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Characterization of acid river dilution and associated trace element behavior through hydrogeochemical modeling: A case study of the Banyu Pahit River in East Java, Indonesia

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ABSTRACT

Kawah Ijen volcano in East Java, Indonesia emits hyperacid ($pH \approx 0$) brines rich in toxic elements including F, Al, Cd and Tl, which are transported downstream by the Banyu Pahit River, which is eventually used to irrigate farmland on the Asambagus Plain. The fate and behavior of major and trace elements are investigated, in the region of greatest change to the Banyu Pahit River, where thermal springs and the neutral Kali Sat and Kali Senggon Rivers increase its discharge 6-fold and pH increases from 1.9 to 4.5 with the development of abundant precipitates. The conservative behavior of Cl, F and SO_4 allows determination of the proportions of the mixing constituents at each confluence. Comparing a mass balance model based on the resulting proportions with measured concentrations demonstrates conservative behavior for most cations, with the exception of Si, Zr, Sn and Ba, which precipitate as amorphous silica, barite, and Zr and Sn phases, respectively. Iron is added as particulate Fe-(oxy)hydroxide in mixing with thermal spring outflow, and dissolves in the lower pH water. This also contributes Co, Cd, Mn, Y, and the rare earth elements, which are desorbed from the Fe-(oxy)hydroxide upon entering the acid water. Subsequent saturation in Fe-(oxy)hydroxide after mixing with the neutral rivers leads to a reverse response. Still, element behavior is close to conservative, which means that the volcanogenic toxic element load is almost entirely transferred to the Asambagus Plain with ensuing environmental and health impacts. This study shows that compositions of these acid waters can be understood and reproduced in a thermodynamic model, but only when fine-tuned using measured compositions and field observations. Therefore, the model's utility in assessing the fate of toxic elements and in planning the environmental mitigation is limited.

1. Introduction

Trace elements display a dualistic behavior in their interactions with the Earth's flora and fauna. Many trace elements are essential to the growth and health of flora (e.g., Cu, Zn, Mn, Fe, Mo and B) and fauna (e.g., Se, Co – He et al., 2005), where they act as catalysts in the processes of life. A deficiency in these essential nutrients is one of the most common checks on the proliferation of specific organisms (e.g., Fe limited plankton growth in parts of the ocean – Morel et al., 1991; and health effects from lack of Se – Maksimovic et al., 1992). However, at elevated concentrations, these essential nutrients commonly have a detrimental effect, and can become toxic to organisms, including people, through both direct exposure, and transportation and bioaccumulation in food chains (Agusa et al., 2006; Buschmann et al., 2008; He et al., 2005).

Elevated concentrations of trace elements in the environment occur as a result of anthropogenic activities, through mining, milling, or smelting of ores (Parsons et al., 2001), application of agricultural fertilizers (Otero et al., 2005), and combustion of fuels (Kelly et al., 1996). Elements can also be enriched by natural processes, such as redistribution and mobilization of trace elements from host rock or regolith by surface and subsurface waters, and flooding events (Adamo et al., 2006; D'Ascoli et al., 2006; Gasparon and Matschullat, 2006). A combination of these processes is at work in the case of acid mine drainage, where exposure of ore fragments to the atmosphere in tailings or abandoned mine workings results in acidification of stream waters and mobilization of trace elements to locally high, and toxic, concentrations (Johnson, 2003; Parsons et al., 2001).

Volcanic systems are another important natural source of trace elements to the atmosphere and hydrosphere, especially in terms of metals, which regularly reach elevated levels (e.g., Mount Ruapehu volcano in New Zealand and its associated Whangeahu River, Deely and Sheppard, 1996; the Rio Agrio draining Poas volcano in Costa Rica, Rowe et al., 1995; and Kawah Ijen volcano and the Banyu Pahit River in Indonesia, Delmelle and Bernard 1994, 2000; Sumarti, 1998; Delmelle et al., 2000; Takano et al., 2004; van Hinsberg et al.,

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2010; and this work). Emissions take the form of vapor and gas, crater lakes and their outflow, and springs linked to the underlying hydrothermal system. Their element load is derived from both magmatic degassing and from scavenging of elements from host rocks during water–rock interaction in the hydrothermal system. Emissions are not restricted to periods of volcanic activity, but are generally persistent and may outlive magmatism. In the examples above, the volcanic waters are highly concentrated in anions, cations and trace elements and they are strongly acidic, with a pH commonly <3, and in several cases <1. This makes them comparable to acid mine drainage in terms of toxicity and environmental impact (e.g., Delmelle and Bernard, 2000).

In both natural and anthropogenic acid streams, the dominant process that reduces their dissolved element concentrations and acidity as they move downstream is dilution by circum-neutral ground- and surface waters. Mineral precipitation, as well as sorption of elements onto precipitates and onto the streambed (organic and inorganic components), is also important, especially as pH increases (Kulik, 2009; Morel and Hering, 1993; and references therein). Precipitation and sorption remove dissolved elements from the solution as opposed to decreasing concentration by dilution. At the same time, the highly acidic nature of these fluids can result in dissolution and leaching of the streambed, scavenging rather than depositing elements, and lead to an increase in the total element load (e.g., the upstream Banyu Pahit River in Indonesia, van Hinsberg, 2001; van Hinsberg et al., 2010). However, this water–rock interaction does contribute to acid neutralization of these waters (van Hinsberg, 2001). Because of the varied and competing processes operating in such acid waters as they move downstream, it is difficult to predict the fates of the constituents. This is especially true for the toxic elements, which are commonly present at trace element levels and do not saturate their own minerals. This is unfortunate, because the lack of a proper understanding of the fate and behavior of (trace) elements in these waters limits the ability to understand and predict the potential impact of these waters on the surrounding environment, and to devise interventions to minimize negative impact.

