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International Journal of Water Resources and Environmental Engineering

Full Length Research Paper

Influence of suspended matters on iron and manganese presence in the Okpara Water Dam (Benin, West Africa)

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Iron and manganese, which their concentrations are seasonally high in the Okpara Water Dam, have a high mobility links to suspended matters (SM). The presence of the water plants constitutes SM retention support within the water column. The anthropoid disturbances caused by the fishermen activities constitute a factor of sediments renewing in the suspension. Solid (>0.45 µm)-liquid (< 0.45 µm) fractionation has been carried out and enabled us to observe that SM are responsible for iron content for more than 10 to 98% and for Manganese content about 23 to 93% filtration removes from 10 to 98% of the colloidal iron which is related to filtrated SM. The phosphorus constitutes a combined factor of the iron mobility in the dam. We have noticed in the top water layers a high proportion (low repartition coefficient) of dissolved (and colloidals) iron respectively. The iron retained by SM is more concentrated in the middle of the water column than anywhere. The west side of the dam is identified as a manganese enrichment source. The manganese ion concentration influences positively on pH (r = 0.57), conductivity (r = 0.78), color (r = 0.66), and SM (r = 0.66) after decantation. Furthermore, the iron concentration is negatively influenced by the pH (r = -0.52) and positively by the TDS (r = 0.51) after filtration. A pre-filtration or a pre-decantation could reduce the quantity of chemicals used during water treatment.

Key words: Iron, manganese, suspended matters (SM), surface water, fractionation, mobility.

INTRODUCTION

Okpara Dam water constitutes a very significant source of supply drinking water of population of Parakou in the north of Benin. This water is polluted, that pollution can be observe through the eutrophication of the dam (Zogo, 2010). Otherwise, the concentration of iron and manganese are influenced by season. Iron, and in a lesser extent, manganese, are the most abundant metallic elements in the earth's crust. It had been shown that both iron and manganese found in water coming from the lixiviated grounds and industrial pollution. These elements

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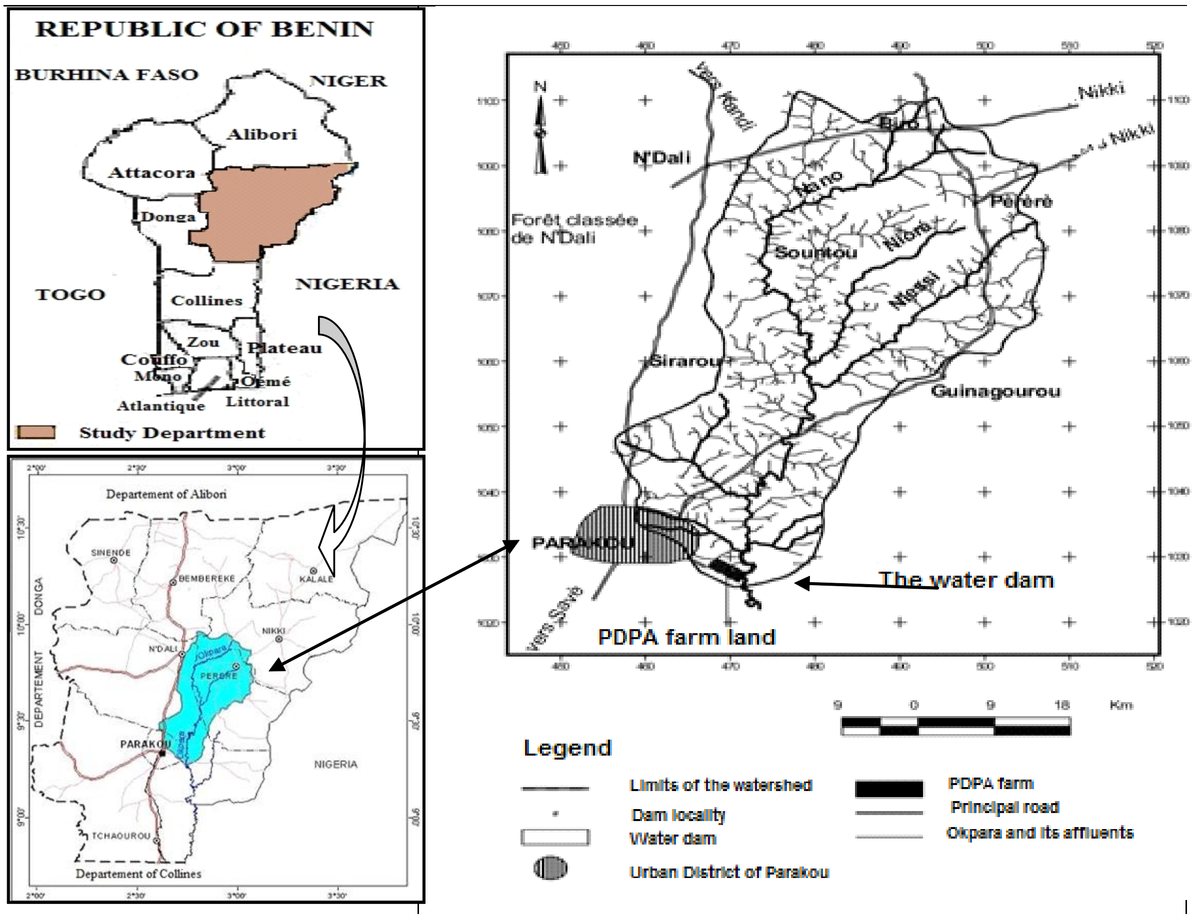

Figure 1. Localization of Benin, Parakou's town and hydrographic system in the under catchment of Okpara's Dam. Source: CENATEL (2003).

do not damage human health or environment. But they cause esthetic and organoleptic damages. Iron and manganese are found in surface or underground water. Removal of iron and manganese from Okpara raw water has been highlight through some studies (Zogo, 2010). This technique consumes a high quantity of potassium permanganate. Furthermore, the origins of iron and manganese, and their transfer in the water column remained not understood. The objective of this study consists of determining the mobility of iron and manganese along the water column across solid-liquid fractionation in raw water.

MATERIALS AND METHODS

Context

This study is focused on Okpara water dam built on an affluent of the Ouémé River called Okpara to supply the town of Parakou (located at the North-East of Benin with 450 kilometers from Cotonou) in drinking water. The dam under catchment is located at the East of the town of Parakou and has been studied in some previous papers. This pouring under catchment of reserve located between 9° 16' and 9° 58' of Northern latitude and 23° 6' and 3° 05' of East on longitude, covers mainly the districts of Pèrèrè in the East, Nikki in the North-East, N'dali in the West, Tchaourou in the South and a small part of the Commune of Bembèrèkè in North (Figure 1).

Analysis methods and testing

Water samples were carried out from five sampling points in December 2011 (D), April 2012 (A) and in June (2012) (Figure 2).

Two samples sites (N1, N2) were more focused. Raw water samples were taken 20 cm from the surface and from 1.5 m depth to 6.5 m in 1.5 L polyvinyl chloride (PVC) plastic containers the day of the tests. The samples were identified as follows: Sampling level in the water column profiles "surfaces (S); middle (M) and bottom depth (P) "followed by the etiquette of the sampling point (N) and period" as indicated in the Table 1. Example: The water sample taken from the surface of water at the research point N1 in April is identified as follows"S-N1-A". Filtration: Samples of raw water were filtered in an erlenmeyer by using a 0.45 µm pore size Durex folded filter paper. Decantation: A portion of the raw sample water was left for decantation in anoxic condition during one to two days, and some physic-chemical parameters were determined. The difference between the total solids in suspension and the non-decantable solids in suspension gives the concentration of decantable solids in suspension. SM are responsible of water turbidity; these SM are various such as silt, clay, organic and inorganic matter in small

Figure 2. Localization of the sampling points in station on the reserve of Okpara.

Table 1. Geo-referred situation of the sampling stations on the reserve.

Sampling points	Localization	Water column depth	Period
N1	N 09° 17' 08.88'' E 002°43'58.67''	2.5 m to 4 m	(A) ; (Jn)
N2	N 09° 17' 02.06'' E 002° 43'58.66''	6 m to 7.5 m	(D) ; (A) ; (Jn)
N3	N 09° 17' 02.04'' E 002° 43'58.57''	2 m to 3.5 m	(A)
N4	N 09° 16' 58.25 E 002° 44'00.00''	4 m to 6.5 m	(Jn)
N5	N 09° 17' 1589'' E 002° 43'43.25''	0.2 m to 0.5 m	(A) ; (Jn)

particles, made up of soluble colored organic matter, plankton and other micro-organisms (American Public Health Association, 1989). Electric conductivity, the total dissolved solids (TDS) and the pH of the samples were measured using a Waterproof pH-meter. The turbidity, the color and the SM were measured by using a HACH colorimeter. The total iron and manganese content were measured; also dissolves and colloidal iron and manganese content were also determined in the raw, filtrated and decanted water samples. Iron concentration was determined by using the orthophenanthroline method and measure at 510 nm wavelength. Manganese concentration was determined according to the potassium periodate acidic oxidation method at 525 nm wavelength. A JENWAY spectrophotometer model 6305 was used for the absorbencies measurement. The iron and manganese analysis methods where based to the standards of the French Standardization Association (AFNOR) of the water quality, Tome3 (1997).

Statistical analyses were performed on SPSS 16.0 software.

