

Potential impacts on the ecology and on human health from petroleum hydrocarbons and metals in sediment found in the Ecuadorian Oriente

By Joy McGrath

Author's biography:

Ms. Joy A. McGrath, Head Project Manager at HydroQual, has more than 15 years of experience in the field of environmental engineering. Her experience includes the development of sediment quality criteria, evaluations of wastewater treatment processes, and fate transport modeling of contaminants. She specializes in the development of water quality criteria and sediment, with particular emphasis on Polycyclic Aromatic Hydrocarbons (PAH) and metals. She is the co-author of draft documents for the United States Environmental Protection Agency (USEPA) on Equilibrium Partitioning Reference Values in Sediments for mixtures of PAHs and Metals Mixtures. She is currently working on applying this type of standard to locations contaminated with PAH from oil. Ms. McGrath has more than five years of experience working in oil-related matters for a major oil company.

Author certification:

The attached report truly represents my knowledge and opinions on the matter.

Author's Signature:

A handwritten signature in black ink that reads "Joy McGrath". The signature is written in a cursive style with a long horizontal flourish extending to the right.

[Handwritten] October 25, 2007

Date:

Potential impacts on the ecology and on human health from petroleum hydrocarbons and metals in sediment found in the Ecuadorian Oriente

Co-Author: John Slocomb, Ph.D

Biography of Co-Author:

John Slocomb is a Head Consultant at ENTRIX, Inc., and has more than 25 years of experience in risk assessment, environmental impact analysis, natural resource management, and environmental statistics. He has managed risk assessment on the ecology and on human health at sites in the Superfund program in the United States, and he has played a fundamental role in design, analysis and public communications matters. Dr. Slocomb has worked closely with natural resource managers in the United States to develop spatial statistical methods that are used to evaluate economic impacts on complex environments, and he has performed forensic geo-chemical analyses and identified sources of contaminants by employing multi-varied statistical methods. Dr. Slocomb has conducted numerous inventories and environmental reference assessments, and he has developed risk management strategies for the oil and gas industry in the United States, South America and Indonesia. He has worked with corporate leaders and upper management to create risk management strategies to mitigate threats to public health arising from exposure to discharge of wastewater, invasion of operating assets and harmful dependency. He has developed a systematic process for environmental risk management that is used to identify environmental threats, evaluate risks, prepare cost efficient responses, and to develop and implement risk management plans. Dr. Slocomb has also carried out numerous natural resource damage assessments (NRDA) associated with leaks of chemical and oil substances, and he has used habitat equivalence analysis to determine the loss of ecological services and the magnitude of restoration projects. He has vast experience in applying statistical methods to environmental problems, using Monte Carlo simulations in probabilistic risk assessments for the ecology and human health, as well as in research that has ranged from analysis of the structure of fish-farming communities to control of industrial processes. He is also an expert in designing statistical sampling for vegetation and fauna studies, brand research and recapture, preparation of estimates of statistical parameters from census data and estimates of sample size. Dr. Slocomb has provided statistical support to process engineers, solid waste management personnel, specialists in energy recovery, environmental scientists, and biologists specialized in flora and fauna, and environmental toxicologists. He has provided his services in litigation in matters of environmental investigations in large lakes, assignment of Total Maximum Daily Load (TMDL), oil spills and chemical substance spills, and in the toxicity of industrial effluents on fish, aquatic invertebrates and benthic organisms. He has designed and statistically analyzed evidence of sediment toxicity to evaluate the impacts of drilling mud on organisms in sediment. He has also provided technical support to the oil, mining and chemical industries in matters of ecological risk and risk to human health associated with exposure to PAH, BTEX, DDT, PCB, MTBE and metals. Dr. Slocomb is a member of the American Statistical Association, the Society of Environmental Toxicology and Chemistry, and the Society for Risk Analysis.

Author certification:

The attached report truly represents my knowledge and opinions on the matter.

