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THE SEDIMENTOLOGY, ICHNOLOGY AND HYDROGEOCHEMISTRY OF THE LATE MIOCENE, MARGINAL MARINE, UPPER PEBAS AND NAUTA FORMATIONS, AMAZONIAN FORELAND BASIN, PERU

by

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The thesis consists of a summary and the following papers referred to in the text by their Roman numerals (**I–IV**):

I Rebata-H., L.A., Räsänen, M.E., Gingras, M.K., Vieira Jr., V., Barberi, M., Irion, G. (2006b) Sedimentology and ichnology of tide-influenced Late Miocene successions in western Amazonia: The gradational transition between the Pebas and Nauta formations. In: Hoorn, C. & Vonhof, H. (Eds) New contributions on Neogene Geography and Depositional Environments in Amazonia. *Journal of South American Earth Sciences* 21 (1-2), 96-119.

II Rebata-H., L.A., Gingras, M.K., Räsänen, M.E., Barberi, M. (2006a) Tidal-channel deposits on a delta plain from the Upper Miocene Nauta Formation, Marañón Foreland Sub-basin, Peru. *Sedimentology* 53, 971-1013.

III Hovikoski, J., Gingras, M., Räsänen, M., Rebata-H., L.A., Guerrero, J., Ranzi, A., Melo, J., Romero, L., Nuñez del Prado, H., Jaimes, F., Lopez, S. (2007) The nature of Miocene Amazonian epicontinental embayment: High-frequency shifts of the low-gradient coastline. *Geological Society of America Bulletin* 119, 1506-1520.

IV Rebata-H., L.A., Korkka-Niemi, K., Heikkinen, P-M., Räsänen, M.E. (2009) Hydrogeochemical characterisation of the Miocene Pebas and Nauta formations in Peruvian Amazonia. (*Boletín de la Sociedad Geológica del Perú 103, 125-151*).

ABSTRACT

This thesis includes detailed sedimentological and ichnological studies on two geological units: the Pebas Formation, with a special focus in its informal upper member, and the Nauta Formation. Both formations were deposited during the Miocene in Northeastern Peruvian Amazonia, in the Amazon retroarc foreland basin. The Pebas and Nauta successions mainly consist of non-consolidated, clastic sedimentary deposits arranged into sand- to mud-dominated heterolithic successions, which can be upward-coarsening to upward-fining. Sediments in both the Pebas and Nauta successions range from mud to fine- to medium-grained sand. The main facies observed were 1) mud-dominated horizontal heterolithic couplets; 2) rooted brownish mud; 3) lenticular, mud-draped, cross-stratified sand; 4) mud- to sand-dominated, inclined heterolithic stratification; 5) sand-dominated horizontal heterolithic couplets; and 6) mud-draped, trough cross-stratified sand. Locally, tidal rhythmites were documented. The facies are interpreted as: 1) muddy, shallow, subaqueous flats/shoals; 2) palaeosols; 3) secondary tidal channels or run-off creeks; 4) tidally influenced point bars; 5) shoreface deposits; and 6) subtidal compound dunes. *Thalassinoides*-dominated *Glossifungites* ichnofacies, low-diversity expressions of the *Skolithos* ichnofacies and depauperate suites consisting of elements common to the *Cruziana* ichnofacies strongly indicate brackish-water conditions. However, continental trace fossil assemblages, with possible elements common to the *Scoyenia* ichnofacies, have also been identified. In addition to the palaeoenvironmental study, a local hydrogeochemical characterisation of the Pebas and Nauta formations was also conducted. The geochemistry of the groundwaters reflects the characteristics and the soil geochemistry of the geological formations studied. The Pebas formation has low hardness, acid to neutral waters, whereas the upper Pebas has high hardness, acid to neutral waters. In both units, the arsenic content is locally high. The Nauta formation has low hardness acid groundwaters. A regional review of the Pebas and Nauta formations placed the local observations into a continental perspective and suggests that the whole Pebas-Nauta system was a probably shallow (some tens of metres at maximum), brackish- to freshwater, tidally-influenced epicontinental embayment with a probable semi-diurnal to mixed tidal regime and a microtidal range, surrounded by continental environments such as forest floors, lagoons, rivers and their flood plains, and lakes.

Keywords: *Amazonia, tidal, sedimentology, ichnology, hydrogeochemistry, marine incursion, groundwater*

CONTENTS

1. INTRODUCTION

The aim of the present doctoral dissertation is to provide a detailed sedimentological and ichnological description and genetic interpretation of two Miocene geological units – the upper Pebas and Nauta formations – important to the ongoing debate regarding the Neogene history of Amazonia. Some of the current sedimentological interpretations, which do not take the ichnological or the more detailed sedimentological evidence into consideration, regard the Nauta system as fluvial (see e.g. Martínez-V. et al., 1999; Sánchez-F. et al., 1999) and the overall Pebas system, mainly based on palynological, palaeontological and/or isotope data, as freshwater dominated (see e.g. Hoorn, 1994; Wesselingh et al., 2002; Vonhof et al., 2003; Wesselingh, 2006). In contrast, the sedimentological and ichnological data together, and to a minor extent also the hydrogeochemical data, presented in this thesis support previous studies on the Miocene history of Amazonia that regard the system as a complex shallow, tidally-influenced, brackish-water-dominated environment with adjacent floodplains, lakes and forest floors (Räsänen et al., 1995; Hovikoski, 2001; Gingras et al., 2002a, b; Hovikoski et al., 2005, 2007; Rebata-H. et al., 2006a, b).

In addition, the work provides a brief description of the quality of the groundwater in these two formations, information that will have increased value in future applied environmental studies in Peruvian Amazonia.

This research was carried out as part of the Amazon Research Team of the University of Turku, whose one long-term aim has been the understanding of the geological history of the area leading to the current edaphic, weathering, floristic, faunistic up to socio-economic patterns in Amazonia (e.g. see Salo et al., 1986; Räsänen et al., 1987; Linna et al., 1998; Ruokolainen & Tuomisto, 1998; Räsänen et al., 1998; Salovaara, 2005). The present study was conducted as part of the Graduate School on Environmental Geology of the University of Turku and the Finnish Biodiversity Research Programme (FIBRE). Fieldwork in Peruvian Amazonia was carried out in co-operation with the Geological Survey of Peru (INGEMMET).

An explanation of some of the basic concepts utilised in this thesis, together with some terminology updates to the four published papers are provided at the end of this chapter (Section 1.3).

1.1. Geological background

Detailed geological studies that include both sedimentology and ichnology, the study of biogenic sedimentary structures, are relatively uncommon, and have only recently been undertaken in Amazonian geological research (Hovikoski, 2001; Gingras et al., 2002a,b; Hovikoski et al., 2005, 2007ab; Rebata-H. et al., 2006a, b). The joint application of both sedimentology and ichnology has opened up a path for the refinement of the geological history of Miocene Amazonia, by restricting the depositional settings to more specific palaeo-depositional environments. The combination of physical sedimentary structures and biogenic evidence pointing to specific physicochemical water conditions (salinity, oxygen content, etc.) allows a detailed discrimination of the depositional environment, e.g. a tidally-influenced palaeo-depositional environment for the present study.

The oldest and most extensively outcropping Miocene geological units in Western Amazonia correspond to the Pebas (in northern Peru and Colombia), Curaray (Ecuador), Solimões (in Brazil) and Madre de Dios (in southern Peru) formations. At outcrops in northern Peruvian Amazonia where this work was carried out, the Pebas Formation is conformably overlain by the Nauta Formation. The transition between these two formations is so distinctive in its lack of fossil content that it is worthy of a separate description as the informal upper member of the Pebas Formation (see Rebata-H. et al., 2006b; Table 1).

All Miocene geological formations outcropping in northern Peruvian Amazonia comprise poorly to non-consolidated, siliciclastic deposits (i.e. composed of sand, silt and clay, and their admixtures, locally with some calcareous content –mostly marly layers to limestone nodular layers). Most palaeoenvironmental reconstructions agree that these Miocene geological units were deposited in shallow water systems. However, researchers differ in their interpretation of the actual depositional setting, which has been proposed as: 1) shallow, brackish-water epicontinental embayments with associated continental sub-environments (Räsänen et al., 1995; Hovikoski, 2001; Gingras et al., 2002a,b; Hovikoski et al., 2005; Rebata-H. et al., 2006a, b); 2) a shallow, inland saline lake (Whatley et al., 1998); 3) a long-lived lake complex (hence a freshwater system), although with occasional marine incursions reaching the complex (Wesselingh et al., 2002; Vonhof et al., 1998; 2003; Wesselingh, 2006); and 4) a shallow but large freshwater wetland, including lake and swamp complexes, and also with intermittent connections to the sea(s) (see Hoorn & Vonhof, 2006 and references therein).

There is a great need for further sedimentological, ichnological and hydrogeochemical research in Amazonia, and their integration. This is especially because of the sparse nature of currently available data, which is mostly due to the limited accessibility and patchy nature of outcropping geological units. Recently, the difficulty in dating the Amazonian sedimentary units, and the current poor chronostratigraphic framework, has been pointed out as a drawback in the understanding of the Neogene history of Amazonia, especially during the Miocene (cf. Hoorn & Vonhof, 2006).

1.2. Purpose of this synopsis

As this doctoral thesis comprises four independently written scientific articles (I–IV), this synopsis provides the scientific background to the research and a coherent summary to guide the reader.

Article **I** includes the sedimentological and ichnological details of the transition between the Pebas and Nauta formations: the upper Pebas Formation. Although lacking the fossiliferous content of the Pebas Formation *proper*, the upper Pebas Formation is treated as the informal uppermost member of the Pebas Formation. The upper Pebas Formation is interpreted as part of a shallow, marginal marine system where the tidal influence was important, probably with the paralic depositional setting of an epicontinental embayment.

Article **II** contains the first detailed sedimentological and ichnological description of the stratotype area of the Nauta Formation, providing a novel interpretation of its origin. The sediments are interpreted as estuarine in character, although the deposits are positioned on an abandoned delta plain. The depositional setting is ascribed to a tidally dominated channel complex, and associated coastal plain environments are denoted by the preservation of palaeosoils.

Article **III** provides a regional sedimentological and ichnological overview, including localities from the Pebas and Nauta formations in northern Peru, the Madre de Dios and Ipururo formations in southern Peru, the Solimões Formation in Brazil and the Quendeque Formation in Bolivia. This paper puts the two previous articles (I–II) into a larger palaeogeographical perspective and highlights the depositional complexities.

Article **IV** characterises the groundwater quality in the two formations studied. These results consist of the geochemical characteristics of the groundwater samples extracted from aquifers located within the Pebas Formation *proper* (i.e. its fossiliferous members), the upper Pebas Formation (i.e. the non-fossiliferous uppermost member of this formation) and the Nauta Formation, and the resulting water types qualifying the aquifers, differentiated by their host formations.

1.3. Explanation of basic concepts and updates to the four published papers

Facies *vs.* Facies Associations

Although in both Articles **I** and **II** the basic sedimentary rock units such as "*rooted brownish mud*" and "*pervasively bioturbated inclined heterolithic stratification*" were termed as *facies associations*, in this synopsis they are now simply referred to as *facies*. This is to better apply current geological terminology and to separate the term **facies**, a more descriptive term identifying distinct rock units with similar characteristics, from the more interpretive **facies associations**, better defined as a group of facies that are genetically related (i.e. typically found together in the geological record) and assigned to a specific depositional setting (e.g. tidal-fluvial estuarine complex facies association, prograding shoreface complex facies association; floodplain facies association).

Brackish-water *vs.* fully marine trace-fossil suites

Brackish-water trace fossil suites are characterised by simple and stunted trace fossil forms that exhibit low diversity, locally high intensity and/or may be monospecific, with impoverished marine assemblages locally common (see e.g. Gingras et al. 2012 and references therein). All these features attest to the stressed physico-chemical conditions inherent in coastal-margin settings, where not only variations and/or a reduction in salinity are important, but also variations in the oxygen requirement related, for instance, to sudden subaerial exposure, an increase in predators, and variations in depositional energy, sedimentation rates, water turbidity, substrate consistency and temperature (Gingras et al. 2011). Thus, brackish-water trace fossil suites encompass the work of trophic generalists and/or opportunistic burrowing organisms that are able to adapt to highly stressful physico-chemical conditions (Gingras et al. 2012).In contrast, fully marine trace fossil suites typically comprise trophic specialist trace fossil forms that develop specific behaviours to survive euryhaline conditions in unstressed environments (e.g. in resource-poor settings prone to very slow, continuous deposition, specialists may develop "farming" techniques and/or highly elaborated deposit-feeding behaviours that allow for the efficient harvesting/exploitation of the limited resources; see e.g. Gingras et al. 2011).

Ichnofacies in the study area

By definition, an ichnofacies is the representation in the geological record of a trace fossil assemblage. All trace fossil suites documented from the Pebas and Nauta Formations during this study can be grossly divided into those supporting brackish-water conditions and those representing freshwater systems. The brackish-water suites commonly include *Ophiomorpha*, *Planolites*, *Laminites*, *Thalassinoides*, *Skolithos* and *Chondrites*. Less common *Arenicolites*, *Teichichnus*, *Palaeophycus*, *Cylindrichnus*, *Phycosiphon*, *Trichichnus* and *Helminthopsis* are also noted. In addition, *Psilonichnus*, *Lockeia*, *Gyrolithes, Rhizocorallium* and escape traces are only recorded within the post-Pebas successions (Hovikoski et al., 2007). The freshwater trace fossil suites within the Pebas Formation appear restricted to the top of the parasequences, commonly below lignitic facies, with rhizoliths and freshwater molluscs also noted. In contrast, freshwater suites within post-Pebas successions are characterised by low-diversity, monospecific assemblages of irregular or meniscus bearing burrows. Other burrows within these suites include *Taenidium*, *Planolites*, *Skolithos*, *Macaronichnus*, *Undichna* and *Diplocraterion*, which are again better preserved at the top of the parasequences. Rhizoliths and traces of insect larvae are also common (Hovikoski et al., 2007). All these ichnogenera can, in turn, be grossly re-grouped into four main ichnofacies: the *Glossifungites*, *Cruziana*, *Skolithos* and *Scoyenia* ichnofacies, with the latter encompassing the continental settings.

