Nitrate and Phosphate Pollution in Surface and Ground Water in Western Malaysia

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Summary: Concentration levels of nitrate and phosphate in river and ground water samples from 9 different states of western Malaysia were determined. It was found that most of the rivers are slightly polluted with nitrate and phosphate. The highest concentration of nitrate (26.0 mg/ L) was found in Melaka state in the river of Batang, while the lowest concentration of nitrate (2.61 mg/ L) was found in the Terengganu state in the river of Besut. The highest concentration of phosphate (0.66 mg/ L) was found in Penang state in the river of Kulim. The minimum concentration of phosphate (0.02 mg/ L) was found in different states. The most important sources that contribute to the pollution were raw crops, irrigated agriculture and over-application of animal wastes.

Introduction

Nitrate and phosphate pollution has been given less attention since the time Malaysia has taken the plunge in the cyber era, leaving behind the agricultural industry. Surface and ground water are the environmental areas that are highly affected by nitrate and phosphate pollution. Nitrates are one of the most problematic and widespread of the vast number of potential ground water contaminants [1]. Nitrate analysis results are expressed as either nitrate-nitrogen ($NO_3 - N$) or as nitrate (NO_3). In order to systematically address the fundamental aspects of nitrate pollution, it is necessary to understand the nitrogen cycle from chemical as well as microbiological perspective. It is important to delineate natural and man-made sources of nitrate in water reservoirs. Health related and other effects of excessive concentrations of nitrate in water must be addressed too.

Nitrogen is essential for all types of life, and most crops require large quantities to sustain high yields. Plants use nitrate from the soil to satisfy nutrient requirements. Sometime rain or irrigation water leaches the highly soluble nitrate into the subsurface drainage system. The compounds containing nitrate ions are highly soluble and can be easily leached away by water, peculating down through the soil. In contrast, the phosphate forms bonds with soil particles which are relatively stable [2]. An increase in nitrate levels can occur from man made sources such as septic systems, fertilizer runoff and improperly treated wastewater. The World Health Organization recommends that drinking water should not contain more than 10 mg/ L of nitrate [3]. Nitrogen is present in our environment in several forms including dissolved molecular nitrogen, ammonia / ammonium, nitrate, nitrite and numerous organic forms. Nitrogen is also the most abundant gas in the atmosphere but plants cannot use nitrogen in this form. Nitrogen cycle starts when nitrogen-fixing bacteria fix the nitrogen (changed to a useful form) by combining it with hydrogen to make ammonia (NH_3) some of which combine with H^+ in H_2O to become ammonium (NH^+_4). Nitrite-forming bacteria combine ammonia with oxygen-forming nitrites, (NO_2^-). The nitrate-forming bacteria convert nitrites into nitrates (NO_3^-). Now the nitrogen is in a form that can be absorbed and used by green plants [4].

Sources of nitrogen include atmospheric inputs (precipitation and fallout), biological fixation, and inputs by ground water and man-made influences such as the effluent from sewage and runoff from agricultural areas. Since nitrogen compounds are important, high nitrate concentration in wastewater effluents or from agricultural runoff can affect primary productivity and community structure [5]. The point sources of nitrate and phosphate pollution are sewage treatment plants, factories, accidents, gas stations.

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Non-point sources are agriculture, urban runoff, and septic systems.

Phosphorus in nature exists mainly as phosphate but in water it may occur in several forms, including soluble reactive phosphate and total phosphorus. Phosphates in waster are the primary sources of excess amounts of nutrients in water.

Phosphorus is essential for plant growth and is often the limiting nutrient in aquatic ecosystem. Phosphates are used in fertilizers, pesticides, industry and cleaning compounds. Phosphate deficiency retards plant growth whereas additional contribution of phosphate to ecosystem accounts for eutrophication. The threshold value of phosphate for drinking water is 0.1 mg/ L [6].

In general, nitrate and phosphate have important impacts on environment and human health. Both nitrate and phosphate initiate eutrophication - an aging process that slowly fills water bodies with sediments and organic matter that use up dissolved oxygen.

Humans, if consume high concentrations of nitrate though drinking water, may develop cancer causing agents known as N-nitroso carcinogens, which cause lymphatic cancer. Infants, if exposed to high level of nitrate, will exhaust supply from their blood hemoglobin that is storing the baby's system of oxygen. In the worst cases, brain damage or death results. This is methemoglobenemia, also known as blue baby syndrome. In some cases, nitrate may have been the cause of miscarriages in pregnant women.

