

# Acid mine drainage arising from gold mining activity in Johannesburg, South Africa and environs

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**“Capsule”:** *Ground water within the mining district is heavily contaminated and acidified.*

## Abstract

The Witwatersrand region of South Africa is famous for its gold production and a major conurbation, centred on Johannesburg, has developed as a result of mining activity. A study was undertaken of surface and ground water in a drainage system in this area. Soils were also analysed from a site within the mining district. This study revealed that the ground water within the mining district is heavily contaminated and acidified as a result of oxidation of pyrite ( $\text{FeS}_2$ ) contained within mine tailings dumps, and has elevated concentrations of heavy metals. Where the water table is close to surface, the upper 20 cm of soil profiles are severely contaminated by heavy metals due to capillary rise and evaporation of the ground water. The polluted ground water is discharging into streams in the area and contributes up to 20% of stream discharge, causing a lowering of pH of the stream water. Much of the metal load is precipitated in the stream: Fe and Mn precipitate as a consequence of oxidation, while other heavy metals are being removed by co-precipitation. The oxidation of iron has created a redox buffer which controls the pH of the stream water. The rate of oxidation and of dilution is slow and the deleterious effect of the addition of contaminated water persists for more than 10 km beyond the source.

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## 1. Introduction

Gold mining commenced in the Johannesburg area in 1886 (Werdnauer, 1986), the gold being won from 1 to 2 m thick tabular conglomerate layers of the Witwatersrand Supergroup, which extend in an east–west direction over a strike length of some 45 km. Mining activity gave rise to a large conurbation centred on Johannesburg, which today accommodates more than 6 million people.

Gold was initially extracted using a mercury amalgam method, but as mining operations became deeper, unoxidized ore containing pyrite ( $\text{FeS}_2$ ) was encountered, which interfered with the extraction. At about this time, the MacArthur-Forrest process of gold extraction, using cyanide, was developed, and was successfully applied to Witwatersrand ores. This was

phased in during the 1890s. Mining operations in the Johannesburg area continued until the early 1960s, and reached final depths in the region of 2500 m below surface, at which point they tended to become uneconomic.

The Witwatersrand conglomerates consist of quartz pebbles, typically 1–3 cm in diameter, set in a matrix of quartz sand. The matrix typically contains about 3% pyrite (about 1.6% S), and lesser amounts of a wide variety of other sulphide and oxide minerals, in addition to gold. Some 70 different ore minerals have been identified in the conglomerates (Feather and Koen, 1975), the most abundant of which, after pyrite, are uraninite ( $\text{UO}_2$ ), brannerite ( $\text{UO}_3\text{Ti}_2\text{O}_4$ ), arsenopyrite ( $\text{FeAsS}$ ), cobaltite ( $\text{CoAsS}$ ), galena ( $\text{PbS}$ ), pyrrhotite ( $\text{FeS}$ ), gersdorffite ( $\text{NiAsS}$ ) and chromite ( $\text{FeCr}_2\text{O}_4$ ).

Ore mined underground was brought to the surface, where it was milled to a fine sand, during and after which it was exposed to a film of mercury spread on copper plates. These were periodically removed, and the mercury–gold amalgam scraped off and distilled to

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recover the gold. The tailings were transported to dumps near the extraction plant, producing the so-called “sand dumps”. The cyanide process required finer milling of the ore, after which it was treated with a cyanide containing solution, which dissolved the gold. Lime was usually added to regulate the pH of the solution. The solution was then separated for further processing, while the tailings were pumped to large dumps, known as “slimes dumps”. Both the mercury amalgam and the cyanidation processes are highly selective for gold, and other ore minerals were unaffected, and hence reported to the tailings dumps. Gold was not completely recovered by the process, and small quantities remained in the tailings, typically around 0.5 g/t. In the last two decades, many of these dumps have been and are being retreated to recover the remaining gold, and the tailings are pumped to disposal sites to the south of the city. Current retreatment operations usually involve extraction of pyrite as well, using flotation methods.

Many of the tailings dumps have remained undisturbed in the Johannesburg area for almost a century, during which time they have been exposed to oxygenated rainwater. This has resulted in oxidation of the pyrite and other sulphides in the material, particularly an outer layer of the dumps several meters thick. The sand dumps, being more permeable, and older, are generally more seriously affected by this oxidation, and oxidation has typically reached a depth of about 5 m in these dumps, and about 2 m in the slimes dumps (Marsden, 1986). Oxidation of the pyrite acidifies the water percolating through the dumps, which then enters the ground water regime beneath the dumps. This acidic water is believed to be entering streams along the Witwatersrand (Jones et al., 1988). In this paper we report the results of a detailed investigation of a site where seepage of acidic ground water into a stream which drains the south-eastern suburbs of Johannesburg and the western portions of the adjoining municipality of Germiston is taking place. The investigation was carried out in order to obtain insight into chemical processes operating at the pollution source. Moreover, the study was extended downstream in order to determine the rate of decay of the pollution signature.

## 2. Previous investigations

Although extensive investigations have been carried out on the pollution problems arising from gold mining on the Witwatersrand, most of these appear in limited circulation reports of the Water Research Commission, and very few have been published in the open literature. Marsden (1986) undertook an inventory of tailings dumps, mainly in the Witwatersrand area, and concluded that most of the available sulphur had been oxidized, and that the pollution problem was past, if it ever

existed. However, consulting engineers Steffan, Robertson and Kirsten Inc. were contracted by the Water Research Commission in the early 1980s to investigate the contribution of mine tailings to the steadily rising dissolved solid load in the principal water supply to Johannesburg, the Vaal River, whose catchment includes the gold mining districts. From a spatially restricted but detailed study carried out in the Johannesburg area, they concluded that the dumps were indeed a source of serious pollution, especially the older sand dumps. While erosion of dump material into water courses contributed to pollution, they concluded that the major contribution came from rain water which had percolated through the dumps, creating polluted ground water plumes beneath the dumps which were emerging at surface in streams (Jones et al., 1988). Audouin (1997) examined one of these sites, and was able to delineate a plume using electrical geophysical techniques.

Rosner and van Schalkwyk (2000) reported the results of an investigation into the condition of the soil exposed after reclamation of slimes dumps to the east of Johannesburg. They found that the topsoil is highly acidified and contaminated with heavy metals, notably Co, Ni and Zn. While most of these metals were apparently not bioavailable, they considered that in the longer term these metals could be leached into the ground water, resulting in sustained pollution. They did not, however, examine the ground water in their study.

## 3. The study area

Annual rainfall in Johannesburg is about 750 mm (Tyson and Wilcocks, 1971), and is strongly seasonal, while potential evaporation is about 1600 mm/annum. Most rain falls during the summer, between October and February. Thunderstorms of short duration account for most of the rainfall. Temperature averages about 20 °C during the summer months and about 15 °C in winter.

The Natalspruit stream was selected for this study. Its headwaters lie in an area in which tailings dumps abound, but one small tributary arises to the north of the mining belt (Fig. 1). The stream is perennial over all of the reaches sampled, and is also susceptible to severe flash flooding during summer thunderstorms. During the dry season, discharge in the stream is sustained by ground water emerging through the bed of the stream, and by seepage through the banks.

Water samples were collected along the major tributaries and along the Natalspruit over a distance of 10 km downstream of the mining area (Fig. 1). In addition, a detailed study was undertaken in a small area adjacent to the stream within an area of concentrated tailings dumps, where ground water emerges and discharges into the stream.