Here the behavior and fate of both major and trace elements in the acidic Banyu Pahit River in East Java, Indonesia, upon its first major dilution by circum-neutral waters have been investigated. The Banyu Pahit originates on the flanks of Kawah Ijen volcano and is characterized by low pH and high concentrations of potentially toxic elements, including Cd, Al, Tl, Pb and F (Delmelle and Bernard 2000; van Hinsberg et al., 2010; this study). This study extensively builds upon the work of P. Delmelle and co-workers, who identified two domains in the river (Delmelle and Bernard, 2000); an upstream section where the acid waters remain essentially undiluted and conservative element behavior dominates, and a downstream section where significant modifications of the river water are induced by inflow of circum-neutral rivers, and non-conservative element behavior becomes progressively more important. Recently, it was shown that elements are actually added to the acid waters in this upstream section due to aggressive water–rock interaction (van Hinsberg et al., 2010), whereas the non-conservative behavior downstream suggests removal of elements. Here this downstream section of the Banyu Pahit River is focused on, where confluence with neutral tributaries results in a sharp, stepwise increase in pH, and the formation of abundant precipitates. The descriptive modeling conducted by Delmelle and Bernard (2000) is extended to a predictive geochemical mixing model to quantify the behavior of trace elements in these acidic waters during neutralization and to evaluate the ability of thermodynamic modeling packages to predict their behavior. In particular, the results allow for assessment of the use of thermodynamic tools to predict the extent of degradation of river water quality further downstream, where, in the case of the Banyu Pahit River, these waters are used for irrigation.

2. Banyu Pahit River system

The Banyu Pahit River originates on the western flank of Kawah Ijen volcano; an active stratovolcano of basaltic to andesitic composition that is part of the large Ijen Caldera Complex in easternmost Java (Fig. 1). This volcano is renowned for its crater lake, which represents the world's largest naturally occurring body of hot hyperacid brine (Kemmerling, 1921; Delmelle and Bernard, 1994; Delmelle et al., 2000; Takano et al., 2004; van Hinsberg et al., 2010). Seepage of crater lake water through the strongly altered western flank of the volcano was previously regarded as the predominant source of the Banyu Pahit stream, but recent work has shown that this forms only a minor contribution based on field observations in 2008 and 2009. In contrast, the primary source of the Banyu Pahit River is a set of springs approximately 375 m below the elevation of the lake. The spring waters represent outflow from the hydrothermal system and distinctly lack a crater lake contribution (Palmer, 2009).

Downstream of these springs up to the village of Watucapil (Fig. 1a), no surface hydrological contributions to the river are observed. Modeling of water compositions indicates that water–rock interaction and dilution control the changes in composition in this section (Delmelle and Bernard 1994, 2000; Palmer, 2009; van Hinsberg et al., 2010). At Watucapil, the river cascades off the lava flow into an inaccessible canyon of porous volcaniclastics.

The Banyu Pahit River emerges from the canyon to the south of the village of Blawan (Fig. 1b) onto the remnant plain of an old lake (Kemmerling, 1921) that is now used extensively for agriculture. On this plain, the river receives circum-neutral water from a number of thermal springs, derived from locally heated groundwater (http://www.vsi.dpe.go.id/pbumi/java/blawantxt.html), and merges with the neutral Kali Sat and Kali Senggon Rivers, which drain the western and eastern parts of the Ijen caldera, respectively. It finally cascades out of the caldera in a waterfall, and is now named Banyu Putih ("White River"), owing to its milky-white color. This color results from the formation of a white precipitate upon mixing of the Banyu Pahit with the various inflows of neutral water (Fig. 2a and c). The streambed of the thermal springs is covered in orange to brown precipitates, and these are also found coating the waterfall (Fig. 2c).

After leaving the caldera, the Banyu Putih flows on the outer slopes of the Ijen Caldera Complex towards the Strait of Madura. However, most of the water is used in irrigation on the coastal Asembagus plains resulting in a strong toxicological impact on soil and crops, and the health of the local population (Heikens et al., 2005a,b,c; Löhr et al., 2005; van Rotterdam-Los et al., 2008a,b).

3. Methods

3.1. Field methods and sampling

Water and precipitate samples were collected during the dry season from mid-July to mid-August 2008. No rainfall was observed in the study area during the sampling period, or upstream in the catchment area of the Banyu Pahit, Kali Senggon and Kali Sat Rivers. Therefore, the hydrology is concluded to represent baseflow conditions. For this project, water samples were taken at several locations along the Banyu Pahit River, of the Kali Sat and Kali Senggon Rivers just upstream of their confluence with the Banyu Pahit, and from the outflow of six thermal springs that contribute to the Banyu Pahit River (Fig. 1b). At each sample site, water and air temperature were measured with a type-K thermocouple, and electric conductivity and pH were measured. The pH and EC electrodes were calibrated daily using certified pH standards of 2.0, 4.0 and 7.0, and KCl solutions of varying concentrations, respectively.

