



This is an author produced version of a paper published in
Acta Agriculturae Scandinavica, Section B - Soil and Plant Science.
This paper has been peer-reviewed but may not include the final publisher
proof-corrections or pagination.

Citation for the published paper:

Ulén, Barbro & Etana Ararso. (2014) Phosphorus leaching from clay soils
can be counteracted by structure liming. *Acta Agriculturae Scandinavica,
Section B - Soil and Plant Science*. Volume: 64, Number: 5, pp 425-433.
<http://dx.doi.org/10.1080/09064710.2014.920043>.

Access to the published version may require journal subscription.

Published with permission from: Taylor & Francis.

Standard set statement from the publisher:

*"This is an Accepted Manuscript of an article published by Taylor & Francis Group in
Acta Agriculturae Scandinavica, Section B - Soil and Plant Science on 12/06/2014,
available online: <http://www.tandfonline.com/doi/abs/10.1080/09064710.2014.920043>.*

Epsilon Open Archive <http://epsilon.slu.se>

Phosphorus leaching from clay soils can be counteracted by structure liming

Barbro Ulén^a and Ararso Etana^a

Corresponding author:

^aSwedish University of Agricultural Sciences, Department of Soil and Environment, PO Box 7014, SE-750 07 Uppsala, Sweden. barbro.ulen@slu.se Tel +4618671251, Fax +4618673156

Other addresses:

ararso.etana@slu.se

Abstract Two field experiments with drained plots on clay soils (60 and 25 % clay) demonstrated a significant reduction in leaching of total phosphorus after application of structure lime. Aggregate stability, was significantly improved. Phosphorus leaching in particulate form was significantly reduced following structure liming at the site with a very high clay content. Sites representing low (50 mg kg^{-1}) and high (140 mg kg^{-1}) levels of phosphorus extractable with acid ammonium lactate in topsoil displayed differing effects on leaching of dissolved reactive phosphorus. This form of phosphorus was only significantly reduced compared with the control at one site with high topsoil P status and relatively high (17-18%) degree of phosphorus saturation in the subsoil. Laboratory experiments with simulated rain events applied to topsoil lysimeters from the same site also demonstrated a significant reduction in leaching of dissolved reactive phosphorus. These findings indicate that structure liming is an appropriate leaching mitigation measure on soils with both a high clay content and high soil phosphorus status.

1

2 **Key words:** *Aggregate stability, drainage water, mitigation method, nutrients, turbidity*

3

4 **Introduction**

5 Phosphorus (P) and nitrogen (N) are both nutrients which have the potential to seriously
6 increase eutrophication of surface waters if available in high concentrations in the water and
7 with proportionally high contribution of P (low N:P ratio) (Smith & Schindler, 2009). In
8 Swedish clay soil areas, P leaching either in particulate (PP) or dissolved reactive (DRP) form
9 is a major environmental problem for water quality (Ulén et al., 2007). Structure liming is
10 officially recommended as a measure to improve clay soil structure, in order to reduce P
11 leaching (SBA, 2013). This amendment is applied either in the form of quicklime (calcium
12 oxide, CaO), or hydrated (slaked) lime (Ca(OH)_2), the latter being more common. When these
13 forms of lime are mixed with a clay soil, several reactions take place at soil aggregate level
14 and an immediate improvement in soil stability, porosity and aggregate strength has been
15 reported (Choquette et al., 1987). The reactions include cation exchange, flocculation and
16 agglomeration, together with slower cementing and the virtually irreversible pozzolanic
17 reaction (Kavak & Baykal, 2012). In addition, complex binding of amorphous P occurs (Zhu
18 & Alva, 1994), as well as precipitation to β -tricalcium phosphate at higher pH (Gray &
19 Schwab, 1993). Liming may stabilise clay soils by moderating swelling and shrinking

20 processes. These are known to form cracks, which apart from enhancing fast macropore flow
21 redistribute larger macroaggregates to smaller sizes (Grant & Dexter, 1990). Limited swelling
22 is partly due to the suppressive effect of Ca^{2+} ions in the diffuse double layer of clay particles
23 and the limited shrinkage is partly due to more uniform spatial arrangement of particles or
24 structural entities in limed soil (Ledin, 1981). The neutral salt gypsum (CaSO_4) has a
25 corresponding stabilising effect and aggregation may follow from the compressed diffuse
26 double layer and increased rate of P adsorption (e.g. Uusitalo et al., 2012). This compression
27 is a result of increased electrolytic concentrations, while the corresponding process after
28 adding lime mainly is a result of dehydration and increased pH. Carefully mixing $\text{Ca}(\text{OH})_2$
29 into soils with a high clay content can result in an effective pozzolanic (cementing) reaction,
30 forming aluminium-silicate hydroxides, silicate hydroxides and/or aluminate hydroxides
31 (Almukhtar et al., 2012). These reactions take place since clay soils have a high sum of silicon
32 and aluminium oxides (He et al., 1995). The cementing effect has the potential to increase the
33 resistance to dissolution of soil aggregates in water and thus reduce P leaching. The resistance
34 is commonly analysed by the aggregate stability test and a gentle method demonstrating
35 disruptive forces close to the field phenomenon is most appropriate (Oades & Waters, 1991).
36 For soils with a high concentration of available P any reduced P leaching may also be the
37 result of decreased P concentration in water caused by the above-mentioned P complex
38 formation and increased adsorption of orthophosphates and phosphate ions. These P forms are
39 included in the analytical method dissolved reactive P (DRP) (e.g. Haygarth & Sharpley,
40 2000).

