Effect of Land Use Changes on Water Quality in an Ephemeral Coastal Plain: Khambhat City, Gujarat, India

Pankaj Kumar 1,*, Rajarshi Dasgupta 1, Brian Alan Johnson 1, Chitresh Saraswat 2,* Mrittika Basu 3, Mohamed Kefi 4 and Binaya Kumar Mishra 5

1 Natural Resources and Ecosystem Services, Institute for Global Environmental Strategies, Hayama, Kanagawa 240-0115, Japan; dasgupta@iges.or.jp (R.D.); johnson@iges.or.jp (B.A.J.)
2 Institute for the Advanced Study of Sustainability, United Nations University, 4-53-70, Jingumae, Shibuya, Tokyo 150-8925, Japan; saraswat.chitresh@gmail.com
3 Laboratory of Landscape Ecology and Planning, The University of Tokyo, Tokyo 150-8925, Japan; mrittika.basu@gmail.com
4 Laboratory of Natural Water Treatment (LabTEN), Water Researches and Technologies Center (CERTE), University of Carthage, Carthage 273-8020, Tunisia; moh_kefi@yahoo.fr
5 Faculty of Science and Technology, Pokhra University, Pokhra 56305, Nepal; mishra_binaya@hotmail.com
* Correspondence: kumar@iges.or.jp; Tel.: +81-070-1412-4622

Received: 8 February 2019; Accepted: 3 April 2019; Published: 8 April 2019

Abstract: Rapid changes in land use and land cover pattern have exerted an irreversible change on different natural resources, and water resources in particular, throughout the world. Khambhat City, located in the Western coastal plain of India, is witnessing a rapid expansion of human settlements, as well as agricultural and industrial activities. This development has led to a massive increase in groundwater use (the only source of potable water in the area), brought about significant changes to land management practices (e.g., increased fertilizer use), and resulted in much greater amounts of household and industrial waste. To better understand the impacts of this development on the local groundwater, this study investigated the relationship between groundwater quality change and land use change over the 2001–2011 period; a time during which rapid development occurred. Water quality measurements from 66 groundwater sampling wells were analyzed for the years 2001 and 2011, and two water quality indicators (NO$_3^-$ and Cl$^-$ concentration) were mapped and correlated against the changes in land use. Our results indicated that the groundwater quality has deteriorated, with both nitrate (NO$_3^-$) and chloride (Cl$^-$) levels being elevated significantly. Contour maps of NO$_3^-$ and Cl$^-$ were compared with the land use maps for 2001 and 2011, respectively, to identify the impact of land use changes on water quality. Zonal statistics suggested that conversion from barren land to agricultural land had the most significant negative impact on water quality, demonstrating a positive correlation with accelerated levels of both NO$_3^-$ and Cl$^-$ concentrations. The amount of influence of the different land use categories on NO$_3^-$ increase was, in order, agriculture > bare land > lake > marshland > built-up > river. Whereas, for higher concentration of Cl$^-$ in the groundwater, the order of influence of the different land use categories was marshland > built-up > agriculture > bare land > lake > river. This study will help policy planners and decision makers to understand the trend of groundwater development and hence to take timely mitigation measures for its sustainable management.

Keywords: groundwater; water pollution; land use change; sustainable water management
1. Introduction

In many regions, already-scarce freshwater resources are under an unprecedented amount of stress from different drivers and pressures, including urbanization, land use change, population growth, increased food/water demand, and climate change [1,2]. It has been well reported that the cumulative effects of both natural and anthropogenic activities have significant impacts on land use, which ultimately affects the services provided by the local ecosystems (e.g., their ability to provision and regulate fresh surface water and groundwater) [3,4]. This is exacerbated by the lack of water governance and inadequate infrastructure in many developing countries [5,6]. Recognizing this problem, the United Nations Sustainable Development Goals (SDGs) highlights the necessity of clean water for achieving different goals pertaining to environmental (e.g., Goal 14, Life below water) and human well-being (e.g., Goal 6, Clean water and sanitation; and Goal 2, Zero hunger) [7]. Also along these lines, a recent study found that more holistic and integrated land use management practices could help achieve SDGs related to water, food, health, and climate change [8]. Water governance has an important role to play in this kind of holistic/integrated land use management.

Water governance is also a particularly important issue when it comes to coastal aquifer systems because of their vulnerability to salt water intrusion. More than sixty percent of the global population is living in coastal regions or low-lying deltaic zones, so it is imperative to monitor the effects of different factors affecting water quality in coastal plains [9]. Furthermore, because of the limited amount of freshwater resources in many coastal areas, it is essential to change water consumption patterns to achieve a stable hydrodynamic state in future [10,11]. Among different groundwater quality parameters, nitrate is particularly significant because of its great leachability in soils and its significant connection with fertilizer use, as well as with inadequate domestic/industrial wastewater treatment [12,13]. Long-term consumption of water with nitrate concentrations exceeding the permissible limit (>45 mg/L) set by [14,15] can lead to low oxygen levels in the blood of infants, a life-threatening situation also known as methemoglobinemia [16]. In addition to nitrate, chloride is another important groundwater quality parameter that is sensitive to land use and land management practices, especially in coastal zones due to seawater intrusion [17,18]. When groundwater levels are reduced in coastal areas (e.g., due to drought or excessive groundwater pumping), salt water with high levels of chloride can infiltrate into the groundwater aquifer. The main reason behind this is inland movement of sea water- fresh water interface and approaching the well screen. Although the health effects of consuming groundwater with levels of high chloride are not well reported, this degraded groundwater is less suitable for other important purposes (e.g., crop irrigation).

