

# Chemical Contamination and Radiological Risk Assessment of Water Sources in Richards Bay

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**Abstract:** South Africa is pronounced a dry country. Though KwaZulu-Natal has a higher rain fall than most part of the country, it has recorded cases of austere droughts. The present study was aimed at examining the quality of water within Richards Bay precinct in relation to South African target water quality range (TWQR). Fifty water samples were collected from five water sources (effluent, stream, Mzingazi River, Indian Ocean and Esikawini drinking tap water) and analyzed using ICP-MS technique to determine the concentrations of some traced metals i.e., Fe, Cu, Tl, Zn, Pb, Cr, and Ni. The main impurities were found to be Cd, Mn and As with concentrations of  $2.21 \times 10^0 \text{mg.l}^{-1}$ ,  $7.19 \times 10^{-1} \text{mg.l}^{-1}$  and  $2.72 \times 10^{-3} \text{mg.l}^{-1}$  respectively. The surface gross alpha contamination of mineral stores within the facilities ranges from  $1.00 \times 10^{-4} \pm 1.5 \times 10^{-2} \text{Bq.cm}^{-2}$  to  $1.45 \times 10^{-2} \pm 4.20 \times 10^{-3} \text{Bq.cm}^{-2}$  with a mean concentration of  $1.15 \times 10^{-2} \pm 1.36 \times 10^{-2} \text{Bq.cm}^{-2}$  while the gross beta contamination ranges from  $1.00 \times 10^{-3} \pm 1.14 \times 10^{-2} \text{Bq.cm}^{-2}$  to  $4.15 \times 10^{-2} \pm 2.17 \times 10^{-2} \text{Bq.cm}^{-2}$  with a mean concentration of  $2.15 \times 10^{-2} \pm 1.80 \times 10^{-2} \text{Bq.cm}^{-2}$ . The result indicated that the water quality was acceptable.

**Key words:** Water, heavy metals, contamination.

## 1. Introduction

Water is scarce in South Africa and further deterioration of the already limited sources should not be allowed to happen. Urbanization and industrial activities commonly introduce pollutants into the nearby environment [1] thereby contaminating surrounding soil and water sources. Therefore, water source intended for human use within an industrial region should not be assumed to be free from pollution [2]. Contaminated water can transport pollutants and cause a variety of diseases [3]. Thus, it may be described as a vehicle for the spread of diseases. In 1990, Schalekamp estimated about 50,000 people all around the world die every day from disease associated to water [4]. Over 12 million people in South Africa do not have access to adequate

potable water supply [5]. South Africa's earth crust is rich in minerals resources [6] foremost among them are gold, uranium, iron ore, phosphate rock and coal [7]. Mined, milled and processed minerals have raised the concentration of naturally occurring radioactive materials and toxic metals in the environment [8], which can reach surface and underground waters in different ways including run-off and leaching [9]. Though natural radioactive nuclides and heavy metals are natural constituent of the earth's crust and are present in all ecosystems [10], their concentrations in the environment have been radically increased by urbanization, industrial and agricultural activities [11]. Therefore, knowledge of their quantitative and qualitative distributions is important to monitor environmental contaminations [12]. In South Africa, studies have been conducted on water quality from different water sources [3, 13-16] but no work has been done on water quality within and around

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phosphate storage facilities in Richards Bay. This study is conducted in Richards Bay about 190 km north of Durban. The study is important because it will form the baseline data for environmental contamination within facility. Port of Richards Bay, commissioned in 1976 has triggered the establishment of many industries including Foskor (pty). The company produces fertilizer, phosphor and sulphuric acid as well as magnetite from rock phosphate mined and beneficiated in Limpopo province and transported to Richards Bay via railways. Since the rock phosphate occurs as a fine powder, it may spill over or disperse into the air during offloading from freight wagon and tipper truck and subsequently settled on water, soil and vegetation within and around the facility.

