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نمذجة الفسفور الغير عضوي علي الغبار المتساقط علي جون الكويت

[*] فاطمة الشمري، [*]علي الدوسري، [*]إقبال العنزي

* مركز أبحاث البيئة والعلوم الحياتية– معهد الكويت للابحاث العلمية– الكويت

خلاصة

لقد تم البحث في سلوك الامتصاص والامتزاز للفسفور الغير عضوي بإستخدام المحاكاة بالنمذجة الرقمية. قد جمعت العينات باستخدام مصائد الغبار خلال الصيف 2011 علي طول ساحل جون الكويت. نتائج العواصف الترابيه بينت انها أساس زيادة المغذيات في جون الكويت والتي تؤدي إلي زيادة نمو الطحالب ومن ثم بدورها إلي الضغط البيئي. وأن العديد من العمليات الفيزيائية المتمثلة في عمليات الامتصاص و الامتزاز والتي تسبب في زيادة أو نقصان مستوي المغذيات. وهذه العلاقه قد أدمجت في نموذج ثلاثي الابعاد للنمذجة الهيدروديناملك (Delft 3D flow) ونمذجة جوده المياه الثلاثي الابعاد (Delft 3D WAQ) التابع للمعهد الهولندي، وقد تم ربطه بنموذج نقل الرواسب. وأظهرت المحاكاة في تعزيز التنبؤ من الفسفور الذائب في مياه خليج الكويت خلال عاصفة ترابية في عام 2011.

Modeling adsorption of inorganic phosphorus on dust fallout in Kuwait bay

EQBAL AL-ENEZI*, ALI AL-DOUSARI* AND FATEMA AL-SHAMMARI*

**Environmental and Life Sciences Research Center*
Kuwait Institute for Scientific Research, Kuwait.
**Corresponding author: eenezi@kisr.edu.kw*

ABSTRACT

Phosphorus (P) adsorption-desorption behaviors on the airborne dust have been investigated by using simulation with numerical modeling. Dust samples were collected during summer 2011 along coastline of Kuwait Bay. Dust storms results showed that substantial nutrients increase in Kuwait Bay which is led to, subsequently, frequent algal blooms and ecological stress. Numerous physical processes give rise to nutrient levels including sediment adsorption/desorption processes. This correlation was incorporated into a three-dimensional hydrodynamic model (Delft3D-FLOW) and a 3D water quality model (Delft3D-WAQ), originated by Deltares, the Netherlands and was linked to a sediment transport model. Simulations showed an enhanced prediction of dissolved phosphorus in Kuwait Bay during the last dust storm in 2011.

Keywords: Adsorption; desorption; dust; nutrient; water quality model

INTRODUCTION

Dust storms have become one of the most important phenomena occurring in Kuwait, formed by the action of strong winds on dry, fine-loose sediment, which have been given high attention as a potential source of environmental pollution (Khalaf *et al*.,1985; Al- Awadhi, 2005; Al-Dousari *et al*., 2012).

The major source of dust fallout in Kuwait are derived from the dry Mesopotamian flood plain in the central and southern Iraq, due to the NW-SE wind direction, that settle over the northern part of the Arabian Gulf and Kuwait Bay (Khalaf *et al*.,1985; Al-Awadhi, 2005; Al-Dousari & Al-Awadhi, 2012).

After the dust fallout settlement in the marine water as suspended sediment, serious marine environmental problems may occur, due to adverse effects on the water quality and marine life. Therefore, suspended sediments play an important role in the increase and distribution of pollutants, and could adsorb a variety of pollutants, such as toxic metals, nutrients and hydrocarbons; they can also release them again into the marine environment.

Sediments play an important role in minimizing the risk of eutrophication, as they may act as sinks for important nutrients such as phosphorus. However, if the environmental conditions change (i.e salinity and pH), the phosphorus-associated sediments may release phosphorus into the water column and sediment may serve as phosphorus sources, which could stimulate the growth of cyanobacteria and algae (Harrison, 2001).

In aquatic systems, phosphorus is found as orthophosphate, and plays an important role in photosynthesis (i.e. primary productivity). The orthophosphate ion is a significant form of inorganic phosphorus and is directly taken up by aquatic plants for nutrition. The dissolved inorganic phosphorus (DIP), is a very important fraction as it is the most readily available phosphorus fraction to aquatic plants, and often is considered the most critical fraction contributing to accelerated eutrophication of surface waters. The total amount of phosphorus bound to particles can be broadly divided into two components; exchangeable phosphorus and non-exchangeable phosphorus.

