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ORIGINAL PAPER

Cl and Na Fluxes in an Andean Foreland Basin of the Peruvian Amazon: An Anthropogenic Impact Evidence

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Abstract The dissolved load of the Amazon River is generally considered to be lowly impacted by anthropogenic activities. In this work, based on the chemical and hydrological database of the Environmental Research Observatory—HYBAM (<http://www.ore-hybam.org>), we explore the importance of the Peruvian Foreland petroleum activity on the dissolved Na and Cl fluxes of the Amazon River. The main result of this study allows us suggesting that oil extraction activity, concentrated in the El Tigre River basin, a small

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foreland watershed in the Peruvian Amazon, influenced drastically the Na and Cl exportation of the Amazon River during the 2006–2007 period. During these years, the dissolved exportations of this basin represented almost 20 % of the annual dissolved Cl Amazon flux and almost 12 % of the annual dissolved Na Amazon flux for a mean annual discharge <1 % of the Amazon River discharge. Since the last decades, the anthropogenic activities are increasing over the whole Amazon basin, especially in Andean countries. In this context, our results demonstrate that extractive activity cannot be considered as negligible on the hydro-chemistry of the Amazonian Rivers especially for the weathering budget estimation based on river-dissolved loads. Moreover, Cl and Na can be used to trace the formation waters derived from oil extraction at a large spatial scale. The environmental impacts of contaminants associated with deep water released to the hydrosystem (polycyclic aromatics hydrocarbons, metallic trace elements, etc.) at local and regional scales are still underestimated and should be monitored to map their local and regional influence and to prevent their risks on human health.

Keywords Oil extraction · Anthropogenic impact · Amazon basin · Dissolved load · Deep water · NaCl · Peru

1 Introduction

Human activities are generally considered to have a negligible effect on the dissolved load of the Amazon River and on its main tributaries (ex: Stallard and Edmond 1983; Gaillardet et al. 1997; Mortatti and Probst 2003). Nevertheless, it can locally affect the environment and the river chemistry throughout the deforestation (ex: Uhl and Jordon 1984; Fritsch 1986; Williams and Melack 1997; Biggs et al. 2002; Markewitz et al. 2004; Callède et al. 2008), the mining exploitation (Salvarredy-Aranguren et al. 2008) or the gold extraction (Vinson et al. 1997; Roulet et al. 1998; Maurice-Bourgoin et al. 1999) for example. In particular, oil extraction can release high amounts of toxic elements into the environment like heavy metals and polycyclic aromatics hydrocarbons (PAHs) and lead to serious health problems in local and indigenous populations living in the upper part of the Amazon basin (mainly in Peru and Ecuador). These impacts are documented locally in Ecuador, and several epidemiological studies describe the links between oil extraction and health impacts on local populations (e.g., San Sebastián et al. 2001; Hurtig and San Sebastián 2002). The populations of this Amazonian region are in close contact with the aquatic environment and sometimes directly consume polluted waters. The prevalence of several benign conditions, dermal or upper aero-digestive routes, appears significantly higher in the exploited region than in the control areas (San Sebastián et al. 2001). Other observations concerning the increase in incidences of spontaneous abortions (San Sebastián et al. 2002) support the hypothesis of an alarming health impact in the regions heavily exposed to this pollution. Further still, these same authors published a series of articles in which they describe an overall increase in incidence of adult cancers and leukemia among children (San Sebastián et al. 2001; Hurtig and San Sebastián 2002; Hurtig and San Sebastián 2004). In Peru, even if since February 2009, the petroleum activity practices were improved due to a more responsible policy, the past practices had severe consequences on the environment and local population health (Orta Martinez et al. 2007). The social issue associated to the land colonization and the oil extraction interests is at the origin of various, sometimes virulent, social conflicts (Anaya 2009 and Romero 2009 in Finer and Orta-Martinez 2010) between indigenous communities (ex: Jivaros, ashuar, kichwas, Urainas) or local population and governmental and petroleum representatives (ex:

Finer et al. 2008; Finer et Orta-Martinez 2010). In any case, the impacts of oil extraction on large rivers hydrochemistry are poorly documented, even if they are still increasing these last decades especially in the Peruvian and Ecuadorian Amazon basins.

Throughout the production of around 62,368 BPD (barrels per day) of oil, oil extraction is one of the main important economic resources of Peru rising each year and represents one of the main exportation products of this country (INEI—<http://www.inei.gob.pe/>). The foreland basin of the El Tigre River is one of the main petroleum areas of Peru. The petroleum concessions of this basin were successively exploited by PeruPetro, Occidental Petroleum and, since 2000, by PlusPetrol. The total oil extracted from these concessions represents a major economic interest for the country as it represents 24 % of the total national petroleum production (INEI, MINEM in Gutierrez Choquevilca and Huboux 2006). During the oil exploitation process, petrol and deep water are extracted together and separated later inland. This deep water is old sedimentary water and is dated back to about 150.10⁶ years ago (Reyes and Ajamil 2005). Because of its long residence time and the presence of evaporite formation near the petroleum reservoirs, these waters are highly mineralized especially in Cl and Na elements. Smith (1989) studied the Cretaceous formation of the oriental basin of Ecuador and measured NaCl concentrations between 500 and 160,000 mg l⁻¹ (8.55 and 2,738 mmol l⁻¹). For reference, the average concentration of NaCl in seawater reaches ~30,000 mg l⁻¹ (~500 mmol l⁻¹), while natural riverine NaCl concentration is about 3 mg l⁻¹ (0.05 mmol l⁻¹) (Meybeck and Helmer 1989).

As highlighted by an environmental impact study carried out by the Peruvian Energy and Mines Ministry (Ministerio de energia y minas—Dirección General de asuntos ambientales 1998), the deep waters extracted during petroleum exploitation in the Northern Peruvian Amazon were directly released in the environment, mainly in rivers. To reduce the environmental impacts of oil activities and to regularize the industrial practices of the petroleum firms, a decree has been adopted in March 2006: the Environmental Protection Regulations for Hydrocarbon Activities DS No 015-2006-EM that prohibits the dumping of production waters into rivers, lakes and requires that saline deep water are re-injected more than 3,000 m depth. But in the El Tigre basin petroleum concessions, this norm has been applied only since early 2009 (Peruvian Ministry of Energy and Mining note NP. 349-09).

The NaCl fluxes exported annually by the Amazon River are mainly produced over the upper Solimões basin in Peru (Stallard and Edmond 1983; Gaillardet et al. 1997; Moquet et al. 2011), the main tributary of the Amazon River in terms of water discharge (Molinier et al. 1993). In this basin, the main part of this dissolved load is produced in the Andes by evaporites dissolution (Stallard and Edmond 1983) and, in a lower proportion, by hydrothermal sources associated with volcanic activity (Moquet et al. 2011). Nevertheless, few studies describe the origin of NaCl fluxes at the scale of the Andes and foreland-associated sub-basins (Moquet et al. 2011). The environmental impacts of the release of major elements and their implications on aquatic and human populations are still poorly known.

In this study, we explore the role of oil extraction activity as a significant source of dissolved NaCl in a foreland Amazon basin, El Tigre River basin (Peru), and we evaluate this riverine contribution relatively to the whole Amazonian production of NaCl.

2 Study Area

The El Tigre River basin covers 42,850 km², representing <1 % of the entire Amazon basin area (Fig. 1). It is located in Peru between latitudes 1°3'S and 4°2'S and longitudes 77°3'W and 74°1'W. Ranging between 65 and 674 m.a.s.l., the mean elevation is