Several scientific works have used different analysis techniques, including regression modeling, time series analysis, and geospatial modeling (e.g., using remote sensing and geographical information systems), to identify the spatio-temporal relationships between groundwater quality changes and different anthropogenic activities [19–24]. With the above background, it is of utmost importance to understand the relationship between land use changes and water quality in developing countries like India with burgeoning populations. This kind of analysis not only helps to identify possible threats to water quality, but also provides vital information to decision makers to allow them to take adaptive measures to ensure sustainable water development. This work strives to quantify the effect of land use changes from 2001 to 2011 on groundwater quality of Khambhat city, a coastal city located in the Gujarat state, Western India. Khambhat was selected as our study site due to the rapid changes in groundwater development and land use practices witnessed there in recent years, along with the absence of guidance and regulations for its sustainable management. In addition, water bodies in the area have recently experienced algal blooms [25] and salt water intrusion [26]. In this study, nitrate is used as an indicator to trace the link between land use changes and groundwater quality changes because of its high solubility, while chloride is used to evaluate the effect of increased groundwater use and its impact on groundwater salinization. Our evaluation is based on an integrated predictive physically based modeling system (spatial interpolation and zonal statistics) of groundwater–agriculture–urbanization.
In addition, different management policies are proposed as adaptive measures to minimize further deterioration of groundwater quality.

2. Study Area

Khambhat, formerly known as Cambay, is a city located in the Anand district of the Indian state of Gujarat (Figure 1). It lies on a sedimentary plain at the north end of the Gulf of Khambhat, which is noted for the extreme rise and fall of its tides, ranging by as much as 9.1 m (the highest in the world) in the vicinity of Khambhat. The average elevation of the area is 8 m above mean sea level. The main alluvial sediment formation is of the quaternary age, and principally deposited by the Mahi River; therefore, the soil is highly fertile. The area to the south of Khambhat consists of muddy wetlands following along the coastline. The climate is warm and humid, with an annual average temperature of 27.4 °C and an average rainfall of 739 mm/year, most of which is received during the south-west monsoon between June and September. Monthly average rainfall and temperature for both year 2001 and year 2011 are shown in Figure 2, which indicates that there are no significant changes (data procured from Indian Meteorological Department web portal). The average groundwater level is 6–8 m below ground [27]. As of the 2011 census, Khambhat had a population of 99,114 (census, 2011), which was 80,439 in year 2001 with a growth rate of 4.1% per year. However, in the recent past, Khambhat city has witnessed drastic population growth, rapid urbanization and sizable growth in agricultural activity because of the high fertility of the land. These factors have led to a significant change in land use, which is still continuing.

Figure 1. Study area map with sampling locations.
were recorded using Global Positioning System (GPS III, Garmin), and on-site measurements of the pH and electrical conductivity (EC) were recorded using an inline flow cell ensuring the exclusion of atmospheric contamination and minimized fluctuations. The transportable “Orion Thermo water analyzing kit (Model Beverly, MA, 01915)”, with a precision of 5%, was used for all kind of on-site measurements. Using thoroughly rinsed polyethylene bottles, the groundwater samples were collected from each location and filtered using 0.2 µm Millipore membrane filters. The samples collected for major cation analysis were acidified by 1% HNO₃ to stabilize trace metals (pH ~ 2), while samples collected for nitrate were acidified with H₃BO₃. The concentration of HCO₃⁻ was analyzed by acid titration (using Metrohm Multi-Dosimat), while other anions Cl⁻, NO₃⁻, SO₄²⁻ and PO₄³⁻ were

Figure 2. Monthly average rainfall and temperature for the study area in 2001 and 2011.

