



## CADMIUM FOUND IN THE BAHIA BLANCA ESTUARY

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### ABSTRACT

The present work was conducted within the frame of the research project "Study of the temporal and spatial dynamics of liquid effluents, either industrial or urban, in the Bahía Blanca Estuary Port Area and Petrochemical Hub". Its aim was to investigate the sources of origin of the Cadmium (Cd) detected in the waters, sediments and fish in this estuary.

Firstly, updated theoretical data concerning Cd is introduced. This framework includes: source of origin, effects on human health and the environment (detection in water, sediments and fish), sources and products containing Cd, related international environmental agreements and proposals, as well as the Argentine legislation and decrees in which this element is mentioned.

Later, a description of the Bahía Blanca Petrochemical Hub and Port Area located on the Estuary, which are under Buenos Aires Province Act No 12530/01, is made. All the point source discharges (industrial, sewage, stormwater and natural watercourses) into the estuary, as well as those from diffuse ones (e.g., waste dump on the floodplains) are identified.

The abovementioned discharges and monitoring points in the estuary, geolocated using a GPS, were entered into a Geographic Information System (GIS) in order to be able to visualize them and to assess their correlation.

Results concerning urban and industrial discharges were also compared with the maximum values permitted by the legislation in force taking into account, in each case, the receiving bodies.

The concluding remarks and suggestions arise from processing and evaluation of records.

To summarize, a single discharge could not be identified as the only source of contamination or the determining factor for the presence of Cd. Diffuse discharges from the former wastedump together with point source sewage discharges were identified as the most significant ones. Accordingly, further sampling and deeper research into these discharges is regarded to be required.

As important conclusions, it should be highlighted that in no case were the assessed industrial or urban results found to be above the values permitted by regulations in force and that, even when the presence of Cd in the estuary was detected, it should be reminded that this metal is a natural component of seawater.

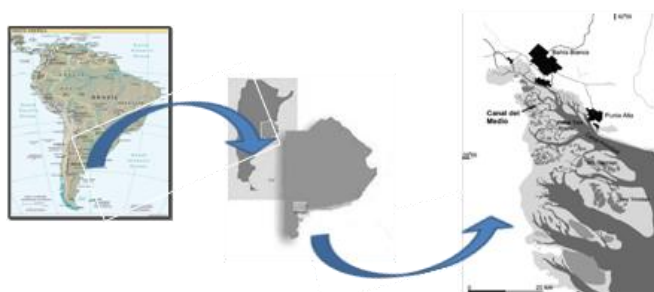
**Keywords:** Pollution; Cadmium; Estuary.

### INTRODUCTION

The present study was motivated by the detection of Cd and other metals in the waters, sediments and fish of the Bahía Blanca Estuary, which is located between 38°45' - 35°10' south and 61°45' - 62°30' west, in the southwestern region of the Buenos Aires Province in the Argentine Republic (**Fig. 1**).

In 2001, the Comité Técnico Ejecutivo (CTE - Executive Technical Committee) of the Bahía Blanca Municipal Government was created under Act No 12530 of the Province of Buenos Aires. This committee implements an Integral Monitoring Program (IMP) comprising various sub-programs, which involve - among other - monitoring the waters of the Bahía Blanca Estuary as well as the industrial and urban discharges of liquid effluents from the Port Area and the Petrochemical Hub. In addition, other public and/or private agencies perform the monitoring of the estuary waters and that of the water courses and drainage channels flowing into the estuary. Based upon such monitoring, the source of origin of Cd in the estuary was researched considering the various point sources (industrial, sewage, stormwater and natural watercourses) and diffuse discharges (former waste dump).

**Fig. 1: Location of the Bahía Blanca Estuary**



**METHODS**

Research started by delimiting the study area, the Bahía Blanca Estuary, which is the sector under the jurisdiction of Act No 12530/01 of the Buenos Aires Province, and by identifying each natural and anthropic discharge into its waters.

Later, both national and international bibliography on Cd was consulted so as to count on an updated theoretical frame including: sources, effects on the environment and human health (Cd detection in water, sediments and fish), sources and products containing this metal, international environmental legislation and agreements as well as the Argentine acts and decrees in which Cd is mentioned.

Data bases containing the results of assessments provided by CTE and IADO - Instituto Argentino de Oceanografía (2001-2010), VALE – Potassium Chloride Project (2011) and CGPBB - Consorcio Gestión del Puerto de Bahía Blanca (2003-2011) were consulted.

Once compiled, the results of the Cd analyses made on the receiving waters and the various discharges were processed, validated and assessed:

The various point and diffuse source discharges, geolocated using a GPS, were entered into a Geographic Information System (GIS) in order to be able to visualize them and their relationships.

- **The waters of Sauce Chico River under regular water flow. Data provided by CTE. [1]**

MONITORING STATIONS ON THE BAHIA BLANCA ESTUARY (IADO)				
NAME	DESCRIPTION	LOCATION		
		LATITUDE	LONGITUDE	
E 1	Bouy 24	62° 10' 59.2" W	38° 52' 34.5" S	
E 2	Bahía Blanca Main Sewage Discharge (Ballena Channel)	62° 12' 14.0" W	38° 50' 24.9" S	
E 3	In the proximity of Ingeniero White Port	62° 15' 48.6" W	38° 47' 54.1" S	
E 4	Galván Port (Flammables Pier)	62° 18' 0.2" W	38° 47' 22.7" S	
E 5	Down-load Collecting Channel Petrochemical Hub	62° 18' 36.4" W	38° 46' 17.9" S	
E 6	Maldonado Discharge Channel	62° 20' 25.1" W	38° 45' 54.1" S	
E 7	Cuaterros Port	62° 23' 2.9" W	38° 45' 1.7" S	
E 8	Surroundings of Sewage Discharge Third Basin	62° 20' 31.6" W	38° 43' 47.2" S	

IADO analyzed Cd in the water, sediments and fish in this basin. [1][2] (Fig. 2)

DISCHARGES FROM THE PETROCHEMICAL HUB AND PORT AREA MONITORED BY CTE				
NAME	DESCRIPTION	TYPE OF DISCHARGE	LOCATION	
			LATITUDE	LONGITUDE
D 1	Petrobrás Refinery 1	Industrial	62° 18' 19.7" W	38° 44' 28.5" S
D 2	Petrobrás Refinery 2	Industrial	62° 18' 2.8" W	38° 44' 41.4" S
D 3	Cargill Plant	Industrial	62° 16' 15.9" W	38° 47' 12.3" S
D 4	Profertil Plant	Industrial	62° 17' 4.9" W	38° 47' 14.7" S
D 5	Dow Chemical - LHC I Plant	Industrial	62° 17' 29.0" W	38° 46' 12.4" S
D 6	Dow Chemical - LHC II Plant	Industrial	62° 17' 34.0" W	38° 46' 8.8" S
D 7	Dow Chemical - LDPE Plant	Industrial	62° 17' 34.0" W	38° 46' 51.3" S
D 8	Dow Chemical - Barcaza Plant	Industrial	62° 18' 9.0" W	38° 46' 51.3" S
D 9	Dow Chemical - Plant HDPE	Industrial	62° 17' 12.1" W	38° 46' 25.4" S
D 10	Dow Chemical - EPE Plant	Industrial	62° 17' 39.9" W	38° 46' 4.3" S
D 11	Solvay Indupa Plant	Industrial	62° 17' 12.2" W	38° 46' 25.5" S
D 12	Luis Piedrabuena Thermoelectric Powerstation 1	Industrial	62° 15' 2.0" W	38° 47' 19.8" S
D 13	Luis Piedrabuena Thermoelectric Powerstation 2	Industrial	62° 15' 28.0" W	38° 47' 19.7" S
D 14	Luis Piedrabuena Thermoelectric Powerstation 3	Industrial	62° 15' 23.1" W	38° 47' 15.7" S
D 15	Air Liquide Plant	Industrial	62° 16' 47.1" W	38° 46' 25.1" S
D 16	Mega Plant	Industrial	62° 17' 33.4" W	38° 47' 3.4" S
D 17	TGS Cerri	Industrial	62° 23' 21.4" W	38° 41' 15.6" S
	Main Sewage Treatment Plant of Bahía Blanca Discharge	Urban	62° 13' 40.8" W	38° 45' 57.6" S
	Sewage Treatment Plant of Ingeniero White Discharge	Urban	62° 16' 28.0" W	38° 46' 54.3" S
	Third Basin Sewage Treatment Plant of Bahía Blanca Discharge	Urban	62° 20' 56.6" W	38° 42' 59.8" S

CTE analyzed Cd in the water and sediments .<sup>[1]</sup> (Fig. 2)

MONITORING IN THE PROXIMITY OF THE MOUTH OF THE NAPOSTA STREAM AT THE POTASSIUM CHLORIDE PROJET LOCATION			
NAME	MONITORED SPACE	LOCATION	
		LATITUDE	LONGITUDE
Naspotá 1 AS	Surface water	38° 46' 15.1" S	62° 13' 57.5" W
Naspotá 2 AS	Surface water	38° 47' 11.4" S	62° 14' 12.3" W
Naspotá 3 AS	Surface water	38° 47' 17.8" S	62° 14' 17.6" W
Naspotá 1 S	Sediments	38° 47' 58.4" S	62° 15' 16.8" W
Naspotá 2 S	Sediments	38° 48' 1.4" S	62° 15' 12.6" W

Monitoring and results provided by VALE. (Fig. 3)

