Chemical and petrochemical industry site: Coatzacoalcos region in Mexico

Report by
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Coatzacoalcos – Mexico City – April 2013

Chemical and petrochemical industry site: Coatzacoalcos region in Mexico

IPEN Mercury-Free Campaign Report

Prepared by Ecología y Desarrollo Sostenible en Coatzacoalcos, A.C. and Centro de Análisis y Acción en Tóxicos y sus Alternativas – CAATA (Mexico) and Arnika Association (Czech Republic) and the IPEN Heavy Metals Working Group

Coatzacoalcos – Mexico City – 3 January 2013

Introduction

In 2009, the Governing Council of the United Nations Environment Programme (UNEP GC) decided to develop a global legally binding instrument on mercury to reduce risks to human health and the environment (UNEP GC25/5). The UNEP GC noted that mercury is a substance of global concern due to its long-range transport, persistence, ability to bioaccumulate, and toxicity. Its conclusions were based in part on the 2002 UNEP Global Mercury Assessment which noted that mercury is present in fish all over the globe at levels that adversely affect humans and wildlife. (UNEP 2002) In humans, hair is widely accepted as a matrix for reliable estimations of the body burden of methylmercury, which likely comes from eating fish (Grandjean, Weihe et al. 1998); (Harada, Nakachi et al. 1999); (Knobeloch, Gliori et al. 2007); (Myers, Davidson et al. 2000).

This report focuses on the area of Coatzacoalcos-Minatitlán, where a chlor-alkali plant and waste incinerator are located inside of a petrochemical complex, and where an oil and gas refinery is located. We examined levels of mercury in hair of population living in this area with a special focus on fishermen and people consuming fish caught in the area to confirm whether mercury releases in from nearby industrial processes can be traced in human hair from these locations. In addition, since local mercury releases become global problems due to long range transport we considered how the draft treaty text will address these sources.

Chemical and petrochemical industry complex in the Coatzacoalcos – Minatitlán area

The municipality of Coatzacoalcos, located in the southern state of Veracruz, is included in the so-called Olmec region, comprising 25 municipalities and dominated by the cities of Coatzacoalcos and Minatitlán. The area has a population of nearly two million and comprises approximately 41% of the economic activity in the state.

There are two main sources of mercury pollution in the study area; a chlor-alkali plant inside of a petrochemical complex near the city of Coatzacoalcos (which also includes a waste incinerator) and an oil and gas refinery in Minatitlán.

The chlor-alkali plant is Industrias Químicas del Itstmo, S.A. (IQUISA), which is part of a company named Cydsa. The facility began chlorine production in 1968 using mercury cell technology. In 1981, Cloro de Tehuantepec (Mexichem) began operation using mercury but currently employs diaphragm cells and does not release mercury in their discharges.

The oil and gas refinery known as General Lázaro Cárdenas refinery was established in 1906, as the first major refinery in Latin America. A reconfiguration of the refinery was completed

in 2011 to increase the processing capacity of crude oil to 350,000 barrels per day (BPD), an increase in the percentage of Maya crude.

In addition to the chemical production facilities, two incinerators were operating in the Pajaritos petrochemical complex at different times in the period of 1995 – 2002. The units burned chemical industry by-products and one incinerator had a capacity to burn 1.5 tons per hour (approximately 100 tons at day). A third incinerator started its operation in 2005 and burns mainly the wastes from vinyl chloride monomer (VCM) production.

Other potential sources of mercury emissions include private chemical industries established in the three petrochemical complexes (Pajaritos, Cangrejera and Morelos). In addition, there are regional hospitals and crematoria located in the area.

Materials and methods

Ecología y Desarrollo Sostenible en Coatzacoalcos, A.C.Agenda conducted sampling of human hair using protocols developed by IPEN (2011). Twenty-two hair samples were taken in total for this study in the Coatzacoalcos chemical industry area. Biodiversity Research Institute (BRI) measured mercury levels (total mercury content = THg) in hair samples in their laboratory in Gorham, Maine, USA. Ecologia y Desarrollo Sostenible en Coatzacoalcos, A.C. and CAATA characterized the site and provided information about its history and presumptive mercury sources.

