

Reservoir sediments: a sink or source of chemicals at the surface water-groundwater interface

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Received: 23 May 2014 / Accepted: 12 August 2015 / Published online: 21 August 2015
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Abstract This study delineates the physical, chemical, and biological effects resulting from anthropogenic and endogenic activities in a sensitive dammed reservoir situated in a semi-arid region. The reservoir is characterized by two major flow regimes: a wet fill hydrologic regime and a dry spill one. A seasonal sampling campaign was carried out over a period of 2 years (2011–2013) where water samples were collected across the water column and from piezometers just outside the

perimeter of the reservoir. Similarly, sediments were collected from the corresponding areas beneath the water column. The water samples were analyzed for environmental isotopic ratios, elemental composition, and physical, biological and chemical parameters, whereas the sediment and algal samples were subjected to physical, mineralogical, spectroscopic, and microscopic analyses. This investigation indicated that the dam had resulted in the alteration of the biogeochemical cycle of nutrients as well as the degradation of the sediment and water quality. The hydrological and biogeochemical processes were found to induce vertical downward transport of chemicals towards the fine grained calcareous sediments during the fill mode, whereas the sediments acted as a source of a chemical flux upward through the water column and downward towards the groundwater during the spill mode. The geomorphological characteristics of the reservoir enhanced the strong hydrological connectivity between the surface water and the groundwater where the reservoir responded quickly to natural and anthropogenic changes in the upper watershed. The water and sediments in the sensitive spill mode were of poor quality and should receive more attention due to the potential hazard for the associated hydro-project and the sustainability of the agricultural soil in the long term. Thus, a safe water and sediment management plan should be implemented in order to improve the dam functionality and to safeguard the precious water resources.

Electronic supplementary material The online version of this article (doi:10.1007/s10661-015-4791-0) contains supplementary material, which is available to authorized users.

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Keywords Reservoir, Sediments, Surface water,
Ground water, Hydrological connectivity

Introduction

Dams are major tools for water management where they are used for irrigation and hydropower production. They also contribute significantly to the industrial activity and socio-economic development (Wei et al. 2009; Delsontro et al. 2010; Wildi 2010). However, the environmental cost of dam constructions manifests in the modification of the hydrological regime, alteration of the biogeochemical cycles, and degradation of both sediment and groundwater quality. The degradation results from the accumulation of chemical contaminants in the sediments and the potential leaching of the contaminants to groundwater due to the long residence time of water (Wei et al. 2009; Wildi 2010, Akin et al. 2010; Mikac et al. 2011; Kraus et al. 2011; Yang et al. 2012). Reservoirs are considered as a transitional zone between rivers and lakes. They reveal complex hydrodynamics and shorter water residence times as compared to lakes (Wall et al. 2005). They also have higher water temperature as compared to rivers, which could result in a decrease in the level of dissolved oxygen, thus reducing the rate of decomposition of pollutants and potentially enhancing the hazard of these pollutants in the aquatic system (Wei et al. 2009). The increase in the concentration of nutrients in reservoirs during flushing events could induce high primary production leading to reservoir eutrophication. As a consequence, the nutrient biogeochemical cycle will be altered (He et al. 2008; Wildi 2010, Yuan et al. 2011).

The fate of chemicals in lacustrine systems is dependent on their transport mechanism, solute mixing, and redox environment (Peretyazhko et al. 2005). Despite the fact that some chemicals, mainly metals, are essential for growth, they are able to denature cell proteins, therefore increasing their hazards for living organisms (Balkis et al. 2010). However, binding of these metals with organic matter and minerals, mainly clay, can minimize their toxicity (Gadd and Griffiths 1978). Blais and Kalff (1993) classified the reactions being able to remove elements from aquatic systems into two categories, adsorption reactions (cation/ligand exchange) and precipitation reaction (with oxides and carbonates). Korfali and Davies (2004) reported that limestone lining had the capacity of buffering pollutant concentrations in aquatic systems. Heavy metals could partition between dissolved phases in the water column and solid phases in the suspended matter and entrapped in the sediments (Korfali and Davies 2004). Delfino (1976) described

the lack of attention to sediments in environmental studies and their impact on aquatic systems in the past as out of sight-out of mind (Delfino 1976). However, researchers have recently intensified their efforts to develop innovative approaches to understand the implications of sediment contamination. Sediments reflect the varied land use of the watershed and act as historical archives of land-use alteration and geomorphological changes (Miller et al. 2003; Tuna et al. 2007; Balogh et al. 2010; Mikac et al. 2011). Thus, in order to trace contaminants and their fate in the aquatic environment, scientists rely on sediments as a tool to document their chemical behavior under different aquatic conditions (Duman et al. 2007; Alaoui et al. 2010; Yuan et al. 2011).

Sediments represent a potential reservoir for contaminants brought in by rivers, surface runoff, and atmospheric deposition (Callender and Rice 2000, Roussiez et al. 2006). Thus, lake bottom-sediments act as sink for contaminants derived from the upper watershed in the form of suspended matter (Skoulikidis et al. 2008; Hiller et al. 2010; Akin et al. 2010). Nutrient retention and metal adsorption to sediments are controlled by various factors such as pH, temperature, redox state, sediment texture, and organic matter content. Any change in these factors could release the sorbed chemicals to the water system (Hiller et al. 2010). The physiochemical properties of the water column and sediments in addition to the metrological and hydrodynamic particularities of the watershed may cause the sediment to be resuspended and act as a source of contaminants, thus impacting the overlying water quality (Miao et al. 2006; Atkinson et al. 2007; Chon et al. 2012). In other words, the geochemical interaction at the sediment-water interface may trap chemicals in the sediments, or it could also release them upward to the overlying water column or downward ultimately to the groundwater (Wildi 2010; Kraus et al. 2011; Banks et al. 2012).

The hydrological settings of the Qaraaoun reservoir in a sensitive semi-arid watershed provide a particular example of sediment behavior under different environmental conditions. This study aims to identify the sediment behavior in the reservoir and the fate of various contaminants in an oxic/anoxic hypolimnion altered by different hydrological regimes. Moreover, it will assess the impact of the sediments at the water-sediment interface on the overlying water column and the ground water quality. The objectives of this work were to understand the sediment behavior in the reservoir under

various hydrodynamic regimes, to investigate the biogeochemical processes in a sensitive semi-arid and strongly hydrologically connected reservoir, and finally, to pinpoint potential sediment management plans for the onsite hydropower project.

Materials and methods

Study area and sampling

Qaraaoun reservoir is an artificial dammed lake established in 1956 that captures the flow of the Litani River (170 km) in a 2.2-km² lake for hydropower production and irrigation purposes. The Litani basin is the largest watershed in Lebanon known for its farming lands and characterized by a semi-arid climate. This basin has an important socio-economical value. It constitutes about 15–20 % of the total area of the country, 20 % of the total population, 20–30 % of the total national water budget, more than 60 % of the agricultural industry, and about 30 % of the total energy production. The dam construction resulted in a significant increase in agricultural and industrial activities in the upper watershed. Farming and agricultural practices act as non-point sources whereas industrial units distributed along the river water course act as direct point sources since they discharge raw liquid and solid wastes without pretreatment into the river or its tributaries. The number of industries is quite large and the type is quite varied. There are about 288 different industries in the Qaraoun

basin as illustrated in the supporting material (Supplemental material Table 1). The Litani basin is of karstic structure characterized by high infiltration capacity to a shallow groundwater table and it has an estimated capacity of 104 million m³ (MCM) (El-Fadel et al. 2003; BAMAS 2005; Saad et al. 2006; Saadeh et al. 2012).

The lacustrine sediment samples in this study were obtained from three different zones (Table 1) crossing the center of the reservoir longitudinally north to south (river inlet [Ri], central zone [Cz], and dam zone [Dz]). The samples were collected using a stainless steel sediment grabber during both spill and fill modes over a period of 2 years from 2011 to 2013 (Fieldmaster Mighty Grab II Dredge). Water samples were collected from the water column above the location of the sediment samples using a depth-dependent sampler at successive depths of 5 m. More samples in the top 5 m were collected to investigate the biological activity at the level of epilimnion (0, 1, 3, 5, 10, 15, 20, and 25 m). Furthermore, in order to understand the hydrological connectivity between the main components of the watershed comprised by the river, reservoir, and groundwater, additional samples were also collected from piezometers around the dam during the study period as shown by the work of Tuna et al. (2007). The coordinates of all samples are presented in Table 1.