Most of the phosphorus percentage in the water body is incorporated into particulate inorganic matter (e.g. apatite and other minerals) and is adsorbed by iron-manganese oxide/oxyhydroxides (Paytan & McLaughlin, 2007). The sediment particles which have iron and aluminium oxyhydroxides on their surface possess a high phosphorus capacity to adsorb more phosphorus from the water column (Paytan & McLaughlin, 2007), as the negative charge of phosphorus ions in the sediment solution is bonded to positively charged mineral surfaces by covalent bond through ion exchange (Valsami-Jones, 2004). The phosphorus adsorption and desorption processes are affected by the sediment particle size and mineralogy, salinity, charge density and the temperature as most important control factors. This study focuses on the concentration of phosphorus adsorption on the dust particles.

Some researchers have studied the mineralogical, composition and sources of dust fallout deposition in Kuwait. The dominant minerals in the dust fallout samples are plagioclase, quartz, calcite, dolomite and feldspars as described by Khalaf *et al*.,1985; Al- Ghadban &Al- Sammak 2005; Al- Awadhi, 2005. There is very limited study on the effect of the dust fallout on marine water quality and marine life. Al-Yamani *et al*. 2006 studied the effects of eolian dust on phytoplankton in the water off Kuwait, and found a positive correlation between the Algal growth and dust fallout.

The aim of this study is Determining the relationship between the water quality and the production of phosphorus adsorption from the dust particles through the water column in the Kuwait Bay.

METHODOLOGY

A dust collector sampler was used to collect the dust fallout during the summer months. Annually, the most intensive dust starts sometime between April and July. In this project, the dust fallout samples were collected from May and August during the summer of 2011 from six stations, close to the coastline of the Kuwait bay. Figure 1 shows the locations of dust fallout samples, which were close to the Kuwait Bay coastline. Some laboratory experiments were carried out at the dust samples, such as loosely sorbed phosphorus and maximum adsorption isotherm on the dust particles, as described below.

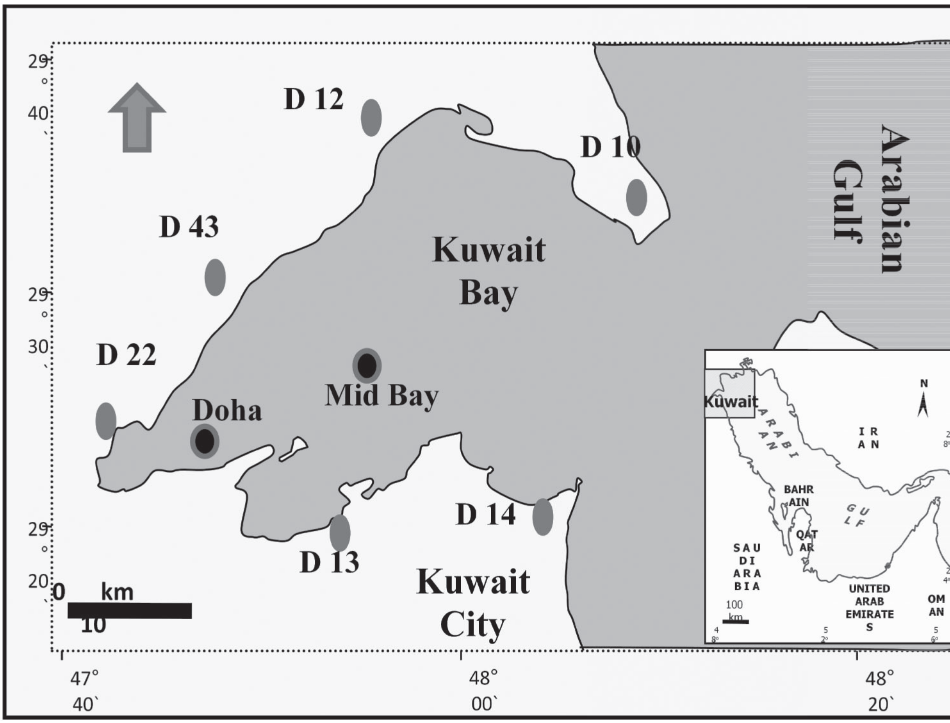

Fig. 1. Locations of dust collector sampler stations.