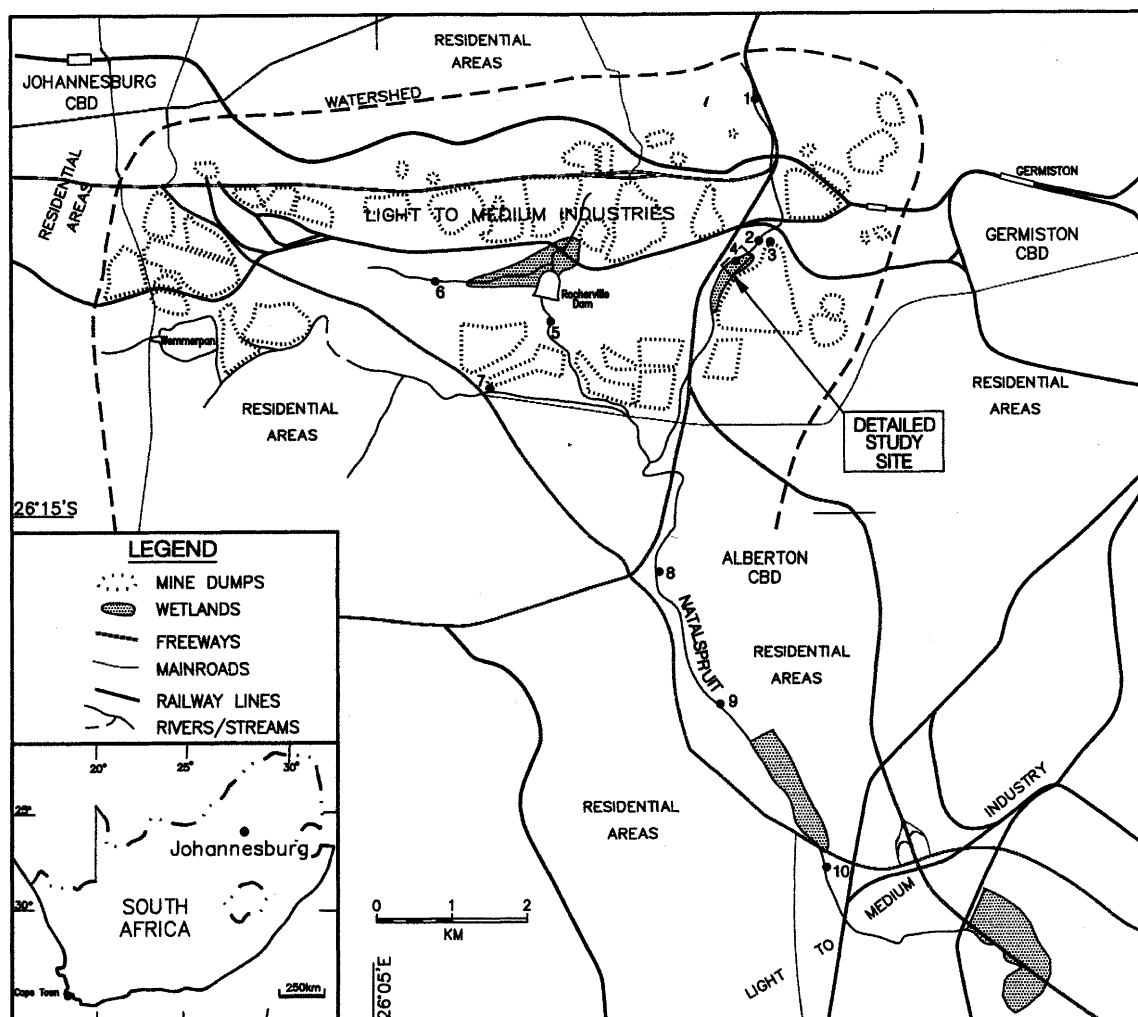


Fig. 1. A map of study area showing sampling localities and the locations of tailings dumps.

## 4. Materials and methods

### 4.1. Sampling procedures

At the detailed study site, the water samples were collected at 3-month intervals four times over a period of a year, starting in winter 1999 through to autumn 2000. Two lines of auger holes were made to a depth of about 1.2 m below the water table on the north bank of the stream. Soil samples were collected at 20-cm intervals. Ground elevation at each of the auger holes was accurately surveyed, using stream water surface as datum. The soil samples were stored in a PVC bags. Ground water samples were collected from the auger holes. The ground water level was allowed to equilibrate and depth to water table was measured during each sampling session. The surface water samples were taken from the middle of the stream (the width ~2–5 m and the depth ~30–60 cm, water discharge 0.1–0.3 m<sup>3</sup>/s). In addition, seepage water was sampled at the site where it had formed shallow puddles on the bank, which were

sufficiently deep to collect samples. The water samples were collected in clean, acidified PP bottles (Radojević and Bashkin, 1999), filtered immediately on return to the laboratory (after about 1 h) and stored in a refrigerator at 4 °C.

### 4.2. Field measurements

The measurements of pH, redox potential, temperature, and conductivity were taken for each water sample during sample collection using standard procedures (Hemond and Fechner-Levy, 2000) employing field meters.

### 4.3. Analytical methods

Field measurements were recorded using a Universal Multiline P4-SET3 field meter (WTW, Germany) equipped with pH combined electrode with integrated temperature probe (SenTrix 41), standard conductivity cell (Tetra Con 375) and oxidation-reduction potential probe (SenTrix ORP).

Soil samples were analysed for selected trace elements using X-ray fluorescence spectrometry. Samples were dried and milled in a carbon steel swing-mill. Approximately 5-g aliquots were pelletised prior to analysis. Samples were analysed on a Philips PW1400 spectrometer. Sample excitation was obtained using an Rh tube, operated at 50 kV and 50 mA. Wavelengths were separated using a LiF (220) crystal. K alpha spectral lines were used in all cases, and background correction applied. Mass absorption correction was made using the Rh K alpha Compton peak. Calibration was carried out using international rock standards (Geo-chemical Reference Standards—US Geological Survey and Canadian CRMP).

The concentrations of metals in water samples were determined using Atomic Absorption Spectrophotometry (Varian SpectrAA 10 (Varian) equipped with hydride generator (VGA). Calibration was carried out using the certified standards (Varian). The low concentrations of metals were determined by Anodic Stripping Voltammetry using Metrohm potentiostat/galvanostat (Mehrom PGSTAT 12) with General Purpose Electrochemical System software and a model 663VA stand (Metrohm). A multimode electrode (Metrohm, cat. No 6.1246.020) was employed as the working electrode in the hanging mercury electrode mode. A silver/silver chloride electrode and platinum electrode (both Metrohm) were used as reference and auxiliary electrodes, respectively. The stripping steps were recorded as a differential pulse voltammograms. All measurements were performed in a Metrohm jacketed glass vessel, equipped with a magnetic stirrer, and thermostatted at 298 K from a constant temperature water bath. The internal standard addition method was used for determination of concentration. The most important anions were determined using the closed system isotachopheresis (ITP analyser, Villa-Labeco, Spiska Nova, Slovakia) with conductivity and UV detection. Leading and terminating electrolytes were:  $\text{Cl}^-$ , pH 3.55 with counter ion BALA ( $\alpha$ -alanine), co-counter ion BTP and citric acid, pH 3.00 with counter ion  $\text{H}^+$ , respectively.

All solutions were prepared with purified water obtained by passing deionised water through a Milli-Q-water purification system. All chemicals used were of analytical grade obtained from Aldrich and Merck.

The chemometric data evaluation was performed using 'Statistica' computer software (Statsoft, Inc, 2000).

## 5. Results

### 5.1. Physical setting

The catchments area of the Natalspruit lies on the southern flank of the major Witwatersrand watershed, which separates rivers that drain into the Atlantic

Ocean from those that drain into the Indian Ocean. The topographic relief is moderate but locally rugged, and run-off is high, largely due to the urbanization. Although underground mining ceased in the area some decades ago, retreatment of the remaining tailings dumps is still in progress. The area between the dumps has been developed for light to medium industry.

At the detailed study site (Fig. 2), the active channel is confined to the north bank of the flood plain and is in the region of 10 m wide. The bank, consisting of alluvial soil, rises up from the channel (Fig. 3), and is sparsely vegetated with grass species, which become more abundant further from the stream. The southern bank marks the edge of the flood plain, about 100 m wide, which is heavily vegetated by *Phragmites* spp. reeds. To the south of this lies a large tailings dump which is presently being removed for retreatment. Some 250 m to the northwest lay another dump, which has since been removed for retreatment. During the winter months, a white crust several metres wide develops on the soil surface along the north bank of the channel.

