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Historical mass balance of cadmium decontamination trends in a major European continent-ocean transition system: Case study of the Gironde Estuary

Pougnet Frédérique [1, *], Gil-Díaz Teba [1], Blanc Gerard [1], Coynel Alexandra [1], Bossy Cécile [1], Schäfer Jörg [1]

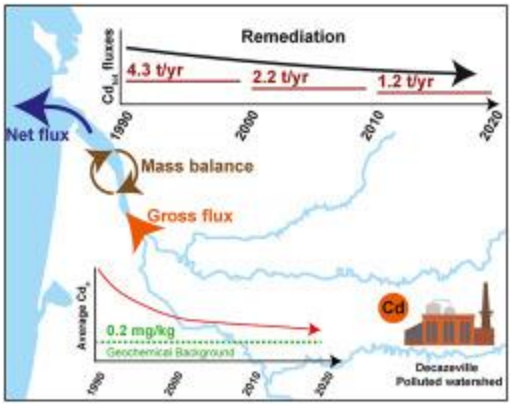
[1] Univ. Bordeaux, CNRS, EPOC, EPHE, UMR 5805, F-33600, Pessac, France

* Corresponding author : Frédérique Pougnet, email address : frederique.pougnet@u-bordeaux.fr

Abstract :

Despite the effective remediation efforts following the end of the metallurgic activity thirty years ago upstream the Lot River watershed, the levels of cadmium (Cd) accumulated in wild oysters from the downstream Gironde Estuary still exceed nowadays the admissible human consumption limit (5 mg/kg, d.w.). The main goal of this work is to quantify the role of sediments as long-term intra-estuarine sources or sinks of Cd and the transport of this contaminant towards the estuary mouth taking as case study the example of the highly turbid Gironde Estuary. The original estimation for the annual net fluxes of the suspended particulate matter (and particulate Cd () presented in this work between 1990 and 2020 indicates that 80% of the Cd discharged into the ocean is in dissolved form (Cdd). The values of vary proportionally to those of and ranged between 0.1 and 1.4 t/y, with a ten-year average decreasing from 0.8 to 0.6 t/y for the past 30 years. The differences between ten-year total (Cdp + Cdd) gross and net fluxes show that Cd has effectively been stored in estuarine sediments. This Cd storage was of about 43, 22 and 13 t for the 1990s, 2000s and 2010s, respectively. However, during years of low gross fluxes, estuarine sediments act as additional, secondary sources of bio-available/dissolved Cd into the water column, potentially relating to the continued observations of high Cd concentrations in wild oysters at the estuary mouth. In addition to the natural solubility of Cdp along the salinity and turbidity gradients of the estuary, natural and anthropogenic remobilization of bottom sediment particles further contribute to its mobilization from the particle phase, along with other numerous inorganic/organic pollutants. The mass balances presented in this work could support a new sediment management policy potentially more beneficial to the estuarine ecosystem.

Graphical abstract



Highlights

► Thirty years record of Cd contamination in Lot-Garonne-Gironde continuum. ► Estimation of corresponding annual gross and net fluxes of SPM and Cd are provided. ► Estuarine Cd storage decreases by decades from 43t in 1990s to 13t in 2010s. ► Intra-estuarine sedimentary dynamics act as long-term sources/sinks of stored Cd. ► Remediation efforts are still required to achieve intra-estuarine background level.

Keywords : Continent-ocean interface, Suspended particulate matter, Monitoring, Cadmium fluxes, Remediation

1. Introduction

Cadmium (Cd) is an element widely present in the environment from both natural (e.g., earth's crust, volcanic activities, forest fires) and anthropogenic sources (e.g., industrial activities, manufacturing of Ni-Cd batteries, as stabilizer in PVC products, and recently in photovoltaics as CdTe, among other applications; Suhani et al., 2021; USGS, 2021). It does not show any biological function, though its accumulation in organisms and biomagnification along trophic chains has shown to have harmful effects for organisms and humans (e.g., oxidative stress leading to carcinogenic effects; Chiffoleau et al., 2001; Martin-Garin, 2004; Suhani et al., 2021). For this reason, Cd is classified within the elements of concern for human health in several European and American priority lists of toxic substances (e.g., EPA, 2008/105/EC), has the 7th position in the Agency for Toxic Substances and Disease Registry (ATSDR, 2019), and appears in the candidate list of elements to be considered as a Substance of Very High Concern (SVHC, ECHA, 2021). Several environmental studies on the reactivity and dispersion of Cd exist in the literature for many environmental compartments. However, these works are still ongoing nowadays, suggesting that this classical element is yet of current interest concerning its environmental fate (e.g., sources/sinks, fluxes), bioaccumulation, and human health risk assessment (e.g., Ramteke et al., 2021; Tzempelikou et al., 2021).

Aquatic systems are highly impacted by anthropogenic activities (e.g., industrial activities, surface runoff, urban discharges, etc.) and favour a wider dispersion of trace elements compared to terrestrial environments. Aquatic organisms thrive within these systems, being of both economic (e.g., seafood) and regulatory interest for environmental monitoring programs (e.g., bivalves used as sentinel species in Mussel Watch programs, etc.). There are several historical records of biological concentrations of Cd in mussels and oysters (RNO/ROCCH, 2016) serving as monitors of ecological status of coastal areas as well as first alerts or indicators for human consumption. Nevertheless, there is little information behind the geochemical processes responsible for the registered biological concentrations. In addition, there is a general lack of long-term geochemical surveys (i.e., more than a few years long) with relevant sampling resolution scales (i.e., more than once per year at a single point) capable of providing a robust registry and comprehensive view (i.e., both dissolved and particulate phases) of the geochemical behaviour of trace elements in the environment. Furthermore, this behaviour is required not only at identified point sources but also along aquatic continuums, showing both spatial-temporal reactivity and evolution of Cd over time.

Among all aquatic systems, estuaries are the most sensitive areas to anthropogenic contamination, from both upstream, river point sources and local, estuarine direct discharges. Estuaries are also highly dynamic environments, showing contrasting salinity and turbidity gradients which affects the exchange of trace elements between dissolved and particle phases, ultimately determining the impact on organism bioaccumulation. In this case, it is known that Cd is subjected to chloro-complexation along the salinity gradient of estuaries (Boyle et al., 1982; Gonzalez et al., 2006), enhancing the transfer of Cd from suspended particles to dissolved forms. The latter are generally considered to provide more bioavailable elemental species to aquatic organisms, though recent studies have also reported that fine sediments may show a non-negligible impact from non-residual Cd species to filter-feeding organisms such as oysters (Ramteke et al., 2021). Nevertheless, there is no available information in the literature providing long-term interannual variability on both hydro sedimentary properties and Cd transfer (i.e., mass balances) along estuarine environments, complementing the observed trends from biomonitoring programs in estuarine systems.

The aim of this work is to provide a comprehensive view and understanding of the transport/retention of Cd in a highly dynamic continent-ocean transition system, explaining reported trends in biological accumulations of oysters at the estuary mouth. Specifically, (i) we report a compilation of historical/published and updated data regarding dissolved (Cd_d) and particulate (Cd_p) Cd concentrations, water discharges (Q) and suspended particulate matter (SPM), and (ii) we provide an unprecedented data evaluation showing estimations between 1990 and 2020 (i.e., interannual total Cd gross and net fluxes with subsequent mass balances for a consistent, 30 years record), with the Gironde Estuary as the ideal case study area. This approach with the mass balance calculations allows verifying the role of sediments as intra-estuarine sinks or sources of Cd and the resilience of the Gironde fluvial-estuarine system to its known historical contamination in Cd. We define the resilience of the system as the processes explaining its gradual return to an acceptable state of decontamination, that is, the processes responsible for the observed, slow recovery of the system to a status where the impact of Cd contamination is no longer present. The status of decontamination will be achieved when (i) the biological concentrations such as those continuously measured in bivalves are below the standard levels for acceptable human consumption of oysters (Water Framework Directive: EC, 2001) and (ii) the environmental concentrations reach levels close to the natural geological background (Larrose et al., 2010). The added value of this work is the use of a high-resolution database (quite scarce in environmental studies) and the comprehensive data evaluation, being capable of estimating in a reasonable manner mass balances for Cd, serving as a guideline for further studies/approaches for other trace elements in continent-ocean transition systems.

2. Material and Methods

2.1. Area of study

2.1.1. Characteristic hydro-sedimentary dynamics

The Lot-Garonne-Gironde fluvial-estuarine continuum is in the southwest of France (Fig. 1). It is a system composed by: (1) the Lot River (i.e., source of historical anthropogenic contamination from its affluent, the Riou Mort River), (2) the Garonne River (i.e., originally draining from the Pyrenean Mountains and where the Lot River eventually discharges), and (3) the Gironde Estuary (i.e., collecting water and suspended particles from its main contributors, the Garonne River, the Dordogne River and the Isle River). These main rivers contribute ~64%, ~31% and ~5% respectively for both the overall water discharge and suspended particle load present the Gironde Estuary (DREAL Aquitaine/HYDRO-MEDDE/DE, 2019; Masson et al., 2006).