Loosely Sorbed Phosphorus Experiment

To remove the adsorbed phosphorus (P) from the surface of the dust particles, an extraction method for exchangeable or loosely sorbed P described in Ruttenberg (1992) and Smith *et al*. (2006) was used. The extraction by a solution of $MgCl_2$ was used in this experiment to remove the P attached or loosely sorbed on the sediment surface. Before experiments commenced, the wet sediment samples were centrifuged at 2,500 rpm for 15 minutes to remove the pore water. Samples of wet sediment weighing 0.5 g were placed into 50 ml centrifuge tubes and 10 ml of the 1M $MgCl_2$ solution was added. The tubes were shaken for 2 hours and centrifuged at 2500 rpm for 15 minutes. The supernatant was then filtered through a 0.45 µm filter membrane and the solution kept for analysis. Another 10 ml of $MgCl_2$ was added to the residue sediment in the centrifuge tubes and the same process was repeated. The analysis was performed twice on the all dust samples. The residue sediment was washed with deionised water twice, then shaken and centrifuged as described above. The solutions were analysed using ascorbic acid according to methods of Murphy & Riley (1962). The loosely sorbed phosphorus was then calculated.

Sorption Isotherm Experiment for Phosphorus

According to the procedure described in SERA-IEG17 (2000), 1 g of wet sediment sample was individually placed into 100 ml Erlenmeyer flasks and treated with 50 ml of a KH_2PO_4 solution with an initial P concentration (P_0) of 0.2, 0.4, 0.6, 0.8 and 1 mg/l in a 0.01 M $CaCl_2$ matrix for low P concentrations and P_0 of 0.5, 1, 2, 5, 10, 20, 30, 40 and 50 mg/l for high P concentrations. The mixture was sealed with parafilm and centrifuged at 150 rpm for 24 hour at 25 ± 1 °C and then filtered through a 0.45 µm membrane filter. The filtrate was then analysed for Soluble Reactive P (SRP) using a spectrophotometer at a wavelength of 880 nm according to Murphy & Riley (1962) and the SERA-IEG17 (2000) methods.

Hydrodynamics and Water Quality Simulation

Coupled hydrodynamic and water quality numerical model was developed for Kuwait Bay, taking into account effects of dust fallout to the surface water. The model was developed based on Delft3D modeling software (Deltares, 2011a; 2011b). Hydrodynamic modeling applied the calibrated Kuwait Bay model of Pokavanich & Al-Bannaa (2012). The hydrodynamic model simulates movement and mixing of water due to effects of tide, wind, and water density difference induced by variation of water temperature. Water quality model used in this study applied Delft3D-WAQ model. The water quality modeling is used to monitor changes of inorganic phosphorus in the water column (PO4), inorganic phosphorus absorbed by sediment (APO4) and dissolved oxygen (DO). Figure 2 shows conceptual diagram of water quality model applied in this study. Water quality model was calibrated and validated against limited field data in terms of overall nutrient concentration and distribution, which is not shown here. Further details of water quality process descriptions are given in Deltares (2011b).

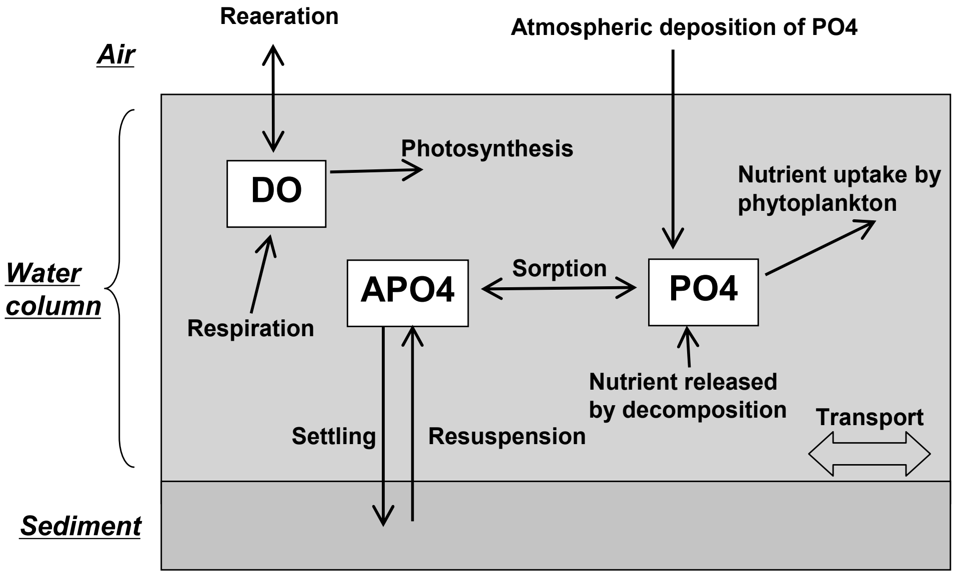

Fig.2. Conceptual diagram of water quality model for phosphorus budget modeling taking into account phosphorus absorption and direct atmospheric deposition.

