Reduction of industrial iron pollution promotes phosphorus internal loading in eutrophic Hamilton Harbour, Lake Ontario, Canada

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A B S T R A C T

Diagenetic sediment phosphorus (P) recycling is a widespread phenomenon, which causes degradation of water quality and promotes harmful algal blooms in lakes worldwide. Strong P coupling with iron (Fe) in some lakes is thought to inhibit diagenetic P efflux, despite elevated P concentrations in the sediment. In these sediments, the high Fe content leads to P scavenging on ferric Fe near the sediment surface, which increases the overall P retention. Reduced external Fe inputs in such lakes due to industrial pollution control may lead to unintended consequences for sediment P retention. Here, we study sediment geochemistry and sediment-water interactions in the historically polluted Hamilton Harbour (Lake Ontario, Canada) which has undergone 30 years of restoration efforts. We investigate processes controlling diagenetic P recycling, which has previously been considered minor due to historically high Fe loading. Our results demonstrate that present sediment P release is substantial, despite sediment Fe content reaching 6.5% (dry weight). We conclude that the recent improvement of wastewater treatment and industrial waste management practices has reduced Fe pollution, causing a decrease in diagenetically reactive Fe phases, resulting in the reduction of the ratio of redox-sensitive P and Fe, and the suppression of P scavenging on Fe oxyhydroxides.

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1. Introduction

Excessive phosphorus (P) concentrations in aquatic ecosystems fuel eutrophication, including algal blooms and bottom water anoxia, and impact biodiversity (Smith and Schindler, 2009). Perpetuated sediment P release, or internal loading, is a common issue in many lakes. However, in eutrophic lakes, P enriched sediments and favorable biogeochemical conditions promote the recycling of the legacy P accumulated in the sediments at higher rates relative to P inputs and permanent P burial. Consequently, internal P loading can potentially delay the water quality improvements gained by reducing the external P inputs. Therefore, to delineate the future ecosystem response to the remediation efforts, it is critical to understand the mechanisms controlling sediment P release and retention. While elevated sediment Fe concentrations are generally considered to promote P retention and reduce P release, due to P sorption on Fe oxyhydroxides, it is unclear how concurrent Fe and P loading reduction impacts this Fe–P coupling. This study focuses on one such unique system, where historically high Fe and P inputs were followed by a sharp reduction of Fe and P loading due to the improvement of industrial and residential wastewater treatment and management practices.

Sediment P recycling is controlled by multiple factors, which include hypolimnetic oxygen levels, gross sedimentation fluxes of reactive forms of organic matter, P and Fe forms, and lake water sulfate concentration (Katsev et al., 2006; Hupfer and Lewandowski, 2008; Dittrich et al., 2013; Orihel et al., 2017). The primary factors controlling short-term summer P release are organic matter mineralization, hypolimnetic oxygenation and Fe–P coupling in surface sediments (Dittrich et al., 2009). Long-term sediment P dynamics are controlled by P chemical speciation of the input source material, diagenetic transformation and
recycling of labile P forms and permanent burial of authigenic P phases in anoxic sediments (Ruttenberg and Berner, 1993; Katsev and Dittrich, 2013). The scavenging of dissolved P on Fe oxyhydroxides in surface sediments is critical for both short- and long-term P release and retention. It prevents diffusive P efflux out of sediments into the overlying water column, while the eventual burial of Fe-bound P forms in the anoxic sediments promotes long-term P sequestration through the authigenesis of apatite (Slomp et al., 1996) or vivianite (Rothe et al., 2015). Although sediment Fe content is often invoked as a predictor of its P binding capacity (Geurts et al., 2008), the dynamics of Fe–P coupling in lakes undergoing the remediation of Fe pollution have received less attention.

Hamilton Harbour (Lake Ontario, Canada) is one of the sites in the Laurentian Great Lakes that has had a record of cultural eutrophication and anthropogenic pollution since the 19th century. Historically, most P and Fe pollution can be traced to the raw discharge from industrial and municipal wastewater facilities, with a significant contribution of urban runoff from the surrounding population centers. Eutrophication and pollution issues were noted very early in the 19th century (HHRAP, 1992), with serious water quality degradation being present throughout the 20th century. The Harbour is identified as one of the most polluted regions in North America by the Water Quality Board of the International Joint Commission (HHRAP, 1992).

The water quality has significantly improved since the control measures to curb excessive pollution were implemented (1970-present). In the period between 1987 and 1997, the total phosphorus (TP) concentrations decreased by 50% in response to external loading reduction (Hiriart-Baer et al., 2016). However, phytoplankton biomass proxies have remained unchanged in the past 4 decades (Hiriart-Baer et al., 2016). The unchanged algal biomass despite falling nutrient levels has been explained in terms of light limitation (Pemberton et al., 2007). However, other factors, such as the increased bioavailability of P, are likely supporting the persistently high algal biomass and the development of harmful algal blooms. For instance, the ratio of the soluble reactive P (SRP) to TP in the water column has consistently increased concurrently with the large increase of hypolimnetic SRP accumulation rates (up to 0.5–1 μg/l/d in the past decade, Hiriart-Baer et al., 2016; up to 8 mg/m²/d normalized for the hypolimnion area, Fig. 1).