The Gironde Estuary (81 000 km^2) is characterized by a semidiurnal tide regime, classified as a stratified estuary during high water discharges and neap tides (e.g., during winter and spring), and as a partially mixed estuary during low river discharges (e.g., in summer and autumn; Jouanneau and Latouche 1981). In addition, the residual circulation and the asymmetric tidal wave promote the formation of a maximum turbidity zone (MTZ) presenting surface concentrations of suspended particle matter (SPM) varying from 1 g/L to > 500 g/L with depth (Sottolichio and Castaing 1999). Otherwise, average SPM concentrations range between 100 mg/L and 1000 mg/L along the estuarine salinity gradient. The MTZ is mostly found in the low salinity region and migrates seasonally along the estuary due to hydrological influence, e.g., reaching the city of Bordeaux in low discharge conditions (Fig. 1). Expulsion events of the MTZ to the coastal area are partial along the year, explaining why the sediment annual supply of ~1.5 – 3 million tons from the Garonne and Dordogne Rivers mounts up to ~4 – 6 million tons within the MTZ (i.e., SPM residence time within the estuary of 1-2 years, established by Castaing and Jouanneau 1979, and verified in this work).

2.1.2. Historical background and current setting

The Lot River is known for its historical mid-19th century multiple metal contamination (mainly zinc, Zn, and cadmium, Cd) mostly from the Aveyron-based zinc metallurgy industry in the Riou Mort River (Latouche, 1988; Jouanneau et al., 1990, 1993, 1999; Lapaquellerie et al., 1995; Blanc et al., 1999; Grousset et al., 1999; Schäfer and Blanc, 2002; Schäfer et al., 2002a; Robert et al., 2004; Audry et al., 2004a, 2004b; Blanc et al., 2006; Coynel et al., 2009). The contaminating metallurgical activities ended in 1987, but metal exportation and fluvial contamination from the industrial area continued to occur due to the drainage and erosion of both landfills containing coal ashes from the former power station and tailings from the ore treatment plant. Remediation works have been implemented overtime to treat the identified point sources ever since, driving parallel efforts regarding the environmental surveillance of the system, including recurrent fluvial monitoring and oceanographic campaigns concerning dissolved, particulate, and biological concentrations. These studies reported Cd concentrations and identified its reactivity along the Gironde fluvial-estuarine continuum (e.g., chloro-complexation along the estuarine salinity and turbidity gradient) at contrasting water discharges and SPM loads, providing a unique and extensive database, uncommon/scarce in environmental studies. Recent works have also reported the decreasing environmental concentrations in the dissolved and particle loads over time, in accordance with the remediation efforts upstream (Bossy et al., 2013; Schäfer et al., 2002). Despite the corresponding decrease in the accumulation levels of Cd in wild oysters at the Gironde Estuary mouth (i.e., KP 82 by Ifremer (RNO-ROCCH), published in Pougnet et al. 2021), bioaccumulation levels evidence that these economically relevant organisms are still unsafe for human consumption even nowadays (EC, 2001). These means that the full cultivation cycle of oysters cannot be performed entirely within the estuary, despite the reclassification of the North Medoc marshes from Class D (i.e., banned cultivation and consumption) to Class B, allowing the maturing of oysters inland. Therefore, there is a need for a comprehensive view including the diverse processes involved in the transfer of Cd along the continent-estuary-coastal continuum (Lot-Garonne-Gironde) in order to understand if the sediments act as sources or sinks of Cd, explaining the estuarine resilience to Cd contamination.

2.2. Implicit calculations

2.2.1. Annual gross fluxes of Cd and SPM

Gross SPM fluxes ($\mathrm{F}^{\mathrm{year}}_{\mathrm{gross}_{SPM}}$), and those of $\mathrm{Cd_p}$ $\left(\mathrm{F}^{\mathrm{year}}_{\mathrm{gross}_{Cdp}}\right)$ and $\mathrm{Cd_d}$ ($\mathrm{F}^{\mathrm{year}}_{\mathrm{gross}_{Cdd}}$) entering into the Gironde Estuary correspond to the sum of the gross fluxes from the three major tributaries, namely the Garonne, the Dordogne and the Isle rivers (Fig. 1). The geochemical data used in this study to quantify the fluxes in the Garonne River are the result of the compilation of data (i.e., SPM and $\mathrm{Cd_p}$/$\mathrm{Cd_d}$ concentrations) acquired as part of the daily monitoring programme carried out since 1990 at La Réole site, upstream of the dynamic tide (Fig. 1, *cf. section 3.1.*), on behalf of the Adour Garonne Water Agency (Bossy et al., 2013; Coynel et al., 2016b, Coynel et al. 2018). During this monitoring, both total Cd and SPM concentrations are quantified to calculate $\mathrm{Cd_d}$ ($\mathrm{F}^{\mathrm{year}}_{\mathrm{gross}_{Cdd}}$) and $\mathrm{Cd_p}$ $\left(\mathrm{F}^{\mathrm{year}}_{\mathrm{gross}_{Cdp}}\right)$ as shown in equations 1 and 2 (i.e., as previously reported in Boyle et al., 1974).

$$\mathbf{F}^{\mathbf{year}}_{\mathbf{gross}_{\boldsymbol{Cdd}}\,(\boldsymbol{Gar.})} = \sum_{365}^{i=0}(\mathbf{Q}^{i}_{(\boldsymbol{Gar.})} \times [\boldsymbol{Cd_d}]_{\boldsymbol{Gar.}}) \ (1)$$

- $\mathbf{Q}^{\mathbf{i}}_{(\boldsymbol{Gar.})}$: Daily discharges from the Garonne River (at Tonneins; DREAL Aquitaine/HYDRO-MEDDE/DE)
- $[\boldsymbol{Cd_d}]_{\boldsymbol{Gar.}}$: Daily Cd_d concentrations between 1990 and 2019 estimated from point sampling campaigns with a 24-day frequency at La Réole in the Garonne River (*cf. section 2.3.1.*).

$$\mathbf{F}^{\mathbf{year}}_{\mathbf{gross}_{\boldsymbol{Cdp}(\boldsymbol{Gar.})}} = \sum_{365}^{i=0}(\mathbf{F}^{\mathbf{daily}}_{\mathbf{gross}_{\boldsymbol{SPM}(\boldsymbol{Gar.})}} \times \left[\boldsymbol{Cd_p}\right]_{\boldsymbol{Gar.}}) \ (2)$$

- $\mathbf{F}^{\mathbf{daily}}_{\mathbf{gross}_{\boldsymbol{SPM}(\boldsymbol{Gar.})}} = \boldsymbol{SPM}_{\boldsymbol{Gar.}} \times \mathbf{Q}^{i}_{(\boldsymbol{Gar.})}$: Estimated daily SPM gross fluxes in the Garonne River, with $\boldsymbol{SPM}_{\boldsymbol{Gar.}}$ representing the quantified, daily SPM concentration in the Garonne River (*cf. section 3.1.*) between 1990 and 2019.
- $\left[\boldsymbol{Cd_p}\right]_{\boldsymbol{Gar.}}$: Daily Cd_p concentrations between 1990 and 2019 estimated from point sampling campaigns with a 24-day frequency at La Réole in the Garonne River (*cf. section 2.3.1.*). Note that units are not accounted for in neither equation 1 nor 2.

The annual gross fluxes of Cd_p and Cd_d from the Dordogne and Isle rivers were determined from on-site sampling campaigns respectively at Pessac sur Dordogne and Abzac sur l'Isle during four years of monitoring from 1999 to 2002 (Masson, 2007). This simultaneous monitoring over four years together with that of the Garonne River was already used to establish a relative contribution of SPM fluxes of about 65%, 30% and 5% for the Garonne, Dordogne and Isle rivers respectively (Masson et al., 2006). This comparison and results were applied in the present work to obtain a realistic estimate of the $\mathrm{F}^{\mathrm{year}}_{\mathrm{gross}_{Cdd}}$ and the $\mathrm{F}^{\mathrm{year}}_{\mathrm{gross}_{Cdp}}$ for the non-regularly monitored tributaries in the 30-year record, Dordogne and Isle, according to equations 3 and 4:

$$\mathbf{F}^{\mathbf{year}}_{\mathbf{gross}_{\boldsymbol{Cdd}}\,(\boldsymbol{Dord./Isle})} = \mathbf{Q}^{\mathbf{year}}_{(\boldsymbol{Dord./Isle})} \times \overline{[\boldsymbol{Cd_d}]}^{\mathbf{1999-2002}}_{\boldsymbol{Dord./Isle}} \ (3)$$

- $\mathbf{Q}^{\mathbf{year}}_{(\boldsymbol{Dord./Isle})}$ Annual discharges from the Dordogne (at Pessac sur Dordogne) or the Isle (at Abzac sur l'Isle; DREAL Aquitaine/HYDRO-MEDDE/DE)
- $\overline{[\boldsymbol{Cd_d}]}^{\mathbf{1999-2002}}_{\boldsymbol{Dord./Isle}}$: Annual averages of Cd_d concentrations between 1999 and 2002 for the Dordogne or Isle River (Masson, 2007)

$$\mathbf{F}^{\mathbf{year}}_{\mathbf{gross}_{\boldsymbol{Cdp}(\boldsymbol{Dord./Isle})}} = \mathbf{F}^{\mathbf{year}}_{\mathbf{gross}_{\boldsymbol{SPM}(\boldsymbol{Dord./Isle})}} \times \overline{\left[\boldsymbol{Cd_p}\right]}^{\mathbf{1999-2002}}_{\boldsymbol{Dord./Isle}} \ (4)$$

