Chapter 15 Petroleum Hydrocarbons in Atlantic Coastal Patagonia



Marina L. Nievas El Makte, Rosana Polifroni, Marcela A. Sepúlveda, and Ana Fazio

Abstract The Patagonian Atlantic region is known as a pristine area with more than 3000 km of coastline. It includes two productive oil basins, Golfo San Jorge and Austral from where oil production (about 14 million m³/vear) is transported by sea from five terminals. The maritime and coastal areas of the Argentine continental shelf are relevant for marine conservation, tourism and fishing, being spawning and nursery areas of many species. In this chapter, we describe the main aspects of oil production in the coastal basins and its maritime transport throughout the Atlantic Patagonia. Offshore oil exploitation and future development prospects on the Argentine continental shelf are introduced. We also present the main oil spills that occurred in Atlantic Patagonia and a review of hydrocarbon levels in coastal marine sediments and organisms. Some episodes of chronic contamination are depicted. The reported levels range from pristine uncontaminated areas to heavily polluted ones, affected by oil or fuel spills. Hydrocarbon pollution has a punctual distribution pattern near the sources, with the most polluted sites located in ports and oil exploitation areas. In addition, possible interactions of sensitive areas for marine conservation, fishing activities and maritime transport are discussed.

Keywords Hydrocarbon · Pollution · Oil spill · Harbor · Patagonia

M. L. Nievas El Makte Facultad Regional Chubut, Universidad Tecnológica Nacional, Av. del Trabajo 1536, Puerto Madryn, Chubut, Argentina

M. L. Nievas El Makte (🖂) · R. Polifroni · M. A. Sepúlveda · A. Fazio Centro para el Estudio de Sistemas Marinos (CESIMAR-CONICET, CCT CONICET-CENPAT), Blvd. Brown 2915, Chubut U9120ACD Puerto Madryn, Argentina e-mail: nievas@cenpat-conicet.gob.ar

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15.1 Petroleum Hydrocarbons Nature and Its Fate into the Marine Environment

Petroleum or crude oil is a natural and complex substance containing hydrocarbons as major components, nitrogen-sulfur-oxygen heteroatom compounds (NSO compounds) in minor proportions and minor quantities of nickel, vanadium and other trace elements. Hydrocarbons can be subdivided based on their structures into aliphatics (n-alkanes, branched alkanes, cycloalkanes) and aromatics (monoaromatic and polycyclic aromatic hydrocarbons (PAHs)), while NSO compounds are resins and asphaltenes. All these types of compounds have different biodegradation susceptibility and toxicity. The monoaromatic benzene, toluene, ethylbenzene and xylene (BTEXs), PAHs (2-6 rings compounds) and their alkylated derivatives are found in crude oil. Low molecular weight (LMW) PAHs comprise compounds with 2-3 aromatic rings, while high molecular weight (HMW) PAHs 4-6 aromatic rings compounds. Some PAHs are classified as priority pollutants, known as possible or probable human carcinogens and having also mutagenic and teratogenic properties. Aromatic compounds are responsible for most of the ecotoxicological issues caused by oil and fuel spills and thus are used as indicators of oil pollution in water, sediments and biota (Beiras 2018).

When hydrocarbon product spills occur in aquatic media, like the marine environment, a complex process called "weathering" occurs. This involves physical, chemical and biological processes that change the composition, the physical state, the toxicity and the distribution of the spilled oil into different environmental compartments: seawater, sediments, air and biota. The initial transformations are spreading, dispersion, dissolution and evaporation, where winds, tidal, marine currents, environmental variables (i.e., temperature, salinity) and the chemical properties of each hydrocarbon compound are involved. Highly energetic coasts may generate water-in-oil stable emulsions ("chocolate or oil mousse"), which have a long environmental half-life and reduced biodegradation susceptibility (Beiras 2018). Initially, light compounds evaporate, photo-oxidation occurs, and the overall toxicity of the spill is reduced. Only a small fraction of the hydrocarbons is dissolved in water, mainly LMW PAHs with high toxicity. In the next weeks and months, sedimentation and biodegradation are the predominant processes, carried out by microorganisms naturally occurring in the marine environment (Chapman et al. 2018). Finally, the heaviest hydrocarbons and droplets settle on the bottom sediments. Shorelines are more sensitive to deleterious effects to the ecosystem through oiling biota, fouling fine-grained sediments and impacting subtidal macroinfauna (Filler et al. 2014). Sediments are considered as sink for pollutant hydrocarbons and act as long-term reservoirs and secondary sources of pollution, while bivalves are filtering organisms that accumulate hydrophobic compounds. Thus, these matrices are used for evaluating ecotoxicological effects and the hydrocarbon pollution status of a certain site.

Oil spills have acute toxicity effects on wildlife, causing death by direct ingestion when the oiled animals try to clean themselves or by oil-contaminated prey ingestion and through the loss of the feathers or fur waterproof property, altering the animal thermoregulation ability (i.e., birds, particularly penguins). Chronic or long-term oil spill effects are evident at the population or community levels in an ecosystem. Changes in feeding, mobility, reproductive behaviors and malformations are often found as responses to oil pollution (Beiras 2018; Chapman et al. 2018).

15.2 Eastern Patagonia

Patagonia is the southernmost region of the South American continent $(37-56^{\circ} \text{ S})$, comprising portions of Argentina and Chile. The Argentinean Patagonia extends for more than 2200 km in a straight line with N–S direction, including on its coast the provinces of Río Negro, Chubut, and Santa Cruz, the southern portion of Buenos Aires Province and the Tierra del Fuego Island, with a total coast length of more than 3000 km (Coronato et al. 2008, Gil et al. 2019) (Fig. 15.1). It has a semi-arid temperate and cold climate, with almost permanent westerly winds with strong intensities that frequently exceed 100 km/h. Few cities on the coast concentrate the major population and industrial activities, such as oil, coal, fishing, aluminum, cement, renewable energy, textile, electronic production and tourism.