Characterization of water samples

Water pH, temperature, electric conductivity (Ec), total dissolved solids (TDS), and dissolved oxygen (DO)

Table 1 The geographical location and nature of samples in the agricultural watershed collected over biannual years

Sample nature	Sample ID	Coordinates		Depth (m)	Altitude (meter above sea level)
Lacustrine sediments	Ri	33.586996° N	35.699037° E	na	815
	Cz	33.571739° N	35.695442° E	na	815
	Dz	33.555250° N	35.690590° E	na	815
Water column	Ri	33.586996° N	35.699037° E	15	815
	Cz	33.571739° N	35.695442° E	25	815
	Dz	33.555250° N	35.690590° E	25	815
Piezometers	S1	33.5517° N	25.6824° E	1.81	856.88
	S5	33.5484° N	35.6852° E	6.06	861.07
	S6	33.5481° N	35.6976° E	3.78	859.03
	KCO309	33.5502° N	35.6828° E	21.93	871.8
	KCO209	33.5527° N	35.6841° E	20.91	874.39
	RM Bis 17	33.5470° N	35.6904° E	9.88	807.55

were measured simultaneously onsite using a pH meter (HANNA pH211 microprocessor pH meter), conductivity meter (WTW cond i), a portable LaMotte pocket multi Tracer-1766, and an oxymeter (JLO30 Jeulin), respectively. In addition, alkalinity and dissolved ammonium were measured by colorimetry (smart3 Lamotte) onsite. Water samples were filtered directly onsite using 0.45- μm minisart filters and stored in two divided batches of 50-ml polyethylene tubes. The first group of water samples were filled to the rim with no head space to avoid aqueous air exchange prior to environmental isotopic analysis, whereas the other samples were acidified using concentrated HNO_3 to reach pH 1 for metal analysis. All collected samples were stored at 4 °C until analysis. The acidified samples were analyzed for (Ca), magnesium (Mg), cadmium (Cd), and copper (Cu) using atomic absorption spectrometry (Rayleigh WFX-210 AA Spectrophotometry with flame and graphite furnace mode), whereas aluminum (Al), zinc (Zn), nickel (Ni), cadmium (Cd), cobalt (Co), chromium (Cr), and lead (Pb) were analyzed using and ICP-MS (Thermo Scientific). The major anions Cl^- , NO_2^- , NO_3^- , PO_4^{3-} , and SO_4^{2-} were measured using ion chromatography (Shimatzu—shim pack IC-A3). Oxygen and hydrogen stable isotopes in the water samples were measured using a laser detection for isotopic ratios (Liquid Water Isotope Analyzer—LWIA-24d) with precision <0.1 ‰ for $\delta^{18}\text{O}$ and <0.3 ‰ for $\delta^2\text{H}$. The isotopic ratios were expressed as delta ($\delta^{18}\text{O}$ - $\delta^2\text{H}$) according to a standard calibration curve using V-SMOW-certified standards in consistency with the International Atomic Energy Agency (IAEA) norms. Two additional water samples at 0- and 3-m depth below the water surface were also collected and directly frozen for dual isotopic approach ($\delta^{15}\text{N}$ and $\delta^{18}\text{O}$) in order to delineate the nitrate source in the reservoir (Liang et al. 2013). Denitrifier method was used to measure the isotopic signature of nitrogen and oxygen at the Vrije University of Brussels (VUB) according to Sigman et al. (2001) and Casciotti et al. (2002). Briefly, nitrate is biologically converted to N_2O gas by *Pseudomonas aureofaciens* bacterial strain, which is later purified by gas chromatography and measured by isotopic ratio mass spectrometer (V IRMS- Thermo Scientific) coupled with open split interface. The method of bacterial culture, and nitrate conversion to nitrous oxides, purification, and measurement is detailed in Mangion (2011).

For chlorophyll-a, water samples (100 ml) were filtered on glass fiber filters and then extracted with

acetone according to the method described by Arnon (1949). The extracted chlorophyll was measured using a photometer (SP 2000 UV Spectrophotometer VWR) over two wavelengths, $\lambda = 645$ and 663 nm. The total chlorophyll was calculated according to Eq. 1:

$$\text{Chlorophyll (total)} = 20.2 (A_{645}) + 8.02 (A_{663}) \quad (1)$$

where A_{645} and A_{663} are the absorbance values detected at $\lambda = 645$ and $\lambda = 663$ nm, respectively.

Characterization of sediments and algae

The grain size distribution of the lacustrine sediment samples was measured using a laser scattering particle size distribution analyzer (Patrica LA-950V2 Horiba) equipped with laser diodes of 1.6 mW with $\lambda = 405$ –650 nm. An ultrasonic probe was used to break up any aggregates at 20-kHz frequency before analysis. The chemical functional groups were determined using FT-IR-6300 (Fourier transform infrared spectrometer (FT-IR)) from JASCO. The samples for Ft-IR were prepared by mixing the powdered samples with potassium bromide (1 % wt/wt) and compressed into 0.7-cm-diameter pellets. The total and particulate organic carbon content in sediment samples were measured using a CNS analyzer from Interscience FISONs (NA-2000, series 2). The mineralogical phases in the sediment samples were determined by X-ray powder diffraction (XRPD) using a D8 Bruker X-ray diffractometer (copper anticathode of wavelength $\lambda\text{K}\alpha = 0.154060$ nm). The data were collected in the 2θ range of 10° to 60° with a step size of 0.02° per second. The collected diffractograms were analyzed using the EVA software and the powder diffraction files provided by the International Centre for Diffraction Data. Sediments were also examined by scanning electron microscopy (SEM) using a JEOL JSM 6360LV, accompanied by a silicon drift detector (SDS), PGT Sahara.

The sediment samples were digested in concentrated acid before elemental analysis using a microwave digestion oven. The samples were first homogenized using pestle and mortar and sieved through 63- μm acid-cleaned nylon mesh. An amount of 50 mg of the 63- μm sieved samples was digested in Teflon bombs along with suprapur acids: 1 ml of 10 N HCl, 2 ml of concentrated HNO_3 , and 250 μl of 40 % hydrofluoric acid (HF). The filters, used for sample filtration of the water column and containing thus the suspended matter,

were stored and digested following the same method used for the sediments. Digested sample solutions were analyzed for major, minor, and trace element contents by graphite furnace atomic absorption spectroscopy (GFAAS) with Zeeman-effect background correction (Varian AA-400) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Varian Liberty series II). Certified standard materials (UN 3264 from Merck) along with blanks were measured with sample batches.

Algae material collected from the eutrophicated reservoir water was examined by SEM. The algae samples were prepared for SEM analysis in a similar way to the preparation of the sediment samples as described in “Characterization of sediments and algae.” In addition, the morphology of algae samples and the presence of chlorophyll were examined by epifluorescence microscopy (Leica—DMRXA) equipped with a bright-field and dark-field inspection and coupled with motorized sextuple type nosepiece and HC PL Fluotar BD objectives: $\times 5/\times 10/\times 20/\times 50/\times 100$. The tilting trinocular viewing head with $\times 10/25$ eyepieces is associated with a 12 V/100 W lamp and automatic Koehler illumination. Finally, a DAPI staining analysis was performed with chlorophyll filter as described by Sherr et al. (1993) to investigate the nature of the material.

Results and discussion

Characterization of reservoir sediments

The sediments showed a fine grain size distribution composed entirely of particles with diameters less than 230 μm (Fig. 1a). Moreover, about 50 % of the sediment particles have a diameter less than 63 μm (Fig. 1a), and such sediments are expected to have dominant clay and silt textures (Roussiez et al. 2006). Fine grain particles have higher affinity to metals and higher tendency to be resuspended under active hydrodynamics; furthermore, researchers found that clay fraction control the distribution of chemical species (Taher and Soliman 1999; Roussiez et al. 2006). Since metals are retained through particle surface actions, it is expected that fine particles with high surface area exhibit higher surface actions (Balkis et al. 2010).

XRPD analysis showed that calcite and montmorillonite are the prevailing mineral phases in the lacustrine sediments (Fig. 1b). In addition, chemical

characterization of sediments using SEM indicated enrichment of the sediments with trace metals such as Cr (Fig. 1b). Conversely, the FT-IR spectra for the reservoir sediment organics (Fig. 1d) exhibited various functionalities. They showed strong peaks corresponding to abundant O–H and C=C and C–O vibrations linked to various organic compounds with weak intensities as reflected by their corresponding narrow absorption bands (Fig. 1d).

The sediments at all locations (Ri, Cz, and Dz) showed some variations in the concentration of the major elements (Fig. 2). However, all sediments exhibited the same abundance for major elemental contents in the order $\text{Ca} > \text{Si} > \text{Al} > \text{Fe} > \text{Mg} > \text{K}$. For different sampling sites, sediments collected at the river inlet exhibited the highest Al, Fe, K, and Mg contents and the lowest Ca value. In contrast, sediments in the central zone showed the highest Ca content and lowest Al, Fe, K, Mg, and Si concentrations. The high calcium content (about 20 %) in the reservoir sediments of the agricultural watershed (Fig. 2) could be due to limestone bedrock weathering and rock cutting industries prevalent in the drainage basin. The Ca concentrations in the central zone of the reservoir are relatively high as compared to those of other major elements and to those of other zones. The high Ca concentration in the central zone of the reservoir could be due to the low turbulence in that zone allowing the deposition of carbonate phases as reflected by the sediment composition. In addition, some of the calcium carbonates could be endogenic or could be trapped in a particular zone through endogenic means. Martín-Puertas et al. (2009) used the ratio of Ca/Al to address the nature of carbonates in lacustrine sediments and to delineate the origin of sediments where a high Ca/Al ratio indicated an endogenic source. In our case, the Ca/Al ratio registered the highest values in the central zone (10.2) as shown in Fig. 2 for samples collected in spill mode, suggesting the in situ origin of Ca and the importance of the biogeochemical cycle of weathered Ca and its precipitation taking place in the reservoir (Martín-Puertas et al. 2009). In contrast, the dam zone reveals more contaminated sediments that have the highest content of aluminum silicates (Fig. 2), with the highest metal content observed during dry season and low river flow (Supplemental material Table 2). This may suggest more lithogenic and anthropogenic sources of metals which may have been transported with the fine fraction to the dam zone especially during the low river flow.

