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METI-LIS MODEL TO ESTIMATE H2S EMISSION RATES FROM TO LICH RIVER, VIETNAM

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ABSTRACT

This paper assessed the water quality in To Lich River through contaminated indicators such as DO, COD, and BOD_5. The emission of H_2S from the river water had impacted the ambient air quality in the riparian areas of To Lich River in Hoang Liet Ward, Hoang Mai District, Ha Noi City. The measured concentration of H_2S in ambient air in the riparian area varied within the range of $48.7 \pm 23.1 \mu g/m^3$. The H_2S emissions rate from wastewater in the To Lich River was estimated about 2, 828.0 mg/m/h. METI-LIS model can be applied to forecast H_2S emission rate from To Lich River. The predicted results showed the close relationship with the measured values by correlation coefficient $R^2 = 0.9197$.

Keywords: hydrogen sulfide, gas emission, wastewater, To Lich River, METI-LIS model.

INTRODUCTION

To Lich River is one of four major sewerage rivers in Ha Noi City (Figure-1). Wastewater in To Lich River is mainly domestic wastewater and a partly industrial wastewater and leads to the pollution of this water body and ambient air in riparian areas (Ha Noi People's Committee, 2005).
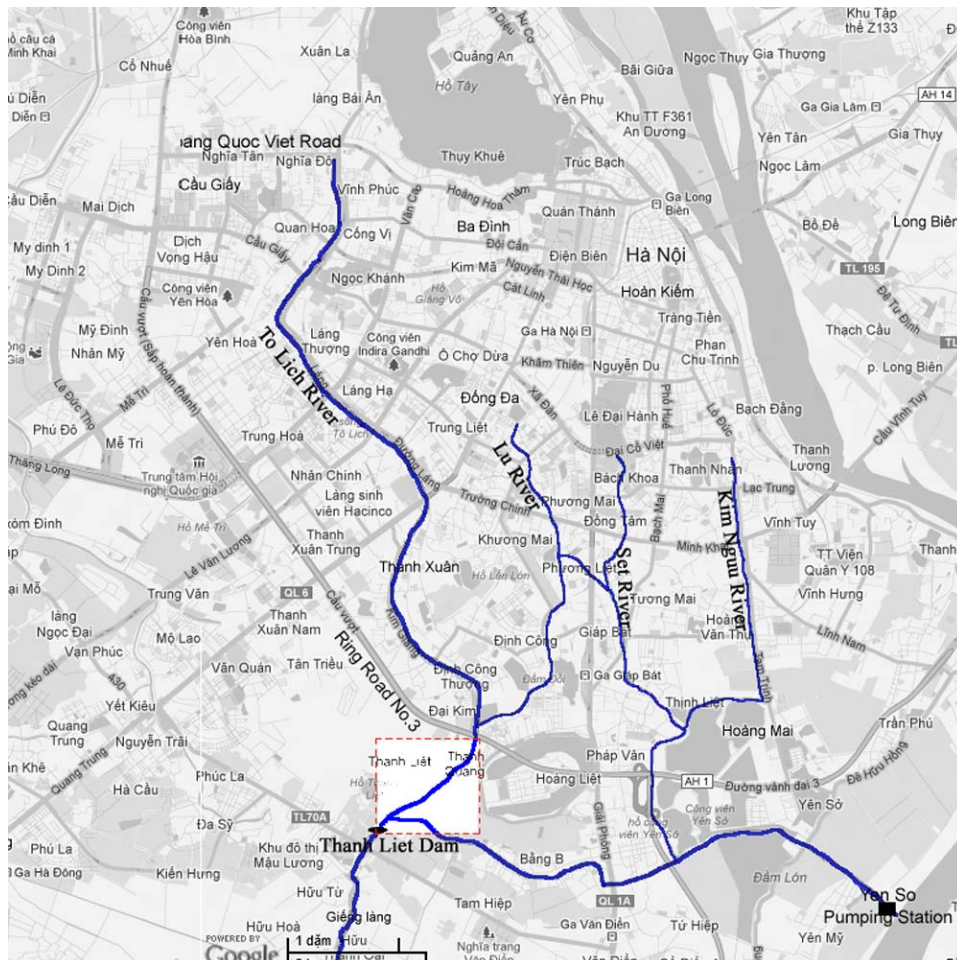

Figure-1. Map of major sewerage rivers in Ha Noi City.

