Sediment–water interaction, acidity and other water quality parameters in a subtropical setting, Pimpama River, southeast Queensland

M. Preda · M.E. Cox

Abstract The geological setting and landuse activities of the Pimpama River catchment are typical for many drainage systems in southeast Queensland. The river originates in coastal ranges of Late Paleozoic age, crosses a floodplain developed during the Late Pleistocene-Holocene sea-level fluctuations and flows into the southern part of the Moreton Bay. The formation of sedimentary pyrite associated with the mid-Holocene transgression is an important feature of this coastal setting. The oxidation and hydrolysis of pyrite and the consequent production of sulfuric acid are controlled by the amount and seasonality of rainfall and influenced locally by landuse activities. The acid production and the leaching of dissolved metals from river alluvium and estuarine sediments impact substantially on land and aquatic habitats. The water quality of the Pimpama River and its tributaries reflects the lithology of the bedrock and can vary largely depending on season, tidal regimes, sediment lithology, local topography and agricultural activities. Monitoring of river water for several seasons revealed four types of events, each with a different response in terms of water quality: (a) occasional showers during the dry season cause low pH and high amounts of dissolved metals in the water, (b) the first heavy rain of the wet season can produce very toxic conditions (low pH and high concentrations of metals) that can result in a fish kill, (c) towards the end of the wet season, prolonged flushing of pyrite oxidation products leads to short-term recovery of the aquatic system (neutral pH and lower amounts of dissolved metals in the water) and (d) a flood event can produce low pH, salinity and high concentrations of metals, which can represent lethal conditions for aquatic life. Assessment of saturation indexes for representative weathering and oxidation products such as clays, goethite, gibbsite and jarosite shows that these mineral phases can precipitate only when the water reaches neutral pH.

Key words Water quality · Acid sediments · Mineral solubility · Estuarine plain

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Introduction

The catchment of the Pimpama River is typical of many eastern Queensland river systems, in terms of geomorphology, geology and landuse. The headwaters rise in heavily timbered ranges and the central course passes through foothills with a mixture of small farms and sparse residential areas. The lower course enters the floodplain and is heavily modified by a variety of small farms, residential pockets and extensive sugarcane production. The physical setting of the lower river and its history result in certain features of water quality that have now been shown to be characteristic of such environments. To understand the variations in water quality, sampling programs were conducted throughout the catchment during different seasons. The results obtained from these programs have been assessed to consider in particular the relationship between chemical composition of the water and different influencing factors such as (a) lithology of the bedrock and alluvium, (b) rainfall patterns, and (c) landuse. A specific feature that is considered is the production of acidic conditions in streams and in adjacent sediments.

Study area and physical setting

Location

The Pimpama River is located 80 km south of Brisbane, in southeast Queensland, and drains a catchment of approximately 100 km^2. The river originates in Darlington Ranges at an elevation of 300 m and flows eastwards along a 30-km course, discharging into the southern part of Moreton Bay (Fig. 1). The main tributary is Hotham Creek which joins the Pimpama River on the floodplain, 7 km from its mouth. The lower course of the Pimpama River develops into a large estuary in which a low-lying mud-sand island, Woogoompah Island, has formed; the mouth of the river is protected from the open ocean by sand dunes which form South Stradbroke Island. The lower 12 km of this drainage system is tidal.

Geological setting

The geological materials which form the area consist of two main groups: (a) basement rocks of Late Paleozoic to Early Mesozoic age, and (b) unconsolidated deposits of the coastal plain, laid down during sea-level fluctuations of the Late Pleistocene–Holocene periods.

Bedrock

The Paleozoic rocks are represented by Carboniferous age flysch-type metasediments deposited on the continental slope and the adjacent abyssal plains of the Late Paleozoic continental margin; these sediments were folded and metamorphosed to greenschist facies in the Early Carboniferous period (Day and others 1983). Various types of sandstones interbedded with shale and chert constitute the main formation, the Neranleigh-Fernvale Beds (Lohe 1980), which forms the basement of the entire catchment and is exposed in the Darlington Range to the west of the floodplain. In the Pimpama headwaters, greywacke is the dominant rock type exposed and it is massive, moderately foliated and contains quartz, K-feldspar, plagioclase, and hornblende (Cooper 1979; Lohe 1980).

Drilling to the basement on the floodplain shows that the eastern one third is underlain by Triassic–Jurassic age sedimentary rocks such sandstone, siltstone, and conglomerate. These sequences apparently conformably overlie the Neranleigh-Fernvale Beds and were intersected at a depth of approximately 40 m in the very east of the floodplain (D. Lockhart, unpub. data). Peripheral to the shoreline, there are limited outcrops of conglomerate which represent localized basement highs of these younger sequences, such as immediately west of the village of Jacobs Well and at location 6 on the Pimpama River (Fig. 1). The general form of this geological setting is of a large embayment, now filled with unconsolidated material.