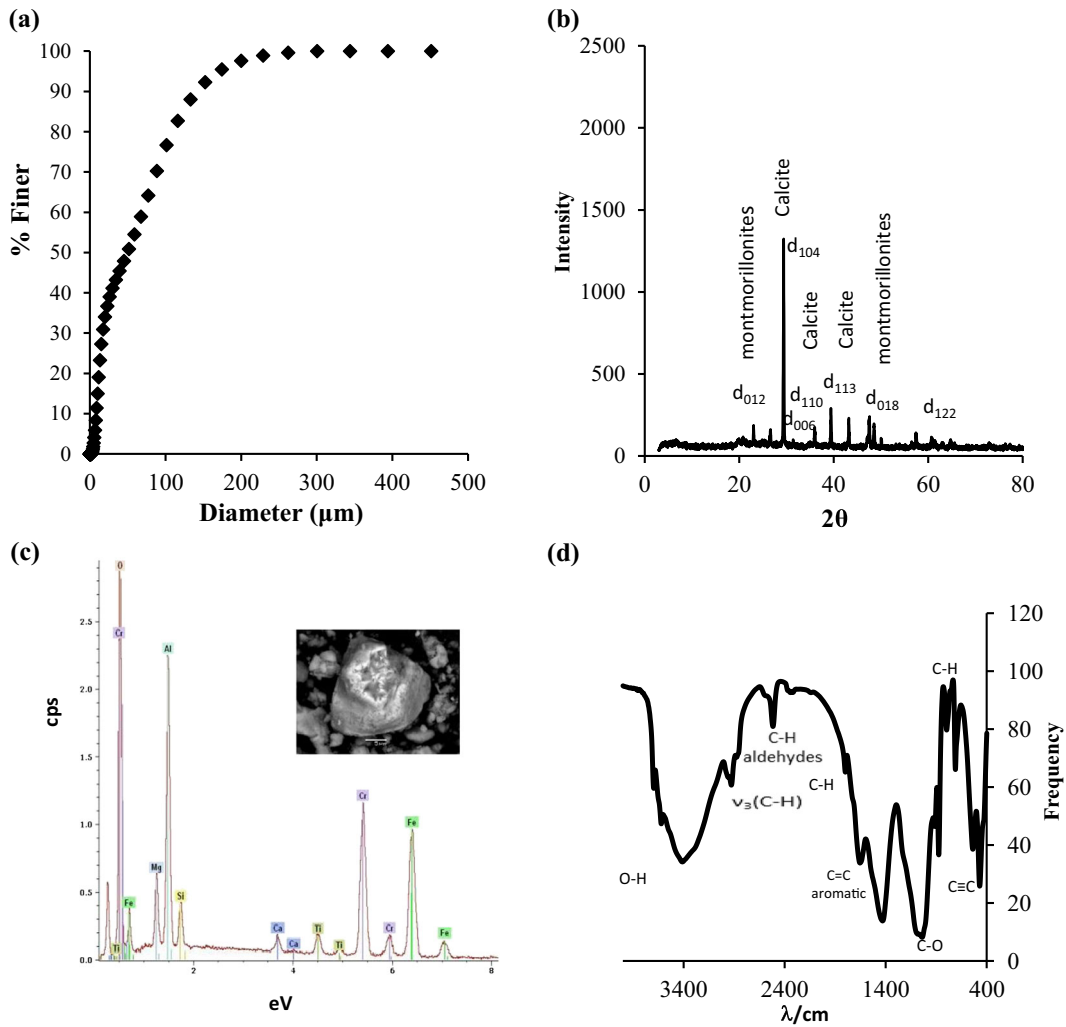
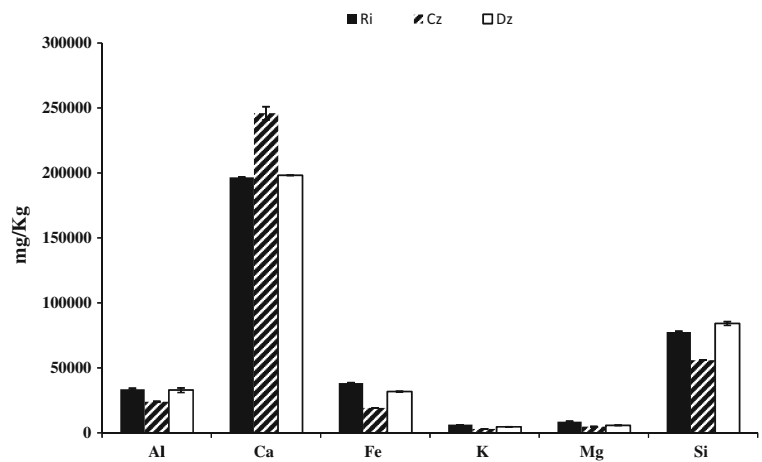


Fig. 1 Characterization of reservoir lacustrine sediments. **a** Grain size, **b** mineralogy, **c** elemental analysis, SEM image of the sediments sample (Dz) and **d** functional groups at the dam zone (Dz) during spill hydrological mode (September 2011)

Fig. 2 Geochemical characterization and spatial variation in lacustrine sediments at Ri, Cz, and Dz during spill hydrological mode (November 2011)



The particulate organic carbon in the sediments ranged between 2 and 3 % which corresponds to an organic matter content of 5–7.5 %, assuming a converging factor of 2.5 (Broadbent 1953). Delsontro et al. (2010) reported that agricultural watersheds are important sources of carbon and nutrients for reservoirs, inducing biological growth. Furthermore, methane emissions are expected to register the highest values at the dam zone during summer (Delsontro et al. 2010). Thus, in our discussion, we will focus on the Dz because of its sensitive location with regard to the reservoir, and the potential hazardous impact of this zone on the utilized water drawn from the reservoir.

The presence of carbonate phases, such as calcite, in lacustrine sediments may dilute metal enrichment in the reservoir sediment bed, whereas the presence of clays may aid in trapping trace metals such as Pb and Cu, through sorption and precipitation (Korfali and Davies 2004). Conversely, the formation of metal-organic complexes may mobilize the metals (Balkis et al. 2010).

Reservoir hydrodynamics

The reservoir hydrodynamics is characterized by two major flow regimes: the fill hydrologic regime and the spill hydrologic regime. During the wet fill mode, water flows to the reservoir from surface and road runoff, springs, and the main river course, whereas during the dry spill mode, the river flow decreases and water level in the reservoir is lowered due to water withdrawal for various usages. Similarly, the reservoir is characterized by three distinct spatial zones, the dam zone (Dz), the central zone (Cz), and the river inlet zone (Ri). The Dz is subjected to weak hydrodynamic regime in the winter season where settling of suspended matter are expected to be more favored. However, the Dz is expected to be under more active hydrodynamics in the summer season due to the turbine flux that is installed at the bottom of the dam, where the withdrawn water is expected to be used for irrigation and hydropower purposes. The Cz exhibits a similar hydrodynamic behavior as the Dz, but it is subjected to weaker hydrodynamic influence since it is situated in a transient zone between Ri and Dz in the river pathway prior to the construction of the dam. Nonetheless, the river inlet zone is where the reservoir connects with the Litani River, and it serves as the major inlet of water to reservoir. Sediments in this

zone are expected to bear the highest metal content in both spill and fill modes (Korfali et al. 2006).

Fill hydrological mode

Physicochemical characteristics and transport direction of chemicals The physicochemical characteristics of the water column above the retrieved sediments collected in the fill hydrological mode of the reservoir are shown in Fig. 3. During the fill mode and as a result of high river flow and surface runoff, the water column is alkaline and shows a decrease in pH from 8.79 at the surface to 8.17 at the bottom (Fig. 3a). Like pH, the temperature decreased along the water column by about 2.5 °C (Fig. 3b). However, the total dissolved solids (Fig. 3c) and conductivity (Supplemental material Table 3) increased by 13 mg/l and 19 µS/cm with depth, respectively. Measured alkalinity fluctuated in the water column where it reached its maximum concentration (167 mg/l as CaCO₃) at 3 m below the surface, and then decreased along the water column (Fig. 3d).

