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HEAVY METALS TRANSPORT FROM WASTEWATER SPILLS INTO A COASTAL AQUIFER AND SEAWATER

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Abstract

Wastewater generated from industrial activities has delivered elevated heavy metal concentrations into fresh and salted aqueous systems. Herein, the migrated trace metals were studied from their initial location through a coastal aquifer up to the seawater. The experiments were carried out at lab scale using a sandbox with glass beads and two attached chambers containing natural groundwater and seawater. The study focused on the transport behaviour of heavy metals such as copper, zinc and lead into freshwater and seawater. Plasma optical emission spectrometry (ICP-OES) analysis was performed to detect the heavy metal concentrations from the water samples taken with time from the experiments. The simulation work adopted Groundwater Modelling System (GMS) codes were used for validation of the experimental outcomes. Results showed that the heavy metals concentrations in wastewater effluents affect the water quality of the aquifer. The water quality and resistance of the aquifer to heavy metals pollution increased with the presence of a renewable recharging of freshwater along with the contamination source. Heavy metal ions in seawater exhibited a gradual increase in their concentrations with time in all studied cases.

Keywords: groundwater, heavy metals, seawater intrusion, trace transport, water quality

Received: November, 2018; *Revised final:* March, 2019; *Accepted:* March, 2019; *Published in final edited form:* December, 2019

1. Introduction

Nowadays, the number of the synthesised chemicals used for industry, agriculture, domestic and medicinal applications has increased exponentially and improved human life. However, these chemicals have also brought new risks. Many hazardous solid wastes and

Wastewater streams characterised with high heavy metal contents are introduced, which then find their way into different components of the environment through various pathways, especially food and water supplies. Heavy metals can mobilise and pollute the groundwater aquifers via direct and indirect discharges such as leachate runoff and infiltrations (Perez-Lopez et al., 2003; Wright and Mason, 1999). One of these important pathways is the

discharge of treated or untreated wastewater into the coastal groundwater system to recharge the aquifers. Therefore, the heavy metals ions in these wastewaters might also reach the seawater through means of the groundwater.

In fact, selecting a suitable treatment method for surface wastewater is important for protecting the groundwater and seawater. Many methods for removing heavy metal ions from industrial and domestic wastewater streams have been widely adopted such as physico-chemical methods, which include chemical precipitation, chemical oxidation or reduction, filtration, ion exchange etc. However, these technologies usually produce wastes with high concentrations of metals, which are considered significant sources of groundwater pollution (Ahluwalia and Goyal, 2007; Lyczko et al., 2017). On

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the other hand, many recent studies investigated the bioremediation methods and deemed them as effective and inexpensive alternatives, particularly, because they do not yield high concentration solutions (Jacob et al., 2018; Karthik et al., 2017; Pugazhendhi et al., 2014; Pugazhendhi et al., 2018; Sobariu et al., 2017; Sridevi et al., 2016; Shanmugaparakasha et al., 2018; Zhang et al., 2017).

In recent times, the degradation of water quality via heavy metals pollution has become a global concern. It introduces indirect toxicity through the food chain, or direct toxicity to human and aquatic life through drinking water. Heavy metals such as chromium, copper, lead and zinc exhibit human toxicity at higher concentrations while, cadmium is toxic at extremely low concentrations (Peters and Bhattacharyya, 1978). Low concentrations of chromium, especially Cr (VI) as reported by Karthik et al. (2017), significantly increased the cardiac function for living organisms.

Heavy metals exist naturally in the environment and have a role in bio-geochemical reactions. They are normally transferred between different compartments of the earth, but due to human activities, this natural transfer is altered (Tayab, 1991). Industrial activities, for instance, have led to a high level of release of heavy metals into the environment, which are approximately 100-1000-fold more than that found naturally in the earth's layers (Carral et al., 1995; Fan, 1996).

The negative impact of this high concentration of heavy metals is quite clear, not only due to decreasing diversity of the aquatic species, but also by exposing human beings to these metal ions through the food chain, which has a negative impact on human health (Andersen et al., 1996; Perez-Lopez et al., 2003). Thus, understanding of heavy metals mobilisation in coastal areas is crucial in the management of coastal water resources to keep the natural equilibrium in these aquatic ecosystems and to provide a healthy and safe environment for human beings (Zhang et al., 2002).

In unconfined coastal aquifers, groundwater discharges into the seawater due to differences in hydraulic head. Since seawater is denser than freshwater, it tends to interfere with the aquifer water under freshwater to form a seawater toe. A freshwater-saltwater interface is established once the seawater encounters the freshwater. The intrusion thickness depends on some physiochemical parameters and the flow characteristics of the water (Volker and Rushton, 1982). Many researchers investigated the transport of solute plumes in the porous medium by experimentation (Schincariol and Schwartz, 1990; Oostrom et al., 1992; Zhang et al., 2002). These studies focused mainly on the instability of the plumes with the horizontal flow field. The investigations concluded that the development of instabilities relies on the density variance between the plume and the ambient groundwater, the groundwater flow velocity, and the hydraulic conductivity of the medium. However, the chemical interaction of these infiltrated

solutions with fresh and salt waters was not taken into consideration.

The migration of pollutants in coastal aquifers is a complicated process. At the fresh and salt waters interface, a saltwater diffusion zone exists between the outflowing freshwater and the seawater, where hydrodynamic dispersion occurs. Few research work exists on the pollution migration in this diffusion interface zone (Zhang et al., 2002). The processes at the seawater-freshwater interface are controlled by the contrast in physiochemical properties and variations in sea and aquifer levels. Physical processes at this interface have been studied extensively, with respect to flow and transport of miscible fluids of different densities (Bear et al., 1999; Reilly and Goodman, 1985). Limited attention has been drawn towards the chemical processes. Several studies have examined the coupling between the flow and transport processes and the geochemical processes as they occur at the interface in a coastal aquifer (Andersen et al., 2005; Carlyle et al., 2004; Snyder et al., 2004).

