Arsenic in the rivers of the Amazon Basin

Wilson Scarpelli
Mineral Exploration Consultant
wiscar@attglobal.net

ABSTRACT *The rivers flowing from the Andes bring more than 5 tons of arsenic per year to the Atlantic Ocean as part of their load of transported sediments and also dissolved in the waters. The combined arsenic content, of about 1 mg/m^3, is close to the 10 mg/m^3 maximum acceptable for potable waters in most of the countries. Following their deposition in the Amazon Fan area, the most important carriers of arsenic, iron oxides and hydroxides, are diagenetically reduced to sulfides, carbonates and phosphates, liberating additional soluble arsenic which causes higher concentrations of arsenic along the shore.*

KEYWORDS *Arsenic, arsenic in Amazon Basin waters, Amazon Basin, Andean rivers, iron oxyhydroxide reduction*

Introduction

The Amazon Basin, defined as the area drained by the rivers that contribute to the Amazon River, covers about 6,110,000 km^2, over large portions of the territories of Brazil, Bolivia, Peru, Ecuador, and Colombia. As shown in Fig. 1, the basin expands in two quite different geomorphological areas, and each one contributes in a different way to its development.

In the west, for 3,200 kilometers the basin drains the eastern cordilleras of the Andes, from south of La Paz, in Bolivia, to near Bogota, in Colombia. This area has high elevations and is made up of very long ridges, with elevations greater than 4,000 meters, steep slopes, a thin cover of vegetation, and a very intense rate of erosion. The rivers leaving it contain a high bedload of sediments, which gives them a distinctive brown color.

To the east of the Andes, surface elevations rarely surpass a few hundred meters, rainfall is intense, vegetation cover is thick, the rocks are deeply weathered and the rate of erosion is relatively low. The rivers draining this portion of the basin transport a small bedload of sediments, and the waters are relatively free of sediments and are occasionally dark due to accumulations of organic matter.

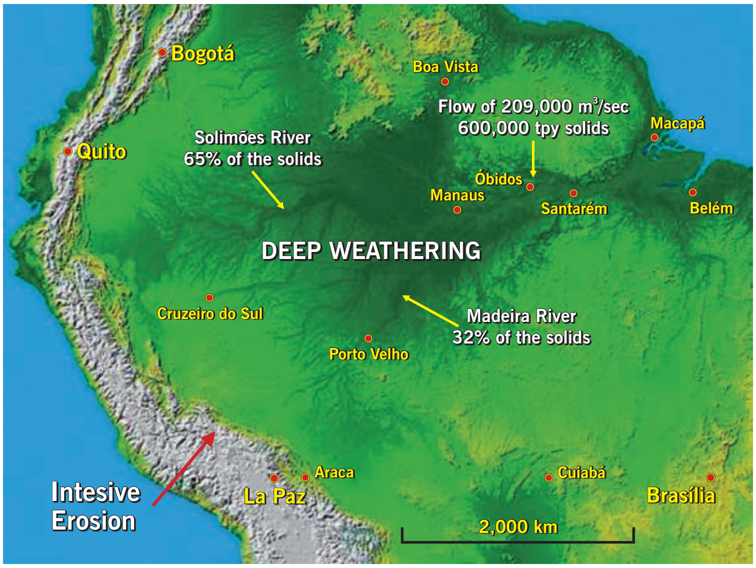


Figure 1 – The western portion of the Amazon Basin, shown in light gray, covers the eastern cordilleras of the Andes, where the erosion is intensive and responsible for 97% of the sediment which is transported seaward. The eastern portion, shown in variations of green, is characterized by deep weathering and low levels of erosion

