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Linking Groundwater Quality and Quantity: An Assessment of Satellite-Based Groundwater Storage Anomalies from GRACE against Ground Measurements of Contaminants in California

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Abstract: Groundwater comprises a large portion of irrigation for California's agriculture, and sustains a wide diversity of ecosystems as well as consumptive use, but pumping is occurring faster than replenishment. At the same time, contaminants from fertilizers and pesticides are infiltrating into the groundwater, becoming increasingly concentrated as water is extracted. It compared space-based observations of groundwater anomalies from California's San Joaquin Valley using the GRACE (gravity recovery and climate experiment) against measurements of 42 organic and inorganic chemicals from 41,667 wells in the valley from 2003 to 2010. It compared Arsenic, Boron, Cadmium, Chloride, Selenium, Trichloroethylene, and TDS (total dissolved solid) concentrations with the groundwater storage anomaly from 2003 to 2010. The results show strong correlations for groundwater depletion against increasing chloride ($r^2 = 0.78$, $p < 0.05$) and boron ($r^2 = 0.88$, $p < 0.05$). This indicates increasing contaminant concentrations while groundwater was depleting over the last eight years. Solubilization by complexation with Cl, CO_3 and/or organic chelates may account for the increasing concentration of some heavy metals when groundwater depletion occurs. These results are the first to link space-based groundwater mass change with groundwater contaminant concentration change.

Key words: Ground water, environment, San Joaquin Valley, groundwater geochemistry.

1. Introduction

High quality groundwater plays an important role for agricultural and industrial activities in the California's Central Valley, USA. Groundwater comprises nearly half of the water used for municipal supply in California [1] and nearly 2 million people rely on that as a primary source of drinking water and for irrigated agriculture [2]. Moreover, the groundwater in this region has a long history of being adversely affected by point and non-point source pollution such as industrial and municipal waste disposal, animal waste, hazardous spills, and air deposition of particulates, urban and barnyard runoffs, failed septic systems, fertilizers and pesticides. According to U.S. Department of Agriculture (1997) [3] there are 8,000 km^2 (2 million acres) of irrigated cropland in SJHR (San Joaquin Hydrologic Region) and 13,350 km^2 (3.3 million acres) in the TLHR (Tulare Lake Hydrologic Region) [3]. To maximize the productivity of agricultural lands, large amounts of nitrogen and phosphorus fertilizers are applied. Due to regulations, the quality of discharges to the surface and groundwater has continuously improved over the last several decades [4]. The need for such regulation is backed by the importance of groundwater to CA, such as: (a) the volume consumed (35% of total, 60% in dry years), (b) its geographic distribution (found in many areas of the state where

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surface water resources are limited), and (c) the degree to which it is protected from contamination (very difficult or even impossible to remediate once contaminated) [5]. Degradation of water quality due to TDS (total dissolved solids) or chloride threatens the long-term sustainability of a very important water resource for SJV (San Joaquin Valley), since water high in TDS and/or chloride is unusable for either urban drinking water needs or for irrigating crops.

Moreover, water quality and quantity are inherently interdependent [6]. To understand the groundwater quality and the extent of damage to crops and agriculture in the SJV, CA, it needs to understand the groundwater chemistry in the region. Chemical composition varies largely depending on its source, primarily marine deposits on the east and micaceous deposits on the west side of the valley. Recharge originating on the Coast Ranges is rich in sodium-calcium bicarbonate, whereas the Sierra Nevada side of the valley is largely sodium sulfate rich [7]. According to Toth [8], the chemistry of the groundwater and soils of the SJV is dictated by the regional groundwater flow patterns. In his conceptual model, Toth [8] considers the groundwater's role as a geologic agent including interaction between the water and its surrounding environment and systematic and hierarchical flow paths. It is an appropriate basis for understanding the evolution of groundwater chemistry from areas of recharge to areas of discharge [8, 9]. The SJV's deep groundwater system supplies 30% of the salt load to the San Joaquin River. In arid regions like SJV, less water percolates through the soil profile than the humid regions. Over time, relatively soluble minerals- calcium carbonates, sulfates, and other salts accumulate in the lower part of the soil profile at the depth where percolating water evaporates. Thus, the buildup occurs because rainfall is not sufficient to flush these dissolved materials through the soil. In the western SJV, the bedrock source for the alluvial parent material is the marine sediments of the Coast Ranges. As a result, the natural salinity of the soil is high, and also soils in this area are particularly high in selenium-bearing minerals [10].

The GRACE (gravity recovery and climate experiment) satellite mission detects time variations of the Earth's gravity field over a few 100 km above earth's surface 10-day per month [11]. According to Tapley, Wahr et al. [11-13], water storage volume have changed in continental hydrology since 2003, when GRACE data has revealed signals [12, 14]. GRACE depends on the interaction of two twin satellites producing some of the most accurate data on the planet's gravitational variations [15]. When they fly over areas of bigger and smaller gravity, they move slightly toward and away from each other. Gravity variation caused by surface and subsurface water such as snow, glaciers, soil moisture, and deep aquifers [16]. A device aboard each spacecraft measures variation in their relative speed very accurately, and scientists interpret this data into maps of the Earth's gravitational field. The obtained information including soil moisture, snow water, surface, and groundwater storage anomalies reveal the total water storage [16]. Prior to GRACE it was very difficult to estimate how the total volume of groundwater is changing over large areas. At the same time, the surface sampling techniques are too limited in accuracy and frequency to provide good estimates. Indeed, through GRACE, it recognized the magnitude and the trends in groundwater changes and to measure other parameters such as evaporation [17].

GRACE data show aquifers under the California's agriculturally productive Central Valley were drawn down by 25 million acre-feet (the water tables have been lowering at the rate of 2 cm/year) from October 2003 to March 2010 and the problem is most severe in the southern region around the city of Tulare [15].