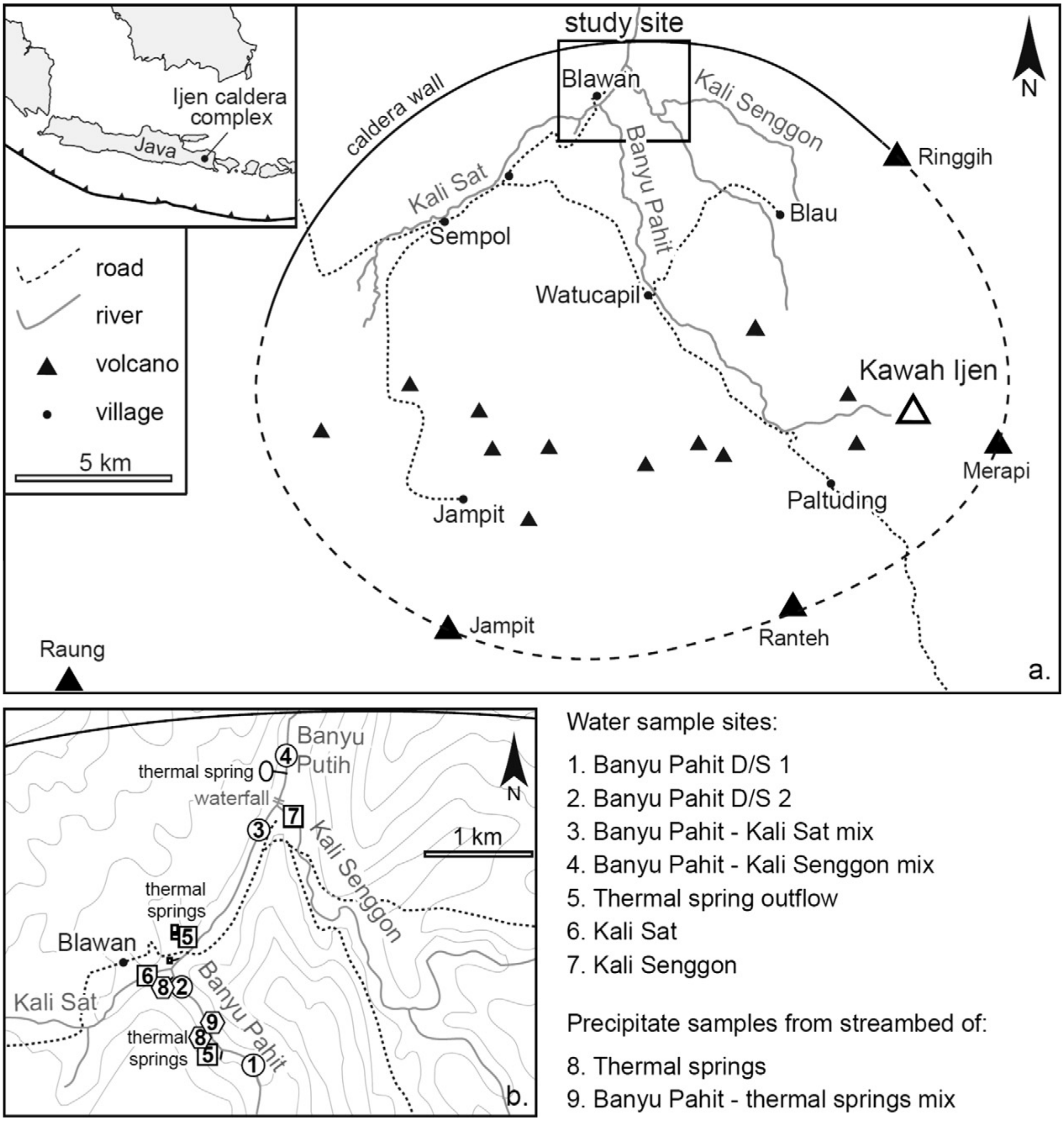

Fig. 1. (a) Overview map of the Ijen Caldera Complex, showing the locations of Kawah Ijen volcano and the major rivers, and (b) sample locations shown on a close-up map of the study area.

Two 60 mL water samples were collected in completely filled, sample-rinsed polyethylene bottles, one for cations and trace elements, and the other for anion analysis. Both samples were filtered using 0.45 μm disposable filters. Cation and trace element samples of the neutral waters were acidified with two drops of dilute trace metal grade HNO_3 to preserve samples for later analyses. Precipitates were collected by sampling boulders coated in precipitate from the streambed of the thermal springs and the Banyu Pahit River (Fig. 1b).