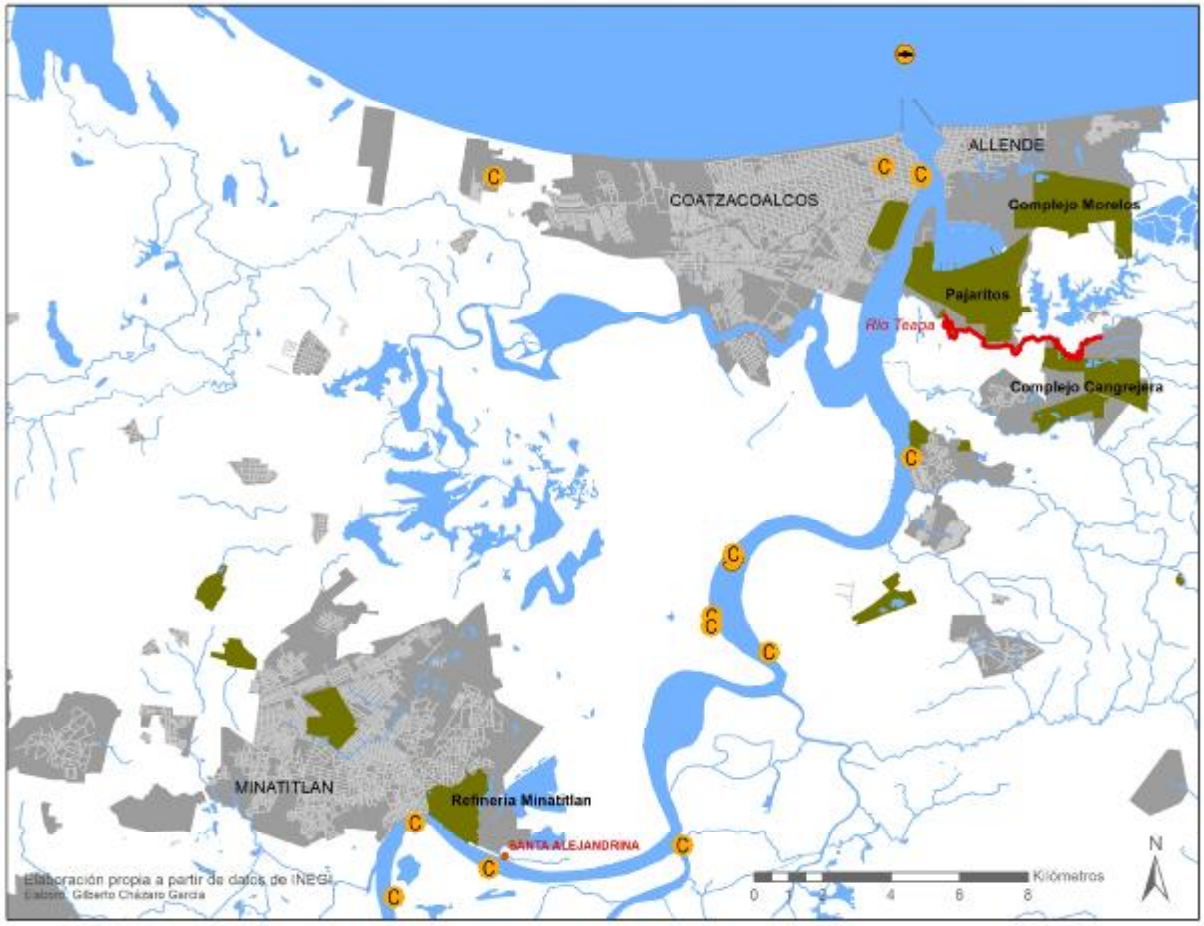

Figure 1: Map of Coatzacoalcos – Minatitlán region with marked location of the sites of people who donated hair for mercury analysis.

Results and discussion

There is extensive literature on the presence of mercury in aquatic ecosystems in the area of Coatzacoalcos and some measurements of mercury in fish and hair. However, most of the data is 35 years old and there is no publically available clinical or epidemiological assessment of the impacts on the population. In these previous studies, the Minatitlán Refinery has never been considered as a possible source of mercury releases nor has its contribution to mercury content in fish or humans in the region been considered. According to Lang, Gardner, Holmes (2012) global concentrations of mercury in crude oil and gas range from 0.1 to 20.000 mg/kg in crude oil and 0.05 to 5000 mg/m^3 of natural gas. Acosta et al. (2001) note that it is likely that most of the mercury in present in crude oil processed in refineries in Mexico, although a portion of it could be passed to the lighter fractions as diesel or gas generated in the atmospheric cooling tower.