RESULTS AND DISCUSSION

Figures 3 and 4 indicate a positive correlation between quartz and dolomite concentration with adsorption/desorption processes of phosphorus in dust samples, with some exceptions. However, Figure 5 shows a negative correlation found between calcite and adsorption/desorption processes. This may be due to the fact that "Seawater is characterized by high ionic strength, high pH values, the dominant P form is HPO_4^{2-} and high availability of cations, such as Ca^{2+}, Mg^{2+}, and Na^{+}, which form ion pairs with the P species, resulting in significantly changing the dissociation of phosphoric acid" (Jahnke, 2000). All the adsorption isotherms models such as (Linear, Freundlich and Langmuir) can describe the orthophosphate adsorption process in most natural estuaries, including the Kuwait bay. The Linear model is preferred, owing to its simplicity and efficiency. The Langmuir or Frendulich adsorption isotherm fitted a wider range of experimental data and used for high concentration level (Valsami-Jones, 2004). The Linear adsorption model had the advantage of being simpler, making the Linear model more efficient, when incorporated into the numerical model. Therefore, the linear model was used to calculate the adsorption process.

The dust fallout contain several minerals such as quartz, calcite and dolomite. The chemical compositions of these minerals are SiO_2, $CaCO_3$ and $CaMg(CO_3)_2$, respectively.

Figure 6 shows that in the concentration of dominant metals in dust samples, calcium (Ca) was to be found in a higher concentration than aluminum (Al) and iron

(Fe), especially in location D 22 and D 43. The results also show that the adsorption of phosphorus is highest in locations with high Ca, Al and Fe with some exceptions, which may be caused by the phosphorus being very reactive in seawater, thus reacting with many metals to form insoluble compounds, thereby controlling metal solubility. The chemical reactivity of phosphorus in the aqueous systems depends on the sediment composition and pH values. For example, the highest phosphorus availability in sediment ranges from pH values 6 to 7. At a high pH value of > 7, the availability of P is as calcium phosphate, whereas, at lower pH values below 7, phosphorus may be associated with Al and Fe metals (Valsami-Jones, 2004). Therefore, the pH value is considered a function of the surface charge of the mineral surface area of the sediment.

