

Remediation of a Eutrophic Bay in the Baltic Sea

Emil Rydin,^{*,||,†} Linda Kumblad,^{||,†} Fredrik Wulff,^{⊥,‡} and Per Larsson[§]

[†]BalticSea2020, Box 50005, SE-104 05 Stockholm, Sweden

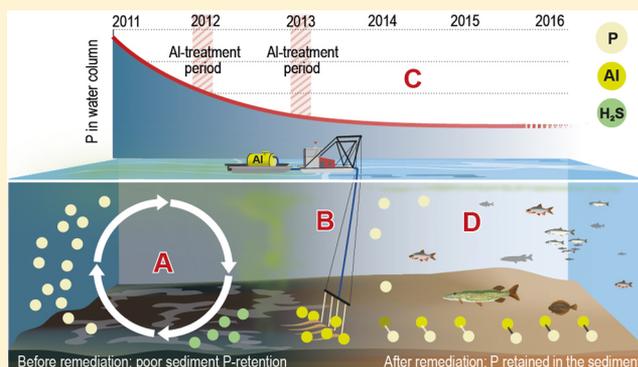
[‡]Stockholm University Baltic Sea Center, Stockholm University, SE-106 91 Stockholm, Sweden

[§]Department of Biology and Environmental Science, Linnaeus University, SE-391 82 Kalmar, Sweden

Supporting Information

ABSTRACT: Eutrophication of coastal ecosystems is a global problem that often results in bottom water oxygen deficiency and in turn promotes sediment phosphorus (P) release (A). In order to increase sediment P retention, we injected dissolved aluminum into the anoxic sediment of a eutrophic semienclosed bay in the Baltic Sea, thereby inhibiting P recycling and further eutrophication (B). The P concentration in the bay remained at half, as did phytoplankton biomass (C), compared to pretreatment conditions and compared to the reference bay. Four years after treatment the water column transparency was increased, allowing submerged vegetation to penetrate deeper, and the habitat suitable for fish and benthic fauna had expanded (D). The lowered P concentration in the bay decreased the P export to the surrounding archipelago.

This is the first full-scale marine remediation project using a geo-engineering method that demonstrates a quick recovery. For successful remediation in coastal areas, permanent binding of mobile P in anoxic sediments may be needed together with measures in the catchment area to obtain faster recovery of eutrophicated marine ecosystems.



1. INTRODUCTION

Throughout the world, many coastal ecosystems have experienced eutrophication, often resulting in harmful algal blooms, increased sedimentation of organic matter, and bottom water oxygen deficiency¹ that in turn may promote sediment phosphorus release.² The brackish Baltic Sea is one of the most polluted seas in the world. Excess nutrient loads from the catchment area have caused severe eutrophication effects that have been exacerbated by overfishing of predatory fish,³ creating a system with frequent algal blooms.⁴ Whether nitrogen (N) or phosphorus (P) regulates primary production varies both spatially and temporally in the Baltic Sea,⁵ with P reduction being of prime importance for reducing cyanobacterial blooms.⁶ Massive sedimentation of organic matter has aggravated hypoxia in deeper areas (>70 m), an effect enhanced by the long retention time of water (30 years) in the Baltic Sea. The bottom water oxygen depletion may stimulate recycling of P from the sediment to the water column; the vicious circle.⁷ P recycling from sediments is now the main factor maintaining high P concentrations, even though external P inputs have been decreasing for over three decades.⁸

Baltic Sea archipelagos have many sheltered basins, where organic matter accumulates through sediment focusing, leading to hypoxic conditions even at shallow depths,⁹ and creating hot spots for nutrient recycling. Like the Baltic Sea, these bays often have sills that hamper water exchange with adjoining basins, resulting in nutrient accumulation and pronounced

eutrophication effects such as elevated water column nutrient concentrations, algal blooms and bottom water oxygen deficiency. While much of the added combined nitrogen has been lost through denitrification, most of the P has accumulated in the sediment and water column.

To break this pattern and restore good water quality, as required by the EU Water Framework Directive (WFD; 2000/60/EC), we increased anoxic sediment P retention by injecting dissolved aluminum chloride into the sediment in one bay, besides measures to decrease nutrient losses from agriculture, private sewers, and horse keeping in the catchment area. By increasing the supply of a binding agent naturally involved in permanent P burial in the sediment, Al addition strengthens P-binding in anoxic sediments. A nearby reference bay allowed us to separate changes in water quality variables caused by remediation from natural changes, due to weather or inflow from the open sea. The overall aim was to test if it is possible to remediate heavily eutrophicated coastal bays in the Baltic Sea.

2. MATERIALS AND METHODS

2.1. Study Sites. The treated bay (Björnöfjärden) (area 1.5 km², maximum/mean depth 25/6 m) and the reference bay

Received: December 14, 2016

Revised: March 16, 2017

Accepted: March 28, 2017

Published: March 28, 2017

(Fjällsvikviken) (area 0.7 km², maximum/mean depth 15/4 m) have many characteristics in common (Supporting Information (SI) Table S1, Figure S1 & S2); limited water exchange with the outside archipelago due to sills and straits, several sub-basins with the deepest basin in center (SI Figure S1), similar morphometry, salinity, and catchments (SI Table S1), as well as a morphometry that leads to stable temperature stratification (SI Figure S2) and subsequent hypoxic conditions in the bottom water. Both bays are in many ways “Baltic Seas in miniature”. The Al-treatment of Björnöfjärden was performed in 2012–2013 and results from the sampling program are reported from September 2011 to May 2016 (ongoing). The catchment area of the treated bay is 13 km², with a bedrock of granites and gneisses covered by glacial and postglacial till, moraine and clay deposits, with mixed forests, pastures and open landscape (SI Table S1). The catchment of the reference bay is similar, but smaller (5 km²) and lacks arable land.

2.2. Aluminum Treatment. Dissolved poly aluminum (Al) chloride “PAX XL 100” (Kemira Kemwater, Sweden) was used as sediment P binding agent and injected into anoxic sediments below 6 m depth. The total dose during eight summer weeks in 2012 and 2013 was 50 g Al/m² on 0.73 km², summing up to 36 tons of Al. Sediment mapping, GPS navigation, and camera monitoring allowed controlled application in the top c. 0.1 m of sediment through tubes mounted on a 10 m wide steel bar, furnished with 25 two meter long plastic tubes pointing downward, carried on a barge. Bay water was pumped through the tubes at high pressure to cause turbulence at the nozzles where the Al was emitted. Treatment was repeated three times with the same Al dose, to ensure homogeneous application.