The ambient temperature and the mineralized water with increased loads of nitrogen enhanced the photosynthetic production of organic matter which was then degraded via oxic respiration, causing oxygen depletion in the reservoir as indicated by the anoxic epilimnion (Fig. 3e) (Peretyazhko et al. 2005). Dissolved oxygen level is minimum in the epilimnion (top 5 m) ranging from 1.6 to 4.8 mg/l, which then increases with depth reaching maximum levels in the hypolimnion (Fig. 3e). Vertical profiles of dissolved inorganic nitrogen are shown in Fig. 3 where ammonium levels decreased with depth (Fig. 3f) and nitrites and nitrates increased mainly between 5 and 10 m as shown in Fig. 3g, h. The profile of heavy metal concentrations along the water column (Fig. 3i–l), mainly in the top 5 m, resembled the trend observed for alkalinity and nitrate/nitrite. The sharp fluctuation of chemical concentration at 3 m indicates the presence of an additional biological community such as phytoplankton which could be responsible for this fluctuation. A drop in the concentration of DO in the water column accompanied by a drop in pH, as that observed during the fill mode at 5 m below the surface, could be a result of proton release from aerobic respiration of organic matter and/or oxidation of reduced species such as NH₄, known as the nitrification, that decreases with

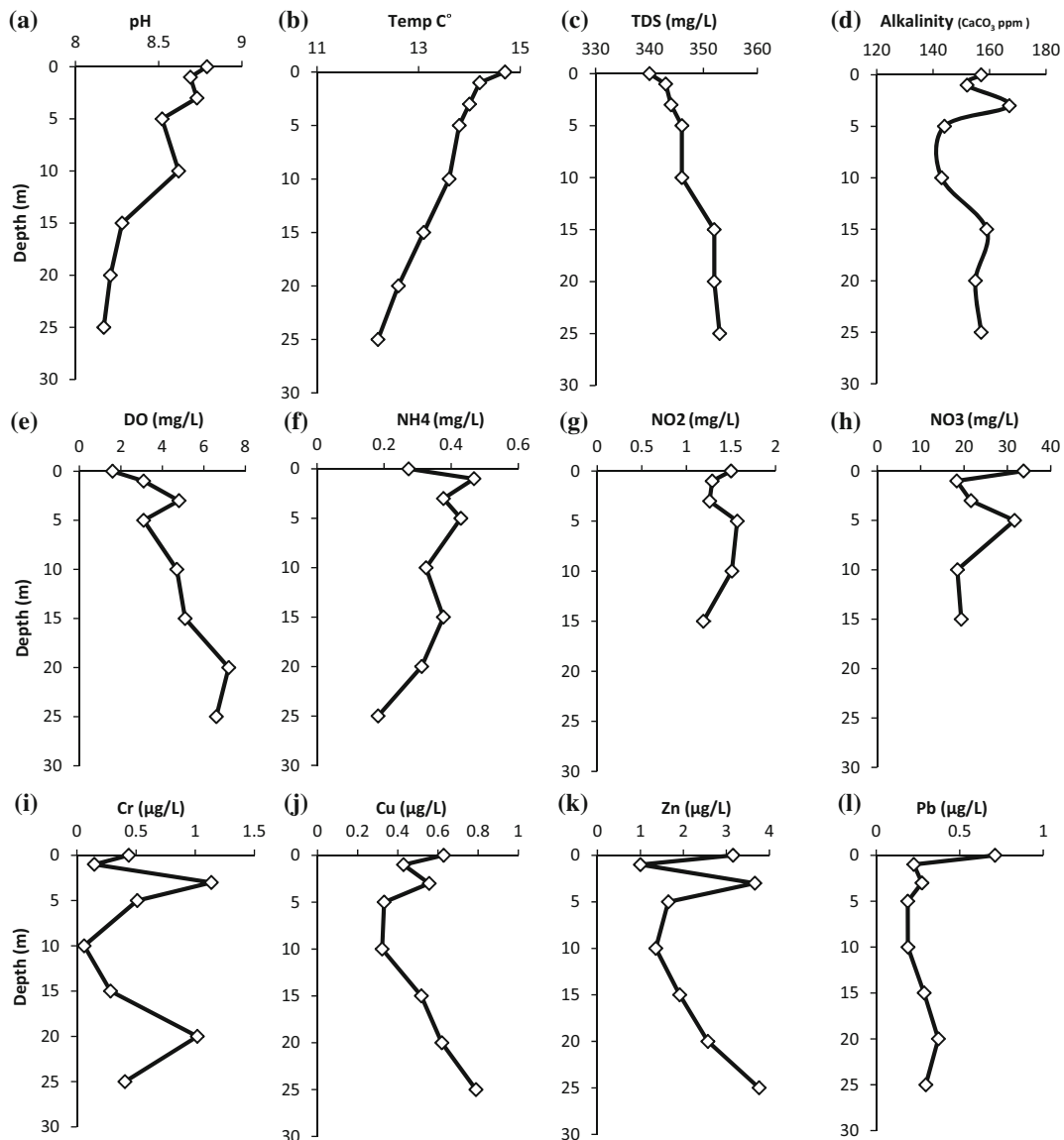


Fig. 3 Physicochemical characteristics of the water column during fill mode (April 2013), showing chemical stratification and the bottom water enriched by chemicals at the level of oxic hypolimnion at Dz

decreasing DO according to Eq. 2 (Peretyazhko et al. 2005).



In the epilimnion, NO_3^- (33.71 ppm) and Mn^{2+} (0.54 ppb) concentrations (Supplemental material Table 3) in the lake are relatively high, thus indicating that nitrification and Mn reduction are taking place when O_2 levels are low (Peretyazhko et al. 2005). Ec gradient increasing from 501 $\mu\text{S}/\text{cm}$ at the surface to

520 $\mu\text{S}/\text{cm}$ at 25-m depth (Supplemental material Table 3) supports the presence of biogenic meromixis (Taillefert et al. 2000). This biogenic meromixis may induce a density gradient which may slow down the transport of dissolved species from monimolimnion to epilimnion, where chemical species accumulate at a depth of 5 m from the surface. The general vertical direction of water in the fill mode is expected to be from the top to the bottom, as groundwater has not yet developed enough pressure head in the aquifer at the bottom of the reservoir to force an upward flux (dissertation).

Moreover, diffusive transport in general is very slow and is not expected to result in large gradients over relatively short time intervals, so the chemical and temperature gradients, if any, would be due to advective-dispersive flow (Boehrer and Schultze 2008). The water temperature gradient decreasing from approximately 14.7 °C at the surface to approximately 12.3 °C at the bottom supports the top-down transport. Similarly, the concentration profiles of Cr, Cu, and Zn (Fig. 3i–k) show an increase in concentration with depth also indicating transport direction from top to bottom during the fill hydrological mode. Thus, the river is expected to exert the most chemical stress on the epilimnion during the fill hydrological mode.

Sediments act as a sink for chemicals The chemical stratification or enrichment in the water column can be expressed as

$$e\% = \frac{(x_{\text{hypolimnion}} - x_{\text{epilimnion}})}{x_{\text{epilimnion}}} \times 100 \quad (3)$$

where x stands for the concentration of the chemical species of interest and epilimnion and hypolimnion are taken at the water surface and bottom, respectively. The TDS enrichment of approximately 3 % clearly indicates an ongoing chemical stratification in the dam zone in the reservoir during the fill hydrological mode (Supplemental material Table 4). The calcium enrichment, estimated to be approximately 4.3 %, could be due to surface and groundwater flows. During the fill mode, the surface runoff and groundwater inflow from karst springs and the corresponding calcite dissolution are reported as factors in calcium enrichment (Jeelani et al. 2011). Thus, the high calcium concentration in the water column mainly found at the bottom (Supplemental material Table 3), in addition to the high Ca content in the sediments (Fig. 2), suggests more alkaline conditions which may scavenge metals from aquatic systems and precipitate them as insoluble oxyhydroxides at the water-sediment interface (Gadd and Griffiths 1978; Korfali and Davies 2004). However, the sorbed metals may be later released in the spill mode when the environmental conditions change in the sediments.

Similarly, the enrichment percentage of Ni, Cr, Cu, Zn, and Cd increased by 5.5, 24.1, 31.0, 21.5, and 46.5 %, respectively, from surface to bottom, in the

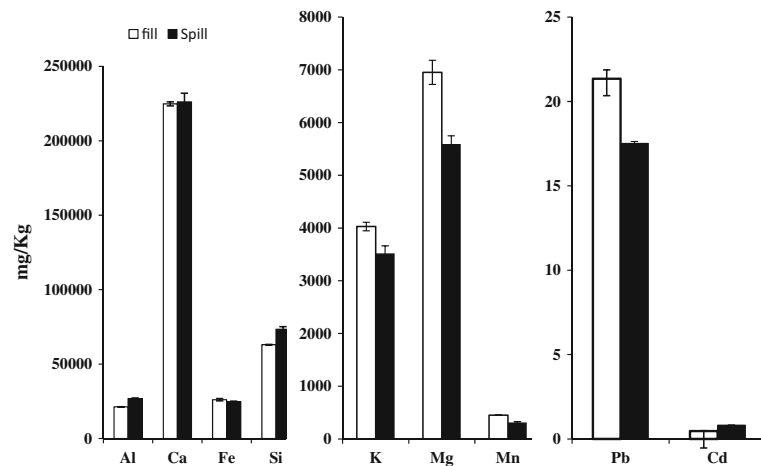
water column (Supplemental material Table 4). This enrichment confirms the presence of heavy water layer at the bottom. Metal input such as Cd and Zn could have originated from various industries such as paint manufacturing, agricultural application of phosphate fertilizers that are extensively applied in the watershed during the fill hydrological mode, in addition to domestic and industrial effluents. The higher enrichment observed for Cd compared to other metals, mainly Zn, and the unexpected negative enrichment for Pb (Supplemental material Table 4), is consistent with higher particulate Pb concentration and lower Cd concentration in the reservoir sediments during the fill mode (Fig. 4). This difference in partitioning behavior of Cd and Pb between the dissolved and the particulated phases at the water-sediment interface could be attributed to their different behavior in response to water physicochemical characteristics. Pb is more influenced by dissolved oxygen changes, salinity, conductivity, and redox state in the water column; thus, it may effectively be adsorbed to finer grained particles and transferred to the sediments (Ekpo and Ibok 1998). The transport of chemicals downward to oxygenated hypolimnion (Fig. 3e) may further allow the entrapment of these chemicals by sediments at the sediment-water interface. Oxidizing conditions will lead to metal immobilization and its entrapment by its adsorption to sediment (Miao et al. 2006).