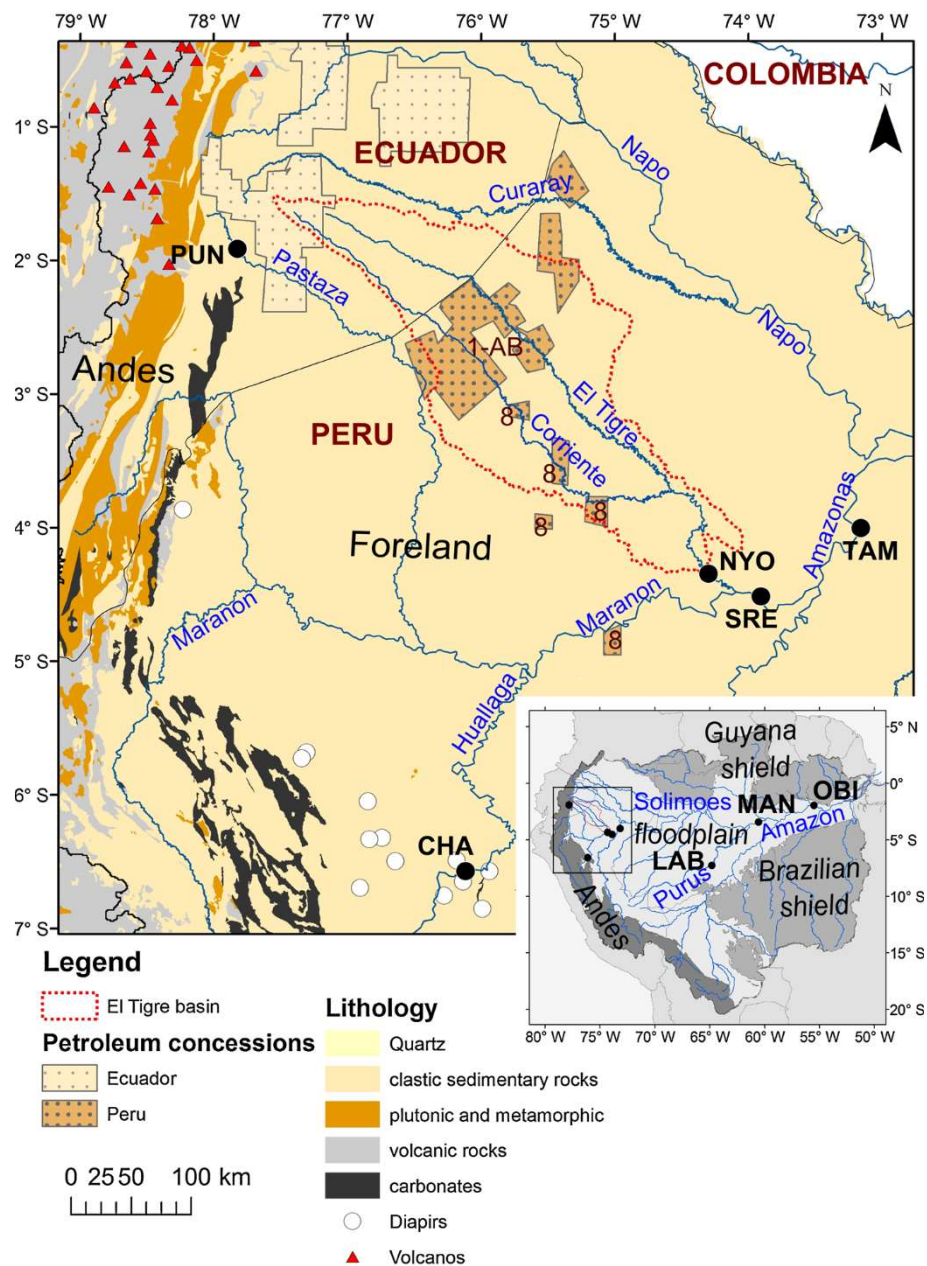


Fig. 1 Lithological map and drainage area of the El Tigre River at the NYO (Nueva York) gauging station. Complementary gauging stations used in this study are also located (CHA—Huallaga River, SRE—Marañon River, TAM—Amazonas River, LAB—Purus River, MAN—Solimões River, OBI—Amazon River). The location of oil concession area (San Sebastián and Hurtig 2004; PeruPetro website) is also reported. The concessions number 1-AB and number 8 in Peru were characterized by 17 and 38 extraction wells, respectively (Ministerio de Energía y Minas—Peru)

205 m.a.s.l. This river is a northern tributary of the Marañón River, upper Solimões tributary, located in the foreland area at the Andean foothill. The climate of this region is characterized by a total rainfall of $\sim 2,500$ mm year⁻¹ (extracted from 1970 to 1999 rainfall interpolated data; Espinoza et al. 2009) and an annual runoff value of $\sim 1,550$ mm year⁻¹ (www.ore-hybam.org). The annual discharge of this river reaches $2,100$ m³ s⁻¹ (over the 2006–2009 period), which corresponds to <1 % of the Amazon River annual discharge. The hydrological regime exhibits a low seasonality. During the 2006–2009 period, the higher daily discharge values, near $3,000$ m³ s⁻¹, were registered between January and June, and the lowest daily discharge values, around $1,250$ m³ s⁻¹, were registered between August and November. This seasonality reflects the South American Monsoon System that depends on the Intertropical Convergence Zone (ITCZ) north–south oscillation and on seasonal changes in the thermal contrast between the continent and adjacent Atlantic Ocean region. This area is entirely covered by the Amazon rainforest.

The upper part of the El Tigre basin is located in the Pastaza Megafan region (Bernal et al. 2010), while the lower part is in the Andean northern foreland, corresponding to the Cenozoic back-arc basins (Roddaz et al. 2006). The lithology is mainly composed of detrital sediments such as conglomerates, sand, clay, lutites and sandstone produced by the Andean Cordillera erosion during the end of the Miocene and the Cenozoic periods (INGEMMET 1999). There is no superficial evaporite and carbonate outcrop over the basin.

Since 1971, this basin is exploited for its hydrocarbon-bearing formation. The petroleum concessions of the El Tigre River basin (IAB and 8) are located in the El Tigre and Corriente river basins upstream their confluence with the Marañón River, in the Amazonian lowlands (Fig. 1). The main exploited petroleum formations are the Vivian and Chonta formations (Cretaceous) located between 2,500 and 4,000 m depth (Ministerio de Energía y Minas—Peru 1998).

3 Materials and Methods

In this study, we used the available data of the Environmental Research Observatory (ORE) HYBAM (Geodynamical, hydrological and biogeochemical control of erosion/ weathering and material transport in the Amazon basin) (<http://www.ore-hybam.org>). This international database offers daily river discharge on several gauging stations located in five countries of the Amazon basin. We extracted the available data from the Nueva York (NYO) gauging station located at the outlet of the El Tigre River for the period Oct. 03rd, 2006—May, 15th, 2009. Water levels were measured daily or twice daily using a conventional hydrological scale. Gauging measurements were realized four times a year using a 600 kHz Acoustic Doppler Current Profiler (ADCP). Daily discharge series were calculated from rating curves (discharge/water level relationship) using the HYDRACCESS software (Vauchel 2005; free download from the ORE-Hybam website).

At this same gauging station, monthly surface water samples were collected for dissolved major elements analysis (Cl⁻, SO₄²⁻, HCO₃⁻, Ca²⁺, Mg²⁺, K⁺, Na⁺ and Si) between April 11th, 2006 and October 11th, 2009 and some other samples were collected punctually during field work. Two previous samples have been analyzed before this period, August, 06th, 2003 and October, 19th, 2005. The sampling protocol and analytical methods did not change during the entire monitoring period. The surface water samples were filtered through a 0.45 μm porosity cellulose acetate membrane. Major element concentrations were determined at the GET laboratory (Toulouse, France). Cl⁻ and SO₄²⁻ concentrations were measured by Ionic Chromatography ([®]Dionex ICS 2000), while Na⁺, Ca²⁺, Mg²⁺,

K^+ and Si were analyzed by ICP-OES, inductively coupled plasma-atomic emission spectroscopy ([®]Horiba Jobin–Yvon Ultima2). Alkalinity was determined by acid titration. The error based on the certified reference material (PERADE20, ION 915 and SLRS 4) analysis is <5 %. Suspended load (>0.45 μm diameter) content, pH and conductivity of surface water have been measured on a 10-day frequency sampling.

The normalized inorganic charge balance ($\text{NICB} = (\text{TZ}^+ - \text{TZ}^-)/(\text{TZ}^+ + \text{TZ}^-)$ with $\text{TZ}^- = \text{Cl}^- + \text{SO}_4^{2-} + \text{HCO}_3^-$ and $\text{TZ}^+ = \text{Na}^+ + \text{Ca}^{2+} + \text{Mg}^{2+} + \text{K}^+$ in meq l^{-1}) is <15 %. Only the two samples of February, 2009 display an excess of negative charge of about 20 %. This excess of anionic charge could be linked to the dissociation of soil organic acids, producing H^+ ions and organic anions, as reported by numerous other authors for tropical catchments (see references in Moquet et al. 2011) (Table 1).

For comparison with natural surface waters located in the upper Amazon basin not impacted by human activities, from our knowledge, we analyzed hydrological data and major elements concentration series of three other gauging stations: Labrea (LAB) on the Purus River, Chazuta (CHA) on the Huallaga River and Puente la Union (PUN) on the Pastaza River (Fig. 1; Table 2); the composition of these rivers typically reflects atmospheric, halite and volcanic chlorides inputs, respectively (Moquet et al. 2011). In order to evaluate the importance of the anthropogenic inputs at the whole Amazon basin scale, we also present the hydrological and NaCl concentration data of the lower gauging station of San Regis (SRE) on the Marañón River, Tamshiyacu (TAM) on the Amazonas River (downstream the confluence of the Marañón and Ucayali rivers), Manacapuru (MAN) on the Solimões River (downstream the Amazonas river) and Óbidos (OBI) the last gauging station of the Amazon River before the estuary (Fig. 1; Table 2). The discharge and hydrochemical data of these rivers are determined following the same protocol than that applied for the El Tigre River at the NYO gauging station.

