The Sick Lagoon

DIOXIN AND OTHER PERSISTENT ORGANIC POLLUTANTS (POPs) IN THE LAGOON OF VENICE

Edited by Stefano Guerzoni and Stefano Raccanelli

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Foreword

This timely collection of studies is of special significance for our city. In this condensed volume, the editorial team gives an accurate description of the "state of the art" of scientific research in the delicate and controversial field of environmental monitoring. It is common knowledge that uncontrolled release into the environment of such substances as dioxins, furans, chlorinated compounds and micro-pollutants in general lead to the worst industrial disasters to which mankind has been subjected over recent decades - Seveso and Bhopal above all. However, it is not only the unexpected or casual "gas leak", "line out of order", "leakage", explosion, or fire which periodically occurs (events covered by European legislation and Ministerial decrees on high-profile industrial accidents) which disturbs the sleep of local inhabitants exposed to "chemical risk": a much higher level of anxiety is induced by fear of the effects of a silent, imperceptible, but constant release into the atmosphere or water of toxic substances which, even if they are only assimilated in minute quantities, may accumulate and have lasting effects, poisoning our bodies.Too often have requests for information been side-tracked, if not purposely misunderstood - there is always someone ready to take advantage of another's ignorance. The undeniable complexity of the subject is no excuse for restricting information to a closed circle of experts or "authorised personnel". If there is one thing we have learnt from the many inquiries carried out by the competent authorities over the years, it is that not only public bodies but also company administrators do not have direct responsibility for the possible effects of unforeseen or "undesirable" events. Thus, it is essential that information be rendered more accessible, "transparent", comprehensible and - consequently - available to all those directly involved, including information referring to even remotely possible events. Worries and fears are always justified, as are diffidence or mistrust due to excessive underestimation, as we have seen in the past. However, alarm and panic must also be avoided, as they are inevitably the outcome of incorrect information, which does nothing to help us understand the causes of danger and the changes which may be applied to remove or reduce it. The other pitfall to be avoided is fatalism. It has been said that this is the era of uncertainty. The future frightens us; we have no confidence in the present. Perhaps this is because the outcomes of our actions have evaded control by the community in general. Science itself does little to help us, and it must be said that the sole *certainty in the study of the evolution of complex systems is uncertainty. Hence, the many recommendations from the various Earth Summit Meetings (Rio de Janeiro 1992, Johannesburg 2002) that the most attentive researchers send to their political leaders concerning the importance of introducing the "principle of precaution", namely "sustainable development", long-term and shared, an estimate of the (limited) capacity of ecosystems to tolerate pollutants, waste and alterations of all kinds introduced by man's transformations of the land and the natural resources of the planet. We are all aware that no human activity represents "zero risk". We are compelled to cohabit with risk. It must be "calculated". But how, and by whom? In our society, delegating risk management to "those who know" is no longer acceptable; neither is the cynicism of the experts who limit themselves to "gauging" (for the insurance companies) the damage caused by factories, transport systems or current levels of consumption. Nor can so-called "scientific evidence" ever be considered complete or sufficient, since it is based on statistical methods that only ascertain the presumed level of average physiological tolerance. But the sensitivity of each member of the species exceeds the "weight" of its bodily mass. It is an established fact that individual and social acceptability of exposure to a given risk is a subjective variable, depending on the degree of in-depth study achieved by scientific research and the level of awareness of the danger as perceived by the population. It is for this reason that available information is of special significance. Psychological, cultural and social conditioning and evidence in a wider sense determine the behaviour and attitudes of individuals and social groups. These also deserve attention, to the extent that the success of policies to contain exposure to risk, recovery and reclamation of contaminated sites, and reduction of environmental impact depends on informed public opinion. These factors are taken into consideration in the joint efforts of the City Council and Province of Venice in calculating past emissions and events and monitoring the current situation, so as to create a group of institutions, a network, which will be able to induce the proper authorities to intervene to protect public health. This is long overdue in Venice. Only in this way will it be possible to move from an indulgent tolerance towards the inconveniences suffered by the population (and by personnel directly involved in dangerous operations), to a culture of shared acceptance of modern, safe industry which is both compatible with the environment and a source of wealth.*

Paolo Cacciari
Councillor for the Environment, City Council of Venice

Ezio Da Villa
Councillor for the Environment, Province of Venice

Preface

The idea for this publication came as a result of the conference "*Environmental control of dioxin and persistent organic pollutants (POPs): experiences from Europe and the United States. The need for monitoring in the Lagoon of Venice*", organised by the Italian Inter-university Consortium for Environmental Chemistry in Venice, November 7-8 2002.

The proceedings of that conference have been put into book form with the aim of providing a general picture of conditions in the Lagoon of Venice in terms of contamination by persistent organic pollutants (POPs), a term which include dioxins (PCDD/Fs), polychlorobiphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), hexachlorobenzene (HCB) and chlorinated organic pesticides (POCs). The various sections of the lagoon ecosystem were taken into consideration: water, atmosphere, sediments, organisms and foods.

Dioxins and PCBs are two groups of persistent toxic substances which have negative effects on the health of human beings and on the environment, including skin toxicity, immunotoxicity, negative effects on reproduction, teratogenicity (which causes foetal anomalies), disturbances of the endocrine system, and a predisposition to cancer. The simplest way for humans to be exposed is through the consumption of food contaminated by dioxins and PCBs. Bio-accumulation and long-term exposure to these pollutants mean that even minimal doses of dioxins and PCBs can result in negative effects on health.

The Committee of Experts on Food of the European Commission has proposed a dose called "Tolerable Weekly Intake" (TWI), given by the total of dioxins and PCBs, of 14 picograms per kg of body weight, i.e., an average of 2 pg per day (per kg of body weight). At present, the TWI is normally exceeded by the majority of the population in Europe. The most effective way of reducing intake levels through the food chain is by reducing environmental pollution. With the aim of attaining this goal on a global scale, in October 2001 the European Commission adopted an EU strategy covering dioxins, furans and PCBs[1]. This document also proposes developing procedures for promoting and improving the availability of reliable and comparable environmental data,

[1] EC strategy on dioxins, furans and polychlorobiphenyls. Communication from the Commission for the Council, to the European Parliament and the Economic and Social Committee, Brussels, 21/10/2001, COM(299) 593.

concerning emissions and covering various environmental sectors, and it is our hope that this book will contribute to that end.

Satellite image of the Lagoon of Venice, showing sites mentioned in the text [Landsat 7-ETM, 15/2/2001, provided by Water Authority].

In greater detail, the first chapter is a short introduction to the problem of contamination in Venice by POPs, and explains several concepts related to the most dangerous type: dioxin. This is followed by an analysis of data on water from the Venetian *Magistrato alle Acque* (Water Authority) (Giorgio Ferrari, Chapter 2) and on atmospheric depositions, prepared by the Italian Research Council (CNR) and the University of Venice (Stefano Guerzoni, Emanuela Molinaroli and Paolo Rossini, Chapter 3). The following three chapters summarise what is known about the relationship between sediments and organisms (Stefano Raccanelli, Davide Tagliapietra, Chapters 4 and 5) and present eloquent data about all waste dumps examined around the Lagoon (Alberto Spoladori, Chapter 6). Then preliminary data on dioxin and PCB monitoring in foodstuffs consumed in the Veneto are set out, with particular regard to fish and molluscs (Paolo Camerotto, Chapter 7). Chapter 8 examines a problem which lies close to the heart of the authors of this book: the publication of data and transparency of information. Patrizia Bidinotto, a recent graduate who wrote an original thesis on the subject at Venice's Ca' Foscari University, presents the varying aspects of the question. The conclusions (Chapter 9) restate the current importance of the risk problem (for the ecosystem and public health), which will be developed in the next volume in this series.

These chapters lead to the conclusion that there is a clear need for constant monitoring in the Lagoon of Venice, so that this fragile ecosystem, which has succeeded in cohabiting with man for over a thousand years, can heal the wounds which man has inflicted upon it and be protected against the threat of further pollution. Monitoring is essential if adequate information about risks is to be made publicly available, for the health and well-being of all.

Stefano Guerzoni and **Stefano Raccanelli**

We would like to thank Mauro Masiol for his invaluable editorial work.

Consiglio Nazionale delle Ricerche

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Stefano Guerzoni, born in 1951, is a biologist and senior scientist at the Institute of Marine Sciences (ISMAR) of the Italian Research Council (CNR), located in Venice. ISMAR has recently been re-organised into a broader national institute which previously included two separate Venetian CNR institutes (IBM, Marine Biology, and ISDGM, Physical Oceanography) plus several other units located around the Italian coastline and covering varying disciplines. A new department called "Lagoon and Coastal Transitional Environments" (LACTE) was created, and is devoted to detailed study of the Lagoon of Venice and its watershed, together with the Northern Adriatic Sea. The main study aim is to integrate the various disciplines and apply as well as possible the considerable experience gained in more than 30 years of work in the Lagoon of Venice and elsewhere. In the Department , several environmental compartments are studied (air, water, sediments) following various approaches (hydrodynamics, chemistry, biology, genetics, modelling). Transport and

Buildings of two previous institutes in Venice sedimentation of pollutants, transport pathways of toxic substancess, biotic and abiotic environmental quality indicators, and risk evaluation are among current studies at LACTE.

ISMAR has developed close links with the personnel of the Veneto Region, Province and City Council of Venice, and the Water Authority, in collaboration with whom several important researches in the Lagoon of Venice have been carried out in the last 30 years. The Department hosts the Italian focal point of LOICZ (Land Ocean Interaction in the Coastal Zone) and actively works in developing a network of research groups devoted to the study of transitional coastal ecosystems (Lagunet, www.dsa.unipr.it/lagunet). According to European legislation, LACTE will be a reference point for researches related to the European Water Framework Directive (2000/60/EC) and for its national application.

Sampling of sediments and landscape of the Lagoon (left) and discharge of wastewater (right).

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Stefano Raccanelli, born in 1960, environmental chemist, heads a specialised laboratory for analysing POPs (Persistent Organic Pollutants), which was established in 1998 in Marghera (Venice) by the Inter-university National Consortium (INCA). The Consortium was founded in October 1993, its head office is in Venice and it comprises about thirty Italian universities. Special interests of INCA include monitoring of poly-chloro-dibenzo-dioxins (PCDDs), poly-chloro-dibenzo-furans (PCDFs), poly-chloro-biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs).

The POPs Lab performs both scientific research (testified by 12 publications and 27 communications to congresses in 3 years) and chemical analytical services for third parties.

INCA promotes the Italian Inter-Calibration Circuit for Dioxins (CIND), currently in its 4th edition; participants are 15 Italian laboratories and 31 foreign ones.

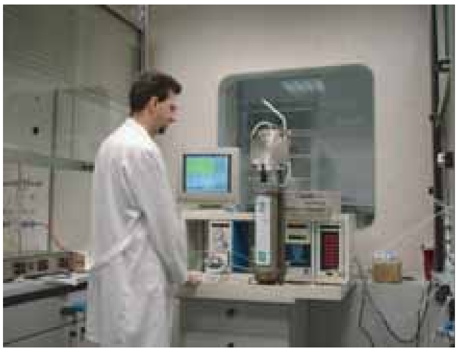
For the first time in Italy, this initiative allowed national laboratories to compare their results at both national and international level, as regards analysis of the 17 cogeners of PCDD/Fs, 12 dioxin-like PCBs, and PAHs, using standard materials obtained via homogenisation of ashes from incinerators of solid urban waste and sediments of the Lagoon of Venice. INCA owns sophisticated equipment which allows the design and application of highly sensitive, selective methods of analysis for determining organic micro-pollutants at an ultra-trace level:

- High Resolution Mass Spectrometer (HRGC/HRMS Autospec Ultima);
- Low Resolution Mass Spectrometer (HRGC/LRMS/MS Saturn 2000);
- Automatic sample purifiers (no. 3 Power-Prep, no. 2 Dioxin-Prep);
- Rapid extractor for solid samples with low use of solvents (ASE 100, ASE200, ASE300);

- INFILTREX system for sampling of high water volumes;
- DEPOBULK for sampling atmospheric depositions.

Analysable samples are: waters (wastewater, underground, surface, drinkable and rain waters), environmental samples (including macrobenthos, macrophytes, gastropods, bivalve molluscs), air and gaseous emissions (incinerators, foundries, power plants, workspaces), food (milk, butter, meat, fish, eggs, fats, oils, animal feed), atmospheric depositions (raw materials and intermediate reaction products).

INCA performs determination of PCDD/Fs in surface and waste waters with a sensitivity limit as low as 10 fg/L for 2,3,7,8-TCDD using an INFILTREX sampler, operates according to *UNI CEI EN ISO/IEC 17025*, and is accredited by *SINAL (no. 0298) for PCDD/Fs, PCBs, HCB and PAHs* using high resolution mass spectrometry.



Headquarters are located in the **VE**nice **GA**teway for Science and Technology (**VEGA**).

Chapter 1

Introduction

1.1 The Lagoon of Venice

The Lagoon of Venice is a complex ecosystem which formed as a result of detritus and other materials transported downstream by rivers to the sea and influenced by tides. Covering a surface area of approximately 550 km^2, it is made up of islands, *barene*, or tidal flats (areas with vegetation, barely above the mean sea level), *velme* (generally a little below average sea level), *valli*, or *valli da pesca* (extensive and intensive fish-farming areas), and channels and man-made canals. It is linked to the Adriatic Sea by way of three inlets (Lido, Malamocco and Chioggia), involving an exchange of water and sediments during tidal cycles. The average depth is 0.6-0.7 m. Eleven small rivers flow into the Lagoon; the total surface area of the channels is 65 km^2, the terrain above water totals 44 km^2, and the average volume of water is estimated at 1000 million cubic metres.

Lagoons are generally coastal environments characterised by extreme fragility and rapid evolution, which originate in delta areas where rivers and sea interact. Solid materials transported in suspension by rivers, meeting the contrasting waves of tides, are deposited as sediments a short distance from the coastline and distributed by currents and wave motion; over time, river debris accumulates and forms littoral belts, strips of sand which gradually extend and enclose a body of water. Thus, the first characteristic of a lagoon is that of an environment in transition, continually reshaped by opposing forces. In the long term, if the eroding effect of the sea is prevalent, a lagoon is gradually transformed into a stretch of sea, or, if the silting tendency of the rivers intensifies, into part of the mainland.

An aerial view of the Lagoon of Venice shows dozens of small islands dotted over its surface. In the past, these islands were envisaged as the "gateway" to the sacred watery "walls" of Venice which, according to a Venetian edict from the 1500s, was "*founded on water, enclosed by water, defended by water, in place of walls*". These very "walls" acted as the outposts of Venetian civilisation and were not crossed for over a thousand years, except by friendly visitors: the water - and the powerful Venetian fleet - always kept foreign armies at the margins of the Lagoon. The islands were called *monasteries* after the religious communities they hosted, complete with relics and sacred images venerated by the lagoon dwellers. The Venetians set up activities appropriate to each island, according to its characteristics and location, and followed a policy of decentralisation which included, for example, removal from the city centre of the kind of work which today would be termed "*polluting*" [*Santarossa*, 1996]. The old inhabitants of Venice were constantly aware of the fact that their city's survival and strength closely depended on the state of the Lagoon. The inspiring principle behind all the substantial work undertaken in it lay in the knowledge that protection and survival depended on the proper hydraulic management of the surrounding region.

In 1501, the Most Serene Republic of Venice established the "*Magistrato alle Acque*", the Water Authority, a council appointed to investigate and solve the problems of the lagoonal environment: the Republic's survival was heavily dependent on the system of waterways of the Veneto region and the Lagoon, which the Authority supervised. With the change in socio-economic conditions and the start of industry at Porto Marghera in the 1930s, the task of defence against pollution was entrusted specifically to the Water Authority (*Royal Decree and Law no.1853 of 18/06/1936*) which was further to carry out checks and controls on any modifying factors asociated with water pollution in the Lagoon. The Water Authority, which currently comes under the Ministry for Public Works, must ensure the survival of Venice, its Lagoon, and the animal and vegetal species which inhabit it, and defend it from natural and anthropic events [*D'Amico et al.*, 1990].

1.2 Pollution in the Lagoon of Venice

The indiscriminate exploitation of the environment as a resource and an inappropriate container for all manner of human waste products has meant that the self-governing and self-regulating capacities of many ecosystems have been lost. Because of their unusual state as semi-closed basins with slow water turnover, lagoons are extremely vulnerable to external influences. In addition, as regards Venice, the choices of economic development drastically modified the very concept of the word: the Lagoon was no longer a bastion of the city, a setting intimately linked to Venice and her survival, but a marshy and malaria-ridden place, in dire need of reclamation. Plans for constructing the port of Marghera were launched in 1917, and gave rise to the first industrial zone, that subtracted some 500 hectares from the lagoon. The decision to locate highly polluting industry, which required large quantities of fresh water and power in the face of relatively low employment levels, was to reveal itself as a progressively negative choice on many fronts. On one hand, industry affected the lagoonal environment by lowering the water-table and polluting it; on the other, it turned out to be incapable of taking an active part in the economic fabric of the Veneto, remaining essentially extraneous in terms of development.

The problem of water pollution in the Lagoon of Venice is a very complex phenomenon, due to the many sources of pollution and the unusual nature of the environment. The Lagoon in fact receives wastewater from a whole series of industries and towns which include:

- the cities of Venice and Chioggia, with their considerable influxes of tourists, and beaches, coastal strips and islands which, for the main part, lack a proper sewage network and water treatment facilities;

- the Venetian mainland, which again has an incomplete sewage network and only a few treatment facilities in operation;

- the two industrial zones and the power station of Porto Marghera;

- the municipalities of the Venetian hinterland, which discharge their wastewater into the watercourses draining into the Lagoon;

- approximately 185,000 hectares, where agriculture is practised using organic and inorganic fertilisers, pesticides, etc., which drain into the Lagoon by way of natural watercourses and channels for the reclamation zones;

- the passage of shipping which discharges into the Lagoon waste deriving from incomplete fuel combustion, including leakage of hydrocarbons;

- road traffic in neighbouring areas, which presumably also affects the Lagoon.

The massive pollutant load deriving from these sources exceeds the capacity of the Lagoon to regenerate water successfully, re-mineralise organic compounds, and dilute inorganic ones so that the concentrations of the various substances can return to levels comparable with those in sea water [*Ghetti* and *Passino*, 1980; *Venice City Council - WWF*, 1985; *MAV - CVN*, 1999; *Venice Water Authority*, 2000].

Over the past decade, *organic micro-pollutants* have taken on particular significance in studies of pollution in the Lagoon. Known as POPs, these compounds are difficult to degrade or only partially degradable. They are the cause for greatest concern, together with several heavy metals, including mercury and arsenic, which are both extremely unstable as well as potentially highly toxic in biological terms [*Marcomini et al.*, 1997; *WWF*, 2001; *Critto* and *Marcomini*, 2001].

1.3 Dioxin: the most toxic persistent organic pollutant

The term *persistent organic pollutants* (POPs) is used in modern environmental science to refer to families of organic compounds which are chemically stable and characterised by marked toxicity and a long life-span in the environment. The best-known are polychlorobiphenyls (PCBs), polychlorinated dibenzo-p-dioxins (PCDDs), polychlorodibenzofurans (PCDFs), chlorinated organic pesticides (POCs, which include DDT), polycyclic aromatic hydrocarbons (PAHs) and hexachlorobenzene (HCB). Years ago, the competent authorities of many countries, faced with the need to protect public health and the environment, launched studies and monitoring programmes of environmental contamination levels of POPs, with the aim of evaluating the risks associated with their spread throughout the planet [e.g., *Swedish Environmental Protection Agency*, 1998]. The Stockholm Convention (22 May 2001) should be mentioned with regard to POPs. Signed by 151 countries and entailing 30 articles and 6 attachments, it recommends cessation of production of PCB (not its use or transport) and the reduction and/or elimination of dioxins and furans (PCDD/F) produced and released "unintentionally" [*Johansson*, 2002]. The Convention will become fully operative when at least 50 countries have incorporated it into their national legislation. The 12 POPs which were banned include insecticides such as HCB, industrial products (PCBs) and unwanted by-products (PCDD/Fs).

The large-scale industrialisation that came in the wake of the Second World War brought not only development and well-being, but also an unexpected and negative environmental impact, due to emissions of by-products into the ecosystem, with a rapid rise in contamination levels starting in the 1960s. The infertility and death in birds of prey (caused by DDT) and mink (caused by PCBs), which had been observed since the mid-1960s, were the early warning signs which led to awareness of the danger of contamination by substances considered indispensable and until then, not dangerous. The studies that followed highlighted the toxicity of POPs for living organisms, and revealed the full extent of their ubiquitous distribution. Moreover, thanks to the chemical stability and lipophilic character of POPs, studies showed that they are subject to processes of bioaccumulation and biomagnification. In other words, environmental contamination at levels even lower than one part per billion can create dangers for man, the final link in the food chain. Mother's milk, rich in fat, is an example of one substance in which POPs accumulate: breast-feeding thus becomes the main source of intake of these substances for newborn babies.

The most infamous POP is undeniably dioxin, known all over Europe in the wake of the Seveso accident in 1976. The word usually refers to a group of 210 cogeners, made up of 75 PCDDs and 135 PCDFs. Of these, only seventeen 2,3,7,8 chlorine-substituted cogeners have demonstrated significant toxicity, related to that of the more toxic 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD), classified as a cancer-causing agent for man by the International Agency for Cancer Research and other authoritative international associations. At present, after a number of preliminary passages, a scientific agreement has been reached on the use of equivalent factors of toxicity, which allow the contents of PCDD/Fs to be defined as equivalents of toxicity (I-TE) with reference to 2,3,7,8-TCDD [*NATO CGMS*, 1988a,b]. International Toxicity Factors (I-TEF) are also used for environmental legislation, whereas those of the World Health Organisation (WHO) are applied to foods (see Chapter 1.6).

It should be noted that dioxins were not produced deliberately, but are unwanted by-products of a series of chemical processes and combustion. As they are highly persistent, they remain in soil and sediments, which become true polluting reservoirs. The main pathway of exposure to dioxin in humans is food, which contributes over 90% to overall exposure.