3. Materials and Methods

3.1. Water Quality Analysis

To estimate the effect of land use changes on the water quality, measurements from sixty-six groundwater sampling stations were collected during 2001 and 2011. These sampling well locations were selected such that the different geological formations, screen depths, and land use patterns of the area were sampled. The sixty-six samples were divided into three categories, namely: (a) deep aquifers (screen depth >50 m below ground level) for eleven samples, (b) intermediate aquifers (screen depth ranges between 26–50 m below ground level) for twenty samples, and (c) shallow aquifers (screen depth <25 m below ground level) for thirty-five samples. Groundwater sampling for both years was accomplished during the pre-monsoon period on the 15–25 May. During the monsoon period, mostly there is an abrupt change in water quality due to the surface runoff, which is statistically hard to quantify. The pre-monsoon season is the most water-scarce period, and that is why May was selected as the water sampling period. The depth of the well and the level of the water top were measured using string and weight and string and fishing float, respectively. In the string and weight method, a small but heavy steel weight was tied to a string. It was lowered into the sampling well until it reached the bottom of the well. After that, the string was taken back and the distance between the bottom of the steel weight and the ground level mark on the string was measured, giving a value for well depth. For the string and fishing float method, the fishing float was lowered into the sampling well until it stopped dropping. Marking that string at ground level gave a value for water level. Sampling coordinates were recorded using Global Positioning System (GPS III, Garmin), and on-site measurements of the pH and electrical conductivity (EC) were recorded using an inline flow cell ensuring the exclusion of atmospheric contamination and minimized fluctuations. The transportable “Orion Thermo water analyzing kit (Model Beverly, MA, 01915)”, with a precision of 5%, was used for all kind of on-site measurements. Using thoroughly rinsed polyethylene bottles, the groundwater samples were collected from each location and filtered using 0.2 µm Millipore membrane filters. The samples collected for major cation analysis were acidified by 1% HNO₃ to stabilize trace metals (pH ~ 2), while samples collected for nitrate were acidified with H₃BO₃. The concentration of HCO₃⁻ was analyzed by acid titration (using Metrohm Multi-Dosimat), while other anions Cl⁻, NO₃⁻, SO₄²⁻ and PO₄³⁻ were
analyzed by DIONEX ICS-90 ion chromatograph with an error percentage of less than 2%, using duplicates. The major cations were evaluated by inductively coupled plasma-mass spectrometry (ICP-MS) with a precision of less than 2%, using duplicates. For each instrument, after the analysis of every five samples, one replicate was used to check the accuracy of the instruments. For major ions, analytical precision was checked by normalized inorganic charge balance (NICB) [28]. This is defined as \([\frac{(Tz^+ - Tz^-)}{(Tz^+ + Tz^-)}]\) and represents the fractional difference between total cations and anions. Here, \(Tz^+\) and \(Tz^-\) represent the total mille-equivalent of cations and anions, respectively. The observed charge balance supports the quality of the data points, which is better than ±5%, and generally this charge imbalance was in favor of positive charge. For statistical analysis, a multivariate analysis technique was used, where the data was subjected to correlation analysis using Spearman’s rank coefficient ranking of the data and not their absolute value using Social Science Statistical Software (SPSS) version 21.0.

3.2. Decadal Land Use Changes

To quantify the decadal (2001–2011) land use changes, remotely sensed, multi-temporal satellite data from the Landsat series (Thematic Mapper (TM) / Enhanced Thematic Mapper Plus (ETM+)) were used as the primary input. These satellite images, acquired on 10 November 2001 and 14 November 2011, respectively, were downloaded from the United States Geological Survey (https://earthexplorer.usgs.gov/). Both the images were subjected to a series of pre-processing techniques, including geometric and radiometric correction, using the ErDAS ImagineTM 9.3 image processing software. Both the images were spatially referenced in the Universal Transverse Mercator (UTM) projection system (zone 43 north) with World Geodetic System (WGS) 1984 as datum. The details of the satellite images, along with the bands used for this study are furnished Table 1.

| Satellite/Sensor | Date of Pass | Path/Row | Spatial Resolution (m) | Band Considered with Spectral Resolution (µm) |
|------------------|--------------|----------|------------------------|---------------------------------------------|
| Landsat-7 ETM+   | 10th November, 2001 | 148/45 | 30                      | 0.45–0.52 (blue)                           |
|                  |              |          | 30                      | 0.52–0.60 (green)                          |
|                  |              |          | 30                      | 0.63–0.69 (red)                            |
|                  |              |          | 30                      | 0.77–0.90 (NIR)                            |
|                  |              |          | 30                      | 0.45–0.52 (blue)                           |
| Landsat-5 TM     | 14th November, 2011 | 148/45 | 30                      | 0.52–0.60 (green)                          |
|                  |              |          | 30                      | 0.63–0.69 (red)                            |
|                  |              |          | 30                      | 0.76–0.90 (NIR)                            |

For land use classification, both images were processed separately and were subjected to supervised maximum likelihood classification using onscreen digitation of training polygons. Based on the authors field experiences, a total of six major land use classes were present, including (1) Agriculture, (2) Barren land, (3) Built-up areas, (4) Lake, (5) Marshland, and (6) River. Here, barren land represents dryland ecosystem. The quality of the classified images was tested separately for both the classified images through a rigorous accuracy assessment technique. We adopted the confusion matrix approach to calculate the overall accuracy and kappa statistics. To compute this matrix, 200 Ground Control Points (GCPs) were randomly generated and verified against the Google EarthTM High-Resolution temporal images. The overall accuracy for the 2001 and 2011 land use were observed 79.8 % and 81.2%, respectively.

To identify the dominant changes in the land use category and to compute the spatial trend of change, we utilized the change analysis tab onboard the Land Change Modeller of the TerrSetTM geoprocessing software. At first, the land use maps from 2001 and 2011 were both calibrated using the onboard harmonization tool to match the exact spatial extent and then, the status each pixel from its initial (2001) to final (2011) state was compared. Thereafter, we cross-tabulated the loss and gains among the six land use categories. To identify the patterns of changes, the spatial trend was
mapped using the third-order polynomial to fit the changed pixel. Identification of spatial trends is an
effective way to visualize and understand underlying drivers of change, and a third-order polynomial
is generally preferred for this purpose [29].