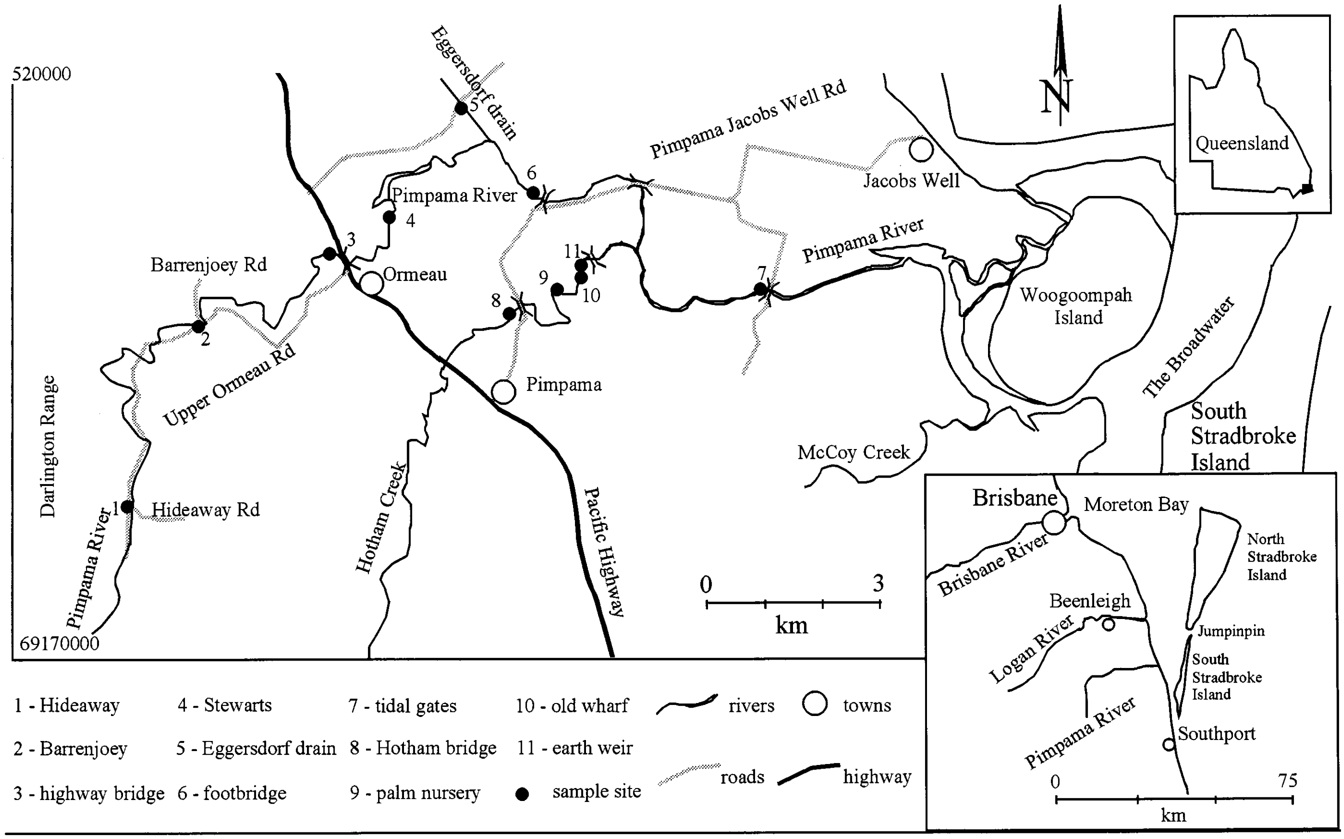

Fig. 1
Study area and sample locations

Quaternary deposits

The overlying sedimentary materials are comprised of fluvial gravels, marine sands, and estuarine clayey sands or sandy clays, which were deposited in the last several thousands of years as a result of sea-level fluctuations and changing estuarine and fluvial regimes. Important in this variability is the fact that about 6000 years ago sea-level was approximately 1 m higher than at present (Stephens 1992). The recent deposits of fluvial origin represent weathering products of the Paleozoic bedrock and their lithological character has the signature of the parent rocks. The marine sands of the floodplain are largely formed of quartz with scarce heavy minerals; it is accepted that they are reworked terrestrial material that has been moved northwards by longshore currents (Stephens 1992) and deposited on the coastal plain during the Holocene transgression. The clays occurring within the alluvium of the catchment as a whole are largely kaolinite, illite and smectites, the later being often randomly mixed with illite (Preda and Cox 1999). The speciation of these clay minerals is, however, not solely influenced by bedrock composition but also by the chemical character of the aqueous system they have deposited from. An important lithological feature of Holocene history here is the formation of sedimentary pyrite, the oxidation of which and subsequent production of sulfuric acid represents one of the main environmental issues of the area.

Features that influence water quality in the drainage system

Oxidation of sedimentary pyrite

In general terms, over the last 6000 years, Holocene sedimentation has kept pace with sea-level fluctuations and has formed a broad, stable tide-influenced zone. This type of setting has provided the required conditions for iron sulfide accumulation on many of the world's coastal plains (Dent 1986) and in the Pimpama area. As the sea-level fell to its present position, the onshore sediment supply resulted in the closure of ancient Jumpinpin bar (Fig. 1), between North and South Stradbroke Islands (Kelly and Baker 1984), which limited wave action and the tidal influence. In the late 1800s, a series of cyclones breached this bar, resulting in flooding of low-lying areas for the second time in the Late Holocene. This opening provided a new opportunity for pyrite accumulation in the tidal section of the Pimpama River system.

The growth of pyrite crystals requires sources of sulfur, iron and the presence of organic material. Specific anaerobic bacteria can decompose organic matter and reduce sulfate (SO_4^{2-}) from seawater contained in sediment pore space to sulfide. Iron is supplied by detrital ferrous phases occurring as concretions, coatings or adsorbed by clay minerals. The most reactive iron compounds are very fine-grained oxides such as goethite (FeOOH) and hematite (Fe_2O_3) (Berner 1971, 1984; Rickard 1973). Hydrogen sulfide (H_2S) is produced by the reduction of sulfate followed by reaction with iron phases to form metastable iron sulfides which are then converted to pyrite. This series of reactions is now well documented for a range of coastal settings (Berner 1971, 1984; Rickard 1973; Lord and Church 1983; Raiswell and others 1993). The iron sulfides formed are stable under undisturbed anoxic conditions; however, when exposed to oxidizing conditions the following chain of chemical reactions that produce sulfuric acid is triggered (Nordstrom 1982; Bierens De Haan 1991):

$$FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2H^+ + 2\ (SO_4)^{2-} \tag{1}$$

$$Fe^{2+} + 1/4\ O_2 + H^+ \rightarrow Fe^{3+} + 1/2\ H_2O \tag{2}$$

$$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 16\ H^+ + 2\ (SO_4)^{2-} \tag{3}$$

Equation (1) shows that the initial driving force for pyrite decomposition is the oxygen from air or water. As the pH drops due to release of H^+, the concentration of ferric iron increases as in Eq. (2), and this phase then becomes the most important oxidizing agent. The sequence continues with major production of acid in Eq. (3). A comparison of Eqs. (1) and (3) shows that ferric iron is more efficient in terms of acid production than oxygen. In addition to this, the inorganic rate of oxidation can be speeded up five or six times if the reactions are catalysed by microorganisms such as *Thiobacillus*. These bacteria commonly play an active role at a pH around 4 by increasing the oxidation rate of ferrous to ferric iron (Nordstrom 1982) and therefore, in the rate of acid production.

