of amelioration projects can be used to detect the spatial impact of artificial drainage. A more sophisticated way of acquiring such data is overlay mapping of a soil map with land use data, where agricultural fields on hydromorphic soils are interpreted as anthropomorphic landscape units. The coincidence of soil and vegetation boundaries at the studied sites corresponds to the assumptions of the German-Russian school of landscape research (Passarge 1919), previous cases of soil and vegetation boundaries (Webster 1973; Wierenga et al 1987) and the common practice in delineating wetlands in the United States (US Army Corps of Engineers Waterways Experiment Station 1987). The vegetation dissimilarity curves in the natural moisture sites were mostly symmetrical. The generalised curve of dissimilarity, which was obtained by averaging transects at non-drained histosols, resembled the Gaussian curve (similar to the derivative of the logistic curve; Figure 9A). The Gaussian curve is the most common model used to link vegetation composition to physical landscape features (Coudun & Gégout 2006). As a function of distance, the model describes ecotones having a varying degree of steepness, patchiness and transect length (Hufkens et al 2008). Most of the curves obtained in this research also resembled the peaks from boundary detection analyses (Webster 1973; Turner et al 1990). The vegetation boundaries probably marked the line where the extended amount of nutrients

ceased to support mesomorphic vegetation, and hydromorphic plants began to prevail. The results of the analysis of the correspondence of vegetation boundaries to redox barriers and the observed topographic position of the vegetation boundaries in the studied Estonian till plain provide a hypothesis of the correspondence of these boundaries in other cultivated till plains of the Northern European mixed forest zone and other meso-scale landforms in the same region (Publication III). However, the actual redox and denitrification potentials of the ecotones ought to be invstigated in the near future.

3.5. Position of vegetation boundaries relative to slope talus

Overall, the vegetation boundaries were exposed in the lower part of the slope. Out of the 24 transects, 23 showed topographic inclinations of more than 1° (Publication III). The transects in natural moisture conditions showed vegetation borders from 6.6 m below the talus (towards the wet soil) to 15 m above it (towards the dry soil). The lower ecotone limits ranged from 21.5 m below the talus to 7.5 m above it, and the higher ecotone limits from 4.4 m below the talus to 36 m above it. Between the types of vegetation transition from naturally wet to dry site, few differences were detected, with the medians of each type ranging from 1.6 m towards the wet soil to 6.0 m towards the dry soil. In the vicinity of the taluses at drained forest/forest sites, multiple small vegetation borders were detected. Transects No 11 and 18 were exceptional among the drained forest sites, showing sharp borders at, subsequently, 6.2 and 1.5 m from the talus towards the dry soil. The borders between the drained agricultural fields and adjacent lands at dry soils ranged from 5 m from the talus towards the histic soil to 32.5 m towards the mesomorphic soil (Publication III). The differences in the vegetation composition of these fields were described in the previous paragraph.

Table 3. Land-use dynamics in the Porijõgi in the period 1987–2008.

	1987	1997	2008
Fallow land	2	11	6
Arable land	42	24	29
Cultivated grassland	6	7	13
Natural grassland	7	10	3
Wetland	3	4	4
Forest	40	45	45

3.6. Land use changes in the agricultural catchment of Porijõgi in 1997–2008

Between 2001 and 2008, the land use changes that had taken place in the years 1987–1997 were reversed (Publication V; Pärn & Mander 20XXb). Table 3 shows the changes of land use types grouped in main classes. The proportion of abandoned land decreased to 6%, while arable land and grasslands rose to 28% and 18% respectively. Forested areas and wetlands remained at 45% and 4% respectively. The forested upper course sub-catchment saw little change, while the agricultural Sipe and Vända sub-catchments returned to their previous land use. In the Sipe, arable land rose to 56% and abandoned land fell to near zero, whereas forested areas showed great depletion. In the Vända, the grasslands were returned to arable land. The changes were followed by an increase in fertiliser use. While almost no P and N was added between 1992 and 1997, the rates rose to an average of 100 kg N ha⁻¹ y⁻¹ and 40 kg P ha⁻¹ y⁻¹ in 2007–2009. The same amounts were applied in the Vända, while the rates in the Sipe were 50 kg N ha⁻¹ y⁻¹ and 25 kg P ha⁻¹ y⁻¹.

