HEAVY METALS IN SEAWATER ALONG THE MEXICAN PACIFIC COAST

Víctor Pérez-Moreno, Miguel Ángel Ramos-López, Carlos Eduardo Zavala-Gómez and Miguel Ángel Rico Rodríguez

SUMMARY

In order to evaluate the presence of heavy metals, samples of seawater were taken over one year, covering the four seasons, at three sites along a 100km section of the Mexican Pacific Ocean coastline, which extends for 7338km. The central point was Playa Blanca, Guerrero, while the two extremes of the sampling area are open sea regions (El Calvario and Troncones) located 50km away along the northern and southern coastline, respectively. Mixed samples were prepared from without regard to zones of anthropogenic disturbance (touristic and urban areas). Field parameters were determined using a multimeter for pH, conductivity, and temperature. In the laboratory, alkalinity, bicarbonate, carbonate, and the following heavy metals: arsenic, cadmium, copper, chrome, mercury, nickel, lead and zinc were analyzed. All the metals analyzed had concentrations below the values allowed in the official Mexican standard. Lead and cadmium showed the highest values. For cadmium they were 0.0527, 0.0608 and 0.0934mg·l^{-1} in summer, autumn and winter of 2013, and 0.0793mg·l^{-1} in spring 2014. For lead, in the same seasons, they were 0.2422, 0.3542, 0.3104 and 0.3725mg·l^{-1}. The official Mexican standard allows for cadmium and lead concentrations of up to 0.1 and 0.2mg·l^{-1}, respectively.

Introduction

The substances dissolved in seawater may have a natural origin, issuing from geological sources, residues of plants and animals, dissolution of atmospheric gases, reactions in the water itself, or they can be the result of human activities.

The average amount of dissolved salts in seawater is constant, but their proportion and concentration varies geographically and seasonally. Salinity varies with basin latitude and depth, and with the seasons. Evaporation leads to a higher salinity and, thus, it is higher in tropical latitudes. Surface waters typically have higher levels of salt due also to evaporation (Pérez-Moreno *et al.*, 2012). Freshwater input decreases salinity in the mouth of rivers or after a large amount of rainfall.

Seawater is a solution of many different substances. It is mainly composed of sodium chloride, but it may also contain almost all natural elements, many of them only as traces. Six elements, in ionic state, represent nearly 99% of the solute composition of seawater; they are chlorine, sodium, potassium, calcium, magnesium, and sulfur (as sulfate). These ions allow salinity to be measured by the electrical conductivity of the water. However, in order to calculate the exact salinity of seawater it is necessary to know the total amount of solids present, the individual quantity of each salt compound, or the concentration of the dissolved substances. The difference in salinity between bodies of water, combined with temperature, produce density differences, resulting in the formation of ocean currents, a phenomenon termed thermohaline circulation (Delcroix *et al.*, 2005).

A very large variety of natural organic compounds is present in seawater. Most nutrients are transferred to the depths of the oceans as dead organisms sink. In the deeper layers, remineralized organic matter and nutrients return to the environment in the form of solution or sediment, a process that requires oxygen. Nutrient concentration generally increases with depth, while the oxygen concentration decreases, except in areas where there is a large amount of organic matter. This matter is a result of both plankton and detritus of marine and terrestrial organisms, and is a constituent of seawater in both particulate and dissolved form. Among dissolved material, high molecular weight molecules such as sugars and vitamins can be found. This is in addition to true colloidal substance solutes such as polysaccharides, proteins, urea, among others, not to mention hydrocarbons in some regions, which can be naturally occurring or from anthropogenic sources (Yiantsios *et al.*, 2005).