RESULTS

According to Figure 3, the suspended matters are well eliminated after filtration and decantation. This condition is favourable to the measurement of the true color. Filtration allowed more SM removal than decantation. The pH of these raw water samples reveals an acid

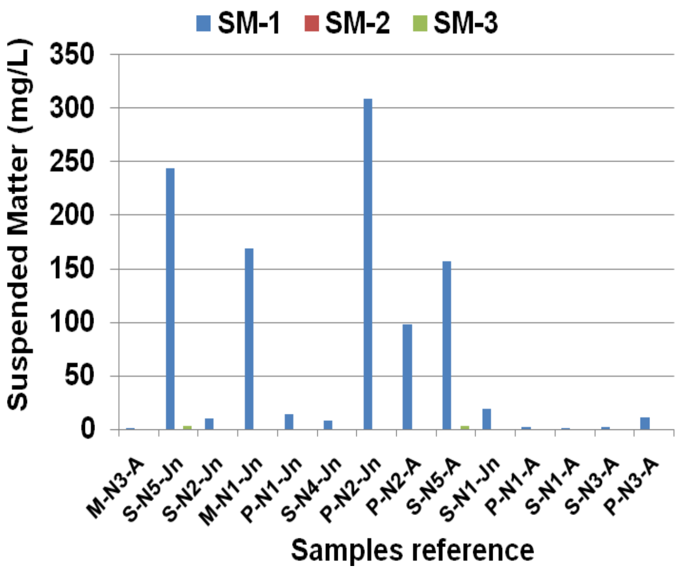

Figure 3. Suspended matter of each sample before filtration (SM-1), after filtration (SM-2) and after decantation (SM-3).

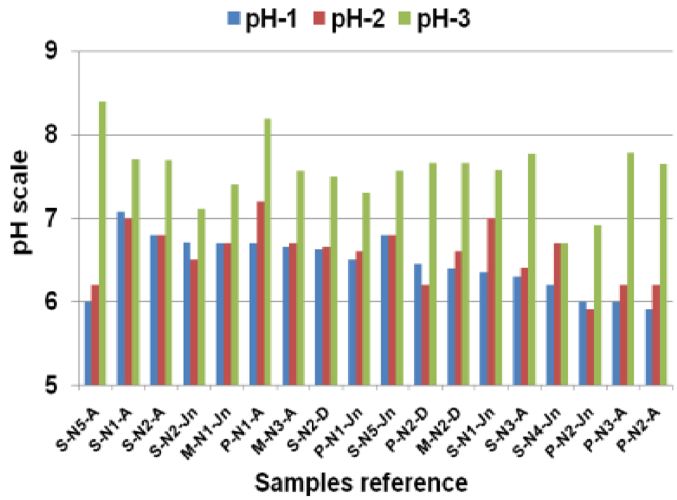

Figure 4. Samples pH values before filtration (pH-1), after filtration (pH-2) and after decantation (pH-3).

character higher from the surface to the bottom of water column (Figure 4). For these waters, there is an average value of all the points which is about 6.51 for raw waters, 6.62 after filtration and 7.56 after one to two days of decantation in anoxic condition. Thus there is an average variation of one unit of pH. All the collected water samples have pH increasing during their storage to a basic pH ranging between 7 and 8.5. The pH is one of the factors (other that the potential rédox) which has a strong influence on the behavior of oligo-elements in the external environment. For example, the reduction in the pH of one unit can lead to an increase of more than one order of magnitude in the concentration of certain metals like aluminum, beryllium (Edmunds and Smedley, 1996). The Metals and metalloids concentrations in the oxy-anions form increase in the aqueous phases when the pH increases (Bonnet, 2000).

Two types of surface water's colors can be measured. One type is the apparent color taking into account the SM (Coul-1) and the second type which is true color measured after SM removal by centrifugation or filtration (Coul-2). We observed according to Figure 5 that whatever is the sampling point, the elimination of SM is always accompanied by the reduction of the color. This fact can be explained by the inorganic matter contribution (sand, clay, etc), and the presence of organic matter and other renewed mineral matters (iron and manganese) in the suspension carried by the surface water during rainy season. The samples taken in the bottom, points NI, N2, N3 and surface in April at point N5 are less suitable for color elimination after filtration or decantation because they presented color values more than 55 color unities.

We have also observed on Figure 6, a light increase of conductivity following the SM removal. This increase varies from 1 to 17 µS/cm except in the point (N5) for the two distinct periods April and June. Water samples from point (5) presented higher conductivity (>100 µS/cm) which decreases after filtration. We could think about a precipitation reaction of the dissolved ions or their adsorptions on eliminated SM. According to Graeme and Jameson (1999), ventilation during filtration can also lead to the flotage of the iron particles, by linking bubble to particle, which can more concentrate the particles in the flocks and give a better turbidity reduction after filtration (Béchir et al., 2007). In these conditions, waters which have high conductivity with strong rate of TDS will be unbalanced and one will observe the decrease of TDS which also involve a conductivity reduction. On the other hand the decantation process of samples from point N5 show conductivity increase with value around 485 µS/cm. Phenomena after decantation process at point N5 are the same, with less values for points N1 and N2 water samples.

Figure 8 reveals that the turbidity of raw water samples varies from 13 to 885 NTU which are results like the values found on the surface water by Hector (2006) which varies from 1.8 to 1948 NTU. The rate of turbidity elimination after filtration is 10 to 94%. December water samples have lowest turbidities and vary from 13 NTU on the surface and 80 NTU in the bottom (4 m) with the rate of turbidity elimination after filtration around 46 to 80%. For waters which turbidities are lower than 100 NTU, the turbidity elimination tends to be 100% after the decantation. The rate of turbidity elimination after decantation is a function of initial turbidity (before and after SM elimination turbidity correlation r = 0.76). In dry season where there is no movement of the water the reduction of turbidity by the sedimentation of the suspended matter (SM) must be observed. However, the presence of the water plants, combined with the daily

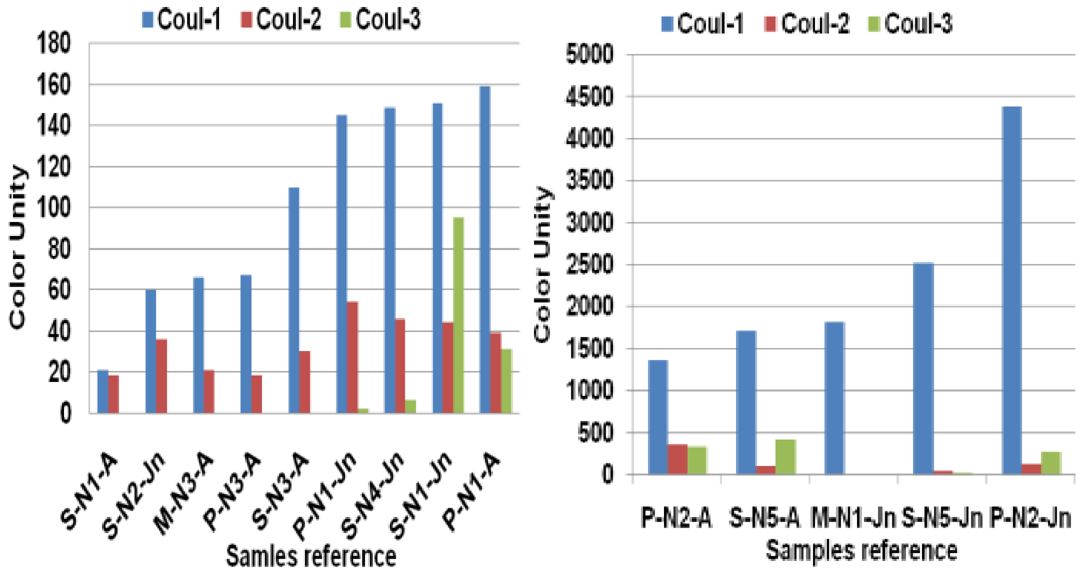

Figure 5. Samples color before filtration (Coul-1), after filtration (Coul-2) and after decantation (Coul-3).

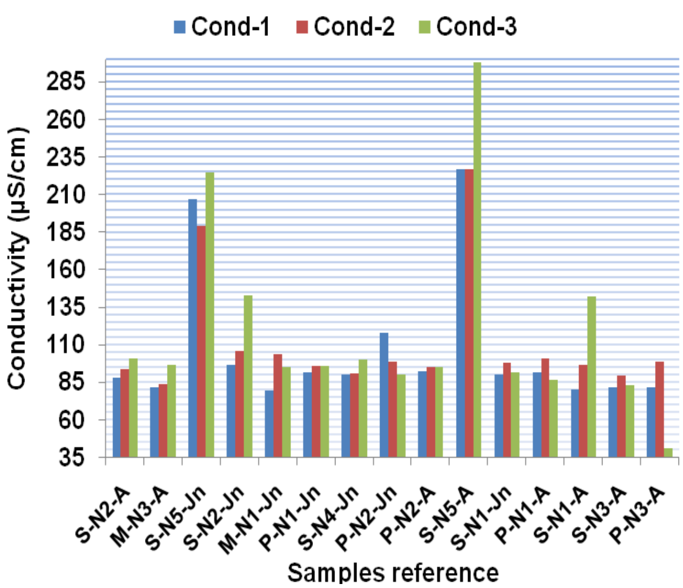

Figure 6. Samples conductivity before filtration (Cond-1), after filtration (Cond-2) and after decantation Cond-3).

impact of fishermen' activities are not favorable to the decantation process *in-situ*. The biological perturbation of the sediment is also a permanent factor of exchange of SM between sediment and water column (Santschi et al., 1997).