4 Results

4.1 Geochemical Characteristics of El Tigre River Surface Waters

The range of major cation and anion concentrations, conductivity and pH value for the El Tigre River waters are reported on Table 1. Based on the chemical composition and TDS (Total Dissolved Solids) concentration, the temporal record can be separated in two periods. The El Tigre River displays high mineralization during the February 2006–January 2009 period (conductivity = 53–425 $\mu\text{S cm}^{-1}$) and since February 2009, conductivity falls drastically (conductivity = 15–36 $\mu\text{S cm}^{-1}$) (Fig. 2).

During the first period, the chemical composition is mainly sodium chloride; Na dominates for about 65 % of the cationic charge and the Cl accounts for about 70 % of the anionic charge. Consequently, these two salts control the mineralization of the water during this period (Fig. 3A). We can note that only 2 samples in 2007 are calcium-bicarbonate type. The correlation between Cl and Na concentrations is significant ($R^2 = 0.94$; $p < 0.001$) (Fig. 3b). This is characteristic of halite dissolution process. From February 2009, Na ions account for about 37 % of the cationic charge, while chlorides account for only 14 % of the anionic charge.

The pH of the El Tigre River water samples shows a high variability between 4.0 and 7.7. The pH values are significantly correlated with Ca+Mg concentrations ($R^2 = 0.45$; $p < 0.001$) and also with conductivity ($R^2 = 0.44$; $p < 0.001$) (Fig. 3C). This suggests that higher pH values can be associated to carbonate dissolution. With the exception of one

Table 1 Chemical composition and total surface suspended solids concentration (TSS) of the El Tigre River at NYO station (TDS concentration: total dissolved solids = cations + anions + SiO₂ in mg l⁻¹, NICB: Normalized inorganic charge balance = (TZ⁺ - TZ⁻)/(TZ⁺ + TZ⁻) with TZ⁻ = Cl⁻ + SO₄²⁻ + HCO₃⁻ and TZ⁺ = Na⁺ + Ca²⁺ + Mg²⁺ + K⁺ in meq l⁻¹)

| Date | Conductivity ($\mu\text{S cm}^{-1}$) | pH laboratory | MES (mg l ⁻¹) | Cl ($\mu\text{mol l}^{-1}$) | SO ₄ | Na | Ca | Mg | K | SiO ₂ | HCO ₃ | TDS (mg l ⁻¹) | NICB (%) |
|------------|---|------------------|------------------------------|-------------------------------|-----------------|-------|-----|----|----|------------------|------------------|---------------------------|----------|
| 06/08/2003 | 149 | 6.5 | | 1,018 | 7 | 905 | 124 | 36 | 27 | 162 | 125 | 82 | 4 |
| 19/10/2005 | 378 | 5.8 | | 3,003 | 13 | 2,294 | 307 | 86 | 46 | 261 | 225 | 206 | -2 |
| 21/02/2006 | 227 | 5.8 | 24 | | | | | | | | | | |
| 21/03/2006 | 109 | 5.6 | 80 | | | | | | | | | | |
| 01/04/2006 | 113 | 5.5 | 55 | | | | | | | | | | |
| 11/04/2006 | 204 | 6.0 | 46 | 1,812 | 18 | 1,190 | 179 | 50 | 24 | 195 | | | |
| 21/04/2006 | | 5.8 | 46 | | | | | | | | | | |
| 09/05/2006 | 101 | 5.9 | 42 | 869 | 27 | 582 | 114 | 35 | 16 | 126 | | | |
| 11/05/2006 | 89 | 5.4 | 51 | 766 | 4 | 543 | 82 | 26 | 14 | 95 | | | |
| 21/05/2006 | 163 | 6.1 | 70 | | | | | | | | | | |
| 01/06/2006 | 237 | 6.2 | 72 | | | | | | | | | | |
| 11/06/2006 | 130 | 6.3 | 47 | 1,149 | 15 | 803 | 138 | 38 | 23 | 91 | | | |
| 21/06/2006 | 162 | 6.0 | 94 | | | | | | | | | | |
| 01/07/2006 | 123 | 5.9 | 103 | | | | | | | | | | |
| 11/07/2006 | 105 | 5.5 | 126 | 1,140 | 52 | 720 | 162 | 49 | 20 | 145 | | | |
| 21/07/2006 | 149 | 6.0 | 90 | | | | | | | | | | |
| 01/08/2006 | 243 | 6.2 | 75 | | | | | | | | | | |
| 11/08/2006 | 280 | 5.7 | 90 | 2,649 | 51 | 1,772 | 290 | 90 | 33 | 240 | | | |
| 21/08/2006 | 219 | 5.8 | 91 | | | | | | | | | | |
| 29/09/2006 | 305 | 6.2 | 48 | 3,068 | 14 | 1,914 | 253 | 76 | 33 | 235 | | | |
| 11/10/2006 | 241 | 6.5 | 70 | 1,847 | 98 | 1,598 | 318 | 99 | | 157 | 224 | | |

Table 1 continued

| Date | Conductivity ($\mu\text{S cm}^{-1}$) | pH laboratory | MES (mg l^{-1}) | Cl ($\mu\text{mol l}^{-1}$) | SO ₄ | Na | Ca | Mg | K | SiO ₂ | HCO ₃ | TDS (mg l^{-1}) | NICB (%) |
|------------|---|------------------|-------------------------------|----------------------------------|-----------------|-------|-----|-----|----|------------------|------------------|-------------------------------|----------|
| 21/10/2006 | 136 | 6.4 | 44 | | | | | | | | | | |
| 01/11/2006 | 227 | 6.7 | 88 | | | | | | | | | | |
| 11/11/2006 | 254 | 6.5 | 73 | 1,674 | 13 | 1,468 | 210 | 72 | | 159 | 244 | | |
| 21/11/2006 | 218 | 6.6 | 71 | | | | | | | | | | |
| 01/12/2006 | 213 | 6.6 | 66 | | | | | | | | | | |
| 11/12/2006 | 154 | 6.2 | 87 | 1,049 | 30 | 811 | 147 | 46 | | 78 | 153 | | |
| 21/12/2006 | 136 | 6.5 | 63 | | | | | | | | | | |
| 01/01/2007 | 118 | 5.8 | 76 | | | | | | | | | | |
| 11/01/2007 | 358 | 5.9 | 30 | 2,320 | 15 | 2,054 | 292 | 102 | | 275 | 407 | | |
| 21/01/2007 | 143 | 5.8 | 61 | | | | | | | | | | |
| 23/02/2007 | 370 | 7.0 | 33 | 180 | 143 | 273 | 906 | 121 | 32 | 142 | 2,702 | 240 | -15 |
| 01/03/2007 | 425 | 7.7 | 30 | | | | | | | | | | |
| 11/03/2007 | 248 | 7.5 | 87 | 1,953 | 60 | 1,645 | 280 | 96 | | 169 | 254 | | |
| 21/03/2007 | 166 | 7.2 | 69 | | | | | | | | | | |
| 01/04/2007 | 123 | 6.1 | 65 | | | | | | | | | | |
| 11/04/2007 | 152 | 5.9 | 120 | 1,076 | 33 | 901 | 155 | 49 | | 147 | 142 | | |
| 21/04/2007 | 121 | 5.9 | 81 | | | | | | | | | | |
| 01/05/2007 | 158 | 6.0 | 59 | | | | | | | | | | |
| 11/05/2007 | 129 | 5.9 | 82 | 862 | 28 | 740 | 130 | 39 | | 146 | 142 | | |
| 21/05/2007 | 90 | 6.6 | 73 | | | | | | | | | | |
| 01/06/2007 | 117 | 6.0 | 46 | | | | | | | | | | |
| 11/06/2007 | 136 | 6.2 | 74 | 852 | 12 | 736 | 115 | 36 | | 116 | 152 | | |
| 21/06/2007 | 79 | 6.8 | 104 | | | | | | | | | | |
| 01/07/2007 | 87 | 6.6 | 63 | | | | | | | | | | |
| 11/07/2007 | 111 | 5.7 | 106 | 716 | 11 | 616 | 106 | 36 | | 92 | 142 | | |