Argentina has ratified international treaties for the prevention of oil pollution of the sea by means of national regulations such as OILPOL, MARPOL and UNCLOS. The most important are summarized in Table 15.1. The Prefectura Naval Argentina (PNA) is the competent authority dealing with oil and other noxious substances pollution in marine and freshwater environments. The same standards



Fig. 15.1 Argentinean continental shelf. Argentinian maritime spaces (left), frontal zones, priority areas of Pampa Azul initiative and marine protected areas (right). *Source* COPLA (2017), and adapted from Allega et al. (2020), Pampa Azul (2017; 2021) and Laws 26,875/13 and 27,490/18

established by the MARPOL convention were adopted for the national order, applying them to ships with Argentine flag in international or national navigation. Two PNA rules are particularly relevant for the Atlantic Patagonian zone: (1) The declaration of special protection zones (SPZs) (Ordinance Nº 12/98 PNA 1998a), in agreement with the particularly sensitive sea areas (PSSA) criteria of the International Maritime Organization (IMO), which bans the discharges of any hazardous wastes from ships, including hydrocarbons in any type; and (2) the tanker maritime route, ruled by the Ordinance N°13/98 PNA (PNA 1998b), which states that vessels transporting hazardous substances, such as oil and distillates, must take a route keeping them within 20 nautical miles of their stranded isobaths. The Argentine continental shelf (ACS) outer limit beyond 200 nautical miles was recently established by the Law N° 27,557/17, in accordance with Article 76 of UNCLOS, incorporating 1.782,500 km² from the 200 mile limit (COPLA 2017, Fig. 15.1). The ACS has unique characteristics worldwide where many frontal zones are generated, producing high primary productivity, turning it into one of the largest and most fertile maritime spaces in the Southern Hemisphere. In the exclusive economic zone (EEZ) (1,529,585 km²), commercial fisheries, hydrocarbon basins and mineral deposits occur (Koutoudjian 2011; Baruj and Drucaroff 2018; MEM-SE 2021). In the Patagonian Sea, its varied fauna, especially birds and marine mammals that approach the coast, gives it an additional ecologic and economic value.

The Argentinean Patagonia economic relevance is based on natural resources exploitation. The main fishing species are red shrimp, squid and hubbsi hake. Total fishery exportation reached 2148 US million dollars in 2018 (ME-SSPME 2019).

| Convention | Subject | Argentine law |
|---|--|--------------------|
| OILPOL 54 | International convention for the prevention of pollution of the seas by oil | Nº 21.353/ 1976 |
| London Convention, 1972 | Convention on the prevention of marine pollution by dumping of wastes and other matter | Nº 21.947/ 1979 |
| Intervention 1969, IMO | International convention relating to intervention on the high seas in cases of oil pollution casualties | Nº 23.456/ 1987 |
| MARPOL 73/78 | International convention for the prevention of marine pollution from ships | Nº 24.089/ 1992 |
| OMI conference, 1990 | International convention on oil pollution preparedness, response and co-operation (OPRC) | Nº 24.292/ 1994 |
| Convention on Biological Diversity, UN 1992 | Establishes among its objectives the sustainable use of biological diversity | Nº 24.375/ 1994 |
| UNCLOS, 1992 | United Nations Convention on the Law of the Sea | Nº 24.543/ 1995 |

 Table 15.1
 International treaties and Argentine regulations intended for the prevention of marine oil pollution

Source http://www.infoleg.gob.ar/

Regarding oil and gas (O&G) resources, Argentina produced in 2019 29.5 million m³ of oil and 49,350 million m³ of gas, being 49% of oil and 34% of gas of the total country from Easter Patagonia basins. Moreover, the economic potential of O&G offshore exploitation for the next 25 years is estimated between 40 and 60 US billion dollars (Baruj and Drucaroff 2018). On the other hand, tourism activity related to the sea on the Patagonian coast has exponentially grown in recent years. Puerto Madryn and Ushuaia are the major touristic cities, especially in relation with ecotourism with wildlife watching. For example, whale watching in Peninsula Valdés has been developed based on the observation of Southern right whales, becoming an important source of income and employment for Chubut Province (Argüelles et al. 2016).

In 2014, the Argentinean Ministry of Science, Technology and Productive Innovation promoted the "Pampa Azul" initiative, aiming to develop actions to promote the conservation and sustainable use of marine natural resources. Based on their oceanographic characteristics, five priority geographic areas were defined, four of them in Patagonia (Pampa Azul 2017, Fig. 15.1).

15.3 Petroleum Basins in Atlantic Coastal Patagonia

Argentina has two productive O&G basins in Eastern Patagonia, Golfo San Jorge (GSJ) and Austral (IAPG 2020) (Fig. 15.2). Golfo San Jorge basin (GSJB) extends over the southern part of Chubut and northern Santa Cruz provinces and to the east, over the ACS (45°–47° S and 65°–71° W), with nearly 180,000 km² being a third part of it situated offshore (Sylwan et al. 2011) (Fig. 15.2). It is a mature basin exploited for more than a century in onshore areas, being the most productive oil zone from Argentina in the last decade. In 2019, it reached nearly 13.3 million m³ of oil and 4681 million m³ of gas, with near 61% of the proven oil reserve of the country in 2018 (Fig. 15.3). The GSJB produces paraffinic medium oils (typically 24°API, TERMAP 2020): Escalante and Cañadón Seco from the north and south flanks of the basin, respectively.

The Austral Basin, also known as Austral-Magallanes basin, is located in the southernmost part of South America. It comprises the southern mainland region of Argentina and Chile, part of the Tierra del Fuego Island, and an east offshore area edging the Malvinas Basin (Fig. 15.2). It extends in NNW-SSE direction between $46^{\circ}30'-54^{\circ}30'$ S and $66^{\circ}30'-73^{\circ}$ W over 170,000 km² (Cuitiño et al. 2019). The basin produces mainly gas and light oil to a minor degree (~API 47°, Petrotecnia 2004). In 2019, the Austral Basin's total production reached 1.25 million m³ of oil and 12,040 million m³ of gas, being the gas proven reserves 29% of the total Argentine reserves in 2018 (Fig. 15.3). Thus, it is a promising area to increase gas production, considering that the country has an annual gas deficit of near 9–12 million m³ for the last 6 years (IAPG 2020). Actually, offshore O&G production is only exploited at Austral Basin, representing 2% of the oil and 17% of the gas produced in Argentina (MEM 2017). Offshore facilities are located in the east mouth