Signature of Co-Author:

Date: October 1, 2007



**POTENTIAL IMPACTS ON THE ECOLOGY AND ON HUMAN HEALTH FROM
PETROLEUM HYDROCARBONS AND METALS IN SEDIMENT FOUND IN THE
ECUADORIAN ORIENTE**

Dominic M. Di Toro² and Joy McGrath¹
HydroQual, Inc., Mahwah, New Jersey

John Slocomb³
Entrix, Inc., Houston, Texas
October 1, 2007

Abstract. It is alleged that the presence of metals, polycyclic aromatic hydrocarbons (PAH), and benzene, toluene, ethylbenzene, xylene (BTEX) in the sediment of the water courses (rivers and estuaries) located in the Ecuadorian Oriente has caused adverse impacts to the ecology and to human health. To verify the validity of that allegation, the concentrations of these components were compared, measured in 55 sediment samples collected during the Judicial Inspections of the sites undertaken from 2004 to 2006, both at the production stations as well as at well sites, using the Sediment Quality Guidelines (SQG) of the United States Environmental Protection Agency (USEPA) and with the reference values for Equilibrium Partitioning Sediment Benchmarks (ESB) established to protect organisms in sediment, and the Soil Screening Levels, or SSL, were also compared, which levels were established in order to protect human health. The objective consisted of determining whether any of the components was a component of potential concern (COPC), which would indicate the possibility of adverse impacts. The results of this conservative analysis of assessment values indicate that by comparing the concentrations of metals, BTEX and PAH with the appropriate criteria, the concentrations of hydrocarbons and metals present in the sediment do not constitute a significant risk to either the environment or to human health. Therefore, remediation of that sediment is not justified.

INTRODUCTION

The objective of this study consists of determining whether the concentrations of metals, PAH and BTEX measured in the sediment in bodies of water in the Ecuadorian Oriente are high enough to have potentially damaging impacts on aquatic organisms present in the sediment, and on people who might come into contact with that sediment. In order to comply with that objective, the concentrations of these components in the sediment samples were compared with

Impact on Sediment
Page 1

Page 1779

¹ (NEED footnote language)

² Collaborated in the analysis of PAH, BTEX and metals in relation to the protection of organisms in sediment.

³ Collaborated in the analysis of PAH, BTEX and metals in relation to the protection of human health and in the analysis of metals in relation to protection of organisms in sediment.

the evaluation criteria established to protect human health and aquatic life. If the measured concentration of a component were found to be above the respective criteria, that component would be considered a component of potential concern (COPC) for human health or aquatic life. To the contrary, if the concentration were found to be below its criteria, the component would not be considered a COPC, and therefore it would not be considered to represent a potential ecological risk or a risk to human health.

Comparisons with the criteria were done using concentrations of PAH, BTEX and sedimentary metals measured in samples collected during the Judicial Inspections of the well sites and the production stations in the Sacha, Lago Agrio, Shushufindi and Aguarico fields up to March 2006. The sediment sample set consisted of 55 samples, collected from depths of between 0.0 meters (surface) and 1.9 meters. It is typically considered that sediment between at a depth of between 0 and 15 centimeters is within the biologically active zone, given that the majority of organisms are found within these confines. However, in this assessment, all of the sample depths were used in order to obtain even more conservative results. The following is a list of sites where sediment samples were collected, which were used in the assessment presented in this study:

Sacha	Shushufindi	Production Stations
SA 21	SSF 13	SSF Southeast
SA 85	SSF 67	SSF South
		SSF North
		LA North
		SA Central
		Aguarico
		SA South
		SA North 2

ASSESSMENT CRITERIA

The United States Environmental Protection Agency (USEPA) has established Sediment Quality Guidelines (SQG) for specific metals and reference values for Equilibrium Partitioning Sediment Benchmarks (ESB) specifically for PAH, that are protective of the organisms that live in sediment (US EPA 2000; 2003) (**Table 1**). Note that the ESB for BTEX presented in **Table 1** were calculated using the methodology derived for PAH (see the explanation that appears below). These SQG and ESB specify the concentrations above which chronic toxicity may be present.

Neither Ecuador, the World Health Organization (WHO), the USEPA, nor other Latin American countries have established guidelines or quality criteria for sediment based on human health. The USEPA, however, has established soil screening levels (SSL) whose purpose is to protect human health (**Table 2**). In order to determine whether levels of metals, PAH and BTEX in sediment can be considered COPC for human health, SSL were used as criteria (US EPA 1996 (a) and (b)), based on the conservative assumption that human exposure to sediments could be comparable to chronic exposure to soil. The method that is generally accepted to evaluate threats to the environment and to public health that result from exposure to oil hydrocarbons consists of measuring specific components of hydrocarbons that are known to be dangerous, for example, PAH and BTEX. The concentration values of each of these compounds are analytically quantified and subsequently utilized to evaluate the impacts on the ecology or on public health.