Figure 9 reveals that the manganese concentration decreases after filtration and this is more significant after the decantation except the point N5 where we observe the contrary phenomenon. The great values of concentrations are recorded in June (Jn) and more in the water samples taken on the surface. The water samples taken in April thus present the greatest manganese concentrations after filtration; the dissolved form of manganese has significant values and this in the middle and the bottom of the water column. Less than 50% of manganese is eliminated in this point but this is not observed with other samples. The measured manganese concentrations in the point N5 water samples are higher than the results obtained by Zogo (2010) on the waters dam whatever is the season. One measured values are about the double of Zogo results. This sampling point (N5) on Figure 2 represented a water collecting point coming from the rivers located in the districts of Eastern of Parakou town, the water treatment plant of "Soneb", the agro-pastoral farm (Figure 1). This point N5 thus represented a source of manganese which enriches the reserve water.

We deduced from the obtained iron values presented on Figure 10 that the content of particular iron varies from 5 to 78% of the total iron content. The ratio between metal fixed by SM and dissolved metal corresponding to the partition coefficient (Kd) allowing the distribution between the dissolved and colloidal form and the particular form. Weak values of Kd indicate a strong contribution of dissolved metals to their total concentration (Vignati, 2004). For analyzed water samples, Kd is very high and varies between 1 and 70 with an average value around 17. According to the work of Valérie (2009) Kd measured for metallic traces elements vary typically in range of 1 to 3 for a given metal according to the sites. Kd is often considered as a site - specific parameter at a given time (Fournier-Bidoz and Garnier-Laplace, 1994). For that, we cannot expect a sufficient reproductibleness of the partition coefficient

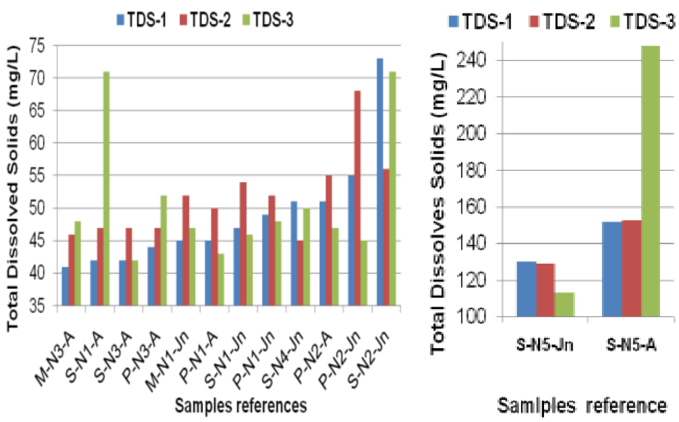

Figure 7. Samples total dissolved solids (TDS) before filtration (TDS-1), after filtration (TDS-2) and after decantation (TDS-3).

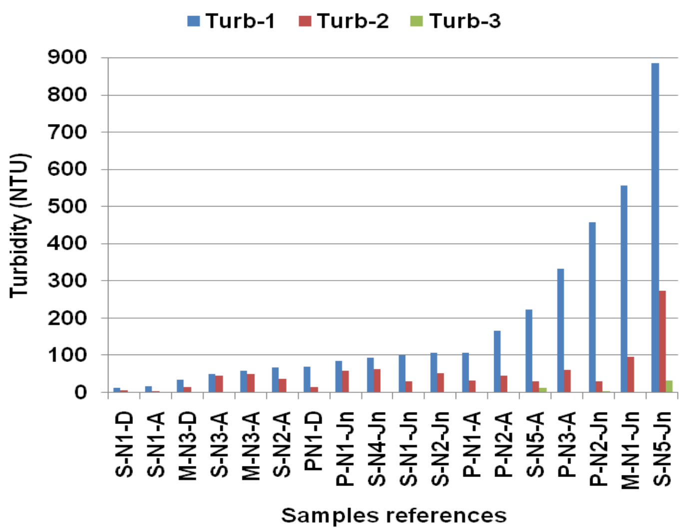

Figure 8. Samples turbidities before filtration (Color-1), after filtration (Turb-2) and after decantation (Turb-3).

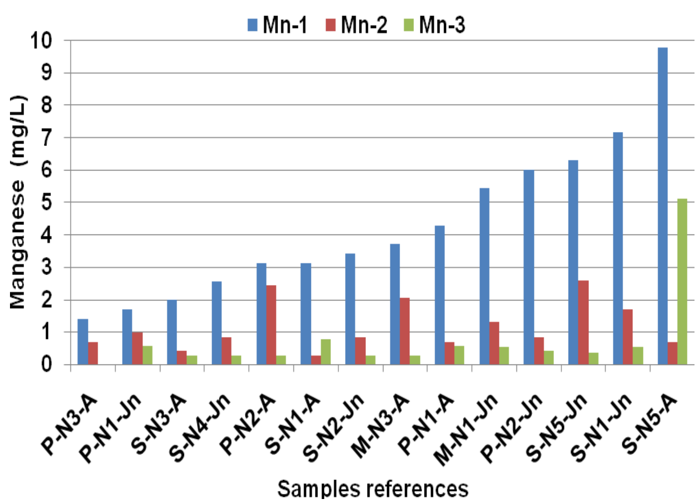

Figure 9. Manganese concentration of the samples before filtration (Mn-1), after filtration (Mn-2) and after decantation (Mn-3).

(Kd) value. The water samples taken on the surface (S) presented the weaker Kd and are less concentrated in dissolves and colloidal iron (< 5mg/L) than those of the bottom (P) from 5 to 30 mg/l whatever in December, April or June. SM contained iron in range of 53 to 99% in the water column. After filtration, all the collected water samples present lower values than 5 mg/L of iron, with an average around 0.96 mg/L in the surface layer and 2.57 mg/L in the bottom waters.

DISCUSSION

The main goal of a drinking water station production is to provide high quality water with a cheaper cost for the consumer. The various water quality parameters included such as turbidity, color, pH, SM, iron, manganese, relied on the water treatment process. To achieve the desired goal, each water treatment will ensure a good water quality and use high qualified human resources (Valentine, 2000).

Correlations are often established between turbidity, suspended matter, total solids and color. Analyzed water turbidity and to a lesser extent the color of analyzed water have show high decrease after filtration or the decantation and this is conform to result found by Zogo et al. (2011) which show that the rates of elimination of turbidity are higher at pH 6.50 and 40 mg/L of aluminum sulphate on the level of water of Okpara. After intense rains, there is SM increase with a good decantation. SM is strongly concentrated at the bottom of the water column from 2 to 310 than surfaces from 1 to 20. Simple filtration does not allow a correct elimination of the color and turbidity in the case of Okpara water in any season and any sampling point. The elimination of the color and turbidity by simple filtration is weak, probably because of the presence high content of iron and manganese seasonally. This weak turbidity elimination could be due to the TDS because (Figure 7), the turbidity of raw water can also be reinforced by the presence of inorganic solids like metallic oxides and hydroxides (iron or manganese) and biological organisms like the seaweed, the zooplankton and the filamentous bacteria or in cluster (Foley, 1980). The manganese ion concentration influences positively on pH (r = 0.57), conductivity (r = 0.78), color (r = 0.66), and SM (r = 0.66) after decantation. After decantation dissolved manganese form is strongly positively correlated (r = 0.72) with TDS-2 and, in contrast of results before filtration (r = 0.07) and after decantation (r = -0.15)

.This observation point out the particular forms of manganese in which concern their natural removal from water samples with the environment physic-chemical condition afferent. Furthermore, the iron concentration is influenced by the pH and in a less proportion by the TDS.

The average measured pH observed is 6.51. Zogo et al. (2011) has used the same pH value for pre-chlorination followed coagulation-flocculation to reach 50

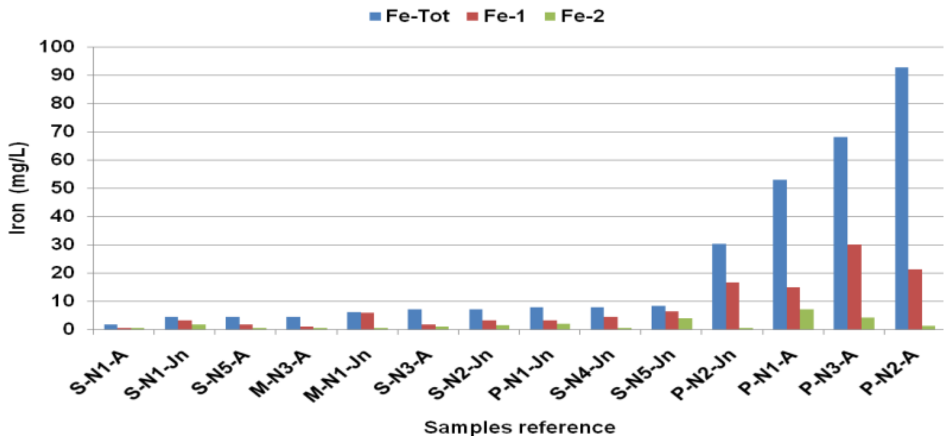

Figure 10. Total iron concentration (Fe-Tot); dissolved and colloidal iron before filtration (Fe-1) and after filtration (Fe-2).

to 95% of iron removal or 20 to 45% of manganese. The initial iron concentration variable was between 8.00 and 35.00 mg/L and an initial manganese concentration in range of 1.00 to 4.00 mg/L for experiences carried out by Zogo. The fact that we have observed a little increase in the pH after filtration and decantation, can be explained by an oxidation or a reduction of organic matters rate in the presence of the humic acids. Kedziorek and Bourg (1996) also showed that the humic substance presence could increase the pH; cation metals react then like anions (Bonnet, 2000). According to Soetaert et al. (2007) reoxidation by oxygen and the reduction of manganese and iron oxides tends to increase the pH. In addition, certain geochemical processes as the dissolution of calcite involve a consumption of hydronium ions (H_3O^+) and thus increase the pH. This can also justify in certain cases the increase of TDS after decantation.

