# ESTIMATION OF PCDD/FS FLUXES IN THE VENICE LAGOON

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## Introduction

The Venice lagoon (northern Italy) has a long history of industrial activity and from the 1950's the inner lagoon area of Porto Marghera expanded as chemical and oil refining plants were developed. Although emissions from the industrial area have reduced because of the decline of the chemical industry and the adoption of new abatement technologies, high concentrations of PCDD/Fs, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and heavy metals still remain in sediments, especially in the central lagoon. This provides a potential source for the lagoon ecosystem and for human exposure, through the ingestion of seafood. Other sources are represented by atmospheric deposition, the discharge of untreated municipal effluents from the historical centre and the emissions associated with heavy aquatic traffic, due to local transportation, fishing activities, cruisers and oil tankers[1]. Extensive sampling campaigns have been conducted in recent years, especially in the central part of the lagoon. Surface sediment, water, settleable particulate matter (SPM) and biota (clams, mussels, crabs and fishes) have all been analysed and physico-chemical data and environmental parameters have been recorded[2] (i.e. temperature, pH, organic carbon fraction in sediment and particulate matter, particulate matter concentration and fluxes). Four sites in the central lagoon have been the focus of investigation, selected to represent contamination gradients. These are (Fig 1): Alberoni, close to the Malamocco Channel (site A); Sacca Sessola (site B), in an area of intense fishing activity; San Giuliano (site C), close to the mainland and to the Osellino Canal and Fusina (site D), in front of the industrial area and the industrial canals. The contaminant contribution of rivers from the catchment area and of atmospheric deposition were also investigated. The central part of the lagoon, between the Malamocco and Lido channels linking the lagoon to the Adriatic Sea, covers a water surface of ca. 132 $km^2$ and is quite well mixed hydrologically. PCDD/F emissions are now much lower than in the past[3], but contaminated sediment in some areas of the industrial canals and surrounding areas may act as a significant long-term secondary source of PCDD/F to elsewhere in the lagoon as it becomes transported and re-distributed. High re-suspension of bottom sediments is caused by intensive fishing for clams (*Tapes philippinarum*), shipping activity and tidal currents. These processes favour high sediment-water exchange, whilst the shallow warm waters of the lagoon encourage high biological productivity and air-water exchange.

The objectives of the study were to: compile the environmental budgets for PCDD/Fs for the area; estimate the actual flux direction for each congener; obtain the information necessary to develop a mass-balance model in order to predict the concentrations of these chemicals in each environmental compartment (sediment, water, air, water and air particles).

## Methods and materials

The central part of the lagoon was chosen to evaluate the equilibrium status and to develop a mass-balance model to predict the steady state concentrations and fluxes of individual PCDD/F congeners

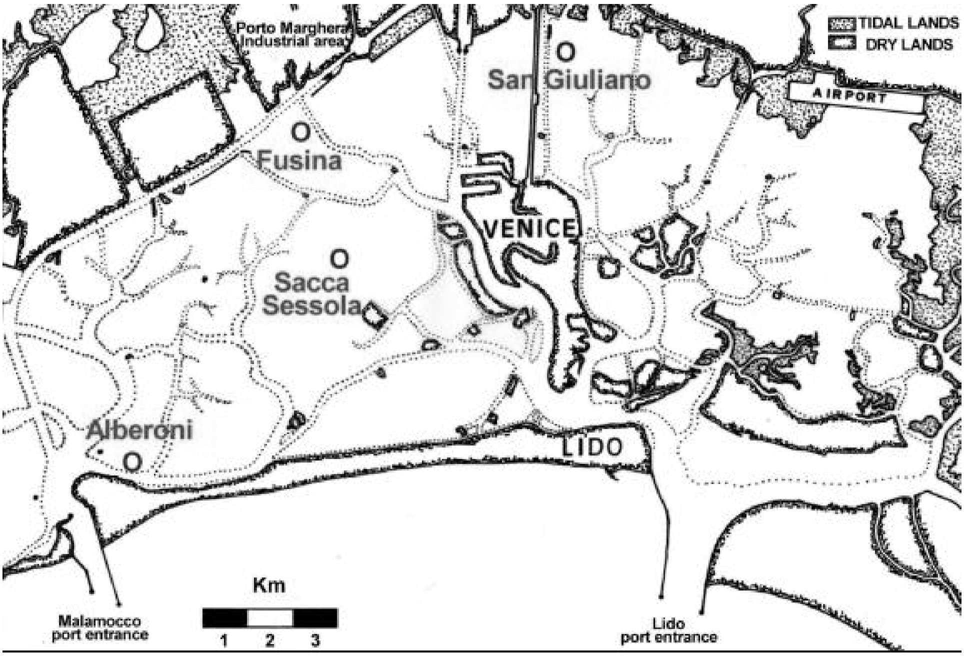


**Figure 1.** Map of the central part of the Venice lagoon.

for key environmental compartments. Firstly the distance from the equilibrium of the congeners distribution was assessed by comparing fugacity values in each compartment. In fact, the comparison of fugacity values of a congener in the different environmental compartments allows to estimate the proximity to the equilibrium and fluxes direction. Actual fugacity values can be easily calculated from experimental concentrations in the compartments from the relationship: $C = Z \cdot f$. Since air concentration values were not available, they had to be estimated from experimental findings resulting from an atmospheric deposition survey.