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The generation of hydrogen sulfide in wastewater is the decomposition of organic compounds containing sulfur or sulfide-oxidizing bacteria in the sediment of the sewerage. Sulfide (H_2S, HS^-, S^{2-}) appears in wastewater of sewerage under these conditions: less dissolved oxygen, long time residual in the sewerage, the quantity of organic compounds containing sulfur (Lehua Zhang, *et al.,* 2008; U.S.-EPA, 1986; U.S.-EPA, 2004).

There are four sources of sulfur in sewage - namely (Rudolfs W., Baumgartner H., 1932; Gostenlow P., 2001):

- Sulfur in inorganic combinations as sulfates, thiosulfates, etc., present in the supplied water of the community.
- Sulfur in inorganic combinations as sulfates, thiosulfates, etc., present in the ground or surface waters which find their way by infiltration into the sewer.
- Sulfur in inorganic combinations, proteins, etc., or as inorganic sulfates from human excreta.
- Sulfur in organic or inorganic combination present in industrial wastes.

In nature, hydrogen sulfide is generated due to the volcanic activity and the process of proteins decomposition by the activity of bacteria. Wide variety of bacteria, fungus can emit hydrogen sulfide in the process of decomposition of sulfur-containing amino acids and in the directly reduction of sulfate. H_2S in the wastewater is generated by the activity of the anaerobic bacteria of *Desulfovibrio* (gram-) and *Desulfotomaculum* (gram +) (Grrrit Voordouw, 1995).

Currently, there are many studies on water supply and drainage system as well as the environment of wastewater receiving rivers in Hanoi City. However, most of these studies have not mentioned the possibility of some toxic gas emissions that affects people's health and costly

as well as damage to the sewerage of Hanoi City. This paper presents the conducted research on To Lich river water quality assessment, the ability to hydrogen sulfide emissions and application of the METI-LIS model to forecast the spreading of hydrogen sulfide from this river.

METHOD

Sampling and preservation methods
The water samples were collected and stored in accordance with TCVN 6663 - 14:2000.

Methods of analysis of water samples
The water quality analysis methods are applied as shown in Table-1.

Calculation methods of hydrogen sulfide emissions
The formula used to calculate the amount of hydrogen sulfide in the sewerage with the parameters from the results of monitoring and references. Forecast and calculate the amount of hydrogen sulfide emissions according to the formula for calculating the emission rate of gas per unit volume (Chaturong Yongsiri, 2008). The length of To Lich River (from Hoang Quoc Viet road to Thanh Liet Dam) is about 13, 500 m; with the estimated water volume is about 650, 000 m^3. The section of the To Lich River applied for calculating emissions of hydrogen sulfide is 2, 000 m, from the Ring Road N^o3 to the Thanh Liet Dam.

Dispersion of hydrogen sulfide
METI-LIS model version 2.03 is a Gaussian dispersion model. The model is developed on the basis of the ISC model of the U.S.-EPA. In 1996, Ministry of Economy, Trade and Industry (METI - Japan) has developed and used this model, when air contamination issues are included in the Air pollution prevention Act in Japan (METI, 2006).

Table-1. Analysis methods.