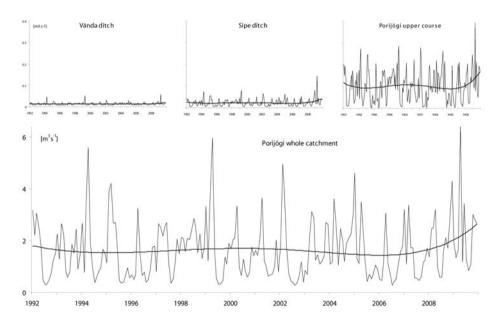


Figure 11. Dynamics of monthly average water discharges in the Porijõgi river (Reola gauge), 1992–2009 (regular line) and polynomial trend line (bold line). Note the rises in the last two years.

3.7. Nutrient losses in the Porijõgi in 1997–2009

While a rapid change in land use and fertilisation rates had caused a significant reduction of nutrient losses from the Porijõgi River catchment in 1987–1994 (Mander et al 1998), the recovery of the agricultural land use in 1997–2008 brought about a respective rise in nutrient runoff, which was magnified by the relatively great water discharges (Publication V). A detailed report is presented in the following paragraph.

During the study period (1997–2009) the water discharges magnified with 2.03 and 2.29 m³ s⁻¹ as the average runoffs in 2008 and 2009, respectively, set against the average 1.69 during the period 1998–2009. Similar dynamics were followed in the sub-catchments (see Figure 11 for the hydrographs). The flow of nutrients amplified from both the entire catchment and sub-catchments (Figure 12). Annual runoff of total-N increased in the catchment from 4.4 to 3.8–6.6 kg N ha-1 y-1, rising just above those observed in the forested area. The agricultural sub-catchments were supplemented even more (from 0.7 to 1.3– 3.3 kg N ha⁻¹ y⁻¹ in the Sipe; from 4.4 to 8.1–11.2 kg N ha⁻¹ y⁻¹). The relatively high nitrogen losses from the Vända were due to the intensification of the use of mineral fertilisers and manure application. However, these values are still much lower than documented in other papers on rural catchments (Miller 1979; Kronvang et al 1993; Larsen et al 1998). Average annual losses of total P from the catchment showed a slight increase between 1997 and 2007-2009 (from 0.08 to 0.06–0.11 kg P ha⁻¹ y⁻¹). The greatest increase was in the cultivated Sipe and Vända sub-catchments, where P runoff rose from 0.02 to 0.02-0.07 kg P $ha^{-1} y^{-1}$ and from 0.09 to 0.16–0.22 kg P $ha^{-1} y^{-1}$ respectively. On the one hand, the overall increase owed to greater water discharges, with 2.03 and 2.29 m³ s⁻¹ as the average runoffs in 2008 and 2009, respectively, set against the average 1.69 in 1998–2009. On the other hand, the water flow could not account for the whole nutrient accretion, as in 1998, when the average water discharge was 2.05 m³ s⁻¹, the substance runoffs were one and a half times lower than in 2008– 2009. Therefore the rise in the agricultural sub-catchments was co-explained by increases in concentrations.

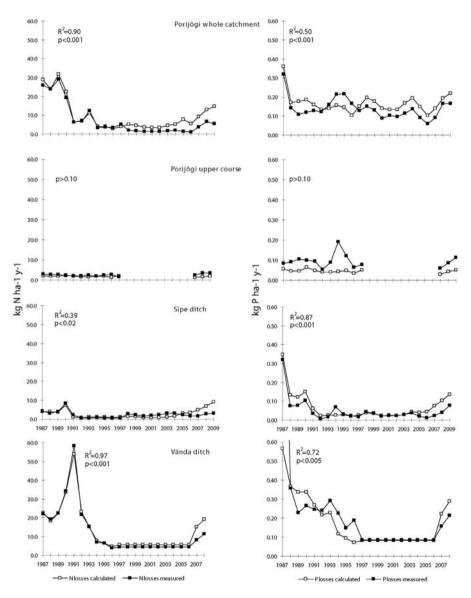


Figure 12. Dynamics of nitrogen and phosphorus runoff in the Porijõgi and sub-catchments set against the calculations of the model. See the considerably higher predictions compared to actual measurements in 2007–2009.