Fig. 15.2 Argentina's hydrocarbon basins (left). Productive basins in Atlantic coastal Patagonia. GSJ (top right), Austral (bottom right) basins. Adapted from https://sig.se.gob.ar/visor/visorsig. php

of the Magellan strait and at eastern Tierra del Fuego Island (52°28' S-53°40' S) near the Atlantic shore in shallow water areas (less than 100 m depth) (Figs. 15.2 and 15.4). Enap Sipetrol S.A. is the major offshore operator in Argentina with 5 platforms nearly located 20 km from shore, with 43 km of submarine collector pipelines and two submarine 22-km pipelines to transport the production to the onshore reception plant, located near Cabo Vírgenes, the end point of Argentinean mainland territory (Petrotecnia 2002; ENAP 2021). ENAP (Chile) has another 40 platforms in operation in the Chilean territory of the Magellan strait (ENAP 2021). The east offshore areas of Tierra del Fuego are operated by Total Austral S.A. or by a consortium of Total Austral S.A., Wintershall Energía S.A. and PanAmerican Energy S.A. (TAU-WS-PAE) companies. This consortium has operated the Cuenca Marina Austral-1 block since 1989, with various oilfields and a network of submarine pipelines connected to onshore plants. The most recent Vega Pléyade offshore area (20 km east from the coast in the south of Bahía San Sebastián, 50 m depth water) constitutes the southernmost offshore platform in the world starting its operation in 2016 (Petrotecnia 2016). Onshore plants on the Atlantic coast of Tierra del Fuego receive the oil and gas production from the marine platforms. The gas is injected into the main gas pipeline that runs from Tierra del Fuego to Buenos Aires $(\sim 4500 \text{ km})$, which crosses the Magellan strait parallel to the international limit between Argentina and Chile by means of a 36-km submarine pipeline. The oil is dispatched by maritime terminals.



Fig. 15.3 Argentina oil and gas production in 2019 and proven reserves in 2018. *Sources* MEM-SE (2021) and SGE (2019a)

15.3.1 Prospects for Offshore O&G Development in Argentina

Argentina hydrocarbon policy promotes the development of offshore hydrocarbon activities with current regulations establishing tax deduction and a 30-years concession period for developments in the ACS (IAPG 2020). The most promising offshore areas that have concentrated the exploration efforts until now are the Colorado Marina basin at south-east of Buenos Aires province and GSJ, Austral and Malvinas Oeste basins in Atlantic Patagonia (Fig. 15.4). In 2008, the YPF Company carried out a shallow water drilling campaign in offshore GSJB, recovering hydrocarbons from wells drilled at 70–110 km from shore in the center of the gulf, but they are not actually exploited as they are considered subcommercial discoveries (YPF 2011). In addition, in 2014, the company reactivated an oil exploitation project in shallow waters in the Restinga Alí area, a maritime sector contiguous to the shore in Comodoro Rivadavia, up to 55 m depth over 167 km². Directed (horizontal) wells from the shore were used, up to 1600 m from the



Fig. 15.4 Offshore prospects in the ACS. Main marine areas with perspectives of O&G offshore development (left). Right: 2D seismic prospection (orange lines). Offshore O&G exploration areas granted in 2018 in contour black lines (A and C), and offshore exploitation areas in Austral basin in black areas (C). Adapted from https://sig.se.gob.ar/visor/visorsig.php, and SGE (2019b)

coastline. The company plans to increment the number of wells for the Restinga Alí offshore area, being 21 wells drilled until 2019 (Van Wyk et al. 2019).

Aiming to increase the offshore O&G development the Argentinean government carried out an international bidding in 2017 to enlarge the potential production, leading to a significant increase of exploration permission in marine zones. Eighteen new marine areas were concessioned, being 94,800 km² granted to 13 companies in three sedimentary oceanic basins (Fig. 15.4, SGE 2019b), being 48,036 km² in the Cuenca Argentina Norte (CAN) Basin in deepwater (200–1300 m) and ultradeep water (1200–4000 m) blocks, 42,328 km² in the Cuenca Malvinas Oeste (MLO) Basin in deepwater blocks (100–700 m) and 4439 km² from the Cuenca Marina Austral (AUS) Basin in shallow water blocks (less than

100 m depth). The two last basins are located in the Patagonia maritime region (Fig. 15.4). Other offshore development projects have also promising perspectives of concretion. Recently, Enap Sipetrol acquired an exploitation permission in the Octans Pegaso area, located 20 km east of Santa Cruz Province. In addition, the consortium TA-WS-PAE is projecting a new development in the Fenix area in the CAM-1 block. The project includes the drilling of three wells and the construction of an underwater pipeline to Tierra del Fuego Island. The oil would be dispatched through the oil terminals in Tierra del Fuego Island.

15.3.2 Hydrocarbon Transport in Patagonia Argentina

Most of the oil production from the coastal Patagonic Basins is commercialized for local market distillation (e.g., in 2019, 78% of total production of the GSJB had this destiny). Distilleries are located near Buenos Aires and along the coast of internal rivers of the country. Thus, maritime voyages from Patagonic terminals to distilleries often take 1800–2500 km (Fig. 15.5).



Fig. 15.5 Harbors, oil terminals and the oil maritime route in Atlantic Patagonia. Data of oil route from https://www.shipmap.org/

The GSJB oil production is concentrated in two exit terminals, Caleta Córdova and Caleta Olivia, operated by Terminales Marítimas Patagónicas S.A. (TERMAP S.A.) (TERMAP 2020) (Fig. 5.5). The former terminal is located 20 km north of Comodoro Rivadavia city, at Caleta Córdova village, in the Chubut Province and the latter in Caleta Olivia city in Santa Cruz province in the GSJ, 70 km south of Comodoro Rivadavia. Both terminals have onshore tank farm facilities with crude storage capacities of 283,000 and 209,000 m³, respectively, and a single point mooring (SPM) monobuoy system for tanker loading, connected to the terminal by submarine pipeline extended along the seabed. Tankers are loaded by connecting to the monobuoy by a floating hose. Both terminals admit tankers up to 160,000 DWT (TERMAP 2020).

The oil production from the Santa Cruz territory of the Austral Basin is delivered by the maritime terminal Punta Loyola (Fig. 15.5). This is an oil and coal terminal operated by YPF S.A., located in the mouth of the Gallegos River, 40 km from Río Gallegos city. It has an oil storage capacity of 180,000 m³ and a pier for vessel loading, admitting tankers up to 60,000 DWT (Petrotecnia 2004). In the Atlantic coast of Tierra del Fuego Island two oil terminals operate: Río Cullen and Cruz del Sur. The Río Cullen terminal is part of the homonymous onshore oil and gas treatment plant located 32 km south of the international limit between Argentina and Chile. The terminal has an oil storage capacity of 92,000 m³ and a SPM monobuoy charge system, operated by Total Austral S.A. It receives mainly the offshore production from the complex operated by the consortium TAU-WS-PAE at east Tierra del Fuego. The terminal operates with tankers up to 150,000 DWT (Petrotecnia 2004). The Cruz del Sur or San Sebastian terminal is located in the south inside the San Sebastian Bay and is operated by YPF S.A. It has a tank farm with crude storage capacity of 70,000 m³ and a SPM monobuov system for tanker loading. The terminal admits tankers up to 60,000 DWT (Petrotecnia 2004). Both terminals of the Tierra del Fuego Island are located in non-populated places at 140 and 75 km, respectively, away from the only city of this province at the Atlantic coast, Río Grande, with 66,000 inhabitants. The three Argentinean terminals of the Austral Basin operate with light oils.