Table 1 continued

| Date | Conductivity ($\mu\text{S cm}^{-1}$) | pH laboratory | MES (mg l^{-1}) | Cl ($\mu\text{mol l}^{-1}$) | SO ₄ | Na | Ca | Mg | K | SiO ₂ | HCO ₃ | TDS (mg l^{-1}) | NICB (%) |
|------------|---|------------------|-------------------------------|-------------------------------|-----------------|-------|-------|-----|----|------------------|------------------|----------------------------|----------|
| 21/07/2007 | 156 | 6.5 | 81 | | | | | | | | | | |
| 01/08/2007 | 244 | 6.6 | 91 | | | | | | | | | | |
| 11/08/2007 | 256 | 6.0 | 73 | 1,727 | 155 | 1,645 | 253 | 71 | | 211 | 163 | | |
| 21/08/2007 | 179 | 6.5 | 36 | | | | | | | | | | |
| 24/08/2007 | | | 35 | 678 | 268 | 808 | 1,019 | 227 | 37 | 159 | 1,921 | 243 | 3 |
| 01/09/2007 | 304 | 6.5 | 72 | | | | | | | | | | |
| 11/09/2007 | | | 78 | 1,107 | 11 | 1,056 | 140 | 40 | 19 | 195 | 183 | 95 | 4 |
| 21/09/2007 | 231 | 6.6 | 103 | | | | | | | | | | |
| 01/10/2007 | 236 | 6.7 | 76 | | | | | | | | | | |
| 11/10/2007 | 256 | 6.8 | 65 | 1,672 | 13 | 1,622 | 215 | 58 | 34 | 241 | 234 | 138 | 7 |
| 21/10/2007 | 229 | 6.5 | 114 | | | | | | | | | | |
| 01/11/2007 | 178 | 6.5 | 75 | | | | | | | | | | |
| 11/11/2007 | | | 109 | 869 | 10 | 896 | 142 | 41 | 27 | 180 | 163 | 81 | 10 |
| 21/11/2007 | 139 | 6.2 | 54 | | | | | | | | | | |
| 01/12/2007 | 114 | 5.8 | 57 | | | | | | | | | | |
| 11/12/2007 | 136 | 6.1 | 60 | 840 | 12 | 841 | 137 | 42 | 26 | 229 | 173 | 82 | 8 |
| 21/12/2007 | 214 | 6.2 | 92 | | | | | | | | | | |
| 01/01/2008 | 140 | 6.8 | 63 | | | | | | | | | | |
| 11/01/2008 | 96 | 6.4 | 58 | 787 | 79 | 751 | 212 | 65 | 19 | 211 | 142 | 85 | 10 |
| 21/01/2008 | 73 | 6.3 | 81 | | | | | | | | | | |
| 01/02/2008 | 75 | 6.2 | 55 | | | | | | | | | | |
| 11/02/2008 | | | 35 | 978 | 10 | 964 | 164 | 51 | 25 | 297 | 275 | 101 | 5 |
| 21/02/2008 | 114 | 6.1 | 73 | | | | | | | | | | |
| 01/03/2008 | 74 | 6.1 | 65 | | | | | | | | | | |
| 11/03/2008 | | | 5 | 770 | 121 | 702 | 263 | 81 | 26 | 200 | 193 | 92 | 8 |

Table 1 continued

| Date | Conductivity ($\mu\text{S cm}^{-1}$) | pH laboratory | MES (mg l^{-1}) | Cl ($\mu\text{mol l}^{-1}$) | SO ₄ | Na | Ca | Mg | K | SiO ₂ | HCO ₃ | TDS (mg l^{-1}) | NICB (%) |
|------------|---|------------------|-------------------------------|-------------------------------|-----------------|-------|-----|----|----|------------------|------------------|----------------------------|----------|
| 21/03/2008 | 142 | 6.0 | 108 | | | | | | | | | | |
| 01/04/2008 | 83 | 6.2 | 42 | | | | | | | | | | |
| 11/04/2008 | | | 175 | 446 | 12 | 459 | 113 | 28 | 20 | 215 | 142 | 55 | 11 |
| 05/05/2008 | | | 25 | | | | | | | | | | |
| 11/05/2008 | 128 | 5.6 | 64 | 909 | 7 | 776 | 92 | 39 | 21 | 155 | 231 | 80 | -4 |
| 21/05/2008 | 83 | 5.5 | 93 | | | | | | | | | | |
| 01/06/2008 | 69 | 5.4 | 84 | | | | | | | | | | |
| 11/06/2008 | 99 | 5.5 | 84 | 684 | 5 | 568 | 79 | 32 | 18 | 156 | 201 | 64 | -5 |
| 21/06/2008 | 121 | 5.5 | 101 | | | | | | | | | | |
| 01/07/2008 | 94 | | 104 | | | | | | | | | | |
| 11/07/2008 | 86 | 5.1 | 104 | 547 | 5 | 482 | 65 | 26 | 17 | 156 | 216 | 57 | -6 |
| 21/07/2008 | 86 | 5.5 | 88 | | | | | | | | | | |
| 01/08/2008 | 63 | 5.4 | 104 | | | | | | | | | | |
| 11/08/2008 | 71 | 5.5 | 109 | 416 | 4 | 382 | 59 | 27 | 16 | 162 | 231 | 51 | -7 |
| 21/08/2008 | 61 | 5.6 | 118 | | | | | | | | | | |
| 01/09/2008 | 140 | 5.8 | 81 | | | | | | | | | | |
| 11/09/2008 | 195 | 5.8 | 90 | 1,411 | 7 | 1,182 | 118 | 56 | 25 | 190 | 268 | 113 | -4 |
| 21/09/2008 | 53 | 5.5 | 98 | | | | | | | | | | |
| 01/10/2008 | 60 | 5.4 | 116 | | | | | | | | | | |
| 11/10/2008 | 62 | 5.4 | 92 | 350 | 5 | 333 | 46 | 22 | 17 | 139 | 194 | 44 | -7 |
| 21/10/2008 | 84 | 5.5 | 237 | | | | | | | | | | |
| 01/11/2008 | 70 | 5.9 | 62 | | | | | | | | | | |
| 11/11/2008 | 67 | 5.6 | 81 | 379 | 4 | 351 | 46 | 24 | 16 | 135 | 201 | 45 | -7 |

Table 1 continued

| Date | Conductivity ($\mu\text{S cm}^{-1}$) | pH laboratory | MES (mg l^{-1}) | Cl ($\mu\text{mol l}^{-1}$) | SO ₄ | Na | Ca | Mg | K | SiO ₂ | HCO ₃ | TDS (mg l^{-1}) | NICB (%) |
|------------|---|------------------|-------------------------------|-------------------------------|-----------------|-----|----|----|----|------------------|------------------|----------------------------|----------|
| 21/11/2008 | 83 | 5.7 | 66 | | | | | | | | | | |
| 01/12/2008 | 85 | 5.6 | 80 | | | | | | | | | | |
| 11/12/2008 | 91 | 5.6 | 72 | 557 | 5 | 494 | 68 | 35 | 18 | 169 | 253 | 61 | -7 |
| 21/12/2008 | 162 | 5.8 | 62 | | | | | | | | | | |
| 01/01/2009 | 134 | 6.1 | 43 | | | | | | | | | | |
| 11/01/2009 | 126 | 5.9 | 94 | 773 | 6 | 706 | 93 | 52 | 23 | 213 | 335 | 83 | -5 |
| 21/01/2009 | 27 | 5.4 | 119 | | | | | | | | | | |
| 01/02/2009 | 23 | 5.2 | 52 | | | | | | | | | | |
| 11/02/2009 | 20 | 5.3 | 72 | 31 | 3 | 46 | 23 | 14 | 13 | 132 | 164 | 22 | -20 |
| 19/02/2009 | 18 | 5.2 | 71 | 26 | 4 | 40 | 25 | 15 | 13 | 126 | 169 | 22 | -21 |
| 21/02/2009 | 19 | 5.2 | 83 | | | | | | | | | | |
| 01/03/2009 | 18 | 6.3 | 72 | | | | | | | | | | |
| 11/03/2009 | 19 | 5.7 | 59 | | | | | | | | | | |
| 21/03/2009 | 18 | 5.8 | 52 | | | | | | | | | | |
| 01/04/2009 | 19 | 5.7 | 53 | | | | | | | | | | |
| 11/04/2009 | 25 | 5.7 | 78 | | | | | | | | | | |
| 21/04/2009 | 20 | 5.8 | 86 | | | | | | | | | | |
| 01/05/2009 | 16 | 5.8 | 49 | | | | | | | | | | |
| 11/05/2009 | 15 | 5.7 | 40 | | | | | | | | | | |
| 16/05/2009 | 17 | 6.0 | 48 | | | | | | | | | | |
| 21/05/2009 | 18 | 5.2 | 66 | | | | | | | | | | |
| 01/06/2009 | 16 | 4.0 | 73 | | | | | | | | | | |
| 11/06/2009 | 17 | 4.9 | 66 | 14 | 4 | 33 | 19 | | 10 | 148 | | | |