All previous work studied the contamination migration using visual monitoring only for the tracer transport. Herein, besides the visual monitoring, there are water samples collected for chemical analysis to help facilitate the research gap mentioned above. To the best of the author's knowledge, so far, no one has conducted laboratory experiments to monitor by chemical analysis the transport processes occurring between fresh and salt waters through sample collection from sandbox scheme. The main aim herein is to conduct well-controlled heavy metal contaminant transport experiments to study the migrated traces of heavy metals from their sources up to the seawater. This study focused on the transport behaviour of heavy metals such as copper, zinc and lead into fresh and salt waters. The physiochemical interaction among fresh, polluted and salt waters in the experiments was simulated using a numerical model by MT3DMS and SEAWAT codes.

2. Materials and methods

2.1. Experimental works

The experiments were conducted at laboratory scale using a sandbox and two attached chambers of freshwater and seawater. Glass beads were used inside the sandbox to simulate porous media. The chemical analysis was conducted using a Plasma optical emission spectrometer (ICP-OES) for the collected water samples. Fig. 1 shows a schematic representation for the adopted sandbox kit used in this particular study. The tank contained three distinct flow chambers; the right inlet chamber was used to supply seawater flow using a feeding top tank. While the left inlet chamber was used to supply flow of freshwater. The central porous media chamber was filled uniformly with glass beads of a diameter approximately 1.09 mm. The test domain, i.e. central chamber, of the flow tank had dimensions of $38 \times 13.5 \times 1.0$ cm in length, height and width, respectively. The

beads were packed under wet conditions to prevent air bubbles being trapped within the tank. The hydraulic conductivity (K) of the tank was $85 \text{ cm}\cdot\text{min}^{-1}$. To separate the side chambers, (i.e. boundary conditions), plastic meshes were used on the sides of the porous media chamber. By adjusting a drainpipe level in both outlet chambers, freshwater and seawater levels were set at 13.37 and 12.97 cm, respectively. The water levels were measured with electrical sensors attached to the top of the chambers. Natural seawater obtained from Seaboard beach in Belfast city, UK and freshwater from coastal groundwater aquifer at Queen's University Belfast area were used in the experiments. The values of freshwater and saltwater densities were 1.0 and $1.025 \text{ g}\cdot\text{cm}^{-3}$, respectively. An elevated tank was used to feed the heavy metal-polluted water through a pipe fastened on the top edge of the porous media beside the freshwater boundary as shown in Fig. 1. Polluted water sources were made artificially by mixing ionized water with 7.85, 5.21 and 2.64 g of copper, zinc and lead precursors respectively, to produce a solution with a concentration of 50 mg/L. Although this concentration of pollutants is much higher than concentrations found in wastewater, it is required to allow easy tracking of pollutant migration. In each experiment, three water samples were taken at different time intervals, namely; 1, 3, 6 and 24 hours. Samples were collected from the mixing zone and freshwater zone using two fine needles of lengths 6 and 2 cm, respectively. These needles were fastened to the top of the porous media and located at 2 and 4 cm, respectively, from the seawater boundary (Fig. 1). The third sample was taken directly from the seawater chamber with a pipette (Fig. 1). The three different types of waters used in the scheme were coloured as follows: colourless for freshwater, dark blue for polluted waters and red for seawater using safe and inert food dyes.

Images for the experiments were captured with a high-speed camera with a resolution of 1280×1024 pixels. The camera was triggered in intervals every 30

seconds and ten images were taken at each interval. The average of these images was used in the measurement analysis of the salt toe length and visualisation recording of the pollution transport. For the test procedure, the test started with flashing the porous media chamber by freshwater, thus the whole domain was without any salt intrusion. The two water levels were set to their specified values mentioned above. Once the desired levels were achieved, the camera then started its interval cycle mentioned above.

There are two feeding tanks to maintain the levels and the densities of the fresh and salt waters. The saltwater wedge started advancing up to the reach of the steady state condition at approximately 60 min. Then, two different experimental scenarios were adopted. One stopped the freshwater feeding and started the heavy metal spill feeding the domain by the flow rate of $25 \text{ cm}^3\cdot\text{min}^{-1}$ as in case of the copper spill experiment. This is to simulate the case of recharging non-renewable aquifers by wastewater effluents only. The second scenario, as in zinc and lead spills, adopted running heavy metals spills in the presence of the normal feeding of freshwater. This is to simulate the infiltrations of wastewater effluents in renewable aquifers. Water samples were collected initially from freshwater, seawater and mixing zone water before commencing the discharging of the polluted waters. These water samples were analysed for full chemical compositions of waters in the scheme prior to pollution.

Table 1 presents the result of these analyses. Each experiment was run for 24 hours. Water samples from the three positions were taken with time as described above. Temperature, pH and conductivity were monitored at the same time intervals of the sample collections, i.e. 1, 3, 6 and 24 hours. A sorption test for beads was carried out to determine whether these glass beads would absorb any heavy metals from the media or not according to ASTM E1195-01(2008). The results of sorption beads showed no absorption activity for the used glass beads.

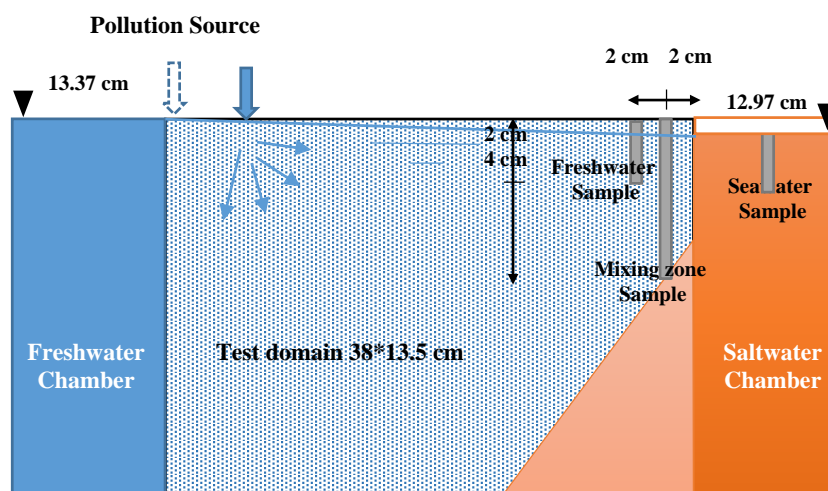


Fig. 1. A schematic representation of the sandbox and sample collection locations

