Estimation of the natural background of phosphate in a lowland river using tidal marsh sediment cores

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Abstract. Elevated phosphate (PO_4) concentrations can harm the ecological status in water by eutrophication. In the majority of surface waters in lowland regions such as Flanders (Belgium), the local PO_4 levels exceed the limits defined by environmental policy and fail to decrease, despite decreasing total phosphorus (P) emissions. In order to underpin the definition of currents limits, this study was set up to identify the pre-industrial background PO_4 concentration in surface water of the Scheldt river, a tidal river in Flanders. We used the sedimentary records preserved in tidal marsh sediment cores as an archive for reconstructing historical changes in surface water PO_4. For sediment samples at sequential depths below the sediment surface, we dated the time of sediment deposition and analysed the extractable sediment-P. The resulting time series of sediment-P was linked to the time series of measured surface water-PO_4 concentrations (data 1967-present). By combining those datasets, the sorption characteristics of the sediment could be described using a Langmuir type sorption model. The calibrated sorption model allowed us to estimate a pre-industrial background surface water PO_4 levels, based on deeper sediment-P that stabilised at concentrations smaller than the modern. In three out of the four cores, the sediment-P peaked around 1980, coinciding with the surface water PO_4. The estimated pre-industrial (~1800) background PO_4-concentration in the Scheldt river water was 62 [57; 66 (95%CI)] µg PO_4-P L^{-1}. That concentration exceeds the previously estimated natural background values in Flanders (15-35 µg TP L^{-1}) and is about half of the prevailing limit in the Scheldt river (120 µg PO_4-P L^{-1}). In the 1930s, river water concentrations were estimated at 140 [128; 148] µg PO_4-P L^{-1}, already exceeding the current limit. The method developed here proved useful for reconstructing historical, background PO_4 concentrations of a lowland tidal river. A similar approach can apply to other lowland tidal rivers to provide a scientific basis for local, catchment specific PO_4 backgrounds.

1 Introduction

Excess phosphorus (P) concentrations in surface waters is a global problem (Azevedo et al., 2015; Dodds and Smith, 2016; Elser et al., 2007). Eutrophication by excess nutrients, including phosphate (PO_4), nitrogen (N) can lead to hypoxia, acidification, and harmful algal blooms (Azevedo et al., 2015; Correll, 1998; Watson et al., 2018). Therefore, limiting P concentrations in the surface water is crucial to ensure a good ecological status. Lowland river systems are at higher risk for eutrophication than upland streams (Watson et al., 2018). As a result, eutrophication of lowland rivers is on the international agenda (Jarvie et al., 2006; Mainstone and Parr, 2002; Reynolds, 2000). This study focuses on dissolved orthophosphate (PO_4), almost identical to the reactive P determined by a colour reaction. Other P forms present in surface water include organic P fractions, and P adsorbed to mineral colloids. Total P (TP) refers to all P forms together. The environmental limits for P are either expressed as reactive P (equated to PO_4-P limits), as TP limits or both.

The lowland rivers of densely populated regions do not achieve good water quality mainly due to the excess of nutrients (Bitschofsky and Nausch, 2019; Huet, 1990; Van Der Molen et al., 1998; Van Puijenbroek et al., 2014; Rönspieß et al., 2020; Schulz and Herzog, 2004). For example, since 2004, the average PO_4 concentration in Flemish waterways has stabilised at 290 µg PO_4-P L^{-1}. That concentration is well above the limits varying between 70-140 µg PO_4-P L^{-1} for different river types (Smolders et al., 2017; VMM, 2018). Despite the current net-zero P-balance in agricultural soils in that region, the situation did not improve since 2004 (VMM, 2017). The question arises when, or even if these limits can be achieved.

Since 2000, the European Union has regulated surface water quality with the Water Framework Directive 2000/60/EC (WFD), which does not prescribe limits but provides a framework for local regulations. The WFD has identified a high ecological status of a river if nutrient conditions remain within the range associated with undisturbed conditions, i.e natural background levels (European Commission, 2000). However, the definition of the natural background has been subject to debate for many river basins (Matschullat et al., 2000; van Raaphorst et al., 2000). The natural background can be defined as the situation (concentration range) found in the environment without any human activity, reflecting only natural geochemical processes (Laane, 1992; Reimann and Garrett, 2005). This definition implies that concentrations must be estimated before human activity, which is not always feasible. Therefore, a pre-industrial background can be defined instead, inferred from samples dating before the industrial revolution (Reimann and Garrett, 2005). The pre-industrial background can logically be affected by anthropogenic processes. Alternatively, natural background concentrations can be estimated by sampling regions with an expected minimal anthropogenic influence, i.e. reference lakes and rivers (Cardoso et al., 2007). Natural background concentrations have been established for different chemical elements in rivers in Europe, however that did not include TP or PO_4-P (Salminen et al., 2005).

65   For P in densely populated regions such as Flanders, the natural background concentrations can only be inferred indirectly. Natural background TP concentrations for Flanders were set at 15-35 µg P L^{-1}, inferred from reference lakes sampled in Central and Baltic states in Europe (Cardoso et al., 2007). However, the natural background PO$_4$-P concentrations of lowland rivers may be higher than those of upland rivers. For example, diatom assemblages revealed natural eutrophic conditions in The Spree river in Germany with TP concentrations of 80 µg L^{-1}, compared to recent data of 120 µg TP L^{-1} (Schönfelder and

70   Steinberg, 2004; Zak et al., 2006).

Lowland rivers can be significantly loaded with P derived from the river bed sediment, defined as internal loading (Froelich, 1988). The internal loading of P better explains temporal and spatial trends in river P concentrations than the P emissions of the lowland river system of Flanders (Smolders et al., 2017). Biogeochemical processes in the sediment explain that result.

75   Ferric iron- (Fe(III)) and aluminium-oxyhydroxides have a high affinity for PO$_4$-anions and limit the PO$_4$ in solution (Borggaard, 1990; Holtan et al., 1988). However, anoxic conditions lead to the reductive dissolution of those Fe(III) minerals releasing the associated P to the overlying water when the sediment is strongly reduced (Baken et al., 2015; van Dael et al., 2020). The small rivers and ditches in lowland regions have a low water velocity and are nutrient-rich, leading to anoxic conditions during summer and fall. Those anoxic events explain the typical summer peaks in PO$_4$ in small rivers. Moreover,

80   regional differences in sediment P/Fe concentration ratios explain regional differences in surface water PO$_4$ concentrations (Smolders et al., 2017).

Sediment analysis is linked to surface water P and can be a valuable tool for assessing historical river water quality. In surface waters, sediments can serve as a sink or a source of PO$_4$, depending on the sediment surface chemistry and water concentrations

85   (Froelich, 1988; House and Denison, 1998; Simpson et al., 2021; van der Zee et al., 2007). For example, P storage on fine bed sediments can amount to 60% of a catchment nutrient budget (Ballantine et al., 2009; Svendsen and Kronvang, 1993). The essential processes for PO$_4$ are adsorption and desorption from Fe oxy-hydroxides, present in the suspended matter or bed sediments (Froelich, 1988; van Raaphorst and Kloosterhuis, 1994; van der Zee et al., 2007). Sediments-P concentrations can likely predict surface water P concentrations and has been relevant for the long term reconstruction of P in the environment

90   (Wang et al., 2009; Zhou et al., 2005). For example, Boyle et al. (2015) used P profiles from lake sediments in the UK to infer catchment P inputs over the last 10.000 years and linked that to the historical evolution in population density. Similarly, banded iron formations in deep oceanic waters allowed inferring oceanic P concentrations of over two billion years ago (Bjerrum and Canfield, 2002). Likewise, the sediments deposited by rivers or lakes react with surface water PO$_4$ and are deposited in regularly flooded areas. Thus, those sediments can serve as an archive for reconstructing historical P emissions trends and

95   provide useful information on historical P concentrations in adjacent water bodies (Birch et al., 2008).