The aim of this study was to examine the radiological surface contaminations and chemical quality of water sources within and around Richards Bay in order to assess their suitability for domestic and agricultural use in relation to South African TWQR (target water quality range) [16]. This was done by: (1) Determining the gross alpha and gross beta activity concentrations of the water sources. Should these concentrations be higher than the recommended values of  $5.0 \times 10^{-1} Bq.l^{-1}$  and  $1.00 Bq.l^{-1}$  for the gross alpha and gross beta respectively [16, 17]? Further analysis will be required to determine the contributions of specific nuclides. (2) Assessing the concentration of ten heavy metals Fe, Zn, Cu, Cd, Cr, Pb, Tl, Mn, Ni, and As in relation to South African water quality guideline for domestic and agricultural uses [16]. A toxic heavy metal is any relatively dense metal or metalloid that is noted for its potential toxicity, especially in environmental contexts [18]. The term has particular application to cadmium, mercury, lead and arsenic [19]. All these appear in the world Health Organization list of 10 chemical of major public concern [20]. Others examples include manganese, chromium, nickel, zinc, selenium, silver, thallium, vanadium and mercury. To maintain the quality of water resources in South

Africa within a range of no health effect on human health, the department of water affairs and forestry set up various range to monitor the concentrations of these metals in water.

## 2. Materials and Methods

After a pre-field survey to map out the major water sources within and around the Richards Bay Precinct facilities, a total of fifty water samples, ten each from five sampling sources; Mzingazi River, Esikawini water tap, effluent, Indian Ocean and a stream within the Richards Bay were collected in March 2016. The samples were collected directly into a two-liter size high density plastic in accordance with the South Africa National Standard water quality sampling technique [21]. To prevent interaction between radionuclides and the container walls, samples were immediately acidified with  $HNO_3$  to a  $pH < 2$  [22]. Furthermore, five swipe samples were also collected from storage facilities using what-man filter paper to assess the surface contamination of such storage facilities. All samples were prepared and analyzed at the nuclear energy corporation of South Africa (NECSA).

Water samples were pressure filtered through a  $4.5 \times 10^{-1} \mu$  pore size membrane with 142 mm in diameter. 10 mL of each sample was acidified with  $5.0 \times 10^1 \mu l^{-1}$  of ultra-pure concentrated  $HNO_3$  and analyzed using inductively coupled plasma mass spectrometry (ICP-MS, series-7900) technique for elemental composition. The pH value, total dissolve solid and conductivity were measured using pH meter and conductivity meters respectively.

The wipe samples from rock phosphate, rutile, magnetite, zircon and major transfer stores were analyzed for gross alpha and beta activity concentration based on analytical methods adopted by NECSA from Radio Analysis Quality Management System [23].

## 3. Results and Discussion

The concentrations of heavy metals in water

sources were analyzed and the results are presented in Table 1. Mn, Cu, Fe, and Zn were the most dissolved elements in the samples from effluent, Esikawini drinking tap, Indian Ocean and Mzingazi River. The least contributors were Tl, Pb, Cr, Ni, Cd and As seen in Table 1. In contrast to the foregoing, Cd, Mn, and Cu are the most dissolved minerals in stream samples were as Fe, Tl, Zn, Pb, Cr and Ni dissolved least in stream sample. Water sources investigated in this study can be classified into two: (1) raw water sources i.e. Indian Ocean, Mzingazi river and stream; (2) Treated water sources i.e. effluent water and tap water. Indian Ocean and Mzingazi River are the major sources of raw water within the study area. Though the river runs continuously into the Indian Ocean, the concentrations of Mn, Fe, Zn and Ni were observed to be higher in Mzingazi River compared to Indian Ocean. This observation can be attributed to the ability of water to purify itself through a natural process of sedimentation and dilution over a long period of time.

The stream within Richards Bay is fed by effluent spillage, industrial water run-off as well as other anthropogenic activities within the facilities utilizing water. The stream was found to contain high concentrations of Cd, Mn, Cu, Fe, and As. However, only the concentrations of Mn ( $7.19 \times 10^{-1} mg.l^{-1}$ ) and Cd  $2.21 \times 10^0 mg.l^{-1}$  in Table 1 were found to be above TWQR as shown in Fig. 1.