No.	Parameters	Method
1	pH	TCVN 6492-1999 pH - Determination
2	COD	TCVN 6491-1999 Determination of COD
3	BOD_5	TCVN 6001-1995 Determination of BOD (5 days)
4	H_2S	TCVN 4567-1988 Determination of sulfur, sulfate
5	DO	TCVN 4564-1988 Determination of dissolved oxygen

TCVN: Stands for Vietnamese national standard

RESULTS AND DISCUSSIONS

To Lich river water quality
Water samples are taken in the downstream areas (at Hoang Liet ward, Hoang Mai district, Hanoi City) and analyzed for assessment of water quality and calculating

the ability to generate hydrogen sulfide from water of To Lich River.
Water sampling locations: $20^057'47''N$, $105^049'05''E$. Parameters of the natural conditions during sampling are presented in Table-2.

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Table-2. Parameters of the natural conditions at sampling time.

Date	Rainfall	Cloudy	T (^{0}C)	Humidity (%)	P (mbar)	Wind direction	Wind speed (m/s)
25/3/2009	Small	8/8	25.2	91.9	1,011.5	Calm	-

Table-3. Analysis results of water samples.

Date	H_2S	BOD_5	COD	DO	pH
	Mg/l	mg/l	mg/l	mg/l	-
25/3/2009	5.32	139	152	0.2	7.57

The dissolved concentration of hydrogen sulfide in To Lich river water (5.32 mg/l) is higher than the average of domestic sewerage about from 2 to 3 times, and need to consider in to the environmental impact of H2S (Hvitved-Jacobsen *et al*., 2002).

pH value in the To Lich River (in Hoang Liet) is 7.57, and meets with Vietnamese national technical regulations on surface water quality (QCVN 08:2008/MONRE), and Vietnamese national standard on water quality for irrigation (TCVN 6773-2000). At this pH values, the conversion between the ions S^{2-}, HS^- and H_2S gas is equilibrium. In fact, existences in the form of water are mainly HS^-, H_2S and a part of S^{2-}. If surface disturbance, H_2S is released from the aqueous phase and transferred to the gas phase and the ions S^{2-}, HS^- converted to H_2S replace, maintain balance in the water. At normal domestic sewage pH levels, from one-quarter to one-third of the dissolved sulfide exists as molecular hydrogen sulfide, H2S, which is released to the air (Kienow *et al.,* 1991).

Values of COD and BOD_5 were 3.1 to 5.5 times higher than the recommended values of QCVN 08:2008 / MONRE, respectively. The high values of COD and BOD_5 also means water contains much of organic matters. The ratio of BOD_5/COD is approximately 0.9 is quite high, which suggests that the organic matters mainly can be decomposed by biological processes. The higher ratio, the greater ability to generate H_2S gas, the reduction process is dominated. Therefore the DO is low (0.2 mg/L).

The results of monitoring of hydrogen sulfide in ambient air in riparian areas along to Lich River

Ambient air in the riparian areas along To Lich River showed the odor contamination, the concentration of hydrogen sulfide was approximately 2 times higher than the recommended values (42 µg/m^3) of the Vietnam national technical regulations on toxic substances in the ambient air (QCVN 06:2008 / MONRE) (Table-4). Average values of H_2S observed in riparian ambient air of To Lich River (250m landward from river) was 48.7 ± 23.1 µg/m^3 (n = 15).

Table-4. Observed values of H$_2$S in the ambient air and forecasted values by the METI-LIS model (µg/m^3).