In lowland rivers with tidal influence, like the Scheldt, vegetated tidal marshes develop along the river banks. Tidal marshes directly adjacent to tidal rivers are regularly flooded during high tides: these flooding events deposit sediments and associated

elements like P on the densely vegetated marsh surface (Friedrichs and Perry, 2001; De Swart and Zimmerman, 2009; Temmerman et al., 2004a). The net accumulation of sediments increases the elevation of tidal marshes over time (Temmerman et al., 2003a). Therefore, researchers have used tidal marshes as sediment archives of deposited substances other than P, such as organic carbon (Van de Broek et al., 2019) and silicon (Struyf et al., 2007). However, it remains to be investigated to what extent P concentrations measured in tidal marsh sediment archives can be used to reconstruct historical changes in PO_4 concentrations in the adjacent estuary.

This study tested and evaluated a methodology to estimate the pre-industrial background water PO_4 concentrations based on the analysis of tidal marsh sediment. Those sediments had been deposited over multiple centuries on the banks of Flanders largest tidal river, the Scheldt. Using sediment analysis and a sorption model provided the first estimate of pre-industrial PO_4 levels in a large lowland river. First, we described the tidal marsh sediment sorption characteristics by linking the P concentration of tidal marsh sediments to historical measurements of PO_4 in the Scheldt river water. Those sorption characteristics allowed an estimation of historical river water PO_4 concentrations. This estimate was based on an analysis of sediments deposited in the 1800s or before industrialisation. The underlying assumption is that sediment-P remains immobile and that the sediments depth profile reflects the historical trend of PO_4 in the Scheldt river. Accordingly, we argue that the sediment P-composition in deeper sediment layers of tidal marshes provides an archive of the historic PO_4 concentration of the adjacent river. A database containing measurements of the PO_4 concentration in the Scheldt river's surface water (1967-current) verified this assumption. This study hypothesises that the previously estimated natural background P of this major lowland river is larger than that estimated earlier for lakes (15-35 μg P L^{-1}).

2 Materials and methods

2.1 Study area

Freshwater tidal marshes were sampled at four locations along the Scheldt river (Fig. 1, Table S1). The Scheldt estuary is located in northern Belgium and the south-western Netherlands and flows into the North Sea. The river basin of the Scheldt covers a large part of Flanders (71%) and the adjacent region of Northern France; the total catchment area is approximately 22.000 km^2. The population living in the river basin is about 10 million (Meire et al., 2005). The tidal wave extends from the mouth (Vlissingen) to 160 km upstream near Ghent, where sluices stop the tidal wave. The estuary's freshwater tidal zone reaches from Ghent to Rupelmonde (Fig. 1). This research focused on freshwater tidal marshes, i.e. located in this freshwater tidal zone of the estuary. Brackish waters experience the mixing of seawater, making it difficult to distinguish the anthropogenic sources from seawater influence. Furthermore, saltwater in the North Sea has PO_4 concentrations about a factor ten lower than fresh water in the Scheldt river (Burson et al., 2016). This research was focused on freshwater, lowland river systems and the human influence on the P concentrations, saltwater environments were beyond the scope of this study.
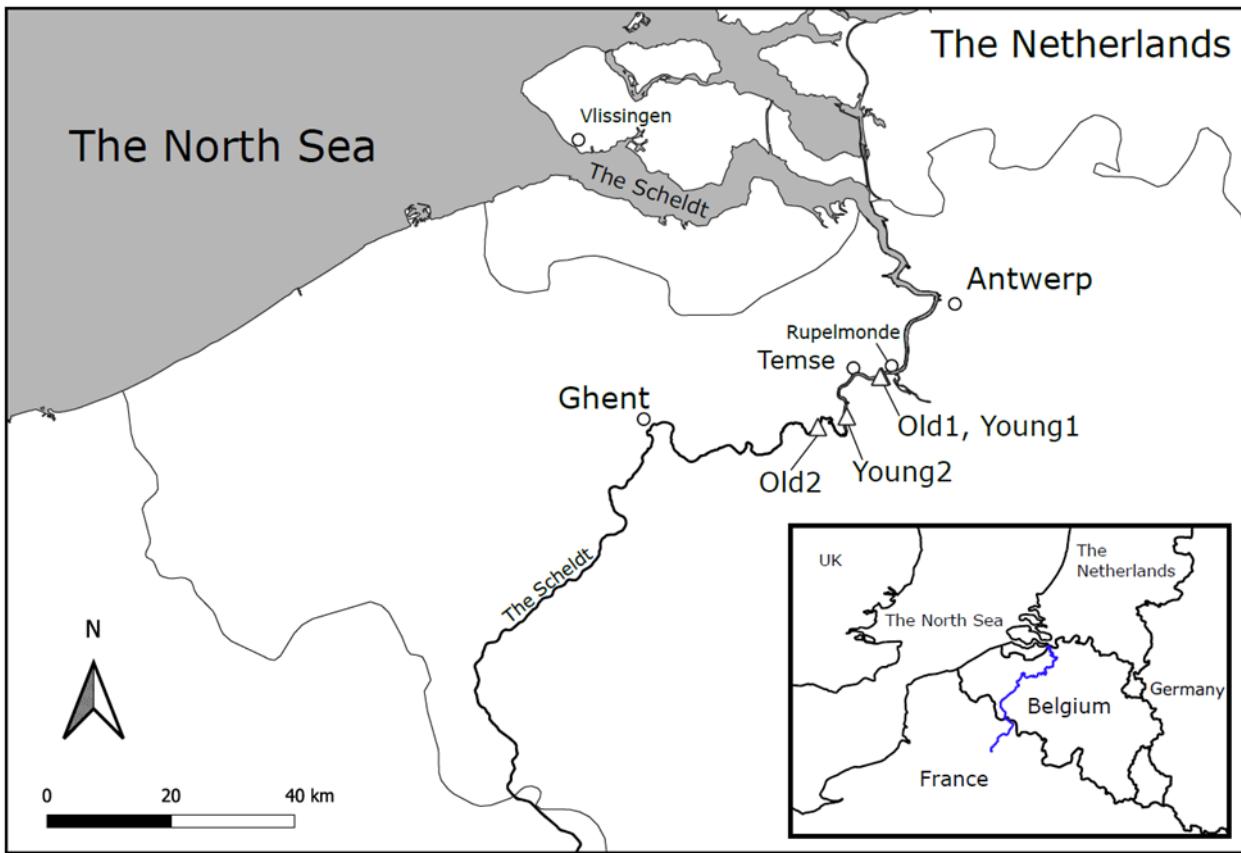
Figure 1: Map of the Scheldt Estuary, triangles indicate the locations of the sampled tidal marshes, Old1 and Young1 were only 250 m apart, and on the scale of the map, they overlap

Sediment accreting in tidal marshes originates from the deposition of riverine suspended matter, including inorganic mineral sediment and organic matter (Callaway et al., 1996). We discriminate between old and young tidal marshes, hereafter referred to as marshes. Old marshes have a higher elevation compared to young marshes. As a general mechanism, young marsh surfaces accumulate sediments quickly and increase their elevation asymptotically up to an equilibrium level, which is around the mean high water level (MHWL)(Pethick, 1981; Temmerman et al., 2003a). Temmerman et al. (2003a) defined an old marsh as visible on topographic maps of Ferraris (1774 - 1777), so it was formed before the 19th century (Temmerman et al., 2003a). Young marshes in the Scheldt estuary were formed more recently, by the natural establishment of pioneer marsh vegetation on formerly bare tidal mudflats, generally after 1944. During the last decades, the young marshes had a surface elevation below MHWL. As a result, young marshes experienced more frequent inundations and had larger sediment accretion rates than old marshes. For example, between 1931 and 1951, young marshes accumulated at rates of 1.6 to 3.2 cm yr^{-1}. In contrast, the elevation of old marshes was very close to the yearly MHWL increase rate of 0.3 to 0.6 cm yr^{-1} in the Western Scheldt (Temmerman et al., 2003a).