3.3. Preparation of Contour Maps and Spatial Analysis of the Impacts of LU Changes of GW Quality

To create the temporal contour maps of Cl$^{-}$ and NO$_3^-$, we applied the Inverse distance-weighted
(IDW) interpolation technique to compute the contour profile from 64 sampling points. IDW is an
algorithm widely used to spatially interpolate point data, and allows for estimating the values at
locations other than the measured sample points. It works on the assumption that each measured
point has a local influence that fades with distance, and the highest influences are always close to the
point of observations. Thereafter, we classified the predicted groundwater quality (Cl$^{-}$ and NO$_3^-$),
well depth and water level contours, as shown in Figure 3a,b, Figures 4 and 5, respectively, and
resampled the contour maps to 30 m spatial resolution to match that of the land use maps. All spatial
analysis was conducted in ArcGIS 10.5TM. To understand the influence of the six land use categories
on groundwater quality, the zonal statistics tool in ArcGIS was applied. This tool summarizes the
values of a raster against the zones of another dataset, and results are reported in form a table. Here,
we used the tool to compute the maximum, minimum and average values of Cl$^{-}$ and NO$_3^-$ for each
land use category, in both 2001 and 2011, respectively.

Figure 3. Spatio-temporal distribution of Cl$^{-}$ (a,b) and NO$_3^-$ (c,d) in the study area.
4. Results

4.1. Water Quality Changes

From the well depth of the sampling point (Figure 4), it is found that most of the shallow aquifers are located in north and northwestern region, whereas medium to deep aquifers are located in the
south and southeast parts of the study area. Figure 5 shows the change in water level in the monitored wells from 2001 to 2011. It is found that water level changed significantly, especially for the shallow aquifers. A summary of the water quality of the groundwater samples for both 2001 and 2011 is supplied in Table 2. The results suggest that the anionic abundance was in the order of $\text{Cl}^{-} > \text{HCO}_3^{-} > \text{SO}_4^{2-} > \text{NO}_3^{-} > \text{PO}_4^{3-}$, while cationic abundance was found in the order of $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Na}^{+} > \text{K}^{+}$. Here, most of the parameters are within the permissible limits prescribed by [13,14], with the exceptions of $\text{Cl}^{-}$ in both 2011 and 2011 and $\text{NO}_3^{-}$ in 2011. Also, it is found that the water level in 2011 was lower, with an average of 3.9 m dropdown, which was primarily due to the high usage rate (Table 2). To evaluate the effects of well depth, we plotted the relationship between $\text{NO}_3^{-}$ and $\text{Cl}^{-}$ and well sampling depth, as shown in Figure 6a,b, respectively. Also, from the spatial distribution of changes in $\text{NO}_3^{-}$ and $\text{Cl}^{-}$ concentrations shown in Figure 3, it was found that shallow aquifers were mainly affected by nitrate enrichment in the year 2011 (Figure 6a), which at spatial scale corresponded to the sample numbers ranging from 40–64 (Figure 1), which were collected from regions dominated by agricultural activities (as seen in Figure 3c,d). Most of the sampling location also lies in the northern and northwestern part, near to the river, as shown in Figure 1, where because of high water table and fertile land, agricultural activities have intensified over the last decade and resulted in nitrate enrichment. Looking into the temporal variation of $\text{Cl}^{-}$ concentration with depth, a temporal shift in sea water–fresh water interface is observed, as shown in the shaded rectangle (6b), which results in a higher concentration of chloride in deeper wells, too. This is a clear case of salt-water intrusion because of the higher groundwater extraction. For chloride, the maximum deviation was found in sample numbers ranging from 31–37, which lay mainly in the southern part or coastal region of the study area, as shown in Figure 1, which signifies the impact of the coastal environment and/or local anthropogenic activities in the region.

### Table 2. Statistical summary of water quality for the years 2001 and 2011.

| Parameter          | 2001        | 2011        |
|--------------------|-------------|-------------|
| Well depth (mbgl)  | 10.0–90.0   | 10.0–90.0   |
| Water level (mbgl) | 4.0–73.5    | 6.0–78.0    |
| pH                 | 6.8–7.8     | 6.4–7.7     |
| EC (µs/cm)         | 362.0–8230.0| 478.0–9792.0|
| Na⁺ (mg/L)         | 29.0–611.7  | 41.1–737.5  |
| K⁺ (mg/L)          | 4.2–36.7    | 4.2–36.7    |
| Ca²⁺ (mg/L)        | 13.8–251.6  | 40.2–303.7  |
| Mg²⁺ (mg/L)        | 6.0–424.7   | 11.5–558.6  |
| HCO₃⁻ (mg/L)       | 62.1–1032.3 | 68.2–1204.8 |
| SO₄²⁻ (mg/L)       | 13.3–234.8  | 20.0–366.7  |
| Cl⁻ (mg/L)         | 9.8–4874.9  | 31.0–5804.5 |
| NO₃⁻ (mg/L)        | 8.9–119.8   | 12.1–211.9  |
| PO₄³⁻ (mg/L)       | 1.3–44.1    | 5.4–78.6    |