The ***Glossifungites*** **ichnofacies** represents a substrate-controlled trace fossil assemblage commonly associated with clastic semilithified or firm substrates. This ichnofacies typically includes dewatered muddy sediments due to subaerial exposure, or burial and subsequent exhumation. It is characterised by robust, sharp-walled simple domichnia and demarcates a discontinuity/omission surface that reflects a pause

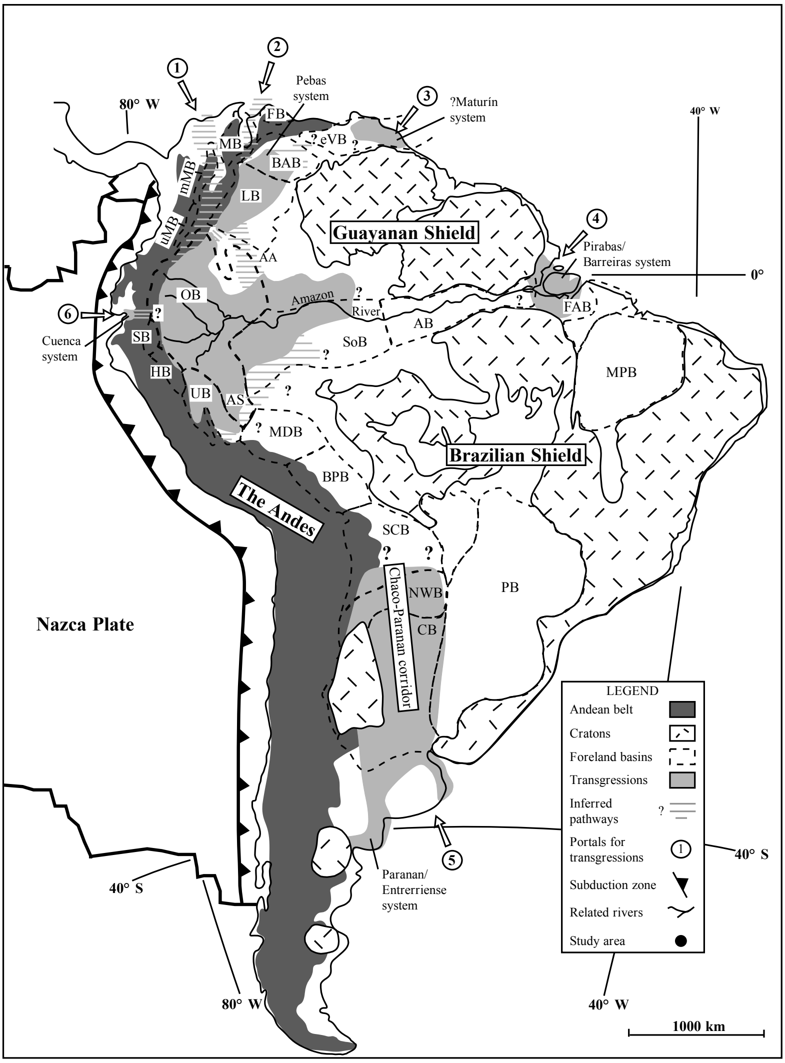


Figure 1. Map of South America showing its tectono-sedimentary elements (Andes, foreland basins/sub-basins and shields), Miocene portals (1–6) and the extent of marine incursions during the Miocene (cf. Rebata-H. et al., 2006a and references therein). eVB, Eastern Venezuela Basin; FB, Falcon Basin; MB, Maracaibo Basin; LB, Llanos Basin; mMB, Middle Magdalena Valley Basin; uMB, Upper Magdalena Basin; AA, Apaporis Area; OB, Oriente Basin; SB, Santiago Basin; HB, Huallaga Basin; UB, Ucayali Basin; AS, Acre Sub-basin; SoB, Solimões Basin; AB, Amazonas Basin; FAB, Foz do Amazonas Basin; MPB, Maranhao (Paranaiba) Basin; MDB, Madre de Dios Basin; BPB, Beni Plain Basin; SCB, Santa Cruz Basin; NWB, Northwest Basin; CB, Chaco Basin; PB, Paraná Basin. Note that the extension of transgressions formed different systems adjacent to the portals: the Pebas, Maturín, Pirabas/Barreiras, Paranan/Entrerriense and Cuenca systems.

in sedimentation and associated erosion (MacEachern et al., 1992). In the study area, the Pebas Formation deposits consist of sharp-based, upward-fining or coarsening parasequences that exhibit a lower contact characterised by a *Thalassinoides*-dominated *Glossifungites* ichnofacies, with this surface possibly reflecting a transgressive surface of erosion (Hovikoski et al., 2007).The ***Cruziana*** **ichnofacies** represents low energy, circalittoral marine substrates deposited between a daily wavebase and storm wavebase that typically have a good preservation potential and may result in high ichnodiversity (Bromley, 1996).The Pebas and Nauta successions, however, range from moderate to low, rarely high diversity, and as such are considered to represent low-diversity, proximal expressions of this ichnofacies. The ***Skolithos*** **ichnofacies** typically encompasses high energy, shallow marine shifting substrates subject to abrupt erosion and or deposition. It is commonly dominated by low-diversity and low-density vertical ichna (Bromley, 1996). In the study area, however, some of the elements of these successions are locally highly diverse and highly densely distributed, supporting the interpretation that some of the elements of this ichnofacies represent a comparatively more distal setting. The ***Scoyenia*** **ichnofacies** consists of firmground associations in nonmarine substrates connected with shallow lacustrine and fluviatile settings that are subject to subaerial exposure (Bromley, 1996). In the study area, these successions are closely associated with palaeosols.

2. STUDY AREA, MATERIALS AND METHODS

2.1. Geological history of South America

The latest phase of the geological history of present South America started after its separation from Africa c. 112–105 Ma (cf. Lundberg et al., 1998). This history is very much connected with plate tectonic mechanisms such as the subduction of the oceanic Nazca Plate below the continental South American Plate, which caused the birth of the Andes as a continental magmatic arc and its continuing development to the current high mountain chain (for a comprehensive summary of the geological evolution of South America, see Lundberg et al., 1998 and references therein). These and other major tectono-sedimentary elements of South America (cf. Jacques, 2003; see also Díaz de Gamero, 1996) are depicted in Figure 1. As a result of the dynamic uplift of the Andes, consisting of alternating loading and unloading cycles (cf. Gil, 2001; Hermoza et al., 2005; Roddaz et al., 2005) a (retro-arc) foreland basin was formed between the Andes to the west and the cratonic shields fringing the eastern margin of the South American continent (Fig. 1). The foreland basin is subdivided in several sub-basins today (see Fig. 1). These sub-basins are under the control of different subsidence rates according to their position along the Andes, mainly in relation to the differential subduction angle and rate of the Nazca Plate along the western coast of South America (see Jordan et al., 1983). The main foreland sub-basins included in the study area, commonly grouped as the Amazon foreland basin, are the Oriente (also called Marañón), Ucayali, Acre, Solimões, Madre de Dios and Beni basins (see Fig. 1 for the location and extension of these basins). Most of the study area for papers I, II and IV is located on the Oriente Basin and has been interpreted as the forebulge of the slowly eastward migrating Andean orogeny (see Roddaz et al., 2005). During the Miocene, there were several periods of overall subsidence in the Amazon foreland basin, which, together with the then existing low elevation openings in the Andean mountain chain, gave room for the entry of seawater through different portals into South America. The main Miocene portals (1–6) and the extension of their adjacent documented marine-incursion systems, including the Pebasian system pertaining to the present study area, are illustrated in Figure 1, based on previous malacological, palynological, sedimentological, isotopic and general stratigraphic studies (cf. Nuttall, 1990; Hoorn, 1994; Hoorn et al., 1995; Räsänen et al., 1995; Vonhof et al., 1998; Steinmann et al., 1999; Wesselingh et al., 2002).

2.2. Sedimentological and stratigraphical framework for Neogene Amazonia

As several authors have pointed out (see Hoorn,1994; Hoorn & Vonhof, 2006; and references therein for a comprehensive summary), the scientific study of the sedimentary units deposited in Amazonia during the Neogene, encompassing approximately the last 23 million years, already began in the 19th century. The main focus was first centred on the fossils found within the sediments. Starting in the late 1980s, the palynological and sedimentological work carried out by Carina Hoorn for her doctoral dissertation (see Hoorn, 1994) marked a breakthrough that provided a stratigraphic framework for northwestern Amazonia during the Neogene. Other sedimentological, palaeontological and stratigraphical studies followed (Räsänen et al., 1995; 1998; Vonhof et al., 1998; Hovikoski, 2001; Gingras et al., 2002a, b; Wesselingh et al., 2002; Hovikoski et al., 2005, 2007ab).

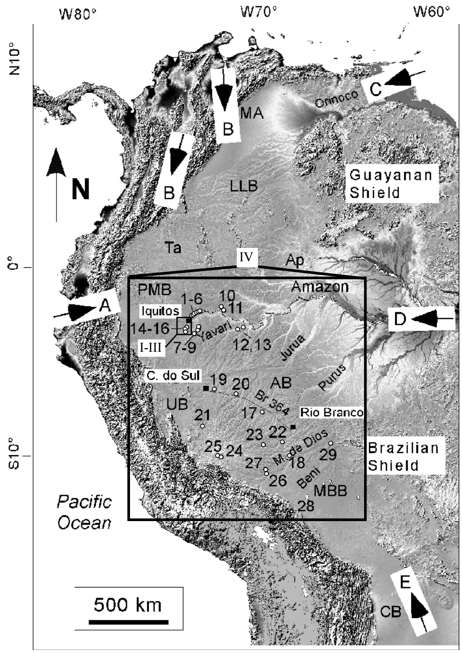


Figure 2. Map modified from Hovikoski et al. (2007) showing the study locations by paper (Roman numerals refer to papers I to IV. See Fig. 3 for detailed location of localities studied for papers I, II & IV. The numbers indicate the study locations for paper III), the main geological units of Western Amazonia, possible sea connections during the Miocene (A–D), and probable hydrographical connection (E) (cf. Hovikoski et al., 2007 and references therein). AB – Acre Sub-basin, Ap – Apaporis sand unit, CB – Chaco Sub-basin, MA – Mérida Andes, MBB – Madre de Dios-Beni Sub-basin, LLB – Llanos Sub-basin, PMB – Pastaza-Marañón Sub-basin, Ta – La Tagua, UB – Ucayali Sub-basin. Courtesy NASA/JPL-Caltech.

The most extensively described outcropping lithostratigraphical units in northwestern Amazonia are the Solimões Formation (described in Brazil; see Maia et al. 1977) and its Peruvian equivalent, the Pebas Formation (see Hoorn, 1994; Gingras et al., 2002b; Wesselingh et al., 2002; Vonhof et al., 2003; for up to date synopsis). Recently, the Nauta Formation has been distinguished as a conformable unit above the Pebas Formation on the outcrop belt in Peru (e.g. Räsänen et al., 1998; Sánchez-F. et al., 1999, Rebata-H. et al., 2006a). Recent tectono-sedimentary studies have concluded that during the Late Miocene, the present study area belonged to the forebulge depozone of the Northwestern Amazonian foreland basin system and was characterised by a transition from marine through estuarine to fluvial facies (Gil-R., 2001; Hermoza et al., 2005; Roddaz et al., 2005).

2.2.1. The fossiliferous members of the late Early to early Late Miocene Pebas Formation

The Pebas sediments consist of fossil-rich, light grey to bluish grey mud (mainly smectitic clay) to variegated sand or sandy mud, organised in 3- to 10-m-thick parasequences capped by less than 1-m-thick lignite layers and/or mollusc shell lags, locally forming coquinas (Hoorn, 1993; Räsänen et al., 1998; Hovikoski, 2001; Gingras et al., 2002b; field observations of the author). The parasequences are characterised by laterally continuous, horizontal to sub-horizontal layers arranged in upward-fining or coarsening successions and locally by inclined heterolithic stratification (IHS). The horizontal to sub-horizontal successions have been interpreted as marginal marine shorefaces, whereas the IHS successions have been interpreted as point bar deposits (Räsänen et al., 1998; Hovikoski, 2001; Gingras et al., 2002b).

The Pebas Formation is strongly characterised by its fossil molluscan fauna, although fossils of ostracods, foraminifers, barnacles, turtles, fishes, mammals, shark teeth, plants and palynomorphs have also been reported (Hoorn, 1994; Räsänen et al., 1998; Whatley et al., 1998). The main signature of the fossil molluscs in the Pebas parasequences indicates freshwater conditions during deposition, but brackish water conditions have been reported toward the upper members of the formation (Hoorn, 1993; Räsänen et al., 1998; Vonhof et al., 1998, 2003; Wesselingh et al., 2002). Based on the malacological and isotopic studies of Wesselingh et al. (2002) and Vonhof et al. (1998, 2003), respectively, the Pebas Formation has been interpreted to represent a long-lived lake complex, with intermittent connections with the sea(s).

2.2.2. The transition between the Pebas and Nauta formations: the non-fossiliferous, upper Pebas Formation

This, the uppermost informal member of the Pebas Formation, although maintaining the characteristic lithological features and stratigraphic relations of the Pebas Formation, lacks the typical Pebas fossil content. However, a decreasing upward trend in the quantity of mollusc fossils preserved and/or mollusc-barren gaps of up to 15 m are reportedly also visible in the fossil-rich lower members of this formation (Hoorn, 1994; Vonhof et al., 2003).

The upper member of the Pebas Formation was originally reported as the "Unidad Canalizada de Porvenir" by Räsänen et al. (1998). Locally, the upper Pebas Formation has also been interpreted as part of the Ipururo Formation (Martínez-V. et al., 1999; Sánchez-F. et al., 1999).

The upper member of the Pebas Formation consists of 3- to 7-m-thick, upward fining to coarsening parasequences, commonly capped by layers of lignite or organic-rich mud (especially smectitic clay with a typical Pebas signature) (Räsänen et al., 1998). The parasequences are also characterised by IHS and laterally continuous sand-mud couplets, interpreted as a channelized unit with point bars and shoreface successions, respectively (Räsänen et al., 1998). Fossil vertebrae of *Purussaurus* (Räsänen et al., 1998; Martínez-V. et al., 1999) have been reported from these successions.

2.2.3. The Late Miocene Nauta Formation

The Nauta Formation was first described as the "Unit C" of Räsänen et al. (1998). A detailed sedimentological study of well-preserved exposures of this formation was carried out by Rebata-H. (1997) near Nauta, a small town along the Marañón River in Loreto, Peru. Later on, Martínez-V. et al. (1999) formally named the unit described by Rebata-H. (1997) and Räsänen et al. (1998) as the Nauta Formation based on the concept of composite stratotypes (cf. Salvador, 1994).