Specific long- and short-term pathologies associated with accumulation of POPs in organisms have been identified. They come from contamination but also from accidents and deliberate release. Studies on the toxic effects of TCDDs at varying levels of exposure have been conducted on numerous animal species. However, little is known about their toxic effects on man; most of the information comes from studies carried out after accidental exposure or contact during work. There is a great deal of controversy in scientific circles on this subject, between those who believe that serious biological effects occur in humans, and those who point to the dearth of experimental proof. There have been somewhat controversial results in terms of carcinogenicity, teratogenicity, effects on foetuses and birth rates, and presumed effects on the endocrine and immune systems. However, the majority of the scientific community and the American Environmental Protection Agency (EPA) agree that currently available epidemiological data [*Fingerhut et al.*, 1991, 1992; *Kogevinas et al.*, 1997], other data soon to become accessible, and toxicological data from laboratory studies, all indicate a reasonable correlation between exposure to TCDDs and the appearance of tumours such as soft tissue sarcomas and lung and liver cancer.

In 1997, 2,3,7,8-TCDD was classified as a group I carcinogen, and reported in volume 69 of the International Agency Research Cancer (IARC). As a tolerable daily dose (i.e., the daily quantity taken in food or in other ways, acceptable by the organism with no danger for health), in 1998 the World Health Organisation established a limit between 1 and 4 picograms, expressed in TE per kilogram of body weight per day. The goal set by the WHO is to achieve levels below one picogram of TE per kilogram of body weight per day. The European Community recently recommended a weekly limit of 14 pg WHO-TE/kg body weight. Recent data and documentation concerning daily intake values indicate that the average rates of dioxins and "dioxin-like" PCBs taken in diet in the European Union are between 1.2 and 3 pg/kg body weight/day, which means that significant numbers of the European population are still above the limit of the tolerable daily and weekly doses. It was also found that children are already exposed 2 to 4 times more than adults, and newborn babies may even reach exposures of 160 pg/kg body weight [*Official Gazette of the European Community*, 2001].

1.4 Sources of dioxin in the Lagoon of Venice

The deposition of PCDD/Fs in the environment is mainly due to man's activities, through the various aspects of the chemical industry, most combustion processes (incineration, metal-working, production of power, heating, traffic, etc.) and discharge of wastewater and sewage. Contamination from PCDD/Fs in the Lagoon of Venice is due to industrial and urban discharges, with further contributions from river drainage basins, atmospheric depositions, and illegal dumping through the water-table. The reactions that lead to the formation of PCDD/Fs (210 cogeners) enhance the formation of certain cogeners rather than others: the results can often be correlated with production. The distribution of identified cogeners provides "signatures", or *fingerprints*, which can identify the type of process leading to their formation. The characteristic fingerprints of PCDD/Fs forming during various industrial and combustion processes have been documented: in the case of a single substance, it is possible to identify the exact point of entry into the environment. The cogeners of dioxins and furans are grouped together, according to their degree of chlorination, from 4 to 8. In this way, fingerprints composed of 5 dioxins and 5 furans can be obtained. Fingerprints for combustion and urban discharges are normally dominated by octachlorodibenzodioxin (OCDD), together with light furans (TCDF, PCDF), whereas those due to chemical processes entailing chlorine are dominated by octachlorofuran (OCDF), with the notable presence of heptachlorofuran (HpCDF). During the industrial production of vinyl chloride and PVC, organic chlorine derivatives and chloro-alkalis, dioxins with characteristic fingerprints are produced and can be identified by the so-called "chlorine fingerprinting" [*Greenpeace*, 1995, 2001; *Ferrari*, 1997; *Rabitti*, 1998].

1.5 Other POPs

1.5.1 *Polychlorobiphenyl (PCB)*

Polychlorobiphenyls are compounds in which the atoms of hydrogen of the biphenyl molecule are wholly or partly replaced by atoms of chlorine. Production of these substances, which commenced in 1929, has now ceased. However, millions of tons of PCB (under the names of Aroclor, Clorphen and Kanchlor) were produced and used worldwide in a range of sectors (dielectric fluids, insulators, lubricants, cutting oil, adhesives, etc.). By varying the number and position of the chlorine atoms in the molecule, it is possible to form 209 different PCB cogeners. However, as their persistence in the environment increases with the degree of chlorination, PCBs with a high degree of substitution are the most abundant in the environment. The persistence and toxicity of the various cogeners depend not only on the degree of chlorination but also on the position occupied by the chlorine atoms inside the molecule. In this regard, PCBs in which chlorine is present in the *meta* and *para* positions but not in the *ortho* position, in relation to the carbon-carbon link, are characterised by the maximum toxic effect. This is because the aromatic rings of these compounds are on the same level (coplanar PCBs), making their molecular structure and toxicological properties very similar to those of dioxin ("dioxin-like" PCBs).

1.5.2 *Hexachlorobenzene (HCB)*

The molecular structure of hexachlorobenzene (HCB) consists of a single aromatic ring in which all the hydrogen atoms have been substituted with chlorine atoms. Although HCB had very limited use in the past as a fungicide for treating seeds, its importance as an environmental contaminant is due to the fact that it is formed as a by-product during the production of chlorine and chlorinated hydrocarbons. It is highly soluble in fats, and is persistent and toxic. In addition, its great chemical stability and especially low biodegradability have contributed to its large-scale environmental dispersal.

1.6 The Concept of TEQs (Toxicity Equivalents)

As already mentioned, the polychlorobiphenyls are a family of 209 cogeners containing from 1 to 10 atoms of chlorine. Several of these cogeners (non-*ortho* and mono-*ortho* PCBs) have toxicological properties comparable with those of dioxins, and are called "dioxin-like" PCBs. Each cogener of the dioxins or "dioxin-like" PCBs has a different level of toxicity. The concept of toxicity equivalent factors (TEFs) is based on the fact that "dioxin-like" compounds have a mechanism for action, interacting with the Ah-receptor. The most toxic compound, 2,3,7,8-tetrachlorodibenzendioxin (TCDD), is assigned the maximum toxicity factor of 1. The 17 cogeners of PCDD/Fs (see Chapter 1.3) and the 12 cogeners of "dioxin-like" PCBs are assigned TEFs lower than or equal to the toxicity of TCDD in relation to that demonstrated by each compound compared with TCDD. Toxicity factors mean that analytical results can be expressed for each of the 17 single dioxin cogeners and the 12 cogeners of "dioxin-like" PCBs by a single quantifiable unit, i.e., "TCDD toxicity equivalent concentration" (TEQ). In June 1997, the World Health Organisation established the levels of toxicity factors (WHO-TEFs) to be applied in evaluating risk for humans and animals. These values became official in May 1998, during the WHO Consultation "*Assessment of the health risk of dioxins: re-evaluation of the Tolerable Daily Intake (TDI)*". The Consultation set the TDI between 1 and 4 pg TEQ/kg body weight, emphasising that the aim was to lower the TDI to a level under 1 pg TEQ/kg body weight.

As regards Venice, recent studies have demonstrated that, on average, the city's population assumes approximately 42 pg TEQ/day (range 15-128). Fish and shellfish account for approximately half the daily intake, and other foods the remaining half [*Zanotto et al.*, 1999]. If the values for "dioxin-like" PCBs are added to dioxin, the values are as high as 108 pg TEQ/day [*Alcock et al.*, 2002].

Chapter 2

Monitoring POPs in the Lagoon of Venice

Giorgio Ferrari
Water Authority - Venice

2.1 Introduction

Monitoring the quality of water (and of wastewater) is seen as a response, one of the steps necessary for reducing causes of changes to the environment and their consequent impacts. Clearly, proper understanding of the quality and quantity of water, and of how pollutants are introduced into it, is essential for monitoring and protecting the evolution of the environment, in terms of policies and relative norms. The importance of this was recognised in *EC Directive 2000/60, October 23 2000*, which is a frame of reference for water monitoring and intervention, and EC member states will need to bring their practises in line in developing their individual environmental policies over the coming decades. The aim of the directive is to furnish a clear legislative picture which is both effective and consistent, in order to further co-ordinate, integrate and develop the long-term policies and actions of member states for the protection and sustainable use of water in the EC.

The organisation of monitoring requires an initial learning phase, defined as one of "operative or investigative monitoring". Its aim is firstly to define the state of environmental quality and evaluate any variations in that state after measurements have been carried out and data collated. During this phase, the maximum number of investigative parameters must be taken into consideration. In addition, monitoring must be sufficiently frequent to give a reliable picture of the state of each qualitative element. This operative monitoring phase must then be followed by "*supervisory monitoring*", with the purpose of checking whether the environmental goals set previously have been attained.

Supervisory monitoring data must also allow for validating and, where relevant, integrating impact assessment procedures, refining the project design of future monitoring activity, and evaluating long-term variations in natural conditions and those resulting from widespread human activity. Supervisory monitoring also entails consideration of the parameters indicating all the elements of biological, hydromorphological and chemical-physical quality, as well as pollutants (priority and others) which top the list and which are discharged into the Lagoon or its nearby watercourses.

Directive 2000/60/EC applies to *internal surface waters*, *transitional waters*, *coastal and underground waters*, and basically aims at preventing further deterioration, and protecting and improving the state of the aquatic and terrestrial ecosystems and the wetlands directly dependent on them in terms of water requirements. In a last analysis, these results will be achieved by gradually reducing the input of dangerous substances into water, to the point when concentrations of natural substances in the sea are the same as those of the natural background levels, and close to zero for man-made substances.

> 1. *Member states will gradually have to make the effort to reach an exemplary ecological situation for water, through integrated programmes and initiatives undertaken respecting the requisites established in the EC Directive.*

In order to achieve these objectives, member states will need to proceed in a homogeneous fashion, with a consistent approach common to the whole Community. For this reason, the Directive lays down common environmental definitions, criteria and objectives to be adhered to for appropriate action. The most important aspects considered include:

- definition of a list of priority substances which present a significant risk for or through the aquatic environment;
- indication of qualitative elements for defining ecological state;
- definition of norms for classifying ecological state;
- guidelines for introducing monitoring of ecological and chemical states of surface waters;
- classification and presentation of ecological state.

Member states will also need to establish the reference hydromorphological, physical-chemical and biological conditions for each type of surface water. These conditions represent the values of specific elements referring to the term “elevated ecological state”, and may be based on spatial criteria, the results of modelling, or a combination of the two. Where this is impossible, reference conditions may also be established according to expert appraisal. Defining elevated ecological state with regard to the concentrations of specific synthetic pollutants, threshold concentrations correspond to those which may

BIOLOGICAL ELEMENTS		
	Composition, abundance and biomass of phytoplankton	
	Composition and abundance of other aquatic flora	
	Composition and abundance of benthic macro-invertebrates	
	Composition and abundance of fish	
HYDROMORPHOLOGICAL EFFECTS SUPPORTING BIOLOGICAL ELEMENTS		
	Morphological conditions	Variations in water depth Mass, structure and substrata of bed Structure of intertidal zone
	Tides	Flow of fresh water Exposure to waves
CHEMICAL AND PHYSICAL-CHEMICAL ELEMENTS SUPPORTING BIOLOGICAL ELEMENTS		
	General elements	Transparency Thermal conditions Oxygenation Salinity Nutrients
	Specific pollutants	Pollution by all substances on the list of priorities for which discharge has been ascertained Pollution by other substances for which discharge has been ascertained in significant quantities

Table 2.1: *Qualitative elements for classifying the ecological state of transitional waters (Reference:* Dir 2000/60/EC, All. V, transitional waters*).*

be achieved by analytical techniques available at the time when the specific typical conditions are established. Table 2.1 lists qualitative elements for classifying the ecological state of transitional waters in terms of *Directive 2000/60/EC*.

2.2 Monitoring in the Lagoon of Venice

Already in the late 20th century, attention was growing in the Italian and international scientific community for in-depth study of the phenomena regulating lagoonal environments. In the case of the Lagoon of Venice and its drainage basin, the quality aims concerning physico-chemical elements were established by the *Ministerial Decree of 23 April 1998* (the so-called "*Ronchi-Costa*" decree), by defining "imperative" and "guideline" values for various parameters. "Imperative" values refer to a "good" ecological state of physico-chemical quality, defined for transitional waters by the 2000/60 EC Directive; "guideline" values refer to the "elevated" state. A "good" state for waters must be attained by the year 2015.

The Water Authority, both directly and through the *Consorzio Venezia Nuova*, has undertaken a monitoring campaign of the lagoon water aimed at reaching the quality objectives of the above Decree. The campaign, launched according to the Inter-ministerial Decree of 30 July 1999 "Limitations to industrial and city discharges into the Lagoon of Venice and its drainage basin, in accordance with Art. 5 of the Inter-ministerial Decree of 23 April 1998, covering requisites of water quality and characteristics of water treatment plants to safeguard the Lagoon of Venice", is structured as a monitoring network managed directly by the Water Authority through the "*Sezione Antinquinamento*" (anti-pollution section, or SAMA) and a series of measuring points in the Lagoon and sea managed by the *Consorzio Venezia Nuova*, as part of the study "Environmental Monitoring Activity in the Lagoon of Venice - implementation of the first three-year plan (2000-2003), with initiatives for controlling quality objectives and maximum allowable discharges according to the Decree of the Ministry for the Environment of 23.4.1998", conventionally referred to as "MELa 1".

2.2.1 *Monitoring by the anti-pollution section (SAMA) of the Water Authority*

Monitoring by SAMA began in 1999. The initial phase involved 12 measuring and sampling points, located around the Lagoon's central and southern basins near the main sources of pollution (Porto Marghera, Venice, Chioggia, Lido, Pellestrina). Starting in January 2001, four more points in the northern lagoon were added (Murano, Burano, Ca' Savio, Saline).

Most of the sampling points are located close to sources of urban and industrial pollution, in order to quantify the direct influence of substances discharged into the Lagoon. For purposes of comparison, three points (M, N, R), relatively distant from points of discharge, were added, with the aim of checking the extent of variations in parameters with respect to the points closest to the sources. Table 2.2 lists the characteristics of the 16 SAMA monitoring points; Figure 2.1 shows sampling point locations.

Starting in 2000, the number of parameters was progressively increased by adding analyses of metals, thanks to voltammetric techniques capable of measuring the concentrations of several heavy metals (cadmium, copper, lead) in "dynamic" form (dissolved, non-colloidal) and totally dissolved forms. During 2001, with the aim of obtaining parameters in line with the quality objectives of the Ronchi-Costa decree, measurements for total dissolved nitrogen and phosphorus were added. A preliminary campaign was also undertaken to determine several POPs using techniques of pre-concentrated sampling.

2.2.2 *Experimental part*

Work was conducted on a monthly basis with "in situ" measurements, samples of water being taken and later analysed in the laboratory. Each campaign

AREA	POINT	LOCATION
Venice	A	Grand Canal — Rialto
	B	Fondamente Nuove
	C	Canale della Giudecca — Punta della Salute
	D	Canale Industriale Nord
	E	Canale Industriale Ovest
	F	Canale Malamocco — Marghera
Lido	G	Santa Maria Elisabetta
Pellestrina	H	Pellestrina residential district
Chioggia	I	Canale Lombardo
	L	Canale del Lusenzo
Lagoon	M	Canale Perognola
	N	Fondi dei Sette Morti
Murano	O	Canale degli Angeli
Burano	P	Canale esterno lato Est
Treporti	Q	Canale Pordelio
Le Saline	R	Canale di San Felice

Table 2.2: *The 16 SAMA sampling points.*

was conducted over two or three excursions, mainly on consecutive days, in the various basins. Both "in situ" measuring and water sampling were always carried out in the first 50 cm of the water column, since it was the most suitable for evaluating the influence of pollution sources in the lagoonal environment, because both thermal and haline stratification and the mean water depth were the most representative for a general description of the Lagoon's aquatic ecosystem.

As regards POPs, samples were collected with an automatic system capable of concentrating organic micro-pollutants on a solid base. This system (INFILTREX 100-II, Axys Environmental System) collects all POPs, both adsorbed on suspended particulate matter (SPM) and dissolved in large volumes of water (up to 100 litres) on a glass wool filter and resin cartridges. In terms of total concentrations of POPs in water (sum of the fraction dissolved and adsorbed on SPM), the extraction, elution and successive analysis of samples resulted in measurements with a sensitivity one hundred times higher than that of traditional methods of analysis.

2.2.3 *Polychlorinated dibenzo-p-dioxins and dibenzofurans*

Due to the unusual conditions in which such compounds form, the distribution and relative abundance of the cogeners that make up the families of PCDDs and PCDFs are characteristics of the specific process which produced them. For example, mixtures of PCDDs and PCDFs emitted as a result of combustion (both industrial emissions and those due to traffic) have an excess

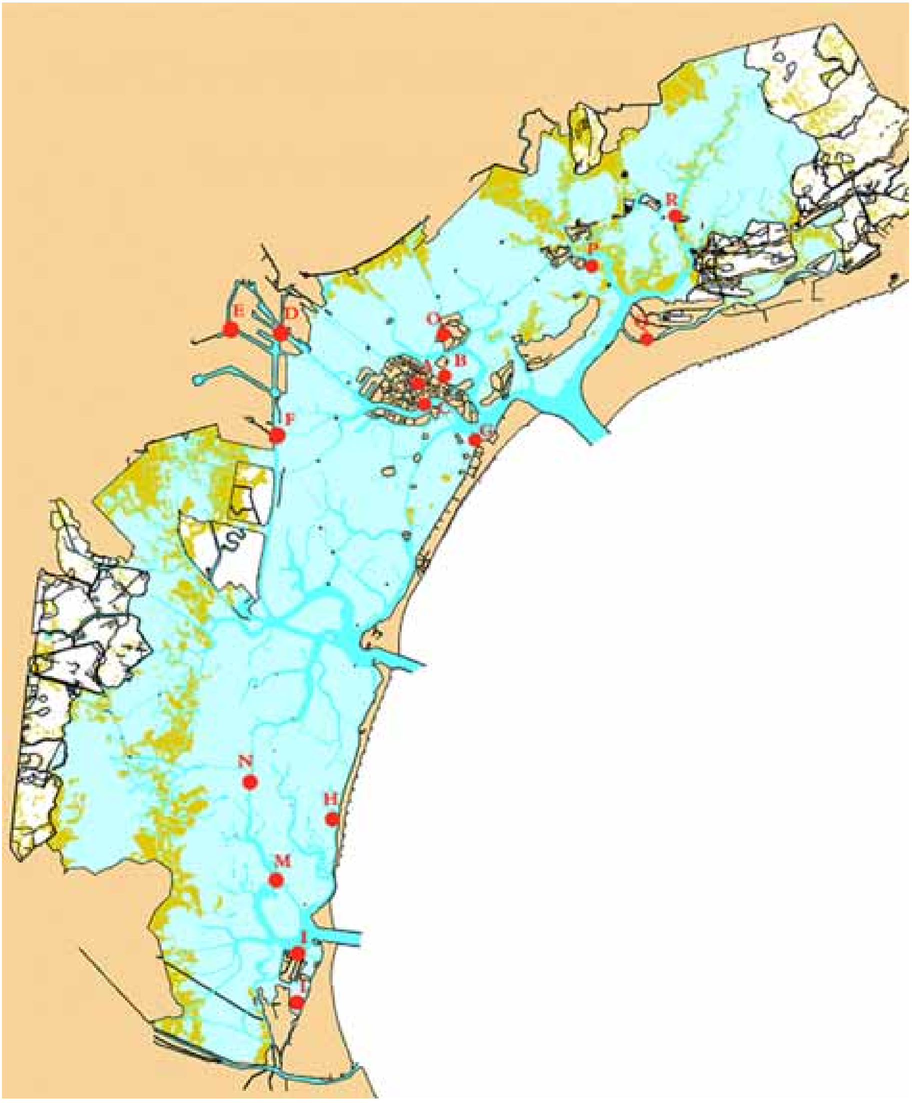


Figure 2.1: *Map showing location of sampling points.*

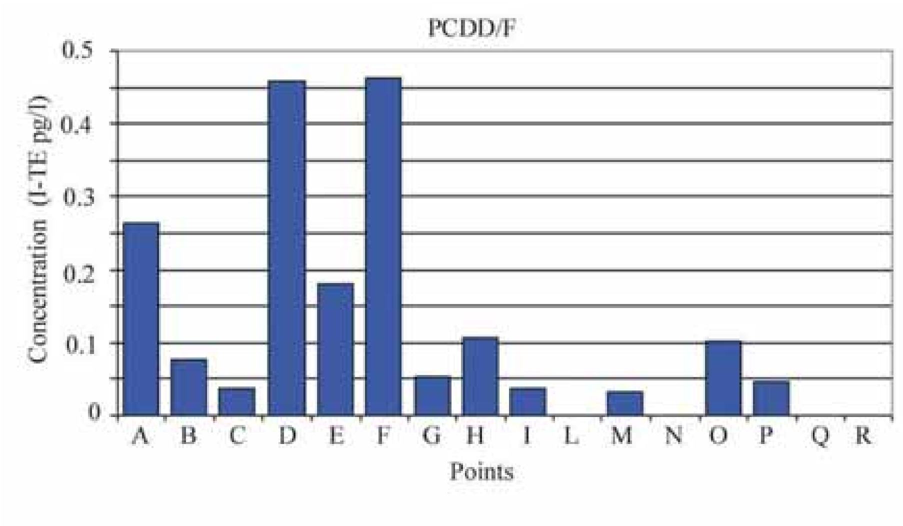


Figure 2.2: *Comparison between concentrations of PCDD/F at all sampling points.*

of PCDDs compared with PCDFs, as do sewage and civilian wastewater. In contrast, PCDFs are preponderant in other industrial activities, such as production involving chlorine, as both raw material and final product (chlorine-soda plants, production of vinyl chloride and volatile organic chlorine derivatives). So unusual is this distribution that, for these processes, environmental contamination can be precisely identified by the so-called *chlorine fingerprinting*. The difference between the overall values of PCDD/Fs (expressed as I-TE) at various points is shown in Figure 2.2.