This study analysed depth profiles of sediment cores originating from tidal marshes along the freshwater Scheldt river. The analysis contained two old and two young marshes, Old1, Old2, Young1 and Young2 (locations indicated in Fig. 1). The coordinates of sampling locations can be found in (Van de Broek et al., 2018; Van De Broek et al., 2016) and supplementary information (SI.I). Marshes Old1 and Young1 originated from the Tidal marsh named the Notelaer, Old 2 from Grembergen
150 and Young2 from Mariekerke. Eight cores were analysed; three replicate cores for both sites Old1 and Young 1 and one core for Old2 and Young2.

2.2 PO_4 concentration in surface waters

The Flanders Marine Institute (IMIS) provided surface water phosphate (PO_4) data measured colourimetrically on a filtered water sample and total phosphorus (TP) by acid digestion and a segmented flow analyser. Concentration data of PO_4 in Scheldt
155 river were available from 1967 to 2019, originating from different sources and compiled by the Research program environmental effects Sigmaplan (OMES). The OMES program did additional quality controls on the data (ECOBE - UA; The Flemish Waterway, 2019). The different sources described in the supplementary information (SI.V) (De Pauw, 2007; ECOBE - UAntwerpen, 2007; Institute for Hygiene en Epidemiology (IHE), 2007; *OMES: Monitoring physical-chemical water quality in the Zeeschelde*, 2016; Van Meel, 1958).
160 The open-source software R (R Core Team, 2020) was used to compile all available datasets for PO_4 closest to the study sites (Temse) and to calculate annual means by averaging all observations within a year. The annual means of PO_4 were used to visualise the evolution of PO_4 in the Scheldt river (Fig. 2). The emissions of P mainly originate from point sources due to domestic loading (Billen et al., 2005). As a result, the increasing surface water P concentration between 1950 and 1975 can be related to the rise in the number of households connected to sewer systems. At first, no wastewater treatment was in place,
165 resulting in a sharp increase in nutrient loads to the river. However, since 1985, wastewater treatment has significantly improved the situation (Billen et al., 2005).
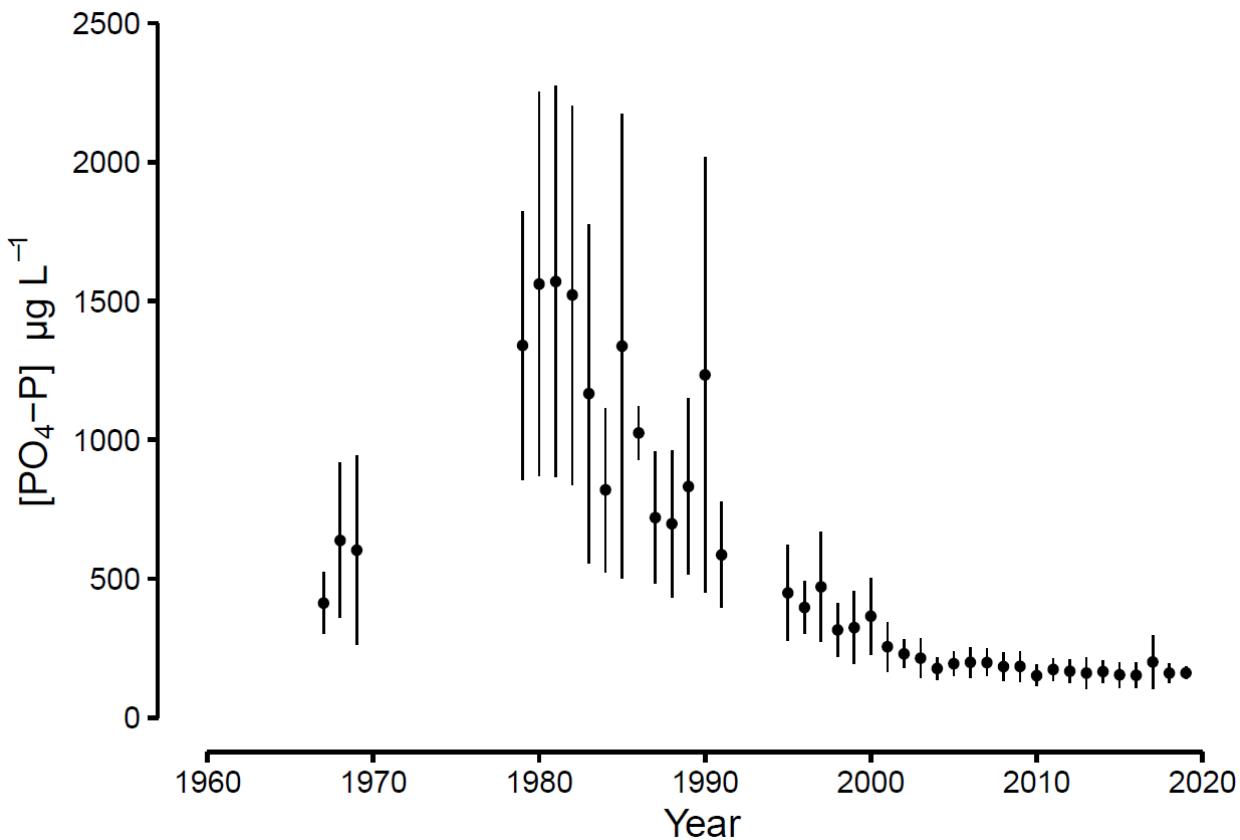
Figure 2. Concentrations of phosphate in the Scheldt River at Temse, annual means and standard deviation (error bar) around the annual mean. Samples were taken in Temse close to tidal marsh sites. (data sources: (ECOBE-UA and De Vlaamse Waterweg, 2016; ECOBE - UAntwerpen, 2007; Institute voor Hygiëne en Epidemiologie (IHE), 2007; Van Meel, 1958; De Pauw, 2007)

2.3 Sediment sampling

The sediment samples used here had been collected during a previous study about carbon sequestration in tidal marsh sediments in the Scheldt estuary (Van de Broek et al., 2018; Van De Broek et al., 2016). Collection of undisturbed sediment profiles on the tidal marshes took place between July and September 2016 (Old1, Young1, Old2, Young2; Fig. 1). Undisturbed sediment cores were taken at each sampling location using a gauge auger (0.06 m diameter). The cores were divided into subsamples with a 0.03 m interval. The sediment samples were dried at a maximum temperature of 50 °C for 48 hours, crushed and sieved to a <2 mm grain size. Macroscopic vegetation residues were removed manually using tweezers (Van de Broek et al., 2018). Bulk density, grain size distribution and organic carbon (OC) content were analysed by Van de Broek *et al.* (2018). We refer to Van de Broek et al. (2016, 2018) for further sample collection and processing information.