Despite these trends that are indicative of internal loading, previous studies have suggested that sediment P release is not a significant issue (Barica, 1989; Mayer and Manning, 1990). High Fe loading from nearby steel mills has generally been thought to prevent P release (Barica, 1989; Hiriart-Baer et al., 2016), yet external Fe loading has dramatically decreased from up to 34,000 kg Fe/d in the 1970s to 500 kg Fe/d at present (Nriagu et al., 1983; Mayer and Manning, 1990; Harlow and Hodson, 1988; HHRAP, 2018, Fig. 1). The impact of up to 70-fold decline in Fe loading on sediment P internal loading has not been examined.

This study aims to understand the interplay between the changes in Fe and P loading and P diagenesis in the historically highly polluted Hamilton Harbour. Considering the large reduction of Fe external pollution, we expected that sediment P retention was impacted, and depending on the Fe speciation, redox conditions and organic matter supply, historically low P efflux into the water column may have increased. In order to prove this hypothesis, we characterized the Fe and P diagenetic processes and quantified the sediment P release, using a combination of long-term comprehensive data on P and Fe external loading into the Harbour and our experimental data on sediment P binding forms and corresponding metal contents, porewater chemistry and physicochemical gradients across the sediment-water interface (SWI).

2. Methods

2.1. Site description

Hamilton Harbour is a triangular-shaped embayment located at the western tip of Lake Ontario. The area of the Harbour is approximately 21.5 km², with a mean depth ($Z_{\text{mean}}$) of 13 m and a maximum depth $Z_{\text{max}}$ of 25 m (HHRAP, 1992). The watershed area is ~25 times the surface area of Hamilton Harbour and occupies...
approximately 500 km². The geology of the watershed comprises Paleozoic shales, limestones and dolostones overlain with Quaternary glacial till and glaciolacustrine sediments (McCann, 1987). The watershed is highly urbanized and receives municipal and industrial wastewater from the cities of Hamilton and Burlington. Direct tributaries include Red Hill, Indian and Grindstone Creeks. To the west is Cootes Paradise Marsh, which is connected to Hamilton Harbour through the Desjardins Canal. To the east, Hamilton Harbour is connected to Lake Ontario by the Burlington ship canal (BSC). The exchange through BSC represents ~80% of the total inflows (Yerubandi et al., 2016). The hydraulic residence time in Hamilton Harbour is highly variable, modulated by episodic large-scale intrusions of hypolimnetic waters from Western Lake Ontario (Barica, 1989; HHRAP, 1992; Yerubandi et al., 2016).

Two long-term monitoring sites were sampled during the summer months of 2014–2016: station HH 9031 (43.27722 N, 79.87833 W; depth – z_max = 7 m, Fig. S1), which represents the shallow western part of the basin, and the centrally located station HH 1001 (43.28750 N, 79.83833 W; z_max = 24 m), which represents the deepest part of the basin.

2.2. Sediment and porewater chemistry and calculation of diffusive P fluxes

Samples were collected from the HH 1001 and HH 9031 stations, using a gravity corer (UWITEC, Austria) and polycarbonate core liners 5.5 cm in diameter and ~70 cm in length. Sampling dates are shown in Table S1. Six or 7 cores per station were collected during each sampling. The sediment cores were sealed and transported to the laboratory in a thermo-isolated box at ~4 °C.

One core per site was used to extract the porewater using Rhyzon samplers fitted with porous polymer 0.1 μm membrane filters. Upon extraction, the porewater was immediately pulled into a syringe and divided into separate vials for analysis of Fe²⁺ and SRP (see SI). Samples were preserved following standard U.S. EPA (1982) guidelines. Porewater SRP and Fe (II) were analyzed at the University of Toronto using the micro-spectrophotometric methods described in detail in Laskov et al. (2007).

Measurements of H₂S, pH and redox potential were carried out ex situ onshore, immediately after sampling using microelectrodes, on at least 1 core per site (see SI). Vertical profiles were measured simultaneously from the overlying water into the sediment. Prior to microelectrode measurements cores were kept tightly capped with no airspace between cap and water overlying sediment. Intact cores were exposed to the air only during measurements which did not exceed 40 min.

Prior to sectioning, the sediment cores were first logged to differentiate the visually distinct sedimentary layers, then sectioned within 24 h after sampling for the analysis of P binding forms, metal contents in P fractions, porosity, dry weight, total organic matter and dissolved substances (see SI for more details). Composition of freeze-dried bulk sediments was analyzed on a Philips PW2404 X-ray fluorescence spectrometer (see SI).

Sediment P release rates were estimated using porewater diffusive fluxes (J_pore), calculated using Fick's first law and diffusion coefficients from Boudreau (1997) (See SI for more details).

Geochemical equilibrium calculations were performed using PHREEQC version 3 with the thermodynamic database 'phreeqc.dat' (Parkhurst and Appelo, 2013). The input values included pore water chemistry (Fe²⁺, SRP), redox potential (pe), pH (varying between 7 and 8.1) and hypolimnetic temperature at the time of the sampling (10–15 °C and 15–20 °C at HH1001 and HH9031, respectively). Thermodynamic calculations were used to simulate activities of Fe²⁺ and SRP, exchange between solid-liquid phases and the saturation state of vivianite in lake water and porewater was calculated assuming solubility constant of vivianite of K_{sviv} = 1 × 10^{-36} from Nriagu (1972).