Then the QWASI[4] (Quantitative Water Air Sediment Interaction) model was applied, as it allows - once environmental parameters (e.g. total water surface, mean depth, organic carbon content in sediment), physical-chemical characteristics (such as PLs, log(Kow) and the Henry's law constant), inputs and advective flows are known - to predict concentration values in all environmental media. The model, based on the fugacity concept, enables also to estimate the intermedia fluxes at the steady state condition.

**Results and discussion**

The air/sediment fugacity ratios show a different behaviour in the different zones of the central lagoon. In the industrial district the ratio is close to 1 for the heavier congeners (HpCDD, OCDD and OCDF) while it is well below 1 for the lighter ones (TCDF, PeCDF and HCDF). For these congeners a net transfer from the sediment to the water column and then to the atmosphere is likely to occur. For the rest of the lagoon, a net deposition is likely to occur for HpCDD and OCDD, while the other congeners are close to equilibrium, except for TCDF, for which the fugacity ratio is between 0.24 and 0.36 (possible volatilisation).

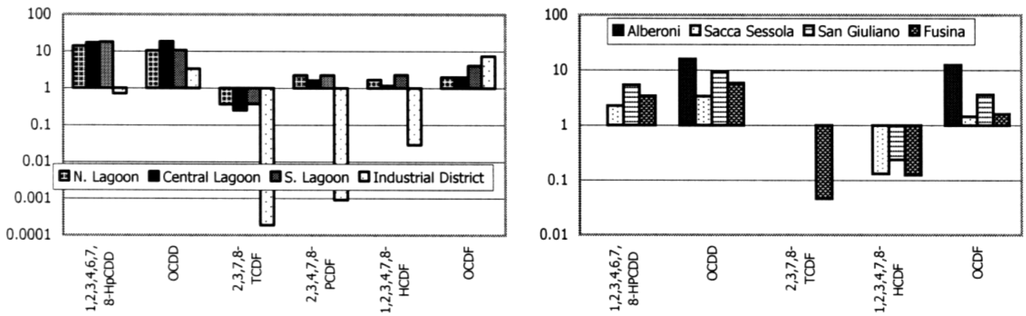


**Figure 2.** Air/Sediment (left) and air/water (right) fugacity ratios in the Venice Lagoon

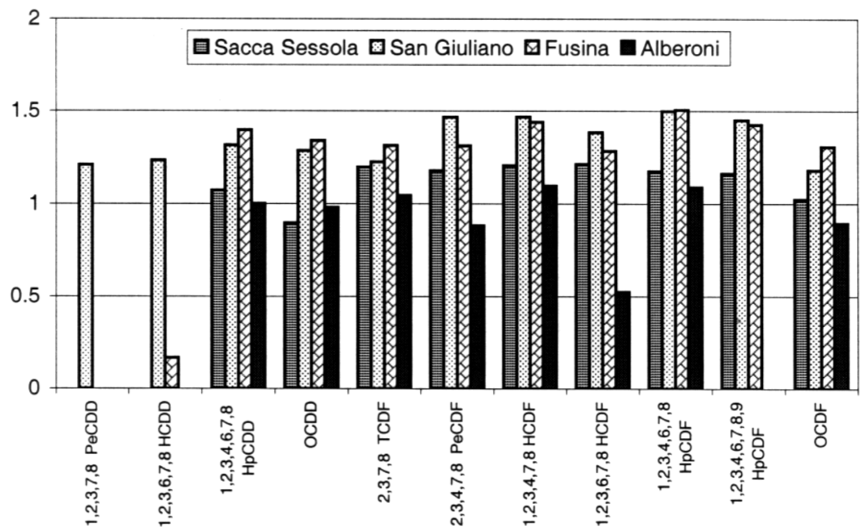


**Figure 3.** Sediment/SPM fugacity ratio

The air/water fugacity ratio is calculated using non-filtered water samples, thus fugacity values, when above the detection limit, refer to bulk water. Fugacity ratios in this case exhibit the same result, suggesting deposition for the heavier congeners and volatilisation for the lighter ones.

The sediment-SPM ratio was calculated from fugacity values obtained from matched samples of sediment and suspended particulate matter in four sampling sites located in the central part of the lagoon. The ratio is always very close to 1, with minor differences among the stations, suggesting conditions very close to equilibrium.

The PCDD/F pattern predicted by the QWASI model for the sediment reflects exactly the input profile, with a dominance of OCDD, HpCDF and OCDF over the other congeners. In water (non filtered) the profile is almost identical, due to the influence of SPM, while the profile of the freely dissolved congeners is enriched in TCDD, TCDF, PeCDF and HCDF, while the importance of the heavier furans is similar. The atmospheric profile is completely different, with a clear dominance of TCDF, due mainly to its higher values in vapour pressure and in the Henry's law constant. In the gaseous phase TCDF represents about 90 % of the total dioxins and furans concentration.

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