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Determination of sub-pico-molar levels of platinum in the pristine Krka River estuary (Croatia) using improved voltammetric methodology

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Environmental Context

Platinum concentrations in natural waters (ocean, rivers, lakes) are extremely low, hindering extensive studies of Pt distributions and biogeochemical cycles. An improved electrochemical method was applied for reliable determination of Pt in the estuarine conditions at concentrations <0.5 pM. A near-conservative behaviour of Pt along the salinity gradient was found with around 90% of Pt present in the dissolved form.

Abstract

Extremely low concentrations of platinum in natural waters require very sensitive analytical techniques, with adsorptive cathodic stripping voltammetry (AdCSV) as one of the most frequently used. Fine "tuning" of the voltammetric parameters, along with advanced data treatment based on derivative transformations, allowed us to determine reliably Pt levels down to 50 fM (0.05 pM). Using short modulation and interval times of the differential pulse stripping waveform, and applying a 4th derivative transformation of the voltammograms, the LOD was lowered down to 10 fM. Although very small concentrations of surface-active substances (e.g.

0.025 mg/l fulvic acid) strongly influence the method sensitivity, recoveries of spiked samples were not impacted (~100%). The application of a desorption step (E_{ds} = -1.35 V; t_{ds}=2 s) at the end of the accumulation significantly improved the sensitivity, presumably through the removal of adsorbed surface-active substances (SAS).

Using this optimized methodology, we determined the Pt distribution in the pristine Krka River estuary in winter and summer period by performing both horizontal transects and vertical profiles (salinity ~1 to 39). In surface waters, dissolved Pt concentrations gradually increased towards the seawater end-member (from ~0.15 pM to ~0.3 pM). A small deviation from the conservative mixing line was observed at salinities below 10, which may reflect changes in Pt redox speciation. In bottom waters, the trend is opposite with dissolved Pt concentrations increasing towards the freshwater end-member, probably due to progressive accumulation related to seawater residence time. On average, 90% of Pt is present in the dissolved form.

Keywords: Platinum, Catalytic stripping voltammetry, Derivative transformation, Estuaries, Salinity gradient

Introduction

Platinum (Pt) abundance and distribution on the Earth's surface is impacted by anthropogenic activities, which accounts for ~80% of Pt fluxes, with ~45% of produced Pt being used for catalytic converters in cars (Sen and Peucker-Ehrenbrink 2012). Insufficient data on Pt distribution, behaviour and role in aquatic environment placed Pt on the list of potentially eco-toxic elements (Mashio *et al.* 2017). Platinum is a Technology Critical Element (TCE) and thus there is an emerging need for its assessment of distribution and impacts in different environments (Cobelo-Garcia *et al.* 2015). The most extensive application of Pt is in catalytic converters for vehicles, which is the most demanding Pt need (Matthey 2018). Pt emissions from vehicles exhaust over the decades increased Pt concentration in many environmental compartments, especially in atmosphere, urban soils, sediments and natural waters (Schafer *et al.* 1999, Rauch *et al.* 2005, Obata *et al.* 2006, Soyol-Erdene *et al.* 2011, Abdou *et al.* 2019). Despite growing efforts to improve the understanding of biogeochemical Pt cycles, there is still a lack of relevant environmental data. One of the reasons for this scarce Pt data is the extremely low concentration of Pt (<1 pM) that are encountered in natural waters (Van Den Berg and Jacinto 1988, Cobelo-Garcia *et al.* 2013, Mashio *et al.* 2017, Fischer *et al.* 2018). There are only few studies that report Pt distribution and behaviour in coastal environments (Van Den Berg and Jacinto 1988, Obata *et al.* 2006, Cobelo-Garcia *et al.* 2011, Cobelo-Garcia *et al.* 2013, Cobelo-Garcia *et al.* 2014a, Mashio *et al.* 2017, Fischer *et al.* 2018, Abdou *et al.* 2019). The concentration of Pt in natural waters ranges from below 0.1 pM to several pM (Van Den Berg and Jacinto 1988, Cobelo-Garcia *et al.* 2013, Mashio *et al.* 2017, Fischer *et al.* 2018). Higher concentrations are found in coastal regions impacted by urban pressure, while in open marine water the concentration is usually below 0.5 pM. Up to now, only few studies were conducted in estuarine environments (Obata *et al.* 2006, Cobelo-Garcia *et al.* 2011, Cobelo-Garcia *et al.* 2013, Cobelo-Garcia *et al.* 2014a), with a non-conservative behaviour reported during estuarine mixing (Cobelo-Garcia *et al.* 2013).

Because of such low concentrations, the determination of Pt in natural water require extremely sensitive analytical techniques. Inductively coupled plasma mass spectrometry (ICP-MS) with a preconcentration step (Turetta *et al.* 2003, Mashio *et al.* 2017, Fischer *et al.* 2018) and catalytic stripping voltammetry (Van Den Berg and Jacinto 1988, Locatelli 2005, Obata *et al.* 2006, Cobelo-Garcia *et al.* 2013) are the techniques most widely used. The limit of detection (LOD) of both methods is low and adequate for studying Pt behaviour in unpolluted natural waters: a LOD of 30 fM has been reported for the voltammetric method (Cobelo-Garcia *et al.* 2014b) and 15-20 pM for the more complex ICP-MS pre-concentration technique (Mashio *et al.* 2017, Fischer *et al.* 2018).

In this work, we focused on (1) optimizing the analytical protocol in order to improve the reliability of Pt determination by voltammetry (which consists in the fine adjustment of the voltammetric procedure and the treatment of the voltammograms); (2) assessing and removing the interference of surface-active substances on the voltammetric signal and (3) evaluating the level, distribution and behaviour of Pt under estuarine mixing of the pristine Krka River estuary.

Experimental

Study site

The Krka River estuary is located on the eastern coast of the Adriatic Sea (Croatia). It is a typical, highly stratified estuary along its entire length of 22 km. The halocline depth and the extension of the low salinity surface brackish water is mainly regulated by the Krka River flow, with an average flow of around 40 m^3s^{-1} (over the last 50 years, it ranged from 5 to 450 m^3s^{-1}, (Prohic and Kniewald 1987, Cindric *et al.* 2015). Figure 1 presents the map the sampling area with the location of the 16 sampling sites used in the transect as well as an extra site near Marine station where a vertical profile was obtained (open triangle in Fig. 1). The potential anthropogenic sources of Pt along the estuary are motorways with intensive traffic during summer period and Šibenik harbour.

Sampling

At each sampling site, samples were collected using a van Dorn horizontal acrylic sampler for bottom waters or by using grab sampling with 1 L FEP bottle (previously cleaned with 1% HNO3 (suprapur) and MQ water) for collection of surface waters (~0.3 m below the surface). Four sampling campaigns were conducted: summer and winter 2017, summer 2018 and winter 2019. Surface and bottom waters (filtered and unfiltered) were always collected except for the winter 2017 campaign where only surface water was sampled. Sampling for the vertical profile was performed using the horizontal acrylic sampler at all depths, including surface. Samples were filtered either immediately onboard or in the laboratory (within few hours) using syringe filters 0.22 µm (Minisart, Sartoris). Both filtered and unfiltered samples were collected and stored in 125 mL FEP bottles which were previously washed using trace metal clean procedure. Samples were acidified to 0.2% v/v conc. suprapur HCl (Merk) and UV-digested for 24h using 250 W high pressure Hg-lamp in order to decompose organic matter and release Pt from potential Pt-organic complexes. We used hydrochloric acid to acidify the samples because the acidification by nitric acid led to a higher baseline current and a decrease of the sensitivity. Vertical profiles of physico-chemical parameters (S, T, O_2, pH and Chl-a) were recorded using a EXO2 multiparameter CTD probe (YSI).

Because of the extremely low concentrations of Pt, obtaining reliable "blanks" and eliminating any contamination was challenging. During the first sampling in summer 2017, high and uniform Pt concentrations were obtained in filtered samples, with values slightly above the level expected for the coastal sea. We found that this was due to contaminations caused by the release of Pt from the silicone ring on the syringe plunger used for filtration (Pt or peroxide is used in the silicon production process ("Platinum- or Peroxide-cured Silicone")). The release of Pt from the silicone ring generated Pt concentration in sample between 0.5 and 0.7 pM. Thereafter, all samples were filtered with syringes free of any silicone ring. Thus, for the July 2017 campaign, only unfiltered concentrations are reported.

