

## Estimation of nitrous oxide emissions (GHG) from wastewater treatment plants using closed-loop mass balance and data reconciliation

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**Abstract**—The amount of greenhouse gases (GHG), especially, nitrous oxide ( $N_2O$ ) emitted from wastewater treatment plants (WWTP) using data reconciliation and closed-loop mass balance was estimated. This study is based on a flow-based emission estimation approach which depends on the accuracy of the measurement data. To reduce the (random) measurement error, data reconciliation was used to enhance the accuracy of the flow measurements. After performing data reconciliation,  $N_2O$  emission was estimated with more precision by using the closed-loop mass balance. The results in both pilot-scale and full-scale plants show that the suggested method can easily obtain the precise flow measurement for GHG emission, which in turn, results in the accurate estimation of the  $N_2O$  amounts emitted from WWTP. Moreover, it is shown that the estimated flowrate values can be used as a software sensor, which can replace the faulty sensors and can validate the existing field measurements.

Key words: Climate Change, Data Reconciliation, Greenhouse Gases (GHG), Mass Balance, Nitrous Oxide Emission, Wastewater Treatment Plant (WWTP)

### INTRODUCTION

In the biological nutrient process, removal of nitrogen by nitrification and denitrification has been used in many wastewater treatment plants to produce effluent of better quality, thereby reducing its impact on the river. Generally, nitrogen gas is an end product of the nitrogen removal process. However, unexpected gas, nitrous oxide ( $N_2O$ ) which is a well known GHG is also emitted through nitrification and denitrification processes [1].  $N_2O$  generated in nitrification (which is in dissolved form) is stripped from the liquid by aeration and mixing. Nitrous oxide contributes to global warming, 310 times higher than carbon dioxide. In the real WWTP process, emitted gases generally are not measured because of process' characteristics. Especially, biological reactors are not covered with a roof, which means that it is impossible to measure emitted gas from the reactor. Hence, it is not easy to estimate emitted gases in WWTP directly, though it is possible to estimate  $N_2O$  emission in lab-scale and pilot scale experiment with a roof. Several researches have been reported in the literature to measure and estimate the nitrous oxide emission of WWTP. IPCC (Intergovernmental Panel on Climate Change) has suggested the default value of nitrous oxide emission factor, which is  $0.0032 \text{ kg } N_2O \text{ person}^{-1} \text{ yr}^{-1}$  (0.035%  $N_2O$  emission of nitrogen load of WWTP) in a wastewater treatment plant [2]. Foley et al. [3] have studied the estimation of  $N_2O$  emissions from full-scale and lab-scale wastewater systems, and have reported the emission factor as  $0.01 \text{ kg } N_2O\text{-NkgN}^{-1}$ .

In this study, a closed-loop mass balance based on data reconciliation is applied to estimate the amounts of  $N_2O$  gas emitted from a pilot-scale membrane bioreactor (MBR) plant. The data obtained from the plant usually suffer from poor quality due to improper functioning of measurements in the plant. The malfunctioning of measurements causes gross errors in the data obtained from the plant. Wrong data (or data with gross errors) affect the estimation result of  $N_2O$  emission in WWTP. Before the data reconciliation, such wrong data needs to be prevented. Gross error detection (GED) is used to find gross error in the plant data. After GED is carried out, data reconciliation is performed to reduce the random errors between the measurement (obtained after discarding gross error data) and the model values. Hence, data reconciliation helps to estimate  $N_2O$  more accurately by reducing the measurement error. After data reconciliation, a closed-loop mass balance is performed. The mass bal-

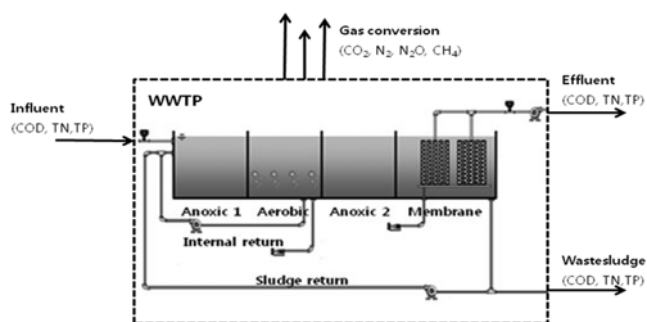


Fig. 1. Overall mass balance of COD, nitrogen, phosphorus and GHGs in a pilot-scale MBR plant.

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ance diagram of a wastewater treatment plant is shown in Fig. 1.

Closed-loop mass balance, mass balance based on phosphorus (which is present in three streams, namely, influent, effluent and waste sludge, and involves no gas conversion) is carried out first, which in turn helps to estimate the nitrogen present in the waste sludge stream. Therefore, more accurate estimation of mass balances can be possible [4]. In particular, the reconciled flowrate values can be used as a soft sensor since it can reduce the measurement error of the field flowrate sensor with accurate plant information.

The contents of this paper are as follows: 1) detailed explanation of GED and data reconciliation concepts; 2) detailed explanation of closed-loop mass balance in WWTP; 3) WWTP process description; 4) estimation of  $N_2O$  emission in pilot-scale WWTP (case 1) based on data reconciliation and closed-loop mass balance (The effect of data reconciliation is analyzed); 5) estimation of  $N_2O$  emission in full-scale WWTP (case 2) based on the closed-loop mass balance, in which the effect of phosphorus and nitrogen ratio of waste sludge is analyzed.