This study does not evaluate the potential adverse effects on receiving bodies of water or on human beings caused by exposure to Total Petroleum Hydrocarbons (TPH), since the USEPA has not established either SSL or SQG for TPH. TPH measurements alone cannot be used to assess risk to the environment or to public health due to the inability to distinguish between hazardous and non-hazardous materials. This point is clearly illustrated through the numerous non-hazardous materials existing in nature that contain high concentrations of TPH. For example, elevated concentrations of TPH are found in many natural materials, such as, for example, peat (3700 mg/kg), pine needles (19,000 mg/kg), cow manure (12,000 mg/kg) and hay (4,500 mg/kg). High concentrations are also found in dry leaves (7,100 mg/kg), grass (14,000 mg/kg), and maple seeds (7,100 mg/kg) (US EPA Method 418.1 1991/92). TPH is also found in Vaseline used in the home, which contains approximately 750,000 mg of TPH/kg. Therefore, even small amounts of these organic materials in sediment can result in high levels of TPH that do not reflect the presence of oil hydrocarbons.

SEDIMENT CHARACTERISTICS

Sediment is generally defined as a mix of natural organic and inorganic materials found beneath the water surface in flowing water. Sediment is comprised of water, an inorganic phase consisting of clay, sand, gravel and other mineral fragments, and an organic phase made of natural organic material in various states of decomposition (Ingersoll 1995). Water is the principal component that surrounds organic and inorganic particles, and it is often called interstitial or porous water, which normally represents 20-50% of the volume of the sediment. The component with the second-highest presence is the inorganic phase, which represents 45-80% of the volume of the sediment. The component with the smallest presence is the organic phase, which in general consists of 1-4% of the volume of the sediment.

The physical characteristics of the sediment vary from one place to another along the trajectories of waterways, depending mainly on the speed of the water (Wetzel 1983). In fast-flowing sections, the smallest particles of organic and inorganic sediment are transported downstream

and deposited in areas where the water flow is sufficiently decreased to allow the particles to settle on the surface of the sediment. In sections of relatively fast-flowing water, the sediment consists mainly of heavier inorganic and organic particles, such as sand, gravel, rounded stones, trunks and stems of large plants that resist the movement of the water flow. In sectors of slower-flowing water, the sediment contains comparatively large amounts of clay, sand and large-grained organic material. Those slow-moving bodies of water are typical of the Ecuadorian Oriente.

The original inorganic materials that occur naturally in the land adjacent to a water course to a large extent determine the concentrations of inorganic components in the sediment (Allan 1995). For example, the concentrations of metals found in the soil adjacent to water courses and the quantities found in sediment are frequently similar, which indicates the natural connection that exists between land and aquatic ecosystems. Similarly, the organic content of the sediment indicates the natural presence of original materials in the surrounding land. Materials in the form of particulates, such as leaves and plant stems in various stages of decomposition, fall into water courses or are dragged to them during rains, and they become part of the sediment. Once in the sediment, that material continues decomposing due to the actions of bacteria and fungus, which are part of the flora and fauna that naturally live in sediment. A large part of the energy that is required to sustain other organisms in a water course (for example, fish) is derived from this original organic material.

The sediment forms a critical habitat for bacteria, fungi, algae, insects and other organisms that collectively form a community of organisms that reside mainly in the top 15 centimeters of the sediment. This area where the majority of organisms are found is often called the biologically active zone. Among other factors, the size of particulates, the water current, the temperature, the dissolved oxygen and the amount of living and not-living organic material, determine the composition and diversity of this community.

Sediment is considered to be the cement of aquatic ecosystems in the same way that soil is the cement of land-based systems. Sedimentary organic material provides a source of nutrients that are critical for many aquatic organisms, and in turn these organisms are a source of nutrients for large predatory aquatic insects and fish. Finally, the health of the entire aquatic trophic chain, including fish, birds and mammals who feed on fish, depends on the quality of the sediment and the health of these organisms.

POTENTIAL TOXICITY TO ORGANISMS IN THE SEDIMENT

Hydrocarbons

Impact on Sediment
Page 4

Page 1782

The concentrations of benzene, toluene, ethylbenzene, xylene (commonly known as BTEX) and 16 polycyclic aromatic hydrocarbons (PAH) were measured from various sediment samples collected in the Oriente during the Judicial Inspections undertaken from August 2004 to March 2006. **Table 3** contains a list of the samples and concentrations of BTEX and the 16 PAH. That table also includes the percentage of total organic carbon (TOC). The concentrations that were left blank indicate that all of the chemical substances came back with results lower than those values reported as detection limits.