The maritime transportation route from the Austral and GSJ Basins runs along the coast of Argentinean Patagonia from the oil terminals to the distilleries in the north of the country. The same route back is used to transport refined products from distilleries to fuel storages plants in Patagonia, from where fuels are distributed by trucks to the end user cities and industries. Three main fuel plants are located on the coast: the YPF pier in Comodoro Rivadavia (Chubut), the Caleta Paula plant in Caleta Olivia (Santa Cruz) and the Orion plant at Ushuaia (Tierra del Fuego Province). Distillate products are usually transported in 60,000 DWT tankers. The most frequent tanker's route is depicted in Fig. 15.5.

15.4 Oil Spills in Atlantic Coastal Patagonia

Eastern Patagonia has a low population density and low pollution compared with other sites worldwide. However, some oil spill episodes have taken place on its coast. Even minor but quite frequent episodes contribute to chronic pollution, particularly, in those areas around crude oil terminals and ports. Below, we depict the most relevant and documented oil or hydrocarbons spills in Atlantic Patagonia and include some low volume spill episodes that account for chronic pollution (Fig. 15.6).

Metula oil spill in 1974. The worst oil spill suffered in Patagonia up to date is the Metula accident, where 52,300 tons of Arabian light crude oil and approximately 2000 tons of Bunker C fuel oil were spilled in the Magellan Strait, in Chilean territory in August 1974. This strait connects the Atlantic with the Pacific Oceans separating the South America mainland from the Tierra del Fuego Island, with the east mouth of the strait being Argentine territory and Chilean territory the rest of the strait up to the Pacific Ocean embouchure (Fig. 15.6C). We include this spill here even though it is not strictly in the Atlantic coast, because the predominant West-East direction winds and currents spreaded the oil reaching Punta Dungeness, in the Atlantic mouth of the strait. "Oil mousse" formation occurred rapidly and around 250 km of coast were oiled, being Espora marshes (EM) heavily polluted (Fig. 15.6). Wang et al. (2001) reported 24 years after the accident, in a



Fig. 15.6 Location of oils spills. OT: oil terminals (monobuoys), red lines: coastlines impacted by oil spills. Adapted from Gundlach (2017) and Commendatore et al. (2008)

site of east EM, oil mousse poorly weathered, showing the *n*-alkanes series from *n*-C12 and exhibiting still 27–40% of the alkylated PAHs of the reference oil, with a whole weathered percentage of only 25–32%. This confirmed a low biodegradation process. They highlighted that the PAHs and fresh oil mousse remaining in the area were expected to persist for many decades. Gundlach (2017) reported in 2015 in the same site relatively fresh oil mousse with 4–5 cm of subsurface oil mousse layers, 41 years after the spill. The high persistence of oil mousse was once again demonstrated in a low energy environment (marshes) with cold climate, even with light oil as the Arabian Light of the Metula spill. Evidence up to date makes researchers believe that predictions of 100 years of impact of the Metula spill are still likely (Gundlach 2017).

Magallanes area spills. A series of oil spills took place at the offshore Magallanes exploitation block in the Austral basin, between 2004 and 2006 (Fig. 15.6). The sources of some of the events were leakages from the submarine pipeline that connects the Enap Sipetrol S.A. platforms with the onshore storage plant near the Cabo Virgenes Natural Reserve (CVNR), where 90,000 Magellan penguins breeding pairs together with a diverse and rich marine ecosystem are protected. In 2004, the company declared a minor oil spill from a submarine pipeline. Later, tar balls appeared on the high tideline over 600 meters on the CVNR beach. In September 2005, an oil spill occurred between platforms connecting pipelines, which did not reach the shore but 50 oiled penguins died. The oil company took responsibility for both events. In April 2006, almost 400 seabirds were found oiled in CVNR and in Isla Magdalena (Chile). Around 33% of the animals died while the rest were rehabilitated. Non-impact signs were reported on the beach, probably because the oil spills drifted to the open sea to the East. The source of the 2006 event oil spill remains unknown, and the company denied responsibility (de Haro 2007; Rouppolo et al. 2007).

Caleta Córdova oil spill. In December 2007, nearly 300 m³ of Escalante crude oil were spilled from contaminated ballast water from the Presidente Arturo Illia tanker while loading oil at TERMAP S.A. terminal. The spill affected 7 km of Caleta Córdova's shore, a fishery village (PJN 2020) (Fig. 15.6). This event constitutes the major oil spill known impacting the shore in the GSJB up to date, since the beginning of oil production in 1907 (Fig. 15.7). The oil spill occurred with East wind causing the oil to reach the highest tide zone of the beach, affecting more than 800 seabirds (FPN 2011). Analysis of sediments carried out 50 days after the spill showed patchy oil pollution with up to 55,784 and 676 mg/kg dw of total petroleum hydrocarbon (TPHs) and total aromatic hydrocarbon, respectively, the highest levels of hydrocarbons recorded in the Patagonian Atlantic coast (Commendatore et al. 2008). Furthermore, 30 months after the spill, the sediment PAHs individual concentration remained above the probable effect level (PEL) for the protection of aquatic life (Marcos et al. 2012). The local community was affected as the Caleta Córdova's coast became dangerous for recreational activities and artisanal fishing. The legal responsibility of the oil spill could not be demonstrated; nevertheless, the tanker owner company subscribed a judicial deal with the provincial state paying 5 million dollars as punishment but without assuming the spill authorship (Decreto N° 701/14). The tanker was scrapped in 2009. Other minor spills happened in the CC zone in 2017 and 2018, most of them denounced by neighbors of the village.

