Fachhochschule Köln
Cologne University of Applied Sciences

UNIVERSIDAD AUTÓNOMA DE SAN LUIS POTOSÍ

FACULTADES DE CIENCIAS QUÍMICAS, INGENIERÍA Y MEDICINA

PROGRAMA MULTIDISCIPLINARIO DE POSGRADO EN CIENCIAS AMBIENTALES

AND

COLOGNE UNIVERSITY OF APPLIED SCIENCES

INSTITUTE FOR TECHNOLOGY AND RESOURCES MANAGEMENT IN THE TROPICS AND SUBTROPICS

CONSTRUCTION OF A MULTIDISCIPLINARY SCENE OF RISK IN "HUASTECA SUR"

THESIS TO OBTAIN THE DEGREE OF

MAESTRÍA EN CIENCIAS AMBIENTALES
DEGRRE AWARDED BY UNIVERSIDAD AUTÓNOMA DE SAN LUIS POTOSÍ

Y

MASTER OF SCIENCE
"TECHNOLOGY AND RESOURCES MANAGEMENT IN THE TROPICS AND SUBTROPICS
FOCUS AREA "ENVIRONMENTAL AND RESOURCES MANAGEMENT"
DEGREE AWARDED BY COLOGNE UNIVERSITY OF APPLIED SCIENCES

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SAN LUIS POTOSÍ, MÉXICO OR COLOGNE, GERMANY **JULY, 2010**

Fachhochschule Köln
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LA MAESTRÍA EN CIENCIAS AMBIENTALES RECIBE APOYO A TRAVÉS DEL PROGRAMA NACIONAL DE POSGRADOS (PNP - CONACYT)

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ABSTRACT

Manganese is an essential element for human, animal and plant species but high concentrations exposure can adversely affect human and ecological health. Manganese has been associated with neurotoxicity in children and psychiatric damage in adults. No studies were found for effects to biota in a polluted area with manganese. In the southern Huasteca area around the city of Tamazunchale, high levels of manganese have been found in sediments of the “Rio Claro”, and in soil and dust samples of the communities next to it. Interestingly, however, urinary manganese was found in children living in them. The source of manganese is the mining industry located in the nearby State of Hidalgo. This mine discharges manganese material into the regional aquatic ecosystem. In the region, humans and biota are exposed to high concentrations of manganese; therefore, there is a need for an integrated risk assessment. The construction of the protocol for this assessment was the objective of the present work. Pathways of exposure were identified and susceptible species were selected for the study, children, rodents (*Peromyscus spp* and *Rattus sp*) and amphibians are recommended as biomonitors for this approach.

Key words: *manganese, integrated risk assessment*

RESUMEN

El manganeso es un elemento esencial pero la exposición a concentraciones altas puede afectar la salud de los seres vivos. Se ha reportado que el exceso de manganeso es neurotóxico para niños y ocasiona daños psiquiátricos en adultos. Por otro lado, no encontramos estudios sobre los efectos del manganeso en organismos de la biota en sitios contaminados por este metal. En la Región Huasteca Sur, próximos a la ciudad de Tamazunchale, se han registrado niveles altos de manganeso en sedimentos del “Rio Claro", y en el suelo superficial y en el polvo de las comunidades de su ribera. Es más, un estudio preliminar reportó valores de manganeso urinario mayores en estas comunidades que en una comunidad de referencia. La fuente de manganeso es la industria minera localizada en el estado cercano del Hidalgo. Esta minera emite manganeso al ecosistema acuático regional.

Por todo lo anterior, podemos concluir que en esta región, los humanos y los organismos de la biota se encuentran expuestos a concentraciones altas de manganeso; por lo tanto, se requiere de una evaluación de riesgo integrada. La construcción del protocolo para esta evaluación fue el objetivo del presente trabajo. Se identificaron las rutas de exposición y fueron seleccionadas las especies susceptibles para el estudio. Recomendamos a niños, roedores (*Peromyscus spp* y *Rattus sp*) y anfibios.

Palabras clave: *manganeso, evaluación de riesgo integrada*

ZUSAMMENFASSUNG

Mangan ist ein essentielles Element für den Menschen, die Tiere und die Pflanzen. Jedoch kann die Aufnahme von hohen Konzentrationen erhebliche menschliche und ökologische Gesundheitsschäden hervorrufen. Es ist bekannt, dass zu viel Mangan neurotoxische und psychische Schäden in Erwachsenen und Kindern verursacht. Bis heute wurden noch keine Studien für Effekte in der Biota in einem spezifischen manganangereicherten Gebiet gefunden. Diesem soll mit Hilfe dieser Studie abgeholfen werden. Bei der Stadt Tamazunchale im südlichen „Huasteca Potosina“ sind hohe Konzentrationen von Mangan im Sediment des "Rio Claros", im Boden sowie in Staubproben in den dortigen Gemeinden gefunden worden. Selbst in Urinproben von Kindern aus den Gemeinden wurden beachtliche Konzentrationen von Mangan gefunden. Das Mangan stammt aus einem Bergbau aus dem nahe gelegenen Staat Hidalgo. In „Huasteca Potosina“ sind Menschen und Biota hohen Konzentrationen von Mangan ausgesetzt. Deshalb ist es von grosser Wichtigkeit eine ganzheitliche Risikoanalyse durchzuführen. Der Aufbau des Protokolls der Risikobewertung war das Ziel der vorliegenden Arbeit. Es wurden Pfade und Medien der Aussetzung identifiziert sowie empfindliche Arten für die Studie ausgewählt. Kinder, Nagetiere (*Peromyscus spp* und *Rattus sp*) und Amphibien werden als Biomonitor für die Riskobewertung empfohlen.

Schlüsselwörter: *Mangan, ganzheitliche Risikoanalyse*

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1. INTRODUCTION

1.1. THE SCENARIO

In the southern Huasteca area around the city of Tamazunchale, high levels of manganese have been found in sediments of the “Rio Claro”, and in soil and dust samples of the communities next to it. More importantly, urinary manganese was found in children living in them. The source of manganese is one of the mines of “Minera Autlán” which is located in the nearby State of Hidalgo. This mine discharges manganese material into the regional aquatic ecosystem and emits dust and smoke into the air. The dust and smoke produced by mining processes are manganese oxides (MnO_2 and Mn_3O_4) (Merian, 1991).

Considering the levels that have been reported in it, the “Rio Claro” is the most contaminated river of manganese presently known in the world. Because of this, a group from the Autonomous University of San Luis Potosí (UASLP) performed a health risk assessment in the area. Four villages were chosen, three exposed to manganese (Santa María Picula, Tenexco, Texojol) and Cautlamayán as a reference community. Taking into account the results, Santa María Picula was the village with the highest risk (Medina-Fernández, 2008).

According to Medina-Fernández (2008) samples were taken in Santa María Picula in order to defined pathways of exposure for humans, including: dust, drinking water, water of the river, sediments, and surface soil. Samples of children´s urine were taken as a biomarker of exposure for manganese. Samples were characterized in dry and wet seasons.

Urinary manganese in children living in Santa María Picula showed a concentration of 22.8 ± 8.8 µg/L in the high rainy season and 29.4 ±7.5 µg/L in the low rainy season, which is up to 10 times higher than the concentration found in children living in Cuatlamayán (<3.4 µg/L). According to ATSDR (2009) the occurrence of manganese in human’s urine is 1 to 8 µg/L. Dust samples in Santa María Picula showed a manganese concentration of 5,271.7 ± 1,355.5 and 6,871.0 ± 1,345.0 mg/kg depending the high or low precipitation season. This concentration is 15 times higher than that found in Cuatlamayán (452.2 ± 63.7 mg/kg). According to ATSDR, (2009) the background level of manganese in sediments and soil is 900 mg/kg. The concentration of manganese in sediments found in the Rio Claro were 100 times higher than the limit: 4,488.3 – 1,3154.2 mg/kg in the high and 15,455.1 mg/kg in the low precipitation season. Whereas, soil samples showed a concentration between 22,127.2 – 23,737.7 and 13,080.2 ± 5,958.7 mg/kg also depending of the high and low raining season; that is, 100 times higher than the limit which is 900 mg/kg (ATSDR, 2009) and can be up to more than 56% higher than the concentration found in Cuatlamayán (394,7 ± 59,7). In the water for human consumption as well as in the water of the river, the concentrations of manganese were below guidelines.