The intention of this collaborative research study is to evaluate the linkage between space-based groundwater storage change using the GRACE and ground-based well measurements of groundwater quality from the GAMA (groundwater ambient monitoring & assessment). Potential for monitoring large scale changes in groundwater quality using GRACE motivates the implications of this work. That is to say this study is the first to link space-based groundwater quantity with groundwater quality.

2. Methods and Data

2.1 Study Area

The Central Valley is located in the middle of CA, USA with an average elevation of 122 m; the annual precipitation of approximately 250 mm; and with the size of about 108,779 km^2 (42,000 square miles) [18]. It consist of two connected valleys including (1) the Sacramento with Mediterranean climate, with warm, dry summers and cool, wet winters and (2) the SJV with much hotter and drier, approaching a desert climate [18]. The late spring and summer months are the driest, each with monthly rainfall below 10 mm [5]. Flay [7] states high evapotranspiration rates necessitate large irrigation rates and subsequent declines in groundwater over time [7]. Yet, the most important trade and industry activity of the area is farming. The principal crops are grapes, raisin, cotton, garlic, potato, and wheat. Consequently this area is prone to groundwater depletion problem. Historical records show that since 1925 over pumping of ground water subside an average of more than 3 m with a max of 9 m [19] (Fig. 1).

The groundwater pumping in Santa Clara, CA shown in green, increased significantly from 1915 through 1960. As expected, the increase in pumping caused reduced groundwater levels. It also had the unanticipated effect of dropping the land surface by subsidence (shown in brown), until water was imported beginning in 1963 to recharge the groundwater. As a result, the subsidence nearly was stopped by recharging water and reduced groundwater pumping.

The GRACE study area is 52,000 km^2 for the Central Valley. It is surrounded on all sides by mountain ranges including Coast Range, to the west, and the Sierra Nevada range to the east. The first part of this study is focused on the San Joaquin and Tulare Basins, which make up most of the southern two-thirds of the Central Valley.

GRACE has the potential for the estimation of groundwater storage anomalies [20] so that the regional-scale groundwater storage changes in SJV were estimated from monthly GRACE TWSC (total water storage capacity) data and *in situ* soil moisture measurements for 36 consecutive months during 2003-2010. To calculate the GWSA (groundwater storage anomaly), the mask (1° × 1°) with the coordinates of longitude: -179.5 to 179.5 and latitude: -89.5° to 89.5° was selected. The GRACE zone coordinates covers latitudes 36° to 43° N and longitudes 118° to 122° W for three basins: Sacramento, San Joaquin, and Tulare basins. The scaling factor for the processing of GRACE data is 2.35 [21]. The map shows four study areas, the distribution of grid cells used for well selection, and grid well sampled in the San Joaquin [22].

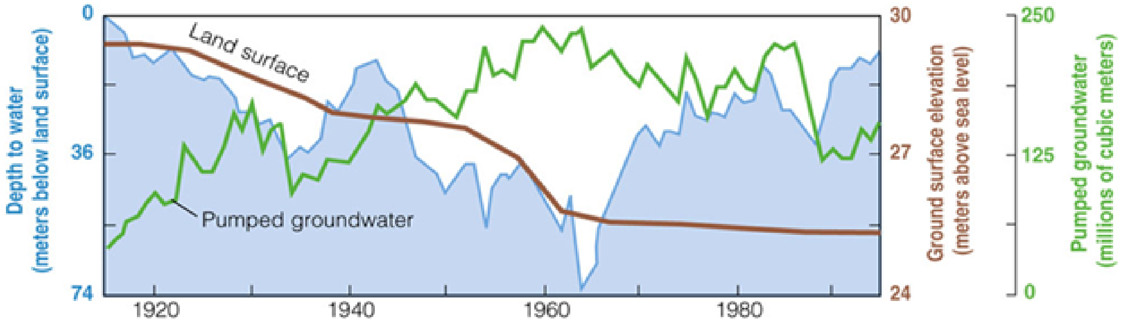

Fig. 1 The history of groundwater pumping in Santa Clara, CA. Around 1940 the ground subsidence slowed briefly due to a recharge program. According to the diagram fastest subsidence and groundwater pumping occurred in 1960. Reduction in pumping and in recharge raised water levels and nearly stopped subsidence (modified after Hyndman & Hyndman, 2007 [19]).

The filtering process, spectral truncation and spatial smoothing reduce the error in the GRACE measurements, but this comes at the price of also reducing actual geophysical signal amplitudes [23]. As discussed in their model, signal attenuation in the Sacramento-San Joaquin basin is relatively strong, due to both the small basins size, the proximity to a land-ocean boundary, and the prevailing north-south orientation of the basin. To restore damped signal amplitudes, a gain factor is applied to the filtered and smoothed basin-mean water storage. GRACE measures terrestrial water storage without respect to form (ice, snow or liquid) or position relative to the surface (surface, soil or groundwater) [17].

The TWS (total water storage) in this region is the sum of all these sub-components (Eq. (1)):

$$\Delta \mathit{TWS} = \Delta \text{SoilM} + \Delta \mathit{SWE} + \Delta \text{RES} + \Delta \mathit{GW} + n \quad (1)$$

where, SoilM (soil moisture), SWE (snow-water-equivalent), and RES (reservoir) storage are either obtained from model simulations (soil moisture), or observed estimates (SWE and RES). GW (groundwater) storage changes can then be estimated as a residual from the other storage quantities, with an additional uncertainty n that arises from possible biases and uncertainties in the models or observations, or non-hydrological physical process that are not taken into account (such processes, e.g., solid Earth changes, are not expected to give rise to sizable signal amplitudes over the Sacramento-San Joaquin basin, but can have larger effect in other regions).