2.3. Sediment Sampling and P Bound to Al. Nine sediment cores evenly distributed in the area to be Al-treated were collected in December 2011 and March 2012 with a gravity corer (inner diameter 63 mm). Sampling was repeated after the Al-treatment, in March 2014 and 2016. The cores were sliced into 1 or 2 cm thick layers down to 20 cm depth on the day of sampling, and stored in airtight containers in the dark at 4 °C until analyses within a week of sampling. Besides water and organic content in the sediment, P associated with Al (Al–P) were separated by sequential extraction,¹⁰ and formed Al–P due to treatment was calculated.¹¹

2.4. Sampling and Analyses of Water Chemistry and Phytoplankton. The main streams and ditches draining 70% of the total catchment area of the treated bay were sampled 15–20 times a year, with shorter intervals during periods of precipitation and large runoff. The three sub-basins of the treated bay, and the two sub-basins of the reference bay, were monitored on 85 sampling occasions from September 2011 to May 2016, with lower frequency in winter. Water samples above the thermocline was collected following a procedure¹² that results in a vertically and horizontally integrated volume-weighted composite samples for the surface water (epilimnion) of each sub-basin. Discrete bottom water samples, evenly distributed in the water column below the thermocline at the deepest sites of each sub-basin were also collected. At these sites, oxygen, salinity, and temperature profiles and Secchi depth were also measured.

Phosphate,¹³ total P after persulfate digestion,¹³ nitrate,¹⁴ total nitrogen as nitrate after persulfate digestion,¹⁴ and ammonia¹⁵ were measured spectrophotometrically. Bottom water sulfide content was measured colorimetrically.¹⁶ Water column profiles of dissolved oxygen were determined¹⁷ using an Oxygard Handy Polaris device; and electrical conductivity (salinity) and temperature¹⁸ with an YSI Pro 30 probe. Chlorophyll *a* was

spectrophotometrically determined after acetone extraction.¹⁹ Phytoplankton community composition was determined using inverted microscopy (Utermöhl technique)²⁰ after Lugol fixation of the sample. All chemical and phytoplankton analyses were performed at the Erken analytical laboratory of Uppsala University, Sweden.

2.5. Sampling and Analyses of Biota. Vegetation composition, cover, and depth distribution were monitored yearly in April along SCUBA diving transects.²¹ The same transects were revisited each year. Benthic macrofauna was sampled yearly in May with a 0.1 m² Van Veen grab, sieved (metal gauze, mesh size 1.0 × 1.0 mm), fixed in ethanol, sorted and determined to lowest possible taxon.²² The same sampling sites were revisited each year. Fish were sampled yearly in July or August using 29 bottom-set Nordic type standardized multipanel survey gill nets²³ per bay, set overnight at sites chosen randomly in proportion to the area of each depth zone. The same net positions were used each year.

2.6. Calculations of Water Column Concentrations. To calculate the epilimnetic mean concentration of chemistry and phytoplankton variables for each bay at a given time, the measured composite concentration in each sub-basin was weighted in proportion to the volume of the respective sub-basin. In addition, to calculate whole water column mean concentration of TN and TP, concentrations of discrete samples for the water strata below the thermocline were included. For unsampled water strata, concentrations were linearly interpolated from water depths with known concentrations, and the concentration in each sub-basin of the respective bay, was weighted in proportion to its volume.

Both the epilimnetic, and whole water column mean concentration, at a given time (sampling occasion), contributed to the summer (1 June–30 October), winter (1 November–31 May) and yearly mean concentration in proportion to the number of days between samplings.

2.7. Calculations of Internal, External, And Exchange Load of N and P. To quantify the internal recycling of dissolved N and P from the sediment due to diffusion, the ammonia and phosphate accumulation rates in stagnant bottom water of the bay was calculated during the pretreatment period. Water strata not measured were linearly interpolated. The relation between released N and P in the reference bay, was used to calculate the post-treatment reduction in P release in the treated bay, based on the bottom water–ammonia accumulation during anoxic periods. Nutrient fluxes due to erosion and resuspension was not calculated. Weekly runoff data from the Swedish Meteorological and Hydrological Institute,²⁴ and nutrient concentrations in the inlets, were used to calculate the monthly nutrient load to the treated bay. From mid-2014, the treated bay outlet water movement (both directions) was logged at 15 min interval with a bottom-mounted acoustic Doppler current profiler device (SonTek IQ+). When water movement in one direction exceeded the volume of the 300 m outlet channel, a water exchange with the adjoining basin was considered to have occurred. N and P outflow from the treated bay was calculated as the volume of the water body multiplied with the epilimnetic N and P concentrations in the bay, and vice versa for N and P inflow occasions, using N and P concentrations in the adjoining bay (data not shown).

2.8. Statistics. The time trend in depth distribution of benthic vegetation in the treated bay was tested using mixed effects models (“lme4”-package²⁵) in R 3.2.3.²⁶ The community structure of fish and benthic macrofauna was analyzed using the MDS (nonmetric multidimensional scaling), SIMPER (sim-

ilarity percentages) and ANOSIM routines in the Primer-E V6 package.²⁷ Data was square root transformed to down-weight high abundances. The resemblance matrix (Bray–Curtis) used for MDS analysis was zero-adjusted.²⁸ Differences between years were analyzed with a one-way ANOVA followed by a LSD multiple comparison, using the software IBM SPSS Statistics 22. The homogeneity of variances for all data sets was tested with Levene statistics.

3. RESULTS

3.1. Sediment Response. A pronounced increase in Al–P concentration was detected in the surface layers of the sediment

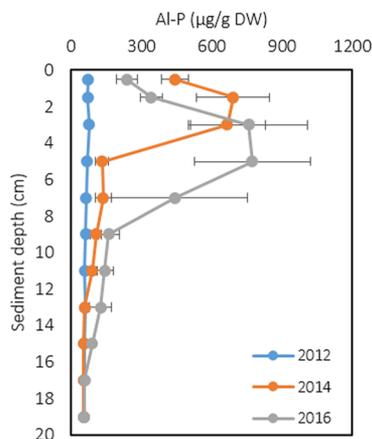


Figure 1. Phosphorus bound to aluminum in the sediment. Concentrations of Al–P (Al–P, $\mu\text{g/g DW}$) before the Al-treatment (2012) as well as 2 and 4 years after the treatment, 2014 and 2016 respectively, in the sediment of the treated bay (Baltic Sea, Sweden).

in the treated bay after the Al-treatment, with the Al–P peak at 2–4 cm depth in 2014, and at 4–6 cm in 2016 (Figure 1). The Al–P content increased at an average rate of 1.3 mg P/m^2 day. The P trapped until March 2016 was 1.5 g/m^2 , corresponding to an extra sequestration of 1.3 tons of P whole treated sediment area (0.7 km^2) since treatment in 2012.