- $\overline{[\boldsymbol{Cd_p}]}_{\boldsymbol{Dord./Isle}}^{\mathbf{1999-2002}}$: Annual averages of Cd_p concentrations between 1999 and 2002 for the Dordogne or Isle River (Masson, 2007)
- $\mathbf{F}_{\mathbf{gross}_{SPM\mathrm{Dord.}}}^{\mathbf{year}} = \boldsymbol{P_{Dord.}} \times \mathbf{F}_{\mathbf{gross}_{SPM\mathrm{Ga.}}}^{\mathbf{year}}$: Estimated annual SPM gross fluxes in the Dordogne River, with $\boldsymbol{P_{Dord.}}$ representing the percentage of gross SPM fluxes of the Dordogne compared to that of the Garonne, equal to 30% (1999 – 2002).
- $\mathbf{F}_{\mathbf{gross}_{SPM\,Isle}}^{\mathbf{year}} = \boldsymbol{P_{Isle.}} \times \mathbf{F}_{\mathbf{gross}_{SPM\mathrm{Ga.}}}^{\mathbf{year}}$: Estimated annual SPM gross fluxes of the Isle River, with $\boldsymbol{P_{Isle}}$ representing the percentage of gross SPM fluxes of the Isle compared to that of the Garonne, equal to 5 % (1999 – 2002).

We are aware that the estimated fluxes at Isle and Dordogne are first approximations based on point observations between 1999 - 2002, probably not sufficiently representative of all the hydrological conditions of each year for a time series of 30 years. Nevertheless, and as aforementioned, having high-frequency records in a whole watershed is challenging in environmental science and we have decided to use this approach for the case of the Dordogne and Isle rivers to serve here as a first conservative approach in the classical sense of predictive model calculations (i.e., not related to chemical reactivity). Given the low contribution of the Isle River for both water discharges and SPM to the overall loads into the Gironde Estuary, the error induced in using such approach is considered very low compared to the effective contributions of the Dordogne and Garonne rivers. For the case of the estimations of the Dordogne River it is difficult to estimate the error in this approach concerning intrinsic the interannual variability given the fact that this river generally shows a similar contribution in water discharges and SPM to the Gironde Estuary relative to the Garonne River, and that lower Cd loads proceed due to the less anthropogenically impacted sites and different orogenic sources (i.e., Massif Central) of the Dordogne River. Nevertheless, this variability may be relatively small compared to the historical, measured contamination from the Garonne River (*c.f. section 4.1*), not changing the observed overall trend.

2.2.2. Annual net fluxes of SPM and particulate Cd

By definition, the daily particulate metal flux at the estuary mouth is proportional to the concentration of Cd carried by particles and the net fluxes of SPM transiting to the sea during one day (i.e., the product of the SPM concentration and the water discharge, Q_j; the subscript *j* indicating daily discharges within the estuary, i.e., the sum of the individual Q_i from discharging rivers). To access a multi-year record on annual net fluxes of Cd_p ($F_{\mathrm{net}_{\mathrm{Cdp}}}^{\mathrm{year}}$), this study has summarized Cd concentrations carried by estuarine particles and estimated annual net flux values of SPM since 1990 at radial levels between the Grave Point and the Suzac Point (GP-SP, Fig. 1), defined as the geographical and biogeochemical boundary between the Gironde Estuary and coastal waters. This means, six sampling campaigns were performed at the same radial between 2006 and 2014 (*cf. section 2.3.2*), ~66% of them carried out during low discharge conditions ($Q_j < 700$ m^3/s).

More specifically, in order to quantify the SPM net fluxes, it is necessary to make a mass balance of SPM flowing out of the estuary during the ebb and entering the estuary during the flood at GP-SP from repeated radials over a tidal cycle. These residual calculations are obtained by coupling measurements of water velocity by "Accoustic Doopler Profiler Currentometer" (ADPC) and SPM concentrations from vertical samples collected along the GP-SP radial (Dabrin, 2009; Pougnet, 2018). The obtained results at this radial were contrasted and in accordance with simulated results from the hydrosedimentary model SIAM-3D, originally designed from satellite images and widely used for calculations regarding hypoxia development and dynamics of the MTZ in the Gironde Estuary (Sottolichio et al., 2000; Benaouda, 2008; van Maanen et al., 2018; Lajaunie-Salla et al., 2017). This means that the point, daily net SPM fluxes of specific sampling campaigns are in accordance with a stablished model estimating net SPM fluxes from daily water discharges. This integrative approach shows that for discharges below 700 m^3/s, residual SPM fluxes (i.e., the difference between the outgoing flux during ebb and the incoming flux with the tide) are almost zero; and that >70% of SPM fluxes exported to the sea only occur during major expulsions of the MTZ (i.e., during recurrent high-water discharges and tidal coefficients; Castaing and Allen, 1981).

Therefore, during this study, we could estimate daily net SPM fluxes between 1990 and 2020, by analysing the record of historical daily water discharges (DREAL Aquitaine/HYDRO-MEDDE/DE), including an estimate of the number of annual expulsion events of the MTZ by including information about the tidal coefficients (Grand Port Maritime de Bordeaux, GPMB). The criteria followed to account for expulsion events is based on previous results evidencing sediment transport and the positioning of the MTZ to estuarine hydrology (Allen and Castaing, 1973; Allen et al., 1977, 1980; Castaing and Allen, 1981; Lane et al., 1997; Sottolichio and Castaing, 1999; Doxaran et al., 2006, 2009; Benaouda, 2008). An expulsion event is considered to happen when either (1) isolated flood events ($Q_j > 3500$ m^3/s) occur during mean discharge conditions ($Q_j \approx 1000$ m^3/s) and spring tidal coefficients (>70), or when (2) two subsequent high discharge events ($Q_j >$ 2500 m^3/s) occur over a duration of at least ten consecutive days, during high tidal coefficients (>70) and separated by discharges exceeding 1000 m^3/s (Pougnet, 2018). Moreover, when a major expulsion is retained by this analysis, it excludes the likelihood of a second successive expulsion, even if favourable conditions for expulsion persist.

This means that, daily net SPM fluxes (i) in dry conditions (Q_j < 700 m^3/s) do not account significantly to the overall annual flux, (ii) at intermediate Q_j (700 m^3/s< Q_j< 2500 m^3/s, bounded range defined in SIAM-3D) are calculated from the SIAM-3D model of Benaouda (2008), and (iii) for high Q_j (Q_j > 2500 m^3/s) are estimated from a realistic, reference SPM net flux quantified in 2007 by Dabrin (2009), only when expulsion events are identified along the year. Thus, the $\mathrm{F}_{\mathrm{net}}^{\mathrm{year}}$ of SPM for the period from 1990 to 2019 were estimated as explained by equation 5:

$$\mathbf{F}_{\mathbf{net}_{SPM}}^{\mathbf{year}} = (\boldsymbol{nb}_{\mathbf{700}}^{\mathbf{2500}} \times \boldsymbol{F}_{\boldsymbol{SPM}_{\boldsymbol{n}}})/\boldsymbol{n} \times (\boldsymbol{nb}_{\mathbf{700}}^{\mathbf{2500}} \times \boldsymbol{F}_{\boldsymbol{SPM}_{\boldsymbol{n}}}) + \boldsymbol{nb}_{\boldsymbol{expul.}} \times \boldsymbol{F}_{\boldsymbol{SPM}_{\boldsymbol{flood}}}^{\boldsymbol{ADCP}} \quad (5)$$

- $\boldsymbol{nb}_{\mathbf{700}}^{\mathbf{2500}}$: Number of days in the year when discharges range between 700 m^3/s < Q_j < 2500 m^3/s
- $\boldsymbol{F}_{\boldsymbol{SPM}_{\boldsymbol{n}}}$: the corresponding SPM net fluxes for 700 m^3/s< Q_j< 2500 m^3/s, modelled to be 0.5 Mt (Benaouda, 2008)
- $\boldsymbol{n}$: Number of days in 2007 (base year) when discharges were between 700 m^3/s and 2500 m^3/s (Dabrin, 2009)
- $\boldsymbol{nb}_{\boldsymbol{expul.}}$: Estimated number of potential expulsion events
- $\boldsymbol{F}_{\boldsymbol{SPM}_{\boldsymbol{flood}}}^{\boldsymbol{ADCP}}$: SPM net fluxes determined in 2007 along the GP-SP radial during a flood event (set at 1.1 Mt/event; Dabrin, 2009)

Subsequently, the estimate of $\mathrm{F}_{\mathrm{net}_{Cdp}}^{\mathrm{year}}$ can be calculated from equation 6:

$$\mathbf{F}_{\mathbf{net}_{Cdp}}^{\mathbf{year}} = \mathbf{F}_{\mathbf{net}_{SPM}}^{\mathbf{year}} \times \boldsymbol{Cd}_{\boldsymbol{pGi}} \quad (6)$$

- $\mathbf{F}_{\mathbf{net}_{SPM}}^{\mathbf{year}}$: Annual SPM net fluxes, calculated from equation 5.
- $\boldsymbol{Cd}_{\boldsymbol{p}\,\boldsymbol{Gi}}$ = 0.45 mg/kg corresponding to the average Cd_d concentration in surface waters of the Gironde Estuary between 2002 and 2017. The reason for this concentration is explained in section 4.1.1.

