This report summarizes the results of a three-year study on the effect of gypsum amendment on the losses of phosphorus from cultivated fields. A substantial reduction in runoff turbidity and in particulate and dissolved phosphorus were found at a catchment-scale. The finding was corroborated by a comparison to a reference catchment with no gypsum amendment, and by mathematical modelling. The potential side effects of the method are also discussed. Gypsum treatment is best suited for coastal catchments with soils sensitive to erosion or showing a high phosphorus level.
The effect of gypsum on phosphorus losses at the catchment scale

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FOREWORD

The potential of an industrial by-product, gypsum, in reducing phosphorus losses from crop production and animal husbandry was examined in the TraP project (‘Novel gypsum-based products for farm-scale phosphorus trapping’). This 3.5-year (2007–2010) joint project was led by Yara and funded by Yara and the Finnish Funding Agency for Technology and Innovation (Tekes). The core research partners included the Finnish Environment Institute (SYKE), MTT Agrifood Research Finland, TTS (the Work Efficiency Institute), and Luode Consulting Ltd.

The main tasks of SYKE in the TraP project were to 1) estimate the effect that spreading gypsum on fields has on nutrient losses on the catchment scale, 2) scale up the effect, and 3) examine the impact of gypsum-derived sulphate on water bodies. Several researchers with SYKE took part in these tasks. Petri Ekholm calculated the material fluxes from the Nummenpää catchment and was principally responsible for writing this report. Sirkka Tattari and Elina Jaakkola performed the ICECREAM modelling, with Jaakkola also gathering the spatial background information on the Nummenpää catchment by interviewing the farmers and performing the GIS analyses. Jouni Lehtoranta and Petri Ekholm planned the sediment and soil incubations for examination of the sulphate’s effect on phosphorus release. The incubations were largely conducted by Visa Mäkelä, who also studied the relationship between catchment characteristics and sulphate concentrations in lakes. Sari Väisänen scaled up the potential gypsum effect with the assessment tool VIHMA. Ljudmila Vesikko participated in data handling.

Mikko Kiirikki, from Luode Consulting Ltd, was responsible for the instrumentation of the catchment and for quality assurance for the on-line data. Pasi Valkama and Kirsti Lahti from the Water Protection Association of the River Vantaa and Helsinki Region took part in the catchment studies and provided additional data from the Nummenpää and the reference catchments. Pasi Valkama took the manual samples, which were analysed in SYKE’s laboratory under the guidance of Teemu Näykki. Yara’s Liisa Pietola was responsible for the entire TraP project and actively collaborated with SYKE in all phases of the project.

The authors wish to thank
• The two collaborating institutes, MTT and TTS, for their fruitful co-operation;
• The steering and co-ordination groups of the TraP project for their active discussions;
• Markku Puustinen (of SYKE) for help in the VIHMA estimations;
• Risto Uusitalo (of MTT) for providing the soil sample for incubation;
• SYKE’s laboratory for analyses;
• Irmeli Ahtela and the others at the Uusimaa Centre for Economic Development, Transport and the Environment for help in the initial phases of the study;
• Irina Lähteenmaa and others with the Municipality of Nurmijärvi for their communication with farmers and provision of local data;
• All the farmers of the Nummenpää catchment for their positive attitude toward the catchment studies performed in their fields; and
• Asko Simojoki and Juha Grönroos for thorough commenting on the manuscript.
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1 Introduction

Many water bodies in Finland will not achieve the good ecological state demanded by the EU’s Water Framework Directive (2000/60/EC) unless nutrient loading from agriculture is drastically reduced (Ministry of the Environment 2009). Erodible fields and sites with high soil phosphorus levels constitute high-risk sites for agricultural phosphorus losses. In addition to sloping fields, flat fields on fine soils may show considerable erosion due to so-called diffusion or dispersion erosion (Aura et al. 2006). Sites with high soil phosphorus levels are found to include fields that have a long history of manure application or that are under strongly fertilised high-value crops (Uusitalo et al. 2007).

Novel remedies may aid in reducing phosphorus losses from the agricultural high-risk sites (Turtola et al. 2010). Recently, several experiments have been performed with different types of amendments in Finland (e.g., Närvänen et al. 2008; Muukkonen et al. 2009; Lillunen et al. 2011). Gypsum (CaSO$_4$ · 2H$_2$O) is a natural mineral, but it is also voluminously formed in industrial processes and flue-gas desulphurisation. Gypsum was used as a soil amendment already by the ancient Greeks (Shainberg et al. 1989), but its use in controlling phosphorus losses, both those in a particulate and in a dissolved form, is relatively new.

Amendment of soil with gypsum increases the ionic strength and calcium concentration in the soil solution (Aura et al. 2006; Pietola 2008), which should promote the flocculation of the smallest soil particles and reduce erosion. In addition, adsorption of anions should become stronger. Thanks to these processes, phosphorus losses to waters should be lessened without reduction in the bioavailability of phosphorus to plants.

The effect of gypsum has been studied mostly under laboratory conditions (Aura et al. 2006; Pietola 2008; Watts and Torbert 2009; Murphy and Stevens 2010; Uusitalo et al. 2010; Kumar and Saha 2011). For example, gypsum was shown to reduce phosphorus losses from the slightly acidic Finnish soils in incubation-leaching studies (Pietola 2008) and in experiments with soil cores under artificial rainfall (Uusitalo et al. 2010). Here, the effect of gypsum on phosphorus losses was examined at catchment scale by means of automatic and manual water quality monitoring and with the aid of modelling. In addition, the losses and impact of sulphate, a side effect of the gypsum spreading, was examined by means of the water quality data and laboratory incubations. Finally, the potential of gypsum to reduce phosphorus losses on a regional scale was estimated.
2 Material and methods

2.1 The experimental catchment and reference catchment

Gypsum was spread and its effects on nutrient losses were monitored in the Nummenpää catchment, a 2.45 km² sub-catchment of the river Lepsämänjoki (a tributary of the Vantaa) in the village of Nummenpää (in Nurmijärvi municipality, southern Finland; Figure 1). In the TraP project, runoff in the catchment was monitored from February 2008 to November 2010. Additional data (for 2005–2007) were available from earlier studies performed in the catchment (Särkelä et al. 2006; Valkama et al. 2007b).

Figure 1. The location of the Nummenpää catchment, the monitoring sites therein, and the nearby reference catchment. In the Nummenpää catchment, the upper site was visited only infrequently, to estimate the level of background loss, while the central and lower sites in the field area (marked in yellow) were instrumented with online sensors.
The Nummenpää catchment was delineated from a digital elevation model (DEM; National Land Survey of Finland, Licence 7/MML/11) with a minimum vertical resolution of 0.3 m and a grid cell size of 2 × 2 m. The DEM was based on laser-scanned data and was corrected in consideration of, for example, culverts. According to the soil classification data of the Geological Survey of Finland, the upper part of the catchment is forested and has rocky areas (Dystric Leptosol) and eskers (Haplic Podzol; Figures 1 and 2). Some forestry actions have been performed there, but their estimated contribution to the nutrient load is negligible. The lower part is mainly cultivated and has clayey soils (Vertic Cambisol). The topsoil texture of the fields is mainly silty clay loam. Of the catchment area, fields account for 41% and forests 44%, with the remaining area being used for such purposes as housing (Table 1). In total, the catchment has 73 inhabitants. None of the houses are connected to central sewerage systems.
The mean slope of the fields was 1.6% (range: 0.6%–4.8%). Information on the location, directions, and condition of drainage pipes was not available for all fields. Most of the pipes were installed in the 1950s and 1960s, but some renovation has taken place more recently. Approximately 83 ha of the field area had sub-surface drains. In comparison to the catchment delineation based on surface runoff, this is approximately 72% of the field area.

