# IDENTIFYING SOURCES AND PATHWAYS OF PERSISTENT ORGANIC POLLUTANTS IN AQUATIC ENVIRONMENTS

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## INTRODUCTION

During past decades, environmental scientists, engineers, and regulatory authorities around the world have devoted considerable resources to the assessment, management, and remediation of chemical contaminants in sediments (Wenning and Ingersoll, 2002). Though in many cases the situation is evolving toward an improvement, environmental problems caused by chemical contamination are still a priority in many cases, especially in those areas undergoing a fast development. Within this context, aquatic environments represent the temporary or permanent sink of all contaminants because bottom sediments can accumulate all kind of chemicals, which usually display an affinity for particles and organic matter and follow their fate. In some cases concentrations can become dangerous from an ecological point of view, but also for human beings, as final consumers of fishery resources.

For the sake of environmental safeguard, the remediation of contaminated sediments is an important management issue. However, many steps are required in the process of a knowledge-based decision making. Finding sources and trends, and assessing the risk are priority needs for the design of measures aimed at the protection and/or the recovery of contaminated environments, and also for understanding whether or not discharge restrictions set by the modern legislation are respected or not.

In this paper we will discuss our point of view about the study of the quality of an aquatic environment as a necessary condition for any decision about its safeguard. Sediments and biota are the key compartments that need to be taken into consideration but source identification and knowledge of pathways have also

to be addressed.

## RATIONALE

The individuation of contaminated area comes first, through surficial sediment sampling and analysis of the most important and harmful chemicals. At this stage, a comparison of contaminant concentrations with sediment quality guidelines (SQGs) will provide first insight into the probable effect of sediment contamination of benthic fauna (Long & Morgan, 1990; Long et al., 1995; Mc Donald et al., 2000). Furthermore, the determination of concentration-depth profiles in sediment cores can make available information into input trends, while the determination of mass accretion rates (using short lived radiotracers such as $^{210}Pb$ and $^{137}Cs$) will allow the calculation of fluxes. These data are particularly important to understand whether the sediment quality is recovering or not. In the latter case, the residual sources should be determined. Therefore, the screening of the sources and the assessment of their relative importance is an important requirement.

## DEFINING THE SOURCES

The first step toward the identification of sources is the discrimination between point or nonpoint ones. It is based on spatial gridding of contaminant distribution compared to the morphology of the territory. This is the simplest way to locate the sources that can then be confirmed by other data related to the specific case. For example, an oil spill in a semi-closed coastal area (such harbours or ports) represents an easy case of source identification.

Actually, coastal aquatic environments are strongly affected by human activities and the same contaminants may have various sources, thus finding specific sources can be difficult in absence of specific evidences (e.g., the closeness of a sewage outfall). However, contaminants themselves can be considered as tracers of their sources, especially certain classes of organic chemicals. Polychlorinated Biphenyls (PCBs) are the less specific but, despite the selective processes that may have modified the original mixtures and changed the relative importance of congeners, sometimes it is possible to find sediments with unusual PCB congener profiles. For instance, Frignani et al. (2001a) found, in a

Porto Marghera industrial canal, a different compositions with respect to the usual congener pattern found in the Venice Lagoon. A similar situation happened in the Thi Nai Lagoon in the Binh Dinh Province of Vietnam (unpublished data). Differently, Piazza et al. (2008) found patterns throughout Mexican aquatic environments that were very similar to that of Aroclor 1254. Excluding special cases due to direct discharges, in general PCBs account for a general contamination. It is not a case that, presently, landfills are considered among their most important sources, as wastes contain a relatively larger amount of PCB. Examples of papers addressing this topic are Frignani et al. (2001b, 2004).

A variety of methods are useful to recognize and unravel Polycyclic Aromatic Hydrocarbons (PAH) sources from urban and industrial activities (Stout et al., 2004, Stout and Graan 2010). They generally fall under two categories: chemical fingerprint and receptor modelling. Chemical fingerprint relies upon qualitative or quantitative comparison of PAH concentration profile (fingerprint) or diagnostic ratios (based on the concentration of an individual PAH or PAH groups or on the concentration of source–specific tracers), versus those of possible sources or referent materials (Frignani et al., 2003; Bertolotto et al., 2003; Giuliani et al., 2008). Receptor modelling involves the application of multivariate statistical methods to identify and quantify pollutant sources (Gordon, 1988).

Similarly, sources of Polychlorinated Dibenzo Dioxins and Furans (PCDD/Fs) can be discriminated based on the relative importance of congeners. For instance, octadioxin is produced by combustion, whereas octafuran can originate during the production of vinyl chloride, and a decreasing pattern of furans, from octa to tetra, can represent the metallurgic industry (that, by the way, is the most important source of this kind of contamination). Our results about this subject are described in Bellucci et al. (2000) and Frignani et al. (2001b).

