Supplementary information:

Reactivity and fluxes of antimony in a macrotidal estuarine salinity gradient: insights from single and triple quadrupole ICP-MS performances

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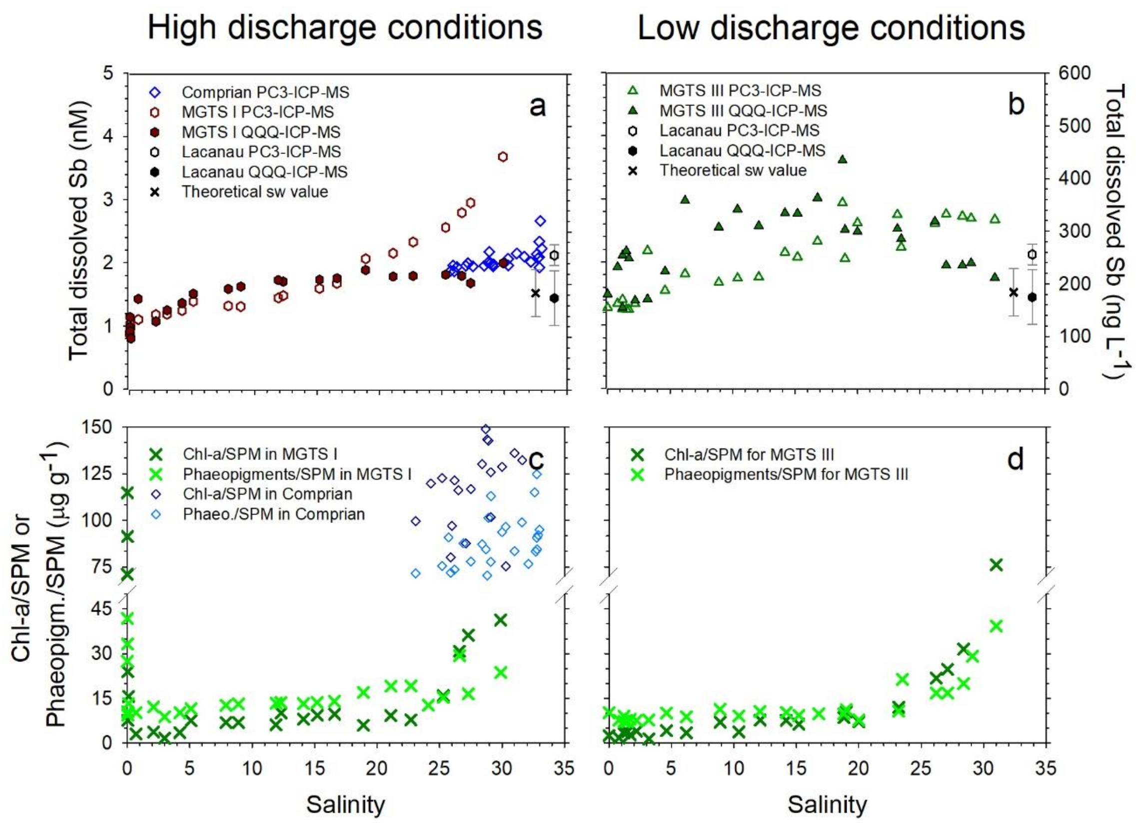

Fig. S1. Comparison between ICP-MS analytical techniques. Sb dissolved concentrations from non-UV-irradiated samples measured with PC3-ICP-MS (empty symbols, Gil-Díaz et al. 2016) and from UV-irradiated samples measured with QQQ-ICP-MS (filled symbols, this study) are compared for (a) intermediate (MGTS I) and (b) low discharges (MGTS III). Dissolved Sb values from Comprian Station in the Arcachon Bay (Gil-Díaz et al. 2016) are also shown in (a). Seawater endmembers are represented in (a,b) by (i) an independent sampling point at Lacanau site, also measured by both techniques, and (ii) by the theoretical range of seawater values of 1.51 ± 0.37 nM (184 ± 45 ng L^{-1}, cross; Filella et al. 2002). Corresponding Chlorophyll-a and Phaeopigment levels are presented normalized to SPM concentrations along the salinity gradients during (c) MGTS I and (d) MGTS III (Pougnet 2018). Corresponding values for the Arcachon Bay (Abdou et al. 2020) are also included in (c).