### 4.2. Land Use Changes

Land use maps for both year 2001 and 2011, derived from the Landsat satellite images, are shown in Figure 7. A statistical summary of the spatial extent of each land use class in each year is presented in Table 3. For the year 2001, the most dominant feature was barren land, having an area of 465.64 km² (54.45% of the study area), and lying mainly in the southeast region of the study area. Barren land was followed by agriculture, which made up approximately 35.44% of total area and was spread mainly around the river and in the north and northwestern region of the study area. This was followed by marshland, which occupied around 4% of the study area. Marshland includes both fresh water marshes because of the presence of river and lake, and salty marshes due to presence of estuary in the southern part of this study area. Marshland was followed by built-up area, with 3.7% of the total area sparsely distributed in both the north and south regions. The fifth category is river, which is the presence of the Mahi River flowing from the north to the south direction. The last class is lake, which
occupies about 1.8% of the total area and is located in the northern part of the study area. Looking at the map for the year 2011, significant changes were observed for almost all of the land-use categories except for lake and river. The most drastic changes were observed for agricultural and barren land categories. It was found that nearly all of the barren land that was lost was due to conversion to agricultural lands. This change can be attributed to a recent increase in agricultural activity to meet the food demand of the newly developed human settlements. Changes in the marshlands and lakes were mainly attributed to coastal development, and human encroachment of water bodies for urban sprawl. To support the finding, cubic trend considered the conversion of barren land to agricultural land, which seems to be the most dominant driver of decadal land change (Figure 8). Here, it is evident that the conversion was highest in the central and southwest parts of the study area, in proximity to the river. The most obvious reason behind this trend is the presence of riparian fertile land and shallow aquifers, as mentioned above.

**Figure 6.** Spatial distribution of (a) NO$_3^-$ and (b) Cl$^-$ in the groundwater with relation to water level.
It was found that nearly all of the barren land that was lost was due to conversion to agricultural lands. This change can be attributed to a recent increase in agricultural activity to meet the food demand of the newly developed human settlements. Changes in the marshlands and lakes were mainly attributed to coastal development, and human encroachment of water bodies for urban sprawl. To support the finding, cubic trend considered the conversion of barren land to agricultural land, which seems to be the most dominant driver of decadal land change (Figure 8). Here, it is evident that the conversion was highest in the central and southwest parts of the study area, in proximity to the river. The most obvious reason behind this trend is the presence of riparian fertile land and shallow aquifers, as mentioned above.

**Figure 7.** Land use/land cover map of the study area for the year 2001 and 2011.

**Table 3.** Statistical summary for various categories in land use/land cover maps for the years 2001 and 2011.

| Category      | 2001 Area (km²) | 2001 Proportion (%) | 2011 Area (km²) | 2011 Proportion (%) | Change in Area (km²) | Change in Proportion (%) |
|---------------|-----------------|---------------------|-----------------|---------------------|----------------------|-------------------------|
| Agriculture   | 303.06          | 35.44               | 344.81          | 40.32               | 41.75                | 4.88                    |
| Barren land   | 465.64          | 54.45               | 429.45          | 50.21               | −36.19               | −4.23                   |
| Built-up land | 31.67           | 3.70                | 42.32           | 4.95                | 10.65                | 1.25                    |
| Lake          | 6.83            | 0.80                | 6.33            | 0.74                | −0.50                | −0.06                   |
| Marshland     | 33.87           | 3.96                | 18.96           | 2.22                | −14.91               | −1.74                   |
| River         | 14.18           | 1.66                | 13.37           | 1.56                | −0.81                | −0.09                   |

**Figure 8.** Spatial trend showing the conversion of barren land to agricultural land.

**4.1. Relationship Between Land Use Change and Water Quality**

To evaluate the impact of land use on groundwater quality, the principal changes among the different categories between the years 2001 and 2011 are shown in Figure 9. As can be seen in this map, five major types of land-use transitions took place between the two years, namely the conversions from: barren land to agricultural land, agricultural land to barren land, built-up land to barren land, marshland to barren land, and barren land to built-up land. Among the above-mentioned five categories, conversion from barren land to agriculture was most dominant, and should be one of the main drivers of groundwater change. The barren land to agricultural land change was most prevalent in the western half of the study area. Geologically, this area is alluvial fertile land with a high water table. This triggered a swift increase in agricultural practices, which is
Table 3. Statistical summary for various categories in land use/land cover maps for the years 2001 and 2011.

| LULC (Category) | 2001 | 2011 | Change in the Area | Change in Proportion (%) |
|-----------------|------|------|-------------------|-------------------------|
|                 | Area (km²) | Proportion (%) | Area (km²) | Proportion (%) | | |
| Agriculture     | 303.06 | 35.44 | 344.81 | 40.32 | 41.75 | 4.88 |
| Barren land     | 465.64 | 54.45 | 429.45 | 50.21 | −36.19 | −4.23 |
| Built-up        | 31.67 | 3.70 | 42.32 | 4.95 | 10.65 | 1.25 |
| Lake            | 6.83  | 0.80 | 6.33  | 0.74 | −0.50 | −0.06 |
| Marshland       | 33.87 | 3.96 | 18.96 | 2.22 | −14.91 | −1.74 |
| River           | 14.18 | 1.66 | 13.37 | 1.56 | −0.81 | −0.09 |

4.3. Relationship between Land Use Change and Water Quality

To evaluate the impact of land use on groundwater quality, the principal changes among the different categories between the years 2001 and 2011 are shown in Figure 9. As can be seen in this map, five major types of land-use transitions took place between the two years, namely the conversions from: barren land to agricultural land, agricultural land to barren land, built-up land to barren land, marshland to barren land, and barren land to built-up land. Among the above-mentioned five categories, conversion from barren land to agriculture was most dominant, and should be one of the main drivers of groundwater change. The barren land to agricultural land change was most prevalent in the western half of the study area. Geologically, this area is alluvial fertile land with a high water table. This triggered a swift increase in agricultural practices, which is well supported by both Figure 3, i.e., spatial distribution of nitrate, and Figure 6a, i.e., changes in nitrate with well depth.