Table 1. Full chemical compositions for used seawater, freshwater and mixing zone (mg/L) according to ICP-OES technique

Sample	Na	Mg	Ca	K	Cl	SO ₄	TDS	pH	Cu	Pb	Zn
Sea Water	11000	1168.9	218.8	300	23330	1900	35000	8.07	0.07	0.1	0.01
Mixing Zone	3900	618.5	372	200	12200	1600	22000	8.19	0.11	0.1	0.02
Fresh Water	31.8	21.8	31.8	1.08	18.9	30	200	8.34	0.13	0.08	0.01

ICP-OES analysis was utilised to detect the heavy metal concentrations accordingly. The solution of each sample was analysed with an ICP Optical Emission Spectrometer (Optima 4300 DV, Perkin-Elmer). Herein, an Agilent 5100 ICP-OES was used for the ultra-fast determination of trace elements where standards were prepared from single element standards and diluted with 2% HNO₃. To validate the method, the following trace metals in drinking water (TMDW) Certified Reference Materials (CRM) were analysed: TMDW-A, and TMDW-B (High Purity Standards, Charleston, South Carolina, USA). An accredited ICP standard solution was ordered from inorganic Ventures in a concentration of 1000 ppm ($\mu\text{g}\cdot\text{mL}^{-1}$). 1 mL of the standard solution was added to a 100 mL volumetric flask, followed by adding 2 mL of HNO₃, helping to form a homogeneous solution, then made up to 100 mL (to prepare 10 ppm solution). 10 mL of that solution was diluted to prepare 1 and 0.1 ppm standard solutions.

The blank solution was prepared by diluting 2 mL of HNO₃ up to 100 mL using deionised water. It is worth noting that the same acid was used in standard and blank solutions. The sample was then digested in 10 mL HNO₃ using the microwave, removed after digestion and the vial heated on a hotplate to reduce the acid down to 5 mL then dilute it with deionised water before the analysis. Water samples can contain a wide range of elements at varying concentrations. Inter Element Corrections (IEC) have been established as the preferred correction technique for these spectral interferences in labs running US EPA methods. However, in this case Agilent's powerful spectral deconvolution Fast Automated Curve-fitting Technique (FACT) was used. Herein, IEC factors were setup using the ICP Expert v7 software. Once the factors had been determined, they were stored in a template and reused in subsequent analyses.

2.2. Numerical simulation

The simulation and validation works were implemented by the MODFLOW, MT3DMS and SEAWAT codes (Guo and Langevin, 2002). The model comprised of a rectangular area of the same dimensions as the porous media chamber in the experimental sandbox. A uniform two-dimensional grid of 0.25 cm dimension (152 cells in the x-direction and 53 cells in the z-direction) was used to discretize the tank. The lowest edge of the model was set as a no-flow boundary. The longitudinal dispersivity values were determined by a trial and error process and were taken normally around the bead sizes. The transverse dispersivity values were taken as 1/10 of the

longitudinal ones, but both values ultimately fell within the range specified by Abarca and Clement (2009) for beads of a close size. A freshwater hydrostatic boundary condition was forced on the left side boundary and a hydrostatic saltwater boundary condition was applied to the right side. The polluted water was applied as a discharging well in one cm (four cells) in the upper left edge of the grid as it was carried out in the sandbox. Two pumping wells were used close to the salt boundary to simulate the two needles used for the sample collection. The adopted physical parameters of porous media are as follows: Hydraulic conductivity of 85 $\text{cm}\cdot\text{min}^{-1}$; porosity of 0.38; molecular diffusivity of 0.06 $\text{cm}^2\cdot\text{min}^{-1}$; longitudinal dispersivity of 0.05-0.13 cm; and transverse dispersivity of 0.005-0.013 cm.

3. Results and discussion

3.1. The mobility of heavy metals

3.1.1. Copper

The copper spill with an average flux of 25 $\text{cm}^3\cdot\text{min}^{-1}$ was applied through the porous domain, i.e. aquifer, over a period of 24 hours. The spill was applied only without freshwater supply to simulate the recharging case of the wastewater effluent for non-renewable aquifers. Fig. 2 presents copper concentrations in the fresh water, mixing and seawater zones.

The results showed that the copper concentration in fresh water significantly increased after one hour and then it continued in a slight increase up to 24 hours. The copper concentration after one hour was around 85% of the total concentration measured at 24 hours. Thus, the freshwater reached the concentration level of wastewater contamination in just one day after exposure to the contamination spill. For the mixing zone, copper concentrations increased significantly with time for the first six hours, as water in the mixing zone gained around 95% of its final contamination level after 24 hours. At the end of the test, mixing zone water absorbed the copper with a total concentration of approximately 44% from the spill concentrations. On the other hand, seawater behaved differently, as it absorbed a small amount of the copper ions reached at 24 hours, 0.5 mg/L, which equals approximately 1% from the copper spill concentration.

The rate of absorption was high and did not reach the steady-state conditions after 24 hours, which refers to the continuity of copper absorption process with time. These results agreed with Dahmouni et al., (2019) who monitored the impacts of using

wastewater in irrigation on the shallow groundwater in a real site in Tunisia. They reported that the concentrations of Cu increased significantly with time in the groundwater. The results herein, showed also that both Mg and Ca concentrations, the most changeable elements accompanying with the copper change, reduced in seawater slightly, whilst in the fresh water these elements were significantly eliminated. This is perhaps due to the formation of a precipitate form of calcium and magnesium of CaCO_3 and MgCO_3 , respectively. It is well known, that the molar concentration of Mg in seawater is around five times that of Ca and this is in line with results herein.

3.1.2. Zinc

In the zinc spill case, the simulation scenario was changed from using the heavy metal spill as the only recharging source for the aquifer to a polluted source point in a running renewable aquifer. This alteration in simulation scenario is to study different realistic situations for the aquifer contamination by

heavy metals effluents. The zinc spill with an average flux of $5 \text{ cm}^3 \cdot \text{min}^{-1}$ was applied to the porous domain as described earlier in the method section across a period of 24 hours. Freshwater was also applied from the freshwater chamber with a flow rate of $20 \text{ cm}^3 \cdot \text{min}^{-1}$. The monitoring of zinc concentrations in freshwater, mixing zone and seawater was presented in Fig. 3. Results showed a significant increase of zinc concentration in freshwater after one hour; however, the concentration then declined up to 24 hours.