### 5.2. Surface-ground water relationships

The water table on the north bank rises with distance from the stream, and both the stream level and the water table rise during the summer (Fig. 3). Throughout the year, the water table is more elevated than the stream water surface, and a seepage zone is developed between the edge of the stream and the line of intersection of the water table and the land surface. This seepage produces shallow pools along the edge of the stream, and rivulets, which flow down to the stream. Similar seepage zones were observed along other reaches of the Natalspruit drainage network, especially during the summer sampling period. These relationships indicate that the stream is effluent, i.e. is sustained, particularly during the winter months, by inflow of ground water from seepage zones and through the bed of the stream.

Above the intersection line of the water table with the surface, the soil surface is moist for a distance of several metres from the stream, reflecting capillary rise of the ground water above the water table. The width of the moist zone varies seasonally in response to fluctuations in the water table.

The ground water seepage zones are characterized by precipitation of limonite, which forms a bright red crust within seepage ponds and surrounding the rivulets on the stream bank.

### 5.3. Soil chemistry

The detailed study area falls within the Kimberley Shale, which divides two gold bearing reefs namely Bird Reef (comprising of quartzite, grits and conglomerates)

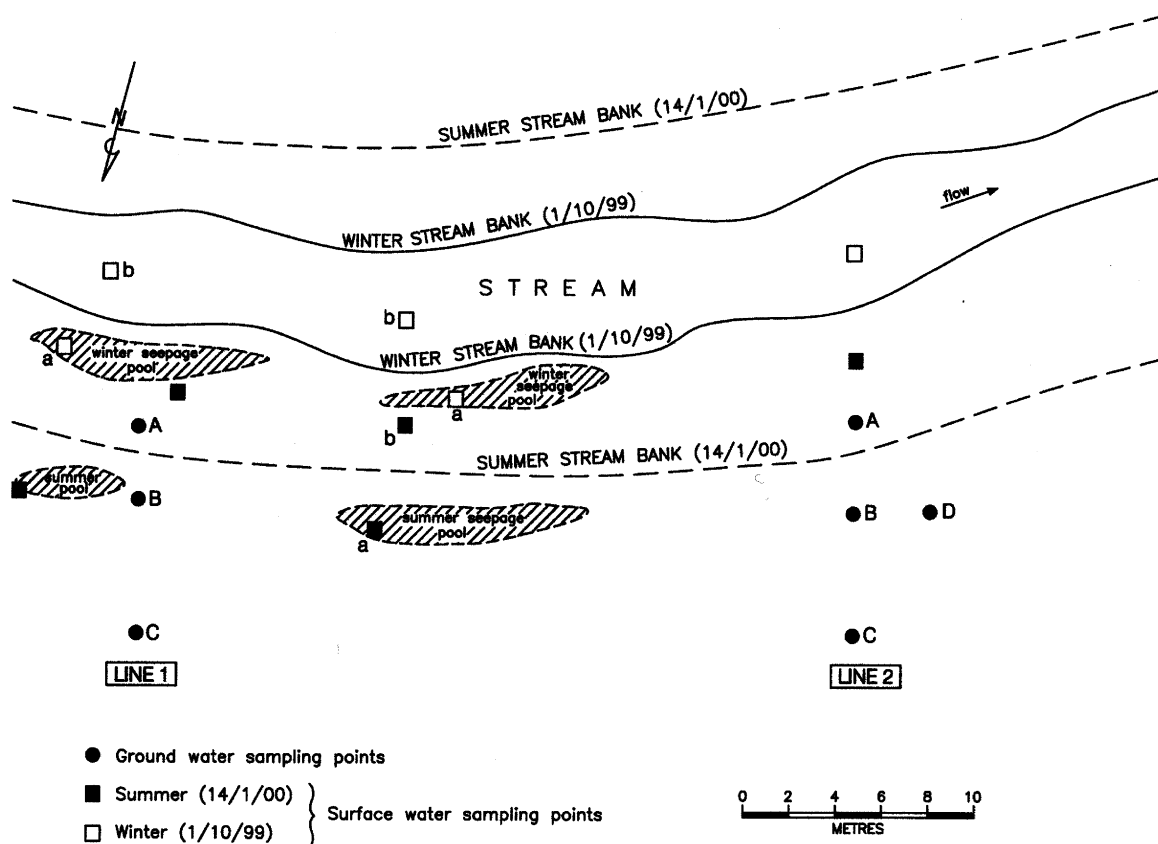


Fig. 2. A map of the detailed study site showing sampling localities. See Fig. 1 for location.

on the north and Kimberley Reef (comprising of course quartzite, grits, conglomerates and shale) on the south.

The white surface crust, which develops along the banks of the stream during winter, was identified by X-ray diffraction as gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). The analysis of the gypsum indicated relatively high concentrations (2000–5000 ppm) of several metals including Co, Ni, and Zn. The soil samples all show a marked gradient in trace element concentration with depth. Maximum concentrations occur in the upper 20 cm of the profiles (Fig. 4).

#### 5.4. Water chemistry

Fig. 5 shows the Eh/pH diagram of water samples. The pH ranges from 3.08 to 7.9. It is evident that the water samples cluster into four groups, namely surface water from the seepage area and downstream of it (Group 1), ground water (Group 2), seepage water collected from shallow pools along river (Group 3) and water collected upstream of the seepage area (Group 4). The surface water within the seepage area and downstream of it defines a linear array with a slope of 120 mV/pH unit.

Table 1 shows the regional variation of surface and ground water quality. Both surface and ground water samples collected upstream of the mining area have

neutral pH and relatively low conductivities. Within the mining area surface water and ground water have low pH and very high conductivities. These samples generally have elevated sulphate, iron and trace metal concentrations. In general the ground water at the seepage site has much higher dissolved solid concentration, conductivities and lower pH relative to surface water.

The chemical characteristics of surface and ground water from the detailed study site are shown in Table 2, for line 1 and 2 only (Fig. 2). The surface water chemistry, as expected, shows the biggest seasonal changes. The ground water preserves the low pH and high redox potential during all seasons. The pH is generally below 6. Sulphate concentrations are high.

Fig. 6 shows the change of conductivity as a function of season for surface and ground water.

## 6. Discussion

### 6.1. Surface and ground water

Little is known of the shallow ground water in the study area, although the water contained within the abandoned mines has been studied in some detail (Scott, 1995). Samplings carried out by Jones et al. (1988)