Table 1 shows the levels of mercury (Hg) in hair samples from the Coatzacoalcos - Minatitlán area (see map at Figure 1).

Table 1: Mercury content in hair samples from the Coatzacoalcos - Minatitlán area in Mexico

	Sample Size	**Hg Mean (ppm)**	**St Dev**	**Min Hg (ppm)**	**Max Hg (ppm)**	**Reference dose (ppm)[a]**	**Fraction of samples over Reference Dose**
All samples	22	1.754	1.075	0.289	4.318	1.00	73%
Boca del Uxpenapa	4	1.495	0.881	0.721	2.761	1.00	75%
Municipio Cosoleacaque	3	1.267	0.290	0.940	1.491	1.00	67%
Municipio de Minatitlán	4	1.754	1.060	0.812	3.132	1.00	75%
Ixhuatlán del Sureste	6	2.262	1.037	1.409	4.318	1.00	100%
Coatzacoalcos	5	1.647	1.614	0.289	3.464	1.00	40%

Abbreviations: Hg, mercury; ppm, parts per million or mg/kg; st dev, std deviation; min, minimum; max, maximum

The results in Table 1 show that the mean mercury level in all 22 hair samples is more than 1.7-times higher than the US EPA reference dose of 1 ppm. Nearly three-fourths of the people sampled had mercury levels in their hair higher than the reference dose. The maximum mercury value observed in the hair sample from Ixhuatlán del Sureste, Mexico exceeded the US EPA reference dose by more than 4-fold. All six samples from this site exceeded the reference dose.

As demonstrated in Figure 2, three-fourths (16 of 22) of the samples exceeded the reference dose level (red line). We focused mainly on fishermen or people selling fish in our survey. Most of them also eat fish relatively often however there are differences between the

[a] U.S. EPA's RfD is associated with a blood mercury concentration of 4-5 μg/L and a hair mercury concentration of approximately 1μg/g." US EPA (1997). Mercury study report to Congress, Volume IV, An assessment of exposure to mercury in the United States. EPA-452/R-97-006**:** 293.

individuals in the group. The highest levels were observed in people who consumed the greatest amount of fish.

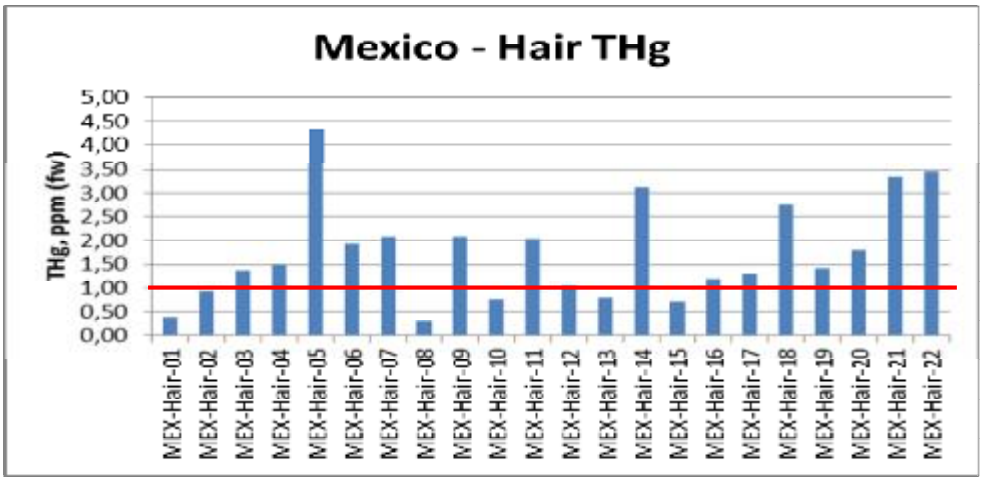

Figure 2: Levels of THg in hair samples from Coatzacoalcos - Minatitlán area, Mexico in ppm.