In 2008, 86% of the fields were planted with spring cereals and 12% in cabbage, with 2% fallow or uncultivated fields (Figure 3). In 2009, 81% of the fields were under spring cereals, 15% under cabbage, and 4% fallow. Autumn ploughing accounted for 75% and 65% of the field area in 2008 and 2009, respectively; the remaining area was under reduced tillage (2008: 22%; 2009: 32%) or directly drilled (3% in both years).

Soils from the fields were taken to a depth of 20 cm in spring 2008 (before sowing and fertilising; Figure 4). In addition, soil data owned by the farmers were collected. Furthermore, TTS took soil samples from 17 GPS-defined sites, mostly in the cabbage plots, once before and four times after the gypsum amendment (Figure 4). The soil analyses involved extraction of dry soil with a solution of 0.5 M ammonium acetate and 0.5 M acetic acid at a pH of 4.65 (Vuorinen and Mäkitie 1955).

Of the 101 hectares of fields in the catchment, 93 hectares (91.3%; Table 1 and Figure 3) were amended with gypsum (4.1 t ha⁻¹) after the harvest and before the tillage in 8 September – 5 November 2008. Spreaders for moist lime and dry manure were both used and found appropriate for gypsum field spreading (Palva and Alasuutari 2009). The gypsum consisted of phosphogypsum, a by-product from the manufacturing of phosphoric acid by digestion of phosphate ore concentrate with sulphuric acid. The phosphate ore originates from igneous phosphate rock in Siilinjärvi, Finland.
The nearby upper reaches of the Lepsämänjoki served as a ‘reference’ catchment, where no gypsum was used (Figure 1). This catchment has been intensely monitored by the Water Protection Association of the River Vantaa and Helsinki Region since 2005 (Valkama et al. 2007a). Although larger (23 km²) and receiving occasional sewage load, the catchment resembles the Nummenpää catchment; that is, it has no lakes, the field percentage is 36%, the fields have mostly clayey soils, and their mean slope is 1.7%.

2.2 Monitoring of nutrient fluxes

Water quality was monitored at three sites (representing the upper, central, and lower reaches; Figure 1 and Table 1) along the main channel in the Nummenpää catchment from February 2008 to November 2010 – i.e., before, during, and after the gypsum amendment. Spring 2008, together with the first week of September 2008, formed a reference period to which the data collected after gypsum amendment were compared. Automatic on-line sensors for recording values such as turbidity, nitrate levels, and temperature were deployed at the central and lower site for, in total, six measurement periods, in spring and autumn (Figure 5). No sampling or measurement was performed in summer or mid-winter, when agricultural runoff levels are typically low in Finland. In 2008, the measurement periods accounted for 66% and in 2009 75% of the annual water flow as estimated from the hydrograph for the Lepsämänjoki (Figure 5).
Table 1. Monitoring sites in the catchment.

<table>
<thead>
<tr>
<th>Site</th>
<th>Area (km²)</th>
<th>Fields (%)</th>
<th>Gypsum spread (% of fields)</th>
<th>Forest (%)</th>
<th>Other (%)</th>
<th>Inhabitants</th>
</tr>
</thead>
<tbody>
<tr>
<td>Upper</td>
<td>0.97</td>
<td>0.3</td>
<td>0</td>
<td>92.4</td>
<td>7.3</td>
<td>6</td>
</tr>
<tr>
<td>Central</td>
<td>1.77</td>
<td>22.7</td>
<td>90.2</td>
<td>60.2</td>
<td>17.1</td>
<td>62</td>
</tr>
<tr>
<td>Lower</td>
<td>2.45</td>
<td>41.4</td>
<td>91.3</td>
<td>44.1</td>
<td>14.5</td>
<td>73</td>
</tr>
</tbody>
</table>

* Based on Agency for Rural Affairs (Mavi) statistics (Tike, Decision 008/411/2008).
* Based on the CORINE land cover database 2000; includes, e.g., wetlands, built areas, and roads.

Figure 5. Hourly (blue line) and cumulative runoff during the six measurement periods in the Nummenpää catchment. The green line shows the runoff in the river Lepsämänjoki (source: the database of the Finnish Environment Institute).

Because of frequent flooding of the lower reaches, the water level at the lower site does not always correctly describe the runoff volume (Figure 6). Therefore, a V-notch weir was constructed at the central site (Figure 7). The runoff (in millimetres) at the upper and lower site was assumed to be the same as that at the central site. The central site was also equipped with a precipitation recorder. In addition, the temperature of the surface soil was measured.

The ‘basic’ sensor (YSI 600 OMS, from YSI, Inc.) was set to record turbidity, conductivity, and water temperature every hour. On occasion, the turbidity exceeded the upper detection limit (approximately 1,000 NTU). The first sensor deployed at the lower site had an exceptionally low upper detection limit (about 850 NTU) and was soon replaced by another. In collaboration with the Water Protection Association of the River Vantaa and Helsinki Region, the sites were also instrumented with S::CAN Spectro:lyser sensors that recorded nitrate nitrogen and dissolved organic carbon in addition to turbidity. They enabled the measurement of turbidity values of up to 5,000 NTU.

To obtain reference data for the YSI sensor, to get calibration data for the S::CAN sensor, and – most importantly – to analyse a larger set of variables than possible with the sensors alone, 123 manual runoff samples were taken, in total. To ensure comparability, the samples from the central and lower sites were usually taken at the time of sensor recording. The upper site was visited only infrequently, to estimate
the background load from the forested area. Although the sampling occasions were chosen to represent flood periods, the highest peak flow events were missed (Figure 8). The manually obtained samples were analysed for temperature, conductivity, turbidity, total suspended solids, total phosphorus, dissolved phosphorus, dissolved reactive phosphorus, total nitrogen, nitrate nitrogen, ammonium nitrogen, total iron, sulphate, and other major anions and cations. Analyses were performed in the laboratory of the Finnish Environment Institute, a testing laboratory accredited to the requirements of the standard SFS-EN ISO/IEC 17025. The details of the manual and sensor determinations are given in the appendix.

Figure 6. Left: The lowest part of the Nummenpää catchment is frequently flooded. Right: Flow measurements based on water level are not reliable during the floods (photos by Petri Ekholm).

Figure 7. Left: A V-notch weir was constructed at the central site. Right: In April 2010, the weir did not operate properly, because an exceptionally large amount of snow accumulated in the main channel (photos by Pasi Valkama and Petri Ekholm).
Figure 8. The timing of the manual sampling.
3 Runoff monitoring results

3.1 Source apportionment

Water coming from the forested upper catchment was brownish but clear, and it had low concentrations of nutrients and dissolved ions. On the agriculturally affected central and lower sampling sites, the turbidity levels and nutrient and ion concentrations were appreciably higher (Table 2).

To estimate the proportion of agriculture in the total load, a source apportionment was made on the basis of land use, specific loads (from the literature), and the number of inhabitants in the various parts of the catchment. The nutrient load from the rural population was estimated on the basis of treatment type, obtained from the municipality of Nurmijärvi. Of the 73 inhabitants, 58 lived in houses either having just a septic tank and leading of overflow to a ditch or for which there was no information on the treatment system. Their phosphorus loading was set, according to the Onsite Waste-water System Decree (209/2003), at 0.80 kg y⁻¹ (2.2 g d⁻¹), of which 60% (Rontu and Santala 1995), or 0.48 kg y⁻¹, was assumed to be transported to waters. In other cases, the share of phosphorus in different wastewater types (all waters and grey waters) was taken from the above-mentioned decree and a 70% reduction in phosphorus was assumed, as required by the decree. In cases where wastewaters were transported to a municipal treatment plant outside the catchment, the load was evidently zero. From these assumptions, the phosphorus load from the rural population was estimated at 2.9, 23.1, and 28.8 kg y⁻¹ in the upper, central, and lower sites, respectively.