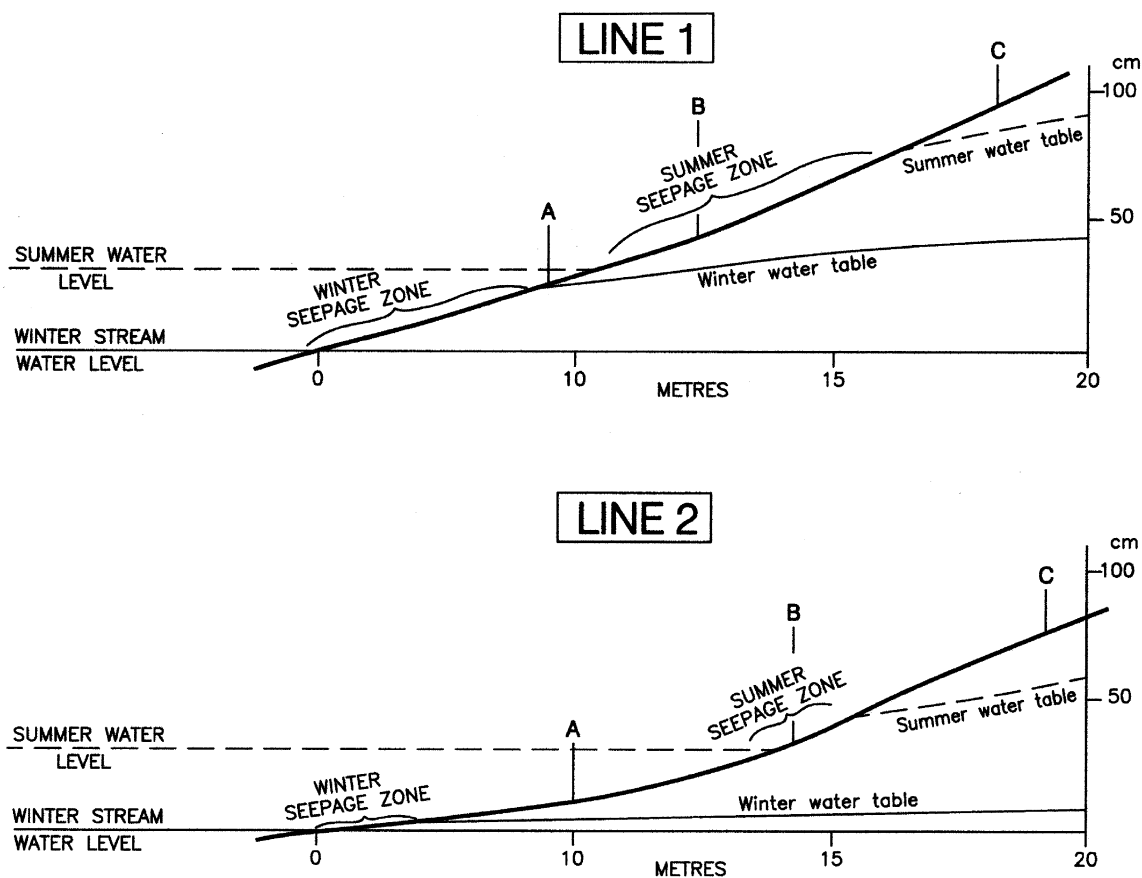


Fig. 3. Topographic sections along the two sample transects, showing the stream water level and water table in winter and summer.

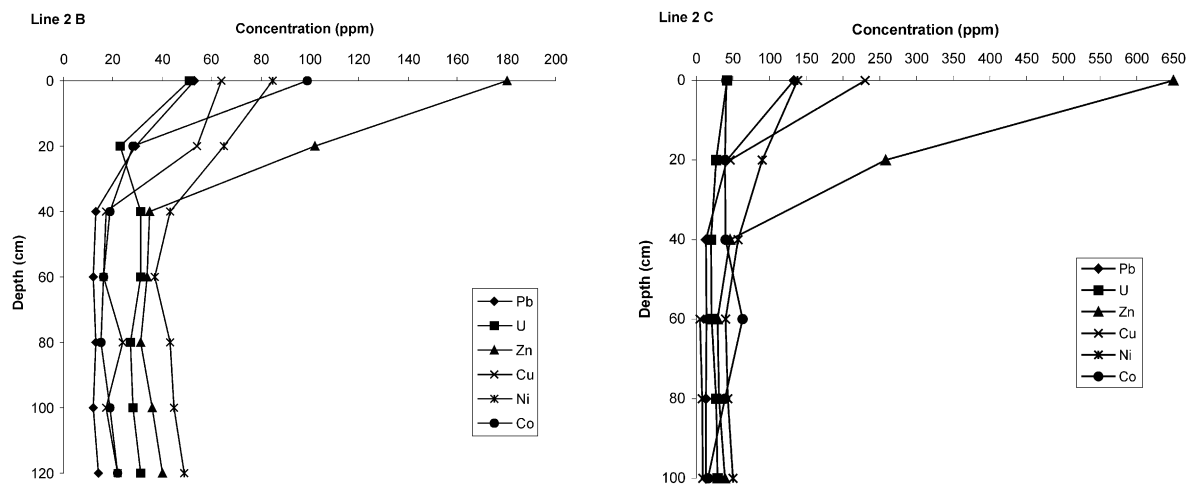


Fig. 4. Concentration of selected metals as a function of depth in two soil profiles.

indicate that shallow ground water in the vicinity of dumps may be contaminated to depths exceeding 18 m below surface. Soils in the catchment area are generally thin, and the bedrock, which consists of quartzites and shales, is hard and impervious. It is likely that most of the ground water is contained within rock fractures (Jones et al., 1988), and a small amount in alluvial aprons that flank certain reaches of the drainage net-

work. The water table within the fractured bedrock most likely follows the ground surface, but with considerably less relief. The shallow ground water is perched above a deeper reservoir of ground water which partly fills abandoned mine workings within the mining belt, where the water table lies at about 750 m below surface. This deeper water table is maintained by pumping from the few isolated mines, which are still in

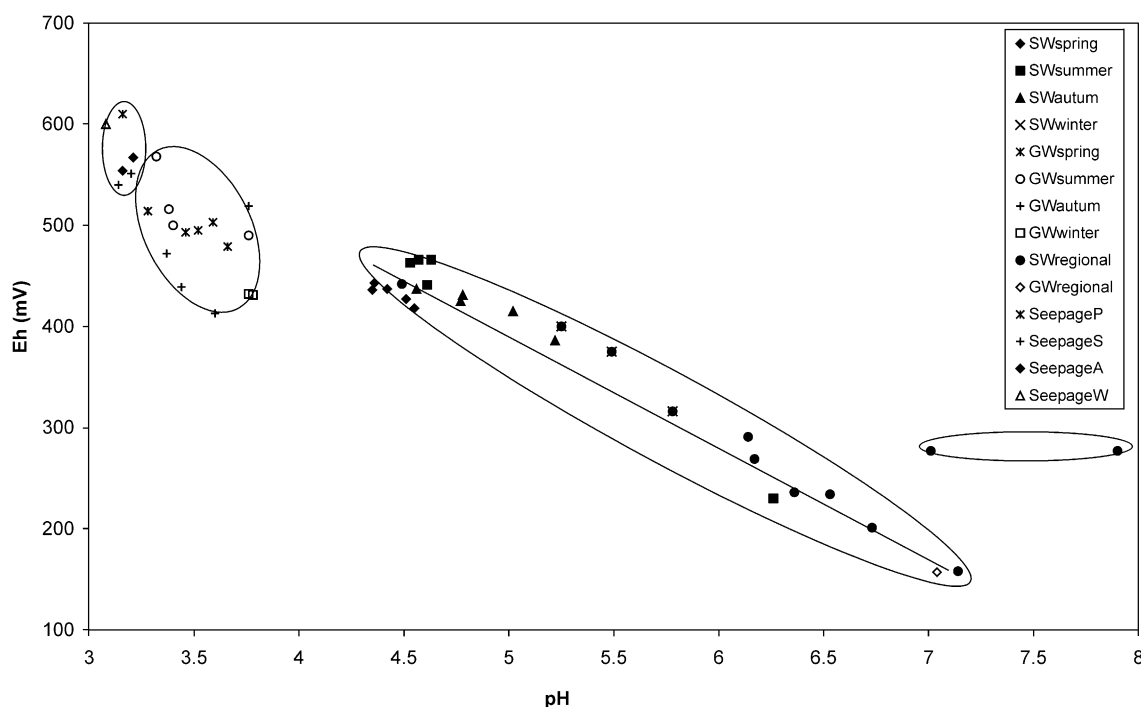


Fig. 5. Eh–pH relationships of all seepage, surface and ground water samples.

Table 1

Analytical results for ground and surface waters collected over 10 km reach of the Natalspruit<sup>a</sup>