Hence there is a tendency of neurotoxic effects due to Mn as well as likelihood of severe renal damage with kidney failure due to Cd [16] if water from this stream is continually for drinking and agricultural purposes without treatment. The high concentrations of Mn, Cd, etc. in stream shown in Fig. 1 may be ascribed to two factors viz.: (1) the ubiquity of these metals in rock soil and water; (2) anthropogenic activities within the facility. Though the concentration of Arsenic (As) is within the TWQR, ingestion at high concentration is known to cause cancer [24]. Evidence revealed population cancer risk due to arsenic in U.S. water supplies may be comparable to those from tobacco smoke and radon in homes [24], hence the need to constantly monitor arsenic in this stream.

Basic parameters of water such as pH values, TDS (total dissolved solid) and EC (electrical conductivity) were also measured and the results are presented in Table 2. The result reveals that the pH values of analyzed samples range between 7.24 and 8.22 with a mean value of 7.65. Water sources within this study area can therefore be pronounced alkaline which is the measure of its capacity to neutralize acid. In other words, its ability to absorbed hydrogen ion without significant pH changes [25]. Since lime in water softening and coagulants for turbidity removal react with alkalinity [25] as reflected in low concentration of TDS in effluent ( $1.01 mg.l^{-1}$ ) and tap water ( $4.8 \times 10^{-1} mg.l^{-1}$ ), it is essential that these parameters

**Table 1 Average heavy metals concentrations in five water sources.**

Metals/sources	Concentrations in $mg.l^{-1}$					
	Effluent	River	Ocean	Stream	Tap	TWQR [16]
Mn	$2.46 \times 10^{-1}$	$1.77 \times 10^{-2}$	$<3.00 \times 10^{-3}$	$7.19 \times 10^{-1}$	$5.34 \times 10^{-3}$	$0 - 5.00 \times 10^{-2}$
Fe	$1.04 \times 10^{-2}$	$4.31 \times 10^{-3}$	$3.83 \times 10^{-3}$	$3.53 \times 10^{-3}$	$2.24 \times 10^{-2}$	$0 - 1.00 \times 10^{-2}$
Cu	$1.06 \times 10^{-2}$	$2.56 \times 10^{-3}$	$3.69 \times 10^{-3}$	$2.17 \times 10^{-2}$	$1.69 \times 10^{-2}$	$0 - 1.00 \times 10^{-2}$
Tl	$1.92 \times 10^{-5}$	$8.15 \times 10^{-7}$	$8.15 \times 10^{-5}$	$5.57 \times 10^{-6}$	$9.03 \times 10^{-6}$	NA
Zn	$2.89 \times 10^{-2}$	$4.49 \times 10^{-3}$	$1.35 \times 10^{-3}$	$9.12 \times 10^{-4}$	$4.24 \times 10^{-3}$	$0 - 5.00 \times 10^{-1}$
Pb	$<1.50 \times 10^{-5}$	$<1.50 \times 10^{-5}$	$<1.50 \times 10^{-5}$	$<1.50 \times 10^{-5}$	$<1.50 \times 10^{-5}$	$0 - 1.00 \times 10^{-2}$
Cr	$1.02 \times 10^{-3}$	$2.37 \times 10^{-4}$	$2.48 \times 10^{-4}$	$5.51 \times 10^{-5}$	$1.02 \times 10^{-3}$	$0 - 5.00 \times 10^{-2}$
Ni	$6.59 \times 10^{-3}$	$8.06 \times 10^{-4}$	$1.01 \times 10^{-6}$	$8.63 \times 10^{-4}$	$7.84 \times 10^{-5}$	NA
Cd	$2.03 \times 10^{-5}$	$2.01 \times 10^{-4}$	$2.11 \times 10^{-5}$	$2.21 \times 10^0$	$7.87 \times 10^{-5}$	$0 - 3.00 \times 10^{-3}$
As	$4.60 \times 10^{-4}$	$2.71 \times 10^{-4}$	$5.91 \times 10^{-4}$	$2.72 \times 10^{-3}$	$2.11 \times 10^{-4}$	$0 - 1.00 \times 10^{-3}$

NA = Not applicable.