Equipment and analysis

All measurements were performed using a µAutolabIII or a PGSTAT12N potentiostats (EcoChemie) coupled with a three-electrode cell (663 VA Stand, Metrohm) with a static mercury drop working electrode (SMDE), Ag|AgCl|sat. NaCl electrode as reference electrode and a glassy carbon rod as the auxiliary electrode. Measurements were performed by coupling the potentiostat with a home-made fully automated system which consisted of a sample-changer, five Cavro XE 1000 syringe pumps and a home-made software (VoltAA: https://sites.google.com/site/daromasoft/home/voltaa).

Platinum was analysed using catalytic adsorptive cathodic stripping voltammetry (Cat-AdCSV) along the method proposed by Van den Berg and Jacinto (1988). UV-digestion is here an important step, as this method is sensitive to the presence of organic matter (Obata *et al.* 2006, Cobelo-Garcia *et al.* 2013). Prior to the measurement, 30 mL of sample was added in acid-clean 50 mL PP vials, and sulphuric acid was added to a final concentration of ~0.6 M (Trace Select, Fluka). This solution was then poured into a Teflon or quartz voltammetric cell and additions of formaldehyde (final concentration 3.5 mM; Riedel-de-Haen) and hydrazine sulphate (final concentration 0.45 mM; Fluka) were done using using the automated burettes, leading to a total dilution factor of 1.04.

Detection was done by differential pulse anodic stripping voltammetry (DPASV) using a deposition potential of -0.65 V and deposition times of 5 or 7.5 mins, which were found sufficient for reliable measurements. The parameters of the differential pulse voltammetric (DPV) technique were varied in order to find optimal conditions where Pt peak is well expressed.

Before each set of measurements, the blank of MQ and chemicals was checked. The blank level was below 30 fM, which was found to originate mainly from the MQ water and not from chemicals used. Thus, the blank was not used for correcting any measured Pt concentrations.

Results and Discussion

Optimisation of the voltammetric procedure

Considering the expected low Pt concentrations (<1 pM), our first aim was to optimise the voltammetric procedure and data treatment, to increase the reliability of the measurement and lower the limit of detection. Concentration of formaldehyde, hydrazine and sulfuric acid had already been optimized by other authors (Van Den Berg and Jacinto 1988, Obata *et al.* 2006, Cobelo-Garcia *et al.* 2013), and we focused first on the optimisation of the stripping parameters (interval time, modulation time and amplitude) and deposition potential(s). The purpose was not to obtain the higher peak intensity, but to obtain a well-resolved Pt peak in relation to the steep baseline current that exists at that peak position. A small shoulder, representing no more than 20% of the Pt analytical signal, is overlapping the Pt peak. Its position varies depending on the voltammetric procedure and its intensity is independent of the deposition time. In addition, due to the very acidic conditions, the current range of 100 nA had to be used (in place of the usual 10 nA), leading to a higher current noise which consequently led us to increase the DP amplitude pulse to 40 mV so as to maintain a good signal to noise ratio. Finally, we found that lowering the pulse time and interval time resulted in a better resolved Pt peak (see example in Fig. S1). The deposition potential used to accumulate the Pt-formazone complex varied between authors: -0.3 V (Cobelo-Garcia *et al.* 2013), -0.7 V (Obata *et al.* 2006) and -0.95 V (Van Den Berg and Jacinto 1988). This latter study reported a stable response when using deposition potentials above -0.8 V, a sharp increase in peak height between -0.85 and -1.0 V and a sharp decrease at more negative potentials. In our experiment, the peak intensity increased gradually up to ~-0.7 V, followed by a sharp decrease at more negative potentials (Fig. 2). From such response, a deposition potential of -0.65 V was chosen as the optimum.

The voltammetric determination of Pt is very sensitive to the presence of even small concentrations of organic matter. This interfering effect has been attributed to the adsorption of electroinactive surface-active compounds on the electrode surface that inhibits the catalytic reaction of hydrogen evolution that is occurring during Pt analysis (Van Den Berg and Jacinto 1988). Other studies have found that full Pt recovery could not be achieved if the samples were not UV irradiated, suggesting the presence of electroinactive Pt-organic complexes (Obata *et al.* 2006, Cobelo-Garcia *et al.* 2013). Here, we looked at the effect of small concentrations of fulvic acid (FA = 0.025 mg/L) in UV-digested estuarine water, spiked with Pt, on its voltammetric peak. Two different voltammetric procedures were used: with and without a short 2 seconds desorption step (DS) at -1.35 V (Fig. 2). This short negative desorption step was previously found to help removing adsorbed organic surface-active substances from the electrode surface, providing a significantly better shaped voltammograms for Cu analysis

(Louis *et al.* 2008). In case of Pt, in UV digested sample without FA additions, slightly higher signals were obtained without DS. Upon addition of FA, the Pt peak intensity for both voltammetric procedures strongly decrease but the Pt peaks obtained with DS are twice higher than those without, showing clear evidence of its beneficial effect. It is however not clear if this significant decrease is due to competitive adsorption at the electrode surface due to surface activity of this low level of FA (0.025 mg/L, equivalent to ~0.0125 mg/L DOC) or if strong complexation of Pt(II) with organic matter can occur, even in these acidic conditions. Van den Berg and Jacinto (1988) noted that in seawater Pt(II) could be complexed by natural organic ligands. Thermodynamic calculations of Cobelo et al. (2013) showed that in seawater Pt(IV) predominates over Pt(II), in agreement with the observation of a rapid oxidation of spiked Pt(II) to Pt(IV) in the presence of the macroalgae *Ulva lactuca L* (Cosden *et al.* 2003), and agree also with results of another study (Mashio *et al.* 2017). In contrast, in freshwater, speciation calculation suggest that Pt(II) should predominate over Pt(IV). Up to date there are no reported studies which focused on the interaction of Pt with natural organic ligands. The extension of our experiment with added FA and with two voltammetric procedures (with and without DS) included testing whether the recovery of Pt would be impacted upon addition of small concentration of FA (having strong influence on peak intensity/shape).

Experiments performed with spiked Pt in MQ (0.85 pM) showed that under these experimental conditions, the analytical determination was not compromised. The obtained recoveries were ~103% for both voltammetric procedures (Fig. S2). However, the sensitivities differed strongly depending on the conditions. While the sensitivity (2nd derivative, 5 min accumulation time) without added FA was 606 /pM, addition of FA decreased it down to 345 /pM and 219 /pM with and without DS respectively. For seawater samples no peak was detected in samples which were not UV irradiated if DS was not applied, whereas weakly noticeable peak was detected if DS was applied. However due to much higher concentrations of organic matter in natural samples, the analytical determination of Pt could be unreliable if the water sample is not UV irradiated, despite using DS. At least, applying both procedures (with and without DS) on the same sample could provide a clear answer if the UV-irradiation was complete or if some surface active organic matter still remained in the sample (test method). Test performed on real samples (UV-irradiated) showed that the difference in peak intensity between two applied procedures was within 10%, which is within the expected experimental uncertainty.

In conclusion, our optimized procedure was: deposition potential of -0.3 or -0.65 V, deposition time 300-450 s, a short DS (-1.35 V for 2 s, in some cases), interval time = 0.1 s, modulation time = 0.025 s and amplitude = 40 mV. Typical catalytic voltammograms at increasing concentrations of Pt obtained in a seawater sample, together with the associated standard addition plot, are presented in Figure S3. The Pt concentration in that sample was measured at 0.29±0.02 pM with obtained LOD of 15 fM. Even lower LOD down to below 10 fM were obtained for low Pt concentration samples.

Voltammograms treatment

We wanted here to explore whether higher derivative transformations could improve the determination of low levels of Pt in comparison to the 2nd derivative treatment, as shown previously (Cobelo-Garcia *et al.* 2014b). Fig. 3 shows typical raw DP voltammograms, along with the corresponding 2nd and 4th derivative transformations. For small Pt peaks, the use of a 4th derivative gives a slightly better peak than with a 2nd derivative because it provides a flatter baseline. Due to the relatively low noise and smooth voltammograms (no unexpected "shoulders"), both the 2nd and 4th derivative peaks are well expressed. In our study we used differential pulse (DP) as the stripping technique, but square wave voltammetry (SW) (Locatelli 2005) or linear scan voltammetry (LSV) (Van Den Berg and Jacinto 1988) can also be used. Given that the DP forward current scan is analogous to that of LSV, it could also be used for quantification of Pt. Although the peak at low concentrations is not well expressed in the raw forward current voltammogram, the 2nd and 4th derivative both provided clear peaks (Fig. S4) and same concentrations (within 10%) were determined using either of them. In this study, we used the 4th derivative transformation of DP voltammograms because of the flatter baseline that should lead to lower detection limits.