Similar behaviour is also recorded in the mixing zone concentrations. For the seawater, zinc concentration increased significantly with time. This behaviour relatively resembled the previous case of the copper spill but with higher concentrations. The concentration was 15 mg/L in 24 hours and exhibited a tendency for increasing because it did not reach the steady-state conditions as seen in Fig. 3. This different behaviour for zinc concentrations in the fresh and mixing zone waters from that of copper is mainly due to the change in the flow system in the aquifer.

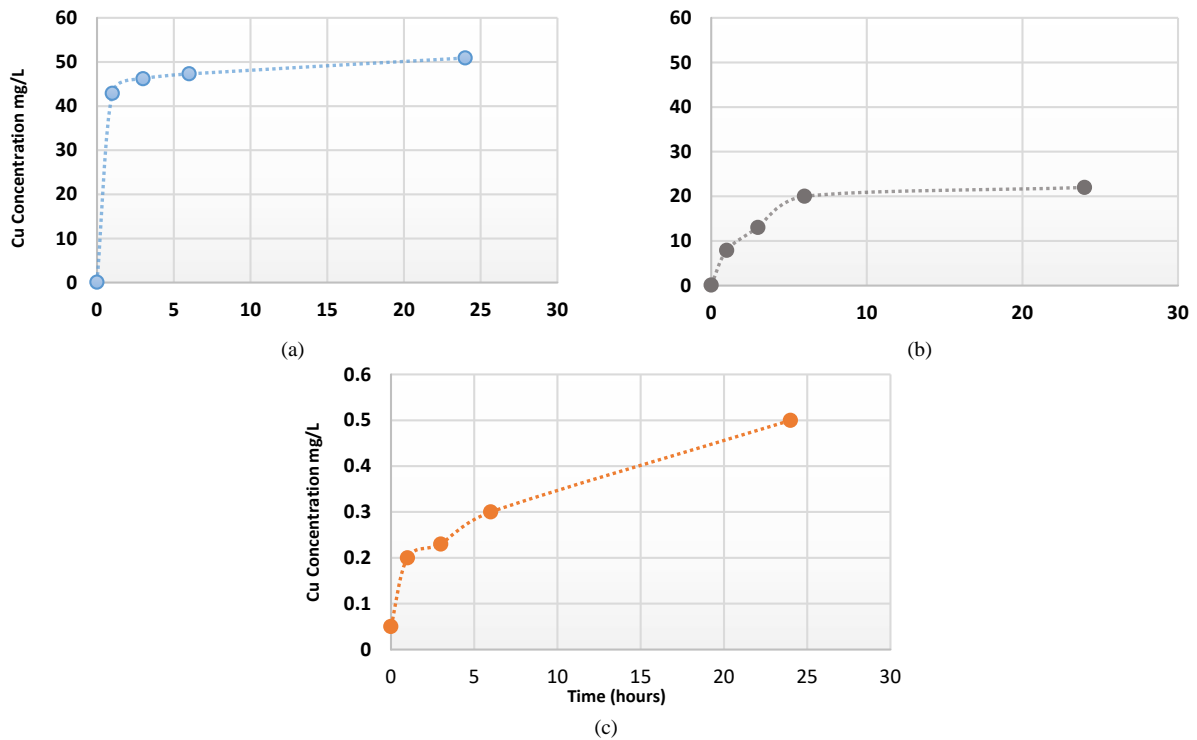
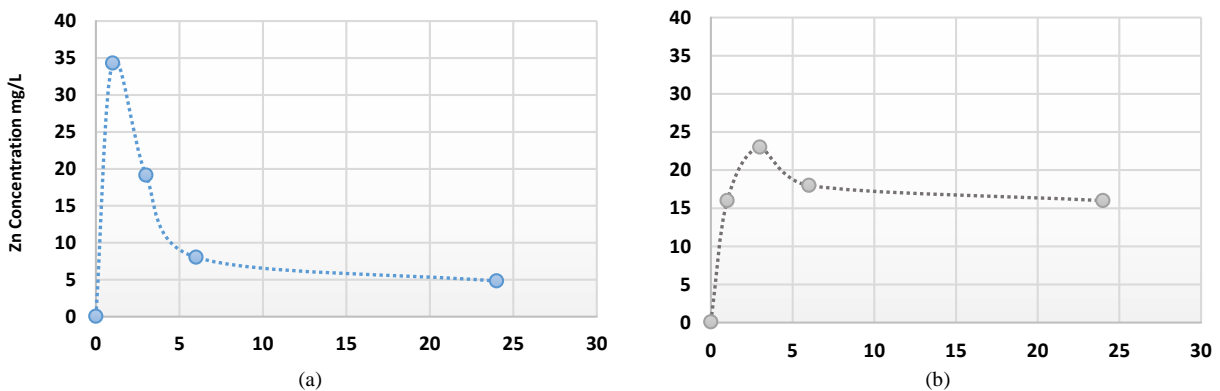


Fig. 2. Copper transport results in freshwater (a), mixing zone (b) and seawater (c)



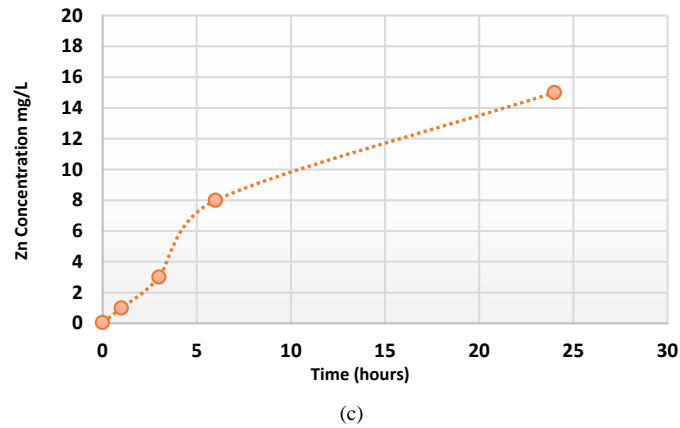
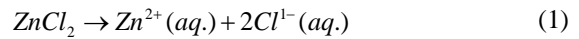


Fig. 3. Zinc transport results in freshwater (a), mixing zone (b) and seawater (c)

In the zinc spill scenario, the freshwater feeding led to wash the aquifer, restrict the vertical advection and diffusion impacts of the zinc spill into the deep water and produced a unique path for the contamination on the top of the aquifer as shown in Fig. 4. This Figure presents photos from the experiments showing clearly the difference between the flow behaviour of copper and zinc spills over 24 hours. When copper was used as a main feeding source spreaded into all porous media, while in the case of the zinc spill used along with freshwater feeding moved into the top path only. Fig. 4 also shows that there is a reduction happening for the contamination path width between 6 hours and 24 hours. This can be explained by the reduction in the water head governing the spill feeding which led to reduce the flow rate with time.