3.2. Nutrient Supply. The pretreatment internal P loading was an order of magnitude larger than the external supply of dissolved P from the catchment (Table 1). After treatment, accumulation of phosphate in the bottom water (>6m) during summer effectively ceased (Figure 2, Table 1) due to the

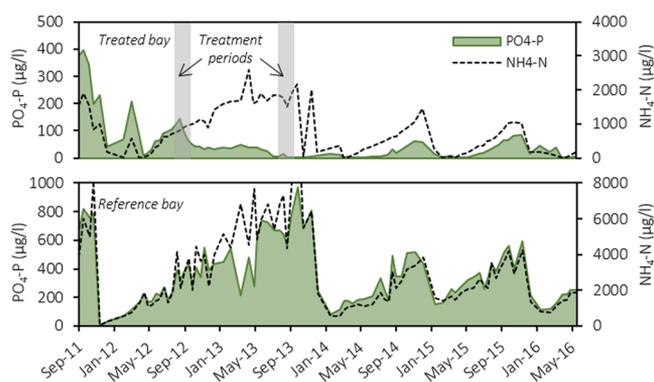


Figure 2. Dissolved nutrient concentration development in the bottom water. Phosphate ($\mu\text{g PO}_4\text{-P/L}$) and ammonium ($\mu\text{g NH}_4\text{-N/L}$) concentrations one meter above the seabed of the treated (above) and reference (below) bay (Baltic Sea, Sweden), September 2011 to May 2016. Periods of Al-treatment indicated by gray shading.

precipitation of dissolved P by the added Al. In the anoxic sediment of the reference bay, anaerobic mineralization of

Table 1. Annual Mean Nutrient Load to the Treated Bay (Ton/Year) And Relative Amount of Dissolved P (%), Divided into Load from the Atmosphere, The Catchment Area and the Sediment

source		PO_4^-	TP	PO_4^-	NH_4^+	NO_3^-	TN
atmospheric load ^a		–	0.02		–	–	0.9
external catchment load ^b							
	2012	0.08	0.25		0.24	1.70	5.71
	2013	0.05	0.15		0.23	1.08	3.33
	2014	0.11	0.24		0.28	1.36	3.80
	2015	0.15	0.44		0.22	1.82	6.92
	mean	0.10	0.27	36%	0.24	1.49	4.94
internal sediment load ^c							
pretreatment	4–6 m	0.24			1.7		
	6–25 m	1.03			7.3		
	sum	1.27		100%	9.0		
post-treatment	4–6 m	0.24			1.7		
	6–25 m	0			7.3		
	sum	0.24		100%	9.0		
exchange with adjoining basin ^d							
pretreatment	Export		0.8				
	Import		0.2				
	net flux		0.6				
post-treatment (2014–2015)	Export	0.1	0.4	14%	0.3	0.4	10.6
	Import	0.1	0.2	31%	0.1	0.2	3.0
	net flux	0.0	0.2		0.2	0.3	7.6

^aMean atmospheric deposition of P^{47} and N^{48} to the treated bay. ^bCalculated from measured nutrient concentrations in inlets and modeled estimates of catchment water runoff.²⁴ ^cCalculated from stagnant bottom water accumulation rate (measured), pre/post-treatment is < July 2012/ >August 2013. ^dCalculated from epilimnetic nutrient concentration inside or outside the water exchange channel multiplied with water exchange (see Materials and Methods).

Table 2. Water Quality Parameters (Volume Proportionate Mean Concentrations, $\mu\text{g/L}$) Before (<2012) and after Treatment (>2013) in the Treated (T), and Reference (R) Bay (Baltic Sea, Sweden), during the Summer (1/6–31/10), Winter (1/11–31/5) Period, and over the Year

variable	unit	bay	summer		winter		yearly	
			before	after	before	after	before	after
TP epilimnion ^a	$\mu\text{g P/L}$	T	26	17	50	23	40	20
		R	24	24	40	36	33	30
PO_4^- epilimnion ^a	$\mu\text{g P/L}$	T	3	2	19	5	12	4
		R	2	1	9	7	7	5
TN epilimnion ^a	$\mu\text{g N/L}$	T	465	442	598	543	540	498
		R	467	491	582	552	532	524
NH_4^+ epilimnion ^a	$\mu\text{g N/L}$	T	14	16	46	42	33	31
		R	9	6	78	43	49	28
NO_3^- epilimnion ^a	$\mu\text{g N/L}$	T	0.4	3	94	77	55	46
		R	0.1	1	57	56	33	33
TN/TP epilimnion ^a	mole/mole	T	41	61	27	54	33	57
		R	43	47	33	36	37	41
TP whole system ^b	$\mu\text{g P/L}$	T	40	22	54	25	48	23
		R	44	45	44	48	44	46
TN whole system ^b	$\mu\text{g N/L}$	T	514	545	611	598	568	573
		R	617	621	610	636	610	626
PO_4^- hypolimnion ^c	$\mu\text{g P/L}$	T	246	34	95	23	157	28
		R	529	470	99	306	277	373
NH_4^+ hypolimnion ^c	$\mu\text{g N/L}$	T	1147	942	276	679	635	784
		R	3730	3930	730	2639	1968	3160
$\text{NH}_4^+ / \text{PO}_4^-$ hypolimnion ^c	mole/mole	T	11	263	6	104	8	169
		R	16	18	63	19	43	18
Chl <i>a</i> epilimnion ^a	$\mu\text{g/L}$	T	4.9	3.0	10.2	5.7	8.0	4.6
		R	5.9	6.0	9.3	10.5	7.8	8.6
Secchi depth	m	T	4.2	5.5	2.8	3.3	3.4	4.2
		R	4.0	4.1	3.3	2.9	3.6	3.4
phytoplankton epilimnion ^a	mm^3/L	T	1.55	0.93	2.35	1.66	2.01	1.35
		R	2.65	2.06	1.74	3.24	2.10	2.74
chlorophyta	mm^3/L	T	0.09	0.05	0.00	0.01	0.04	0.03
		R	0.26	0.11	0.03	0.02	0.13	0.06
chrysophyta	mm^3/L	T	0.16	0.08	0.34	0.13	0.26	0.11
		R	0.22	0.20	0.27	0.37	0.25	0.30
haptophyta	mm^3/L	T	0.01	0.04	0.00	0.03	0.01	0.03
		R	0.04	0.05	0.02	0.07	0.03	0.06
dinophyta	mm^3/L	T	0.36	0.24	0.52	0.25	0.46	0.25
		R	0.30	0.27	0.48	0.61	0.40	0.47
cryptophyta	mm^3/L	T	0.15	0.16	0.03	0.08	0.08	0.11
		R	0.18	0.34	0.07	0.21	0.11	0.26
ciliophora	mm^3/L	T	0.32	0.17	1.39	1.09	0.94	0.71
		R	0.63	0.16	0.73	1.86	0.69	1.15
cyanophyta	mm^3/L	T	0.33	0.14	0.01	0.00	0.14	0.06
		R	0.88	0.81	0.01	0.03	0.37	0.35
euglenophyta	mm^3/L	T	0.00	0.00	0.00	0.00	0.00	0.00
		R	0.00	0.01	0.02	0.00	0.01	0.00
incertae sedis	mm^3/L	T	0.12	0.05	0.07	0.07	0.09	0.06
		R	0.12	0.10	0.10	0.08	0.11	0.09