3.2. Water analyses

Sulfate, Cl and F were determined by ion chromatography (IC) at the Hydrogeology Laboratory, Department of Earth and Planetary Sciences, McGill University (Dionex DX-100 with Dionex AS14 column, guard and suppressor). Samples and standards for IC were prepared by mass in distilled water and a NaOH solution was used as the eluent. Dissolved concentrations of the major cations Si, Ca, Fe, K, Li, Mg and Na were determined by atomic absorption spectrometry on a Perkin Elmer AAnalyst 100 at the Trace Element Analytical Laboratory (TEAL) at McGill University. Silicon was determined using an acetylene-nitrous oxide flame, whereas the other cations were determined using O_2 as the oxidant. Samples and standards were prepared by mass in 3% trace metal grade HNO_3. Dissolved trace element concentrations were determined at TEAL by ICP-MS using a Perkin Elmer Elan 6100 DRCplus with dilutions of samples and standards prepared in 2% trace metal grade HNO_3. A set of dilutions was measured for each sample to cover the range in element concentrations and to check for enhancement and suppression effects, and blanks were run

Fig. 2. Photographs of precipitates in the Banyu Pahit system. (a) Orange-brown precipitates in the streambed of a thermal spring and development of a white precipitate upon mixing with the Banyu Pahit River. No orange precipitates are present at the confluence. Field of view is *ca.* 1 m. (b) Extensive precipitates in a recent channel of thermal spring outflow dug through a field. The channel width is *ca.* 30 cm. (c) Orange precipitates coating the wall of a waterfall immediately after the confluence of the Banyu Pahit and Kali Senggon Rivers. The waterfall is *ca.* 20 m high. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

regularly to check for element build-up in tubing and on cones, though none was found.

3.3. Analysis of precipitates

Precipitates were scraped off the surface of the sampled boulders and dried overnight at 90 °C. An aliquot of this material was fixed to double-sided tape, C-coated and subsequently analysed for major elements by standard-less electron microprobe EDS at the Department of Earth Sciences, Utrecht University, using a JEOL JXA-8600 Pioneer electron microprobe. Operating conditions were 15 kV acceleration voltage, and 10 nA beam current. The remaining material was crushed and ground in an agate mortar, pressed into a tablet and analysed by XRD at the Department of Earth Sciences, Utrecht University using a Philips PW1800 XRD with Cu $K\alpha_1$ radiation. Spectra were collected from 3° to 73° at 0.02° spacing and 10 s dwell time.

4. Results

Results of field and laboratory analyses for each sample site are presented in Tables 1 and 2, respectively. The thermal waters have temperatures between 40 and 80 °C, whereas the temperature of the river waters is constant at circa 22 °C. The pH of the Banyu Pahit stream increases from 1.9 at the furthest upstream sample site to 3.3 after mixing with the Kali Sat River (pH = 7.8), and to 4.5 after its confluence with the Kali Senggon River (pH = 7.6). As the pH increases, the conductivity and concentrations of anions and cations decrease. Fluid properties and compositions are similar to those reported by Delmelle and Bernard (1994, 2000), Löhr et al. (2005), Sumarti (1998), van Hinsberg (2001), and Zelenov (1969) with differences mostly within the seasonal variability observed by Sumarti (1998).

The relative, 1 sigma precision of the analyses by AAS and IC is better than 5%, as determined from duplicate analyses, and better than 10% for ICP-MS results with the exception of Be (19%).

Table 1
Field measurements of pH, electric conductivity, and air and water temperature at sample sites.

Sample	Banyu Pahit DS 1	Banyu Pahit DS2	Banyu Pahit – Kali Sat mix	Banyu Pahit – Kali Senggon mix	Thermal springs	Kali Sat	Kali Senggon
Site	1	2	3	4	5	6	7
pH	1.9	2.0	3.3	4.5	6.4	7.6	7.7
Electric conductivity (mS)	9.7	8.8	1.8	1.4	2.2	0.5	1.2
Temperature (air) (°C)	23.7	26.6	24.2	22.2	26.1	24.6	25.0
Temperature (water) (°C)	22.0	22.4	22.1	23.7	48.2	19.8	22.3

Table 2
Element concentrations measured for each sample site.