The concentration of chloride in fresh water varied with time for the zinc test. The precursor for

zinc was in chloride form of $ZnCl_2$, so it not surprising that the chloride content increased in fresh water due to the continual chloride flow in freshwater as seen in Fig. 5 and derived from Eq. (1).



3.1.3. Lead

The lead was chosen to simulate the behaviour of one of the heaviest elements of the heavy metals group. The lead spill experiment was carried out using the same test procedure of the zinc experiment. Fig. 6 presents the monitoring of lead concentrations in the fresh water, mixing zone and seawater. Results showed a significant increase in the lead concentration in freshwater after one hour as it reached 8.3 mg/L; however, the concentration then declined up to 24 hours to read 1.3 mg/L.

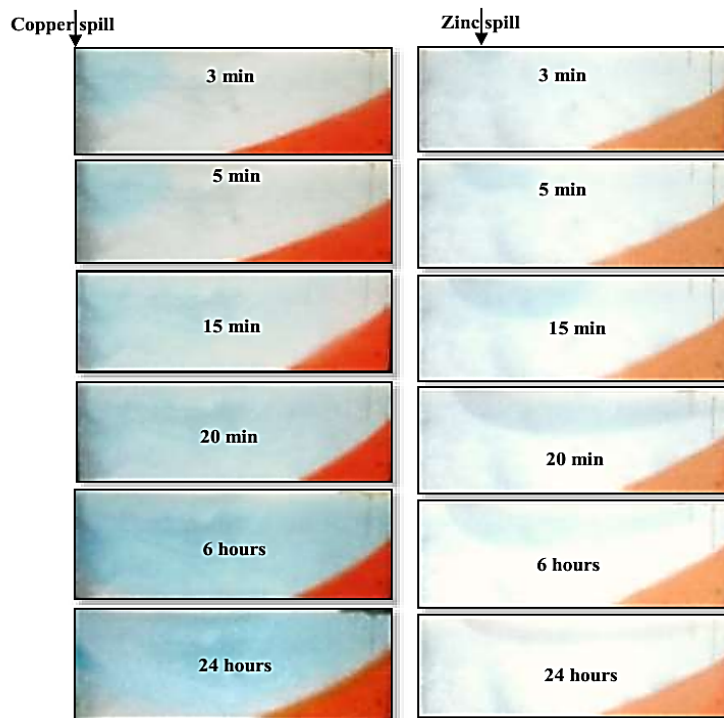


Fig. 4. Photos by an ordinary camera for copper (a) and zinc (b) spill behaviour over 24 hours

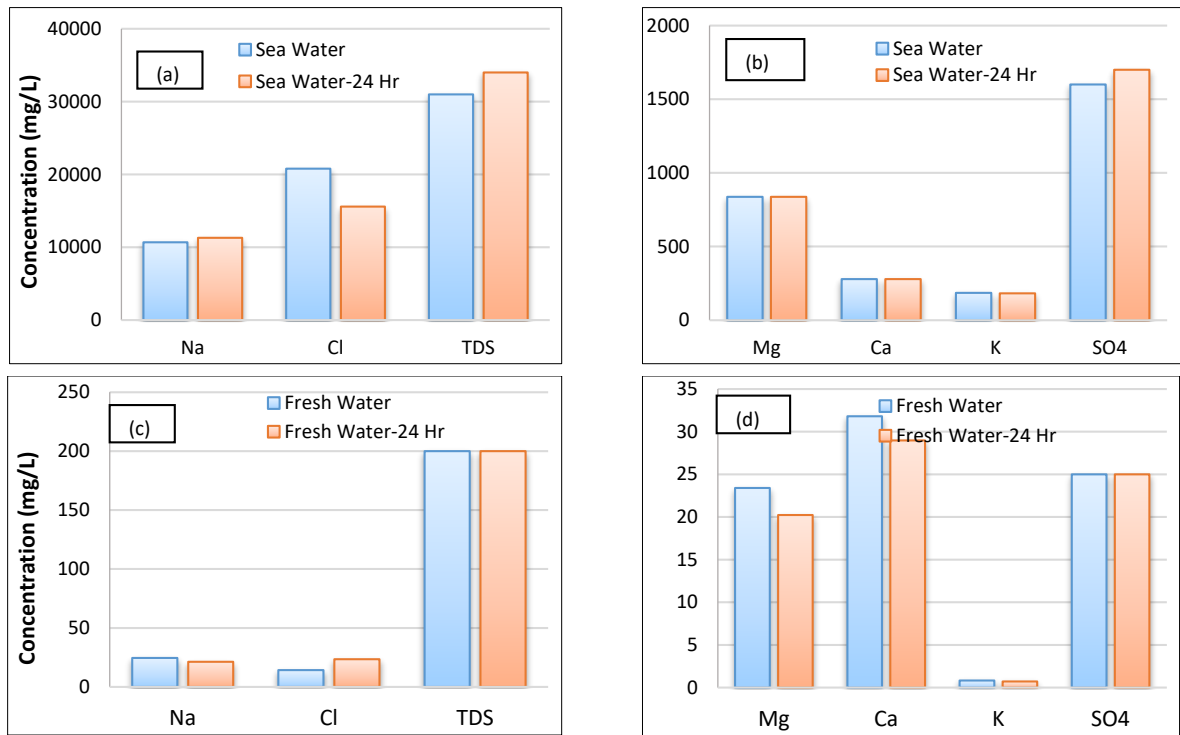


Fig. 5. Element concentrations in seawater (a, b) and fresh water (c, d) before and after zinc spill test