The main objective of the current study was to determine the concentration of nitrate and phosphate in rivers and wells of Peninsular western Malaysia and compare the results, with the guidelines set for water quality in Malaysia (2000). The study will also relate the extent of nitrate and phosphate pollution to current agricultural and animal farming activities.

Results and Discussion

The nitrate content of drinking water has been rising at an alarming rate in both developed and developing countries owing largely to a lack of proper sewage treatment, and excessive fertilizer application. Nowadays, nitrate risk analysis (including exposure consequences and control) is warranted in high exposure areas of Europe, USA, Japan, South-East Asia and Latin America [5].

The addition of phosphorus, as phosphate ion, to natural waters is one of the most serious environmental problems because of its contribution to the eutrophication process. Nitrate pollution also contributes to eutrophication but phosphate appears to be the main source of this pollution in fresh water reservoirs.

In natural waters, phosphorus is often the limiting nutrient, i.e. algal growth is inhibited by the supply of phosphorus but not, in general, by the supply of carbon and nitrogen. Throughout the world, there are numerous examples of increasing eutrophication, or algal blooming of lakes and water reservoirs, e.g. Great lakes in USA, water reservoirs along the Volga River in Russia and many artificial water reservoirs in Asia [6]. The nitrate and phosphate concentrations of river and ground water samples from 9 states, i.e., Kedah, Perak, Penang, Selangor, Negeri Sembilan, Melaka, Johor, Padang, and Terengganu, of Peninsular Malaysia were determined.

Determination of Nitrate and Phosphate in Kedah State

Kedah is in the northwestern part of Peninsular Malaysia. Three major rivers namely: Sg. Krian (river is called sungai in Bahasa Malayu language abbreviated as Sg), Sg. Muda and Sg. Padang Terap in the state were tested for nitrate and phosphate pollution. Three stations were selected at each of the three rivers for sample collection.

The average nitrate concentration at three stations in Sg. Krian was 5.69 mg/ L, and in Sg. Muda, was 4.30 mg/ L. High average concentration of nitrate i.e. 16.57 mg/ L was found in Sg. Padang Terap. The average phosphate concentration in Sg. Krian was 0.04 mg/ L, and in Sg. Muda, was 0.05 mg/ L. High average concentration of phosphate i.e. 0.30 mg/ L was found in Padang Terap as shown in Table-1. The high concentration of nitrate and phosphate in Padang Terap may be due to the application of artificial fertilizer to paddy and

Table-1: Nitrate and Phoshpate Concentration in the Major Rivers of Kedah State

River	Nitrate Concentration (mg/ L)				Phosphate Concentration (mg/ L)			
	Station 1	Station 2	Station 3	Average	Station 1	Station 2	Station 3	Average
Krian	5.75	5.54	5.77	5.69	0.04	0.05	0.03	0.04
Muda	4.30	4.22	4.38	4.30	0.05	0.05	0.06	0.05
Padang Terap	16.74	16.05	16.91	16.57	0.32	0.27	0.31	0.30

Table-2: Nitrate and Phosphate Concentrations in the Rivers of Perak State

River	Nitrate Concentration (mg/ L)				Phosphate Concentration (mg/ L)			
	Station 1	Station 2	Station 3	Average	Station 1	Station 2	Station 3	Average
Larut	22.09	23.03	23.00	22.71	0.57	0.58	0.57	0.57
Selinsing	18.60	18.90	18.78	18.76	0.01	0.03	0.02	0.02
Raia	11.00	10.50	11.51	11.00	0.04	0.03	0.05	0.04
Kinta	5.70	6.20	5.88	5.93	0.02	0.01	0.03	0.02

rubber trees plantation. Over application of fertilizer causes the nutrient to leach into the river.

Four rivers namely, Larut, Selinsing, Raia and Kinta were tested for nitrate and phosphate pollution in the state of Perak. The high average concentration of nitrate (22.71 mg/ L) and phosphate (0.57 mg/ L) were found in Sg. Larut. The average nitrate concentration in Selinsing was 18.76 mg/ L, in Raia, was 11.00 mg/ L, and in Kinta, was 5.93 mg/ L. The average phosphate concentration in Selinsing was 0.02 mg/ L, in Raia, was 0.04 mg/ L and in Kinta, 0.02 mg/ L as shown in Table-2. The high concentration of phosphate and nitrate may be caused by the application of fertilizer by palm oil planters. Palm oil plantation utilizes high amounts of nitrate and phosphate based fertilizer to feed the crops. These nutrients may run-off and leach to the river, hence causing pollution. Pig farming near Larut may also be one of the contributors to the pollution. Overflow of pig sewage pond during rainy days may induce nitrate contamination. Irresponsible practice of letting the effluent of pig farm straight to the river without treating it may worsen this condition.