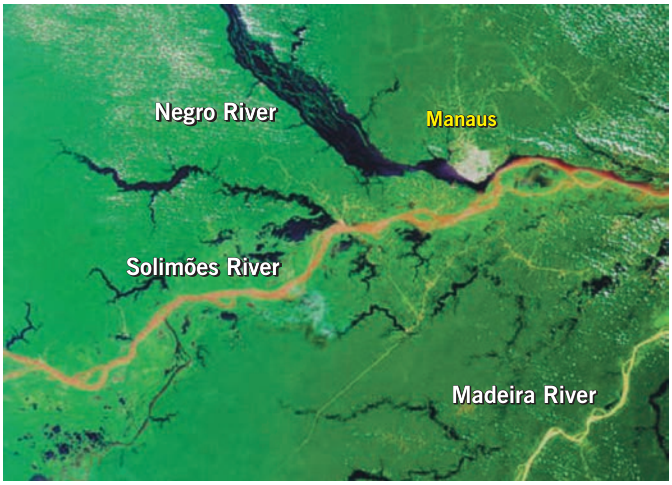


Figure 2 – The encounter of the brown waters of the Andean Solimões River with the dark clean waters of the Rio Negro in the north. The Andean Madeira River is shown in the lower right

Figure 3 – The encounter of the brown waters of the Amazon River with the clean waters of the Tapajós river, at Santarém, Pará

As result of the contrasting bedloads of the rivers draining the two areas, a characteristic of the Amazon Basin are the "encounters of waters", as those of Manaus and of Santarém (Figs. 2 and 3), when the brownish and sediment loaded waters coming from the Andes encounter and mix with the dark clean waters of the other rivers.

ANEEL sampling

An unpublished paper by S.F.P. Pereira, of the Laquanam (the environmental and analytical chemistry laboratory of the University of Pará) triggered the interest to search through the literature to find out about the distribution of arsenic in the Amazon Basin. As mentioned later, the paper indicated high values of arsenic in both the Amazon and the Guamá Rivers at the mouth of the Amazon.

High quality information regarding water flow volume and the transported materials is available from the sampling, measurements, and assay work done by ANEEL (the national agency of electrical energy) at its 60 monitoring stations located along the most important rivers of the Brazilian portion of the basin.

The information is being compiled and comprehensively studied through the HiBAM Project (Hidrology and Geochemistry of the Amazon Basin), a joint program made up of an association of the CNPq (Research National Council, of

Brazil) with the IRD (institute of research for the development, of France). The activities of HiBAM are carried out with the participation of ANA (the national water agency), ANEEL, UnB (University of Brasília), and the IRD.

Among the many papers presenting the information compiled by the HiBAM Project, Seyler and Boaventura (2001) presented tables with good quantitative information obtained at the ANEEL sample stations. They show that from 1965 to 1990 the flow of the Amazon River averaged 209,000 m^3 per second at the Óbidos station, in the state of Pará. This rate of flow corresponds to 6,500,000,000 m^3 annually. They also show that the river carried 600,000,000 tons of sediments to the ocean each year, and that 62% of this tonnage arrives from the Solimões River, 35% from the Madeira River, and only 3% from all of the other rivers.

These numbers explain quite well the reasons for the brownish color of the rivers with waters coming from the Andes, like the Beni, the Madeira, the Solimões, the Amazon and others. They also explain the reason for the contrast of color of the waters of these rivers and the waters of rivers that originate in the Brazilian Shield, like the Negro, the Tapajós, and others.

In their tables, Seyler and Boaventura (2001) also present figures of the amount of solids being transported, and of the arsenic content in both the transported solids and dissolved solids in the waters. Their numbers are shown in the columns on the left hand side of Table 1. They made it possible to calculate, for each sampling station, the percentage of arsenic transported as solids, the total concentration of arsenic in the rivers, and the total mass of arsenic being transported in tons per day.