2.3. Sequential extraction for assessing phosphorus binding forms

Sediment P binding forms were extracted following the P fractionation technique from Psenner and Pucsko (1988), with modifications by Hupfer et al. (2009). This technique separates sediment P into the following fractions: (a) loosely adsorbed P (total P extracted with NH₄Cl, NH₄Cl–P); (b) redox-sensitive P bound to Fe and Mn oxhydroxides (total P extracted with bicarbonate dithionite (BD), BD–P); (c) P bound to aluminum hydroxide and clays (dissolved P extracted with NaOH, NaOH–SRP); (d) organic bound P (particulate P extracted with NaOH, NAOH-NRP); (e) calcium-bound P (HCl–P) (total P extracted with HCl); and (f) refractory P (Ref-P) (Hupfer et al., 1995; Hupfer et al., 2009). The concentrations of the major elements (including P, Fe, Al, Ca, Mn, Si) in the P extraction pools were measured by inductively coupled plasma mass spectrometry (ICP-MS).

3. Results and discussion

3.1. Dynamics of dissolved and solid P forms are closely coupled with Fe cycling

The vertical pH and redox (Eh) profiles across the SWI show decreasing pH (by 0.5–0.75 units) and redox potential (100–300 mV) in the top 2 cm (Fig. S2). Sediments are highly reducing with Eh < 100 mV below 3 cm and present visual evidence of gas, most likely methane or CO₂ ebullition pockmarks, or both (Fig. S3). The measured Eh range in the top 2 cm (<200 mV) at circumneutral pH values is consistent with the shallow iron reduction zone (Sigg, 2000; Weber et al., 2006), contradicting earlier studies that suggested that redox potential near the SWI remains above the range expected for iron reduction and between the range of denitrification and manganese reduction (MOE, 1985; Mayer and Manning, 1990).

Fe reduction is intimately linked to organic matter degradation, thus promoting the simultaneous release of P bound to organic compounds and Fe oxhydroxides. In the presence of sufficient amounts of Fe²⁺, released P can precipitate in authigenic phases, such as vivianite Fe₃(PO₄)₂·8H₂O (Rothe et al., 2015). This takes place only in environments where sulfide, a strong binding partner of Fe²⁺, is absent in porewater. Hamilton Harbour sediments are highly enriched in organic matter (Fig. 2), which enhances S²⁻ production through dissimilatory sulfate reduction and organic matter desulfurisation (Rothe et al., 2015). However, sediment Fe content is exceptionally high (5–6.5% Fe d.w. at the sediment surface, Table S2 and S3), indicating the presence of an almost inexhaustible pool of available Fe to bind excess sulfide. Indeed, porewater sulfide concentrations were below the microsensor detection limit (0.3 µM H₂S) throughout the top 5–6 cm of sediment, suggesting the presence of active sulfide sink, likely due to the precipitation of Fe sulfides, as suggested by Loh et al. (2013). Alternatively, this may also reflect vigorous sulfur cycling by sulfide-oxidizing bacteria (MOE, 1985).

Dissolved Fe²⁺ accumulates in the porewater, reaching concentrations of 20–50 mg/L (HH 1001) and 3–28 mg/L (HH 9031) in the depths between 20 cm and 30 cm (Fig. 3). Concurrently, the porewater SRP concentrations mirror the increase of porewater Fe²⁺, rising below the SWI and reaching maximum concentrations between 2 and 3 mg P/L at station HH 1001 and 2.5–5.5 mg P/L at station HH 9031 in the depths between 5 cm and 10 cm. From this maximum SRP, the concentration decreases with depth, apart from the porewater sampled at station HH 1001 in July 2016, which
shows increase with depth. The porewater ratio of Fe$^{2+}$ to P reflects availability of reactive iron species and consequently P binding capacity of sediments (Smolders et al., 2001). A ferric Fe-rich layer, formed by the oxidation of Fe$^{2+}$ at surface sediment can quantitatively trap P when porewater ratio of Fe$^{2+}$:P $>$ 1–3.5 (Smolders et al., 2001; Geurts et al., 2008). In Hamilton Harbour, this ratio is largely <1, indicating that the sediment surface contains an insufficient amount of reactive Fe to bind all the P released during diagenesis (Fig. S4).

At station HH 1001, the sediment P concentrations decrease from 3 mg P/g d.w. in the surface sediment to 2 mg P/g d.w. in the depths between 15 cm and 25 cm, increasing to 2.5 mg P/g d.w. in the deepest sampled interval (Fig. 2). At station HH 9031, the sediment P concentration decreased from a maximum of 2.7 mg P/g d.w. in the surface sediment to 2–2.3 mg P/g d.w. in the depths between 10 cm and 25 cm (Fig. 2). The total concentrations of sediment P measured using the XRF technique confirmed these values, ranging between 0.33 and 0.23% d.w. (equivalent of 3.3–2.3 mg P d.w.) at station HH 1001, and 0.27 and 0.18% d.w. (equivalent of 2.7–1.8 mg P d.w.) at station HH 9031 (Table S2 and S3).

The redox-sensitive bound BD-P fraction accounts for 33–35% of the total P in the surface sediment, decreasing rapidly with sediment depth at both stations (Fig. 2). In contrast, the NaOH-SRP fraction, which ranges between 20% and 30% of the total P in the surface sediment at stations HH 9031 and HH 1001 respectively, increases with depth, reaching 40% and 50% at stations HH 9031 and HH 1001 respectively. This fraction represents P, which is
exchangeable with hydroxyl ion, e.g., P sorbed on Al hydroxides, clays and non-reducible inorganic P compounds. The accumulation of this fraction with the sediment depth suggests that this P binding form is the most important burial sink for P.