MONITORING STATIONS OF CGPBB				
NAME	MONITORED SPACE	DESCRIPTION	LOCATION	
			LATITUDE	LONGITUDE
M 1	Sea	Near Bahía Blanca Main Sewage Discharge	62° 13' 17.0" W	62° 13' 17.0" W
M 2	Sea	Main Channel Bouy 32 (near Main Sewage Bahía Blanca)	38° 48' 7.6" S	62° 15' 23.0" W
M3	Sea	Piedrabuena Powerstation's Pier	38° 47' 34.1" S	62° 15' 32.2" W
M 4	Sea	Bahía Blanca Terminal	38° 47' 31.3" S	62° 15' 51.30" W
M5	Sea	Cargill Pier	38° 47' 31.2" S	62° 16' 13.3" W
M6	Sea	Fisherman's Dock	38° 47' 25.6" S	62° 16' 15.3" W
M 7	Sea	Multi-purpose Harbour	38° 47' 28.0" S	62° 16' 32.2" W
M 8	Sea	Ministro Carranza Pier - Site 19	38° 47' 18.5" S	62° 16' 35.0" W
M9	Sea	Profertil Pier	38° 47' 20.8" S	62° 17' 5.2" W
M 10	Sea	Mega Pier	38° 47' 16.8" S	62° 17' 21.3" W
M 11	Sea	Dreyfus Pier	38° 47' 11.4" S	62° 17' 41.0" W
M 12	Sea	Galván Port - Site 5	38° 47' 5.2" S	62° 17' 56.20" W
M 13	Sea	Galván Port - Sites 2/3	38° 47' 1.2" S	62° 18' 4.7" W
M 14	Sea	Flammables Pier 1	38° 47' 6.1" S	62° 18' 21.1" W
M 15	Sea	Flammables Pier 2	38° 46' 59.6" S	62° 18' 38.5" W
M 16	Sea	Arroyo Galvñn frente muelle ESSO	38° 46' 14.8" S	62° 18' 34.5" W
M 17	Sea	Arroyo Galvñn frente Esso sur	38° 46' 9.6" S	62° 18' 23.8" W
M 18	Sea	End Canal S02 Cerri	38° 46' 32.3" S	62° 19' 29.2" W
M 19	Sea	End Confluence Canal at S06 Cerri	38° 45' 42.2" S	62° 20' 39.4" W
M 20	Sea	End Confluence Canal at S07 Cerri	38° 45' 19.1" S	62° 21' 33.6" W
M 21	Sea	Cuaterros Port	38° 44' 45.8" S	62° 22' 41.7" W
M 22	Sea	Natural Channel - Third Basin's Sewage Discharge	38° 43' 27.0" S	62° 20' 53.8" W

The CGPBB performed analyses at those stations for Cd in waters and sediments (Fig. 4)

MONITORING STATIONS OF CGPBB				
NAME	MONITORED SPACE	DESCRIPTION	LOCATION	
			LATITUDE	LONGITUDE
T1	Ground	Landfill near ex Route 229 around waste dump drainage	38° 46' 33.5" S	62° 9' 34.2" W
T2	Ground	Bahía Blanca Main Sewage Discharge - Home channel	38° 47' 55.3" S	62° 13' 17.7" W
T3	Ground	Bahía Blanca Main Sewage Discharge - Right side channel	38° 47' 54.0" S	62° 13' 19.0" W
T4	Ground	Bahía Blanca Main Sewage Discharge	38° 47' 53.0" S	62° 13' 18.3" W
T5	Ground	Napostá Stream	38° 46' 13.7" S	62° 13' 58.1" W
T6	Ground	Drainage channel Loma Paraguaya - Petrobrás Refinery	38° 45' 13.1" S	62° 18' 14.8" W
T7	Ground	Sauce Chico River and Route 3 intersection	38° 42' 7.5" S	62° 27' 26.1" W
T8	Ground	Cuenca interior SE de Brio Colón	38° 44' 57.3" S	62° 18' 53.8" W
T9	Ground	Ex waste dump Belisario Roldán - Almte Brown Club	38° 45' 0.5" S	62° 19' 29.1" W
T10	Ground	Saladillo Dulce Affluent Route 3 Km 701.5	38° 41' 16.6" S	62° 23' 19.7" W
T11	Ground	Natural Canal - Third Basin Sewage Discharge	38° 43' 37.3" S	62° 20' 47.7" W
T12	Ground	Third Basin Sewage Discharge - Home canal	38° 43' 26.9" S	62° 21' 14.5" W

The CGPBB performed analyses at those stations for Cd in waters and sediments (Fig. 4)

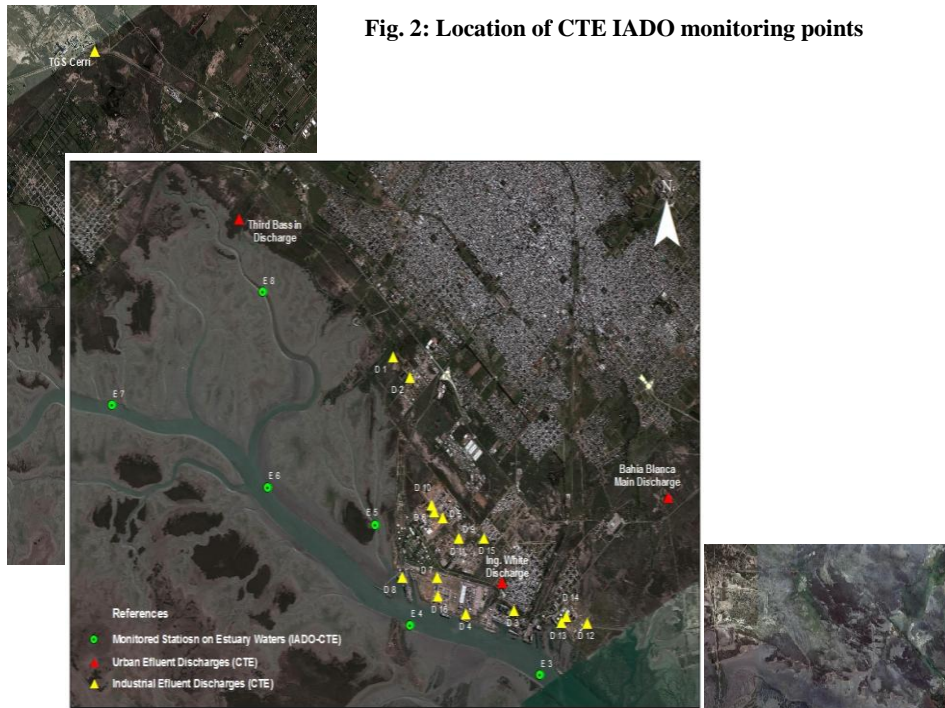


Fig. 2: Location of CTE IADO monitoring points

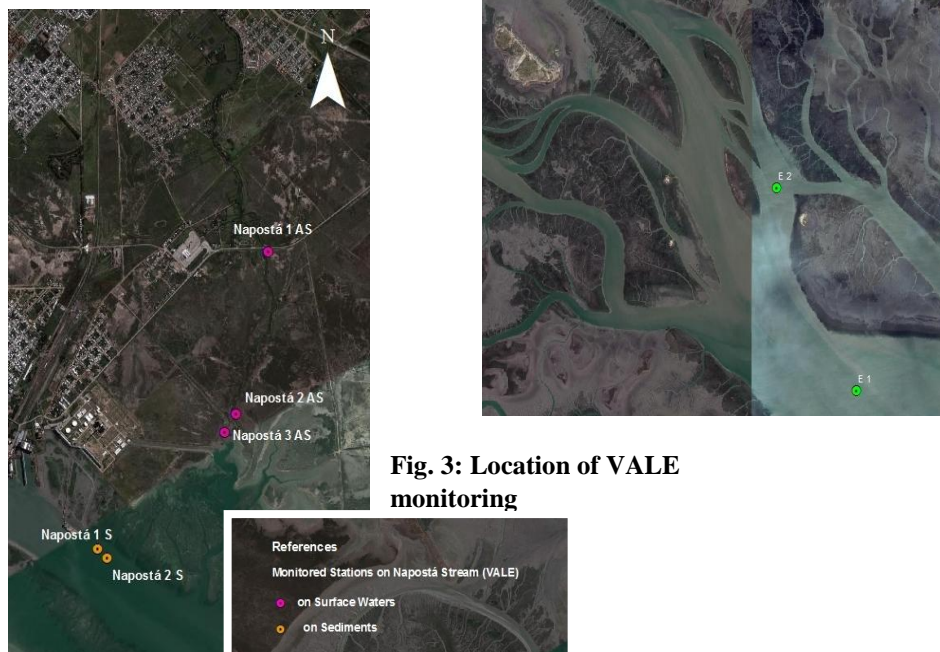


Fig. 3: Location of VALE monitoring

Fig. 4: Location of CGPBB monitoring points



As for industrial and urban effluent discharges, results were compared with the maximum discharge values established by Regulatory Decree N° 336/03, Buenos Aires Province corresponding to Act N° 5965. This decree establishes a permitted maximum for Cd of  $\leq 0.1$  mg/l for surface water discharges (this being the case for the Bahía Blanca Estuary), and  $\leq 0.5$  mg/l for discharges to sewerage collector.

Considering that there are no national, provincial or local regulations establishing standards for the water, sediments or fish in the Bahía Blanca Estuary, the guideline levels of National Oceanic and Atmospheric Administration (NOAA) were used as reference values in order to evaluate the concentration levels of Cd found. Such guideline levels are established as follows:

- Cd dissolved in water: chronic exposure: 8.8 ppb – acute exposure: 40 ppb.<sup>[1]</sup>
- Cd in surface marine sediments: Effects Range Low – ERL : 1.2 ppm; Effects Range Median - ERM: 9.6 ppm.<sup>[1]</sup>

The definition of Acute Exposure to Cadmium dissolved in water is formulated for average concentration per hour of exposure. It should be stated that NOAA does not establish any reference concentration levels for periods shorter than one hour.

The definition of Chronic Exposure refers to average concentration for 96 hours of exposure (4 days). NOAA has not established reference concentration values for longer periods.