Table 1 continued

| Date | Conductivity ($\mu\text{S cm}^{-1}$) | pH laboratory | MES (mg l^{-1}) | Cl ($\mu\text{mol l}^{-1}$) | SO ₄ | Na | Ca | Mg | K | SiO ₂ | HCO ₃ | TDS (mg l^{-1}) | NICB (%) |
|------------|---|------------------|-------------------------------|-------------------------------|-----------------|----|----|----|----|------------------|------------------|----------------------------|----------|
| 13/06/2009 | 17 | 6.0 | 81 | | | | | | | | | | |
| 21/06/2009 | 17 | 4.9 | 71 | | | | | | | | | | |
| 01/07/2009 | 18 | 4.9 | 85 | | | | | | | | | | |
| 11/07/2009 | 15 | 4.9 | 80 | 11 | 3 | 28 | 16 | | 10 | 134 | | | |
| 21/07/2009 | 16 | 4.9 | 94 | | | | | | | | | | |
| 01/08/2009 | 20 | 4.9 | 83 | | | | | | | | | | |
| 11/08/2009 | 24 | 5.3 | 121 | 22 | 5 | 66 | 29 | 9 | 12 | 215 | | | |
| 21/08/2009 | 19 | 5.1 | 107 | | | | | | | | | | |
| 01/09/2009 | 19 | 5.1 | 98 | | | | | | | | | | |
| 11/09/2009 | 21 | 5.2 | 100 | 22 | 4 | 54 | 26 | 6 | 13 | 175 | | | |
| 21/09/2009 | 36 | 5.4 | 72 | | | | | | | | | | |
| 01/10/2009 | 26 | 5.3 | 74 | | | | | | | | | | |
| 11/10/2009 | 22 | 5.3 | 84 | 19 | 5 | 57 | 26 | 7 | 14 | 184 | | | |
| 21/10/2009 | 25 | 5.4 | 69 | | | | | | | | | | |

Table 2 Gauging station characteristics and Na and Cl concentrations of the studied rivers

| River | Gauging station | Symbol | Latitude | Longitude | Surface area (km ²) | Period hydrological data | Annual discharge available (m ³ s ⁻¹) | Period Chemical data | Cl avg (mmol l ⁻¹) | Na avg (min-max) (mmol l ⁻¹) |
|--|-----------------|--------|----------|-----------|---------------------------------|--------------------------|--|----------------------|--------------------------------|--|
| <i>Studied river (per period)</i> | | | | | | | | | | |
| El Tigre | Nueva York | NYO | -4.1620 | -74.3823 | 42850 | 10/2006–01/2009 | 2,100 | 4/2006–1/2009 | 0.982 (0.165–3.067) | 0.866 (0.273–2.054) |
| | | | | | | | | 2/2009–10/2009 | 0.02 (0.010–0.030) | 0.046 (0.027–0.065) |
| <i>Reference Rivers (CHA: evaporites, PUN: Volcanic inputs, LAB: atmospheric inputs)</i> | | | | | | | | | | |
| Huallaga | Chazuta | CHA | -6.5704 | -76.1193 | 68,741 | 01/2005–12/2010 | 3,006 | 4/2005–11/2010 | 0.975 (0.327–4.397) | 1.078 (0.396–4.217) |
| Pastaza | Puente la Union | PUN | -1.9141 | -77.8258 | 12,687 | 01/2002–05/2005 | 704 | 4/2000–5/2005 | 0.074 (0.024–0.183) | 0.308 (0.137–0.562) |
| Purus | Labrea | LAB | -7.2522 | -64.8111 | 226,552 | 01/2004–12/2010 | 5,555 | 9/2004–8/2011 | 0.016 (0.002–0.081) | 0.078 (0.028–0.292) |
| <i>Downstream stations (per period)</i> | | | | | | | | | | |
| Maranon | San Regis | SRE | -4.5162 | -73.9081 | 357,255 | 01/2003–12/2008 | 16,333 | 5/2003–1/2009 | 0.663 (0.165–3.404) | 0.622 (0.224–2.083) |
| | | | | | | 01/2009–12/2011 | 16,733 | 2/2009–3/2011 | 0.184 (0.091–0.381) | 0.285 (0.163–0.613) |
| Amazonas | Tamshiyacu | TAM | -4.0031 | -73.1617 | 722,089 | 01/2002–12/2008 | 28,873 | 5/2002–1/2009 | 0.396 (0.070–0.790) | 0.467 (0.130–0.951) |
| | | | | | | 01/2009–12/2011 | 28,110 | 2/2009–3/2011 | 0.251 (0.124–0.67) | 0.369 (0.209–0.956) |
| Solimões | Manacapuru | MAN | -3.3083 | -60.6094 | 2,203,303 | 01/2003–12/2008 | 102,938 | 4/2003–10/2008 | 0.096 (0.044–0.167) | 0.139 (0.081–0.278) |
| | | | | | | 01/2009–12/2009 | 116,161 | 4/2009–12/2011 | 0.09 (0.048–0.188) | 0.147 (0.056–0.3) |

Table 2 continued

| River | Gauging station | Symbol | Latitude | Longitude | Surface area (km ²) | Period hydrological data | Annual discharge available (m ³ s ⁻¹) | Period Chemical data | Cl avg (min-max) (mmol l ⁻¹) | Na avg (min-max) (mmol l ⁻¹) |
|--------|-----------------|--------|----------|-----------|---------------------------------|--------------------------|--|----------------------|--|--|
| Amazon | Obidos | OBI | -1.9225 | -55.6753 | 4,669,201 | 01/2003–12/2007 | 171,000 | 4/2003–9/2007 | 0.062 (0.026–0.180) | 0.095 (0.049–0.249) |
| | | | | | | 01/2009–12/2012 | 180,233 | 4/2009–8/2012 | 0.052 (0.006–0.104) | 0.093 (0.050–0.179) |

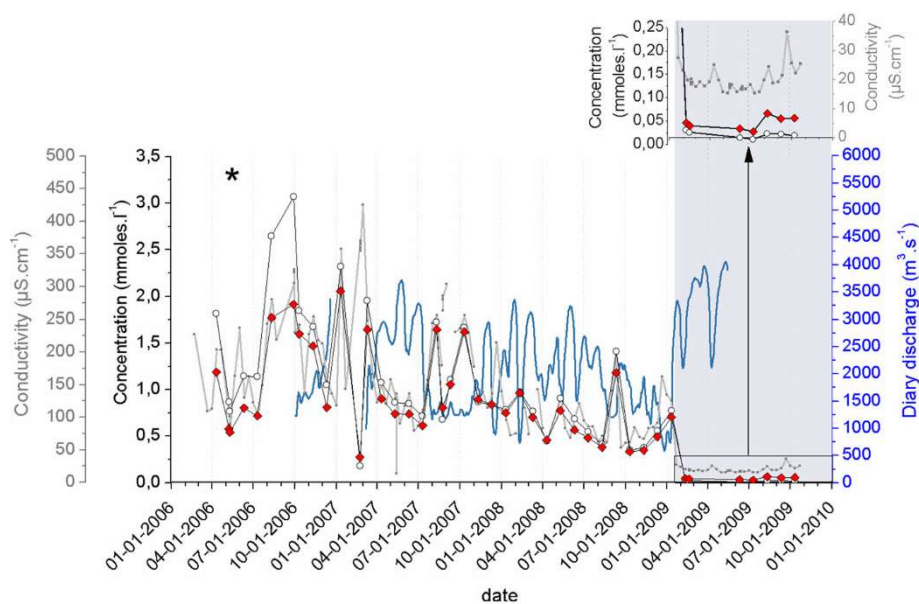


Fig. 2 Temporal variation of the daily discharge, Na concentration (red points), Cl concentration (white points) and conductivity (small gray points) of the El Tigre River during the January 2006—October 2009 period at the NYO station. The asterisk corresponds to the publication of the Supreme decree 048-2006 EM in Peru, which regulates the deep waters treatment in March 2006. The gray area corresponds to the practical application period of this norm in the study area starting from February 2009

extreme value with a pH 4, the lowest pH values are generally around 5 and correspond to the lowest dissolved load concentrations. These lowest pH values are recorded after February 2009 and are typical of natural Amazonian lowland rivers (Stallard and Edmond 1983).

During the first period, Ca, Mg and K are significantly correlated with Na and Cl ($R^2 > 0.75$; $p < 0.001$; $N = 36$ with the exclusion of 2 outliers waters sampled on February 23rd 2007 and August 28th 2007) (ex: Fig. 3D, E). This observation suggests an homogenous origin of these elements, which could be attributed to the association of halite with carbonates (dolomite, calcite) or other evaporites (gypsum for example) that are not outcropping over the study area. As Cl and Na and other cations (Ca, Mg and K) concentrations are correlated; since February 2009, they decrease drastically with the conductivity (Table 1). SO_4 and Ca are significantly correlated ($R^2 = 0.72$; $p < 0.001$) (Fig. 3F). This suggests that gypsum (CaSO_4) dissolution can control part of these elements production and that the sources of both elements are common or dependent. The value of 1:20 for SO_4 :Ca ratio shows that gypsum dissolution can control only a small percentage of Ca fluxes. Ca and Mg concentration are well correlated ($R^2 = 0.84$; $p < 0.001$). The Ca:Mg ratio is 3:1. As dolomite Ca:Mg ratio is 1:1, this 3:1 ratio value might reflect the association of dolomite and calcite in Ca and Mg production (Fig. 3G).

For both periods, the fluxes of Ca, Mg, K, SO_4 and HCO_3 in the El Tigre River account for <10 % of their fluxes downstream, at the SRE station on the Marañon River (Moquet et al. 2011). As the behavior of Na and Cl best exemplify the influence of oil extraction on large river fluxes, we consider in the following only these two elements.