Both NaOH-NRP and HCl–P concentrations decline with depth at both stations. While NaOH-NRP is generally thought to be composed of diagenetically reactive organic P phases, HCl–P is the immobile fraction of P, composed mainly of Ca-bound phases, chiefly (hydroxy)apatite (Lukkari et al., 2007). However, HCl–Pi is sensitive to pH and thus it is possible that some apatite dissolution takes place during burial, as pH typically decreases with sediment depth (Fig. S3). Exchangeable P (NH₄Cl–P) is in equilibrium with porewater and represents 1–2% of the total P and decreases with depth from the maximum in the surface sediment to the minimum in the deepest interval.

The total Fe increases with depth from minima in the surface sediments (4.98% Fe d.w. and 6.34% Fe d.w. at HH 9031 and HH 1001, respectively, Table S2 and Table S3, Fig. S5), to maximum concentrations in the deepest sediment layer (6.37% and 13.05% Fe d.w. at HH 9031 and HH 1001, respectively). At present, surface Fe enrichment at HH1001 (Fig. S5) is comparable to the tailings lakes impacted by mining activity (>60 mg Fe/g d.w., Kleeberg et al., 2013). The downward increasing Fe concentration reflects a history of continually decreasing wastewater Fe discharges, which declined from 34,000 kg Fe/d to 500 kg Fe/d at present (Nriagu et al., 1983; Harlow and Hodson, 1988; Mayer and Manning, 1990, Fig. 1). In comparison, the Ti and Al concentrations are constant with depth, representing an inert detrital supply from watershed erosion and resulting in a downcore increase of Fe/Ti and Fe/Al ratios. However, sediment Fe concentrations are still considerably higher than watershed erosion inputs estimated to be 4.0–4.5% Fe d.w. (Mayer and Manning, 1990). Excess Fe, despite diminished external inputs (Fig. 1), leads to diagenetic Fe migration toward the surface due to Fe reduction in deeper sediment, diffusive fluxes to the sediment surface, subsequent oxidation to Fe³⁺, and precipitation near the sediment surface.

Sediment Fe enrichment has a profound effect on P mobility. Jensen et al. (1992) have shown that P release is strongly suppressed in sediment with Fe/P ratio >15 (w%/w%) at a circumneutral pH range (Jensen et al., 1992). The Fe:P ratios of the surface sediments in Hamilton Harbour are higher (Fe:P > 18; Table S2 and S3) than this empirical cutoff, suggesting the presence of excess Fe, which can scavenge P. However, Fe enrichment itself does not translate into P retention, because sediments are comprised of a mix of different Fe phases with variable reactivity toward P. While composition of historical Fe load cannot be reconstructed with certainty, most of the Fe inputs can be traced to industrial effluents with amorphous Fe³⁺ phases, hematite and wüstite from industrial waste, and subordinate chlorite from the watershed, which combined represented ~95% of the total Fe load prior to the pollution control (Mayer and Manning, 1990). Mineralogical characterization of Fe inputs using X-ray diffraction and Mössbauer spectral determination has shown that only up to 40% of the total sediment Fe loading was in the form of reactive amorphous Fe oxyhydroxides at the time when industrial waste inputs prevailed (Manning et al., 1980; Mayer and Manning, 1990). Considering that these industrial inputs have recently been reduced (Fig. 1), presently we find that amorphous BD-reducible Fe oxyhydroxides make up to

![Fig. 3. (a) Porewater P (black square) and Fe (red circle) concentrations at station HH 1001 - top left panel; (b) Porewater P (black square) and Fe (red circle) concentrations at station HH 9031 - top right panel; (c) Diffusive fluxes of P (diagonal lines) and Fe (grey) at station HH 1001 - left bottom panel; (d) Diffusive fluxes of P (diagonal lines) and Fe (grey) at station HH 9031 - right bottom. Note the different scales in the subplots of panels a) and b).](image-url)
0.6—0.93% and 0.6—0.95% sediment d.w. at stations HH 1001 and HH 9031, respectively. Diagenetically less reactive phases are magnetite and hematite, as well as a portion of Fe bound in silicates (Raiswell et al., 1994). These less reactive phases are extracted by cold HCl in the present dataset (HCl–Fe acid extracted and refractory fraction, Raiswell et al., 1994) and account for a larger proportion of the total Fe.

The importance of P sorption on Fe oxyhydroxides is supported by a strong correlation between BD-Fe and BD-P (Fig. S6). The ratio of BD-Fe:BD-P can be used to estimate the spare sorption capacity of Fe oxyhydroxides, the principal P binding partner (Anschutz et al., 1998). At station HH 1001, the BD-Fe:BD-P ratio is 4.2:1, considerably lower than the ratio of 6.7:1, which corresponds to the supersaturation of the surface binding sites of nanoscale ferrhydrite, the phase with the highest P sorption capacity (Sigg and Stumm, 1981; Anschutz et al., 1998). While this suggests that the Fe oxyhydroxides at station HH 1001 have a limited spare capacity to bind excess P, the low BD-Fe:BD-P ratios can also denote the precipitation of ferric phosphate during the rapid oxidation of Fe²⁺ in p-enriched water, which produces a phase with a maximum Fe and P ratio of 2.1 (Thibault et al., 2005). Since station HH 1001 experiences seasonal hypolimnetic anoxia, it can be suggested that the oxygenation of hypolimnion during turnover or periodic intrusion of oxygenated Lake Ontario water results in the precipitation of iron oxyhydroxides and ferric phosphate. Conversely, BD-Fe:BD-P ratios at the shallow station HH 9031 are 7.9 and thus over the saturation limit of 6.7:1 (Anschutz et al., 1998), indicating some spare binding capacity. This modest spare BD-P binding capacity can be related to the local pollution and hydrodynamic patterns, as HH 9031 is located distally from major industrial and municipal wastewater plants and receives lesser inputs from those point sources (see map at Fig. S1).