Seasonal regime of rainfall

Another important factor that has been found to influence water quality of the drainage system is the regime of rainfall. The climate here is subtropical humid with a hot wet summer and a mild dry winter. On the coastal plain the average precipitation is 1300 mm, increasing westward to 1600 mm in the ranges (Bureau of Meteorology 1983). About 70% of this rainfall occurs during the summer wet season, from November to April (Fig. 2). Rainfall influences water quality directly by increasing suspended material and dissolved ions after storms, but this is usually a short-lived phenomena. However, the most significant aspect is that rainfall amount and periodicity control the reactions of hydrolysis which take place in the pyritic layers, and finally the fate of oxidation products. It was observed that during a long, dry period there is continual build up of pyrite oxidation products such as acid, sulfates, iron, and other metals in pore waters. These products can be adsorbed within the structure of clays that host the pyrite, or they can be scavenged by iron during the formation of pyrite. With occasional showers during a dry period water infiltrates rapidly and can partially leach these phases into the rivers with noticeable reduction of water quality. The first heavy rain of the subsequent wet season, or a flood, are critical events when large quantities of released iron, aluminum and other toxic metals are flushed into the rivers,

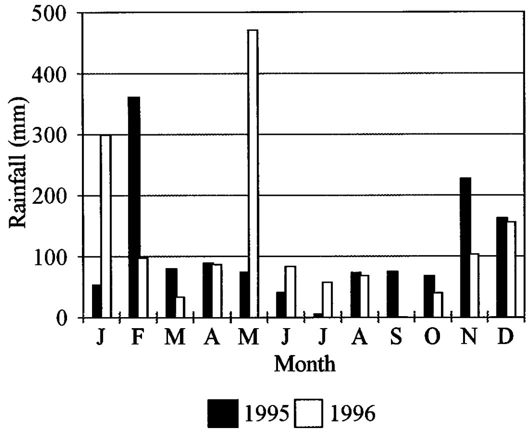

Fig. 2
Rainfall records for 1995 and 1996, the period of the study. The recording position is the palm nursery on Hotham Creek (location 9)

often with a substantial impact on the aquatic habitat. Prolonged rainfall causes high volume flushing of oxidation products and the drainage system is able to reestablish non-toxic conditions. The effect of tidal flushing and the buffering capacity of estuarine marine water also assist natural remediation of these rainfall-related fluxes.

Landuse

During extended dry periods, the production of acid is increased due to lowering of the water table and the consequent increased volume of sediment available for oxidation. However, the major cause of acidity in such coastal settings is related to the range of landuse activities that physically disturb and expose the pyritic layers. The coastal plain of the mid-lower Pimpama catchment was extended as a sugarcane growing area by the development of a flood mitigation scheme to limit the area affected by tidal flooding. Drainage canals were dug between the Pimpama and Logan Rivers (Fig. 1) and a tidal gate was constructed on the Pimpama River (location 7: Fig. 1). One of the largest canals built recently is Eggersdorf drain (location 5: Fig. 1) which became an artificial tributary of the Pimpama River and connects the Pimpama by drain networks to the Logan River in the north. During winter, stream input from the upper Pimpama River can in fact cease at the junction with the Eggersdorf drain. Under these circumstances, the lower course of the river is then supplied mainly by tidal waters that enter the drainage system through two paths, (a) the Pimpama mouth from the east, and (b) Eggersdorf drain from the north. In addition to this, the flow regime on Hotham Creek has also been modified by an earth weir (location 11: Fig. 1) which restricts direct upstream migration of salt water in the creek enabling cultivation of the adjacent land.

Sampling and analytical methods

Sampling sites

A number of water quality surveys were conducted throughout the catchment during different seasons. To provide an understanding of the character of each sampling location, the main features are summarized in Table 1. As the rainfall regime and the tidal fluctuations have an important influence on water quality, these characteristics were also recorded each time a water quality survey was carried out (Table 2).

Table 1
Sampling sites and their morphological and lithological features

Site	Main features
1	Steep valley (1–3 m wide, 10–50 m deep), cobble river bed with thin layer of clays, undisturbed bushland
2	Moderate slope valley, silty river bed (2–3 m wide), bushland and pastures
3	Beginning of the floodplain, meandering channel (3–6 m wide), alluvium and silty sand deposits, partly cleared for pastures
4	Shallow, narrow river bed (1 m wide), swamps, silty alluvium, edge of sugarcane
5	Supplies water during the dry season, steep sides due to tides (2–3 m wide), silty and clayey river bed, pyrite-rich sediments on river banks, sugarcane
6	enlarged artificially mid-1960's (3–4 m wide), steep sides with clayey pyrite-rich sediments on river banks, outcrop of Triassic conglomerate, animal farms and sugarcane
7	Wide and deep river (20 × 4 m), silty and sandy banks, mangroves on banks
8	Narrow, shallow river with pyritic clays on banks (3 m wide), nil flow during dry season, sugarcane and cattle grazing
9	Shallow and narrow meander (3–4 m wide), pyritic clays, palm nursery using river water for irrigation, grazing
10	Cliff of chert (Neranleigh-Fernvale Beds), wider river (up to 10 m)
11	Wide and deep creek (5 × 2 m), silty sediments rich in pyrite, during wet season overflow above the earth weir level, sugarcane, grazing area

Table 2
Rainfall and tidal influence at the time of sampling

Date of sampling	Days after x mm of rain	Tides
6/95	6 days/25 mm	Low tide
8/95	1 day/40 mm	High tide
10/95	1 day/4 mm	Low tide
12/95	1 day /30 mm	High tide
3/96	1 day/10 mm	Low tide
5/96	10 days/50 mm	High tide
9/96	16 days/45 mm	High tide

Analytical methods

At each sample location, pH and salinity were measured mid-stream using a field water testing meter. Samples of water for cation analyses were collected in polyethylene bottles aged in nitric acid for at least 4 days; samples for anion analyses were collected in non-acidified bottles. The water samples were not filtered.

Cations and sulfate were analyzed using inductively coupled plasma emission spectroscopy (ICP). The ICP was calibrated against appropriate standards and against a blank prepared with nitric acid. The chloride was determined by Mohr titration with 0.1 M $AgNO_3$, and the alkalinity as HCO_3, by titration with 0.02 N Standard HCl following procedures described in Greenberg and others (1992).

Solubility modelling

The saturation state of the water for a number of common mineral phases occurring in silty sediments was calculated using PHREEQC, a computer program based on an ion-association aqueous model (Parkhurst 1995). PHREEQC has capabilities for speciation and saturation-index calculations (SI); SI is expressed as a ratio between the ion activity product (IAP) and the solubility product (K) of the phase's components: $SI = \log(IAP/K)$. For $SI = 0$, there is equilibrium between the mineral and the solution. Where $SI > 0$ reflects supersaturation of the water sample in respect to a mineral phase and the mineral can precipitate; $SI < 0$ indicates undersaturation and a condition where the mineral phase may be dissolved (Appelo and Postma 1994).