Groundwater storage is estimated by subtracting the observed or forward-modeled components of soil moisture, snow-water-equivalent and reservoir storage from the total GRACE TWS. Assuming uncorrelated errors in each of these sub-components, the uncertainty of a monthly groundwater anomaly is approximately ± 48.2 mm-H_2O [23].

From April-2006 through March-2010, the groundwater storage in Central Valley, CA decreased by 39 ± 12 mm/yr (averaged over the combined Sacramento-San Joaquin basin), equivalent to a cumulative mass loss of approximately 27 ± 8.3 km^3 for this time period. The trend values are estimated with a seasonal Kendall-Mann test, accounting for auto-correlation, and are similar to within uncertainties to previously published values [20].

The distribution of the wells in the study area is laid out by DWR (department of water resources) in each hydrogeological basin. The well grid basins are semi quantitatively reprehensive for the entire GRACE area for SJV. The well distribution is uniform in the hydrogeological basin in study region. However, according to Henry et al. [24] for a quantitative and unbiased analysis the monthly field data needed to be converted from raster to polygons using GIS (geographic information system) ArcView, clipped to the study region, and re-converted to raster in Arc-GIS [24]. This will minimize the influence of TWS (total water storage) changes outside the region on the study area. The means of the clipped raster thus will represent a spatial average of TWS change during the course of that month in the study region [24].

According to SWRCB (State Water Resources Board), the targeted groundwater wells, which were selected for groundwater quality data in SJV including:

(a) shallow wells such as monitoring wells at regulated cleanup sites, or private domestic wells usually < 20 ft deep;

(b) intermediate wells, which are deeper than shallow wells, and typically tap deeper aquifers, such as water supply wells;

(c) deep wells as typically 100s to 1,000 s of ft deep, which could pump large volumes of water from deeper aquifers such as water supply wells used for public supply purposes [22].

To access the data, first basin # 5-22 from Tulare Lake Hydrologic Region Map was selected (Fig. 2). This basin is divided into seven sub-basins. The 42,031 wells were matched for chemical data search investigation. The groundwater quality data then were sorted and narrowed down based on their time of sampling (from October 2003 to March 2010). The

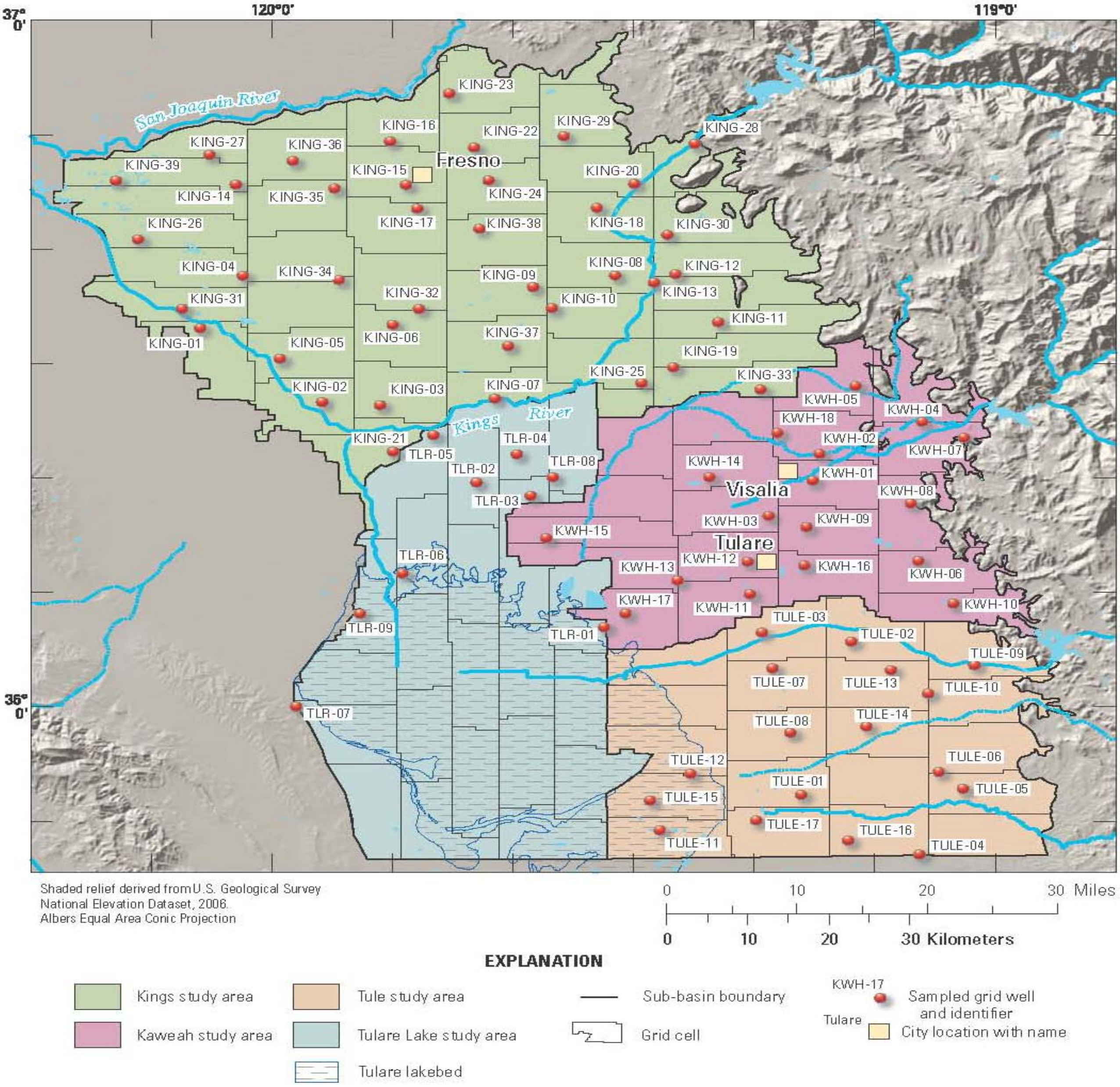

Fig. 2 Distribution of wells in Groundwater Basins of the SJV (San Joaquin Valley) as defined by Department of Water and Power (SWRCB). Source: http://www.swrcb.ca.gov/gama/report_depot.shtml [22].

data (mean value of month/well) were correlated with GRACE data. Table 1 lists the sub-basins selected in this study along with the number of wells and surface area covered.