The specific loads for forested areas (9 kg km⁻² y⁻¹), for agricultural areas (110 kg km⁻² y⁻¹), and for natural background losses (5.4 kg km⁻² y⁻¹) were obtained from the literature (Vuorenmaa et al. 2002; Mattsson et al. 2003). From these values, the annual phosphorus flux at the upper site was calculated to be 12 kg km⁻² y⁻¹. A 5% higher value was obtained from the water quality monitoring data at the site.

Table 2. Mean values of the water quality variables by site in the Nummenpää catchment before the gypsum amendment (13 February – 3 September 2008).

<table>
<thead>
<tr>
<th>Site</th>
<th>n</th>
<th>pH</th>
<th>Conductivity (mS m⁻¹)</th>
<th>Sulphate (mg l⁻¹)</th>
<th>Turbidity (FNU)</th>
<th>Total suspended solids (mg l⁻¹)</th>
<th>Phosphorus (µg l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Upper</td>
<td>7</td>
<td>6.3</td>
<td>4.4</td>
<td>6.8</td>
<td>8.1</td>
<td>8.5</td>
<td>14</td>
</tr>
<tr>
<td>Central</td>
<td>13</td>
<td>6.8</td>
<td>9.6</td>
<td>9.9</td>
<td>93</td>
<td>75</td>
<td>120</td>
</tr>
<tr>
<td>Lower</td>
<td>13</td>
<td>7.0</td>
<td>13.2</td>
<td>13</td>
<td>240</td>
<td>210</td>
<td>300</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>
The same approach was used for the lower site. For the period before the gypsum amendment, the calculated load was 37% lower than the flux obtained from monitoring data. If the assumption as to the load from other sources than agriculture is correct, as suggested by the good match between the calculated and measured fluxes in the forested upper reaches, agricultural nutrient flux should have been as high as 170 kg km\(^{-2}\) y\(^{-1}\) in the catchment (Figure 9), a value that is within realistic bounds in view of the high phosphorus level and erosion of the soil. If so, 79% of the total flux in the lower reaches originated from the fields.

![Figure 9. The estimated origin of phosphorus fluxes in the lower reaches before the gypsum amendment.](image)

3.2 Turbidity and particulate phosphorus

As found in other Finnish agricultural catchments (Linjama et al. 2009; Koskiaho et al. 2010), the turbidity recorded by the on-line sensors in Nummenpää strongly correlated with the turbidity found in the laboratory (Figure 10). The recorded turbidity values increased with flow at the central and the lower site (Figure 11). The scatter in the relationship was partly brought about by positive hysteresis – i.e., turbidity tended to be higher for a rising than a decreasing flow. After the gypsum amendment, turbidity values were generally lower and their correlation to the flow weaker. Before the gypsum, turbidity increased at the lower site by 2.95 NTU (95% confidence interval: 2.83–3.07 NTU) when flow increased by one unit (\(1\) s\(^{-1}\)). After the gypsum, the increase was only 0.82 NTU (95% confidence interval: 0.79–0.85 NTU). Yet some high turbidity values were seen after the gypsum treatment too (Figure 11). Note that, in contrast to the slope, the intercept was higher after than before the gypsum. The reason for this is not known, but the result suggests that the effect of gypsum is realised only with higher flow values.

There was also a good correlation between turbidity measured on-line and the concentration of particulate phosphorus determined in the laboratory from manual samples, both before and after the gypsum amendment (Figure 12). Accordingly, online data could be used as a proxy for the changes in particulate phosphorus due to gypsum amendment.
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Figure 10. Left: Turbidity recorded by on-line sensors correlated with turbidity determined in the laboratory from manually taken samples (central and lower site). Right: Turbidity standards of 0, 20, 200, and 1,000 FNU (photos by Timo Yanni and Teemu Nätäkkä).

Figure 11. Turbidity and runoff before (22.5.2008–8.9.2008, 2,313 hourly values) and after (5.11.2008–18.6.2010, 8,761 hourly values) the gypsum amendment at the lower (left) and the central (right) site.

Figure 12. The relationship between turbidity recorded on-line and particulate phosphorus determined in the laboratory (particulate phosphorus = the difference between total phosphorus and dissolved total phosphorus).
The impact of gypsum on phosphorus losses cannot be estimated by simply comparing the concentrations before and after the amendment, as other factors affecting phosphorus concentrations may be present. Fortunately, agricultural practices remained practically the same throughout the study period (see Subsection 2.1). The effect of fluctuating hydrological conditions was taken into account via analysis of the difference in the relationship between phosphorus concentration and flow before and after the gypsum amendment, with the aid of analysis of covariance. By means of the SAS/STAT procedure, the relationship between the concentration of particulate phosphorus (CPP, \(\mu g \text{ l}^{-1}\)) and runoff (\(l \text{ s}^{-1}\)) was estimated with gypsum amendment as a classification variable and with consideration for the interaction between the gypsum amendment and flow. The resulting models were the following (see also Figure 13):

Before gypsum: \(C_{pp} = -5.4 + 4.1 \text{ Flow}\)

After gypsum: \(C_{pp} = 47 + 1.1 \text{ Flow}\)

The models (and the intercepts and slopes) were highly significant \((p < 0.001, n = 10,557)\), although, because of strong autocorrelation in the data, the probability values are overestimated to some extent. The equations were then used to estimate the concentration of particulate phosphorus for all measurement periods in spring 2008 – spring 2010, with the assumption that gypsum had been applied already at the start of the monitoring period or had not been used at all. With this approach applied, the reduction in the loss of particulate phosphorus due to gypsum was 57%.

The concentration of dissolved reactive phosphorus could not be estimated from the on-line data. Since there were only much less frequent manual data available, the effect of gypsum on this form of phosphorus could not be estimated as reliably as the equivalent for particulate phosphorus. Before gypsum amendment, the mean concentration of dissolved reactive phosphorus on the lower site was 48 \(\mu g \text{ l}^{-1}\), with the concentrations increasing with runoff (Figure 14). After gypsum, the mean con-

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**Figure 13.** Particulate phosphorus and runoff before (22.5.2008–8.9.2008, 2,313 hourly values) and after (5.11.2008–18.6.2010, 8,761 hourly values) the gypsum amendment at the lower (left) and the central (right) site.

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### Dissolved phosphorus

The concentration of dissolved reactive phosphorus could not be estimated from the on-line data. Since there were only much less frequent manual data available, the effect of gypsum on this form of phosphorus could not be estimated as reliably as the equivalent for particulate phosphorus. Before gypsum amendment, the mean concentration of dissolved reactive phosphorus on the lower site was 48 \(\mu g \text{ l}^{-1}\), with the concentrations increasing with runoff (Figure 14). After gypsum, the mean con-
The concentration of dissolved reactive phosphorus was 35 µg l\(^{-1}\) and there was no correlation of concentrations to flow (as the figure shows). At the central site, the same pattern was found. Analysis of covariance gave the following equations for the lower site:

Before gypsum: \( C_{\text{DRP}} = 16 + 0.48 \text{ Flow} \)

After gypsum: \( C_{\text{DRP}} = 33 + 0.04 \text{ Flow} \)

Figure 14. Dissolved reactive phosphorus and runoff before and after gypsum amendment at the central and lower site.
However, the model was significant only with $p = 0.053$ ($n = 33$; here, there was no autocorrelation bias due to relatively infrequent sampling). Using these equations for the spring 2008 – spring 2010 data suggested that the loss of dissolved reactive phosphorus was 34% lower after the gypsum amendment.