^aVolume proportionate composite samples above the thermocline. ^bVolume proportionate means of the whole water column. ^cDiscrete samples 1 m from the sediment at the maximum depth, of the respective bay.

organic matter kept the proportional phosphate and ammonia release close to the Redfield ratio, indicating mineralization of phytoplankton (Figure 2). In the remediated bay, almost only ammonia was released, approximately doubling the epilimnetic TN/TP ratio (Table 2). Nutrients dissolved in hypolimnion reached the photic zone mainly during autumn and winter mixing (Table 2). During winter, ammonia was nitrified, resulting in a winter nitrate peak that declined during late winter and spring (Figure 3).

3.3. Water Column Response. The treatment caused a clear ecological response. The primary effect was a lowered overall water-column TP concentration, from on average 48 before to 23 $\mu\text{g/L}$ after treatment (Figure 4, Table 2). The TP concentration in the reference bay remained at about 45 $\mu\text{g P/L}$ during this period. Pretreatment surface water (epilimnetic) characteristics as yearly means were 40 $\mu\text{g P/L}$, a phytoplankton biomass of 8.0 $\mu\text{g chlorophyll } a/\text{L}$, and a water transparency as Secchi depth of 3.4 m (Table 2, Figure 5). After treatment, yearly

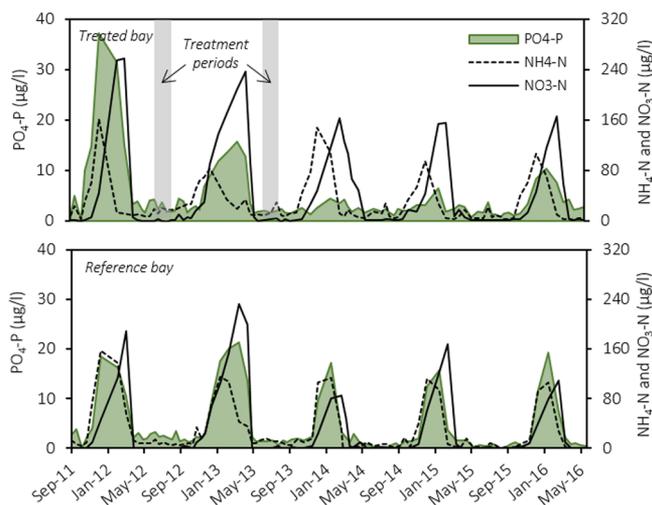


Figure 3. Dissolved nutrient concentration development in the water column. Phosphate ($\mu\text{g PO}_4\text{-P/L}$), ammonium ($\mu\text{g NH}_4\text{-N/L}$) and nitrate ($\mu\text{g NO}_3\text{-N/L}$) concentrations in epilimnion of the treated (above) and reference (below) bay (Baltic Sea, Sweden), September 2011 to -May 2016. Periods of Al-treatment indicated by gray shading.

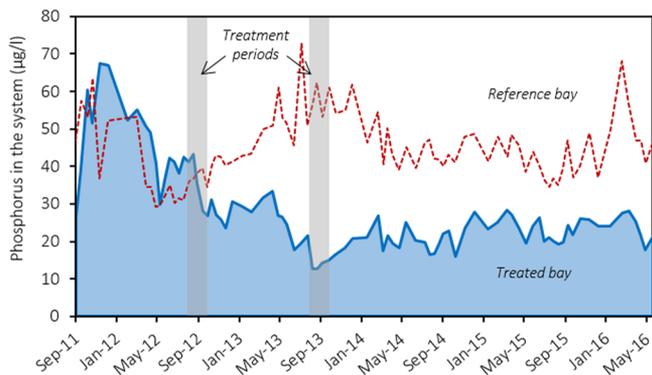


Figure 4. Water column phosphorus concentration development. Mean total phosphorus concentration ($\mu\text{g TP/L}$) in the water whole column of the treated (blue area) and reference (red dashed) bay (Baltic Sea, Sweden), Sep. 2011 to May 2016. Periods of Al-treatment indicated by gray shading.

TP and chlorophyll *a* concentrations decreased by about half, and the Secchi depth increased to 4.2 m, with no such changes in the reference bay (Table 2).

Phytoplankton biovolume averaged $2.0 \text{ mm}^3/\text{L}$ before the treatment, with pronounced autumn and spring blooms after nutrient supply from bottom water during water column turnover (Table 2). Dominant taxa were Ciliophora, Dinophyta, and Chrysophyta. After treatment, the lower availability of P reduced the spring and autumn blooms, as well as the summer cyanobacterial bloom. Post-treatment, the main chlorophyll *a* concentration peak occurred in February, and was dominated by the ciliate *Mesodinium rubrum*, resulting in a yearly mean phytoplankton biovolume of $1.4 \text{ mm}^3/\text{L}$ (Table 2, Figure 5).