Due to the design characteristics of the monitoring of the Bahía Blanca Estuary, the values obtained in each campaign may be compared to Acute Exposure Values. However, since it is unknown whether the concentration values found persist during the subsequent 96 hours, the Chronic Exposure value is used, being the latter established for a shorter span of time and allowing thus a more conservative criterion for comparison.<sup>[1]</sup>

Regarding fish, because of lack of national, provincial or local legislation establishing guideline levels or a maximum limit for Cadmium content in fishery products for human consumption, the values found were compared to the maximum value permitted for striped weakfish's muscle meat by:

- UE - European Union - Regulation N° 1881/06: 0.20 – 1.0  $\mu\text{g/g}$  muscle meat, based on wet weight.
- FAO - United Nations Food and Agriculture Organization: 1  $\mu\text{g/g}$  muscle meat, based on wet weight.
- WHO – World Health Organization: 1.5  $\mu\text{g/g}$  muscle meat, based on wet weight.
- CAA - Código Alimentario Argentino - Act No 18284: Not regulated.

The final considerations and remarks in this document result from the processing and evaluation of these results.

### DESCRIPTION OF THE STUDY AREA

The Bahía Blanca Estuary System, which has an extension of approximately 80 km NW-SE, comprises an area of around 2,300 km<sup>2</sup> including a channel with a length of 68 km as well as a number of islands, low marshes and intertidal plains divided by tidal channels (Ángeles, 2001). The tidal pattern is semidiurnal with mean amplitude of 2 - 3.3 m (Perillo et al., 2001, Pícolo et al., 1990).

Within the estuary, specific sectors are determined by the distribution of its islands, the extension of its plains, the presence of salt flats and marshes, fresh-water inputs and geographical location (Melo et al., 2001).

The rivers and streams flowing into the inner sector of the estuary provide fresh-water input, which varies with rainfall levels thus determining local changes in salinity levels (Botté et al., 2007, Freije et al., 2004). Among the fresh-water tributaries, the Sauce Chico River and the Napostá Grande Stream (having 1,600 km<sup>2</sup> and 920 km<sup>2</sup> drainage basins, respectively) should be highlighted (Campuzano et al., 2008, Perillo et al., 2001). The watercourses tribute sediments which –together with those derived from the erosion of tidal plains and the channel sandbanks, - are redistributed into the system (Bokuniewicz, 1995). This inner sector further comprises Salitral de la Vidriera, which stretches north-westwards into the continent, and includes lagoons and salt flats (Freije & Marcovecchio, 2004)<sup>[2]</sup>.

On the other hand, the external area of the estuary shows a significantly more pronounced marine influence.

A number of localities lay in the proximity of the head of the estuary, on the northern coast: General Cerri, Ingeniero White, Bahía Blanca, the Nature Reserve, the Municipal Beach, the Petrochemical Hub (136 ha, 106 industrial sites and still growing), and the Port Area which comprises Cuatreros, Galván and Ingeniero White Ports, the two latter being of national importance due to their draft, production and export volumes. The Navy Base Puerto Belgrano, Punta Alta City, Rosales Port, the Marine's Base Baterias and the Multi-purpose National Reserve (a series of islands and islets), are located in the outermost zone on the same margin.

Historically, the variety of activities conducted in the area has resulted in the estuary receiving an input of exogenous substances from sewage and industrial discharges, leachate from wastelands, agrochemicals and other type originated from port activities. These substances are incorporated to the estuary - whether directly or indirectly- through its fresh-water tributaries both natural and artificial (see Fig. 5):

- The Saladillo de García Stream: this is regarded as a superficial receiving water body. It also receives discharges from Transportadora Gas del Sur, Villa Olga Coldhouse and the Sewage Treatment Plant of the Third Basin (Depuradora Tercera Cuenca).

- Point source discharges made by a number of companies: Petrobrás, Mega, Profertil, Piedra Buena Powerstation, Cargill (since 2005; before that, they used to discharge into the sewage system) and Dow Chemical - PBB Polisor (LLDPE-Barcaza Plant; discontinuous discharges).
- Point source discharges from the Sewage Treatment Plants (Depuradora Bahía Blanca) which, in turn, receive discharges from Air Liquide and other type of industries located in the Industrial Park and the urban area.
- Petrochemical Hub Collector Canal (Canal P. Petroquímico): it receives effluents from Solvay Indupa (unified discharge point chlorine/caustic soda, PVC and VCM) and PBB Polisor (unified discharge from LHC I - LHC II cracking plants and discharges from EPE, LDPE and HDPE Plants).
- The Napostá Stream, which runs from north to south across the city and flows out into the estuary.
- The artificial Maldonado Canal, a derivation of Arroyo Napostá, which collects storm drains and receives domestic and illegal industrial effluents.
- The Sauce Chico River, which flows into the estuary after crossing an area of small farms in General Cerri.

It should be remarked that the former city waste dump Belisario Roldán (Ex Basural B. Roldán) is located on the estuary's flood plains because, even when this site is not operating at present, its sanitation has not been performed and its leachate turns into diffuse discharges.

**Fig. 5: Natural and anthropic discharges into the Bahía Blanca Estuary**



### THEORETICAL FRAMEWORK

After having researched the bibliography available, it was regarded as necessary to transcribe part of the information contained in "Analysis of trade flow and revision of rational environmental management practices concerning products containing cadmium, lead and mercury in Latin America and the Caribbean"<sup>[4]</sup> as it briefly provides basic information about Cd, should be included in this work in order to identify the source of origin of this metal found in the Bahía Blanca Estuary.

### Cadmium

Cadmium is a bright white metal, ductile, malleable and corrosion resistant. Its density is 8.64 g/cm<sup>3</sup>, and its vapors are 3.88 times heavier than air. Its vapor pressure is relatively high, therefore it passes easily into the vapor state and in this state is rapidly oxidized producing cadmium oxide, which remains in the air. When in the atmosphere there are reactive gases or vapors such as sulfur dioxide or carbon, cadmium oxide reacts with these gases to produce carbonate, sulfite, hydroxide, sulfate and chloride respectively.

Because of its similarity to the essential metal zinc, plants absorb cadmium from irrigation water, therefore, the use of phosphatized-based fertilizers containing cadmium in ionic form as a natural contaminant or its presence in the beds of rivers and seas contaminated by industrial discharges increases levels of the element in soil and therefore in the plants. Bioavailable cadmium concentration increases when the pH of soil decreases, therefore a further undesirable effect of acid rain is the increasing levels of cadmium in food (Osorio Saldivar, 1997).<sup>[4]</sup>

In its elemental form it is a soft metal, silvery white color that is easy to cut with a knife. It belongs to Group II B of the Periodic Table; it is present in nature as complex oxides, sulfides and carbonates of zinc, lead and copper and is not recovered as the main product of the mines, but is a byproduct of the extraction of other non-ferrous metals, mainly zinc ores. About 18 percent of the world consumption comes from recycling. The main uses of refined cadmium are: batteries (Ni-Cd batteries), pigments for plastics, ceramics and enamels, stabilizers for plastics, iron and steel plates, as well as an alloy for lead, copper and tin.

### **Main effects of cadmium on health**

Emissions of cadmium to the environment occur in three major environmental media (air, water and soil) and are highly variable; however, its life in the atmosphere is relatively short compared with other substances such as mercury. In the environment, cadmium is toxic to plants, animals and microorganisms. Cadmium is a persistent element; it cannot be decomposed into less toxic substances in the environment. The degree of bioavailability and potential effects depend on the form of cadmium. Cadmium mainly bioaccumulates in the kidneys and liver of vertebrates, aquatic invertebrates and algae.

Cadmium is a non-essential element that is toxic to humans and primarily affects the kidneys and skeleton; cadmium is also a carcinogen by inhalation and accumulates in the bones. Excess exposure to cadmium causes adverse health effects in humans and the main sources of human exposure to cadmium include air pollution, occupational exposure and cigarette smoke.

The main adverse effects of cadmium include kidney damage and pulmonary emphysema, the population most at risk are women with nutritional deficiencies or low iron, also people with kidney disease, fetuses and infants with low iron content in body reserves. The World Health Organization (WHO) has established a Provisional Tolerable Weekly Intake (PTWI) for cadmium in 7 µg/kg of body weight. The kidney is considered critical to control the toxicity of cadmium in humans; the main critical effect is the increased protein excretion in the urine as a result of proximal tubular cell damage and the severity of the effect depends on the duration and magnitude of exposure. Bone alterations are another critical effect of chronic exposure to elevated cadmium levels (UNITED NATIONS ENVIRONMENT PROGRAMME, 2008).<sup>[4]</sup>

Cadmium is a human carcinogen through inhalation, epidemiological data from the workplace confirm lungs as the organs affected; cadmium is not considered a carcinogen by ingestion. It is stored in the liver and kidneys, the excretion is slow, with a very long (decades) average life in the human body; cadmium is stored in more tissues as age increases.

Tobacco is a significant source of cadmium uptake in smokers and may also affect nonsmokers through passive exposure to secondhand smoke. People living near industrial areas and other sources that release cadmium may be exposed to higher levels of cadmium.

Cadmium is found in different kinds of foods, but the crops (particularly irrigated rice) generally represent the bulk of the intake, vegetarians and groups of high cereal consumption may have increased exposure compared with general population.

People with a high consumption of shellfish and organ meat of marine animals can have a particularly high consumption of cadmium.

Cadmium in crops is due to the uptake of cadmium from soil and the absorption rate is influenced by factors such as soil pH, salinity, humus content, vegetal species and varieties and the presence of other elements (e.g. zinc).