Figure 9. Principal changes among different categories in land use/land cover from year 2001 to 2011.
4.4. Zonal Statistics

Finally, zonal statistics was calculated to estimate the association between different land categories and changes in mean concentration for both NO$_3^-$ and Cl$^-$, as shown in Figure 10a,b, respectively. The order of influence of each land use type on NO$_3^-$ concentrations in the groundwater was agricultural land > bare land > lake > marshland > built-up > river, with the magnitude of NO$_3^-$ concentrations from 2001 to 2011 increasing by factors of 11.9, 9.7, 7.4, 6.3, 4.9 and 3.6, respectively.

Agricultural practices in the farmlands and converted barren land involving high use of fertilizers causes nitrate enrichment in the shallow aquifers, especially, because of high leaching ability. The process of nitrification responsible for the conversion of ammonia within nitrogen fertilizers into nitrate is shown with Equation (1):

\[ \text{NH}_3 + 2 \text{O}_2 \rightarrow \text{NO}_3^- + \text{H}^+ + \text{H}_2\text{O} \]
\[ \text{NH}_3 + 2\text{O}_2 \rightarrow \text{NO}_3^- + \text{H}^+ + \text{H}_2\text{O} \] (1)

Next, bare land has a high increase in NO\(_3^-\) concentration compared to the other classes. This is because bare land is typically located near to agricultural land, so it is affected by the nearby fertilizer use. The next most dominant land use category is lake, as lakes act as a receiving body for locally generated nitrate-enriched runoff, which is quite evident with algal blooms in the lake throughout the year. This nitrate-enriched lake water recharges shallow aquifers, and thus contributes to increasing the concentration of nitrate in the nearby groundwater sources. Following this, the next land use category in terms of contribution to nitrate enrichment is marshland. Because of the very little amount of water in the marshlands in this area, particularly during the dry season, decomposing organic matter leads to nitrate enrichment, which finally seeps into groundwater sources nearby. Marshland was followed by built-up in terms of the land uses responsible for high nitrate concentration in the groundwater. High nitrate in the groundwater here can be attributed to leaching from open dump yard sites, landfills, untreated domestic sewerage and industrial effluents. Finally, river is the least contributing land use type for nitrate enrichment in the groundwater samples, probably because they transport the nitrate runoff that they receive to the nearby sea.

In terms of concentrations of Cl\(^-\) in the groundwater, the order of influence for the different land use categories was marshland > built-up > agriculture > bare land > lake > river, with the magnitude of Cl\(^-\) concentrations increasing between 2001–2011 by factors of 1.75, 1.73, 1.63, 1.51, 1.41 and 1.26 in each land use category, respectively. The largest contribution here is from marshland located near the coastal region in the southern end of the study area. This is mainly a mixture of salt marshes and tidal marshes. Because of the high contribution from sea tides, the Cl\(^-\) concentration in the groundwater increases. This was followed by built-up, agriculture and barren land. This can all sum up the pressure from anthropogenic activities on groundwater development mainly in the southern part of the study area. Because of the increase in demand for groundwater for agriculture and household consumption, the seawater–groundwater equilibrium has become disturbed, and brackish plumes are encroaching into the inland shallow aquifers, as evident from the elevated Cl\(^-\) concentrations in the groundwater. Other possible reasons for the higher groundwater salinity may include high evaporation rate during recharge and increased infiltration of sewage effluents. Lastly, lakes and rivers had the least impact on the elevated Cl\(^-\) concentrations found in the groundwater.

To support the above finding, correlation analysis was performed, and the results are shown in Table 4. It gave a clear picture to trace the prime factors responsible for the change in water quality parameter (NO\(_3^-\) and Cl\(^-\)) concentrations. It was found that changes in land use categories like agriculture and built-up and water level have a significant positive correlation with change in NO\(_3^-\) concentrations, whereas they were negatively correlated with barren land. This supports the arguments that with an increase in population growth, agricultural practices and built-up areas increases at the cost of other land cover type namely barren land, marshland, etc. Thus, high usage of fertilizers in agricultural activities and leakage from untreated sewerage in the rapidly urbanizing areas leads to increase in NO\(_3^-\) concentrations in the groundwater. Also, these combined activities caused a disturbance in sea water-fresh water equilibrium in the coastal part of the study areas. As a result, the effect of groundwater salinization increased, and hence so did the Cl\(^-\) concentration in the groundwater.