Observed variations in water quality

The most representative results for the different sites and times are presented in Appendix 1 and 2. In Appendix 1 the analytical results are listed by site number and in Appendix 2 they are grouped by relative amounts of rainfall (i.e. wet or dry seasons).

Variations in pH and salinity

Pimpama River

The freshwater section of the Pimpama River (sites 1–4) has salinities ranging between 170 and 320 mg/l and neutral pH. These low salinity waters are, however, of a dominant Na-Cl composition, which is a result of local precipitation containing aerosols of marine origin.

The saltwater input in the tidal section of the drainage system (sites 5–7) varies greatly. The input is difficult to assess because there is influence from two sources: Eggersdorf drain which is linked to the Logan River to the north and the Pimpama estuary. Rainfall can also have an immediate or a long-term effect by influencing the chemical composition and pH fluctuations of the water. For example, at site 7 (upstream of tidal gates) the salinity can be 30 000 mg/l in conditions of high tide, but can decrease to 3000 mg/l after heavy rainfall. At site 5 (Eggersdorf drain) the salinity is usually between 10 000 and 20000 mg/l, but can drop below 10 000 mg/l during wet periods when tidal waters coming in from the Logan River are pushed back by freshwater and the flow in the drain is subsequently reversed.

Monitoring of the sites, in particular 5–7, enabled the acid-production sequence to be observed. At the beginning of the dry season, for example, June 1995, the acid started to build up in the sediments adjacent to drains and rivers. The tidal effect initially offset the seepage of acid pore-waters into the river and the pH was maintained at 5 to 6. During 1995, drought conditions prevailed and the only significant rain in August (40 mm) was on the night before sampling; the impact of this rainfall is clearly reflected by the low salinity measured at sites 5 and 6 even during high tide. The acid stored in the sediments was consequently flushed into the river and the pH fell to less than 4. At the tidal gates (site 7) the mixing with salt water buffered the acidity and the pH was higher (6.2). By October 1995, a substantial volume of acid had been produced and leached into the rivers and the tides were more or less able to buffer it. At site 5, the pH was 4.9 under conditions existing at low tide, while at site 6, the incoming tides increased the pH to 6.2. These observations suggest that the buffering capacity of estuarine high tides is effective in conditions of low-level discharge of acid. Note that the measurements in October 1995 were conducted one day after several millimetres of rain (Table 2).

The beginning of the wet season was marked by heavy rain at the end of November 1995. By mid-December, even under conditions of high tide, the salinity was still very low due to the large input of freshwater and the low pH reflects the rapid discharge of acid from bank sediments. Towards the end of the wet season, neutral pH reestablished due to the prolonged rainfall which had flushed much of the acid produced in the sediments during dry conditions. This condition is reflected by the measurements conducted in March 1995, when neutral pH dominates despite rainfall one day before sampling and low-tide conditions.

The dry season of 1996 had higher rainfall than 1995, and notably resulted in the floods in May (Fig. 2); the values of both salinity and pH during September 1996 reflect the difference between these two years. The flood event in May 1996 (see Appendix 2) occurred at the end of the wet season and produced a different response to the pattern described above. The floods, triggered by more than 400 mm of rain in a week, caused a substantial drop in salinity and pH, even in well buffered locations such as the tidal gates (site 7). Two weeks after the event and at high-tide, low salinity and pH persisted in the lower Pimpama River. This sudden flood-related change in the system shows that the production of acid is not diminished during the wet season, rather it is masked by dilution; high rainfall and associated high stream discharge and runoff can mobilize in addition the oxidation products.

Hotham Creek

The smaller drainage of Hotham Creek is fresh for most of its course, down to the earth weir (site 11), 0.9 km from the junction with the Pimpama River. The weir is very effective in restricting the tidal influence and causes a substantial difference in water quality between the up- and downstream sides. Upstream of the weir, the salinity is typically between 1000 and 2000 mg/l but hundreds of metres upstream (between site 9 and 10) salinities can be up to 10 000 mg/l. This local increase in salinity occurs only during the dry season and is due to the leaching of salts from a low-lying area between meanders which was a supra-tidal swamp before the construction of the Pimpama tidal gates. Immediately downstream of the weir the salinity can vary largely (10 000–20 000 mg/l) depending on tides and the pH is greater than 5. Due to the absence of buffering by tides above the weir, the creek has a pH of approximately 3 throughout the dry season. Such low values confirm that a relatively freshwater environment can be at least, or even more acid-productive than a tidal-influenced setting, and that the history of sedimentation is an important factor. In Hotham Creek, only a prolonged period of rainfall can increase the pH to neutral levels after a dry period. As with the Pimpama River, the floods decreased the salinity and pH to very low levels (330 mg/l and 4.8, respectively).

Variations in metal content of river waters

Pimpama River

In the upper Pimpama River, the uniform presence of low levels of Fe, Al and Mn and the limited seasonal variation of metal content suggest that they are derived from the Palaeozoic bedrock. Higher amounts of Al and Fe (site 3, December 1995) are produced by normal, slightly acid rain percolating through soils and sediments and not by pyrite oxidation.

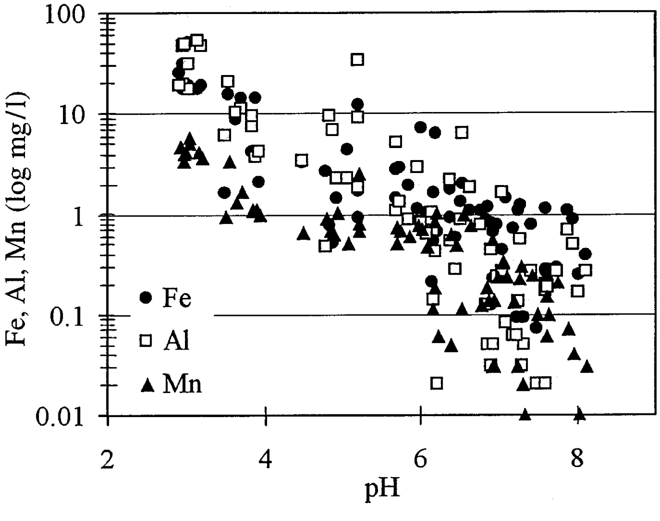

Fig. 3
Variation of metals Fe, Al, Mn compared with pH in river water on a semi-logarithmic plot. The highest values are associated with low pH for both the main river and its tributary