Hydrography of the estuary

Physico-chemical parameters for the sampling period are presented by contour plots in Fig. S5. The vertical and horizontal salinity profiles are typical for those two sampling periods (summer and winter). The halocline is positioned deeper in winter than in summer, with a low salinity upper layer extending more towards the lower part of the estuary, due to higher freshwater flow. The variation of pH (not shown) was minimal, starting at 8.4 in the upper estuary (freshwater side) and finishing at around 8.2 in the seawater end-member. Slightly higher pH in freshwater part is related to the degassing (removal of CO_2) that is occurring at the waterfalls which precede the estuarine transect (Cindric *et al.* 2015). The suspended particulate matter (SPM) level was not measured in this work, but previous studies found relatively low concentrations, not exceeding 5 mg/L. Dissolved organic carbon (DOC) concentrations were higher in summer (up to ~150 μM) than in winter (up to ~80 μM). Typically, DOC was lower (~50 μM) in winter at the freshwater end-member than at the seawater end-member, whereas for the summer period, an opposite trend is observed due to the high biological productivity that occur in freshwater Visovac Lake preceding estuary (Petricioli *et al.* 1996) (Figure 1). Typical DOC profiles (Fig S5) for the Krka estuary were obtained at both seasons; those are rather unusual compared to other estuaries which show a decreasing trend in the seaward direction. Temperature profiles follows those of salinity for both seasons. The oxygen saturation profile was the most variable; in summer, high oxygen levels (up to 140 % saturation) were found below the halocline between Station P3 and Station P11 (Figure 1) while very low levels were found in the upper part of the estuary in winter. Such trends were already reported in a previous study (Legović *et al.* 1991). The former case is related to the high productivity at the lacustrine part of the estuary (Prokljan lake). The low oxygen levels in winter are due to the degradation of organic matter produced during the summer period associated with the high residence time of the bottom seawater layer in that upper part of the estuary.

Distribution of platinum along the estuarine transect

Horizontal distributions of dissolved and/or total Pt concentrations in surface layer along the estuarine horizontal transect are presented in Fig. 4A (in relation to salinity) and Fig. 4B (in relation to distance from the waterfalls, station E0). In most cases, Pt concentrations increased with salinity, reaching a maximum value of ~0.3 pM at the seawater end member, similar to those reported in the North Pacific (~0.3 pM) (Fischer *et al.* 2018) or in the Venice Lagoon (Turetta *et al.* 2003). The concentrations of Pt in the freshwater end-member were low (down to 0.11 pM), higher than those measured in Lérez River (~0.05 pM) (Cobelo-Garcia *et al.* 2013), but significantly lower than those reported by Obata *et al*., (2006) in Ara and Tama Rivers (Japan) or in the urban Como channel (Italy) (Monticelli *et al.* 2010). Dissolved Pt concentration measured in major rivers of East Asia ranged between <0.1 and 5.8 pM, with median values mainly lower than 0.5 pM, with some samples having concentration below 0.1 pM (Soyol-Erdene and Huh 2012). In the Gironde estuary, the decreasing trend of dissolved Pt concentrations with salinity was observed, with Pt concentrations on the level of ~0.55 pM at the freshwater part and ~0.25 pM in the seawater end-member (Cobelo-Garcia *et al.* 2014a). In studies of Gironde and Lérez estuaries Pt (Cobelo-Garcia *et al.* 2013, Cobelo-Garcia *et al.* 2014a), as well as Tokyo Bay's estuaries (Obata *et al.* 2006, Mashio *et al.* 2017) a non-conservative behaviour was found for dissolved Pt. Our results suggest a near-conservative behaviour. A slight positive deviation from the conservative mixing line of dissolved Pt at salinities below ~10 is observed, followed by a clear linear increase toward higher salinities. Taking into account that Pt(II) is predicted to dominate over Pt(IV) in freshwater while the latter is the dominant species in seawater (Cobelo-Garcia *et al.* 2013), this slight positive deviation from the conservative line might be due to a change in Pt redox speciation, favouring the desorption of small amount of Pt from the particulate matter. Indeed, Pt(IV) has a low affinity at higher salinities due to weak electrostatic attraction between inorganic Pt(IV) complexes and the negatively charged suspended particles (Turner 2007). In contrast, in freshwater conditions, Pt(II) is easily adsorbed on the suspended particles (Turner *et al.* 2006). No systematic differences in the level of dissolved Pt concentrations between summer and winter period were found.

Our results show that Pt exist predominantly in the dissolved form, with no evident Pt partitioning trend regardless of salinity. Fig. 4B presents Pt levels measured in unfiltered surface samples as function of distance from E0. Linear increases were obtained for all campaigns. In summer 2017, a slight increase was observed in the region of Šibenik town (distance of ~ 18 km), suggesting an anthropogenic source, connected to more intensive traffic during the summer season. However, this was not observed in summer 2018, maybe due to the lower salinity for which is characterised to have generally lower concentrations of trace metals in the bay (Cindric *et al.* 2015).

On average, ~90% Pt was present in the dissolved form (min/max=54%/112%), similar to previously reported in the Lérez River estuary (Cobelo-Garcia *et al.* 2013). In few samples, Pt concentrations in filtered samples were slightly higher (up to ~10%) than those in unfiltered samples. This was not attributed to contamination issues but more to the uncertainly of the analytical technique (10-15%; error bars in Fig. 4).

Along with the horizontal surface profiles shown in Fig. 4A and 4B, Pt concentration profiles in unfiltered samples in the bottom seawater layer are plotted in Fig 4C. In this case, an increasing trend in the landward direction is evident in both summer 2017 and 2018. Such increase is due to the progressive accumulation occurring in that bottom layer while moving upstream, slowly collecting particles from the upper layer, which might explain why the upstream bottom water has the highest concentrations (Cindric *et al.* 2015). This trend is not unique to Pt and has been observed for few other trace metals (Cindric *et al.* 2015). Another possibility is sediment input. Pt concentrations in the range of 2.8–40 µg/kg were found in estuarine sediments of the Tagus Estuary with dissolved porewaters concentrations of 0.7–3.6 pM (Almecija *et al.* 2016). These concentrations are higher than that of seawater, implying that sediments and interstitial waters can also be a source of Pt in the bottom waters. As the Pt concentrations in the Krka River sediments and porewaters are not know, the contribution of the sediment as a source of Pt to the bottom layer remains an open question.

In winter 2019, the profile shows a different behaviour with an increase low in the estuary and a strong decrease higher in the estuary. Such trend might be explained by the low Pt levels in the Krka river (~ 0.11 pM) and its relatively high flow at that period. Indeed, in summer, the seawater layer was extending all along the estuary, up to the freshwater end while in winter, the freshwater later extended ~3 km down the estuary. Such strong freshwater flow caused mixing of the bottom layer, thus diluting this bottom layer and reducing its Pt concentration levels.

A vertical profile was also collected at a site located in Šibenik bay, ~10 m from the shore (Fig. 1). Fig. 5 shows the Pt concentrations as a function of depth measured in summer 2017 and 2018 as well in winter 2019. A significant increase is observed at the position of the halocline, as observed for many other metals (Cindric *et al.* 2015). Concentrations in the surface (brackish) and bottom (seawater) layers are in general agreement with those of the horizontal transect for that particular location. Small differences are attributed to the different locations, as observed for other metals in that bay (Cindric *et al.* 2015). If plotted against salinity, the concentrations follow a linear trend (Fig. S6), similar to those reported for the transect. For comparison purposes, a typical level of procedural MQ blank was plotted, showing no practical influence on the measured Pt concentrations in samples.

Conclusions

Very low concentrations of Pt in marine/estuarine waters require extremely sensitive analytical methods. In our work, we used a well-known adsorptive cathodic stripping voltammetry, with addition of formaldehyde, hydrazine and sulphuric acid. In order to obtain well resolved voltammograms at low Pt concentrations (e.g. ~0.1 pM), we tested different combinations of voltammetric parameters. Optimum signal to noise ratio was obtained using short interval and modulation times of the differential pulse stripping waveform (0.1 s and 0.025 s, respectively), along with a relatively high pulse amplitude (40 mV). Data treatment is done using a 4th derivative transformations that provides slightly better resolution than the 02nd derivative, that is normally applied (Cobelo-Garcia *et al.* 2014b). Using the optimized voltammetric procedure, LODs were lowered down to 10 pM (LOD based on the standard addition method). The presence of very small concentrations of surface-active substances (SAS) from natural organic matter was found to strongly impact the sensitivity of the method. However, in model solutions, the obtained recoveries were ~100%, implying that under our acidic experimental conditions, Pt was not complexed to the added fulvic acid (0.025 mg/L FA). Further studies would be needed in order to resolve whether the strong decrease in measurement sensitivity in natural samples is due to the complexation of Pt with organic ligands or due to the adsorption of these organic substances on the electrode surface that interfere with the stripping signal. Here, UV-irradiation is required to be able to obtain a signal.