3.4 Major cations and anions

The reliability of ion determinations was evaluated by 1) summing the concentrations (meq l$^{-1}$) of anions and cations and examining the balance and 2) comparing the calculated and the measured conductivity. The relationship between anions and cations showed relatively little scatter but did exhibit slight overestimation of cations (Cations = 1.08 Anions + 1.37, $r^2 = 0.95$). This overestimation may result from the analysis of cations with ICP-OES (see appendix), which may capture cations on/in particles, in addition to those in solution, because of the only modest pre-treatment of samples (centrifuging). By contrast, anions were analysed by IC, which had a pre-filtration and a pre-colony that prevent particulates entering the measurement colony. The calculated conductivity (mS m$^{-1}$) also correlated strongly with the observed one, again with slight overestimation (Cond$\text{calc} = 1.3$ Cond$\text{obs} - 5.0$, $r^2 = 0.95$). On the basis of these two relationships, the ion determinations can be considered sufficiently reliable for the purpose of the study – i.e., to examine whether gypsum triggered major changes in the losses of ions, particularly sulphate ions.

Sulphate concentrations were strongly correlated to calcium concentrations, yet the molar ratio was not that of gypsum (1:1) but 1:0.79 (Figure 15). Sulphate has a relatively low tendency to be adsorbed to soil particles, whereas calcium may be taken up by exchange reactions. As also shown by the results of MTT, it seems that magnesium has been exchanged by calcium to some extent (Figure 15).

![Figure 15. Left: molar ratio of sulphate to calcium in the Nummenpää runoff. Right: molar ratio of sulphate to magnesium in the runoff.](image-url)
The gypsum used originated from fluoroapatite and contained less than 0.3% fluoride, of which 60% consisted of water-extractable forms (Reetta Puska of Yara Suomi Oy, personal communication). Theoretically, fluoride pollution could form a potential adverse side effect of the measure. There were no data on fluoride in Nummenpää runoff before the gypsum treatment. After the gypsum, the maximum fluoride concentration was 0.32 mg l\(^{-1}\). Given that the upper limit for fluoride in the EU’s Drinking Water Directive (98/83/EC) is a full 1.5 mg l\(^{-1}\), fluoride appears not to pose problems.

3.5 **Sulphate**

The losses of sulphate give an indication of the duration of gypsum’s effect. In addition, they give insight on the potential side effects of the method (see Section 5). The concentration of sulphate (C\(_{\text{SO}_4}\)) in the manual samples correlated with conductivity recorded by the on-line sensors (C\(_{\text{SO}_4}\) = 0.22 Cond\(^{1.68}\), \(r^2 = 0.84\), \(n = 94\)). The relationship allowed calculation of the losses of sulphate for the central and lower site from the on-line data. For the upper site, only manual samples were used.

If one assumes the spring 2008 data to represent the entire year, the specific sulphate losses were 44 kg ha\(^{-1}\) y\(^{-1}\) from the forested upper reaches and 140 kg ha\(^{-1}\) y\(^{-1}\) from agricultural land. Soon after the gypsum amendment, the sulphate concentrations increased substantially (Figure 16). As there were heavy rains before the surface-applied gypsum was incorporated into the soil through tillage practices, some of the losses may be due to direct washout of the gypsum. After the first autumn, the losses were smaller; the mean sulphate loss after the gypsum amendment remained as high as 460 kg ha\(^{-1}\) y\(^{-1}\).

Sulphate losses from agriculture are a topic seldom studied in Finland. According to Korkman (1973), they ranged in the 1960s from 8 kg ha\(^{-1}\) y\(^{-1}\) in mineral soils to 500–1,000 kg ha\(^{-1}\) y\(^{-1}\) in acid sulphate soils. More recent data (from a database of the Finnish Environment Institute) show that the losses are 42–180 kg ha\(^{-1}\) y\(^{-1}\) in small agricultural catchments in southern Finland but as high as 920 kg ha\(^{-1}\) y\(^{-1}\) in catchments on acid sulphate soils in western Finland.

![Figure 16. Estimated sulphate concentrations in runoff in the six measurement periods, based on conductivity recordings by the YSI sensor. The numbers show the mean sulphate concentration for each period.](image-url)
The total amount of gypsum spread in the Nummenpää catchment was 369 tons. On the assumption that the moisture content of the gypsum was 16.5 %, 172 tons of sulphate, in total, was applied in gypsum. An upper limit for the gypsum loss can be obtained by assuming that all sulphate lost from agricultural land after the gypsum amendment originated from gypsum. In this case, 45 % of the gypsum had been lost through runoff. The true figure is smaller, since sulphate is lost from cultivated soil on account of factors such as mineralisation; well over 95% of the total sulphur in many types of soil is held in the organic matter (see Nriagu 1978).

3.6 The reference catchment

The conclusion that gypsum reduced phosphorus losses was further supported by the comparison of the runoff concentrations in the Nummenpää catchment to those in the reference catchment. Figure 17 shows the concentrations of total suspended solids, particulate phosphorus, and dissolved reactive phosphorus in the Nummenpää and the reference catchment on those days when a sample had been taken from both sites. The graphs are divided into two sets: the period before the gypsum amendment in Nummenpää (3 October 2005 – 10 April 2008) and the period after the gypsum amendment (10 November 2008 – 3 November 2010).

Before the gypsum amendment, the concentrations of total suspended solids in these two catchments, located near each other, were well correlated, with total suspended solids in the Nummenpää catchment being approximately 1.1 times those in the reference catchment (Figure 17). After the gypsum amendment, the correlation was lower and the concentrations in the Nummenpää catchment tended to be lower than in the reference catchment.

For particulate phosphorus, a similar but clearer change was found; the concentrations in the Nummenpää catchment were about 1.2 times those in the reference catchment before the gypsum amendment, whereas they were markedly lower afterward (Figure 17). For the dissolved reactive phosphorus, however, the differences were smaller (Figure 17).

Finally, the Nummenpää and the reference catchment were compared on the basis of concomitant turbidity recordings by the YSI sensor (Figure 18). The comparison showed a clear change toward lower turbidity values in the Nummenpää catchment after the gypsum amendment.
Figure 17. Concentrations of total suspended solids, particulate phosphorus, and dissolved reactive phosphorus in the Nummenpää catchment (lower site) and in a nearby reference catchment during spring 2005 – autumn 2010, divided into two periods: before (autumn 2005 – spring 2008) and after (autumn 2008 – autumn 2010) the gypsum use in the Nummenpää catchment. Particulate phosphorus is calculated here as total phosphorus less dissolved reactive phosphorus. The solid line shows a 1:1 ratio. Data come from the Water Protection Association of the River Vantaa and Helsinki Region and the TraP project.
3.7 Soil analyses

According to the determinations performed in the TraP project, as complemented by farmers’ own data, the soil test P of fields in the Nummenpää catchment before gypsum amendment ranged from 8.4 mg l\(^{-1}\) to 86 mg l\(^{-1}\). The mean value over all of the plots was 20 mg l\(^{-1}\). For cabbage plots, it was as high as 50 mg l\(^{-1}\) and for spring cereals 16 mg l\(^{-1}\). Both values exceeded the national average (about 12 mg l\(^{-1}\)). Soil pH ranged from 5.9 to 7.6 (mean: 6.6). The dominant soil type was silty clay loam but there were also some coarser soils.