3.2. Sediment P release is a significant P source to the water column

The diffusive P fluxes during summer 2016 ranged between 2.0 and 5.2 mg P/m²/d and between 3.5 and 6.5 mg P/m²/d at stations HH 1001 and HH 9031, respectively (Fig. 3). These diffusive P fluxes are comparable with hypolimnetic P accumulation rates (Hiriart-Baer et al., 2016, Fig. 1). Therefore, it can be concluded that the declining Fe pollution reduced the sediment capacity to bind excess P. Simultaneously with declining Fe pollution, P external inputs did not decline by a comparable rate during the last 20–30 years and consequently P originating from organic matter nowadays cannot be retained in the sediment as much as it did before, leading to increasing SRP hypolimnion accumulation (Fig. 1).

3.3. P immobilization is controlled by P scavenging on Fe oxyhydroxides and Fe—P authigenesis

An intriguing feature of the sediment P binding form dynamics is sink switching from redox-sensitive BD-P to NaOH-SRP with sediment depth. The latter extraction pool has been linked to P sorbed on amorphous Al hydroxides, which is stable at reducing conditions and, therefore, not vulnerable to diagenetic recycling during burial (Kopacek et al., 2005). The relative sorption capacity of available “free” Al hydroxides compared with available reducible Fe oxyhydroxides is reflected in the ratio of Al and Fe extracted in the first 3 extraction pools (NH₄Cl, BD, NaOH-SRP fraction). Al:P ratios indicate the overall availability of Al oxyhydroxides relative to the amount of P bound in the diagenetically most reactive phases (sum of NH₄Cl—P and BD-P). Kopacek et al. (2005) showed that if Al:Fe(NH₄Cl, BD, NaOH-SRP):P(NH₄Cl—P, BD-P) > 25, there are enough Al oxyhydroxides to adsorb P released during the reductive dissolution of BD-P. This is not the case in the Hamilton Harbour sediments, where Al:Fe(NH₄Cl, BD, NaOH-SRP) ratios are 0.2—2 and Al(NaOH-SRP):P(NH₄Cl—P, BD-P) vary between 0.4 and 18 (Fig. S7), implying that Al hydroxide concentrations are too low to explain diagenic sink switching from BD-P to NaOH-SRP.

This poses the question of the nature of the NaOH-SRP pool, which is often termed “metal bound P” but includes a complex pool of P phases with a varying degree of diagenetic reactivity, including P associated with Al hydroxide, vivianite, clays and some hydrolyzed organic P (Lukkari et al., 2007; Rothe et al., 2015). Notably, in our dataset, the Fe and P in the NaOH-SRP extraction pool are correlated (albeit moderately, Pearson r = 0.76), unlike Al and P (Pearson r = −0.33 and 0.06 at stations HH 9031 and HH 1001 respectively, Fig. S8). The Fe:P ratios vary between 0.5 and 2.5 (average~1), which is fairly similar to the molar ratio of vivianite Fe₅PO₄H₂O (Fe:P = 1.5). Therefore, similar to the Rothe et al. (2015) study, we propose that sink switching to the NaOH-SRP extraction pool is likely associated with vivianite authigenesis.

Rothe et al. (2015) have also identified the S:Fe molar ratio <1.1—1.5 (total S to reactive Fe measured by digestion with aqua regia) as an empirical threshold/indicator of vivianite formation. The basis of this indicator is the presence of an excess amount of reactive Fe relative to the production of sulfide during sulfate reduction. Hence, vivianite formation is not restricted by the supply of reactive Fe and Fe sulfide precipitation. While we did not quantify the aqua regia extractable Fe, we propose that the sum of Fe extracted by the BD reagent and digested HCl (BD-Fe, HCl–Fe and Fe-Ref) (Fig. S5) represent a reasonable approximation of the total Fe that is reactive toward sulfide (Rothe et al., 2015). Thus, the estimated reactive Fe varies between 0.50 and 0.72 mmol Fe/g d.w. at station HH 1001 and between 0.41 and 0.72 mmol Fe/g d.w. at station HH 9031, giving S(reactive Fe)/Fe(reactive Fe) ratios well below the empirical threshold value of 1.1 (Table S2 and S3).

Another indicator for possible authigenic vivianite formation is porewater supersaturation (Fig. 4). However, porewater supersaturation in respect to vivianite alone is not enough to prove vivianite precipitation, which must be demonstrated through mineralogical identification (Rothe et al., 2016). Manning et al. (1980) have suggested that due to high concentrations of porewater Fe and P, vivianite would be expected to precipitate in Hamilton Harbour;
accumulated a large amount of excess Fe, which still modulates P cycling through sorption on reducible Fe oxyhydroxides and the precipitation of vivianite in anoxic sediment. However, the diminished industrial Fe inputs reduce the availability of reactive Fe species relative to P and S. Gächter and Müller (2003) have shown that in anoxic sediments, the permanent P retention is sustained if the molar ratio of reactive Fe:P is > 2. If we assume that the entire Fe and P external loading in Hamilton Harbour is composed of reactive species, the threshold value for Fe:P in the external loading sources has been breached around the year 2000 (Fig. 1).