We applied our optimised methodology to study the distribution and behaviour of Pt along the salinity gradient of the stratified Krka River estuary. We found that Pt was mostly present in the dissolved form and total concentrations (unfiltered) ranged between 0.10 and 0.5 pM, with on average ~50% higher concentrations in the bottom seawater layer than in the surface layer. In the latter, Pt concentrations gradually increased towards sea end-member, following a near-conservative behaviour, with a slight increase in the dissolved Pt at salinities below ~10. Speciation modelling predicts change in the redox speciation of Pt, from Pt(II) in freshwater (with higher affinity to particles), to Pt(IV) in seawater in the form of $PtCl_5(OH)^{2-}$. There is a clear increase of Pt concentrations in the bottom seawater layer when moving upstream; this increase might be due to progressive accumulation of Pt, consistent with the residence time of that bottom layer in the estuary and/or from the sediment (Mashio *et al.* 2017). This question remains open and will require further studies.

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Conflicts of Interest

The authors declare no conflicts of interest

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Figure Captions

Figure 1. Left: Map of the Krka River estuary with indicated locations of sampling sites (open squares). Open triangle is location where water column was sampled. Right: horizontal bottom depth profile with positions of sampling sites and specific regions along the estuary.

Figure 2. (A) Voltammograms and (B) relationship of the peak intensity (2nd derivative) on the adsorption potential for ~1.2 pM Pt in seawater obtained with and without added fulvic acid (FA) and with and without desorption step (DS).

Figure 3. Raw DP voltammograms and corresponding 2nd and 4th derivative transformations. Blue dashed line approximates the "tangent fit" line used for peak determination.

Figure 4. Dissolved (A) and “total” (B) Pt profiles in surface layer in relation to salinity (A) and distance from waterfalls (B), and “total” Pt profiles in seawater layer (C). Error bars correspond to 95% CI of each Pt determination.

Figure 5. Vertical profiles of dissolved Pt obtained in summer 2017/2018 and winter 2019 in Šibenik bay.

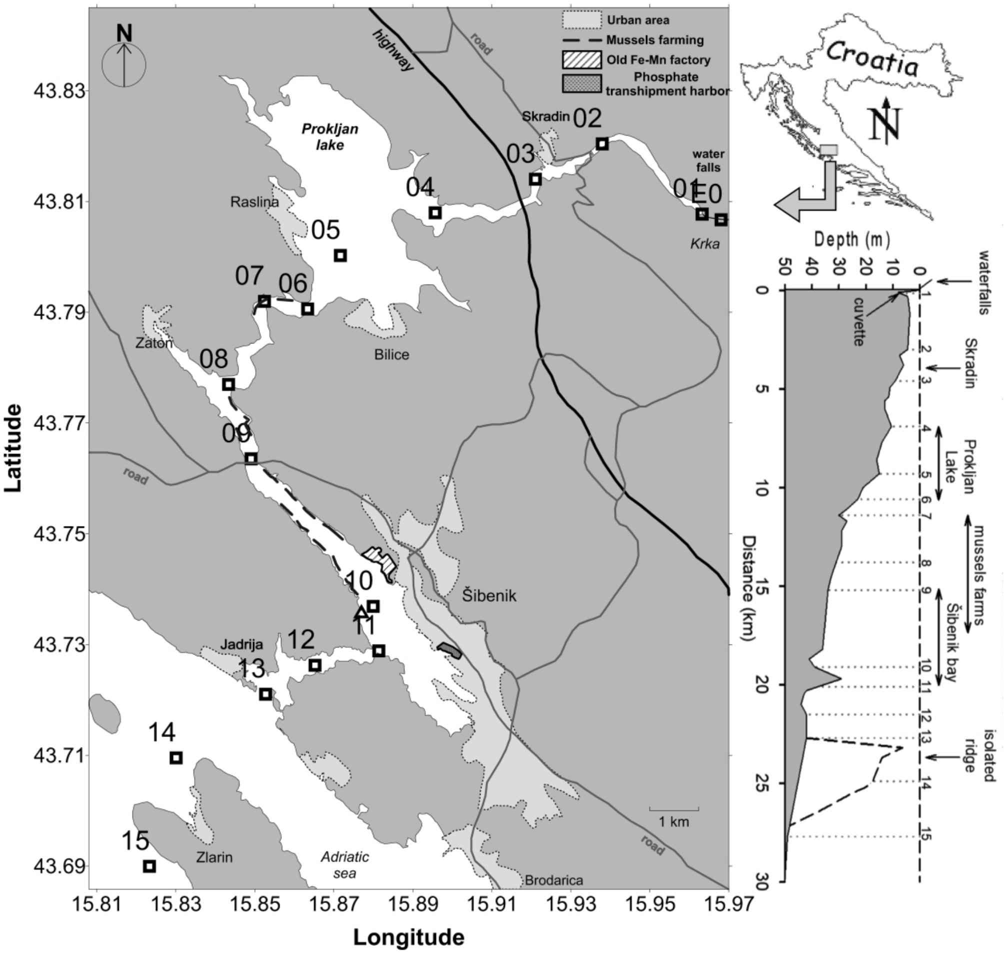

Figure 1

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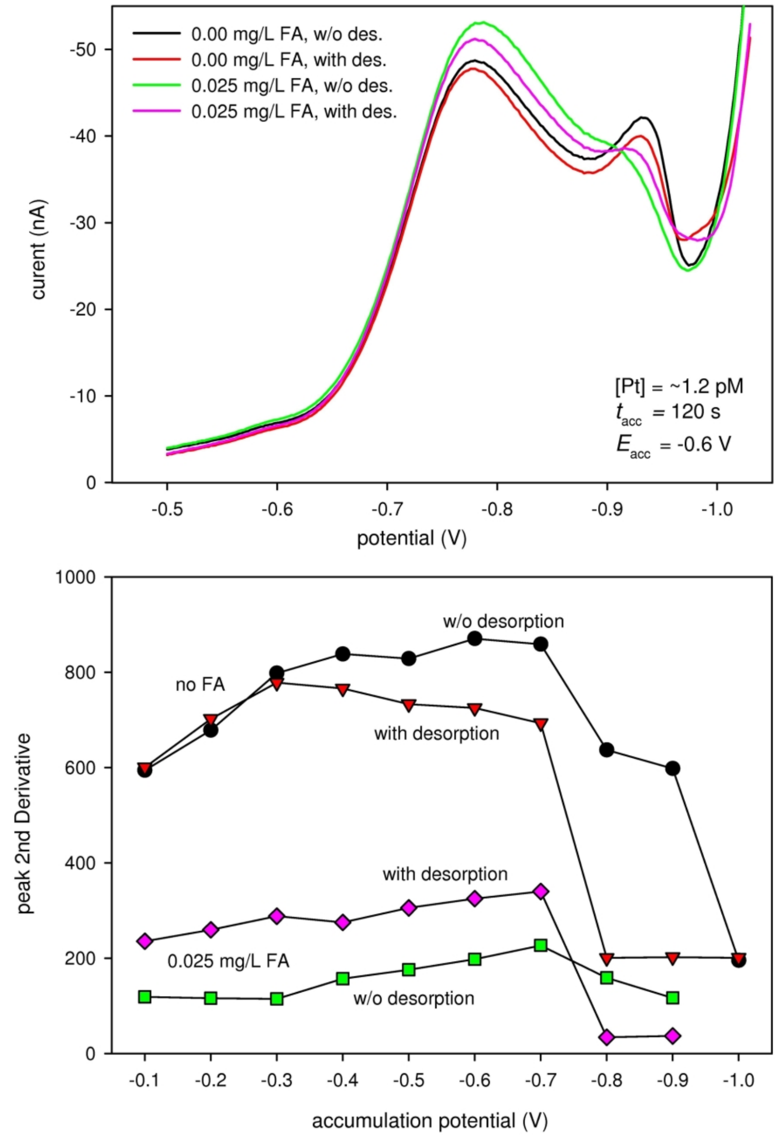