Undeclared oil spills event in 2010. Some hydrocarbon spills in the ocean remain unknown as they do not reach the shore. In September 2010, around 400 oiled penguins were found in Chubut coasts (FPN 2011). The largest breeding colony of Magellanic penguins in Patagonia is located at Punta Tombo. Penguins migrate annually from Punta Tombo up to southern Brazil (\sim 2000 km), following a corridor within 250 km of shore (Stokes et al. 2014). They leave the colony from January to April returning from September to December. In the 2010 pollution event, oiled penguins found from San Lorenzo ranch (42°08.3' S, 63°58.2' W) to Punta



Fig. 15.7 Caleta Córdova (CC) oil spill in December 2007 at Golfo San Jorge, Argentina. Oiled animals in a CC rescue center (top), oil impacted beach (yellow arrows), with wastes absorbent booms and waste tank on the beach (orange arrows). *Photos* courtesy of Martin Levicoy https://martinlevicoy.com

Tombo (44°03.6' S, 65°13.3' W) beaches were studied (Fig. 15.8). Oiled penguin feathers were analyzed to assess hydrocarbon type and distribution, showing the chromatographic profiles of a common source of pollution with aliphatic series from nC12 to nC37 and the presence of unresolved complex mixture (UCM) compatible with oil, as shown in Fig. 15.8 (Nievas et al. 2010). The *n*-heptadecane/pristane (nC17/Pri) and n-octadecane/phytane (nC18/Phy) ratios, indicators of early biodegradation, were around 1.5 and 3.5, respectively, indicating fresh or slighted biodegraded oil. The oil in penguin feathers lost the lighter compounds up to nC15, with the exception of the northern sample site (San Lorenzo ranch) where the nalkane series started from nC12, suggesting that penguins that reached this location were nearer to the oil spill. Escalante crude oil shows close hydrocarbons profile matching with oiled penguin, with an *n*-alkane profile from nC8 to nC37, UCM and nC17/Pri and nC18/Phy ratios of 2.9 and 3.9. Diesel fuel and bilge waste from fishing ships and Bunker C were unlikely sources of the pollution found in oiled penguins, as they had lower *n*-alkane/isoprenoids ratios than those found in these animals (Nievas 2006; Wang et al. 1997). The penguins returning route to the Punta Tombo colony matches with the oil route in Patagonia (Fig. 15.8). No shore pollution was reported associated with this event, neither declaration of tanker owner, cruises or other ships in the zone at the event time. The overall evidence let us hypothesize that the most probable situation was that an undeclared oil spill of Escalante crude oil happened in the oil route of northern Patagonia. The predominant west wind likely drove the oil slick to the open sea. The penguins returning to Punta Tombo hit the oil slick, and the most affected reached the nearest coast where they were found. No one responsible for the event was found. The oil spill is just known because of the sights of oiled penguins.

In Patagonia Argentina other events of declared or mystery oil spills affected mainly penguins (García-Borboroglu et al. 2006; 2008; FPN 2011; Ruoppolo et al. 2007). For example, from 1982 to 1991, estimates indicate that 40,000 penguins died by oil pollution along the Patagonian coast each year. In September 1991, 17,000 oiled penguins appeared in Punta Tombo by a mystery oil spill, suspected from a tanker. In 2005 and 2006, 50 and near 400 oiled penguins, respectively, appeared at Cabo Vírgenes Provincial Reserve, Santa Cruz. The cause was an oil spill from a broken submarine pipeline from offshore facilities at the Magellan strait in 2005 and by an undeclared oil spill in 2006 (see Magallanes area spills, in this section). In December 2007, more than 800 seabirds were registered at the Caleta Córdova spill, Chubut (see Caleta Cordova oil spill, in this section). The number of oiled penguins found along the coast varied among years but showed a dramatic increase in the mid-1990s, showing a close match with the increase Argentinean oil exportations from 1987 to 2002 (García-Borboroglu et al. 2006). After 1998, when the oil and hazardous substances route was moved 20 miles away from the tanker stranding depth, the number of oiled penguins arriving to the Chubut coast decreased, indicating that this was a useful measurement (García-Borboroglu et al. 2008).

Cabo San Sebastian oil spill at Puerto Madryn's harbor. In August 2015, a storm capsized a wrecked fishing ship, Cabo San Sebastián, in the Almirante Storni harbor area at Puerto Madryn city (Figs. 15.6 and 15.9). Around 20,000 L of fuel



Fig. 15.8 Oiled penguins in Chubut coast in a mysterious oil spill event, September 2010. Positions of sampled oiled penguins (left), oiled penguin in recovery center in Puerto Madryn (bottom), chromatographic hydrocarbon profiles from penguin feathers (PF) and Escalante crude oil (CO) as reference adapted from Nievas et al. (2010). *Photo* Courtesy of Maxi Jonas Fotos https://www.facebook.com/maxijonasFotos/, Data of oil route from https://www.shipmap.org/

and an undetermined amount of bilge wastes were released, the slick drifting into the Golfo Nuevo and impacting the harbor beach. Pollution levels in the intertidal sediments 15 days after the event were 5–30 ppm of TPH with fresh hydrocarbon signature of medium distillates (Nievas El Makte and Sepúlveda 2016; Sepúlveda et al. 2016). This hydrocarbon spill happened in Golfo Nuevo, which is a SPZ due to its environmental sensitivity, and besides generating dock area pollution coincided with the peak of abundance of Southern right whales, which visit the gulf for their reproduction and calving every year (Fazio et al. 2015). Furthermore, the spill site (industrial pier) is less than 3 km from the busiest recreational beach in the city.

Silent hydrocarbon pollution in Puerto Madryn Harbor. In the same event that wrecked the Cabo San Sebastian ship, another seven fishing ships drifted and were hauled up on the nearby beach from the Almirante Storni harbor pier, in Puerto Madryn, in 2014. The ships increased the number of stranded vessels in a ship graveyard area of the dock (Fig. 15.10). A hydrocarbon spill was detected from one of the grounded vessels, Codepeca I, in January 2016. The ship presented hull damage after being grounded on the beach and was partially flooding inside