The successions of the Nauta Formation were originally interpreted as tidally-influenced, estuarine deposits composed of channelized successions, mostly dominated by pointbar deposits, assigned by stratigraphic position to the Late Miocene (Rebata-H., 1997; Räsänen et al., 1998). However, recent studies by other authors interpreted the Nauta Formation as fluvial and assigned it to the Pliocene-Pleistocene (e.g. Cerrón-Z. et al., 1999; Martínez-V. et al., 1999; Sánchez-F. et al., 1999; see also Roddaz et al., 2005).

2.3. Hydrogeochemical characterisation of the Pebas and Nauta formations, and the transition between them

2.3.1. Previous water quality studies in Northern Peruvian Amazonia

Previous studies on water quality (groundwater, river water and/or potable water for household consumption or the elaboration of food/drinks) in Northern Peruvian Amazonia are very local and rare, commonly strictly confined to studies carried out by biologists

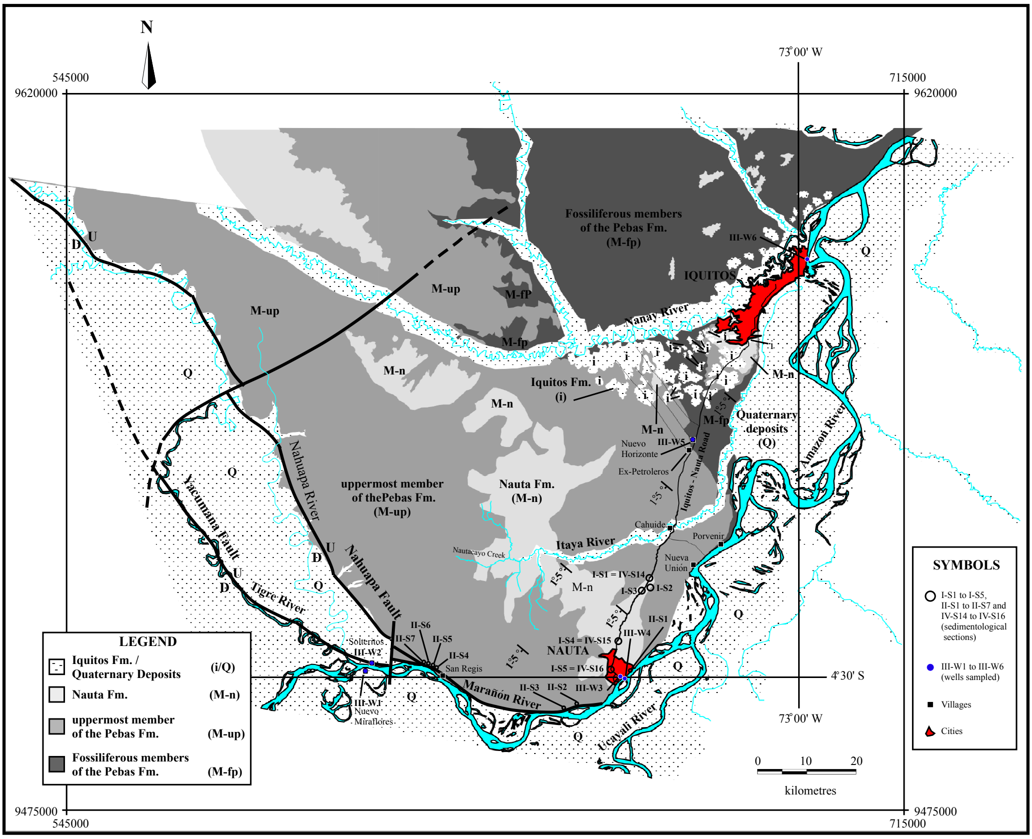
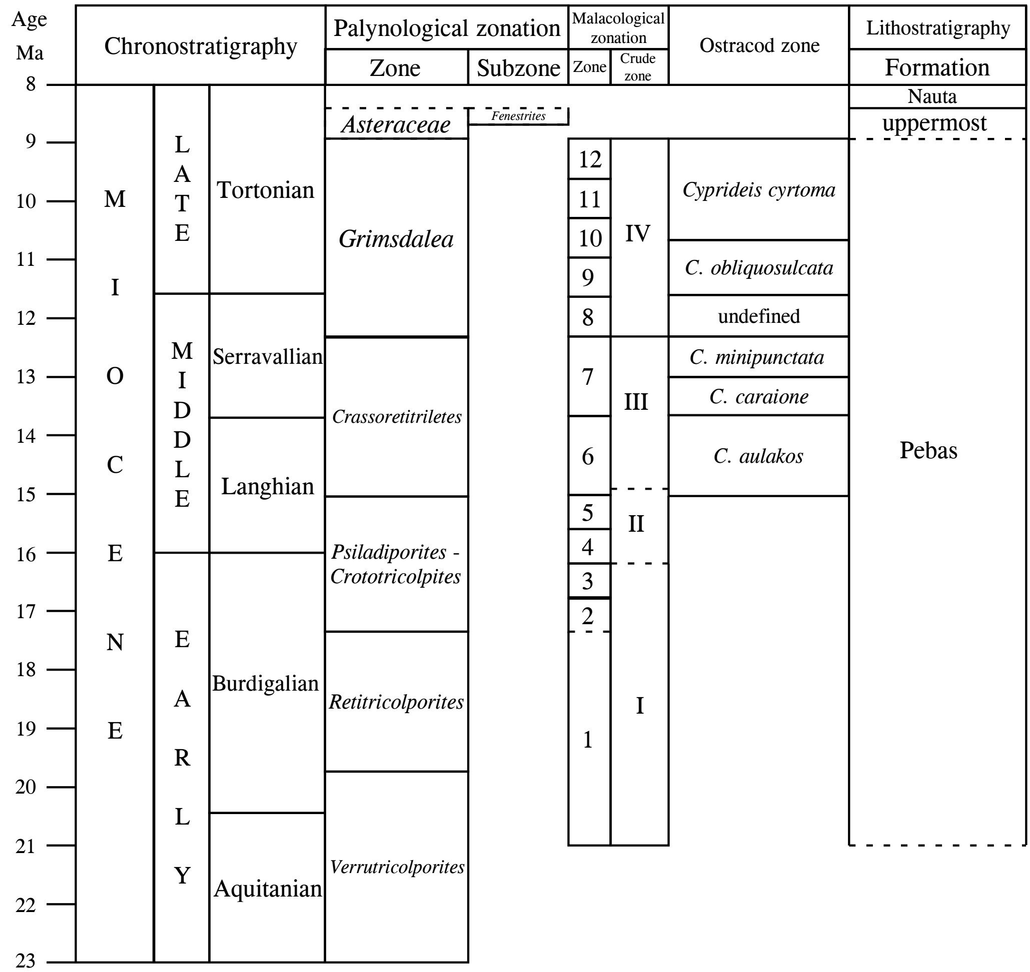


Figure 3. Local geological map of the study area for papers I, II & IV, and partially for paper III, in the Loreto Region, Peru. Note the locations of the sedimentological sections studied for papers **I** (I-S1 to I-S7), **II** (II-S1 to II-S5), and the wells studied for paper **IV** (IV-W1 to IV-W6). Notice also that the Nauta localities from paper **III** (14 to16) are included in this map.

or chemical engineers for their academic degree or professional title (see e.g. Arrué-F., 1974; Zamora-C., 1977; Bardales-G., 1979; Cornejo-S., 1987; Sánchez-G., 1991). In the 1990s, research was started by the Research Institute of Peruvian Amazonia (Instituto de Investigaciones de la Amazonía Peruana - IIAP) on environmental contamination in the region, mostly centred on water quality analyses (see Gómez, 1994). In 1999, the Geological Survey of Peru (Instituto Geológico Metalúrgico – INGEMMET) included water quality analyses (mostly of rivers, but also some from groundwaters) in their regional geological mapping of Amazonia (see e.g. Martínez-V. et al., 1999; Sánchez-F. et al., 1999). In summary, these studies concluded that river waters near to populated areas in Northern Peruvian Amazonia are contaminated by total coliform and faecal coliform bacteria (up to 1100 NMP ml^{-1}; cf. Gómez, 1994) due to the direct input of untreated sewage water. Cornejo (1987) found high concentrations of mercury (in fish up to 1.7 mg L-1), chromium (up to 0.055 mg L^{-1}), copper (up to 1 mg L^{-1}), nitrates (measured as nitrogen, up to 3.2 mg L^{-1}), and zinc (up to 0.4 mg L^{-1}). High concentrations of nitrates are most probably the result of agricultural activities. Martínez et al. (1999) reported high concentrations of iron (up to 4.3 mg L^{-1}) and manganese (up to 20 mg L^{-1}). In addition, high contents of

Table 1. Stratigraphic framework for Miocene Amazonia modified from Wesselingh et al. (2006, their fig. 2). These authors based their framework on the palynological zonations of Hoorn (1993, 1994) and Lorente (1986), their own malacological zonation and lithostratigraphy, and the ostracodan zonation from Muñoz-Torres et al. (2006). Please note that the age of the lower Pebas boundary ranges from c. 23 to 19 Ma and that of its upper boundary between 10 and 8 Ma (cf. Wesselingh et al., 2006, their fig. 2). Please also notice that the actual age of the upper limit of the *Asteraceae* palynological zone (cf. Lorente, 1986, her Table 15) is, although in the Late Miocene, uncertain (dashed lines).



hydrocarbons (up to 7 mgL^{-1}; Gómez, 1994) and lead (up to 0.11 mg L^{-1}; Martínez et al., 1999) have been found. According to Gómez (1994), these high contents of hydrocarbons and lead are probably leftovers of fluvial transportation and the activities of the petroleum industry. Locally, relatively high contents of arsenic (cf. Gómez, 1994) near Iquitos have been reported. According to Gómez (1994), arsenic contamination mostly results from the use of wood preservatives in the activities of the forestry industry.

2.3.2. The hydrogeochemistry of aquifers within the Pebas and Nauta formations

There is no previous literature regarding the further hydrogeochemical characterisation of the stratigraphical units described in the present thesis with the water types of their embedded aquifers.

2.4. Fieldwork methods

2.4.1. Study area, fieldwork periods and sites

The main study area for this thesis and papers I, II & IV is located between the cities/villages of Iquitos, Nauta and San Regis in the Loreto Region of Northern Peruvian Amazonia, with the Nanay, Amazon, Marañón and Tigre rivers limiting the area to the north, east, south and west, respectively (Fig. 3). The sedimentology and ichnology of the deposits exposed by road cuts along the Iquitos-Nauta Road, with emphasis on its last 40 km, were investigated in detail during 14thAugust to 16thNovember 1999; some outcrops near San Regis (along the left bank of the Marañón River) were also studied during this field trip. Fieldwork was carried out together with Drs Matti Räsänen and Murray Gingras, in collaboration with INGEMMET and the San Marcos National Major University (Lima – Peru) represented by Elba María Ponce Arias and Edward Córdova Romero, respectively. During a second field trip from1st-September to22ndOctober 2000, Miocene outcrops along the Marañón River between Nauta and San Regis were studied in detail; additional sedimentological observations were carried out along the Iquitos – Nauta Road and along the riverbanks of the Itaya River (to the Nautacayo Creek; see Fig. 3 for location). Fieldwork was carried out in collaboration with INGEMMET and Eddy Marcello Imaña Osorio. Final sedimentological fieldwork was carried out during18thSeptember to 10thOctober 2001, mainly logging the left bank of the Marañón River. Fieldwork was carried out in collaboration with INGEMMET represented by Iván Vílchez Burga. During this field trip the first groundwater samples were taken (2nd–4thOctober 2001) from five wells located in Iquitos, Nuevo Horizonte (along the Iquitos-Nauta Road), Nauta and Nuevo Miraflores (along the left and right bank of the Marañón River, respectively; see Fig. 3 for location). Three additional groundwater samplings were carried out in 2002, from 14th–15thJanuary, 6th–7thMay and 13th–14thAugust, including a sixth well located in Solteritos, on the left bank of the Marañón River (see Fig. 3 for location), in collaboration with Eddy Marcello Imaña Osorio and INGEMMET represented by Iván Vílchez Burga. The total time spent on fieldwork for this study was then about 115 days.

2.4.2. Description of physical sedimentary structures

The detailed field observation of physical sedimentary structures included the description of bedding types, the shape of beds, lower and upper bedding contacts, grain size, mineralogical composition using hand lenses, the upward trend in grain size, vertical and lateral continuation of the beds, and even, if possible, a three dimensional view. A graphical sedimentological log, with actual drawings of the sedimentary structures, was compiled during the description, commonly extending no more than c. 1 metre laterally. To locate the logged strips, a detailed sketch of whole outcrops, extending laterally for c. 100 m., was prepared in the field. A group of lithologically similar conformed beds were grouped into facies in the field, which were subsequently up-scaled into interpretive, genetically-related facies associations. Syndepositional deformation such as slumping, translation or rotation of stratified blocks, and post-depositional features such as faults and nodules were also noted.

2.4.3. Description of biogenic sedimentary structures

Ichnological field observations included the identification of trace fossils based on their shape, position in/on beds/bedding planes, lateral or vertical development, the type of wall lining, the type/texture of filling, and their association with other trace fossils (e.g. cross-cutting relationships, if any, or reburrowing). A graphical representation of all these data was also prepared in the field, paying close attention to the drawing of the traces as they actually appeared. In the case of the Nauta Formation (Rebata et al., 2006a), once trace fossils were identified, their abundance in each bed/facies was numerically assessed by assigning a percentage to them and, based on that, an ichnofabric index was determined (i.i.) (cf. Gingras et al., 2002a,b). In detail, the ichnofabric index depicts the strength or extent of bioturbation by utilising a scale from 1 to 5, with 20% increments for each class. In this way, i.i. =1 where bioturbation in the studied area ranges between 1–20%, i.i. =2 between 21–40%, and so on. Finally, related and repetitive trace fossils were grouped into trace fossil assemblages.

2.4.4. Measurement of palaeocurrents and depositional planes

Field measurements of the orientation and declination of ripple and dune foresets and troughs were taken with a compass to estimate the dominant palaeocurrents during deposition. Likewise, the orientation and inclination of major depositional planes were also measured to obtain the orientation of the master bedding in the depositional setting.