The above-mentioned poor management of water resources has resulted in environmental deterioration, increases in water-related health diseases, and loss of income for farmers, among other problems in the last few years. Henceforth, as a mitigation measure for the above issues related to water scarcity, there is a need for better policy implementation regarding water resource management, including management of data inventory for both water quality and budget, conjunctive use of both surface and groundwater, and citizen awareness; all of these aspects are matters for future research.
Table 4. Correlation matrix showing relationship change in LULC and water quality parameters from 2001 to 2011.

|              | Agriculture | Barren Land | Built-Up | Lake | Marsh Land | River | Nitrate | Chloride | Water Level Reduction |
|--------------|-------------|-------------|----------|------|------------|-------|---------|----------|-----------------------|
| Agriculture  | 1.00        |             |          |      |            |       |         |          |                      |
| Barren Land  | −0.78       | 1.00        |          |      |            |       |         |          |                      |
| Built-Up     | 0.59        | −0.62       | 1.00     |      |            |       |         |          |                      |
| Lake         | 0.12        | 0.16        | 0.40     | 1.00 |            |       |         |          |                      |
| Marsh Land   | −0.51       | 0.20        | 0.37     | 0.03 | 1.00       |       |         |          |                      |
| River        | −0.22       | −0.13       | 0.06     | 0.09 | 0.08       | 1.00  |         |          |                      |
| Nitrate      | 0.84        | −0.65       | 0.55     | 0.41 | −0.44      | 0.45  | 1.00    |          |                      |
| Chloride     | 0.47        | 0.33        | 0.17     | 0.12 | 0.67       | 0.36  | 0.24    | 1.00     |                      |
| Water level reduction | 0.79 | −0.45 | 0.88 | −0.23 | −0.31 | −0.28 | 0.66 | 0.80 | 1.00 |

5. Conclusions

The findings from this work revealed that the major factors for the change in the groundwater quality between 2001–2011 in Khambhat city were the rising water demand along with groundwater withdrawal (for domestic, agricultural and industrial need) and land use/land cover changes. As a result of the above-mentioned drivers and pressures, sharp declines in fresh water resources in terms of both quality (high nutrient content, salt water intrusion) and quantity (lowering of water table) have been observed. More precisely, NO$_3^-$ concentration in the groundwater increased mainly for the shallow wells near the agricultural field because of high fertilizers input, whereas Cl$^-$ concentration in the groundwater increased for the samples located near the coast due to high water extraction and salt-water intrusion. The vulnerability of these water resources can be further exacerbated by different climate-related pressures like climate change, especially rainfall and temperature. This study will be helpful for both scientific communities and decision makers involved in water resource management. The poor management of water resources results in environmental deterioration, increases in water-related health diseases, and loss of income for farmers, among other problems. As a mitigation measure for the above issues related to water scarcity, there is a need for better policy implementation regarding water resource management, including management of data inventory for both water quality and budget, conjunctive use of both surface and groundwater, and citizen awareness.

Author Contributions: Conceptualization (P.K. and R.D.); methodology, (P.K. and R.D.); software, (P.K. and R.D.); validation, (P.K. and R.D.); formal analysis, (P.K. and R.D.); investigation, (P.K. and R.D.); writing—original draft preparation, (P.K. and R.D.); writing—review and editing, (P.K., R.D., B.A.J., C.S., M.B., M.K., B.K.M.).

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Dabrowski, J.M.; De Klerk, L.P. An Assessment of the Impact of Different Land Use Activities on Water Quality in the Upper Olifants River Catchment. *Water Sa* 2013, 39, 231–241. [CrossRef]
2. Saraswat, C.; Mishra, B.K.; Kumar, P. Integrated urban water management scenario modeling for sustainable water governance in Kathmandu Valley, Nepal. *Sustain. Sci.* 2017, 12, 1037–1053. [CrossRef]
3. Chu, H.J.; Liu, C.; Wang, C. Identifying the Relationships Between Water Quality and Land Cover Changes in the Tseng-Wen Reservoir Watershed of Taiwan. *Int. J. Environ. Res. Public Health* 2013, 10, 478–489. [CrossRef]
4. Gardner, K.K.; Vogel, R.M. Predicting Ground Water Nitrate Concentration from Land Use. *Ground Water* 2005, 43, 343–352. [PubMed]
5. Zeilhofer, P.; Lima, E.B.N.R.; Lima, G.A.R. Spatial patterns of water quality in the Cuiaba river basin, Central Brazil. *Environ. Monit. Assess.* 2006, 123, 41–62. [CrossRef] [PubMed]
6. Ding, J.; Jiang, J.; Fu, L.; Liu, Q.; Peng, Q.; Kang, M. Impacts of Land Use on Surface Water Quality in a Subtropical River Basin: A Case Study of the Dongjiang River Basin, Southeastern China. *J. Water* 2015, 7, 4427–4445. [CrossRef]
7. United Nation Sustainable Development Goals. *The 2030 Agenda for Sustainable Development*; A/RES/70/1; United Nation Sustainable Development Goals: New York, NY, USA, 2015; p. 41.
8. Keesstra, S.; Mol, G.; de Leeuw, J.; Okx, J.; de Cleen, M.; Visser, S. Soil-related sustainable development goals: Four concepts to make land degradation neutrality and restoration work. *Land* 2018, 7, 133. [CrossRef]