1.2. Manganese

Mn is wide spread in nature and the occurring concentrations are barely toxic. Manganese can have natural and anthropogenic sources (ATSDR, 2009). Mn is an essential metal, which can be found in human, animals, soils and plants. In cells it is used as an activator for some enzymes (Merian, 1991). It plays an important role in the bones, the urea cycle and it has a key role in wound healing (ATSDR, 2009).

The deficiency but also the excess of manganese can bring up severe health disadvantages such as Manganese pneumonia or Manganism (Merian, 1991) especially by inhaling a high concentration or via oral exposure. Manganism is a serious neuro-psychotic disease which is very similar to Parkinson. Neurological symptoms are: decreased memory, fatigue, headache, vertigo, equilibrium loss, insomnia, tinnitus, trambling of fingers, muscle cramps, rigidity, alteration of libidio, and sweating (Menezes-Filho, et al., 2009).

1.3 Humans

Manganese is classified as an essential nutrient. Human needs 2.5 – 5.0 mg/day, which is a dose absorbed within a good diet. The most important source of the metal is diet (Greger, 1998). Mainly, manganese accumulates in mitochondria and that is why it is stored in organs like the liver, the kidney, the pancreas and also in the hypophysis. It is excreted by bile and intestinal tract. Manganese is able to get into the fetus and concentrates in liver and brain. Newborns and infants do have a higher risk for dangerous accumulation of manganese (Merian, 1991).

The absorption of manganese occurs generally through the diet but absorption through inhalation can be important for occupationally exposed persons. Normally the level of manganese in the tissues is maintained through dietary intake of manganese, (ATSDR, 2009).

Manganese is eliminated through hepatobiliary excretion. The elimination through maternal milk and urine are expected to be small. Manganese can be found the brain and in all mammalian tissues, but in liver, pancreas, and kidney the concentration is higher than in other tissues (Dorman, et al., 2006).

According to ATSDR (2009) especially MnO_2 and Mn_3O_4 can cause an inflammatory response in the lung. Manganism is also caused by inhaling a high concentration of manganese, probable more than 100 mg/d during some months or years. It is said, that Mn(III) is more cytotoxic to human neural cells than other manganese complexes. But also Mn(II) may also involved in neurotoxicity. It could be a substitute for Ca(II). The transport of Mn(II) into brain cells is still uncertain but it preferentially accumulates in the mitochondria in the areas of the brain, which are associated with manganism and neurological symptoms.

Manganese shares characteristics with iron (Fe). In physiological conditions both have the valences of 2^+ and 3^+ and similar ionic radius. Also, both are bind strongly to transferrin and accumulate in the mitochondria. Low Fe stores is associated with increasing Mn uptake (Mertz, et al., 1994).

Mn can accumulate in the central nervous system. Exposure to Mn was shown to interfere with several neurotransmitter, especially in the dopaminergic system which is responsible for motor coordination, attention, and cognition. Mn is a potent dopamine oxidant, which could explain the toxicity in some dopaminergic brain regions. Mn could destroy or inactivate the membrane by free radicals or cytotoxic quinines (Medina-Fernández, 2008).

1.4. BIOTA

Manganese is required for the healthy growth of animals and plants but it can also have negative effects on biota.

In animals, manganese is needed for carbohydrate and lipid metabolism and growth as well as for reproduction and skeletal development (dpi, 2010). High levels of manganese may produce neurotoxic response such as hypoactivity, nervousness, tremors and ataxia, negative effects on the liver and decrease growth. In plants manganese participates in the oxygen-evolving system of photosynthesis and in the photosynthetic electron transport system (EPA, 2007).

Chronic inhalation by animals of concentrations higher than 5 mg/m^3 of manganese is known to produce adverse neurobehavioral, respiratory and reproductive effects (Pfeifer, et al., 2004). The excess of Manganese has a negative effect in the metabolism of animals and can produce an impairment of hemoglobin formation because of the reduced intake of iron into the porphyrin ring. In the case of sideropenic anemia, hemoglobin formation is produced by 45 ppm manganese in feed (Merian, 1991). The concentration in the tissue depends on the extent of exposure, nutritional status (regarding iron), and the body’s metabolic control mechanisms for manganese (Pfeifer, et al., 2004).

When neonate and adult rats are exposed to manganese, neonate obtain a higher concentration and manifest more extensive brain pathology than adults. Juvenile animals have an increased absorption through the gastrointestinal tract and it is important to remember that in these animals the blood-brain barrier is incompletely formed. Manganese can induce an alteration in the brain dopamine concentration (ATSDR, 2000).

Rats inhaling a water soluble form of Mn show a higher Mn concentration in the lung than an insoluble form (Pfeifer, et al., 2004).

Inhaled Mn may migrate up the olfactory nerves to the olfactory bulb in rodents. Still it is not known, if in primates have the same process, because the olfactory structure is quite different (Pfeifer, et al., 2004). However, studies in rodents and primates reported that Mn may bypass the blood-brain barrier when it comes in contact with the olfactory mucosa and is transported to the olfactory bulb (Riojas-Rodríguez, et al., 2006). According to Erikson, et al., (2002) animals with iron-deficient anemia accumulate more Mn in brain. Rodents with an iron-deficient have a higher risk to accumulate Mn in brain.

According to a study of Kuperman, et al., (2004) manganese in soil can be toxic to invertebrates like earthworm (*Eisenia fetida*), enchytraeid (*Enchytraeus crypticus*), and collembolan (*Folsomia candida*). The toxicity depends on the species of the invertebrates and the concentration of manganese. Effects were observed in adult survival, cocoon production and juvenile production. The lowest effect of manganese was observed at 116 mg/kg Mn/soil in E. crypticus.

Dissolved Manganese can reduce the function of the gill epithelium, disrupts the balance and may impact the hematology of fish. The toxicity of manganese on fish depends on the fish species and can be between < 1 and ≥ 50 mg/L. Next to the species it also depends on the life stage and ambient water chemistry. The lower the hardness of the water the higher is the toxicity. Rainbow trouts for example are very sensitive to manganese in water where the hardness is approximately 50 mg/L or less (Fish, 2009).

In plants, manganese is involved in chlorophyll synthesis, the activity of oxidase enzymes and growth (dpi, 2010). Manganese concentrates in plants. Plants absorb manganese as Mn(II) which is also influenced by the pH and the oxidation-reduction potential (ATSDR, 2000). The most diagnostic symptom of manganese toxicity in plants is the darkening of leaf veins. The accumulation of dark crystal is the insoluble manganese dioxide in tissues or along the veins. This is expressed by plants as pothos, hibiscus and rose-of-Sharon, bean, soybean, potato, chrysanthemum, tomato and cucurbits. Another symptom is the interveinal chlorosis with leaf cupping or necrotic blotching of foliage. These symptoms produced by manganese can mostly found in the cabbage and lettuce (Schubert, 1992).

The main manganese sources in food are grain, whole meal bread, vegetables, nuts, and tea. Milk products and fish contain relatively low concentrations (Merian, 1991).

1.5. Conclusion

Taking all this antecedents into account, it can be concluded that the area impacted by the manganese present in the Rio Claro sediments, has to be declared a high risk area both for humans and biota. Therefore, there is a need for an integrated risk assessment.

THE ELABORATION OF THE PROTOCOL FOR AN INTEGRATED RISK ASSESSMENT

IN THE AREA OF THE RIO CLARO WAS THE MAIN PURPOSE OF THE PRESENT THESIS

2. METHODS

As mentioned before, the exposure to a high concentration of manganese in human and/or biota can produce negative health effects. Thus an integrated risk assessment that includes both human and biota species is recomended for the area impacted by this metal.

Integrated Risk Assessment is a tool that combines human health and ecological risk assessments. The aim of the method is to analyse if a certain concentration of a stressor could have a negative effect on humans and/or biota, as a result of exposure (Diaz-Barriga, et al., 2001).

Actually, human health and ecological risk assessments methodologies have been developed independently. However, with the growing need to protect human and biota, an integrated approach has evolved. In this type of assessment, the risk of exposure is addressed to situations of multi-stressors, multi-media, multi-pathways, and multi-species (WHO, 2010). With an integrated analysis, the quality and the efficiency of the assessment is improved, as there is an exchange of information between human and biota, making more coherent the decision making processes (Suter, et al., 2003). Furthermore, it is also important to include in the same assessment, humans and biota because the protection of humans will not inevitably conclude in the protection of an ecosystem. Nonhuman receptors can be more exposed or more sensitive to contamination than humans (Reyes, 2009).