### **Main effects of cadmium on the environment**

The life of cadmium in the atmosphere is relatively short compared with substances such as mercury or persistent organic pollutants, most cadmium in the air is of nominal size as particulate matter (less than 1 micron) (EC, 2001). Cadmium is emitted into the atmosphere from anthropogenic sources such as elemental cadmium and/or cadmium oxide, some sources are emitted as sulfur or chloride (EC, 2001), and atmospheric combustion sources, due to gaseous elemental cadmium, but as it cools, cadmium binds rapidly to particles (UNITED NATIONS ENVIRONMENT PROGRAMME, 2008).<sup>[4]</sup>

Due to condensation of water vapor and other gases in the atmosphere, particle size increases due to the interaction between particles of different sizes. Cadmium and many of its compounds have relatively low vapor pressure, and therefore are not particularly volatile. However, high heat processes can volatilize cadmium, and output in the form of vapor, where vapor quickly condenses cadmium into aerosols as they enter the atmosphere (EC, 2001). Therefore, most cadmium in the atmosphere is in the form of particles, which can be very small when produced in combustion processes (ATSDR, 1999). According to a study on the presence of cadmium aerosol types in the atmosphere, based on measured size distributions and vapor pressure data, cadmium chloride, cadmium sulfate and cadmium oxide appear to be the predominant species in ambient air (EC, 2001) and the atmospheric transport mechanism is governed by the transport mechanism of aerosols (UNITED NATIONS ENVIRONMENT PROGRAMME, 2008).<sup>[4]</sup>

The mobility of cadmium in aquatic environments is enhanced by low pH, low hardness, low suspended matter, and redox potential of high and low salinity (Government of Canada, 1994). In natural water, bioavailability of cadmium is reduced by absorption of suspended particles and water is responsible for biologically controlling the highest levels of cadmium (ECB, 2005). In aquatic systems, cadmium is more easily absorbed by organisms directly from water in its free ionic form (AMAP, 1998).

The chemistry of cadmium in the soil environment is largely controlled by pH. The U.S. EPA (1999) reported that under acidic

conditions, cadmium solutions increase, and there is very little absorption of cadmium from soil colloids, hydrous oxides and organic matter specific to the site.

For pH values above 6 units, cadmium is absorbed by the soil solid phase or is precipitated and concentrated by cadmium solutions which are considerably reduced. Cadmium forms soluble complexes with inorganic and organic ligands, in particular chloride ions. The formation of these complexes increases with the mobility of cadmium in soils (McLean and Bledsoe, 1992, quoted by the U.S. EPA, 1999). Adriano et al., (2005) claim that in general, chloride can form a soluble complex with  $Cd^{2+}$  and  $CdCl^+$ , thus decreasing the adsorption of  $Cd^{2+}$  in soil particles.

### **Sources of cadmium and supply of products containing cadmium**

Cadmium is widely distributed in the earth's crust at an average concentration of 0.1 mg/kg. In sedimentary rocks, the concentrations are higher; environmental conditions, such as erosion, transport large quantities of cadmium to oceans where the content of this metal is about 0.1 ug/kg; ocean sediments near areas of high human activity may contain cadmium at very high concentrations associated with biological waste discharge; volcanic activity is the largest natural source of cadmium release into the atmosphere. It is estimated that the total annual increment due to this source is 100 to 500 tonnes; underground volcanoes also release cadmium to the environment but it is not yet quantified the effect of this process (Osorio Saldivar, 1997).<sup>[4]</sup>

Mining activities of non-ferrous metals are the main source of cadmium released to the aquatic environment, pollution may come from the water of mine drainage, waste water of minerals processing, spill of deposits, waste from mineral processing, rainwater that falls in the general area of the mine and ore lighter particles that pass through the sieves in concentration and purification operations. The wet deposition of cadmium in fresh and salt water causes a very large increase of the metal globally (...)

Cadmium content in fertilizers is highly variable and depends on the origin of the rock. It was estimated that the fertilizer from West Africa contain between 160 and 225 grams of cadmium per ton of phosphorus pentoxide, while the concentration of cadmium fertilizers from the southeastern United States is 36 g/ton. There is a 1% increase in the level of cadmium in surface soil where U.S. fertilizers are applied. Although the rate of increase is relatively small, it has shown that the continuous application of fertilizers containing cadmium caused a discernible increase in metal concentration of soil where plants join the food chain, as it happened in Japan with the "itai-itai" case (Osorio Saldivar, 1997).<sup>[4]</sup>

There are two main sources of production of cadmium, the primary source is from the recovery of smelting zinc and cadmium, the secondary source is from the recycling of nickel-cadmium batteries, copper-cadmium alloys, iron and others, as well as the recycling of iron and cadmium powders (...)

Cadmium is released by several natural and anthropogenic sources to the atmosphere, aquatic environments (freshwater and saltwater) and terrestrial environments, including flows between these systems. Cadmium released into the atmosphere can be deposited to land and water, and eventually eliminated in the aquatic environment and over the long-term it is eliminated in deep-sea sediments and to some extent in controlled landfills, in cases where, due to their physical-chemical

properties, cadmium is immobilized and remains undisturbed by anthropogenic or natural activity (climatic and geological) (Osorio Saldivar, 1997).<sup>[4]</sup>

Cadmium, once emitted to the atmosphere, is subject to atmospheric transport in the form of particulate cadmium. Its transport in the atmosphere is governed by aerosols (particles) and transport mechanisms: cadmium in the atmosphere can be transported at a local, national, regional and intercontinental scale, depending on several factors, including natural and anthropogenic sources, particle size, the height of emission points and meteorology. Cadmium spends relatively short amount of time in the atmosphere (days or weeks); however, this metal is transported over long distances local, national, regional and even intercontinental.

Other bibliography consulted indicates industrial boilers, elemental lead smelters, manufacture of portland cement, oil refining and hazardous waste incinerators as air pollutants containing cadmium.<sup>[5]</sup>

The European Commission mention that most of the compounds of lead and cadmium, including those used in PVC are dangerous for the environment and pose a risk of cumulative effects. The two metals are persistent and some of the compounds are accumulate in certain organisms.

### **Products containing cadmium**

Cadmium coating and electroplating is applicable to certain metals to prevent corrosion. The amount of cadmium consumed for coatings and electroplating worldwide has declined in recent years; several cadmium-plated parts were removed from motor vehicles. However, cadmium coatings are still used by the aerospace industry and military for some critical applications where the replacement of the coating may endanger safety. Cadmium is commonly used for fasteners, plates in aircraft landing devices and parachutes, due to a combination of properties not seen in other anti-corrosive coatings (US Geological Survey, 2008).<sup>[4]</sup>

Reactions within a NiCd rechargeable battery are produced between nickel compounds in the positive electrode and cadmium

compounds in the negative electrode. NiCd batteries have a high number of charge-discharge cycles, a high rate of energy discharge and wide operating temperature range. For their duration of energy they are widely used in portable electronic products (especially power tools) and to provide backup power for industrial and electrical systems in aircrafts (US Geological Survey, 2008).<sup>[4]</sup>

The use of NiCd battery in consumer electronics was thought to be declining due in part to the preference for the Rechargeable chemical battery of Lithium ion (Li-ion), which has replaced the NiCd batteries for cell phones and laptops due to their high energy density. However, NiCd batteries have a cost advantage compared to other chemical batteries, so they are still used in cheaper consumer electronic devices (Minerals Yearbook US. Department of the Interior US Geological Survey, 2008).<sup>[4]</sup>

Another use given to NiCd batteries at the industrial level is to store energy produced by solar or wind energy (solar cells and wind farms). Storing energy in a battery mass system is necessary to regulate the load, which is later sent during periods of high electricity demand. Chemical batteries of NiCd are the best (favorite) for this use because of its stability in very harsh weather environments and high sea (US Geological Survey, 2008).<sup>[4]</sup>

The inorganic cadmium pigment is based on cadmium sulfide, which is golden yellow in color; the color spectrum of cadmium pigments can change from bright yellow to brown. Cadmium pigments are mainly used to color plastics processed at higher temperatures; the pigments are capable of withstanding high temperatures without degrading (US Geological Survey, 2008).<sup>[4]</sup>

The main compound used is cadmium telluride (CdTe), a thin flexible film of solar cells which is an alternative to crystalline silicon and practical for commercial applications on the roof and large-scale ground-mounted supply systems. CdTe solar cells were considered safe and an environmentally friendly application for cadmium because cadmium content is maintained in the structure and is recyclable. CdTe cells contain an average of 7 grams (g) of cadmium per square meter. This is equivalent to 70 g of cadmium per kilowatt of electricity produced, assuming that the cells are 10% efficient (US Geological Survey, 2008).<sup>[4]</sup>

Summarizing, the products that contain Cd come from electric storage batteries or Ni-Cd cordless power tools, wireless radio communication devices, emergency lighting, cordless phones, walkie –talkies: appliances for household and personal care (toothbrushes, shavers, cutters, etc.), sun lamps, mobile phone (cellulars), portable computers, video cassette recording equipment, specialized devices of measurement techniques (laboratory, medical, etc.), solar cells and wind farms, electroplating products, alloys of low melting point, rectifiers and accumulators coatings, welding pipes, cans of paint pigments and preparations based on cadmium compounds (fluorescent paints), antioxidants and other compounds stabilized cadmium-based stabilizers for rubber or plastics, phosphate fertilizer, animal manure applied to food crops, mineral or chemical fertilizers and phosphatic materials, ash and residues (other than the manufacture of iron and steel) containing antimony, beryllium, cadmium, chromium and mixtures thereof, switches (digital logic device networking of computers), toners, cartridges, printer ink, monitors, televisions (components fluorescent of black and white TV and activators to produce blue and green in color TV tubes), old PVC cables, power lines, fuses for automated systems, fire alarms and electrical fuses, photographic film, dye wastes and printing, glass, among other things.

### **International Environmental Agreements and Proposals Mentioning Cadmium:**

- The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal (1992).
- The Rotterdam Convention, applicable to certain pesticides and hazardous chemicals in international trade (2004).
- The Aarhus Protocol on Heavy Metals (2003).
- Strategic Approach to International Management of Chemicals (2006).