9. Steyl, G.; Dennis, I. Review of coastal-area aquifers in Africa. *Hydrog. J.* 2010, 18, 217–225. [CrossRef]

10. Anderson, F.; Al-Thani, N. Effect of Sea Level Rise and Groundwater Withdrawal on Seawater Intrusion in the Gulf Coast Aquifer: Implications for Agriculture. *J. Geosci. Environ. Prot.* 2016, 4, 116–124. [CrossRef]

11. Grundmann, J.; Khatri, A.A.; Schütze, N. Managing saltwater intrusion in coastal arid regions and its societal implications for agriculture. *Proc. IAHS* 2016, 373, 31–35. [CrossRef]

12. Puckett, L. *Nonpoint and Point Sources of Nitrogen in Major Watersheds of the United States*; USGS Water Resources Investigations Report 94–4001; United States Geological Survey: Reston, VA, USA, 1994.

13. Pérez-Fernández, M.A.; Calvo-Magro, E.; Valentine, A. Benefits of the symbiotic association of shrubby legumes for the rehabilitation of degraded soils under Mediterranean climatic conditions. *Land Degrad. Dev.* 2016, 27, 395–405. [CrossRef]

14. WHO. *Guidelines for Drinking-Water Quality*, 4th ed.; World Health Organization: Geneva, Switzerland, 2011; p. 563.

15. Bureau of Indian Standards (BIS). *Indian Standard Drinking Water Specification*, 2nd ed.; BIS 10500:2012; Bureau of Indian Standards: New Delhi, India, 2012.

16. Manassaram, D.M.; Backer, L.C.; Messing, R.; Fleming, L.E.; Luke, B.; Monteilh, C.P. Nitrates in drinking water and methemoglobin levels in pregnancy: A longitudinal study. *Environ. Health* 2010, 9, 60. [CrossRef]

17. Alfarrah, N.; Walraevens, K. Groundwater overexploitation and seawater intrusion in coastal areas of arid and semi-arid regions. *Water* 2018, 10, 143. [CrossRef]

18. Kumar, P. Multi isotopic approach to study temporal variation of groundwater quality in coastal aquifer of Saijo Plain, Shikoku Island, Japan. *Water Resour.* 2013, 40, 208–216. [CrossRef]

19. Hua, A.K. Land use land cover changes in detection of water quality: A study based on remote sensing and multivariate statistics. *J. Environ. Public Health* 2017, 2017, 7515130. [CrossRef]

20. Huang, J.; Zhan, J.; Yan, H.; Wu, F.; Deng, X. Evaluation of the impacts of land use on water quality: A case study in the Chaohu Lake Basin. *Sci. J.* 2013, 2013, 329187. [CrossRef]

21. Khan, A.; Khan, H.H.; Umar, R. Impact of land-use on groundwater quality: GIS-based study from an alluvial aquifer in the Western Ganges Basin. *Appl. Water Sci.* 2017, 7, 4593–4603. [CrossRef]

22. Narany, T.S.; Aris, A.Z.; Sefie, A.; Keesstra, S. Detecting and predicting the impact of land use changes on groundwater quality, a case study in Northern Kelantan, Malaysia. *Sci. Total Environ.* 2017, 599–600, 844–853. [CrossRef]

23. Persky, J.H. *The Relation of Ground-Water Quality to Housing Density*; USGS Water Resources Investigation Report 86–4093; USGS: Cape Cod, MA, USA, 1986.

24. Kumar, P.; Kumar, A.; Singh, C.K.; Saraswat, C.; Avtar, R.; Ramanathan, A.L.; Herath, S. Hydrogeochemical Evolution and Appraisal of Groundwater Quality in Panna District, Central India. *Expo. Health* 2016, 8, 19–30. [CrossRef]

25. Sarangi, R.K.; Chauhan, P.; Nayak, S.R. Inter-annual variability of phytoplankton blooms in the northern Arabian Sea during winter monsoon period (February-March) using IRS-P4 OCM data. *Indian J. Mar. Sci.* 2005, 34, 163–173.

26. Kumar, N.; Kumar, P.; Basil, G.; Kumar, R.; Kharrazi, A.; Avtar, R. Chemo-metric analysis for evaluating geochemical processes responsible for spatio-temporal variation of surface water quality at Narmada estuarine region in Gujarat, India. *Appl. Water Sci.* 2015, 5, 261–270. [CrossRef]

27. Central Ground Water Board (CGWB). *District Groundwater Brochure*; CGWB: Anand District, Gujarat, India, 2013; p. 20.

28. Kumar, P.; Kumar, M.; Ramanathan, A.L.; Tsujimura, M. Tracing the factors responsible for arsenic enrichment in groundwater of the middle Gangetic Plain, India: A source identification perspective. *Environ. Geochem. Health* 2010, 32, 129–146. [CrossRef] [PubMed]

29. Yen, S.T.; Liu, S.; Kolpin, D.W. Analysis of nitrate in near-surface aquifers in the Midcontinental United States: An application of the inverse hyperbolic sine Tobit model. *Water Resour. Res.* 1996, 32, 3003–3011. [CrossRef]

© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).