Figure 2

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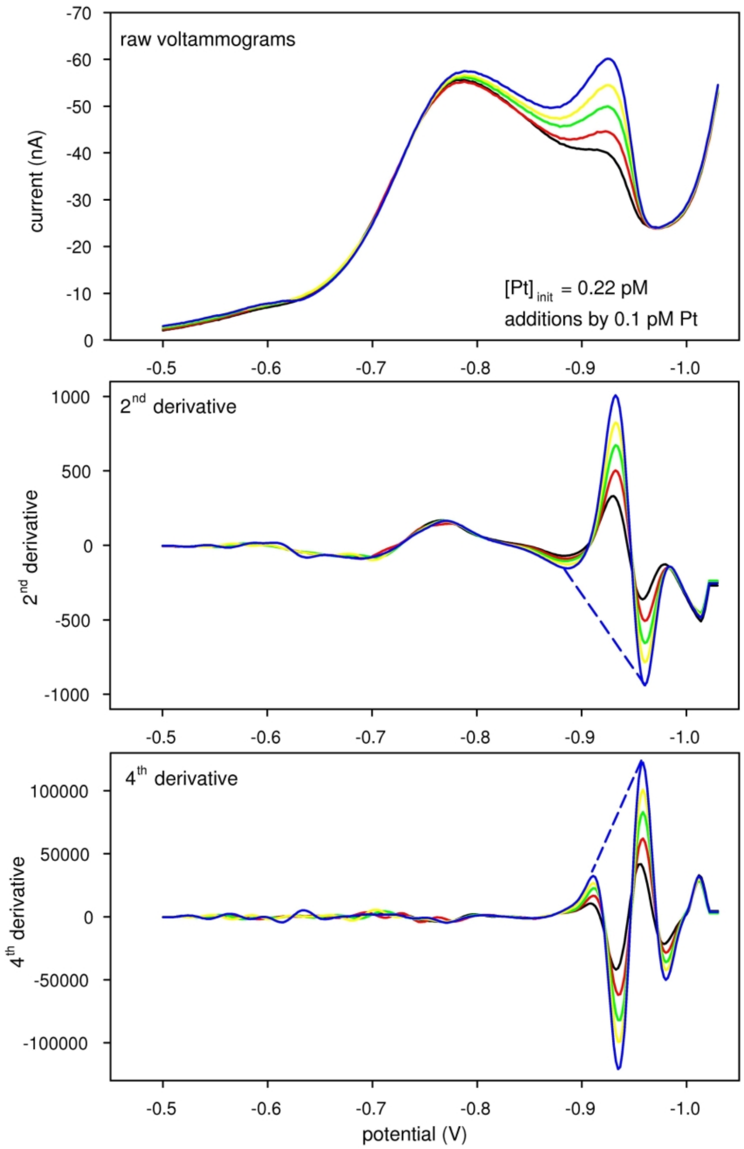

Figure 3

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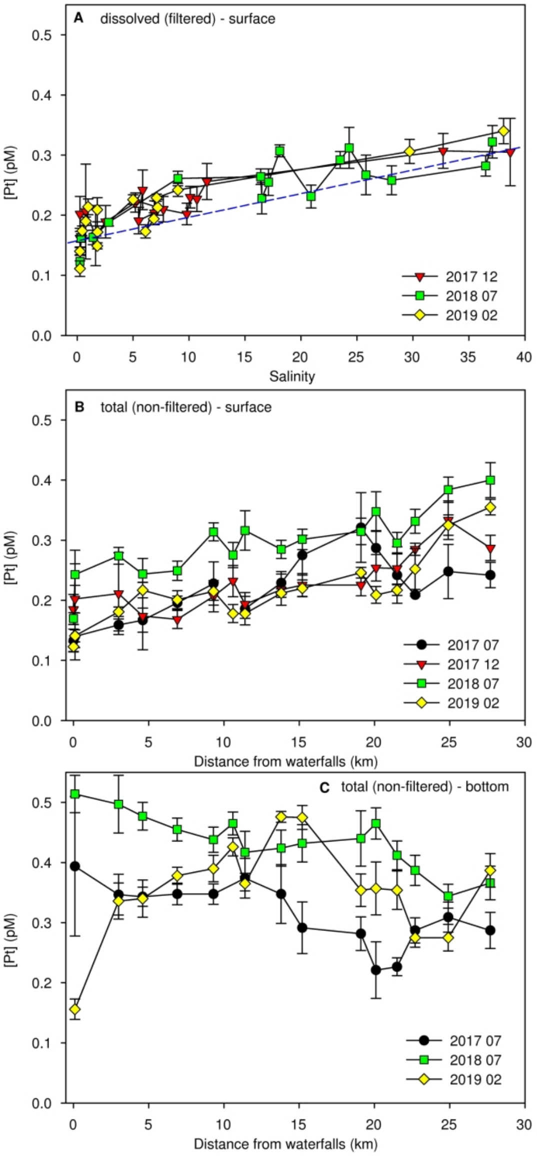

Figure 4

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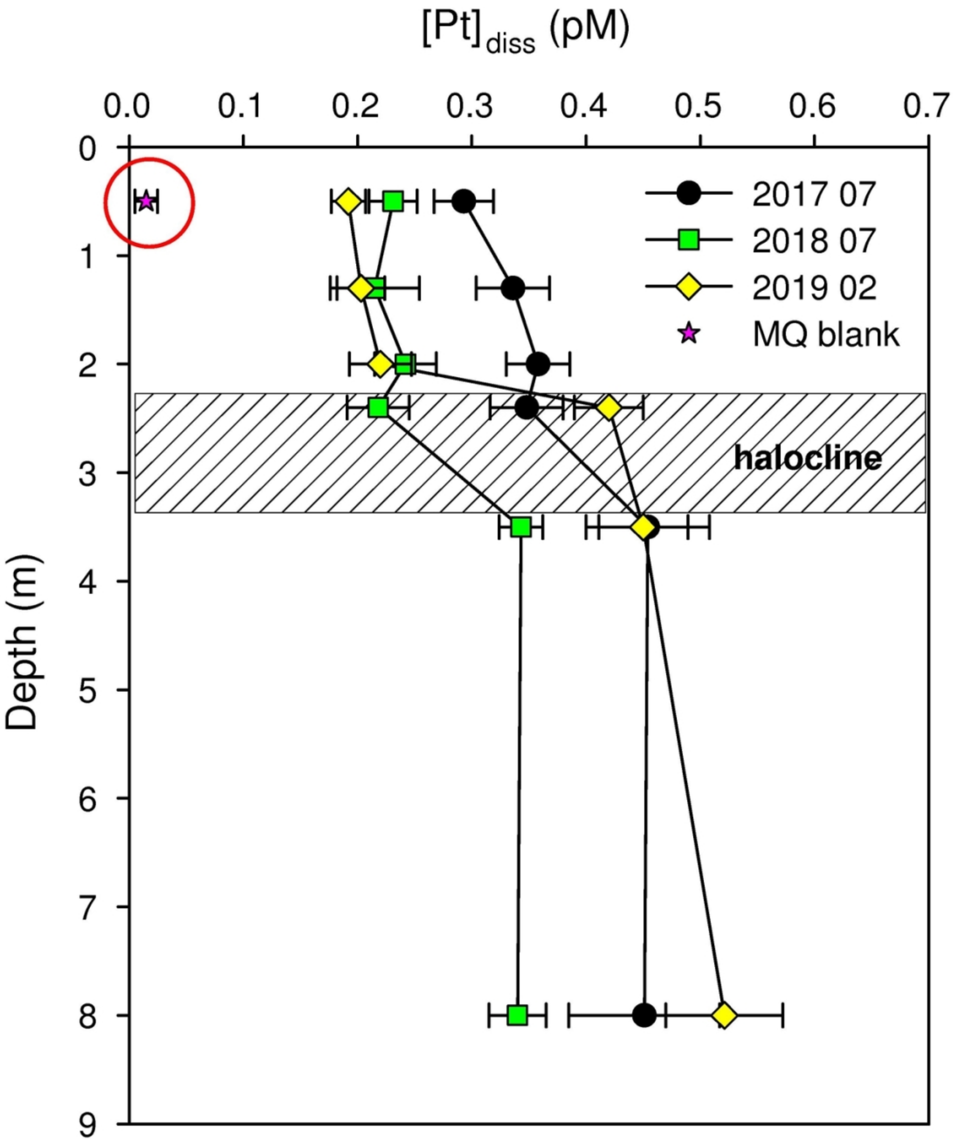