3. Results

The GAMA groundwater samples taken between 2003 and 2010 in all of the wells of study area showed a pH range of 7.9-10.5 with average pH of 8.2; the EC (electric conductivity) ranged from 1,610-460,000 µmhos/cm and average of 5,047 µmhos/cm; and HCO_3^- ranges between 680-5,600 mg/L and average of 745 mg/L (Table 2). Furthermore, drinking water pH and EC ranges from 6.5-7.5 and 0.005-0.05 dS/m respectively.

The results indicated that all samples had the high concentration of NO_3^- (above the recommended guidelines of the World Health Organization WHO; 50 mg/L; WHO, 2003). Moreover, the maximum and

Table 1 List of all groundwater sub basins in San Joaquin Valley (SJV). (GW SBN = Groundwater Sub-Basin Number) (Source: modified after CDWRB-GAMA data [22]).

Sub-Basin	GW SBN	# of wells	Surface area km^2	Sub-Basin	GW SBN	# of wells	Surface area km^2
5-22.02	Modesto	4,540	993	5-22.10	Pleasant Valley	639	585
5-22.03	Turlock	5,031	1,398	5-22.11	Kaveah	6860	1,795
5-22.04	Merced	5,056	1,978	5-22.12	Tular Lake	2461	2,110
5-22.05	Chowchilla	2,216	639	5-22.13	Tule	4636	1,891
5-22.06	Madera	2,216	1,584	5-22.14	Kern	18,604	7,843
5-22.07	Mendosa	8,991	3,018	5-22.15	Tracy	6,171	1,390
5-22.08	Kings	13,761	3,947	5-22.16	Cosumnes	1,336	1,132
5-22.09	west side	7,987	2,580		Total	90,511	32,889

Table 2 Range and mean chemical compositions and standard deviation in the eight sub-types of groundwater samples (Source: modified from GAMA data [22]).

		2003	2004	2005	2006	2007	2008	2009	2010
pH	Min	NA	8.1	7.91	7.91	7.91	8	8	7.95
	Max	NA	8.1	10.5	9.7	9.31	8.9	9.2	9.31
	Mean	NA	8.1	8.3	8.2	8.2	8.3	8.4	8.5
	SD	NA	0	0.6	0.3	0.3	0.3	0.4	0.4
# of wells		N/A	1	62	73	34	16	18	13
EC µmhos/cm	Min	1,640	1,670	1610	1610	1610	1610	1610	1,610
	Max	4,340	14,000	29,000	16,000	52,000	460,000	45,000	38,000
	Mean	2,395	3,958	3,246	3,984	6029	10,699	5,702	4,363
	SD	754	3,898	3,212	2,972	7,715	45,909	7,505	5,489
# of wells		11	32	130	159	124	181	169	146
HCO_3^- mg/l	Min	333	340	336	333	335	340	333	334
	Max	680	1,400	1,200	1,500	5,500	5600	5,500	5,000
	Mean	439	471	488	519	985	988	1,262	973
	SD	93	152	159	225	1,249	1,187	1,464	1,151
# of wells		32	89	209	155	168	154	88	133

NA = not applicable.

minimum concentrations ranged from 63.59 mg/L to 1,519.07 mg/L during the 7 years sampling period.

GRACE groundwater storage anomalies show continuously negative trend and this trend is evident from 2005 to 2010. It was found strong correlations with groundwater depletion against increasing chloride ($r^2 = 0.78$) and boron ($r^2 = 0.88$), but no relationship with benzene ($r^2 = 0.03$).

According to WHO [25], chloride concentrations > 250 mg/L can give rise to noticeable taste in water, but the threshold depends upon the associated cations. Based on WHO factsheet chloride increases the electrical conductivity of water and thus increases its corrosivity [25]. In the same way, in metal pipes, chloride reacts with metal ions to form soluble salts, thus increasing levels of metals in drinking-water [25]. Our results showed that the chloride concentration decreased from 2008 to 2010 but still far above the concentration limit.

In addition, TDS (total dissolved solids) ranged from 50 mg/L to 10,000 mg/L. TDS and chloride constitute a problem in groundwater in SJV as well. The values obtained from GAMA for these parameters were generally above WHO (2003) guidelines for drinking water (1,000 mg/L, 250 mg/L, respectively).

VC (vinyl chloride) showed also an increase in concentration from 2004 to 2010. Additionally, solvents such VC are used for a number of purposes, including manufacturing and cleaning. In the SJV study area, solvents were detected at high concentrations in less than 1% of the primary aquifers, at moderate concentrations in about 2%. For this reason, VC in the study area is above the MCL (maximum contamination limit) of 0.5 µg/L.

According to ATSDR (Agency for Toxic Substances and Disease Registry) (www.atsdr.cdc.gov) Naphthalene (NAPHT) enters the environment from industrial uses, from the burning of wood, and from accidental spills. Additionally, NAPHT at hazardous waste sites and landfills can dissolve in water. NAPHT can become weakly attached to soil or pass through the soil into groundwater [26]. NAPHT values in some monitoring wells showed up to 700 times more concentration than MCL = 17 μg/L as well.