Analysis of the soil samples taken from exactly the same 17 locations five times in the course of the project gave indications of the effect of gypsum on soil chemistry. The mean soil test P at these locations was 41 mg l\(^{-1}\) before the gypsum amendment and remained at that level on the four sampling occasions after the gypsum amendment. No change was found in pH (mean: 6.9), Ca (mean: 4,300 mg l\(^{-1}\)), K (mean: 290 mg l\(^{-1}\)), or Mg (mean: 410 mg l\(^{-1}\)) either. By contrast, conductivity increased by about one unit from the mean level of 170 µS cm\(^{-1}\). In addition, sulphur concentration roughly doubled from the initial value of 34 mg l\(^{-1}\).
4 Modelling of the effect of gypsum on phosphorus losses

4.1 The effect of gypsum in the Nummenpää catchment as estimated with the ICECREAM model

A field-scale mathematical model, ICECREAM, was applied to simulate phosphorus losses in the Nummenpää catchment. This is a dynamic model that calculates soil and nutrient losses at a daily time step (Rekolainen and Posch 1993; Tattari et al. 2001; Yli-Halla et al. 2005). The hydrology component simulates daily runoff by using the empirical SCS curve number method (USDA-SCS 1972). The original version of the model was found to overestimate dissolved phosphorus and underestimate particulate phosphorus when parameterised for the rather flat field area in the Nummenpää catchment (Jaakkola 2009). In addition, Finnish clayey soils have been found to have short response times between rain events and drainage flow, and high nutrient concentrations in the drainage flow soon after fertilisation, which suggest macropore flow to be the main source for drainage flow (Paasonen-Kivekäs et al. 2008). Therefore, before the effect of gypsum was added to the model, the model was modified to take into account macropores, which enables more particulate phosphorus to be routed out from the soil.

To simulate the macropore flow, three new parameters were introduced to the model. First, the area of macropores controlling the proportion of water routed via macropores was used instead of matrix flow. Second, a threshold for moisture in the two upper soil layers was used, representing the soil moisture level above which macropore flow starts. Third, the model used a P-specific parameter referring to the fraction of total particulate phosphorus transported from the phosphorus pools to macropores.

Simulations were performed for three distinct field types typical of the Nummenpää catchment: 1) spring barley with autumn ploughing, 2) spring barley with shallow cultivation, and 3) cabbage with autumn ploughing. The results from these three simulations were then combined via weighting for the share of each cultivation type in the full area. The mean slope, fertilisation rates, soil type, and soil phosphorus status of the fields as well as cultivation and tillage practices were set as found at the study site. Simulations were run with climate data for the years 2001–2010, aggregated from the data of the Finnish Meteorological Institute, and the precipitation recorded for each day at the study site. Model parameters related to the soil’s hydraulic properties and its physical and chemical characteristics (e.g., SCS curve number, soil erodibility factor, field capacity, and wilting point) were based on the work of Bärlund et al. (2009). The origin of the crop parameters used is presented by Tattari et al. (2001). There exist no previous modelling studies of phosphorus losses from cabbage fields, so the plant parameters for cabbage were collected from various sources, such as agricultural fact sheets (e.g., median yield and sowing interval) and
the GLEAMS manual (Knisel 1993) (e.g., C:N and N:P ratios). Some parameters had to be based on expert judgement.

The model was first calibrated for the reference period: 21 Feb. 2008 – 21 May 2008. With the new macropore parameters, ICECREAM simulated phosphorus losses (units: kg ha⁻¹) clearly better than without them (Figure 19). However, despite efforts to improve its performance through, for example, finetuning of the snow melt parameters, ICECREAM was not able to predict the extreme flow event in the middle of April 2008. The underestimation may be due to processes such as in-stream erosion or so-called diffuse erosion of clay particles that the model does not describe.

![Figure 19. Observed and modelled loss of total phosphorus (TP) before the gypsum amendment. Model simulations were performed with macropores open and closed.](image)

The effect of gypsum was added to the model as follows: 1) the equation that calculates the labile phosphorus pool was adjusted so that the concentration of water-extractable phosphorus in the soil fell by approximately half, 2) the SCS curve number was lowered by five units and the erodibility factor of the soil by 10%, and 3) the proportion of particulate phosphorus taken from the phosphorus pools to macropores was lowered by 20%. The modified model was used for simulating gypsum amendment under the Nummenpää conditions for the period 5 Nov. 2008 – 18 Jun. 2010 (‘Simulated gypsum amendment’; Figure 20). In addition to gypsum, the effect of another efficient erosion control measure was simulated with the model (including the macropores): direct sowing applied on spring cereal plots (85% of the fields, ‘Simulated direct sowing’; Figure 20).

ICECREAM simulated well the effect of gypsum in three out of the four monitoring periods (see ‘Simulated gypsum amendment’ and ‘Monitored load’ in Figure 20). During the dry autumn of 2009, simulation overestimated the phosphorus load. For that period, the model predicted most of the phosphorus coming through macropores, which suggests occasional overestimation of loading through macropores in the model.

If no gypsum was applied (‘Simulated autumn ploughing & shallow cultivation’ in Figure 20), the cumulative total phosphorus loss was 3.4 kg ha⁻¹ for the simulation period. With gypsum amended to 91% of the field area, as was the case in Nummenpää, the load was 45% lower (1.9 kg ha⁻¹). According to the model, gypsum reduced the total phosphorus load clearly more than did direct sowing, which reduced the load by 24%. The ICECREAM model simulated reduction for both dissolved and
particulate phosphorus loading when the cultivation method was changed to direct sowing, although it has been shown that dissolved reactive phosphorus loading may increase in a move from autumn ploughing to direct sowing (Muukkonen et al. 2007; Puustinen et al. 2010). Therefore, the ICECREAM simulation for direct sowing should only be considered tentative.

4.2 The potential of gypsum for reducing phosphorus discharge into the Archipelago Sea

The Archipelago Sea suffers from eutrophication, partially caused by Finnish agriculture. The phosphorus load to the Archipelago Sea from Finland was 610 t y⁻¹ in 2005–2009. According to a commitment made by former Finnish Prime Minister Matti Vanhanen in February 2010, the area shall achieve the good ecological status demanded by the Water Framework Directive already in 2020 rather than 2027 as forecast by the national implementation assessment. According to a Finnish Government Decision-in-Principle (Water Protection Policy Outlines for 2015), the load of phosphorus to the Archipelago Sea should be lowered by 120 t y⁻¹ (Anon. 2007).

The potential of gypsum amendment for reducing the phosphorus load of the Archipelago Sea was estimated by means of VIHMA assessment tool (Viljelyalueiden valumavesien hallintamalli, Puustinen et al. 2010). This tool was originally developed to estimate the nutrient losses from field areas and to compare the effect of different agri-environmental measures.

Proceeding from laboratory measurements performed by Yara and MTT, and from the results presented here, we assumed that gypsum reduced the load of particulate phosphorus by 60% and that of dissolved reactive phosphorus by 50%. As all experi-
ments in the TraP project were performed with clayey soils, the VIHMA model was applied only to this soil type.

The input data for the VIHMA model included the cultivation areas of different plants, soil types, field slopes, tillage practices, and soil test results for phosphorus. These were obtained from the WSFS-Vemala hydrological and water quality simulation and forecasting system (see Huttunen et al. 2008), from the Agency for Rural Affairs (Mavi), and by means of expert judgement (Väisänen and Puustinen 2010).

Gypsum treatment with traditional autumn ploughing was compared to winter stubble and implementation of buffer zones. These measures were applied to 5%, 25%, and 75% of the clayey soils under cereals and high-value crops (e.g., sugar beet) in the catchment. All three measures were always allocated to the steepest fields possible, because the effectiveness of winter stubble and buffer zones in reducing loading increases with field slope. In the absence of data, the performance of gypsum was assumed to be independent of the slope. Clayey soils accounted for 55% of the total field area in the catchment of the Archipelago Sea, and cereals and high-value crops accounted for 75% of the clayey soils.

According to the VIHMA exercise, gypsum was the most effective of the three measures (Figure 21). The larger the area treated, the better gypsum performed in comparison with the other two measures. If 5% (4,650 ha) of the clayey soil were treated with gypsum, the potential reduction would be 12 tons of phosphorus per year. With 25% (23,250 ha) of clayey soil treated, the reduction would be 36 tons. Finally, if the area treated were 75% (69,750 ha, approximately one third of the total field area), the phosphorus load could decrease by 62 tons.