Clearly, the highest values were measured at Porto Marghera (points D, F) and in the Grand Canal (point A), both areas where concentrations of these compounds are at a maximum in sediments as well. At points further away

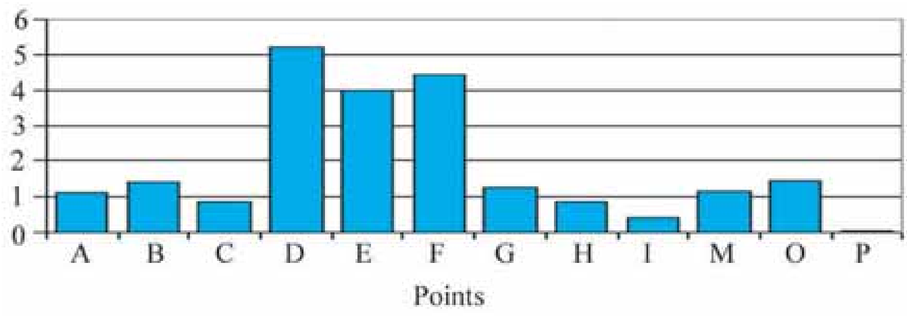


Figure 2.3: *OCDF/OCDD ratios at sampling points.*

from the generating sources, concentrations are lower or even absent (points L, N, Q, R). For the OCDF/OCDD ratio, peak values appear once again at points D, E and F (Figure 2.3).

Comparison of the relative abundances of cogeners reveals several differences between the fingerprints at the various points. Those close to the industrial zone of Porto Marghera (points D, E, F) highlight the clearcut superiority of OCDF (50-60%, compared with all cogeners), as well as 1,2,3,4,6,7,8 HpCDF and OCDD (10-20%). This picture ("Marghera fingerprint") is comparable with that reported in the literature concerning discharges and waste from the production of dichloroethylene (DCE) and vinyl chloride (VCM), and confirms that the characteristics of the water in the Porto Marghera industrial zone have the PCDD/PCDF fingerprint typical of chlorinated hydrocarbons (DCE/VCMs), which continue to be produced in the petrochemical plant (Figure 2.4).

A second group of points (I, P, L) is characterised by the clearcut dominance of OCDD over the other cogeners. These points are the furthest from the industrial zone and consequently may not be affected by fluxes from that area. The dioxin fingerprint at these points is typical of the general processes of combustion and contamination due to urban discharges (Figure 2.5).

A third group of points (A, B, C, G, H, M, O) has OCDD and OCDF in comparable concentrations ("Venice fingerprint"). These points are clearly influenced by a combination of the two main sources: Porto Marghera for OCDFs and the widespread urban contribution for OCDDs (Figure 2.6). The industrial component, in addition to influencing the quality of water at these points through wastewater discharge, contaminated areas and sediments from the industrial zone, is also detected in atmospheric fall-out of industrial origin, as has been clearly demonstrated in recent studies (see Chapter 3).

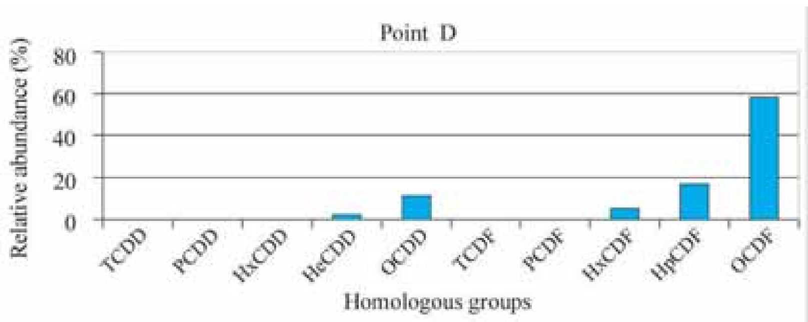


Figure 2.4: *Example of "Marghera fingerprint", revealing production of chlorinated hydrocarbons.*

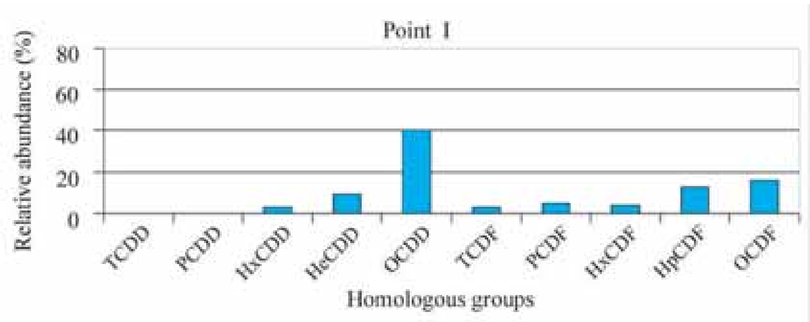


Figure 2.5: *Example of fingerprints of generalized processes of combustion and urban waste.*

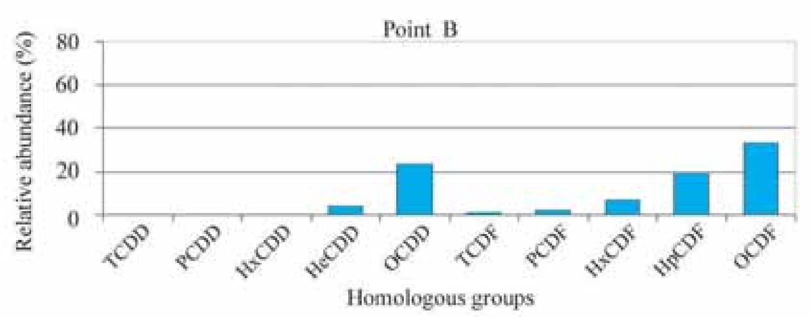


Figure 2.6: *Example of "Venice fingerprint".*

2.2.4 *Polychlorobiphenyl and Hexachlorobenzene*

Figure 2.7 shows the concentrations of coplanar PCBs, which peak at point A in the historical city centre of Venice, where high levels also occur in sediments. Relative peaks are also encountered in the three points opposite the petrochemical plant (D, E, F) and at Murano (O), all with concentrations about three times lower than those in the Grand Canal (A).

Figure 2.8 shows HCB concentrations at the various sampling points. As may be seen, peaks are evident in Porto Marghera (D, E, F), where concentrations are three times higher than in the Grand Canal (point A) and 10 times higher than at other points in the Lagoon, confirming the specificity of this contaminant, a by-product of the processes of the chlorine cycle under way at Porto Marghera.

As a final note, on the basis of these data, a provisional estimate (Table 2.3) may be made of POPs deriving from discharges into the Lagoon off Porto Marghera, the zone with the highest levels of all pollutants.

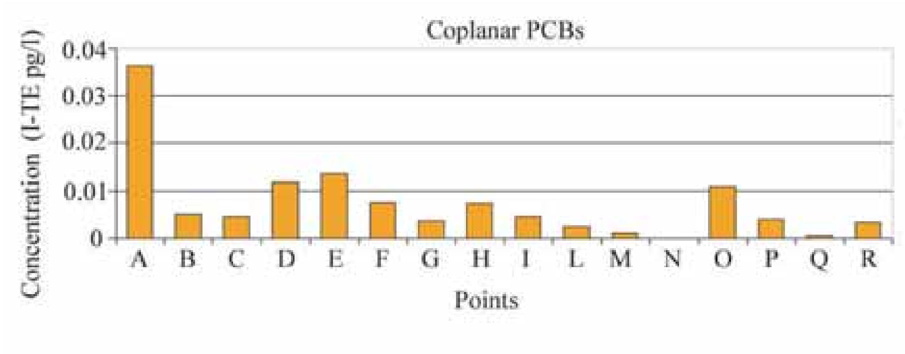


Figure 2.7: *Concentrations of coplanar PCBs at all sampling points.*

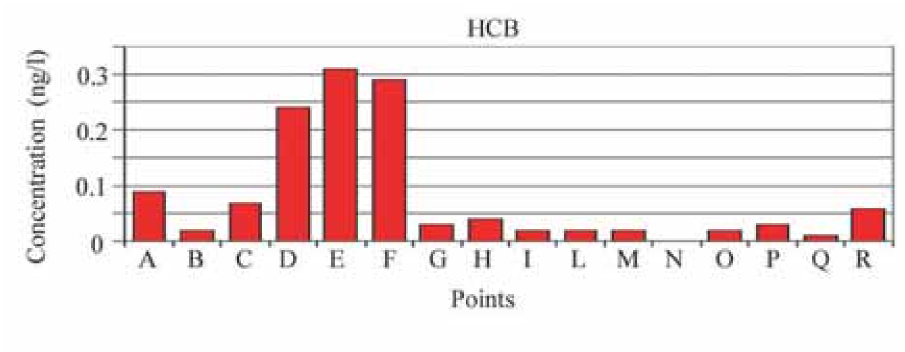


Figure 2.8: *Concentrations of HCB at all sampling points.*

2.3 Conclusions

Monitoring of water in the Lagoon of Venice, undertaken by the Water Authority in 1999 and over the following two-year period (2000-2001), yielded an initial picture of the state of its physico-chemical elements, in accordance with the *Ministerial Decree of 23 April 1998 and Directive 2000/60/EC.*

Monitoring results identified zones in the Lagoon which are subjected to considerable pressure by man (Porto Marghera industrial zone and Venice's historical city centre), which influences the qualitative characteristics of the lagoonal water and those areas which are still free from contamination. In general, the threshold level established by the Ronchi-Costa decree is easily exceeded in the above areas, in terms of most of the parameters analysed.

These observations confirm the need for intervention with strict anti-pollution measures, both as regards discharges directly into the Lagoon and throughout the drainage basin, and interventions aiming at reducing sources of pollution everywhere (e.g., dredging of contaminated sediments,

PAH	25 kg
PCB	0.5-1.0 kg
HCB	0.25 kg
PCDD/F	0.5-1.0 g TEQ

Table 2.3: *Provisional estimate of POPs from discharges into Lagoon off Porto Marghera, in 2001.*

work on the margins of the Porto Marghera area to eliminate leakages from contaminated industrial soil).

Monitoring of POPs in the environment is an essential activity, which the competent authorities must ensure in order to guarantee the application of environmental norms and policies. Therefore, work will be continued over time, to ascertain whether the objectives of quality according to the Ronchi-Costa decree are being achieved.

The anti-pollution section of the Water Authority will undertake progressive integration of work, both in terms of the type of parameters analysed and of the number and location of monitoring points. In particular, a laboratory will be set up for separate determination of the dissolved fraction of organic micro-pollutants.

Chapter 3

Atmospheric deposition of POPs in the Lagoon of Venice and surrounding areas

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3.1 Introduction

Study of atmospheric depositions - that is pollutants which reach marine and terrestrial environments - is of special importance because, indirectly, it concerns the quality of the air we breathe. Research carried out in sea and lagoonal areas in the vicinity of industrial zones, as in the case of Venice with its petrochemical plant, have demonstrated that atmospheric depositions may be of considerable importance when calculating the quantities of pollutants introduced into the environment.

The first studies on atmospheric depositions conducted by ENEA (the Italian authority for alternative energy) in the Lagoon of Venice were carried out in the 1990s, and dealt mainly with nutrients (nitrogen and phosphorus) and inorganic micro-pollutants (heavy metals, HMs). Other data on HMs from a single sampling point in the historical city centre of Venice were published recently [*Rossini et al.*, 2001].

The first specific research on POPs was part of *Progetto 2023* [*MAV - CVN*, 2000a] and presented the first complete set of data available on the Lagoon of

Venice (a summary is available at www.salve.it). More recently, in collaboration with provincial and city authorities, work was carried out near the Porto Marghera industrial zone and the town of Mestre, on the mainland, and results became available at the end of 2003. In this chapter, preliminary results of the *Progetto 2023* study are briefly described in terms of depositions of dioxins and furans (PCDD/Fs), polychlorobiphenyls (PCBs) and hexachlorobenzene (HCB).

3.2 Sampling and analysis

Sampling lasted for 13 months (July 1998-July 1999; total number of samples 109), using bulk deposition samplers (passive collectors of wet and dry depositions, see Figure 3.1) at four points inside and in the proximity of the lagoon drainage areas, as follows: Point 1: Historic City Centre, 2: Northern Lagoon, 3: Southern Lagoon, 4: Industrial Zone. The criterion for selecting the sites was based on a review of the different gradients of inorganic and organic pollutants between land and lagoon and between north and south. The four representative sites were located in zones not directly affected by the sources of heavily polluting urban and industrial emissions, in line with criteria proposed by the World Meteorological Organisation [*UNEP/MAP/WMO*, 2001].

The sampling system used has the advantage of being simple and functioning "passively" and without electricity, so that any site in the Lagoon is viable, even places without facilities. Although this method does entail a number of inaccuracies, they were analysed and found on the whole not to exceed 10-20%.

Table 3.1 gives a summary of the total fluxes of the organic micro-pollutants studied (one year's figures for points 1 and 4, nine months for points 2 and 3). Considerable differences between the four points are immediately apparent, the highest often at point 1 (city centre of Venice) and 4 (industrial zone), and the lowest at 2 and 3 (northern and southern parts of the Lagoon).

The specific loads of PCDD/Fs in the lagoon as a whole are reasonably homogeneous and range from 10 to 20 ng m^{-2} per year; $\sim$ 50 ng m^{-2} per year were measured at point 4. The deposition of PCBs is similar at points 4 and 1, i.e., approximately 500 ng m^{-2} per year, or 5 times higher than that in the northern and southern basins. HCB produces an annual load of over 8000 ng m^{-2} in the industrial zone, almost 6 times higher than in the rest of the Lagoon ($\sim$1500 ng m^{-2} per year).

When the monthly rate of flux is considered (Figures 3.2, 3.3, 3.4), variability between months is even more accentuated, although the values for point 4 (industrial zone) are always the highest. Exceptions to this repetitive rate are PCBs (Figure 3.2), where in some cases (November-December 1998, April 1999) fluxes in the northern lagoon (point 2) exceeded or were similar to those of all the other points. In the case of dioxins (PCDD/Fs) and hexachlorobenze (HCB), several absolute peaks stand out for point 4, in August

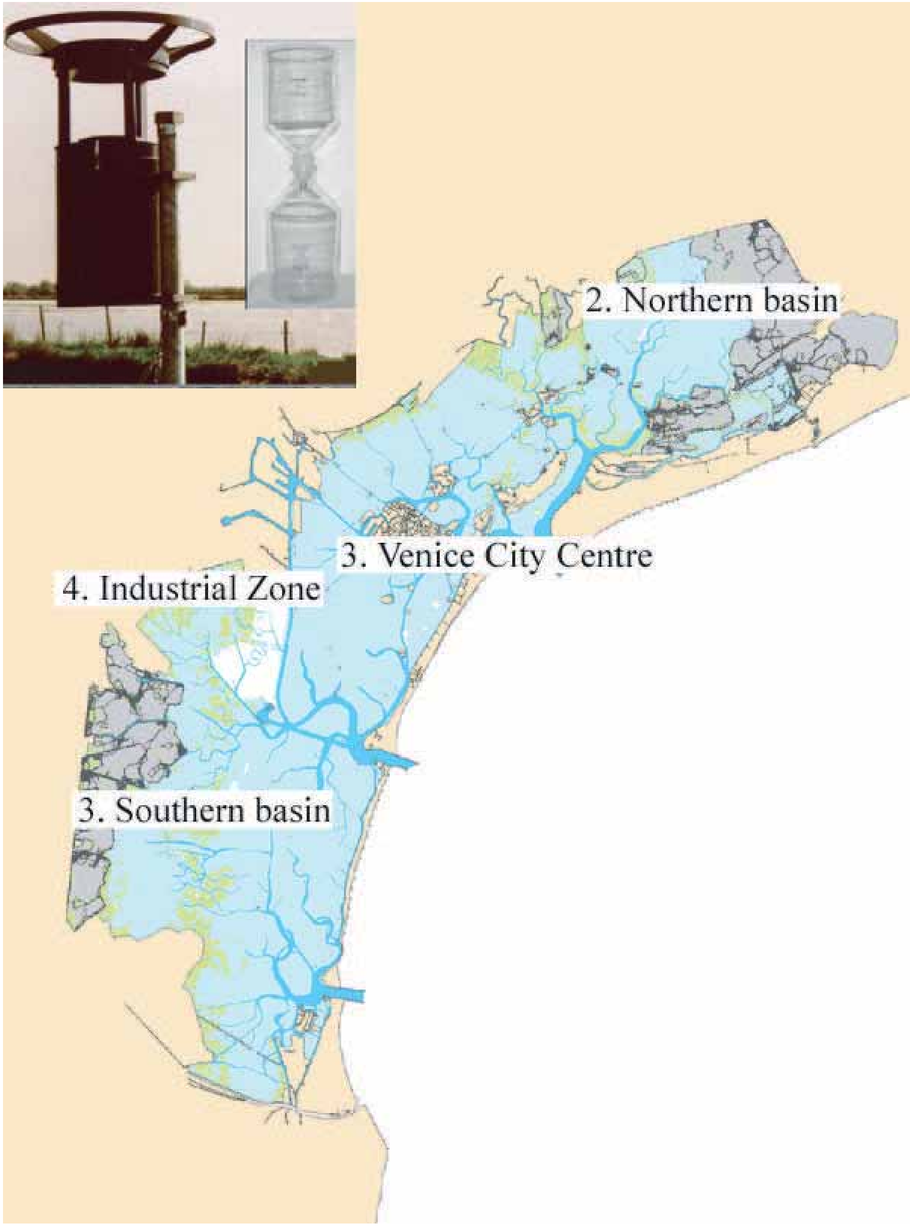

Figure 3.1: *Map of Lagoon of Venice, showing sampling points. Inset: bulk deposition sampler used for research [MAV - CVN, 2000a].*

	PCB ng $m^{-2}a^{-1}$	**PCB** pgTE $m^{-2}a^{-1}$	**HCB** ng $m^{-2}a^{-1}$	**PCDD/F** ng $m^{-2}a^{-1}$	**PCDD/F** pgTE $m^{-2}a^{-1}$
Point 1	2479	731	1547	18	747
Point 4	2737	1023	8611	47	733
Average	2608	877	5079	32	740
Point 1(*)	864	163	678	12	657
Point 2(*)	425	59	558	8	338
Point 3(*)	378	57	425	10	469
Point 4(*)	1026	223	4397	29	528
Average	673	126	1515	15	498

Table 3.1: *Fluxes of organic micro-pollutants at four points. * = 9 months.*

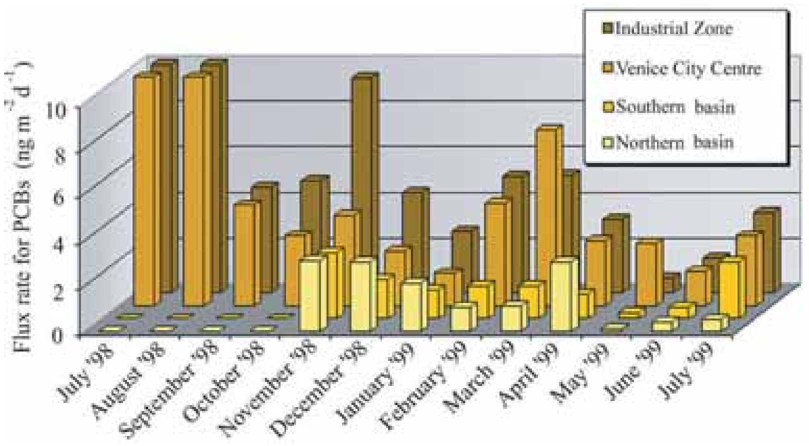

Figure 3.2: *Monthly fluxes of PCBs (ng m^{-2} d^{-1}).*

1998 and February 1999 (Figure 3.3) and October 1998 and January-February 1999 (Figure 3.4) respectively.

Results clearly demonstrate that the sampling point near the industrial zone had higher POP deposition. In particular, they highlight the existence of an important source of PCDD/Fs and HCB linked to industrial processes - not to mention PCBs close to the city centre. The great variability between one month and another shows that, in addition to constant discharges, there were probably also "leakages" and/or discontinuous emissions.