2.2.3. Annual net fluxes of dissolved Cd

The annual net fluxes of Cd_d ($\mathrm{F}_{\mathrm{net}_{Cdd}}^{\mathrm{year}}$) presented in this work correspond to the sum of daily net fluxes of Cd_d calculated from an already published, empirical numerical model for the Gironde Estuary (Pougnet et al. 2021). This model was developed based on the long-term record on Cd_d concentrations acquired along the estuarine salinity gradients since October 1982 (i.e., selected salinity ranges between 15 and 25 from 36 campaigns, *c.f. section 2.3.2*), allowing to (i) determine the theoretical Cd concentrations at zero salinity (Cd_0) following the method described in Boyle et al. (1974) and (ii) correlate these values to estuarine, daily water discharges (Q_j). These correlations over time were computed by using truncated exponential functions with thresholds corresponding to the 10-year-stage decreases in Cd contamination observed in wild oysters from the Gironde Estuary (Pougnet et al., 2021), allowing to extrapolate non-measured days based on measured, known Q_j (DREAL Aquitaine/HYDRO-MEDDE/DE).

The truncated model was further developed in order to directly compute/predict $F_{\mathrm{net}_{Cdd}}^{\mathrm{year}}$ for a given 10-year-stage based on annual water discharges (i.e., calculated from DREAL Aquitaine/HYDRO-MEDDE/DE) measurements). In this current work, we have updated the database of Cd_d with more recent sampling campaigns to complete the historical trend of 30 years (compared to that in Pougnet et al. 2021) and report annual net fluxes of Cd_d computed from the aforementioned model by Pougnet et al. (2021). Noteworthy, the measured net fluxes from the recent years (i.e., 2019) match the predicted values when the current 10-year-stage is used, serving as a post-validating step of the robustness of the model.

2.3. Oceanographic campaigns and data acquisition

2.3.1. The fluvial system (gross fluxes)

The Lot–Garonne–Gironde fluvial-estuarine system has been continuously monitored since 1990 as part of a long-term decontamination-monitoring program from the Adour Garonne Water Agency (e.g. Audry et al. 2004a; Masson et al. 2006; Schäfer et al. 2002). Consequently, La Réole site has been sampled periodically ever since. Daily water samples for analysing SPM concentrations have been taken by hand (1 sample per day). This sampling frequency and accuracy of subsequent calculated gross fluxes of SPM have been assessed and validated (Coynel et al., 2004). Trace element concentrations are accounted by another frequency sampling (i.e., every ~24 days, with additional sampling during flood events) collecting water and sediment samples manually (i.e., at ~0.5 m depth, 1 m away from the riverbank). From these, Cd_d (i.e., filtered onsite with 0.2 µm Minisart® cellulose acetate filters) and Cd_p (i.e., 40 L of sample, then centrifuged by a Westfalia 12000g for retrieval of particles) are quantified. Briefly, Cd_p is extracted from the SPM after a total, tri-acid digestion and both Cd_p and Cd_d are quantified by ICP-MS. Further details of the sampling strategy and the analytical methodology for determining fluvial concentrations of Cd_d and Cd_p are reported in many previous studies (Masson et al., 2006; Coynel et al., 2007a, 2007b; Bossy et al., 2013, Coynel et al., 2016b). The representativeness of the sampling methods, sampling conditioning and river water analyses allowing to access reliable values of Cd_d and Cd_p for calculating inter-annual gross fluxes have also been described elsewhere (Blanc et al., 1999; Schäfer and Blanc, 2002; Schäfer et al., 2002a; Audry et al., 2004a; Coynel et al., 2004).

2.3.2. The estuarine system (net fluxes)

The data used for calculating Cd net fluxes released into the sea result from several oceanographic campaigns carried out in the Gironde Estuary including (i) historical data from twenty-seven past oceanographic cruises undertaken between 1982 and 2009 (Elbaz-Poulichet et al., 1987; Jouanneau et al., 1990; Kraepiel et al., 1997; Boutier et al., 2000; Michel et al., 2000; Dabrin et al., 2009; Strady, 2010), and (ii) recent data from twelve sea cruises from March 2014 until June 2015 (Pougnet, 2018; Pougnet et al., 2021). These campaigns were performed between Bordeaux and the Safe Water buoy (BXA) at the estuary mouth (Fig. 1). All sampling campaigns were implemented by the University of Bordeaux (OASU, EPOC Laboratory), mobilizing the in-sea resources of the National Institute for the Sciences of the Universe (*Institut National des Sciences de l'Univers*, INSU) as part of the annual programme of the National Coastal Fleet Commission (*Comité National de la Flotte scientifique océanographique Côtière*, CNFC). Within the recent campaigns, four cruises (*Métaux Gironde Transferts et Spéciation*, MGTS) were carried out on board the R/V Thalia (Ifremer), and the other nine campaigns were conducted on board the *Côte de la Manche* (INSU) as part of the GIRonde Observation Service (*Service d'Observation de la GIRonde*, SOGIR) of the Aquitaine Observatory of Sciences of the Universe (*Observatoire Aquitain des Sciences de l'Univers*, OASU). All campaigns carried out between 1982 and 2017 cover a wide range of freshwater discharge conditions, calculated as the sum of the daily flows of the Garonne, Dordogne and Isle rivers (Fig. 1). It is noteworthy that the campaign MGTS 2 (March 2015) corresponds to the highest freshwater discharge conditions ever sampled (3450 m^3/s).

Both dissolved and particulate fractions were sampled from the same estuarine water body in each oceanographic campaign. The particulate fraction results from the recovery of particles after centrifugation of a large volume of water (30 to 80 L) on a Westfalia Separator, 12000 g with a flux rate of 40 L/h. This centrifuging procedure allows a particle recovery of at least 96% of total solid content (Schäfer and Blanc, 2002). Concentrations of Cd_p are determined according to a widely tested procedure performed at the EPOC laboratory, including dissolution by total tri-acid digestion (HCl, HNO_3, HF) and analysis on an ICP-MS Thermo X7 (e.g. Schäfer et al., 2002a; Gil-Díaz et al., 2016). Dissolved Cd was quantified from filtered samples (0.2 µm) recovered along the estuarine salinity gradient after pre-concentration with ion exchanging resins (Strady et al., 2009, 2011b; Dabrin et al., 2009; Pougnet et al., 2021).

4. Results and Discussion

4.1. Concentrations and fluxes

4.1.1. Overview of the historical trend of concentrations of average particulate Cd (Cd_p in mg/kg) at the estuary mouth

The historical record of average Cd_p on SPM from surface estuarine waters presenting salinities from 10 to 25 shows a characteristic trend over time (Fig. 2). The data acquired in the 1980s ranged ~0.9 mg/kg and then decreased, varying between 0.4 and 0.7 mg/kg in the period of 2002 to 2006. The average concentrations of Cd_p measured between 2012 and 2017 are between 0.3 and 0.5 mg/kg (i.e., excluding the anomalous point of 0.8 mg/kg) and are comparable to those reported between 2007 and 2009. Thus, it seems likely that Cd_p concentrations have decreased in stages over time (e.g., Pougnet et al. 2021). However, the data before 2002 are insufficient to confirm this hypothesis. Furthermore, recent Cd_p concentrations do not confirm the apparent downward trend indicated by the data acquired until 2009, as the values from 2012 to 2017 remain higher than the regional geochemical background (0.2 mg/kg), which corresponds to non-bio-available geological Cd (Larrose et al., 2010). Thus, it seems that the SPM outside the Maximum Turbidity Zone (MTZ), potentially stores the same amount of bio-available Cd since 2006, despite the remediation efforts concerning the last stage of metallurgical waste containment from the Aveyron region (Fig. 2). These recent concentrations based on sampling campaigns along the turbidity gradient are comparable to the average Cd_p measured at GP-SP radials, showing recurrent concentrations of 0.45±0.10 mg/kg (Dabrin, 2009; Strady, 2010; the present study). These concentrations have been set and correspond to the residual value in Cd_p reaching coastal waters, resulting from the sorption/desorption reactions within the Gironde Estuary (Robert, 2003; Schäfer et al., 2002b; Blanc et al., 2006).