To evaluate whether the PAH have a potential adverse impact on the benthic community at the measured concentrations, the US EPA method was used to assess the toxicity of the sediment with PAH Mixtures (USEPA 2003) based on the Target Lipid Model developed previously (Di Toro *et al.*; 2000; Di Toro and McGrath 2000). The method requires that the toxicity of the PAH mixture be calculated in each sediment sample. One toxicity unit (TU) is calculated for each PAH i measured in the sediment, TU_{PAHi} , dividing the concentration of sediment normalized to organic carbon, $C_{OC,PAHi}$, by the US EPA's Equilibrium Partitioning Sediment Benchmarks (ESB), $C_{OC,PAHi,FCVi}$, in the following way:

$$TU_{PAHi} = \frac{C_{OC,PAHi}}{C_{OC,PAHi,FCVi}}$$

where the units of the concentrations in the numerator and the denominator are similar (that is, $\mu\text{g/g OC}$). For each sediment sample, the toxicity of the PAH mix is calculated, adding together the Toxic Units (TU) of the individual components.

$$TU_{mix} = \sum_i TU_{PAHi}$$

In theory, if the mix of Toxic Units is greater than or equal to one, it is likely that an adverse impact will present as a result of exposure to that sediment. However, it should be pointed out that a value of 1.0 for the Toxic Unit parameter does not constitute an absolute value. Di Toro *et al.* (2000) reported an uncertainty factor of two in calculating Toxic Units. For mixes with a total of Toxic Units greater than 2.0, it was likely that impacts would present. Similarly, for mixtures with a total of Toxic Units less than 0.5, it was not very likely that there would be impacts. The effects for mixtures with total Toxic Units between 0.5 and 2.0 were uncertain.

Sixteen PAH were measured in the sediment samples from the Oriente. To evaluate the sediment, however, the USEPA defines the total toxicity of PAH as the sum of Toxic Units of 34 PAH, which includes the original PAH and their analogous alkylates. The USEPA provides average adjustment factors to convert the Toxic Units calculated from the subsets of 13 PAH or 23 PAH of the total of 34 PAH to obtain the toxic equivalent of 34 PAH. This conversion is done

when there are no concentrations of the 34 PAH available, as is the case of the sediment samples in this study. For the sediment samples, the 13 PAH that comprised the subset of the 13 PAH were measured. Since only 16 PAH were measured, in this case the subset of 23 PAH is not the guide. To convert the toxicity of the 13 PAH to the toxicity of total PAH, the sum of Toxic Units of the 13 PAH is multiplied by 2.75. After adjusting the toxicity of the 13 PAH to their equivalent of 13 PAH, the uncertainty associated with the unquantified PAH is reduced.

The toxicity associated with BTEX in sediment cannot be ignored in the calculation of total toxicity. BTEX are hydrocarbons whose modality of action is similar to that of PAH (Di Toro *et al.* 2000). To be consistent with the theory of additivity used in the derivation of ESB for PAH, the toxicity associated with BTEX is calculated and the toxicity of total PAH is added. The toxicity of BTEX is calculated using the US EPA's ESB methodology. For each component of BTEX, the Toxicity Unit is calculated dividing the concentration in normalized sediment to organic carbon by the specific ESB for that chemical substance. ESB were calculated for BTEX and these varied between 208 $\mu\text{g/g}$ OC for benzene and 315 $\mu\text{g/g}$ OC for xylene. In this analysis, it was assumed that the BTEX and the PAH had similar levels of toxicity. This is a conservative focus since PAH are slightly more toxic for benthic communities than BTEX (Di Toro *et al.* 2000).

Table 3 contains a summary of toxicity evaluation for PAH and BTEX. For each sediment sample, the Toxic Units for BTEX, 16 PAH, 13 PAH and total PAH are presented. The Toxic Units of each sample were calculated by adding together the Toxic Units of the BTEX and the Toxic Units of the total PAH. For sediments that did not have a corresponding concentration of TOC, the average concentration (3.2%) of TOC was used. For the calculations, all results qualified with "J" (estimated values) were considered to be real values. An initial evaluation was performed ~~done~~ assuming that the values reported below the detection limits were equal to zero. For this scenario, the total of Toxic Units for all sediment samples was less than 0.5, which indicates that it is not likely that there were adverse impacts due to exposure to sediment. The Total Toxic Units for sediment at one station, SSF-SO-JI-SED 3, was 1.13, which is within the area of uncertainty. In this situation it is possible that the impacts may or may not be seen. **Figure 1** (upper section) shows a probability distribution of the total Toxic Units calculated for each sediment sample. It should be noted that the BTEX contribution to the total Toxic Units calculation is very low.