Figure 5

112x134mm (300 x 300 DPI)

Supporting information

Determination of sub-pico-molar levels of platinum in the pristine Krka River estuary (Croatia) using improved voltammetric methodology

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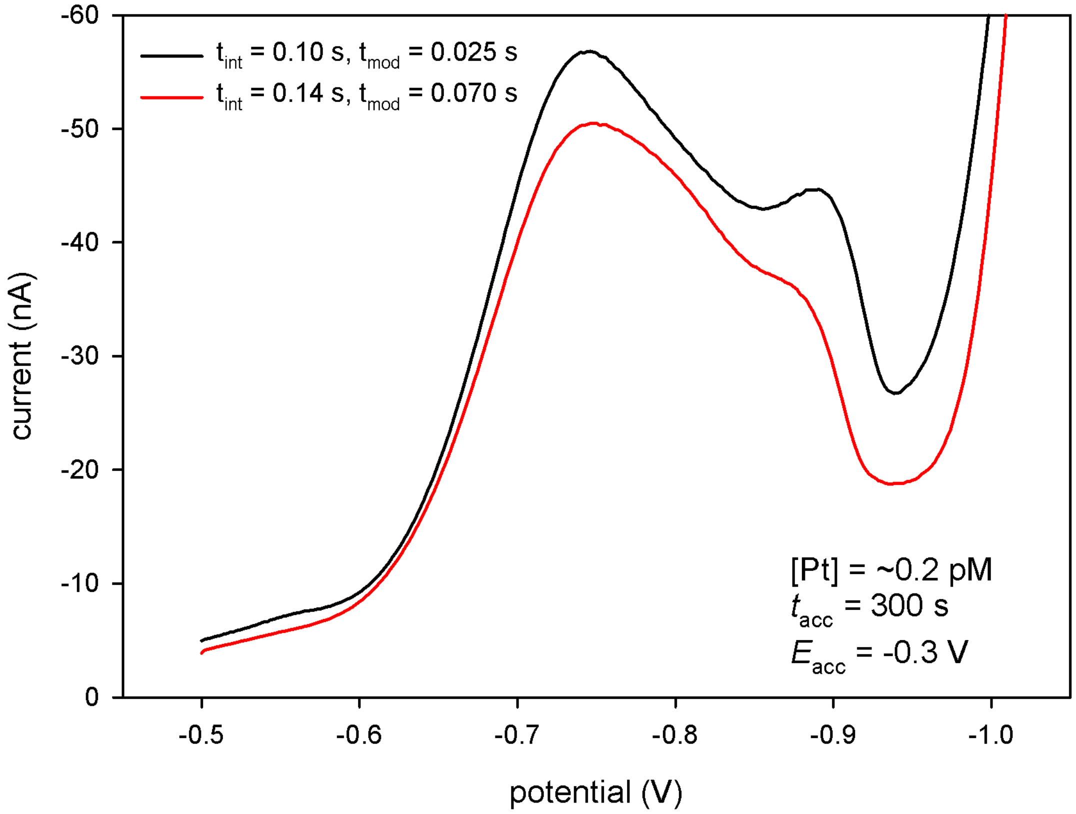


Figure S1. Voltammograms of Pt obtained under two different experimental parameters.

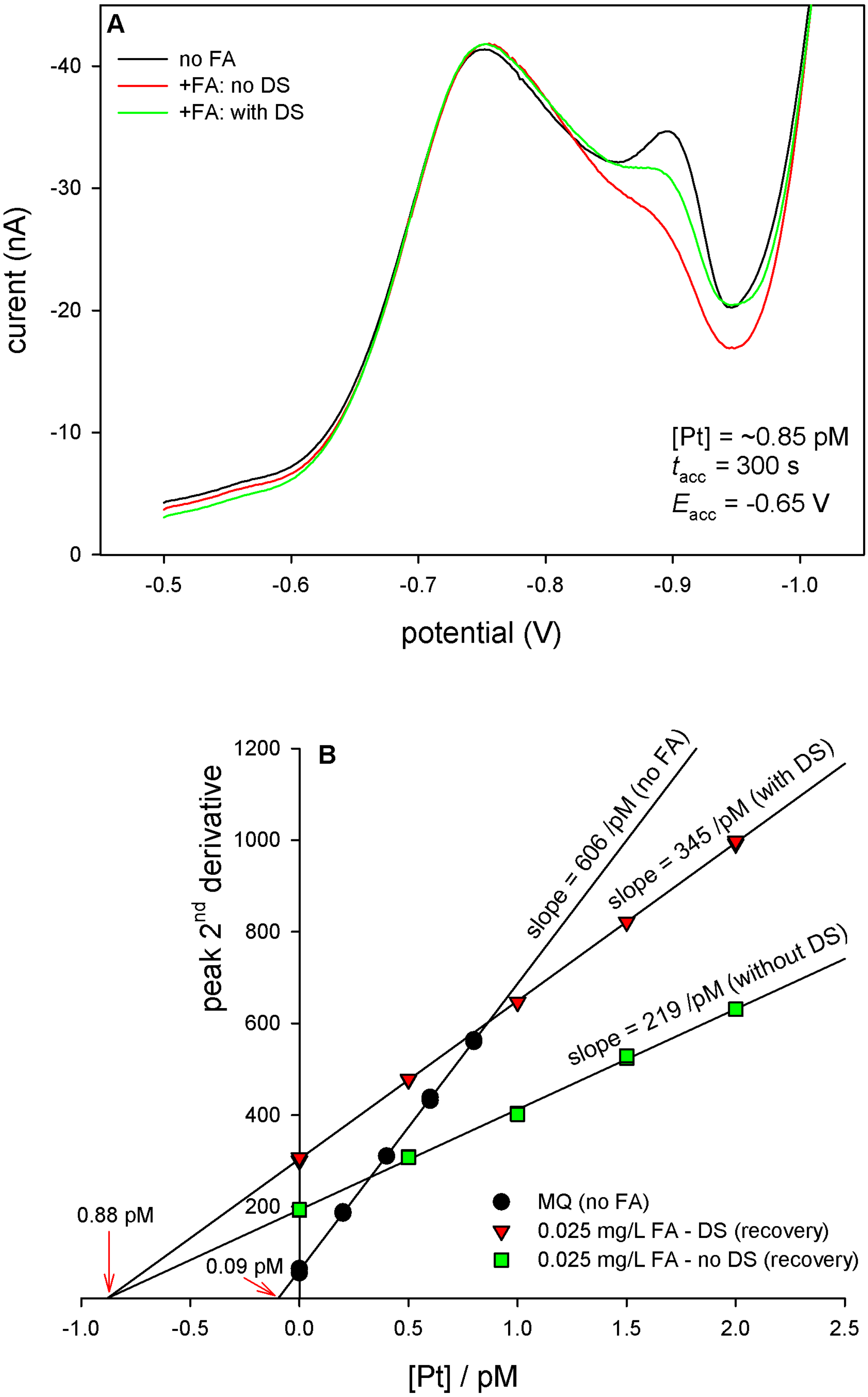


Figure S2. (A) Voltammograms of Pt obtained without added fulvic acid (FA) and with added FA (0.025 mg/L) applying (or not) short desorption step (DS) (E_{ds} = -1.35 V, 2 s). (B) Standard addition plots of Pt in MQ water without added FA, and recovery plots (with and without DS) of Pt after addition of FA.