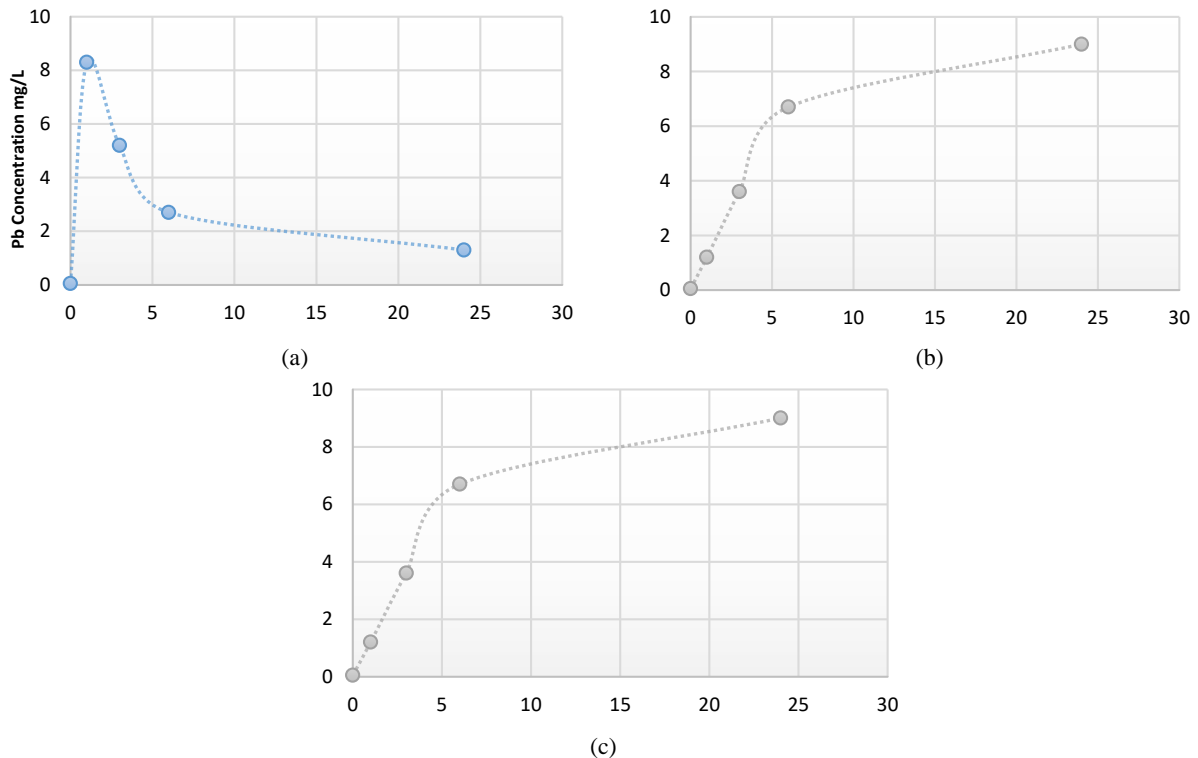


Fig. 6. Lead transport results in freshwater (a), mixing zone (b) and seawater (c)

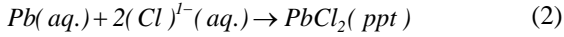
For the seawater, lead concentrations increased significantly with time. This behaviour relatively resembled previous cases of other spills. For lead especially, the relation between time and concentration insinuates a linear behaviour that indicates the possibility of the relative high progress with time. This is in line with Dahmouni et al., (2019) who reported that concentrations of some heavy

metals such Cd, and Pb were significantly correlated with water salinity.

Again, similar behaviour is nearly recorded, herein, in the mixing zone concentration. Lead showed a different behaviour with mixing zone compared with other previous spills because it exhibited linear increase with time. This is perhaps because lead is the heaviest metal among the three adopted elements,

which led to precipitate and transport from the top spill to the mixing zone area.

Unlike the Zinc test, the chloride content in fresh water dramatically decreased in the lead spill test as each mole of lead consumed two moles of chloride to form the precipitate of $PbCl_2$ as seen in Fig. 7 and shown below in Eq. (2):



3.2. Aquifer water quality

As described above, when the heavy metals spill was used as the only recharge source for the aquifer, the concentrations of the whole aquifer reached the spill concentrations in a short period which happened in the case of copper.

On the other hand, when it was used as a discharging point accompanying a feeding freshwater source into the aquifer, the contamination reached 70% maximum in the upper boundary of the aquifer at the contamination path. This happened in the case of the zinc experiment. To sum up, the resistance of the aquifer to heavy metals pollution and the water quality increased with the presence of a renewable freshwater source along with the spill contamination.

This is because the freshwater stream makes the contamination path in the top boundary of the aquifer only. This refers to the risk of the argument of using these untreated effluents as a sole source for recharging the aquifers. The allowable values of these heavy metals for drinking water from different specifications shows that 3 and 5 mg/L is the

maximum for copper and zinc respectively. While 0.1 mg/L is the maximum for lead (WHO, 1985). These restrictive values indicate that any small concentrations of heavy metals in wastewater effluents may affect the quality of aquifer water. In fact, no concentration of heavy metals elements even being low will be safe. Especially, if it continues in water for long-term exposure. Cabezaa et al. (2012) studied the occurrence of emerging contaminants in treated wastewater and groundwater between 2008 and 2010 in Spain. They reported that regardless of the advanced wastewater treatment not all contaminants are totally removed from the treated wastewater. 98 out of the 170 elements analysed are still detected although at low concentrations generally below 100 mg/L.

3.3. Sea water quality

In this study, the heavy metal ions in seawater exhibited a gradual increase in their concentrations with time in all studied cases. However, while copper and lead transported into seawater with only 1% from their spill concentrations, zinc contaminated the seawater by 30% after 24 hours. This refers to the different behaviours of metal ions in transporting into saltwater. Even small concentrations of heavy metals transmitted into seawater are equally harmful to the marine life. Ostapezuk et.al. (1997) reported that the heavy metals ions were markedly found in maritime animals of coastal regions having a flow of contamination in comparison to regions located in unpolluted areas.