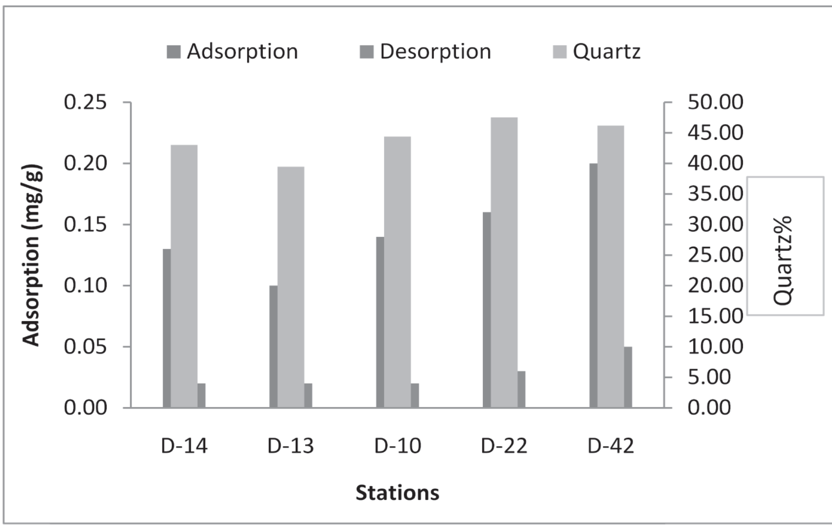

Fig. 3. Phosphorus adsorption/desorption processes on quartz

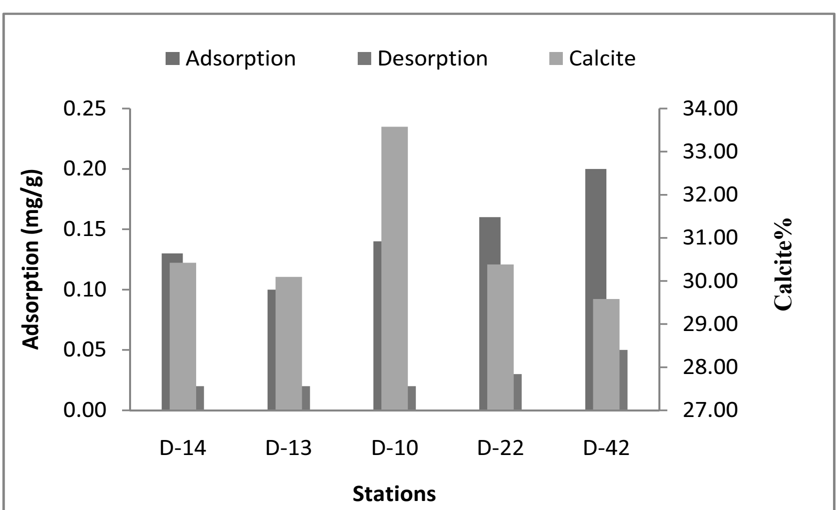

Fig.4. Phosphorus adsorption/ desorption processes on calcite

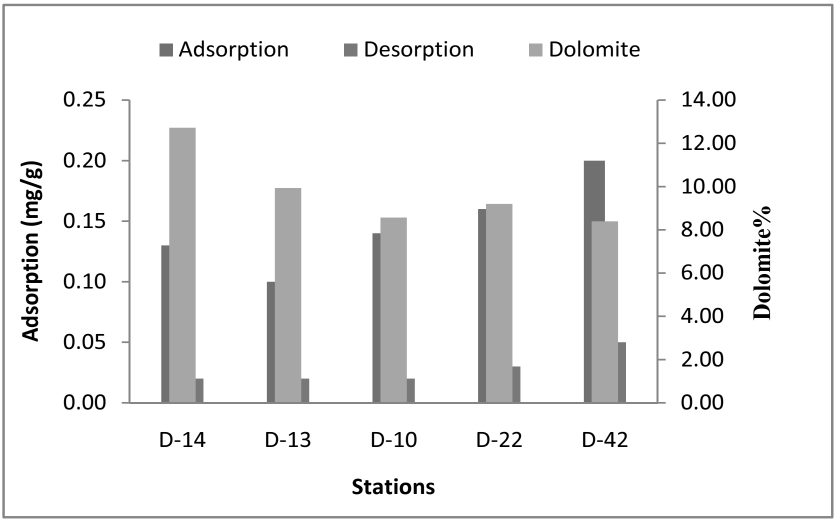

Fig. 5. Phosphorus adsorption/desorption processes on dolomite

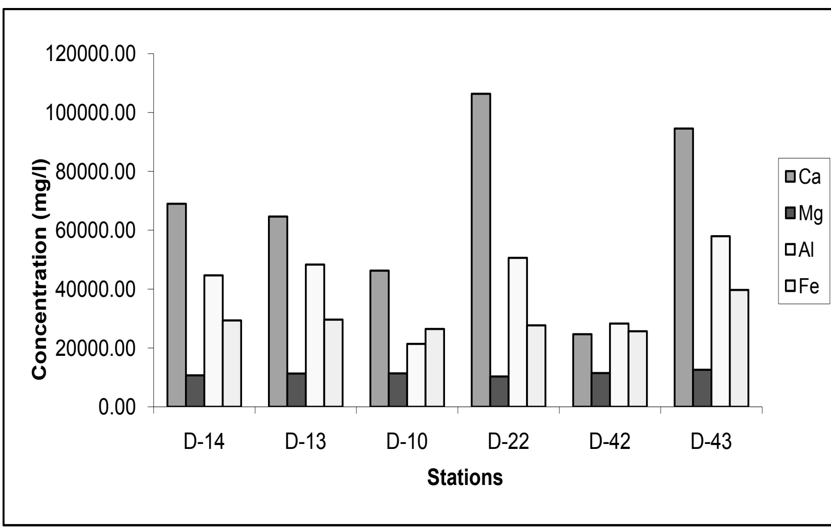

Fig. 6. Dominant metals concentration at different locations

Also, the results found show that the maximum phosphorus adsorption was in very fine silt and clay samples. Fox *et al*. (1989) summarized the different factors affecting the adsorption processes such as phosphorus concentration, pH value, clay fraction of the sediment, depth of water, ion concentration and organic matter of the sediment. Sharma & Reddy (2004) studied other factors affecting the sorption of contaminants on the sediments, which relate to the sediment characteristics, such as mineralogy, permeability, porosity, texture, homogeneity, organic carbon content, surface charge, surface area and pH value. Andrieux-Loyer & Aminot (2001) studied the relationship between phosphorus and the grain size of sediments in French coastal areas in the Bay of Seine Loire and Gironde estuaries. They noted that the exchangeable phosphorus (exch-P) and Fe/A/- bound phosphorus are related significantly to the fine fraction (<63μm).

Therefore, the suspended particles play an important role in phosphorus concentration and recycling between the suspended particles and overlay water column in marine environments. They provide a large surface area for phosphorus adsorbed and can strongly affect the phosphorus concentration in the water column (Li *et al*., 2006). Reddy *et al*. (1996) measured the P flux during sediment resuspension under laboratory conditions and found that the resuspension flux of P was higher than the diffusive flux.