During an integtated risk assessment, the human being is seen as a part of the ecosystem. This has the consequence that stressors are not reduced to chemicals, biologicals and/or physical stressors, but also the concept includes those factors that have a negative effect in the environment decreasing the quality of life of the population (Ilizaliturri, et al., 2009). It has to be seen that both, biota and humans, deserve protection, remembering every time that some types of contamination may do not harm humans as they do harm biota. In this case, the effects on biota is the leading reason for restauration (Diaz-Barriga, et al., 2001).

The integrated risk assessment consist of three phases: the first is the *Problem Formulation*, followed by *Analysis* and ending with *Risk Characterization.* The assessment starts with the Problem Formulation where goals, objectives, scope and activities in the assessment are identified (Diaz-Barriga, et al., 2001). During the Analysis data are collected and modeling exercises are done to characterize the exposure in time and space in order to define its effects on humans and ecological systems. In the Risk Characterization step, exposure and effect information are synthesized in order to estimate the risk, the uncertainties are considered, and the results are explained to stakeholders (WHO, 2010). In Ecological and Health Risk Assessments the step of risk characterization is the key step providing a description of the evidence concerning the hazard, potential exposures, uncertainties, variability, and assumptions used in the assessment. Thus, the integration of risk assessment approaches is encapsulated in the analytical processes (Orme-Zavaleta, et al., 2010).

2.1. Problem Formulation

The objective of this step is the description of the risk scenario (Site Description), including information regarding (Ilizaliturri, et al., 2009):

- The source of the stressor
- The media through which the stressor has contact with the receptor
- Description of the receptor

The problem is that in contaminated places, different stressors (multiple toxics) may impact different media (multiple pathways) and different receptors.

Stressors can be classified as chemicals (natural, industrial, etc.), biologicals (microorganisms), and physical (radiation, temperature, etc). It is always important to analyze both, the time of exposure and the concentration of the stressor; as the toxic dose depends in these factors. Also, the toxic concentration depends on the biological characteristics of the receptor, such as gender, age, diet sources, etc. For example, pregnant women and children deserve higher attention due to the windows of susceptibility that are present during these periods (Ilizaliturri, et al., 2009).

The “descripition of the site” also includes geografical and socio-economical data, use of soil, biological information, information regarding access to potable water, meteorological data, etc. Using this information and knowing more about the stressor and its sources, a model of the site can be obtained where the most important pathways of exposure and the identification of the biota and the population receptors are described (Diaz-Barriga, et al., 2001). However, it is important to considered that identification of the biota receptors is a more complex issue because various species may be susceptible to the same stressor (Ilizaliturri, et al., 2009); thus, prioritization factors have to be developed in each site.

2.2. Analysis

This step includes three phases: “analyses of the environmental contamination”, the “assessment of the components of the biota”, and the “assessment of the components of the human population” (Diaz-Barriga, et al., 2001):

1. Information about environmental contamination include: data about time of the year where samples have to be collected, the media where stressor concentrations are needed for exposure assessment, sample locations, frequency of the sampling, and issues regarding transport and quality control. Thus, in the whole concept, physicochemical characteristics of the stressor have to be considered. Furthermore, sampling also depends on the receptor, because biota receptors could be exposed to different pathways of exposure than humans. Samples are taken at the time of the highest probability of exposure. However, at this point, a critical analysis of the stressor bioavailability is a fundamental issue. Using environmental levels in different media, and defining bioavailibity issues, an estimation of the exposure is then performed for the different receptors.

2. For an integrated risk assessment, the components of biota can be the individual organism, the population, the community, the ecosystem and/or its habitat. At first,

the whole biota of the area has to be analysed. After prioritization, for the selection of the most susceptible species in the area, exposure/risk assessment can be performed using different biomarkers, such as: for individuals (chemical concentration, death, growth), population (abundance, morbility), communities (number of scpecies, diversity of species), and ecosystem (productivity, biomass). In this scientific evaluation of risk, also the local knowledge and experiences of the changes of the nature should be taken into account. The use of biomarkers of exposure may define the level of the stressor bioavailability.

3. Regarding humans, the population with the highest risk are those with the highest exposure and the highest susceptibility, like children or pregnant women. In humans, exposure assessment includes the quantification of biomarkers. In order to increase the knowledge about exposure, questionnaires are important. About health effects, biomarkers of effects or clinical anaylises are useful.

2.3. Risk Characterization

In this last step, all the information is included; also a discussion of environmental or health guidelines regarding contamitants of concern and the analyses of uncertainties and the limitations of the study are important issues. As a conclusion, identification of the pathways of exposure that need remediation as a part of a risk reduction program for a biota or humans, is a priority. At the end a concept of the site has to be completed and reassessed. This concept may include socioeconomic, political, or climatical factors (Orme-Zavaleta, et al., 2010).

3. RESULTS

3.1. PROBLEM FORMULATION

High levels of manganese have been reported in the sediments of the Claro River which is located in the Huasteca Region (South Huasteca). Thus, there is a health risk for the communities located on the banks of the river. Preliminary data showed a high risk in one of these communities, Santa María Picula.

3.1.1. SITE DESCRIPTION

Santa María Picula is located in the county of Tamazunchale in San Luis Potosi (Image 1). During 2005 (last census in Mexico) the population includes 922 inhabitants, 463 male and 459 female. In this indigenous community, ten percent of the population do not have direct access to health services. This is important, as almost half of the population are children (aged below 14 years) (INEGI, 2005). Regarding urban infraestructure, the inhabitants have almost to 100 % access to potable water though electricity, and only twenty percent of the dwellings have dirt floors (INEGI, 2005). Thus, according to CONAPO (2005), Santa María Picula belongs to a migration level of “middle” with a margination index of -0,80361. Table 1 shows some of the social indicators of this community.

Table 1: Social Indicators of Santa María Picula

INDICATORS	PERCENT
Population aged 15 years or more which are illiterate	20
Population aged 15 years or more without having completed primary education	31
Habitation without sewage and lavatory	0
Habitation without electricity	3
Habitation without access to water pipes	0
Habitation with dirt floors	20
Habitation without fridges	41

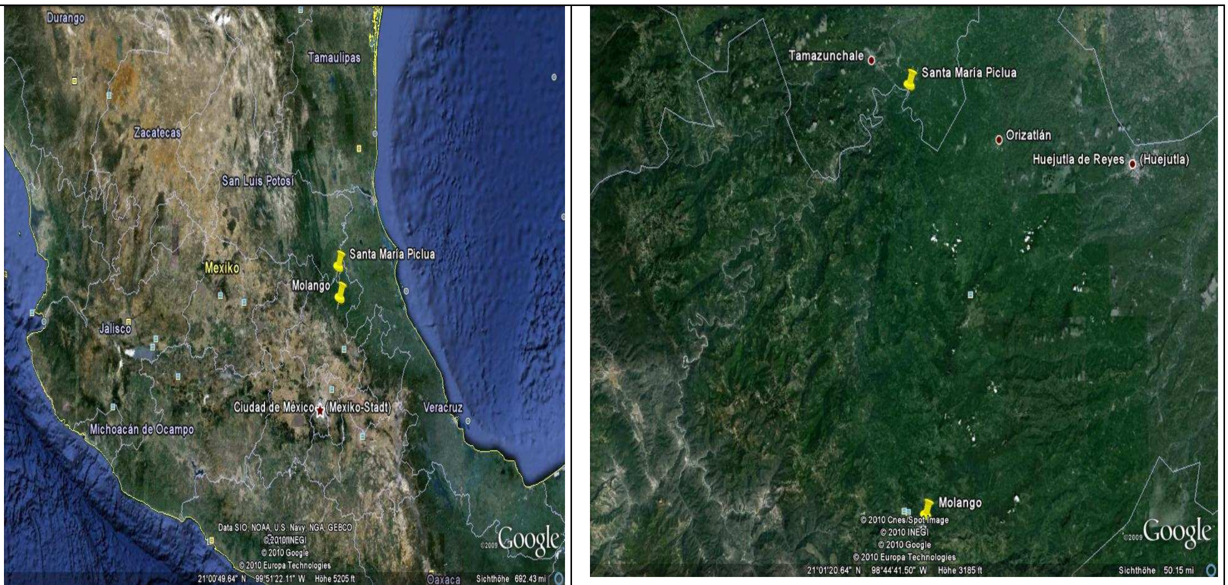

Image 1: Santa María Picula Location

In the left map is seen Mexico with the state borders and Santa María Picula. In the right picture the area of Tamanzunchale, Santa María Picula and Molango can be seen (Google Earth, 28.6.2010).