The results present the first account of the impact of the recovery of agricultural activities on nutrient runoff in Estonian rural areas. Until now, mainly downward trends have been reported after the restoration of the country's independence (Mander et al 1998; Stålnacke et al 2002; Kull et al 2005; Mourad et al 2006; Iital et al 2010; Moore et al 2010; Nõges et al 2010). Knowing that only

minor progress has been made in studying the effect of large-scale disturbances on nutrient fluxes (Burt et al 2010), the case can be viewed as a sort of disturbance on the scale of decades. Although the nutrients increased noticeably, the discharges remained considerably below the amounts measured during the Soviet era. The findings show the predictions of the moderate land use scenario of the nutrient runoff model by Mander et al (2000) to be significant overestimations. Nevertheless, the inertia between increases in input and output was anticipated by Piirimäe et al (2007) and Mourad (2008) using the PolFlow model to simulate the nutrient fluxes in the neighbouring small Ahja River basin and the Gulf of Finland catchment respectively. According to their model, the limited effect of emission changes is explained by the presence of the relatively thick aguifers with long transit times in the soilwater and groundwater (Mourad 2008), probably causing a substantial time lag between changes in the input and output of nutrients (Stålnacke et al 2002). The diffuse load of nutrients depends greatly on their storage in the soil (Goodchild et al 1996; Piirimäe et al 2007). Water residence times are relatively long in Estonia (compared to Norway; Stålnacke et al 2002). In addition to the deep water-permeable Quaternary sediments, this is due to the wide spacing of lateral tile drains in the soil (10-15 m and up to 30 m; Jansons et al 2002). Furthermore, in-river retention has a great impact, reducing the surplus N and P loads to Lake Peipus by about 62% and 72% respectively (Mourad et al 2006).

Another possible explanation of the discrepancy may be the developments in the timing and methods of fertiliser application. The date at which nutrients are applied has a significant influence on their uptake. There is a higher utilisation of fertiliser N when application is delayed, because uptake and translocation within the soil are greater during the filling of seeds (Bigeriego et al 1979; Pearce 1998). Also, recent techniques have involved the ploughing of substances into the soil. The surprisingly low nutrient fluxes may also be the result of the undisturbed development of riparian buffer zones during the period of low agricultural activity, especially their expansion and the depletion of the excess nutrients. It can be assumed the strips were relatively uncontaminated and therefore fresh to start processing the new loads. The N saturation effect is discussed by Hanson et al (1994) and Sabater et al (2003; Publication V).

3.8. Modelling results in the Porijogi in 1997–2009

The modelling results were compared against the measured N and P losses from the Porijõgi catchment and its three sub-catchments (Publication V). In general, the modelling results overestimated the measured values (Figure 12). This may be due to a lack of consideration of the methods and timing of fertiliser application. The greatest misjudgement occurred in the Sipe, probably owing to the model's inability to account for the efficient functioning of the well-developed riparian buffer zones. These had received minimal amounts of nutrients prior to the study period, and were therefore relatively uncontaminated and fresh to remove the N

and P. On the contrary, in the forested upper course sub-catchment, the model underestimated N runoff. This may be due to the fact that most of the leaching nutrients in this area do not originate from agriculture (Mander et al 2000). Models of this type are not applicable to catchments where the agricultural influence is very low. Analogous empirical models of annual nutrient runoff from rural catchments developed in Sweden (Joelsson & Hoffmann 1998) and Denmark (Andersen et al 1998) can be applied in order to obtain better results. It is planned for these to be used in further analysis. Clearly, the application of more complex simulation models that consider the physical, chemical and biological properties of soils and more precise hydrological parameters would offer more satisfactory results, because in large mosaic catchments, land use pattern plays the main role. Factors accounting for fertiliser application methods and timings and the amount of buffer strips would add to the accuracy of predictions. However, in terms of landscape analysis the simple empirical models based on readily available data are more applicable in further landscape and regional planning of the whole region (Mander et al 2000; Publication V).