### **Argentine Environmental Legislation mentioning Cadmium (National level and Buenos Aires Province)**<sup>[6]</sup>

Main regulations concerning products which contain Cadmium are:

- National Act No 21947/79, *Agreement on the prevention of sea pollution caused by discharges of waste and other substances*. It comprises: international agreements, water pollution, waste discharges, and waste discharges permits. This Act regards cadmium –among other- as a hazardous substance, which requires controls.
- National Act No 23922/91, *Approval of The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal*. It covers: International treaties, Basel Convention, environmental protection, hazardous waste, hazardous waste transportation, illegal traffic in waste, international border control, waste treatment. This Act approved *The Basel Convention on the Control of Transboundary Movements of Hazardous Wastes and their Disposal*, which classifies both cadmium and elements containing cadmium as hazardous substances.
- National Act No 24051/92, *Hazardous Waste* and Regulatory Decree No 831/93. They cover: hazardous waste, hazardous waste producers and operator's record, - hazardous waste treatment plants - environmental certificate – hazardous waste transport – pathological waste – contamination incidents - risk or damage due to defect – extra contractual liability – abandoned things – third party opposition – adulteration of fresh water. Cd is included in this Act as a hazardous substance.
- National Act No 26184/06, *Portable Electric Power Act*. It covers: electric power - portable electric power – primary batteries – power imports. This Act specifically bans manufacturing, assembling, trading or importing primary batteries containing 0.015% of Cd in weight throughout the whole national territory.
- Buenos Aires Province Act No 5965/58, *Protection of water supply sources, watercourses, water receiving bodies and the*

atmosphere. It covers: waters – underground waters – surface waters – water policies – water pollution – water treatment. Specifically, Regulatory Decree No 336/03 establishes cadmium discharge values for effluents in view of its receiving body.

- Buenos Aires Province Act No 11720/95, *Handling, storage and transportation of special waste within the territory of the Buenos Aires Province Act*. It covers: Environmental Law – industrial waste- waste treatment. In Annex A, cadmium and its compounds are included on the list of waste requiring management controls.
- Buenos Aires Province Act No No 13592 /06, *Integral Management of Urban Solid Waste Act*. Regulated by Decree No 1215/10. This act establishes procedures for urban solid waste management in accordance with National Act No 25916/04, *Minimum Budgeting for Environmental Protection concerning Domestic waste Integral Management*. The guidelines, obligations and responsibilities for USW management are set: eradication, treatment and prevention of the establishment of new locations.
- Buenos Aires Province Act No 14321/11. This Act establishes a set of rules, obligations and responsibilities for the sustainable management of waste generated from electric and electronic appliances in the Province of Buenos Aires, in concordance with the Basil Convention, ratified by National Act No 23992 and Provincial Acts 11720 (Special Waste) and 13592 (Urban Solid Waste).

Even though the last two Acts do not explicitly include cadmium, they are relevant to the development of this study.

## RESULTS

After analyzing the results obtained from the various monitoring procedures, the following conclusions were reached:

### IADO's Studies on the Estuary

The information contained in this section results from the final reports of the Bahia Blanca Inner Estuary Environmental Quality Monitoring Program <sup>[2]</sup>, included in PIM 2009. <sup>[1]</sup>

The graphs in this paper showing the monitoring results of the estuary's waters and sediments corresponding to the last period reported were analyzed in order to identify the points with the most significant values, and to reach conclusions concerning the evolution of results over time. Annual mean values were compared to the values of the last four programs: 2002, 2005, 2007 and 2008.

As previously stated in Methods, due to the fact that there are no national, provincial or local regulations or guideline level values to be used as reference for the Estuary of Bahia Blanca, it was decided to use the NOAA guideline levels as a reference framework:

- ✓ Dissolved Cd in water: chronic exposure: 8.8 ppb – acute exposure: 40 ppb.
- ✓ Cd in superficial marine sediments: ERL: 1.2 ppm - ERM: 9.6 ppm.

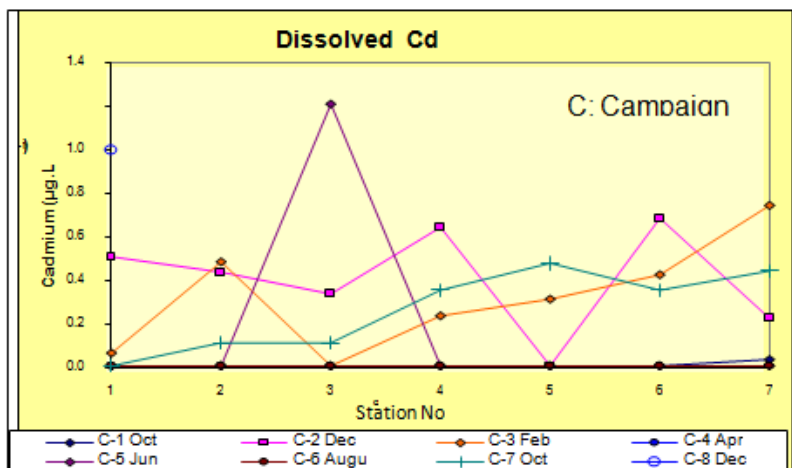
In addition, information on studies concerning the fish of the Estuary was included.

### • Surface Waters

Considering data for Cd dissolved in water for a period of 10 years, it can be stated that 100% of the corresponding historic values stay well under reference NOAA values and 95% of the historic values were under 0.51 ppb. Also, over the period 1999 – 2009, out of 244 determinations of dissolved Cd, 73% of non-detectable values were recorded. The highest value recorded was 1.79 ppb for a sample taken at E4 - Galván Port (Flammables Pier) in June/99. <sup>[1]</sup> This value is not included within the period of this study (2001-2011).

In particular, during the period 2006 - 2007, concentrations of Cd dissolved in the estuarine waters within the study area, reached levels of 0.69 ppb (December/06), 0.75 ppb (February/07), 1.21 ppb (June/07) and 0.48 ppb (October/07), being these values the highest for the last periods analyzed. As it can be seen in **Fig. 6**, the most significant values were detected at E3 - Ingeniero White and E6 - Discharge Maldonado Channel. <sup>[2]</sup> These locations are respectively located near the former sewage discharge of Ingeniero White and the former waste dump.

**Fig. 6: Distribution of cadmium dissolved in water**



More recently, during the period 2008-2009, a maximum value of 0.4 ppb was recorded for a sample taken in October/08 at E6 - Maldonado Channel Discharge.<sup>[1]</sup>

Even when the values obtained are below NOAA’s guideline levels, the report by IADO highlights that the detection of dissolved metals indicates their recent incorporation into the system; this phase is extremely ephemeral for metal compounds and quickly displaced to other system compartments (e.g., suspended particulate matter, sediments and organisms). Consequently, the already mentioned concentrations of Cd dissolved in water show present incorporation and, in turn, the existence of one or more sources introducing it into the system.<sup>[2]</sup>

• **In marine sediments**

Considering the data of Cd in superficial marine sediments, which comprises 10 years, 63% of the historic values of this parameter fell bellow the ERL reference guideline value and 100% of the historic values stayed well bellow the ERM guideline value (both established by NOAA).

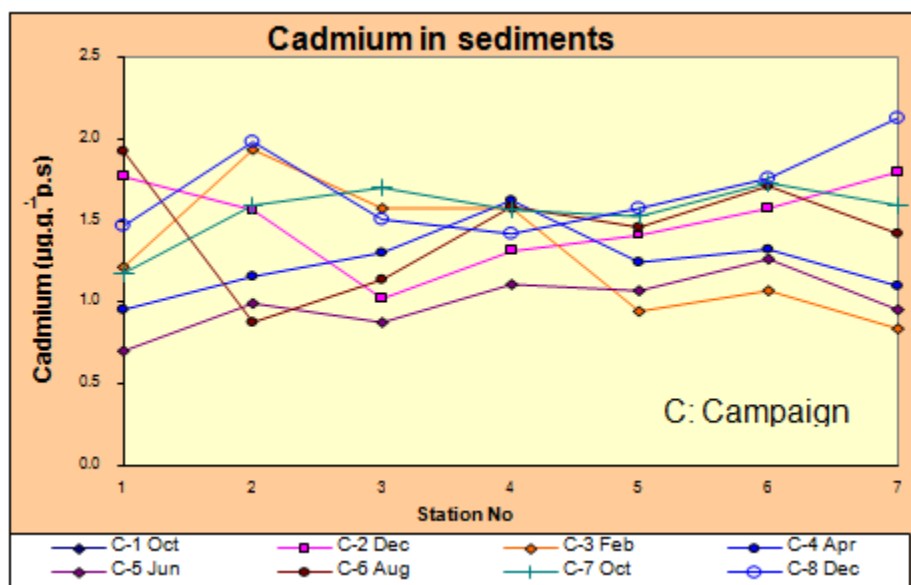
The highest values found in the decade of 1999-2009 were: 2.2 ppm (October/06) and 2.13 ppm (December/07), both in the samples taken at E7 - Cuatros Port; and 1.98 ppm (December/07) at E2 - Bahía Blanca Main Sewage Discharge.

Over the period 2008-2009, the highest recorded value was 1.94 ppm, in the sample taken in October/08 at E2 - Bahía Blanca Main Sewage Discharge<sup>[1]</sup>

On the other hand, the 2006-2007 analysis performed by IADO in order to detect Cd in superficial waters, showed a steady trend in the period with similar values at the various stations included and a slight increase (not significant from the point of view of statistics) towards the inner stations of the estuary, as seen in Fig. 7 .