The results from evaluating the toxicity of BTEX and PAH were based on quantified concentration values. However, the majority of the data ended up being below the method's detection levels. In these cases the detection limit values were reported. In those toxicity calculations, it is unlikely that the detection limit values for each compound are the real concentration. In order to prove the importance of undetected compounds, it is assumed that the concentration is equal to half of the limit of detection. The BTEX and PAH total Toxic Units are calculated using half of the limit of detection values. The results are summarized in

Table 3 and **Figure 1** (lower section). This focus changed the prediction of toxicity for just one sediment sample: SA-C-JI-SED4. However, this seems to be a consequence of the low concentration of TOC in this sample. In the initial evaluation, a toxicity prediction could not be made since all concentrations of PAH and BTEX were below the detection limit values. The total Toxic Units at this location were 0.76, which places the toxicity level within the area of uncertainty. However, the TOC concentration in this sediment was below 0.2%, and normalization with organic carbon is not valid at such a low concentration of TOC (Di Toro *et al.* 1991). Therefore, the toxicity evaluation using this methodology overestimated the toxicity in this sample. Consequently, even by using the very conservative method of integrating the limit of detection values for the toxicity evaluation shows that there is no toxicity due to BTEX and PAH in these sediment samples.

Metals

Metals do not have a common toxicity mechanism; therefore, it does not make sense to calculate a toxicity index for a mix of metals. It is assumed that metal toxicity occurs as a result of the reaction of the free metal ion with specific binding sites that are physiologically active at the reaction site (USEPA 1999). For example, the binding sites of metals in fish seem to be the surface membranes of the gills. For fish and organisms in the sediment, it is accepted that the total concentration of a metal is not a good measurement of exposure that can be related directly to the toxicity of organisms in the sediment. Notwithstanding this, the bioavailability of a metal (that is, the amount of metal available in the sediment that might cause toxicity) is typically lower than the total concentration. Given that the maximum concentrations of total metals are below the SQG values, it is certain that the bioavailable portion with respect to the total is also not toxic for the organisms in the sediment.

The USEPA has derived ESB values for mixtures of cadmium, copper, lead, nickel, silver and zinc (USEPA, 2005). The data that supports this method were recently reported, as was an extension of the method (Di Toro *et al.* 2005). In order to use this methodology one must have simultaneous acid volatile sulfur (AVS) and metal extraction concentrations such that one mol of AVS adheres to one mol of SEM. The bioavailability of these metals is related to the amount of acid volatile sulfur such that one mol of AVS adheres to one mol of SEM. The exception is silver, which requires that two mols of silver adhere to one mol of AVS. If the total molar concentration of SEM is less than or equal to the total molar concentration of AVS, adverse impacts are not projected from the SEM. Impacts may occur when there is an excess of SEM. Since neither the SEM nor the AVS were measured, this methodology cannot be used to evaluate the toxicity of these metals.

However, total concentrations of metals may be compared to USEPA consensus-based guidelines. A discussion has been published on the usefulness of these guidelines and their relationship to available mechanistic guidelines (Wenning and Ingersoll, 2005). The consensus-based guidelines are not based on causality. To the contrary, they were developed based on the

sediment collected in the field, which may have been contaminated by many constituents, including metals. The idea is that if the sediment is contaminated, it will have high concentrations of many constituents. The consensus-based guidelines are actually parameters that qualify those sediments that are contaminated and that may cause toxic impacts. This method is reasonable in light of the available data.

The comparative results show that the maximum concentrations of metals in all of the samples, with the exception of one, are below the EPA's associated SQG values, and therefore the metals cannot be considered as COPC for ecological receptors (**Table 4**). One single sample collected from a marsh approximately 100 meters north of the drainage pipe on the northern edge of the Shushufindi Southwest production station (SSF-SO-JI-SED2) slightly exceeded the SQG for nickel by 5.4 mg/kg. With this sole exception, the concentrations of all metals are below the levels at which toxicity could present. Therefore, it is not justified to further evaluate the risks that metals present to organisms living in the sediment. It is important to point out that the background concentrations of metals in the sediment must be considered, since the SQG values of some metals may be equal to the background values of the metals in some areas of the world or even lower than those values. The background values of the metals in the soil in the Ecuadorian Oriente are presented in Table 5.