Báez et al. (1976) note the results of mercury concentrations in hair in two groups of individuals. The first consisted of adult individuals without occupational exposure to mercury that had concentrations ranging from 1 to 12 ppm in hair. The second group was made up of adults who worked in the petrochemical complex of Pajaritos and experienced occupational exposure to mercury. This group had mercury values ranging from 1.81 to 35.5 ppm in hair with an average level of 7.36 ± 7.12 ppm. No overt symptoms of poisoning were recorded among selected adult individuals in a medical examination. Our survey was focused on non-occupational exposure group in comparison with this older research in Coatzacoalcos.

Guentzel, Portilla et al. (2007) performed measurements of mercury in people living near the Alvarado lagoon system. Levels of total mercury in hair ranged from 0.10 to 3.36 ppm (n = 47) and 58% of the samples were above the US EPA reference dose. The results of this study are similar to other studies which exhibit exposure resulting from fish consumption. Results from the Coatzacoalcos- Minatitlán area presented in our report show slightly higher levels of mercury in hair.

The transport of mercury in the atmosphere was inferred by Báez (1976) in Coatzacoalcos acid rain from air emissions generated by the 3 petrochemical complexes of Morelos, Pajaritos and Cangrejera that are carried by wind currents prevailing in the region of Coatzacoalcos going south and southeast. The population potentially exposed to these emissions includes those living in the New World in the municipality of Coatzacoalcos, Nanchital of Lázaro Cárdenas, Ixhuatlán del Sureste, as well as the urban center of the city of Coatzacoalcos. Also located within 40 km zone is an extensive cattle ranching and commercial poultry broiler. The atmospheric emissions from the Minatitlán refinery reach the people municipality of Isle of Capoacán and surrounding rural area.

Chlor-alkali plants using mercury, oil refinery, and waste incinerators in the mercury treaty

The chemical industry hotspot in the Coatzacoalcos – Minatitlán area provokes questions about how the mercury treaty might mandate actions to eliminate mercury pollution of the

environment and fish from chlor-alkali facilities along with releases from other significant sources of mercury pollution.

More recent studies by (Pirrone, Cinnirella et al. 2010); (Mukherjee, Bhattacharya et al. 2009) estimate that the chlor-alkali sector produces 3-times higher total mercury releases to air than original the UNEP Chemicals (2008) air emissions inventory, while global releases to water caused by chlor-alkali plants were not estimated at all. These findings as well as case documented in this study underline need to set up an early date for phasing out mercury use in chlorine production. There are still two options (2020 or 2025) in current proposed treaty text (UNEP (DTIE) 2012) [b] and both permit continued use of mercury for a long time. In addition, no agreement exists on whether countries have to identify and characterize mercury use at chlor-alkali facilities or whether to allow new mercury-using chlor-alkali facilities under certain circumstances in the future. (UNEP (DTIE) 2012).[c]

In the case of Coatzacoalcos would be also helpful to insure protection of human health and environment from toxic mercury wastes. To prevent problems related to the generation of mercury waste in the future, it would be helpful for the treaty to require the minimization and prevention of generating mercury-containing waste, but the current text does not do this (UNEP (DTIE) 2012). [d]

To prevent continuous mercury pollution of the Coatzacoalcos – Minatitlán area including all water ecosystems and people depending on these ecosystems it is necessary to prevent further releases from the chemical industry complex, wastes and especially stop the use of mercury in chlorine production. Until these problems are addressed, mercury will continue to contaminate both the local area and contribute to global mercury pollution.

Significant levels of mercury were found also in the neighborhood of oil refinery in Minatitlán, which has increased processing capacity of crude oil to 350,000 barrels per day (BPD). This may lead to significant increases in mercury emissions in the broader region of Coatzacoalcos- Minatitlán according to US EPA (2001) and recent findings in UK (Lang, Gardner et al. 2012). The current treaty text does not address emissions of mercury from oil refineries (UNEP (DTIE) 2012).[e]

Acknowledgements:

Ecología y Desarrollo Sostenible en Coatzacoalcos, A.C., CAATA, Arnika Association and IPEN gratefully acknowledges the financial support the governments of Sweden and Switzerland, and others, as well as the technical support provide by the Biodiversity Research Institute (BRI) to analyze the data. The content and views expressed in this report, however, are those of the authors and IPEN and not necessarily the views of the institutions providing financial and/or technical support.