Sample	pH	Eh mV	Cond mS/cm	SO <sub>4</sub> <sup>2-</sup> mg/l	Cl <sup>-</sup> mg/l	Cr mg/l	Zn mg/l	Pb mg/l	Cu mg/l	Fe mg/l	Mn mg/l	Co mg/l	Ni mg/l	Na mg/l	Ca mg/l	Ca mg/l
1S	7.01	277	0.37	250	21.00	1.65	0.1	0.00	0.10	2.38	0.30	0.00	0.13	10.24	84.60	84.60
1G	7.04	157	0.81	300	12.00	2.01	5.0	0.10	0.20	9.78	0.40	0.00	0.10	19.07	125.20	125.20
2S	6.17	269	1.5	500	12.00	2.01	1.5	0.10	0.10	26.61	6.20	0.69	1.02	49.26	125.80	125.80
3S	7.90	277	0.5	360	17.40	2.01	0.0	0.10	0.10	0.62	0.00	0.00	0.10	18.06	69.40	69.40
4E	3.08	600	5.71	2080	80.00	5.90	8.0	0.40	6.00	384.30	86.60	14.30	17.88	25.64	133.10	133.10
4S-A	5.78	316	1.31	680	17.50	2.19	1.0	0.10	0.10	19.19	8.30	0.37	1.06	38.99	121.00	121.00
4S-B	5.49	375	1.37	570	17.40	2.19	1.1	0.10	0.10	23.82	8.00	3.10	1.26	24.36	141.60	141.60
4S-C	5.25	400	1.38	530	18.06	1.65	1.2	0.10	0.20	24.84	8.50	0.62	1.38	46.81	145.20	145.20
4G-A	3.76	432	5.45	1750	36.40	9.97	8.0	0.70	6.00	453.40	68.00	11.40	15.28	22.60	125.70	125.70
4G-B	3.78	431	4.77	1400	26.70	5.82	7.0	0.30	5.00	379.00	72.00	10.30	15.38	23.28	116.40	116.40
5S	7.14	158	0.94	430	17.40	2.01	0.1	0.10	0.10	12.09	1.40	0.00	0.35	36.05	127.30	127.30
5G	4.56	408	1.33	570	23.50	2.01	1.4	0.20	0.40	3.69	2.40	0.00	0.57	29.09	204.10	204.10
6S	6.73	201	0.85	370	18.20	2.01	0.3	0.20	0.20	10.09	0.60	0.00	0.43	44.95	117.30	117.30
6G	3.96	394	5.7													
7S	4.49	442	1.14	530	16.00	2.01	1.5	0.20	0.30	77.60	2.00	0.00	1.27	29.31	100.90	100.90
8S	6.36	236	1.2	500	12.00	2.01	0.5	0.20	0.20	17.38	2.80	0.00	0.64	44.55	122.90	122.90
9S	6.14	291	1.04	430	10.80	2.01	0.4	0.10	0.10	14.70	2.50	0.00	0.59	35.40	127.10	127.10
10S	6.53	234	1.01	490	12.00	2.01	0.4	0.10	0.20	13.06	2.10	0.00	0.55	40.55	115.30	115.30

S, surface water, G, ground water; E, seepage water.

<sup>a</sup> See Fig. 1 for sample locations. Samples were collected in October 1999.

operation, as all of the mine workings on the Witwatersrand are interconnected. There is infiltration of shallow ground water into the mine workings (Scott, 1995), but the rate of infiltration is evidently slow, and has not disrupted the discharge of shallow ground water into the streams in the area, as indicated by the seepage zones observed along the stream banks.

Along all of the reaches of the Natalspruit sampled in this study, there is inflow of ground water into the stream. In summer, this is augmented by surface run-off from rainfall. Infiltration of rainfall also raises the water table during summer (Fig. 3), seepages become more active, and hence there is a general increase in stream discharge.

Table 2  
Subset (for the auger hole ‘B’ only) of analytical results for water samples collected over four seasons at the detailed study site (Fig. 2)<sup>a</sup>

Sample	pH	Temp. °C	Eh mV	Cond mS/cm	NO <sub>3</sub> <sup>-</sup> mg/l	PO <sub>4</sub> <sup>3-</sup> mg/l	SO <sub>4</sub> <sup>2-</sup> mg/l	Cl <sup>-</sup> mg/l	Cr mg/l	Zn mg/l	Cd mg/l	Pb mg/l	Cu mg/l	Fe mg/l	Mn mg/l	Co mg/l	Ni mg/l	Na mg/l	Ca mg/l	As µg/l	Hg µg/l	Se µg/l
1Sp	4.55	21.80	418	1.45	6.49	7.56	348.86	42.83	4.78	20.98	10.07	1.11	1.62	5.03	5.12	2.16	1.49	12.46	111.24	8.94	18.00	0.79
1Ss	6.26	15.30	300	0.37	3.79	3.02	424.92	9.22	5.76	0.76	1.50	0.14	0.03	2.99	1.20	0.65	0.30	5.95	34.94	8.90	11.60	0.45
1Sa	5.22	22.30	386	0.60	19.00	3.40	500.00	16.66	6.50	1.24	0.10	0.63	0.10	12.00	5.35	0.97	0.08	12.00	73.28	3.28	2.76	0.39
1Sw	5.78	13.50	316	1.32	7.82	1.40	680.00	17.50	2.20	1.00	0.00	0.10	0.10	19.19	8.30	0.37	1.06	38.99	121.00	0.57	2.16	0.00
1Ep	3.10	23.40	712	5.10	18.39	9.65	1398.34	31.48	4.38	23.70	0.24	2.74	3.89	7.75	8.44	26.11	15.20	39.71	415.88	26.90	20.00	1.23
1Es	3.20	16.30	551	6.64	13.42	7.85	1989.74	14.18	10.06	2.91	2.32	0.10	1.84	18.36	67.50	1.44	13.80	6.23	518.00	14.04	12.70	1.23
1Ea	3.21	28.60	567	4.39	56.20	37.50	2108.33	20.56	14.80	11.12	0.84	0.83	1.26	2.47	7.05	12.87	10.77	12.08	455.46	7.02	3.16	0.69
1Ew	3.08	19.40	600	5.71	22.79	13.10	2080.00	80.00	6.00	8.00	0.01	0.40	6.00	384.30	86.60	14.30	17.88	25.64	133.10	2.86	0.16	0.00
1Gp	3.52	18.50	495	6.63	4.17	22.56	1518.92	26.94	3.13	20.22	5.09	1.05	8.01	76.80	7.90	29.75	20.39	14.00	363.51	3.65	18.00	1.21
1Gs	3.40	17.60	500	4.33	2.13	11.07	2048.08	24.82	6.72	3.04	2.79	0.09	2.94	20.30	95.03	24.93	20.30	8.65	619.00	11.04	13.50	0.99
1Ga	3.44	20.90	439	4.17	17.40	11.60	2000.00	18.08	16.73	12.38	1.30	0.59	1.49	135.33	128.73	8.38	11.23	19.02	359.44	7.03	5.12	0.57
1Gw	3.76	12.30	432	5.45	12.39	17.10	1750.00	36.40	10.00	8.00	0.02	0.70	6.00	453.40	68.00	11.40	15.28	22.60	125.70	2.96	0.78	0.00
2Sp	4.42	21.70	437	1.53	7.32	11.52	439.29	42.83	5.64	20.60	10.00	1.08	1.57	6.31	5.19	3.63	1.96	19.71	85.05	7.77	15.00	0.74
2Ss	4.61	15.20	441	0.58	3.60	2.33	419.08	9.93	5.97	0.96	1.71	0.15	0.07	8.80	3.84	1.01	0.90	5.94	47.30	10.01	11.80	0.50
2Sa	4.78	22.60	431	0.70	14.20	3.00	553.00	16.66	6.20	1.42	0.18	0.56	0.13	16.13	5.59	1.10	0.19	16.03	70.73	1.32	1.98	0.39
2Sw	5.25	14.30	400	1.39	7.82	1.98	530.00	18.06	1.70	1.20	0.00	0.10	0.20	24.84	8.50	0.62	1.38	46.81	145.20	0.65	0.40	0.00
2Ep	3.16	22.80	610	6.81	5.71	10.48	1620.79	35.45	4.54	19.12	0.24	3.15	4.81	5.64	10.68	24.70	21.98	2400	196.64	29.25	15.30	1.28
2Es	3.14	16.50	540	4.62	14.03	5.78	1634.58	17.02	8.90	3.06	2.52	0.09	2.40	22.52	105.01	27.08	21.20	9.03	329.20	17.14	13.10	1.40
2Ea	3.16	28.80	554	4.17	29.00	12.60	1975.00	18.08	17.35	10.80	0.74	0.73	2.26	1.65	3.24	13.07	12.34	11.37	324.30	3.10	2.18	0.71
2Gp	3.46	15.20	493	6.17	27.20	29.44	1400.42	26.38	2.15	21.24	2.04	1.03	5.03	43.80	6.78	24.16	21.61	28.29	328.40	3.25	18.00	1.11
2Gs	3.76	17.60	490	3.69	13.41	4.40	1672.12	24.82	8.36	2.85	2.05	0.16	0.95	14.85	52.50	15.58	11.60	10.13	489.90	13.78	14.50	0.81
2Ga	3.60	20.80	413	3.80	17.50	19.20	2150.00	18.88	14.38	13.22	0.87	0.66	0.60	179.82	168.91	15.69	11.73	17.09	339.41	5.12	4.33	0.63
2Gw	3.78	12.30	431	4.77	12.39	20.00	1400.00	26.70	5.80	7.00	0.02	0.30	5.00	379.00	72.00	10.30	15.38	23.28	116.40	6.00	0.19	0.00

S, surface water; G, ground water; E, seepage water; p, Spring; s, Summer; a, Autumn; w, Winter.