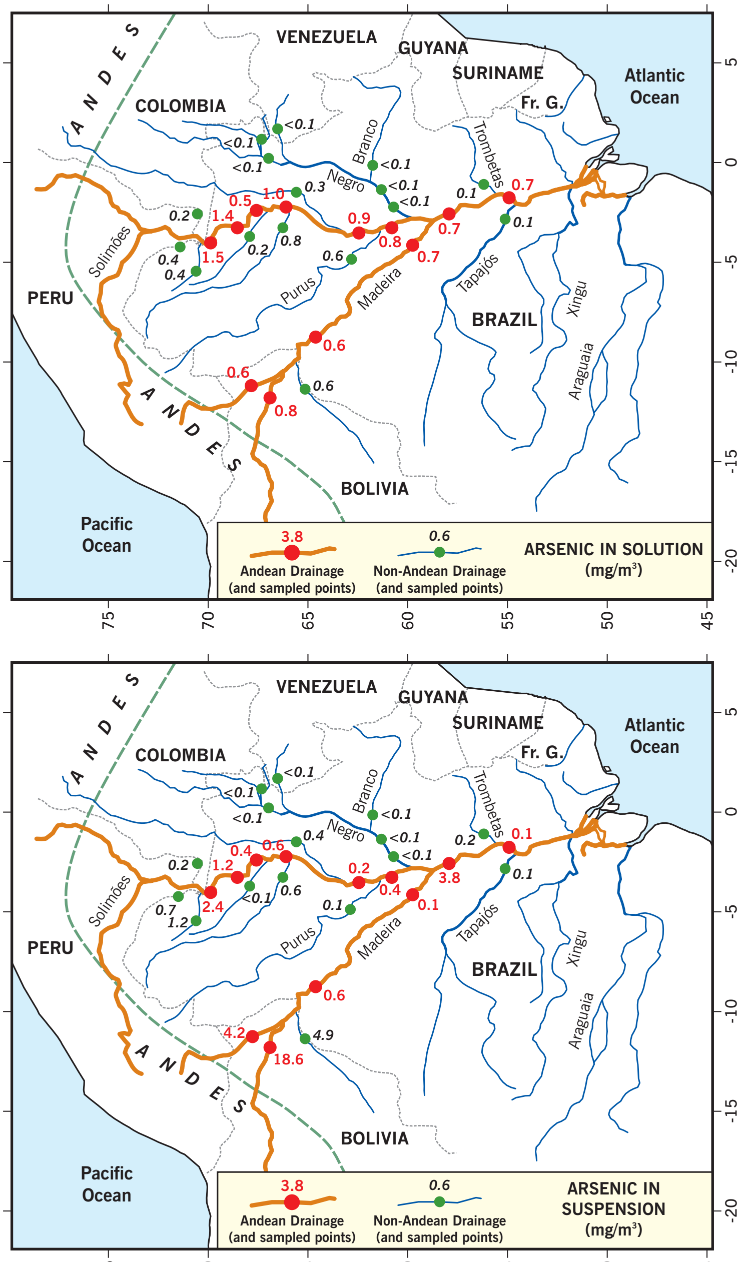


Figure 4 – Arsenic content of the rivers of the Amazon Basin as determined by sampling at ANEEL monitoring stations. Andean rivers are shown in brown to represent their high load of sediments. They show higher concentrations of arsenic in both soluble (above) and suspended (below) forms

HiBAM data on arsenic in the Amazon Basin

The concentrations of arsenic in the rivers are shown in Figures 4 and 5, on which the rivers with Andean waters are drawn in brown. The illustrations show the contents of arsenic in soluble form, in suspended solids, the total concentration of

Table 1 – Arsenic transported in the rivers of the Amazon Basin as observed with samples collected under the framework of the HiBAM project at the network of stations operated by ANEEL in the Brazilian Amazon. Rivers with Andean waters and sediments are shown in negrite