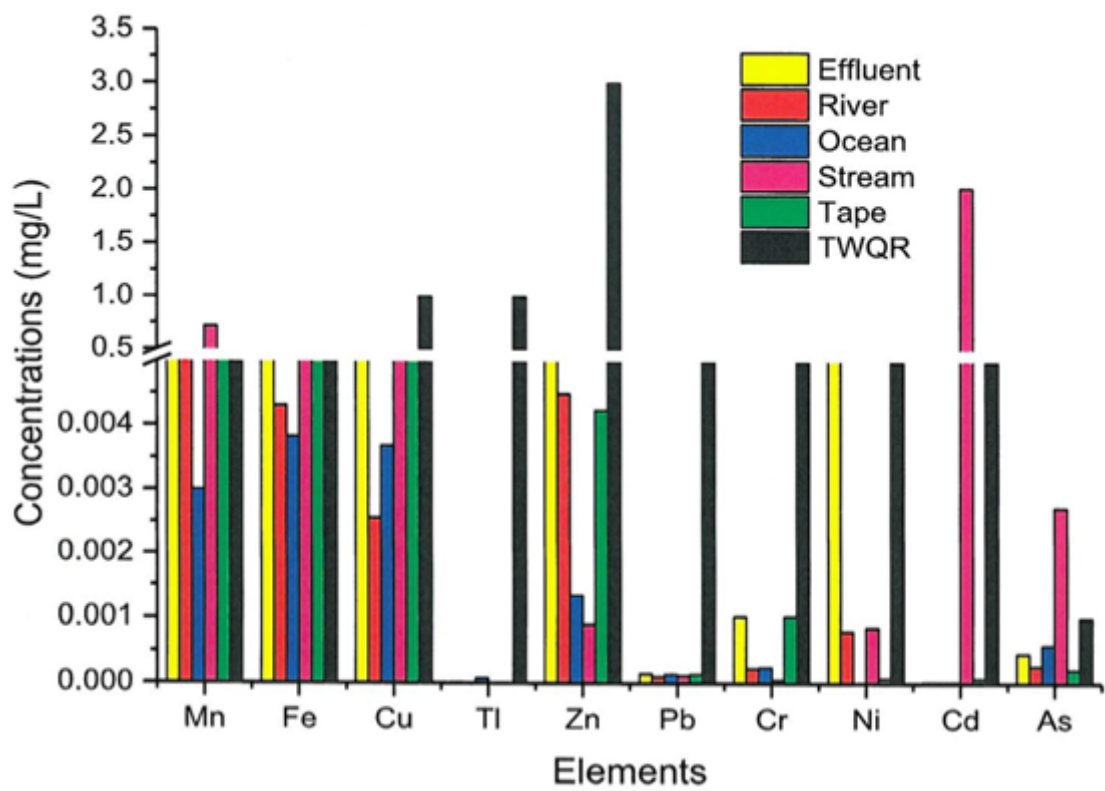


Fig. 1 Comparison of heavy metals concentrations in water samples with TWQR.

(alkaline and TDS) should be monitored in both raw water and treated water to ensure optimum dosage treatment chemicals in turn govern the water quality.

In this study, TDS, pH, EC were observed to show a direct proportionality relation (see Table 2) such that the higher the TDS, the higher the pH and the higher the conductivity. The high concentration of TDS values  $6.96 \times 10^1 \text{ mg.l}^{-1}$ ,  $4.57 \times 10^1 \text{ mg.l}^{-1}$  and  $3.38 \text{ mg.l}^{-1}$  in Indian ocean, Mzingazi river and stream respectively are a direct indication of the extend of pollution [25] which could be used in turn to determine the water quality.

The conductivity of the effluent water  $2.12 \mu\text{s.cm}^{-1}$  and the tap water  $9.6 \times 10^{-1} \mu\text{s.cm}^{-1}$  in this study were observed to be low compared to those of raw water samples. This can be traced to the low dissolved mineral concentrations as reflected in TDS values of  $1.01 \text{ mg.l}^{-1}$  and  $4.8 \times 10^{-1} \text{ mg.l}^{-1}$  in effluent and tap water samples respectively. This observation agrees with the report of the American Public Health Association that conductivity can be

used to estimated TDS in a sample by multiplying the conductivity value by the empirical factor of 0.9 [25].