No.	Sample description	Location	Monitoring data	METI-LIS
1	River bank, near the paint factory	20^{0}57'32.1'' N; 105^{0}48'40.1'' E	96.5	95.3
2	Van hamlet, 10m from river bank	20°50'32.10" N; 105°48'48.58" E	39.0	44.3
3	Residential area of Van hamlet, 200m from river bank	20°57'29.16" N; 105°48'53.00" E	30.0	28.8
4	At the gate of Trung Thu textile dyeing factory, Van hamlet, 50m from river bank	20^0 57' 32" N; 105^0 48' 58" E	58.0	44.9
5	Bang A hamlet, 50m from river bank	20°57'37.64" N; 105°48'53.39" E	47.0	56.3
6	Bang A hamlet, 200m from river bank	20°57'36.68" N; 105°48'58.19"	39.0	42.8
7	Bang A hamlet, 250m from river bank	20°57'48.50" N; 105°49'15.77" E	26.0	17.4
8	At the gate of Bang A hamlet, 50m from river bank	20^0 57' 48" N; 105^0 49' 09"E	82.0	74.4
9	Bang A hamlet, 100m from river bank	20°57'51.40" N; 105°49'14.64" E	35.0	37.8
10	At the gate of Phuong Liet secondary school	20^0 57' 51" N; 105^0 49' 06" E	65.0	67.7
11	Bridge of Trung hamlet, 50m from river bank	20°57'48.10" N; 105°49'2.86" E	38.0	37.7
12	Near the fork of Trung hamlet, 250m from river bank	20°57'52.97" N; 105°48'59.28" E	25.0	13.6
13	Residential area of Trung hamlet, 100m from river bank	20°57'40.69" N; 105°48'46.07" E	30.0	24.1
14	Road side, Trung hamlet, 50m from river bank	20°57'40.53" N; 105°48'47.66"	42.0	42.5
15	River bank, Trung hamlet	20°57'38.38"N; 105°48'46.32" E	78.0	72.3

The values of hydrogen sulfide in the ambient air of seven out of total 15 observed samples were exceeding QCVN 06:2008 / MONRE (Figure-2).
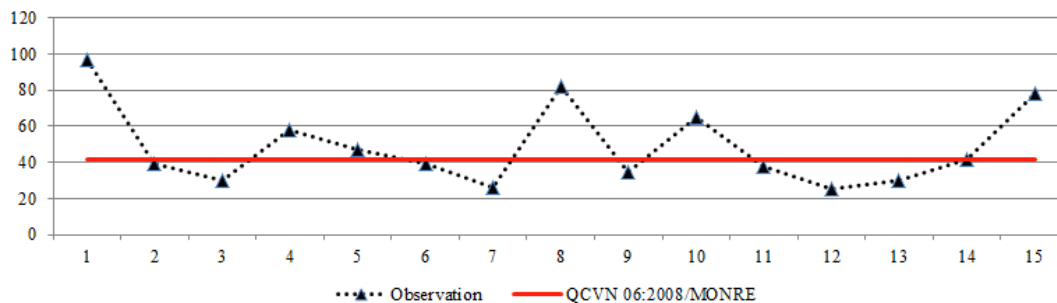
QCVN: stands for Vietnamese national technical regulations

Figure-2. Observed values of hydrogen sulfide in ambient air at Hoang Liet areas (µg/m^3-1h).

Calculation of H$_2$S generated from wastewater from to Lich River

There are many methods that can estimate the amount of H$_2$S gas generation from sewerage, including method of Yongsiri by using the following equation (Chaturong Yongsiri *et al.,* 2009).

$$R_{H2S} = -\frac{dC_W}{dt} = \alpha[0.86f]\left[\frac{0.86(1+0.2F^2)(su)^{3/8}}{d_m}\right]$$
$$\times\left[C_W - \frac{\beta C_{A,H2S}}{fH_{c,H2S,cw}}\right]1.034^{(T-293)} \quad (1)$$

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Where

R_{H2S} = H₂S emission rate (gS/m³/h)
f = H₂S $_{(aq)}$ fraction relative to total sulfide (-)
F = u ✕ g $^{(-0, 5)}$ ✕ d$_m$ $^{(-0, 5)}$
u = mean velocity (m/s)
s = slope

d_m = mean hydraulic depth (m)
C_w = dissolved sulfide concentration in water phase (gS/m³)
$C_{A, H2S}$ = H₂S concentration in air phase (gS/m³)
$H_{C, H2S, Cw}$ = nondimensional Henry's law constant for H₂S
A_{cr} = cross section (m²)

Table-5. The parameters applied for calculating of H₂S emission rate.