41 Only two field experiments on the effect of structure liming on P leaching from Swedish
42 clay soils have been carried out to date. The effects of drain backfilling with burnt shell-ash
43 from Estonia when draining clay soils is currently being studied in Lithuania (Šaulys &
44 Bastienė, 2007) and is to our knowledge the only ongoing long-term experiment monitoring
45 drainage water quality. The aim of the present paper was to investigate any mitigating effect
46 of structure liming on phosphorus losses from two agricultural clay soils with similar
47 mineralogy but different clay and soil P status. Any effect on nitrogen leaching was
48 simultaneously monitored. The following hypotheses were tested: After structure liming, (i)
49 leaching losses of particulate phosphorus (PP) are significantly reduced; (ii) leaching losses of
50 dissolved reactive P (DRP) are significantly reduced; and (iii) dissolution of soil aggregates
51 by water disruption is significantly reduced.

53 **Materials and methods**

54 *Field experiments with drained plots*

55 The two field experiments with drained plots (Figure 1) were carried out in eastern Sweden,
56 20-30 km southwest of Stockholm city. Both sites have clay soil (Table 2) dominated by the
57 2:1 mineral illite. The Bornsjön experimental field, with a soil with high clay content (57-61%
58 clay), is situated 20 km from the coast of the Baltic Sea, while the Wiad site is situated near
59 the coast of the Baltic Sea and with a topsoil clay content which is significantly lower (22-
60 29%). The experimental setup comprised 28 drained plots at Bornsjön and eight drained plots
61 at Wiad. Number of replicates was four for each treatment, including structure liming, at both
62 sites. The acid ammonium lactate-extractable P (P-AL) content in topsoil, determined
63 according to Egnér et al. (1960), is 30-43 mg P-AL kg soil⁻¹ at Bornsjön and more than three-
64 fold higher (110-170 mg P-AL kg soil⁻¹) at Wiad. Due to this and to a high content of
65 aluminium (Al) in Bornsjön soil, the degree of P saturation (DPS-AL), determined according
66 to Ulén (2006), is very low at Bornsjön but quite high at Wiad (Table 2). In both field
67 experiments, the soil was amended with structure lime, at Bornsjön in the form of burnt lime
68 (CaO) and at Wiad in the form of a commercially available product with active lime in slaked
69 form (Ca(OH)₂) (Table 1). Total amount applied, recalculated to active CaO, was 5 t ha⁻¹ at
70 Bornsjön and 2 t ha⁻¹ at Wiad. At both sites, application took place under dry conditions in
71 September (2007 at Bornsjön and 2011 at Wiad) and the structure lime was immediately and
72 carefully cultivated into the topsoil in several directions with a good cultivator machine. The
73 crop sequence after structure liming was spring barley, spring barley, oats, pea and spring
74 barley at Bornsjön and spring barley and oats 2011/2013 after liming at Wiad. In the
75 monitoring period 2006-2009 before liming at Wiad 2006-2007, grass ley was grown and
76 ploughed under, followed by winter wheat.

77 At Bornsjön, water was sampled flow-proportionally in six agrohydrological years (1
78 July-30 June). A composite sample from each plot was stored for at most one week in an
79 underground chamber (10-15°C) before being sent to the laboratory for analysis. At Wiad,
80 water flow was measured with tilting vessels and water samples were manually collected
81 weekly when drainage occurred in two agrohydrological years. The samples were sent
82 immediately to the Water Laboratory at the Department of Soil and Environment, Swedish
83 University of Agricultural Sciences.

84 *Experiments on leaching from topsoil (0-20 cm)*

85 Twelve topsoil lysimeters, 20 cm in diameter and 20 cm high (plastic tubes with sharp iron
86 rims) were extracted from Bornsjön unfertilised fallow, between the experimental plots
87 (Figure 1), using a tractor-powered hydraulic double-action piston in October 2010. The
88 monoliths were extracted under moist soil conditions, in order for the samples to be as
89 undisturbed as possible. The soil monoliths were then trimmed by hand and stored under cold
90 conditions (+4°C) until the start of the rain simulation experiments, which was within 3
91 months of sampling. The base of the monoliths was prepared and a special base cap fitted to
92 each lysimeter. In the laboratory, eight lysimeters were amended with the same amount of
93 structure lime as in the field experiment, with a theoretical dose of 5 t ha⁻¹ as CaO, but using
94 both pure burnt lime (4 lysimeters) and pure slaked lime (4 lysimeters) (Table 3). The lime
95 was mixed into the soil, which was then reconsolidated for six months after the disturbance
96 through repeated gentle wetting of the soil, followed by drying. Artificial rain events were
97 applied to Bornsjön soil using a laboratory rain chamber, with a rain intensity of 8-10 mm h⁻¹
98 and a distance to the soil surface of 1.5 m (Svanbäck et al., 2013) (Table 3). Three artificial
99 rain events were applied for 3 hours per event, with 1-2 days drying between events. Since the
100 soil had frequent macropores, no problems with ponding occurred and all water discharged
101 rapidly through the soil. A total leached volume of 50-64 mm was discharged, equal to the
102 theoretical pore volume of the Bornsjön soil. Corresponding experiments at this site on
103 application of pesticides and bromide have demonstrated breakthrough curves equal to less
104 than 25% of the theoretical pore volume, thus indicating preferential flow (Larsbo et al.,
105 2013).