<sup>a</sup> The whole data sets are excluded due to very large sizes.



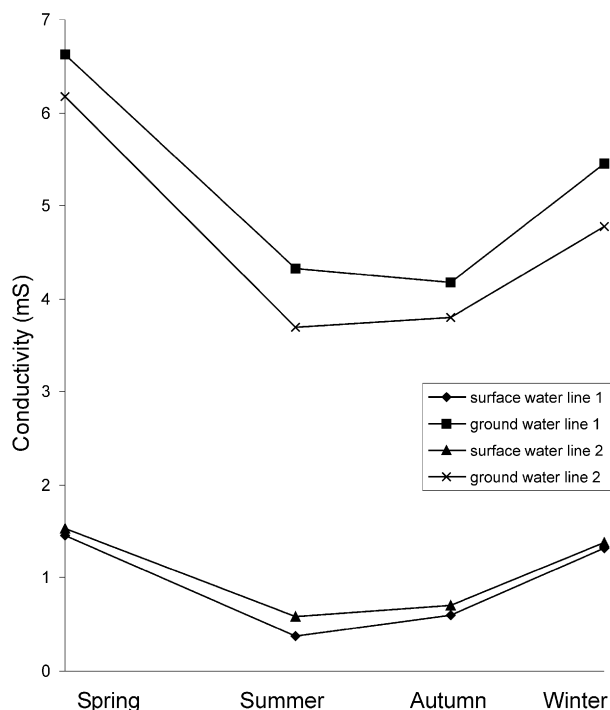


Fig. 6. Seasonal changes in conductivity for surface and ground waters.

One of the tributaries sampled rises to the north of the mining belt, but most of the others derive their inflow from within the area of tailings dumps (Fig. 1). To the south of the mining belt, there are few active streams, and the downstream increase in discharge is primarily due to inflow of ground water along the length of the Natalspruit. This ground water to the south of the mining belt is unaffected by mining activity.

### 6.2. Condition of the ground water

Ground water from outside the mining area (Table 1, 1G) is sulphate dominant and has a neutral pH. In the mining area, the ground water becomes very acidic (pH 3.4), and has high sulphate and heavy metal concentrations (Table 1, 4G, A/B). Seepage water in the mining area is also characterised by high sulphate and heavy metal concentration, and the pH is slightly lower than the ground water. This is probably the result of oxidation of iron as the ground water emerges at the surface, which further lowers the pH.

### 6.3. Soil – ground water relations

The soil profiles on the north bank all show increasing metal concentration towards the surface, with the highest concentration in the top 20 cm of the profile. Similar profiles have been reported from sites where dumps had been removed (Rosner and van Schalkwyk, 2000), which were attributed to downward migration of metals

from the dump. The study site described here has never been covered by tailings, and we attribute the concentration gradients in the soils to the effect of capillarity and surface evaporation. Metal rich ground water is drawn upwards by capillarity and evaporates on the soil surface producing a gypsum crust, which is very enriched in metal sulphates. During the rainy season this is partially dissolved and enters the soil profile. There is a water deficit in the region (evaporation > rainfall) and hence insufficient rainfall to completely flush out the metal salts, which consequently accumulate in the soil profile. Erosion of both the soil and the gypsum crust into the Natalspruit undoubtedly adds to the metal load in the stream.

### 6.4. Stream water composition

Upstream of the mining area, the surface water is neutral and has low metal concentrations—lower than ground water in the region, as a result of dilution by rain (Table 1, 1S). Within the mining area, the pH falls to 5–6, and heavy metals and sulphate concentrations rise dramatically, due to the inflow of acidic ground water. South of the mining area, the pH rises (Table 1, 8S, 10S, Fig. 1). Fe and Ni concentrations decrease by about 50%, while Mn concentration decreases by about 70%. It is noted that along the entire sampled reach of the Natalspruit, rocks on the river bed are coated by a thin layer of orange-coloured limonite, which has accumulated over many decades. The stream supports virtually no animal life and very little aquatic vegetation.

The Eh–pH diagram (Fig. 5) indicates that these parameters are strongly negatively correlated in the surface water within and downstream of the mining area (Group 1). The gradient of this line corresponds closely with the predicted equilibrium between Fe (II) and Fe (III) hydroxide (Pourbaix, 1988), suggesting that the Eh and pH are buffered by the presence of precipitated Fe (III) hydroxide. Ground water in the seepage area is not buffered by this redox equilibrium, and lies within stability field of Fe (II; Group 2, Fig. 5). Surface water collected upstream of the mining area is also not buffered by the iron redox reaction (Group 3, Fig. 5).

The outflow from the Rosherville Dam (Table 1, 5S) is unusual in that it has neutral pH, and metal concentrations not very different from water outside the mining area. Sulphate however is slightly elevated. This is surprising, as the entire catchment of the dam lies within the mining belt (Fig. 1). The better quality of water is also reflected in the greater variety of aquatic animal and plant life in the stream below the dam.

We attribute the superior quality of the outflow and presumably dam water itself to the major contribution which surface water runoff makes to the water stored in this reservoir, which dilutes the contribution of acidic ground water.

An indication of the contribution of acid mine seepage in the Natalspruit over the sampled region can be obtained by using the sulphate concentration as a marker, i.e. a conserved species. Water upstream of the mining area contains about 300 mg/l of sulphate. At site 4 (Fig. 1) sulphate rises to 600 mg/l, indicating the addition of about 20% of acidified ground water. At site 10, some 10 km downstream, the sulphate concentration has fallen to about 500 mg/l, indicating the presence of about 12% of acidic mine water in the stream. Although the mining belt where acidic groundwater is generated is relatively narrow (Fig. 1), its rate of dilution is clearly very slow and hence acidity and the associated deleterious effects persist for a considerable distance downstream. It is emphasised that these are minimum estimates of the proportion of acidified ground water in the stream, as sulphur is probably not completely conserved along the river system. Sulphur may be lost from the water by precipitation of less soluble sulphates, and also by reduction to insoluble sulphide in the organic-rich, marshy reaches along the stream.

The admixture of 20% contaminated water to the stream, as indicated by the sulphate content, should increase the iron and nickel concentrations to 80 and 4 mg/l respectively. However, observed concentrations of iron and nickel are 20 mg/l and about 1 mg/l. This indicates that both Fe and Ni are being rapidly precipitated in the mixing zone, and the analyses suggest that about 70% of the Fe and Ni have been removed from the mixed water. The precipitation of Fe is due to redox effects (Fig. 5). Ni would normally be soluble under the prevailing pH conditions, and we attribute its removal to co-precipitation processes. Similar calculations for Mn indicate that about half of the Mn is precipitated in the zone of mixing, probably also due to oxidation. The downstream decrease in Fe is largely due to dilution and continuing precipitation, but the rate of precipitation is evidently relatively slow, because Fe concentration falls from about 20 mg/l in the mixing zone to about 13 mg/l 10 km downstream. In contrast, Mn concentration decreases more rapidly from about 8 mg/l in the mixing zone to about 2.5 mg/l over 10 km. The slow precipitation of these metals, particularly Fe, accounts for the very extensive development of limonite coatings in the stream bed, and the downstream persistence of the pH control by the iron redox buffer (Fig. 5).

The contribution of acidic ground water to the stream at the study site varies seasonally, but not by much. Prior to the summer rains, sulphate concentration at site 4 indicates about 22% ground water contribution. After the rainy season the proportion of acid ground water in stream water falls to about 18%. The reason for this limited range is probably due to the rise in the water table during summer (Fig. 3), which results in increased the groundwater seepage. However, there must be times

during flash floods, when the contribution of ground water becomes extremely small, although these would be of very short duration (a few hours).