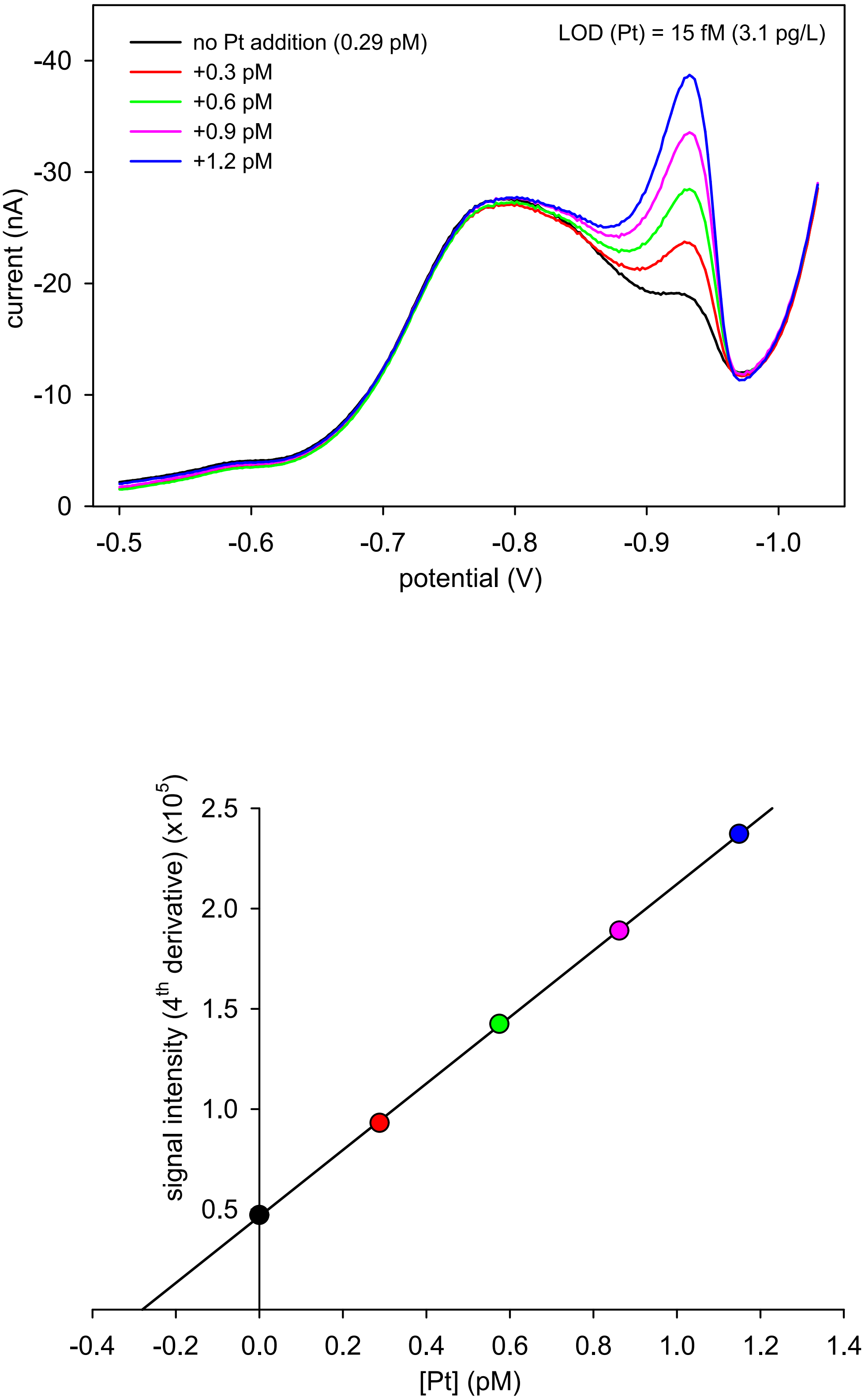


Figure S3. (A) Typical voltammograms of Pt obtained during analysis using standard addition method, along with (B) the corresponding standard addition plot.

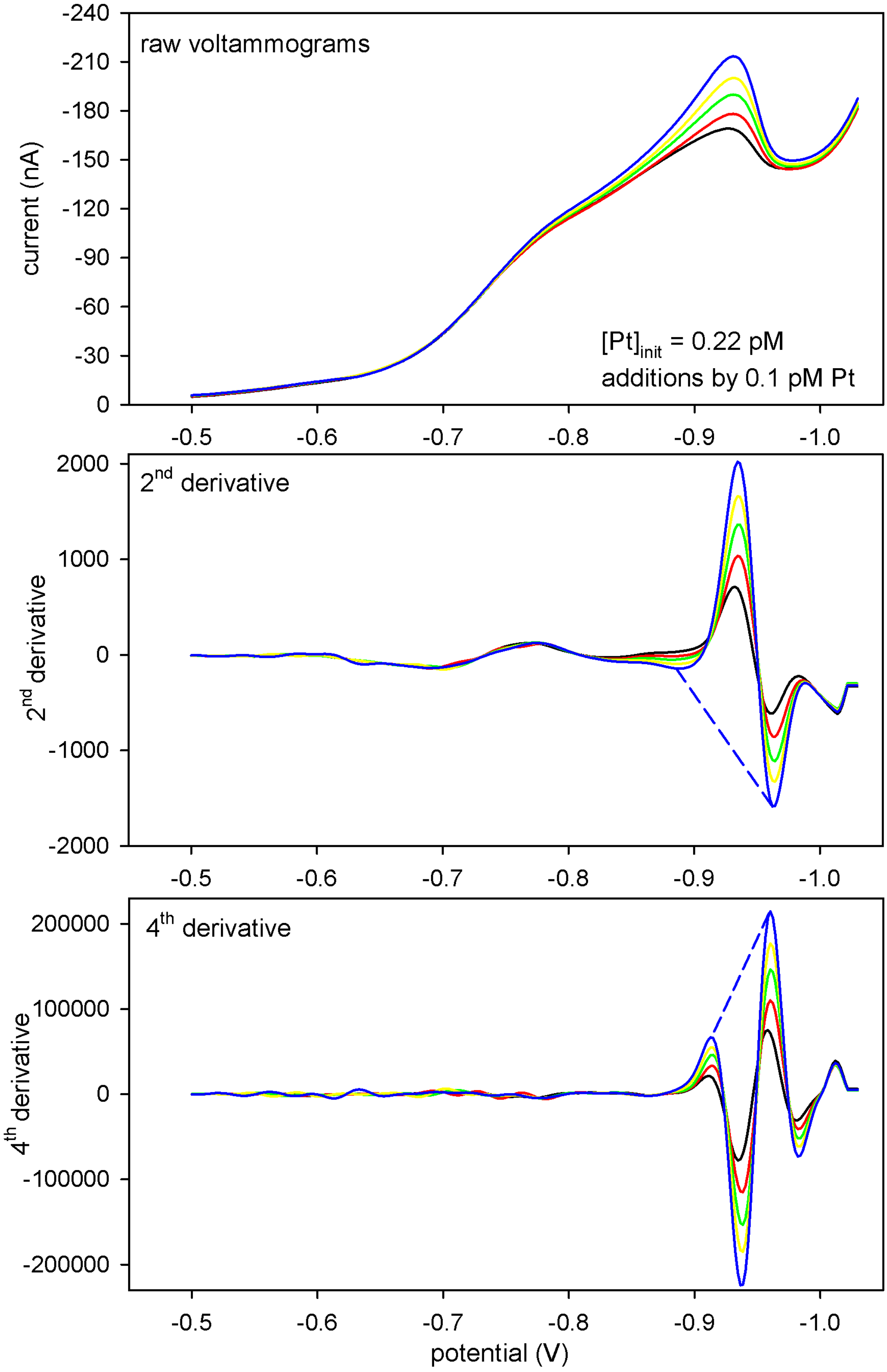
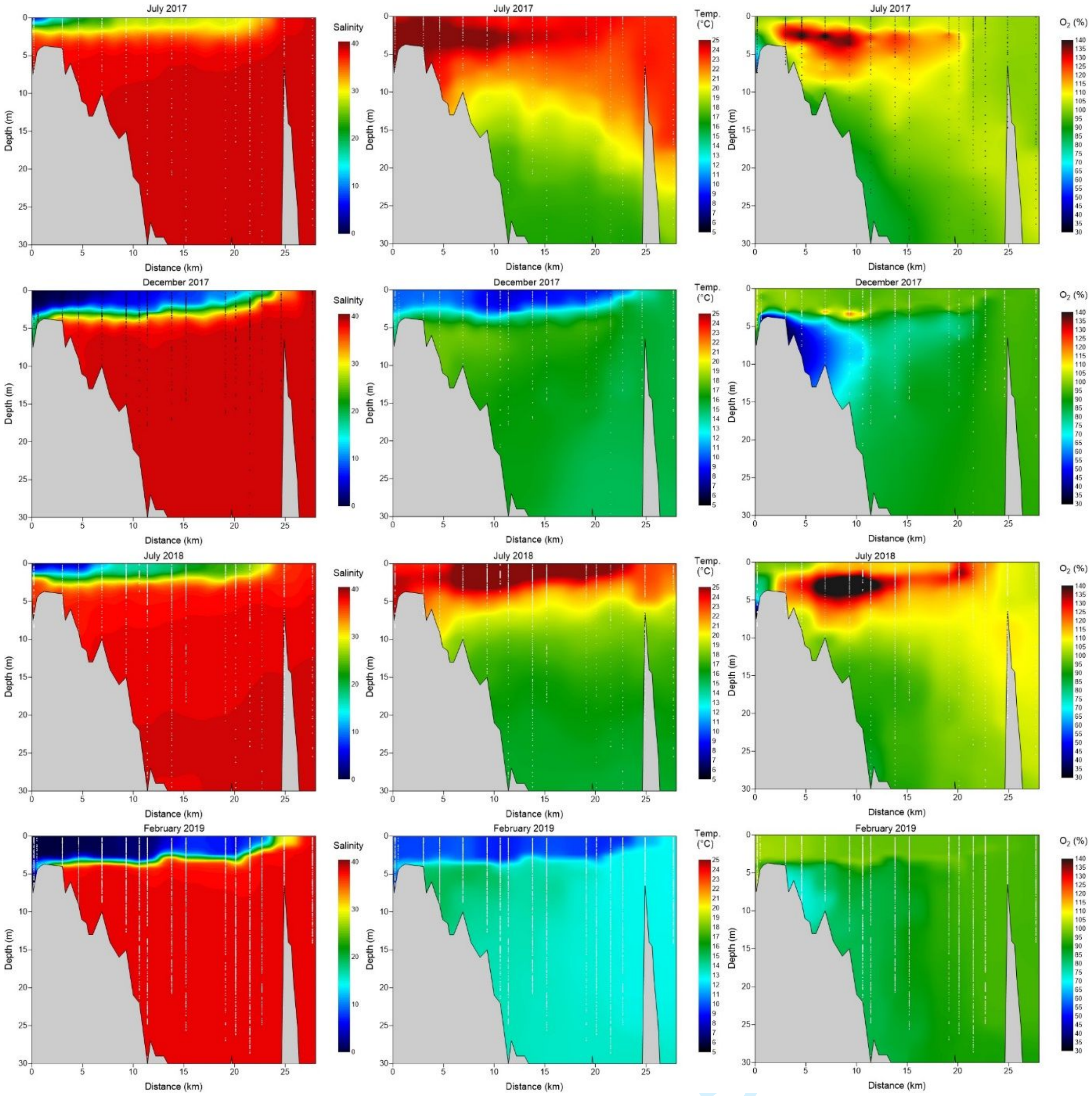