3.9. Chemical and hydrological trends related to organic carbon in Estonian rivers in the period 1992–2007

The non-seasonal Mann-Kendall test yielded significant slopes for five of the six small streams of northern Estonia (p<0.05) showing upward trends (M-K slope>2.35; Figure 13; Publications II; IV; Pärn et al 2009; Pärn & Mander 20XXa). In the Pärnu River, the positive trend of 1.98 was close to significance (0.05<p<0.1). In the rivers of southern Estonia, the slopes were considerably flatter (0.45 < M-K slope < 1.48; p > 0.1). A zero magnitude trend was observed in the Narva, the largest of the rivers. The seasonal test provided no statistically significant results (p>0.05). No significant slopes were observed in either water discharges or annual numbers of drought days. The greatest downward slopes in discharges were shown by the Narva, and four of the six small northern Estonian rivers, while in the rest of the streams, the slopes were below 1.00. The Narva, the Suur Emajõgi and the small rivers of southern Estonia did not have any drought days below the set threshold. At the same time, five of the small northern Estonian rivers showed Mann-Kendall slopes over 1.03, and the Pärnu River also had a positive trend of drought days. None of the three gauges with data on phenolics showed a significant Mann-Kendall statistic. However, in the case of the Keila River, this was only due to the shortness of the time series, starting from 2004, as the phenolics varied from 13.8–74.9 µg L⁻¹ from June 2004 to April 2005 and then plummeted below $2\mu g L^{-1}$ for the entire period from June 2004 to December 2007. Significant downward slopes of SO₄²⁻ were ascertained in eight of the eleven investigated streams (p<0.05; -3.61<M-K slope<-1.88). Among the exceptions were the Narva River and the small Vihterpalu River in northern Estonia, which had slightly positive trends (Publications II; IV).

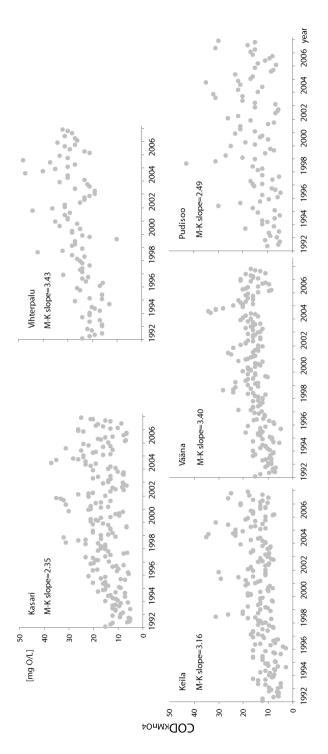


Figure 13. Trends of organic carbon surrogate in five small northern Estonian streams.

3.10. Trends in organic carbon explained

In order to explain the increase in TOC concentrations in the small rivers of northern Estonia and the Pärnu River while the exports remained the same in the Narva, Suur Emajõgi and the two small rivers of southern Estonia, trends in COD_{KMnO4} were found to be closely correlated with the rising trends in drought days (Publications II; IV). A significant correlation of 0.82 was obtained between the magnitudes of trends in COD_{KMnO4} , and trends in drought days (ρ^2 =0.68; p<0.01; n=11; Figure 14). Neither the land use percentages nor trends in water discharge or SO_4^{2-} showed significant correlations with the slopes of COD_{KMnO4} . Significant Spearman's correlation coefficients were accomplished between TOC and COD_{KMnO4} for the six small rivers situated in northern Estonia that possessed 0.95> ρ^2 >0.72; p<0.01. Pärnu showed a determination coefficient of ρ^2 =0.38; p<0.05. The rest of the streams of southern Estonia had 0.25< ρ^2 <0.5; p>0.05.

The dependence of TOC concentrations on the parameter of hydrological droughts corresponds with what has been proposed on droughts affecting the decomposition processes that produce dissolved organic carbon through the enzymic 'latch' mechanism (Tipping et al 1999, Freeman et al 2001, Worrall & Burt 2005). This is also somewhat supported by a drop in the phenolics, as observed in 2005 in the Keila River, the gauge which showed a significant upward trend in the TOC surrogate, while in the Narva and Suur Emajõgi rivers, which had no significant trend in TOC, no noticeable change was present. The correlation with droughts, however, conflicts with the conclusions of Freeman et al (2004) and Blodau et al (2004) suggesting a negative or non-existent relationship with droughts. No significant correlation of COD_{KMnO4} concentrations or trends with respective total runoff parameters was acquired. The findings contradict the general pattern of organic carbon export following a rise in discharge as explained by Pastor et al (2003). Nor do they correspond with the analysis of terrestrial organic carbon transport to Lake Võrtsjärv by Tamm et al (2008), which proposes that the total load is mainly dependent on water discharge.