2.4 Sediment analysis

The dried sediment samples were analysed for oxalate-extractable P, Fe, Al and Mn (P_{ox}, Fe_{ox}, Al_{ox}, Mn_{ox}; Schwertmann, 1964). The preparation of extraction solution and dilutions were made with ultrapure water (Milli-Q®), and all glassware was acid-soaked overnight in a 1% HCl acid bath to prevent P contamination. That acid oxalate extractant, a mixture of ammonium oxalate (0.2 M) and oxalic acid (0.2 M) at pH = 3, targets poorly crystalline oxyhydroxides of Fe, Al and Mn and the associated P (Schwertmann, 1964). Those poorly crystalline oxyhydroxides are the most reactive due to their large specific surface area (Hiemstra et al., 2010). The extraction was done with 1 g of dry sediment in 50 ml extraction solution over two hours in an end-over-end shaker at 20°C (26 rpm). The suspension was filtered through a 0.45 µm membrane filter (CHROMAFIL ® Xtra PET - 45/25). Analytical blanks, internal reference samples, and duplicate samples were included in every batch to ensure the analysis's quality, purity, and reproducibility. The extracts were diluted 20 times and measured by inductively coupled plasma optical emission spectrometry (ICP-OES). The degree of P-saturation (DPS; %) was calculated as in Eq. (1). The DPS represents the extractable (P_{ox}) ratio to the P sorption capacity of the sediment. This P sorption capacity is estimated as half of the sum of oxalate Fe_{ox} and Al_{ox}, because not all the Fe and Al in the soil is available for P sorption with Fe_{ox}, Al_{ox} and P_{ox} in molar units.

$$DPS = \frac{P_{ox}}{0.5(Fe_{ox} + Al_{ox})} 100\%, \tag{1}$$

The DPS is expressed in percentage and can be interpreted as the ratio of sorption sites on the sediment occupied by P. Previous research used the DPS to identify agricultural areas sensitive to phosphate leaching and showed a good correlation with pore water P concentrations (Breeuwsma et al., 1995; Lookman et al., 1995; Schoumans and Chardon, 2015; Schoumans and Groenendijk, 2000; van der Zee, 1988). The DPS relation for porewater-soil systems was developed and verified by van der Zee et al. (1990). Lexmond et al. (1982) illustrated that the maximal sorbed P was about half the pool available after a long-term precipitation experiment. Therefore, the factor 0.5 is an empirical value representing the soil's sorption capacity. The parameter α primarily affects the maximum sorption capacity. So they set α at 0.5 ± 0.1. However, even among soils, this parameter varied between 0.3 and 0.6 (Lexmond et al., 1982). For this research, low background concentrations are to most important, so maximal sorption occurring at high PO_4 concentrations is less relevant.

2.5 Age-depth model

The sediment analysis and the surface water PO_4 data had to be linked by a corresponding date and location to fit a sorption model. Therefore, an age-depth model was used to calculate the time since deposition of each sediment sample. Temmerman et al. (2004b, 2004a) developed a time-stepping marsh sedimentation model (MARSED). That model estimates sediment deposition rates and the resulting evolution of the tidal marsh elevation in the Scheldt estuary. Hence, we could use MARSED to determine the time since deposition of sediments throughout the sampled sediment profiles. The MARSED model simulates the tidal supply of suspended sediments and the settling to the marsh surface during tidal inundation cycles integrated over the

years. The model was calibrated and validated against measured sediment deposition rates on the Scheldt estuary tidal marshes from 1945 until 2002 (Temmerman et al. 2003; 2004). The empirical data on sediment deposition rates were derived from radiometric and paleoenvironmental dating of sediment cores at the exact locations sampled for the present study (Temmerman et al., 2004a, 2004b).

For our current study, we extrapolated the MARSED model simulations of sediment accretion from 2002 until 2016, the sampling date of the sediment cores (Van de Broek et al. 2018). However, simulations overestimated the observed marsh surface elevation in 2016 by 25 cm for sampling location Old1, 29 cm for Young1, 19 cm for Old2, and 8 cm for Young2 (observed by RTK GPS surveying; Van de Broek et al. 2018; Poppelmonde, 2017). The MARSED model was initially designed to simulate the overall sediment accretion and surface elevation changes in tidal marshes in response to sea-level rise scenarios, for which those errors were acceptable. In contrast, the most important was the time of sediment deposition throughout the sediment profile for the present study. Therefore, the original age-depth relation calculated by MARSED was recalibrated using observed age-depth points. The observed age-depth points originated from GPS measurements of marsh elevation in 2016 (M. Van de Broek, unpublished data) and previously published radiometric and paleoenvironmental dating (Temmerman et al. 2003; 2004). This rescaling procedure is explained in the Supporting Information (Fig. S1, S2, S3, S4).

An approximate extrapolation procedure was used to estimate the sediment deposition time from depths below the oldest measured age-depth points (mentioned in the previous sentence). The observed age-depth points were available from 1958 for sampling site Old1, 1947 for Young1, 1963 for Old2 and 1968 for Young2 (Temmerman et al. 2004). This extrapolation procedure could only be applied for old marshes, which were defined as marshes that existed at least since the end of the 18th century (Temmerman et al. 2003a; 2004). Two sediment cores originated from old tidal marshes (Old1 and Old2). Based on observed age-depth points, it has been proven that the old marshes reached equilibrium with the MHWL before 1944. After 1944, Old marshes have built up their elevation at a rate comparable to local MHWL rise (Temmerman et al., 2003a). Here, we assumed that also between 1800 and 1944, these old marshes accreted at a rate comparable to the MHWL rise.

Historical tide gauge data of MHWL rise was available from 1901 for site Old1 and 1930 for site Old2 (ScheldeMonitor Team and VNSC, 2020; Temmerman et al., 2003a) and linear regression of the MHWL against time was used to estimate the marsh surface elevation before 1944 (Fig. S6, S7). However, the dating accuracy will be lower going further back in time. Furthermore, such extrapolation to earlier dates is not appropriate for young marshes, as they were only formed after 1950 by pioneer vegetation establishment on formerly bare mudflats (Temmerman et al. 2003a; 2004). Those mudflat sediment profiles do not have continuous sedimentary records as tidal marshes and are likely to be disturbed by erosion and sedimentation alternations (Belliard et al., 2019). Therefore, the sediment deposition time could not be extrapolated for the young marsh sampling locations.

2.6 Relating surface water PO₄ with sediment P: the sediment-water model

The age-depth model and linear regression of MHWL provided a deposition year for each sediment sample. Thereby, the dataset of water PO_4 between 1967-2016 was linked to the sediment DPS for each core. The resulting dataset contained all

245 available surface water PO$_4$ readings between 1967 and 2016, closest to the tidal marshes in Temse (n = 1932) and a corresponding DPS value. The DPS value of a sediment sample originates from a specific layer of one sediment core or a mean DPS of the replicate sediment samples. This dataset allowed to fit a sorption model further termed the sediment-water model. Schoumans and Groenendijk (2000) presented a Langmuir-type sorption model to predict PO$_4$ concentration leaching from a soil layer based on the DPS Eq. (2).