In the tidal Pimpama River, the high levels of major elements such as Na, K, Mg and Ca largely reflect the tidal influence and it is difficult to assess how much is leached by acid from sediments. Other metals such as Fe, Al and Mn show a clear relationship with pH and are released in greater amounts during "acidic" episodes. The highest values for these metals were recorded at the peak of the dry season (August 1995), during the floods (May 1996) and at the beginning of the wet season (December 1995), all periods of low pH (Fig. 3). An extreme example of metal release is site 6; here, one day after 40 mm of rain and at high tide, the river water contained Fe = 13.8 mg/l, Al = 11.0 mg/l and Mn = 1.7 mg/l. In comparison, background values for these metals measured in the freshwater section are typically: Fe = 0.07–1.7 mg/l, Al = 0.02–2.0 mg/l and Mn = 0.03–0.12 mg/l. In the open estuary, near the junction with McCoy Creek, a water sample collected in the dry conditions of August 1995 contained Fe = 0.9 mg/l, Al = 0.5 mg/l and Mn = 0.04 mg/l.

Hotham Creek

The content of Fe, Al and Mn are much higher in Hotham Creek than Pimpama River. This is not only due to the absence of tides but also local features such as land-use, low magnitude of flow and limited topography which can significantly influence the discharge rate of dissolved metals. For example, at Hotham bridge (site 8) the flow is reduced considerably during the dry season and the river channel has been enlarged and the banks disturbed. These natural and artificial changes both result in high production of acid and seepage of metals, which is here concentrated in a limited volume of water. In addition, upstream of site 8, is a hardrock quarry from which there is discharge of the fine fraction into the creek. The existence of this quarrying operation can explain the presence of high amounts of metals in August 1995 when the flow in the creek was reduced to a minimum (Fe = 49.4 mg/l, Al = 17.1 mg/l and Mn = 5.6 mg/l). Downstream, at sites 9 and 10 there is limited disturbance on the banks; on the south side of the creek is the low-lying area which is not cultivated due to the high remnant content of salts. Large amounts of pyrite are stored in such "relict" tidal flats. The continuous oxidation of this pyrite, especially during the dry season when the water table is lowered, is reflected in the water quality at these sites. Another feature of site 10 is that it is below high-tide level and the width of the creek increases. Thus, high gradient flow can induce increased seepage of metals from the adjacent pyritic sediments. At sites 9 and 10, the maximum concentrations of dissolved metals measured in stream water are: Fe = 18–30 mg/l, Al = 30–47 and Mn = 5.1–4.2 mg/l. Just upstream of the earth weir, site 11 has both fresh and brackish input, plus the tidal dilution and buffering is impeded by the weir. The highest values here were recorded in dry conditions (Fe = 17 mg/l, Al = 51 mg/l and Mn = 4 mg/l). It is of note that at site 8 the dominant dissolved metal is iron while for sites 9–11 the dominant metal is aluminum. This situation suggests different sources of these metals. Site 8 is influenced by artificial input from the upstream quarrying activity, while the other sites receive metals from the adjacent "relict" tidal flats. Overall in Hotham Creek, during wet periods, the water quality improves and the amount of dissolved metals can decrease 10–20 times.

Mineral solubility

In addition to the metals released to rivers during acidic episodes, the aqueous system also carries suspended chemical components that reflect weathering processes. The solubility of certain mineral phases was therefore examined to further identify the type of geochemical processes that may be occurring.

The saturation state of several representative mineral phases was assessed using PHREEQC. The results for six common weathering products at different locations and under wet and dry conditions are summarized (Figs. 4 and 5).

Kaolinite is the main clay mineral that has been identified throughout the catchment; montmorillonite and illite are present to a lesser extent and are usually randomly mixed (Preda and Cox 1999). This finding from X-ray diffraction analysis of sediments is reflected by the commonly occurring saturation of waters with respect to these minerals, especially in higher rainfall periods and when pH tends towards neutral. Hydroxides and sulfates such as goethite (FeOOH) and jarosite ($KFe_3(SO_4)_2(OH)_6$) are the most common pyrite oxidation products that form on river banks. Gibbsite ($Al(OH)_3$) is considered the most stable weathering phase of aluminum.

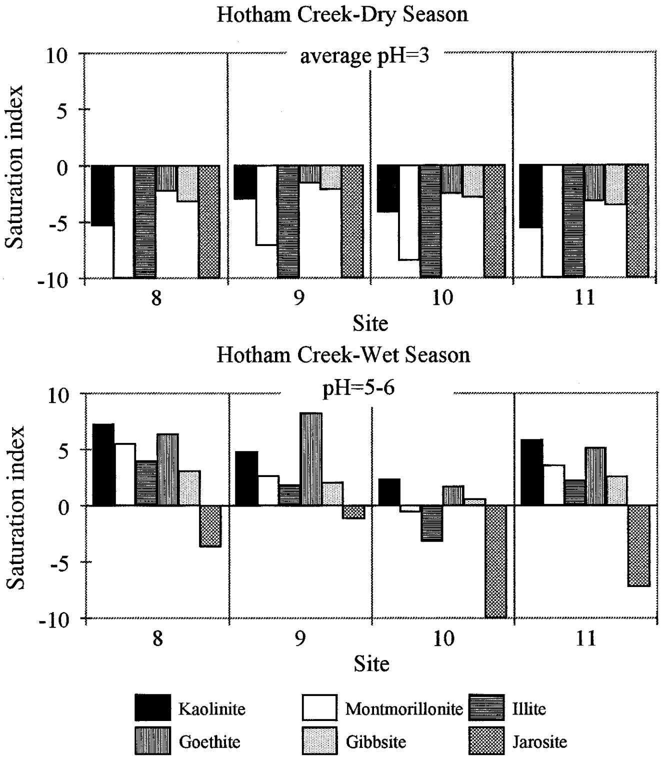

Fig. 5
The saturation indexes for major mineral phases at different sites on Hotham Creek, determined using PHREEQC