3.2.1 *Sources*

For a thorough study of the origin of dioxin emissions, the "fingerprint" method described in Chapter 2 was applied. Briefly, this entails identifying samples

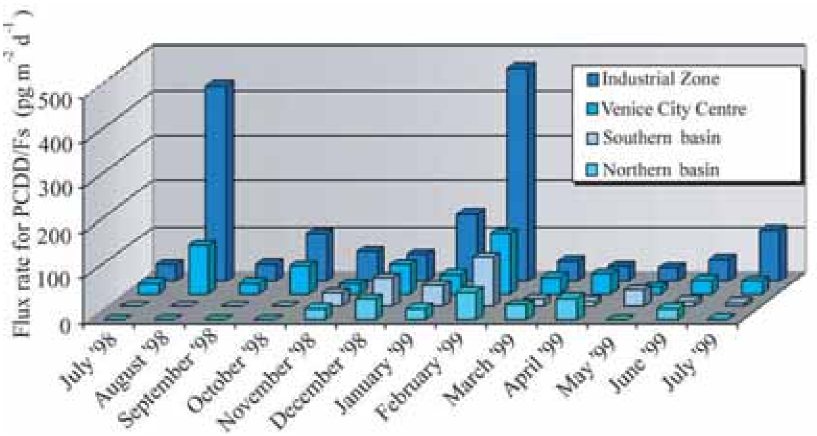

Figure 3.3: *Monthly fluxes of PCDD/Fs (pg m^{-2} d^{-1}).*

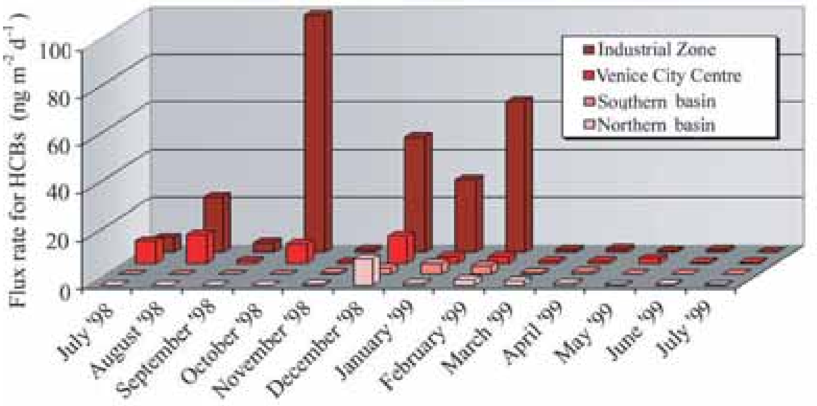

Figure 3.4: *Monthly fluxes of HCB (ng m^{-2} d^{-1}).*

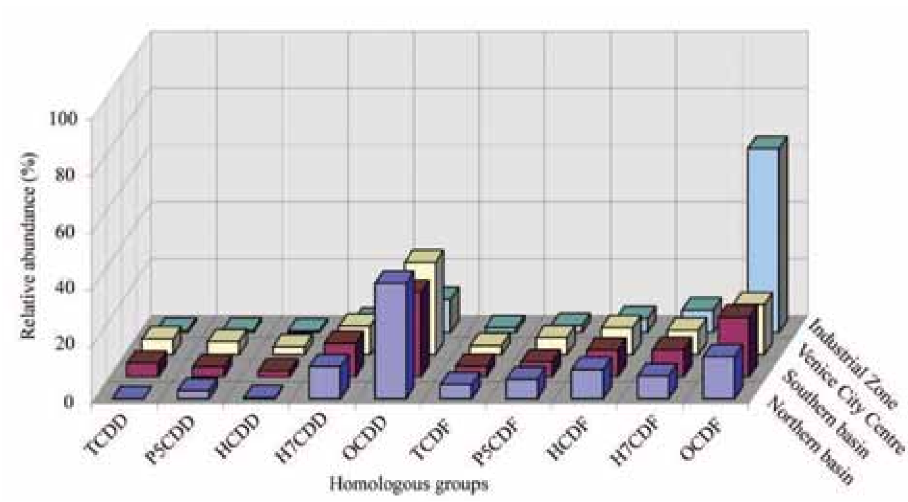

Figure 3.5: *Average fingerprints of dioxin at four points from November 1998 to July 1999. Note great differences between fingerprints for the industrial zone (high levels of OCDFs) and three other points, which are similar to each other (high levels of OCDDs).*

of atmospheric depositions by homologous groups of dioxins and furans, the characteristics of which are associated with well-defined industrial and/or combustion processes.

As regards the Lagoon of Venice, Figure 3.5 shows the average annual fingerprints for the four points examined. The unusual nature of point 4, close to the industrial zone, stands out immediately, as it is characterised by a source of atmospheric emissions of dioxins and furans with high levels of OCDFs, probably due to production of vinyl chloride monomer. The annual average fingerprints for these pollutants regarding atmospheric deposition at the other three points is quite different, with high levels of OCDDs, typical of non-industrial combustion (incinerators, traffic, heating, etc.). In several cases, the industrial source occasionally also influenced the other points (as happened during the June-July 1998 leakage) which, however, preserved very different average fingerprints.

These comparisons were also made possible thanks to analyses and data produced by Enichem concerning industrial emissions (from chimneys and incinerators; see Figure 3.6), routinely checked while the plant was producing DCE and VCM.

To study this aspect further, even more sophisticated data processing (multivariate analyses, PCA) was applied (see Chapter 4). In short, these methods apply analytical mathematical procedures to compare the fingerprints of atmospheric samples with “markers” which are typical of the different possible sources of polluting substances. Mathematical comparisons can

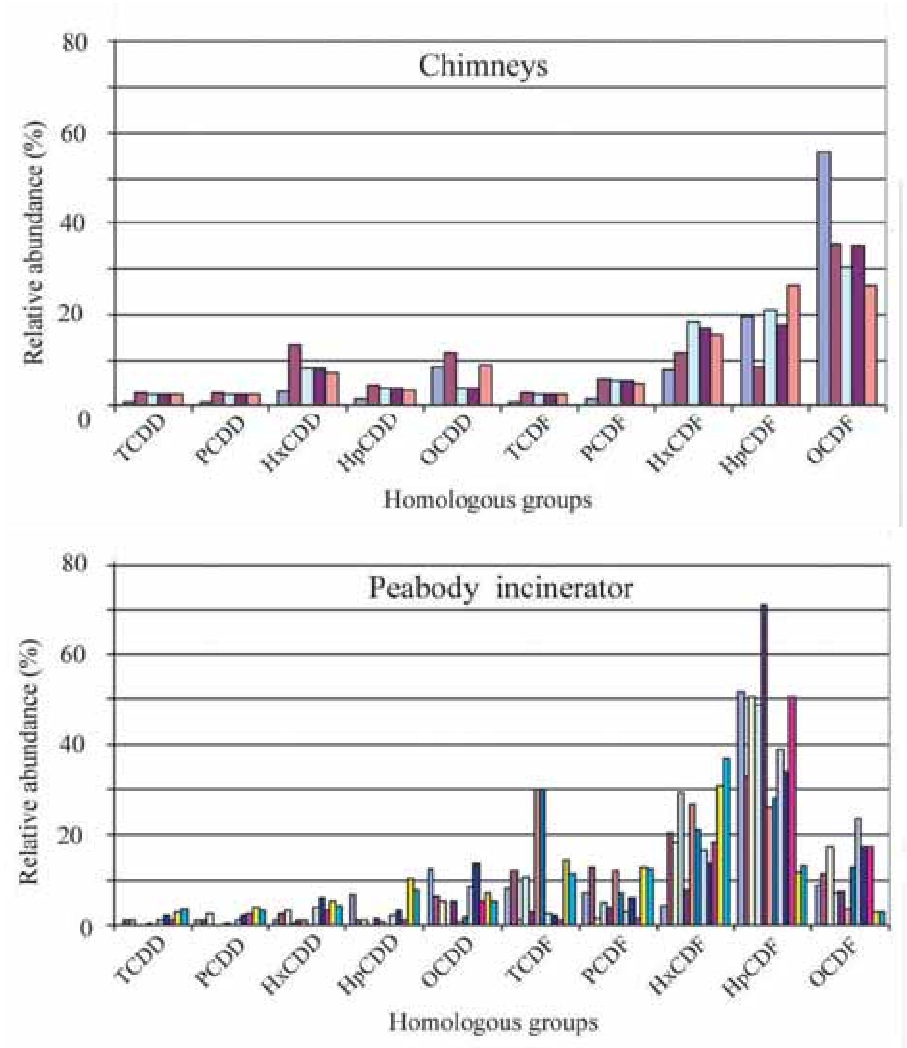

Figure 3.6: *Examples of emission markers in industrial atmosphere at Porto Marghera (European Vinyl Corporation EVC chimneys and Peabody incinerator).*

establish the degree of "similarity" between environmental samples and sources. Figure 3.7 shows the result of one of these procedures: the areas circled in red and blue contain samples closest to the markers of industrial activity shown in Figure 3.6.

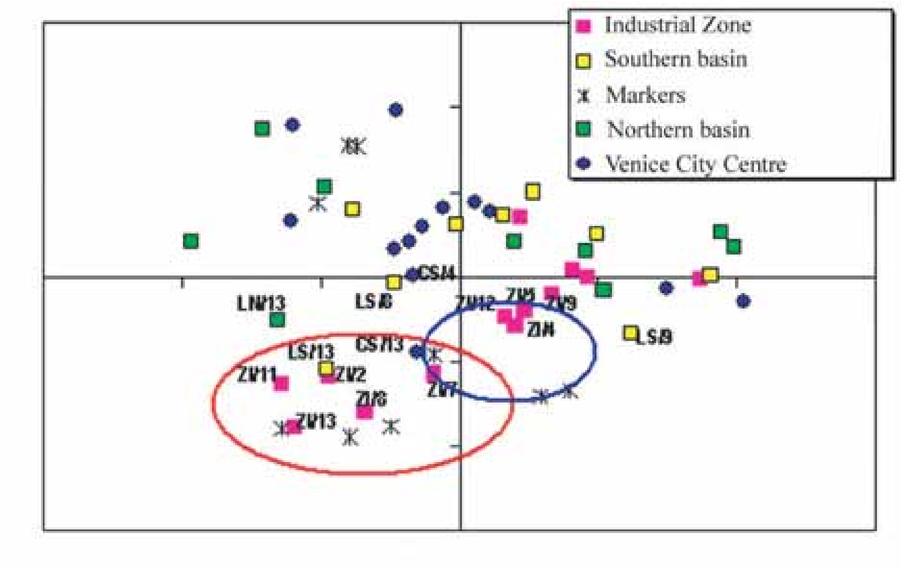

Figure 3.7: *Multivariate processing (PCA). Filled symbols: monthly depositions at four sampling points. Red and blue areas: samples which are most similar to markers of industrial processing of dichloroethylene (DCE) and vinyl chloride monomer (VCM).*

3.3 Conclusions and ideas for the future

1. Measurements of atmospheric deposition of POPs using the bulk deposition samplers gave good results, and fluxes measured at the four sampling points around the Lagoon are relatively different.
2. PCA is a useful tool for identifying sources, especially when production "markers" exist, as is the case for dioxins and furans.
3. The fingerprint identifying procedures of the chlorine cycle, with OCDF>OCDD, was found at point 4, closest to the petrochemical plant.
4. The average fingerprints of depositions at the more distant lagoon points (> 10 km) are characterized by OCDD>OCDF, similar to those of the sludge from the Fusina treatment plant, and typically found in urban aerosols.

5. During June and July 1999, an increase in OCDFs was measured at all sampling points, presumably due to the leakage of 3000 kg of VCM chlorine which took place on June 8 1999.

6. Between 9% and 27% of the average monthly samples exceed the guideline values for atmospheric depositions for protecting health and the ecosystem, recently proposed by the Environmental Agency of Belgium (Figure 3.8).

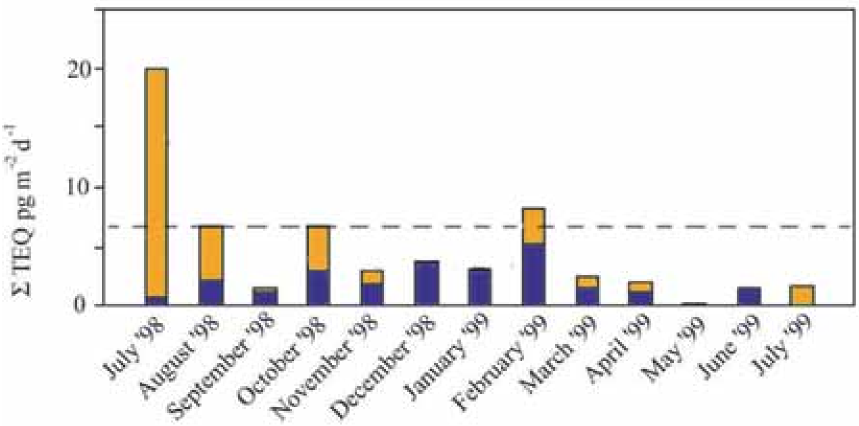

Figure 3.8: *Average fluxes of dioxin and PCBs. Each histogram represents sum of fluxes of PCDD/Fs (blue) and PCBs (ochre), expressed as toxicity equivalent. Dashed line (7 pg* m^2 d^{-1}*): threshold value recommended by Environmental Agency of Belgium to protect public health [De Fré et al., 2000].*

In the light of the above results, ideas for improving the quality of the air over the Lagoon of Venice are listed below:

- identifying and monitoring “sensitive areas”;
- reducing inputs of dioxin into the Lagoon to as low a level as possible (see point 6 of Ministerial Decree of April 1998);
- improving and increasing analyses of emissions - work to be carried out by the competent authorities.

Further short-term intervention - in conjunction with issue of permits - would be to impose supplementary controls (continuous sampling, biomonitoring, deposition sampling, etc.), especially in the case of incinerators for solid urban waste, industrial incinerators, power plants, and the use of fuels derived from waste.

Chapter 4

POPs from sediments to the food chain: the need for monitoring

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Micro-pollutants Laboratory, INCA Consortium, Marghera

Together with soil and living organisms, sediments from seas, lakes and rivers are the environmental compartments most affected by the input and consequent accumulation of PCDDs, PCDFs and other POPs. Contamination is caused by the direct introduction into the environment of industrial and urban wastewater, run-off from contaminated soils, atmospheric deposition and dumping of waste, both treated and untreated. The sediments on the bottom of the Lagoon of Venice play a fundamental role in determining the overall quality and equilibrium of the ecosystem and have consequently been the subject of many studies in the past [e.g., *Orio* and *Donazzolo*, 1987; *MAV - CVN*, 1999]. These sediments preserve the "memory" of the processes of introduction, dispersal and deposition of pollutants, whether of man-made or natural origin, and with them the main physical phenomena in the Lagoon.

In past years, monitoring POPs in the Lagoon of Venice has almost exclusively concerned sediments, due to the fact that the high concentrations detected could be analysed by relatively simple analytical methods. Several studies used radiometric techniques to define the chronology of sediment contamination. Human activities, canal dredging, the transit of ships and smaller craft which disturbed even deep sediments, and the fishing and harvesting of molluscs carried out with special turbo-blowers have left very few zones undisturbed. Thus, it is difficult if not impossible to carry out a

ZONE	**PCDD/Fs** (ng TE/kg)	**PCBs** (ng TE/kg)
Industrial zone	∼300	∼50
Shallows	2—6	0.3—1
Lagoon channels	∼3	∼0.5

Table 4.1: *Average values of toxicity equivalent of dioxin and "dioxin-like" PCBs in sediments of Lagoon of Venice [MAV - CVN, 2000b].*

chronological study of lagoon sediments in areas characterised by large-scale human activity. The decision was therefore made to monitor POPs in surface sediments, in order to define their distribution in space, and to measure contamination levels in the habitat of living organisms, which is the compartment responsible for transferring POPs to man.

The first complete study on the presence of PCDD/Fs in surface sediments (first 15 cm) in the Lagoon of Venice was carried out in 1997 and 1998 by the *Consorzio Venezia Nuova* on behalf of the Water Authority. As Figure 4.1 shows, the highest concentrations (∼500 ng I-TE/kg) were detected in the industrial zone. In other studies carried out in the same area, a concentration of 2857 ng I-TE/kg was found [e.g., *Bellucci* et al., 2000].

Table 4.1 gives the results in terms of mean values for sediments in the Lagoon, expressed as toxicity equivalent, dioxin and "dioxin-like" PCBs. Sediments with low contamination were found in the southern and northern parts of the Lagoon at concentrations between 1 and 2 ng I-TE/kg. The 18/12/95 circular from the Ministry for the Environment prohibited canal dredging and sediment dumping at sea in locations where concentrations of dioxins and furans expressed in equivalent toxicity (I-TE) exceeded 0.48 ng I-TE/kg, which can thus be taken as the reference level for the Lagoon.

Analysis of industrial waste and sludge at the city's treatment plants resulted in two fingerprints (see Chapter 1.4), the key to understanding PCDD/F contamination in Lagoon of Venice. The first fingerprint is that of the chlorine production cycle, the second that of human sewage. The most obvious difference between the two is the ratio between octachlorodibenzofuran (an OCDF cogener, relatively abundant in the production of VCM and the chlorine cycle) and octachlorodibenzodioxin (an OCDD cogener, relatively more abundant in sewage and some types of combustion). The OCDF/OCDD ratio varies from 4 to 8 in the industrial zone to 0.3-0.5 in the Chioggia area, in the southern part of the Lagoon.

Comparisons of average fingerprints indicate that the sediments from the industrial zone are contaminated by industrial waste resulting from chlorine production, whereas those in the canals of the city centre of Venice are mostly contaminated by human faeces (Figure 4.2).

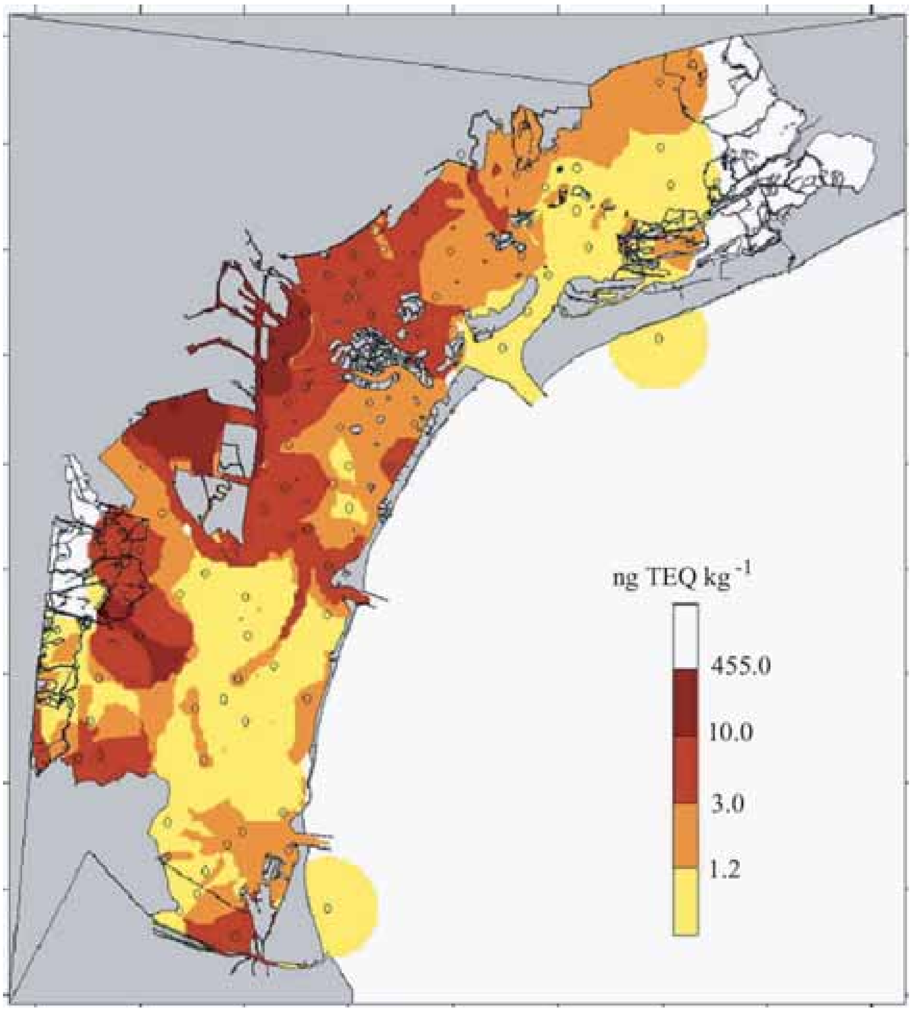

Figure 4.1: *Concentrations of PCDD/Fs in sediments [MAV - CVN , 1999].*

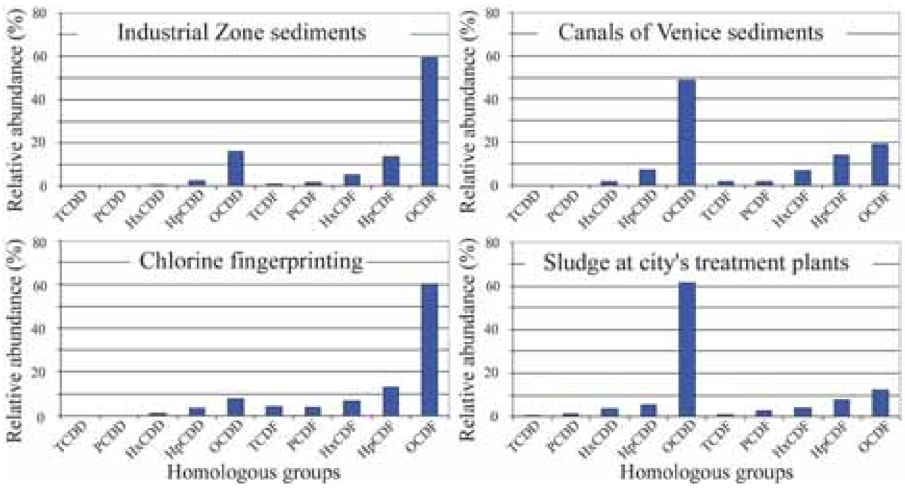

Figure 4.2: *Comparisons of fingerprints.*

4.1 Principal Components Analysis (PCA)

Fingerprints have the advantage of reducing the amount of information needed for inferring the main source of contamination. Up to 210 cogeners can be detected in one sediment sample, 17 of which are toxic, although only 10 are taken into account in the fingerprint. However, the number of variables needed to describe the overall contamination of a given sample may be further reduced by applying appropriate statistical methods.

Principal Components Analysis is a reliable method of achieving this goal [*Kurzl*, 1988], since it can identify sets of new variables, the "principal components, which are linear combinations of the original ones. Each component is associated with a given fraction of data variance, so that components associated with a very small fraction of the variance can be eliminated. This method was applied to a data set which included the fingerprints of the PCDD/Fs in the surface sediments of the Lagoon, industrial channels, and the canals of Venice. For purposes of comparison, the data set included fingerprints of the city's wastewater treatment plants and industrial waste from inspection pits inside the petrochemical plant, and several fingerprints taken from the literature on the production of VCM and the chlorine cycle.

The data were organised into a matrix (with variables in columns, representing the 10 relatively abundant items, and samples on rows). Principal Components Analysis reduced the number of variables necessary for describing data variability and visualising objects in a space with two and three dimensions instead of 10. This meant that the majority of the variance of the original data could be explained by two or three new variables, a linear combination of the original variables. The fraction of variance explained by the first three components always exceeded 90%.

The results of PCA are summarised in Figure 4.3, which shows the distribution of samples on the plane of the 1st and 3rd components. As can be seen, the ellipse on the left encircles most of the sediments sampled from the industrial channels, industrial waste and fingerprints from the literature for VCMs; the ellipse on the right encompasses the fingerprints of the treatment plants. The central ellipse, closer to the right-hand one, contains most of the samples from the central part of the Lagoon - largely affected by industrial contamination, in addition to human sewage. Sample PA100 at the edge of the right-hand ellipse is an isolated case: as it was taken very close to the city of Chioggia, it was affected almost exclusively by urban waste water.