2.4.5. Sampling for grain size, XRD clay mineralogical analyses, soil geochemistry and pollen content

During the sedimentological logging and sketching, several locations were selected for sampling. Samples for grain-size analyses were taken from each facies, starting from the bottom of the logged strip toward the top. In addition, samples were taken from special locations along the lateral extent of the outcrops (for instance, where organic-rich rhythmites occurred).

Samples for clay mineralogical analyses and for the characterisation of the weathering and edaphic features of the study area were taken from the top of the logged strips (or actual surface) downward to the bottom of the outcrops, according to the following depths: at 20 cm, 50 cm, 1 m, 2 m, 4 m, 6 m, 8 m, 10 m, and so on. On some special occasions, for instance when there was a noticeable textural/mineralogical change between the assigned depths, extra samples were taken.

Samples for palynological analyses were only taken from organic-rich sediments in the Nauta Formation during the first fieldwork in 1999. However, in 2000, samples from the upper Pebas sections were taken at several logged strips every 5–10 cm, starting from the top of the outcrops, because the preservation of pollen was expected to be better in this unit.

2.4.6. Groundwater sampling

Groundwater samples were taken to analyse the geochemical characteristics of the local aquifers. During a second sampling period, the bacteriological content of the groundwater samples was also analysed.

The groundwater analyses were divided into seven main groups (listed below): physical parameters, anions, cations, Hg, Si and dissolved organic carbon (DOC), as well as total coliform bacteria and faecal coliform bacteria. The water for each group was sampled in a different bottle.

Six large wells, which are widely distributed in the study area, were selected for the study. The groundwater wells (W1–W6) were sampled four times in different seasons during the hydrological year from September 2001 to August 2002 in order to study possible seasonal variation.

Well W1 is owned by the Nuevo Miraflores community (c. 50 households). The water intake is at a depth of less than 10 m and there is no reservoir. The samples were taken manually by directly pumping the borehole with a hose. The aquifer of this well is in the upper Pebas Formation.

Well W2 is also a communal well, and c. 25 households use it for potable water. The depth of the well is less than 10 m. The samples were taken directly from the reservoir above the well. The aquifer of this well is also within the upper Pebas Formation.

Well W3 is located inside the University Campus of the Faculty of Engineering Systems of the National University of Peruvian Amazonia (FISI-UNAP) and is used by the students and university personnel (c. 200 users). Well W3 is c. 50–60 m deep (Abreu-P., 1999) and has a large reservoir. The samples were taken directly from the well. The aquifer of this well represents the Pebas Formation.

W4 is situated in the inner yard of the “Nuestra Señora de Loreto” Primary and Secondary School and used by c. 800 persons, including pupils and staff. The well is c.15 m deep. The samples were taken from the reservoir. The aquifer of this well represents the Nauta Formation.

Well W5 is used by the “National Fund for the Development of Fisheries” (FONDEPES) for potable water and for fish farming. The total depth of the well is 16 m (Abreu-P., 1999). The samples were taken directly from the well. The aquifer of this well represents the Pebas Formation.

Well W6 is owned and used by a local soft-drink company (Industrial Iquitos S.A) located in Iquitos, the largest city in Peruvian Amazonia (~332 000 inhabitants; INEI, 2000). The well is 32 m deep (Industrial Iquitos S.A., 2001). The samples were taken directly from the well. The aquifer of this well represents the Pebas Formation.

Prior to sampling, the wells were pumped for about 5 to 10 minutes and water was collected into buckets for field measurements. After field measurements, sampling bottles were washed with distilled water and with water from the well. Bottles were additionally marked with the well identification and elements to be analysed. All samples for cation and anion analyses were pre-filtered (except for October 2001 for INGEMMET) with a membrane filter 1.2 μm in pore diameter. In addition, samples for the analysis of cations, Hg, Si and DOC were filtered using a filter 0.45 μm in pore diameter and preserved if necessary. Bacteriological samples were collected without filtering into special sterilised polyethylene bags provided by the laboratory. All samples were stored in a cool box immediately after sampling and transferred to a refrigerator in less than 12 hrs.

2.5. Laboratory methods

2.5.1. Grain-size analysis

The grain-size distribution of the sediments studied was determined with a Coulter LS 200laser diffraction grain-size analyser. Prior to this measurement, samples were pre-treated (according to van Reeuwijk, 1992 and Siiro et al., 2005) with i) 1 M HCl if the sample was not calcareous, or with a buffer solution of Na acetate adjusted to pH 5.0 with glacial acetic acid, and a saturated solution of sodium chloride if the sample was calcareous, both in warm water baths, for the removal of carbonates; ii) 10% H_2O_2 in a warm water bath for organic matter removal; iii) a buffer solution of sodium citrate and sodium bicarbonate, and sodium dithionite in a warm water bath, for deferration; and iv) 0.005 M sodium pyrophosphate with ultrasonification for the dispersion of the samples. The actual grain size measurement was followed by the classification of the sediments and the calculation of sand/mud ratios according to Folk (1954).

2.5.2. XRD-clay mineralogical analysis

Duplicate samples were sent to the Laboratory of Sediment Petrography of the Senckenberg Institute in Wilhelmshaven, Germany for X-ray diffractometry (XRD) analysis of the clays. The methodology followed and the scientific background to XRD analyses are well explained by Irion (1984) and Räsänen et al. (1998). A clay fraction of all samples was obtained using settling tubes. Smear slides of clay (diameter < 2 μm) were pre-treated with Mg^{2+}, K^+ and ethylene glycol before the actual clay-mineralogical analysis.

2.5.3. Soil geochemistry analysis

The easily leachable nutrients (Ca, Mg, Na, K and Al), pH and loss on ignition (LOI) of the sediment and soil samples were analysed at MTT

Agrifood Research Finland. Extractable bases (Ca, K, Mg and Na) were measured with ammonium acetate at pH 7, aluminium was measured with 1 M KCl and pH was measured with KCl.

2.5.4. Palynological analysis

Samples were pre-treated to remove organic matter and the concentration of pollen was determined according to Hoorn (1994) and Ybert et al. (1992) at the Laboratory of Palaeoecology of the Catholic University of Goiás in Goiania, Brazil. First, samples were manually mixed and an exotic pollen was added for the concentration calculations; then, carbonates, inorganic silicates and organic debris were removed; finally, the samples were mounted on a glass slide and covered with glycerine. The actual identification and quantification of the pollen content was carried out under the microscope. A minimum of c. 300 angiosperms together with gymnosperms was counted, and palynological diagrams were constructed based on this.

2.5.5. Groundwater analysis

Groundwater geochemical analyses were performed at INGEMMET and also, although only for the first two sampling periods for comparative purposes, at the Geological Survey of Finland (GSF). Physical parameters and bicarbonate contents were not measured at GSF due to the temporal constraints in these analyses.

Bacteriological analyses were carried out using the "filtration by membrane" method with a 24-hr incubation period. The total coliform bacteria were reported at 35°C and the faecal coliform bacteria at 44.5°C. The laboratory results consisted of only a presence/absence report of the bacteria identified in a 100 ml sample.

Alkalinity was measured in the laboratory of INGEMMET by titration using the phenolphthalein and methyl orange indicators during all field periods. During May 2002, alkalinity was additionally analysed in the field with a HACH Digital Titrator for comparison purposes. Titration was performed with 1.6 N sulphuric acid for all wells and 0.16 N sulphuric acid for wells W3 and W4. Phenolphthalein and bromcresol green-methyl red were used as indicators. The alkalinity of well W1 was not measured in the field because of logistical problems.

The Lahti Research Institute used the Ströhlein Instruments C-Mat 5500 carbon analyser at 600°C for the detection of DOC.

3. RESULTS AND INTERPRETATION

3.1. Sedimentology and palynology

A brief general description is presented here, comprising the two formations studied. A detailed description of each of the three geological units follows below. All three geological units studied (see Table 2 for a summary of the units) are exposed and poorly to non-consolidated (Figs 4 and 5). The sediments are mostly composed of clay to fine-grained sand, with an average mode for sands coarser (158.3 μm = 2.7ϕ) in both the upper member of the Pebas Formation and the Nauta Formation than in the underlying fossiliferous members of the Pebas Formation (116.3 μm = 3.1ϕ; cf. Siiro et al., 2005; see also Table 2).

Likewise, all geological units are characterised by trace fossils assemblages mainly indicative of brackish-water conditions and composed of admixed ichnological elements of both the *Skolithos* and *Cruziana* ichnofacies. However, ichnofossil evidence of freshwater and subaerially exposed surfaces, with expressions of the *Scoyenia* ichnofacies, has also been reported (cf. Hovikoski et al., 2007).

Fossil pollen has been reported from both the Pebas and Nauta formations. The Pebas pollen content has been well studied by Hoorn (1993, 1994) and placed in three consecutive palynological zones: the Early to Middle Miocene *Psiladiporites*-*Crototricolpites* Concurrent Range Zone, the Middle Miocene *Crassoretitriletes* Interval Zone, and the Middle to Late Miocene *Grimsdalea* Interval Zone. New data from the upper member of the Pebas Formation obtained during this research indicate palynological correlation to the *Asteraceae* palynological zone, which immediately succeeds the *Grimsdalea* zone and expanded during the Late Miocene proper. The Nauta fossil pollen content does not include diagnostic material that could be used for dating, but merely allows the interpretation of the palaeo-environment as a depositional setting in the vicinity of mangrove forests.

The clay mineralogy of the Pebas Formation is characterised by smectite, whereas the Nauta Formation is characterised by kaolinite (cf. Räsänen et al., 1998). Both formations share a similar weathering process for their clays, typical of tropical environments (see Irion, 1984). Pebas sediments are enriched in nutrients (K, Mg, Ca), which is partly related to the high concentration of mollusc (aragonitic) shells in its beds, whereas strong lateritic weathering in the Nauta sediments has caused the loss of most of the nutrients (K, Mg, Na, Ca), and resulted in the formation of very poor soils (cf. Räsänen et al., 1998). In the Nauta Formation, kaolinite mostly comes from the weathering of feldspars, and in the topmost parts illite is transformed into Al chlorite (cf. Räsänen et al., 1998; see also Rebata-H., 1997).

3.1.1. The fossiliferous members of the Pebas Formation (Fig. 4e)

Exposures of this formation (and its equivalents) were studied together with post-Pebas strata at c. 5- to 40-m-high river banks or road cuts in 29 localities (sites 1–29 in Fig. 2; please note that sites 14 to 16 correspond to sites II-S1, II-S4 and II-S5 in paper **II**), expanding c. 1500 km from near Iquitos in Northeastern Peru to Beni in Northern Bolivia (cf. Hovikoski et al., 2007). Localities 1–14 correspond to the Pebas Formation *sensu stricto* (i.e. the fossiliferous members of the Pebas Formation). The un-weathered sediments of these members are characterised by finer-grained sands (see above and Siiro et al., 2005) than the overlying non-fossiliferous upper member of the Pebas Formation and the Nauta Formation (see below). The Pebas Formation *sensu stricto* is characterised by bluish clay to sandy/clayey mud and yellow-

Table 2. Summary of the geology of the Pebas and Nauta formations. Modified from Rebata et al. (2010) based on a compilation from Hoorn, 1994; Vonhof et al., 1998; Wesselingh et al., 2002; Rebata-H. et al., 2006a, b; Hovikoski et al., 2007.

Characteristics	**Pebas Formation – fossiliferous members (Unit 1)**
Time range	- late Early Miocene to early Late Miocene (c. 23- c.12 Ma)
Facies	- 3- to 10-m-thick, repetitive, heterolithic parasequences of bluish mud, variegated sand, shell-lags and lignite; - Very common organic-rich layers (with the lignite) with pyrite nodules - Common $CaCO_3$-rich mud - Channels are present - Tidally influenced (rhythmites) - Localities mostly at up to 28-m-high river banks but also at ~ 1-m-high road cuts
Grain size	- Mud to fine- to medium-grained sand; - Average mode (sand): 116.3 mm (muddy sand; finest-grained unit)
Clay mineralogy	- Smectite-rich $[(Si_8\ Al_{3.3}\ Mg_{0.7})\ O_{20}\ (OH)]$ clays - Also kaolinite and illite. - Superficial weathering; sometimes, un-weathered deposits can be observed at 1 m depth - Loss of c. 50% of K, and the formation of kaolinite and pyrophyllite - Sediments are enriched in nutrients (K, Mg, Ca)
Fossils	- Mainly freshwater molluscs (evidence from stable isotopes; aragonitic shells), but some brackish-water molluscs as well. - Also brackish-water ostracods, gastropods, barnacles, fish, sting rays, turtles, freshwater caimans, euryhaline (30-40 psu) shark teeth, marine foraminifers, etc.
Pollen	- Mangrove pollen (*Zonocostites ramonae*) among others; used for dating this formation as late Early to early Late Miocene
Trace fossils	- Indicate brackish-water to locally normal marine conditions (*Glossifungites* and/or admixed ichnological elements of both the *Skolithos* and *Cruziana* ichnofacies), to freshwater conditions (continental trace fossil associations, with possible elements of the *Scoyenia* ichnofacies)
Groundwater geochemistry	- Groundwaters are acid to neutral in pH (4–7), and have low hardness (≤1-60.8 mg$CaCO_3$/l), and high As (<5–27 mg/l), Fe (<0.01–25.4 mg/l), Mn (<0.1–0.56 mg/l), Na (0.3–28 mg/l), and Cl (<1–48.3 mg/l) concentrations. DOC is relatively high (<1–7 mg/l). Water type ranges from Fe/Ca/Na-HCO_3/Cl to Na-Fe-Cl-HCO_3.
Soil geochemistry	- Ca (from 1539 to 42 mg/kg), Mg (from 179 to 12 mg/kg), K (from 74 to 66 mg/kg) & Na (from 117 to 25 mg/kg) concentrations decrease, but Al (from 225 to 1133 mg/kg) and LOI (from 1.98 to 2.22%) concentrations increase, from the un-weathered to the weathered layers. Ca & Mg high concentrations in the un-weathered sediments are probably related to a mollusc-rich layer.
Interpretation of the palaeo-environment	- Complex association of transgressive-regressive bay-margin successions including shoreline, disoxic distal bay, delta/channel facies and freshwater swamp and lagoon environments
Whole system	- Probably a shallow (some tens of metres in maximum), brackish-water, tidally-influenced epicontinental embayment - The system was "prone to low energy, stagnant conditions that promoted dysaerobic conditions in the water column".
- Tidal regime	- Probably semi-diurnal to mixed
- Tidal range	- Probably mesotidal (2-4 m)
- Salinity	- Fluctuating (from low salinity, locally high salinity, to freshwater)

ish to greyish (silty/muddy) sand, and intervals rich in organic mud and/or lignite and shell-hash, although sporadic calcareous white mud is also present. This formation is composed of upward fining and/or upward coarsening 3- to 10-m-thick parasequences. Some successions are composed of heterolithic bedding that can be laterally extensive (from tens to hundreds of metres). The characteristic sedimentary structures observed are: mud-draped wave ripples, combined-flow ripples and/or current ripples (some bearing organic matter in their foresets and some where current reversals can be measured); double mud drapes; mud-draped cross-stratification, locally with bi-polar dune foresets; mm-scaled sand-mud-organic matter triplets; and dm-scaled sand-mud couplets. In addition, root-bearing mud, organic-rich mud or lignitic intervals bearing freshwater fossils (e.g. molluscs, turtles, caimans, undifferentiated bones of continental vertebrates), synaeresis cracks, and soft-sediment deformation occurs.