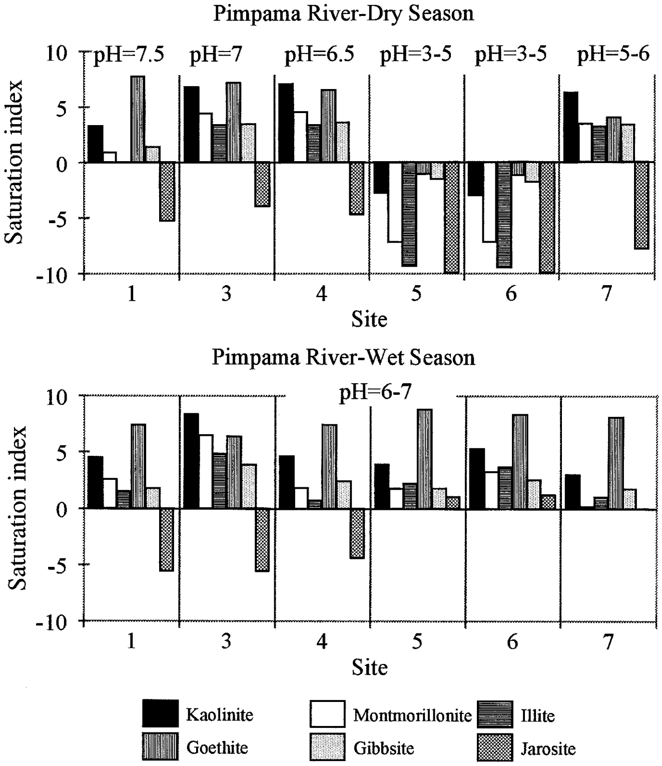

Fig. 4
The saturation indexes for major mineral phases at different sites on Pimpama River, determined using PHREEQC

The SI fluctuation for all mineral species tested is pH-dependent and is therefore indirectly controlled by season. In the freshwater section of the Pimpama River (sites 1, 3 and 4), regardless of season, the aqueous system is saturated with respect to the main clay species, plus iron and aluminum oxides, while jarosite remains undersaturated. In the tidal section of the Pimpama River and in the lower section of Hotham Creek, the SI values exhibit a distinct pattern. During a dry month when pH is low, the river is undersaturated with respect to these mineral phases and this condition enables their dissolution. The converse is usually the case during the wet season when the water is saturated with respect to most of the phases assessed and their precipitation may result. The strong tendency of iron to be mobilized, transported and deposited is reflected by the variations in goethite.

These SI plots show that the rivers are usually strongly undersaturated with respect to jarosite; the only time when jarosite saturation occurs is in the wet season, and it was identified at Pimpama sites 5–7. It should be noted that jarosite commonly forms on river banks and on heaps of excavated sediments (well developed at sites 5 and 6), and that river waters do not represent these conditions except as a result of runoff in wet periods. Such runoff can also result in the formation of some combined organic and inorganic phases. An example of this is shown in a transmission electron microscope (TEM) photograph of material collected from the surface of the wa-

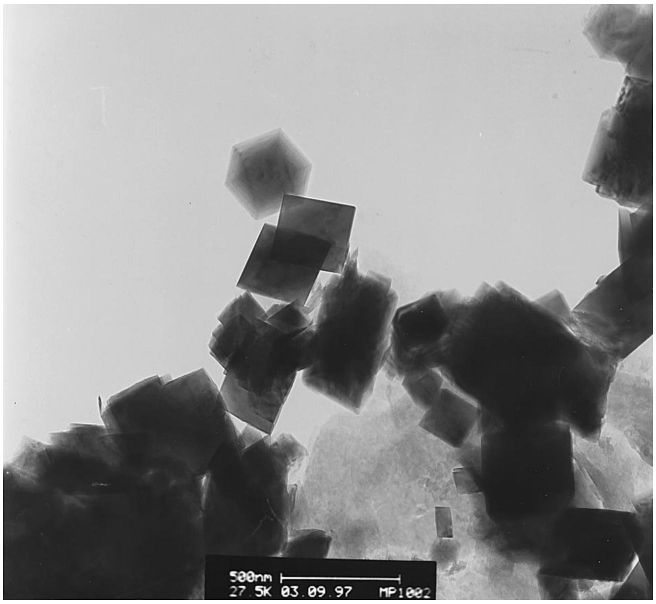

Fig. 6
Transmission electron microscope photograph of well developed crystals of jarosite and natrojarosite in material collected from the surface of river water

ter at site 6 (Fig. 6). This material is shown to be a mixture of clay particles, amorphous iron phases and well-developed crystals of jarosite and natrojarosite.

Discussion

Feldspars and their weathering products are major components of the bedrock and also dominate the composition of river alluvium and the estuarine sediments of the coastal plain. In subtropical coastal settings with abundant sedimentary pyrite, the high seasonal rainfall and the production of acid increase the rate of weathering and promote the leaching of cations from unconsolidated sediments. In such materials, kaolinite is the main secondary product of silicate weathering as its formation requires acid conditions. Tidal flooding can bring additional ions of Mg, Na and K into the system to enable ion exchange and alteration of kaolinite to montmorillonite or illite (Berner 1971).

The silicate rock-forming minerals of the basement Neranleigh-Fernvale Beds, and to a lesser extent their weathering products (clays and hydroxides) represent the main source of aluminum, iron and other minor metals found in river waters. For example, some of the titanium-rich ilmenite grains found in bedrock sandstone contain manganese (M. Preda, unpub. data). Both major and minor metals become available during weathering, particularly when assisted by acid conditions, and can be absorbed or adsorbed by clays or scavenged by iron during the formation of sedimentary pyrite. The sulfuric acid produced through pyrite oxidation and hydrolysis releases these metals into the rivers, changing the composition of the original mineral phase and of the water that promoted dissolution. The composition of major cations fluctuates with the tides and therefore it is difficult to assess the extent to which these metals may be leached from sediments. The amounts of minor metals are influenced by their availability in the system, while their leaching is determined by pH which fluctuates seasonally.

Conclusion

During the two-year duration of monitoring, there were four main events observed within the streams on the coastal plain, each of which had a specific response.

1. During the dry period, the river pH is very low especially in the freshwater section. The water is in an undersaturated state relative to the main mineral phases and the amounts of toxic metals are high.
2. With the first heavy rain of the wet season, large quantities of acid and metals are leached concurrently into the rivers. If the river flow is restricted and the acidity of the water is not buffered by tidal input, the impact on the aquatic system can be enough to result in a fish kill.
3. During the sustained wet period, large quantities of freshwater flush the acid and the oxidation products from the system, then the water quality improves over several months. The amounts of metals are lower and the slightly acid to neutral pH favours the precipitation of mineral phases.
4. A flood event will result in low pH associated with toxic metals, although in lesser amounts than during a dry season. In terms of saturation indexes, this period is characterised by undersaturation with respect to the main mineral phases.