The rainy season is between June and October. February is the month with the lowest and September with the highest precipitation. Agriculture is the main economic occupation of the community, and the principal cultivates are orange, corn and beans.

3.1.2. Stressor Identification

The first environmental assessment in the area was performed in 2005 by the Autonomous University of San Luis Potosi, in that study, high levels of manganese were reported in river sediments of the Claro River (Table 2). To our knowledge, the levels found in this water body are the highest ever reported in literature for a river polluted with this metal (Mejía-Saavedra et. al; (2005).

Table 2: Concentration of manganese in sediments.
Rivers of the Huasteca Region

RIVERS	[µmol/kg]
Salado - Upgradient	18,9 ± 2,8
Huitznopala – Claro	966,5 ± 246,0
Tamala – Claro	201,8 ± 80,2
Tenexco - Claro	270,8 ± 38,0
Tancuilin-Reference	10,4 ± 0,95
Axtla-Reference	8,8 ± 0,62
Huichihuayan-Reference	10,6 ± 0,91

The studies done by Mejia-Saavedra et. al; (2005), showed that manganese oxide was the main species found in sediments. This can be explained due to the source (mining); however, it is important to take into account that in reductive conditions Mn(II) dominates, whereas in oxidative conditions, manganese dioxide is the most common species. Normally the main concentration of manganese can be found at the surface where organic material is also found. It is transported through the B-horizon to the C-horizon where it is accumulated (Riojas, 2001).

The diffusion rate into the soil of Mn depends on the natural abundance and solubilization or precipitation processes but also on the soil characteristics including the pH, organic matter content, cation exchange capacity, particle size, and presence of other metals in the soil (Bhuie, et al., 2005). The availability of manganese salt for plants depends on the characteristics and pH of the soil. Plants absorb part of the Mn which is found in the surface through the roots (Riojas, 2001). Alkaline soil cannot absorb manganese (Merian, 1991).

The chemical form of manganese in water depends on the pH of the water, anions present and its oxidation–reduction potential (ATSDR, 2000). Furthermore, Mn can form a complex with humus in the water which could be more stable.

The size of manganese particles in the atmosphere is decided by the sources of manganese. In ferro-manganese and dry-cell battery plants, small particles dominate the size distribution of manganese aerosols, whereas in mining operations, larger particles are usually predominant (Davis, 1984).

3.1.3. SOURCE OF THE STRESSOR

The source of manganese is the mining area of Molango-Otongo located in the nearby State of Hidalgo. Mining started in the 1960’s with the ”Molango Facility”; where manganese nodules are being produced. These nodules are then transformed at the “Nonoalco Facility” (located in the same county) into manganese dioxide for try-cell batteries, ceramic grade manganese dioxide for the ceramic industry, and manganous dioxide for the micro-nutrient and fertilizer industry (Autlan, 2010).

The mine contains the largest deposit of manganese ore in North America (Autlan, 2010). According to Camamex (2010) “Minera Autlán” belongs to the principal producers of manganese in the world. During 2006 Hidalgo produced 98% of the manganese in Mexico (Camamex, 2010). The deposits is one of the largest Mn deposits around the world, covering an area of 125 km^2 and has a proven reserve of 32 million tons of Mn (Yaneth, et al., 2009). The forms of manganese found in the deposit are manganese carbonate and manganese dioxide (Riojas, 2004).

3.1.4. Environmental Contamination

In this chapter the environmental contamination in sediments, soil, dust and water can be seen (Table 3 - Table 6).

Table 3: Manganese levels in sediments Claro River close to Santa María Picula

Season	n	[mg/kg]
High Precipitation	2	4,488 – 13,154
Low precipitation	1	15,455

Results from (Medina-Fernández, 2008)

Table 4. Manganese concentration in surface soil in Santa María Picula

Season	n	Mean Concentration [mg/kg]	%>900 mg/kg
High Precipitation	2	22,127 – 23,737	100
Low precipitation	6	13,080	100

Results from (Medina-Fernández, 2008)

Table 5. Manganese concentration in dust in Santa María Picula

Season	n	Mean Concentration [mg/kg]	Size < 1 µm	Size < 9 µm
High Precipitation	8	5,271	1,6 ± 0,1*	35,1 ± 4,5*
Low precipitation	8	6,871	1,6 ± 0,2*	38,4 ± 8,9*

Results from (Medina-Fernández, 2008). Manganese concentration in dust samples in the reference community (Cuatlamayan) 452 mg/kg.

Table 6: Manganese concentration in water sources in Santa María Picula

Season	Drinking Water		Water of the Rio Claro River		Reference Community
	n	[µg/L]	n	[µg/L]	[µg/L]
High Precipitation	2	4.9 – 14.0	1	36.2	nd
Low precipitation	-	-	1	26.6	-

nd (not detectable, LOD 3.4 µg/L). Results from (Medina-Fernández, 2008)

3.2. Receptors

Taking into account the manganese levels in different environmental media (Table 3 - Table 6); selection of the receptors needs to take into account those species in contact with soil, dust and sediments.

3.2.1. Description of the Human Receptor

Selection of the Human Receptor .

Children are not small adults. A child's exposure may differ from an adult's exposure in many ways. Children drink more fluids, eat more food, breathe more air per kilogram of body weight, and have a larger skin surface in proportion to their body volume. A child's diet often differs from that of an adult's. The developing human's source of nutrition changes with age: from placental nourishment to breast milk or formula to the diet of older children who eat more of certain types of foods than do adults. A child's behavior and lifestyle also influence exposure. Children crawl on the floor, put things in their mouths, sometimes eat inappropriate things (such as dirt or paint chips), and spend more time outdoors. Children also are closer to the ground, and they do not use the judgment of adults to avoid hazards (ATSDR, 2009; WHO 2006). Taking all this information into account, children can be identified as the population at the highest risk.

EFFECTS OF MANGANESE IN CHILDREN ..

Children are exposed *in utero* because manganese in maternal blood crosses the placenta to satisfy the fetus' need for manganese. The compound has been measured in cord blood plasma of infants and their mothers. The average manganese concentration in the cord blood of full term babies was 5.5 µg/L (Wilson, et al., 1991). No correlations were observed between maternal and infant concentrations of manganese. In a normal scenario, the main source of exposure of children to manganese is through food; however, young children often eat dirt and exhibit frequent hand-to-mouth activity; they can be exposed to manganese through this unique pathway if the soils contain the metal (ATSDR, 1995).

Both manganese and iron are bound by transferrin and these elements compete for the binding protein in the body. Therefore, diets that are low in iron allow transferrin to bind more manganese. For this reason, it is important to provide children with a balanced diet to maintain optimal iron and manganese stores in the body. Studies show that adults absorb only 3–5% of manganese ingested from the diet (Davidsson et al. 1988, 1989; Mena et al. 1969); infants have increased absorption relative to adults (Dorner et al. 1989). Neonatal animals also exhibit increased absorption relative to older animals (Ballatori et al. 1987; Miller et al. 1975; Rehnberg et al. 1981).

Manganese concentrations in blood serum of children of different ages indicate that manganese concentrations decrease slightly from the time the infant is 5 days of age until he or she is 12 months of age (Alarcón et al. 1996; Rükgauer et al. 1997). Manganese concentrations increase after this time, and they have been measured as an average of 1.4±1.25 µg/L in children aged 1 month to 18 years (Rükgauer et al. 1997).

We have defined that in the area of concern due to the high environmental levels of manganese, children are the population at risk and the principal pathways of exposure for them are inhalation/ingestion of dust either from sediments or surface soil. Therefore, an exposure-effect assessment is needed. In the following sections the biomarkers of exposure and the biomarkers of effect that can be studied are discuss.

BIOMARKERS OF EXPOSURE .

Manganese can be measured in biological fluids like serum, blood or urine; in tissues like hair; and in feces (ATSDR, 2009). Manganese has a life of 30 hours in urine and between 10 and 42 days in blood (Medina-Fernández, 2008). Both can be taken as a biomarker to analyze a recent exposure (ATSDR, 2009).

A study showed the correlation between manganese levels in total dust and in blood of chronically exposed workers (Roels, et al., 1987). Also in Canada higher levels of blood manganese were correlated with high levels of airborne manganese. Blood manganese also can be related with intake from food, water, and air. However, as urinary samples are easy to collect, in the studied done by Medina-Fernández (2008), manganese in urine was selected as the biomarker of exposure. Children in the exposed area had higher levels than in the reference communitiy.

Hair is a possible biomarker for manganese, but it is influenced by the colour, bleaching or other factors. Nevertheless, there are several studies which show the relation between manganese in hair and behavioral deficits (ATSDR, 2009).