If we assume that gypsum would be spread to all clayey fields under cereals and high-value crops (93,000 hectares of ploughed fields) in the catchment, the total load to the Archipelago Sea could be reduced by 11%. With the current tillage situation and the implementation of other agri-environmental measures in the Archipelago Sea catchment taken into account, the phosphorus reduction by gypsum would be 68 t y⁻¹ at best – that is, 57% of the reduction target value set by the Finnish Government.

![Figure 21. Reduction in the phosphorus load of the Archipelago Sea with gypsum application, fields being on winter stubble, or buffer zones being implemented. The percentages refer to the treated area of clayey soils under cereals and high-value crops.](image-url)
The effect of sulphate on benthic phosphorus release in lakes

Most aquatic studies related to sulphate have been focused on acidification, while the impact of sulphate itself has received less attention. Yet it is known that high concentrations of sulphate may adversely affect freshwater biota, such as mosses (Davies 2007). Furthermore, to prevent corrosion in the delivery system, the concentration of sulphate in drinking water should not exceed 250 mg l\(^{-1}\). Recent advances in sediment microbiology have, however, revealed the crucial role of sulphate in biogeochemical cycling of many elements, phosphorus in particular (Burgin et al. 2011).

Sulphate-mediated eutrophication refers to a situation wherein an accelerated flux of sulphate increases primary production in a body of water without an increase in external phosphorus load. In the Netherlands, sulphate has caused major deterioration of the fen systems and riverine floodplains (Loeb 2008), with the River Rhine as the source of sulphate-rich waters. Sulphate-mediated eutrophication is restricted to nonsulphidic fresh-water systems, as marine and brackish waters are inherently rich in sulphate. For example, the brackish surface water of the Gulf of Finland off the city of Helsinki contains about 500 mg l\(^{-1}\) of sulphate. In oceans, the concentration is as high as 2,700 mg l\(^{-1}\).

That sulphate accelerates eutrophication was already known to Hasler and Einsele (1948), but the mechanism was clarified much later (see Hasler and Einsele 1948; Ohle 1953; Caraco et al. 1989; Smolders and Roelofs 1993). Provided that there is labile organic C present, a prerequisite met in eutrophic waters, sulphate promotes microbial sulphate reduction in sediments. The end product of sulphate reduction, hydrogen sulphide, reacts with iron oxides to form solid iron sulphides, thereby allowing phosphorus to escape freely from sediments to the productive water layers (Roden and Edmonds 1997). Without sulphate, much of the released phosphorus would be recaptured by iron.

In the Nummenpää catchment, the mean concentration of sulphate in runoff before gypsum amendment was 19 mg l\(^{-1}\). After the amendment, the maximum values were about 300 mg l\(^{-1}\), with the mean concentration being 60 mg l\(^{-1}\) in autumn 2008 and 30 mg l\(^{-1}\) in spring 2010 (estimated from the conductivity values recorded by the on-line sensor; see above). For the sake of comparison, the present-day sulphate concentration in the Rhein is about 60 mg l\(^{-1}\) (Loeb 2008).

Sulphate in runoff and agriculturally loaded lakes

The sulphate concentration in runoff increases with the proportion of agricultural land in the catchment (Korkman 1973; Mattsson et al. 2007; Figure 22). In the small agricultural basins monitored by the Finnish Environment Institute, the mean sulphate concentration was 11 mg l\(^{-1}\) in the Savijoki (south-west Finland), 29 mg l\(^{-1}\) in
Hovi (southern Finland), 56 mg l\(^{-1}\) in Löytäneenoja (western Finland), and as high as 290 mg l\(^{-1}\) in Haapajyrä – an area of acid sulphate soil in western Finland (figures taken from the database of the Finnish Environment Institute).

In the TraP project, the relationship between the percentage of fields in the catchment and the sulphate concentration in the near-bottom water layer of Finnish lakes was examined with the aid of a database of the Finnish Environment Institute. Some high concentrations appeared to result from a mine, landfill, or wastewater treatment facility in the catchment. Such sites were omitted from further analysis. In the remaining sites, mean sulphate concentrations ranged from 0.71 to 22 mg l\(^{-1}\) (\(n = 99\)) and correlated with the percentage of fields in the catchment (Figure 23). However, no relationship was found between sulphate and phosphorus concentration.

Sulphate in agricultural runoff may originate from fertilisers, including 2–4% of the sulphur (Yli-Halla et al. 2011), and from the soil itself, especially in areas with Litorina clays. Also, a south-to-north gradient of decreasing concentration has been observed for sulphate (Mannio and Vuorenmaa 1995). Since the agricultural area and the acid rainfall in Finland have a distinctly decreasing south-to-north gradient as well, acid rain may have an effect on sulphate values. In conclusion, it appears that even without any gypsum amendment, agricultural land is not only a source of phosphorus and nitrogen losses but also a source of sulphate, which may further deteriorate the state of receiving waters.

![Figure 22. Sulphate concentration in runoff increases with the proportion of agricultural land in the catchment. Redrawn from the work of Mattsson et al. (2007). Catchments with acid sulphate soils are excluded.](image-url)
5.2 Experiments to examine the effect of sulphate in lakes

Analysing the impact of gypsum use on eutrophication requires considering the effect of sulphate loss on the biogeochemical cycling of iron and phosphorus in freshwater systems. Here, the effect was investigated by means of laboratory incubations of sediment cores sampled from a brackish estuary and from an agricultural lake. Additionally, the behaviour of clayey soil in a sulphate-rich environment was studied.
Estuarial sediment

The bay Ahvenkoskenlahti is a shallow (mean depth: 4.3 m) semi-enclosed eutrophic estuary located in the eastern part of the Gulf of Finland. The western branch of the Kymijoki (catchment: 37,200 km²) discharges into this estuary. Eight sediment cores (20–30 cm in length) were sampled in polycarbonate cylinders with a gravity corer in October 2007. Within a few days, the overlying water was replaced by a brackish phosphorus-free nutrient medium in the laboratory of the Finnish Environment Institute. Sulphate was added to four of the sediment cores as K₂SO₄ with a needle syringe to obtain an initial concentration of about 400–500 mg l⁻¹ (a level found in the Gulf of Finland), while the concentration in the remaining cores was an order of magnitude lower.

The cores were incubated in the dark at 10 °C for 60 days. On Day 10, labile organic carbon (lactate and acetate) was added to half of the cores, to boost anaerobic mineralisation processes. The cores were first kept in contact with air, then closed with rubber stoppers, and finally reopened. All of the time, magnetic stirrers gently mixed the overlying water (Figure 24 shows the equipment).

When the cores were sealed, sulphate started to decline in the overlying water (Figure 25, A), suggesting the onset of efficient sulphate reduction. More ferrous iron, Fe(II), the end product of iron reduction, was released from the sediment in the low sulphate treatment than in the high (Figure 25, B). The opposite was true for phosphorus release (Figure 25, C). At the end of the experiment, when oxygen was allowed to penetrate the cores through removal of the stoppers, dissolved phosphorus was scavenged in the low sulphate cores, while it remained in solution in the high sulphate treatment (Figure 25, C). The poor scavenging ability while sulphate was present may be explained by the inactivation of the iron – i.e., formation of hydrogen sulphides capable of precipitating iron out as solid iron sulphides unable to bind phosphorus. Figure 26 shows the cores after their incubation.
Figure 25. Concentrations of A) sulphate; B) ferrous iron, Fe(II); and C) dissolved phosphorus (DP) in overlying water of incubations with estuarial sediments in which oxygen delivery was manipulated. Black symbols denote sediment cores with sulphate, and white symbols denote cores where sulphate was removed. Both treatments had two replicates. Labile carbon was added in all of the cores on Day 10. Incubations were performed at 10 °C. Arrow denotes carbon addition.
Lake sediment

Similar incubation was performed for clayey lake sediments. Lake Pusulanjärvi is located in southern Finland. It is currently loaded by agriculture (fields constitute 23% of the catchment). In July 2008, eight sediment cores were taken from the lake and the overlying water was replaced with a phosphorus-free fresh-water nutrient medium (0.5 mg l⁻¹ of sulphate). As in the experiment with estuarial sediment, the cores were divided into four subsets amended with sulphate and/or carbon (two replicates in each). The sediments were incubated at 15 °C for 25 days, after which they were allowed to contact the air, resealed, and monitored for a further 21 days.