α	β	f	F	u	g	d$_m$	C$_w$	C$_{A, H2S}$	H$_{C, H2S, Cw}$
- 0.6	- 1	-0.176	0.077	0.35	9.81	2.06	5.32	0.078 (*)	600
K$_a$	$_p$K$_a$	pH	s	A$_{cr}$	w	b	h	T	V$_{ww}$
1.26 ✕ 10$^{(-7)}$	6.8996	7.57	0.05	48.125	35	20	1.75	298.2	650,000

(*) Sample N⁰:15 Table-4

Table-6. H₂S emission rate of wastewater from To Lich River.

H₂S emission rate	Unit		Value
R$_{H2S}$	g S/m³/h	20⁰C	0.053
		25.2⁰C	0.059
R$_{H2S}$	kg S/day	20⁰C	822.5
R$_{H2S}$		25.2⁰C	916.3
R$_{H2S}$	ton S/day		0.916

H₂S emissions rate per day is R_{H2S} = 0.916 tons S/day at 25.2⁰C. The average emission of H₂S from To Lich River water converted to mg/m/h is: 916.3 (kg/day)/24 (h)/13, 500 (m) * 10⁶ = 2, 828 (mg/m/h).

Forecasted values by METI-LIS model

The model is applied to the end section (2, 000 m) of To Lich River, with the weather conditions described in Table-2.

By using above-mentioned formula (1), the minimum value of $C_{A, H2S}$ = 0, the R_{H2S} will reach the maximum value with the same calculating conditions. By using the value of $C_{A, H2S}$ = 0 in formula (1), the values of R_{H2S} = 2, 825.441 (mg/m/h). Then, using this R_{H2S} value for application of METI-LIS model, the maximum value of $C_{A, H2S}$ = 200.277 (µg/m³).

Average value of $C_{A, H2S}$ = ($C_{A, H2S}$ min + $C_{A, H2S}$ max)/2 = 100.1395 (µg/m³).

By using the value of $C_{A, H2S}$ = 100.1395 (µg/m³) to verify the model with the value of R_{H2S} = 2, 825.9 (mg/m/h), and using the METI-LIS model with the same conditions as mentioned above, the results were shown in Table-4, Figure-3 and Figure-4.
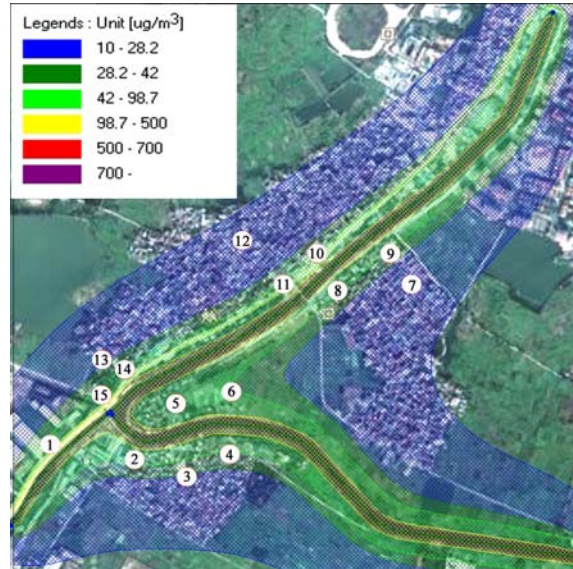