POTENTIAL RISKS TO HUMAN HEALTH

In order to evaluate the potential risks to human health, the maximum quantified concentrations of metals—PAH and BTEX—were compared with the SSL (**Table 5**). As mentioned previously, there are no sediment quality criteria to assess the risks to human health, therefore the SSLs for soil were used to evaluate whether any of the constituents in the sediment should be considered a COPC. The use of SSL values to evaluate assess the risks of the soil are based on specific exposure factors, such as the frequency of exposure, duration of exposure, and direct ingestion rates, as well as inhalation, among others. For example, the USEPA (1996 b) uses an exposure frequency of 350 days/year and soil ingestion of 200 mg/day to develop an SSL value associated with ingestion of a non-carcinogenic constituent in residential soil. However, it is likely that the duration of exposure and the ingestion or inhalation rate of the sediment are significantly less than for residential soil, which makes the comparisons of concentrations of sedimentary components with SSL values very conservative. Detected concentration in the soil (or sediment) above an SSL signifies that it is justified to consider and evaluate the site in greater depth. It does not mean that impacts to human health have occurred, or that it is likely that they will occur.

The results of these comparisons show that the constituents did not exceed the corresponding SSL (**Table 5**). Therefore, it is evident that no constituent is a COPC and there are no significant

risks to human health due to exposure to sediments in the Ecuadorian Oriente.

RISK-BASED REMEDIATION ACTIONS

The USEPA has developed a risk-based decision-making process (1989; 1998) to decide whether remediation actions are necessary to protect human health and the environment from exposure to damaging constituents present in a location. Canada, New Zealand and the Netherlands have also adopted risk-based decision-making in their programs for managing and cleaning up contaminated sites. In the United States, an evaluation of the need for remediation actions at a site is normally done in a series of increasingly complex steps. The first step consists of evaluating the detected values to determine if potentially toxic chemical substances are present, and if there are is, it is then determined if those concentrations exceed the conservative reference values that indicate a potential threat to human health (SSL). If the concentration levels of the detected chemical substances do not exceed the SSL the presence of chemical substances does not exceed the limit of detection values, then that means there are no COPCs. If no COPC components are identified, the need to take additional steps, including remediation actions, is eliminated. Given the results presented in this study, it is not necessary to take additional remediation actions.

CONCLUSIONS

Based on the results presented in this study, it is unlikely that there are adverse ecological impacts or impacts to human health due to PAH, BTEX and metals in the sediment in the Oriente. Petroleum hydrocarbons were detected (PAH and BTEX) in the sediment in bodies of water, but the concentrations found were below the levels that could produce chronic toxicity in organisms or result in risks to human health. The additive toxicity of the mix of PAH and BTEX was also found to be below levels that could be toxic. Similarly, no metals were found at concentrations above those at which adverse ecological impacts could occur (with the exception of a single sample in one marsh). The metals found were also determined to be below the SSL values for impacts on human health, and could simply be representative of values of metals that are naturally occurring in the earth that surrounds waterways. There is no need to initiate remediation actions to remove contaminated sediment from the waterways (rivers and estuaries) analyzed in the Oriente to date, given that no constituent (PAH, BTEX or metals) represents a significant risk to health or to ecological receptors.

BIBLIOGRAPHY

- Allan JD. 1995. Stream Ecology: Structure and Function of Running Waters. Chapman Hall, London, 388 pp.
- American Petroleum Institute (API). 1995. Metals Criteria for Land Management of Exploration and Production Wastes: Technical Support Document for API Recommended Guidance Values. API Publication Number 4600, Washington, D.C.
- Di Toro DM, Zarba CS, Hansen DJ, Berry WJ, Swartz RC, Cowan CE, Pavlou SP, Allen HE, Thomas NA, Paquin PR. 1991. Technical basis for establishing sediment quality criteria for nonionic organic chemicals by using equilibrium partitioning. *Environmental Toxicology and Chemistry*. 10:1541-1583.
- Di Toro DM, McGrath JA, Hansen DJ. 2000. Technical basis for narcotic chemicals and polycyclic aromatic hydrocarbon criteria. I. Water and tissue. *Environmental Toxicology and Chemistry*. 19:1951-1970.
- Di Toro DM and McGrath JA. 2000. Technical basis for narcotic chemicals and polycyclic aromatic hydrocarbon criteria. II. Mixtures and sediments. *Environmental Toxicology and Chemistry*. 19:1971-1982.
- Di Toro DM, McGrath J M, Hansen DJ, Berry WJ, Paquin PR, Mathew R., Wu KB, Santore RC. 2005. Predicting Sediment Metal Toxicity Using a Sediment Biotic Ligand Model: Methodology and Initial Application. *Environmental Toxicology and Chemistry*. 24:2410-2427.
- Ingersoll, CG. 1995. Sediment Tests, In (G. M. Rand, ed.). *Fundamentals of Aquatic Toxicology: Effects, Fate and Risk Assessment*, Taylor and Francis, Washington, SC, 1125 pp.
- U.S. Environmental Protection Agency. 1989. Risk Assessment Guidance for Superfund, Volume I, Human Health Evaluation Manual, Office of Emergency and Remedial Response, OSWER Directive 9285.7-01a, September 29, 1989.