4.1.2. Annual gross fluxes of particulate ($\mathbf{F}_{\mathbf{gross}_{Cdp}}^{\mathbf{year}}$ in t/year) and dissolved ($\mathbf{F}_{\mathbf{gross}_{Cdd}}^{\mathbf{year}}$ in t/year) Cd

The values of all gross Cd_p and Cd_d fluxes are reported in Table S2 (Supplementary information) and presented in Fig. 3 and Fig. 4. In general, Cd_p concentrations vary by a factor of 10 to 20 in the three rivers, while SPM concentrations vary respectively by factors of ~1500 in the Garonne, ~600 in the Dordogne and ~200 in the Isle River (Masson et al., 2006). As a result, gross Cd fluxes are mainly dependent on SPM load variability. The values of total $\mathbf{F}_{\mathbf{gross}_{SPM}}^{\mathbf{year}}$ vary by a factor of 30 (from 0.3 to 8.8 Mt/year) with ten-year average values of 3.2 ± 2.7 Mt/year in the 1990s, 1.7 ± 0.8 Mt/year in the 2000s and 1.4 ± 0.9 Mt/year during the 2010s (Fig. 3). The values of $\mathbf{F}_{\mathbf{gross}_{Cdp}}^{\mathbf{year}}$ and of $\mathbf{F}_{\mathbf{gross}_{Cdd}}^{\mathbf{year}}$ vary by factors of 18 (1.5 to 27 t/year) and 6 (0.5 to 2.3 t/year), respectively (Fig. 4). As observed with the net fluxes, the highest annual gross fluxes occurred in the 1990s and the lowest in the 2010s. From the local perspective, these changes in annual fluxes are significant as slightly larger systems such as the Rhône River (i.e., 98 800 km^2 with average annual flow of 1700 m^3/s and > 3000 m^3/s during flood events) have registered annual SPM fluxes between 1.2 – 22.7 Mt/y (i.e., within the registered values in Fig. 3) but equivalent Cd$_p$ fluxes of 2.69 – 6.22 t/y (Ollivier et al., 2011), which are only similar to the registered $\mathbf{F}_{\mathbf{gross}_{Cdp}}^{\mathbf{year}}$ in the Gironde watershed for the latest decade (Fig. 4).

4.1.3. Annual net fluxes of SPM ($\mathbf{F}_{\mathbf{net}SPM}^{\mathbf{year}}$ in Mt/year) and Cd$_p$ ($\mathbf{F}_{\mathbf{net}_{Cdp}}^{\mathbf{year}}$in t/year)

Following the description of section 2.2, the compilation of the number of days (nb) when discharges (Q$_j$) are < 700 m^3/s, between 700 and 2500 m^3/s, and > 2500 m^3/s, as well as the number of potential expulsion events used in equation 5 to determine the SPM net fluxes for each year between 1990 and 2020 are presented in Table S1 (Supplementary information). The resulting values of $\mathrm{F}_{\mathrm{netSPM}}^{\mathrm{year}}$ are between 0.2 and 3.1 Mt/year and show ten-year averages between 1.4 and 1.8 Mt between 1990 and 2020 (Fig. 3). These values are consistent with the average value of 1 Mt/year derived from satellite data for the same area of study (Doxaran et al., 2009). Moreover, Castaing and Jouanneau (1979) suggested that the renewal of particles in the estuary is 50%/year, i.e., an average residence time of ~ 1 to 2 years, which would correspond to an annual expulsion of 2 to 3 Mt/year with reference to the estimated mass of the MTZ.

The values of $\mathrm{F}_{\mathrm{net}_{Cdp}}^{\mathrm{year}}$ vary proportionally to the $\mathrm{F}_{\mathrm{net}_{SPM}}^{\mathrm{year}}$ and are between 0.1 and 1.4 t/year, showing decreasing 10-year averages from 0.8 to 0.6 t/year. The net fluxes of SPM and Cd$_p$ showed in Fig. 3 and Fig. 4 and reported in Table S1 must be considered as a first estimate, probably slightly below reality since the parameters used in sedimentary hydrodynamic models result from under-documented field data at the estuary mouth (Benaouda, 2008). However, this estimate is the most realistic one until now, based on the current knowledge of the dynamics of particle expulsion from a macro-tidal estuary. The obtained results of net fluxes will enable us to discuss pertinently the resilient trajectory of the Gironde Estuary with regard to its contamination in Cd (*c.f. section 4.2.*).

4.1.4. Annual net fluxes of dissolved Cd ($\mathbf{F}_{\mathbf{net}_{Cdd}}^{\mathbf{year}}$ in t/year)

The annual net fluxes of Cd$_d$ reported in Table S1 and presented in Fig. 4, range from 9.5 to 1.5 t/year and have decreased accordingly to the decontamination stages of the Aveyron metallurgical site (Pougnet et al. 2021). The amount of the Cd$_d$ added along the estuarine salinity gradient due to chloro-complexation effects and/or particle remobilization has decreased over time because the Cd particle load from the Lot River has also decreased. As a result, maximum values of Cd$_d$ in the estuary during low-water discharge periods (dry seasons) have halved between the 2000s (Dabrin et al., 2009) and October 2015 (i.e., from 140 ng/L to 70 ng/L, Pougnet, 2018). From a regulatory perspective, Cd_d concentrations in the estuary have always ranged below the values of the Annual Average Environmental Quality Standard (EQS-YA) for coastal surface waters, set at 200 ng/L (Directive 2013/39/UE, n.d.). In 2015, the amplitude of Cd_d addition reached concentrations below 90 ng/L, i.e., the EQS-YA (Directive 2013/39/UE, n.d.) value used for inland surface waters, applicable upstream of the estuarine fluvial limit (e.g. La Réole; Bossy et al., 2013; Coynel et al., 2016b). Therefore, the estuarine and river water bodies downstream of the Garonne River are in good ecological status regarding stablished WFD guidelines for aqueous elements. Nevertheless, the oysters located at the Gironde Estuary mouth remain unfit for human consumption (>5 mg/kg d.w.; EC, 2001), despite the decrease of a factor of 5 in their Cd concentrations since the 1980s.

4.2. Mass balances in the Gironde fluvial-estuarine system

4.2.1. Mass balance of SPM fluxes

The inter-annual mass balance of gross and SPM net fluxes (Fig. 3) indicates that the Gironde Estuary is generally in sedimentary equilibrium, or even in erosion. From 1990 to 2000, from 2000 to 2010, and from 2010 to 2020, the ten-year averages of $F_{gross_{SPM}}$ decreased from 3.2 Mt/year to 1.7 Mt/year and then to 1.4 Mt/year, while the ten-year averages of $F_{net_{SPM}}$ were relatively constant (1.6 ± 0.1 Mt/year on average from 1990 to 2020, with a slight decrease to 1.4 Mt/year in the 2010s; Fig. 3). This sedimentary transport is obviously related to water discharges with, nevertheless, disparities in the transport regime from one year to another. For example, 1992 presents a $F_{gross_{SPM}}$ close to twice as much as that in 1994 for equivalent average discharge rates. This contrast could result from the strong water regime in 1992 after the dry period of 1990-1991. However, the ten-year decline in $F_{gross_{SPM}}$ by a factor of ~2 since the late 1990s is not directly explicit with the data in this study. External climatic and internal forcing of watershed and river development is probably to be considered. Actually, in the 1990s, the strong $F_{gross_{SPM}}$ in 1992, 1993, 1994 and 1996 determine a ten-year storage period of ~15 Mt. In the 2000s and 2010s, the ten-year sedimentary budget was in deficit by ~25Kt. If the $F_{net_{SPM}}$ determined in this study are underestimated, then the sediment deficit would be greater. However, this sediment deficit is consistent with other recent and independent investigations. Cartographic analysis of estuarine bathymetry indicates a deepening of the downstream estuarine zone and an expansion of the anthropogenic overcutting areas in the tidal Garonne (Sottolichio et al., 2013). These results are consistent with the observation of a recent increase in estuarine turbidity and the duration of the presence of the MTZ in the tidal Garonne (Sottolichio et al., 2011, van Maanen and Sottolichio, 2018). The hypothesis mainly used to account for this situation is an anthropogenic change in the river regime (Etcheber et al., 2011), without the partition due to global climate change and river water pumping for irrigated agriculture being clearly established. Intra-estuarine dredging efforts are a secondary hypothesis that should be considered. In addition to the fact that estuarine dredging alters an average of 8 Mt/year of sediment, which is more than the estimated mass of the MTZ (4 to 6 Mt, Castaing and Jouanneau, 1979), it seems that the morphological balance of the widest downstream section of the estuary (KP 70-80 km) may be disturbed by dredging activities (Sottolichio et al., 2013). This study indicates that the sediment deficit appears to have increased since 2000. It is unclear if the internal anthropogenic forcing has become more significant ever since, particularly in connection with the increase in the draft of ships going up to Bordeaux (Fig. 1). In any case, this erosive balance is detrimental to the natural functions of an estuary, namely areas of high sedimentation and the creation of purifying wetlands suitable for biological development.

4.2.2. Mass balance of total Cd fluxes

Figure 4 presents both annual total cadmium (Cd_{tot}) gross fluxes, corresponding to the sum of the gross fluxes of Cd_d and Cd_p from the three major tributaries of the Gironde Estuary (the Garonne, the Dordogne and the Isle rivers), and the annual Cd_{tot} net fluxes, corresponding to the sum of the annual net fluxes of dissolved (Cd_d, Pougnet et al., 2021) and particulate (Cd_p) Cd exported to the ocean between 1990 and 2020. This figure shows that the contribution of Cd_p annual net fluxes to total net fluxes is in the order of 15 ± 5%, a relatively small and constant proportion over the entire observation period. The consistency of these net flows of Cd_p is related to the stability of Cd_p concentrations in surface waters and in the water column outside the MTZ. Thus, the potential underestimation of these fluxes, induced by equation 1, can be considered negligible when analysing the global mass balance of exports to the ocean, which is, by more than 80%, dominated by Cd_d net fluxes.