There are also new and relatively new contaminants such as synthetic musks and polybrominated diphenyl ethers (PBDE), respectively. They represent ideal tracers of domestic activities, and hence of the urban contribution to environmental contamination. The first class includes synthetic polycyclic musks, the most common of which are HHCB (1,3,4,6,7,8-Esaidro-4,6,6,7,8,8-esametil ciclopenta[g]-2-benzopyran), commercially known as Galaxolide[®] and AHTN (7-acetyl-1,1,3,4,4,6-hexamethyltetralin ), known as Tonalide[®], both used as synthetic

fragrances in personal care products and household cleaners. The others are flame retardant, whose mixtures were widely employed in electric appliances, and can reach very high concentrations in indoor environment (e.g., Zhang et al 2009 ).

## FLUXES AND PATHWAYS

Usually, the release of a chemical into the environment can occur especially as dissolved in water or suspended in air (gas or particulate phase). In the first case it is delivered directly into the water system (a river, a lagoon, a lake or the coastal zone), whereas in the second it is transported by wind. In both cases, contaminants interact with particles and eventually accumulate in aquatic sediments and/or in the biota. Depending on the energy of the environment and the presence of benthic fauna, particles and related contaminants are either buried in the sediment or released into the environment, due to resuspension, diffusion, redox processes, and transfer through the food web. Key information in assessing the contaminant behaviour in an ecosystem are inputs and outputs, suspended particle concentration, OC contents in particles and sediments, water-particle partitioning, sedimentary mass accumulation rates, contaminant concentrations in both surficial and subsurficial sediments and in organisms. This information can be used to understand the mechanisms that regulate aquatic system dynamics.

Contamination refers simply to the presence of a substance where it should not be or the concentration above background; in turn pollution may results in adverse biological effects (Chapman, 2007). In this case the chemical analysis alone is not sufficient, but information on bioavailability and toxicity are needed for key organisms. However, all these "lines of evidences" cannot be used independently to determine the pollution status because living species interact actively and passively with environmental changes, therefore, variability of natural adaptation to contamination and tolerance can be confused and/or misinterpreted.

## MATERIALS AND METHODS

Sampling is a key step in environmental studies: the collection of undisturbed sediments and the study of biota are of paramount importance. Therefore, the choice of correct sampling strategies in specific locations is critical to maximize the amount of information provided by sediments, as well as the

choice of key species may allow discriminating whether or when contamination becomes pollution.

The list of basic determinations includes: a) suspended particle concentrations; b) sediment grain size; c) activity-depth profiles of radioactive tracers ($^{210}$Pb e $^{137}$Cs); d) mineralogical composition; e) organic carbon (OC) and total nitrogen (TN); f) stable isotopes ($\delta^{13}$C e $\delta^{15}$N); g) major (Fe, Al, Mn) and trace metals (Ag, As, Cd, Cr, Cu, Hg, Pb, Zn); h) organic contaminants (IPA, PCB, PCDD/F, PBDE, musks, hydrocarbons, pesticides). Effect-based measures such as laboratory or field toxicity tests and the evaluation of the status of resident, exposed communities provide key information. Both heavy metals and organic chemicals should be determined in these environmental compartments.


## DECISION MAKING

As a first order information, contaminants of potential concern (COPCs) and their concentration in surficial and deeper sediments are measured to determine the level and extent of contamination. At the same time, information on sediment stability is obtained to determine whether investigation can be restricted to surficial sediment or needs to be extended to deeper layers, to reconstruct the story of contamination in the area and the first link to causalities.

The second step is to determine whether or not contaminants could cause harmful effects to the receptor compartment/study area. In this case, the easiest way is to compare measured contaminant concentrations with international Sediment Quality Guidelines (SQGs) (Chapman, 2007; Gómez-Gutiérrez et al., 2007), such as the NOAA ERL (Effect Range Low) and ERM (Effect Range Median), or the Canadian TEL (Threshold Effect Level) and PEL (Probable Effect Level). However, the best way would be to use Site Specific Sediment Quality Guidelines. If hazard exists (i.e, the concentration is higher than the upper SQG) a further investigation is required to address toxicity to individual organisms and to assess the extent of toxicity, before undertaking any decision.

This comparison with SQGs provides an initial screening-level ecological risk assessment (ERA), which gives the first identifications of sources and causes of toxicity, but may be followed by a detailed-level ERA if key uncertainties need to be resolved and the causalities are indentified (Chapman, 2007).

Another approach to face with the study of pollution and to undertake environmental decisions consists in the use of mathematical models, such as multimedia fate and transport models. They provide a mechanicistic understanding of the environmental processes from input-output to transport and distribution. Models can be used as management tools, to quantify the reactions of environmental components to both natural and anthropogenic induced changes (Diamond et al 2004). However, a reliable modelling approach may be expensive because it requires a suitable amount of input data and a high degree of expertise, especially in the calibration and validation steps. The uncertainty associated to complex models may be particularly high, and in most cases the simplest approach (identification of source-to-sink pathways) is commonly used.

The availability of historical data, and the collection of new ones could be particularly troublesome for developing countries. Ongley and Booty, (1999) suggested a realistic approach that takes into account these difficulties. They defined the formulation of a decision-support system (DSS) for water management, which probably can be used also for sediments. That allows to game with alternative remediation options with outputs expressed in degree of uncertainty in the assumption and analytical processes included in the DSS system.

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