[b] **UNEP**(DTIE)/Hg/INC.5/3; Two phase out dates options bracketed in Annex D Part I: Processes subject to Article 7, paragraph 2

[c] **UNEP**(DTIE)/Hg/INC.5/3; Paragraph 5 in Article 7 is still bracketed. Alternative text provides opportunity to use mercury in newly established facilities.

[d] **UNEP**(DTIE)/Hg/INC.5/3; Not present in Article 13 on Wastes

[e] **UNEP**(DTIE)/Hg/INC.5/3; Oil and gas production and processing facilities is in brackets in Annex F proposal with not threshold proposed so far

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Chemical and petrochemical industry site: Coatzacoalcos region in Mexico.
Mercury levels in fish in the Coatzacoalcos River

IPEN Mercury-Free Campaign Report

Prepared by Ecología y Desarrollo Sostenible en Coatzacoalcos, A.C. and Centro de Análisis y Acción en Tóxicos y sus Alternativas – CAATA (Mexico) and Arnika Association (Czech Republic) and the IPEN Heavy Metals Working Group

Coatzacoalcos – Mexico City – 3 April 2013

Introduction

In 2009, the Governing Council of the United Nations Environment Programme (UNEP GC) decided to develop a global legally binding instrument on mercury to reduce risks to human health and the environment (UNEP GC25/5). The UNEP GC noted that mercury is a substance of global concern due to its long-range transport, persistence, ability to bioaccumulate, and toxicity. Its conclusions were based in part on the 2002 UNEP Global Mercury Assessment which noted that mercury is present in fish all over the globe at levels that adversely affect humans and wildlife (UNEP 2002).

This report focuses on the area of Coatzacoalcos-Minatitlán, where a chlor-alkali plant and waste incinerator are located inside of a petrochemical complex, and where an oil and gas refinery is located. This report is based on analyses of mercury levels in fish.

Levels of mercury in hair of population living in this area were examined in our previous report published in January 2013 (Ecología y Desarrollo Sostenible en Coatzacoalcos, CAATA et al. 2013).[1]

In addition, since local mercury releases become global problems due to long range transport we considered how the draft treaty text will address these sources.

Chemical and petrochemical industry complex in the Coatzacoalcos – Minatitlán area

The municipality of Coatzacoalcos, located in the southern state of Veracruz, is included in the so-called Olmec region, comprising 25 municipalities and dominated by the cities of Coatzacoalcos and Minatitlán. The area has a population of nearly two million and comprises approximately 41% of the economic activity in the state.

There are two main industrial sources of mercury pollution in the study area; a chlor-alkali plant inside of a petrochemical complex near the city of Coatzacoalcos (which also includes a waste incinerator) and an oil and gas refinery in Minatitlán.

The chlor-alkali plant is Industrias Químicas del Itstmo, S.A. (IQUISA), which is part of a company named Cydsa. The facility began chlorine production in 1968 using mercury cell

[1] See Mexico in Country Hot Spot Report at http://ipen.org/hgmonitoring/

technology. In 1981, Cloro de Tehuantepec (Mexichem) began operation using mercury but currently employs diaphragm cells and does not release mercury in their discharges.

The oil and gas refinery known as General Lázaro Cárdenas refinery was established in 1906, as the first major refinery in Latin America. A reconfiguration of the refinery was completed in 2011 to increase the processing capacity of crude oil to 350,000 barrels per day (BPD), an increase in the percentage of Maya crude.

In addition to the chemical production facilities, two incinerators were operating in the Pajaritos petrochemical complex at different times in the period of 1995 – 2002. The units burned chemical industry by-products and one incinerator had a capacity to burn 1.5 tons per hour (approximately 100 tons at day). A third incinerator started its operation in 2005 and burns mainly the wastes from vinyl chloride monomer (VCM) production.

Other potential sources of mercury emissions include private chemical industries established in the three petrochemical complexes (Pajaritos, Cangrejera and Morelos). In addition, there are regional hospitals and crematoria located in the area.