As discussed above, and as a consequence of the reservoir hydrological setting and the water physicochemical characteristics, sediments can act as sink for chemicals during the fill hydrological mode. Furthermore, the thermal gradient in the water column, accompanied with the chemical stress exerted by the river on the surface of the reservoir, can cause an indwelling water movement of water molecules enriched in chemicals toward the bottom. The thermal gradient and the enriched water movement toward the bottom will result in a heavier water layer at the level of hypolimnion where it can resist the water turnover during the fill hydrological mode (Boehrer and Schultze 2008).

Spill hydrological mode

Physicochemical characteristics and transport direction of chemicals The water column exhibits chemical profiles in the spill mode different from those observed in the fill mode. The chemical stress exerted by the river is weak due to low river flow and the absence of any

Fig. 4 Sediment characterization in fill (March 2012) and spill (November 2011) hydrological modes at dam zone (Dz)



surface runoff, which is reflected by the reservoir's limnology. The alkalinity in the reservoir in the spill mode increased as compared to that in the fill mode (Fig. 5a); however, pH was lower in the spill mode than that exhibited during the fill mod. Many factors could have contributed to this change in alkalinity and pH including biological and manmade activities. For example, algal growth is reported to result in the consumption of alkalinity concomitant with pH increase during the algal growth season in the fill mode (Peavy and Row 1985). Analogously, surface runoff from adjacent rock cutting industries next to the reservoir could have also contributed to the increase in alkalinity in the reservoir in the spill mode since the main river flow becomes more concentrated in limestone cuttings during the spill mode (very low flow rate as compared to the fill mode).

Nevertheless, the water column still exhibited a thermal stratification (Fig. 5b). The TDS concentration increased with depth, where the recorded concentration at the level of hypolimnion was 308 mg/l (Fig. 5c). The same trend was observed for alkalinity where the hypolimnion was more enriched than the upper water column by almost onefold (Fig. 5d). The dissolved oxygen and nitrogen species in the water column are affected by increased temperature and the presence of favorable conditions for biological growth. The DO (Fig. 5e) showed an opposite trend to that exhibited in the fill mode by which oxygen level decreased with depth and the water at the bottom of the reservoir was depleted in oxygen. Denitrifying bacteria could explain the higher concentration of NH_4^+ in the hypolimnion (Fig. 5f) (Krivtsov and Sigee 2005). In addition, the lower ammonium level in the epilimnion (Fig. 5f) could be due to

its assimilation by photosynthetic phytoplankton which explains the high levels of DO , NO_2^- , and NO_3^- (Fig. 5e, g, h). Anthropogenic effluents are reported to be the major source of trace metals in the aquatic system (Roussiez et al. 2006; Callender and Rice 2000, Chon et al. 2012). The metal contamination is manifested in the higher concentration of dissolved Cr and Cu in spill mode and the corresponding fluctuation in the water column as shown in Fig. 5i, j. The high metal concentration in the top layer could be related to the use of algacides by the Litani River Authority to control algal bloom in the irrigation canals which are then recycled to the reservoir, or it could be related to the use of herbicides by farmers in the upper watershed where irrigation is active during the dry season. Moreover, industrial effluents are more concentrated dissolved metals when the river flow is low. However, dissolved Zn (Fig. 5k) and Pb (Fig. 5l) concentrations increased with depth; thus, in the spill hydrological mode, the water at the hypolimnion level was highly enriched with chemicals as compared to the upper water layers, and to the water column during the fill mode. The vertical distributions of dissolved elements indicate an opposite trend to that exhibited during the fill mode.

Sediments act as a source for chemicals The enrichment of dissolved chemical species in the water column during the spill mode is relatively high at the bottom layer where Ec, TDS, alkalinity, and Ca increased by 20 %, 20 %, 34.8, and 27.8 %, respectively. Similarly, dissolved Ni, Zn, and Pb were enriched by 7.6, 119, and 133 %, respectively (Supplemental material Table 4). The high enrichment in Zn and Pb suggests a flux of

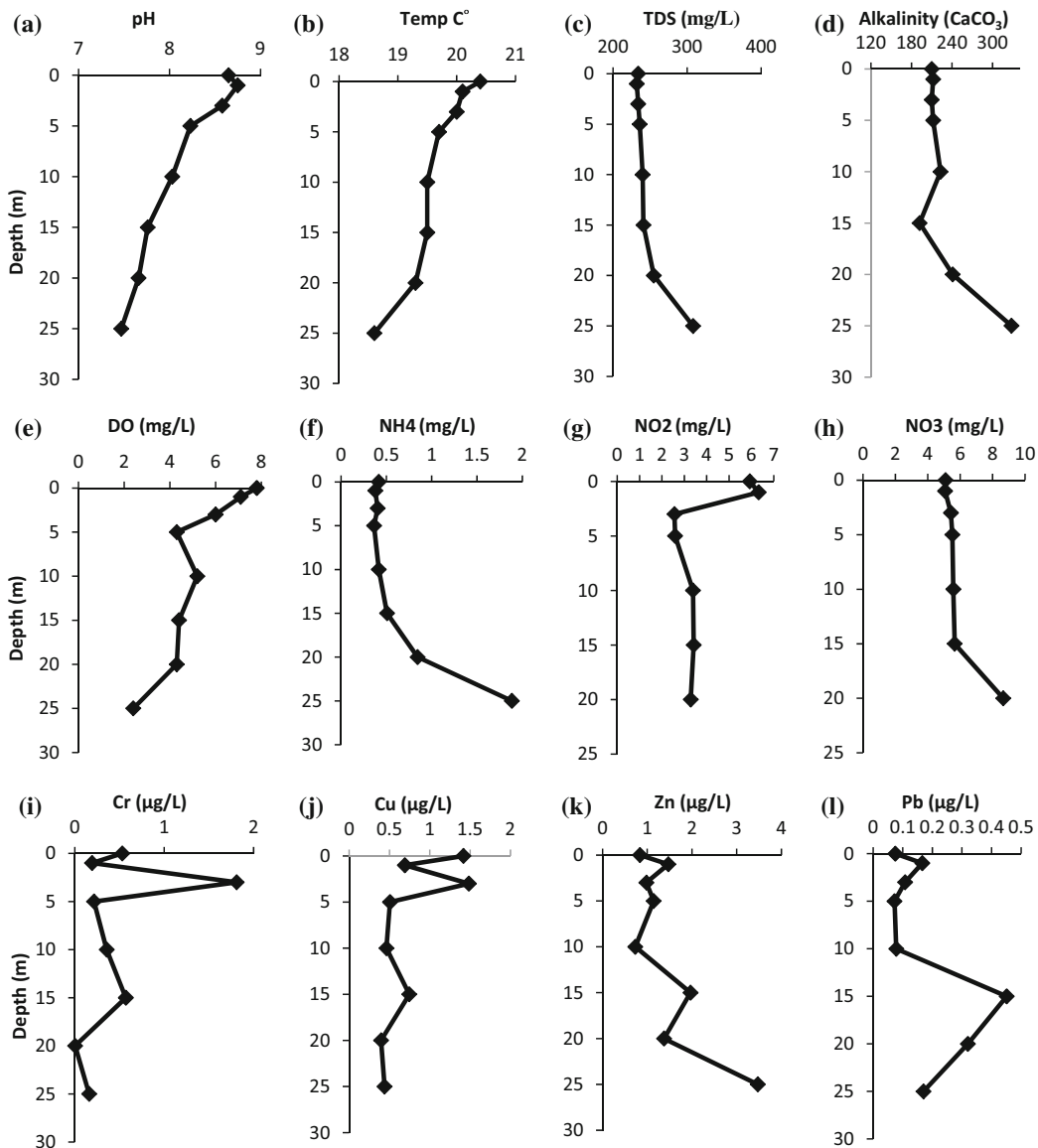


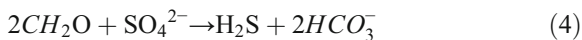
Fig. 5 Physicochemical characteristics of the water column during spill mode (October 2012), showing the presence of an anoxic hypolimnion and a flux of nutrients from resuspended sediments upward the water column at Dz

chemicals from the sediments beneath the water column. Due to the physicochemical changes in the overlying water column in the spill mode as compared to the fill mode (Figs. 3 and 5), and the change in the redox state at the sediment water interface, metals may be subjected to exchange fluxes between sediments and the overlying water column (Argese et al. 1997). Metals are expected to form complexes with the abundant carbonate ions in the reservoir during the fill mode, and as pH decreases during the spill mode (Figs. 3a and 5a) at the level of hypolimnion, the carbonate/metal

complexes are expected to liberate the metals to the water column. Witness observation of gas bubbles in the spill mode during sediment sampling supports possible dissolution of CaCO_3 by fugitive CO_2 gas emanating from methanogenic reactions in the hypolimnion. The dissolution of CaCO_3 will result in an increase in the concentration of Ca^{2+} and metals as shown in Fig. 5 and Supplemental material Table 4. Similarly, the high enrichment of dissolved Pb at the level of hypolimnion (Supplemental material Table 4) can be explained by the high affinity of Pb complexes for residual oxide phases

and the possible dissolution of these oxides due to physicochemical changes at the sediment-water interface. Similarly, ammonium levels in the hypolimnion increased by 2.5-folds whereas dissolved oxygen decreased by 46.8 % at the dam zone (Supplemental material Table 4). This is in agreement with Wall et al. (2005) who reported that sediment denitrification is highest in the deep dam zone during summer. In their study, they found that nitrate concentration was high in the spring and low in the summer.