Sample	Banyu Pahit DS 1	Banyu Pahit DS 2	Banyu Pahit – Kali Sat mix	Banyu Pahit – Kali Senggon mix	thermal springs	Kali Sat	Kali Senggon
Site	1	2	3	4	5	6	7
Flame atomic absorption							
Si[a]	55.6	58.8	39.4	38.0	54.8	33.7	38.2
Al[a]	345.2	344.5	81.0	47.0	0.0	0.0	30.0
Fe[a]	93.9	97.2	13.2	1.4	1.2	0.2	0.6
Mg[a]	150.6	147.1	47.4	46.4	89.1	30.7	44.6
Ca[a]	302.7	299.9	74.7	72.1	85.4	23.0	64.3
Na[a]	176.6	93.9	68.1	77.9	161.4	36.5	63.1
K[a]	59.2	59.3	16.6	16.5	33.6	4.9	9.5
Ion chromatography							
Cl[a]	972.5	888.3	210.1	178.5	81.7	26.0	74.0
F[a]	64.5	59.2	13.1	7.3	0.9	0.7	1.1
SO_4[a]	3076.3	2838.1	561.7	484.8	256.5	87.5	212.9
ICP-MS							
Li[a]	0.089	0.091	<d.l.	<d.l	0.225	0.001	0.005
Cs[a]	0.005	0.005	0.003	0.001	0.001	0.005	0.006
Rb[a]	0.173	0.173	0.050	0.044	0.046	0.023	0.025
Be[b]	10.370	9.220	1.861	<d.l.	0.100	<d.l.	<d.l.
Sr[b]	2.429	2.377	0.721	0.514	0.691	0.209	0.393
Ba[a]	0.035	0.035	0.037	0.027	0.051	0.019	0.028
Sc[a]	0.075	0.078	0.024	0.022	0.026	0.014	0.017
Cr[b]	7.960	7.620	2.750	0.422	1.783	0.754	0.062
Mn[a]	7.462	7.409	1.467	0.994	0.563	0.126	0.253
Co[b]	91.117	90.692	17.599	9.577	0.530	0.326	0.729
Ga[b]	38.493	38.430	7.731	1.235	1.144	0.547	0.709
Y[b]	194.335	191.974	31.286	22.031	0.025	0.095	3.313
Zr[b]	14.299	12.166	0.069	<d.l.	0.219	0.060	0.060
Cd[b]	3.625	0.012	1.061	0.697	0.068	0.135	0.048
Sn[b]	1.869	1.493	0.121	<d.l.	0.021	<d.l.	<d.l.
Pb[b]	74.610	72.981	15.117	4.908	0.268	1.622	1.277
Tl[b]	17.770	17.614	2.923	<d.l.	<d.l.	<d.l.	<d.l.
La[b]	81.487	82.555	15.722	8.466	0.010	0.050	1.331
Ce[b]	205.731	218.406	39.958	27.293	0.090	0.049	3.208
Nd[b]	148.611	150.975	27.458	15.443	0.040	0.091	2.191
Sm[b]	35.239	35.546	6.291	3.680	0.011	0.028	0.505
Eu[b]	9.331	9.398	1.664	0.995	0.006	0.015	0.108
Gd[b]	36.484	36.802	6.199	4.036	0.009	0.026	0.566
Tb[b]	5.963	6.002	1.022	0.667	0.035	0.009	0.086
Dy[b]	33.492	33.334	5.623	3.756	0.011	0.022	0.508
Ho[b]	6.761	6.719	1.186	0.766	0.005	0.007	0.099
Er[b]	19.864	19.678	3.319	2.265	0.006	0.014	0.301
Yb[b]	17.386	17.116	2.820	1.950	0.006	0.014	0.262
Lu[b]	2.660	2.653	0.860	0.305	0.035	0.008	0.036

[a] mg/L.
[b] μg/L.

Accuracy is better than 11% (21% for Be), as determined from standards and a series of upstream Banyu Pahit River samples that were previously analysed at the Department of Earth Sciences, Utrecht University.

The XRD spectra for the precipitates show a large bulge centered at 30°, together with minor peaks for plagioclase and clinopyroxene in one sample. This indicates that the precipitates are XRD amorphous, with mineral peaks derived from contamination by the host boulder. The precipitates were too fine to obtain compositions for individual grains by EMP-EDS. Area scans showed that several phases are present in each sample, and that these phases are (hydr)oxides with only minor S and Cl. The precipitates from the streambed of the thermal springs are dominated by an Fe phase, but also contain a component rich in Si, Al, Mg and Ca (in decreasing order of abundance). The precipitate just downstream of the confluence of a thermal spring and the Banyu Pahit (location shown in Fig. 2a) predominantly contains Si, with Al, Fe, Ca and P as the main additional elements. The Banyu Pahit River precipitate contains the same constituents as reported by Delmelle and Bernard (2000) and Zelenov (1969), but in different proportions and with a smaller S content (no sulfates were found in repeated scans of these precipitates). However, element proportions are variable within a given precipitate sample. Although a mineralogy could not be established owing to the fine grain-size of the precipitates, it is suggested that they are composed of amorphous silica and (oxy)hydroxides of Fe and Al, based on their compositions and previous work (Delmelle and Bernard, 2000; Zelenov, 1969).

5. Discussion

5.1. Determining mixing proportions from conservative tracers

The dissolved element concentrations in the Banyu Pahit River decrease downstream, as a result of progressive dilution by meteoric-derived, neutral waters, such as the Kali Sat and Kali Senggon Rivers. This mixing has been quantified using a step-wise, two-component mixing model for each sample site (Fig. 3), using the anions Cl, SO_4 and F as conservative tracers. Conservative behavior has been well established for these anions in the upstream Banyu Pahit River (Delmelle and Bernard, 1994, 2000; Sumarti, 1998; van Hinsberg, 2001; van Hinsberg et al., 2010). Delmelle and Bernard (2000) suggest a deviation from conservative behavior for the river section discussed here, especially for SO_4, owing to the formation of SO_4-bearing precipitates. However, calculations using only Cl as the tracer, which is not a major component of any precipitate phase, indicate that even after the confluence with the Kali Senggon River, a minimum of 99.3% of SO_4 behaves conservatively in both previous studies (Delmelle and Bernard, 2000; van Hinsberg, 2001) and in the present dataset. This negligible deviation from conservative behavior is within the analytical uncertainty, although it is likely real, and reflects the small amount of S in precipitate relative to the S concentration in the river water. Combined with the observation of excellent agreement between mixing proportions derived from Cl, F and SO_4 (see below), the authors prefer to calculate an average mixing proportion from all anions.