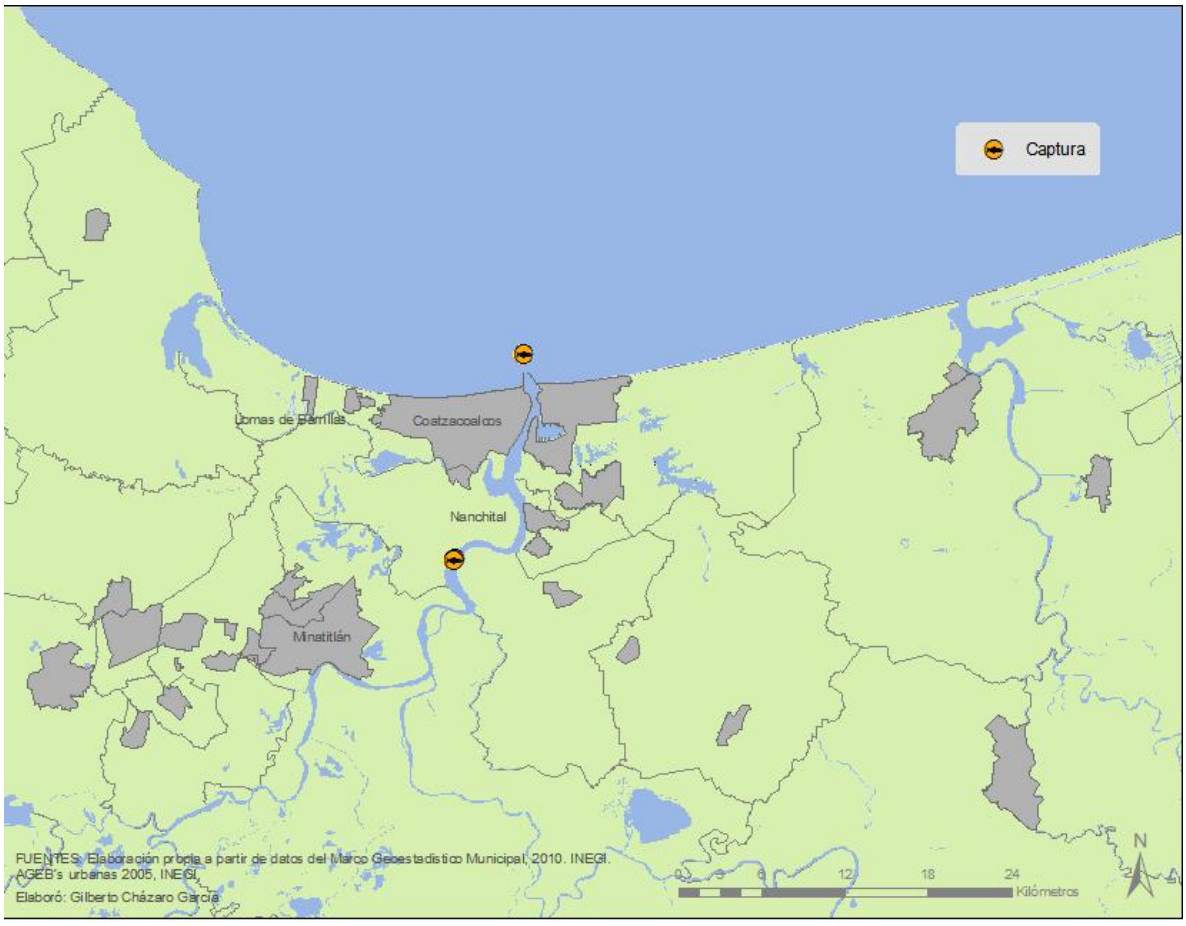

Figure 1: Map of Coatzacoalcos – Minatitlán region with marked location of the fish sampling sites.

Materials and methods

Ecología y Desarrollo Sostenible en Coatzacoalcos, A.C. conducted sampling of fish in cooperation with local fishermen using protocols developed by BRI (2011). Fifteen fish

samples were taken in total for this study in the Coatzacoalcos chemical industry area. Biodiversity Research Institute (BRI) measured mercury levels (total mercury content = THg) in fish samples in their laboratory in Gorham, Maine, USA. Ecologia y Desarrollo Sostenible en Coatzacoalcos, A.C. and CAATA characterized the site and provided information about its history and presumptive mercury sources.