However, a gross external loading Fe:P ratio may overestimate the availability of the reactive Fe species relative to P. The sources of Fe and P are distinctly divergent, with present-day P originating mostly from wastewater treatment, and Fe representing erosional sources from the watershed (Fig. 1). It has been demonstrated that P originating from wastewater treatment effluents is mostly bioavailable (e.g., Qin et al., 2015). Watershed Fe inputs are predominantly composed of clays (Manning et al., 1980; Mayer and Manning, 1990), which are less reactive during diagenesis. Thus, it is likely that recent sediments are receiving much lower inputs of reactive Fe than suggested by the total Fe loading. This decreases the sediment ability to bind excess P.

The reduced external Fe inputs relative to the historical values decreases the inventory of reactive Fe. The current Fe pool in the surface sediment (top 1 cm, dry bulk density -0.2 g/cm²) is approximately 100 and 127 g/m² (stations HH 9031 and HH 1001, respectively). The decrease rate of the Fe inventory can be calculated based on the total Fe profiles (Fig. SS; Table S2 and S3) and the sediment accumulation rates (assuming 0.15 g/cm²/yr; Nriagu et al., 1983; Jonilija, 2014) is 2 and 12 g/m²/yr at stations HH 9031 and HH 1001, respectively. Therefore, assuming the current sediment accumulation rates, within the next 5 years surface sediments will reach Fe concentration in watershed erosion inputs (4.0–4.5% Fe d.w., Mayer and Manning, 1990) which is equivalent to total Fe of 80–90 g Fe/m².

One important consequence of decreasing Fe inventory is a decline of the sediment capacity to scavenge P on Fe oxyhydroxides in the surface sediments. Still, there is another feedback mechanism, namely that Fe oxyhydroxides are known to enhance the preservation of organic matter in sediments (Lalonde et al., 2012). Thus, reduction of Fe oxyhydroxides inventory reduces organic matter preservation thereby promoting degradation and release of organic P, whose sedimentation rates likely did not change significantly over the past 2 decades, considering that algal biomass during this period has remained at present levels (Hiriart-Baer et al., 2015). Furthermore, following the argument by Rothe et al. (2015), lake productivity and organic matter export are the primary controls of sulfide production through sulfate reduction and desulfuration of organic S. Hence, it can be presumed that sediment sulfide production will be sustained if primary productivity does not change, as is the case in Hamilton Harbour (Hiriart-Baer et al., 2016). Since Fe sulfides preferentially precipitate over vivianite (Gächter and Müller, 2003; Rothe et al., 2015), lower amounts of Fe will be available to bind with P and, consequently, it will lead to decreasing P retention and act as a positive feedback on water column eutrophication.

Presently, we estimate that a considerable amount of legacy P in the sediment is being recycled. The sediment P diffusive fluxes during summer are estimated to be 2–6.5 mg P/m²/d. Extrapolating these values across the surface of sediment over lain by a hypolimnetic layer leads to a P flux of ~200± 100 kg P/day in the range of all combined external inputs (Fig. 1). However, this is a worst-case scenario and likely an overestimate, as this calculation does not take into account flushing from Lake Ontario and the fact that legacy P is not uniformly concentrated throughout the Harbour.
Nonetheless, one can expect that this P release from the sediment to the water column will deteriorate the water quality of Hamilton Harbour during prolonged periods of stagnation.

One uncertainty about this adverse impact comes from the sporadic hypolimnion exchange with Lake Ontario (e.g., Yerubandi et al., 2016). Considering that hypoxic episodes may persist (Yerubandi et al., 2016), the possibility of extensive surface water P enrichment originating from sediments should, therefore, be considered and factored into the expectations of the area recovery by the water managers. Understanding sediment impact on the water quality is particularly important in the context of climate change, which has a potential to alter the hydrodynamic regime within the Harbour, likely reducing the frequency of Lake Ontario intrusion events and increasing the duration of the stratification period (Yerubandi et al., 2016), thus exacerbating the impact of the hypolimnetic P accumulation and feedback associated with reduced Fe pollution.

4. Conclusions

In this study, we delineated the processes controlling the sediment P dynamics in eutrophic Hamilton Harbour, a unique system undergoing the reduction of Fe industrial pollution. We found that the external loading and diagenetic processes are responsible for the redistribution of mobilized P and Fe within the anoxic sediment. These processes drive an effective sink switching to a stable authigenic Fe(II) phase, most likely vivianite, and contribute to P retention. However, reducing Fe sediment levels limit the surface sediment capacity to bind newly deposited P, which emphasizes the importance of external P loading reduction.

Our results demonstrated that the reduction of Fe loading has accelerated the P recycling processes, which contrasts with earlier studies that concluded that historically high Fe levels effectively trap P in sediment. The Hamilton Harbour case is, therefore, an example of a system where controlling industrial pollution leads to an unintended increase of sediment diagenetic P recycling.

Currently, the diagenetic P efflux from sediment into the water column has considerable impact on the overall P budget in eutrophic Hamilton Harbour. In the worst-case scenario, 2.65 mg P/m²·d of sediment P is released into the hypolimnion, which is within the range of external P loading during summer months. Remediation plans should consider that these internal P subsidies will exert a growing influence over nutrient balance and productivity and delay recovery process.