The Pimpama River system is a good example of a case where both natural and man-made influences affect the water quality. The lithology of the bedrock ultimately determines the availability of chemical elements and the speciation of weathering products. The recent geological history provided appropriate conditions for the formation of sedimentary pyrite, the oxidation of which is controlled by the rainfall regime and locally by landuse activities. The common acid conditions of surface and shallow groundwaters in such a subtropical setting play an active part in the weathering of primary minerals and in further alteration of secondary weathering minerals and pyrite oxidation products. The sequence of events observed during monitoring are likely to occur to some extent during the normal annual seasonal variations, as well as in other similar settings.

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Appendix 1

Water pH, salinity and chemical composition at selected sites in the study area

Date	Site	pH	Salinity g/l	Major cations (mg/l)				Minor cations (mg/l)			Major anions (mg/l)		
				Na	K	Mg	Ca	Fe	Al	Mn	Cl	HCO3	SO4
6/95	1	7.5	0.18	44.4	1.8	11.6	17.2	0.07	0.02	0.10	89	56	28
9/96	1	7.3	0.20	40.7	1.7	10.9	13.6	0.09	0.06	0.03	78	54	22
6/95	2	6.9	0.32	81.4	2.2	20.2	28.9	0.22	0.00	0.03	124	35	98
9/96	2	6.9	0.29	47.0	1.3	11.7	12.4	1.16	0.05	0.14	82	45	44
8/95	3	6.8	0.22	57.4	6.1	12.4	14.6	1.07	0.78	0.12	101	37	37
12/95	3	6.4	0.17	42.4	2.9	8.3	11.0	1.76	2.09	0.05	78	24	29
9/96	3	7.0	0.25	55.5	2.0	12.5	12.7	0.64	0.05	0.14	92	52	24
8/95	4	6.5	0.23	59.9	8.5	13.5	15.4	1.33	0.88	0.11	110	28	58
9/96	4	6.9	0.31	53.1	2.9	11.6	10.2	0.88	0.12	0.18	99	38	15
6/95	5	5.9	24.50	7865.0	243.4	1046.0	483.7	1.90	0.86	0.60	15 193	12	2022
8/95	5	3.8	12.40	3788.2	188.1	650.2	242.5	7.50	9.18	1.07	6466	0	1225
10/95	5	4.9	20.90	6171.0	258.7	936.4	371.5	1.41	2.18	1.04	12 762	0	1765
12/95	5	3.9	2.36	598.3	28.2	138.4	69.7	2.08	4.19	1.00	1007	0	545
3/96	5	7.6	7.87	2456.0	91.3	430.3	133.3	1.13	0.20	0.25	4538	67	650
9/96	5	5.8	11.95	3178.0	114.4	520.0	180.8	2.85	1.31	0.67	5672	6	1055
6/95	6	5.2	23.70	7715.0	247.1	1027.0	476.7	1.64	1.80	0.81	14 535	6	1972
8/95	6	3.7	12.50	4103.0	216.0	702.0	251.5	13.79	10.95	1.67	7274	6	1293
10/95	6	6.2	24.50	6458.0	300.0	1020.0	429.2	1.61	0.67	0.83	14 889	22	1949
12/95	6	4.5	0.69	155.9	12.5	37.2	22.9	3.20	3.32	0.66	284	0	200
3/96	6	7.3	17.20	5085.0	190.0	758.3	257.0	1.20	0.56	0.30	9075	46	1196
5/96	6	3.6	0.93	214.2	9.4	54.6	37.0	8.73	9.90	1.29	567	0	367
9/96	6	6.4	18.40	4484.0	154.6	690.6	243.7	0.89	0.53	0.62	7941	17	1347
6/95	7	5.7	25.40	7740.0	225.2	1001.0	466.8	2.78	5.14	0.75	14 180	12	1940
8/95	7	6.2	30.70	9128.8	572.6	1153.0	503.5	0.21	1.04	0.11	16 165	21	2071
12/95	7	3.5	11.39	3565.0	105.4	456.3	156.2	1.60	5.93	0.93	5105	0	1283
3/96	7	7.6	25.40	7953.0	309.2	1021.0	391.3	0.26	0.17	0.15	14 464	66	1743
5/96	7	6.0	2.60	793.9	30.9	126.8	49.5	1.11	2.80	0.78	1560	18	325
9/96	7	7.1	24.36	5965.0	201.2	858.5	319.7	0.44	0.26	0.34	10 919	60	1665
6/95	8	3.9	0.54	126.0	10.3	21.7	19.0	13.76	3.58	1.12	213	0	176
8/95	8	3.1	1.43	249.5	15.4	56.6	45.7	49.38	17.08	5.65	404	0	598
10/95	8	2.9	1.95	352.6	14.6	60.4	44.5	24.74	19.02	4.65	500	0	523
3/96	8	6.2	0.38	101.0	5.7	18.1	15.6	6.13	0.42	1.01	142	22	105
9/96	8	6.0	0.64	121.3	3.7	18.4	12.1	6.99	0.79	0.71	199	15	59
8/95	9	3.6	1.90	490.4	22.5	107.7	64.0	14.92	19.95	3.29	878	0	606
10/95	9	3.1	1.90	334.8	15.3	92.3	59.4	18.82	30.25	5.12	550	0	674
3/96	9	7.1	0.63	110.0	5.3	18.3	14.0	1.39	0.08	0.23	163	40	70
6/95	10	3.0	1.47	338.3	15.6	84.1	63.8	30.46	19.38	3.95	634	0	656
8/95	10	3.2	2.27	517.1	19.7	136.2	77.0	18.48	46.00	3.61	1008	0	864
10/95	10	3.0	2.63	577.9	21.2	160.6	86.3	19.16	47.87	4.19	993	0	947
5/96	10	4.8	0.33	72.8	5.0	14.1	12.6	2.62	0.47	0.89	113	0	81
8/95	11	3.0	2.30	584.4	18.4	129.0	71.0	16.94	46.04	3.40	1043	0	821
10/95	11	3.2	2.59	544.0	21.0	169.0	88.1	17.08	51.44	4.07	1134	0	990
12/95	11	5.1	0.31	81.5	6.0	13.5	12.0	4.29	2.21	0.51	128	0	70
3/96	11	6.2	0.78	229.0	9.8	35.5	19.2	0.54	0.14	0.18	376	18	122