The mixing proportions calculated for the Banyu Pahit River give average proportions of 9 ± 0.6% thermal springs and 91 ± 0.6% Banyu Pahit water at Site 2, 79 ± 0.2% Kali Sat and 21 ± 0.2% Banyu Pahit River water at Site 3, and 23 ± 0.8% Kali Senggon and 77 ± 0.8% Banyu Pahit water as the river leaves the caldera at Site 4 (Figs. 1b and 3), and are in excellent agreement between the three tracers used. The contribution of thermal springs to Sites 3 and 4 was not modeled, because it is dwarfed by the input from the neutral rivers. These calculations indicate that the water leaving the Ijen caldera consists of only 15% acidic Banyu Pahit River water as it flows onto the plain at the first sampling site of this study, and is predominantly made up of Kali Sat (61%) and Kali Senggon (23%) waters.

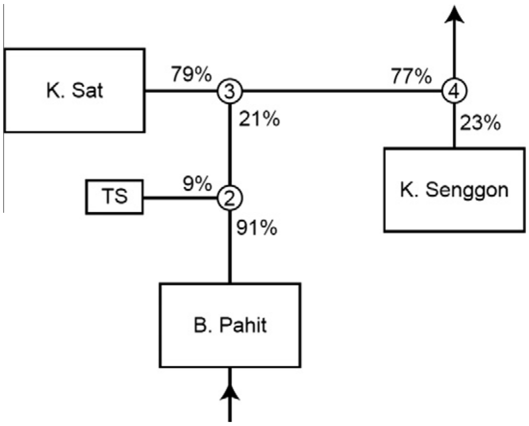

Fig. 3. Box representation of the mixing model with the proportions of each component to the mixture as determined from conservative tracers. TS – thermal springs, B. – Banyu, K. – Kali.

5.2. Conservative mass-balance

The major and trace cation composition of the river water at each sample site can be predicted from simple conservative mass balance using the anion-derived mixing model in a forward modeling approach (i.e., the composition at Site 2 is predicted from measured compositions of Site 1 and thermal spring waters, mixed in the proportion 91:9, and this predicted composition is subsequently used in the next mixing step, see also Fig. 3). These predictions and the actual measured concentrations are compared in Fig. 4 for a range of major and trace elements. There is overall good agreement between predicted and measured concentrations, suggesting that conservative behavior also predominates for the cations. However there are deviations, with predicted concentrations of Si, Sn and Zr being too high, and Fe, the rare earth elements (REE), Co, Cd, Mn, Pb and Y initially too low and subsequently being too high. These deviations indicate that these elements do not show conservative behavior, with predicted values greater than measured concentrations indicating an unaccounted for sink, and predicted values less than measured concentrations indicating an additional source for that element.

5.3. Mass balance modeling with mineral precipitation

The visual appearance of precipitates upon each mixing step (see Fig. 2) makes these a likely element sink, as was also suggested for deviations from conservative behavior along the full length of the Banyu Pahit River by Delmelle and Bernard (2000). Semi-quantitative analyses indicate that this precipitate is XRD-amorphous and dominantly contains Si, Al and Fe, in agreement with results of Zelenov (1969), but significantly lower in S compared to reported precipitate compositions of Delmelle and Bernard (2000). To explore the interactions with precipitates in more detail the mixing was modeled using PHREEQC 2.17 and the Lawrence Livermore National Laboratory database of thermodynamic properties (Parkhurst and Appelo, 1999). The simulations were run with the full suite of elements reported here, and with an O_2 buffer controlled by the Fe^{2+}–Fe^{3+} ratio in the solution, from Delmelle and Bernard (2000). Mixing proportions were those derived from the conservative anions, and the same forward modeling approach was applied as outlined for simple mass balance above. Schwertmannite ($Fe_8O_8(OH)_{5.5}(SO_4)_{1.25}$, data from Acero et al., 2006) was added to the database because it is a common Fe-phase in SO_4-rich acid mine drainage, but never reaches saturation.

Calculations predict that the solutions are thermodynamically saturated in amorphous silica, goethite, jarosite, barite and a Zr-phase, and these phases were subsequently allowed to precipitate in each mixing step (ZrO_2 was selected as the precipitating phase for Zr). Tin oxide was close to saturation (saturation index −0.3), and precipitation of a Sn phase likely accounts for its deviation from conservative behavior. That Ba, Zr and Sn minerals were not identified in the precipitates is likely due to the exceedingly small amounts that precipitate owing to the low concentrations in the river water (see Table 2), although sorption rather than precipitation may also play a role (see also below). Minor differences in the precipitate mineralogy compared to those predicted by Delmelle and Bernard (2000) are the result of the use of different thermodynamic databases.