Deep seawater and surface water samples from the different bodies of water have been analyzed for heavy metals such as Cd, Pb, Cu, Ni and Co. It has been demonstrated that concentration levels of surface and deep seawaters may differ significantly in different bodies of water. The

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Víctor Pérez-Moreno. Chemical Engineer, Universidad Veracruzana, Mexico. M.Sc. in Chemical Engineering, Instituto Politécnico Nacional (IPN), Mexico. Doctor in Catalysis and Materials, Université Claude Bernard Lyon 1, France. Professor-Researcher, Universidad Autónoma de Querétaro (UAQ). Address: Centro de Estudios Académicos sobre Contaminación Ambiental (CEACA), Facultad de Química, UAQ. Cerro de las Campanas, C.P. 76010, Santiago de Querétaro, Qro; México. e-mail: vperez@uaq.mx

Miguel Ángel Ramos-López. Agronomical Engineer, Universidad Autónoma Metropolitana (UAM), Mexico. M.Sc in Ecology and Environmental Sciences, Universidad Nacional Autónoma de México (UNAM), Doctor en Ciencias Biológicas, UAM, Mexico. Professor-Researcher, UAQ, Mexico.

Carlos Eduardo Zavala-Gómez. Chemical Engineer and M.Sc. in Environmental Technology, UAQ, Mexico.

Miguel Ángel Rico-Rodríguez. Biologist, Universidad Autó-noma de Nuevo León (UANL), Mexico. M.Sc. in Ecology and Environmental Sciences, UNAM, Mexico), Doctor in Environmental Sciences, Universidad Autónoma del Estado de Hidalgo, Mexico. Professor-Researcher, UAQ, Mexico.

METALES PESADOS EN EL AGUA DE MAR A LO LARGO DE LA COSTA PACÍFICA DE MÉXICO

Víctor Pérez-Moreno, Miguel Ángel Ramos-López, Carlos Eduardo Zavala-Gómez y Miguel Ángel Rico Rodríguez

RESUMEN

A fin de evaluar la presencia de metales pesados se tomaron muestras de agua de mar durante un año, abarcando las cuatro estaciones, en tres sitios a lo largo de una sección de 100km de la costa pacífica de México, la cual se extiende por 7338km. El punto central es Playa Blanca, Guerrero, y los extremos del área de muestreo se hayan en mar abierto, 50km al norte (El Calvario) y al sur (Troncones) de ese centro, a lo largo de la costa. Se prepararon muestras mixtas, sin tomar en cuenta la presencia de zonas con afectaciones antropogénicos (turísticos y zonas urbanas). Los parámetros de campo se determinaron con un multímetro de pH, conductividad y temperatura. En el laboratorio se midieron alcalinidad, bicarbonato, carbonato, y los contenidos de los metales pesados arsénico, cadmio, cobre, cromo, mercurio, níquel, plomo y zinc. Todos los metales analizados presentaron concentraciones menores a las permitidas por la Norma Oficial Mexicana. Plomo y cadmio tuvieron los valores más altos. Para cadmio éstos fueron de 0,0527; 0,0608 y 0,0934$mg\cdot l^{-1}$ en verano, otoño e invierno de 2013, y 0,3725$mg\cdot l^{-1}$ en la primavera de 2014. Para plomo fueron, en las mismas estaciones, 0,2422; 0,3542; 0,3104 and 0,3725$mg\cdot l^{-1}$. La Norma Oficial Mexicana permite para cadmio y plomo hasta concentraciones 0,1 y 0,2$mg\cdot l^{-1}$, respectivamente.

METAIS PESADOS NA ÁGUA DO MAR AO LONGO DA COSTA PACÍFICA DO MÉXICO

Víctor Pérez-Moreno, Miguel Ángel Ramos-López, Carlos Eduardo Zavala-Gómez e Miguel Ángel Rico Rodríguez