3.1.2. The non-fossiliferous upper member of the Pebas Formation (Fig. 4a-d)

Exposures of this geological unit were studied along the left-side margin of the Marañón River (sites I-S1 to I-S7 in Fig. 3) at c. 5- to 12-m-high river banks. The un-weathered sediments of the upper member of the Pebas Formation are characterised by tan to variegated silty sand (average mode: 131.6 μm = 2.9ϕ) and bluish to light grey mud (average mode: 53.5 μm = 4.2ϕ). The member is composed of heterolithic sand-mud cou-

Pebas Formation – non-fossiliferous, upper member (Unit 2)	**Nauta Formation – non-fossiliferous (Unit 3)**
- Late Miocene (c. 12 – c.10 Ma)	- Late Miocene (c. 10 – c.9-8 Ma)
- 3- to 7-m-thick parasequences of heterolithic variegated sand- bluish to grey mud couplets - Some organic-rich layers - Some interspersed calcareous layers - Channels are very common - Probably tidally influenced - Palaeosoils; carbonate cementation - Localities mostly at ~ 12-m-high river banks	- 1- to 7-m-thick heterolithic successions of variegated sand- light grey to reddish mud couplets; Common mud balls/blocks giving a brecciated texture to the successions. - Organic-rich trough-crossbedded beds & rhythmites with pyrite nodules - Rare marly layers - The whole unit is channelized - Tidally-influenced: rhythmites - Palaeosoils; rare limestone nodular layers - Localities mostly at up to 13-m-high road cuts
- Mud to fine- to medium-grained sand - Average mode (sand): 120.4 mm (silty sand; fine-grained unit)	- Mud to fine- to medium-grained sand; - Average mode (sand): 178.3 mm (silty sand; coarser-grained unit)
- Smectite-rich $[(Si_8\ Al_{3.3}\ Mg_{0.7})\ O_{20}\ (OH)]$ clays - Also chlorite, illite, goethite, kaolinite, quartz, pyrophyllite and Al chlorite - Superficial weathering; sometimes, un-weathered deposits can be observed at 1 m depth - Sediments are enriched in nutrients (K, Mg, Ca)	- Kaolinite-rich $Al_4\ [[Si_4O_{10}]\ (OH)_8$ or $Al_2O_3\ .\ 2\ SiO_2\ .\ 2\ H_2O]$ clays (as a result of feldspars' transformation) - Also Al chlorite (as a result of illite transformation on the top levels, passing first from smectite/vermiculite; illite, quartz, goethite, gibbsite & lepidocrocite - Strong (post-depositional) lateritic weathering - Loss of most of K, Mg, Na & Ca resulting in poor soils
- No molluscs but rare vertebrae of a crocodile (*Purussaurus*)	- No fossils
- Used for estimating the age of this formation as Late Miocene	- Mangrove-related pollen (*Zonocostites*) among others; Valid only for palaeoecological interpretation
- Indicate brackish-water (low salinity; admixed ichnological elements of both the *Skolithos* and *Cruziana* ichnofacies) to freshwater conditions (continental trace fossils associations, with possible elements of the *Scoyenia* ichnofacies)	- Indicate brackish-water (low salinity; admixed ichnological elements of both the *Skolithos* and *Cruziana* ichnofacies) to freshwater conditions (continental trace fossils association, with possible elements of the *Scoyenia* ichnofacies)
- Groundwaters are neutral in pH (6.7-7.6), and have high hardness (131-285 $mgCaCO_3/l$), As (14-130 mg/l), Fe (0.02-4.86 mg/l), and Mn (1.46-3.82 mg/l) concentrations. Na (9.5–14 mg/l) and Cl (<1-3.24 mg/l) contents are lower than in the fossiliferous members. DOC is relatively high (3–8.3 mg/l). In the study location, the waters contain total and faecal coliform bacteria that indicate anthropogenic contamination. Water type is Ca-(Mg)-HCO_3.	- Groundwater is acid in pH (4.2-5.6), and show low hardness (21-28 $mgCaCO_3/l$), and high NO_3 (45.9-50 mg/l), Al (300-609 mg/l), Mn (0.32-0.4 mg/l), Na (24.2-38 mg/l) and Cl^- (45.3-56.4 mg/l) concentrations. DOC is low (1 mg/l). **At the study location** faecal coliform bacteria are present in the water pointing to anthropogenic contamination. Water type is Na-(Ca)-Cl-NO_3.
- Sediments change from neutral (6.96) to acid (3.52) in pH from the un-weathered to weathered layers in the section. Ca (from 3355 to 32.3 mg/kg), Mg (from 346.3 to 15 mg/kg), K (from 174.1 to 137.9 mg/kg) & Na (from 31.39 to 15.89 mg/kg) concentrations decrease, whereas Al (from 40 to 1994 mg/kg) & LOI (from 1.77 to 4.06%) concentrations increase from the un-weathered to weathered parts of the section. Ca & Mg high concentrations in the un-weathered sediments are probably related to calcareous concretions and/or carbonate cementation.	- Sediments are acid in pH both in the un-weathered (1.93) and weathered (3.78) layers of the section. Ca (from 6.1 to 1.5 mg/kg), K (47.4 to 35.4 mg/kg), Mg (from 14.6 to 2 mg/kg), Na (from 2.72 to 0.4 mg/kg), Al (from 1001 to 557 mg/kg) & LOI (from 8.9 to 2.52%) concentrations decrease from the un-weathered to weathered layers.
- Transgressive/regressive bay-margin successions more channelized than the Pebas Formation *proper*.	- Tidally influenced, estuarine channel complexes developed in the inactive parts of delta plains.

plets organised in approximately 3- to 7-m-thick repetitive parasequences. Individual parasequences can be upward fining or upward coarsening. Some successions include organic-rich layers and/or interspersed calcareous layers. The sedimentary successions are mainly composed of a facies dominated by *sand-to mud-prone IHS*, which include superimposed dm-, cm-, and mm-scale, rhythmical sand-mud alternations characteristic, but not diagnostic, of tidal influence. The variation from sand to mud and vice versa was observed not only vertically but also laterally in the outcrops, a reportedly common feature in estuarine environments. This facies is thus interpreted as tidally-influenced, laterally-accreting bars, mainly point bars (but see Dalrymple et al., 2003), deposited in primary channels on an estuarine depositional setting. Other facies recorded in the upper member of the Pebas Formation are *mud-dominated horizontal heterolithic couplets* interpreted as deposited in muddy, shallow, sub-aqueous flats or shoals, *rooted brownish mud* interpreted as palaeosols fringing the flats, *lenticular mud-draped cross-stratified sand* interpreted as channel-floor dunes, indicating the presence of secondary channels as tributaries of the main channels on the flats, and *sand-dominated horizontal heterolithic couplets*, mostly upward-coarsening, interpreted as deposited in a more energetic sandy shoreface environment. These five facies may be grouped into three facies associations: i) **tidal flats and surrounding floodplain**; ii) **tidal channels** including both primary and secondary channels (tidal creeks)

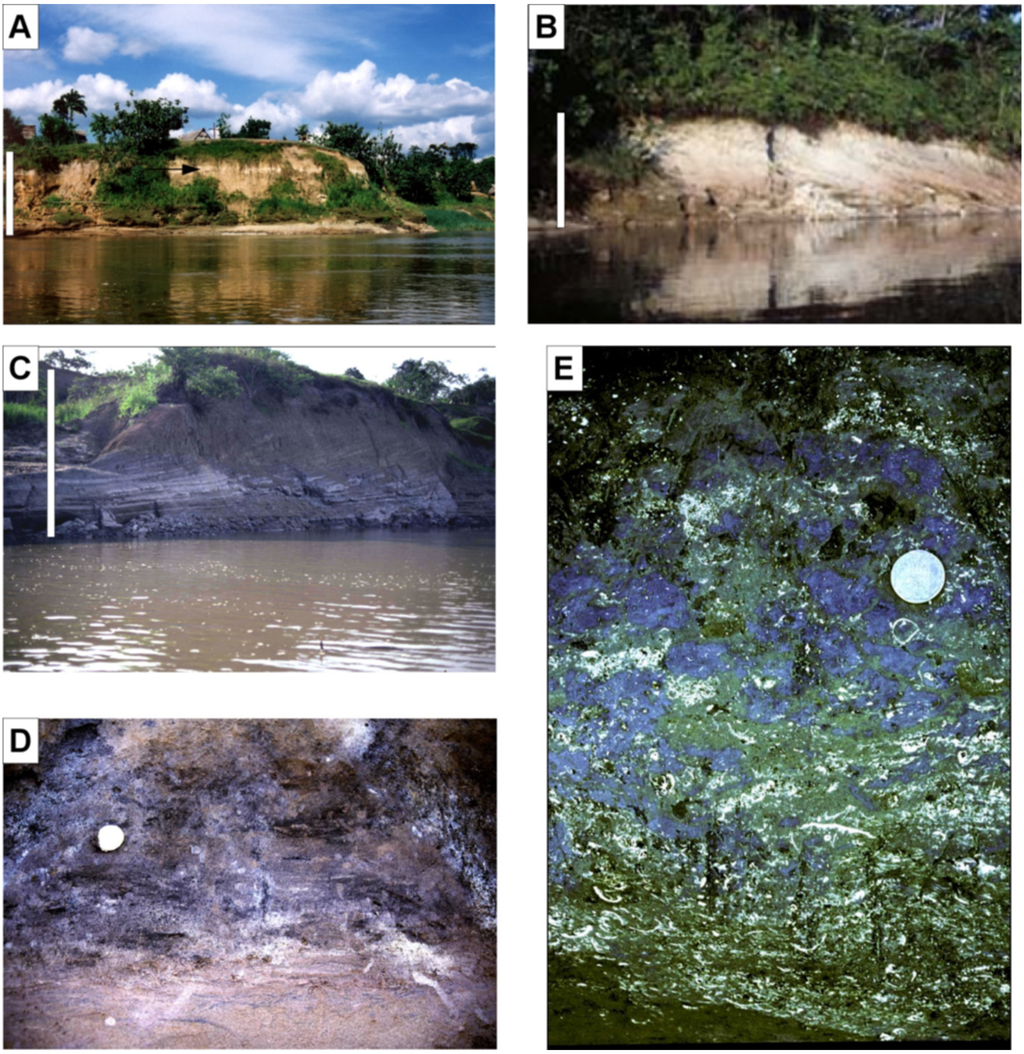


Figure 4. Examples of the outcrop localities and facies interpreted to represent the Pebas Formation. A) Panoramic view of laterally continuous gradational sand to mud couplets with interspersed calcareous layer (black arrow). Locality Monte Verde (UTM coordinates: 619203, 9502803), left-side river bank of the Marañón River. Vertical bar is *c.*10m high. B) Panoramic view of sand to mud-dominated inclined heterolithic stratification, left-side river bank of the Marañón River near to San Regis; UTM coordinates 618096, 9503554. The vertical bar is *c.*3m high. C) Example of the IHS channels in the upper Pebas Formation, Nueva Unión; UTM coordinates: 677094, 9528013. Left-side river bank of the Amazon River. Photo by M. Räsänen. Vertical bar is *c.*20m. D) Bioturbated, organic-rich ripple sandy mud. Locality Monte Verde; UTM coordinates: 619080, 9502876. The coin is 25mm in diameter. E) Example of the fossiliferous lower Pebas Formation. Note the fossil mollusc shells, which are mainly interpreted as a freshwater fauna (see e.g. Wesselingh et al., 2002). Right-side river bank, Amazon River, near to Tamshiyacu; UTM coordinates: 704547, 9556721. The coin is 25mm in diameter.

crosscutting the tidal flats and iii) **shoreface**. Palaeocurrent measurements from the troughs of dunes and ripples indicate a predominant NW orientation, whereas the orientation of the main depositional planes indicates a preferential NE, SE and W direction.

Ichnology in the upper member of the Pebas Formation is mainly characterised by low-diversity, impoverished admixed ichnological elements of both the *Skolithos* and *Cruziana* ichnofacies, including *Planolites*-reburrowed *Taenidium* and/or *Thalassinoides*, *Skolithos*, *Arenicolites, Chondrites*, *Teichichnus*, and some monospecific (*Thalassinoides*-dominated) ichnoassemblages. Rare *Laminites* were reported in paper I, which were interpreted as a variant of *Scolicia* (commonly attributed to the burrowing of spatangoid echinoids; cf. Plaziat & Mahmoudi, 1988). Although the traces described as *Laminites* are in agreement with their first description by Ghent and Henderson (1966), these occurrences lack some diagnostic features of echinoid burrows (e.g. drains in the lower part of the trace fossil) and display size variation uncommon for irregular echinoids, and an alternative trace maker should thus be considered. Delineation of the palaeoenvironmental significance of this trace fossil requires more work in the future (Matti Räsänen and Jussi Hovikoski, personal communication).

The impoverished assemblage with proximal to distal expressions of the *Skolithos* ichnofacies and low-diversity, proximal expressions of the *Cruziana* ichnofacies in the upper Pebas successions preclude a continental setting. Instead, the impoverished nature of the suites (the trace fossil suites documented within these ichnofacies hardly show more than 4 or 5 ichnogenera) and the diminutive expression of their elements argue for brackish-water conditions. Brackish-water trace fossil suites of this type are reportedly common in estuarine environments (Ekdale et al., 1984; Pemberton & Wightman, 1992; Pemberton et al., 1992; Ainsworth & Walker, 1994; Buatois et al., 1998; Zonneveld et al., 2001). In these environments, fluctuating physicochemical conditions in the water (e.g. changes in salinity, oxygen content and sediment supply) create stressed conditions for the organisms colonising the sediments. The *Taenidium*-dominated suite may represent interchannel facies and is probably associated with subaerially exposed surfaces. In the latter case, if the *Taenidium*-dominated suite reported in paper I is associated with palaeosols, it is more likely that they actually represent *Scoyenia* or *Naktodemasis* trace fossil forms, and as such could represent traces generated by insects (particularly beetles) and correspond to the nonmarine *Scoyenia* ichnofacies. This would be in agreement with the continental trace fossil assemblages reported in paper IV at a more regional level. This uncertainty requires further detailed investigation.