Selenium concentration also varies in different region of SJV. According to Velicogna and Wahr [21] the data showed selenium concentration from 63 μg/L to 384 μg/L. The average concentration from 2003 to 2010 was 149 μg/L. The recorded values for selenium were overall above WHO (2003) guidelines MCL for drinking water 50 μg/L.

A list of all tested wells is shown in the Table 2. The Hydrologic basin 5-22.10 (Pleasant Valley) has the most contaminated with 50% results of chemicals above the contamination limit. Tracy showed the highest percentage among the hydrologic basin in SJV with 13% of the all wells sampled above MCL. Following Tracy (5-22.15), Chowchilla (5-22.05), and Mendosa (5-22.07) showed higher percentage of wells with above MCL. Fig.3 shows different chemicals (including trace metals and anions) with different concentrations from 2003 to 2010.

According to USGS, arsenic and boron were the trace elements that most frequently occurred at high concentrations in SJV [27]. The GAMA data showed the annual min and max arsenic level 24 μg/L to 107 μg/L, which for all years exceeded the MCL of 10 μg/L. Overall, the arsenic concentration decreased but fluctuates in drought and wet periods. This is associated with basin-filled deposits of alluvial-lacustrine origin particularly in arid and semi arid regions and also with areas of sedimentary rocks derived from volcanic areas in Sierra Nevada and gold and mining districts. Additionally, irrigation in some areas has liberated arsenic to the extent that concentration of up to 1 mg/L was found in shallow groundwater beneath irrigated field.

Boron also was detected in high concentration in groundwater between 2003 and 2010. In fact, boron concentrations in groundwater are derived from leaching of rocks and soils that contain borate and borosilicate minerals in SE region of study area. According to Ref. [27], boron was detected at high concentrations in about 13% of the primary aquifers, and in moderate concentrations in about 25% in this region. The GAMA data showed the annual minimum and maximum level for boron from 1.6 mg/L to 24.7 mg/L, which for all years is exceeded the MCL of 1 mg/L.

The trichloroethylene (TCE) level also ranged from 24 μg/L to 104 μg/L exceeding the MCL (5 μg/L). According to EPA [28], TCE is a colorless liquid, which is used as a solvent for cleaning metal parts. Based on EPA factsheet drinking or breathing high levels of TCE may cause nervous system effects, liver and lung damage, abnormal heartbeat, coma, and possibly death [29]. Besides, the possible source for TCE is point source pollution as a result of the fabricating, employing, and discarding of the chemicals [28]. TCE results show that in SJV the annual concentration have been higher in 2005, 2006 and 2007 (drought period) and slightly lower in 2003, 2004, 2009 and 2010 (non drought period).

Similarly, we compared arsenic, boron, cadmium, chloride, selenium, TDS and organic substances such TCE concentrations with the groundwater storage anomaly from 2003 to 2010. There was a statistically significant ($p < 0.05$) increase in chloride and boron against depleting groundwater (Fig. 4). Moreover, salinity concentration is also increasing with decreasing groundwater, primarily from saline surface (residual irrigation) conditions. For this reason, this saline water can percolate into the underlying groundwater. If the groundwater is later pumped and used for additional irrigation, the evaporation cycle is repeated and salinity levels will continue to increase.