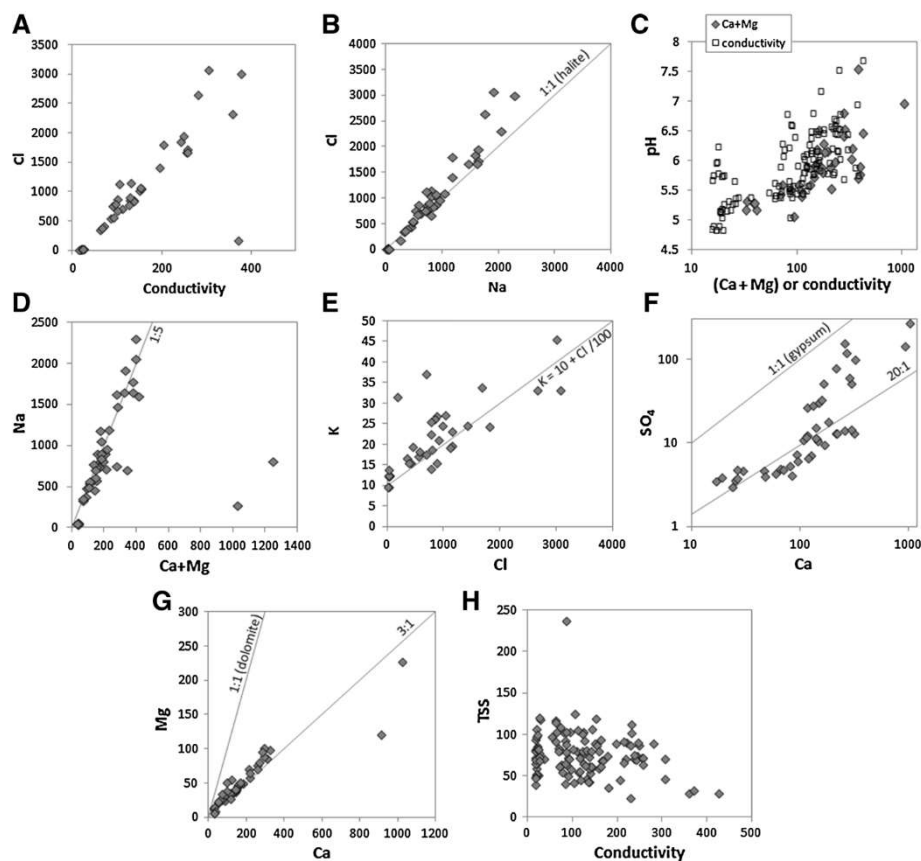


Fig. 3 Relationships between physicochemical parameters, major elements concentration and total suspended solids (TSS) concentration monitored in the El Tigre River at the NYO gauging station. The Cl concentration versus conductivity (A), Cl versus Na concentration (B); pH versus (Ca + Mg) concentration and conductivity (C); Mg versus Ca concentration (D); Na versus Ca + Mg concentration (E); K versus Cl concentration (F); SO_4 versus Ca concentration (G) and TSS concentration versus conductivity (H). The concentration of major elements is given in $\mu\text{mol l}^{-1}$, the conductivity in $\mu\text{S cm}^{-1}$ and the TSS concentration in mg l^{-1}

Taking into account the entire study period, we also note that the total suspended solids (TSS) concentrations in the El Tigre surface waters vary between 5 and 237 mg l^{-1} and do not follow the same trends than the total dissolved solids load (Table 1; Fig. 3H).

4.2 Seasonal Variability of Na and Cl Concentrations

The seasonal variations of both Na and Cl concentrations at the NYO station are reported on the Fig. 2. There is no relationship between the water discharge and the Na or Cl concentrations. The highest concentrations of Na and Cl ions are mainly observed in September, during the low water stage, but there is no clear seasonality in the major elements distribution (Figs. 2, 4). Na and Cl concentrations fluctuate over a large range during the 2006–2007 hydrological year (Cl 0.17–3 mmol l^{-1} ; Na 0.27–2 mmol l^{-1}),

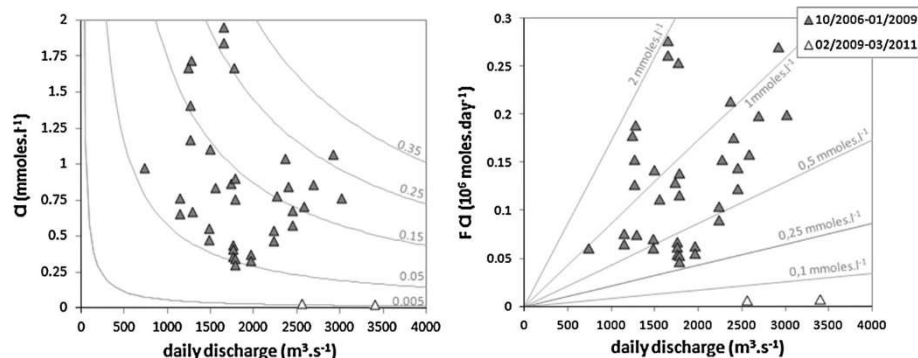


Fig. 4 Relationship between Cl concentrations and Cl fluxes with daily discharge of the sampling days at NYO gauging station along the El Tigre River. Lines of constant flux (in 10^6 mol day $^{-1}$) and lines of constant concentration are added for reference

while they show more stable high values between April 2007 and January 2009 (Cl 0.3–1.7 mmol l $^{-1}$; Na 0.33–1.6 mmol l $^{-1}$). On the other hand, Na and Cl concentrations are well correlated for both periods ($R^2 = 0.90$; $p < 0.001$ and $R^2 = 0.98$; $p < 0.001$, respectively). From October 2006 to January 2009, Na and Cl concentrations show large and erratic variations. No correlation is observed between Cl concentration or daily Cl flux with the water discharge of the sampling day (Fig. 4). After February 2009, the concentrations of Na and Cl decrease drastically (Cl ~ 0.02 mmol l $^{-1}$; Na ~ 0.04 mmol l $^{-1}$).

4.3 Na and Cl Concentrations in the El Tigre River and Comparison with Natural Inputs

According to the evolution of the major elements concentrations, two periods are distinguished.

During the first period, from April 2006 to January 2009, with values ranging between 0.17 and 3.07 mmol l $^{-1}$, the Cl and Na concentrations of the El Tigre River are similar to the concentrations measured in rivers influenced by evaporite inputs (Huallaga River at CHA station). The Cl and Na concentrations are correlated and follow a 1:1 ratio characteristic from water influenced by halite (Fig. 5). Concentration inputs of these two major elements are one order of magnitude higher than in volcanic areas (Upper Pastaza River at PUN) and two orders of magnitude higher than in surface waters of sedimentary areas where chlorides mainly come from atmospheric inputs and Na originates from atmospheric and Na-silicate weathering inputs (Purus River at LAB) (Fig. 5)

During the second period, from February 2009 to October 2009, the Na and Cl values are commensurate to the Purus River values (Fig. 5).

We note that Bouchez et al. (2012) observed an increase in the Na flux carried by suspended load, especially associated to the fine fraction, on the Marañon River between the outlet of the Andes (Borja station) and the confluence with the Ucayali River (TAM station). The suspended solid samples analysed by Bouchez et al. (2012) were taken in April 2008; hence, during the high dissolved NaCl flux that we measured in the El Tigre R. We can suggest that adsorption of Na from the El Tigre River on the suspended sediment transported by the Marañon can occur. Even if Na is not known to sorb on fine particles, at

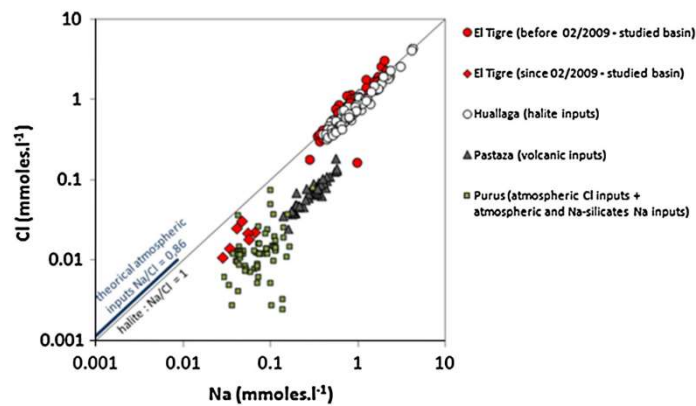


Fig. 5 Relationship between Cl and Na concentration in the El Tigre River (NYO station), Huallaga R. (CHA station), Pastaza R. (PUN station) and Purus R. (LAB station) for the 2006–2009 period. Theoretical curves for halite dissolution ($\text{Na}/\text{Cl} = 1$) and atmospheric inputs ($\text{Na}/\text{Cl} = 0.86$ and $\text{Cl}_{\text{atm}} < 0.01 \text{ mmol l}^{-1}$; Moquet et al. 2011) are also plotted

very high Na concentrations, such process might start to be significant. In the present study, we do not explore potential exchange between solid and dissolve phase of major cations.