- U.S. Environmental Protection Agency 418.1. Total Recoverable Hydrocarbons by IR, Groundwater Analytical Bulletin, Buzzards Bay, MA, Groundwater Analytical Inc., Winter 1991/92.
- U.S. Environmental Protection Agency. 1996a. Soil Screening Guidance: Technical Background Document. EPA/540/R95/128, Office of Solid Waste and Emergency Response, Washington, D.C.
- U.S. Environmental Protection Agency. 1996b. Soil Screening Guidance: User's Guide. Publication 9355.4-23, Office of Solid Waste and Emergency Response, Washington, D.C.
- U.S. Environmental Protection Agency. 1998. Guidelines for Ecological Risk Assessment. Office of Research and Development, April 1998, EPA/630/R-002F, Washington, D.C.
- U.S. Environmental Protection Agency. 1999. Integrated Approach to Assessing Bioavailability and Toxicity of Metals in Surface Water and Sediment. EPA-822-E-99-001, Office of Water and Research and Development, Washington, D.C.
- U.S. Environmental Protection Agency. 2000. Prediction of Sediment Toxicity Using Consensus-Based Freshwater Sediment Quality Guidelines, EPA 905/R-00/007.
- U.S. Environmental Protection Agency. 2003. Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: PAH Mixtures. EPA/600/R-02/013. Office of Research and Development. Washington, D.C., USA

U.S. Environmental Protection Agency. 2005. Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: Metals Mixtures (Cadmium, Copper, Lead, Nickel, Silver and Zinc. EPA/600/R-02/011. Office of Research and Development. Washington, D.C., USA.

Venezuela, Decree 2635. Rules to control recovery of hazardous materials and management of hazardous waste. Extraordinary Official Gazette No. 5245.

Wenning RJ and Ingersoll CG. (Eds.). 2005. Use of Sediment Quality Guidelines and Related Tools for the Assessment of Contaminated Sediments. Pensacola, FL. SETAC Press.

Wetzel RG. 1983. Limnology (2nd edition). Sanders College Publishing. New York, 767 pp.

Table 1. Sediment quality guidelines (SQG) and Reference Values for equilibrium partitioning in sediments (ESB) for metals, BTEX and PAH. SQG and ESB were used to evaluate the sediment quality for protection of organisms that live in sediment.

CONSTITUENT	CAS No.	SQG OR ESB	REFERENCE
-------------	---------	------------	-----------

ND = has not been determined for this constituent; *NA* = does not apply in this case.

¹ US EPA methodology was used to obtain this criterion.

Table 2. US EPA Soil Screening Levels (SSL) were used for metals, benzene, toluene, ethylbenzene, xylene (BTEX) and Polycyclic Aromatic Hydrocarbons (PAH) that protect human health. SSL were used to evaluate the quality of the sediment

CONSTITUENT	CAS No.	SOIL SCREENING LEVEL (MG/KG)	REFERENCE
-------------	---------	------------------------------	-----------

* The only potential source of barium associated with activities in the oil fields is barite (barium sulfate). The US EPA has determined that: “Data on human beings and animals indicate that barium sulfate is practically not toxic for human beings and other species of mammals.” (USEPA, 1993).

Table 3. Summary of toxicity assessment.

Station location	Concentrations for assumed detection values of 0 mg/kg								Concentrations for assumed detection values of ½ DL					
	Total BTEX (µg/kg) ¹	Total PAH (µg/kg) ²	TOC (%) ³	BTEX Toxic Unit	16 PAH ⁴ Toxic Unit	13 PAH ⁵ Toxic Unit	Total PAH ⁶ Toxic Units	Total Toxic Units PAH + BTEX ⁷	BTEX Toxic Unit	16 PAH ⁴ Toxic Unit	13 PAH ⁵ Toxic Unit	Total PAH ⁶ Toxic Units	Total Toxic Units PAH + BTEX ⁷	Impacts?