Fig. 15.9 Cabo San Sebastian oil spill at Puerto Madryn harbor (Chubut, Argentina) in August 2015. *Photo* courtesy of Maxi Jonas Fotos https://www.facebook.com/maxijonasFotos/

with every high tide. Water flowing out the ship percolated through the sand under the vessel and blew up in the perimeter of the ship settlement. At the spill event, the water flowing out contained a significant amount of a yellowish non-aqueous liquid phase (NALP), which formed little pools in sediments while running off down the intermareal up to the sea (Fig. 15.10). Analysis concluded that NALP was fuel from the ship assimilable to diesel oil. The nearest sediments presented high fuel pollution (up to 22% dw), being the lighter compounds quickly lost by evaporation and dissolution (Fig. 15.10). The hydrocarbon concentrations ranged from 100% for the NALP to nearly 5 ppm of total petroleum hydrocarbons for sediment away from the spill plume (Nievas El Makte and Sepúlveda 2016). The amount of spilled fuel was estimated between 10 and 20 L throughout low tide. The findings of this case indicate that the ship internally contained some amount of fuel that floated over the water column that flooded the grounded vessels at each tide cycle. The event was noticed at an extraordinary low tide day. This situation, with a longer time between flooding cycles, enabled the water to drain and also the hydrocarbons layer over it. The wrecked ship became a slow-release hydrocarbon buoy generating small fuel spills over time. As the ship was abandoned and declared unrecoverable, and no obvious hydrocarbon spills were easily appreciated, the situation remained unnoticed for 16 months, until the hydrocarbon spill event was reported. After the episode, the ship was conditioned until removed, and finally scrapped in December 2019. In Patagonia, as worldwide, harbors usually remain as hot spots regarding hydrocarbon pollution and other contaminants (Jupp et al. 2017; O'Brian 2006; NRC 2003). Thus, the management of ship graveyards at ports and programs to scrap abandoned ships are highly recommended, as they can not only enhance the visual contamination, but also avoid the invisible chronic pollution. This management became particularly relevant if the sites are in sensitive environments or nearby recreational beaches as the case of Puerto Madryn harbor.

Cruz del Sur terminal oil spill at San Sebastian Bay. A minor oil spill happened in 2019 in an episode from the terminal monobuoy at the Austral Basin (Fig. 15.6). Nearly 1500 L of released oil were declared by authorities, while only 200 L were admitted by the operator company. The spill was contained, partially recovered and did not reach the shore (Tiempo fueguino 2019). The monobuoy stopped operations due to technical problems for nearly a year, restarting in August 2020. No further information is available up to date regarding the ecological impact of the event. San Sebastian Bay, located on the Atlantic coast of Tierra del Fuego Island, is a sensitive environment declared SPZ and RAMSAR site (Fig. 15.6).



Fig. 15.10 Chronic hydrocarbon pollution by fuel spill at Puerto Madryn harbor. Chromatographic profiles (left). Center and right: Almirante Storni harbor (top), and CODEPECA I ship (middle) locations, NAPL pools in sediments in the spill runoff (bottom). Adapted from Nievas El Makte and Sepúlveda (2016)

15.5 Petroleum Hydrocarbons Levels in Atlantic Coastal Patagonia

15.5.1 Hydrocarbons Levels in Coastal Sediments

Coastal areas are usually classified according to the hydrocarbon pollution in sediments as non-polluted (hydrocarbon content <10 mg/kg dw), low to moderate polluted sediments (concentration of 10–100 mg/kg dw), moderate to high hydrocarbon levels (100–1000 mg/kg dw) and highly polluted sediments (concentration above 1000 mg/kg dw) (Commedatore et al. 2000; Commentore and Esteves 2007). While regarding PAHs levels, according to Baumard et al. (1998), the parent PAH levels (the sum of 18 compounds) can be considered as low, moderate, high and very high when they are in the ranges of 0–100, 100–1100, 1000–5000 and >5000 μ g/kg, respectively.

Reports of hydrocarbon levels in coastal sediments or organisms in Atlantic Patagonia are quite scarce, even more taken into account the extension of its coastline estimated at more than 3000 km (Gil et al. 2019). Some baseline level assessments were performed along the coast (Commendatore et al. 2000; 2012; 2015; Commendatore and Esteves 2007; Esteves et al. 2006; Esteves and Commendatore 1993). Other sites description were performed in spill event reports (Iantanos et al. 2008; Commendatore et al. 2008; Nievas El Makte and Sepúlveda 2016; Sepúlveda et al. 2016), studies focused on bioaccumulation and effects of hydrocarbons on marine organisms (Massara Paletto et al. 2008; Amin et al. 2011; Primost et al. 2018; Sturla Lompré et al. 2018) or gene and enzyme prospection of microbial hydrocarbon metabolism (Guibert et al. 2012; Marcos et al. 2012). Based on this information, hydrocarbon levels in sediments can be resumed as follows: levels of hydrocarbon from low to high concentrations were found in many harbors and nearby areas in Atlantic Patagonia. Considering TPH or total aliphatics (TAl) were found: (1) in the low-moderate pollution range: coast of Comodoro Rivadavia (1995), (2) in the moderate to high range: San Antonio Oeste harbor (1995), Rawson harbor (2001), Comodoro Rivadavia harbor (1995), Caleta Córdova (1995), Ushuaia commercial port, Nautical pier and Aspirante Creek (2006) and (3) in the highly polluted levels Puerto Madryn (2016), Ushuaia combustible pier (2006) and Caleta Córdova (after the 2007 oil spill). Moreover, regarding the PAHs a similar pattern was found: low PAHs pollution in Camarones harbor (2010) as in north and south beaches of Puerto Madryn (2001); in Puerto Madryn harbors, Storni pier moderate to very high (2001 and 2005) and in Piedra Buena Pier moderate to high (2005 and 2012). In Comodoro Rivadavia harbor, the concentration was low (in 2005) and very high in Caleta Córdova after the oil spill (2007), decreasing to moderate 2.5 years after the spill in two evaluated sites. In Ushuaia Bay, moderate pollution was found in commercial harbors and nearby areas (2006), while in the Orion combustible plant, low to high PAHs pollution levels were reported in intertidal and subtidal sediments (2004-2010). Thus, the hydrocarbon pollution type seems to be associated with sources: anthropogenic activities at ports and oil industry. Typical polluted sediments from areas related to port and industrial activities are reported in the range of 650-1200 mg/kg dw of petroleum hydrocarbons (Commendatore et al. 2000). Sites where hydrocarbon spills happened recently were particularly polluted, as expected. Concentrations measured early after the spills showed the highest hydrocarbon values in sediments of the coast. The Caleta Córdova sediments showed up to 55,108 mg/kg dw of total hydrocarbons in 2008 (Commendatore et al. 2008), while in the Puerto Madryn chronic spill (see Sect. 15.4) reached a hydrocarbon content of 22% dw in the fuel spill point up to near 5 mg/kg dw away the site (Nievas El Makte and Sepúlveda 2016). These concentrations represent an acute situation which requires a following up to assess the attenuation of hydrocarbons over time, after spreading, adsorption onto the sediments and subsequent weathering. Commendatore and Esteves (2007) concluded that three types of zones could be identified in the Atlantic Patagonian coast: harbors affected by chronic pollution with concentrations in the range of 6-741 mg/kg dw of TAl and 2.5-7.7 mg/kg dw of total PAHs, an accumulation zone likely an area where an oil spill impacted the north zone of GSJ with concentrations up to 1305 mg/kg dw TAl and the rest of the assessed sites with unpolluted character with hydrocarbons concentrations in the range of 0.27-5.4 mg/kg dw TAl. Since then, more recent reports have confirmed this tendency. Sites away, even short distances, from punctual hydrocarbon pollution likely sources, have low levels of hydrocarbons and usually with biogenic character. To this category belong beaches of Golfo San Jose (1989 and 2005), Península Valdés (1989, 2009 and 2012), beaches 8 km north and 3 km south of the Puerto Madryn center in Golfo Nuevo (1989, 1995 and 2001), Chubut Atlantic coasts from Punta Ninfa to the north edge of GSJ (except Rawson harbor) (1989,1995 and 2001), most of the sites of the North Zone of GSJ in the Patagonian Austral Inter-jurisdictional Marine Coastal Park (with exception of an accumulation point in Faro Aristizabal and Camarones harbor) (1989, 1995 and 2010), Rada Tilly (1989 and 1995), Santa Cruz coast at south of GSJ (1995), the Atlantic shore of Tierra del Fuego Island (2001), the Beagle channel (with the exception of the Ushuaia bay) (2001) and Isla de los Estados (2003).