The range of Cd in sediments values for the period was 0.70 – 2.12 ppm in dry weight vs. reported results for the period 2008-2009, which was 0,08-1,92 ppm.<sup>[2]</sup>

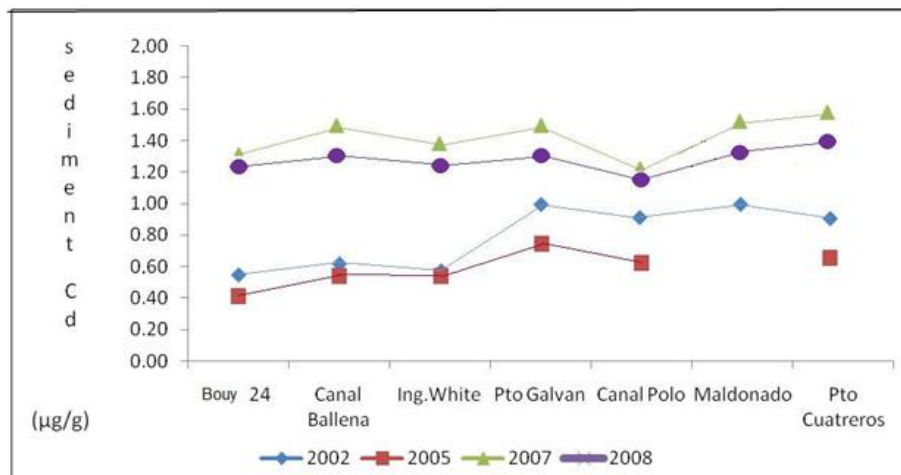
**Fig. 7: Distribution of Cadmium during the period 2006-2007 (IADO, 2008)<sup>[2]</sup>**



From the IADO report (2009)<sup>[2]</sup> on comparative distribution of Cd in surface sediments for the last four monitoring programs in the Estuary (Fig. 8), it can be concluded that, even when there is a slight decrease in values against the previous year, both are higher than the results for 2002 and 2005.

In addition, it can be seen that E2 - Bahía Blanca Main Sewage Discharge (Ballena Channel), E4 - Galván Port, E6 - Maldonado Channel Discharge and E7 - Cuatros Port showed the highest concentration of Cd in sediments for the monitored periods.

Fig. 8: Comparative distribution of Cd in surface sediments during monitoring 2002 -2008 (IADO, 2009)<sup>[2]</sup>



### • Fish

Values for Cd in tissue for striped weakfish (*Cynoscion guatucupa*) showed a sustained trend: the values in muscle meat were below the detection limit of the method implemented, up to 0.31 µg Cd/g in wet weight, while the values in liver varied from 0.01 to 3.11 µg Cd/g in wet weight. The values in muscle meat obtained in this study are similar to historic antecedents for the same species in the Bahía Blanca Estuary (Marcovecchio, 1988; Marcovecchio et al., 1988.a; 1988.b; IADO, 2000, 2002, 2004, 2006, 2008). However, those found in liver happen to be significantly higher and demand further detailed study.<sup>[2]</sup>

In this case, the trend observed does not allow to state that biological accumulation of Cd in muscle meat for striped weakfish in the Estuary but there seems to be evidence of this process in the liver of the specimens that were studied. A probable explanation to this finding could be that the Cd values in muscle (which were very low) are below the threshold that triggers bioaccumulation, while those values in liver significantly surpass such threshold. This is the first time that Cd bioaccumulation is detected in this species within the Estuary.<sup>[2]</sup>

Anomalous results of cadmium and lead for two samples of striped weakfish initiated the technical reports made by CTE, which were referred to Servicio Nacional de Sanidad (SENASA) by the Undersecretariat of Municipal Management. SENASA, in turn, opened up an administrative record to communicate the results for these heavy metals.<sup>[1]</sup>

### CGPBB's Studies on the Estuary

The CGPBB holds more than 35 monitoring stations at the Estuary, some of them outside the scope of this study (e.g., Rosales Port, Belgrano Port, and Bouy 24, among others). To the purpose of this research, the 20 more representative stations were included. In these stations, Cd in water and sediments has been analyzed since 2001.

The selected stations were identified by their geographic coordinates, determined by means of a GPS and entered into a GIS. The resulting map can be seen at **Fig. 4**.

### • Surface Waters

Only 11.5 % out of 191 records of Cd dissolved in water for the Estuary showed measurable values while 9% exceeded the Acute Exposure Limit established by NOAA. The latter results correspond Terminal Bahía Blanca's Sites (up to 120 ppb); Fishermen's Basin (110 ppb); Ministro Carranza Wharf (up to 130 ppb) and sites of Galván Port (up to 120 ppb). **See Table N° 1**

It should be remarked that 9% of the samples showing results above the Acute Exposure Limit were taken between 2003 and 2004. Among these results, the concentrations at Ministro Carranza Wharf should be noticed. This point coincides with the sewage discharge from Ingeniero White Sewage Treatment Plant, which has derived its effluents to the Bahía Blanca Sewage Main Treatment Plant since 2009. Besides, the high concentration levels detected in Galván Port belong to mooring sites 2/3 in the proximity of DOW - PBB – Polisur floating PVC plant and Site 5, where phosphate fertilizers are occasionally unloaded.

### • Marine Sediments

Considering the 233 Cd sediments determinations made in Bahía Blanca, 45% showed detectable values and 23% stayed above the 1.2

ppm ERL limit established by NOAA. No result was found above the 9.6 ppm ERM.

At Site 5 in Galván Port, values above ERL were found 8 times, reaching a maximum of 3.6 ppm. At Ministro Carranza Wharf Values went over ERL in 2 cases, reaching a maximum of 3.4 ppm. (See Table N° 2).

In 2011, sediment sampling started in the area near the former waste dump Belisario Roldán, at a point named Almirante Brown Club. The value obtained was 2.3 ppm and it is still under validation.

### **Studies on industrial discharges at the Petrochemical Hub and Port Area**

Taking the 322 results for Cd analysis for the ten-year monitoring of industrial liquid effluents at the Petrochemical Hub and Port Area, which was conducted by CTE, no value was found above the maximum permitted by the regulations in force: 0.1 mg/l for discharge into surface waterbodies (this is how the Bahía Blanca Estuary is classified) and 0.5 mg/l for discharge to sewage collector. On the whole, with only a few exceptions, values were always reported to be below quantification limit : <0.005 mg/l.

PIM 2010<sup>[1]</sup> reported that analyses researching Cd that were started in 2007 are still on course. In 2010, no presence of the metal was detected and every determination fell below the quantification limit.

All the results are available and can be consulted in the correspondin PIM <sup>[1]</sup>. However, the summary of the results can be seen in:

- **Table N° 3:** Effluents industrial discharges to Superficial Course (Bahía Blanca Estuary)
- **Table N° 4:** Effluents industrial discharges to Sewage Collector
- **Table N° 5:** Effluents discharge from Industrial Park into Sewage Collector

Regarding effluent discharges from the Industrial Park to the sewage collector, as from 2009 and because of the detection of some heavy metals such as cadmium and mercury resulting from the monitoring performed in the area by IADO, a series of screening samplings were taken using an inspection chamber located downstream at the Industrial Park.<sup>[1]</sup>

It should be taken into account that around 106 companies discharge into the Park's collector, among other: accumulators industries, PVC dyeing, cleaning products, all whose effluents may contain Cd. Even when the screening threw results below the 0.005 mg/l limit, periodical monitoring is suggested.

The assessment of these results lead to posing the question whether it would be necessary to continue investing efforts and budget resources in order to monitor this parameter in every industrial effluent just to conclude that results are always below the 0.005 mg/l detection limit and well under the maximum permitted for discharge by the regulations in force.

Probably, it may be more convenient to implement a procedure to follow changes in the materials processed by each industry in order to focus efforts on those which, according to what is stated by the theoretical framework, may generate effluents containing Cd. Additionally, detection limits should be lowered in order to determine whether this parameter is detected and to verify its trend, if that were the case.

### **Studies on the Petrochemical Hub Collecting Canal**

This canal discharges effluents from Dow Chemical and Solvay Indupa's Plants.No values above the quantification limit of 0.005 mg/l<sup>[1]</sup> were recorded for Cd dissolved in water.

Unlikewise, the results for sediment sampling in 2009 ranged between 2.6 and 2.9 ppm, that is above NOAA's ERL (1.2 ppm).<sup>[1]</sup>

Sediments leachate analysis threw results well under the reference value established by Decree No 891/92 (National Act No 24051/92).<sup>[1]</sup>

### **Studies concerning sewage discharges**

Results from the analyses corresponding to the two Sewage Treatment Plants are scarce. Although monitoring started in 2011, values are being validated and are not available. The few data provided by CTE indicates that the values for Cd in water stay below the maximum established by the legislation in force.

No results were obtained from the analyses made to the sediments in these dicharges. However, as it can be seen from **Fig. 7 and 8** showing the distribution of Cd concentrations in sediments at E2-Bahía Blanca Main Sewage Discharge (Canal Ballena), a sustained trend for Cd can be appreciated in the campaigns conducted by IADO.

For this reason, it should be required to solve the information void (whether due to lack of existence or availability) concerning the

monitoring of the discharges from both treatment plants, in order to discard the possibility that urban effluents may contain Cd and to establish controls on the industries located in the urban area which discharge into the collecting network and may generate Cd in effluents.

**Study on the former waste dump Belisario Roldán located on the flood plain of the Estuary**

As the leachate from the former waste dump is diffuse, not from a point source, the monitoring references for this source are the studies concerning surface waters and sediments conducted by IADO at E6 - Maldonado Channel. It has already been mentioned that this monitoring point shows a steady trend as far as values of Cd dissolved in water and surface sediments are concerned (See Fig. 6 - 8).

It should be warned again that the presence of this dissolved metal at the time of being monitored indicates its recent incorporation to the system.