In the reducing medium, the iron and manganese oxides are reduced and dissolved. This followed by a departure of the heavy metals from the different compartments of the sediment such as the organic matter, clay and especially the sulphides to the water column (Tack et al., 1996). This phenomenon appears observable in the deep layer of water column where Zogo (2010) observed high contents of organic matter. Filtration has eliminates 10 to 98% of colloidal iron which is related to SM filtrated. There would thus exist in water samples an important adsorbed iron. Because of their small size, the colloidal particles have specific surfaces

(report/ratio surfaces/mass) significant (> 10 $m^2.g^{-1}$) and can thus represent adsorbent or absorbent form for the chemical elements in general and the metallic elements in particular (Citeau, 2004). According to IUPAC (1997), the colloids are molecules or polymolecular particles dispersed in a medium and having, at least in a direction, a dimension ranging between 1 nm and 1 µm. if the lower limit is considered without ambiguity around 1 nm (Lead et al., 1997), determination of the higher limit seems more complex. It can vary, according to authors, from 0.2 to 0.5 µm (Singhal et al., 2006), and can even reach 1 µm (Lead and Wilkinson, 2006). Then a part of the colloids could be eliminated with the SM.

After filtration, the content of iron dissolved and colloidal in water varied from 0.41 to 7.10 mg/L. Physical treatment like filtration has thus a beneficial effect in terms of the reduction of chemical quantity to carry out the treatment without a pre-filtration of these water samples. The iron form in the surface layer of the Okpara Dam water in dissolved and colloidal which that is combined more with SM, and this could explain the weak rate of variation of the iron content related to SM after the filtration of surface water. The iron concentration is negatively influenced by the pH (r = -0.52) and positively by the TDS (r = 0.51) after filtration. In the absence of oxygen and nitrates, metallic oxides are the most powerful oxidants and are reduced in the anoxic area. According to Audry (2003) the redox species of metals which have more than one oxidation step in natural water have different mobility, solubility, toxicities and reactivity. According to Boust et al. (1999), reduced iron and manganese will be found in dissolved form Fe (II) and Mn (II) in porous water. In this form, they can either (i) diffuse towards the oxic layers or re-oxidize into oxides or (ii) precipitate, if the products of solubility are reached, with the chemical species produced by the degradation of the organic matter (sulphides, phosphates, carbonates). Manganese precipitates in carbonate salts form $MnCO_3$ (rhodochrosite), iron precipitates under carbonates salts form $FeCO_3$ (siderite) and salts of monosulphurs FeS (mackinawite) (Boust et al., 1999). In fact the form of precipitated iron and manganese will be higher in the presence of phosphate ions which are mainly present in Okpara water (Zogo et al., 2011). The anoxia and acidity in the sediments are favorable with the dissolution of oxidize-hydroxylated forms. Thus, certain metals, like Fe,

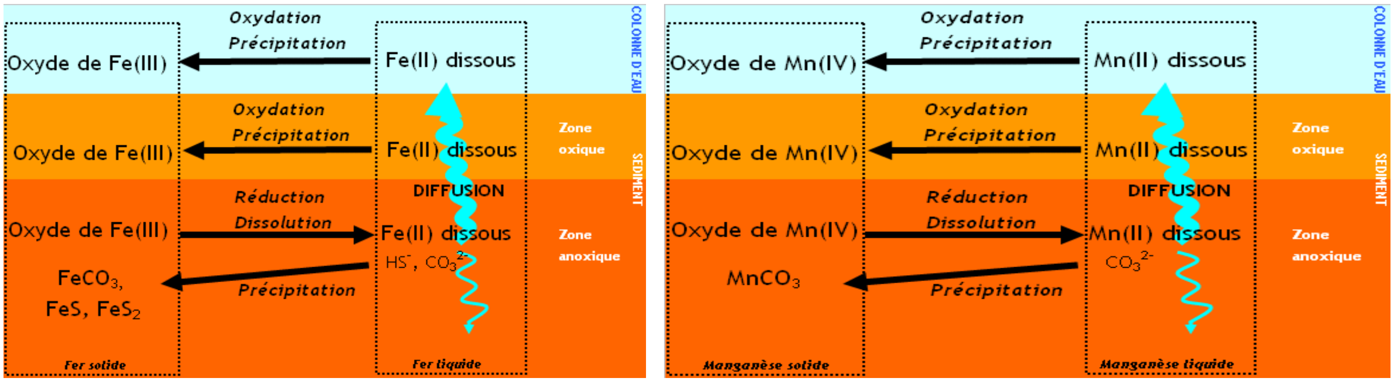

Figure 11. Behavior of iron and manganese in the sedimentary area of the rivers. (Boust et al., 1999).

Mn and Cr are more movable in their reduced form. The work archived by Zogo (2010) has show that the surface water layer in a given sampling point of the reserve of Okpara presented 10% of oxidized form (Fe III) against 90% of particular form iron with a total concentration of 2.015 mg/l. The redox conditions can increase or decrease the quantities of oxyhydroxydes and sulphides adsorbed (Lions, 2004). Reducing media will support the solubilization of the metal species (oxides) and then increase or decrease the mobility of the metallic trace elements which diffuse from the sediments to the water surface layer (Blanchard, 2000).

The work achieved by Zogo (2010) concluded indeed that the splitting up related to the use of the grounds of under catchment area of the dam for intensive cotton culture and other food products accompanied by significant quantities of artificial fertilizers using are probably at the base of the imbalance observed on the level of this water ecosystem.

The work made possible to identify in the reserve of Okpara six macrophytes species and to count eighteen microphytes species Moreover, according to trophic levels' based on the chlorophyll a contents (OECD, 1982), with a concentration sometimes higher than chlorophyll 25,00 µg/l has and the level of development of the macrophytes in the stopping of Okpara, this reserve can be classified in the category of the eutrophic lakes'. The amount of ortho-phosphorus could reached 30 mg/L in the surface water then.

Phosphorus measured in the bottom water (Tomètin et al., 2013) showed that the total phosphorus could reach to 191 mg/L at station N1 and 397 mg/L at station N2. Also the sediment constitutes a source of phosphorus renewed for the water column. Then the high phosphorus amount in the water and sediment under different forms (mobility) could be control by the iron and manganese. The fraction of phosphates related to iron is very sensitive to the variations of the sediments redox potential. When the redox potential is lower than 200 mV (ESH), a fraction of Fe^{3+} available to the level of the sediments is reduced in Fe^{2+}. Gomez et al. (1999) show that this value of potential redox is variable according to the pH of the sediments, to the presence of organic ligands and to porous water salinity. Phosphorus is thus likely to be salted out in the water column when the interface water-sediment becomes anoxic (Gomez et al., 1999) by various mechanisms of diffusion of interstitial water (Enell and Löfgren, 1988). In anoxic conditions on the surface of the sediments, it formation of iron hydroxide will thus not have there as the straight lines part of the Figure 11 indicates it and thus not of fixing of the phosphorus which is thus released in great quantity in the water column. In oxic conditions on the surface of the sediments, there are however two possible cases: the phosphorus diffuse of the sediment (anoxic) towards the interface water sediment (oxic), where it is trapped the iron hydroxide which is excellent adsorbing phosphorus in the presence of oxygen dissolved (Figure 12).