Figure 7 shows the maximum phosphorus adsorption in very fine silt samples and clay samples. Fox *et al*. (1989) summarized the different factors affecting the adsorption processes such as phosphorus concentration, pH value, clay fraction of the sediment, depth of water, ion concentration and organic matter of the sediment. Sharma & Reddy (2004) studied other factors affecting the sorption of contaminants on the sediments, which relate to the sediment characteristics, such as mineralogy, permeability, porosity, texture, homogeneity, organic carbon content, surface charge, surface area, and pH value. Andrieux-Loyer & Aminot (2001) studied the relationship between phosphorus and the grain size of sediments in French coastal areas in the Bay of Seine Loire and Gironde estuaries. They noted that the exchangeable phosphorus (exch-P) and Fe/A/- bound phosphorus are related significantly to the fine fraction (<63μm).

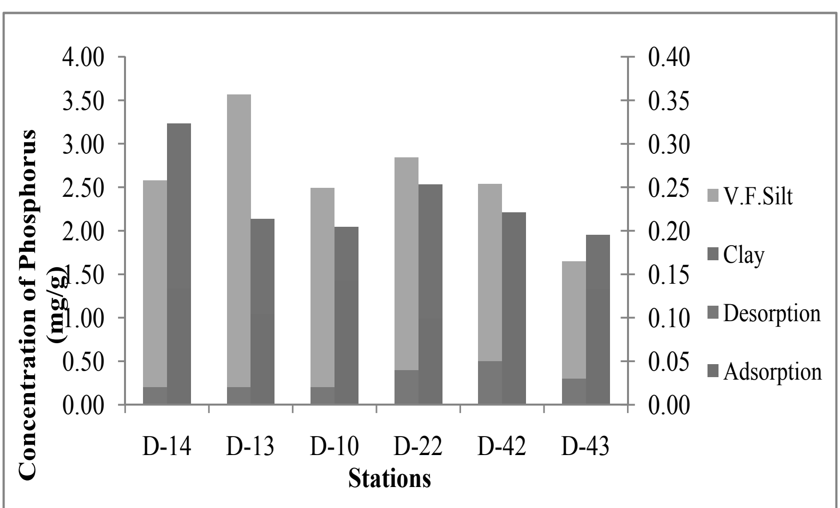

Fig. 7. The relationship between the dust size and phosphorus adsorption/desorption process at different locations.

The tides in Kuwait Bay are classified as mixed and meso-tide, ranging between 3.3 m at spring tide and 2.0 m at neap tide (Pokavanich & Al-Banaa, 2012). The phenomenon is dominated by a semi-diurnal component, which means it often has two high tides and two low tides a day, but, sometimes one high and one low tide a day. Modeled results have found that the tide ranges increase from the mouth of the bay towards the inner part of the bay. Figure 8 shows the influence of the dust particles on the orthophosphate concentration and adsorption process in the water column of the Kuwait bay. From these results it can be observed that the orthophosphate concentration increases in the water column after intensive dust deposition. Therefore, the dust deposition in the Kuwait Bay might have resulted in several problems in water quality, such as high turbidity, high nutrient concentrations and low-dissolved oxygen concentration, which leads to massive fish death, toxicity and low biodiversity. The algal bloom or red tide (excessive growth of phytoplankton in seawater) is usually an indicator of negative anthropogenic influences on the marine environment.