The fraction <2 μm in the clays of the upper member of the Pebas Formation (studied only in section I-S4; see Fig. 3 for location) shows a transitional signature between the typical smectite-rich Pebas mineralogy and the kaolinite-rich Nauta mineralogy. In the upper Pebas weathering profiles there has been no neo-formation of Al chlorite or kaolinite. The un-weathered upper Pebas clays were probably originally characterised by a very high content of smectite and a medium content of chlorite and illite. Now, after chemical weathering, the illite has dissolved and goethite has formed on the top 2 m of the upper Pebas successions.

Several samples from the upper member of the Pebas Formation (from section I-S6; see Fig. 3 for location) were analysed for pollen content, but pollen was only found in one sample. This sample was characterised by a high diversity of pollen species, although in low concentrations (less than 10%), except for the *Monoporites annulatus* (c. 20%) and *Psilatricolporites anconis* (c. 15%) palynomorph types. Based on the presence of *Echitricolporites spinosus*, *Fenestrites spinosus*, *Magnastriatites grandiosus*, *Psiladiporitesredundantis*, *Psilaperiporites minimus*, *Cyatheacidites annulatus* and *Verrucatosporitesusmensis*, the presence and abundance of *Monoporites annulatus*, and the absence of *Echitricolporites mcneillyi* and *Stephanocolpites evansii*, the upper member of the Pebas Formation is correlated with the Late Miocene *Asteraceae* interval zone, the *Fenestrites* interval subzone of Lorente (1986; see also Table 1) [the *Echitricolporitesspinosus* palynological zone of Germeraad et al. (1968) and the X superzone, *Echitri-*

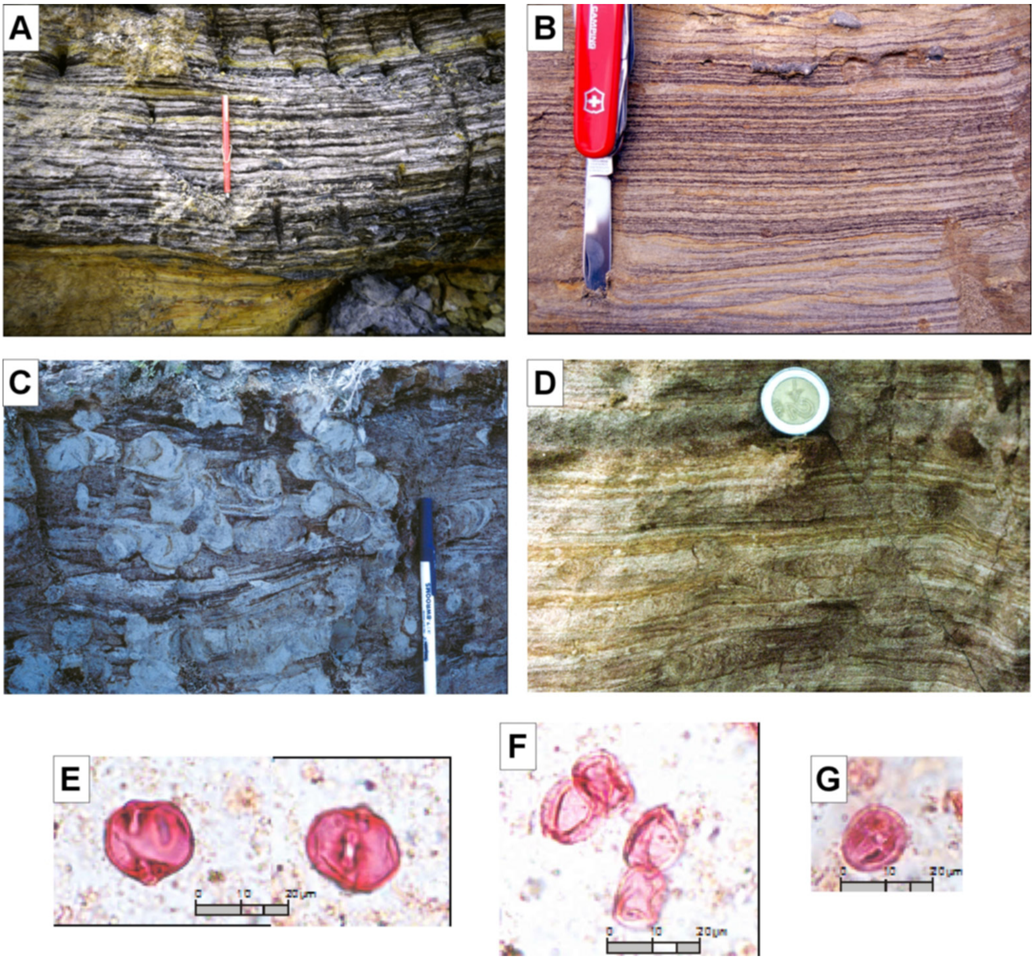


Figure 5. Examples of rhythmites, bioturbation and the pollen content in the Nauta Formation. A) Organic-rich triplet/tetraplet rhythmites comprising sand, mud, elemental sulphur and organic debris laminae. The pen is *c.*14cm long. B) Detail of organic-rich rhythmites. Note the pyrite nodules. The knife blade is *c.*7cm long. Photo by J. Hovikoski. C) Detail of *Laminites*-dominated ichnofabric. The pen is *c.*10cm long. D) Bioturbated rhythmites dominated by *Taenidium* traces. Alternatively, they could represent Scoyenia, Naktodemasis or Edaphichnium, all indicative of a continental suite. The coin is 20mm in diameter. E) Palynomorph Type 3107: Zonocostites sp. Assemblage 1 related to mangrove environments (cf. Rull, 2001). Photo by Maira Barberi. F) Palynomorph Type 3109: Psilatricolporites maculosus. Assemblage 1 related to mangrove environments (cf. Rull, 2001). Photo by Maira Barberi. G) Palynomorph Type 3110: Retitricolpites simplex type 02. Assemblage 1 related to mangrove environments (cf. Rull, 2001). Photo by Maira Barberi.

colporites spinosus concurrent range zone of Muller et al. (1987)]. The palynostratigraphic framework for Miocene Amazonia established by Hoorn (1993, 1994) based on work by Lorente (1986) for the Upper Tertiary in Venezuela is included in Table 1, together with the recently published stratigraphic framework by Wesselingh et al. (2006; their fig. 2) for the Pebas Formation *sensu stricto* (i.e. including only its fossiliferous members), mainly based on their study of molluscs.

3.1.3. The Nauta Formation (Figs 5 and 6)

This geological unit was studied from c. 6- to13-m-high road cuts along the Iquitos-Nauta Road, especially from the last c. 40 km, starting close

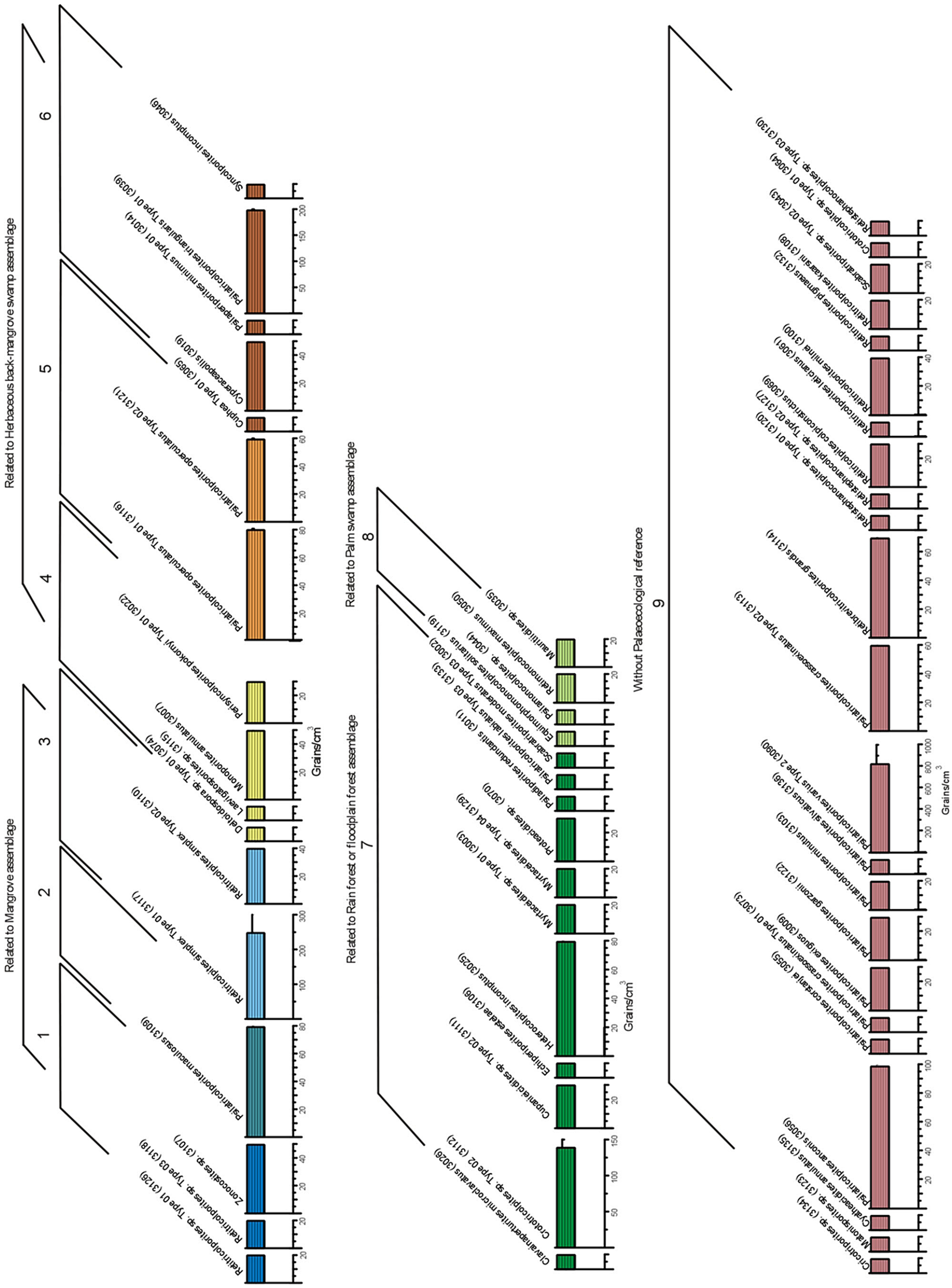


Figure 6. Palynological concentration diagram from organic-rich rhythmites in the Nauta Formation.

to the Itaya River and ending near the left margin of the Marañón River in Nauta (sites II-S1 to II-S5 in Fig. 3). The un-weathered sediments of the Nauta Formation are characterised by beige to variegated muddy sand (average mode: 178.3 μm = 2.5ϕ) and light grey to reddish mud (average mode: 33.86 μm = 4.9ϕ). The Nauta Formation is composed of heterolithic sand-mud couplets arranged in c. 1- to 7-m-thick, upward-fining successions. Some successions include marls, nodular limestone layers and organic-rich mud/sand. One to several successions may make up a facies association. The major repeating facies observed in the Nauta sections were *mud-draped trough cross-stratified sands covered by IHS deposits,* and on top *horizontally bedded sand-mud couplets*. Concave erosional surfaces truncating these facies, both vertically and laterally, are common. They are interpreted to indicate the bases of channels eroded into both the trough cross-stratified sands and IHS facies and deposited within a very dynamic depositional setting, probably dominated by autocyclic changes.

The *mud-draped trough cross-stratified sands* facies is lowest in the individual channels and is slightly bioturbated and presents sedimentary structures characteristic of a tidally-influenced estuarine environment, such as consecutive trough crossbedded sets with opposing palaeocurrent directions, mm- to cm-scale rhythmites with c.7-cm-thick deformed vs. non-deformed repetitive cycles, climbing ripples, continuously mud-draped ripples, both on their lee and stoss side, counter-current ripples at bottom sets, soft-sediment deformation, and synaeresis cracks. The *mud-draped trough cross-stratified sands* facies is subdivided into a sandy and an organic-rich, muddier sub-facies. This facies is interpreted as 3D-migrating dunes deposited on the channel floors of a sub-tidal channel complex or complexes.

The *IHS* facies lies on top of the former facies and is characterised by pervasively bioturbated heterolithic sand-mud couplets subdivided into three sub-facies: a rhythmite-dominated sub-facies where mm- to cm-scale sand-mud couplets arranged in 12–14 groups or cycles have been documented and interpreted as amalgamated spring-neap tidal cycles (cf. Räsänen et al., 1998); a sub-facies characterised by m- to dm-thick sand-mud couplets, with reworked mud preserved as mud balls or blocks in sand, giving a typical mud brecciated texture to the Nauta successions, and where laminated mud blocks typically contain several cm-scaled sand-mud couplets; and a commonly mud-dominated, locally thoroughly bioturbated sub-facies including wavy to undulatory bedding. Discrete root traces were recorded. This facies is interpreted as representing tidal point bar deposits in a channelized system with a seasonal imprint interpreted from the m- to dm-scaled sand- to mud-dominated cycles.

The *horizontally stratified sand-mud couplets* facies lies on top of the channel succession and is moderately bioturbated, includes marly to organic sand/mud couplets, and presents physical sedimentary structures characteristic of tidally-influenced estuarine environments, such as double mud drapes, hummocky cross-strata, flaser bedding and synaeresis cracks. This facies is subdivided into a clastic and a calcareous sub-facies, and is interpreted as deposited in tidal shallow, mostly sub-aqueous flats due to the absence of consistent preservation of root traces or any other evidence of long-term emergence. All these facies are genetically related and can thus be grouped into a tidally-influenced estuarine channel-complex facies association with associated subaqueous flats developed in the inactive parts of delta plains. Measurements of palaeocurrent and bounding surfaces from the troughs of dunes and ripples, and the main depositional planes, respectively, in the Nauta successions indicate a predominant SW orientation for the flow.