Results and discussion

There is extensive literature on the presence of mercury in aquatic ecosystems in the area of Coatzacoalcos and some measurements of mercury in fish and hair. However, most of the data is 35 years old and there is no publically available clinical or epidemiological assessment of the impacts on the population. In these previous studies, the Minatitlán Refinery has never been considered as a possible source of mercury releases nor has its contribution to mercury content in fish or humans in the region been considered. According to Lang, Gardner, Holmes (2012) global concentrations of mercury in crude oil and gas range from 0.1 to 20.000 mg/kg in crude oil and 0.05 to 5000 mg/m^3 of natural gas. Acosta et al. (2001) note that it is likely that most of the mercury in present in crude oil processed in refineries in Mexico, although a portion of it could be passed to the lighter fractions as diesel or gas generated in the atmospheric cooling tower.

For this study, three fish species were sampled from two different localities in the Coatzacoalcos - Minatitlán area (see map at Figure 1): common snook (robalo blanco; ***Centropomus undecimalis***), fat snook (chucumite; ***Centropomus paralellus***) and gafftopsail catfish (bandera o banderilla; ***Bagre marinus).*** Table 1 shows the levels of mercury (Hg) in each type of fish.

Table 1: Mercury content of fish sampled in the river Coatzacoalcos in the area of Coatzacoalcos – Minatitlán, Mexico.

	Sample Size	**Hg Average (ppm, ww)**	**St Dev**	**Min Hg (ppm)**	**Max Hg (ppm)**	**Reference dose[2] (ppm)**	**Fraction of samples over Ref. Dose**
All fish samples	15	0.258	0.065	0.155	0.395	0.22	67%
Common snook	3	0.268	0.062	0.197	0.314	0.22	67%
Fat snook	3	0.306	0.096	0.205	0.395	0.22	67%
Gafftopsail catfish	9	0.239	0.053	0.155	0.339	0.22	67%

Abbreviations: Hg, mercury; ppm, parts per million or mg/kg; ww, wet weight; min, minimum; max, maximum

The results in Table 1 show that the mean mercury level in all 15 fish samples is higher than the US EPA reference dose of 0.22 ppm. Fish containing mercury concentrations of 0.22 parts per million (ppm) should be consumed no more than once per month [3] Two thirds of fish

[2] Figure derived from the reference dose used as U.S. EPA consumption guidelines for fish (0.2 mg.kg^{-1} methylmercury) based on the presumption that methylmercury counts for 90% of THg levels, limit value used by Canada is similar . Japan and/or UK use 0.3 reference dose. Source: US EPA (2001). Water Quality Criterion for the Protection of Human Health: Methylmercury. Final. EPA-823-R-01-001, Office of Science and Technology, Office of Water, U.S. Environmental Protection Agency Washington, DC**:** 303.

[3] Based on the U.S. EPA's reference dose of 0.0001 mg methylmercury per kg of body mass per day, we calculated fish consumption guidelines using an average body mass of 60 kg (132 pounds) and an average fish meal□size of 170 grams (6 ounces). Fish containing mercury concentrations of 0.22 parts per million (ppm)

samples had mercury levels higher than the reference dose. The maximum mercury value observed in the fish samples from Coatzacoalcos – Minatitlán area was observed in fat snook and exceeded the US EPA reference dose by 1,8-fold.

Báez et al. (1976) noted mercury in fish muscles in higher levels than observed in our study. For common snook levels of 0.20 to 0.97 ppm ww values reported in 1973 and 0.08-1.7 ppm ww in 1974. In ground croaker (ronco; ***bairdiella ronchus)*** they reported even higher levels of mercury 0.45-3.54 ppm ww.

Guentzel, Portilla et al. (2007) performed measurements of mercury in people living near the Alvarado lagoon system as well as fish from this ecosystem. Concentrations of total Hg in fish and shellfish harvested from the Alvarado lagoon system ranged from 0.01 to 0.35 ppm ww.

The concentration of mercury in muscle tissue of the hardhead catfish (***ariopsis felis***) in the southern Gulf of Mexico (between the years 2001-2004) ranged from <0.006 to 0.157 ppm dry weight (Vázquez, Florville-Alejandre et al. 2008). Range of mercury per dry weight of fish in samples from our study ranged between from 0.640 to 1.920 ppm dw and thus it can be considered as higher levels however in other fish species than hardhead catfish.

Recently there were found very high levels of mercury in fish from Mexico in carp with mean of 0.87 ppm ww in the study focused on Lake Chapala (Trasande, Cortes et al. 2010).