BIOMARKERS OF EFFECTS .

Regarding respiratory symptoms, in Japan children from a school located near a manganese plant had higher complaints that children from a reference school (ATSDR, 2009).

Manganese concentration in dust samples was up to 100 times higher in San Maria Picula than in Cuatlamayan (reference village). Thus, dust inhalation is an important route of exposure; especially if we take into account that manganese can enter the body not only through lung absorption but also may enter the brain directly through olfactory uptake. Children’s exposure to airborne Mn may be proportionally higher than adults (Yaneth, et al., 2009). Yaneth, et al., (2009) also mentioned further studies where environmental exposure by inhaling dust rich with Mn was related to motor and attention impairments in exposed populations; for example, the exposed group of children in the study of Yaneth, et al., (2009) showed significally lower verbal and performance IQ compared with a control group. Younger children were more affected. In adults the main effect of environmental Mn exposure have been associated with the motor skills and attention, but the effect on children seems to include other function, like the verbal function.

The clinical picture of manganism shows psychiatric and neurological manifestations. The disease normally starts with feeling weakness and lethargy. Within the progress of the illness further neurological symptoms are visible. Although the symptoms are various, the most common are: slow and clumsy gait, tremor, masklike faces, and speech disturbance. At further exposure the symptoms can progress and for example the speech disorder can change into muteness. In the third stage the disease is fully developed and shows difficulties in walking and writing. The patients become disabled and could show in addition syndromes of psychological and psychic disturbance (aggressiveness, hallucination, psychosis) (Nordberg, et al., 2007). According to ATSDR (2009) manganism has typically been observed in occupational settings or in isolated cases of an extreme exposure to manganese. In general, these scenarios do not pertain to children. Studies on neurological effects are rare, but one study shows that a population living in an area rich with manganese suffers from increased neurological disorders (Kilburn, 1987). According to a review by (Menezes-Filho, et al. (2006) studies are found which shows children with a high exposure to manganese having learning problems in Canada, United States and China. Children with hyperactive behaviour are found in Canada, United States and United Kingdom. Symptoms of cognitive deficy are found in studies in Spain and Bangladesh. Neurobehavioural and other general effects are found in China United States and France. The exposure of manganese in one study in United States was mining waste with neuropsychological and neurobehavior effects (Wright, et al., 2006). A study by Yaneth, et al. (2009) in the mining district in Hidalgo figguerd out that non of the children reached the IQ expected for their age (90-110) with a concentration of mangnaese in hair up to 12,6 µg/g and in blood up to 9,5 µg/L.

Platelet monoamine oxidase (MAO) and serum dopamine β-hydroxylase (DBH) activities can be observed in men exposed to manganese via inhalation. Studies showed that exposed men had lower MAO activities, but similar DBH activities than not exposed. To analyse the disease the characteristic pattern of symptoms and neurological signs should be diagnosed. Measurement of altered levels of dopamine and other neurotransmitters in the basal ganglia has proven to be a useful means of evaluating central nervous system effects in animals.

3.2.2. Description of the Biota Receptor

Selection of the Biota Receptor ..

In the region of the Claro River there are 35 species have been defined to be at risk (CONABIO, 2001). Moreover, according to the Soil Screen Levels (SSL) of the Environmental Protection Agency (EPA, 2007) the susceptibility to manganese in soil is: Plants > Invertebrates > Mammals > Birds. In comparison, the distribution of susceptibility in aquatic species is: amphibians > invertebrates > microalgae > protozoa > fish (Howe, et al., 2004). These criteria can be taken into account for the selection or the biota receptor, but further criteria are needed considering the characteristics of a biomonitor.

Biomonitors are able to accumulate contaminants in their tissues without significant adverse effect, so they can be used: i) for risk assessment; ii) to provide early warning of situations; and/or iii) for studies that relate effects to exposures. A biomonitor shares its environment with human generally with the same food and water sources. Thomas talpides, Tarentola mauritanica, terrestrial vertebrates and snakes are used to indicate contamination with metals (Espinosa-Reyes, et al., 2010). Earthworms play an important role in the interaction within ecosystems through the mixing and translocation of soil constituents (Reyes, 2009).

Taking into account these antecedents, the criteria that we used for selection of species of concern are:

i) not to be in the list of species at risk (NOM-059-SEMARNAT);

ii) antecedents of its use for studies in sites polluted with metals;

iii) susceptibility to manganese;

iv) charisma;

v) easy to capture;

vi) simple identification;

vii) big enough to take samples; and,

viii) similar exposure pathways to children.

Using these criteria *Peromyscus spp* and *Rattus sp* of the mammals, and *Rhinella marina (Bufo marinus)* of the amphibian were selected as the most recommended biomonitors. Comparing *Peromyscus spp* and *Rattus sp* it has to be said that *Rattus sp* was brought from Europe and so the *Peromyscus spp* is the favoured species of the mammals.

EFFECTS OF MANGANESE IN BIOTA ..

Manganese can be found in animals, in all tissue and also in feces and blood. Manganese is also responsible for the normal function of the central nervous system. High levels of manganese in animals may produce neurotoxic responses such as hypoactivity, nervousness, tremors and ataxia, negative effects on the liver and decrease growth (EPA, 2007).

Negative effects observed in mammalian wildlife have been biochemical changes, behavior, physiology, pathology, reproduction, growth and survival effects. The most obvious effects in wildlife could be seen almost in all observed effects, whereas the effects of mortality, physiology and pathology were the less observed. In Invertebrates negative effects in mortality and growth could be observed (EPA, 2007).

The excess of Manganese may induce alterations in the metabolism in animals and can produce an impairment of hemoglobin formation because of the reduced intake of iron into the porphyrin ring. In the case of ironic anemia, hemoglobin formation is produced by 45 ppm manganese in feed (Merian, 1991). Manganese can be found in all tissues. The concentration in the tissue depends on the extent of exposure, nutritional status (regarding iron), and the body's metabolic control mechanisms for manganese (Pfeifer, et al., 2004).

BIOMARKERS OF EXPOSURE ..

Manganese can be found in all tissues. The concentration in the tissue depends on the part of exposure, nutritional status (regarding iron), and the body's metabolic control mechanisms for manganese (Pfeifer, et al., 2004).

BIOMARKERS OF EFFECTS ..

In rats neurological effects are known. When neonate and adult rates are exposed to manganese, neonate rates obtain a higher concentration and manifest more extensive brain pathology as adults. Manganese also altered brain dopamine concentration (Pfeifer, et al., 2004). According to Erikson, et al., (2002) animals with iron-deficient anemia accumulate more Mn in brain. Rodents with an iron-deficient have a higher risk to accumulate Mn in brain.

In *bufo spp.* among the effects of manganese we can include delayed development, body bending, microcephaly, defective geills, stunted tail, skeletal malformation, size reduction, organ displacement, abnormal intestine, heart beat reduction and swimming in circles as a result to be exposed to metals reviewed by (Venturino, et al., 2003).

It is known that in nonmammalian vertebrates the exposure to metal produces behavioral abnormalities. Tabpoles exposed to a metal are known to have reduced discriminate avoidance learning or deficiencies in learning and retention (Stricker-Shaw, et al., 1990).

3.3. Pathways of Exposure

Table 7 shows the pathways of exposure for children and in Table 8 can be seen the pathways of exposure for biota.

Table 7: Pathways of Exposure for Children.

<table>
<tr><th>Source</th><th>Media</th><th>Point of Exposure</th><th>Route of Exposure</th></tr>
<tr><td rowspan="2">Sediment</td><td rowspan="2">Dust</td><td rowspan="2">River Banks</td><td>Inhalation</td></tr>
<tr><td>Ingestion
(hand to mouth activity)</td></tr>
<tr><td rowspan="3">Surface Soil</td><td rowspan="2">Dust</td><td rowspan="2">Residential Area

Playgrounds</td><td>Inhalation</td></tr>
<tr><td>Ingestion
(hand to mouth activity)</td></tr>
<tr><td>Food</td><td>Garden, Fields</td><td>Ingestion</td></tr>
</table>

The concentration of manganese found in the water of the river and in drinking water does not represent a health risk for humans and is not further mentioned.