		Reported Sampling and Assay Data					Calculated Values			
River	Distance from sea (km)	Date of sampling	River flow (m^3/sec)	Suspended sediments (g/m^3)	As in the sediments (g/ton)	As in solution (mg/m^3)	As in solution (mg/m^3)	As in the sediments (mg/m^3)	As total grade (mg/m^3)	As total mass (ton/day)
Solimões	**2,500**	**26/oct/1995**	**20,115**	**166.5**	**14.5**	**1.53**	**1.53**	**2.41**	**3.94**	**6.85**
Javari		27/oct/1995	1,565	127.6	5.8	0.36	0.36	0.74	1.10	0.15
Itaquaí		27/oct/1995	793	148.3	7.9	0.44	0.44	1.17	1.61	0.11
Solimões	**2,200**	**28/oct/1995**	**24,251**	**74.5**	**15.7**	**1.38**	**1.38**	**1.17**	**2.55**	**5.34**
Içá		31/oct/1995	5,354	41.4	3.5	0.15	0.15	0.14	0.29	0.14
Solimões		**29/oct/1995**	**32,539**	**46.0**	**9.7**	**0.49**	**0.49**	**0.45**	**0.94**	**2.63**
Jutaí		3/nov/1995	1,143	13.5	3.4	0.15	0.15	0.05	0.20	0.02
Solimões	**1,900**	**3/nov/1995**	**34,333**	**60.9**	**10.0**	**1.01**	**1.01**	**0.61**	**1.62**	**4.80**
Juruá		4/nov/1995	1,045	56.3	10.1	0.85	0.85	0.57	1.42	0.13
Japurá		4/nov/1995	10,264	28.5	13.6	0.33	0.33	0.39	0.72	0.64
Solimões	**1,380**	**7/nov/1995**	**46,847**	**63.7**	**3.0**	**0.88**	**0.88**	**0.19**	**1.07**	**4.34**
Purus		9/nov/1995	2,534	38.6	3.1	0.55	0.55	0.12	0.67	0.15
Solimões	**1,200**	**10/nov/1995**	**52,477**	**127.1**	**2.8**	**0.77**	**0.77**	**0.36**	**1.13**	**5.10**
Branco		8/jul/1996	11,960	22.7	2.1	<0.05	<0.05	0.05	0.05	0.05
Negro		20/jun/1996	9,790	9.9	0.2	<0.05	<0.05	0.00	0.05	0.04
Negro		23/jun/1996	15,840	11.6	0.2	<0.05	<0.05	0.00	0.05	0.07
Negro		27/jun/1996	23,000	10.3	0.2	<0.05	<0.05	0.00	0.05	0.10
Negro		9/jul/1996	52,640	17.0	1.7	<0.05	<0.05	0.03	0.05	0.23
Negro	1,250	12/jul/1996	64,680	8.9	7.9	0.05	0.05	0.07	0.12	0.67
Beni	**2,000**	**1/apr/1994**	**2,856**	**937.0**	**19.9**	**0.83**	**0.83**	**18.65**	**19.48**	**4.81**
Madre Diós	**2,050**	**2/apr/1994**	**5,092**	**424.0**	**10.0**	**0.61**	**0.61**	**4.24**	**4.85**	**2.13**
Mamoré		3/apr/1994	8,391	409.0	11.9	0.61	0.61	4.87	5.48	3.97
Madeira	**1,950**	**12/apr/1998**	**29,000**	**302.0**	**(2)**	**0.59**	**0.59**	**(0.60)**	**(1.19)**	**(2.98)**
Madeira	**1,200**	**15/nov/1995**	**5,132**	**21.3**	**2.7**	**0.69**	**0.69**	**0.06**	**0.75**	**0.33**
Amazonas	**1,000**	**15/nov/1995**	**75,017**	**46.1**	**81.9**	**0.73**	**0.73**	**3.78**	**4.51**	**29.20**
Trombetas		16/nov/1995	1,258	14.8	17.1	0.12	0.12	0.25	0.37	0.04
Tapajós		18/nov/1995	6,027	3.5	17.7	0.11	0.11	0.06	0.17	0.09
Amazonas	**650**	**17/nov/1995**	**81,090**	**44.2**	**2.8**	**0.68**	**0.68**	**0.12**	**0.80**	**5.63**

arsenic, and the tonnage of the element transported per day.

It is quite clear that the Andean waters have dramatically higher concentrations of arsenic, occasionally not too far from the maximum limit of potability, which is 10 μg/liter, or 10 grams per cubic meter, as defined in year 2000 by the Brazilian Health Ministry. When the concentrations of arsenic in solution and in solids are added, the limit of potability is occasionally surpassed.