Despite available data are mostly historical and recent information is very scarce, no unexpected high levels of hydrocarbons were found in remote places away from anthropogenic activities. New assessments of hydrocarbon concentration are needed to update the available information and establish pollution trends. Moreover, some oil spills happened after the last hydrocarbon level assessments in sediments in many sites reported here, so it is expected that levels would be higher than in previous reports. The Atlantic Patagonia possesses many ports where commercial fishery activities and oil transport take place (Fig. 15.5). Minor accidental spills while bunkering ships or in loading tanker operations are frequent reasons of hydrocarbon pollution in harbors and oil terminals worldwide (O'Brian 2006; Krata and Jachowski 2021). Some spill events in harbors and in oil terminals have also contributed to chronic pollution in the Atlantic Patagonian coast.

15.5.2 Hydrocarbons Levels in Bioindicator Organisms

Bivalves are filtering organisms that accumulate hydrophobic compounds, and for this reason, they are used as pollution indicators (Sericano 2000). Many monitoring programs (i.e., Mussel Watch, NOAA) were implemented worldwide to assess persistent organic pollutants (POP) in the marine environment (Sericano 2000; Monirith et al. 2003). In addition, hydrocarbon levels in edible species are of great concern regarding the foodstuffs safety.

In Atlantic Patagonia, some authors reported hydrocarbons levels or PAHs bioaccumulation in organisms. Primost et al. (2018) compared PAHs content in the edible gastropods Buccinanops globulosus in two sites with different maritime influences: Puerto Madryn harbor area and a 20 km nearby beach, presumably non-polluted, finding non-detectable PAHs neither in gastropods nor in sediments of the control site. On the other hand, PAHs levels were higher in gastropod tissues (560 µg/kg dw) than in sediments (270 µg/kg dw) at the harbor area, being the PAH4 level (sum of benzo[a]anthracene, benzo[b]fluoranthene, benzo[a]pyrene and chrysene) exceeding the maximum limit established by UE for PAH4 in foodstuffs (30 µg/kg dw, EUC 2011). While the dibenzo[a,h]anthracene sediment concentration exceeded the level established by the Canadian guidelines for marine sediment quality, being lower than the PEL concentration (CCME 1999). These authors concluded that based on the PAHs levels, the consumption of these animals could be dangerous for humans according to the ingestion frequency. Hydrocarbon levels in mussel and clam were also studied in Bahía Nueva, Golfo Nuevo, Chubut, in 2001 (Massara Paletto et al. 2008). Aliphatic and aromatics compounds were assessed. The highest levels of aliphatic hydrocarbon were found for mussels at both piers, while the highest PAHs levels were also found in both piers, in an effluent discharge site and in the harbor adjacent area. Sediments of the harbor area showed the highest PAHs concentration of the study, particularly, the Piedra Buena Pier. Amin et al. (2011) studied PAHs concentration in Mytilus edulis chilensis (mussel) from Ushuaia Bay reporting an increment between October 1999 and October 2003. In 2003, the PAHs in mussels ranged from 2.25 to 2420 µg/g lipid having petrogenic origin with pyrogenic background, with high concentrations of naphthalenes, fluorenes, phenanthrenes and anthracenes. These facts indicated that the mussels were exposed to relatively fresh petroleum hydrocarbons. The highest levels in both years were found in mussels from the site next to the Orion combustible plant in Ushuaia Bay (Fig. 5.5), with notable high levels. The authors stated that these results reflect the environmental quality of the Ushuaia bay, which atmospheric and oceanographic conditions favors the POP accumulation and long-term permanence. These results closely agree with hydrocarbon pollution determined in the Ushuaia bay sediments (Esteves et al. 2006; Commendatore et al. 2012; Marcos et al. 2012). Evaluation of PAHs levels in the north zone of the San Jorge gulf was carried out in 2010, assessing sediments and bivalves (Mytilus edulis) (Commendatore et al. 2015). Generally, values found in sediments corresponded to non-polluted, except in Camarones that were slightly polluted. In addition, levels of PAHs in bivalve tissues were low and typical for locations distant from contaminant sources.

In summary, studies performed in organisms from the Atlantic coast generally reflected the hydrocarbon pollution levels of its site of origin. Thus, hydrocarbon levels in marine organisms in locations identified as hydrocarbon-polluted ones, likely shows the same trend. Consequently, closed monitoring programs are necessary to assess PAHs levels in hydrocarbon pollution hot points on the Atlantic Patagonian coast, such as near ports or in sites impacted by hydrocarbon spills where coastal artisanal fishing and mollusk gathering are economic activities, such as Caleta Córdova in Golfo San Jorge.