The ichnology of the Nauta Formation is also characterised by admixed ichnological elements of both the *Skolithos* and *Cruziana* ichnofacies, with their low-diversity trace-fossil suites and reduced size supporting brackish-water conditions. These trace fossils suites are, however, comparatively more diverse (locally less stressed, e.g. in terms of salinity) than in the underlying upper member of the Pebas Formation (see above). Trace fossil assemblages observed in the Nauta beds commonly include *Skolithos*, *Thalassinoides*, *Teichichnus*, *Planolites*, *Laminites*, *Chondrites*, *Arenicolites*, and *Taenidium*; rarely *Psilonichnus*, *Palaeophycus*, *Ophiomorpha, Rhizocorallium*, *Cylindrichnus*, *Gyrolithes*, *Siphonichnus*, *Monocraterion*, and diminutive trace fossils possibly burrowed by threadworms. Locally, some of the *Taenidium* traces reported within the bioturbated rhythmites in paper II (see Fig. 5D) could alternatively represent *Naktodemasis*, *Scoyenia* or *Edaphichnium* trace fossil forms, which are indicative of a continental setting (the former two beetle-generated and the latter oligochaete-generated). However, as the rhythmic lamination supports tidal cyclicity, and hence the likelihood of a brackish influence on that unit, the *Taenidium* description is favoured.

The un-weathered fraction <2 µm in the Nauta clays (studied e.g. at section II-S2, II-S4, and II-S5; see Fig. 3 for location) is typically dominated by kaolinite with a subordinate content of quartz, illite, and goethite, and a very minor content of both low- and high-charged smectite. In the top 2 m of the Nauta successions, aluminium chlorite with some and/or a large amount of expandable layers and pyrophyllite have been now formed (Georg Irion, 2001, pers. comm.).

Several samples from organic-rich Nauta beds were palynologically analysed, but a fossil pollen content was only found in one sample from section II-S5 (see Fig. 3 for location). The sample is characterised by a high diversity of palynomorphs but in low concentrations, similarly to the upper member of the Pebas Formation (see above). An exception to this is the high concentration of *Psilatricolporites varius* (25.5%). Palynomorphs were grouped into five assemblages according to their botanical affinities. The groups include an assemblage with a high correlation with mangrove environments (cf. Rull, 2001), where *Psilatricolporites maculosus*, *Retitricolpites simplex*, *Retitricolporites* sp. and *Zonocostites* sp. were observed. The other palyno-assemblages are related to herbaceous back-mangrove swamps (including species tolerant of low-salinity to fresh water such as *Cyperaceapollis*, *Monoporites annulatus*, *Psilatricolporites operculatus* and *P. triangularis*), rain forests or floodplains (dominated by *Crototricolpites* sp., *Heterocolpites incomptus* and *Myrtaceidites* sp.), and palm swamps (including *Equimorphomonocolpites solitarius*, *Mauritiidites* sp., *Psilamonocolpites* sp. and *Retimonocolpites maximus*).

3.2. Geo- and hydrogeochemistry of the Pebas and Nauta formations

The purpose of presenting the weathering profile and soil geochemistry (easily leachable nutrients and LOI) data is to compare the geochemistry of the sediments from the three stratigraphical units studied in this thesis with the geochemistry of the groundwaters (obtained from wells W1, W2, W4 & W5) hosted within them. W3 was excluded because, although the aquifer is within the Pebas Formation, the superficial sediments surrounding the well belong to the Nauta Formation.W6 was also excluded because data on un-weathered sediments were also lacking near this well (see Fig. 3 for the location of the wells; see also paper **IV**).

3.2.1. The fossiliferous members of the Pebas Formation

For comparative purposes, the soil geochemistry from this unit was retrieved from data published by Ruokolainen & Tuomisto (1998) for their site “Ex-petroleros_hu 40 valley”, the nearest site to well W5 [see Fig. 3 for the location of the well and Ruokolainen & Tuomisto (1998) for the location of the soil sampling site]. The un-weathered sample from “Ex-petroleros_hu 40 valley” is from a depth of 1.9 to 2.05 m, whereas the weathered one from a depth of 0.95 to 1.05 m (cf. Ruokolainen & Tuomisto, 1998). The pH of the sediments was not measured near W5. The concentrations of the most easily leachable nutrients (Ca, K, Mg, and Na) in the sediments decrease from the bottom to the top of the sections, with the exception of aluminium and LOI. Calcium and magnesium decrease from 1539.072 to 42.084 mg/kg and from 178.752 to 12.16 mg/kg, respectively. The higher Ca and Mg concentrations at the bottom of the sections are most probably related to one of the typically mollusc-rich layers from this

Table 3. The fossiliferous members of the Pebas Formation (comparison of soil geochemistry from "Ex-petroleros_hu_40_valley" (*) near W5 and groundwater geochemistry from wells W3, W5 and W6 (**)).

Samples	Depth	pH-field	pH-lab	Hardness-lab	HCO3-lab	DOC	Cl	SO_4
Unit	m			$mgCaCO_3/l$	mg/l	mg/l	mg/l	mg/l
Weathered Soil near W5	0.95-1.05	NM	NM	NM	NM	NM	NM	NM
Un-weathered Soil near W5	1.9-2.05	NM	NM	NM	NM	NM	NM	NM
Groundwater in W5_oct 2001	*c.*8–14	6,40	6,40	NM	42,80	NM	1,00	0,50
Groundwater in W5_jan 2002	*c.*8–14	6,10	5,70	52,50	48,20	4,10	1,38	0,50
Groundwater in W5_may 2002	*c.*8–14	5,60	5,50	17,00	27,80	NM	1,00	0,50
Groundwater in W5_aug 2002	*c.*8–14	7,04	5,20	14,00	25,20	NM	1,00	0,50
Groundwater in W6_oct 2001	*c.*20 – 21.5	5,80	6,00	NM	87,04	NM	41,40	13,60
Groundwater in W6_jan 2002	*c.*20 – 21.5	5,50	5,50	60,80	61,60	7,00	48,30	11,70
Groundwater in W6_may 2002	*c.*20 – 21.5	5,40	5,40	22,00	58,20	NM	42,30	11,00
Groundwater in W6_aug 2002	*c.*20 – 21.5	5,69	5,40	15,00	58,20	NM	42,30	11,00
Groundwater in W3_oct 2001	*c.*42	4,70	5,40	NM	8,04	NM	1,00	0,50
Groundwater in W3_jan 2002	*c.*42	4,40	4,20	1,26	3,74	1,00	1,38	0,50
Groundwater in W3_may 2002	*c.*42	4,00	4,50	1,00	2,40	NM	1,00	0,50
Groundwater in W3_aug 2002	*c.*42	4,60	4,40	1,00	2,42	NM	1,00	0,50

(*) Soil samples from Ex-Petroleros_hu 40 valley (*cf.*Ruokolainen & Tuomisto, 1998).
(**) Groundwater wells located at FONDEPES-Iquitos km39,5 (W5; UTM coordinates: 672074 E, 9550329 N), Industrial Iquitos S.A.-Well2-Iquitos (W6; UTM coordinates: 695337 E, 9586744 N) and FISI-UNAP-Nauta (W3; UTM coordinates: 657145 E, 9502107 N).
NM: Not measured

formation. Potassium, on the other hand, decreases only slightly (from 74.29 to 66.47 mg/kg). Sodium decreases from 117.249 to 25.289 mg/kg. In contrast, aluminium increases c. 5-fold (from 224.75 to 1132.74 mg/kg), but LOI increases only slightly (from 1.98 to 2.22%).

The groundwaters in this geological unit studied from wells at sites IV-W3, IV-W5 and IV-W6 (see location in Fig. 3) are acid to neutral in pH (4–7), and have high concentrations of arsenic (from less than 5 to 27 $\mu g\ L^{-1}$), iron (from less than 0.01 to 25.4 mg L^{-1}), manganese (from less than 0.1 to 0.56 mg L^{-1}) and chloride (from less than 1 to 48.3 mg L^{-1}). On the other hand, hardness is low (from less than or equal to 1 to 60.8 mgCaCO3 L^{-1}). The water type in these groundwaters ranges from (Fe)-Ca-HCO_3 through Na-Fe-Cl-HCO_3/HCO_3-Cl to Ca/Na-HCO_3-Cl.

High concentrations of Fe, Mn, SO_4, DOC (dissolved organic carbon) and As are characteristic of the Pebas successions, with some differences between the fossiliferous members and the underlying fossil barren upper member of the Pebas Formation. In particular, the reduction of iron (concentrations as high as 21.1 mg/l in W6) is the main mechanism for the release of arse-

Table 4. The non-fossiliferous upper member of the Pebas Formation (comparison of soil geochemistry from "I-S4; paper I (*) near W1 and W2 and groundwater geochemistry from the same wells (**)).

Samples	Depth	pH-field	pH-lab	Hardness-lab	HCO3-lab	DOC	Cl	SO_4
Unit	m			$mgCaCO_3/l$	mg/l		mg/l	
Weathered Soil near W1 & W2	0,2	NM	3,52	NM	NM	NM	NM	NM
Un-weathered Soil near W1 & W2	10,3	NM	6,96	NM	NM	NM	NM	NM
Groundwater in W1_oct 2001	*<10*	7,00	7,15	NM	237,00	NM	3,24	0,83
Groundwater in W1_jan 2002	*<10*	6,90	6,60	274,10	366,80	3,00	1,38	0,50
Groundwater in W1_may 2002	*<10*	6,70	6,70	252,00	353,80	NM	1,00	0,50
Groundwater in W1_aug 2002	*<10*	7,48	6,80	285,00	373,20	NM	1,00	0,50
Groundwater in W2_oct 2001	*<10*	NM	NM	NM	NM	NM	NM	NM
Groundwater in W2_jan 2002	*<10*	6,90	6,60	130,50	187,40	8,30	1,38	0,50
Groundwater in W2_may 2002	*<10*	6,70	6,60	131,00	202,20	NM	1,00	1,00
Groundwater in W2_aug 2002	*<10*	7,55	6,60	142,00	202,20	NM	1,00	0,50

(*) Soil samples from I-S4 (paper I-Section 4) come from Monte Verde (S4°29'60", W73°55'21"; Rebata et al. 2006a).
(**) Groundwater wells located at Nuevo Miraflores- Marañón River, right-side bank (W1; UTM coordinates: 605602E, 9503385N) and Solteritos- Marañón River, left-side bank (W2; UTM coordinates: 606930E, 9504836N).
NM: Not measured

Al	As	Ca	Fe	K	Mg	Mn	Na	LOI	Groundwater type
mg/l (water) mg/kg (soil)	mg/l	mg/l (water) mg/kg (soil)	mg/l	mg/l (water) mg/kg (soil)	mg/l (water) mg/kg (soil)	mg/l	mg/l (water) mg/kg (soil)	%	
1132,74	NM	42,084	NM	66,47	12,16	NM	25,289	2,22	Not applicable
224,75	NM	1539,072	NM	74,29	178,752	NM	117,249	1,98	Not applicable
0,0290	0,0050	12,20	3,30	2,31	0,33	0,230	1,90	NM	Ca-HCO_3
0,0280	0,0050	9,77	13,80	1,73	0,25	0,500	1,08	NM	Fe-Ca-HCO_3
0,0050	0,0120	6,10	0,66	2,20	0,32	0,560	1,60	NM	Ca-HCO_3
0,0050	0,0050	4,50	0,55	1,70	0,37	0,460	1,50	NM	Ca-HCO_3
0,0240	0,0170	6,10	25,40	6,51	1,29	0,100	26,90	NM	Na-Fe-HCO_3-Cl
0,0200	0,0270	7,66	21,10	7,80	0,86	0,100	26,50	NM	Na-Fe-Cl-HCO_3
0,0050	0,0260	7,30	15,80	8,80	0,81	0,100	25,00	NM	Na-Fe-Cl-HCO_3
0,0150	0,0170	4,70	13,90	8,70	0,77	0,100	28,00	NM	Na-Fe-Cl-HCO_3
0,0100	0,0050	0,50	0,26	0,23	0,09	0,100	0,43	NM	HCO_3-Cl
0,0200	0,0050	0,20	0,28	0,18	0,03	0,100	0,36	NM	HCO_3-Cl
0,0090	0,0050	0,40	0,01	0,19	0,08	0,100	0,30	NM	Ca-HCO_3-Cl
0,0079	0,0056	0,20	0,05	0,11	0,10	0,100	0,38	NM	Na-HCO_3-Cl

nic (concentrations alarmingly reach 130 µg/l in well W1) into the Pebas system.

3.2.2. The non-fossiliferous upper member of the Pebas Formation

The soil geochemistry of this unit was studied from site I-S4, the nearest to wells W1 and W2 (see Fig. 3 for location); un-weathered sediments correspond to 10.3 m depth (sample: Tu01L17), whereas weathered sediments correspond to 20 cm depth (sample Tu01L12; see Fig. 7 in paper **I** for a detailed log of the section and the location of the samples). The un-weathered sediments of this geological unit at the bottom of the section are neutral in pH (6.96), whereas the weathered sediments at the top of the section are acid in pH (3.52). The easily leachable nutrients (Ca, K, Mg, Na, Al) mostly show great differences between the un-weathered and weathered sediments. The concentrations of calcium, potassium, magnesium and sodium in the sediments decrease from the un-weathered to the weathered levels in the section: Calcium varies by c. 100-fold [from 3355 to 32.3 mg/kg; the high calcium concentration at the bottom of the section could be related to calcareous concretions and/or carbonate-cementation (see

Al	As	Ca	Fe	K	Mg	Mn	Na	LOI	Groundwater type
mg/l (water) mg/kg (soil)	mg/l	mg/l (water) mg/kg (soil)	mg/l	mg/l (water) mg/kg (soil)	mg/l (water) mg/kg (soil)	mg/l	mg/l (water) mg/kg (soil)	%	
1994	NM	32,3	NM	137,9	15	NM	15,89	4,06	Not applicable
40	NM	3355,1	NM	174,1	346,3	NM	31,39	1,77	Not applicable
0,0050	0,0460	107,00	3,30	5,20	20,50	3,820	13,10	NM	Ca-Mg-HCO_3
0,0050	0,0200	84,60	0,34	4,15	13,80	2,780	10,60	NM	Ca-HCO_3
0,0050	0,1300	80,00	0,02	4,10	12,60	2,110	12,00	NM	Ca-HCO_3
0,0050	0,0485	87,00	2,56	4,80	15,00	3,000	14,00	NM	Ca-HCO_3
NM	NM	NM	NM	NM	NM	NM	NM	NM	NM
0,0050	0,0140	25,20	0,75	3,25	15,40	1,480	9,95	NM	Mg-Ca-HCO_3
0,0050	0,0150	27,40	0,36	2,70	15,10	1,460	9,50	NM	Ca-Mg-HCO_3
0,0050	0,0550	28,00	4,86	3,70	16,00	3,000	12,00	NM	Ca-Mg-HCO_3

Table 5. The Nauta Formation (comparison of soil geochemistry from "II-S5; paper II (*) near W4 and groundwater geochemistry from the same well (**)).