### 6.5. Chemometric evaluation of data

Chemometric evaluation was performed on 17 surface water samples, 16 ground water samples and selected variables found in Table 1. Trace metals (As, Hg, Se) and temperature were not considered in any chemometric evaluation. Seepage water was excluded from the surface water data set, due to its large chemical differences from surface and ground water (Table 2).

Both sets of data (surface water and ground water) for all river sections were found to be normally distributed. The linear dependency of the variables was assessed by calculating the correlation matrix (Adams, 1995) for both data sets. High correlation of many heavy metals and sulphate exist for both surface and ground water samples.

The most important use of principle factor analysis (PFA) is to represent the n-dimensional data structure in a smaller number of dimensions, usually two or three. This permits the observation of groupings of objects, outliers etc., which define the structure of the data, (Massart et al., 1988). PFA reduced the multivariate data sets for both surface and ground water of 18 variables each to three and five factors respectively. The scree plot was used in deciding the number of factors required for ground water. The cumulative variance of the three factors for the surface waters accounted for

Table 3  
Factor loadings for (a) surface water and (b) ground water

	a			b		
	Factor 1	Factor 2	Factor 3	Factor 1	Factor 2	Factor 3
pH	-0.44	<b>0.77</b>	0.22	-0.19	0.27	0.49
Eh	0.06	<b>-0.82</b>	-0.30	0.29	-0.04	<b>-0.73</b>
Conduct.	<b>0.78</b>	<b>0.53</b>	-0.23	<b>0.56</b>	0.37	0.03
NO <sub>3</sub> <sup>-</sup>	0.02	0.17	<b>0.80</b>	-0.19	0.08	0.08
PO <sub>4</sub> <sup>3-</sup>	<b>0.82</b>	-0.13	0.13	0.35	<b>0.75</b>	0.18
SO <sub>4</sub> <sup>2-</sup>	<b>-0.62</b>	0.36	0.22	<b>-0.88</b>	-0.06	0.12
Ci	<b>0.96</b>	0.09	0.04	<b>0.62</b>	0.50	0.36
Cr	0.10	<b>-0.89</b>	0.35	<b>-0.86</b>	-0.12	0.19
Zn	<b>0.96</b>	-0.10	-0.11	-0.03	<b>0.63</b>	0.07
Cd	<b>0.92</b>	-0.21	-0.20	0.33	<b>0.83</b>	-0.29
Pb	<b>0.88</b>	-0.23	0.34	0.10	<b>0.92</b>	0.15
Cu	<b>0.96</b>	-0.08	-0.12	<b>0.61</b>	0.06	0.24
Fe	<b>-0.57</b>	<b>0.71</b>	0.13	-0.17	-0.09	<b>0.89</b>
Mn	-0.33	<b>0.84</b>	0.12	<b>-0.88</b>	-0.25	0.05
Co	<b>0.81</b>	-0.06	-0.17	<b>0.55</b>	0.35	-0.32
Ni	<b>0.64</b>	0.16	<b>-0.68</b>	<b>0.65</b>	0.49	-0.11
Na	0.08	<b>0.87</b>	-0.04	0.33	0.44	0.31
Ca	0.21	<b>0.92</b>	-0.01	-0.31	-0.11	<b>-0.81</b>
ExpI.Var	7.82	5.48	1.72	4.74	3.64	2.83
% Cum.Var	43.41	73.83	83.39	26.32	46.56	62.43

Marked loadings are > 0.55.

Table 4  
Correlation matrix for all surface water samples

	Ph	Eh	COND	NO <sub>3</sub> <sup>-</sup>	PO <sub>4</sub> <sup>3-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	Cr	Zn	Cd	Pb	Cu	Fe	Mn	Co	Ni	Na	Ca
Ph	1	-0.88	0.01	0.32	-0.48	0.56	-0.37	-0.69	-0.56	-0.64	-0.55	-0.54	0.80	0.82	-0.46	-0.30	0.62	0.63
Eh	-0.88	1	-0.34	-0.39	0.18	-0.39	-0.02	0.67	0.17	0.28	0.17	0.16	-0.58	-0.72	0.20	0.11	-0.70	-0.73
COND	0.01	-0.34	1	-0.07	0.56	-0.34	0.81	-0.50	0.76	0.69	0.50	0.77	-0.09	0.16	0.69	0.77	0.59	0.68
NO <sub>3</sub> <sup>-</sup>	0.32	-0.39	-0.07	1	0.02	0.18	0.06	0.15	-0.09	-0.19	0.26	-0.09	0.24	0.22	-0.11	-0.52	0.12	0.17
PO <sub>4</sub> <sup>3-</sup>	-0.48	0.18	0.56	0.02	1	-0.47	0.83	0.28	0.82	0.78	0.86	0.81	-0.53	-0.32	0.77	0.41	-0.07	0.05
SO <sub>4</sub> <sup>2-</sup>	0.56	-0.39	-0.34	0.18	-0.47	1	-0.59	-0.28	-0.69	-0.73	-0.57	-0.70	0.72	0.65	-0.53	-0.51	0.28	0.13
Cl <sup>-</sup>	-0.37	-0.02	0.81	0.06	0.83	-0.59	1	0.04	0.95	0.90	0.88	0.96	-0.51	-0.21	0.77	0.63	0.17	0.31
Cr	-0.69	0.67	-0.50	0.15	0.28	-0.28	0.04	1	0.15	0.21	0.43	0.13	-0.69	-0.76	0.10	-0.31	-0.81	-0.86
Zn	-0.56	0.17	0.76	-0.09	0.82	-0.69	0.95	0.15	1	0.99	0.87	1.00	-0.69	-0.45	0.82	0.71	0.00	0.11
Cd	-0.64	0.28	0.69	-0.19	0.78	-0.73	0.90	0.21	0.99	1	0.83	0.98	-0.76	-0.55	0.81	0.72	-0.09	-0.01
Pb	-0.55	0.17	0.50	0.26	0.86	-0.57	0.88	0.43	0.87	0.83	1	0.87	-0.65	-0.45	0.66	0.29	-0.12	-0.02
Cu	-0.54	0.16	0.77	-0.09	0.81	-0.70	0.96	0.13	1.00	0.98	0.87	1	-0.67	-0.42	0.81	0.71	0.03	0.14
Fe	0.80	-0.58	-0.09	0.24	-0.53	0.72	-0.51	-0.69	-0.69	-0.76	-0.65	-0.67	1	0.88	-0.49	-0.38	0.61	0.60
Mn	0.82	-0.72	0.16	0.22	-0.32	0.65	-0.21	-0.76	-0.45	-0.55	-0.45	-0.42	0.88	1	-0.33	-0.15	0.73	0.76
Co	-0.46	0.20	0.69	-0.11	0.77	-0.53	0.77	0.10	0.82	0.81	0.66	0.81	-0.49	-0.33	1	0.70	-0.06	0.13
Ni	-0.30	0.11	0.77	-0.52	0.41	-0.51	0.63	-0.31	0.71	0.72	0.29	0.71	-0.38	-0.15	0.70	1	0.23	0.28
Na	0.62	-0.70	0.59	0.12	-0.07	0.28	0.17	-0.81	0.00	-0.09	-0.12	0.03	0.61	0.73	-0.06	0.23	1	0.84
Ca	0.63	-0.73	0.68	0.17	0.05	0.13	0.31	-0.86	0.11	-0.01	-0.02	0.14	0.60	0.76	0.13	0.28	0.84	1

83.39% of the data (Table 3a). The first three factors for the ground water accounted for 62.4% of the total variance of the data, (Table 3b).

A varimax rotation of the loadings (Einax et al., 1997; Sharaf et al., 1986; Table 3a,b) indicates some structure. For the surface water (Table 3a), factor 1 is loaded with variables (conductivity, phosphates, chlorides, and all metals which have a single stable oxidation state), which suggests a strong impact of solubility product chemistry and the effects of co-precipitation. Factor 2 indicates the influence of oxidation-reduction processes controlled by redox chemistry, particularly Fe and Mn. These ele-

ments are present in their reduced states in the ground water, and precipitate due to oxidation once the water comes into contact with the atmosphere. The kinetics of the oxidation are evidently slow, the iron redox buffer persists for many kilometers along the stream. The clear separation of the behavior of Fe and Mn from the other heavy metals is also indicated by the correlation matrix (Table 4), which shows the heavy metals with single stable oxidation states to be highly positively correlated, while their correlation with Fe and Mn is poor. Factor 3 is loaded with nitrates and Ni, which could be linked to industrial sources.