250 $$[PO_4] = K^{-1} \frac{DPS}{100-DPS},$$ (2)

With [PO$_4$] phosphate concentration in (kg L^{-1}), K the sorption constant (L kg^{-1}), DPS (degree of P-saturation; %). This model adequately described P sorption in soil across a wide range of pH values, including the Scheldt river pH (Schoumans and Groenendijk, 2000; Warrinnier et al., 2018). The model relies on surface complexation between PO$_4$ and Fe-, Al-oxyhydroxides in the sediment. That complexation is determined by a chemical equilibrium between solid (adsorbed) and

255 dissolved PO$_4$ phase (Warrinnier et al., 2019). The parameter K of existing soil models has been calibrated for soil - pore water system, and the sediment-water parameter (K) is unlikely equal. Therefore, the model was calibrated by fitting parameter K (Eq. 2) on sediment DPS measurements and recent Scheldt water PO$_4$ measurements. As a result, the fitted K-value is adapted to the local geochemistry of tidal marsh sediments and the surface water.

We explored 16 different scenarios to fit the sediment-water model Eq. (2). These scenarios illustrate the statistical uncertainty

260 surrounding the estimated PO$_4$ concentrations. The model was fitted separately for each site sediment core or on the combined replicate cores for Old1 and Young1 (SI.VI). Every sediment sample had between one and three replicates, depending on the depth and the site. The average value of these replicates was used or the individual replicates DPS values. One sediment sample covered several deposition years, so multiple PO$_4$ observations corresponded with each sediment sample. Again, the average of all corresponding PO$_4$ readings was taken, or all available values were used separately. The combination of mean or

265 individual DPS and PO$_4$ resulted in 16 models (Table S2). For each of these, the parameter K was fitted by non-linear least squares regression with R using Rstudio interface (R Core Team, 2020; RStudio Team, 2015).

2.7 Evaluation Model Performance

The predictions of the sediment-water model were evaluated based on several parameters; the Residual Standard Error (RSE), the Nash Sutcliffe Model Efficiency (E) and by plotting the measured surface water PO$_4$ against predicted PO$_4$ between 2007

270 and 2016 (Table S2; Fig. S10). Additionally, the percentage bias (Pbias) was calculated for data points between 2007 and 2016. The Pbias measures the average tendency of the simulated data to be larger or smaller than their observed counterparts. That difference is expressed as a percentage of deviation from the observations (Moriasi et al., 1983; Eq. 3). The predictions of recent years is interesting to evaluate the model's performance for two reasons. First, the most recent surface water PO$_4$-concentrations are relatively low and more representative of background concentrations. Second, the monitoring data have a

275 high temporal resolution, and the age-depth model is more accurate at shallow depths.

$$PBias = \frac{\sum_{i=1}^{n}(Y_i^{obs} - Y_i^{sim})}{\sum_{i=1}^{n} Y_i^{obs}} \qquad (3)$$

3 Results

3.1 History of surface water PO_4 concentrations

280   The Scheldt PO_4-concentrations varied greatly over the past decades, with the peak in surface water PO_4-concentrations between 1975 and 1985 (Fig. 2). In Temse, the annual mean concentrations rose from 410 µg PO_4-P L^{-1} in 1967 and peaked in 1980 with 1570 µg PO_4-P L^{-1}. Between 1990 and 2003 concentrations decreased and stabilised between 160 and 200 µg PO_4-P L^{-1} in Temse. The current PO_4-levels are a factor two lower than in 1967 and almost a factor ten lower than the peak in 1980 (Fig. 2; Table 1).

285   ### 3.2 Sediment cores

The P_{ox} in the sediments ranged between 370 mg P kg^{-1} and 13,000 mg P kg^{-1}, while the DPS ranged between 13% and 94% (Table 1). In all soil cores starting at the surface, the DPS and P_{ox} increased with depth and peaked at about 0.5 m below the surface (Fig. S7, Fig. S8). In deeper (>1.0 m) sediment layers, P_{ox} and DPS decreased and stabilised for Old1, Young1 and Young2 (Table 1). Overall, the P_{ox} increased by an average factor of 3.5 between the surface and the maximum concentrations

290   (Fig. S8, Table1). The sediments with these peak DPS were deposited between 1960 and 1985 in three of the four sediment cores (Fig. 2). Only the core Old2 peaked earlier (ca. 1940-1950). Most importantly for this work, DPS for Old1 showed an apparent stabilisation in deeper or older layers, which indicated undisturbed sediment layers (Fig. 3, Fig. S7).

Table 1: The sediment oxalate extractable P (P_{ox}) and its Degree of Phosphate Saturation (DPS) of the top, bottom, peak sediment layers at four different tidal marsh locations. Top layers are the sediments closest to the surface, peak layers had maximal P_{ox} and DPS, and bottom layers are those sediments sampled at the largest depth. Values of P_{ox} and DPS are means (± standard deviation) of N sediment samples, between top and bottom (cm) depth.

Location		N	Top – Bottom (cm)	P_{ox} (mg kg^{-1})	Fe_{ox} (mg kg^{-1})	Al_{ox} (mg kg^{-1})	DPS (%)
Old1	**Top**	4	0 - 9	2300 (± 2400)	21000 (± 1400)	1200 (± 130)	36 (± 3)
	Peak	7	27 - 57	5400 (± 1300)	24000 (±4700)	1800 (± 300)	70 (± 8)
	Bottom	8	147 - 180	540 (± 110)	8500 (± 750)	660 (±41)	20 (± 4)
Young1	**Top**	4	0 - 9	2700 (± 320)	24000 ± 1200	1400 (± 91)	37 (± 2)
	Peak	6	27 - 57	8500 (± 3200)	31000 (±7500)	2000 (± 120)	85 (± 15)
	Bottom	6	129 - 144	910 (± 440)	7000 (± 3900)	650 (±120)	40 (± 4)
Old2	**Top**	3	0 - 9	2800 (± 90)	19000 (± 230)	1700 (±36)	45 (± 1)
	Peak	3	54 – 69	8000 (± 1600)	25000 (± 6500)	2600 (± 360)	94 (± 2)
	Bottom	3	132 - 147	1700 (± 620)	11000 (± 3900)	1700 (± 300)	43 (± 6)
Young2	**Top**	3	0 - 9	2700 (± 410)	39000 (± 7800)	1300 (± 240)	23 (± 1)
	Peak	3	48 - 63	7000 (± 1200)	42000 (± 5400)	1900 (± 57)	55 (± 7)
	Bottom	3	144 - 183	3200 (± 110)	34000 (± 770)	1400 (± 78)	31 (± 2)

Within the first meter, Fe_{ox} was stable in the three soil cores (Old1, Young1, Old2) with concentrations around 20,000 mg kg⁻¹, except for Young2 for which Fe_{ox} was a factor two larger (Fig. S9). For Young1 and Young2, Fe_{ox} concentration decreased at depths > 1 m. For Old1, Fe_{ox} showed a steady decline from 20,000 mg kg⁻¹ at the surface to 10,000 mg kg⁻¹ at the bottom of