Appendix 2

Water pH, salinity and chemical composition sorted by season

Date	Season	Site	pH	Salinity (g/l)	Major cations (mg/l)				Minor cations mg/l)			Major anions (mg/l)		
					Na	K	Mg	Ca	Fe	Al	Mn	Cl	HCO3	SO4
6/95	Dry	1	7.5	0.18	44.4	1.8	11.6	17.2	0.07	0.02	0.10	89	56	28
6/95	Dry	2	6.9	0.32	81.4	2.2	20.2	28.9	0.22	0.00	0.03	124	35	98
6/95	Dry	5	5.9	24.50	7865.0	243.4	1046.0	483.7	1.90	0.86	0.60	15 193	12	2022
6/95	Dry	6	5.2	23.70	7715.0	247.1	1027.0	476.7	1.64	1.80	0.81	14 535	6	1972
6/95	Dry	7	5.7	25.40	7740.0	225.2	1001.0	466.8	2.78	5.14	0.75	14 180	12	1940
6/95	Dry	8	3.9	0.54	126.0	10.3	21.7	19.0	13.76	3.58	1.12	213	0	176
6/95	Dry	10	3.0	1.47	338.3	15.6	84.1	63.8	30.46	19.38	3.95	634	0	656
8/95	very Dry	3	6.8	0.22	57.4	6.1	12.4	14.6	1.07	0.78	0.12	101	37	37
8/95	very Dry	4	6.5	0.23	59.9	8.5	13.5	15.4	1.33	0.88	0.11	110	28	58
8/95	very Dry	5	3.8	12.40	3788.2	188.1	650.2	242.5	7.50	9.18	1.07	6466	0	1225
8/95	very Dry	6	3.7	12.50	4103.0	216.0	702.0	251.5	13.79	10.95	1.67	7274	6	1293
8/95	very Dry	7	6.2	30.70	9128.8	572.6	1153.0	503.5	0.21	1.04	0.11	16 165	21	2071
8/95	very Dry	8	3.1	1.43	249.5	15.4	56.6	45.7	49.38	17.08	5.65	404	0	598
8/95	very Dry	9	3.6	1.90	490.4	22.5	107.7	64.0	14.92	19.95	3.29	878	0	606
8/95	very Dry	10	3.2	2.27	517.1	19.7	136.2	77.0	18.48	46.00	3.61	1008	0	864
8/95	very Dry	11	3.0	2.30	584.4	18.4	129.0	71.0	16.94	46.04	3.40	1043	0	821
10/95	Dry	5	4.9	20.90	6171.0	258.7	936.4	371.5	1.41	2.18	1.04	12 762	0	1765
10/95	Dry	6	6.2	24.50	6458.0	300.0	1020.0	429.2	1.61	0.67	0.83	14 889	22	1949
10/95	Dry	8	2.9	1.95	352.6	14.6	60.4	44.5	24.74	19.02	4.65	500	0	523
10/95	Dry	9	3.1	1.90	334.8	15.3	92.3	59.4	18.82	30.25	5.12	550	0	674
10/95	Dry	10	3.0	2.63	577.9	21.2	160.6	86.3	19.16	47.87	4.19	993	0	947
10/95	Dry	11	3.2	2.59	544.0	21.0	169.0	88.1	17.08	51.44	4.07	1134	0	990
12/95	Wet	3	6.4	0.17	42.4	2.9	8.3	11.0	1.76	2.09	0.05	78	24	29
12/95	Wet	5	3.9	2.36	598.3	28.2	138.4	69.7	2.08	4.19	1.00	1007	0	545
12/95	Wet	6	4.5	0.69	155.9	12.5	37.2	22.9	3.20	3.32	0.66	284	0	200
12/95	Wet	7	3.5	11.39	3565.0	105.4	456.3	156.2	1.60	5.93	0.93	5105	0	1283
12/95	Wet	11	5.1	0.31	81.5	6.0	13.5	12.0	4.29	2.21	0.51	128	0	70
3/96	Wet	5	7.6	7.87	2456.0	91.3	430.3	133.3	1.13	0.20	0.25	4538	67	650
3/96	Wet	6	7.3	17.20	5085.0	190.0	758.3	257.0	1.20	0.56	0.30	9075	46	1196
3/96	Wet	7	7.6	25.40	7953.0	309.2	1021.0	391.3	0.26	0.17	0.15	14 464	66	1743
3/96	Wet	8	6.2	0.38	101.0	5.7	18.1	15.6	6.13	0.42	1.01	142	22	105
3/96	Wet	9	7.1	0.63	110.0	5.3	18.3	14.0	1.39	0.08	0.23	163	40	70
3/96	Wet	11	6.2	0.78	229.0	9.8	35.5	19.2	0.54	0.14	0.18	376	18	122
5/96	Flood	6	3.6	0.93	214.2	9.4	54.6	37.0	8.73	9.90	1.29	567	0	367
5/96	Flood	7	6.0	2.60	793.9	30.9	126.8	49.5	1.11	2.80	0.78	1560	18	325
5/96	Flood	10	4.8	0.33	72.8	5.0	14.1	12.6	2.62	0.47	0.89	113	0	81
9/96	Dry	1	7.3	0.20	40.7	1.7	10.9	13.6	0.09	0.06	0.03	78	54	22
9/96	Dry	2	6.9	0.29	47.0	1.3	11.7	12.4	1.16	0.05	0.14	82	45	44
9/96	Dry	3	7.0	0.25	55.5	2.0	12.5	12.7	0.64	0.05	0.14	92	52	24
9/96	Dry	4	6.9	0.31	53.1	2.9	11.6	10.2	0.88	0.12	0.18	99	38	15
9/96	Dry	5	5.8	11.95	3178.0	114.4	520.0	180.8	2.85	1.31	0.67	5672	6	1055
9/96	Dry	6	6.4	18.40	4484.0	154.6	690.6	243.7	0.89	0.53	0.62	7941	17	1347
9/96	Dry	7	7.1	24.36	5965.0	201.2	858.5	319.7	0.44	0.26	0.34	10 919	60	1665
9/96	Dry	8	6.0	0.64	121.3	3.7	18.4	12.1	6.99	0.79	0.71	199	15	59

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