Figure-3. Verification of METI-LIS model.
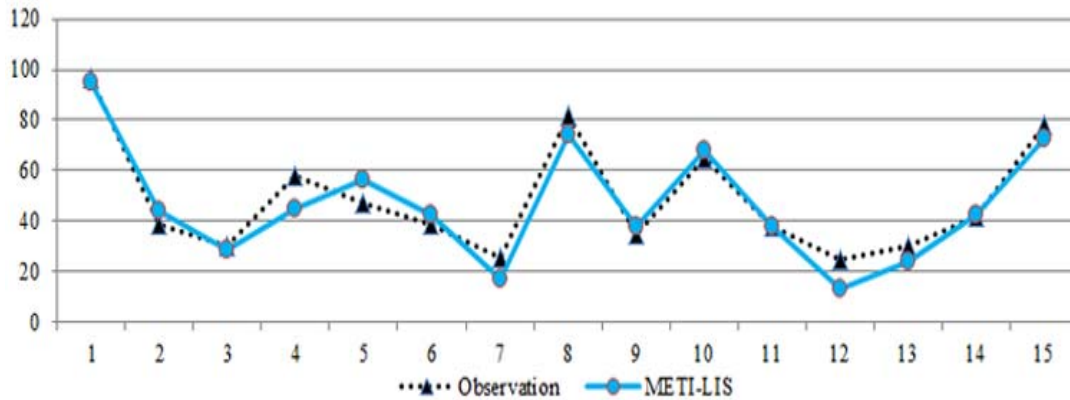
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Figure-4. Observed values of H_2S in the ambient air and forecasted values by the METI-LIS model ($\mu g/m^3$-1h).

The observed results of H_2S in ambient air and by METI-LIS model show the cose relationship with the correlation coefficient $R^2 = 0.9197$ (Figure-5).
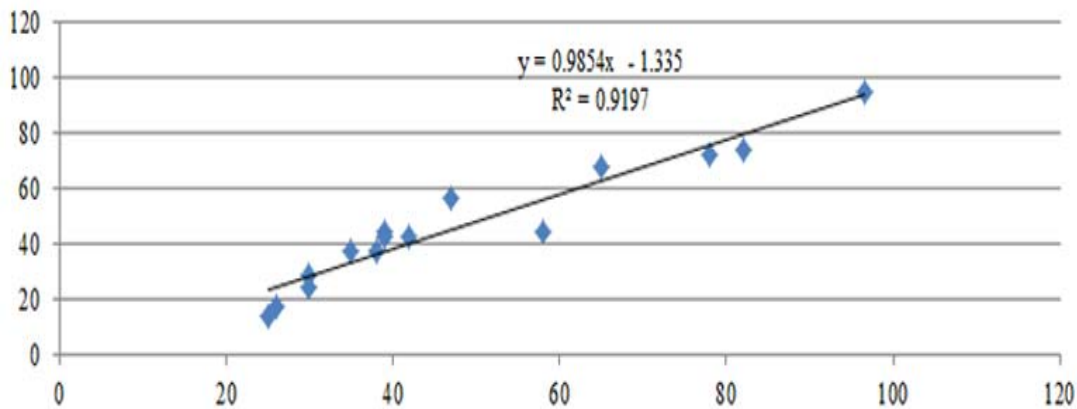

Figure-5. Correlation coefficient between monitoring of H_2S and by using METI-LIS model.

CONCLUSSIONS

a) Water in To Lich River is polluted, the index BOD_5 and COD were so high, and exceeded the recommended values by the Ministry of Natural Resources and Environment (MONRE, Vietnam). Whereas DO was lower than the recommended value, that cause the heavily pollution of organic matters and microorganisms due to the reduction process and limited traffic flow.

b) River water with high content of organic matters in anaerobic condition (low DO) should generate much of H_2S gas that affects to the river water quality itself, ambient air quality in the residential riparian areas. This causes many problem of health of residents, such as gynecological diseases, skin diseases, eye, respiratory, intestinal etc.

c) The measured concentration of H_2S in ambient air in the riparian area within the distance of 250m from the river bank fluctuates in the range of 48.7 ± 23.1 $\mu g/m^3$.

d) H_2S emission rate from To Lich River water was estimated about 2, 828.0 mg/m/h.

e) METI-LIS model can be applied to forecast the H_2S emission rate from To Lich River. The calculated and measured values of H_2S showed the close correlation coefficient: $R^2 = 0.9197$. According to METI-LIS the ambient air in the riparian areas of To Lich River contaminated by H_2S generated from To Lich River water, with the concentration of H_2S higher than recommended value by QCVN 06:2008 /MONRE in the riparian areas, within 50 m from the river bank, due to its diffusion in the atmosphere.

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