3.4. Ecosystem Response. The increased water transparency apparently resulted in benthic vegetation (primarily *Aegagrophila linnaei*) penetrating over 1 m deeper on hard substrates (Figure 6a). Hydrogen sulfide formation above the soft accumulation sediments at intermediate depths (8–10 m) ceased after treatment (SI Figure S3). Light penetration now seemed to be sufficient to allow photosynthesis on the sediment, preventing development of sulfate-reducing bacteria in the

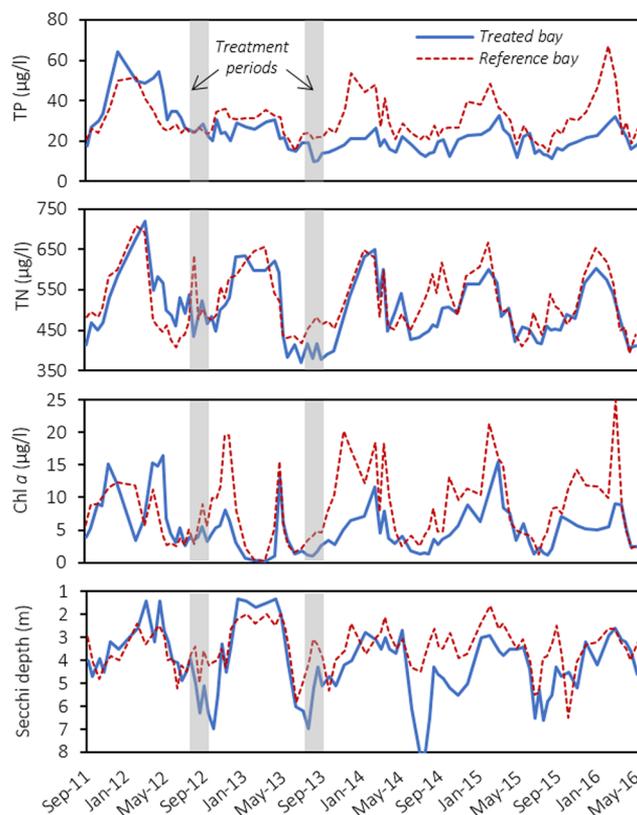


Figure 5. Development of nutrients, a phytoplankton proxy and water transparency. Total phosphorus (TP, $\mu\text{g/L}$), total nitrogen (TN, $\mu\text{g/L}$), and chlorophyll *a* (Chl *a*, $\mu\text{g/L}$) concentration in the epilimnion of the treated (blue) and the reference (red dashed) bay (Baltic Sea, Sweden), September 2011 to May 2016. Periods of Al treatment indicated by gray shading.

bottom water.²⁹ While oxygen concentration did not increase significantly at these depths (SI Figure S3), there were indications of improved oxygen conditions below the thermocline, shown by increased fish abundance and presence of “new” fish species (*Perca fluviatilis*, *Blicca bjoerkna*, *Abramis brama*, *Gymnocephalus cernuus*, *Esox lucius*, *Rutilus rutilus*, *Coregonus clupeaformis*) in the 8–10 m zone, and colonization by benthic macrofauna species with pelagic larvae stages (*Macoma balthica*, *Marenzelleria neglecta*, *Pygospio elegans*, *Potamopyrgus antipodarum*) in the 5–10 m depth interval (Figure 6bc). No such changes were recorded in the reference bay.

4. DISCUSSION

Our results highlight the importance of the sediment P retaining capacity for eutrophication in P-limited coastal marine areas. Dissolved P was trapped in the sediment by the added Al, at a rate corresponding to the pretreatment recycling rate. The accumulation of Al-P and the observed shift in P peak depth from 2014 to 2016 apparently indicates a yearly accumulation of about one cm of unconsolidated sediment on top of the treated layer (Figure 1). After 40 months, 1.3 tons of dissolved P has been trapped by Al in the 0.7 km^2 treated anoxic sediment area, P that no longer supports eutrophication in the bay, turning the treated bay into a sink for P in the Baltic Sea ecosystem.

By enhancing the P retention of the sediment, the vicious circle was broken, resulting in lower water column P, reduced phytoplankton growth and improved light climate.

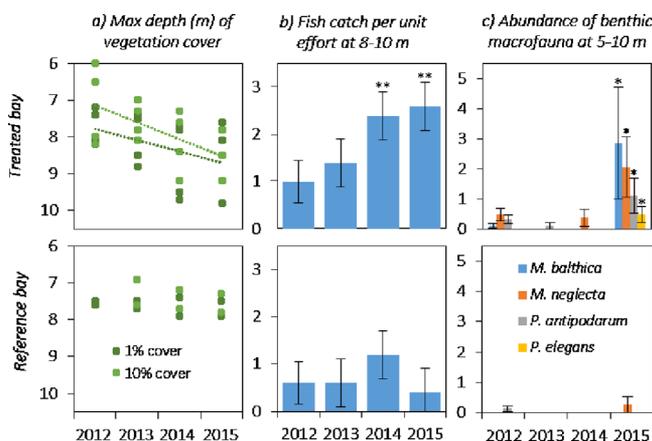


Figure 6. Biological responses to reduced phosphorus availability in the treated bay. (a) Increased maximum depth (m) with vegetation ($\geq 1\%$ and $\geq 10\%$ cover; mainly *Aegagrophila linnaei*). (LME4-package, conditioned by the random grouping factors survey transect ($n = 4$, $n = 2$) nested in water basin, slope $\geq 1\%$ cover 0.376 ± 0.075 SD, $p = 0.0005$; $\geq 10\%$ cover 0.380 ± 0.078 SD, $p = 0.0005$). No significant changes observed in the reference bay. (b) Increased catch per unit effort for fish (yearly means CPUE \pm SE) in the 8–10 m zone in 2014 and 2015 compared to 2012 in the 8–10 m zone in the treated bay (ANOVA, $F = 3.65$, $P = 0.005$). No significant changes observed in the reference bay. (c) Increased abundance (yearly means \pm SE) of benthic macrofauna with pelagic larvae in the 5–10 m zone in the treated in 2015 compared to 2011–2014. (*Macoma balthica* ANOVA, $F = 2.27$, $P = 0.04$; *Marenzelleria neglecta* ANOVA, $F = 2.96$, $P = 0.04$; *Pygospio elegans* ANOVA, $F = 2.68$, $P = 0.05$ and *Potamopyrgus antipodarum* ANOVA, $D = 3.10$, $P = 0.03$). No significant changes observed in the reference bay.