As expected, Fig. 4 also shows that Cd contributions to the Gironde Estuary are generally dominated by Cd_p gross fluxes from the Garonne River, whose source comes mainly from the Aveyron metallurgy via the Lot River. However, the number, the intensity and the origin of floods seem to have a strong impact on the quantities of Cd transferred to the estuary. For example, 2013 was a wet year with an annual water flux of more than 1000 m^3/s, comparable to the wettest years of the 20th century (1992, 1994, 1996), which posted the highest gross Cd fluxes over the past 26 years. However, the high annual water flux in 2013 results from numerous floods in the upstream Garonne River and its Pyrenean tributaries. Thus, Cd inputs this year derive mainly from high erosion of agricultural soils amended with phosphate fertilizers containing cadmium (Coynel et al., 2016b). On the other hand, 2003 was a dry year with an annual average water discharge of ~800 m^3/s. However, this year was characterized by intense low water levels (231 days, $Qj < 700 m^3/s$; Table S1) and by two floods of the Massif Central tributaries, including a centennial flood on the upstream Lot River. Therefore, it severely eroded metallurgical waste and caused, on account of dam flushing, the re-suspension of polluted sediments accumulated over more than 40 years upstream of the hydroelectric dams located along the Lot River (Coynel et al., 2007b). In addition, the development of the Lot waterways may result in the re-suspension of older, more Cd-polluted sediments. This was particularly the case in 2000, when gross Cd flux results mainly from poorly confined development work at Villeneuve sur Lot (Audry et al., 2004a). Thus, cadmium inputs to the Gironde Estuary are dominated by inputs from the Garonne River, whose two main anthropogenic sources are the zinciferous metallurgy from the Aveyron region with the occasional re-suspension of polluted river sediments from the Lot River, as well as agriculture on the Gascony hills, dominated by corn growing.

Overall, total average F_{net} emissions decreased by a factor of 2 in each decade, from 7.9 t to 4.7 t and 2.8 t in the 1990s to 2010s. Although less contrasting, the evolution of total average F_{gross} displayed the same trend as that of the total F_{net}. They both varied from 122 t to 69 t in the 1990s and 2000s and then reached 39 t in the 2010s. The ten-year differences between total F_{gross} and total F_{net} indicate a Cd storage in estuarine sediments of ~43 t in the 1990s, ~22 t in the 2000s and ~12 t in the 2010s (Fig. 5). Thus, the estuary has been storing cadmium despite a lack of sedimentary storage since 2000. These accumulation tonnages result from the combination of Cd_p mass balances and Cd_d solubilisation in the salinity gradient. Cd_p mass balances were in the order of 92, 53 and 25 t, respectively in 1990, 2000 and 2010, with quasi constant Cd_p yearly F_{net}, from 0.8 to 0.6 t/year on a 10-yearly average. The quantities of Cd solubilised in the salinity gradient have decreased each decade and were in the order of 7.1, 4.0, and 2.1 t, with yearly Cd_d average F_{gross} in the order of 2.2 t/year in the 1990s and 0.8 t/year in the 2000s and 2010s. Hence, these mass balances quantify the effectiveness of the remediation work carried out on the Aveyron metallurgical site. They show that the amounts of bio-available Cd in the estuary have decreased significantly, i.e., they were ~7 t/year in the 1990s, then ~4 t/year in the 2000s and ~2 t/year in the 2010s. This decrease in a factor of 5 of the bio-available Cd explains the decrease in contamination observed in wild oysters at the Gironde Estuary mouth by the Ifremer monitoring network, RNO-ROCCH (Pougnet et al., 2021). However, these mass balances indicate that the quantity of desorbed Cd from particles arriving to the Gironde Estuary is still insufficient to allow wild oysters at the estuary mouth to reach edible levels. These observations indicate that the estuarine desorption potential has not been altered, as evidenced by the residual concentrations of estuarine particles, which remain at an average value of 0.45 mg/kg, i.e., above the geochemical background (Fig. 2, *c.f. section 4.1.1.*). In addition, at the 10-year scale, estuarine sediments should be considered as a sink of Cd, although, in the years of low gross fluxes (1990, 91, 95, 97, 98; 2001, 04, 05, 06, 07), estuarine sediments constitute a source of bio-available Cd towards the water column (Fig. 5).

This storage and release of cadmium via estuarine sediments slows down the estuary's resilience to Cd contamination. For cadmium, Audry et al., (2007a) showed that an addition of Cd_d of 20% to 50% is derived from the anthropogenic re-suspension of estuarine sediments due to the fact that almost all the sediments dredged in the estuary are released near the dredging area inside the estuary. Other metals such as Cu, Ag, Ni, Co, Mo, V, Sb..., also show some addition in the salinity gradient (Audry et al., 2007b; Dabrin, 2009; Strady et al., 2009; Lanceleur et al., 2011a; Gil-Díaz et al., 2016). Besides, many biocidal molecules, particularly hydrophobic or mixed molecules carried by estuarine particles (Phillips et al, 1999; Munoz et al., 2015; Budzinski et al., 2016), may also exhibit additive behaviours. Thus, any natural and/or anthropogenic re-suspension of contaminated estuarine sediments will result in a dilution of SPM concentrations by dispersion in the water column. This SPM dispersion takes place at each tide and as the result of dredging operations. Recent studies on the hydro-sedimentary functioning of the Gironde Estuary (Artelia, 2016, personal communication) indicate that the natural winnowing of dredged sediments redistributes particles throughout the estuary, with preferential deposition in intertidal areas, regardless of the location of the sediment clapping area. Thus, clapping followed by the natural winnowing of the dredged sediments favours the contamination of the entire estuarine water column, mainly through desorption of contaminants from the particulate phase to the dissolved phase. This contamination is almost permanent in the Gironde Estuary since it results from the permanent adjustment of numerous thermodynamic balances between the dissolved and particulate phases in the salinity and turbidity gradients controlled by the estuarine hydrodynamics. The dispersion of pelagic and benthic particles is therefore likely to release into the water column a biocidal cocktail of compounds that are bio-available for many living organisms, as shown by numerous studies on the contamination of different links in the estuarine trophic chain (Pasquaud et al., 2010; Masson et al., 2011; Lanceleur et al., 2011b, 2012; Strady et al., 2011b; Daverat et al., 2012; Petit et al., 2013; Abdou et al., 2016; Munoz et al., 2017; Ballutaud et al., 2019; Gil-Díaz et al., 2019).

5. Conclusion

This is the first study presenting a reasonable estimation of annual SPM and dissolved and particulate Cd net fluxes applicable to highly turbid macrotidal estuaries. It includes assumptions from the SIAM-3D model as well as available field data and a detailed analysis of the daily flux chronicles in a case study area such as the Gironde Estuary. The following conclusions can be drawn from this work:

- The multi-year comparison between gross and SPM net fluxes over three decades indicates that (1) average net flux values are comparable to the global estimates previously made by sedimentology and remote sensing (Castaing and Jouanneau, 1979; Castaing et al. 1999; Doxaran et al., 2009) and that (2) the Gironde Estuary has generally been in sedimentary equilibrium or even in erosion since the year 2000. This is consistent with the bathymetric over-scouring of the downstream estuarine zone (Sottolichio et al., 2013; van Maanen and Sottolichio, 2018).

- Cd_p net flux values determined over 30 years since 1990 represent ~20% of total Cd net fluxes (Cd_d + Cd_p). Hence, the Cd_p net fluxes have low influence on the estuarine Cd budgets.

- The mass balances established between the gross and annual net fluxes of dissolved, particulate and total cadmium show that the quantity of bio-available cadmium has decreased by a factor of 5 since the 1990s, with a decrease of a factor of 2 in the maximum Cd_d concentrations. However, estuarine sediments continue to store Cd despite the decrease in the upstream source of the Aveyron metallurgical basin and a deficient estuarine sediment balance. Depending on the annual quantities of Cd brought from the watershed, estuarine sediments constitute both sinks and sources of Cd to the water column, explaining the current, above human consumption levels present in oysters at the estuary mouth. However, this intra-estuarine 4.3 to 1.2 t storage has decreased over time by a factor of two in each decade since the 1990s.

Thus, Cd sources will have to continue to decline in the next years in order to free themselves from this Cd contamination in the coming decades. This requires better controlled management of cadmium fluxes from the Decazeville basin, river works, silted water reservoirs and phosphate agricultural inputs. Nevertheless, to achieve a significant result in the short term, real and innovative efforts should be made in estuarine sediment management. A possible anthropogenic remediation measure could involve performing the summer clapping of controlled quantities of fine estuarine sediments in waters of salinity $\geq$32 (Anschutz et al., 2020). Results on cadmium transfers in coastal areas (Miramand et al., 1998, 2001; Strady et al., 2011a, 2011b; Dabrin et al., 2014) show that this proposed remediation would not impact the current oyster aquaculture area in Marennes-Oléron. Furthermore, this remediation measure would have the advantage of cleaning up the estuary of its cadmium load in a matter of years, as well as that of other metallic and organic contaminants (though their environmental effects are still subject to further research/evaluation), while reducing the dredging effort of the shipping channel and probably the siltation of the tidal Garonne.