106 An undisturbed soil monolith of similar size was sampled from each of the eight
107 experimental plots at Wiad (Figure 1) (4 structure-limed and 4 without lime) by pressing
108 plastic tubes with sharp iron rims into the topsoil. Sampling took place on 17 October 2013,
109 slightly more than two years after structure liming, which at that site had been followed by
110 conventional tillage and cultivation of cereal crops. In the laboratory the soil monoliths were
111 then similarly trimmed by hand, the base was prepared and a special base cap was fitted to
112 each lysimeter. Simulated rainfall was applied using equipment described by Liu et al. (2012),
113 applying a rain intensity of 32 mm hour⁻¹. After 2 or 2.5 hours leaching, a water volume
114 corresponding to 77-90 mm discharge was collected. The procedure was repeated 3 times,
115 with one day in between, with the soil under lid. Total drainage amount was nearly twice the
116 theoretical pore volume of the Wiad soil. There were generally no problems with water
117 ponding for the lysimeters from this site, with the water effectively discharging through the
118 soil columns.

119

120 *Soil aggregate tests*

121 At the Bornsjön site, aggregates (mean 8-11 mm diameter) corresponding to in total 120 g
122 field-moist soil per plot were collected on 27 August 2010, three years after structure liming.
123 This large aggregates were chosen since they are more friable, weaker and have lower tensile
124 strength than smaller aggregates (Utomo & Dexter, 1981). Consequently they can act as more
125 sensitive indicators of aggregate strength than smaller aggregates. Each of 16 replicate
126 samples from each treatment (4 per plot) was placed in a plastic cylinder (100 mm high, 102
127 mm in diameter and with 0.6 mm mesh at the bottom) and manually immersed three times in
128 a beaker with 300 mL synthetic rainwater. The solute was then transferred to a 250-mL plastic
129 bottle, which was shaken with a slow oscillating movement (90 revolutions min^{-1}) for 10
130 minutes. Content of soil particles in solution was then determined by turbidimeter (2100N
131 Hach-Lange company, Düsseldorf, Germany) (Cryz et al., 2002). Large particles and fine
132 aggregates larger than the clay size ($<0.2 \mu\text{m}$) were then allowed to settle for 4.5 hours
133 (Sheldrick & Wang, 1933) and the content of dispersed clay still in solution was determined.
134 The supernatant water was analysed for particulate P (PP) and dissolved reactive P (DRP).

135 Two years after structure liming (October 2013), topsoil samples (0-20 cm) from each of
136 the eight plots (both limed and controls) at Wiad were collected and gently transported to the
137 laboratory. Soil aggregates (8-11 mm, in total 120 g field-moist soil per plot) and dispersed
138 clay content were measured after corresponding pre-treatment as for Bornsjön.

139

140 *Water analysis*

141 For all samples of drain water and leachate, pH was measured on the following day, DRP
142 within two days and total P (TP) and total nitrogen (TN) within 4 days, after storage at $+4^{\circ}\text{C}$.
143 TotP was analysed as soluble molybdate-reactive P after acid oxidation with $\text{K}_2\text{S}_2\text{O}_8$ (ECS,
144 1996), while DRP was analysed after pre-filtration using filters with pore diameter $0.2 \mu\text{m}$
145 (Schleicher & Schüll GmbH, Dassel, Germany) with the same colorimetric determination
146 (ECS, 1996). Particulate P was estimated as the difference between TP before and after
147 filtration of the water with the same filters. TN was analysed with a carbon nitrogen (CN)
148 analyser (Shimadzu, GmbH, Duisburg, Germany).

149

150 *Statistics*

151 Coefficient of variance (CV) was used to reflect differences in discharge and leaching
152 between different plots. To analyse differences in leaching between the different treatments in

153 the field experiments, a general mixed model (SAS software Version 9.2) was used. To
154 account for the time series structure of the data, correlations between measurements over time
155 were modelled with a spatial power covariance structure (Littell et al., 2006). Factors for the
156 spatial variations were used as covariates at Bornsjön, where they showed a distinct spatial
157 pattern (Svanbäck et al., 2014). A significance level of $\alpha=0.05$ was applied, including the p
158 value associated with the F statistics of a given effect ($p_r>F$). Comparisons between
159 lysimeters from the same site, which were all treated in the same simulated rain events, were
160 estimated using basic two-sample test statistics as used in the aggregate studies.

161

162 **Results**

163 *Field experiments*

164 The narrow drain spacing (8 m) at Bornsjön resulted in high discharge (mean 500 mm yr⁻¹).
165 At Wiad, discharge of water was low (mean 140 mm yr⁻¹), but the variation in discharge
166 between different plots was somewhat larger (CV = 30%) than at Bornsjön (CV = 25%).
167 Apart from less intensive tile drainage, the main reason for the low discharge at Wiad is
168 probably the topography and location of the plots, in a gentle slope close to the bank of a
169 stream recipient. Water may leach to the groundwater and thus bypass the tile drains before
170 reaching the stream. Consequently, TP leaching from the Bornsjön control plots (mean 0.97
171 kg ha⁻¹ yr⁻¹) was significantly higher than at Wiad (0.30 kg ha⁻¹ yr⁻¹).

172 The TP leaching losses at Bornsjön (mean 1.0 kg ha⁻¹ yr⁻¹) were significantly ($p_r>F<0.002$)
173 lower from structure-limed plots than from the non-limed control in the six monitoring years.
174 This was also the case for PP leaching, which was 83% of TP leaching. The PP leaching
175 (mean 0.8 kg PP ha⁻¹ yr⁻¹), which demonstrated similar large variance (CV = 75), was
176 significantly reduced following structure liming at this site ($p_r>F<0.002$). In contrast, PP
177 leaching losses were not significantly lower after liming at Wiad, when statistically evaluated
178 with the model and taking the spatial variation in the three previous monitoring years into
179 account. In that pre-period of three agrohydrological years (2006/2009), P leaching was
180 similar to that in the control plots in 2011-2013. Leaching of DRP was on average 0.15 kg ha⁻¹
181 yr⁻¹ and comprised a much lower proportion of TP leaching in the drain water at Bornsjön
182 than at Wiad (45%). In addition, the CV value for DRP leaching was low (20%) between
183 plots at Bornsjön (Svanbäck et al., 2014) and did not change after structure liming. Leaching
184 of DRP was 55% of TP leaching, with a mean value of 0.11 kg ha⁻¹ yr⁻¹ (CV = 70%), at Wiad

185 and was significantly ($p_r > F < 0.002$) lower from plots with structure liming than from the
186 control plots in the two years monitored (Table 4).