Conclusion

Iron and manganese, present in Okpara Dam water have various concentrations according to the season. Their contents and mobility are tied in the major part; with SM quantities are strongly retained more by the water plants. The colloidal SM is the major factor of iron high amount in the water middle and bottom column. The high amount of phosphate in the water column constitutes a factor of iron and manganese precipitation which migrate from the top to the water bottom. Also, these naturals' factors can be added to the anthropological activities which increase the exchange between sediments and water column. SM constituted a major vector of the mobility of iron and manganese within the water column. After decantation or SM removal from the water sample, the pH of this water varies from 6.51 to 7.62. The organic matter decomposition in the sediments and the water column maintains the water column acidity favorable to the increase of the dissolved forms which migrate towards the water surface layer under free form to be oxidized or engaged as ionic or colloid forms, tied with SM which

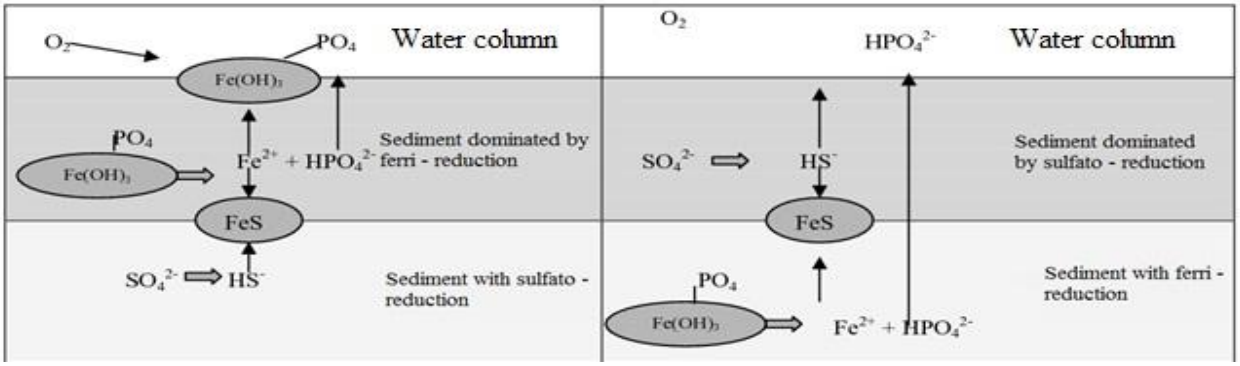

Figure 12. Diagrammatic representation of two possible mobility cases of phosphorus at water sediment interface in oxic conditions. The simple arrows represent flows of diffusion and the double arrows represent the chemical reactions (according to Matthiesen et al., 1998).

concentration increases from the surface to the bottom of the water column. Iron concentration along the water column strongly dependent on the organic matter responsible of the humic acids and the water acidic pH. Organic matter is the fundamental component of the SM. A probable source of manganese enrichment of the dam water is located at the point N5 where one river supplies water to the dam. The high concentration of manganese can be provided by total solid quantity of this river.

Physical treatment like pre-filtration has a beneficial effect in terms of chemical quantity reduction to carry out the treatment without a pre-filtration of these water samples. The fractionation and the speciation of iron and manganese in the water column and the sediments are new concept of control and treatment efficiency of Okpara Dam water.

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Full Length Research Paper

Evaluation of sustainability of groundwater resources in a semi-arid region of the Maharashtra State of India

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This study aims to assess the sustainability of groundwater resources in a semi-arid watershed in the Maharashtra State of India using sustainability indicators proposed by the United Nations Organization for Education, Science and Culture (UNESCO). We have selected seven widely used indicators based on their relevance in the field of groundwater sustainability and proven data collection reliability and methodology. These indicators were applied to a Dhubdhubhi watershed with a semi-arid climate. The integral application of all these indicators in this particular watershed leads us to conclude that at present the groundwater resources of the entire watershed is at a stage requiring sustainable development. However, in some areas groundwater development and use is semi-critical and over-exploited, which may result in a critical situation unless adequate management practices are put in place.

Key words: Groundwater sustainability, semi-arid region, indicators, India.

INTRODUCTION

A large part of the population in the Maharashtra State of India suffers severe and chronic water scarcity due to its unfavorable climatic conditions such as low rainfall, frequent dry spells and high evaporation. Of the total water use in the State, irrigation is about 80% while domestic and industrial uses are 12 and 4% respectively, with the rest used for other purposes (World Bank, 2005). Widespread and progressive depletion of groundwater tables in districts of the Maharashtra State has become a major environmental concern over the past 20 years.

In the State, 19 out of 35 districts show a decline in average groundwater levels of greater than 4 m in 1981 to 2000 (MoWR, 2003). In addition, many districts in the State are concerned about the groundwater pollution problems such as salinity intrusion in the Amravati, Akola and Buldhana districts; fluoride contamination in Bhandara, Chandrapur, Nanded, Yavatmal and Satara; nitrate in the Satara, Sangli and Nagpur districts (GoM, 2003).These problems are more critical in the drought prone areas of Maharashtra State which receives an average annual rainfall of 400 to 700 mm, limiting the availability of surface water and forcing the majority of the population to depend heavily on groundwater.

Most of the population in the State depends on

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agriculture and related activities for their livelihoods. Construction of groundwater wells has increased the pressure on groundwater resources. Excessive groundwater abstraction followed by low rainfall in the watershed is leading to declining groundwater levels. The population of most of the villages and towns depends on water supply bodies for drinking water in the dry season and the situation is worse in drought years. Assessment of the sustainability of groundwater resources; including the stages of development, recharge, extraction, exploitable resources, and quality is therefore extremely essential for the efficient management and development of groundwater resources in the watershed.

'Groundwater sustainability' refers to the development and use of the resource in a manner that can be maintained for an indefinite time without causing unacceptable environmental, economic, or social consequences (Alley, 2004).

Sustainability represents an optimal state; however, this is neither fixed nor constant but rather time and space dependent (De Carvalho et al., 2009) and therefore needs to be quantified in order to evaluate the progress in achieving sustainability over time and space.

As many researchers have stated, sustainability of groundwater bodies is a necessary goal for the long-term welfare of both humans and the environment (Henriksen et al., 2008; Sophocleous, 2000, 2012).

In this context, many findings have been reported on the development of indicators to quantify the degree of exploitation to which a groundwater body is subjected. In fact, groundwater sustainability indicators, based on monitoring programmes help to maintain the sustainable management of groundwater resources, and analyse the extent of natural processes and human impact on groundwater systems in space and time to facilitate communication and public participation in resource planning and policy making (Vrba and Lipponen, 2007).

The objective of such indicators is to define by means of diverse variables and synthetic expressions, specific aspects of the quantitative and qualitative state of groundwater and to permit comparison with different aquifers, as well as proper planning and management of the available water resources. Such indicators can be calculated from data that is relatively easy to gather, providing information about the state of an aquifer and the possible tendencies and/or impacts taking place in it. Some earlier studies (Lavapuro, 2008; Girman, 2007; Hirata et al., 2007; Pernia and Lamban, 2007) have also used such groundwater indicators to generate concise information on the present state and trends in groundwater systems, analyzing the extent of natural processes and human impact on groundwater systems, and facilitating communication and public participation in resource planning.

This study aims to assess the sustainability of groundwater resources in the Dhubdhubhi watershed using selected indicators proposed by UNESCO. These indicators can be easily derived from readily available groundwater related data.

MATERIALS AND METHODS

Study area

The Dhubdhubhi watershed is located in the Southern Maharashtra State of India. The watershed area is 484 km^2 and home to a population of 94,727. The watershed further consists of seven sub-watersheds (BM-138-1, BM-138-2, BM-138-3, BM-138-4, BM-139-1, BM-139-2 and BM-139-3), Figure 1. The size of sub-watershed varies between 10 km^2 to 100 km^2. The watershed is a typical drought prone area in India. It is underlain by hard basalt rock restricting the groundwater recharge to 10 to 20% of annual rainfall (Campbell, 2013). The characteristics of seven sub-watersheds in relation to groundwater are summarised in Table 1.

According to the Groundwater Surveys and Development Agency (GSDA) of the Government of Maharashtra, groundwater is the main source of irrigation, contributing to more than 60% of the State's net irrigated area. More than 80% of the drinking water supply is also groundwater dependent. Widespread and progressive depletion of the groundwater table at various locations in Maharashtra State districts has become a major concern over the past 20 years, with only a partial (temporary) recovery during exceptionally heavy monsoon rainfall years.

According to GSDA, groundwater development is progressing slowly: 55 and 62% for Akkalkot and South Solapur sub-districts respectively. The groundwater development stage here is defined by the ratio of existing gross groundwater draft for all uses to net annual groundwater availability. For domestic water uses, most of the villages and towns depend on tanker (vehicle carrying water tanks) water supply in the dry season with the situation deteriorating in years of drought.

Data collection

Groundwater level data from 35 observation wells for the period of 2002 to 2006 and specific yield (estimated by pumping tests) from 22 locations in the watershed were collected from Shivaji University, Solapur (Sabale, 2008). Records of precipitation, human and cattle population, areas of various crops, and net irrigation were obtained from various government departments. Thematic maps of watershed boundaries, reservoirs, and water bodies were obtained from the Maharashtra Remote Sensing and Application Centre (MRSAC), Nagpur.