The resulting model reproduces measured Zr concentrations, and improves the fit for Si and Ba. However, predicted K and Fe

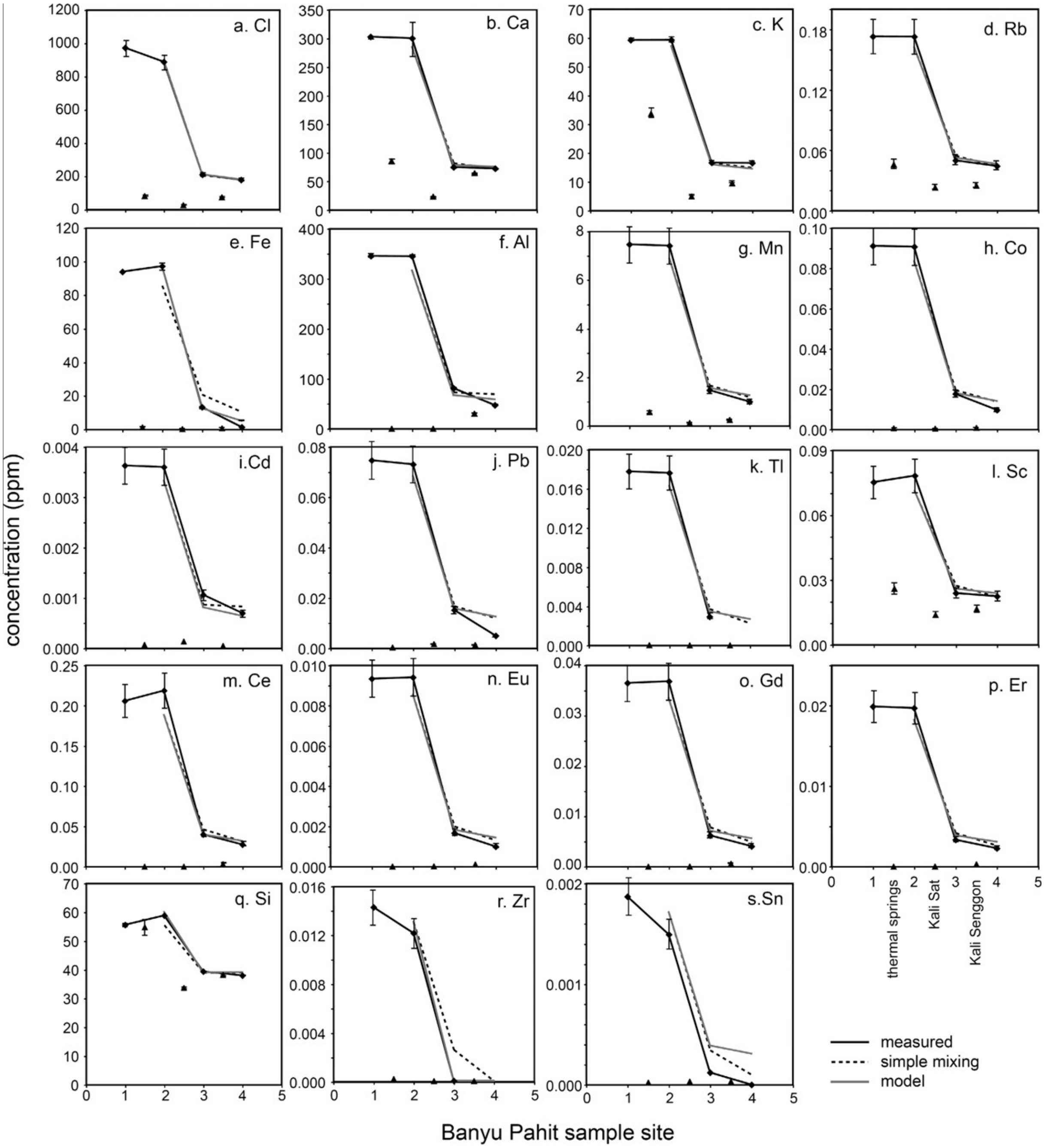

Fig. 4. Concentrations of selected elements in the Banyu Pahit River from upstream to downstream, as measured (solid black line with 1 sigma uncertainty on measured compositions), as derived from conservative mass balance (dashed line), and predicted from a forward model (grey line) calculated by PHREEQC 2.17 (Parkhurst and Appelo, 1999) allowing for precipitation of amorphous silica, barite, ZrO_2 and goethite, and adding goethite in the first mixing step. Conservative mixtures are calculated from the composition of the contributing measured compositions, whereas the PHREEQC model uses the calculated Banyu Pahit River composition from the previous mixing step in subsequent calculations.

concentrations are an order of magnitude too low. Preventing precipitation of jarosite in the model, warranted because of low concentrations of S and K in the EDS spectra of the precipitates, and known sluggish precipitation rates for jarosite (Bigham and Nordstrom, 2000), restored the fit for K, but still left an order of magnitude deficit in Fe owing to increased goethite precipitation. Using amorphous Fe-hydroxide instead of goethite as preferred by Delmelle and Bernard (2000) leads to similar results. The abundance of Fe in precipitates from the Banyu Pahit and the orange-brown coating visible beneath the waterfall (Fig. 2c) indicate that precipitation of a Fe-phase should not be suppressed.