187 The results were thus contrasting for P forms at the two sites. Only P leaching in PP form
188 at Bornsjön and in DRP form at Wiad were significantly reduced following structure liming
189 (Table IV). Simultaneously, there was a significantly lower P-AL content in the topsoil at
190 Bornsjön (38-44 mg kg⁻¹ soil) compared with Wiad (120-140 mg kg⁻¹ soil). At Bornsjön, the
191 pH in the topsoil showed no significant differences between structure-limed plots before (6.3
192 ± 0.1) and two or four years after liming (6.5 ± 0.3 both occasions). Moreover, there was no
193 significant difference in topsoil pH measured before (7.2 ± 0.5) and after (7.3 ± 0.5) liming at
194 Wiad at six months or two years after liming. The pH in drain water was similarly stable and
195 with no significant differences between structure-limed and unlimed plots (Table IV).

196 Nitrogen leaching was nearly 30 kg ha⁻¹ yr⁻¹ at Bornsjön, but quite low from the fallow
197 plots (6 kg TN ha⁻¹ yr⁻¹). Nitrogen leaching was moderate (12-14 kg TN ha⁻¹ yr⁻¹) at Wiad
198 after cereals in the experimental period and lower in the pre-period, when ley was grown
199 (Table IV). The leaching observed after cereals was of the same magnitude as is commonly
200 found on the Swedish east coast (e.g. Kyllmar et al., 2006). The TN/TP ratio in drain water
201 was mostly high, except for the fallow at Bornsjön (9:1) (Table 4).

202

203 *Simulated rainfall events in the laboratory*

204 For Bornsjön topsoil to which structure lime had been added in the laboratory, the differences
205 in topsoil P-AL and DPS-AL between structure-limed and unlimed plots were non-significant
206 after treatments. However, following application of simulated rain, there was a significant
207 reduction in PP leaching (Table 5), as also observed in the field experiments. The DRP
208 concentration was only estimated by difference between TP and PP, since the analysis was
209 disturbed by high pH. Moreover, only small amounts of DRP were measured before liming
210 and the amounts were only marginally lower (0.01-0.02 kg ha⁻¹) and not significantly different
211 from those in lysimeters amended with structure lime.

212 There was no significant difference in topsoil P-AL and topsoil DPS-AL between
213 structure-limed and unlimed plots at Wiad (Table V). However, application of simulated
214 rainfall to these lysimeters resulted in a significant reduction in leaching of TP. Similarly to
215 the field studies (Table 4), for the lysimeters from Wiad the P reduction was statistically
216 significant for DRP, but not for PP

217

218 *Aggregate stability tests*

219 The large-sized soil aggregates (8-11 mm) from Bornsjön showed more resistance to
220 dissolution in water after structure liming (Figure 1a), irrespective of whether the soil had
221 been conventionally ploughed (control) or only shallow tilled (an additional treatment given
222 in Figure 1a). The large-sized soil aggregates from the field plots at Wiad amended with
223 structure lime similarly displayed significantly greater resistance to dissolution in water than
224 aggregates from plots with no such amendment. This was apparent both before and after the
225 clay particles were allowed to settle (Figure 1b). After settling, the supernatant with dispersed
226 clay colloids from Wiad demonstrated significantly lower P concentrations in both PP and
227 DRP form after structure liming and also significantly lower turbidity values *than the*
228 *supernatant from Bornsjön* (Table 4).

229

230 **Discussion**

231 The two field experiments represented sites with high (Bornsjön) and rather moderate (Wiad)
232 TP losses compared with the Swedish average of 0.4 kg TP (and 0.2 kg DRP ha⁻¹ yr⁻¹) (Ulén
233 et al., 2007). At Bornsjön, where the soil has a high clay content, most losses took place in PP
234 form while DRP losses were moderate. This is similar to findings for drained Finnish soils
235 with a high clay content (Uusitalo et al., 2001). At Wiad the moderate leaching losses of PP
236 and DRP via tile drains is a consequence of the low water discharge, while flow-weighted
237 mean concentration was quite high (0.2 mg TP L⁻¹). The two sites compared also represented
238 soils with very high (Bornsjön) and moderate (Wiad) topsoil clay content, but only the
239 Bornsjön soil demonstrated significant effects of structure liming in reducing PP leaching. In
240 addition, the two sites represented soil with a low (Bornsjön) and a high (Wiad) level of AL-
241 extractable P and displayed contrasting effects on DRP leaching after structure liming.
242 Leaching of DRP was only significantly lower *for structure-limed soil* compared with the
243 control for the Wiad site, with its high topsoil P status and relatively high (17-18%) DPS-AL
244 value in the entire subsoil down to the tile drains. One explanation for this could be formation
245 of Ca-P complexes or Ca-precipitates at Wiad owing to a presumed high concentration of
246 DRP in the soil water solution and the high pH after liming. Such types of reactions have been
247 indicated to take place in a clay soil with a history of pig manure addition (Ulén & Snäll,
248 2007).