Samples	Depth	pH-field	pH-lab	Hardness-lab	HCO3-lab	DOC	Cl	SO_4
Unit	m			$mgCaCO_3/l$	mg/l	mg/l	mg/l	mg/l
Weathered Soil near W4	0,2	NM	3,78	NM	NM	NM	NM	NM
Un-weathered Soil near W4	10,1	NM	1,93	NM	NM	NM	NM	NM
Groundwater in W4_oct 2001	*c.15m*	4,50	5,30	NM	9,38	NM	45,30	0,50
Groundwater in W4_jan 2002	*c.15m*	5,60	4,60	28,00	13,40	1,00	55,20	0,50
Groundwater in W4_may 2002	*c.15m*	4,20	4,50	21,00	5,00	NM	56,40	0,50
Groundwater in W4_aug 2002	*c.15m*	4,58	4,30	22,00	7,48	NM	56,40	0,50

(*) Soil samples from II-S5 (paper II-Section 5) come from km 3,55, Nauta-Iquitos Road (S4°29'31", W73°35'52"; Rebata et al. 2006b).
(**) Groundwater well located in the inner yard of the "Nuestra Señora de Loreto" Primary and Secondary School , Nauta (W4; UTM coordinates: 658087 E, 9501790 N).
NM: Not measured

paper I)], magnesium about 20-fold(from 346.3 to 15 mg/kg), sodium around 2-fold (from 31.39 to 15.89 mg/kg), but potassium only slightly (from 174.1 to 137.9 mg/kg). In contrast, aluminium concentrations increase c. fifty-fold from the un-weathered (40 mg/kg) to the weathered sediments (1994 mg/kg). The LOI of the sediments also increases from 1.77 to 4.06% from the bottom to the top of the section.

The groundwaters in this geological unit, studied in wells at two sites (IV-W1 & IV-W2; see Fig. 3 for location) are neutral in pH (6.7–7.6) and in a similar manner to the fossiliferous members of the Pebas Formation show high concentrations of arsenic (14–130 µg L^{-1}), iron (0.02–4.86 mg L^{-1}) and manganese (1.46–3.82 mg L^{-1}). However, in contrast to the fossiliferous members, waters here are high in hardness (131–285 mgCaCO3 L^{-1}) and chloride concentrations are lower (from less than 1 to 3.24 mg L^{-1}). In addition, the waters have total and faecal coliform bacteria. The water type for this formation is Ca-(Mg)-HCO_3.

The high content of Mn, especially in wells W1 and W2, which are emplaced in the upper member of the Pebas Formation, are explained by their location on the modern Marañón River floodplain, where river water easily infiltrates into the wells via the sediments. Likewise, the mostly sandy Quaternary fluvial floodplain deposit cover provides a rapid path for the river water to penetrate into the aquifers. River infiltration in wells W1 and W2 is further supported by the presence of coliform bacteria in the water, and sharp seasonal changes in the ion concentrations (e.g. observed in iron).

3.2.3. The Nauta Formation

The soil geochemistry of this formation was studied from site II-S5 (see Fig. 3 for location); un-weathered sediments correspond to 10.1 m depth, whereas weathered sediments correspond to 20 cm depth (see Fig. 16 in paper **II** for a detail log of the section). In contrast to the upper member of the Pebas Formation, the Nauta sediments increase in pH from the un-weathered to the weathered levels, although the sediments are extremely acid in pH (from 1.93 to 3.78). On the other hand, all easily leachable nutrients decrease in concentration from the bottom to the top of the section: calcium from 6.1 to 1.5 mg/kg, potassium from 47.4 to 35.4 mg/kg, magnesium from 14.6 to 2 mg/kg, sodium from 2.72 to 0.4 mg/kg, and aluminium from 1001 to 557 mg/kg. LOI also decreases from 8.9% in the un-weathered sediments to 2.52% in the weathered topmost levels of the section.

Groundwater from this formation was studied from one well at site IV-W4 (see Fig. 3 for location) and is acid in pH (4.2–5.6). This water has high concentrations of nitrate (45.9–50 mg L^{-1}), aluminium (300–609 µg L^{-1}), chloride (45.3–56.4 mg L^{-1}), manganese (0.32–0.4 mg L^{-1}) and sodium (24.2–38 mg L^{-1}), and low hardness (21–28 mgCaCO3 L^{-1}). The water type in this well is Na-(Ca)-Cl-NO_3 and the water contains non-typical faecal coliform bacteria.

Groundwaters from well W4 (in the Nauta

Al	As	Ca	Fe	K	Mg	Mn	Na	LOI	Groundwater type
mg/l (water) mg/kg (soil)	mg/l	mg/l (water) mg/kg (soil)	mg/l	mg/l (water) mg/kg (soil)	mg/l (water) mg/kg (soil)	mg/l	mg/l (water) mg/kg (soil)	%	
557	NM	1,5	NM	35,4	2	NM	0,4	2,52	Not applicable
1001	NM	6,1	NM	47,4	14,6	NM	2,72	8,9	Not applicable
0,4590	0,0050	8,10	0,05	6,10	1,92	0,320	24,20	NM	Na-Ca-Cl-NO_3
0,3000	0,0050	7,70	0,13	9,40	1,60	0,360	34,90	NM	Na-Cl-NO_3
0,6090	0,0050	5,80	0,01	9,10	1,55	0,380	37,00	NM	Na-Cl-NO_3
0,5690	0,0050	4,90	0,01	9,80	1,70	0,400	38,00	NM	Na-Cl-NO_3

Formation) are extremely low in pH (as low as 4.2), poor in dissolved solids, and have especially low contents of Ca and Mg (means 6.6 & 1.69 mg/l, respectively) (reflecting the lack of fossils in this formation). Aluminium concentrations in the Nauta successions are the highest (up to 609 µg/l), which is readily explained by the kaolinitic-rich clays typical of this formation. Kaolinite is dissolved and/or transformed into illite and Al chlorite, with the release of aluminium into the Pebas system due to the low pH. High nitrate contents (up to 50 mg/l) in well W4 are probably a result of anthropogenic contamination. Sharp seasonal changes in nitrate concentrations are related to their flushing from the soil surface into the aquifer during the rainy season. The presence of faecal coliform bacteria further supports the anthropogenic contamination in the waters of this well.

4. DISCUSSION

4.1. Palaeoenvironmental reconstruction of Late Miocene Western Amazonia

4.1.1. Tidally-influenced, shallow brackish-water embayment

The Pebas epicontinental embayment comprised transgressive-regressive bay-margin successions, including shoreline, disoxic distal bays, delta/channel facies and freshwater swamps and lagoons. The Pebas system became more restricted and channelized upwards in the stratigraphy (from its fossiliferous members to its upper member). The upper member of the Pebas Formation shows a backstepping progradation of the shoreline with deposition in subaqueous tidal flats/shoals through intertidal flats to muddy to sandy shorefaces. Tidal point bars and minor runoff creeks were common in estuaries scattered along the palaeo-coastline, with palaeosoils fringing the estuaries.

The main palaeo-depositional environment for the Pebas Formation is interpreted herein as that of a shallow, brackish-water tidally-influenced epicontinental embayment in agreement with some previous research (Gingras et al., 2002a,b), but in disagreement with other research interpreting the Pebas palaeo-depositional environment as a long-lived system of freshwater lakes/wetlands affected only intermittently by marine incursions (e.g. Hoorn et al., 1995; Vonhof et al., 1998, 2003; Wesselingh, 2006; Wesselingh et al., 2002, 2006).

Nevertheless, both interpretations need not be at odds with each other, because mostly the overall shallow sub-aqueous setting, flat Amazonian topography, the influence of Andean dynamics and sea-level changes combined to form a complex scenario where small rises in the relative sea level caused extensive marine incursions into the continent that created brackish-water conditions in most embayed coasts. Meanwhile, subsequent regressive progradational coastlines allowed freshwater to advance into the system and create a superimposed, predominantly freshwater-dominated depositional setting. These alternations repeatedly occurred during the whole depositional time frame of the Pebas Formation (c. 23–10 Ma), allowing the preservation of its common brackish and freshwater successions (see Hovikoski et al. (2007) for further elucidation of the Pebas regional scenario).

4.1.2 Tidally-influenced channel complex

The change from the Pebas to the Nauta Formation is a transitional one, and as such, their palaeo-depositional environments are very much alike. The Nauta Formation represents a less restricted depositional setting than the Pebas Formation, although still a paralic one. The abundance of channelized successions allows the interpretation of the Nauta Formation as representing a tidally-influenced channel complex or complexes that probably developed in the inactive parts and/or abandoned channels of delta plains fringing the shallow epicontinental embayment. The estimated Nauta Formation depositional frame is much shorter (c. 10–8 Ma), and its lateral continuity is less extensive than the transcontinental Pebas Formation. This is explained by its superficial position, which has caused it to be widely eroded. The erosional rests are not well mapped in Peruvian Amazonia.

4.2. Groundwater characteristics

The groundwaters in the Pebas Formation are highly reducing and low in pH. The high organic content (lignite) in the sediments is reflected by the comparatively high DOC (dissolved organic carbon) in the waters. The decay of the organic matter under reducing conditions favours the reduction of iron, which in turn is linked with elevated concentrations of arsenic in the Pebas groundwaters. Further studies on the regional concentration and distribution of arsenic in groundwaters in the study area are recommended, in view of the potential toxic effects of the high arsenic concentrations observed in the study area (up to 130 μg/l). High iron concentrations are also related to high manganese contents in the waters. The upper member of the Pebas Formation has high calcium and magnesium concentrations, which reflect the carbonate cementation observed in these beds. Comparatively high sodium and chloride contents in the groundwaters from the Pebas Formation may indicate a marine influence, thus supporting the sedimentological and ichnological evidence.

The groundwaters in the Nauta Formation, only studied in one well (W4), are acid in pH (mean 4.7) and show high aluminium concentrations related to the kaolinite clays characterising this formation. High nitrate concentrations and the presence of faecal coliform bacteria indicate anthropogenic contamination. Comparatively high sodium and chloride contents may allow the interpretation of this formation, based on groundwater geochemistry, as the most marine influenced when compared with some of the wells emplaced in the Pebas Formation.

5. CONCLUSIONS

The late Early to Late Miocene Pebas Formation is characterised by up to 10-m-thick heterolithic upward-fining or coarsening parasequences. Individual Pebas parasequences are typically capped by lignites and/or mollusc-rich layers, except for the upper member of this formation, which lacks both the lignites and fossils; however, organic-rich muds are locally preserved. The Pebas mollusc fossil fauna has been reported as mainly developed in freshwater conditions, while widespread moderate- to low-diversity, rarely high-diversity trace fossil assemblages indicate brackish-water conditions, especially in the base of Pebas parasequences. However, this apparent discrepancy can be readily explained by the palaeodepositional setting of the Pebas system. This was a tidally-influenced, shallow brackish-water embayment closely interbedded with and restricted by continental settings. In detail, the Pebas system can be thought of as a complex association of marginal marine, transgressive-regressive bay-margin successions, where the tidal influence was important, and increasingly more channelized towards the end of the Pebas deposition. Forests floors, swamps, lakes and river channels were also present in the hinterland. The presence of freshwater molluscs in the same beds where the ichnological characteristics of the beds indicate brackish-water conditions can be explained by the occurrence of several tens of widespread, shallow, restricted and repetitive ingressions shaping the continental margins of Western Amazonia during the Miocene. The hydrogeochemical characterisation of the Pebas successions provides an additional insight, as the comparatively high sodium and chloride contents in the groundwaters from these successions may indicate a marine influence, supporting the sedimentological and ichnological evidence. In detail, the groundwaters in the Pebas Formation are highly reducing and low in pH. The decay of organic matter under reducing conditions favours the reduction of iron, which in turn is linked with elevated concentrations of arsenic in the Pebas groundwaters. The upper member of the Pebas Formation has high calcium and magnesium concentrations, which reflect the carbonate cementation observed in these beds.

The Late Miocene Nauta Formation is characterised by up to 7-m-thick heterolithic successions, especially including tidally-dominated, inclined heterolithic stratification and mud-draped trough cross-stratified sands. Overall, the Nauta sands are coarser-grained than the Pebas sands, although mud-dominated successions are more abundant in the Nauta system, especially observed in the characteristic brecciated textures exposed by mud blocks/balls with a sand matrix in the inclined stratification. In a similar way as in the Pebas system, trace fossil assemblages in the Nauta IHS channels support brackish-water conditions. The Nauta palaeodepositional setting is interpreted as a tidally-influenced, estuarine channel complex or complexes developed in the inactive parts of abandoned delta plains. Groundwaters in the Nauta Formation are acid in pH (mean 4.7) and show high aluminium concentrations related to the kaolinite clays characterising this formation. The comparatively high sodium and chloride content may allow the interpretation of this formation, based on groundwater geochemistry, as the most marine influenced when compared with some of the wells emplaced in the Pebas Formation.

In summary, the main conclusion of this study is that the documented Pebas and Nauta successions were not deposited in wholly continental settings. Evidence presented in the four papers forming part of this thesis supports the interpretation that these successions were deposited in a tidally-influenced, coastal margin system, possibly affected by semi-diurnal tides and exhibiting a microtidal range. In detail, the low-diversity and diminutive trace fossil suites characteristic of the Pebas and Nauta successions reflect widespread brackish-water conditions. The contrast of these successions with the rare nonmarine deposits and their continental trace fossil suites further supports the predominance of at least some marine influence on sedimentation. Additionally, the nature of the IHS (both horizontal and inclined), and their rhythmicity at various scales clearly indicates that tidal cyclicity was a persistent factor in sedimentation. This demonstrates that Miocene sedimentation in Amazonia must have been part of an epicontinental seaway system.

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