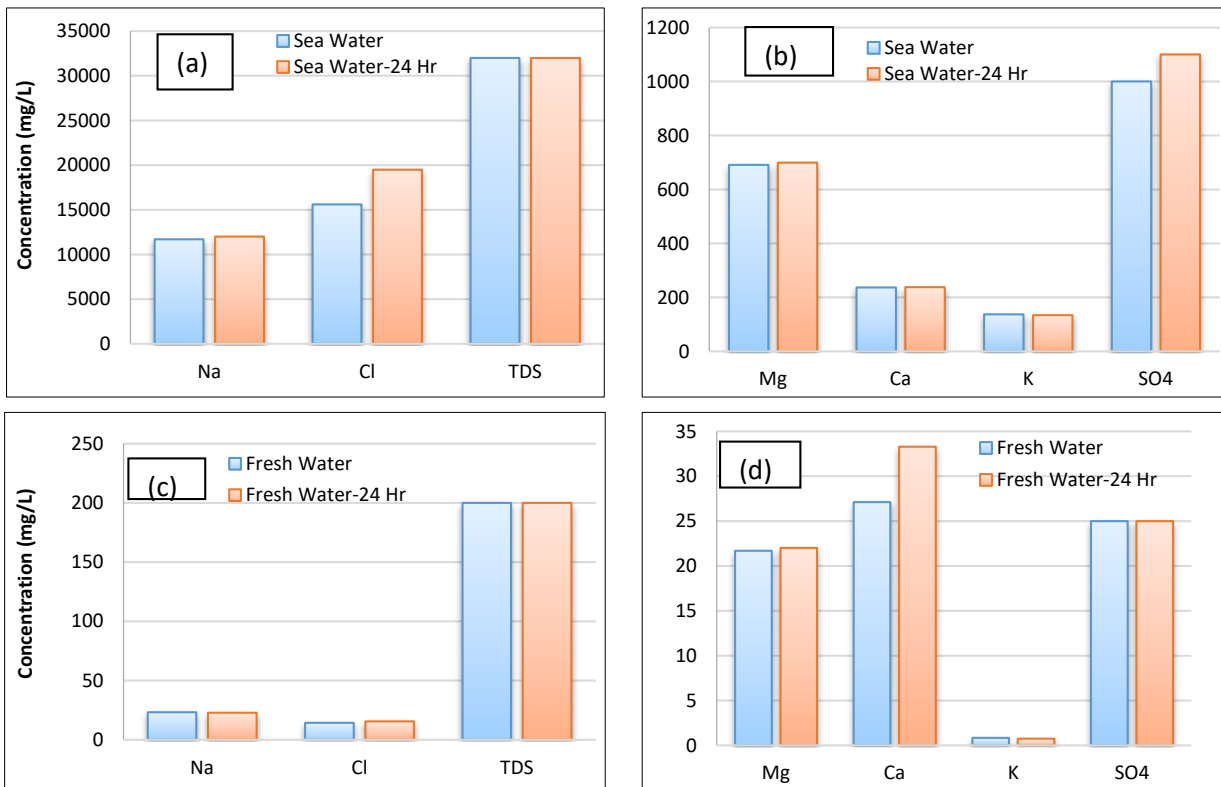


Fig. 7. Element concentrations for seawater (a, b) and fresh water (c, d) before and after lead spill test

This fact proved the transport of these pollutants into marine animals' bodies. Perez-Lopez et.al. (2003) also evidenced that a direct relationship between heavy metals concentrations in seawater and limpet soft tissues was found in the studied area. The levels of Cd and Zn concentrations had the greater spatial differences among other elements. In this sense, there is a general tendency of aquatic organisms to accumulate pollutants of various kinds from the surrounding environment.

Disposal of wastewater containing a trace of heavy metals causes contamination of fish with these metals. Every pollutant in the aquatic environment could affect the physiology, development, growth or survival of the fish; it will also affect humans whom are at the end of this food chain (Khayatzadeh and Abbasi, 2010). By reviewing the maximum daily dose or exposure of some heavy metals for human and animals presented by Govind and Madhuri (2014). The allowable values show that safe concentrations from heavy metals in the day are very small and indicate to the hazardous potential of any additional traces of heavy metals might be transported into the seawater.

3.4. Impacts of heavy metals spills on the seawater intrusion

In another aspect of the relation between fresh water of the aquifer and seawater in the coastal areas, contamination of fresh groundwater by salt intrusion becomes a worldwide alarming problem that threatens many countries depending on groundwater. The important harmful impact of the saltwater intrusion (SWI) is the drop in the available freshwater quantity due to pollution of the groundwater wells by saline. In this section, the influence of the heavy metals spills was investigated on the seawater intrusion process.

3.4.1. Toe length

The toe length (TL) is the length of salt intrusion into a freshwater aquifer measured from the seawater side along the bottom boundary. TL was examined during heavy metals spills for the two different discharging scenarios under a head difference of $dH = 4\text{mm}$ between fresh and sea waters. Intrusion images were captured with the high-speed camera during experiments. Fig. 8 shows TL progression and reduction during the lead experiment. The screenshots in the figure exhibited the progression of the salt incursion into the aquifer before applying the lead spill as TL reached around 19 cm in 60 min measured from the seawater boundary. When the spill recharging was applied, after 60 min, salt intrusion and TL started reducing. With advancing of the spill infiltration into the freshwater, TL keeps reducing up to reach 16 cm after 90 min. Up to six hours, the salt intrusion is stable at 16 cm and then started

advancing into freshwater to reach 18 cm. In the beginning, the spill infiltration pushed the salt intrusion back by generating a circulating motion on the top surface of the salt toe. This scenario could be a permanent case, as it had already ran for more than six hours without a change. Then the toe started advancing again. This advancing behaviour is mainly related to the test procedure, as the spill flow rate decreased due to the head decrease in the feeding tank of heavy metals solution. This can be noted in the last two screenshots of Fig. 8, as the spill plume width decreased at 720 and 1440 min.

This behaviour of the salt toe was observed also in zinc and copper spills, as shown previously in Fig. 4. This proved the physical influence of the spill flows on the salt intrusion without concerning its chemical contents. To sum up, spill discharging from the top of the aquifers, especially, at close locations of seawater beach reduces the seawater intrusion; however, it should be unpolluted flow to be safe to the environment.