5 Discussion

5.1 Identification of NaCl Sources and Quantification of the Anthropogenic Inputs

The Cl and Na concentrations at the NYO station are very high compared with other Andean and foreland basin stations (Moquet et al. 2011 and Fig. 5). As the outcropping lithology of the El Tigre River basin is essentially composed by Holocene detrital sedimentary rocks (INGEMMET 1999) and is comparable to that of the Purus River basin, similar Na and Cl concentrations in these two basins were expected (Cl Purus $0.002\text{--}0.081 \text{ mmol l}^{-1}$; Na Purus $0.028\text{--}0.292 \text{ mmol l}^{-1}$). As the atmospheric inputs for Cl are estimated to be lower than 0.010 mol l^{-1} in this area (Moquet et al. 2011), only atmospheric inputs cannot explain the Cl concentrations measured in this basin. It can be observed that the 1:1 ratio between Na and Cl is characteristic of the halite contribution. We also note that these concentrations are of the same order of magnitude that those of the Huallaga River basin characterized by the occurrence of numerous evaporite domes (Benavides 1968; Stallard and Edmond 1983; Moquet et al. 2011) (Fig. 5). The much higher Na and Cl concentrations measured in the El Tigre River, the absence of discharge–concentration/flux relationship and the absence of evaporites outcrops in the basin suggest a predominant effect of anthropogenic impact due to the oil extraction releasing significant amounts of saline deep water into the drainage basin. We can also highlight that during the second period, the concentrations of Cl are lower than 0.05 mmol l^{-1} with a Na/Cl ratio closer to natural inputs in a sedimentary basin like the Purus River (Fig. 5). These low values of Na and Cl concentration in the El Tigre River between February 2009 and October 2009 suggest that the release of deep water into the river has been stopped.

In order to insure our hypothesis, we compare the measured annual NaCl flux of the El Tigre River based on monthly sampling at the NYO station with the NaCl flux released by

production waters extracted by the oil extraction over the same period and the same basin. The monthly river water sampling frequency has initially been established to monitor the natural temporal variability of the dissolved load in large river basins. For the sampled days, compared to the liquid discharge, the variability of the dissolved Cl and Na concentrations and fluxes is erratic (Fig. 4). There is no chemostatic behavior, nor hydrologic control on Na and Cl elements. Consequently, on the first gauging stations affected by the El Tigre inputs (NYO, SRE and TAM stations), the monthly fluxes of Na and Cl calculated from a unique monthly sample and the mean monthly discharge are not presented here due to the high variability of instantaneous Cl and Na concentrations, which are not controlled by hydrodynamics. Far downstream, at the stations MAN and OBI, the Cl concentrations for both periods are more stable (Fig. 6). This can be due to the buffering effect associated with the dispersion (molecular and turbulent) effect of the river between upstream and downstream stations. For annual fluxes determination, we considered that the monthly sampling carried out on the El Tigre River is representative of the mean dissolved load variation along the year. As there is a high variation of Na and Cl concentrations and considering that there is not direct relationship between the instantaneous concentrations and the corresponding discharge on the NYO station (Fig. 4), we estimated the annual Na and Cl fluxes based on the concentration average and the annual discharge average. At the outlet of the El Tigre River, the average NaCl concentration is 0.94 mmol l^{-1} during the period April 2006–January 2009 for an average water discharge of $2 \cdot 100 \text{ m}^3 \text{ s}^{-1}$. The annual average NaCl flux is consequently $62 \text{ M mol year}^{-1}$ calculated as following:

$$F = Q_{\text{year}} \times C_{\text{average}}$$

with F , C_{average} and Q_{year} the NaCl flux, the mean annual NaCl concentration and the average discharge for the October 2006–January 2009 period on the El Tigre River gauging station NYO (Table 3). This yearly NaCl flux can then be compared with the estimated inputs from oil extraction in the same area and more specifically with the production waters discharges of the drainage area. In 1998, the 1A and 8 concessions wells produced, respectively, 686,512 and 17,341 deep water equivalent barrels per day, respectively (water volume after water–petroleum separation process) (Ministerio de Energía y Minas 1998). This corresponds to $1,263$ and 32 l s^{-1} of water, respectively ($1 \text{ barrel} = 159 \text{ l}$). Around 80 % of the concessions are included in the El Tigre R. basin. If we consider that this activity did not modify their practices since 1998, that the deep water release is proportional to the area of the concession and that the production waters are completely released into the river, the deep water discharge from petroleum activity reaches $1 \text{ m}^3 \text{ s}^{-1}$ [$\sim (1,263 + 32) \times 0.8/1,000$].

As the oil reservoirs exploited in Peru corresponded to the same geologic formations as those exploited in Ecuador and dated from Cretaceous period, we can assume, based on Smith' study (1989), that these waters can reach concentrations between 8.5 and $2,738 \text{ mmol l}^{-1}$ ($500\text{--}160,000 \text{ mg l}^{-1}$) of NaCl. By comparison, the NaCl concentration of seawater is 517 mmol l^{-1} , the Amazon water at Óbidos station is around 0.07 mmol l^{-1} , the Amazonas River downstream the Marañon and Ucayali confluence is around 0.38 mmol l^{-1} and the Huallaga River at Chazuta station (influenced by evaporite inputs) is around 0.89 mmol l^{-1} .

Assuming that the whole volume extracted from the wells is then released to the river, the NaCl flux from the oil extraction activity would range between 0.28 and 89 Mmol year^{-1} from the following equation:

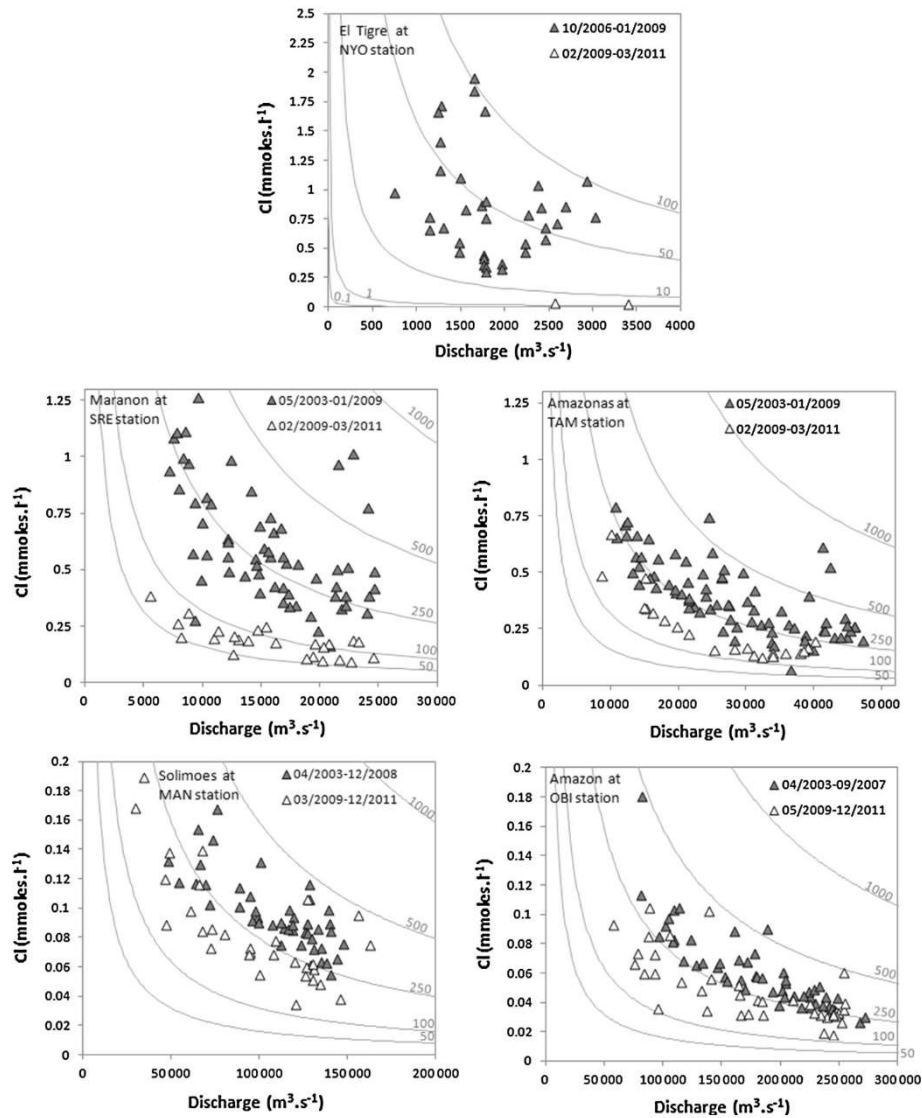


Fig. 6 Relationship between Cl concentration and daily discharge in the El Tigre River (NYO station), Marañon R. (SRE station), Amazonas R. (TAM station), Solimões R. (MAN station) and Amazon R. (OBI station) for the May 2003–January 2009 (Gray triangles) and February 2009–December 2011 (White triangles) periods. Lines of constant annual flux (in $10^6 \text{ mol year}^{-1}$) are added for reference

$$F_{\text{deepwater}} = Q_{\text{deepwater}} \times C_{\text{deepwater}}$$

With $F_{\text{deepwater}}$, $Q_{\text{deepwater}}$ and $C_{\text{deepwater}}$ the annual deep water NaCl flux, discharge and NaCl concentration, respectively.