The discrepancies observed between the sites reflect differences in the flow regimens and should not be taken as representing errors in sampling or assaying. Along the Amazon River itself, one of the reasons for the differences is the continuous process of deposition and erosion of the transported solids on the banks of the river (Martinelli *et al.* 1993).

The largest difference occurred with the samples taken at the last two sampling stations in the Amazon River, near the mouths of the Trombetas and the Tapajós rivers. The values observed at these stations revealed that 29.2 and of 5.6 tons of arsenic were being transported per day, respectively. While the true value could be between these two figures, it is quite clear that 5.6 or 29.2 tons per day of arsenic represent a very large figure.

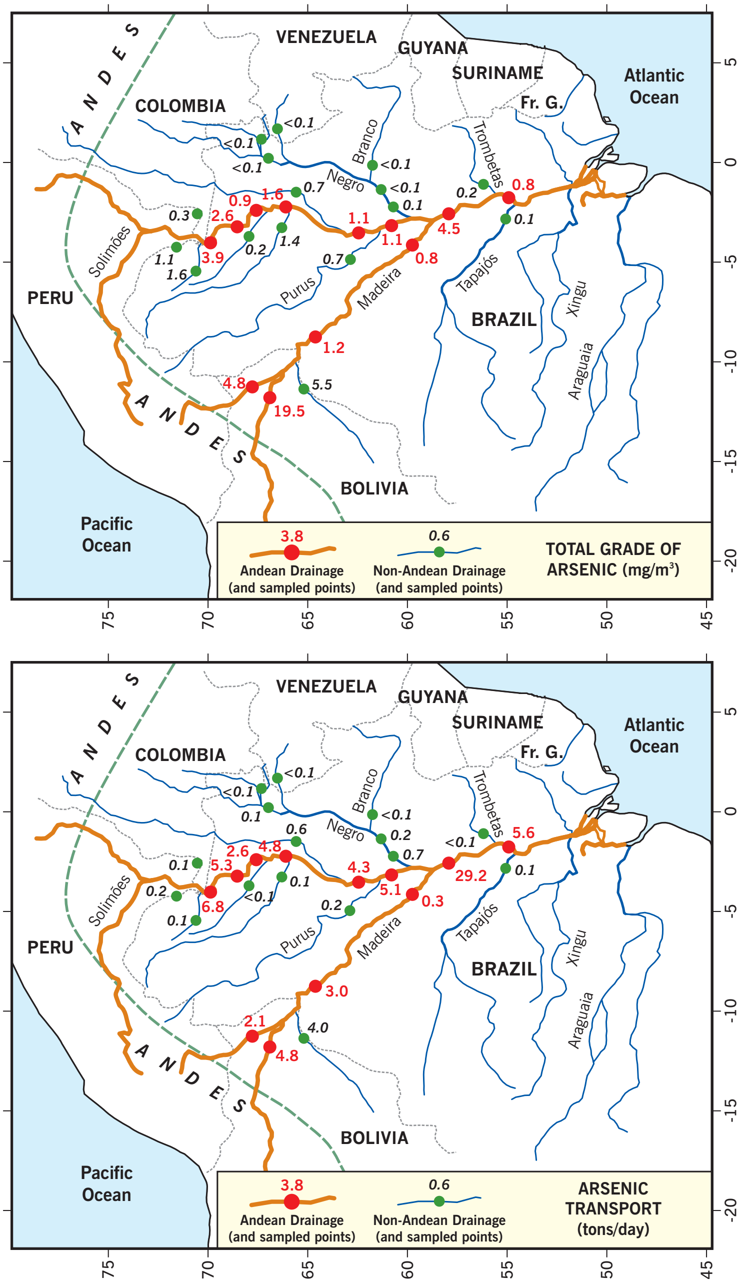
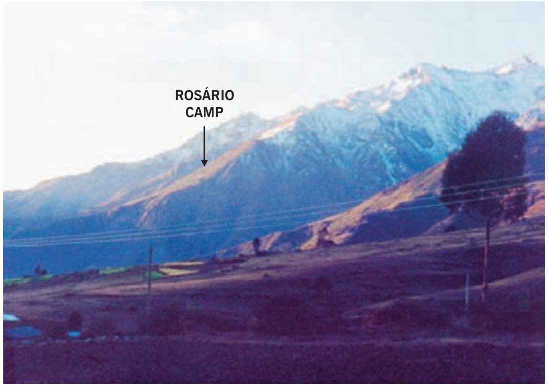