The experiment showed a strong concomitant release of phosphate (analysed as dissolved reactive phosphorus) and iron. Cores with sulphate showed lower phosphate concentrations until Day 25 (Figure 27). When samples came in contact with air, the phosphate concentration in samples with sulphate fell back below those of the samples without sulphate. After resealing, phosphate levels in samples with sulphate and carbon addition rose again. Approximately 90% of the sulphate was consumed in the samples with carbon, while only about 10% of the sulphate was consumed in the samples with no added carbon.

The incubation failed to show any effect of sulphate on phosphorus release, although sulphate reduction was evident from the strong smell of hydrogen sulphide and formation of black iron sulphides. Longer incubation might have revealed larger differences between the treatments. There were also methodological artefacts that lowered the reliability of the results. The carbon addition was greater than intended, because of a dilution error, and the sulphate addition possibly too low, as most of the sulphate was consumed during the incubation and the availability of sulphate may have restricted sulphate reduction.
A new incubation, with a lower carbon and higher sulphate concentrations, was performed for sediments taken on July 2009 from the lake. In view of other experiments being performed at the time, the temperature had to be kept at 10 °C, which, in combination with the lower carbon concentration, slowed the reactions markedly and forced the incubation to be extended to 290 days. Such a prolonged incubation led to previously unexpected problems being encountered with air penetrating the polycarbonate cylinders, which caused the formation of brown iron oxide layers in the sediments (Figure 29). To counteract concomitant iron oxygenation, organic carbon was repeatedly added to the sediments.

The first carbon addition, on Day 2, did not cause any increase in Fe(II) (Figure 28). After another addition, on Day 27, Fe(II) started to increase but later decreased again, apparently because of the unintended diffusion of oxygen in the system. The two following carbon additions triggered iron reduction again. On Day 217, carbon was added to all of the cores, including those previously serving as controls, which caused a rapid increase in Fe(II) in these cores. Surprisingly, the Fe(II) concentration was higher in the cores with sulphate. Phosphate behaved rather similarly to Fe(II). Although there were clear signs of sulphate reduction in the sulphate-amended cores, the behaviour of iron and phosphorus was not as clear as was expected. Unfortunately, the result of the second incubation cannot be considered reliable either, as the diffusion of air could not be prevented. Figure 29 shows the cores after the incubation.

Figure 27. Concentrations of phosphate in overlying water of incubations with lake sediment. Incubation was performed at 10 °C. Practically no P was released from the sediments without carbon addition.
Figure 28. Ferrous iron, Fe (II) and phosphate concentrations in the overlying water of the sediment cores of Lake Pusulanjärvi. Means of two replicates are used. Arrows denote carbon additions. On Day 217, carbon was added to all cores. Incubation was done at 15 °C.
Figure 29. Sediments from Pusulanjärvi after 290 days of incubation. Iron oxidation due to air penetration of the cores is clearly manifested in the brown colour of sediments. However, in sediments 4a and 4b with sulphate and organic carbon, black iron sulphides are also visible.
Soil incubation

Surface soil (sandy clay) taken from a cultivated field located in Tammela (Kaukjärvi, southern Finland) was shipped to the laboratory, courtesy of Risto Uusitalo (MTT). To find out the effect of sulphate on agricultural soil (sandy clay) transported by erosion into sulphate-rich water, an experiment with sulphate and organic carbon additions was performed in airtight 100 ml serum bottles at 20 °C. In addition, marine sediment was added to the bottles to trigger the sulphate reduction by marine micro-organisms. The experiment showed that addition of organic carbon and sulphate leads to iron and phosphorus behaviour similar to that observed in sediment experiments: the concentration of iron first increased in the water but started to decrease when the suspended soil turned pitch-black (Figure 30). However, phosphorus remained in the solution.

The experiments performed failed to yield conclusive results as to the effect of sulphate on phosphorus release from sediments, at least partly in consequence of methodological artefacts. Yet the experiments did indicate that additions of sulphate together with available carbon lead to increased sulphate reduction and formation of iron sulphides, which, according to the literature, should greatly increase phosphorus release.

If sulphate accelerates benthic phosphorus fluxes in lakes, the benefit of gypsum amendment in catchments with sensitive lakes depends on the trade-off between 1) reduced phosphorus fluxes and 2) the reduced phosphorus retention ability of the bottom sediments. It is not yet possible to determine the safe level of sulphate in freshwaters. Until more accurate information on the issue is obtained, it is not recommended to use gypsum extensively in catchments with sulphate-poor lakes.
6 Conclusions

Agricultural water protection measures encompass a great variety of actions, ranging from soil protection and balanced fertilisation to implementation of buffer zones and construction of wetlands. On top of these measures, novel techniques provide an approach with potential to speed up nutrient reduction. The results presented here show that gypsum amendment may effectively reduce phosphorus losses from clayey soils.

Unlike some other field-scale measures, gypsum appeared to cut down the losses of both particulate and dissolved phosphorus in the Nummenpää catchment. Gypsum increased the ionic strength of the soil solution, which apparently decreased the detachment of these forms of phosphorus. The phosphorus fluxes from the catchment remained lower than before the gypsum amendment for at least two years. As more than half of the gypsum applied remained in the soil after these two years, the beneficial effect probably will continue for some time. For determination of how long, the catchment should be monitored for as long as the ionic strength of the soil solution at least reaches the pre-gypsum level (see Figure 31).

Figure 31. It is proposed that the Nummenpää catchment be monitored until the gypsum effect vanishes. The numerical values on the Y-axis are indicative only.
The phosphorus fluxes in the catchment were estimated on the basis of a combination of automatic and manual water sampling and analysis, an approach that proved to provide useful information, especially when complemented with earlier data from the site and when the results were contrasted against those obtained from a nearby reference catchment.

The application of the ICECREAM model supplied further evidence and helped to systematise the effect of various contributing factors. Yet, although the relatively simple modifications to the ICECREAM model described the overall impact reasonably well, gypsum-induced processes such as flocculation and aggregation of the smallest soil constituents should be studied in more detail. Without such data, incorporation of these key processes into any model is impossible, which prevents scaling the gypsum effect up to different environmental conditions with the aid of modelling.

Sulphate losses are an inherent side effect of gypsum amendment. Since sulphate may increase the release of phosphorus from freshwater sediments, massive-scale use of gypsum is not recommended in catchments with sulphate-poor lakes. Under such conditions, the balance between decreased phosphorus losses and increased sulphate losses remains to be resolved. From an environmental standpoint, no other side effects of gypsum use were found in this study.