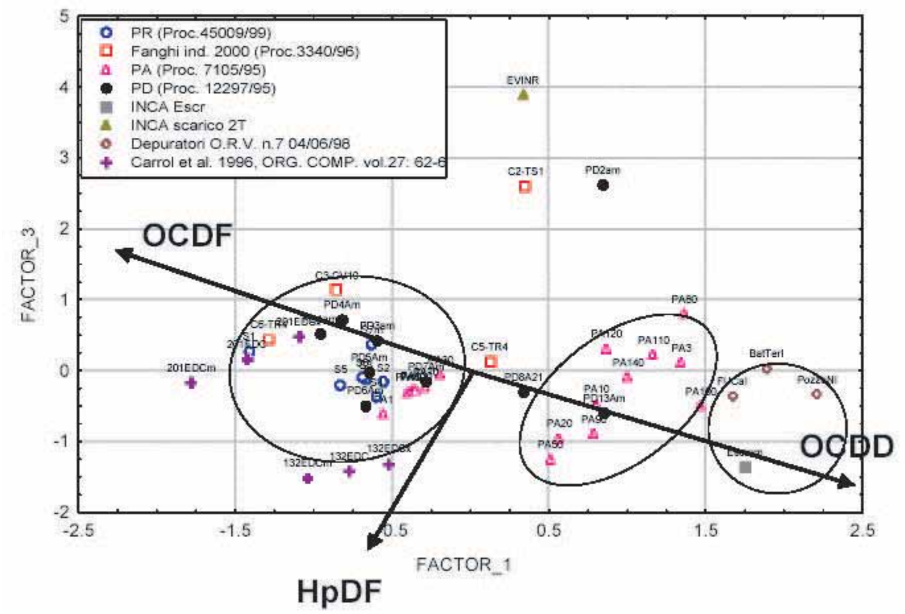

Figure 4.3: *Principal Components Analysis (PCA) of surface sediments*

Statistical analyses also confirmed the petrochemical plant and relative chlorine production as the main source of dioxin contamination in the Lagoon of Venice. PCA analysis also identified the substantial contribution of human sewage, not only as direct discharges but also through treatment plants.

4.2 Sediments and clams

Moving on to concentrations of dioxins and other POPs in the sediments sampled in the areas where the clam *Tapes philippinarum* is farmed and harvested, the following four sites were examined:

1. industrial zone, where all types of fishing and harvesting are forbidden but where unauthorised activities do take place;
2. area north of Venice, where authorised clam farms are located;
3. zone to the north of Chioggia where authorised clam rearing areas are located;
4. the S. Erasmo shallows, where many Venetians are accustomed to gathering clams.

Analysing data concerning concentrations in surface sediments where clams breed, the total of dioxins and polychlorobiphenyls (PCDD/F+PCB), expressed as toxicity equivalent (ng WHO/kg), falls from an average of 46.6 in the industrial zone to 0.2 at S. Erasmo. Values found north of Chioggia are comparable to those of S. Erasmo; those north of Venice (Burano) are even higher than the recommended limits for farming areas.

Two other markers - hexachlorobenzene (a by-product of the chlorine cycle) and the OCDF/OCDD ratio - confirm the fact that, the greater the distance from the industrial zone, the more drastically the mean HCB values drop. Values in the industrial zone (260 ng/kg) were 18 times higher than those at S. Erasmo (1.4 ng/kg) and 4000 times higher than those in Chioggia. Similarly, the OCDF/OCDD ratio fell from an average of 8 in the industrial zone to 0.5 at Chioggia (see Table 4.2).

So far, analysis of POP data shows that the areas north of Chioggia and south of the Malamocco-Marghera channel are almost free from the influence of discharges from the industrial zone.

ZONE	**PCDD/F+PCB** ng WHO-TE/kg	**OCDF/OCDD**	**HCB** μg/kg
Industrial channels	46.6	8	260
Burano	5.9	2.2	0.15
S. Erasmo	0.2	1.5	1.4
Chioggia	0.5	0.5	0.1

Table 4.2: *Average concentrations of POPs in lagoon sediments.*

Taking clams as an example of molluscs which live in sediments, it is clear that contamination by POPs measured in their habitat is transferred to the clams themselves. Table 4.3 shows the average PCDD/F+PCB concentrations, in pg TE-WHO/g of edible part, measured in clams from the four sites. As was the case for sediments, maximum concentrations were found in clams gathered

ZONE	**PCDD/F + PCB** pg WHO-TE/g	**OCDF/OCDD**	**HCB** μg/kg
Industrial channels	1.65	4.7	6.9
Burano	0.45	1.2	< 0.1
S. Erasmo	0.09	0.7	< 0.1
Chioggia	0.11	0.4	< 0.1

Table 4.3: *Average concentrations of POPs in clams.*

(illegally) in the industrial zone, and the minima came from S. Erasmo, with similar levels for Chioggia.

Concentrations of dioxin and "dioxin-like" PCBs in clams from the northern lagoon can be correlated with those found in sediments. Inserting all data on concentrations of PCDD/Fs found in sediments in a logarithmic diagram, together with those for clams gathered at the same point, good levels of correlation are found - further proof that contamination of clams is related to contamination in sediments (Figure 4.4).

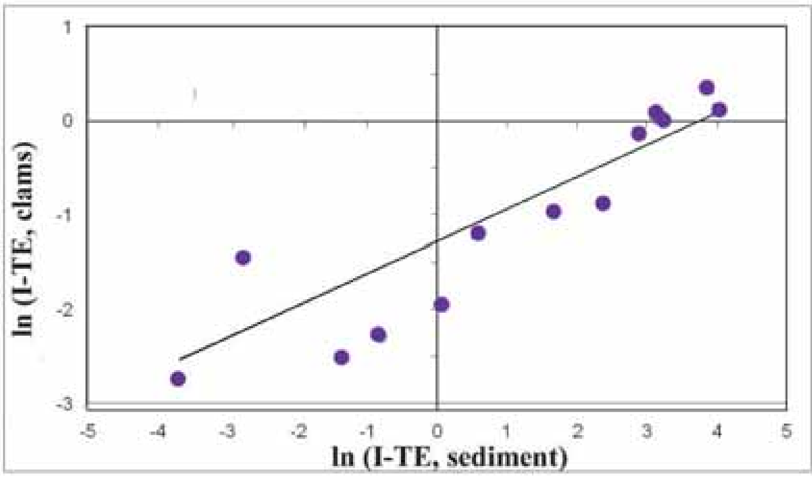

Figure 4.4: *Correlations between concentrations of PCDD/Fs in sediments and clams collected in several areas of the northern lagoon.*

Fingerprints from sediments and clams (despite slight differences due to metabolism) from the four areas confirm correlations between the fingerprint of PCDD/Fs found in sediments and the clams themselves (Figure 4.5).

Proof of the relation between sediment contamination and clam contamination is also provided by the average concentration of HCB in clams (6.9 μg/kg in the industrial zone and practically nil in other areas) and by the OCDF/OCDD ratio, with an average of 4.7 in the industrial zone and values between 0.4 and 1.2 in the other areas.

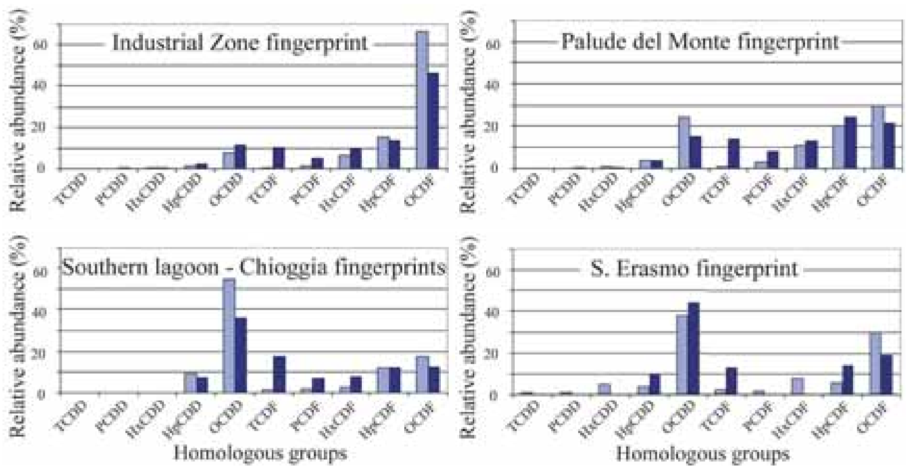

Figure 4.5: *Comparisons between fingerprints in sediments (pale blue) and clams (dark blue).*

4.3 Conclusions

Considering the above data and in the light of possible future recovery of contaminated areas, there is clearly an urgent need for POP monitoring, in order to:

- estimate POP loads from direct discharges into the Lagoon, the drainage basin and emissions;
- quantify discharges during clean-up operations;
- study the transfer of POPs from sediments to water and living organisms;
- protect foods through controls on farming and stop illegal fishing and harvesting.

Chapter 5

Can POPs lower the capacity for reproduction in the lagoon organisms?

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CNR - ISMAR, Venice

The decline in aquatic fauna witnessed in the Lagoon of Venice during the second half of the twentieth century may be attributed to a general loss of environmental quality, due to both the destruction of the habitat and to varying types of pollution. On one hand, the decline is obvious even to amateur fishermen; on the other, with very few exceptions [*Vatova*, 1940; *Giordani Soika & Perin*, 1974; *Venice Water Authority-CVN*, study in progress], systematic counts of aquatic fauna are all but lacking, and data on fishing demand careful attention, since they only deal with limited species of commercial interest.

It must be emphasised that environmental stress acts on the metabolism of ecosystems on different space and time scales. Scenarios change according to the extent and duration of disturbance and the ecosystem's state of biological integrity. For instance, widespread anoxia resulting from proliferation of macro-algae - episodes of which occurred in the 1980s and early 1990s - causes sudden death on a large scale for the majority of marine organisms. And mutagenic agents cause genetic damage, the effects of which (in terms of populations or ecosystems) only become perceptible after a certain period of time. However, masking large-scale events (e.g., anoxia) due to acute effects on the biotic community must not mean that events with chronic effects should be ignored.

This chapter reflects on the possible consequences to the reproductive capacity of aquatic fauna in the Lagoon of Venice due to exposure to persistent organic pollutants (POPs). The hypothesis is that the POPs present in the environment spread to individuals, both directly through water and by way of the food chain, accumulating in fatty tissues. They then concentrate in the gonads, causing fertility problems in adults and, when transferred to gametes, jeopardising development and survival of embryos and larvae. As POPs are persistent - and difficult to metabolise in themselves - with a high affinity for fatty tissues, they are bioconcentrated, bio-accumulated and biomagnified in high percentages along the food chain [*Gray*, 2002; *Moore et al.*, 2002; *Van der Oost et al.*, 2003]. In each organ where they are accumulated, POPs can exert their harmful action. Once a POP has been taken in by an organism and has entered its biological structures, it interacts with the physiological processes of growth, maintenance and reproduction, and can have direct effects on the metabolism of individual organisms or even indirect effects on the growth or survival of their offspring. Consequently, both direct and indirect damage can be hypothesised on reproductive capacity. Indirect damage is inflicted in the body, which then affects reproductive activity; direct damage affects the reproductive line (gametes, eggs, embryos, larvae). This chain of events could cause significant limitations in the annual numbers of new organisms entering the environment, meaning that the loss of adults, due to natural mortality and/or fishing, would not be adequately compensated. The result would be the slow decline in populations. Although very few studies have been conducted to date in the Lagoon of Venice, elsewhere, especially outside Italy, the results of ongoing experiments support the above hypothesis and prove the existence of this impact. The process can be distinguished into the following phases (Figure 5.1):

1. exposure of individuals to POPs;
2. intake of POPs by individuals;
3. accumulation in tissues;
4. biological transfer of pollutants:
    (a) transfer among the same species to gametes, embryos and larvae;
    (b) transfer to species on higher trophic levels, with amplification of effects along the trophic chain.

An example of direct action on reproduction highlighted in the Lagoon of Venice [*Livingstone et al.*,1995; *Pipe et al.*,2000; *Pulsford et al.*, 2000] is the negative impact which several POPs have on the immune system of mussel (*Mytilus galloprovincialis*) and goby (*Zosterisessor ophiocephalus*), causing generalised weakening in organisms subjected to major exposure. PCBs, dioxins and furans act directly and disturb the reproductive system (as they start with endocrine functions, they are catalogued among the Endocrine Disrupters [EDs]). Even at low concentrations, these substances exert a hormone-like action, which profoundly affects the development and functioning

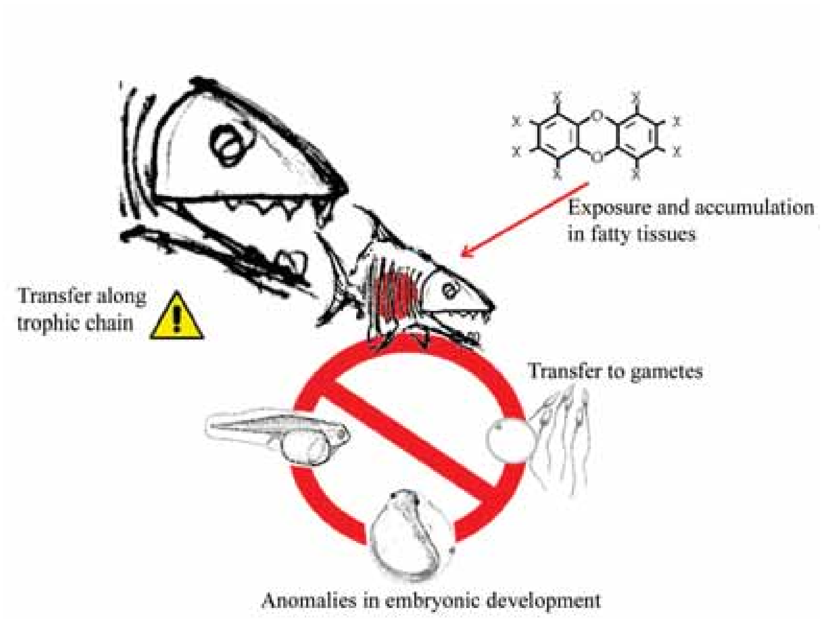

Figure 5.1: *Intra- and inter-species transfer of POPs.*

of the gonads, with results such as feminisation of males or masculisation of females [*US-EPA*, 1997]. These effects may combine with those of other widespread EDs in the environment, such as tributhyltin (TBT) [*Axiak et al.*, 2003].

Other research conducted in the Lagoon of Venice [e.g., *Nasci et al.*, 1998] highlights accumulation of organic pollutants in mussel (Figure 5.2) together with high levels of fat, precisely during the reproduction period when lipids are abundant in the bodies of animals, providing energy at this critical time. Indeed, they are one of the fundamental components of the reproductive organs, [*Pazos et al.*, 1997] and later serve as nourishment (yolk) for developing eggs and larvae [Holland, 1978]. Lipids account for a high percentage, around 15-20%, of total egg weight in invertebrates and fish. This means that organic pollutants can end up directly in oocytes and exert their toxic effect, with negative results on fecundation, hatching, proper development of embryos and the survival of larvae [*Hummel et al.*, 1990; *Monosson et al.*, 1994; *Chu et al.*, 2000].

Different species are influenced in different ways by the above mechanisms, depending on their physiology and ecology [*Gray*, 2002]. Thus, even a slight but constant reduction in reproductive success may be sufficient to cause a slow decline in populations. However, once certain critical levels are reached, imbalance in the relationships between species and between species and their habitat takes place, with amplified effects on the ecosystem. These

Figure 5.2: *Eggs (left) and larvae (right) of Mytilus galloprovincialis (photo by Chiara Fosso).*

effects are translated into an unexpected drop in several species, together, paradoxically, with a similar unexpected increase in the numbers of their competitors. The most vulnerable species are thus those characterised by a high percentage of fatty tissues, a long life-span, and a relatively small number of large eggs, possibly accompanied by care of the young, as is the case for goby (*Zosterisessor ophiocephalus*); the advantaged species probably have the opposite characteristics. The complexity and number of relationships between species may disrupt the biological system, resulting in chaotic fluctuations until a new equilibrium is reached. A complicating factor would be the possible effects of other contaminants [*Matthiessen & Law*, 2002] and environmental stress, which would combine with that of POPs.

In conclusion, we emphasise that the integrity of the environment in which events linked to reproduction take place, are of fundamental importance. Here, too, POPs have a negative influence - the effect of herbicides on marine phanerogams, true seagrasses which represent an extremely important setting where very many species reproduce (called "nurseries" by specialists) - has not yet been evaluated in the Lagoon of Venice, compared with other locations [*Scarlett et al.*, 1999; *Haynes et al.*, 2000]. In order to support the above hypothesis, the following programmes of study and monitoring need to be conducted on:

- contaminants in gonads, eggs and larvae;
- rate of hatching;
- embryonic development;
- survival of embryos;

- malformations;
- death at onset of autonomous feeding.

These studies should be linked to experimental evaluation programmes in the laboratory and mesocosms, on the survival and life-cycle of embryos, larvae, and the young of lagoon organisms exposed to individual contaminants and combinations of them. Such programmes should be planned in an integrated manner and conducted by the scientific community of Venice and Italy, with the help of bodies desirous of protecting Venice.

Chapter 6

Dumps of toxic industrial waste in the drainage area of the Lagoon of Venice

Alberto Spoladori
Commanding Officer, Forestry Commission, Mestre (Venice)

6.1 Introduction

Since 1993, when the State Forestry Commission Office was set up in Mestre (Venice), studies have constantly been conducted both by the Commission itself and on behalf of the competent authorities, on waste cycles and related illegal activities. We found ourselves working in the complex geo-morphological and biological environment of the Lagoon of Venice. Inhabited continuously by man for hundreds of years, its fragile equilibrium has recently been severely jeopardized by the large-scale industrialisation launched in the 1950s - which, among other things, transformed Porto Marghera, in the very heart of the Lagoon, into one of the largest high-risk petrochemical centres in Europe.

Right from the start, attempts were made to identify situations of high-level environmental emergency (waste products and pollution), with the aim not only of investigating and halting illegal activities, but also of creating a map of the state of the habitat. In the Province of Venice alone, 200 unauthorised waste depots have already been registered; 60 of these contained industrial waste posing a grave risk for the environment and public health. Figure 6.1 shows the largest dumps in the Porto Marghera industrial zone.

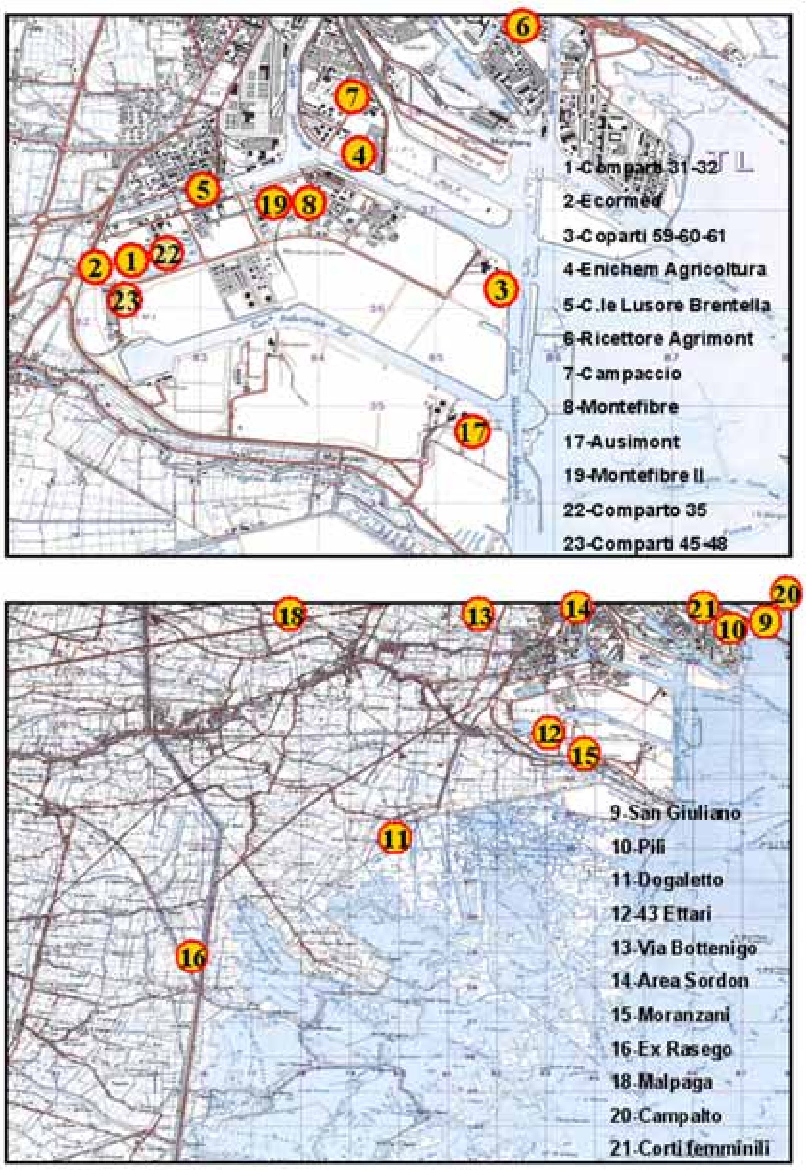

Figure 6.1: *Largest dump sites in Porto Marghera industrial zone and drainage area of Lagoon of Venice.*

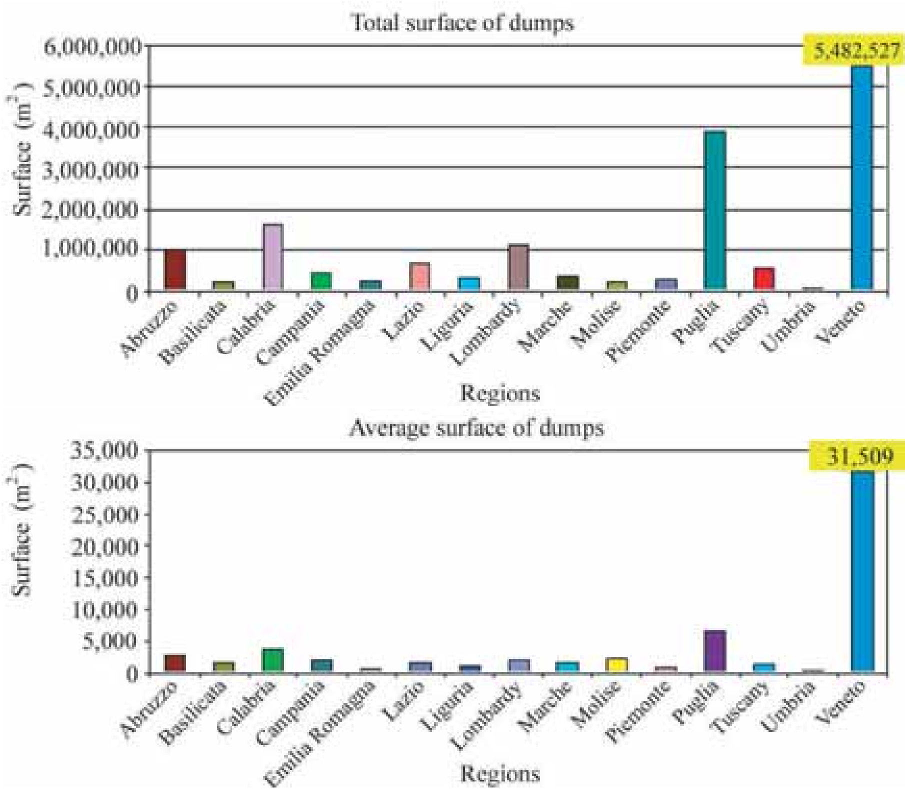

Figure 6.2: *Third national census conducted by State Forestry Commission in 2002. Total surface area (top) and average (bottom) of dumps per region.*

6.2 Registering dump sites

The third census of unauthorised dump sites conducted on a nation-wide level by the State Forestry Commission (www.corpoforestale.it), listed all depots registered - 4866 sites, for a total of almost 20 million square metres. It also demonstrated that, from the viewpoints of both extent and ratio between total surface and number of dumps, the Veneto, together with Puglia (almost 4 million square metres), far exceeds other regions, where figures are rarely higher than one million square metres of total surface area for dumps (Figure 6.2).