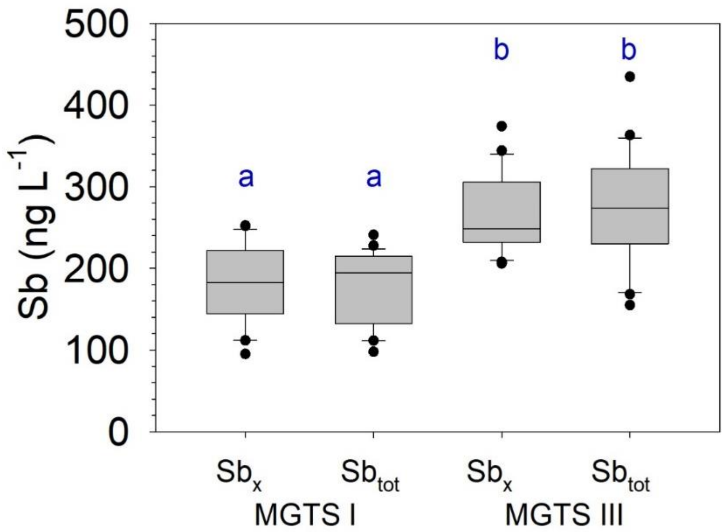

Fig. S2. Box-plots of the Sb_x and Sb_{tot} datasets for MGTS I and MGTS III. The median of each dataset is shown with a line. Normality tests (Shapiro-Wilks tests) were significant for MGTS I (p_value < 0.05) but not for MGTS III datasets (p_value = 0.43). Thus, Mann-Whitney Rank sum test was performed for equal medians on the MGTS I series, showing no statistical significance between Sb_x and Sb_{tot}. The t-test for equal means was run for the MGTS III series, showing no statistical significance between Sb_x and Sb_{tot}. Likewise, differences between MGTS I and III were tested for Sb_x and Sb_{tot}, showing significant differences (p_value < 0.001) in the mean and the median, respectively (i.e., there are significant differences in Sb concentrations between water discharge conditions, drought vs intermediate discharge). These results were obtained via IBM SPSS v20 and are shown in the graph with the letters a and b.