According to the field plot studies performed by MTT Agrifood Research Finland, gypsum does not negatively affect crop yields. It will, however, hamper selenium uptake in the first two years after application, which has to be taken into account when one is planning gypsum use. To what extent gypsum from the practically endless reserves in Siilinjärvi will be spread on Finnish fields depends not only on its agricultural and environmental performance, which both should be further elucidated, but also on whether this measure will be included in the forthcoming Agri-Environmental Programme.
Appendix

**Phosphorus:** The in-house methods were based partially on the withdrawn standards SFS 3025 and SFS 3026. Orthophosphate ions reacted in an acidic solution containing molybdate and antimony ions to form a phosphomolybdate complex. Reduction of the complex with ascorbic acid formed a coloured molybdenum blue complex, the absorption of which was measured at 880 nm by means of a Shimadzu UV-1601 spectrophotometer. For the analysis of total phosphorus, polyphosphates and organophosphorus compounds were converted to orthophosphate by acid peroxodisulphate digestion at 120 °C and under pressure. Total dissolved phosphorus and dissolved reactive phosphorus were analysed for a filtered sample (Whatman nuclepore polycarbonate, pore size 0.4 µm, diameter 47 mm); in the analysis of total dissolved phosphorus, the sample was digested before staining, whereas dissolved reactive phosphorus was determined without digestion. Particulate phosphorus was obtained as total phosphorus less total dissolved phosphorus, except when the text indicates otherwise.

**Turbidity:** In the laboratory, turbidity was measured nephelometrically (from scattering) with a Hach 2100AN IS turbidometer. If turbidity exceeded 1,000 FNU (Formazine Nephelometric Units), the sample was diluted with deionised water. The YSI sensor also determined turbidity from scattering, but in Nephelometric Turbidity Units (NTU), by emitting near-infrared light into the water and measuring the light that bounces back at a 90° angle from the suspended particles. S::CAN determined turbidity (and nitrate and carbon) via inverse modelling of the absorption spectrum of visible light. The raw results of the S::CAN sensor were calibrated against laboratory analyses.

**Total suspended solids** were analysed gravimetrically; a well-mixed sample was filtered through a weighted membrane (Whatman nuclepore polycarbonate, pore size 0.4 µm, diameter 47 mm). The membrane with the residue retained on it was dried to a constant weight at 105 ± 5 °C and weighed.

**Nitrogen:** Total nitrogen and the sum of nitrite and nitrate were measured through an in-house method partly based on the standards SFS-EN ISO 11905-1 and SFS-EN ISO 13395 and by means of an AA3 continuous flow analyser (CFA) by Bran+Luebbe. Nitrate was reduced to nitrite with a copper-cadmium reduction column. Nitrite was then determined by diazotizing with sulphanilamide and coupling with N-(1-naphthyl)-ethylenediamine to form a reddish-purple azo dye measured at 550 nm. Ammonium was analysed with the indophenol blue method. In the analysis of total nitrogen, the ammonia, nitrite, and organic nitrogen-containing compounds were oxidised to nitrate by means of peroxodisulphate in a buffered alkaline system. The off-line oxidation took place in a closed vessel at 120 °C and under pressure.

**Ions:** Figures for cations (sodium, potassium, magnesium, and calcium) were determined with a Varian Vista PRO Radial inductively coupled plasma-optical emission spectrometry (ICP-OES) after centrifuging to remove most of the particles. The method was partly based on the standard ISO 11885:2007 (modified). Anions (chloride, fluoride, and sulphate) were determined with ion chromatography (IC), which should capture only dissolved ions. A Dionex 500 ion chromatograph with CD20 conductivity detector and a selfgenerating suppressor of model ASRS-Ultra II were
used with an AG12A guard column and AS12A analytical column. The method was based on the standard method describe in ISO 10304-1.

**Reliability of on-line sensors:** The upper detection limit of the YSI sensors is about 1,000 NTU, varying roughly from 850 to 1,300 NTU. The majority of turbidity recordings were well below this level, yet, occasionally turbidity in the lower site exceeded the upper detection limit, as revealed by several successive recordings with the same value. In spring 2008, such observations were found 11 times out of the full set of 2,151 recordings. All of these instances occurred with a rising hydrograph and therefore may reflect high incidence of erosion. In the autumn of 2009, only one out of 3,233 turbidity recordings exceeded the upper detection limit. The observation took place under relatively stable flow conditions and might have been caused by, for example, embankment collapse rather than erosion of surface soil. In spring 2009, four of the 2,284 observations exceeded the limit with a rising hydrograph. No exceeding was found in the 2,610 observations from autumn 2009, but seven situations of this type occurred in spring 2010. In all of the calculations, the original recordings were used.
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The ability of novel measures to reduce the loss of phosphorus from fields to surface waters is seeing increasing testing. Gypsum, by elevating the ionic strength in soil solution, has been shown to reduce phosphorus losses from Finnish soils under laboratory conditions. This report presents the results of a catchment-scale gypsum experiment. In a 2.45 km² catchment in southern Finland, 91% of the field area (93 out of 101 hectares, mostly on clayey soils) was amended with gypsum after the harvest in 2008. Runoff volume and quality (e.g., turbidity, nutrients, cations, and anions) were monitored for six high-flow periods in February 2008 to November 2010 – i.e., before, during, and after the amendment – by means of on-line sensors and manual sampling. Additional data were collected by a local water protection association at the site and in a nearby ‘reference’ catchment where gypsum was not used. Moreover, the effect of gypsum was simulated with the ICECREAM model and scaled for the clay fields in the catchment of the Archipelago Sea via the assessment tool VIHMA. Potential changes in soil chemistry were monitored with soil analyses. Finally, the impact on lakes caused by sulphate lost from gypsum was studied by means of laboratory soil and sediment incubations.

The turbidity recorded by the on-line sensors from the runoff correlated with the concentration of particulate phosphorus analysed in the laboratory, which enabled the evaluation of changes in particulate phosphorus loss from the on-line data. Using a covariance model with gypsum application as a qualitative and runoff volume as a quantitative variable, we approximated gypsum as having reduced the loss of particulate phosphorus by 57%. The loss of dissolved reactive phosphorus decreased by approximately one third. The total phosphorus reduction was about 54%. According to the ICECREAM model, the reduction in total phosphorus was 45%. No corresponding changes were found in the reference catchment. Gypsum did not affect soil test values for phosphorus, potassium, magnesium, or calcium but did increase the ionic strength and sulphur in soil. The proportion of gypsum lost in runoff could not be estimated precisely, because there were insufficient background data on sulphate losses. At maximum, 45% of the gypsum was lost, as calculated from conductivity values recorded by the sensors. Since sulphate may aggravate eutrophication in sulphate-poor lakes, the sulphate lost from gypsum may restrict extensive gypsum application to only those catchments discharging directly into the Baltic Sea. Fortunately, most clayey fields in Finland with a risk of erosion are located in the coastal catchments without a great presence of lakes. As an example, the application of gypsum on all clayey fields used for cereals or high-value crops in the catchment of the Archipelago Sea could reduce the total phosphorus load by 68 t y⁻¹, as calculated with the assessment tool VIHMA. That would be more than half of the national target (120 t y⁻¹) for this sea area. The duration of the gypsum effect and impact of gypsum-derived sulphate on the ecology of rivers and lakes has yet to be determined.
The effect of gypsum on phosphorus losses at the catchment scale
(Kipsin vaikutus valuma-alueen fosforikulkeumiin)

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The effect of gypsum on phosphorus losses at the catchment scale
(Gipsens inverkan på utsköljningen av fosfor från avrinningsområde)

Sammandrag

Nyckelord
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This report summarizes the results of a three-year study on the effect of gypsum amendment on the losses of phosphorus from cultivated fields. A substantial reduction in runoff turbidity and in particulate and dissolved phosphorus were found at a catchment-scale. The finding was corroborated by a comparison to a reference catchment with no gypsum amendment, and by mathematical modelling. The potential side effects of the method are also discussed. Gypsum treatment is best suited for coastal catchments with soils sensitive to erosion or showing a high phosphorus level.