A mean deep water NaCl concentration of $1,373 \text{ mmol l}^{-1}$ (which correspond to the mean of the two extreme values reported by Smith 1989), induce a NaCl input of $45 \text{ Mmol year}^{-1}$. Thus, the scenario which considers that all the deep water is released in the

Table 3 Estimation of NaCl inputs from production waters, El Tigre River fluxes and Amazon River fluxes during the study period

| | Period | Discharge $\text{m}^3 \text{ s}^{-1}$ | Concentration | | | Flux | | | % Flux Amazon | | | | | |
|---|---------------------|--|----------------------------|-----------------------|---------|------------------------------------|------------------------------------|----------|---------------|-----|------|-----------------------|--|--|
| | | | Cl mmol l^{-1} | Na l^{-1} | NaCl | Cl $10^6 \text{ mol year}^{-1}$ | Na $10^6 \text{ mol year}^{-1}$ | NaCl | Cl | Na | NaCl | % Mean Amazon flux | | |
| Petroleum activity in no 1 A–B and no 8 concessions | 1998* | 1,036 | | | 8.55** | | | 0.28 | | | | | | |
| | Min | | | | | | | | | | | | | |
| | Max | | | | 2,738** | | | 89 | | | | | | |
| El Tigre River at NYO | Mean | | | 1,711 | | | 56 | | | | | | | |
| | 4/2006–1/ 2009 | 2,100 | | 0.982 | 0.866 | 0.936 | 65 | 57 | 62 | 20 | 12 | 18 | | |
| | 2/2009–10/ 2009 | | | 0.02 | 0.046 | 0.030 | 1 | 3 | 2 | 0.4 | 0.7 | 0.6 | | |
| Amazon River at OBI | 01/2003–12/ 2007 | 171,000 | | 0.062 | 0.095 | 0.075 | 318 ± 58 | 491 ± 85 | 404 ± 72 | 100 | 100 | 100 | | |
| | 01/2009–12/ 2012 | 180,233 | | 0.052 | 0.093 | 0.068 | 241 ± 50 | 459 ± 78 | 350 ± 64 | 100 | 100 | 100 | | |
| | 4/2009–8/ 2012 | | | | | | | | | | | | | |

* From Ministerio de Energia y Minas (1998)

** From Smith (1989) (see text for details)

river is consistent with the NaCl flux of $62 \text{ Mmol year}^{-1}$ recorded in the basin outlet until January 2009, demonstrating that natural inputs during this period are negligible (Tab. 3).

5.2 NaCl Fluxes from El Tigre River to Downstream Stations

Comparing the Cl concentration values measured on the El Tigre River with those recorded downstream on the Marañon and Amazonas Rivers (Fig. 6), it appears that the high Cl signal of the contaminated basin is also recorded 50 and 200 km downstream (respectively for SRE and TAM stations). The shift in Na and Cl concentrations observed in Feb. 2009 for the El Tigre River is also measured in the largest rivers very far downstream in the Solimões River at the MAN station and the Amazon River at the OBI station. This is evidenced by the drastic decrease in the Cl concentrations after February 2009 at these stations (Fig. 6) (student test— $p < 0.01$ for SRE and TAM and $p < 0.1$ for OBI). These observations show the consistency of the Na and Cl variation from the contaminated source to the outlet of this basin.

5.3 Contribution of the El Tigre River to the Amazon River Dissolved Load

From 2006 until January 2009, the oil extraction of the El Tigre basin had a significant impact on the total dissolved load production of the whole Amazon basin. Major element concentration values of the Amazon River at the last gauging station of Óbidos are available for the periods April 2003–Sept. 2007 and April 2009–Jan. 2012. For each period, the mean annual Amazon River fluxes at Óbidos station are calculated as following: we first estimated the monthly flux based on monthly instantaneous concentration and monthly discharge. We then calculated the average of inter-annual monthly fluxes. We finally added the twelve monthly flux averages to evaluate the annual flux. To calculate the error associated to the Óbidos station fluxes, we first calculated the standard deviation of the inter-annual monthly fluxes and then we summed these values to estimate the yearly flux error (Table 3).

At Óbidos station, the mean annual Cl flux reaches 318 ± 58 and 241 ± 50.10^6 mol year⁻¹, respectively for the first and the second period. The estimated annual Na flux is relatively stable with 491 ± 85 and 459 ± 78.10^6 mol year⁻¹ for the first and the second period, respectively. Consequently, during the period 2006–2007, the El Tigre River contribution to the Amazon River at the last gauging station of Óbidos reaches 20 and 12 % of the Cl and Na production, respectively (Table 3).

At the Óbidos station, the Na flux is more stable during the two periods, unlike the Cl flux. This observation can be explained by the difference of natural sources inputs of these two elements over the basin. The main natural processes of Cl inputs in the hydrosystem are atmospheric precipitation and evaporite dissolution (Gaillardet et al. 1997; Moquet et al. 2011), while the natural sources of Na also include the weathering products of silicates dominating the whole basin lithology. Therefore, the relative contribution of anthropogenic inputs appears more significant in the final Cl budget. For Na inputs, the relative contribution of anthropogenic sources is lower than for the Cl inputs and can be hidden by the natural background noise of Na concentration variability during the first period.

The Na and Cl release to the rivers can disturb the ecosystems (Cañedo-Argüelles et al. 2013), but the suite of highly toxic contaminants (PAHs, heavy metals, metalloids) potentially associated to oil extraction can especially affect the local and regional

environment and the riparian population health (Orta Martinez et al. 2007). Unfortunately, these releases are actually unknown and need to be monitored in order to prevent further contamination and to control bad practices.

By comparison, in the foreland part of the Napo River in Ecuador, known for its long history of oil extraction from the 1960s, no high Cl and Na concentration levels on the monitored gauging stations were measured between 2000 and 2008. It seems that the Cl production in this area is mainly attributed to natural hydrothermal activity (Moquet et al. 2011). The environmental policy was more active in Ecuador than in Peru (Finer et al. 2010), the oil extraction activity was more controlled by the authorities and all deep water was re-injected in specific deep wells.

6 Conclusion

This study allows us to show for the first time that oil extraction, and more specifically the direct release of deep waters into a small drainage area, acts as a significant source of dissolved Na and Cl flux of the Amazon River. From mid-2006 to early 2009, the oil extraction in the El Tigre R. basin contributed significantly to the total Na and Cl exportation of the Amazon River. During the 2006–2007 period, this activity produced the equivalent of ~20 % of the dissolved Cl and ~12 % of the dissolved Na Amazon flux at the Óbidos gauging station, for a drainage area that represents <1 % of the Amazon basin and for a mean annual discharge <1 % of the Amazon River discharge. This result highlights that the effect of anthropogenic activity on dissolved load production also has to be considered in the Amazon River dissolved load studies, even at a large scale. This implies that anthropogenic inputs cannot be considered as negligible to estimate the weathering budget based on hydrochemistry of Amazonian rivers. This result also highlights the importance of long-term monitoring for the identification and the control of contamination indexes at large scale but also at local scale. These indexes have to be linked to contaminants, like heavy metals and PAHs that can reflect a potential impact of human activities in the Amazonian environment and lead to local population health risks and vulnerabilities. If the actual activity and the heritage of historical oil extraction practices seem to be an important source of contamination in Amazonian environments (ex: Orta-Martinez et al. 2007; Quarles 2009 in Finer and Orta-Martinez 2010), their direct and indirect impacts on the ecosystem and on local population health are actually unknown (Orta-Martinez et al. 2007; Finer et al. 2013). The actual challenges are to: (1) better quantify the contamination fluxes in the natural compartments (waters–rainfall, surface and groundwaters, soils and biosphere), and study their biogeochemical cycles, (2) evaluate the impacts of the mixture of toxic molecules emitted by these activities on the ecosystems and the associated risks for human health (Orta Martinez et al. 2007), (3) study the impact on socioeconomic development of the oil-rich areas, by placing this development in a wider context of the impact of this activity on the local development of the concerned areas, (4) identify the vulnerability and social disposition involved in dealing with the differing levels of action available (at the national, regional, community and family levels) and (5) develop concrete technical and organizational solutions to respond to the challenges ahead. Taking into account the rapid expansion of oil extraction in the Peruvian Amazon, environmental, sanitary and social issues would increase without any efficient program of remediation and prevention of the contamination. The development of chemical water monitoring sites on local and on the Amazon basin scale would allow for a better survey of

these practices and would help authorities to define a political, ecological and sanitary strategy to be performed for environmental preservation and to prevent health risks.

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