Diffusion from untreated, shallow ($< 6\text{m}$) sediments, as well as erosion and resuspension processes, can be expected to have remained largely unaffected by treatment. These sources, together with the external supply, now regulate water column P input. After treatment, the bay shifted to mesotrophic status (TP $< 30 \mu\text{g P/L}$) using freshwater classification,³⁰ with the mean epilimnetic TP concentration stabilized at $20 \mu\text{g/L}$ (Table 2). This is contrary to model results by Dimberg and Bryhn³¹ that predict virtually no effect on water column TP concentration by Al treatment of the bay. According to the EU Water Framework Directive's water quality classification for TP, chl *a*, and Secchi depth, the treated bay now has regained high or good status, while other bays in the region have moderate, poor or bad status.³² To maintain the remediated bay's improved status in the future, it is however crucial to also reduce its external nutrient load. Measures have therefore been taken to reduce nutrient losses from farmland and built-up areas in the catchment.

Although there were quick improvements in water chemistry variables, and subsequent positive response in biota, oxygen conditions in the bottom water remained poor. There is often a lag in recovery in bottom oxygen status after reduced settling of degradable organic matter,³³ since the sediment has accumulated an oxygen demand after decades of hypoxic conditions, as indicated by the laminated sediments (data not shown) due to the absence of bioturbation. The established poor oxygen conditions in the sediment support the assumption that the pretreatment internal loading rate of P measured was representative for the bay also for the period before the monitoring started.

The concomitant decline in water column P concentration and phytoplankton biomass suggests that P was growth limiting

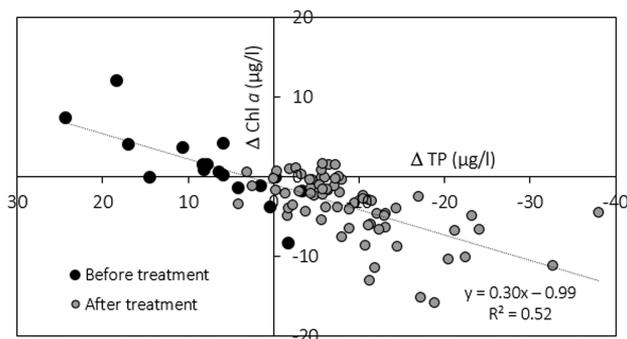


Figure 7. Difference in phosphorus and chlorophyll *a* levels in the studied bays. The difference in epilimnetic concentrations of total phosphorus (ΔTP) and chlorophyll *a* ($\Delta \text{Chl } a$) between the treated and the reference bay. Black circles represent concentration differences before the Al-treatment and gray circles after the treatment. Each dot represents a sampling date, no data was excluded (September 2011 to May 2016).

(Figure 7), but colimitation by nitrogen cannot be ruled out since nitrate and ammonia were both largely depleted in the epilimnion in spring, unexpectedly even after the pronounced reduction of P supply to the water column (Figure 3).

This is the first time Al-treatment was used to remediate a nonlimnic environment. The 36 tons of added Al to the sediment is forecast¹¹ to permanently bind 4 tons of dissolved P that otherwise would have been recycled to the water column within a decade. Although the expected ratio of Al to P binding is up to a factor 5 less effective than chemical precipitation in sewage treatment plants, the mechanism is essentially the same, but avoids the problem of disposal of the sewage sludge. Al-treatment has been used in lakes³⁴ and is one of a few methods available for increasing anoxic P retention, but other means of binding sediment-P may potentially be available.^{35–37} The addition of Al to the sediment can be considered as boosting the natural supply of Al from the catchment, strengthening a natural P-binding process by supplying additional binding sites to inactivate the pulse of excess P supplied from anthropogenic sources. In spite of the quick improvement observed in the remediated bay, Al-treatment should complement, not replace actions to reduce P load from the catchment. If external loading continues, a new “P-legacy” will soon build up and form the basis for future P recycling to the water column, reinvigorating the vicious circle.

Since the turn of the millennium, the Baltic Sea has experienced a marked increase in anoxic sediment areas³⁸ that will result in reduced sediment P binding capacity, and further strengthen the vicious circle. Model simulations indicate that increased recycling of P, due to increased extension of anoxic sediments, has more than compensated for the load reduction, explaining the continued poor trophic state.⁸ As consequence, a decrease of the external P supply to 1950 levels will not be enough to restore the 1950 nutrient status in the Baltic Sea within several decades,⁸ perhaps not even in a century. Similar developments have been seen in numerous lakes that received poorly treated wastewater in the mid-1900s.³⁵ Reduction of nutrient supply through, for example, sewage diversion was often not sufficient to return to former nutrient status within several decades, even though the water retention time in these lakes often was just a fraction of the 30 years of the Baltic Sea. Not until in-lake measures such as biomanipulation³⁹ or geo-engineering³⁵ were employed, were these lakes eventually restored to acceptable water quality.

As in the open Baltic Sea, accumulation sediments in the coastal zone have increasingly turned anoxic,⁹ reducing their function as P traps from matter originated both from land runoff and from the open sea. Instead anoxic coastal basins have become “hot-spot-areas” of, for example, P recycling from formerly deposited matter.⁴⁰ Restoring the former P burial capacity of these areas might thus have a positive effect also on P availability at the Baltic Sea scale.

The application of geo-engineering methods in the Baltic Sea has been criticized⁴¹ as being unrealistic and unproven as means to counteract marine eutrophication,⁴² and even though enclosure experiments in a brackish water environment showed no negative effects on biota,⁴³ potential side effects may need further study.⁴⁴ Aluminum hydroxide has very low solubility at circum-neutral pH, but dissolves at alkaline and acid pH, and might then be toxic to aquatic organisms.⁴⁵ The mean pH was 7.0 in the bottom water in both the studied bays (SI Table S1).

It has been argued that action to boost the P-retention capacity of the sediment may divert attention from reducing the external nutrient load, even if it may take decades⁸ for this to take effect.⁴¹ We have shown, however, that the use of chemical precipitation to permanently bind mobile P in the sediment, and thus break the vicious circle, can be cost-effective¹¹ in enclosed coastal areas, resulting in improved water quality and quick recovery from eutrophication. Reducing the external nutrient supply remains of prime importance, but addressing also sediment P release is necessary to maintain the political momentum needed, in the long run, to implement and sustain land-based measures required to further reduce nutrient load from the catchment area, and thus improve the environmental status of the Baltic Sea.⁴⁶

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b06187.

Table S1, morphometry and catchment data. Figure S1, bathymetry chart. Figure S2, temperature development. Figure S3, oxygen development (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*Phone: +46 (0)8 6739766; fax: +46 (0)8 6739760; e-mail: emil.rydin@balticsea2020.org.