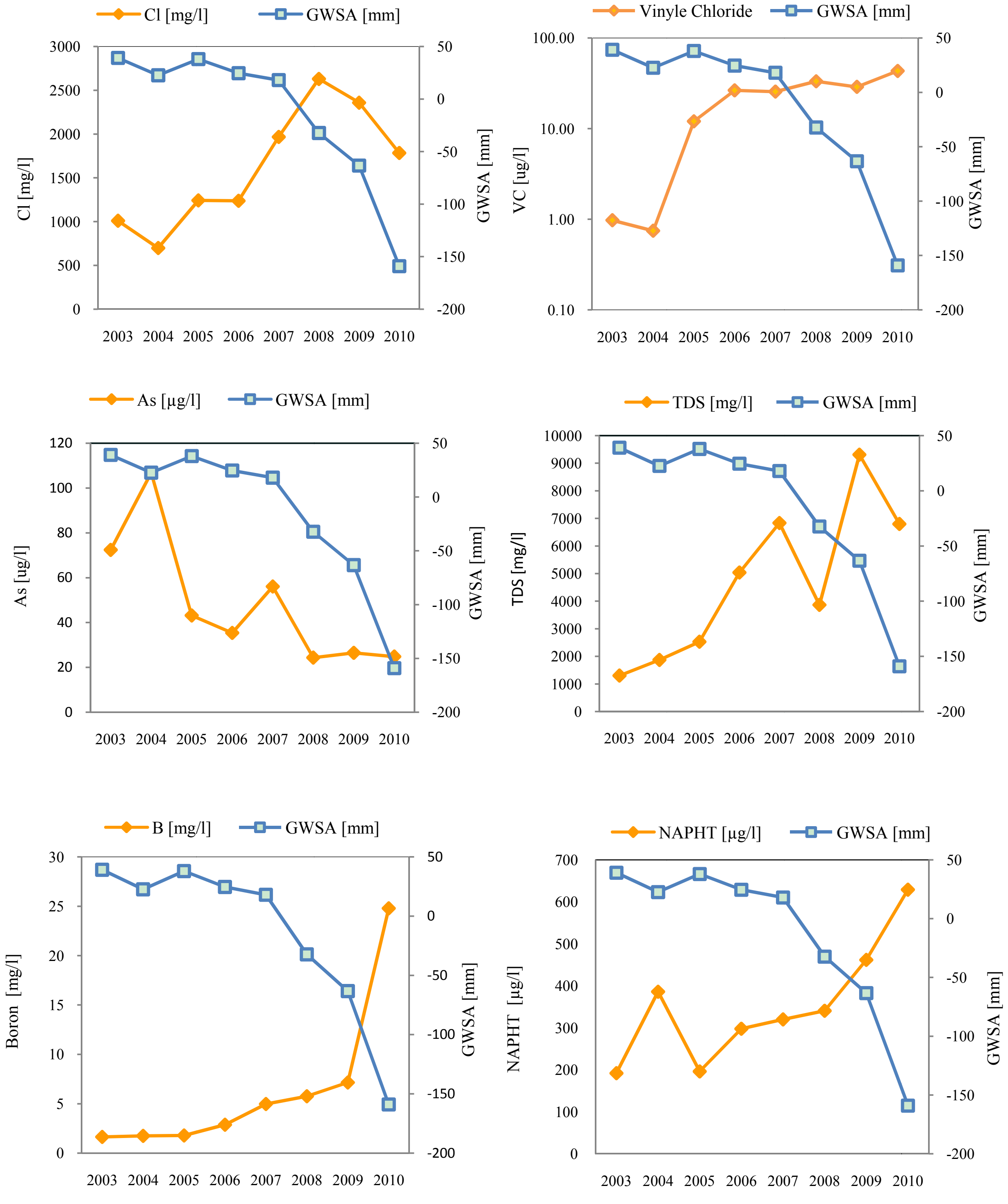

Fig. 3 Concentration of organic and inorganic chemicals vs. groundwater storage anomaly (GWSA). Graphs show the concentration of arsenic, total dissolved solid (TDS), boron, naphthalene, chloride, and vinyl chloride versus Ground Water Storage Anomalies (GWSA) [mm] in SJV groundwater from 2003-2010.

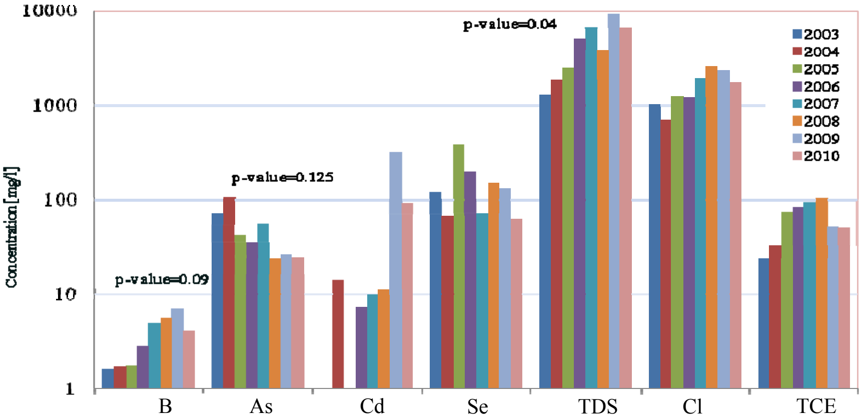

Fig. 4 The concentration of arsenic, boron, cadmium, chloride, selenium, trichloroethylene (TCE), and total dissolved solids (TDS) in different years from 2003 to 2010.

According EPA's estimate, approximately 10% of the soils in the Central Valley have been damaged by buildup of salt. When groundwater lowers by over pumping, the effluent river (losing stream) can add water to aquifer leaching the salt. According to EPA [29] the salinity MCL is 500 mg/L. These results show much higher salinity valued than MCL.

4. Discussion

High concentrations of boron are often related with salty soils in semiarid and/or arid climates with irrigated agriculture [30]. In addition, excess boron often occurs in connection with moderate to high salinity [31]. Knowing that the soil solution of saline soils is composed of a range of dissolved salts, such as NaCl, Na_2SO_4, $MgSO_4$, $CaSO_4$, $MgCl_2$, KCl and Na_2CO_3, each of which contribute to salinity stress [32], but according to Rengasamy and Munze [33, 34], NaCl is the most prevalent salt and has been the focus of much of the work on salinity to date. In order to address the salinity issue in SJV and its relationship with water quality, we emphasize our discussion on boron and chloride in general.

In fact, the salinity problem is not well understood by the authorities in CA. Furthermore in areas where groundwater is pumped heavily from deep aquifers, the water pressures in aquifers will decline significantly. If the declines are sufficiently high, these aquifers will cease to push water up toward the land surface in discharge areas. Instead, contaminated water containing organic and inorganic substances will be drawn down towards the deeper aquifer, impairing chemical quality at depth. Irrigation of arid soil in SJV causes salt to be dissolved and carried to the lower horizons at higher rate that would occur under natural conditions. As water molecules evaporate into the atmosphere, salts remain behind in the irrigation water. In many areas including western SJV, problems occur because of presence of clay layers in alluvial parent material. The clay layers form a barrier to percolating water, causing salt rich irrigation water to build up near the surface (Fig. 5).

A biotechnological investigation reveals the combined effects of boron and salinity on growth and yield of some melon plants [35]; for instance the research results indicate that increasing the water salinity decreased the sensitivity of both grafted and non-grafted plant types and increased boron concentration in leaf [35].

According to Mortensen et al. and Howard et al. [36, 37] dissolution of soil organic matter occurs in the presence of excess salts and this is believed to be a common cause of mobilization of sediment-bound heavy metals in estuaries with chloride concentrations of ≥ 200 mg/L [38]. Besides, this has been attributed to oxidation in the presence of microorganisms and complexation of the released metals with chloride or ligands from the decomposing organic matter [39].