Figure 5 – The total grades of arsenic in Amazonian rivers are shown above in soluble and suspended forms. Below, the tonnage of arsenic transported per day, considering the concentrations of arsenic and water flow volume

Source of the arsenic transported by the Amazon Basin rivers

The information presented clearly indicates that the arsenic is coming from the Andes, which is the source of 97% of the solids being transported by the Amazon River to the ocean.

The source seems to be the sulfide-related mineralizations of gold and base metals that occurs in the eastern Andean ridges, many related to north-south faults and occurring at elevations on the order of 4,000 meters. Most of these steep sloped ridges receive high rainfall due to moisture rich winds from the forest area to the east, and are eroded at a relatively fast rate (Figs. 6 and 7).



Figures 6 and 7 – Rosario de Araca, east of La Paz, Bolivia, one of the source areas for sediments containing arsenic. The Rosario de Araca camp is located over an arsenic-bearing auriferous deposit, at mid-slope of a 4,700-meter high cordillera. The photo at left shows the steep gulleys cutting through the mineralized area, and the photo at right, taken from the camp, shows extensive sedimentary terraces at the base of the mountain, submitted to intense erosion

Arsenic at the mouth of the Amazon River

In the paper which drew attention to the issue of arsenic in Amazon waters, S.F.P. Pereira presented values of dissolved arsenic in waters of the mouth of the Amazon and the Guamá Rivers, that is, at west, north, and south of the Marajó Island. As the two rivers are connected by water channels west of the Marajó Island, Andean water from the Amazon also flows through the Guamá River.

Her paper (Fig. 8) revealed arsenic contents similar to those observed in the upstream sections of the Amazon River, but with an increase of values in direction of the sea. From concentrations of 3 to 5 mg/m^3 in front of Macapá and Belém, the concentration reached 10 to 14 mg/m^3 in the delta. These high concentrations are greater than the maximum presently accepted by most countries for waters for human consumption, which is 10 mg/m^3.

High values of arsenic at the Amazon Fan

There are several reports describing the sediments of the Amazon Fan area, among them those based on cores of the Ocean Drilling Program. The observations support a proposed mechanism to explain the greater values of dissolved arsenic in the coastal area of the state of Amapá.

Nanayama (1997) describes the constituent minerals of the sediments deposited in the Amazon Fan, identifying assemblies derived from the Precambrian Brazilian and Guyana Shields, from the Tertiary Sediments of the Amazon River Basin, from arc-volcanic rocks of the Andean Cordillera and from the foreland region of the Andes. Most of the grains are quartz, feldspars and micas, followed by minor oxides and silicates. Quartz and feldspars are round or angular, usually with iron-rich coatings.

McDaniel *et al.* (2002) detailed the relatively unweathered conditions of the sediments sampled in the fan area and concluded, after comparative studies of Pb and Nd isotopes, “that muds of the Amazon Fan are derived dominantly from the Andean highlands. Furthermore, during their journey to the Atlantic Ocean, they were not affected by the extreme weathering conditions such as those that exist in the Amazon drainage basin today”. This conclusion was similar to that made earlier by Gibbs (1967), who identified angular grains of fresh feldspars in the sediment load of the Amazon River.

Burns (1997) describes the presence of a laterally persistent horizon rich in secondary diagenetic iron sulfides, phosphates and carbonates in the fan area, at about one meter of depth. He points out that these minerals form after dissolution and re-crystallization of iron oxides and hydroxides. The reactions occur under the reducing anoxic conditions created by the continuous burial of the sediments.