Figure S4. Forward current of DP voltammograms and corresponding 2nd and 4th derivative transformations. Blue dashed line approximates the "tangent fit" line used for peak determination.



July 2017

December 2017

July 2018

February 2019

Figure S4. Contour plots of salinity, temperature and oxygen saturation for examined sampling campaigns.

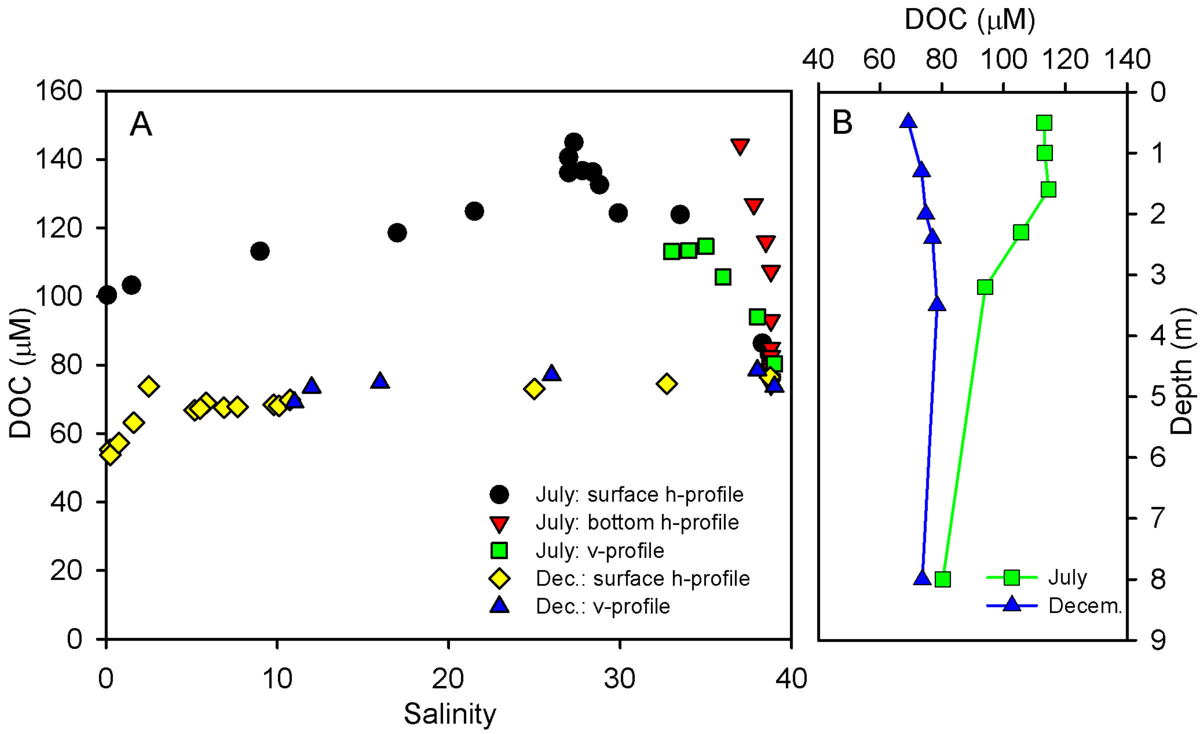


Figure S5. Typical horizontal and vertical profiles of dissolved organic carbon (DOC) for winter and summer period in the Krka River estuary ("h" - horizontal; "v" - vertical)

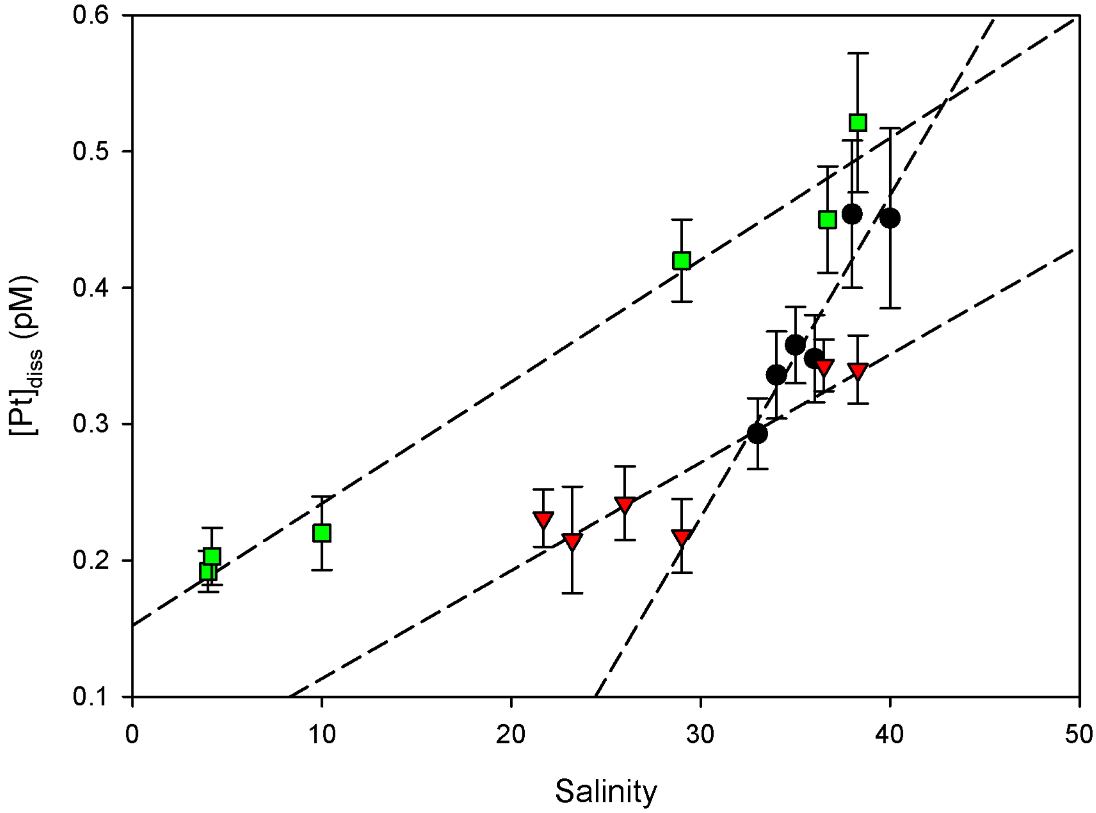


Figure S6. Relationship of dissolved Pt with salinity for examined vertical profiles presented in Fig. 5