The reducing conditions in the sediments in the spill hydrological mode may allow bacteria to reduce sulfate and release sulfides according to Eq. 4. This is further confirmed by the increased alkalinity with depth along the water column (Fig. 5d) concomitant with a decrease in sulfate concentration in the epilimnion from 54.4 to 22.8 ppm in the hypolimnion (Supplemental material Table 5) suggesting the degradation of organic matter according to Eq. 4 (Peretyazhko et al. 2005).



The anoxic conditions may facilitate reduction reactions where metals can be released from sediments and transferred to the overlying water to be later transported by the vertical mixing induced by groundwater influx through the water column at Dz (dissertation). Studies show that Pb, Cu, Zn, and Cd are easily exchanged between sediments and the overlying water; the sediments are mostly anoxic whereas the overlying water is in an oxidized state. Metals which are associated with labile phases such as oxides and organic matter are easily resuspended and solubilized in the water column (Argese et al. 1997; Xue et al. 1997). In addition to the favorable conditions for metal release from sediments created by the variation in redox state between sediments and the overlying water column, the sediment texture is composed mostly of fine grains (Fig. 1a) which will aid in their resuspension. The sediment resuspension and the consequent metal release are further helped by the active hydrodynamic conditions caused by turbine suction during the spill mode and the seasonally dependent groundwater influx (Argese et al. 1997).

The low inflow into the Litani River during the warm spill mode and the reservoir bathymetry in addition to reservoir hydrodynamics influenced by water exploitation for irrigation and hydropower production lead to dramatic decrease in the water level which could induce

intense biogeochemical reactions (El-Fadel et al. 2003; Saadeh et al. 2012). They are more favored in larger surface areas with weak water currents such as those featured near the dam zone, which is the largest and deepest part of the reservoir (Taillefert et al. 2007; Figueiredo et al. 2011). Two possible factors could explain the metal enrichment at the sediment-water interface in the dam zone: the mechanical transport of sediments from the river towards the dam and the subsequent sedimentation of finer clayey sediments, and the precipitation of pollutants due to biogeochemical processes in the alkaline water and/or its resuspension from sediments as a result of redox reaction. Reservoir sediments in the dam zone are composed of fine grains where approximately 50 % of the total sediments consist of grains with size less than approximately 20 μm , and these fine fractions could be easily resuspended with the water current. As a consequence of the increase of particulate metal content in finer fractions, the bioavailability and hazardous impacts of metals increase significantly (Callender and Rice 2000; Ebrahimpour and Mushrifah 2008).

Reservoir eutrophication and biological processes

The physicochemical properties of the reservoir water indicate high mineralization during the fill hydrological mode (Fig. 3). Under this condition, the river is enriched with nutrients and chemicals derived from crustal erosion during the winter and anthropogenic activities such as land use in the upper watershed where fertilizers and agrochemicals are applied in the agricultural plain (BAMAS 2005; Darwish et al. 2011). The nutrient enrichment is clearly shown in Fig. 6, where PO_4^{3-} , NO_3^- , and SO_4^{2-} concentrations are relatively high during the fill mode as compared to the spill mode. These nutrients are brought in by the river at the level of epilimnion (Fig. 6) during the fill mode and may induce the algal blooms when the favorable conditions are provided during the spill mode. The algal proliferation provokes a new biogeochemical cycle in the reservoir (Ocampo et al. 2006). Moreover, the alkaline pH (Figs. 4a and 5a) may reflect photosynthetic assimilation of nutrients and higher primary production in the spill mode compared to fill hydrological mode (Hart et al. 2002).

The eutrophic conditions in the reservoir have recently led to a massive proliferation of algal blooms. These blooms are wreaking havoc with the reservoir and the associated hydro-project. Optical

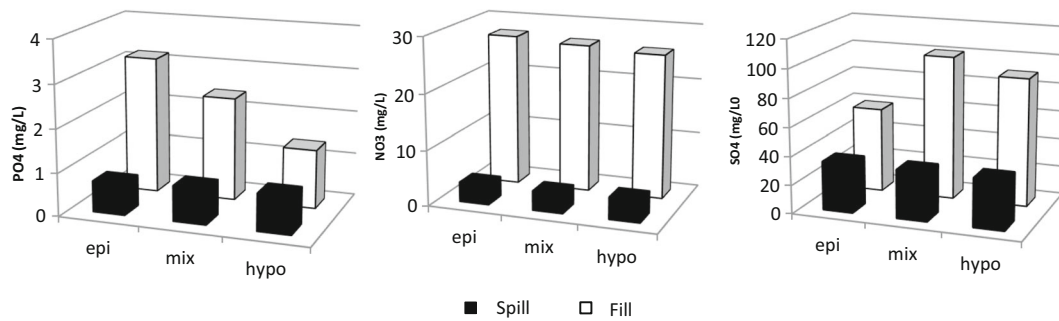


Fig. 6 Anthropogenic influence on the nutrient concentration in the reservoir during fill mode (March 2012) and their assimilation by primary productivity during spill mode (September 2012) at Dz.

Epi denotes epilimnion (top 5 m), *mix* is mixolimnion (5–15 m), and *hypo* is hypolimnion (the bottom water)

and scanning electron microscopy examination of these algal materials indicated the presence of diatoms and other photosynthetic phytoplankton that share the characteristics of cyanobacteria (Fig. 7e). Cyanobacteria are photoautotrophic prokaryotes, able to fix atmospheric nitrogen and enrich sediments with organic matter (Taher and Soliman 1999; Kremer et al. 2008). However, the SEM images indicated the presence of carbonate aggregates with perfect dodecahedral crystal morphology (Fig. 7e). This observation suggests the possibility of in situ precipitation of calcite in the reservoir by cyanobacteria mats, since the photosynthetic cyanobacteria are able to fix CO₂, thus concentrate the bicarbonate ions in the reservoir and as a result increase the calcite saturation state during the spill mode (Merz 1992; Kremer et al. 2008; Kamennaya et al. 2012). The dense biological community could result in the creation of an anoxic layer, whereas the activities of the photosynthetic species may result in an increase in the concentration of dissolved oxygen in the water column (Singh et al. 2008; Lenzi et al. 2013). This may explain the sharp decrease in DO in the upper 5 m as shown in Fig. 5.

During bacterial respiration and denitrification, oxygen and nitrogen molecules fractionate by the preferential consumption of the lighter isotopes ¹⁶O and ¹⁴N leaving the water column enriched by ¹⁸O and ¹⁵N (Brandes and Devol 1997). The measured ¹⁵N ratio during the spill mode in the reservoir at the 0- and 3-m levels are 8.27 and 8.48 ‰, respectively, whereas the ¹⁸O ratio was measured at 6.04 and 5.9 ‰, at the same levels, respectively. This indicates that the source of nitrogen in the reservoir is most likely farming and agritainment practices (Liang et al. 2013).

Hydrological and chemical connectivities of the system

Hydrologic connectivity

Environmental isotopic ratios of oxygen and deuterium were used to investigate the water infiltration from the reservoir to the surrounding piezometers during both hydrological modes. The hydrological setting of the reservoir was explained in details in a previous work; however, the interaction of the reservoir with groundwater is presented in this work. The environmental isotopic investigations in both fill and spill modes in the reservoir and the adjacent piezometers denote the strong hydrological connectivity between surface water and groundwater (Fig. 8). The plot of water samples between global meteoric water line (GMWL) (Siebert et al. 2009; Develle et al. 2010) and local meteoric water line (LMWL) (Saad et al. 2006) signifies the seasonal influence of precipitation and evaporation on the reservoir. In Fig. 8, samples located to the right of GMWL are subjected to evaporation enrichment during spill hydrological regime (Halder et al. 2013), and those located on the GMWL and/or LMWL are more influenced by precipitation (Cartwright et al. 2012). As a consequence, samples located between the two lines are the mixing results of the mentioned groups. In addition, samples located to the left of LMWL indicated by circles and squares in the same figure characterized by the lightest isotopic signature are the result of snow melting and recharge from higher altitudes during the transition season (June 2012) (Cartwright et al. 2012). However, the variation in isotopic signature of groundwater in the investigated hydrological mode shows their recharge by multisources and their rapid response to the changes in the reservoir. During fill mode, piezometers