RESUMO

Com a finalidade de avaliar a presença de metais pesados se tomaram amostras de água de mar durante um ano, abrangendo as quatro estações, em três locais ao longo de um trecho de 100 km da costa pacífica do México, a qual se estende por 7.338 km. O ponto central é Praia Branca, Guerrero, e os extremos da área de amostragem estão localizados em mar aberto, 50 km ao norte (El Calvário) e ao sul (Troncones) de esse centro, ao longo da costa. Prepararam-se amostras mistas, sem considerar a presença de áreas com afetações antropogênicos (turísticos e áreas urbanas). Os parâmetros de campo se determinaram com um multímetro de pH, condutividade e temperatura. No laboratório mediram-se alcalinidade, bicarbonato, carbonato, e os conteúdos dos metais pesados arsênico, cádmio, cobre, cromo, mercúrio, níquel, chumbo e zinco. Todos os metais analisados apresentaram concentrações menores às permitidas pela Norma Oficial Mexicana. Chumbo e cádmio tiveram os valores mais altos. Para cádmio estes foram de 0,0527; 0,0608 e 0,0934 $mg\cdot l^{-1}$ no verão, outono e inverno de 2013, e 0,3725 $mg\cdot l^{-1}$ na primavera de 2014. Para chumbo foram, nas mesmas estações, 0,2422; 0,3542; 0,3104 e 0,3725 $mg\cdot l^{-1}$. A Norma Oficial Mexicana permite para cádmio e chumbo concentrações até 0,1 e 0,2 $mg\cdot l^{-1}$ respectivamente.

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same is valid to a greater extent for coastal waters, particularly those affected by anthropogenic inputs that may be dispersed by tidal currents. The situation is complicated in coastal areas where tidal currents can carry plumes of polluted water over long distances (Mart *et al.*, 1982; Kim *et al.*, 2010).

The spatial distribution of heavy metals (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in dissolved and particulate fractions has been studied in the port of Mazatlán, Sinaloa, and adjacent areas in a coastal lagoon system located on the northwestern coast of Mexico. All metals, salinity, suspended matter, and particulate organic matter showed seasonal variations, with similar patterns (Páez-Osuna and Ruíz-Fernández, 1995; Bozkurt *et al.*, 2014). Also, in sediment samples, the concentrations of seven metals (Al, Cd, Cu, Fe, Pb, Ni, and Zn) were determined over three years at the mouth of the Itata River (south-central Chile) and the adjacent sea area (Chandía and Salamanca, 2012).

The aim of this study was to determine the physicochemical properties of seawater and the presence of heavy metals in the Mexican Pacific in three sites along 100km of coastline.

Experimental

Sampling area

The sampling area included three sites along 100km of coastline of the Mexican Pacific Ocean. The central point was the bay of Playa Blanca, Guerrero (17º34'45"N, 101º27'97"W). The northern point, El Calvario (17º23'08"N, 101º09'64"W) and the southern point, Troncones (17º47'00"N, 101º43'73"W) were both open sea regions located along the coastline 50km to the north and the south of Playa Blanca (Figure 1). Mixed samples were prepared from this region, avoiding zones with anthropogenic discharges (touristic and urban areas), so as to fulfill the criteria of not presenting anthropogenic disturbances (Pérez-Moreno *et al.*, 2013).

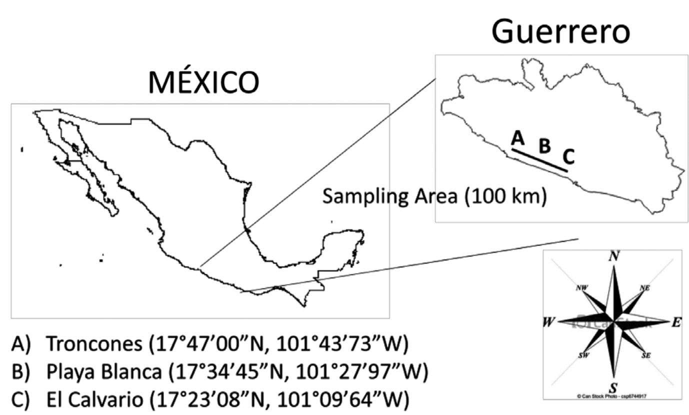

Figure 1. Sampling and seawater characterization area on the Mexican Pacific coast.

Sampling of seawater was based on the NOM-014-SSA1-1993. The samples were collected seasonally (year round) and at the three sites. For each site, one mixed sample was made with 10 single samples from the central point and five samples from 5km towards the north (each separated by 1km) and other five samples from 5km towards the south. They were mixed and taken to the laboratory. This method was used for each tested point of the coastline.