305   the profile (Fig. S9). The Al_{ox} concentrations showed a similar trend as the P_{ox} concentrations, with an initial increase followed by a decrease with depth. The strong correlations of Al_{ox} and Fe_{ox} with P_{ox} (r_{Al} = 0.73 and r_{Fe} = 0.65) illustrate the positive effect of Fe and Al oxyhydroxides on P sorption.
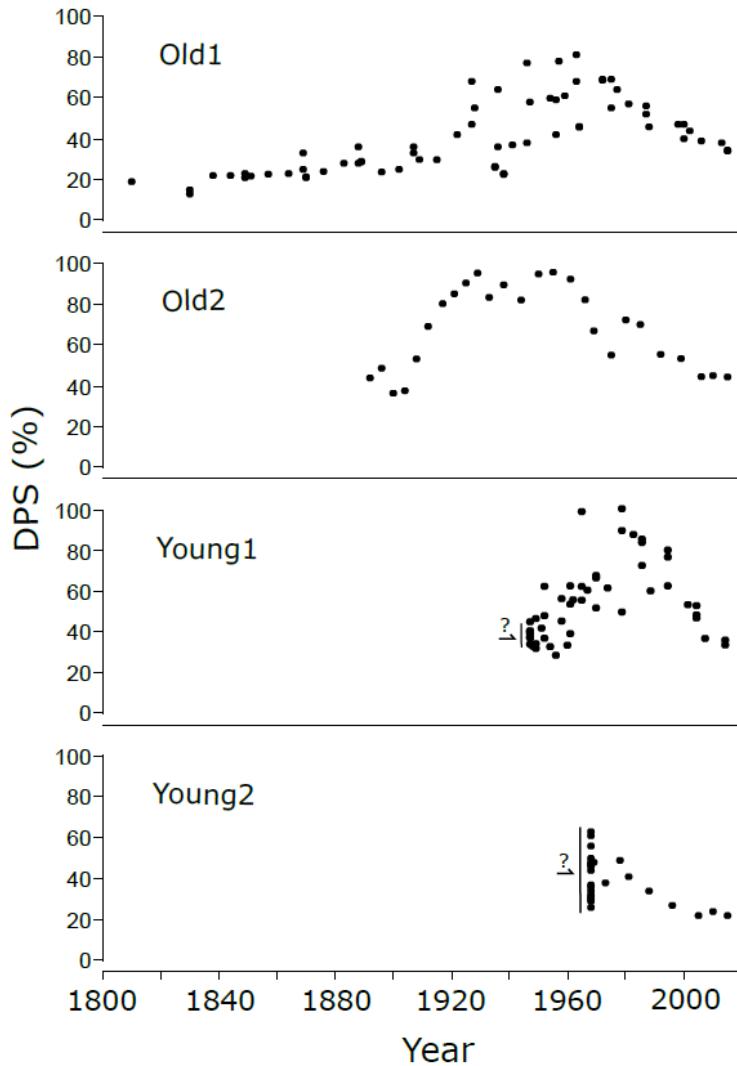
Figure 3: The Degree of Phosphate Saturation (DPS) timeline based on four tidal marsh sediment sites. Each dot represents a
310   **sediment analysis. The year assigned to each sediment analysis was calculated with the age-depth model. Before 1930, no model dates were available. Therefore a linear regression of the MHWL was used to extrapolate the dates for the old marshes. Dates before 1930 are increasingly uncertain going further back in time. For young marshes, such extrapolation was not possible. The points before the formation of the marshes are indicated with a question mark.**

3.3 Sediment core selection

Under the assumption that PO_4 does not migrate, the tidal marsh sediment cores can provide an archive for river water PO_4. Considering P-migration, it is crucial to evaluate the distance from a creek within the tidal marsh. That distance is essential for two reasons. First, within 10 to 20 m of the creeks, the groundwater table fluctuates largely with the tides, which can induce
320 vertical P-migration (Van Putte et al., 2020). Secondly, sediment accretion is more difficult to predict at closer distances to the creeks and can affect the age-depth relation (Temmerman et al., 2003b). The distance from the sediment cores to the nearest creak was 21 m for Old1, 56 m for Young1, 35 m for Young2 and 5 m for Old2.

The assumption that PO_4 does not migrate may be most violated at Old2 and Young2. The profile of Old2 indicated P-migration because it had a peak of P_{ox} at an earlier date (1950) than was expected from surface water data (1980) (Fig. 2). Consequently,
325 Old2 was not taken up to interpret the relation between DPS and PO_4. For core Young2, deeper sediment layers had a larger DPS than the surface layers (Table 2). Additionally, the age estimation of sediments older than 1968 was impossible due to this tidal marsh's young age. Furthermore, Fe_{ox} concentrations were a factor two larger than the other cores (Fig. S9) and a factor two larger than the average sediment Fe-concentration of the Upper-Scheldt basin (VMM, 2019). The local enrichment in iron lowers the DPS values and makes the core less representative of the average situation in the Scheldt. These observations
330 made Young2 inappropriate to fit the relation between DPS and PO_4.

The two remaining soil cores, Old1 and Young1, originated from the same tidal marsh area named "The Notelaer", located near the city of Temse (Fig. 1). That marsh has been the topic of multiple studies on sediment accretion (Temmerman et al., 2004b, 2003a) and soil OC stocks (Van de Broek et al., 2018; Van De Broek et al., 2016). The sediment profiles of both sites Old1 and Young1 rise and fall in DPS comparable to dynamics in surface water PO_4-concentrations (Fig. 2, Fig. 3). In deeper
335 sediment layers, DPS and P_{ox} stabilise below levels of recent deposits (Fig. S7, S8). The time series of Old1 displayed a DPS peak around 1960, indicating a shift of 20 years (Figure 2). However, the core Old1 was taken up for the model fitting because it dates back to 1800 at the deepest levels and is essential to predict the background. Furthermore, the DPS concentrations stabilised before 1920, indicating that P has not migrated to these depths, making it suitable for background prediction. These observations suggested a well-preserved P_{ox} and DPS profile, essential for the DPS-PO_4 relation. Therefore, Old1 and Young1
340 are considered the best profiles for applying the sediment-water model and interpretation of background concentrations.

Table 2: The predicted concentrations of phosphate (PO$_4$-P µgL^{-1}) in the Scheldt river based on the Degree of Phosphate Saturation (DPS) in the sediment layers of marsh Old1, dating back to 1800 (pre-industrial), where DPS values stabilised with depth at 20%. The predicted concentration dated to 1930, where DPS stabilised at 36%. The Pbias is the mean difference of simulated and observed data between 2007 and 2016, expressed as a percentage of the observed data. The conversion of DPS to river phosphate concentration is based on the association of DPS with PO$_4$-P. That association was calibrated to data 1967-2016, thereby using different sediment-water models; the details of models are in Table S2. Model 3b (in bold) is proposed as the most accurate (see text).

Model #	K (L kg^{-1}) [95% CI]	pre-industrial background ~1800 µg PO$_4$-P L^{-1} [95% CI]	~1930 µg PO$_4$-P L^{-1} [95% CI]	Pbias (2007 -2016)
1b	2.1×10^6 [2.0×10^6; 2.3×10^6]	120 [110; 130]	270 [245; 281]	62
2b	4.9×10^6 [4.6×10^6; 5.2×10^6]	51 [49; 54]	120 [109 ; 122]	-28
3b	**4.1×10^6 [3.8×10^6; 4.4×10^6]**	**62 [57; 66]**	**140 [128; 148]**	-15

3.4 Sediment-water model fit

The sediment-water model Eq. (2) was fitted on DPS-PO$_4$ data from the different sediment cores (Table S2). Two observations were omitted because the DPS values were too large (0.99 – 1.02) and produced artefacts in the results. The Nash-Sutcliffe model efficiency (E) ranged between 0.04 and 0.85 depending on the input data (Table S2; Nash and Sutcliffe, 1970). The sediment-water model was fitted on each core's data separately and combined data from Old1 and Young1, as they came from the same tidal marsh location. The models fitted on data from sites Old2 and Young2 were not considered as migration likely affected those cores (crf. section 3.3).