Calculation of indicators

Development of groundwater sustainability indicators (GWSIs) has been taken up by UNESCO under the Sixth Phase of the International Hydrological Programme (IHP), Theme 2: Integrated Watershed and Aquifer Dynamics. The indicators proposed for this group, although simple, are both scientifically based and policy-relevant (Vrba and Lipponen, 2007). In this work, we selected seven main GWSIs based on their importance in the field of groundwater sustainability and because they proved to be the most reliable, based on the use of data collection and methodology. The GWSIs selected are described below:

Renewable groundwater resource per capita (I_1)

The renewal groundwater resources consist of recharge from precipitation (natural recharge), seepage from surface water

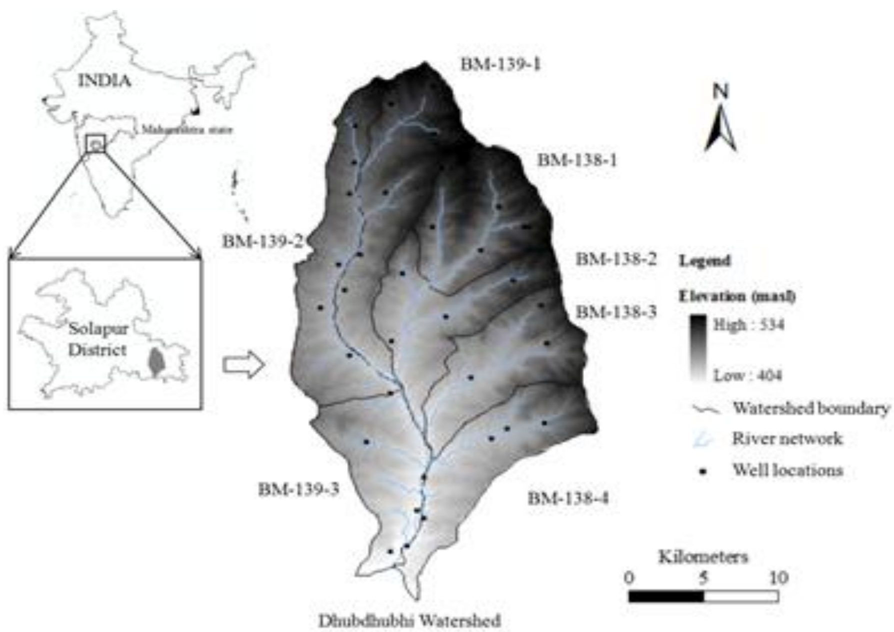

Figure 1. Location map of the Dhubdhubhi watershed including its sub-watersheds.

Table 1. Characteristics of seven sub-watersheds in Dhubdhubhi

Sub-watershed[1]	Area (km^2)	Elevation (masl)	Area under agriculture[2] (km^2)	Area under irrigation[2] (km^2)	Groundwater extraction[3] (MCM/yr)	Average saturated thickness[4] (m)	Average specific yield[4]
BM-138-1	68.81	494	27.09	10.02	5.33	7.47	0.01
BM-138-2	67.02	465	12.82	3.89	2.62	5.67	0.01
BM-138-3	65.23	466	47.51	10.40	4.89	6.13	0.02
BM-138-4	67.24	453	25.93	8.59	4.69	4.78	0.02
BM-139-1	85.83	488	43.78	10.44	5.24	5.66	0.01
BM-139-2	71.73	470	34.21	9.14	4.44	4.54	0.01
BM-139-3	57.79	440	32.14	10.74	5.99	5.01	0.04

[1]MRSAC Nagpur (2010); [2]DSE (2009); [3]Estimated by CROPWAT; [4]Sabale (2008).

bodies, and groundwater discharge to surface water (base flow), groundwater flow across the groundwater basin boundary and artificial recharge. At the initial stage of groundwater development, this preliminary estimate is based on surface observations and the use of direct and indirect estimation techniques depending on data availability. The expression of this calculated amount annually per capita in the study area gives an indication of the availability of groundwater. The indicator I_1 is obtained as:

$$I_1 = G_R / N \qquad (1)$$

Where G_R is a renewable groundwater resource in m^3 and N is the total population.

The renewable groundwater resource is obtained by a simple groundwater budget equation considering the negligible recharge during the non-monsoon season (December-March) (Shirahatti, 2012; MoWR, 1997). According to the norms of the Groundwater Estimation Committee (GEC) (1997) and MoWR (1997), the recharge during the non-monsoon season is considered only if the rainfall in the non-monsoon season is greater than 10% of the average annual rainfall.

In this study, rainfall during the non-monsoon season is less than 10% of average annual rainfall. Hence non-monsoon recharge is not considered in the analysis. The renewable groundwater resource is obtained as:

$$G_R = A - F_I + \Delta S \qquad (2)$$

Where A is the total groundwater abstraction for all uses (irrigation, domestic and livestock), F_I is the irrigation return flow, and ΔS is the change in groundwater storage volume and estimated as:

$$\Delta S = \Delta h \times S_Y \qquad (3)$$

Where Δh is the change in groundwater level and S_Y is specific yield.

Groundwater abstraction for irrigation (referred later as A_I) is obtained as the difference between the total water needed for irrigation (referred later as W_I) and surface water available for irrigation. The W_I for a particular crop is obtained by multiplying the irrigated area of that crop and the gross irrigation requirement (*GIR*). *GIR* is estimated as:

$$GIR = NIR / E_F \quad (4)$$

Where *NIR* is the net irrigation requirement and E_F is the irrigation application efficiency.

The CROPWAT 8.0 model developed by FAO was used to estimate the net irrigation requirement of each crop (Smith, 2012). The *NIR* is the difference between the crop water requirement and effective precipitation. Various inputs were needed to apply the model, such as reference evapotranspiration (ET_O) obtained from the CLIMWAT database (Smith, 1993) for the Solapur station. The average monthly precipitation from the South Solapur and Akkalkot stations, crop characteristics (of all crops grown including crop coefficients for four crop development stages), and soil characteristics, were obtained from available literature (Sabale, 2008; Subramaniam, 1989; Boonstra, 1981; Brouwer and Heibloem, 1986).

Renewable freshwater availability per capita (I_2)

Renewable internal freshwater resource flows refer to internal renewable resources (internal river flows and groundwater from rainfall) in the country. Watersheds with more than 1,700 m^3 of renewable fresh water per person per year will generally experience only intermittent or localised water shortages. As the renewable water supply falls below 1,000 m^3 per person, more serious "water scarcity" begins to occur. In this category, chronic water shortages can hamper food production and economic development and cause serious environmental degradation (Falkenmark and Widstrand, 1992). Renewable freshwater availability (I_2) is obtained as:

$$I_2 = W_R / N \quad (5)$$

Where W_R is renewable freshwater and *N*is the total population.

Percentage of the population served by groundwater for drinking (I_3)

This indicator shows the dependency of the population on groundwater as a source of drinking water. As explained under Indicator I_1, according to the Total Water Resources Analysis Report (GoM, 2006), almost all of the population in the watershed, abstract groundwater for drinking purposes from dug wells, bore wells, and hand pumps. Indicator I_3 is calculated as:

$$I_3 = (N_G / N) \times 100 \quad (6)$$

Where N_G is the population served by groundwater for drinking and *N*is the total population.

Groundwater abstraction for irrigation as a percentage of total irrigation water (I_4)

This indicator signifies the contribution of groundwater to irrigation. The indicator I_4 is obtained as:

$$I_4 = (A_I / W_I) \times 100 \quad (7)$$

Where A_I is groundwater abstraction for irrigation, and W_I is the total water available for irrigation.

Groundwater abstraction as a percentage of the total water available (I_5)

This indicator looks at groundwater abstraction as a percentage of the total available water in the watershed, separated into groundwater and surface water. The indicator I_5 is calculated as:

$$I_5 = (A / W) \times 100 \quad (8)$$

Where *A* is the total groundwater abstraction for all uses and *W* is the total available water. *W* is obtained as the sum of the exploitable groundwater and surface water resources.

Groundwater abstraction as a percentage of recharge (I_6)

Groundwater abstraction means the total withdrawal of water from a given groundwater body by wells, springs, and other methods for the purpose of water supply and other uses against the recharge. Excessive abstraction of groundwater without the understanding of recharge rates can cause problems, in particular, depletion of the resource. The indicator I_6 is obtained as:

$$I_6 = (A / G_R) \times 100 \quad (9)$$

Where *A* is the total groundwater abstraction for all uses and G_R is the renewable groundwater resource in m^3.

Stage of groundwater development (I_7)

The indicator I_7 stage of groundwater development is the ratio of the total abstraction of groundwater resource (*A*) to the exploitable groundwater resource (G_E) as:

$$I_7 = (A / G_E) \times 100 \quad (10)$$

Vrba et al. (2007) classified the stages of groundwater development in three scenarios: scenario 1: I_7 <90% (scope for development), scenario 2: I_7 =100% (fully developed) and scenario 3: I_7 >100% (Overexploited).

RESULTS AND DISCUSSION

The variables needed to calculate seven indicators are estimated at watershed and sub-watersheds levels following the methodology outlined above and discussed in the section below.

Groundwater recharge

The change in groundwater storage volume (ΔS) is obtained for each year as a product of change in groundwater level (Δh) and specific yield (S_Y). The difference between the pre- and post-monsoon groundwater level is Δh. The average groundwater level in the watershed is plotted in Figure 2, showing water

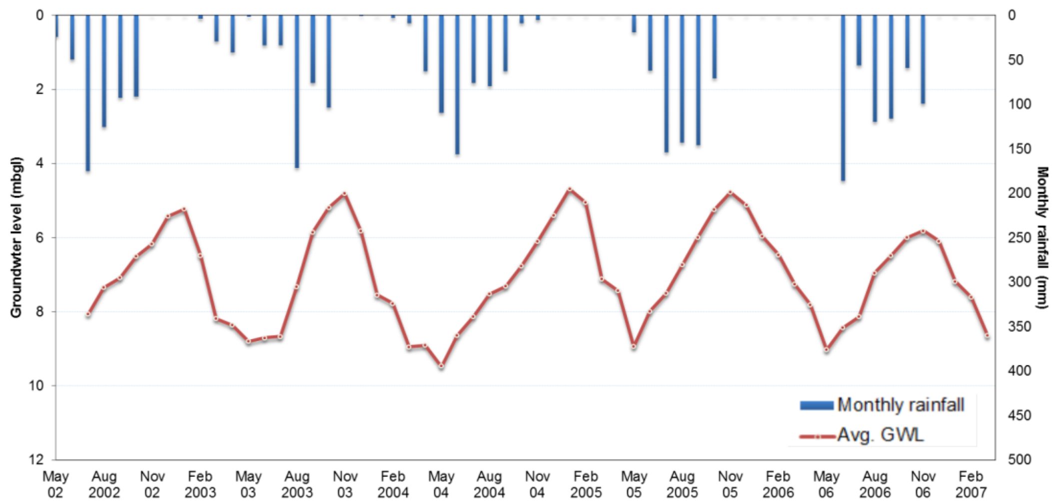

Figure 2. Average groundwater levels in the Dhubdhubhi watershed during 2002 to 2006.