ORCID

Emil Rydin: 0000-0002-2566-8547

Author Contributions

^{||}These authors contributed equally to this work.

Notes

The authors declare no competing financial interest.

[†]Deceased May 20, 2016.

■ ACKNOWLEDGMENTS

We are grateful to Ragnar Elmgren for edits on the manuscript. Fredrik Wulff's too early death prevented his participation in the final preparation of this manuscript. We thank the staff at Naturvatten i Roslagen AB, Sveriges Vattenekologer AB, Loude Consulting, and at the Erken Laboratory at Uppsala University for sampling and analyses, and Vattenresurs AB for the aluminum addition. Jonas Nilsson and Joakim Hansen assisted

with statistics. This work was funded by the BalticSea2020 foundation.

■ REFERENCES

- (1) Diaz, R. J.; Rosenberg, R. Spreading dead zones and consequences for marine ecosystems. *Science* **2008**, *5891*, 926–929.
- (2) Howarth, R.; Chan, F.; Conley, D.; Garnier, J.; Doney, S.; Marino, R.; Billen, G. Coupled biogeochemical cycles: Eutrophication and hypoxia in temperate estuaries and coastal marine ecosystems. *Front. Ecol. Environ.* **2011**, *9*, 18–26.
- (3) Casini, M.; Hjelm, J.; Molinero, J. C.; Lövgren, J.; Cardinale, M.; Bartolino, V.; Belgrano, A.; Kornilovs, G. Trophic cascades promote threshold-like shifts in pelagic marine ecosystems. *Proc. Natl. Acad. Sci. U. S. A.* **2009**, *106*, 197–202.
- (4) Karhu, M.; Savchuk, O.; Elmgren, R. Satellite measurements of cyanobacterial bloom frequency in the Baltic Sea: interannual and spatial variability. *Mar. Ecol.: Prog. Ser.* **2007**, *343*, 15–23.
- (5) Granéli, E.; Wallström, K.; Larsson, U.; Granéli, W.; Elmgren, R. Nutrient limitation of primary production in the Baltic Sea area. *Ambio* **1990**, *19*, 142–151.
- (6) Wulff, F.; Savchuk, O.; Sokolov, A.; Humborg, C.; Mörtz, C. M. Management Options and Effects on a Marine Ecosystem: Assessing the Future of the Baltic. *Ambio* **2007**, *36*, 243–249.
- (7) Vahtera, E.; Conley, D.; Gustafsson, B.; Kuosa, H.; Pitkänen, H.; Savchuk, O.; Tamminen, T.; Viitasalo, M.; Voss, M.; Wasmund, N.; Wulff, F. Internal ecosystem feedbacks enhance nitrogenfixing cyanobacteria blooms and complicate management in the Baltic Sea. *Ambio* **2007**, *36*, 186–194.
- (8) Gustafsson, B.; Schenk, F.; Blenckner, T.; Eilola, K.; Meier, M.; Müller-Karulis, B.; Neumann, T.; Ruoho Airola, T.; Savchuk, O.; Eduardo, Z. Reconstructing the development of Baltic Sea eutrophication 1850–2006. *Ambio* **2012**, *41*, 534–548.
- (9) Conley, D.; Carstensen, J.; Aigars, J.; Axe, P.; Bonsdorff, E.; Eremina, T.; Hahti, B.-M.; Humborg, C.; Jonsson, P.; Kotta, J.; Lännergren, C.; Larsson, U.; Maximov, A.; Medina, M. R.; Lysiak-Pastuszak, E.; Remeikait Nikien, N.; Walve, J.; Wilhelms, S.; Zillen, L. Hypoxia is increasing in the coastal zone of the Baltic Sea. *Environ. Sci. Technol.* **2011**, *45*, 6777–6783.
- (10) Psenner, R.; Boström, B.; Dinka, M.; Pettersson, K.; Puckso, R. Fractionation of suspended matter and sediment. *Arch. Hydrobiol. Beih. Ergebn. Limnol.* **1988**, *30*, 98–103.
- (11) Rydin, E. Inactivated phosphorus by added aluminum in Baltic Sea sediment. *Estuarine, Coastal Shelf Sci.* **2014**, *151*, 181–185.
- (12) Blomqvist, P. A proposed standard method for composite sampling of water chemistry and plankton in small lakes. *Environ. Ecol. Stat.* **2001**, *8*, 121–134.
- (13) Swedish Standards Institute (SIS). Water quality - Determination of phosphorus - Ammonium molybdate spectrometric method (ISO 6878:2004), 2004; <http://www.sis.se>.
- (14) Swedish Standards Institute (SIS). Water quality - Determination of nitrite nitrogen and nitrate nitrogen and the sum of both by flow analysis (CFA and FIA) and spectrometric detection (ISO 13395:1996), 1996; <http://www.sis.se>.
- (15) Swedish Standards Institute (SIS). Water quality - Determination of ammonium nitrogen - Method by flow analysis (CFA and FIA) and spectrometric detection (ISO 11732:2005), 2005; <http://www.sis.se>.
- (16) Swedish Standards Institute (SIS). Determination of sulphide content of pure water and non-polluted natural water; Colorimetric method (SS 28115:1976), 1976; <http://www.sis.se>.
- (17) Swedish Standards Institute (SIS). Water quality - Determination of dissolved oxygen - Electrochemical probe method (ISO 5814:2012), 2012; <http://www.sis.se>.
- (18) Swedish Standards Institute (SIS). Water quality - Determination of electrical conductivity (ISO 7888:1985), 1985; <http://www.sis.se>.
- (19) Swedish Standards Institute (SIS). Determination of chlorophyll in water - Extraction with acetone; Spectrophotometric method (SS 28146), 1980; <http://www.sis.se>.