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This project was funded by the Great Lakes Sustainability Fund and NSERC Discovery Grant to MD. We are thankful for the generous support of Environment and Climate Change Canada, the Hamilton Harbour Remediation Action Plan and the Ontario Ministry of the Environment and Climate Change. Debbie Burniston is acknowledged for providing water-quality monitoring data for Fig. 1. Furthermore, the field and laboratory assistance of Elaine Lu is kindly acknowledged.

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.envpol.2019.05.124.

References


Supplementary Information

Reduction of industrial iron pollution promotes phosphorus internal loading in eutrophic Hamilton Harbour, Lake Ontario, Canada

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<td></td>
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**Table S1.** Sampling dates. Note that sediment samples were collected on all sampling dates, but data for porewater used in this paper were sampled during 2016.

### Analysis of dissolved H₂S, pH and redox potential

The pH and redox potential (reduction potential measured in mV) were measured with a Unisense needle electrode relative to Radiometer Analytical reference electrodes. The pH electrodes (Unisense pH-N, Denmark) were calibrated with commercial pH buffers (pH 4, 7 and 9, HACH). The offset between the reference electrode and the standard hydrogen electrode redox potential was calibrated prior to measurement using freshly prepared quinhydrone redox buffers with known redox potentials. The porewater \( \text{H}_2\text{S}_{(g)} \) was measured using a Unisense amperometric ferricyanide microsensor. Since ferricyanide electrolyte is sensitive to light, sensor was calibrated in a darkened calibration chamber and all measurements were conducted in the dark. A 3-point calibration in the range of 0 to 100 \( \mu \text{mol} \) \( \text{H}_2\text{S} \) was conducted using oxygen-free standards prepared from 10 mM \( \text{Na}_2\text{S} \) stock solution.

Each pH and redox profile presented hereafter represent the average of the replicate measurements from the same sediment core. The standard deviation of the repeated pH measurements was <5%, while it was <10% for the \( \text{H}_2\text{S} \) and redox measurements.

### Analysis of chemical and physical properties of sediments and porewater

Sediment water content was measured by drying at 105°C for 60 h. Loss on ignition (LOI) was calculated as the loss of weight during ignition at 550°C for 4 h. The total carbon has been estimated as \( \text{OC} = \text{LOI}_{550}/2.5 \) (i.e., assuming organic matter composition as \( \text{CH}_2\text{O} \), Burdige 2006). Dry weight (water
content), porosity (calculated using moisture loss during drying) and loss on ignition represent the average of 2 samples from the same layer.

For bulk sediment analysis, freeze-dried sediment samples were compressed in pellets and analyzed on a Philips PW2404 X-ray fluorescence spectrometer. XRF analysis provides quantitative results for major and certain minor elements, with detection limits down to 1 ppm. Analytical precision of XRF measurements was evaluated through repeat measurements averaging ± 1% for major elements and ±1.5% for trace elements. To ensure measurement accuracy, the international reference standards were analyzed along with the samples. The samples were run in triplicate, and the relative standard deviation for the different measured variables was under 10%. The data quality assurance and control were ensured through the use of standard procedures, including method blanks and blind reference samples.

**Estimation of P release from sediment and Fe diffusive fluxes**

The SRP diffusive flux was calculated from concentration gradients across the sediment-water interface (SWI) using Fick’s first law (Berner 1980):

\[
J_{SRP} = D_{sw} \frac{\varphi}{\theta^2} \frac{\partial C}{\partial x}
\]

where \(\varphi\) is the porosity, \(\partial C\) represent SRP concentration, \(\partial C/\partial x\) represent concentration gradient in the depth interval over which gradient is calculated (uppermost 1-2cm), and \(\theta\) represents the tortuosity, or the degree of deviation around particles; \(\theta^2\) factor was calculated using the empirical relationship \(\theta^2 = 1 - \ln(\varphi^2)\), where \(\varphi\) is porosity (after Boudreau 1997), and \(D_{sw}\) is a molecular diffusion coefficient of PO\(_4\) in the pore water, assuming ambient hypolimnion temperature (values after Boudreau 1997). Similarly, diffusive fluxes of reduced iron were calculated from their respective measured concentration gradients in pore water. The depth interval used for calculation of concentration gradient was the top 1-2cm. Diffusion coefficients for Fe\(^{2+}\) correspond to ambient temperature freshwater estimates after Boudreau (1997).
Hypolimnetic SRP accumulation rates

A long-term water-quality monitoring dataset for Hamilton Harbour was used to estimate SRP mass accumulation rates in the hypolimnion (MOE 1981, 1985, 1986; Nriagu et al. 1983; Harlow and Hodson 1988; Hiriart-Baer et al. 2016). Weekly water column profiles of water temperature and depth (binned to 1 m strata) from station HH 1001 were used to define the depth of the hypolimnion for each sampling date in a given year. The top of the hypolimnion was chosen as 1 m below the inflection point of the thermocline, and hypolimnetic volumes (m$^3$) were calculated using 1 m depth intervals and 1 m interval bathymetric data for Lake Ontario (www.ngdc.noaa.gov/mgg/greatlakes/ontario.html). Concentrations of SRP collected from the hypolimnion (depths of 19 to 22 m) were assumed to be representative of SRP concentrations throughout the hypolimnion. The mass of SRP in the hypolimnion (SRP$_H$) at the respective sampling time was calculated as:

$$SRP_H = SRP \times V_H$$

where SRP is the concentration of SRP in the hypolimnion at the time of sampling (mg/m$^3$) and $V_H$ is the volume of the hypolimnion (m$^3$). SRP mass accumulation rates were calculated via linear regression of SRP$_H$ over day of year during the stratified summer period for each year with available records. To facilitate comparison with the sediment SRP diffusive flux (J$_{SRP}$) and long-term P recycling rates, obtained from sediment P depth profiles (described in the main text), hypolimnetic volume SRP$_H$ mass accumulation rates (Hiriart-Baer et al. 2016) were normalized to areal rates by dividing by the average hypolimnetic area during the stratified period.
1 Woodward WWTP
2 Skyway WWTP