Table 3. Summary of toxicity assessment.

Station location	Concentrations for assumed detection limit values of 0 mg/kg								Concentrations for assumed detection limit values of ½ DL					
	Total BTEX (µg/kg) ¹	Total PAH (µg/kg) ²	TOC (%) ³	BTEX Toxic Unit	16 PAH ⁴ Toxic Unit	13 PAH ⁵ Toxic Unit	Total PAH ⁶ Toxic Units	Total Toxic Units PAH + BTEX ⁷	BTEX Toxic Unit	16 PAH ⁴ Toxic Unit	13 PAH ⁵ Toxic Unit	Total PAH ⁶ Toxic Units	Total Toxic Units PAH + BTEX ⁷	Impacts?

¹ Total quantified concentration of benzene, toluene, ethylbenzene and xylene.

² Total quantified concentration of PAH.

³ The values in bold represent average concentration of TOC measured at all stations. For these locations, TOC data was not provided.

⁴ Toxic units calculated from the 16 quantified PAH.

⁵ Toxic units calculated from the 13 principal quantified PAH.

⁶ Toxic units calculated from total PAH. That calculation is done taking the toxic units from the 13 principal PAH and multiplying them by an adjustment factor of 2.75.

Table 3. Summary of toxicity assessment.

Station location	Concentrations for assumed detection limit values of 0 mg/kg								Concentrations for assumed detection limit values ½ DL					
	Total BTEX (µg/kg) ¹	Total PAH (µg/kg) ²	TOC (%) ³	BTEX Toxic Unit	16 PAH ⁴ Toxic Unit	13 PAH ⁵ Toxic Unit	Total PAH ⁶ Toxic Units	Total Toxic Units PAH + BTEX ⁷	BTEX Toxic Unit	16 PAH ⁴ Toxic Unit	13 PAH ⁵ Toxic Unit	Total PAH ⁶ Toxic Units	Total Toxic Units PAH + BTEX ⁷	Impacts?

⁷ Toxic units calculated from BTEX and PAH. A toxic unit higher than 2.0 indicates that it is likely that impacts will be observed. A toxic unit lower than 0.5 indicates that it is unlikely that impacts will be observed.

⁸ The concentration of TOC of this sediment is too low (< 0.2); the analysis will overestimate toxicity.



The shaded areas indicate that the toxic units fall within an area of uncertainty.

Table 4. Comparison of the maximum concentrations of metals quantified (mg/kg) in sediment with the base values in the soil in the Oriente and with the sediment quality guidelines based on chronic toxicity (SQG, mg/kg). If the concentration did not exceed the SQG value, then the constituent was not considered to be of potential concern (COPC) for sediment receptors.

CONSTITUENT	SEDIMENT QUALITY GUIDELINE (SQG)	BASE VALUES FOR METALS IN THE SOIL IN THE ORIENTE	ADO DETECTION NUMBER ¹	MAXIMUM CONCENTRATION ²	COPC (YES/NO)?
-------------	----------------------------------	---	-----------------------------------	------------------------------------	----------------

ND = has not been determined for this constituent; *NA* = does not apply in this case.

¹ Number of measurements detected above the analytical detection limit.

² Maximum concentration detection.

³ The maximum concentration exceeds the SQG guidelines by 5.4 mg/kg, which slightly exceeds the criteria for the COPC designation.

* SQG < Background Values

Table 5. Comparison of the maximum concentrations of constituents measured in sediment with the Soil Screening Levels (SSL) established to protect human health. If the concentration did not exceed the SSL value, then the constituent was not considered to be of potential concern (COPC) to human health.

CONSTITUENT	SOIL SCREENING LEVEL (SSL)	NUMBER DETECTED ¹	MAXIMUM CONCENTRATION ²	COPC (YES/NO)?
-------------	----------------------------	------------------------------	------------------------------------	----------------

¹ Number of measurements detected above the analytical detection limit.

² Maximum concentration detection.

* The only potential source of barium associated with activities in the oil fields is barite (barium sulfate). The USEPA has determined that: “Data on human beings and animals indicate that barium sulfate is practically not toxic for human beings and other species of mammals.” (USEPA, 1993).