It turned out impossible to reliably confirm reduced sulphate deposition as a possible cause for an accretion of organic carbon, as previously suggested by Monteith et al (2007), since the recorded decreases in SO_4^{2-} concentrations in Estonian stream water did not correlate significantly with the increased ratios of TOC concentrations. As there has also been a dramatic decrease in the deposition and agricultural input of nitrogen compounds in Estonia (Mander et al 1998; Treier et al 2004), further investigation is needed to clarify the impact of the soil chemistry on the accretion of organic carbon exports (Findlay 2005, Evans et al 2006, Monteith et al 2007). A possible explanation could be the great sulphur supplies that accumulated in the soil during the decades of high air pollution. For example, at the Lake Saare monitoring station, the organic horizon of the pine forest floor contained an average 90 kg S ha⁻¹, and the spruce forest contained 210 kg S ha⁻¹ in 2008 (Frey et al 2010). Therefore it is reason-

able to assume that despite the serious sulphate reductions, the S levels remained high enough not to limit the carbon-consuming function of the archaea.

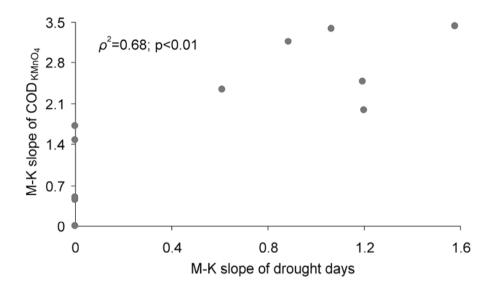


Figure 14. Correlation between trends on drought days and trends in the TOC surrogate. Spearman's ρ^2 =0.68; p<0.01; n=11.

The exceptionally great impact of droughts in the observed catchments can also be explained by the high proportion of man-made drainage systems. 20–53% of the catchments with significant trends in the TOC surrogate are covered with peatlands (Järvekülg 2001), and 60–70% of Estonian peatlands are artificially drained (Ilomets & Kallas 1995). For the catchments examined in this research, no sufficient data currently exist to quantify the influence of ditching. There were only enough historical data available to conduct a preliminary analysis in order to assess the relationship between the loss of natural mires and trends in TOC surrogates in six catchments. The first set of mire percentages in the catchments was based on expert opinion from the period 1955–1960 (provided by Dr August Loopmann, published by Järvekülg 2001), and the second set dated from 2009 (Iital et al 2010). The losses of natural mires expressed as the negative differences between the data sets ranged from 0 to 31% of the catchment area transferred from mire to another land use. The percentages correlated closely with the trends in COD_{KMnO4} (ρ^2 =0.89; p<0.001; n=6), suggesting that the impact of extremely low water tables on organic carbon concentrations is magnified by artificial drainage. Alternatively, the vulnerability of the northern rivers to droughts may result from a greater share of xeromorphic soils. Additionally, the influence of the in-lake removal of TOC could be observed. Three of the six rivers without considerable increases in TOC surrogate (namely

the Narva, Suur Emajõgi and Võhandu rivers), originated from Lake Peipus, Lake Võrtsjärv and Tamula and Vagula lakes respectively, whereas none of the streams with rising TOC concentrations received a significant amount of water from lakes. The mechanisms of in-lake removal have been explained by Schimel et al (2007), and the related processes have been studied by Vuorenmaa et al (2006). In Estonia this case has been investigated by Toming et al (2009). In any case, a further analysis is necessary to clarify the relationship between organic carbon trends and the catchment properties, especially the soil cover parameters (Publications II; IV).

4. CONCLUSIONS

This thesis aims to clarify the impact of landscape factors on the nutrient and organic matter runoff in agricultural landscapes in Estonia. That influence is highly variable in a temperate climate, depending on which fluxes dominate and vary in the subject catchment. In watersheds with varying inputs, soil qualities, the proportion of various land uses, proximity to the water body and runoff factors are the determinants. When the inputs are constant over time, chemical and physical conduits and barriers determine the flows, and the factors of the landscape pattern explain the differences in nutrient losses. Nitrogen is often determined by factors of agriculture and soil characteristics, especially moisture, controlling denitrification. The greatest variance among N losses is found in small catchments. Phosphorus transport is stronger in connection with physical factors, especially flow conduits and barriers. The link with the amount of riparian buffers and landscape pattern is therefore even clearer for P (Publication I).