The concentrations of Fe, Cu, Zn, Pb, and Cr in all the water samples analyzed were within their TWQR of  $1.00 \times 10^{-1} \text{ mg.l}^{-1}$ ,  $1.0 \times 10^0 \text{ mg.l}^{-1}$ ,  $5.0 \times 10^{-1} \text{ mg.l}^{-1}$ ,  $1.00 \times 10^{-2} \text{ mg.l}^{-1}$  and  $5.00 \times 10^{-2} \text{ mg.l}^{-1}$  respectively, as shown in Table 1.

Furthermore, radiological surface contaminations of the mineral storage facilities were analyzed and the results are presented in Table 3.

Rock phosphate store is the most contaminated store within the facility with a gross alpha and gross beta activity concentrations of  $1.45 \times 10^{-2} \pm 4.2 \times 10^{-3} \text{ Bq.cm}^{-2}$  and  $9.10 \times 10^{-2} \pm 10^{-2} \text{ Bq.cm}^{-2}$  respectively as shown in Table 3. This is due to the typical concentration of uranium-238 ( $1,500 \text{ Bq.kg}^{-1}$ ) in sedimentary phosphate deposit [26]. The gross alpha activity concentrations in hematite, rutile and zircon stores were found to be comparable to radioactive phosphate rock store (see Table 3) because they are heavy sand [27] and also considered

**Table 2** Chemical parameters of water samples.

Parameters/sources	Effluent	Stream	Ocean	River	Tap	Average	TWQR [16]	Irrigation limit [16]
pH	7.46	7.30	8.22	7.24	8.05	7.65	6-9	6.50-8.40
TDS ( $mg.l^{-1}$ )	1.01	3.38	69.6	45.70	0.48	24.03	NA	NA
E.C ( $\mu s.cm^{-1}$ )	2.12	6.61	143.20	97.60	0.96	50.09	0-700	NA

NA; Not applicable.

**Table 3** Surface contaminations of mineral storage facilities.

Samples sources	Alpha activity ( $Bq.cm^{-2}$ )	Beta activity ( $Bq.cm^{-2}$ )
Rock phosphate	$1.45 \times 10^{-2} \pm 4.20 \times 10^{-3}$	$9.10 \times 10^{-3} \pm 1.55 \times 10^{-2}$
Major transfer	$1.00 \times 10^{-4} \pm 1.50 \times 10^{-2}$	$4.15 \times 10^{-2} \pm 2.17 \times 10^{-2}$
Hematite	$1.44 \times 10^{-2} \pm 4.20 \times 10^{-3}$	$2.25 \times 10^{-2} \pm 1.82 \times 10^{-2}$
Rutile	$1.43 \times 10^{-2} \pm 2.08 \times 10^{-2}$	$3.36 \times 10^{-2} \pm 2.06 \times 10^{-2}$
Zircon	$1.44 \times 10^{-2} \pm 2.08 \times 10^{-2}$	$1.00 \times 10^{-2} \pm 1.41 \times 10^{-2}$
Average	$1.15 \times 10^{-2} \pm 1.36 \times 10^{-2}$	$2.15 \times 10^{-2} \pm 1.80 \times 10^{-2}$
Contamination limit [17]	$4.00 \times 10^{-2}$	$4.00 \times 10^{-1}$

to be NORM (naturally-occurring radioactive materials) due to the presence of thorium and uranium in mineral grains [27]. Though gross alpha and beta activity concentration are preliminary investigations which give the general contamination of an area without being specific to particular nuclides, the surface contamination of storage facility within Richards Bay precinct is within the safety limits of  $4.00 \times 10^{-2} Bq.cm^{-2}$  and  $4.00 \times 10^{-1} Bq \times cm^{-2}$  [17].

#### 4. Conclusion

This study was planned to provide maiden information that could be used as finger prints to locate polluted water sources in order to work out model for remediation. The results indicated that the water quality is acceptable and the gross alpha and beta surface contamination are within safety limits. However, the stream within Richards Bay was found to be slightly contaminated with Mn and Cd above TWQR, hence the need to minimize spillage, dust spread as well as other anthropogenic activities that are likely to cause further contamination of the stream. Furthermore, periodic constants monitoring of this stream and similar run-off stream from other industrial areas for the presence of radioactive nuclides and

heavy metals are strongly recommended. Determination of these elements plays a vital role in advising water officials whether or not the quality of water from these sources is within the recommended safety limits.

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