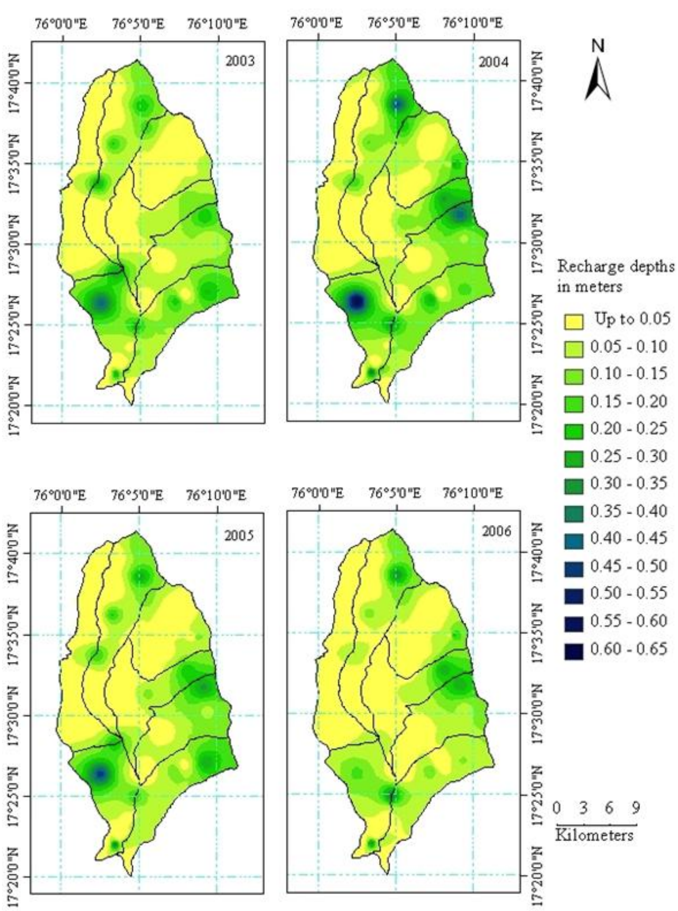

Figure 3. Groundwater recharge in seven sub-watersheds estimated by the hydrograph analysis method (2002 to 2006).

table fluctuations during the period of 2002 to 2006. The observed specific yield ranged from 0.0025 to 0.0751 (generally, for basaltic rock it varies from 0.02 to 0.07) (Deolankar, 1980), mainly due to heterogeneous underground formations and characteristic variations within small distances. The estimated average change in groundwater storage volume is estimated as 38.49 million m^3 for the period of 2002 to 2006.

For the period of 2002 to 2006, the annual average renewable groundwater resource was estimated to be 46.44 million m^3 when considering the estimated annual average change in storage volume (38.49 million m^3); total groundwater abstraction during the monsoon season (10.92 million m^3) and irrigation return flow (2.97 million m^3). The average annual renewable groundwater resource in the study area is 16.7% of annual average rainfall, which agrees with the findings of Singhal et al. 1999 and Limaye et al. (1986). The renewable freshwater is estimated as the sum of the annual average renewable groundwater resource (46.44 million m^3) and surface water available for irrigation (4.44 million m^3), both of which were obtained under IndicatorI_1.

The average depth of dug wells (13.31m) was used to determinate the exploitable saturated soil thickness (WRI, 2003). The product of the saturated soil thickness and specific yield multiplied by the aquifer area is the amount of exploitable groundwater resource (G_E) and was estimated to be 51.44 million m^3. Accordingly, the estimated total available water (W) is 55.88 million m^3. Similarly, the average groundwater recharge estimated in the sub-watershed is shown in Figure 3.

Groundwater for irrigation, domestic and livestock uses

Irrigation water requirements for eleven types of crops (Sorghum, Wheat, Maize, Sunflower, Vegetables, Pulses,

Table 2. Surface and groundwater withdrawal for irrigation, livestock, and domestic purpose in sub-watersheds.

Sub-watershed	Irrigation water requirements and use					Groundwater used for Livestock (million m^3)	Groundwater used for Domestic (million m^3)
	Total water required for irrigation (million m^3)	Surface water used for irrigation (million m^3)	Groundwater used for irrigation (million m^3)	Groundwater use (%)	Surface water use (%)		
BM-138-1	5.7195	0.7868	4.9327	86.24	13.76	0.1412	0.2531
BM-138-2	3.1074	0.7713	2.3361	75.18	24.82	0.112	0.1682
BM-138-3	4.9461	0.3527	4.5934	92.87	7.13	0.1155	0.1807
BM-138-4	4.7087	0.3527	4.356	92.51	7.49	0.1023	0.2354
BM-139-1	6.0768	1.1744	4.9024	80.67	19.33	0.118	0.2155
BM-139-2	4.9352	0.6938	4.2414	85.94	14.06	0.0089	0.1945
BM-139-3	6.0994	0.3178	5.7816	94.79	5.21	0.0689	0.1357

Table 3. Groundwater abstraction vs. recharge in seven sub-watersheds.

Sub-watershed	Groundwater recharge/yr, (million m^3)	Groundwater abstraction/year, (million m^3)	Remarks
BM-138-1	4.80	5.33	Recharge < Abstraction
BM-139-2	3.98	4.44	
BM-138-2	5.70	2.62	Recharge > Abstraction
BM-138-3	8.16	4.89	
BM-138-4	8.70	4.69	-
BM-139-1	8.54	5.24	-
BM-139-3	9.54	5.99	-

Bajara, Groundnuts, Rice, Sugarcane, and Fruit) grown in the watershed were estimated using the CROPWAT model, Table 2. For example, to determine *GIR* for a crop of Sorghum, *NIR* was estimated by the CROPWAT model to be 387.20 mm (it generally varies at around 400 mm (Dara and Raghuvanshi, 1999). E_F of 0.65 (MKVDC, 2011) was used for the Solapur district in Equation (4) above. *GIR* for Sorghum was estimated to be 595 mm. The irrigated area of Sorghum in the watershed is 601 ha. *GIR* volume as a product of the irrigated area of Sorghum and *GIR* is 0.358 million m^3. Similarly, *GIR* volume was estimated for all eleven crops grown in the watershed. The summation of *GIR* volume for all crops over the watershed gives the annual W_I as 35.58 million m^3.

Nearly all of the population in the watershed abstracts groundwater for drinking purposes; from dug wells, tube wells, or hand pumps. Surface water is not used for domestic purposes as it is scarce and not of good quality (GoM, 2006). In other words, the population is almost 100% dependent on groundwater for domestic uses. Groundwater abstraction for domestic use is obtained as a product of the population (*N* = 94,727) to provide an adequate water requirement of 40 L per person per day (GoI, 2001), which equates to1.38 million m^3/year. The groundwater abstraction for livestock as a product of the livestock population (33,375) has a water requirement of 55 L per cattle per day (Datta, 2012), equating to 0.67 million m^3/year. Since there is no industrial development, there is no groundwater withdrawal by industries. Groundwater abstractions merely during the monsoon season for domestic and livestock uses are 0.69 and 0.34 million m^3 respectively. Total abstraction of groundwater (for irrigation, domestic, and livestock uses) during the monsoon season is 10.92 million m^3. The estimated irrigation return flow (assumed to be 30% of groundwater abstracted for irrigation) (GEC, 1997) is 2.97 million m^3. Groundwater use for the domestic and livestock sector is presented in Table 2. Similarly, sub-watershed level groundwater abstraction vs. recharge is presented in Table 3.

Groundwater sustainability indicators

Utilising the values of all variables obtained above, seven indicators were estimated at the watershed and sub-watershed levels and are summarised in Table 4. For the whole watershed level, the renewable groundwater resource per capita (I_1) is estimated at 490 m^3 per capita per year. It is highest (981) in sub-watersheds in BM 139-3 and lowest in sub-watersheds BM 138-1 and BM 139-2. The renewable freshwater availability per capita (I_2) is estimated to be 537 m^3 which shows water scarcity in the

Table 4. Summary of results of estimated groundwater indicators in the seven sub-watersheds and at the watershed level.