- (20) Swedish Standards Institute (SIS). Water quality - Guidance standard on the enumeration of phytoplankton using inverted microscopy (Utermöhl technique) (SS-EN 15204:2006), 2006; <http://www.sis.se>.
- (21) Kautsky, H. Methods for monitoring of phyto-benthic plant and animal communities in the Baltic Sea. In: Plinski, M. (ed.). *Ecology of Baltic Terrestrial, Coastal and Offshore Areas -Protection and Management*. Proc. Conf. in Sopot. Part 1-Marine Environment, Gdańsk, Poland, 1993, 21–59.
- (22) HELCOM. Manual for marine monitoring in the COMBINE Programme of HELCOM, 2001; <http://www.helcom.fi>.
- (23) HELCOM. HELCOM Core Indicators, 2013; <http://www.helcom.fi/Lists/Publications/BSEP136.pdf>.
- (24) Bergström, S. *The HBV model – its structure and applications*, 1992; <http://www.smhi.se>.
- (25) Bates, D.; Maechler, M.; Bolker, B.; Walker, W. Fitting Linear Mixed-Effects Models Using lme4. *J. Stat. Softw.* **2015**, *67*, 1–48.
- (26) R Core Team. *R: A Language and Environment for Statistical Computing*; R Foundation for Statistical Computing: Vienna, Austria, 2015; <https://www.R-project.org>.
- (27) Clarke, K.; Warwick, R. *Change in Marine Communities: An Approach to Statistical Analysis and Interpretation*, 2nd ed.; Primer-E Ltd.: Plymouth, 2001.
- (28) Clarke, R.; Somerfield, P.; Chapman, G. On resemblance measures for ecological studies, including taxonomic dissimilarities and zero-adjusted Bray-Curtis coefficient for denuded assemblages. *J. Exp. Mar. Biol. Ecol.* **2006**, *330*, 55–80.
- (29) Jensen, H.; Andersen, F. Sulfate reduction in a coastal lake during summer stratification. *Arch. Hydrobiol.* **1987**, *108*, 465–481.
- (30) Nürnberg, G. Trophic state of clear and colored, soft- and hardwater lakes with special consideration of nutrients, anoxia, phytoplankton and fish. *Lake Reservoir Manage.* **1996**, *12*, 432–447.
- (31) Dimberg, P.; Bryhn, A. Predicted effects from abatement action against eutrophication in two small bays of the Baltic Sea. *Environ. Earth Sci.* **2014**, *72*, 1191–1199.
- (32) Svealands Kustvattenvårdsförbund (SKVVF). Resultat från karteringar 2001–2015 (p32–25). Svealandskusten 2016. ISBN: 978-91-980325-4-3, 2016; <http://havet.nu/dokument/Svealandskusten2016.pdf>.
- (33) Kemp, W.; Testa, J.; Conley, D.; Gilbert, D.; Hagy, J. Temporal responses of coastal hypoxia to nutrient loading and physical controls. *Biogeosciences* **2009**, *6*, 2985–3008.
- (34) Huser, B.; Egemose, S.; Harper, H.; Hupfer, M.; Jensen, H.; Pilgrim, K.; Reitzel, K.; Rydin, E.; Futter, M. Longevity and effectiveness of aluminum addition to reduce sediment phosphorus release and restore lake water quality. *Water Res.* **2016**, *97*, 122–132.
- (35) Cooke, G.; Welch, E.; Peterson, E. S.; Nicols, S. *Restoration and Management of Lakes and Reservoirs*, 3rd ed.; CRC Press: Boca Raton, 2005.
- (36) Carstensen, J.; Conley, D.; Bonsdorff, E.; Gustafsson, B.; Hietanen, S.; Janas, U.; Jilbert, T.; Maximov, A.; Norkko, A.; Norkko, J.; Reed, D.; Slomp, C.; Timmermann, K.; Voss, M. Hypoxia in the Baltic Sea: Biogeochemical Cycles, Benthic Fauna, and Management. *Ambio* **2014**, *43*, 6–36.
- (37) Stigebrandt, A.; Gustafsson, B. Improvement of Baltic Proper Water Quality Using Large-scale Ecological Engineering. *Ambio* **2007**, *36*, 280–286.
- (38) Spears, B.; Mackay, E.; Yasseri, S.; Gunn, I.; Waters, K.; Andrews, C.; Cole, S.; De Ville, M.; Kelly, A.; Meis, S.; Moore, A.; Nürnberg, G.; van Oosterhout, F.; Pitt, J.-A.; Madgwick, G.; Woods, H.; Lürling, M. A meta-analysis of water quality and aquatic macrophyte responses in 18 lakes treated with lanthanum modified bentonite (Phoslock®). *Water Res.* **2016**, *97*, 111–121.
- (39) Bernes, C.; Carpenter, S.; Gärdmark, A.; Larsson, P.; Persson, L.; Skov, C.; Speed, J. D. M.; Van Donk, E. What is the influence of a reduction of planktivorous and benthivorous fish on water quality in temperate eutrophic lakes? *Environ. Evid.* **2015**, *4*, 7.
- (40) Puttonen, I.; Mattila, J.; Jonsson, P.; Karlsson, M.; Kohonen, T.; Kotilainen, A.; Lukkari, K.; Malmäus, M.; Rydin, E. Distribution and estimated release of sediment phosphorus in the northern Baltic Sea archipelagos. *Estuarine, Coastal Shelf Sci.* **2014**, *145*, 9–21.
- (41) Conley, D. Save the Baltic Sea. *Nature* **2012**, *486*, 463–464.
- (42) Conley, D.; Bonsdorff, E.; Carstensen, J.; Destouni, G.; Gustafsson, B.; Hansson, L.-A.; Rabalais, N.; Voss, M.; Zillén, L. Tackling hypoxia in the Baltic Sea: is engineering a solution? *Environ. Sci. Technol.* **2009**, *43*, 3407–3411.
- (43) Kumblad, L.; Rydin, E.; Sjö Lilliesköld, G.; Mörk, E. Fosforfällning för en förbättrad skärgårdsmiljö: ett mesokosmförsök. (BalticSea2020/Swedish Ecology Consulting, 2011); <http://go.nature.com/o4x6om> (in Swedish) (2012).
- (44) Spears, B.; Bernard, D.; Reitzel, K.; Rydin, E. Geo-Engineering in Lakes - A Call for Consensus. *Environ. Sci. Technol.* **2013**, *24*, 3953–3954.
- (45) Gensmer, R. W.; Playle, R. C. The Bioavailability and Toxicity of Aluminum in Aquatic Environments. *Crit. Rev. Environ. Sci. Technol.* **1999**, *29*, 315–450.
- (46) Elmgren, R.; Kumblad, L.; Rydin, E.; Wulff, F. Political backing to save the Baltic Sea. *Nature* **2012**, *487*, 432.
- (47) Savchuk, O.; Wulff, F.; Hille, S.; Pollehne, F. The Baltic Sea a century ago - a reconstruction from model simulations, verified by observations. *J. Mar. Syst.* **2008**, *74*, 485–494.
- (48) Robertson, L.; Langner, J.; Engardt, M. An Eulerian limited-area atmospheric transport model. *J. Appl. Meteor.* **1999**, *38*, 190–210.