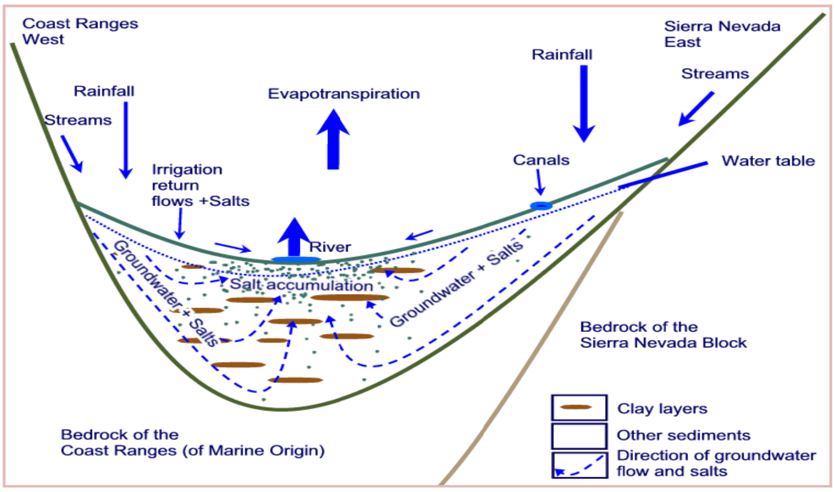

Fig. 5 The Aquifer System of the San Joaquin Valley (not to scale/modified after Flay, 1999 [7]). The arrows show the movement of water as well as salts.

Therefore, chelation with partially decomposed organic matter is probably a major factor contributing to the heavy metals mobility [37].

From a biotechnological perspective, the excess of salts in the soil (such as Na^+ and other ions) taken up by roots are transported to shoots in the transpiration stream (where they accumulate over time) posing an additional challenge to the plant as a barrier for water uptake [40].

Along with, salinity stress limits the productivity of agricultural crops worldwide. As a result, it has been estimated that almost 80 million hectares of arable lands worldwide is currently affected by salinity [32]. In the same way, salt can lessen plant growth by the osmosis cause [41], therefore high salt concentration increases the forces that hold water in the soil and this condition requires plant roots to expend more energy to extract the water [42]. Especially during the dry period, salt in soil solution may become concentrated enough to kill plants by pulling water from them. That is salt moves in water to the soil surface, where they accumulate, sometimes becoming visible as powdery, white salt crusts [43].

Furthermore, three other probable mechanisms for solubilization of metals to be: (in order of decreasing importance): (1) complexation with chloride derived from evapotranspiration; (2) complexation with CO_3 resulting from carbonate dissolution and TDS; (3) high concentration as a result of weathering bedrock (Fig. 6).

Similarly, the high HCO_3^- concentration is most likely formed from carbonate weathering [44]. According to Jalali [44], as a result the excess bicarbonate ions cause the release of the alkali ions (usually Na^+) into the solution by the exchange reactions. He furthermore emphasizes the roll of a) dissolution of dolomite, calcite, and gypsum and b) the evapotranspiration of infiltrating rainwater, causing an increase in the concentrations of Ca^{2+}, Mg^{2+} and HCO_3^- [44] (Fig. 7). Increasing salinity in soil, as a result of irrigation of arid soil in SJV, causes salt to be dissolved and carried to the lower soil horizons at higher rate. The Corcoran clay layer forms a barrier to percolating water, causing salt rich irrigation water to build up near the surface and may cause the increasing of concentrations of metals in water. Another source would be direct anthropogenic source of pollution. According to Taylor [45], a great quantity of chemicals is applied to the farming soils as fertilizers and pesticides annually and such applications may result in the increase of heavy metals particularly cadmium, lead, and arsenic [45].

Taylor and Percival [45] further stated that application of fertilizer reduces soil solution pH and

Fig. 6 Schematic view of geochemical process of heavy metals mobilization in soil. The process shows the effect of salt on mobilization of metals in soil and eventually groundwater contamination.

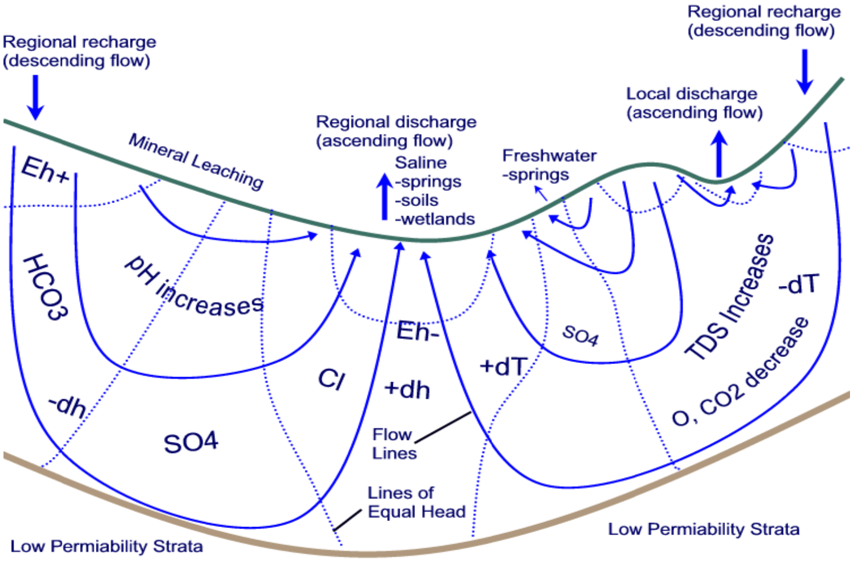

Fig. 7 Effects of Flow on Groundwater Chemistry in a Conceptualized Unconfined Basin. The chemistry of the groundwater and soils of the SJV is dictated by the regional groundwater flow patterns (After Toth and Winter [8, 9]).

increases the heavy metals concentration in soil solution; thus these metals can accumulate in the soil, be taken up by plants, and passed on in the food chain to animals and humans [45]. And this is caused by excessive accumulation of Cl$^-$ and Na$^+$ in the leaves, including exclusion of Cl$^-$ and/or reduction of Cl$^-$ absorption by the roots, and the replacement or substitution of total K$^+$ by total Na$^+$ in the foliar parts [35].