Table 8: **Pathways of Exposure for Biota (***Rhinella marina* and *Peromyscus***).**

<table>
<tr><th>Source</th><th>Media</th><th>Point of Exposure</th><th>Route of Exposure</th></tr>
<tr><td rowspan="2">Surface Soil</td><td>Soil</td><td rowspan="2">Field, Countryside</td><td>Absorption
Ingestion</td></tr>
<tr><td>Dust</td><td>Ingestion
Inhalation</td></tr>
<tr><td rowspan="2">Sediment</td><td>Sediment</td><td>River</td><td>Ingestion</td></tr>
<tr><td>Dust</td><td>River Banks</td><td>Ingestion
Inhalation</td></tr>
</table>

3.4. Environmental Sampling Needed for the Integrated Risk Assessment

For this chapter, pathways of exposure for children and biota were considered; also, because of the high precipitation in the summer and the low precipitation in the winter (INEGI, 2010) the samples have to be taken in February, time with the lowest precipitation (middle 43 mm/month) and during September time with the highest precipitation (middle 425,4 mm/month) (INEGI, 2005a).

3.4.1. Media

As showed, surface soil and indoor dust are the pathways of exposure of concern for humans, whether for biota, river sediments are also important. Taking into account that these matrixes (soil, dust and sediments –in areas-) are sources of air particles, inhalation can also become a relevent route of exposure. Finally, considering that manganese accumulates easily in grain, fruit and vegetables, food items should be analyzed (ATSDR, 2009). *The information in this chapter follows ATSR´s recomendations for hazardous waste sites ATSDR* (ATSDR, 2010).

3.4.2. Surface Soil

Soil samples have to be collected from areas mostly used by children and also used by the environmental susceptible species. Important locations are playgrounds, schools and residences for humans, and habitats for biota species.

Generally, the public is exposed to only the top few inches of soil; therefore, ATSDR has defined surface soil as the top 3 inches. For its evaluation, ATSDR needs concentrations of contaminants found in surface soil reported separately from those found in subsurface soil. Because ATSDR considers past, current, and future exposure scenarios, the Agency needs to know the concentrations of contaminants in the soil before and after removal or remedial actions. Information relevant to ATSDR's evaluation of the soil pathway is listed below.

1. Exact sample locations, including descriptions and map locations, and the purpose of the sampling

2. Depth of sampling points: specify if sample is a vertical composite of soil between specified depth ranges (e.g., 0-3 inches, 3-12 inches, 1-3 feet)
3. Type of sample (e.g., grab)
4. Constituents analyzed for, analytical methods used, detection limits, and concentrations detected
5. Date of sampling
6. Type of soil (sandy, etc).

3.4.3. INDOOR DUST

Samples have to be taken in chairs, at the ground, at the windowsill and the palm of hands of childs. Samples are best collected with a wipe. According to Morato (2009) different methods were compared, but wipes were selected because also the palm of hand can be measured. Data listed below are needed.

1. Surface area sampled (i.e., square feet).
2. Description of the area sampled. Is activity in the area high or low? Is the area accessible (i.e., kitchen floor vs. behind couch, or a combination)? Are floors in the sampled building or area carpeted, hardwood, concrete, linoleum, dirt, etc.?
3. A copy of the indoor dust sampling plan. The detection limits that will dictate how large a sample to collect must be at or below the level of health concern for the contaminants present.

3.4.4. SEDIMENT

Residents and biota may be exposed to contaminated sediment either through direct dermal contact, ingestion, and inhalation or through a secondary pathway: ingestion of contaminated biota (food items). Sediment sampling is needed at possible human or biota exposure points, such as recreational areas or children's play areas, and at locations where contaminated sediment may enter the food chain, such as known fishing and hunting areas, if there is the possibility of uptake of contaminated sediments by wildlife, fish, or shellfish that may be eaten by people later. Upstream sediments may be collected to determine background concentrations of the contaminants.

Sediments may also be mechanically disturbed and transported to possible human and biota exposure points by dredging. Therefore, sampling and analysis of the dredged sediments, as well as the stream channels and impoundments, may be needed at some sites.

To prevent confusion between "soil" and "sediment," ATSDR defines sediment to be any solid material, other than waste material or waste sludge that lies below a water surface; that has been naturally deposited in a waterway, water body, channel, ditch, wetland, or swell; or that lies on a bank, a beach, or floodway land where solids are deposited. For best evaluation of the potential exposure of the public, sediment samples, like soil samples, should be shallow (0-3 inches). The information listed below is needed for ATSDR's analysis of the sediment pathway.

1. Descriptions and locations on map of samples obtained
2. Depths of sampling points: specify if sample is a composite of soil between specified depth ranges (e.g., 0-3 inches, 3-12 inches, 1-3 feet, etc.)
3. Type of sample (e.g., grab or composite)
4. Constituents analyzed for, analytical methods used, detection limits, QA/QC data, and concentrations detected
5. Date of sampling event and site conditions at that time

3.4.5. Food

This media is only considered for humans. Food samples are divided in samples of the fauna and flora. It is important to have a well-designed biota sampling protocol and more than 20 samples are recommended per location.

Biological samples need a special handling to be transported. The transportation of fish for example could be needed to be frozen. It has to be evaluated with each species (ATSDR, 1994).

The season of the samples of the food depends on the season they are consumed by the population. Are they eaten during the whole year, the sample should be taken in February and September.

People may be exposed to site contaminants by eating plants or animals that have incorporated the contaminants into their bodies. Both on- and off-site hunting, fishing, foraging, and farming activities may bring people into contact with those contaminants. Some substances, particularly fat-soluble substances and heavy metals, may reach concentrations in animal tissues that are thousands of times higher than those found in water, soil, and sediment. For discussion in the PHA, it is important that the *edible portions* of such food items be analyzed for contaminants of concern. *Edible portions* of food items need to be determined at each site based on the eating habits of the various ethnic populations that may ingest the various food items being analyzed; e.g., residents of one community may eat skinned fillets of fish, while those in another community eat the whole fish. If several ethnic groups are present in the potentially exposed community, it would be desirable to have samples analyzed based on each ethnic group's eating habits; however, if this is not possible, the worst-case eating habits should be used to determine the samples to be analyzed. It is difficult to draw meaningful human food-safety conclusions when the whole body of a fish is analyzed rather than fillet samples, if the community typically eats only fillets of that type of fish, or when a whole plant is analyzed and only the fruits are normally ingested.

When planning and designing an investigation of food-chain contamination, it is important to have a well-designed biota sampling protocol, with sample size large enough to be statistically significant (more than 20 samples per location per sampling episode are recommended when parametric statistical methods will be used). In particular, organisms of different species, ages, or reproductive status should not be sampled without strong justification. For example, when assessing the impact of contaminated sediment upon the edible fish populations in a stream, results of analyses of tissues from bottomfeeding fish should not be combined with those from water-column feeders; because of their different feeding habits, very different effects may be expected. Discrete (grab) samples are preferred because ATSDR tries to determine the maximum contamination in order to model worst-case scenarios .

Special handling of biologic samples needs to be considered. Some analytical procedures require that live or fresh-frozen fish be transported to the lab immediately for analysis; the accuracy of other procedures may not be affected if formalin-preserved specimens or those held frozen for weeks or months are used. Such considerations, along with any special problems encountered, should be included in an appendix to the document for quality assurance review.

When contamination of consumable plants and/or animals is suspected, specific data are needed by ATSDR to evaluate the food-chain pathway.

A. Nonsampling Information (past/present)

1. Animal and plant species that may be eaten by people if these species are potentially affected by the site (e.g., annual animal population or crop volume harvested)
2. Descriptions of populations consuming each potentially contaminated crop and animal (e.g., residential gardens containing tomatoes, corn, and peas consumed by owners [include ethnicity, if known]; local subsistence hunting for rabbits, dove, and deer; commercial and subsistence fishing for salmon and catfish; commercial beef cattle ranches and feedlots in the area; etc.)
3. Descriptions of past, present, and intended future land use

B. Sampling Information

If contamination exists only on site:

1. Sampling and analysis of edible plants and on-site edible animal species
2. Sampling and analysis of off-site edible animal species likely to pass through the contaminated area

If contamination exists off site, sampling and analysis should include all plant and animal species believed to be exposed to contaminated media if they have potential to be used as human food sources.