No.	Indicator (unit)	Sub-watershed							Watershed
		BM-138-1	BM-138-2	BM-138-3	BM-138-4	BM-139-1	BM-139-2	BM-139-3	
I_1	Renewable groundwater resource per capita (m^3/capita/year)	258.38	474.64	620.14	510.71	543.79	258.53	981.15	490.25
I_2	Renewable freshwater availability per capita (m^3/capita/year)	330.21	501.50	691.89	530.63	618.72	298.50	996.37	537.12
I_3	Percent population served by groundwater as drinking water (%)	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
I_4	Groundwater use for irrigation as percentage of total irrigation water (%)	86.24	75.18	92.87	92.51	80.67	85.94	94.79	87.52
I_5	Groundwater abstraction as percentage of total water available (%)	67.22	69.44	61.77	62.45	26.95	141.87	44.95	59.40
I_6	Groundwater abstraction as percentage of recharge (%)	116.90	81.30	78.00	64.70	32.60	142.00	51.50	71.46
I_7	Stage of groundwater development (%)	80.00	73.00	68.00	64.90	30.40	167.80	45.60	64.50

watershed, since it is far less than the so-called water scarcity limit (1000 m^3/year/capita) (Falkenmark, 1989). This value (537 m^3) agrees with the estimates of the Water Research Institute (WRI) (2003). Similarly, renewable freshwater availability per capita in all sub-watersheds is less than 1000 m^3/year/capita which highlights the water scarcity.

In the entire watershed, the percentage of the population served by groundwater for drinking (I_3) shows that 100% of the population is dependent on groundwater for drinking purposes, depicting the importance of groundwater in people's lives. Generally, in the Maharashtra State, 90% of the rural population uses groundwater for drinking purposes (eSakal News Article, 2013). This difference is due to the comparison of State level results with local levels in a much smaller area.

The groundwater use for irrigation as a percentage of total irrigation water (I_4) ranges from 75 to 95%, showing a higher contribution of groundwater for irrigation purposes. The groundwater abstraction as a percentage of the total water available (I_5), is estimated to be the lowest (27%) in sub-watershed BM-139-1 and the highest (142%) in sub-watershed BM-139-2. These results indicate that the overall dependence of the community on groundwater resources is very high in some sub-watersheds and overexploitation of groundwater is observed.

The groundwater abstraction as a percentage of recharge (I_6) at a watershed level is 71.46%, whereas it is more than 100% for sub-watersheds BM138-1 and BM-139-2. The stage of groundwater development (I_7) in the entire watershed is 64.5% which shows that groundwater resource development falls into the first scenario as reported by Vrba et al. (2007). It means that groundwater resources in the watershed as a whole are not fully utilized, and there is still scope for groundwater development. However, in the sub-watershed BM-139-2, the stage of groundwater development is greater than 100%, showing over-exploitation of groundwater resources. When compared with GEC-1997 norms, a watershed is safe if the stage of groundwater development is at less than 70% and no decreasing groundwater level over the pre- or post-monsoon season is observed. If this is not the case, it is otherwise classified as semi-critical (when I_7 is 70 to 90%), critical (when I_7 is 90 to 100%) and overexploited (when I_7 is >100%) with pre- or post-monsoon decreasing groundwater levels.

In Dhubdhubhi, the stage of watershed groundwater development (I_7) is 64.5% with no decreasing groundwater level. Hence, the watershed is safe in terms of groundwater resource development. However, at sub-watershed level a different situation is observed. In the sub-watershed BM-139-2, I_7 is greater than 100% with a decreasing groundwater level classified as overexploited, Figure 4. This can be attributed to low recharge followed by high groundwater abstraction resulting in a declining groundwater level. Also, for the sub-watershed BM-138-1, I_7 is between 70-90% with a decreasing groundwater level classified as semi-critical, Figure 5, which can result in a state of over-exploitation if adequate management practices are not implemented.

CONCLUSIONS AND RECOMMENDATIONS

Groundwater resource status and its uses were assessed using seven widely applied indicators proposed by UNESCO in a drought prone Dhubdhubhi watershed in the Maharashtra State of India. The integral application of all these indicators in this particular watershed leads us to conclude that, at present, the groundwater resources of the whole watershed is at a stage of sustainable development. Five sub-watersheds have sustainable

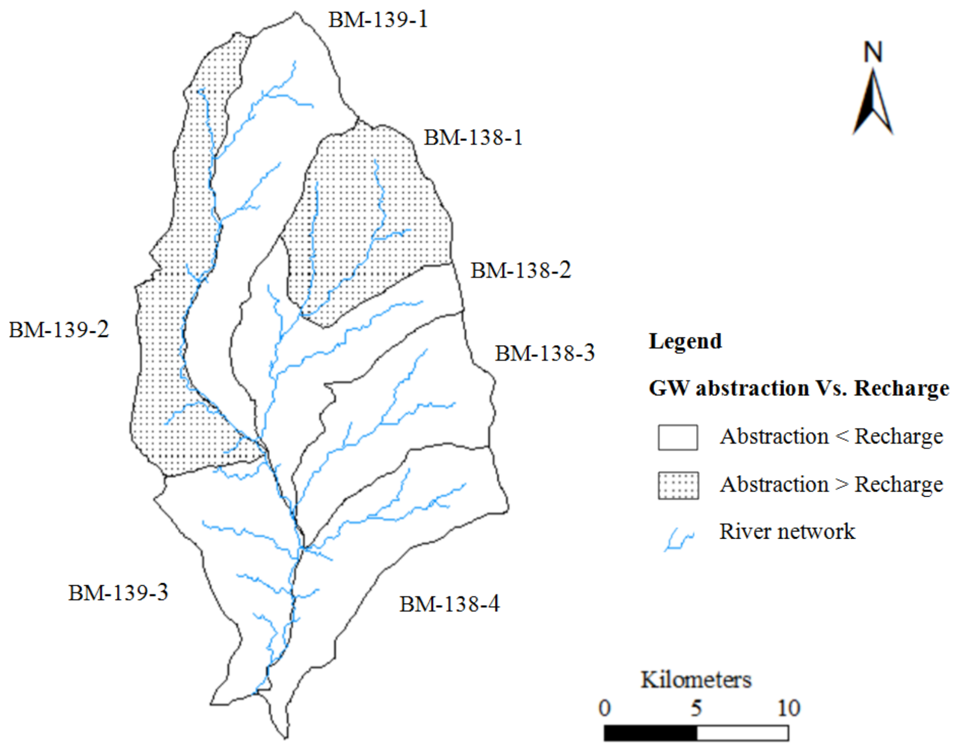

Figure 4. Sub-watershed of Dhubdhubhi watershed showing the status of groundwater abstraction and recharge.

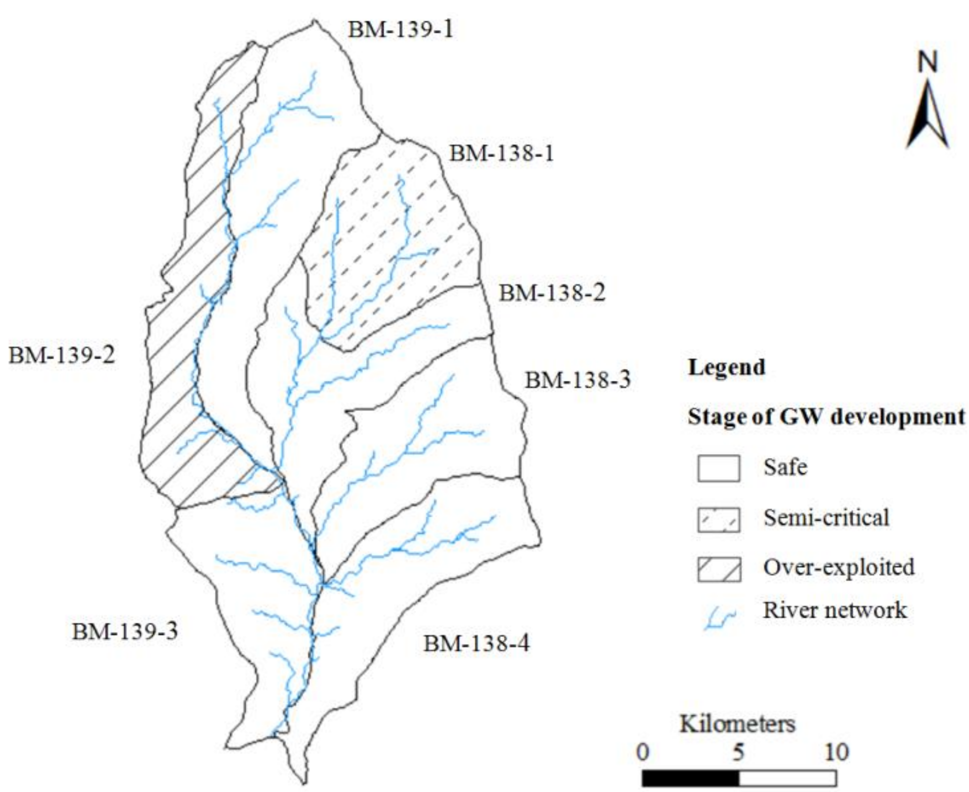

Figure 5. Stages of groundwater development in seven sub-watershed in Dhubdhubhi according to GEC (1997) norms.

groundwater development, and groundwater abstraction use does not exceed the recharge. This shows that there is still scope for groundwater development in these sub-watersheds. However, the stage of groundwater development is semi-critical in BM 138-1 and over exploited in BM 139-2 sub-watersheds, where groundwater abstraction exceeds the recharge, calling the sustainability of the resource into question.

Water management demands a certain degree of action for example: minimising on-farm water loss, adopting water-saving irrigation scheduling, soil-water conservation through mulching, and rainwater harvesting in farm ponds. It is therefore necessary to develop alternative surface water sources such as dams (where feasible), and surface water should be used when and where available to avoid groundwater mining and promote the sustainable use of groundwater resources in these sub-watersheds.

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Conflict of Interest

The author(s) have not declared any conflict of interests.

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