Mexican Pacific seawater physicochemical characterization

Field parameters were determined *in situ* with a Hanna HI 9828 multimeter for pH (NMX-AA-008-SCFI-2011), conductivity (NMX-AA-093-SCFI-2000), and temperature (NMX-AA-007-SCFI-2013). In the laboratory, alkalinity, bicarbonate, and carbonate were determined according to NMX-AA-036-SCFI-2001.

Mexican Pacific seawater heavy metals determination

Heavy metals: arsenic (As), cadmium (Cd), copper (Cu), chrome (Cr), mercury (Hg), nickel (Ni), lead (Pb) and zinc (Zn) were determined by atomic absorption spectrophotometry based on NMX-051-SCFI-2001 with an Atomic Absorption Spectrophotometer (Perkin Elmer, model AAnalyst 200). Traceable standards from High Purity Standards (Charleston, SC, USA) were used for As (#1431419), Cd (#1420605), Cr (#1412804), Cu (#1502704), Hg (#1530716), Ni (#1419192), Pb (#1424101) and Zn (#1502616). The sample recovery percentages were: As 91%, Cd 95, Cr 98, Cu 98, Hg 99, Ni 91, Pb 97 and Zn 99%.

Results and Discussion

Mexican Pacific seawater physicochemical characterization

The physicochemical parameters of the seawater determined in three sites along the Mexican Pacific coastline over one year are shown in Tables I, II and III. The average temperatures, pH, CE, alkalinity, HCO^{3-} and CO^{3-} were similar in Playa Blanca, El Calvario and Troncones. In a study conducted in three different stations from Santa Cruz de Miramar, Nayarit, México (Pacific seawater), Vargas-Machuca *et al.* (2008) reported an annual average pH for each of the sampling points ranging 9.2-9.5 and temperatures of 30.8, 30.7 and 30.7ºC. These results are in contrast to the ones from the present study. This may be due to the fact that the seawater from Nayarit was sampled in three plastic cages and also on a fish farm, conditions that could be factors causing an increase in the mentioned parameters. On the other hand, López-Ortega *et al.* (2012) reported a temperature of 25.08ºC, pH of 7.53 and 42.13mS·cm^{-1} for a samples from Laguna de Tampamachoco, in the state of Veracruz on the Gulf of Mexico. These values are similar to those found in this study.

As can be observed in Table I, alkalinity shows seasonal variation, increasing in summer and winter. CO_2 would be absorbed from the atmosphere by the oceans at an increased rate if ocean alkalinity increased. There is also substantial seasonal variability in pH and other carbon system parameters in the ocean, resulting in cyclic change that cause long-term trends in pH. The changing ocean pH and carbonate chemistry will affect a broad spectrum of physical and biogeochemical properties of the ocean ecosystems including metals chemistry. If CO_2 is high, carbon moves from the ocean to the atmosphere; if low, from the atmosphere to the ocean. CO_2 is, in turn, controlled by the pH of seawater; as pH increases, CO_2 decreases so that the oceans tend to absorb more carbon to re-establish equilibrium (Harvey, 2008).

The Earth's oceans represent the largest surficial carbon reservoir of its carbon cycle. The mean concentration of inorganic carbon in ocean water is ~2.3mmol·kg^{-1} and its residence time is ~200kyr. Ocean and atmosphere exchange carbon in the form of carbon dioxide (CO_2). Atmospheric CO_2 is therefore strongly coupled to the oceanic reservoir. The total amount of dissolved inorganic carbon in the modern ocean is about 60 times greater than that of the pre-anthropogenic atmosphere (Siegenthaler and Sarmiento, 1993).

Dissolved carbon dioxide in seawater occurs mainly in three inorganic forms (Zeebe and Wolf-Gladrow, 2001): free aqueous carbon dioxide (CO_2 (aqueous)), bicarbonate (HCO_3^-), and carbonate ions (CO_3^{2-}). The results obtained from this study showed that pH varied from 7.88 to 8.37. In this interval, the concentration of HCO_3^- tended to increase and that of CO_3^{2-} diminished when pH decreased. If this continues over time, pH may continue to lower, which could affect marine life (Hettinger *et al.*, 2012).