5.4. Final model with dual role for Fe-(oxy)hydroxides

To reconcile the observed discrepancies between predicted and measured dissolved element concentrations requires an additional influx of Fe upon mixing of the thermal waters with the Banyu Pahit River. It is proposed that this source is particulate Fe-(oxy)hydroxide, previously precipitated from the thermal waters as they emerge onto the surface, that are washed into the Banyu Pahit River. There is a distinct change in color of the precipitates from orange-brown in the streambed of the thermal springs to white after mixing with the acid waters (Fig. 2a), and the composition of the precipitates changes concurrently from Fe-dominated to Si-dominated (as determined from EMP-EDS analyses). This suggests that the Fe-precipitates dissolve in the acid water, or are at least leached of their Fe. To include this aspect in the model, up to 2×10^{-4} moles of goethite were allowed to dissolve in the mixing step with thermal waters (equivalent to 18 mg of goethite per kg of river water), which simply saturates the mixture in goethite. This model led to the required increase in Fe, but predicted concentrations were too high. Assuming that this mixture is indeed saturated in goethite, and that the measured Fe concentration, therefore, represents the equilibrium concentration, the log*K* for goethite was changed to match this concentration. This necessary destabilization of crystalline goethite could reflect the amorphous nature of the actual Fe-precipitates. In this final model, Fe concentrations are reproduced perfectly for all sites (Fig. 4).

The correspondence between the deviations in measured and predicted concentrations for Fe, Al, Y, REE, Co, Cd, Pb, Mn and Co, suggests that these are linked (Fig. 4). It is proposed that this link is through sorption of these elements onto Fe-(oxy)hydroxides in the thermal waters, followed by their release upon dissolution, or leaching of these Fe-precipitates as they interact with the acid Banyu Pahit River (for Al, incorporation in the precipitate will also be important). Indeed, sorption of these elements onto the surface of Fe-(oxy)hydroxides is well documented, and this sorption decreases sharply with decreasing pH (Benjamin and Leckie, 1980; Dzombak and Morel, 1990; Gammons et al., 2005; Munk et al., 2002; Verplanck et al., 2004). Sorption was not modeled in detail in the simulations, because the precise compositions, mineralogy and surface properties of the Banyu Pahit precipitates are unknown, and these strongly impact sorption behavior (e.g., Webster et al., 1998). However, qualitative calculations using standard goethite surface properties indicate that these metals would indeed attach to the goethite surface. Furthermore, element sorption strongly decreases from neutral to acid pH, so precipitates washed into the Banyu Pahit River would release these elements even without associated dissolution. Precipitation of goethite upon mixing with the Kali Sat and Kali Senggon Rivers has the opposite effect, in agreement with a change to an excess, rather than a deficit in predicted concentrations (Fig. 4). The persistent decrease in Ba, Sn and Zr downstream, rather than an initial deficit changing to excess as observed for most metals and Y-REE, indicates that these elements are not controlled by sorption. Precipitation of separate phases as discussed in the previous section is, therefore, the most likely explanation for their behavior.

6. Conclusions and implications

Using mass balance mixing models, with the anions as conservative tracers, the contribution of acidic and neutral waters to the Banyu Pahit River has been determined. Despite the continued acidity of this river (pH = 4.5), it only contains 15% of the hyperacid Banyu Pahit water, with the remainder made up by the neutral Kali Sat and Kali Senggon Rivers (61% and 23%, respectively), and neutral thermal waters (1.5%). Comparing modeled predictions of concentrations with measured concentrations indicates that the majority of elements show decreasing concentrations that purely reflect dilution. Silicon, Ba, Sn and Zr are quantitatively removed by precipitation of amorphous silica, barite, and Zr and Sn phases, respectively, and their concentrations downstream are controlled by the solubility of these phases. An important new finding is the role of thermal springs derived Fe-precipitates in controlling element concentrations in the river. Iron is added as particulate Fe-(oxy)hydroxide from thermal springs, and this particulate material subsequently dissolves in the acid waters, leading to an increase in Fe and release of the metals and Y-REE sorbed onto the Fe-(oxy)hydroxide surface. Subsequent saturation in, and precipitation of Fe-(oxy)hydroxides upon mixing with the Kali Sat and Kali Senggon Rivers leads to the reverse with scavenging of these elements onto the precipitate surface.

Despite these precipitate-related effects, the overall element behavior is close to conservative. This means that the vast majority of the toxic element load of the Banyu Pahit River is transported downstream, albeit in diluted form. Indeed, mass balance calculations indicate that essentially all Cd, Al, Tl and F emitted from the springs of the Banyu Pahit on the flanks of Kawah Ijen volcano are released through the Banyu Putih River onto the outer flanks of the Ijen Caldera Complex where these waters are eventually used to irrigate the Asambagus plain. In other words, despite the strong dilution of these fluids, the toxic element load derived from volcanic emissions is quantitatively transferred to the soil, especially given that nearly all the water from this river is used for irrigation in the dry season. This will lead to accumulation of trace elements in the soil and associated, progressively worsening, impact on the soil productivity, a situation that is already being observed (Heikens et al., 2005b; Löhr et al., 2005; van Rotterdam-Los et al., 2008a,b).

More generally, these results show that the major and trace element behavior during progressive neutralization of acid streams, from natural or anthropogenic sources, can be understood and modeled. However, it is shown that for forward models to accurately describe this behavior requires fine-tuning based on constraints from field observations and downstream river water compositions. This need for field observations limits the predictive power of such modeling and highlights the importance of a combined modeling and field-based approach before inferences are made on mitigation of the environmental impact of these waters.

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