Figures 8 and 9 show the effect of dust fallout on the phosphate concentration in the waters of the Kuwait Bay. It can be seen that at Doha stations, without air dust deposition, the phosphate concentration (PO_4^{-3}) was found to be much lower than at the Midbay station. This may be because the phytoplankton in waters at the Doha stations use up the PO_4^{-3} more than those at the Midbay stations. However, the PO_4^{-3} concentration is found to increase at both locations after dust fallout activity, due to the air dust deposition in the water and release of the adsorbed phosphorus on the dust particles into the water column. At the Doha station, the range of phosphorus concentration in the water increased from 0.025 to 0.1 mg/l after dust deposition. Whereas, at the Midbay station, the increase in the water column was slight (0.038 to 0.06 mg/l) due to the water current exchanging and diluting in the seawater.

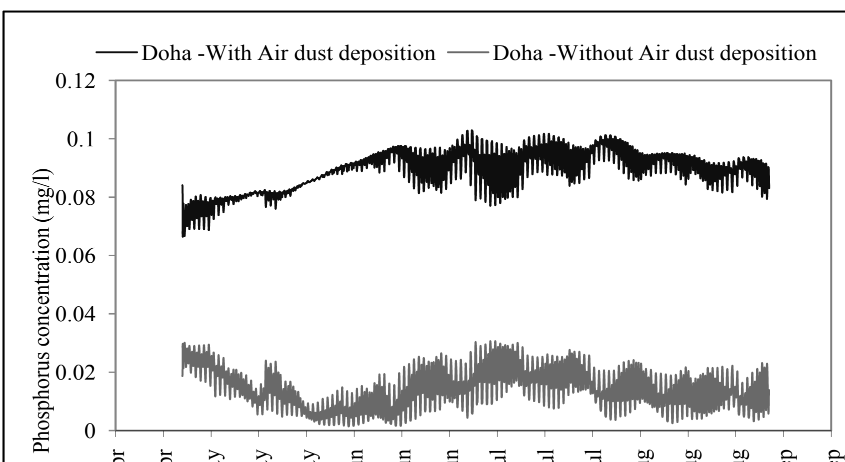

Fig.8. Comparison of time- series of phosphorus concentration for the Doha station with and without dust deposition during 2011.

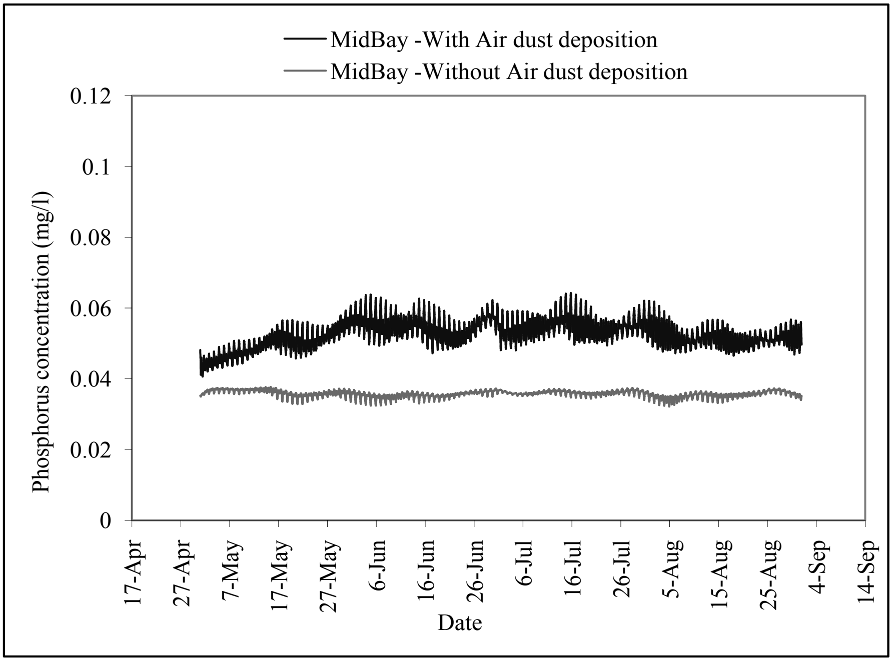

Fig. 9. Comparison of time- series of phosphorus concentration for the Midbay station with and without dust deposition during 2011.