TABLE I
SEASONAL VARIATION OF PHYSICOCHEMICAL PARAMETERS IN PLAYA BLANCA DURING ONE YEAR

Parameters	Summer 2013	Autumn 2013	Winter 2013-14	Spring 2014
Temperature (ºC)	27.5	20.1	19.6	21.5
pH	8.37	7.95	8.35	7.88
CE (mS·cm^{-1})	46.0	57.7	58.4	57.7
Alkalinity (mg·l^{-1})	136.99	130.20	135.21	131.73
HCO_3 (mg·l^{-1})	1.839	1.951	1.843	2.144
CO_3 (mg·l^{-1})	0.955	0.943	0.954	0.861

Values are an average of 3 determinations for each parameter of a mixed sample.

TABLE II
SEASONAL VARIATION OF PHYSICOCHEMICAL PARAMETERS IN EL CALVARIO DURING ONE YEAR

Parameters	Summer 2013	Autumn 2013	Winter 2013-14	Spring 2014
Temperature (ºC)	27.2	19.8	19.2	21.0
pH	8.42	8.27	8.09	7.11
CE (mS·cm^{-1})	54.6	58.3	59.3	58.2
Alkalinity (mg·l^{-1})	136.70	131.73	134.74	130.12
HCO_3 (mg·l^{-1})	1.842	1.823	2.192	1.924
CO_3 (mg·l^{-1})	0.913	0.953	0.889	0.863

Values are an average of 3 determinations for each parameter of a mixed sample.

TABLE III
SEASONAL VARIATION OF PHYSICOCHEMICAL PARAMETERS IN TRONCONES DURING ONE YEAR

Parameters	Summer 2013	Autumn 2013	Winter 2013-14	Spring 2014
Temperature (ºC)	26.9	19.9	19.3	21.3
pH	8.43	8.45	8.05	8.15
CE (mS·cm^{-1})	53.2	58.4	58.4	57.3
Alkalinity (mg·l^{-1})	137.28	131.73	135.12	134.12
HCO_3 (mg·l^{-1})	1.843	1.889	1.921	1.897
CO_3 (mg·l^{-1})	0.907	0.947	0.889	0.852

Values are an average of 3 determinations for each parameter of a mixed sample.

Mexican Pacific seawater heavy metals determination

The mean concentrations of As, Cd, Cu, Cr, Hg, Ni, Pb, and Zn in water are shown in Tables IV, V and VI. The results show that the parameters were similar in all three locations. All the metals but Pb were below the limits established by the Mexican legislation (NOM-001-ECOL-1996),

TABLE IV
SEASONAL VARIATION OF HEAVY METALS IN PLAYA BLANCA DURING ONE YEAR

Metal (mg·l^{-1})	Summer 2013	Autumn 2013	Winter 2013-2014	Spring 2014
Arsenic	<0.0012	<0.0013	<0.0011	<0.0013
Cadmium	0.0527	0.0608	0.0934	0.0793
Copper	<0.0155	<0.0436	<0.0436	<0.0281
Chrome	<0.0397	<0.1456	<0.0966	<0.0706
Mercury	<0.001	<0.001	<0.001	<0.0008
Nickel	0.1714	0.2245	0.3251	0.2448
Lead	0.2422	0.3542	0.3104	0.3725
Zinc	<0.1628	<0.1670	<0.1472	<0.1385

Values are an average of 3 determinations for each parameter of a mixed sample.

TABLE V
SEASONAL VARIATION OF HEAVY METALS IN EL CALVARIO DURING ONE YEAR

Metal (mg·l^{-1})	Summer 2013	Autumn 2013	Winter 2013-2014	Spring 2014
Arsenic	<0.0012	<0.0013	<0.0011	<0.0013
Cadmium	0.0736	0.0650	0.0925	0.0879
Copper	<0.0202	<0.0436	<0.0436	<0.0333
Chrome	<0.0397	<0.1380	<0.0966	<0.0693
Mercury	<0.001	<0.001	<0.001	<0.0008
Nickel	0.1930	0.2484	0.3989	0.2710
Lead	0.2420	0.3560	0.3291	0.3451
Zinc	<0.1526	<0.1492	<0.1502	<0.1380

Values are an average of 3 determinations for each parameter of a mixed sample.