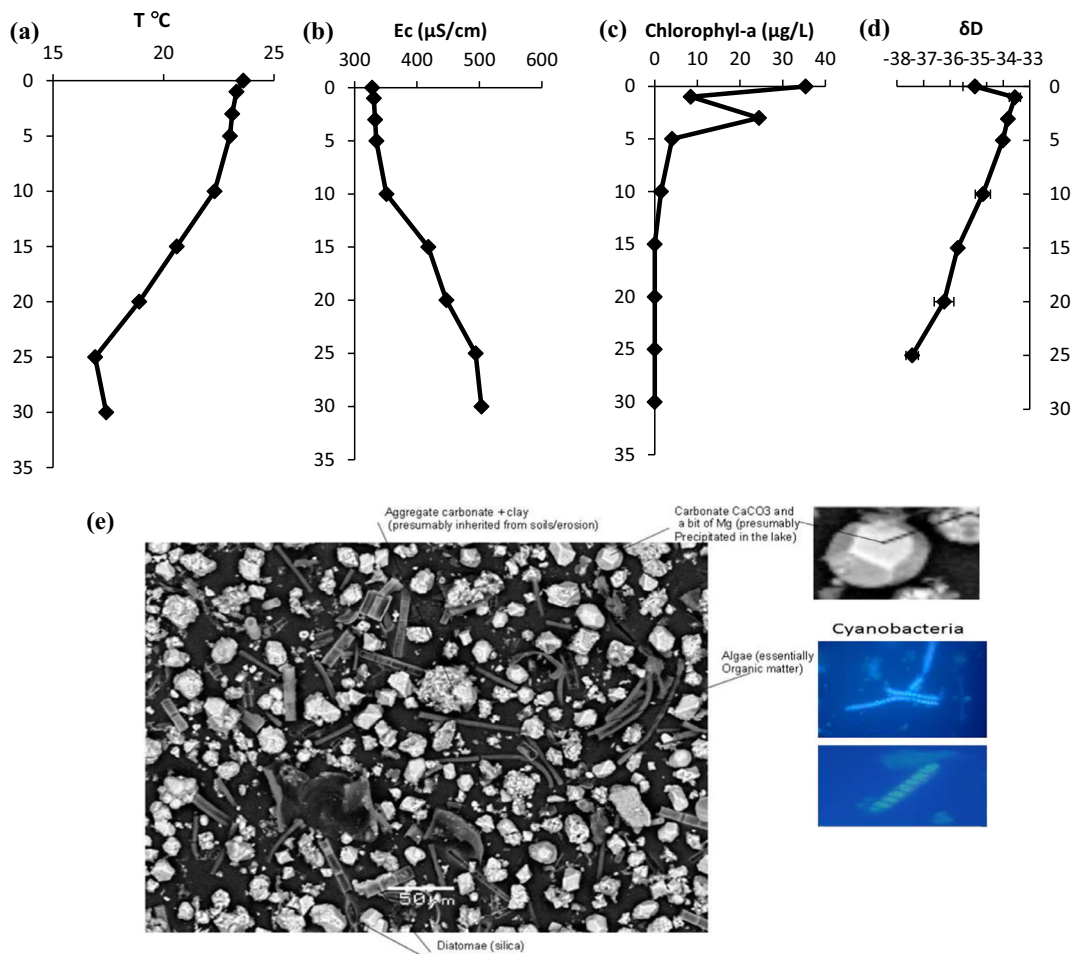


Fig. 7 Vertical distributions of **a** temperature, **b** electrical conductivity, **c** chlorophyll-a, and **d** δD , showing respectively thermal, chemical, biological, and isotopic stratification, and **e** reservoir

eutrophication leading to biogenic precipitation and alternation in the biogeochemical settings of the dam lake at Dz (July 2013)

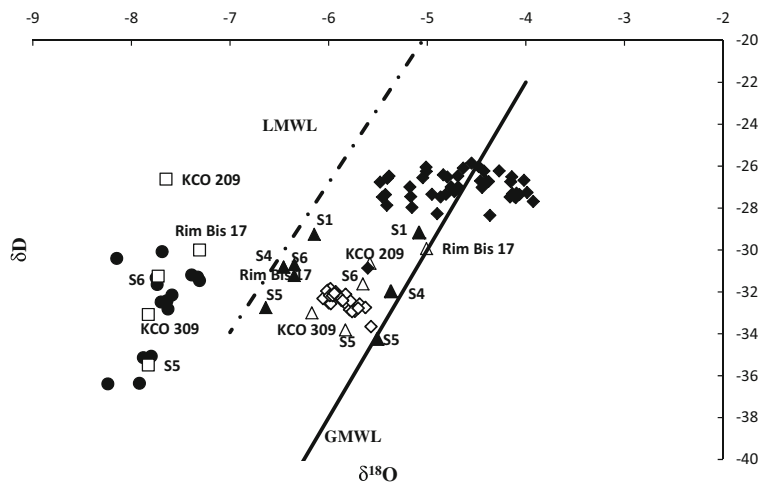
are influenced mainly by precipitation. However, in spill mode, the data on piezometers are plotted close to that of the reservoir signatures in Fig. 8, which indicates the important impact of the reservoir on their isotopic signature. The isotopic compositions confirm the water infiltration from the reservoir to surrounding piezometers, thus aggravating the hazard of metal behavior in sediments during spill mode. Therefore, the mobilized metals from the reservoir sediments during the spill mode pose a potential hazard for the groundwater quality.

Chemical connectivity

In the fill hydrological mode, the hypolimnion is depleted in heavy isotopes and has a similar isotopic

ratio to groundwater represented by both $\delta^{18}O$ and δD (Fig. 9a, b). Groundwater inflow can change water quality in the hypolimnion; even more, it can break down stratification (Krivtsov and Sigee 2005). Contrary to the conditions in the fill mode, water at the hypolimnion level in the spill mode is enriched with heavier isotopes where certain piezometers are affected by the reservoir water (Fig. 9, f). Furthermore, the limnology of the piezometers (Supplemental material Table 6) reflects a similar water composition as observed for the reservoir water. For example, similar TDS values are found in piezometer S6 (315 mg/l) and RM Bis 7 (283 mg/l) as compared to those for the reservoir hypolimnion (308 mg/l) in the spill mode (Fig. 5c). High altitude springs owe their high TDS loads to the sediments

Fig. 8 Strong hydrological connectivity between reservoir (diamonds) and piezometers (triangles) during both fill (open symbols) and spill (filled symbols) and their rapid response to changes in the upper watershed (2011–2013). Data on piezometers (open/white square) and reservoir water (black/filled circle) during transition season in June 2012 are also shown



(Jeelani et al. 2011). This agrees well with a previous study which reported that the Qaraaoun reservoir is recharging the surrounding piezometers (Saad et al. 2009).

During the fill mode, the concentration of dissolved Pb fluctuated in the water column but showed an increasing trend with water depth (Fig. 9c). Similarly, particulate Pb increased at depth but with larger

fluctuations (Fig. 9d). The dissolved Pb concentration in the water column above the retrieved sediments ranged between 0.2 and 0.4 µg/l. The Pb content in the suspended matter increased from 45 µg/g at the water surface to 354 µg/g at 30-m depth, suggesting the enrichment of Pb close to the sediment-water interface in the dam zone. The dam zone in the fill mode is expected to have a quiescent hydrological regime

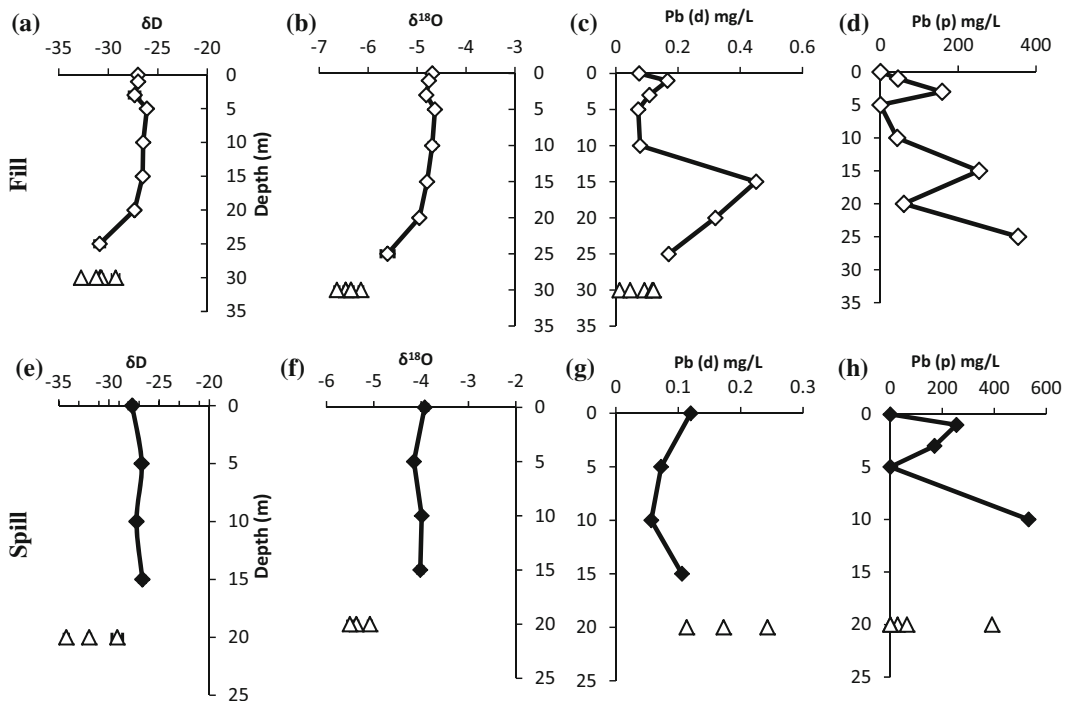


Fig. 9 Environmental isotopic ratios indicating the water infiltration from the reservoir (diamond) to the adjacent piezometers (triangle) where Pb is remobilized from the sediment and migrates with reservoir water to groundwater in spill mode (October 2012) in Dz

favorable for deposition of fine particles. This partitioning of Pb between the dissolved and particulate phases and the similar concentration gradients along the water column suggest a downward transport direction where particulate Pb will precipitate out and deposited at the water-sediment interface. The low concentration of Pb measured in the piezometers as compared to those measured in the hypolimnion exclude the possibility of Pb leaching from the sediment with the infiltrated water (Fig. 9c). It appears that particulate Pb deposition at the sediment surface is the main transport process of Pb from the water column to the sediment bed similar to other reported results (Chon et al. 2012). However, in the spill mode, dissolved Pb concentration in the hypolimnion is higher than that in the epilimnion (Fig. 9g) whereas the particulate Pb is still enriched in the hypolimnion with higher concentrations than those measured in the fill mode. The concentration of dissolved Pb in the groundwater in the spill mode is higher than that in the fill mode (Fig. 9c, g). Moreover, it is higher in the groundwater than in the hypolimnion during the spill mode. This could be explained by the fact that dissolved Pb may originate from the resuspended sediments, enriching the hypolimnion, but it may be ultimately transported by the infiltrated water to groundwater.