A three-dimensional hydrodynamic model (Delft3D-FLOW) and a three-dimensional water quality model (Delft3D-WAQ) were used to predict water circulation and budget of inorganic phosphorus in water column, inorganic phosphorus absorbed to the sediment and dissolved oxygen in the water column. The preliminary results of the numerical model suggested that phosphorus concentrations in the water column were elevated due to direct dust fallout to the bay (Figure10). Increase in concentration of phosphorus nutrient may have direct implications on increasing productivity of phytoplankton in Kuwait Bay. This study summaries the main conclusion as, the dust deposition can be found to have a significant link with algal blooms in the marine environments. Western side of Kuwait Bay is receiving much more dust fallout and finer in size particles compared to the eastern side.

CONCLUSION

This study has found a positive correlation between dust deposition and phosphorus levels in water in the Kuwait bay. The majority of phosphorus adsorption was on finer dust particles, rather than coarser particles. This is believed to be caused by the surface areas present in the fine sediment fractions being larger than those in the coarse sediment fractions. A positive correlation was found between phosphorus adsorption in the dust particles and certain parameters including the tidal range, sediment metal concentration, sediment mineralogy and suspended sediment.

Calcite and dolomite were found to have a negative correlation with the adsorption of phosphorus, whereas quartz was found to give a positive correlation. This may be caused by the type of surface charge and chemical composition in the dust particles. The dust particles after deposition in the water, will act as suspended sediment, because it acts to remove (sink) or release (source) phosphorus from or to the water column depending on the phosphorus concentration in the water column. Therefore, size and chemical composition of the dust particles were found to be important factors controlling the behavior of phosphorus adsorption

This study reports on the development and application of an integrated water quality model (WAQ /Delft3D) for predicting the hydrodynamics, sediment transport, and water quality processes in Kuwait bay waters. The nutrient cycle has been coupled with the sediment transport process, in order to take into account the nutrient exchange between bed sediments and the overlying water column via sediment erosion and deposition. This extra nutrient flux is related to the adsorption/desorption process.

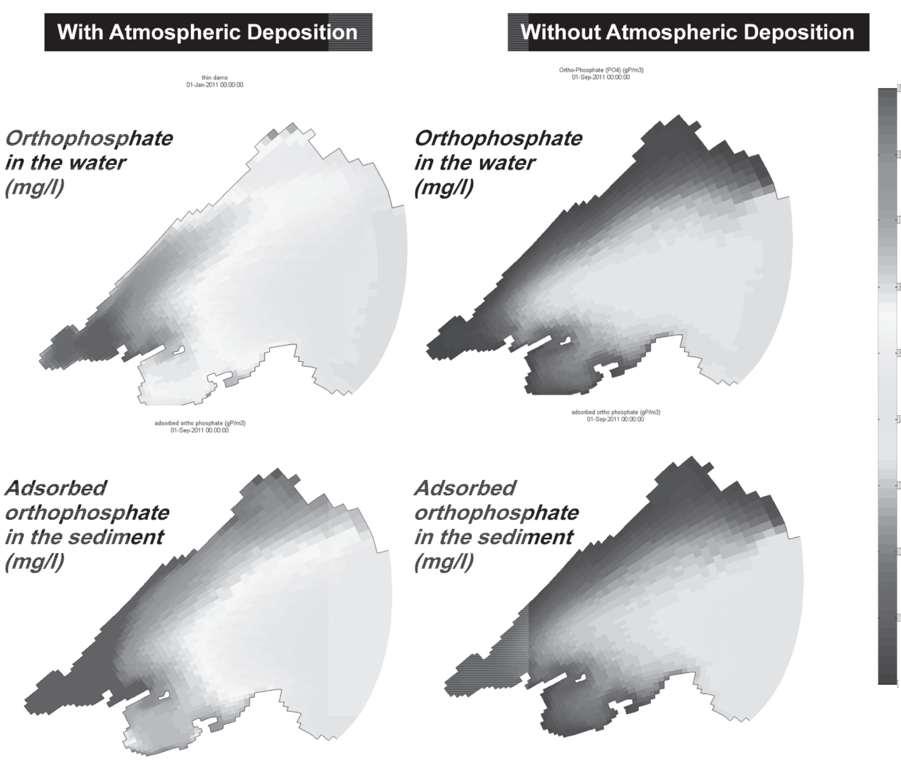

Fig. 10. Comparison of horizontal distribution for the orthophosphate and adsorbed orthophosphate in the Kuwait bay with and without the dust deposition.

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