249 There are concerns that a high pH can suppress P availability and reduce plant uptake of P,
250 especially in coarse-textured soils (e.g. Murphy & Stevens, 2010). However, pH in the field
251 experiments with structure liming seemed to have equilibrated with the clay in the soil, since

252 there were no significant differences in soil pH between structure-limed and unlimed plots at
253 Bornsjön 2 years after liming and at Wiad 0.5 years after liming. Furthermore, quite similar
254 pH was observed in the drainage water from the limed plots compared with the unlimed plots
255 at both sites (Table 4), as well as in leachate water from Wiad (Table 5). A general increase in
256 yield on limed plots has been reported at Bornsjön, especially in the first year after liming
257 (Svanbäck et al., 2014). This was probably an indirect effect, through improved soil structure,
258 but the crop (barley) still had a high P content (0.3% of dry weight), which was similar to the
259 P content in barley crops from non-limed soils. The yields of spring barley and oats at Wiad
260 showed no significant differences in either year after liming compared with the control.
261 Recent tests on seeding of winter wheat three days after structural liming showed good results
262 in the field near the Bornsjön experimental area (data not shown).

263 Gypsum application causes compression of the electronic double layer and clay colloids
264 flocculate as lime, but as a result of the increased Ca^{2+} concentration and electric conductivity
265 (Haynes & Naidau, 1998), and not the increased pH. Any reduction in P by precipitation
266 should be minor using this neutral salt. However the cementing effect may be limited in time
267 and significant effects on P leaching have been reported to end after 2.5 years (Uusitalo et al.,
268 2012). Relatively short-term effects for this and other amendments such as water treatment
269 residuals and coal combustion slag have also been demonstrated in laboratory experiments
270 with simulated rain (O'Connor et al., 2005).

271 Results obtained in lysimeter studies with concentrated simulated rainfall events in the
272 laboratory should be viewed with caution. They may be regarded more as prolonged water
273 extraction, which dissolves high amounts of DRP in the water-saturated soil. In all lysimeter
274 experiments, water flow is also forced into a straighter vertical direction than would occur in
275 the field and horizontal transport of PP, which typically occurs in field conditions, is
276 prevented. Topsoil studies may also give less realistic results due to the critical role of the
277 subsoil (e.g. Sinaj et al., 2002). At Wiad, leaching of DRP may also occur from the subsoil
278 with its relatively high 18% DPS-AL value (Table 2). However, the DRP/TP ratio in leachate
279 from the Wiad lysimeter was high (75-80%) and the reduction in DRP was significant, as
280 found with drainage water from the experimental plots.

281 After application of the lime in the present field experiments, there was visible mixing with
282 the soil, most probably facilitated by subsequent tillage, harrowing and growing crops in the
283 present field experiments. This also illustrates the importance of soil microorganisms and
284 plant roots in the formation and stabilisation of soil aggregates (Oades, 1993). The settled clay
285 particles from Wiad soils might contain more P than the colloids in suspension, since the P

286 concentration was lowered even more than the turbidity (Table 6). The settled material might
287 include biofilms, root exudates, organic macromolecules and other traces of biological glue in
288 a corresponding way to water sediment deposits (e.g. Droppo, 2001; Williams et al., 2008).
289 There is an urgent need for comparable field and laboratory investigations for a better
290 mechanistic understanding of the formation and dissolution of soil aggregates.

291 Due to the necessity to reduce the P load and N load in the Baltic Sea area simultaneously,
292 actions on arable land should focus on soil structure improvements rather than converting
293 arable land to fallow (Svanbäck et al., 2014). In drain water from structure-limed plots at
294 Bornsjön and Wiad, the N/P ratio was 60-110 but only 9 in the water from the fallow plots
295 (Table 4). The latter is close to the level which can promote growth of N-fixing algae in e.g.
296 the brackish water of Stockholm archipelago (Boesch et al., 2006). However, at Wiad the
297 TN/TP ratio in the drain water was higher (20:1) after growing grass, and under such
298 conditions the presence of N-fixing blue-green algae in receiving water is less plausible.

299

300

301 **Conclusions**

302 Dissolution of large macro-aggregates in water was significantly reduced after liming of two
303 soils with a high and very high clay content, respectively. In view of the generally high PP
304 losses from the Bornsjön soil, it could be concluded that at this site efforts to combat
305 eutrophication of the nearby Baltic Sea should concentrate on mitigation of P losses,
306 including P in particulate form (PP). Structure liming was demonstrated to reduce PP losses
307 for at least six years at this site. Results from Wiad highlight the importance of
308 simultaneously reducing leaching of P in dissolved reactive (DRP) form from soils with a
309 high risk of DRP leaching, which was shown to be achieved by structure liming. However,
310 more field studies are needed to clarify the effect of structure liming on P leaching as a
311 function of available soil P content alone, and in combination with different soil clay contents.
312 Such studies should be of a long-term nature, since lime distribution into the soil and soil
313 aggregate formation by biological activities take time.

314 **Acknowledgements**

315 Thanks are expressed to Hans Tallberg for hosting the experiment and taking water samples,
316 and to Stefan Ekberg, Annelie Mejbert, Ana Maria Mingot Soranio and Nargish Parvage for
317 analytical work. Financial support was provided by the Swedish Farmers' Foundation for
318 Agricultural Research (SLF).