The river, Selinsing is polluted with nitrate because of the operation of pig farms upstream it, while Raia seems to be polluted with nitrate by the palm oil estates along the river.

Two rivers Kulim and Kelang Ubi were tested for nitrate and phosphate pollution in the Penang state. In Kelang Ubi the average nitrate concentration was 9.75 mg/ L and phosphate concentration was 0.06 mg/ L while Kulim was moderately polluted with nitrate and phosphate with an average value of 23.05 mg/ L and 0.66 mg/ L respectively given in Table-3. Both the values of nitrate and phosphate exceeded the safe value of 10 mg/ L for nitrate and 0.1 mg/ L for phosphate [4]. The source of pollution may be the chickens farm upstream the sampling stations. Chicken manure contained high level of urea that might contribute to high level of nitrate in river water.

In Selangor state, three rivers Langat, Bernam and Buloh were analyzed for nitrate and phosphate pollution. Bernam is highly polluted with an average value of 15.78 and 0.19 mg/ L for nitrate and phosphate respectively. Nitrate and phosphate concentrations in Langat river were 5.76 mg/ L and 0.02 mg/ L, respectively while in Buloh the concentrations were 6.67 mg/ L and 0.04 mg/ L. The nitrate concentration in both the rivers exceeded the safe level, while the phosphate concentration was very slightly greater than the safe were level of 0.1 mg/ L for both the rivers. The high concentration of nitrate and phosphate in the river of Bernam might be due to the existence of palm oil estate near the river. Nutrient might run-off from the surface of the soil to the river. The results are shown in Table-4.

In Negeri Sembilan state, the concentration of nitrates in the two rivers Gemenchen and Gemas was 8.82 mg/L and 7.72 mg/ L while the phosphate concentration was 0.05 mg/ L and 0.07 mg/ L. Both the levels of nitrate and phosphate were lower than the safe level. Bongek was slightly polluted with an average value of 15.78 mg/ L and 0.47 mg/ L, for nitrate and phosphate respectively as shown in Table-5. The nitrate and phosphate pollution may arise from the palm oil and rubber plantation nearby. Excessive application of fertilizer may stimulate a surge in nutrient concentration in the river water.

Table-3: Nitrate and Phosphate Concentration in the Rivers of Penang State

River	Nitrate Concentration (mg/ L)				Phosphate Concentration (mg/ L)			
	Place 1	Place 2	Place 3	Average	Place1	Place 2	Place 3	Average
Kulim	23.06	23.01	23.08	23.05	0.66	0.67	0.65	0.66
Kelang	9.88	9.70	9.68	9.75	0.06	0.07	0.05	0.06

Table-4: Nitrate and Phosphate Concentration in the Rivers of Selangor State

River	Nitrate Concentration (mg/ L)				Phosphate Concentration (mg/ L)			
	Station 1	Station 2	Station 3	Average	Station 1	Station 2	Station 3	Average
Langat	5.86	5.54	5.87	5.76	0.02	0.03	0.01	0.02
Bernam	15.79	15.70	15.78	15.76	0.20	0.19	0.18	0.19
Buloh	6.88	6.77	6.67	6.77	0.05	0.04	0.03	0.04

Table-5: Nitrate and Phosphate Concentration in the Rivers of Negeri Sembilan State

Rivers	Nitrate Concentration (mg/ L)				Phosphate Concentration (mg/ L)			
	Station 1	Station 2	Station 3	Average	Station 1	Station 2	Station 3	Average
Gemenchen	8.88	8.80	8.77	8.82	0.05	0.05	0.04	0.05
Gemas	7.76	7.68	7.71	7.72	0.08	0.07	0.07	0.07
Bongek	15.87	15.76	15.70	15.78	0.47	0.48	0.47	0.47

Table-6: Nitrate and Phosphate Concentration in the Rivers of Melaka State

River	Nitrate Concentration (mg/ L)				Phosphate Concentration (mg/ L)			
	Station 1	Station 2	Station 3	Average	Station 1	Station 2	Station 3	Average
Batang	26.01	26.67	25.31	26.00	0.47	0.44	0.45	0.45
Melaka	5.83	5.80	5.77	5.80	0.07	0.08	0.09	0.08