Furthermore, Bar-Tal et al. [46] showed also that irrigation water with high salinity can leach native and applied K$^+$ from the soil [46]. In fact, Jalali [44] reported losses equivalent of 63-170 kg·K·ha^{-1} (12%-33% of the initial exchangeable K$^+$) when 196 mm of solution containing 2-30 meq·L^{-1} CaCl$_2$ were applied to soil column in the laboratory [44, 47]. Additionally, this clearly supports the fact that increasing salinity promotes metal desorption from the sediment, which domino effect in increased cadmium concentrations in the water and as a consequence cadmium will get into the food chain. It yet also promotes the formation of chloride complexes (e.g. CdCl complexes) in the water column, which seem to be less bio-available, especially at higher salinities.

Arsenic is assumed to be present in certain sulfide minerals (pyrites) that are deposited within the aquifer sediments [48, 49]. Fazal et al. [48, 49] stated that due to the lowering of water table in dry seasons, arsenopyrite oxidized in the vadose zone releases arsenic, which is adsorbed on iron hydroxide and in wet seasons during the subsequence recharge period, iron hydroxide releases arsenic into groundwater. According to this hypothesis, the origin of arsenic rich groundwater is partially anthropogenic caused by extensive irrigation and/or naturally occurring event by the change of wet/dry period. The latter is a frequent phenomenon in CA. According to GRACE (gravity recovery and climate experiment) data, the intensive irrigation in SJV in dry season may help to lower groundwater table supporting the above hypothesis. Furthermore, another interesting observation of annual

GRACE data and the mean arsenic concentration reveals the fact that the change of arsenic concentration somehow correlates with the drought cycle. For instance 2007 arsenic data (pre-drought) shows much higher value than 2008 to 2010. According to Famiglietti [50], the state-wide drought from 2008 to 2010 led to a significant groundwater decline that totaled about 27 km^3 of water loss over the Central Valley aquifer [50]. The drought period ended in 2010, and the total terrestrial water storage has subsequently rebounded to predrought values so does the arsenic values.

Primary sources of TDS in SJV groundwater are residual and industrial runoffs, discharges from sewage, fertilizers, and soil erosion. Yet, irrigation water is often applied to crops during the summer when evaporation rates are highest. In fact, TDS including chloride could be increased by irrigation. Degradation of water quality due to TDS or chloride contamination threatens the long-term sustainability of a very important water resource for SJV, CA, since water with high TDS and/or chloride contaminant is neither usable for drinking nor for irrigating crops. Therefore, damage to the aquifer system could be irreversible. The saline water intrusion problem is not well understood by the SJV water authority [51]. Therefore, further studies and monitoring methods are necessary to ensure the problem is addressed and monitored adequately. Authors suggest the isotope dating (using the oxygen isotope ratio) of the groundwater and saline water could determine the source of salt water intrusion. Besides, we also believe that the saltwater may have been laterally leaking from an ancient saline aquifer.

Hydrochemical facies including interactions between groundwater and host rocks and groundwater and soil are the main hydrochemical processes controlling chemical characteristics of groundwater in the arid and semi arid regions [44, 47]. The most important parameters used in identifying the groundwater type including major cation and anion concentrations, TDS, and cation and anion ratios [44, 47].

Therefore, the Na-Cl relationship and their parallel enrichment in the soil can be used as an indicator for identifying the mechanism to track salinity and saline intrusions in semi-arid regions [44, 47].

In authors' study area this is evident by a high correlation ($r = 0.92$) between Na^+ and Cl^- and a high correlation ($r = 0.97$) between Na^+ and SO_4, signifying that Na^+ mostly a product from dissolution of sodium chloride and sulfate minerals.

The common groundwater pollution in the region is NO_3^- [18]. Furthermore, concentrations of NO_3^- are the result of different pollution processes, sewage effluents, industrial wastes, and agricultural flows [44, 52, 53]. Other sources of NO_3^- can be derived from fertilizers, wastewater irrigation and breakdown of remnants of the growing crops [54]. Yet, the high concentration of NO_3^- in SJV region could be as a result of urbanization, wastewater outflow from industrial and agricultural practices. Moreover, the intensive use of NO_3^- fertilizers in the study area may contributes to the increase of the concentration of NO_3^- in groundwater.

Lastly, the present-day groundwater salinity is spatially correlated with natural soil salinity in SJV [55]. Additionally, the salinity and selenium concentration in shallow groundwater of the western SJV, CA is a function of the geomorphology and hydrology of the alluvial fans [55]. Deverel, and Gallanthine [55] described two levels of salinity and selenium concentrations in shallow ground water of SJV: (1) The highest salinity and selenium concentrations in shallow groundwater, which occur in alluvium deposited by ephemeral streams and at the margins of the major alluvial fans consisting of naturally saline, fine-grained soils and (2) The low-to-moderate salinity and selenium concentrations in shallow groundwater, which are associated with upper and middle areas of the major alluvial fans deposited by intermittent streams [55]. In the same way, the isotopic data indicate that the highest salinity and selenium concentrations in groundwater present at low altitudes resulted from evaporative concentration when the water table was shallow [55].

Progress has been made to allow the determination of boron isotopes, O and N isotopes in nitrates, O isotopes in phosphates, and S and O isotopes in sulfates [56]. Further work is required to ensure that the techniques are robust enough to produce data of sufficient precision accuracy. In other word, using the latter techniques we will be able to discriminate between different sources of anthropogenic contamination into ground and surface water systems using N, O, and S isotopes [56].

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