Sullivan and Aller (1996), examining the shallow holes drilled along the lines ‘ost’ and ‘rtm’ shown at Figure 8, verified that during the diagenetic formation of iron carbonates, sulfides and phosphates, the arsenic contained in the iron oxides and hydroxides was liberated to the pore water of the sediments, with the maximum grade of arsenic in pore water seen at depths of 0.25 to 1.5 meters (Fig. 9). A sample with 300 ppb (300 mg/m^3) was reported at the horizon rich in iron carbonates, sulfates and phosphates. They express that “maximum porewater arsenic concentrations are one order of magnitude greater than levels reported in most other coastal marine environments”, and “oxidized arsenic is associated with iron oxyhydroxides in surface sediments, then subsequently reduced and released upon burial in the extensive suboxic zone”. To aggravate the matters, “upward diffusion and intense physical reworking of sediments presumably releases the dissolved portion of arsenic fraction to the water column”.

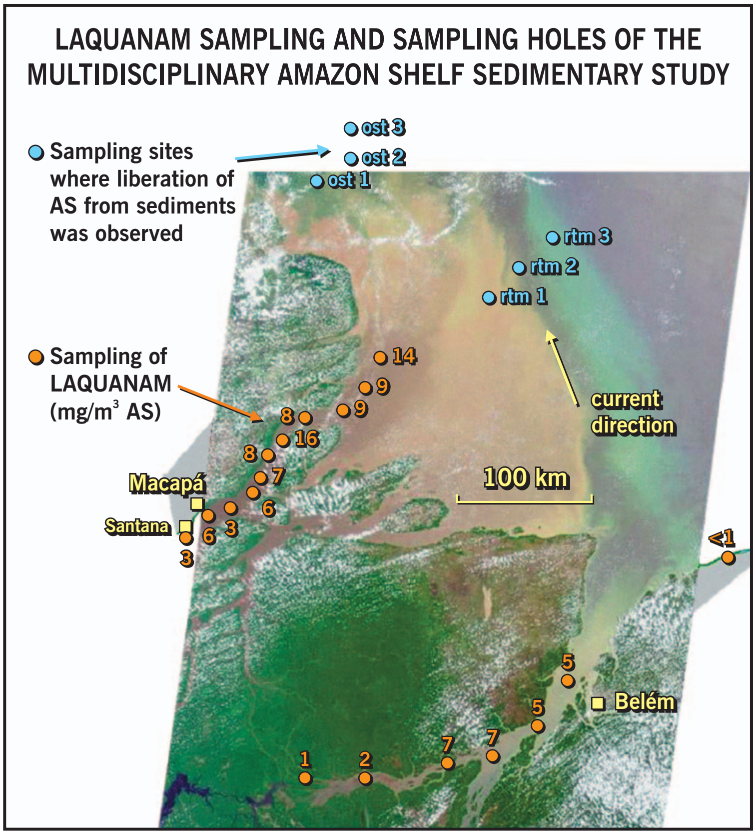


Figure 8 – Soluble arsenic determined by LAQUANAM in the Amazon River in the north, and the Guamá River in the south. There is an increase of soluble arsenic towards the ocean. The figure also shows the location of the two lines of holes, “ost” and “rtm”, of the Amazon Shelf Sedimentary Study, which revealed that the diagenesis of iron oxides and hydroxides liberates arsenic to the ocean waters, a possible reason for the increase of arsenic in the coastal areas.

Summary and conclusions

The high rate of erosion in the Andean cordilleras is the cause of the great volume of sediments transported by the Andean rivers, giving them their characteristic light brown color. These rivers are responsible for 97% of the sediments transported by the Amazon River to the Atlantic Ocean.

Together with their transported minerals, mostly quartz, feldspars and micas, which are often coated with iron oxides and hydroxides, the Andean rivers also transport high concentrations of arsenic, in solution or adsorbed in the iron oxides and hydroxides. The arsenic, which originates from the common occurrences of arsenic-bearing sulfides along the Andean cordilleras, appears with concentrations which approach the maximum value of arsenic accepted for potable water. The samples collected at the monitoring stations of ANEEL indicate that more than 5 tons of arsenic are transported annually to the Atlantic Ocean.