319 **References**

- 320 Al-Mukhtar, M., Khattab, S. & Alcover, J.F. (2012). Microstructure and geotechnical
321 properties of lime-treated expansive clayey soils. *Engineering Geology 139-140*, 17-27.
- 322 Boesch, D., Hechy, R., O'Melia, C., Schindler, D., Seitzinger, S. (2006). Eutrophication of
323 Swedish Seas. Swedish Environmental Protection Agency. Report 5509. ISBN 91-5509-
324 7. ISSN 0282-7298. 2006.
- 325 Choquette, M., Bérube, M-A. & Locat, J. (1987). Minerological and microtextural changes
326 associated with lime stabilization of marine clays from eastern Canada. *Applied Clay*
327 *Science 2*, 215-232.
- 328 Cryz, E.A., Dexter, A.R. & Terelak, H. (2002). Content of readily-dispersible clay in the
329 arable layer of some Polish soils. In Pagliai, M. & Jones, R. (eds) *Sustainable Land*
330 *Management – Environmental Protection. Advances in Geoecology*. Catena verlag,
331 Germany, 115-124.
- 332 Droppo, I. (2001). Rethinking what constitutes suspended sediment. *Hydrological Processes*
333 *15*, 1551-1564.
- 334 ECS. (1996). Water quality. Determination of phosphorus. Ammonium-molybdate
335 spectrometric method. *European Standard EN 1189*. Brussels, Belgium: European
336 Committee for Standardization, 18 pp.
- 337 Egnér, H., Riehm, H. & Domingo, W.R. (1960). Investigations on chemical soil analysis as
338 the basis for estimating soil fertility. II. Chemical extraction methods for phosphorus and
339 potassium determination. *Kungliga Lantbrukshögskolan. Annaler 26*, 199-215.
- 340 Gustafson, A. & Torstensson, G. (1988). Leaching of nutrients after ploughing a ley.
341 *Ecohydrology*, Division of Water Quality Management, Swedish University of
342 Agricultural Sciences, pp. 29-41 (In Swedish).
- 343 Grant, C.D. & Dexter, A.R. (1990). Air entrapment and differential swelling as factors in the
344 mellowing of molded soil during rapid wetting *Australian Journal of Soil Research 28*,
345 361 – 369.
- 346 Gray, C.G. & Schwab, A.P. (1993). Phosphorus-fixing ability of high pH, high calcium, coal-
347 combustion, waste materials. *Water, Air and Soil Pollution 69*, 309-320.
- 348 Haygarth, P.M. & Sharpley A.N. (2000). Terminology for phosphorus transfer. *Journal of*
349 *Environmental Quality 29*, 10-15.

350 Haynes, R.J. & Naidau, R. (1998). Influence of lime, fertilizer and manure application on soil
351 organic and soil physical conditions; a review. *Nutrient Cycling in Agroecosystems* 51,
352 123-137.

353 He, C., Osbreck, B. & Makovicky, E. (1995). Pozzolanic reaction of six principal clay
354 minerals: activation, reactivity assessment and technological effects. *Cement and Concrete*
355 *Research* 25, 1691-1702.

356 HELCOM. (2013). Baltic Sea Environment Proceedings No. 141, *Review of the Fifth Baltic*
357 *Sea Pollution Load Compilation for the 013 HELCOM Ministerial Meeting Helsinki*
358 *Commission*. Baltic Marine Environment Protection Commission Helsinki Commission,
359 Katajanokanlaituri 6 BFI-00160 Helsinki, Finland <http://www.helcom.fi>

360 Kavak, A. & Baykal, G. (2012). Long-term behaviour of lime-stabilized kaolinite clay.
361 *Environment Earth Sciences* 66, 1943-1955.

362 Kyllmar, K., Carlsson, C., Gustafson, A., Ulén, B. & Johnsson, H. (2006). Nutrient discharge
363 from small agricultural catchments in Sweden – Characterisation and trends. *Agriculture,*
364 *Ecosystem & Environment* 115, 15-26.

365 Larsbo, M., Löfstrand, E., van Alphen de Veer, D. & Ulén, B. (2013). Pesticide leaching from
366 two Swedish topsoils of contrasting texture amended with biochar. *Journal of Contaminant*
367 *Hydrology* 147, 73-81.

368 Ledin, S. (1981). *Physical and micromorphological studies of the effect of lime on clay soil*.
369 Doctoral thesis. Department of Soil Sciences, Swedish University of Agricultural Sciences,
370 Uppsala ISSN 91 576 0900 4

371 Littell, R., Milliken, G., Stroup, W., Wolfinger, R. & Schabenberger, O. (2006). *SAS for*
372 *Mixed Models*. 2nd ed. SAS Inst., Cary, NC.

373 Liu, J., Aronsson, H., Ulén, B. & Bergström, L. (2012). Potential phosphorus leaching from
374 sandy topsoils with different fertilizer histories before and after application of pig slurry.
375 *Soil Use and Management* 28, 457-467.

376 Murphy, P.N.C. & Stevens, R.J. (2010). Lime and gypsum as source measures to decrease
377 phosphorus loss from soil to water. *Water Air and Soil Pollution* 212, 101-111.

378 Oades J.M. & Waters, A.G. (1991). Aggregate hierarchy in soils. *Australian Journal of Soil*
379 *Research* 29, 815-828.

380 Oades, J.M. (1993). The role of biology in the formation, stabilization and degradation of soil
381 structure. *Geoderma* 56, 377-400.

382 O'Connor, G.A., Brinton, S. & Silvera, M.L. (2005). Evaluation and selection of soil
383 amendments for field testing to reduce P losses. *Soil and Crop Society of Florida*
384 *Proceedings 64*, 22-34

385 Šaulys, V. & Bastienė, N. (2007). The impact of lime on water quality when draining clay
386 soils. *Ekologija 54*, 22-28.