However, while in the case of Puglia, the large total surface area of the region may be considered in proportion to the high number of dump sites, in the Veneto the extent of the dumps registered in the Venice-Porto Marghera area is quite remarkable. Average dump size in virtually all Italian regions is several thousand square metres, but in the Veneto dumps are very much larger, around 30,000 square metres.

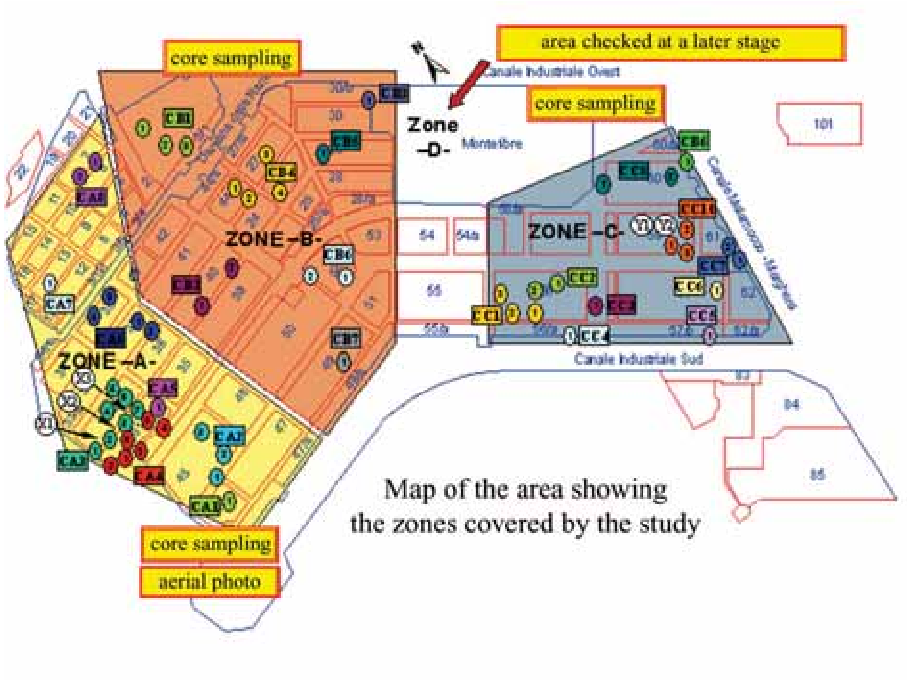

Figure 6.3: *Porto Marghera petrochemical plant: areas subjected to surveys and geognostic measurements.*

The Venice-Porto Marghera zone has been "colonised" by significant numbers of unauthorised, large-scale dumps, containing mainly dangerous toxic waste from industries in the area, particularly chemical plants. In recent years, large-scale legal proceedings have been undertaken, during which the Forestry Commission of Mestre collected detailed new data from inside factories in the industrial zone - thanks to police checks, which represented an essential part of the census.

The geognostic survey conducted by State Forestry personnel from Mestre on behalf of the Italian State Attorney in Venice, provided evidence of serious irreversible pollution of the soil, subsoil and water-table, caused by the presence of depots of industrial waste (Figures 6.3, 6.4). In particular, inside the Porto Marghera industrial zone, from depths of 1 metre to 6-7 metres below ground level, industrial waste was frequently found, covered by landfill and organic matter. This industrial waste was usually blackish in colour, resembled plastic, and had low density, which tended to increase with depth. A strong odour was released when the waste was unearthed. Analysis of soil layers for surveys and compilation of hydro-geological sections revealed that this material rests on the bottom of the basin and levels out to a constant thickness upwards, confirming the presence of an original drainage basin and the liquid or semi-liquid state of

Figure 6.4: *A dump being prepared inside Porto Marghera petrochemical plant .*

the waste deposited, or its discharge directly into the water from the edge of the Lagoon.

Results of analyses on soil and waste samples revealed general soil contamination in the area, due to elements like lead, zinc, cadmium, arsenic and mercury. Mineral oils and phenols were also widespread, and aromatic amines, chlorinated solvents, aromatic hydrocarbons and ammonia were detected (Table 6.1).

The pollution caused by these depots in the water-table, both superficial and deep, is no less serious. Ammonia is widespread even at depths exceeding 15 metres. Chlorinated solvents are found in water deeper than 20 metres, as are high concentrations of aromatic amines, and the water contains aromatic solvents and arsenic. These data are listed in Table 6.2.

Similar situations were found in several of the dumps around the lagoon drainage basin; many had a level of radioactivity 10 times higher than natural background values. Massive pollution was also found in the channels near the industrial zone, which for many years had received waste from factories. One example is the Lusore-Brentella channel (Figure 6.5): at present, its bed contains 15,000 m^3 of sediments, composed of silt and sand with concentrations of mercury up to 150 mg/kg and of chlorinated hydrocarbons up to 10,000 mg/kg.

PHOSPHO-GYPSUMS		
Fertimon Agrimont — production of phosphoric acid (fertiliser)		
CHLORINATED SOLVENTS		
Plants for VCM - TR - TS - DL2 (carbon tetrachloride) as products and production residues (chlorinated pitch)		
AROMATIC AMINES		
Production of TDI (toluene diisocyanate). Process of nitration of toluene to obtain dinitrotoluene. Successively reduction produces toluendiamine. A reaction with carbon monoxide produces TDI.		
PCB		
Electrical fluid in transformers (plants and transformer bleeding)		
PCDD		
VCM, but also from other production of aliphatic chlorine (TR - TS - DL2) and aromatic chlorines (benzyl chloride and benzal chloride) BC1		
HEAVY METALS		
Lead	Pb	Stabilisation in PVC.
Mercury	Hg	Chloro-alkali plant. Mercuric chloride used as catalyser in production of ethylene chloride, VCM and acetates.
Iron	Fe	Ferric chloride — catalyser in trieline and perchloroethylene plants.
Copper	Cu	Catalyser copper chloride used in TD2 (production of carbon monoxide).
Arsenic	As	Present in pyrite ash, production of phosphoric acid and Enichem Agricoltura (Fertimon, Agrimont) sodium arsenite solutions (called “Gianmarco solution” for purifying ammonia).

Table 6.1: *Characteristics and origin of waste unearthed in dumps.*

6.2.1 *Waste treatment*

A preliminary reconstruction of how this massive pollution had occurred was based on interviews with more than 200 people, and was very revealing. Voluminous documentation was confiscated, and furnished a picture of serious environmental degradation, later unequivocally confirmed by geognostic surveys, samples of sediments and organisms. Over 135 criminal acts were reported. The overall picture clearly showed that, since the 1970s, the chemical industry had solved its problems of waste disposal in an expeditious manner, discharging it through sewers, dispatching it in tankers to “unknown” destinations, packing it in drums which were buried inside the factories, or burning it in rudimentary incinerators, with no control of emissions. Liquid waste, tar, end-products of distillation, contaminated solids and residue from chemical processes containing all kinds of toxic substances were dispersed throughout the environment (air, water, soil) around the petrochemical plant. After the 1970s, industrial waste from Porto Marghera was also dumped

	a/b/c						
CHLORINATED	0.02/	PZ37	$\mathbf{4033}_{a,b,c}$	PZTDI	$\mathbf{10}_{a,b,c}$	PZ63	$\mathbf{0.12}_{a,c}$
SOLVENTS	1.00/	PZ56	$\mathbf{289}_{a,b,c}$	PZ15	$\mathbf{9}_{a,b,c}$	PZ64	$\mathbf{0.07}_{a,c}$
	0.03	PZ16	$\mathbf{46}_{a,b,c}$	PZ50	$\mathbf{0.2}_{a,c}$	PZ73	$\mathbf{0.07}_{a,c}$
		PZ55	$\mathbf{20}_{a,b,c}$	PZ43	$\mathbf{9}_{a,b,c}$	PA2	$\mathbf{1.29}_{a,b,c}$
		PZ66	$\mathbf{554}_{a,b,c}$	PZ27	$\mathbf{0.4}_{a,c}$	P18	$\mathbf{1.15}_{a,b,c}$
		PZS1	$\mathbf{76}_{a,b,c}$	PZ67	$\mathbf{3}_{a,b,c}$	P15	$\mathbf{4.4}_{a,b,c}$
AROMATIC	0.01/	P4(TA)	$\mathbf{0.1}_{a,c}$				
SOLVENTS	0.02/	P1	$\mathbf{0.07}_{c}$				
	0.05						
AROMATIC	0.01/	P1	$\mathbf{2}_{a}$	PA3	$\mathbf{0.13}_{a}$		
AMINES	N.L./	P15	$\mathbf{3.4}_{a}$				
	N.L.	P18	$\mathbf{15.9}_{a}$				
COD	80/	PZ53	$\mathbf{171}_{a,b,c}$	P1	$\mathbf{965}_{a,b,c}$	P13	$\mathbf{250}_{a,b,c}$
	160/	PZ45	$\mathbf{183}_{a,b,c}$	PA2	$\mathbf{428}_{a,b,c}$	P15	$\mathbf{210}_{a,b,c}$
	5	PZ1	$\mathbf{736}_{a,b,c}$	PA5	$\mathbf{138}_{a,c}$	P18	$\mathbf{418}_{a,b,c}$
AMMONIA	2/	PZ75	$\mathbf{1972}_{a,b,c}$	PZ46	$\mathbf{40}_{a,b,c}$	P13	$\mathbf{132.7}_{a,b,c}$
	10/	PM2	$\mathbf{312}_{a,b,c}$	PZ64	$\mathbf{28.9}_{a,b,c}$	P18	$\mathbf{300}_{a,b,c}$
	0.05	PZ39	$\mathbf{41}_{a,b,c}$	P1	$\mathbf{774}_{a,b,c}$	PA2	$\mathbf{116}_{a,b,c}$
						PA5	$\mathbf{127}_{a,b,c}$
ARSENIC	0.02/	PZ71	$\mathbf{0.45}_{a,c}$				
	0.05/	PZ73	$\mathbf{0.38}_{a,c}$				
	0.05						
MERCURY	0.005/	PZ30	$\mathbf{0.014}_{a,b,c}$				
	0.005/						
	0.001						
LEAD	0.01/	P4(TA)	$\mathbf{0.1}_{a,c}$				
	0.02/	P1	$\mathbf{0.07}_{c}$				
	0.05						
ZINC	0.05/	PZ25	$\mathbf{4.8}_{a,b,c}$				
	0.05/	PZ63	$\mathbf{0.6}_{a,b}$				
	3						

Table 6.2: *Piezometers in which legal concentrations were exceeded: PZx: piezometer; numbers in bold type: concentrations in mg/l with (below) legal limits exceeded by each piezometer as per: a) D.P.R. 962/73, b) L. 319/76, c) D.P.R. 236/88; second column: legal limits for each substance. N.L. = no limit.*

inland, spread in the immediate vicinity, deposited in disused quarries in the surroundings of Venice, discharged into the Adriatic Sea, and even transported to several European and Third World countries.

In practice, the Lagoon of Venice, the Adriatic Sea and the Venetian mainland all served as dumping sites. Eighty million tons of sludge were dumped in the sea a short distance off the Lido. Industrial residues were sometimes used for reclamation work on beaches. Many structures of the present industrial zone were erected on a substrate composed of waste material, which ended up in the lagoon water due to erosion. Five million m^3 of toxic substances were used to fill internal areas in the industrial plants. The data of Table 6.3 concerning polluting toxic residues produced and introduced into the lagoon ecosystem further highlight the situation.

Figure 6.5: *Lusore-Brentella channel within Porto Marghera petrochemical plant.*

Thus, there is a very serious state of environmental pollution and potential danger for the Lagoon's food cycle and for man. Legislative intervention has been necessary, and the relative areas are now considered at high environmental risk - hence, state funding will be forthcoming to cover clean-up operations.

At this point, it is interesting to reflect on clean-up operations. Experience gained in the investigative field by the State Forestry Commission of Mestre has demonstrated that such operations are often cover-ups for illegal criminal activity and speculation. Recent surveys have revealed that approximately 500 tons of toxic waste, removed from "cleaned-up" areas, were sent illegally to cement factories for re-use or used to construct roads, by means of systematic falsification of documentation and false declarations of completed waste treatment. In addition, there were even cases of fraud against the state - for instance, invoices for waste treatment which had never taken place. This sector has considerable appeal to criminal organisations, mainly because of the meagre penalties inflicted by the law and the ease with which considerable profits can be made. A large proportion of the waste treatment business and the construction of plant infrastructures is therefore controlled by such organisations.

SOLID WASTE PRODUCED ANNUALLY AND DISCHARGED INTO LAGOON AREA IN MID-1970s	
PRODUCT	**TONS / YEAR**
Distillation residue and pitch from TD1 and other plants	9000
Chlorinated residue	11,000
Pyrite ash	7000
Gypsum from hydrofluoric acid	400,000
SOME POLLUTANTS PRESENT IN INDUSTRIAL WASTEWATER DISCHARGED INTO LAGOON IN LATE 1970s	
PRODUCT	**TONS / YEAR**
Ammoniacal nitrogen	4300
Nitrous nitrogen	87
Phosphates	540
Suspended solids	10,080
Cyanides	0.2
Chrome	0.7
Mercury	2
Zinc	8
Chlorinated solvents	1000
Mineral oils	920
Chlorine	176
Copper	20
SOME POLLUTANTS INTRODUCED INTO ATMOSPHERE BY PORTO MARGHERA INDUSTRIES IN 1980s AND 1990s	
PRODUCT	**TONS / YEAR**
Vinyl acetate monomer	187
Acetylene	199
Hydrochloric acid	55
Ammonia	7150
Sulphur dioxide	43,490
Chlorine	37
Vinyl chloride monomer	1685
Benzotrichloride	1269
Hydrocarbons	52
Cyanide	27
Nitric oxide	7000
Carbon monoxide	2900
Plasticisers	2.4
Dust	4500
Sym-tetrachloroethane	7.5

Table 6.3: *Waste produced annually and discharged into Lagoon from the mid-1970s.*

6.3 Conclusions

In the light of surveys conducted and constant expert monitoring and checking by State Forestry staff, it may be realistically stated that the environmental emergency for the entire habitat of the Lagoon of Venice drainage basin has now reached a critical level. Radical intervention is required in order to save this delicate, seriously compromised ecosystem and to safeguard human health. The only possible solution is drastically to reduce the sources of pollutants which continue to enter the Lagoon by way of unauthorised dumps, and to launch in-depth - not superficial - clean-up operations. Setting new and stricter limits serves no purpose, as checks can be avoided simply by diluting waste. Instead, a methodical preliminary study of the consequences of dumping in the environment is essential. Everyone must examine their consciences, all actions produce a certain effect. Resolution is needed to overcome the preference for contingent profits, together with continual surveillance exercised over the environment in which we live and in which future generations should be able to continue to live, in well-being and health. Legislators could certainly contribute by making the appplication of laws harsher and transforming certain offences into crimes, so that greater deterrents face offenders in this sector.

Chapter 7

Plan for monitoring dioxins and PCBs in foods produced in the Veneto

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Veterinary Services, Veneto Regional Authority

With *Law no. 4783 of 28 December 1999*, the Veneto regional authorities approved the sum of 280,000,000 lire (approx. 144 thousand euros) for monitoring the production of foods of animal origin for dioxin and PCBs. Regional management was entrusted with the task and in turn commissioned the laboratories of the Italian Inter-university Consortium of Marghera (INCA) to carry out the necessary analyses. A sampling programme was drawn up, launched in December 2000, and concluded in summer 2001. The veterinary department of the local public health unit carried out actual sampling and the *Istituto Zooprofilattico Sperimentale delle Venezie* (IZSV) collated samples and data. Statistical analysis of data and processing in epidemiological terms was carried out by regional management (further information on the Veneto Region website: www.regione.veneto.it/prevenzione).

7.1 Samples

A total of 100 food samples were analysed, including beef, pork, chicken, rabbit, milk, eggs, fish and shellfish from fish farms, abattoirs and distribution centres. Monitoring was carried out to:

- check average levels of contamination for the first time in the Veneto region;

- integrate Italian and EC data-bases in terms of contamination by dioxin and PCBs in the Veneto;
- check the level of risk due to consumption of foods of animal origin produced in the Veneto;
- evaluate risk factors due to production or processing in the region.

7.2 The plan

In Italy, systematic and periodic checks on POPs do not exist. The few checks carried out to date cover a limited range of products and were only effected as a consequence of emergency situations. With the exception of the "Seveso control group", virtually no checks have been conducted on the population. Similarly, a nation-wide inventory of emissions is lacking, despite requests made several years ago by the European Community. In other EU countries, periodical checks are carried out on the production of PCBs and dioxin. In Germany, the Scandinavian countries and the UK (Ministry of Agriculture, Forestry and Fisheries) have been monitoring milk on an annual basis since 1989. This type of survey has never been carried out systematically in Italy.

The plan for checking production of foods of animal origin in the Veneto involves:

- study and evaluation of the industrial system in the Veneto for producing foods of animal origin;
- determination of the number of samples necessary for reliable measurements (100 to cover all categories);
- identifying environmental areas at greatest risk and planning a monitoring strategy;
- defining environmental compartments for sampling and relative sampling methods.

Samples from cattle came from animals mostly bred in highly industrialised farms, which use feed produced on the farm itself, togther with complementary feed with added minerals and vitamins purchased on the market.

Chickens and rabbits were selected from battery-type farms using complete prepared feed, and from rural farms where animals were fed on mixed feed, i.e., commercial feed and raw material acquired locally.

Fish samples came from fish-farms located on the mainland and from specimens taken from the Lagoon.

Molluscs came from areas in the Lagoon where harvesting had not been prohibited.

It was decided to take 16 milk samples from areas at high risk from contamination due to the presence of incinerators and waste dumps in a 5-km

	Σ **PCDD/F and “dioxin-like” PCBs**
Eel	24.28
Mussel	33.45
Gilt-head bream and sea bass	29.05
Trout	30.11
Beef	1.16
Chicken and rabbit	0.57
Pork	0.05
Milk	1.47
Eggs	1.26

Table 7.1: *Sum of PCDD/Fs and “dioxin-like” PCBs in WHO-TE pg/g fat.*

radius and near busy arterial roads, motorways, and industrial zones. Three milk samples were taken in areas of lower industrialisation in the north of the Veneto Region (Feltre and Belluno).

Veterinary surgeons from the local health unit carried out sampling from March to September 2001. All samples were delivered to the IZSV for coding before going to the INCA laboratories in Marghera (Venice), where they were analysed. Data were processed in our department.

7.3 Results

All samples were examined for 17 cogeners of PCDD/Fs, “dioxin-like” PCB cogeners (according to international nomenclature IUPAC 81-77-123-118-114-105-126-167-156-157-169-189) and “PCB markers” (IUPAC 28-52-101-138-153-180-170). All samples had values lower than the threshold levels set by *EC Reg. 2374/01 of 29 November 2001.*

As regards whole products, higher concentrations for PCDD/Fs plus “dioxin-like” PCBs emerged for fish and shellfish, with average levels of less than 2 pg WHO-TE/g of edible product. If the contribution of PCDD/Fs alone is considered, concentrations in fish and shellfish were comparable with those of clams from authorised harvesting areas in the Lagoon (0.2- 0.4 pg WHO-TE, see Table 4.3).

Data referring to percentages of fats in various foods improved comparisons. Table 7.1 shows that the sum of PCDD/Fs + “dioxin-like” PCBs for fats is considerably higher in fish and shellfish (eel, mussel, gilt-head bream, trout) than it is for beef, chicken, rabbit or pork.

These results are given in Figure 7.1 showing the relative contributions of PCBs and PCDD/Fs to total toxicity; on average PCDD/Fs account for 25%.