The transport of mercury in the atmosphere was inferred by Báez (1976) in Coatzacoalcos acid rain from air emissions generated by the 3 petrochemical complexes of Morelos, Pajaritos and Cangrejera that are carried by wind currents prevailing in the region of Coatzacoalcos going south and southeast.

Chlor-alkali plants using mercury, oil refinery, and waste incinerators in the mercury treaty

The chemical industry hotspot in the Coatzacoalcos – Minatitlán area provokes questions about how the mercury treaty might mandate actions to eliminate mercury pollution of the environment and fish from chlor-alkali facilities along with releases from other significant sources of mercury pollution.

More recent studies by (Pirrone, Cinnirella et al. 2010); (Mukherjee, Bhattacharya et al. 2009) estimate that the chlor-alkali sector produces 3-times higher total mercury releases to air than original the UNEP Chemicals (2008) air emissions inventory, while global releases to water caused by chlor-alkali plants were not estimated at all. These findings as well as case documented in this study underline need to set up an early date for phasing out mercury use in chlorine production, but from the two options (2020 or 2025) in proposed treaty text (UNEP

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should be consumed no more than once per month. Fish with mercury concentrations less than this value (<0.22 ppm) can be consumed more frequently. Fish with mercury concentrations greater than 0.95 should be avoided. Entirely. For more information see Appendix: Methods Behind the data in Global Mercury Hotspots BRI-IPEN Jan 2013. at http://ipen.org/hgmonitoring/pdfs/ipen-bri-report-global-hg-hostpots-2013-01-09.pdf

(DTIE) 2012) [4] the later one was negotiated in the fourth session of the INC (Intergovernmental Negotiating Committee) meeting on future Mercury treaty. It will permit continued use of mercury for a long time.

To prevent continuous mercury pollution of the Coatzacoalcos – Minatitlán area including all water ecosystems and people depending on these ecosystems it is necessary to prevent further releases from the chemical industry complex, wastes and especially stop the use of mercury in chlorine production. Until these problems are addressed, mercury will continue to contaminate both the local area and contribute to global mercury pollution.

Significant levels of mercury were found also in the neighborhood of oil refinery in Minatitlán, which has increased processing capacity of crude oil to 350,000 barrels per day (BPD). This may lead to significant increases in mercury emissions in the broader region of Coatzacoalcos- Minatitlán according to US EPA (2001) and recent findings in UK (Lang, Gardner et al. 2012). The current treaty text does not address emissions of mercury from oil refineries (UNEP (DTIE) 2012).[5]

We recommend that Health authorities conduct regular fish monitoring for mercury in the Coatzacoalcos Basin and develop a consumer alert strategy, with the participation of relevant academia, NGOs, and social organizations including those potentially affected by mercury in fish.

We also recommend that the Federal Government ensure that new industrial facilities in the Coatzacoalcos basin are consistent with the Mercury Treaty and do not utilize mercury catalysts. An example is the new petrochemical complex, Ethylene S XXI, under construction in the Nanchital Municipality near Coatzacoalcos, Veracruz with Mexican and Brazilian investment. The project is planned to produce 1 million of tons a year of ethylene and polyurethane in three polymerization plants beginning in 2015[6] . However, the recently adopted Mercury Treaty includes polyurethane production using mercury catalysts and notes that countries should aim "at the phase out of this use as fast as possible." [7]

Acknowledgements:

Ecología y Desarrollo Sostenible en Coatzacoalcos, A.C., CAATA, Arnika Association and IPEN gratefully acknowledges the financial support the governments of Sweden and Switzerland, and others, as well as the technical support provide by the Biodiversity Research Institute (BRI) to analyze the data. The content and views expressed in this report, however, are those of the authors and IPEN and not necessarily the views of the institutions providing financial and/or technical support.

[4] **UNEP**(DTIE)/Hg/INC.5/3; Two phase out dates options bracketed in Annex D Part I: Processes subject to Article 7, paragraph 2. Final adopted phase out date was 2025.

[5] **UNEP**(DTIE)/Hg/INC.5/3; Oil and gas production and processing facilities is in brackets in Annex F proposal with not threshold proposed so far and the source was taken out in the final adopted text

[6] See http://www.grupoidesa.com/es/content/etileno-xii

[7] http://www.unep.org/hazardoussubstances/Mercury/Negotiations/INC5/INC5Report/tabid/3496/Default.aspx

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