Finally, the transition between the fill and spill hydrological modes is characterized by groundwater influx at the bottom of the reservoir (dissertation). Low river flow accompanied with water withdrawal by the hydropower turbines under high temperature conditions will result in high primary productivity. It appears that the reservoir is subjected at this stage to stratification as indicated by the thermal and chemical trends shown in Fig. 7. The thermal gradient manifests in a 7-degree difference from surface to bottom (Fig. 7a), whereas the chemical gradient manifests in an increase in electric conductivity by about 175 $\mu\text{S}/\text{cm}$ along the depth (Fig. 7b). The thermal and chemical downward gradient trend is opposed by an upward gradient trend for both biological and isotopic indices. The intense biological activity is revealed by the high chlorophyll-a concentration in the top 5 m with the highest level of 35.4 $\mu\text{g}/\text{l}$ at the water surface (Fig. 7c). The environmental isotope analyses using deuterium show unexpected isotopic ratios; the highly heavy isotope-depleted water at the bottom can only be explained by an external recharge from either high altitude or snow thawing at the bottom of the reservoir (Cartwright et al. 2012). As a consequence,

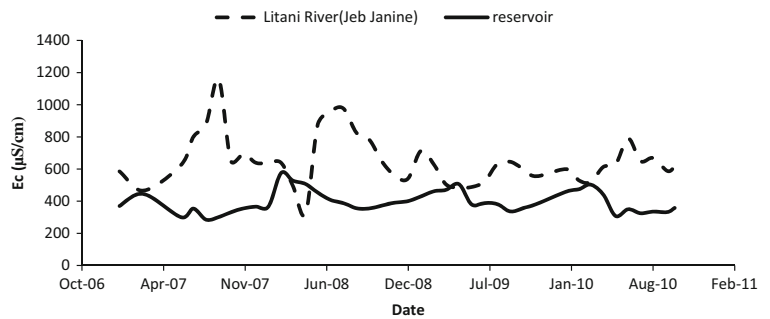
the water column appears to be under chemical stress exerted by the river inflow and phytoplankton in the top layer, and subjected to vertical water mixing induced by the groundwater influx (Fig. 7d).

Reservoir vulnerability and capacity to retain and liberate chemicals

The collected historical data over a period of 5 years reveal the capacity of the reservoir to retain chemicals (Fig. 10). The electric conductivity measured a few kilometers away from the reservoir at Jeb Janinne, which is a representative point for the collective water quality brought up by the Litani River main course, nine (9) tributaries, and surface runoff, is higher than the measured Ec at the reservoir (Fig. 10). The drop in the measured Ec in the reservoir could be a result of precipitation in the more alkaline water of the reservoir and the reservoir hydrodynamics. It appears that the reservoir sediments are responsible for this retention capacity and they show the ability to control reservoir physicochemical settings.

Table 2 summarizes the water quality data for water entering and exiting the reservoir for the fill and spill hydrological modes. The water entering the reservoir at the level of epilimnion is labeled “in” whereas the water exiting the reservoir at the level of the turbines at the hypolimnion level in the dam zone is labeled “out.” In the fill mode, a slight increase was observed in the concentration of Ca, Mg, Al, Ni, Cu, Zn, and Pb in the hypolimnion as compared to the concentration of the same chemical species in the water entering the reservoir. Even though during the fill mode the incoming water is more mineralized as compared to the incoming water in the spill mode, the incoming water during the spill mode is more enriched in anthropogenic heavy metals such as Cu, Zn, and Pb. Furthermore, the water exiting the reservoir during the spill mode is more enriched in chemicals and heavy metals as compared to the incoming water in the spill mode and the exiting water during the fill mode. The exiting water in the spill mode is enriched in metallic pollutants as a result of chemical accumulation in the heavy water layer at the hypolimnion and the leaching of chemical species from the resuspended sediments (“Sediments act as a sink for chemicals”). We can estimate mass fluxes of chemical species exiting the reservoir by multiplying the dam outflow (10.05 m^3/s) by the

Fig. 10 Reservoir vulnerability at the watershed scale and its capacity to retain and liberate chemicals, showing that endogenic process dominates over the watershed impact. Data were provided by the Litani River Authority



concentration of chemical species at Dz hypolimnion (below 10 m) during the spill mode (Peretyazhko et al. 2005). This indicates that water used for irrigation has the following fluxes for metals: Co (3.43 kg/day), Ni (1.02 kg/day), Cu (1.01 kg/day), Zn (5.21 kg/day), and Pb (0.4 kg/day). Furthermore, the nutrient fluxes are estimated to be 1.4 tons/day for NH_4^+ , 3.4 tons/day for NO_2^- , and 7.2 tons/day for NO_3^- . Finally, 3.4 tons of Cl/day is exiting from the reservoir during the spill mode which threatens to salinize the agricultural soil and increase metal bioavailability.

The water quality in the spill mode should receive more attention since this water is used for irrigation during the dry months. In the long term, the concentration of anthropogenic fluxes of chemical species entering the reservoir will increase due to the increasing industrial and agricultural activities in the basin. This will threaten the quality of water exploited from the reservoir and the hydropower project sustainability. As a consequence, the water pumped from the reservoir to the irrigation canal (canal 900) will be enriched with contaminants leading ultimately to accumulation of toxins in the food chain. Furthermore, the increased nutrient flux during the warm spill hydrological mode will induce biofilm proliferation, menacing the turbine and the canal activity.

Conclusions

As a consequence of the reservoir hydrological settings and the water physiochemical characteristics, the hydrological and biogeochemical processes induced a vertical downward transport of chemicals towards the fine grained calcareous sediments during the fill mode. In contrast, during the spill mode, the sediments acted as a source for a chemical flux upward through the water column and downward toward groundwater. The sediment behavior and reservoir eutrophication in the spill mode impacted significantly the quality of the water exiting the reservoir in the hypolimnion near the dam zone. However, local hydrodynamics and sediment behavior buffered partially the chemical and thermal stress on the reservoir water quality during the fill mode. The geomorphological features of the reservoir situated in a Mediterranean semi-arid area enhanced the strong hydrological connectivity between surface water and groundwater where the reservoir responded quickly to natural and anthropogenic changes in the upper watershed. The water used for irrigation is enriched in metals, for example, about 5.2 kg of Zn, 3.4 kg of Co, 1 kg of Ni, and 1 kg of Cu, in addition to 0.4 kg of Pb, are estimated to be pumped per day to the irrigating canal from the reservoir; moreover, nutrients such as nitrogen in the form of ammonia (1.4 tons/day), nitrate (7.2 tons/

Table 2 Physicochemical parameters and dissolved metal concentrations in the incoming water and outgoing water of the reservoir during both fill and spill hydrological modes

Parameters	pH	T (°C)	DO (mg/l)	Alkalinity (mg/l)	Ec (µS/cm)	Ca (µg/l)	Mg (µg/l)	Al (µg/l)	Mn (µg/l)	Co (µg/l)	Ni (µg/l)	Cu (µg/l)	Zn (µg/l)	Pb (µg/l)	
Fill	In	8.1	15.2	5.1	176.2	511.2	60.0	15.28	26.15	1.85	3.94	1.16	0.54	2.96	0.19
	Out	8.2	12.4	6.9	156	518.5	61.7	15.34	31.41	0.46	3.93	1.60	0.70	3.16	0.33
Spill	In	7.9	25.8	6.3	208.7	344	37.5	15.2	4.23	0.52	3.94	0.84	0.89	3.3	0.43
	Out	7.7	25.3	6.4	211	337.5	38.3	15.9	3.53	0.62	3.95	1.18	1.17	6.0	0.54

day), and nitrites (3.4 tons/day) in addition to chloride (3.4 tons/day) are threatening to salinize the agricultural soil and increases metal bioavailability and its potential to bioaccumulate in the food chain. Moreover, the nutrient enrichment in the water withdrawn from the reservoir will induce algal growth that may lead to turbine biofouling, thus disturbing irrigation canal activity and hydro-project sustainability. The water quality in the spill mode should receive more attention due to its potential hazard for the hydro-project and the sustainability of the agricultural soil in the long term.

Acknowledgments This research has been financed by research grant programs of the Lebanese University and the Lebanese Council for Scientific Research. We also acknowledge the support of Azm and Saadé Association, PCSI programs in AUF. Additional funding was provided by the Bureau of International Relations (BRIC) and the Xénophilia Funds of the Université Libre de Bruxelles (ULB). Kind appreciations are extended to the Litani River Authority staff represented by Mr. Ali Tarrif and Ms. Eliane Hayek for their help during fieldwork. We are grateful for the analytical help provided by Prof. Bruno Lartiges (Université Paul Sabatier), Prof. Frank Dehairs (VUB), and Ms. Adriana Anzil (ULB).

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