Author Contributions

Frédérique Pougnet and Gérard Blanc: Conceptualization. **Frédérique Pougnet and Teba Gil-Díaz:** Methodology. **Frédérique Pougnet, Alexandra Coynel and Cécile Bossy:** Sample collection and analysis. **Frédérique Pougnet and Cécile Bossy:** Investigation. **Frédérique Pougnet and Teba Gil-Díaz:** Data curation. **Frédérique Pougnet and Gérard Blanc:** Writing - Original Draft. **Frédérique Pougnet, Teba Gil-Díaz and Alexandra Coynel:** Writing – review and editing. **Frédérique Pougnet:** Visualization. **Gérard Blanc, Alexandra Coynel and Jörg Schäfer:** Supervision. **Gérard Blanc and Alexandra Coynel:** Funding acquisition.

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Figure captions

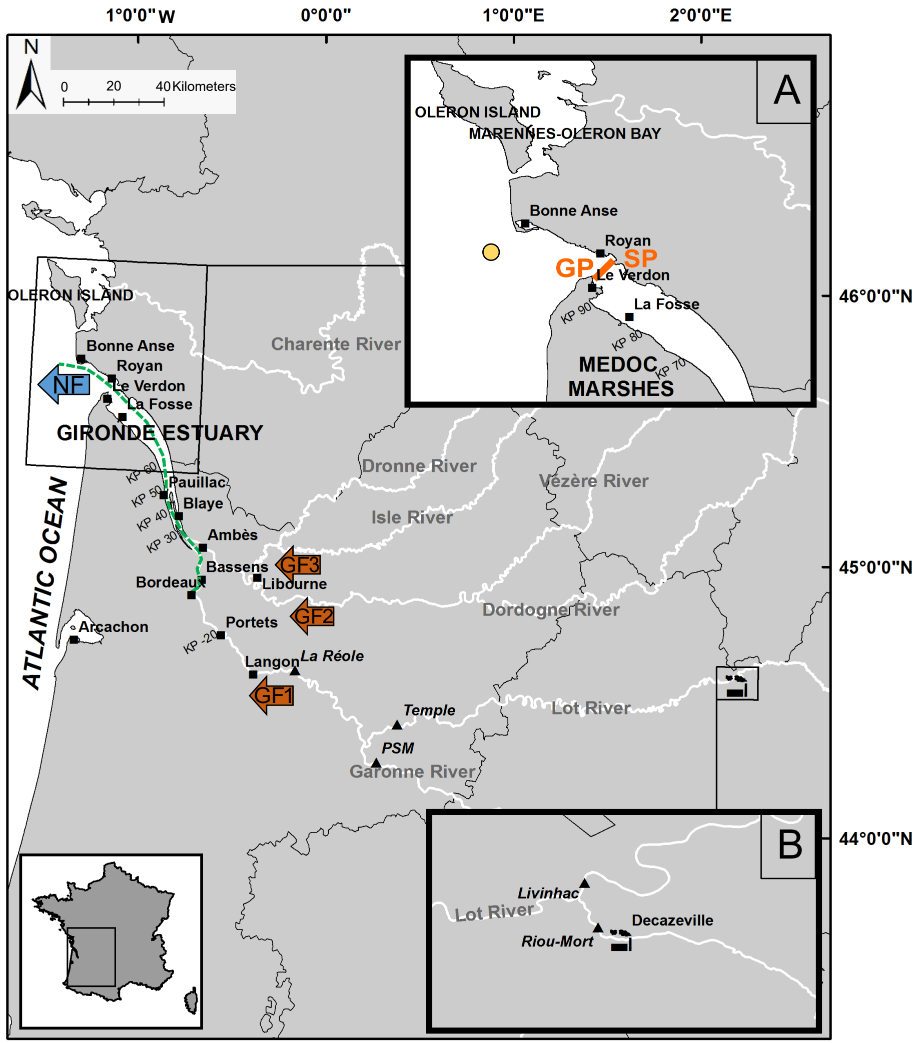
Fig. 1 : Map of the Gironde Estuary. Location of the sampling sites along the Lot-Garonne-Gironde fluvial-estuarine system (black triangles), zoom in on the specific areas of the Medoc Marshes (A) and the small, polluted watershed (B). Kilometric Points (KP; km) show the distance from the city of Bordeaux (KP 0) to the estuary mouth.

Fig. 2 : Temporal variations of average, estuarine particulate Cd concentrations (Cd_p) between 1982 and 2015. The plotted averages were extracted in several sampling campaigns from SPM samples collected from surface waters presenting salinities between 10 and 25 (extended dataset from Strady 2010).

Fig. 3 : Annual SPM gross and net fluxes and annual water fluxes in the Gironde Estuary between 1990 and 2020. The SPM budget is an extended dataset from Bossy et al. (2013) and Coynel et al. (2016b). Black and red lines represent the ten-year averages of gross and net fluxes respectively (extended dataset from Pougnet 2018). *represents an estimation of the SPM budget over 10 years.

Fig. 4 : Annual total gross and net fluxes of Cd between 1990 and 2020. Total ($Cd_{tot} = Cd_d + Cd_p$) budgets are accounted for each affluent of the Gironde Estuary (Garonne, Dordogne and Isle rivers) and annual Cd_{tot} net fluxes are an extended dataset from Pougnet (2018). Gross Cd_d and Cd_p fluxes are in magenta and purple, respectively, for the Isle River; cyan and blue for the Dordogne River; and orange and brown for the Garonne River. Net Cd_d and Cd_p fluxes in the Gironde Estuary are in green and khaki.

Fig. 5 : Annual storage/destocking budget between 1990 and 2020. Calculations are based on the difference between total cadmium fluxes (Cd_{tot}) entering and outgoing the Gironde Estuary. Annual water fluxes in the Gironde Estuary are also included (extended dataset from Pougnet 2018).



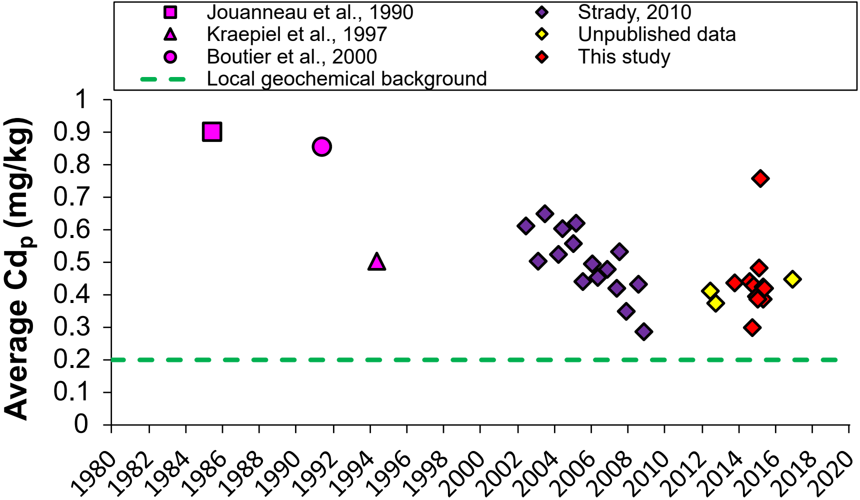
- - - Sampling profile according to the salinity gradient from Bordeaux (KP0) to the estuary mouth (MGTS1,2,3)

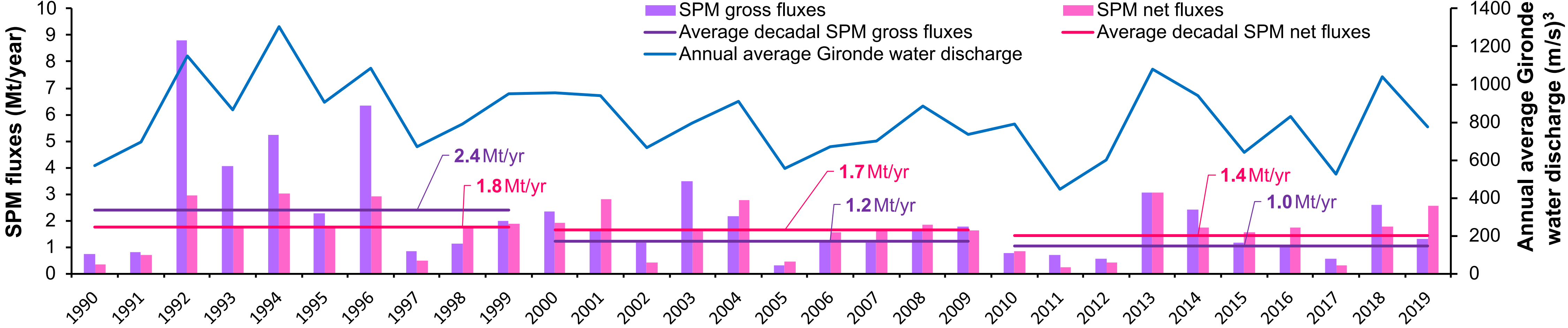
▬ Radial ADCP between Grave Point and Suzac Point (GP-SP ; MGTS 1 and 2)