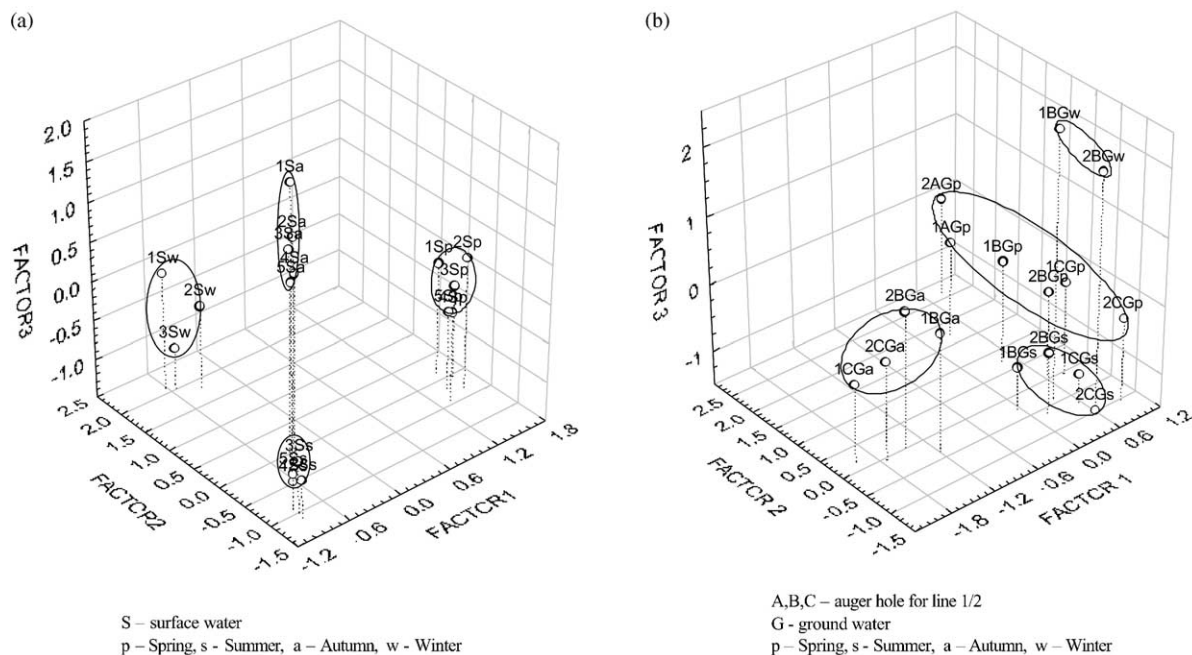


Fig. 7. 3D scatter plots of the first three factors for: (a) surface and (b) ground water data.

For ground waters, the loading of factors does not show clear grouping according to chemical solution equilibria. This may be due to the general homogeneity of the data set, coupled with small-scale effects such as soil mineral surface properties, sorption and exchange reactions, redox chemistry and reaction kinetics in soil–water systems (Evangelou, 1998). However factor 1 and 2 (Table 3b) accounts more for solubility product chemistry. Factor 3 could account for stronger influence of redox processes being loaded with Eh, Fe and Ca.

The 3D score plots (Fig. 7a,b) for both surface and ground water data sets clearly illustrate the seasonal variation of the variables loading the first three factors. The main seasonal effect appears to be dilution, which is also illustrated by the seasonal change in conductivity (Fig. 6). As expected, surface water shows much stronger seasonal changes than the ground water.

## 7. Conclusions

This study has indicated that shallow ground water contaminated as a result of mining activities is contributing significantly to the quality of surface water emanating from the Witwatersrand watershed, and is not only affecting the pH of the water, but is also contributing heavy metals to the surface aquatic environment. Acidified water seeping from the mine tailings dumps contributes an average of about 20% of stream flow from this area. It reduces pH, adds high metal loads to the water and causes extreme iron hydroxide precipitation in the stream, all of which impact negatively on aquatic life. In addition, evaporation of ground water off the capillary zone above the water table has created surface soil layer along the bank of the stream, which is extremely enriched in heavy metals. This zone no longer supports vegetation. During the dry winter months, a gypsum crust enriched in heavy metals also develops on this surface. Dissolution of the crust and the surface soil adds to the metal loads in the stream.

The oxidation of iron introduced into the stream by seepage has established a redox buffer, which controls the pH of the stream water. Oxidation is slow, and the control by the redox buffer persists for many kilometers from the pollution source. The analysis has shown that while iron and manganese concentrations in surface water are controlled by redox equilibria, the chemical control on other heavy metals is different, and these are probably being removed from the stream water by co-precipitation processes. Moreover the rate of dilution downstream of the mining belt is relatively low, so that

the effects of the contaminated water persist for considerable distances downstream of the pollution source.

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## References

- Adams, M.J., 1995. *Chemometrics in Analytical Spectroscopy*. The Royal Society of Chemistry, Cambridge.
- Audouin, J.-C., 1997. Geophysical study of acid rock drainage in the City Deep area, Johannesburg, Gauteng. Unpublished MSc Thesis, University of the Witwatersrand, Johannesburg, South Africa, 112pp.
- Einax, J.W., Zwanziger, H.W., Greiß, S., 1997. *Chemistry in Environmental Analysis*. Wiley.
- Evangelou, V.P., 1998. *Environmental Soil and Water Chemistry. Principles and Applications*. J Wiley & Sons, New York.
- Feather, C.E., Koen, C.M., 1975. Mineralogy of the Witwatersrand Reef. *Mineral Science and Engineering* 7, 189–224.
- Hemond, H.F., Fechner-Levy, E.J., 2000. *Chemical Fate and Transport in the Environment*. Academic Press, San Diego.
- Jones, G.A., Brierly, S.E., Geldenhuis, S.J.J., Howard, J.R., 1988. Research on the Contribution of Mine Dumps to the Mineral Pollution Load at the Vaal Barrage. Water Research Commission Report No. 136/1/89. Water Research Commission, Pretoria.
- Marsden, D.D., 1986. The current limited impact of Witwatersrand gold mine residues on water pollution in the Vaal River system. *Journal of the South African Institute of Mining and Metallurgy* 86, 481–504.
- Massart, D.L., Vandeginste, B.M.G., Deming, S.N., Michotte, Y., Kaufman, L., 1988. *Chemometrics: a Textbook*. Elsevier, Amsterdam.
- Pourbaix, M., 1988. *Atlas of Electrochemical Equilibria in Aqueous Solutions*. Cebalcor, Brussels.
- Radojević, M., Bashkin, V.N., 1999. *Practical Environmental Analysis*. Royal Society of Chemistry, Cambridge.
- Rosner, T., van Schalkwyk, A., 2000. The environmental impact of gold mine tailings footprints in the Johannesburg region, South Africa. *Bull. Eng. Geol. Env.*, v59 137–148.
- Scott, R., 1995. Flooding of Central and Grand Rand Gold Mines: an investigation into controls over the inflow rate, water quality and the predicted impacts of flooded mines. Water Research Commission Report, 486/1/95, South Africa, 238 pp.
- Sharaf, M.A., Illman, D.L., Kowalski, B.R., 1986. *Chemometrics—Chemical Analysis*. Wiley-Interscience publication, New York, Vol. 82, pp. 206–223.
- Tyson, P.D., Wilcocks, J.R.N., 1971. Rainfall variation over Johannesburg—the local climate over Johannesburg. Department of Geography and Environmental Studies, University of Witwatersrand, Johannesburg, occasional paper pp. 428.
- Werdmuller, V.W., 1986. The central rand. In: Antrobus, E.S.A. (Ed.), *Witwatersrand Gold—100 Years*. Geological Society of South Africa, Johannesburg, p. 748.