387 SBA. (2013). *Swedish Board of Agriculture Guidelines for Fertilization and Liming*
388 *2014*. Jordbruksverket 551 82 Jönköping Report Jo 13:11, 2013-11-18 90 pp. (In Swedish).

389 Sheldrick, B.H. & Wang, G. (1993). Particle size distribution. In: Varter, M.R. (ed.) *Soil*
390 *Sampling and Methods of Analysis*. Boca Raton, FL: Lewis Publishers, 499–511.

391 Sinaj, S., Stamm, C., Toor, S., Condon, L. M., Henry, T., Di, H.J., Cameron, K.C. &
392 Frossard, E. (2002). Phosphorus exchangeability and leaching losses from two grassland
393 soils. *Journal of Environmental Quality 31*, 319-330.

394 Smith, V.H. & Schindler, D.W. 2009 Eutrophication science: where do we go from here?
395 Trends in *Ecology & Evolution 24*, 201-207.

396 Svanbäck, A., Ulén, B., Etana, A., Bergström, L., Kleinman, P.J.A. & Mattsson, L. (2013).
397 Influence of soil phosphorus and manure on phosphorus leaching in Swedish topsoils.
398 *Nutrient Cycling in Agroecosystems 96*, 133-137.

399 Svanbäck, A., Ulén, B. & Etana, A. (2014). Mitigation of phosphorus leaching losses via
400 subsurface rains from a cracking marine soil. *Agriculture, Ecosystems and Environment*
401 *164*, 124-134.

402 Ulén, B. (2006). A simplified risk assessment for losses of dissolved reactive phosphorus
403 through drainage pipes from agriculture soils. *Acta Agriculturae Scandinavica, Section B*
404 *Soil & Plant Science 56*, 307-314.

405 Ulén, B. & Snäll, S. (2007). Forms and retention of phosphorus in an illite clay soil profile
406 with a history of fertilization with pig manure and mineral fertilisers. *Geoderma 137*, 455-
407 465.

408 Ulén, B., Bechmann, N., Fölster, J., Jarvie, H. & Tunney, H. (2007). Agriculture as a
409 phosphorus source for eutrophication in the north-west European countries, Norway,
410 Sweden, United Kingdom and Ireland: A review. *Soil Use and Management 23*, Suppl.1, 5-
411 18.

412 Ulén, B., Alex, G., Kreuger, J., Svanbäck, A. & Etana, A. (2012). Particle-facilitated leaching
413 of glyphosate and phosphorus from a marine clay soil via tile drains. *Acta Agriculturae*
414 *Scandinavica, Section B – Soil and Plant Science 62 Suppl. 2*, 241-51.

- 415 Ulén B., Etana, A. & Lindström, B. (2012). Effects of aluminum water treatment residuals,
416 used as a soil amendment to control phosphorus mobility in agricultural soils. *Water*
417 *Science and Technology* 65, 1903-1911.
- 418 Utomo, W.H. & Dexter, A.R. (1981). Tilt mellowing. *Journal of Soil Science* 32, 187-201.
- 419 Uusitalo, R., Turtola, E., Kauppila, T. & Lilja, T. (2001). Particulate phosphorus and sediment
420 in surface runoff and drainflow from clayey soils. *Journal of Environmental Quality* 30,
421 589-595.
- 422 Uusitalo, R., Ylivano, K., Rasa, K., Kaseva, J., Nylund, O., Pietola, L. & Turtola, E. (2012).
423 The effect of gypsum and other nutrients through clay soil monoliths. *Agriculture and Food*
424 *Science* 21, 260-278.
- 425 Williams, N.D., Walling, D.E. & Leeks, G.J.L. (2008). An analysis of the factors contributing
426 to the settling potential of fine fluvial sediment. *Hydrological Processes* 22, 4153-4162.
- 427 Zhu, B. & Alva A.K. (1994). The effect of gypsum amendment on transport of phosphorus in
428 a sandy soil. *Water, Air and Soil Pollution* 78, 375-382.

429

430

431

432

433 Table 1. Experimental set-up in the Swedish field experiments with structure liming, including number
 434 of agrohydrological years with monitoring before and after treatment. Each treatment was represented
 435 by four replicate plots. At Bornsjön there was a stabilisation year after drainage

	Bornsjön ^a	Wiad ^b
Plot size (m)	24x20	55x60
Tile drain spacing (m)	8	14
Lime amendment	CaO	Ca(OH) ₂
Time of application	26 September 2007	13 September 2011
Number of replicates	4	4
Load equivalent to CaO (t ha ⁻¹)	5	2
Control	No lime, no P fertiliser	No lime, no P fertiliser
Pre-period	2006/2007	No lime and P fertiliser
Monitoring before treatment	1 year (2006/2007)	3 years (2006/2009)
Monitoring after treatment	6 years (2007/2013)	2 years (2011/2013)

436 ^a Site description and results in Svanbäck et al. (2014)

437 ^b Site description in Gustafson & Torstensson (1988)..