This former wasteland was operative over more than 30 years. Although it was closed down in 1992, illegal dumping still occurs. Leachate is permanent and aided by constant floodings, which may constitute a permanent diffuse discharge into the system. Due to this study, the CGPBB has incorporated a new monitoring point to that area, called Almirante Brown Club (See Fig. 4), in order to confirm the results found by IADO and CTE. To the presentation date of this document, such results are not available.

Table No 1: Synthesis Monitoring Cd dissolved in water in the Bahía Blanca Estuary – CGPBB

NOAA's Limit Chronic Exposure < 8.8 µg/l (ppb) – NOAA's Limit Acute Exposure < 40 µg/l (ppb)

Monitored Sector	Monitoring Points	Monitoring Period		No Cd Records	Evaluation Cd Results	Times above Limit	Maximum ug/l (ppb)	Dates for Maximum
		From	Until					
Main Canal	Main Sew age B. Blanca	19/02/2009	30/09/2011	3	Values below quantification limit <5 µg/l	0	**	**
Main Canal	Bouy 32	07/01/2009	06/01/2010	3	Values below quantification limit <5 µg/l	0	**	**
Pedrabuena Wharf	Toepfer	03/07/2008	30/09/2011	5	Values below detection limit. Variable QL between <5 and <1 µg/l	0	**	**
TBB Wharf	Sites 5, 6, 7, 8 and 9	24/01/2003	30/09/2011	44	Out of 44 monitoring, 7 threw measurable values. QL between <1 and <10 µg/l	5	120	07/01/2004
Cargill Pier		12/04/2007	20/05/2011	5	Values below detection limit. Variable QL between <5 and <1 µg/l	0	**	**
Fishermen's Basin		15/12/2003	11/04/2008	6	Out of 6 monitoring, 1 valor medible. Variable QL between <1 and <5 µg/l	0	110	15/12/2003
M. Carranza Wharf		07/01/2003	30/09/2011	47	Out of 47 monitoring, 5 threw measurable values. Variable QL between <1 and <10 µg/l	3	130	07/01/2004
Multipurpose Wharf		11/09/2007	20/05/2011	2	Values below quantification limit <1 µg/l	0	**	**
Profertil Wharf		30/09/2011	30/09/2011	1	Values below quantification limit <5 µg/l	0	**	**
Mega Pier		11/04/2008	20/05/2011	5	Values below detection limit. Variable QL between <5 and <1 µg/l	0	**	**
Dreyfus Pier		20/11/2008	20/05/2011	5	Values below detection limit. Variable QL between <5 and <1 µg/l	0	**	**
Galván Port	Turning site	12/04/2007	20/05/2011	8	Values below detection limit. Variable QL between <5 and <1 µg/l	0	**	**
Galván Port	Sites 5/6/7/8	24/01/2003	30/09/2011	34	Out of 34 monitoring, 5 threw measurable values. Variable QL between <10 and <1 µg/l	0	108	27/11/2003
Galván Port	Site 2/3	07/01/2003	01/04/2010	15	Out of 15 monitoring, 4 threw measurable values. Variable QL between <10 and <1 µg/l	3	120	07/01/2004
Flammable Cargo Piers	Pier 1 and 2	06/01/2010	30/09/2011	4	Values below detection limit. Variable QL between <5 and <1 µg/l	0	**	**
End Confluence Canal	SO2 Cerri	30/09/2011	30/09/2011	1	Values below quantification limit <5 µg/l	0	**	**
End Confluence Canal	SO6 Cerri	30/09/2011	30/09/2011	1	Values below quantification limit <5 µg/l	0	**	**
End Confluence Canal	SO7 Cerri	30/09/2011	30/09/2011	1	Values below quantification limit <5 µg/l	0	**	**
Cuaterros Port		30/09/2011	30/09/2011	1	Values below quantification limit <5 µg/l	0	**	**
<b>TOTAL RECORDS</b>				<b>191</b>	<b>22 Values above quantification limit</b>	<b>11</b>		

Table No 2: Synthesis Monitoring Cd marine sediments in the Bahía Blanca Estuary – CGPBB

NOAA's Limit: Effects Range Low – ERL: 1.2 µg/g (ppm); Effects Range Median – ERM: 9.6 µg/g (ppm)

Monitored Sector	Monitoring Points	Monitoring Period		No Cd Records	Cd Results Evaluation	Times above ERL	Maximum µg/g (ppm)	Dates for Maximum
		From	Until					
Main Canal	Main Sew age B. Blanca	07/01/2010	30/09/2011	5	Out of monitoring, 4 threw values above quantification limit. <0.1 µg/g	1	1.2	30/09/2011
Main Canal	Bo anda 32	12/04/2007	06/01/2010	5	Values below quantification limit <0.1 µg/g	0	**	**
Pedrabuena Wharf	Toepfer	01/04/2010	30/09/2011	6	Out of 6 monitoring, 4 threw Values above quantification limit. <0.1 µg/g	4	3.1	20/05/2011
TBB Wharf	Sites 5, 6, 7, 8 and 9	17/05/2001	30/09/2011	46	Out of 46 monitoring, 14 threw measurable values. Variable QL between <0.5 and 0.1 µg/g	8	3.3	20/05/2011
Cargill Pier		30/11/2001	20/05/2011	7	Out of 7 monitoring, 1 measurable value. QL. <0.5 and 0.1 µg/g	1	3.1	20/05/2011
Fishermen's Basin		10/10/2000	11/04/2008	11	Out of 11 monitoring, 7 threw values above below quantification limit. Variable Limits <0.5 and 0.1 µg/g	2	2.35	10/10/2000
M. Carranza Wharf		10/10/2000	30/09/2011	65	Out of 65 monitoring, 40 threw measurable values. QL between <0.5 and 0.1 µg/g	12	3.4	20/05/2011
Multipurpose Wharf		30/11/2001	20/05/2011	3	Out of 3 monitoring, 1 measurable value. Variable QL between <0.5 and <0.1 µg/g	1	1.9	20/05/2011
Profertil Wharf		30/11/2001	30/09/2011	2	Out of 2 monitoring, 1 value above quantification limit <0.5 µg/g	1	2.5	30/09/2011
Mega Pier		30/11/2001	20/05/2011	7	Out of 7 monitoring, 1 measurable value. Variable QL between <0.5 and <0.1 µg/g	1	3.4	20/05/2011
Dreyfus Pier		20/11/2008	20/05/2011	6	Out of 6 monitoring, 2 threw measurable values. QL between <0.5 and <0.1 µg/g	2	3.1	20/05/2011
Galván Port	Turning site	05/06/2007	20/05/2011	9	Out of 9 monitoring, 2 threw values above QL <0.1 µg/g	2	2.7	20/05/2011
Galván Port	Sites 5/6/7/8	17/05/2001	30/09/2011	36	Out of 36 monitoring, 18 threw above QL <0.1 µg/g	8	3.6	20/05/2011
Galván Port	Sites 2/3	17/05/2001	20/05/2011	14	Out of 14 monitoring, 5 threw measurable values. Variable QL between <0.5 and <0.1 µg/g	2	1.9	20/05/2011
Flammable Cargo Piers	Pier 1 and 2	06/01/2010	30/09/2011	4	Out of 4 monitoring, 3 threw values above quantification limit <0.1 µg/g	3	3.4	20/05/2011
Petrobras	Loma Paraguaya Drainage Canal	04/06/2009	07/11/2011	3	Out of 3 monitoring, 1 value above quantification limit <0.1 µg/g	1	1.5	07/11/2011
End Confluence Canal	SO2 Cerri	30/09/2011	30/09/2011	1		1	1.8	30/09/2011
End Confluence Canal	SO6 Cerri	30/09/2011	30/09/2011	1		1	1.8	30/09/2011
End Confluence Canal	SO7 Cerri	30/09/2011	30/09/2011	1		1	1.5	30/09/2011
Cuaterros Port		30/09/2011	30/09/2011	1		1	1.9	30/09/2011
<b>TOTAL RECORDS</b>				<b>233</b>	<b>104 Values above quantification limit</b>	<b>53</b>		

Table No 3: Industrial Effluent Discharges Upper Course (Bahía Blanca Estuary) –Cadmium Maximum Limit permitted <0.1 mg/l

Discharges	Monitoring Period		No Cd Records	Cd Results Evaluation	Times above limit	Maximum mg/l	Dates for Maximum	pH
	From	Until						
CARGILL	24/01/2008	17/12/2010	19	Always below max permitted by legislation	0	<0.005	*	**
CIA MEGA	24/07/2007	24/11/2010	25	Always below max permitted by legislation	0	0.006	27/08/2007	8.9
PBB – EPE	07/08/2007	19/02/2010	22	Always below max permitted by legislation	0	0.005	19/09/2007	8.1
							10/04/2007	8.5
							30/10/2007	8.7
							28/12/2007	8.8
PBB – HDPE	20/08/2007	10/12/2010	16	Always below max permitted by legislation	0	0.005	28/12/2007	7.9
PBB – LDPE	20/08/2007	18/11/2010	14	Always below max permitted by legislation	0	0.005	28/12/2007	8.1
PBB – LHCI	20/08/2007	03/12/2010	25	Always below max permitted by legislation	0	0.005	28/12/2007	7.3
PBB – LHC II	20/08/2007	03/12/2010	23	Always below max permitted by legislation	0	0.005	28/12/2007	9.7
PROFERTIL	05/10/2001	17/12/2010	32	Always below max permitted by legislation	0	0.067	26/12/2007	8.6
REFINERIA PETROBRAS	20/03/2002	29/11/2010	39	Always below max permitted by legislation	0	<0.005	*	***
SOLVA AND – INDUPA	04/04/2002	18/10/2010	49	Always below max permitted by legislation	0	0.007	07/01/2008	7.8
TERMOELECTRICA M6	24/01/2008	07/05/2010	14	Always below max permitted by legislation	0	<0.005	*	****
TERMOELECTRICA OLEO	29/12/2008	03/12/2010	7	Always below max permitted by legislation	0	<0.005	*	*****
TGS SA	17/10/2007	29/11/2010	17	Always below max permitted by legislation	0	<0.005	*	*****
<b>TOTAL RECORDS</b>			<b>302</b>	<b>All values always below max permitted</b>	<b>0</b>			