Table-7: Nitrate and Phosphate Concentration in the Rivers of Johor State

River	Nitrate Concentration (mg/ L)				Phosphate Concentration (mg/ L)			
	Station 1	Station 2	Station 3	Average	Station 1	Station 2	Station 3	Average
Muar	7.65	7.43	7.53	7.54	0.04	0.07	0.05	0.05
Segamat	12.98	13.78	13.05	13.27	0.19	0.22	0.23	0.21
Labis	20.23	21.05	20.10	20.46	0.29	0.26	0.27	0.27

In the state of Melaka, two rivers Batang and Melaka were tested for nitrate and phosphate pollution. The average concentrations of nitrate and phosphate were 5.80 mg/ L and for 0.08 mg/ L in the river of Melaka while in Batang, were 26.00 mg/ L and 0.45 mg/ L respectively which exceeded the safe values (Table-6). The pollution might arise from chicken and pig farm operation nearby. In addition to that, palm oil plantation in the vicinity of sampling stations also contributed to the nutrient pollution.

In Johor state, the three rivers Muar, Segamat, Labis were analyzed for nitrate and phosphate contents. Labis is highly polluted with an average value of 20.46 mg/ L and 0.27 mg/ L for nitrate and phosphate respectively. Nitrate and phosphate concentration in Muar river was 7.54 mg/ L and 0.05 mg/ L, while in Segamat the concentration of nitrate was 13.27 mg/ L and the concentration of phosphate was 0.21 mg/ L. The nitrate and phosphate concentrations in the three rivers are shown in Table-7. This might be due to palm oil plantation and chicken farm near the sampling site. The severity may increase when pig farm is being operated near the sampling station, with the existing palm oil estate.

In Pahang state, the two rivers Lipis and Triang are moderately polluted with nitrate and phosphate. The average nitrate value of 21.05 mg/ L and phosphate value of 0.47 mg/ L were Lipis river and a nitrate value of 21.83 mg/ L and phosphate value of 0.56 mg/ L were for Triang river as shown in Table-8. It may be due to the application of agricultural fertilizer in oil palm and rubber tree plantation near the sampling places. The average nitrate value of 7.82 mg/ L and phosphate value of 0.03 mg/ L for the river of Pahang are lower than the standard values for nitrate and phosphate.

In Terengganu state, the river Terengganu is slightly polluted with an average concentration of

Table-8: Nitrate and Phosphate Concentration in the Rivers of Pahang State

River	Nitrate Concentration (mg/ L)				Phosphate Concentration (mg/ L)			
	Station 1	Station 2	Station 3	Average	Station 1	Station 2	Station 3	Average
Pahang	7.80	7.91	7.76	7.82	0.03	0.03	0.03	0.03
Triang	21.09	22.00	22.40	21.83	0.57	0.55	0.56	0.56
Lipis	21.02	21.03	21.09	21.05	0.48	0.45	0.48	0.47

Table-9: Nitrate and Phosphate Concentration in the Rivers of Terengganu State

River	Nitrate Concentration (mg/ L)				Phosphate Concentration (mg/ L)			
	Station 1	Station 2	Station 3	Average	Station 1	Station 2	Station 3	Average
Besut	2.58	2.64	2.60	2.61	0.02	0.02	0.03	0.02
Kemaman	5.67	5.77	5.85	5.76	0.03	0.04	0.02	0.03
Terengganu	12.38	12.31	12.99	12.56	0.23	0.24	0.22	0.23

Table-10. Nitrate and Phoshpate Concentration in Ground water Samples Collected from Domestic Wells in Different States.

State	Nitrate Concentration (mg/ L)				Phosphate Concentration (mg/ L)			
	Station 1	Station 2	Station 3	Average	Station 1	Station 2	Station 3	Average
Melaka	2.34	2.38	2.39	2.37	0.050	0.070	0.06	0.060
Perak	5.08	5.45	5.70	5.41	0.060	0.060	0.070	0.063
Johar	7.39	7.55	7.71	7.55	0.055	0.061	0.058	0.058
Selangor	5.66	5.85	5.75	5.75	0.058	0.051	0.055	0.054
Pahang	6.67	6.85	6.55	6.69	0.077	0.071	0.075	0.074
Terengganu	6.05	6.50	6.75	6.43	0.080	0.085	0.083	0.083
Kedah	3.24	3.50	3.06	3.26	0.048	0.052	0.054	0.051

nitrate i.e. 12.56 mg/ L and phosphate concentration of 0.23 mg/ L as shown in Table-9. The concentrations of nitrate and phosphate in the other two rivers are lower than the safe level. Terengganu as being the longest river in the state may be accumulated with nutrients from chicken farms, palm oil and rubber trees plantation.