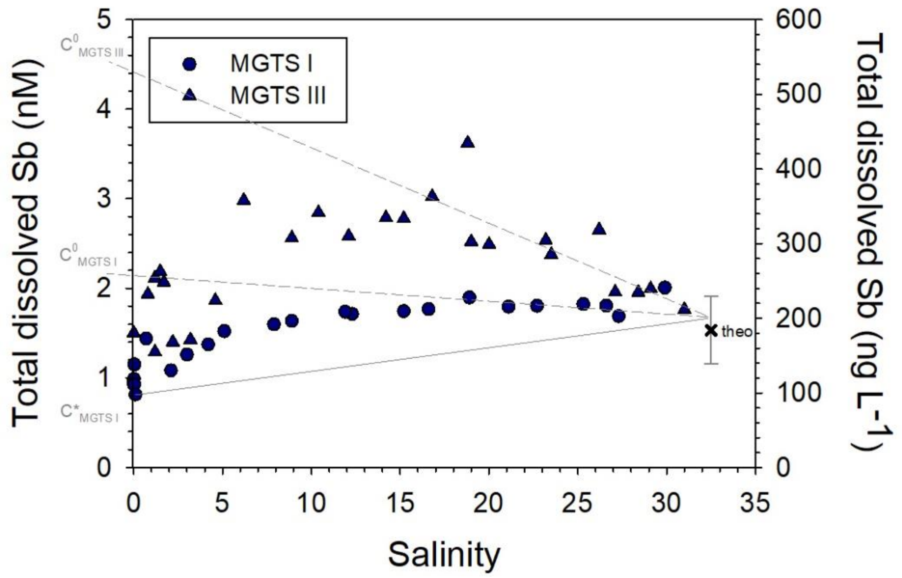

Fig. S3. Estimation of effective and river concentrations for dissolved Sb. Total Sb (inorganic + organic) dissolved concentrations along the salinity gradient of the Gironde Estuary during intermediate (1203 m^3 s^{-1}, MGTS I, filled circles) and low freshwater discharge conditions (248 m^3 s^{-1}, MGTS III, filled triangles) measured directly with QQQ-ICP-MS. Estimated river concentration (C*, only shown for MGTS I, solid line) and "effective" river Sb concentration (C^0, for both MGTS I and MGTS III, dashed lines) are shown together with theoretical (theo) average range of Sb concentrations in seawater (Filella et al. 2002).

Table S1. Influence of onsite filtering/long-term storage and of the UV-treatment on Sb concentrations. Raw data from (i) field blank samples (i.e., Milli-Q water filtered and acidified during field campaigns, like the water samples) and (ii) UV-treatment blanks (i.e., Milli-Q water in Teflon bottles subjected to the same UV-treatment as the water samples for Sb_{tot}).

Conditions		**Samples** Field blanks (N = 3)	**Samples** UV-treatment blanks (N = 6)
Analysis: QQQ-ICP-MS via Standard additions	**Sb concentrations (nM)**	0.02, 0.03, 0.16	0.01, 0.02, 0.12, 0.16, 0.30, 0.32
	Sb concentrations (ng L^{-1})	2.61, 3.79, 19.1	0.7, 1.97, 15.2, 19.3, 36.9, 38.6

Table S2. Overview of Sb_{tot} vs Sb_x differences from MGTS I and MGTS III datasets. Summary table compiling all data values (N = 49) from MGTS I and MGTS III to facilitate the discussion on the potential influence of organo-Sb species on Sb_{tot} and Sb_x differences in the Gironde Estuary. Cases are defined by the ± 15 % criteria attributed to analytical variability (i.e., 15 % diff. threshold). Cases 1 and 4 represent the anomalies in the dataset, where differences between Sb_{tot} and Sb_x concentrations fall beyond the ± 15% threshold*. Differences are accounted as $(Sb_{tot} – Sb_x)/Sb_{tot}$. The number of data that fulfill the criteria are shown as a fraction of the total (i.e., TRUE/total) and the corresponding percentage is also included (i.e., % tot. data). The salinity ranges where conditions are true are included for clarity, as well as the original hypothesis or interpretations of the outcomes.

	Case:	**TRUE / total**	**% tot. data**	**Salinity range**	**Hypothesis/interpretation**
1	$Sb_{tot} > Sb_x$ (> 15 % diff.)[a]	10/49	20%	Mainly S > 15, except: S = 1.5	Potential influence of organic Sb species (< 0.2 µm) OR UV-treatment contamination[+]
2	$Sb_{tot} > Sb_x$ (≤ 15 % diff.)	16/49	33%	0.01 < S < 29	Analytical variability
3	$Sb_{tot} < Sb_x$ (≤ 15 % diff.)	15/49	31%	0.7 < S < 31	Analytical variability
4	$Sb_{tot} < Sb_x$ (> 15 % diff.)[b]	8/49	16%	Mainly S < 5, except: S = 8, S = 12 and S = 27	Inefficient UV-treatment[++]

[a] 7/10 samples show differences which are 20 % to 36 % higher in Sb_{tot} than Sb_x

[b] 5/8 samples show differences which are 23 % to 45 % higher in Sb_x than Sb_{tot}

* The selected threshold is in accordance with the typical/nominal range attributed to analytical variability. This range also agrees with the Tukey 25th - 75th quartiles and the variation coefficients in the study of atypical values, results obtained from the statistical descriptive analysis of each dataset (performed with the IBM SPSS v20)

[+] As evidenced from the UV-treatment blank samples (N = 6), the use of Teflon bottles may influence Sb concentrations in the range of 0.15 ± 0.13 nM (18.8 ± 16.4 ng L^{-1}, raw data shown in Table S1).

[++] Hypothesis: inefficient breakdown of organic compounds could make them more reactive and cause losses of Sb species during measurements at the ICP-MS.

References:

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