\*Monitoring results for the period threw the same results.  
 \*\*For the monitored period, pH varies between 7.5 and 10.3 - Under all pH conditions, Cd results were below detection limits  
 \*\*\*For the monitored period, pH varies between 6.8 and 9.3 - Under all pH conditions, Cd results were below detection limits  
 \*\*\*\*For the monitored period, pH varies between 7.8 and 8.9 - Under all pH conditions, Cd results were below detection limits  
 \*\*\*\*\*For the monitored period, pH varies between 7.5 and 8.8 - Under all pH conditions, Cd results were below detection limits  
 \*\*\*\*\*For the monitored period, pH varies between 6.7 and 10 - Under all pH conditions, Cd results were below detection limits

Table No 4: Discharges from Industrial Park's effluents to Sewage Collector – Cd maximum limit permitted <0.5 mg/l

Discharges	Monitoring Period		Cd Records	Cd results Evaluation	Times above Limit	Maximum mg/l	Dates for Maximum	pH
	From	Until						
AIR LIQUIDE	22/08/2007	10/11/2010	20	Always below max permitted by legislation	0	0.0035	22/08/2007	*****
<b>TOTAL RECORDS</b>			<b>20</b>	<b>All values always under max permitted</b>	<b>0</b>			

\*\*\*\*\*For the monitored period, pH varies between 6.8 and 9.4 - Under all pH conditions, Cd results were below detection limits

Table No 5: Discharges from Industrial Park's effluents to Sewage Collector – Cd maximum limit permitted <0.5 mg/l

Discharges	Monitoring Period		Cd Records	Cd Results Evaluation	Times above Maximum	Maximum mg/l	Dates for Maximum
	From	Until					
INDUSTRIAL PARK (1)	13/04/2010	12/05/2010	6	Not detected (Source: CTE – PIM 2010)	0	Not detected	
<b>TOTAL RECORDS</b>			<b>6</b>		<b>0</b>		

(1) The Industrial Park does not belong to the Petrochemical Hub but is under the jurisdiction of Act. No 12530 (Buenos Aires Province)

### Studies on the Napostá Stream

The results for Cd dissolved in surface water were obtained from three monitoring points in the stream. Such results stayed below the method's quantification limit (0.005 mg/l). Regarding sediments, the results obtained at the two points selected, were also below the quantification limit (0.1 µg/g dry weight) and the values established by NOAA.

### Studies on the Sauce Chico River

The analysis performed in September/08 in the Sauce Chico River threw results for Cd dissolved in water below the detection limit of 0.005 mg/l.

Sampling in the river was carried out under regular flow conditions. [1]

### Volcanic Ashes

Considering that volcanic activity constitutes the most important natural source of emission of Cd into the atmosphere and that it can be transported by the wind to reach long distances, Cd input through the ashes of the Chaintén Volcano – which reached the Estuary in 2008- should not be discarded. Montenegro, R. (2011)<sup>[7]</sup> warned that samples of those ash particles contained traces of cobalt, copper, chromium, molybdenum, nickel, lead, cadmium and uranium. Research did not confirm the presence of cadmium in the ashes from the Puyehue Volcano.

## FINAL REMARKS

The assessment of the estuary's waters shows that the stations with the most significant values of Cd dissolved in surface waters are E3 (Ingeniero White) and E6 (Maldonado Channel), in both cases being these values below the guideline values for Chronic Exposure established by NOAA and with a sustained trend. As regards the analysis of sediments, the stations with results showing the highest concentration are E2 (Bahía Blanca Main Sewage Discharge), E4 (Galván Port) and E7 (Cuatrerros Port). A slight increase (statistically non-significant) was observed towards the Estuary's inner stations. It should be taken into account that presence of Cd in water implies its recent incorporation while in the case of sediments- due to their mobility- the presence of this metal is not necessarily related to the proximity of the source of origin.

Even when the dredging periods for the various sectors in the Estuary were analyzed, no correlation between the results for Cd dissolved in water and those of Cd in sediments could be verified for the period 2004 - 2010.

Regarding the stations showing the most significant values of Cd, it is considered appropriate to recommend the following course of action:

- Carrying out a follow-up of E3 (Ingeniero White) in relation with the sewage discharge of the Treatment Plant of Ingeniero White, whose effluents have been derived to the Main Sewage Treatment Plant of Bahía Blanca, in order to verify whether the values obtained come from the already mentioned sewage discharge. Likewise, monitoring of E2 (Main Sewage Discharge of Bahía Blanca) should be intensified in the future because, if the effluents derived are not properly treated, the trend for that station may become positive in the future.
- Intensifying monitoring at E6 (Maldonado Channel), which shows detectable Cd values in water. This station is located near the former dumpsite Belisario Roldan, located on the flood plain of the estuary and the site's leachate constitutes a diffuse source of pollution, which demands special follow-up.

Concerning fish, it should be advisable to continue researching on cadmium content which—even when below international standards—has shown abnormal results. In addition, it would be necessary to work on legislation establishing local standards.

The values of Cd in industrial liquid effluents resulting from the monitoring of the Petrochemical Hub and Port Area showed no Cd values above the maximum limit established for dumping by the legislation in force. In addition, these values are below the detection limit.

Further analysis of Cd dissolved in water made only to report results below the quantification limit seems not to be justified. The exception would be those industries which definitely use Cd in their process but, in these cases, the limit should be lowered so as to enable detection.

It should be recommended to allocate budgets and efforts to intensify sediments analysis because, as already mentioned, Cd mobility in water environments depends on pH, hardness, levels of suspended matter, redox potential and salinity. Besides, in natural water bodies its bioavailability is reduced through the absorption of suspended particles.

Based on the fact that bibliographical sources support the hypothesis that PVC industries and refineries are liable to become sources of Cd contamination through their effluents, further investigation on these sources should be advised. Also, considering that Cd stearate is used to improve the stability of PVC materials against light and atmospheric agents, effluent analysis should be intensified for those industries manufacturing PVC, mainly in the case of dyeing. Cd oxide is utilized as a catalizer for methane hydrogenation and synthesis as well as for the manufacturing of enamels and sintering.

Increasing controls are suggested for the effluents from companies involved in manufacturing and/or rectifying of accumulators located both at the Industrial Park and the urban area of Bahía Blanca.

Regarding the analysis in the Napostá Stream, it was concluded that this watercourse does not contribute Cd to the Estuary. Notwithstanding, as scarcity of records make them non-representative and considering the use of fertilizers in the upper basin of this stream, the results should be confirmed.

On surveying all the discharges into the estuary, no results could be obtained for some sources (e.g., Maldonado Canal, Napostá Relief Channel; upriver Saladillo de García, stormwater, etc.). It would be necessary to find whether there are results for Cd analyses performed by some organizations or to perform pertinent monitoring in order to determine the existence of diffuse contamination.

It should be necessary to intensify monitoring of sewage effluents (in water and sediments) both in the Bahía Blanca Main Basin as in the Third Basin. This action will allow to define the need for surveying the industries located within the urban area whose effluents may contain Cd, which may be discharging into the collection network without complying with the regulations in force. Once the industries whose effluents may contain Cd have been identified, they should be geolocated to determine into which Sewage Collecting Basin their discharges are made.

One point to be solved is the information gap concerning monitoring of both sewage treatment plants (whether due to the absence of data or to such data not being public), as it shows that the intensive control on industries contrasts with the minimum control on urban effluents.

Diffuse leachate at the former waste dump Belisario Roldan, located on the flood plain of the estuary, should be controlled by means of specific monitoring of waters and sediments as far as this case implies the greatest threat. In case it were certified that the highest concentration of Cd and other metals proceeds from this environmental liability, the challenge of remediation should be faced in compliance with Buenos Aires Province Act No 13592 – Integral Management of Urban Solid Waste Act (Regulation of conditions after the closing of wastedumps is still pending).

Besides, in compliance with Buenos Aires Province Act No 14321, which establishes the guidelines, obligations and responsibilities for the sustainable management of waste from electric and electronic appliances, actions should be taken to avoid that these type of waste be still dumped in the former waste dump or any other “spontaneous” waste dump, in the sense of providing incentives for the reutilization and/or recycling of such appliances. Even when there are municipal campaigns for the collection of this type of equipment, such campaigns are not massive and illegal dumping continues, perhaps due to the fact that people ignore the risks implied for the ecosystem.

As the investigation progressed, it was confirmed that the Estuary’s waters and sediments are analyzed by various public and private organizations (this tests include Cd), and that the results obtained are available. Consequently, it should be convenient to make a joint effort so as to generate a common database which would enable data correlation. Public information would be made available in a reliable manner, which would make validation compulsory by means of a standardized information method which does not depend on personal criteria.

Another concern would be the need to work on legislation for the Estuary of Bahía Blanca providing guideline parameters for Cd in the waters and marine sediments, taking into account that there is no legislation on this subject at national, provincial or local levels.

Summing up, it was not possible to identify a source of Cd contamination as the only one causing or determining the presence of this metal in the study area. However, diffuse discharges from the former and point source discharges of urban sewage effluents were identified as being the most significant, which leads to recommending further research on these sources.

It should be remarked that in the case of all the results evaluated corresponding to industrial and urban discharges, no result stayed above the permitted values as established by legislation in force.

It is still pending to assess the type of agrochemicals used in the basin of the Napostá Stream and the Saladillo de García River, as well as that of the Sauce Chico River, in order to determine whether they contain phosphatic ingredients and, if that were the case, to research on concentration of Cd in waters and sediments.

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