● Position of the Beacon, Safe Waterbuoy (BXA) at the Gironde Estuary mouth

⬅ Gross Fluxes from the Garonne (GF1), Dordogne (GF2) and Isle (GF3) rivers

⬅ Net Fluxes of the Gironde Estuary (NF)


Jouanneau et al., 1990
Kraepiel et al., 1997
Boutier et al., 2000
Local geochemical background
Strady, 2010
Unpublished data
This study
Average Cd$_p$ (mg/kg)
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1980
1982
1984
1986
1988
1990
1992
1994
1996
1998
2000
2002
2004
2006
2008
2010
2012
2014
2016
2018
2020


SPM gross fluxes
SPM net fluxes
Average decadal SPM gross fluxes
Average decadal SPM net fluxes
Annual average Gironde water discharge
SPM fluxes (Mt/year)
Annual average Gironde water discharge (m/s)^3
0
1
2
3
4
5
6
7
8
9
10
0
200
400
600
800
1000
1200
1400
2.4 Mt/yr
1.8 Mt/yr
1.7 Mt/yr
1.2 Mt/yr
1.4 Mt/yr
1.0 Mt/yr
1990
1991
1992
1993
1994
1995
1996
1997
1998
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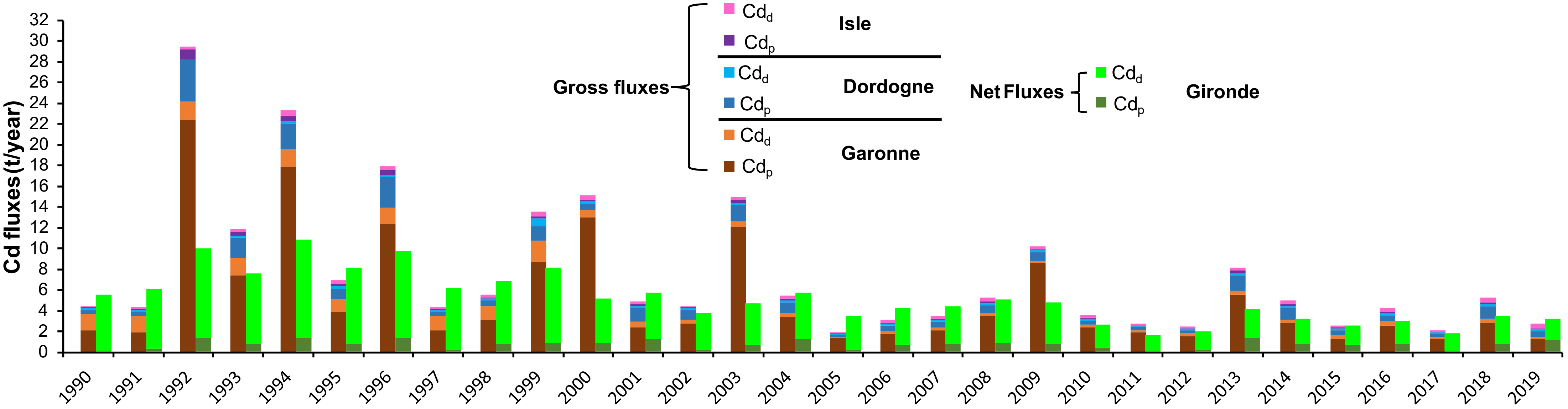
2019


Cd fluxes(t/year)
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30
32
Gross fluxes
Cd$_d$
Cd$_p$
Isle
Cd$_d$
Cd$_p$
Dordogne
Cd$_d$
Cd$_p$
Garonne
Net Fluxes
Cd$_d$
Cd$_p$
Gironde
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
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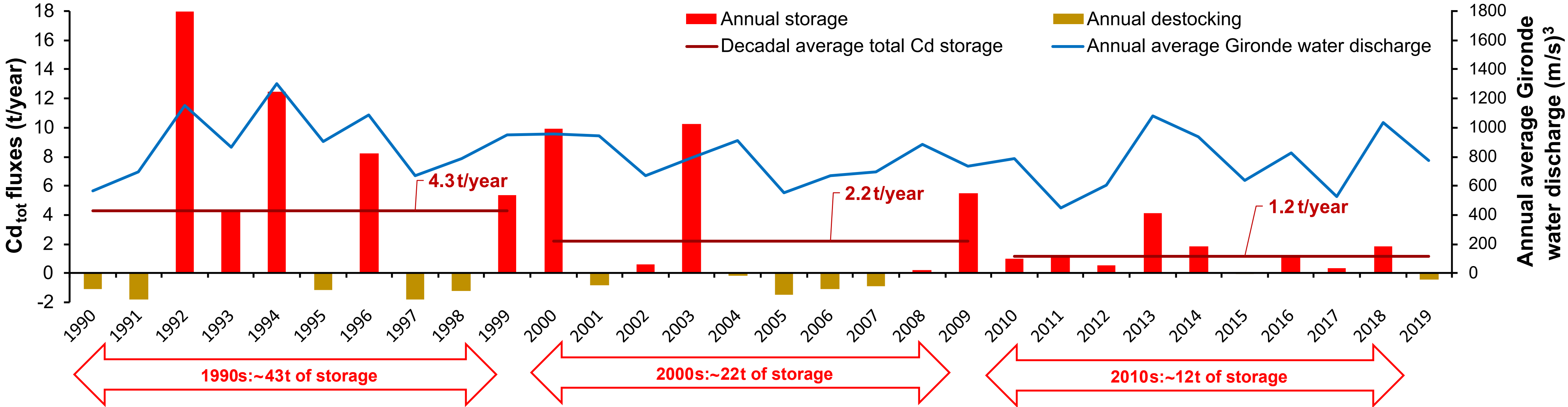
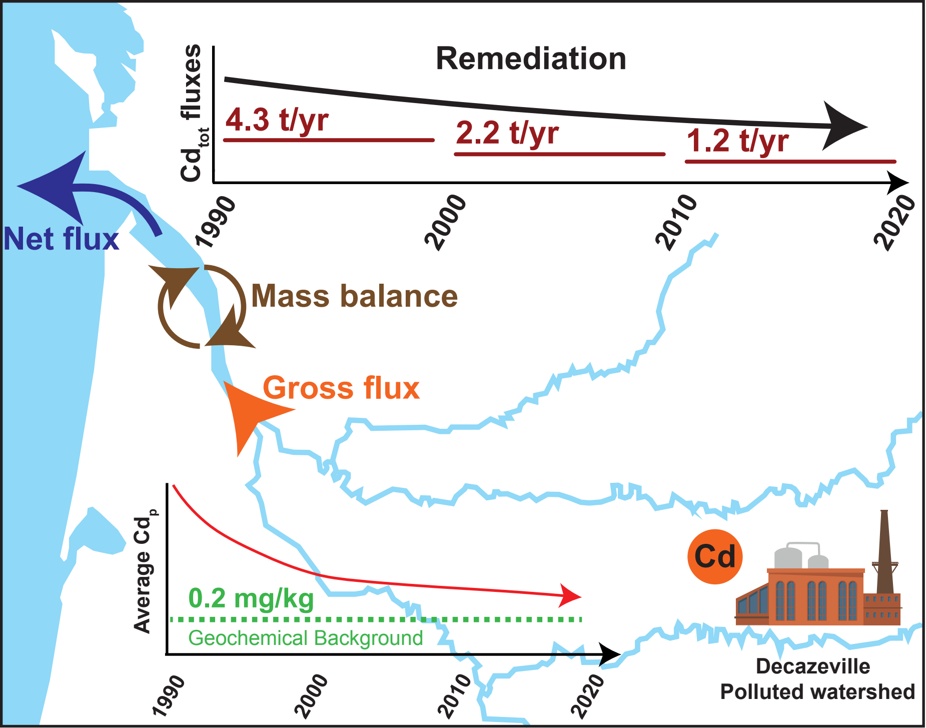
2019


Cd$_{tot}$ fluxes (t/year)
Annual average Gironde water discharge (m/s)^3
Annual storage
Annual destocking
Decadal average total Cd storage
Annual average Gironde water discharge
4.3 t/year
2.2 t/year
1.2 t/year
18
16
14
12
10
8
6
4
2
0
-2
1800
1600
1400
1200
1000
800
600
400
200
0
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
2012
2013
2014
2015
2016
2017
2018
2019
1990s:~43t of storage
2000s:~22t of storage
2010s:~12t of storage


Remediation
Cd_{tot} fluxes
4.3 t/yr
2.2 t/yr
1.2 t/yr
1990
2000
2010
2020
Net flux
Mass balance
Gross flux
Average Cd_p
0.2 mg/kg
Geochemical Background
1990
2000
2010
2020
Cd
Decazeville
Polluted watershed