The riparian mire – upland redox barriers in the soil are marked by corresponding vegetation boundaries in the studied Estonian till plain. Such ecotones can be observed in aerial and satellite imagery at the footslopes, revealing redox barriers and related hot spots in agricultural landscapes. The barriers and corresponding ecotones occur below cultivation terraces in field margins. Man-made drainage removes redox barriers and corresponding ecotones, making the landscape uniform and therefore vulnerable to disturbances. Ecotones may represent functional boundaries for delineating wetlands and planning the sustainable use of agricultural landscapes (Publication III).

The export of organic carbon compounds in Estonian streams increased in the years 1992–2007, in spite of a general decrease in water discharges during that period. The main drivers of the increased dissolution of peat were the extremely low water tables, deepened by man-made drainage, as revealed by the close correlations with rising trends in droughts (Publications II; IV). The accretion of nutrient runoff from the Porijõgi and its sub-catchments during the years 1997–2009 was caused by the rise in water discharge in the last two years and the re-intensification of agricultural land use, although the recovery of nutrient flows fell remarkably short of expectations, probably owing to catchment retention (Publication V).

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SUMMARY IN ESTONIAN

Toitainete ärakande maastikulised tegurid Eesti valglatest

Toitainete liikumine valglas on maastikuökoloogia peamisi uurimisobjekte. Suurt tähelepanu pööratakse keemiliste koormuste määramisele ja nende mõju leevendamisele märgalade ja kaldapuhvrite abil. Vähem on uuritud lammi ja mineraalmaa piiril paiknevaid ökotone. Luhtade servad toimivad geokeemiliste redoksbarjääridena, mis koguvad endasse mineraalmuldadelt leostunud keemilisi elemente. Maastikuelementide mõju ainevoogudele on eriti aktuaalne Eestis, kus kollektiivse põllumajanduse kollaps on põhjustanud toitainete väljakande järsu languse. Samas on Põhja-Euroopa turbamaadel toimuv inimtegevus hoogustanud orgaanilise süsiniku väljakannet. Eesti territooriumist on turbaga kaetud 10 091 km², millest 60–70% on kuivendatud. Viimastel kümnenditel on meil täheldatud põudade sagenemist, mis ähvardab suurendada turba lagunemist ja süsiniku leostumist. Eriti suur on see oht kuivendusobjektidel.

Käesoleva väitekirja üldine eesmärk oli selgitada Eesti põllumajandusmaastikes fosfori, lämmastiku ja orgaanilise süsiniku liikumise protsesse. Täpsemad ülesanded olid:

- a) Anda kirjanduse ülevaade fosfori ja lämmastiku ärakande maastikulistest teguritest parasvöötmes. Viimaste all käsitletakse pinnamoe, pinna- ja põhjavee, mulla, taimkatte ning maakasutuse faktoreid;
- b) Selgitada Rõngu–Palupera moreentasandiku näitel ökotonide vastavust redoksbarjääridele mullas. Peamiseks hüpoteesiks oli ökoloogiliste servade esinemine taimkattes vähemalt 20 m redoksbarjäärist.
- c) Analüüsida Porijõe ja erineva maakasutusega alamvalglate näitel maakasutuse intensiivistumise mõju toitainete ärakandele aastatel 1997–2009 ja katsetada lihtsat empiirilist fosfori ja lämmastiku ärakande mudelit, mis arvestab maakasutuse, väetamise, mulla ja vooluhulga näitajaid.
- d) Selgitada 1992.–2007. a toimunud orgaanilise süsiniku kontsentratsiooni ja ärakande muutumist Eesti jõgedes seoses maakasutuse, hüdroloogilise põua, vooluhulga ja vee keemia näitajatega.

Kirjandusülevaate peamiseks allikaks olid kuni 1993. a ilmunud tööde osas Ülo Manderi ja Tõnu Mauringu poolt loetletud uurimused (Mander & Mauring 1994), hilisemaks materjaliks aga Thomson Reutersi ISI Web of Science'i indekseeritud kirjandus. Kirjanduse põhjal koostati andmebaas kolme analüüsi tarbeks: a) fosfori ja lämmastiku ärakande põhimõtteline skeem parasvöötme põllumajandusmaastikes b) ülevaade determinatsioonikoefitsientidest toitainete ärakande ja maastikuliste tegurite vahel ning c) valgla suuruse mõju selgitamine ainevoogudele.