The consumption of foods contaminated by dioxin and PCBs is the main source of their accumulation in our bodies. Dioxin accumulates in both animals and man and is stored in adipose tissue. Several groups of the population, such as newborn babies and those consuming a fat-rich diet in areas seriously

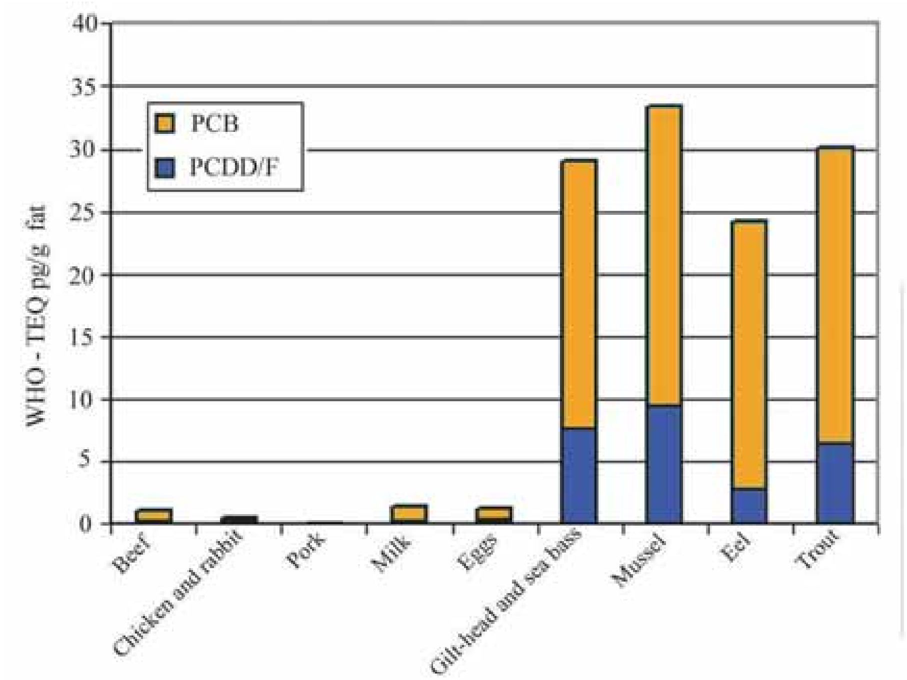

Figure 7.1: *Sum of PCDD/Fs and "dioxin-like" PCBs, calculated in WHO-TEQ pg/g fat, in fish, shellfish and various meats.*

contaminated by environmental discharges, are more exposed to high doses of dioxin. Figure 7.2 shows data for cow's milk: note the variability among the various samples (average 1.2 pg WHO-TE/g ; range 0.4-3.8).

7.3.1 *Data on fish products*

In view of the high consumption of fish products in the Lagoon of Venice, greater attention was given to this type of food over meat. Analyses of fish and shellfish (5 samples of eel, 2 of mussel, 12 of gilt-head bream and sea bass, and 10 of trout) produced the results shown in Figure 7.3 for PCDD/Fs + "dioxin-like" PCBs. The values, calculated for the whole product, range from ∼0.2 pg WHO-TE/g in some river and sea fish, to ∼12 pg WHO-TE/g in a sample of eel. Remarkably, dioxin never actually exceeded the maximum value of 4 pg WHO-TE/g of EU regulations, but high PCB concentrations were found. This situation is clear in Figure 7.3, which highlights the contribution of "dioxin-like" PCBs (in ochre) compared with PCDD/Fs (blue). If EU regulations were to introduce checks on "dioxin-like" PCBs as well, 4 out of 5 samples of eel would exceed the current limit for dioxin; other samples would be below the threshold value.

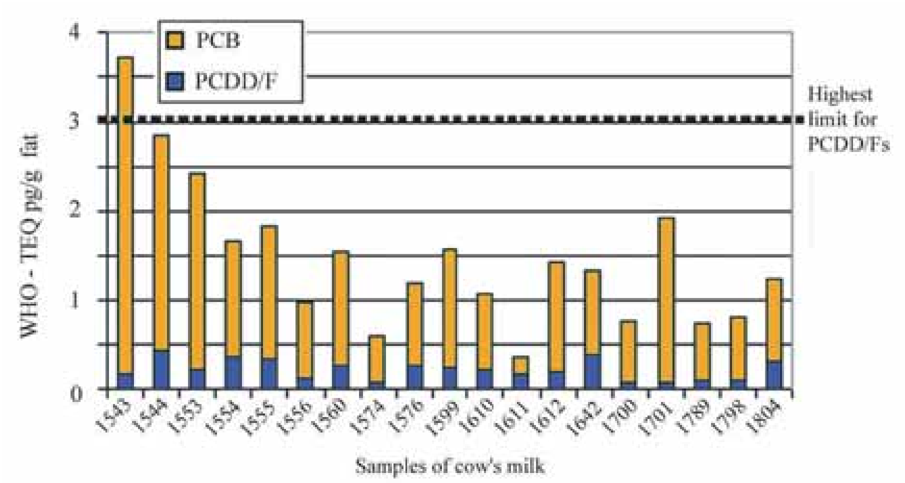

Figure 7.2: *Sum of PCDD/F and "dioxin-like" PCBs in samples of cow's milk.*

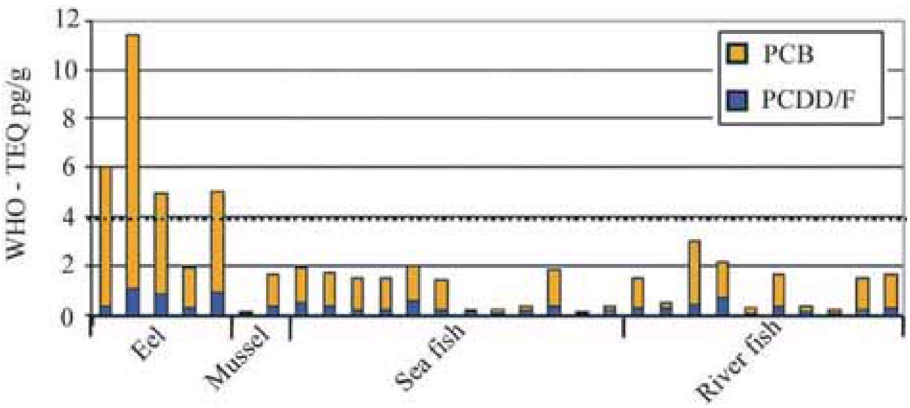

Figure 7.3: *Sum of PCDD/F + "dioxin-like" PCBs in WHO-TEQ pg/g of whole product in individual samples.*

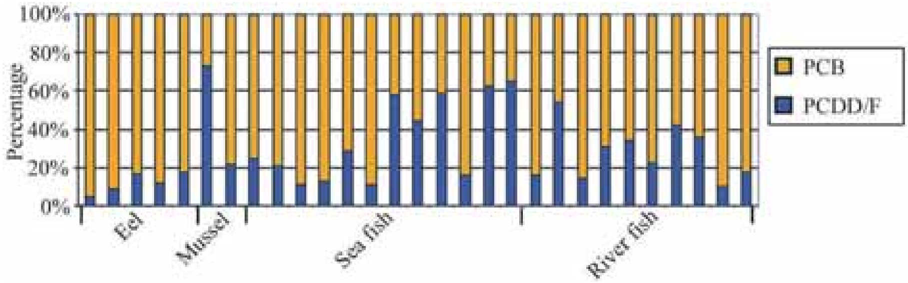

Figure 7.4: *Percentage of "dioxin-like" PCBs and PCDD/Fs in individual samples.*

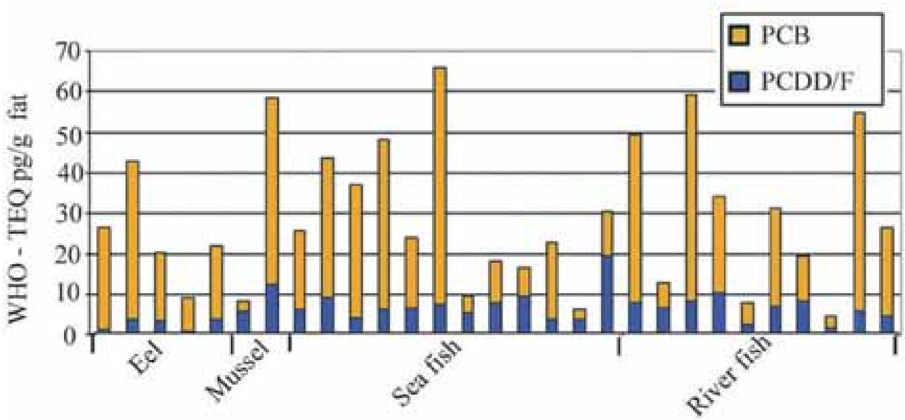

Figure 7.5: *Sum of PCDD/Fs and "dioxin-like" PCBs in samples, with reference to fat contents.*

Examination of the percentages of PCDD/Fs and "dioxin-like" PCBs gives the results shown in Figure 7.4, in which the contribution of PCBs to total toxicity varies considerably, from approximately 20% to over 70%.

Bearing in mind the fat contents of various species of fish is a better method for comparison purposes, the sum of PCDD/F and "dioxin-like" PCBs in fish and shellfish gives average values between 24 pg WHO-TE/g fat for eel to about 33 pg WHO-TE/g fat for mussel (Figure 7.1), with great differences among samples.

7.4 Conclusions

Statistical analyses showed a slight trend for greater contamination of PCDD/Fs in samples from at-risk areas compared with those from "neutral" ones. In particular, samples of poultry (5 out of 9 samples) from at-risk areas had higher levels of PCDD/Fs than battery-raised animals. The opposite was found for contamination by “dioxin-like” PCBs (6 out of 22 samples over the average of 0.43 pg WHO-TE/g fat).

Levels in milk were presumably higher than those yielded by means of conventional sampling of milk on sale, as monitoring essentially involved areas subject to high industrialisation. However, these data must be confirmed, as systematic and constant monitoring was not conducted on Veneto milk destined for human consumption.

Values measured in fish and shellfish are all below the maximum PCDD/F level of 4 WHO-TEQ pg/g whole product, according to the recent EC regulation 2374/2001 of November 29 2001. However, when compared with the other samples, they were by far the highest. WHO-TEQ pg/g values were also calculated, together with those for “dioxin-like” PCBs in WHO-TEQ pg/g fat and the sum of the two (PCDD/F+PCB). In these cases, animals which did not exceed the limit for dioxin alone (e.g., eel) did exceed it when the contribution of the toxicity of the “dioxin-like” PCBs was taken into account.

The results of monitoring food products from the Veneto point to the need for continuity, in both terms of analyses of foods for man and of animal feed, in line with guidelines from international organisations such as FAO, WHO and the EU. Systematic and periodical checks, which need to be specific and carefully designed in view of the expense entailed in analyses, ensure guarantees for consumers as well as safeguarding product quality. The European Community has asked member states, through the above-mentioned Regulation 2374/01, Regulation 178/02 and Recommendations C1541 of 5 June 2001 and 66/2002 of 25 January 2002, to activate official co-ordinated programmes to check on these substances.

Chapter 8

POPs: relationship between scientific investigation and information

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> *"...The industrial zone will mainly host factories which spread smoke, dust or fumes that are harmful to human life, discharge poisonous substances into the water, and produce vibration and noise...".*
>
> *(Art. 15, paragraph 3 of town planning regulations of the Venice City Council Master Plan, approved and applicable as of 17 December 1962).*

The Lagoon of Venice, an extremely fragile ecosystem due to its peculiar physical characteristics, has been the subject of endless controversy concerning pollution in recent years. Since the 1930s, the Lagoon has "hosted" a vast industrial complex, Porto Marghera, with which it has had to share several tragic episodes entailing damage to the environment and to the health of

[1]The problem of communicating scientific data was recently described in the thesis: "Dioxin pollution in sediments of the Lagoon of Venice: scientific inquiry and mass communications", which analysed relationships between scientific data, limited to study of sediment pollution and relative mass communications, and thus included the relationship between science and public opinion.

its residents. Low-grade raw materials for the production of steel, fertilisers and glass (e.g., bauxite, coal, phosphates), unloaded on to the wharves in the first industrial zone, were followed by raw and semi-worked materials for the chemical industry in the second industrial zone. Unfortunately, the success of Porto Marghera's two industrial zones led to considerable changes in the Lagoon, not only in a morphological sense, but above all in terms of environmental conditions, pollution in particular.

November 2 2001 saw the conclusion (with the acquittal of the accused) of the criminal trial against top-level management personnel Enichem and Montedison, corner-stones of the chemical industry in Italy and long-term producers of PVC (polyvinyl chloride) and organic chlorinated compounds at Porto Marghera. As well as sources of urban origin, chlorine production and the activities of numerous other factories in Venice's industrial zone had contributed to the deterioration of the lagoonal ecosystem. In 1995, Greenpeace's alarming dossier was the first report of the presence of dioxin in the Lagoon of Venice. Reports from the media created panic among the Venetian population. The "experts" demanded scientific discipline and therefore tests were begun and new analyses commissioned. The damning report by Greenpeace came only one year after that of Gabriele Bortolozzo, a retired worker from Enichem: a case was presented to Public Prosecutor Felice Casson reporting many cases of cancer in factory workers detailed to carry out synthesis of PVC. An investigation was launched and a criminal trial began in March 1998, concluding, as mentioned, in November 2001.

The indiscriminate exploitation of the environment as a reservoir of resources but also as an inappropriate dumping-ground for residues of human activity, has led to loss of the capacity for self-regulation in many ecosystems. As environments, lagoons are particularly vulnerable to changes in their state, due to the fact that they are semi-closed basins with low water turnover. In the Lagoon of Venice, the problem of water pollution is very complex, with a multiplicity of polluting sources and the unusual nature of the environment. Over the past decade, studies of pollution in the Lagoon have revealed the important role played by organic micro-pollutants, the so-called POPs. As these substances are chemically stable and difficult to break down, they cause great concern, as do several metals, including mercury, which is extremely unstable, and also highly toxic in biological terms [*WWF*, 2001].

This work focuses in particular on dioxins, as their presence in the Lagoon of Venice has given rise to understandable public outcry, especially in the wake of the 1995 report by Greenpeace. The relationship between scientific study and mass communications for the events which occurred in Venice clearly shows that sources of industrial origin have a considerable communication impact. The Porto Marghera industrial zone was the focus of many debates and controversy, provoking public interest - examples are the Petrochimico trial or the case of "clams *à la dioxin*". The Greenpeace report had a remarkable effect on public opinion, especially because it reminded everyone of the accident at Seveso in 1976. The last time the Italian public had been involved in the dioxin problem had been nearly 20 years before. Since then, the problem had been an issue for the scientific community, the subject of very limited interest every so often by Italian regions (above all Lombardy), and had then been forgotten by the majority of people. Thus, controversy, inquiries and discussions arose, during which public opinion, channelled by the mass media, identified the petrochemical plant as the sole source responsible for the state of deterioration of the Lagoon of Venice. In particular, the production of chlorine (which does represent a serious source of dioxin) was very thoroughly examined, since it appeared to be the main cause of the onset of grave illness (initially, a rare form of cancer) in more than 100 technicians working on the production of VCM (vinyl chloride monomer), PVC (plastic), in addition to polluting the Lagoon. This led to continuing reflection on the roles of industry and local administrators in handling the communication of risks to the population. Undeniably, it is limiting to believe that dialogue with the population can only take place through the mass media, especially because communication concerning environmental safeguarding and surveillance is one of the most complex, from the viewpoint of those involved and their responsibility.

8.1 Difficulty in communicating scientific data

Nowadays, nobody can claim exhaustive knowledge and answers to questions such as chemical and radioactive pollution, industrial accidents, the production of waste and residues, climatic change, and desertification. There is even little certainty concerning the origins and possible consequences of phenomena and events which have accompanied mankind since its very beginnings, such as earthquakes, floods, volcanic eruptions, and so on. Thus, we cannot appeal to scientific knowledge to discover the truth on which political decisions about risk and safety are based. Science is only one - albeit a very important - voice of the many in public debates, and it is responsible for transparency for results, methods and procedures. “A new contract must now guarantee that scientific knowledge is socially healthy and that its production is seen by society as transparent and participatory at the same time” [*Gibbons*, 1999]. Due to the different types of uncertainties and value judgements that inevitably influence decisions concerning risks, scientific analysis must be flanked by other types of reflection [*De Marchi* and *Ravetz*, 1999]. Experts, often researchers in a sector somehow implicated in the topic, or popularisers of science, are constantly called upon to pronounce judgement on environmental problems. And here a further, serious difficulty in our era becomes evident: notwithstanding difficulties caused by the fragmentation of its disciplines, scientific knowledge is often capable of mastering environmental issues in both intellectual and technical senses. However, it is only capable of communicating its knowledge through recourse to its typical scientific language, of little use for communicating with public opinion. This makes a “scientist” look like an expert who tends to dodge questions from the public. In order to make contact with public opinion, science should popularise its language and adopt a common, simple mode of speech, although this method may sometimes be dangerous: channelled by ordinary language, scientific knowledge may dissolve (at least partly) and become imprecise [*Marcomini et al.*, 1997].

8.2 The role of communication in science

Until recently, it was commonly thought that scientific information circulated only within certain "*forums*", a sort of "*experts only*" system, although recently it has begun to spread in an increasingly broad manner, gradually involving a vaster public. Changes in society and differences in attitude are there for everyone to see and compare with everything that went before, and the 20th century in particular was characterised by rapidity of change. This was due to the scientific discoveries and technology which were applied to all the varying sectors of our lives. In any case, one crucial factor of these transformations was undeniably communications: the possibility of transferring data, the chance to bring people closer together, tell someone else about your wishes, decisions and problems ... these things have changed the world. After the elation experienced throughout the 1970s and most of the 1980s about discoveries in space and technological progress, now newspapers, radio, TV, websites on the Internet, news and information about science and technology have progressively become distressing, in view of the topics they cover. We no longer get reports about moon landings or reports of advances in research, but news about pollution, mad cows, genetically modified organisms: from certainty to doubt, from faith to fear.

In Italy, in this day and age, the media covering scientific topics are all doing well. Why? Perhaps the manner in which such subjects are presented to the general public has finally changed and, apart for the odd exception, the somewhat old-fashioned and distant figure of the "populariser" has disappeared from both newspapers and TV. Over the last twenty years, science has changed, and with it, its very concept; so has knowledge in possession of the public and, above all, their expectations about what is "churned out by the labs" has changed. In the past, science was considered a subject for the select few; today, the common approach is: "Let's all go and see what the problems are and what can be done about them", instead of "Now we'll tell you what to do and how to do it" [*Media Duemila*, 2002].

The environmental problems of Venice and of its Lagoon were long excluded from the information system: it was the Enichem trial which allowed a kind of "forced communication" to take place. The dossiers of Greenpeace and Gabriele Bortolozzo were the events which triggered the information system. This method of communicating - solely through strongly-worded reports, with no advance warning from the people most closely involved - encourages the ordinary public not to believe what is stated, because they fear that something about which they knew nothing may suddenly happen. The message which the companies wished to transmit had to be effective for their ends, whereas for Greenpeace the accuracy of the information was less important, because the aim was the extreme force of the message for purposes of environmental safeguarding (the situation was similar in the case of Bortolozzo). It was effective in terms of strategy, but as regards the industries, the decision to omit mention of the the risks meant that an accident or something similar would have an especially strong consequent communicative effect. This is how the Lagoon of Venice and Porto Marghera ended up displayed in the public arena, when it was no longer possible to deny what was happening.

The scientific model that guided the conquest of the world and control over nature needs thorough revision. And it is not just the model which needs revision, but the very science that generated it [*Funtowicz* and *Ravetz*, 1992]. Definitive solutions to pertinent problems are continually being demanded of scientists, even when the phenomenon in question may be new, highly complex, variable and not sufficiently understood. Unlike the past, today holds no promise of certainty that application of scientific method will guarantee the affirmation of right over wrong theories and consequently that the adoption of the "right" choices that will be for "the good" of society. For society in general, working in conditions of uncertainty means forgoing the conviction deriving from the possession of scientifically accurate and reliable information. The aim is to learn how to work in conditions of uncertainty, by means of dialogue and participation: for scientists, this means accepting the partial and time-related nature of their results and adopting a new type of scientific method which is first and foremost multidisciplinary [*Funtowicz*, 1995].

There are always experts who express differing opinions on any one subject. This attitude is positive when it acts as the basis for discussion; if anything, scientific homogeneity may always have been illusory, a myth. It is important for different scientific opinions to be expressed in public. In the past, divulgation would have been made in private, in scientific and research circles, but this is no longer the case. Why are such discussions now held in public? What role do scientists have today in a public context? The answer does not depend on the fact that we now have means of mass communication that were previously unthinkable: of much greater importance is the fact that the role and position of experts in terms of development have changed. Thus, we could almost speak of environmental complexity, in which the idea of complexity entails multiple persons, prospects and interactions between the various aspects which make up the environment.

In our specific case, the emergency that affects Venice is a direct consequence of oversight or lack of interest on the part of institutions entrusted with environmental safeguarding and, unfortunately, the health of all. We are now seeing a sort of change in direction, as both public and private bodies gradually assume more responsible attitudes: all this translates into greater knowledge and, consequently, commitment in managing environmental problems. This change begins with talk of clean-up operations, monitoring, epidemiological surveys, etc., but it is clear that these projects are not straightforward in either terms of application or of cost. Information is not lacking these days, as a glance through any local newspaper will reveal (see Chapter 9.5), but it is important to realise that much remains to be done and that the contribution of individuals can also help to create a feasible future. Nevertheless, the most difficult part is managing communications with the public. Strategies should be neither too soft nor too heavy-handed. Starting with institutions and moving all the way down to individual citizens, the best form of "education" is that of conferring responsibility. Each figure should maintain her or his own role while working towards improved collaboration. Only with greater communication, also between individuals and not necessarily channelled by mass media, will it be possible to put into practise collective interests, both present and future. Importance must be given to the fact that, as each environmental issue is different for many reasons - geographical context, environmental aspects, type of pollution, etc. - all-embracing solutions cannot be found. Those who are called upon to decide must be allowed greater freedom of action, within legal limits, so that suitable solutions to environmental problems can be found. Another essential factor which should not be ignored is that each environmental situation lies within a different political, social, economic and cultural context which must be taken into due consideration. Thus, at present, the impediments to straightforward solutions to environmental problems consist mainly of confusion on a legislative level, togther with forms of culture that are not always helpful for environmental issues.