C. Biota Studies

When biota studies are performed:

1. A copy of the protocol used, including how each species was harvested; how representative samples were selected of each species; what portions were sampled and analyzed; size of samples; special specimen-handling procedures, including sample storage procedures; contaminants analyzed for and rationale for their selection; methods used and their detection limits, etc.
2. All analytical results and reports, including any QA/QC data and reports, and a list of samples and their corresponding sample number
3. A sample size of at least 20 individuals per species, per episode
4. Analysis of *edible portions*
5. Analysis of individual (grab) rather than composite samples. If composite samples are necessary because of the size of the species, include compositing strategy.
6. A control population of at least 20 individuals from a comparable uncontaminated location for background levels

3.4.6. Air Samples

A. Ambient Air Data

1. Locations where samples were taken, including descriptions and illustrations on maps
2. Meteorologic conditions, temperature, wind speed, and wind direction when samples were taken (i.e., which samples were upwind, and which were down-wind), cloud cover, (i.e., sunny, overcast), time of year, and time of day or night
3. Sampling log, including descriptions of activities in the area during sampling that may have contributed to concentrations of constituents detected and descriptions of measures taken to reduce emissions if ambient air monitoring is in conjunction with remediation activities (e.g., dust-control measures, etc.)
4. Height at which samples were taken. Samples should be taken in the breathing zone (4-5 feet above ground)

5. Descriptions of sampling methods used and constituents collected by each method.
6. Sampling frequency and dates (duration of continuous or integrated composite sampling, grab samples, etc.). If grab samples are taken, samples may need to be taken both at night and during the day in case the concentrations are affected by the change in meteorologic conditions.
7. Constituents analyzed for, analytical methods used, detection limits, QA/QC, and concentrations detected.
8. Ambient air sampling where people may be exposed at on- and off-site locations.

4. DISCUSSION

4.1. THE CLARO RIVER REGION

The high concentration of manganese in soil (between 22127,2 – 23737,7 and 13080,2 ±5958,7 mg/kg), sediments (4488,3 – 13154,2 mg/kg and 15455,1 mg/kg) and dust (5271,7 ± 1355,5 and 6871,0 ± 1345,0 mg/kg) in the South Huasteca Region next to the Claro River, one of the most polluted areas of manganese in the world. As showed in the antecedents included in this document, the high concentration of manganese in different environmental media is a risk, not only for humans but also for the rest of the biota.

Manganese is a neurotoxic element, therefore, the presence of other neurotoxicants in the area deserves attention, due to the possibility of an interaction with this metal. This is the case for DDT (dichlorodiphenyltrichloroethane) and PAHs (polycyclic aromatic hydrocarbons). DDT was used in the area from 1957 to 1999 in the malaria control program. This insecticide has been found in sediments, household dust and children´s blood (preliminary results, Diaz-Barriga F.) in communities located in the Region. In its turn, PAHs sources are indoor air (wood combustion) and waste fires (burning of community waste); we have found children exposed to PAHs in indigenous communities in the area (Martínez-Salinas, et al., 2009, Fiedler, 2003).

Interestingly, this protocol can be expanded to the analysis of DDT and PAHs. For instance analyzing Mn, DDT and PAHs in environmental samples (dust, food items, etc); and in biological samples (children´s urine or blood and biota tissues). Furthermore, taking into account the presence of these pollutants, the assessment of neurological functions is a priority for the Region.

4.2. Why an Integrated Risk Assessment ?

An integrated risk assessment is needed to support decision making by evaluating the risk effects on human and ecological health from environmental stressors like chemicals (Suter, et al., 2007). With the goal to protect both, human and ecological health in Santa María Picula, integrated risk assessment is necessary. Also appropriate decisions can be taken with the help of integrated risk assessment. Protection of humans will not inevitably result in protection of biota. Some species may be more exposed or more sensitive than humans (Suter, et al., 2003).

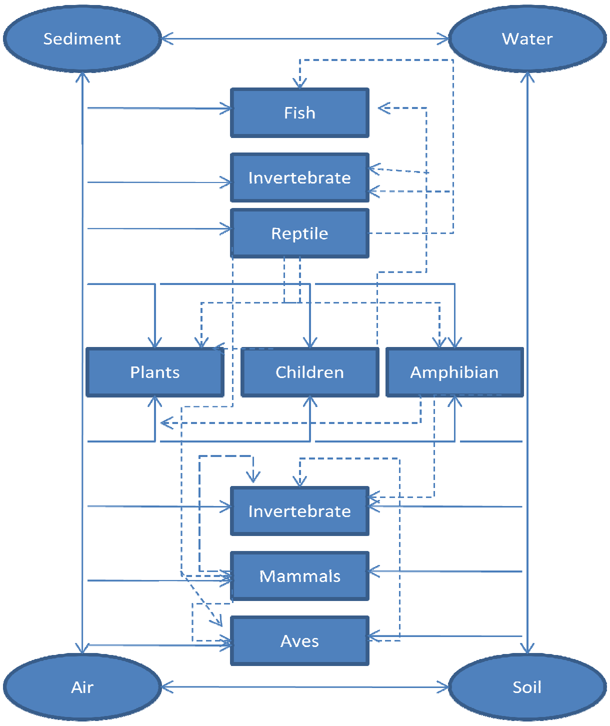

Image 2: Model for an Integrated Risk Assessment of Manganese

The exposure of humans and biota to environmental manganese has the same source and similar pathways of exposure (Image 2). Mice for example, as humans, are exposed to dust and soil; whereas, amphibians are exposed to manganese through sediments, surface soil, and dust particles, so are children.

Table 9: General Characteristics of an Integrated Risk Assessment in the Area Impacted by Manganese.

RECEPTOR	Media		Routes of Exposure		Exposure		Effect	
	Soil/Dust	Sediment	oral	inhalation	Tissues	Blood	neurological	Deformation of the body
Children	√	√	√	√	--	√	√	-
Amphibians	√	√	√	√	√	√	√	√
Mice	√	√	√	--	√	√	√	-

Table 9 shows the characteristic of an integrated Risk Assessement with manganese.

4.3. VULNERABILITY

Risk is a probability function that results from the interaction between a threat (in this case manganese in the environment) and the vulnerability of the receptors (in this case children, mice and amphibians). Thus, an integrated risk assessment needs to take into account, not only the levels and the distribution of manganese, but also, the vulnerability of the biota and the human population in the polluted area.

4.3.1. CHILDREN

Santa María Picula has a margination level of “middle” (CONAPO 2005), in a weak social-economical area. Lack of access to nutritious food, poor and overcrowded houses make people vulnerable to disease (Detels, et al., 2002a).

Malnutrition has an important effect on the brain. The brain development and learning facilities are disturbed as well as social behavior. Furthermore malnutrition brings with it a loss of micronutrients. For example, iron deficiency is one of the most common deficiencies in the world. In tropical countries the deficiency of iron often increases by intestinal parasitosis by the loss of blood of the gastrointestinal tract. The effects of iron are wide. Iron plays a central part in transporting oxygen in the body and is essential for many enzyme systems. The normal defense system against infection is affected. In pregnant women the risk of fetal morbidity, mortality and low birth weight is increased by iron deficiency (Detels R. et. Al., 2002, WHO 2003). Diets low in iron increase the binding of manganese by transferrin, resulting in an increased absorption of the metal (ATSDR, 2009).

It should also be taken into account that the population of Santa María Picula is used to cooking with wood which produces indoor air pollution. Indoor air pollution is often a reason for respiratory disease in socio-economic weak areas (UN, 2006/2007). Often a chimney is missing, so families have to inhale the incomplete combustion of wood. Traditional housing and substandard living conditions can be important facts for respiratory infections in children. Mainly women and children are inhaling smoke from burning wood each day, which is mainly responsible for respiratory infections (Detels, et al., 2002a).

Furthermore, liver disease is a factor that increases as a result of the exposure to manganese, because the main route of excretion for manganese is hepatobiliary transport. Individuals with impaired liver capacity would be expected to have a diminished ability to handle manganese excesses (Hauser, et al., 1994). A further factor to consider decreased liver function is that the alcoholism in the region is high, even among young adolescents.

4.3.2. Mice

The toxicology in rodents is higher in developing organisms (fetus and neonates) than in adults. It is also known that neonates have a higher absorption of toxic metals (Shore, et al., 2000). Also, within mice differences in the dietary levels of iron and calcium can vary the toxicology. Probably there is a transport competition between iron and manganese and calcium and manganese. The most interesting interaction is between iron and manganese (Klimis-Tavantzis, 1994). Individuals with low ferritin absorb 3-5 fold more compared with individuals with high ferritin. Iron (Fe) deficiency is a risk factor for the accumulation of Mn. Mn and Fe schare transferrin as a transporter and partially as a distribution system in the CNS (Solis-Vivanco, et al., 2009). The low-level protein intake appears to increase the effect of manganese on brain neurotransmitter levels in exposed animals (ATSDR, 2009).