15.6 Resource Overlap in the Patagonian Sea: Hydrocarbon Pollution and Its Environmental Implications

The Patagonian Continental Shelf of Argentina presents a highly productive ecosystem, which provides a great richness and diversity of resources. The abundance of plankton along the fronts in Patagonian Sea promotes the reproduction of commercial fish, crustacean and squid species, which supports the development of a large-scale fishing industry (Allega et al. 2020). The Patagonian coast is also an important breeding zone for the same fishing resources since intertidal and coastal benthic communities are the diet of larvae or juveniles of commercial species or offer refuge for the deposition of eggs. Thus, benthic organisms constitute highly structured environments. GSJ and off Tierra del Fuego are hotspots for benthic species richness (Miloslavich et al. 2011). Particularly, GSJ has a relevant hubbsi hake fishery and the most economically important shrimp fishery of Argentina, with the main area of shrimp youth concentration located in the south of the gulf in Mazarredo (46°45' S, 66°30' W) at depths less than 40 m (Góngora et al. 2012). On the other hand, these sites are near the exit zone of oil production of Eastern Patagonia oil basins (see Sect. 15.3). Considering that oil spills are particularly harmful to benthic communities when they reach the coast, and that hydrocarbon pollution events happened in the near past in those sites (see Sect. 15.4), management actions strongly committed to prevent oil spills from hydrocarbon terminals are imperative. Any oil impact in critical areas as Mazarredo raises the risk of a fishery collapse. Adverse ecological and environmental impacts of oil spills have been well documented. For example, in the Exxon Valdez oil spill, the most notable ecological effect was the outright mortality of extensive quantities of biota at all levels, with varying degrees and rates of recovery (Gill et al. 2016). The economic and subsequent social impact of this spill was also extensive. The collapse of fishing industries, the damage of tourism along with ancillary industries, and the implications on community-based health and livelihood were consequences of the spill, together with the ecological damage (Zhang et al. 2019). Similar situations were

reported in other spills as the Prestige in Spain (Martínez-Gómez et al. 2009; Penela-Arenaz et al. 2009). Special protection zones (SPZs) were created to protect sensitive environments. However, despite the rules that ban hydrocarbons discharges from vessels in normal ship operations in SPZs, accidental spills can greatly affect these areas. As an example, the oil spills described here in Caleta Córdova (2007), in Bahía San Sebastian (2019) and in Puerto Madryn (2015) all happened in SPZs. Moreover, three of the five oil terminals in Atlantic Patagonia are located in SPZs (Caleta Córdova, Caleta Olivia and Cruz del Sur), thus, any oil spill near these terminals acquires higher relevance based on the sensitivity of the zone and on the higher risk of damage.

The Patagonian coast and its adjacent waters are valuable in terms of global biodiversity, as they are used as a resting, feeding and mating site for birds and marine mammals. The predictability when those animals arrive on these coasts has given rise to ecological tourism, including tours to see penguins, sea lions, elephant seals and whales. Whale watching in particular is the main tourist activity of Chubut. It is well known the occurrence of acute and chronic toxicity in whales or in other marine mammals when these animals are in contact with hydrocarbons from oil spills or chronic pollution. Consequences of these toxicities as, for example, reduction in reproductive success or increases in respiratory infections have been reported (Hook 2020; Kellar et al. 2017). Another important tourist attraction along the Patagonian shore are the Magellanic penguin breeding colonies. As was described before, oil spill affects particularly penguins and seabirds (see Sect. 15.4). Thus, the risk of oil spills in sensitive areas such as penguin colonies or reproductive areas of marine mammals, like in the example of Golfo Nuevo, would impact on the ecology and also on tourism activities based on wild marine fauna, which is one of the socio-economical pillars of eastern Patagonia.

15.7 Concluding Remarks

The Argentinean O&G production in onshore and offshore areas is expected to increase in the next years to fulfill the country's own needs and also to improve its trade balance. This will imply an increase in platform operations and number of tankers for hydrocarbon transportation across the maritime zone. Thus, with the development of the new offshore activity, the risk of oil spill pollution will also rise. Hydrocarbon pollution in the Atlantic Patagonian coast has been mainly related to oil exploitation zones and to maritime hydrocarbon transport. The Magellan strait suffered a disaster oil spill four decades ago, which impacts still persist today. A more recent and smaller oil spill in GSJ in 2007 impacted a fishery village causing deep environmental and social consequences. The other hydrocarbon pollution focus detected in Patagonian coast is the chronic pollution related to harbors operation. Besides major oil spill, oil terminals had minor but frequent spilling affecting the surrounding area. Commercial and fishing ports are, excepting areas affected by petroleum spills, the more polluted sites in the Atlantic Patagonian

coast. However, information is scarce and frequent monitoring programs would be useful to assess hydrocarbon pollution trends. Some studies have also proven the presence of hazardous PAHs in organisms near ports over safe international standard levels. The hydrocarbon pollution in the Atlantic Patagonian coast does not seem to be an extended situation, instead, it is concentrated in specific points: ports and harbors, oil terminals and nearshore or offshore oil production areas. While the impact of hydrocarbon pollution in the open sea, such as those likely from intense fishing areas near the 200 mile, is unknown.

In summary, Atlantic Patagonia has vast coast areas exempt from hydrocarbon pollution, with high biodiversity and a huge richness in biological resources. To continue this way, modern environmental management tools became indispensable, in order to have a sustainable development. Prevention of oil pollution at sea requires quick response monitoring tools covering the maritime most frequent routes as well as the hot spot fishing areas. While the pollution damage immediately begins after an oil spill, environmental crime responsibilities of its generator may take many years to be proven. Thus, legal tools and procedures of environmental authorities need to be strengthened to achieve a quick and effective response after an oil spill. Regarding chronic pollution, increasing in security requirements for oil terminals and harbor bunkering became obvious measurements. On the other hand, the implementation of programs for ship graveyard elimination, by scrapping or removing abandoned ships at harbors, would greatly enhance the recovery of harbor's nearby impacted area, not only of hydrocarbons, but also of other contaminants associated such as heavy metals. This is particularly important in sensitive environments, or where the same place is used by ports and recreational activities such as in Puerto Madryn, Rawson and Comodoro Rivadavia cities. Argentina faces the challenge to develop economic activities in its maritime continental shelf area without losing environmental quality. Marine research in pollution fields as well as in physical, chemical and biological oceanography seems to be the necessary input to take management and conservation adequate decisions.

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