TABLE VI
SEASONAL VARIATION OF HEAVY METALS IN TRONCONES DURING ONE YEAR

Metal (mg·l^{-1})	Summer 2013	Autumn 2013	Winter 2013-2014	Spring 2014
Arsenic	<0.0012	<0.0013	<0.0011	<0.0013
Cadmium	0.0832	0.0680	0.0902	0.0910
Copper	<0.0204	<0.0436	<0.0436	<0.0333
Chrome	<0.0405	<0.1521	<0.0966	<0.0966
Mercury	<0.001	<0.001	<0.001	<0.0008
Nickel	0.1814	0.2305	0.3812	0.2704
Lead	0.2427	0.3487	0.3238	0.3631
Zinc	<0.1754	<0.1560	<0.1480	<0.1372

Values are an average of 3 determinations for each parameter of a mixed sample.

while for Pb the values reported for the three coastline points and for all the seasons were higher than the value established by the law, which sets the maximum permissible contaminant limit in wastewater discharges into national waters and territories at a maximum value of 0.2mg·l^{-1} for fisheries, navigation and estuaries areas. The average of Playa Blanca was 0.3198mg·l^{-1}, El Calvario 0.3181mg·l^{-1} and Troncones 0.3196mg·l^{-1}.

Páez-Osuna *et al.* (1989) conducted a similar study of heavy metals along the Mexican Pacific coast in the Mazatlán Harbor, and showed the mean dissolved concentration (over 10 months) to be for Cd <0.01, Cr <0.05, Cu 1.2, Pb 0.67, Ni 2.4 and Zn 42µg·l^{-1}, values which are above those resulting from this study. On the other hand, Vázquez-Sauceda *et al.* (2005) found 0.32mg·l^{-1} for Cd and 0.45mg·l^{-1} for Pb in seawater from the Gulf of Mexico, a similar behavior as for Pb, with higher values than permissible limits according to the Mexican legislation, as in our study.

Mexican Pacific seawater bioavailability of heavy metals Absorption from solution in seawater may occur across the general body surface area of an organism or through special areas such as gills. If an animal drinks seawater the absorption occurs across the walls of the gut. However, metal bioavailability is strongly linked to the direct and indirect effects of the abiotic factors that determine chemical speciation reactions in the medium (complexation with the different inorganic and organic ligands in the dissolved and particulate phases) and to the exposure regime (Leao *et al*., 2007).

Nevertheless, there are some studies in marine organisms that indicate the presence of heavy metals along the Mexican Pacific Coast (Nuñez-Nogueira *et al*., 2012; Ruelas-Inzunza *et al*., 2010). This indicates that heavy metals present a serious threat to the marine environment due to their potential toxic effects (Negri and Heyward, 2001). The concentrations of Cd and Pb found in the present study demonstrate the persistence and long-distance transportation of aquatic pollution from input sources. Studies *in vivo* and *in vitro* suggested that acidification could aggravate heavy metal such as Cd and Pb pollution and toxicity for marine organisms (Han *et al*., 2014). Also, metals transferred through aquatic food webs to fish and humans are an environmental and human health concern.

There is increasing evidence that a high concentration of CO_2 in seawater decreases pH and consequently many of the pollutants such as heavy metals become more bioavailable to the organisms that live there. Our results provide complementary information about the state of the seawater contamination with heavy metals in Mexican Pacific Coast and the state of acidification in this zone; the results suggest a trend in the reduction of pH, which has been seen in the seawater around the world.

Conclusions

The heavy metals measured, except Pb, were below the contamination levels allowed according to the Mexican legislation for maximum permissible limits of heavy metals. The levels for Pb were above the allowed contamination level for fisheries, navigation and estuaries areas, and other uses. However, these areas could be used for recreation, because it is below the maximum permissible limits (0.5 mg·l^{-1}).

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