After their deposition in the Amazon Fan area, the iron oxides and hydroxides are slowly reduced to sulfides, carbonates and phosphates when covered by about one meter of new sediment load, and during this reduction, their adsorbed arsenic is liberated in soluble form to the pore water of the sediments. The top layers of sediments are disturbed during storms and the newly formed soluble arsenic is released into the sea water.

As a consequence of this process, the concentration of arsenic is higher in the Amazon Fan than in the Amazon River, and this should be of some concern since this area is a source of marine sea foods.

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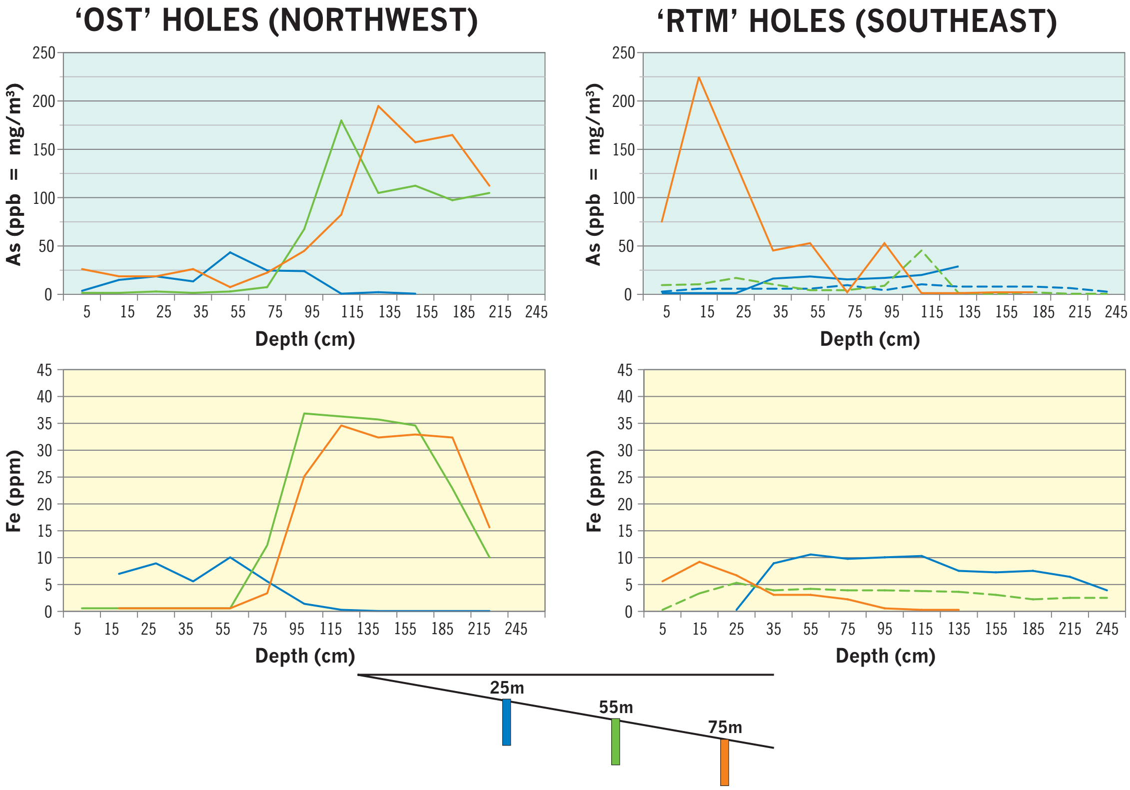

Figure 9 – Arsenic and iron in pore water of shallow sediments in the Amazon Fan area, as observed in holes OST-1,2,3 and RTM-1,2,3. The holes were drilled under sea water columns of 25 (blue lines), 55 (green lines) and 75 meters (red lines) of depth and were sampled every 10 centimeters of penetration to a depth of 2.5 meters. The marked increase of arsenic coincides with the horizon of reduction of iron oxides and hydroxides to iron sulfides, carbonates and phosphates

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