4.3.3. Amphibians

Amphibians are exposed to soil and sediments and in their first life stages to water; which expose them to a wide range on contaminants. They are particularly sensitive to chemicals during their freshwater cycles (Venturino, et al., 2003). Amphibians are highly vulnerable to toxics because of their permeable skin that readily absorbs contaminants. Their eggs are also highly permeable (Ashley, 2000).

4.4. Limitations

4.4.1. Human Health

- Taking into account that dust inhalation may be an important pathway of exposure, it is important to measure manganese concentrations in respirable particles (<10.0 µm).

- Surface soil samples in residences and playgrounds are missing.

- I recommend to make interviews with the population about their dietary habits in order to organize a food sampling.

- The whole analysis of the socio-economic status is missing and should be taken in account.

- Samples of biomarker of effects should be taken

4.4.2. BIOTA

- It would be important to evaluate the bioavailability of manganes for biota to characterize the risk for ecological health.

- The list of species with a special susceptibility to manganese has to be made in the field. Next to amphibians and mammals also plants, reptils, fish, and insects can be very susceptible to manganese.

- The amount and the species of manganese in pore water have to be analyzed considering aquatic fauna.

- Regarding manganese levels in the river water, an assessment is needed for its possible effects in amphibians.

- Samples of biomarker of effects and exposure should be taken

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ANNEX. - CRITERIA FOR BIOMONITOR SELECTION

Taxonomic group	Specie	NOM-059-SEMARNAT	Toxicology	Exposure	Alimiento	Same exposure biomarker	Same effect biomarker	Charisma	Identification	Capture	Size	TOTAL
PLANTS	*Pilosocereus cometes*	1	1	5	1	1	1	5	5	5	3	**28**
	Chysis bractescens (A)	1	1	5	1	1	1	5	5	5	3	**28**
	Euchile marie (A)	1	1	5	1	1	1	5	5	5	1	**26**
	Habenaria umbratilis (Pr)	1	1	5	1	1	1	5	5	5	3	**28**
	Stanhopea oculata (A)	1	1	5	1	1	1	5	5	5	1	**26**
	Stanhopea tigrina (A)	1	1	5	1	1	1	5	5	5	1	**26**
	Chamaedorea microspadix (A)	1	1	5	1	1	1	5	5	5	3	**28**
	Zea mays	5	1	5	5	1	1	3	5	5	3	**34**
	Citrus sinensis	5	1	1	5	1	1	1	5	5	5	**30**
	Mangifera indica	5	1	1	5	1	1	1	5	5	5	**30**
	Cynodon plectostachyus	5	1	1	1	1	1	1	5	5	1	**22**
	Quercus oleoides	5	1	1	1	1	1	1	5	5	5	**26**

	Bursera simaruba	5	1	1	1	1	1	1	5	5	5	**26**
	Piscidia communis	5	1	1	1	1	1	1	5	5	5	**26**
	Coccoloba sp.	5	1	1	1	1	1	1	5	5	5	**26**
	Ficus sp	5	1	1	1	1	1	1	5	5	5	**26**
MAMMALS	*Herparilurus yagouaronid (A)*	1	3	5	1	5	5	5	1	1	3	**30**
	Leopardus pardalis (P)	1	3	5	1	5	5	5	1	1	3	**30**
	Leopardus wiedii (P)	1	3	5	1	5	5	5	1	1	3	**30**
	Peromyscus spp.	5	3	5	1	5	5	1	5	5	1	**36**
	Rattus	5	3	5	1	5	5	1	5	5	1	**36**
	Dasypus novemcinctus	5	3	5	1	5	5	3	1	1	3	**32**
	Sylvilagus floridanus	5	3	5	1	5	5	3	1	1	3	**32**
	Sylvilagus brasiliensis	5	3	5	1	5	5	3	1	1	3	**32**
	Coendu mexicanus	5	3	5	1	5	5	3	1	1	3	**32**
	Puma concolor	5	3	5	1	5	5	5	1	1	3	**34**
	Canis latrans	5	3	5	1	5	5	3	1	1	3	**32**
	Nasu narica	5	3	5	1	5	5	3	1	1	3	**32**
	Procyon lotor	5	3	5	1	5	5	5	1	1	3	**34**
REPTILES	*Ophisaurus incomptus (Pr)*	1	3	3	1	3	1	5	3	1	1	**22**
	Boa constrictor (A)	1	3	3	1	5	1	5	5	1	5	**30**
	Geophis	1	3	3	1	3	1	5	3	1	1	**22**

	mutitorques (Pr)											
	Leptodeira annulata (Pr)	1	3	3	1	5	1	5	5	1	3	**28**
	Masticophis flagellum (A)	1	3	3	1	5	1	5	5	1	5	**30**
	Pituophis deppei (A)	1	3	3	1	5	1	5	3	1	5	**28**
	Thamnophis sumichrasti (A)	1	3	3	1	5	1	5	5	1	5	**30**
	Corytophanes hernandezi (Pr)	1	3	3	1	3	1	5	3	1	1	**22**
	Laemanctus serratus (Pr)	1	3	3	1	3	1	5	3	1	1	**22**
	Trachemys scripta (Pr)	1	1	3	5	5	1	5	1	1	5	**28**
	Coleonyx elegans (A),	1	3	3	1	3	1	5	1	1	1	**20**
	Kinosternon herrerai (Pr)	1	3	3	5	5	1	5	3	1	3	**30**
	Cophosaurus texanus (A)	1	3	3	1	3	1	5	3	1	1	**22**
	Phrynosoma cornutum (A)	1	3	3	1	3	1	5	1	1	1	**20**
	Crotalus atrox (Pr),	1	3	3	1	5	1	5	5	1	5	**30**
	Crotalus scutulatus (Pr)	1	3	3	1	5	1	5	3	1	5	**28**
AMPHIBIAN	*Rana johni (P)*	1	1	5	1	5	1	5	1	3	1	**24**
	Rana montezumae (Pr)	1	1	5	1	5	1	5	5	3	1	**28**

	Notophthalmus meridionalis (P)	1	1	5	1	5	1	5	1	3	1	**24**
	Bufo marinus ó Rhinella marina	5	1	5	1	5	1	1	5	5	5	**34**
FISH	*Cichlasoma labridens (A)*	1	5	1	1	5	1	1	1	3	1	**20**
	Cichlasoma steindachneri (P)	1	5	1	1	5	1	1	1	3	5	**24**
	Cyprinella lutrensis (A)	1	5	1	1	5	1	1	1	3	1	**20**
	Cualac tessellatus (P)	1	5	1	1	5	1	1	1	3	1	**20**
	Ataeniobius toweri (P),	1	5	1	1	5	1	1	1	3	1	**20**
	Xenoophorus captiva (P)	1	5	1	1	5	1	1	1	3	1	**20**
	Ictalurus australis (A)	1	5	1	5	5	1	1	1	3	5	**28**
	Ictalurus mexicanus (Pr)	1	5	1	5	5	1	1	1	3	5	**28**
INVERTEBRATES	*Libellulidae*	5	5	5	1	1	3	3	1	5	3	**32**
	Gomphidae	5	5	5	1	1	3	3	1	5	3	**32**
	Ashmidae	5	5	5	1	1	3	3	1	5	1	**30**
	Calopteryidae	5	5	5	1	1	3	3	1	5	1	**30**
	Protoneuridae	5	5	5	1	1	3	3	1	5	1	**30**
	Plastysticidae	5	5	5	1	1	3	3	1	5	1	**30**
	Lestidae	5	5	5	1	1	3	3	1	5	1	**30**

	Pseudostigmatidae	5	5	5	1	1	3	3	1	5	3	**32**
	Corduliidae	5	5	5	1	1	3	3	1	5	3	**32**
	Megapodagrionidae	5	5	5	1	1	3	3	1	5	3	**32**
	Palaemonidae	5	1	5	5	1	3	1	1	5	5	**32**
	Cambaridae	5	1	5	5	1	3	1	1	5	1	**28**

Table 10: Characteristic of the used criteria

	NOM 059 SEMARNAT	
Yes 1		No 5
	Toxicology	
A lot 1	Media 3	A little 5
	Exposure	
Different like children 1		Same like children 5
	Aliment	
No 1		Yes ^5
	Biomarker of effect/exposure	
Not the same than children 1		Same than children 5
	Charisma	
No 1		Yes 5
	Identification	
Difficult 1		Easy 5
	Capture	
Difficult 1		Easy 5
	Size	
Small 1		Big 5


(Memo Espinosa Reyes)