438

439 Table 2. Soil texture and soil phosphorus (P) characteristics of the field plot experiments at Wiad and
 440 Bornsjön, including degree of P saturation in acid lactate extract (DPS-AL)

Parameters	Bornsjön			Wiad		
	0-23	23-60	60-90	0-23	23-60	60-90
pH (H ₂ O)	6.3	6.6	7.0	7.1	-	-
Clay (%)	59	61	61	26	37	53
Silt (%)	40	38	39	43	39	36
Sand (%)	1	1	0	32	24	12
Organic matter (%)	3.9	1.1	0	2.0	1.2	0
P-AL (mg kg soil ⁻¹)	49	24	16	143	92	93
Al-AL (mmol kg soil ⁻¹)	16	13	14	6	9	9
Fe-AL (mmol kg soil ⁻¹)	6.1	5.3	7.5	6	8	8
DPS-AL (mole-based %)	7	4	2	36	17	18

441

442

443

444 Table 3. Experimental set-up in laboratory experiments with simulated rain events. Each treatment was
445 represented by four replicate topsoil from each of the two Swedish field sites

	Bornsjön	Wiad
Lysimeter sampling year	2010 ^a	2013 ^b
Amendment	CaO and Ca(OH) ₂	Ca(OH) ₂
Load expressed as CaO (t ha ⁻¹)	5	2
Application + incorporation into topsoil	To lysimeters in laboratory	Before, in the field

446 ^a In untreated fallow. After mixing in the amendments, the soil was reconsolidated for 6 months.

447 ^b Two years after application in the field, towards the end of the field leaching study

448

449

450 Table 4. Mean annual discharge, water pH and leaching losses of total P (TotP), particulate P (PP),
 451 and dissolved reactive P (DRP), total percentage of DRP/P total nitrogen (TN) and TN/TP ratio in the
 452 experimental plot experiments (4 replicates). Treatments were: at Bornsjön structure liming (CaO), a
 453 control (without liming and P fertilising) and unfertilised fallow (Fallow); at Wiad structure liming
 454 (Ca(OH)₂), a control (without liming) and a pre-period partly with fallow. All treatments without
 455 fallow were conventionally ploughed.

Period Treatments	Bornsjön ^a			Wiad		2007/2009 Pre-period
	2007/2013 CaO	Control	Fallow	2011/2013 Ca(OH) ₂	Control	
Discharge (mm yr ⁻¹)	505	546	460	137	142	140
pH in water	7.1	6.8	7.1	7.1	7.0	-
TP (kg ha ⁻¹ yr ⁻¹)	0.59**	0.97	0.77	0.13**	0.30	0.29
PP (kg ha ⁻¹ yr ⁻¹)	0.46**	0.82	0.60	0.07	0.14	0.14
DRP (kg ha ⁻¹ yr ⁻¹)	0.13	0.15	0.17	0.08**	0.15	0.11
DRP/TP (%)	20	15	20	50	50	40
TN (kg ha ⁻¹ yr ⁻¹)	30	29	6**	14	12	5
Ratio TN/TP	60	40	9	110	40	20

456 ^a For more details, see Svanbäck et al. (2014).

457 **Significantly lower leaching losses from 4 limed lysimeters compared with 4 control ($p_r > F < 0.002$).

458

459

460

461

462

463

464 Table 5. Mean topsoil lysimeter characteristics, discharge and leaching losses of total P (TP),
 465 particulate P (PP) and dissolved reactive P (DRP) after simulated rainfall in the laboratory

Treatments	Bornsjön laboratory lysimeters ^a			Wiad laboratory lysimeters	
	CaO	Ca(OH) ₂	Control	Ca(OH) ₂	Control
<i>Soil characteristics</i>					
Soil pH	9.5	8.8	5.9	7.5	6.5
P-AL (mg kg soil ⁻¹)	38	41	44	120	140
Al-AL (mmol kg soil ⁻¹)	16	17	15	7	6
Fe-AL (mmol kg soil ⁻¹)	6.6	6.8	4.8	6	7
DPS-AL (mole-based %)	6	9	5	30	37
<i>Lysimeter leaching</i>					
Discharge (mm)	68	68	66	175	179
Water pH	8.5	8.4	7.1	7.3	7.0
TP (kg ha ⁻¹)	0.03**	0.04**	0.15	0.11**	0.13
PP (kg ha ⁻¹)	0.02**	0.03**	0.13	0.03	0.03
DRP (kg ha ⁻¹)	0.01 ^a	0.01 ^b	0.02	0.08**	0.10
DRP/PP (%)	25	25	10	75	80

466 **Significantly (p<0.05) lower leaching compared with unlimed control.

467 ^a For more details, see Ulén et al. (2012).

468 ^b Estimated values, since high pH disturbed DRP analysis.

469

470

471

472 Table 6. Mean concentrations of turbidity (nephelometric turbidity units, NTU), total P (TP),
473 particulate P (PP) and dissolved reactive P (DRP), with standard deviation (SD), after sedimentation of
474 dispersed particles of larger (8-11 mm) aggregates in tests on samples from Wiad and the ratio
475 between the two treatments

Treatment	Turbidity (NTU)		TP (mg L ⁻¹)		PP (mg L ⁻¹)		DRP (mg L ⁻¹)	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
Structure-limed	780**	120	0.24**	0.11	0.18**	0.10	0.05**	0.01
Control	1300	260	0.60	0.07	0.48	0.05	0.10	0.02
Ratio	0.6		0.4		0.4		0.5	

476 ** Significantly lower concentrations from limed plots ($p < 0.05$) compared with unlimed soil.

477

478

479 FIGURE CAPTIONS

480

481 Figure 1. Map of Sweden and the coastal area south of Stockholm where the two experimental
482 fields are situated. Sampling sites of topsoil lysimeters are indicated (dots) relative to the
483 experimental plots (squares) to the right.

484

485

486 Figure 2a) Relative turbidity after settling of dispersed particles in samples taken from
487 Bornsjön in autumn 2010. Control (=100, not structure-limed) compared with structure-limed
488 plot (SL). SL and control were conventionally ploughed but at Bornsjön relative turbidity
489 after shallow tillage with a cultivator is included for comparison (diagram based on Ulén et
490 al., 2012). 2b) Relative turbidity after settling of dispersed particles in samples taken from
491 Wiad in October 2011.

492