**Figure S1.** Sampling site location.
Figure S2. Porewater pH and Eh depths profiles at the sediment-water interface a) HH1001 b) HH9031
Figure S3. Photographs of vertical core splits from core collected on June 5, 2014: Deep site HH 1001 (left) and shallow site HH 9031 (right).
### Table S2. Bulk sediment composition at station HH 1001 (on dry weight basis).

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### Table S3. Bulk sediment composition at station HH 9031 (on dry weight basis).

| Depth | Si | Ti | Al | Fe | Mn | P | S | Fe/Ti | Fe/Al | Fe/P | Cr | Ni | Pb | Cr | Ni | Fe/P | Fe/Ti | Fe/Al |
|-------|----|----|----|----|----|---|---|-------|-------|------|----|----|----|----|----|------|-------|-------|-------|
| cm    | % d.w. | molar | ppm | %/% |
| 0-1   | 22.06 | 0.39 | 5.51 | 4.98 | 0.17 | 0.27 | 0.48 | 0.21 | 80 | 97 | 39 | 18.44 | 12.77 | 0.90 |
| 1-2   | 22.72 | 0.40 | 5.61 | 5.01 | 0.18 | 0.26 | 0.44 | 0.25 | 86 | 104 | 41 | 19.27 | 12.53 | 0.89 |
| 2-6   | 23.00 | 0.40 | 5.66 | 5.11 | 0.20 | 0.26 | 0.52 | 0.34 | 85 | 114 | 42 | 19.65 | 12.78 | 0.90 |
| 6-10  | 23.93 | 0.40 | 5.98 | 5.39 | 0.22 | 0.20 | 0.48 | 0.37 | 102 | 117 | 46 | 26.95 | 13.48 | 0.90 |
| 10-13 | 23.75 | 0.40 | 5.98 | 5.67 | 0.22 | 0.20 | 0.56 | 0.34 | 116 | 126 | 49 | 28.35 | 14.18 | 0.95 |
| 13-15 | 23.56 | 0.40 | 5.93 | 5.96 | 0.22 | 0.21 | 0.60 | 0.36 | 146 | 141 | 55 | 28.38 | 14.90 | 1.01 |
| 15-24 | 23.70 | 0.41 | 6.04 | 6.01 | 0.23 | 0.20 | 0.52 | 0.32 | 175 | 172 | 60 | 30.05 | 14.66 | 1.00 |
| 24-28 | 23.51 | 0.40 | 5.93 | 6.37 | 0.24 | 0.18 | 0.60 | 0.36 | 257 | 203 | 73 | 35.39 | 15.93 | 1.07 |
**Figure S4.** Molar ratios of dissolved Fe and SRP in porewater: (a) HH 1001 and (b) HH 9031. The lower panels represent expanded shaded blue areas in the upper panels. The porewater molar Fe:SRP ratio >3.5 (black solid line) indicates a low risk of internal loading (Geurts et al. 2008). Smolders et al. (2001) similarly suggested a low risk of P release when porewater molar Fe:SRP ratio >1 (gray dashed line).
Figure S5. Fe and Al extracted with P binding forms: a) Total Fe (see Table S2) and Fe extracted in different P extraction pool at HH 1001; b) Total Fe (see Table S3) and Fe extracted in different P extraction pool at HH 9031; c) Al extracted in different P extraction pool at HH 1001 d) Al extracted in different P extraction pool at HH 9031
Figure S6. Molar ratio between BD-extractible Fe and associated BD-P (HH 1001 - filled black squares; HH 9031 - empty red circles). At station HH 1001 molar Fe:P ratio is lower than 6.7, suggesting the supersaturation of surface binding sites of ferrihydrite (Sigg and Stumm 1981) or the coprecipitation of metastable P-ferrihydrate assemblage, which has a maximum Fe:P ratio of 2:1 (Thibault et al. 2009), or both.
Figure S7. Upper panel: Molar ratios of Al vs. Fe against the sum of loosely sorbed (NH$_4$Cl-P) and redox-sensitive (BD-P) fractions, which are the diagenetically most reactive P phases. Kopáček et al. (2005) ratio cutoff is indicated as a red line. Lower panel: Sediment molar ratios of Al (associated with NaOH-SRP) vs. P[NH$_4$Cl+BD-P] against the sum of loosely sorbed (NH$_4$Cl) and redox-sensitive (BD-P) fractions. Kopáček et al. (2005) dataset ratio cutoff is indicated as a red line. Note that all ratios in (a) and (b) represent surface sediments (upper 5 cm).
Figure S8. Scatter matrix showing the correlation between P (NaOH-SRP), Al (Al NaOH-SRP) and Fe (Fe NaOH_SRP) in the NaOH-SRP extraction pool at station HH 1001 (a) and station HH 9031 (b).
References