3.4.2. Chemicals of the mixing zone

The zone where seawater and fresh groundwater mix in a coastal aquifer is often denoted as an underground estuary (Moore, 1999). It is typically characterised by strong physical features such as zone width and chemical gradients. Therefore, it is an important zone for the transformation of groundwater-derived reactive species (Anwar, 2012). The mixing zone limits can be defined as the surfaces of 1 and 95% seawater content, based on total dissolved solids or chloride ion content. Otherwise, Custodio and Bruggeman (1987) stated that the lower value may be chosen equal to the maximum total dissolved solids for drinking water and the upper one depends on the salt concentration of the seawater. Herein, this study focused on the change of the concentrations of this mixing zone and its chemical compositions after applying heavy metals spills. The experimental results exposed that the salt concentrations in the mixing zones ranged between 10 to 90% from seawater content as shown in the experiment images in Fig. 8.

Applying heavy metals spills in the aquifer domain altered the mixing zone properties as it increased its width and diluted the salt consternations. This can be noted from Fig. 8, as starting from minute 70, the mixing zone colours became wider and lighter. This colour alteration indicates to the reduction of salt concentrations in the mixing zone. In addition, it is obvious that the scenario of the copper spill has a significant impact on the mixing zone rather than zinc and lead spills because the former allowed direct mixing between heavy metals and mixing zone chemicals. This can be noted clearly in Fig. 4 at 24 hours.

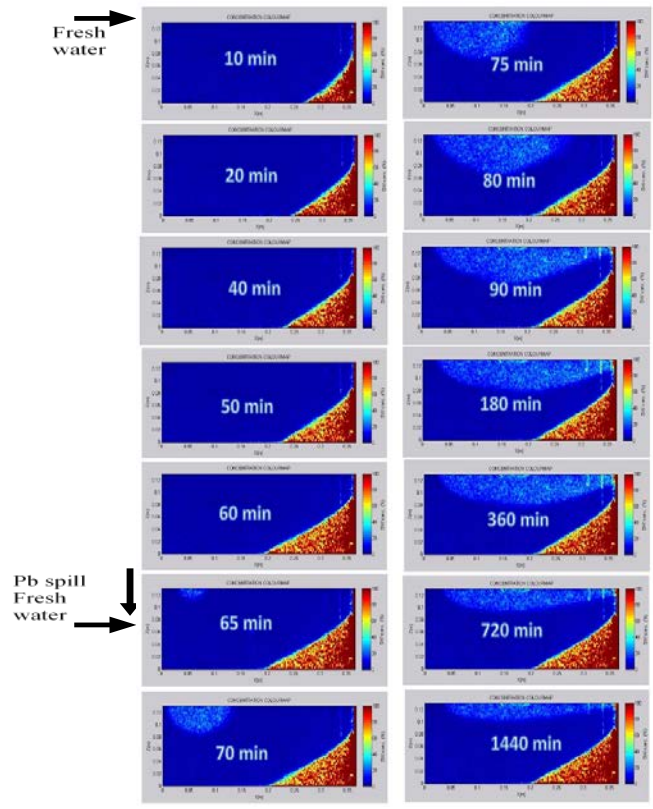


Fig. 8. Screenshots from the video recorded by the high-speed camera for seawater incursion before and after the lead spill

3.5. Numerical simulation results

Numerical models were built for these experimental cases by SEAWAT code. The numerical and experimental measurements matched well, as shown in Fig. 9. The numerical models depicted the reduction of salt intrusion caused by the spill discharging in the two different scenarios; namely zinc and copper spills.

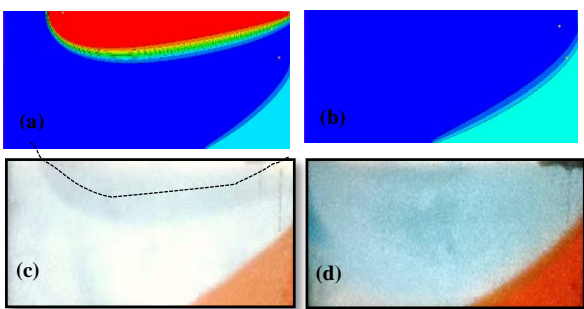


Fig. 9. Screenshots from the and numerical ((a)-Num. Zinc and (b)-Num. Copper) and experimental ((c)-Exp. Zinc and (d)-Exp. Copper) works for seawater incursion status after applying zinc and copper spills by 20 min

There are some minor deviations that are observed in the TLs, especially, at the beginning of each stress period, perhaps this is due to the pressure fluctuations at these moments during experiments. In addition, the width of the spill infiltration plume into

the aquifer was smaller by numerical results than experimental ones. This is perhaps related to the diffusion coefficient values adopted in the numerical models.

4. Conclusions

The resistance of the aquifer to heavy metals contamination increased with the presence of a renewable freshwater source along with the spill contamination. In the case of using the heavy metals spill as a solo recharging source for the aquifer, the concentrations of the whole aquifer reached the spill concentrations in a short period of time.

Any small concentrations of heavy metals in wastewater effluents affect the quality of aquifer water. Therefore, heavy metal ions in seawater exhibited a gradual increase in their concentrations with time in all studied cases. The copper concentration, for instance, after one hour of the test commencing, reached around 85, 44 and 10% from the total concentration at 24 hours in groundwater, mixing zone and seawater, respectively.

Spill discharging from the top of the aquifers, especially, at close locations of seawater beach reduces the seawater intrusion. However, it should be unpolluted effluent to be safe for the aquatic environment. On the other hand, applying heavy metals spills in the aquifer domain altered the mixing zone properties as it increased its width, diluted the salt consternations and added new chemicals.

Acknowledgements

The award of a postdoctoral scholarship by the Egyptian government to pursue this research programme at the Queen's University Belfast (QUB) in the UK is gratefully acknowledged. An extended thanks to all academic staff and technicians of the Queens' Belfast University who supported and helped in this work, especially Dr. Ashraf Ahmed and Professor David Rooney. Thanks also for Mr. Charlie Farrell for his help as a native speaker in revising paper English.

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