The models fitted on an average DPS (across replicates) associated with individual PO$_4$ readings were considered most suitable (Models 1b, 2b, 3b; Table S2). A single sediment sample analysis represents an average P signal over the sediment's deposition period. However, the age-depth relation can vary slightly due to the marsh surface elevation variation. By taking an average DPS from replicate cores, the variation in the independent variable was reduced. Furthermore, the prediction error increased in most models by relating individual rather than mean DPS values with individual PO$_4$ measurements (Table S2). Models using unique DPS associated with single PO$_4$-data duplicated or even triplicated the PO$_4$-data, artificially creating more degrees of freedom (Model 1c, 2c, 3c; Table S2). Using mean PO$_4$-values artificially reduced the degrees of freedom, compromising the model predictions by increasing RSE and widening confidence intervals (Models 1a, 2a, 3a; Table S2). The fitted parameter K (L kg^{-1}) ranged between 1.0×10^6 and 5.4×10^6 for the different input datasets, with the 95% confidence intervals ranging

365 between 0.8×10^6 and 7.2×10^6. The variation of parameter K for the various input datasets was larger than the individual confidence limits variation (Table S2). Thus, the uncertainty was more pronounced due to the variability in sediment samples than due to the model fit.

3.5 Model performance

The sediment-water model performance was evaluated with several parameters (RSE, Pbias, and E) and the actual by predicted
370 PO_4 concentrations over the last decade. Those recent PO_4 concentrations are more comparable to the background (Fig. S10; Table 2; mean Temse [2007-2016] = 170 µg PO_4-PL^{-1}). Model 3b was considered the most suitable for predicting background concentrations. The Pbias was the lowest for recent observations for model 3b. The average tendency of simulated data compared to the observations was only -14.9 %, which is within the acceptable range of ±25% (Moriasi et al., 1983). Model 2b had an underestimation of observed data of more than 28%, and model 1b overestimated recent observations by more than
375 60%. Such an overestimation is unwanted for calculating the background, and therefore, both were considered unsuitable (Table 2). The actual by predicted plots illustrate a similar message (Fig. S10). Based on these observations, model 3b was considered the best model, although the residual standard error (RSE) was lower for model 2b (Table S2). The selected model 3b successfully reconstructs the rise and fall in surface water PO_4-concentrations based on the sediment characteristic DPS (Fig. 4).
380

Maxima of monitored and predicted PO_4-concentrations coincide in time and have a similar size (Fig. 4). For example, in 1973, the average PO_4 concentration predicted by the model was 1200 µg PO_4-P µgL^{-1} and measured concentrations was on average 1300 µg PO_4-P µgL^{-1}. The maximal predicted PO_4 concentration was 2200 µg PO_4-PL^{-1}, while the maximal observed was 3000 µg PO_4-PL^{-1}. Predictions for recent years are within 15% of the observed data (e.g. 2015: Model: 133 µg PO_4-PL^{-1},
385 Measured 155 µg PO_4-PL^{-1}). Between 1940 and 1990, the modelled PO_4-concentrations had more variation. Likewise, monitored PO_4-data are spread more between 1967 and 1990 (Fig. 2). Before 1930, modelled PO_4-concentrations stabilised at levels below current observations (Fig. 4).
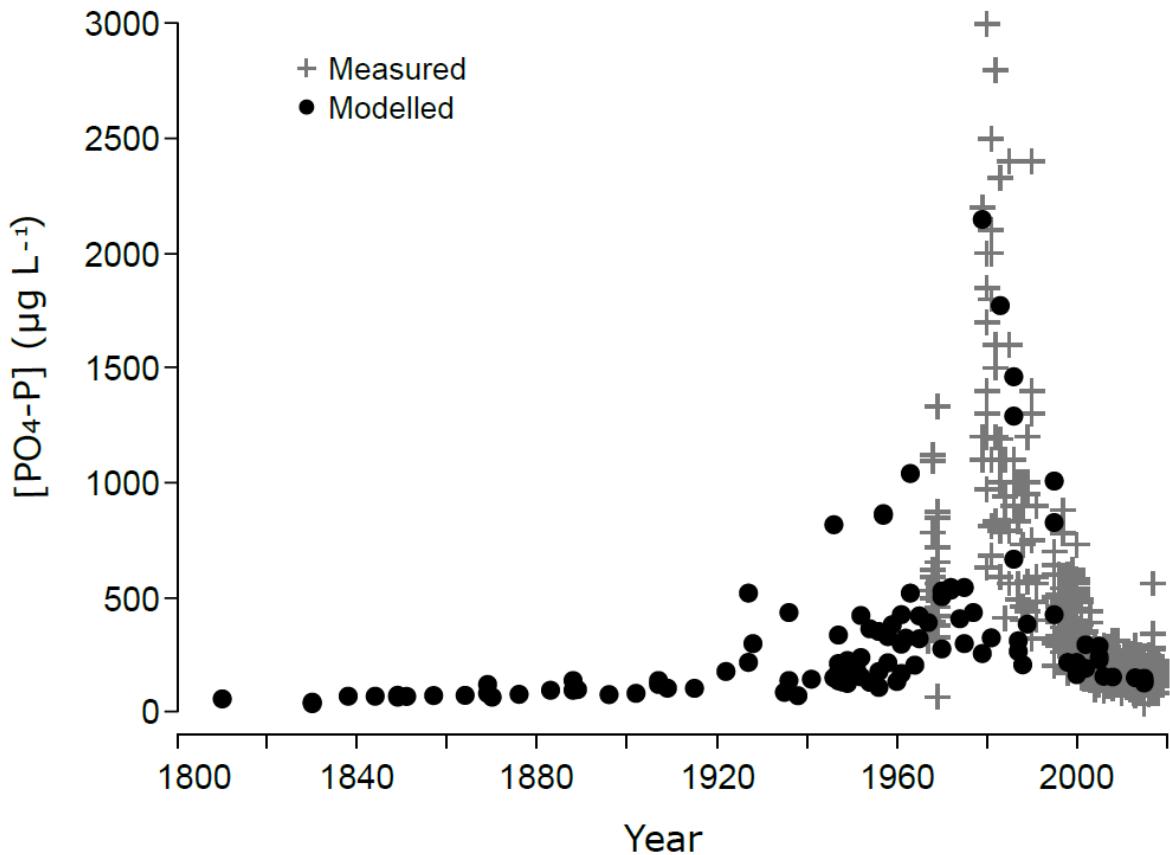
Figure 4: Measured (grey crosses; +) and predicted (black points) of PO₄-P concentrations (µgL⁻¹) in the Scheldt river in Temse. The concentrations are calculated from the sediment phosphate saturation (DPS) of the tidal marshes at Old1 and Young1, using sediment-water model 3b.

3.6 Estimating background PO₄ concentrations in the Scheldt river

The deepest sediment layers are most suitable for predicting background PO₄ concentrations of the Scheldt river water. These layers are the oldest and expected to have experienced the lowest impact of P additions from anthropogenic sources. The Old1 marsh site was appropriate for this purpose as it developed before 1774, before the industrial revolution in Belgium. The average DPS for the bottom sediments, dated between 1800 and 1840, was 20% for core Old1 (Table 1; Fig. 2); these samples are considered to represent the pre-industrial background. That DPS value produced PO₄-concentrations of 62 µg PO₄-PL⁻¹ [95%CI (57; 66)] for the pre-industrial background, using sediment-water model 3b (Table 2). The sediment dated to 1930 had a DPS of 36%. For that value, the same sediment-water model predicted a PO₄-concentration of 140 µg PO₄-P L⁻¹ [95%CI (128; 148)] (Table 2).