> "*News that triggers alarm when there is an environmental crisis may be deontologically correct. And if it generates fear that is positive for activating commitments with the intention of removing the causes, there is no doubt that well-directed fear has been activated. We must not be afraid of providing data, but we must know how to transmit them clearly, so that the risk lies clearly before our eyes*".

This quotation from G. Moriani [*ARPAV*, 1999] is useful in explaining why the generalised presence of dioxin in the Lagoon of Venice, as in any other environment, will no longer make the headlines. Instead, it requires detailed explanatory comments on its possible relevance - environmental, eco-toxicological, hygienic, health-related, etc.. And it is indispensable that means of communication furnish information on a high scientific level.

Chapter 9

Conclusions

9.1 POPs in the lagoon: surprising repetition

The previous chapters supply environmental data that are surprisingly consistent. All samples examined (air, water, sediments, organisms) show a similar spatial pattern. The zone surrounding the Porto Marghera petrochemical plant always has the highest levels of POPs (especially PCDD/Fs and HCB), and the minima are at points on the margins of the Lagoon.

Intermediate values are often encountered in the historical city centre of Venice and in the Lagoon. Peak values in the case of dioxin always have characteristic "fingerprints" which persist in time and are repeated in all cases, i.e., the OCDF/OCDD ratio. This ratio is higher than 2 (up to 10) for all samples from the surroundings of the Porto Marghera industrial zone, as may be seen in Figures 2.3 (water), 3.5 (air), 4.2 (sediments) and 4.3 (clams) in previous chapters. In all the other lagoon sites, this ratio is always below 1 (between 0.1 and 1). For the same points near the industrial zone, values for hexachlorobenzene are always much higher than elsewhere in the Lagoon, as shown in Figures 2.8 (water) and 3.4 (air), and Tables 4.2 (sediments) and 4.3 (clams). In the case of HCB, the very high values are more circumscribed.

As regards PCBs, the situation is slightly different, with peak values almost always near the industrial zone, but also in the city centre of Venice, where these substances have been used for decades (oil for transformers, inks, plasticisers, etc.).

From an environmental viewpoint, these observations should lead us to reflect that the source of these premonitory data is very strong and has long-lasting characteristics, and that the majority of observations link their characteristics to the production cycles of chlorine (DCE, VCM) and chloro-organics, well-developed at the Porto Marghera petrochemical plant, both now and in the past. This unusual situation was probably caused by a combination of "old" contamination (1980s-1990s), which continues to be redistributed by way of leaching from dumps, mobilisation of contaminated sediments, and persisting high levels of emissions in both water and air.

This combination of "old" and "new" contamination may be one explanation for the persistence of the OCDF>>OCDD fingerprint in various compartments which provide differing environmental data. Analyses of water and air may be considered almost immediate, i.e., with significant variations which may be measured from day to day, or month to month, whereas data from sediments and shellfish require longer periods of time, perhaps several months (e.g., the whole life-cycle of an organism) to several years (in the case of sediments).

9.2 Contamination pathways

POPs enter the food chain in different ways. In the case of Lagoon of Venice, the main pathway is environmental contamination. Figure 9.1 illustrates how substances introduced into the Lagoon from different sources interact with sediments and living species, and eventually reach man through contaminated food.

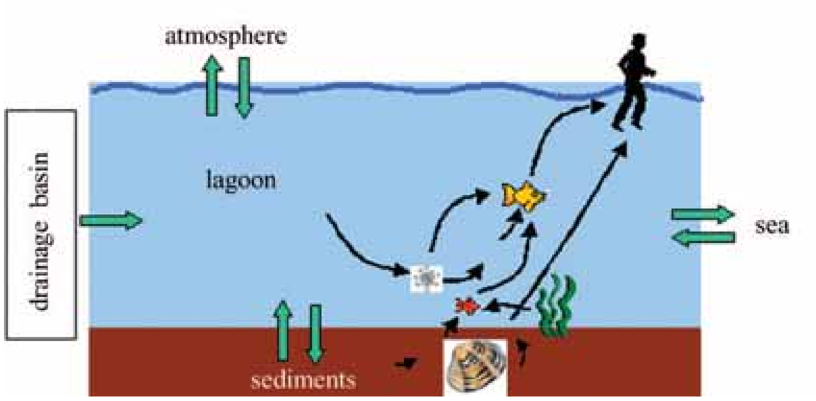

Figure 9.1: *How pollantants are transferred from the environment to man.*

Dioxin and "dioxin-like" PCBs are molecules that do not easily dissolve in water, although water helps them to disperse, once they have been adsorbed on suspended mineral and organic particles. POPs released into the air can be transported on the surface of the sea and concentrate in the marine food chain. The natural place for POPs to accumulate on the mainland is soil, the equivalent of sediments in the lagoon. Contamination passes to organisms which live in contact with sediments. In general, at the same level of contamination, the longer the life of the animal, the greater the accumulation of POPs in adipose tissue. In countries where dioxin and similar compounds have been systematically monitored for years, intake pathways have been calculated.

The two diagrams in Figure 9.2 show that diet is responsible for the intake of over 95% of dioxin and "dioxin-like" PCBs.

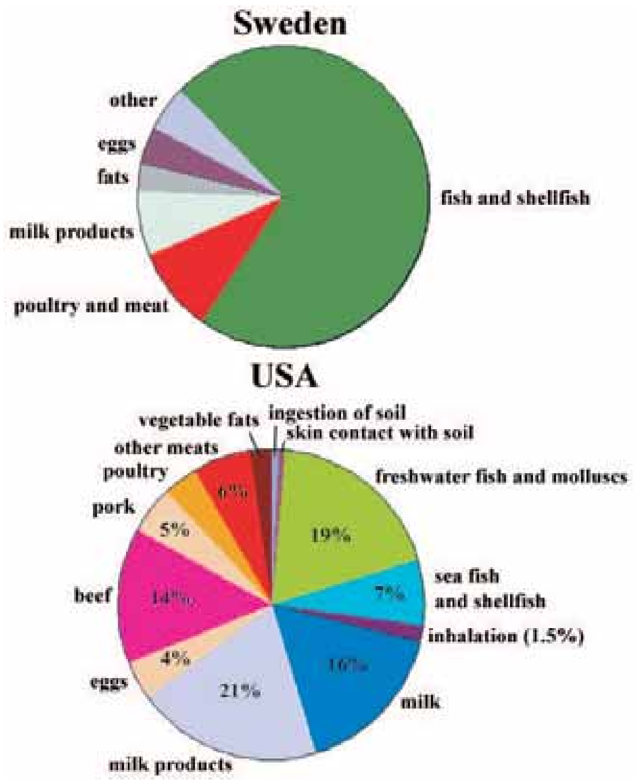

Figure 9.2: *Average daily intake of dioxin and "dioxin-like" PCBs in adults in Europe: Sweden (top) and USA (bottom) [Niklas Johansson (Swedish Environmental Protection Agency and Karolinska Institutet), 1998].*

Moreover in Sweden, approximately 65% of the intake of dioxin and similar substances is through fish and shellfish: something to be borne in mind in view of the fishing and shellfish farming in the Lagoon of Venice.

In general, people who eat a lot of fish, fatty meat and rich cheeses are more highly exposed. Those who live or work in the proximity of contaminated sites containing dioxin, waste incinerators or factories that produce dioxin as a by-product, are subjected to additional exposure (Venice, for example).

The majority of POPs ingested by animals - including man - are fixed in fatty tissues where dioxin, for example, persists for years. Its half-life (that is, the time necessary for the body to metabolise half the pollutant) ranges from 5 to 14 years in human beings. Because POPs stay in the body for so long, their damaging effects may become obvious long after exposure.

9.3 Risk evaluation

One example of risk assessment concerning human health can be found in *Progetto 2023*, sections E-C [*MAV - CVN* , 2000c]. This study was carried out according to internationally recommended procedures [*Guidelines for Exposure Assessment, USEPA, 1996/FRL-24129-5*] and emphasised the main contamination pathways in the case of Venice. The study also made use of available data with a range of objectives, in order to establish a system for evaluating and estimating the distribution of contaminants according to a multi-compartmental model with risk quantification for various targets (using the data in Table 9.1). To this end, the following pathways of exposure were identified:

a) intake of pollutants through local fish products;

b) inhalation of atmospheric contaminants;

c) intake of contaminants through foods.

Matching different levels of contaminants in foods and different levels of food consumption led to the identification of three scenarios characterising carcinogenic risk:

1) standard risk: average intake and average concentrations (geometric mean);

2) high risk: high intake and average concentrations (geometric mean);

3) highest risk: high intake and high concentrations (80^o percentile).

Risk evaluation for the population was reached by matching these scenarios with five classes of population, constructed on the basis of the intake of fish products.

Results provided estimates of the overall risk for the population in both carcinogenic and chronic non-carcinogenic terms. Without going into the results in detail, as regards overall carcinogenic risk, the study shows that arsenic, dioxin and "dioxin-like" PCBs are the major determinants of risk. In particular, dioxin accounts for 30% of overall risk, with 1.8 cases for 10,000 inhabitants in the worst case. Of this percentage, two-thirds is due to fish products and the remaining third to other foods.

The study also analysed contamination scenarios concerning the population or specific sub-groups. In scenario 1 (standard), the risk due to POPs is 3.7 cases per 10,000 inhabitants, rising in case 3 (worst risk) to 3.6 cases per 1000 inhabitants. These figures are 30 to 3000 times higher than those recommended by the US-EPA, which are one case per hundred thousand or one million.

The worst scenario was calculated using the 80^o percentile (Table 9.1). Comparisons of several of these figures with those reported in the preceding chapters for the most contaminated areas (e.g., around the petrochemical plant), show that the values are similar in several cases, whereas in others they are much lower (Table 9.2). Therefore, if a risk estimate were calculated using the POP values of the most contaminated areas of the Lagoon of Venice, an even worse scenario would result. Identification of a diet based on the consumption of local fish as the main source of exposure would require a broader data-base, in order to estimate more precisely pro-capita consumption and the origins of local products.

	HCB	**HCB (80^o)**	**Σ TEQ-PCDD/F and PCB**	**Σ TEQ-PCDD/F and PCB (80^o)**
Fish	706	830	1.03	2.2
Clams	766	3400	0.26	0.7
Mussels	321	2090	0.37	0.7
Crabs	—	—	2.65	5.4

Table 9.1: *Concentrations (pg/g whole product) of HCB and sum of PCDD/Fs + "dioxin-like" PCBs (pgTEQ/g whole product) of Lagoon biota used for risk analysis [MAV - CVN, 2000c]. Left-hand column: geometric mean of each variable; right-hand column: 80^o percentile*

	HCB^1	**HCB**^{2}	**PCDD/F+PCB**^{1}	**PCDD/F+PCB**^{2}
Fish	830	—	2.2	3.0*
Clams	3400	6900$^\wedge$	0.7	1.6$^\wedge$
Mussels	2090	—	0.7	0.9*

Table 9.2: *Comparisons between concentrations (pg/g whole product) of HCBs and sum of PCDD/Fs + "dioxin-like" PCBs (pgTEQ/g whole product) in Lagoon biota [1: 80^o percentile] and those for organisms sampled in the most contaminated areas of the Lagoon [2: $^\wedge$ Raccanelli, Table 4.3; ∗ MAV - CVN, 2000b].*

Evaluation of environmental risk (including that for man) still lacks the threshold values of the effect of PCDD/Fs and PCBs [*Critto* and *Marcomini*, 2001]. Thus, complete analysis of ecological risk necessitates further investigations aimed at evaluating adverse effects. Given the current level of contamination, this should be carried out because, in addition to POPs, there are other sources of risk in the Lagoon, including heavy metals such as arsenic and mercury.

9.4 Reduction of exposure to POPs

9.4.1 *European Community strategy*

As seen in the Preface, the Scientific Committee for Food (SCF) analysed the growing risk for public health represented by the presence of dioxin and "dioxin-like" PCBs in foods. This analysis included calculation of the daily intake of dioxin and "dioxin-like" PCBs with food for the population of the EC, and identification of the main sources of exposure.

These substances are characterised by persistence, and the SCF has established a tolerable weekly assumption level of 14 pg toxic equivalent (TEQ) per kg of body weight for dioxin and "dioxin-like" PCBs. This Tolerable Weekly Intake (TWI) is proportional to the Provisional Monthly Intake (PMI) of 70 pg/kg of body weight/month, set by the Commission of Experts on Food Contaminants of the FAO/WHO, at their 55th Meeting in Rome in June 2001. The level is also in line with the provisions for a Tolerable Daily Intake (TDI) of 1-4 pg WHO-TEQ/kg of body weight, established by the WHO in 1998. Comparison of the EU limits with those of other international scientific organisations shows that the maximum dose of 2 pg/kg body weight/day proposed by the SCF in May 1998 is in line with that of 2-3 pg/kg body weight/day suggested by experts from the World Health Organisation (JECFA-WHO) in June 2001.

Communication 2001/C 322/02 published in the EU's official gazette (C 322/2, 17.11.2001) describes EC strategy on dioxins, furans and polychlorinated biphenyls. The document illustrates the problems connected with exposure to these contaminants, the effects on human health and the environment, and the degree to which emissions have been reduced over a range of activities. The same document also lists the aims: on one hand, reduction of dioxin and PCBs in food and animal feed and, on the other, reduction of these compounds in the environment. The first part of this strategy is mainly regulated by legislative measures defining maximum levels, danger levels, and long-term goals for food and animal feed. The second proposes setting limits on emissions in varying industrial contexts, together with the development of procedures for promoting and improving the availability of reliable and comparable environmental data for both emissions and various environmental compartments[1].

The SCF concluded that, although a considerable proportion of the European population takes in quantities of toxic substances in excess of the maximum daily limit, this does not necessarily imply high risk for the health of individuals, as the established weekly intake (TWI) has an in-built safety factor. However, exceeding the TWI progressively reduces the protection afforded by the safety limit. It is important to remember that intake through diet of these contaminants by Europeans shows broad variability because of the eating habits and types of food which change so greatly in the various countries. For example, a diet based on fish from the highly contaminated areas of the Baltic currently entails much greater risk than the varied diet of southern Europe, and the same may hold true for a diet of fish from the Lagoon of Venice.

[1] 2399th Council meeting - Environment - Brussels, 12 December 2001: *Dioxins, Furans and Polychlorinated Biphenyls (PCB) Conclusions.*
http://europa.eu.int/abc/doc/off/bull/en/200112/p104042.htm.

9.5 The current situation: what the papers say

There is constant talk of working in safety, stricter controls, etc.. But how much has really been done?

This is not the appropriate place for an in-depth investigation concerning the problem of emergency plans, application of the "Seveso Law", and the treatment and use of waste, since each would require specific analysis. Our aim is to present a collection of articles which were published in local Venetian newspapers, in order to demonstrate that the above issues can kindle the interest of the media.

The most worrying aspect is that, despite everything which has been said, environmental disasters continue to happen, frequently affecting people's health. As soon as effective campaigns of study and information on a given environmental issue are organised, something else happens. Strangely enough, one pollutant in particular keeps rearing its head in the Lagoon of Venice: dioxin. A glance through any newspaper is enough to see that dioxin always appears at the top of the list whenever a leakage or an episode of deliberate dumping is reported.

Persistent Organic Pollutants (POPs) are now the main research objective, due to their dangerous nature and consequent risk for the health of the population. As has been emphasised in this publication, rigid limits have been set on an EC level to reduce if not totally eliminate emissions of these compounds, and a number of experts in this sector of environmental health are at work in the Lagoon (Figure 9.3).


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CRONACA DI MESTRE

la Nuova

I cinque anni di attività del laboratorio del Consorzio interuniversitario Inca con sede al Parco Vega di Marghera

I cacciatori di diossine e pop

Punto di riferimento mondiale nelle analisi dei microinquinanti

IDEE E IMPRESA

Uno studio sull'uso di microrganismi nelle bonifiche

Risanare suoli ed acque con l'aiuto dei batteri

Figure 9.3: *Hunting dioxin and POPs. Five years of work at Inter-university Consortium (INCA), based at Parco Vega in Marghera, a world-wide reference point in analysis of micropollutants (*La Nuova Venezia, 25/3/2003*).*

However, this is apparently insufficient when we have to deal with people who turn pollution into a profitable source of income. Much has been said about the "clams *à la dioxin*" harvested in the industrial channels, a zone out-of-bounds to fishermen, inspectors' seals falsified, and products sold at the fish market, ending up on our tables (Figure 9.4).

IL GAZZETTINO Venerdì 1 novembre 2002

CHIOGGIA Il presidente e i 22 soci della cooperativa Ittica Nettuno dovranno comparire davanti al giudice il 19 novembre

Vongole inquinate, chiesto il giudizio

Le accuse sono pesanti: associazione per delinquere finalizzata alla ricettazione, frode, falso

L'attività secondo gli inquirenti sarebbe stata avviata come copertura della pesca abusiva

Figure 9.4: *Polluted clams, trial called for. Chioggia: chairman and 22 members of* Ittica Nettuno *fishing cooperative to appear in court on November 19. Serious accusations: criminal association with the aim of receiving stolen goods, fraud, forgery. (*Il Gazzettino, 1/11/2002*).*

As if this were not enough, Porto Marghera continues to be the site of leakages of toxic compounds from the petrochemical plant. One such episode could have ended in tragedy on November 28 2002. "It could have been a second Bhopal", a fireman on the spot commented. Talk of making the plants safer continues, but we still do not have a real emergency plan, with information available to residents about risks and what to do if there is an accident (Figure 9.5).

And what about the latest scandal? It appears that sludge from the waste treatment plant for industrial and urban waste water at Fusina, with high concentrations of dioxin, PCBs and PAH ended up on cultivated land: vegetables polluted by dioxins and other POPs could have ended up on our plates (Figure 9.6).

There is not much to add to this, except to express our astonishment that current legislation on this subject is still in such a state of superficiality and confusion. Once an accident has happened, it is impossible to find out who

Venerdì 29 novembre 2002

Esplosione in un reparto della Dow Chemical: quattro operai feriti, cittadini invitati a chiudersi in casa

Fiamme a Marghera, ore di paura

Brucia fabbrica chimica
È allarme nube tossica

IL POSGENE

UNA BOMBA FRA LE CASE

di Giorgio Cecchetti

Figure 9.5: *Flames at Marghera, hours of fear. Explosion at Dow Chemical plant: four workers injured, residents advised to stay at home. Chemical factory on fire: toxic cloud alarm. (*La Nuova Venezia, 29/11/2002*).*

Anno III - n. 140
Venerdì
23 maggio 2003

VENEZIA. Allarmanti particolari dall'inchiesta sugli scarichi tossici mentre scoppia la guerra su chi doveva controllare

Montagne di veleni nei campi

Usate come fertilizzanti 96.000 tonnellate di diossina

I controlli del Corpo Forestale sugli scarichi dei fanghi tossici a Fusina

COSA FA MALE

PER FAVORE PARLATE CHIARO

di Andrea Iannuzzi

SEGUE A PAGINA 14

CECCHETTI E VITUCCI
ALLE PAGINE 2 E 3

Figure 9.6: *Heaps of poison in the fields. Alarming details from enquiry into dumping of toxic waste, while a war erupts over who was supposed to be checking. 96,000 tons of dioxins used as fertiliser. (*La Nuova Venezia, 23/5/2003*).*

was supposed to be in charge of preventing it. Currently, there are no precise guidelines to establish exactly who is to carry out checks, what they are to check and how often. This is an inadmissible situation. Perhaps it is still not clear that the aim of checks is not to identify the guilty party once the damage has been done, but to do everything possible to avoid it happening.

Specific analyses aimed at measuring levels of dioxin in body fat, blood and mother's milk do exist (Figure 9.7), but they are expensive and are not usually routinely available to the public.

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CRONACA DI VENEZIA

la Nuova

INDUSTRIE E SALUTE

Risposta «tranquillizzante» all'interrogazione di Luana Zanella circa la presenza di sostanze pericolose

Latte materno in Parlamento

Il caso delle analisi effettuate 4 anni fa su alcune mamme

Figure 9.7: *Mother's milk reaches Parliament. In response to questioning by Luana Zanella (Green Party) about dangerous substances, the answer was "Keep calm". Analyses conducted 4 years ago involve a number of mothers. (*La Nuova Venezia, *14/11/2003).*

Our main aim, always, should be that of reducing the levels of contamination in the environment and in foods, in order to ensure a high level of protection and health for the public. Our message to those responsible for authorising emissions, discharges, waste treatment, and re-use of waste is for stricter controls, in the hope that, in the near future, we will not have to be afraid of taking a breath of fresh air or sitting down to a meal!

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This timely collection of studies is of special significance for the city of Venice and its Lagoon. In this condensed volume, the editors give an accurate description of the "state of the art" of scientific research in the delicate and controversial field of environmental monitoring. For the first time, in a simple manner, the results of various types of research carried out by both public and private institutions are presented, all dealing with the contents of persistent organic pollutants (POPs) in the environment (air, water, sediments, soil, fish) and in foods in Venice and its surrounding area.

Uncontrolled release into the environment of such substances as dioxin, furans, chlorinated compounds and micro-pollutants in general are capable of causing the worst industrial disasters to which mankind has been subjected in recent decades: Seveso and Bhopal above all. But it is not only the unexpected or casual leakage, explosion or fire which disturbs the sleep of local inhabitants exposed to "chemical risk": a much higher level of anxiety is induced by the fear of being subjected to the effects of a silent, imperceptible, but constant release into the atmosphere or water of toxic substances which may accumulate and have lasting effects, poisoning our bodies without our knowledge.

This work clearly reveals the need for continual monitoring of the Lagoon of Venice, so that this fragile ecosystem, which had succeeded in cohabiting with mankind for over a thousand years, can heal the wounds which man has inflicted upon it and be protected against the threat of further pollution. Monitoring is essential if appropriate information about risks is to be made available for people's health and well-being.

The problem of risk for the ecosystem and for human health is emphasised, and has indeed recently been reported by the European Commission which, in October 2001, adopted an EC strategy for dioxin and other toxic substances, confirming that controlling environmental pollution is one of the most efficient methods of reducing intake levels of toxic substances through the food chain.

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