Ökotonide analüüsiks Rõngu–Palupera moreenitasandikul kasutati redoksbarjääride indikaatorina tugevaid mullaniiskuse piire. Uurimisalal määrati 24 redoksbarjääri lõiku ning uuriti nendega risti paiknevatel transektidel ruumilisi erinevusi taimkattes. Selleks võrreldi kahte kõrvuti asetsevat 10 m vööndit ja arvutati nende erinevus. Nihutades sellist kahe poolega "akent" mööda transekte, saadi taimkatte erinevuskõverad.

Uurimuse käigus arvutati ning modelleeriti ka Porijõe ja selle alamvalglate fosfori ja lämmastiku ärakanded. Lisaks arvutati orgaanilise süsiniku tendentsid Eesti vooluvete seire programmi 11 lävendi TOC (kogu orgaanilise süsiniku) ja PHT (permanganaatse hapnikutarbe) mõõtmiste põhjal. Saadud trende korreleeriti hüdroloogilise põua näitajaga ja sulfaatide kontsentratsioonide tendentsidega.

Kirjanduse ülevaate tulemustest järeldus, et vahelduvate sisenditega valglates on toitainete ärakandes määravaks mullatingimused, teatud maakasutuse osakaal ja veekogu kaugus. Ajas samana püsivate sisendite puhul on peamiseks keemilised ja füüsilised voolukoridorid ja -barjäärid ning maastikumuster. Fosfori ärakanne on tugevalt seotud voolunõvade ja -takistustega. Seetõttu on fosfori puhul eriti selged seosed maastikumustri ja puhverribadega. Samas lämmastiku väljakande määravad paljuski põllumajandusega seotud tegurid ja mulla niiskusrežiim (seonduvalt denitrifikatsiooniga). Suurim lämmastiku ärakande varieeruvus tuvastati väikestes valglates.

Lammide ja mineraalmaa piiril paiknevate redoksbarjääride analüüs näitas, et neid tähistavad maastikus taimkatteservad. Selliseid ökotone on võimalik jälgida aerofotodel ja satelliitpiltidel. Sel meetodil on võimalik põllumajandusmaastikes määrata redoksbarjääre ja biogeokeemiliselt "kuumi kohti". Vastavad ökotonid asuvad tüüpiliselt põlluserva vahetus läheduses künniterrasside all. Kuivendamine eemaldab redoksbarjäärid ja vastavad ökotonid, lihtsustades maastikumustrit ja suurendades ökoloogiliste häiringute tõenäosust (näiteks põlengud, üleujutused, põuad). Selliseid ökotone võib kasutada soode ja muude märgalade piiritlemisel ning põllumajandusmaastike jätkusuutliku kasutuse planeerimisel.

Toitainete ärakande kasvu Porijões ja selle põllumajanduslikes alamvalglates 1997.–2009. a põhjustas vooluhulkade suurenemine viimasel kahel aastal ja põllumajandusliku maakasutuse taastumine. Samas jäid ainevood mitmekordselt alla modelleerimise põhjal oodatavale. Vähese tõusu põhjuseks on arvatavasti valgla puhverdusvõime ja väetiste ratsionaalsem kasutamine.

Orgaanilise süsiniku kontsentratsioon ja ärakanne Eesti jõgedes aastatel 1992–2007 kasvas. Seejuures väljakanne tõusis hoolimata vooluhulga vähenemisest. Peamiseks kasvu põhjustajaks olid aastatel 2000–2007 sagenenud erakordselt madalad suvised veetasemed, mille mõju süvendasid omakorda kuivendussüsteemid. Seda tõendab statistiliselt oluline tugev korrelatsioon hüdroloogilise põua näitajaga.

Kokkuvõttes olid käesoleva väitekirja tulemuseks uudsed järeldused Eesti valglate ainevoogudest, eriti mis puudutab süsinikuühendite ärakande intensiivistumise seost kliimamuutustega. Samuti analüüsib käesolev töö luha ja mineraalmaa vahelisi ökotone seni vähe käsitletud maastiku geokeemilisest aspektist. Esimesena lahkab väitekiri 21. sajandi algusaastate põllumajanduse taastumise järel toimuvat toitainete väljakande tõusu Eestis.

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