4 Discussion

4.1 Pre-industrial background vs ambient PO$_4$ concentrations.

This work presents a novel approach to reconstruct background surface water PO$_4$ concentration in a tidal river using the DPS of adjacent tidal marsh sediments. The background concentration is essential in the context of developing local nutrient limits. The predicted pre-industrial background concentration (62 µg PO$_4$-P L^{-1}; Table 2) is about half of the current surface limit of the Scheldt (120 µg PO$_4$-P L^{-1}; Flemish Government, 1995). Remarkably, the predicted background concentrations are about a factor two larger than the background estimates of lake waters for Flanders today (15-35 µg PO$_4$-P L^{-1}; Cardoso et al., 2007). That pre-industrial PO$_4$ concentration is about three times lower than the current concentration in the Scheldt. For example, between 2007 and 2016, the mean PO$_4$ concentration of the Scheldt in Temse was 170 µg PO$_4$-P L^{-1}. However, in the 1930s, the concentration was estimated at 140 µg PO$_4$-PL^{-1} and larger than current limits, at a time before widespread connection to sewer systems, P-loaded detergents, and application of mineral fertilisers.

Those results suggest that the sediment internal loading triggered by summer anoxia in lowland rivers contributes to larger PO$_4$ concentrations than estimated before (see introduction). The summer PO$_4$ peak lasts about five months per year in Flanders and largely affects the rivers' mean P concentrations (Smolders et al., 2017). Summer anoxia can occur in eutrophic lakes or sometimes in oligotrophic brown water lakes (Nürnberg, 1995). Additionally, lowland rivers in Flanders are primarily groundwater-fed, and 73% of streamflow can be attributed to base flow. The groundwater in Belgium has a median P concentration between 150 - 320 µg P L^{-1}(Edmunds and Shand, 2009). Therefore, groundwater feeding the river waters logically affects the river P concentrations. In contrast, primarily rain-fed lakes will have lower P concentrations, with rain P ranging between 1.5 and 120 µg P L^{-1} (Migon and Sandroni, 1999).

4.2 Limitations of the model

Care needs to be taken with background extrapolations to ensure that post-depositional processes have not modified the biogeochemical patterns and that the area represents the area of interest (Reimann and Garrett, 2005). Several factors can obscure the reconstructed background concentrations. First, vertical migration of P can enrich deeper sediment layers, causing an overestimation of the background. Second, the sediment profiles at the tidal marshes are almost permanently saturated, so the intrusion of P-rich groundwater could affect the P concentrations in the tidal marsh sediment. Moreover, depending on the tidal marsh elevation, periodic flooding occurs at an approximate range of 300-350 inundations per year (Temmerman et al., 2003b). These conditions could favour P migration due to the reductive dissolution of Fe (oxy)hydroxides (Baken et al., 2015; van Dael et al., 2020).

Two cores with indications of PO$_4$ migration were removed from the analysis to address the issue (Old2 and Young2). These cores were identified by the DPS age profile and considering the distance from the nearby creeks (Fig. 2; Fig. 1). Additionally, the DPS levels of the deepest sediment layers were compared with layers at the surface. The surface layers had lower DPS

levels than the deepest layers for one core (Young 2). The two remaining cores (Old1, Young1) had lower DPS levels in deeper

435 sediment layers (Fig. S7). More importantly, the modelled peak in PO_4 concentrations based on the cores Old1, Young1 were found within two years of the monitored peak and had a similar magnitude (Fig. 4). The coinciding peaks illustrate little migration of PO_4 in Old1 and Young1, thereby justifying these cores as an archive for water-PO_4.

The limited migration is also logical: at the average DPS of 90 % in sediment showing at the peak; the sorption models predict that the solid-liquid P concentration ratio is 2900 L kg^{-1} with the average K value of models of Table 2. That solid-liquid ratio

440 can be converted to a dimensionless retardation factor representing the ratio of the distance migrated by the PO_4 compared to the distance travelled by percolating water. For example, the retardation was calculated to be 7500 with a bulk density (ρb) of 1.3, porosity (θ) of 0.5 and a net vertical annual water percolation of about 2 meters. That retardation corresponds to a net vertical P migration rate of 2.5 cm over 100 years, i.e. vanishingly small (calculation details not shown).

Secondly, there is uncertainty on the age-depth estimation of the sampled sediment profiles. The age-depth model is expected

445 to be most reliable for the Young1 sediment core, as it is based on a fitting of a modelled age-depth relation to four observed age-depth points, while we only had two observed age-depth points available for the other cores (Temmerman et al., 2004a). Additionally, observed age-depth points were not older than 1944. Hence, the extrapolation of the age-depth model to periods before the older available age-depth points is increasingly uncertain.

4.3 Pre-industrial and natural background values

450 The population increase between 1800 and 1930 can provide a first, very crude estimate of the population-DPS relation in the Scheldt basin. In 1800 the population in Belgium was around 3 million. Later, in 1930, this number had more than doubled to 7 million (Vanhaute, 2003). A linear relation between both suggests that the DPS is 8% for the pre-anthropogenic pristine environment, corresponding with a PO_4-concentration 19-41 µg PO_4-PL^{-1}, i.e. close to what researchers have indicated for pristine lakes. Such predictions need to be corroborated with older sediment observations and other archaeological information.

455 The Scheldt river is logically more aerated than smaller lowland rivers where summer anoxia is naturally more present, i.e. the pristine PO_4-P values will be higher.

5 Conclusions

Our study illustrated that tidal marsh sediments could evaluate pre-industrial background PO_4-concentrations of the freshwater rivers like the Scheldt river. A sediment assessment can record time-integrated environmental events, providing useful spatial

460 and temporal information. Our data estimated the pre-industrial background concentration at 62 µg PO_4-P L^{-1} [95%CI (57; 66)], about half of the environmental limits set for surface waters in Flanders and neighbouring countries. Around 1930, the PO_4 levels were only about 20% lower than today, which is a remarkably large concentration at a time before the massive application of mineral fertilisers, with lower population density and limited connection to sewer systems. The current PO_4 concentrations decreased ten times from the peak found 40 years ago, reflecting wastewater treatment efforts and reducing

465   diffuse P emission. It is also clear from this study that the pristine, pre-anthropogenic PO_4-P concentrations in the Scheldt river are well below the current ambient ones.

Data availability

The supplement provides the sediment data analysis and age depth model results in csv format. In addition, results of surface water data are available upon request at the IMIS (Flanders Marine Institute).

470   **Author contribution**

FL, ES and PC designed the research. FL conducted the investigation process, and developed the methodology under supervision of ES. MVDB carried out the fieldwork and conceptualised the use of the samples. ST prodived the methodology for the age-depth model and software. TM validated the use of the surface water data. EVM and FL placed the results in perspective with historical data. All the authors contributed to discussion and data interpretations, review and editing of the
475   work.

Competing interests

The authors declare that they have no conflict of interest

Acknowledgements

This project was supported by the Research Fund Flanders (FWO), project G089319N. The results of this research greatly
480   depended on the data collected by the OMES-monitoring and The Flemish Waterway. Many years of intensive data collection and quality assessment of the Scheldt river resulted in a unique and valuable phosphate time series. We have the utmost respect for their work and are thankful we could apply the dataset for this research. We acknowledge Dries Grauwels and Kristin Coorevits for technical assistance. We recognise the efforts from the unanimous reviewers for their constructive comments on the work, which improved the quality of the result. Finally, thanks to the Scheldt for providing this beautiful sediment archive
485   to travel back in time and explore environmental history.

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