Ground water samples collected from domestic wells of different states were analyzed for nitrate and phosphate concentration. It is clear from the Table-10 that nitrate and phosphate levels are less than the threshold value for drinking water in Malaysia [4]. It is due to less agricultural and animal farming activities in the vicinity of the domestic well. It is inferred that ground water is affected more by nitrate rather than phosphate. This condition happens due to the nature of nitrate that allows it to leach better through the layers of soil in the ground. The nitrate and phosphate pollution can be related to the agricultural activities [6] and animal farming [7]. Fertilizers used for agricultural land, and animal secretions from livestock farm in Malaysia's tropical climate with monsoon and rainy season induce leaching and run-off that adds to this condition.

Higher levels of nitrate and phosphate, when percolate through the soil to ground water, may pollute drinking water. Nitrate in drinking water is associated with an increased risk of non-Hodgkin's lymphoma (NHL). It has been found that the more nitrate is consumed in the water, the greater is the probability of getting the NHL cancer [8]. In addition, organic nitrogen pollution leads to higher BOD and has adverse effects on aquatic life.

Experimental

Sample Collection and Preservation

Water samples were collected from different rivers in 9 states of Peninsular Malaysia. The samples were labeled according to date, time and weather condition. The samples were taken in a clean container. The containers were rinsed several times with river water before taking the sample. The samples were taken near the middle of water body at least several feet from the shore or edge of the riverbank. Ground water samples were collected from domestic wells in different states. Samples were mostly collected from areas where point sources in the vicinity were not known. After collection, the samples were refrigerated at 4°C as per the standard method for sample preservation.

Sample Analysis

Nitrate determination in water samples was carried out by using Cadmium Reduction method, HR (0.3-30 mg/L NO_3-N) using DR/4000 UV-VIS spectrophotometer [9]. For 2530 N analysis, Nitrate HR program was selected. A blank cell with 15 mL sample was prepared. Nitra Ver ^{R} 5 Nitrate Reagent powder pillow was powdered into another cell with sample. The Timer was adjusted for a one-minute reaction period. The sample cell was shaken vigorously until the timer beeped. When the timer beeped, a five-minute reaction period started. An amber color developed which showed the presence of nitrate. The blank sample prepared was wiped and placed into the cell holder. Zero measurement was adjusted. The sample was placed into the cell holder to obtain the results.

For phosphate determination using Acid Per sulfate digestion method (0.01-1.00 mg/ L Po_4^{3-}), the COD reactor was turned on and fixed at 150 °C. The program 536 P Total/ AH PV TNT was selected. For phosphate, 5.0 mL of sample was added into a Total and Acid hydrolysable test vial. The Potassium Persulfate Powder Pillow was added for phosphate to the vial. The vial was capped tightly and shaken to dissolve. The Vial was placed into the COD reactor for 30 minutes. After 30 minutes, the vial was cooled to room temperature. Then, 2.00 mL sodium hydroxide of 1.54 N was added to the vial. The vial was placed in spectrophotometer to produce baseline reading. One phos Ver ^{R} 3 powder pillow was added to the vial. The vial was shaken and later left to settle. Then, the vial was placed in DR/4000 to obtain the result [8].

Conclusions

The current study shows that two rivers, each in the states of Kedah, Selangor, and Terengganu, have nitrate and phosphate levels less than the threshold value for drinking water. All the other states have nitrate and phosphate level slightly higher than the threshold value for drinking water. Based on the results, it could be concluded that Peninsular Malaysia's river water is slightly polluted with nitrate and phosphate with an average maximum value of nitrate 26.00 mg/ L and phosphate 0.66 mg/ L.

The study is in no way a comprehensive investigation into the problem, but it does provide an indication of the existence of the problem. More data, covering extended areas, are required to make a firm statement about nitrate and phosphate pollution of surface water. The impacts of flow rate in the river as well as the seasonal variation also need to be taken into consideration.

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