## MATERIALS AND METHODS

Equipment (hardware reconciliation) is usually calibrated to take care of the errors associated with the measuring equipment. These errors are caused during the manufacturing of the equipment. Measurement values are nothing but the sensor values, which show different values (small deviation) from that of real process values. The difference between the measurement and the process values is taken care of by using calibration of the equipment. Gross error detection is used to detect gross errors in the data coming from the plant. Gross errors are caused due to the completely or mostly failed equipment. Data reconciliation is a process of reducing random errors in the data coming from the plant. Random error is nothing but the difference in the values of measurement and the model. Measurement values involve both random and gross errors, even though equipment is calibrated well before being installed in the plant. Gross errors are detected using gross error detection and usually eliminated from the data before data reconciliation to reduce random errors. A data-reconciled model (the model which satisfies the plant values and mass balance equations) is used to carry out control and optimization studies of a plant. Elimination of gross and random errors is generally termed as ‘software data reconciliation’. Elimination of gross and random errors is generally termed as ‘software data reconciliation’. Development of software for gross error detection and data reconciliation is carried out in this paper, which can detect gross errors and reduce random errors respectively.

### 1. Data Reconciliation

Data reconciliation [5-7] is a technique to adjust the measured data and to give estimates for unmeasured variables. Data reconciliation can identify erroneous measurements which have random errors. Reliable information obtained by data reconciliation is essential for effective estimation of GHG emission. Measurement can be mathematically described as:

$$\mathbf{y}_{meas} = \mathbf{y}_{model} + \boldsymbol{\varepsilon} \quad (1)$$

where  $\mathbf{y}_{meas}$  is the vector of measurement values of  $n$  process variables;  $\mathbf{y}_{model}$  is the vector of model values of  $n$  process variables;  $\boldsymbol{\varepsilon}$  is a vector of random measurement errors.

Data reconciliation is a process of minimizing sum of squares of errors between measurements and model values, subject to a number of constraints (mean balance equations). A data reconciliation problem can be stated as follows:

$$\begin{aligned} & \text{Min } (\mathbf{y}_{meas} - \mathbf{y}_{model})^T \boldsymbol{\psi}^{-1} (\mathbf{y}_{meas} - \mathbf{y}_{model}) \\ & \text{s.t.} \\ & \mathbf{A}_1 \mathbf{y}_{model} = \mathbf{0} \end{aligned} \quad (2)$$

where,  $\boldsymbol{\psi}$  is the weight matrix,  $\mathbf{A}_1$  is the process matrix (balance equation). The Lagrangian multiplier method is used for solving this optimization problem. A constrained optimization problem can be converted into unconstrained optimization problem by using this method. The Lagrangian can be written as:

$$L(\mathbf{y}, \boldsymbol{\lambda}) = (\mathbf{y}_{meas} - \mathbf{y}_{model})^T \boldsymbol{\psi}^{-1} (\mathbf{y}_{meas} - \mathbf{y}_{model}) - 2\boldsymbol{\lambda}^T \mathbf{A}_1 \mathbf{y}_{model} \quad (3)$$

where  $\boldsymbol{\lambda}$  is a vector of  $n$  Lagrangian multipliers.

Substituting Eq. (1) in Eq. (3) gives

$$L(\boldsymbol{\varepsilon}, \boldsymbol{\lambda}) = \boldsymbol{\varepsilon}^T \boldsymbol{\psi}^{-1} \boldsymbol{\varepsilon} - 2\boldsymbol{\lambda}^T (\mathbf{A}_1 \mathbf{y}_{meas} - \mathbf{A}_1 \boldsymbol{\varepsilon}) \quad (4)$$

The equations obtained after differentiating Eq. (4) with respect to  $\boldsymbol{\varepsilon}$  and  $\boldsymbol{\lambda}$  and equating them to zero are:

$$\frac{\partial L}{\partial \boldsymbol{\varepsilon}} = 2\boldsymbol{\psi}^{-1} \boldsymbol{\varepsilon} + 2\mathbf{A}_1^T \boldsymbol{\lambda} = 0 \quad (5)$$

$$\frac{\partial L}{\partial \boldsymbol{\lambda}} = \mathbf{A}_1 (\mathbf{y}_{meas} - \boldsymbol{\varepsilon}) = 0 \quad (6)$$

Thus, we can get the values of  $\boldsymbol{\varepsilon}$  and  $\boldsymbol{\lambda}$  as:

$$\boldsymbol{\varepsilon} = -\boldsymbol{\psi} \mathbf{A}_1^T \boldsymbol{\lambda} \quad (7)$$

$$\boldsymbol{\lambda} = -(\boldsymbol{\psi} \mathbf{A}_1^T)^{-1} \boldsymbol{\varepsilon} \quad (8)$$

Multiplying and dividing with  $\mathbf{A}_1$  on the right hand side of the above equation gives

$$\boldsymbol{\lambda} = -\mathbf{A}_1^{-1} (\boldsymbol{\psi} \mathbf{A}_1^T)^{-1} \mathbf{A}_1 \boldsymbol{\varepsilon}$$

The above Eq. can be simplified to

$$\boldsymbol{\lambda} = -(\mathbf{A}_1 \boldsymbol{\psi} \mathbf{A}_1^T)^{-1} \mathbf{A}_1 \boldsymbol{\varepsilon} \quad (9)$$

Rearranging Eq. (6) gives

$$\mathbf{A}_1 \boldsymbol{\varepsilon} = \mathbf{A}_1 \mathbf{y}_{meas} \quad (10)$$

Substituting Eq. (10) in Eq. (9) gives

$$\boldsymbol{\lambda} = -(\mathbf{A}_1 \boldsymbol{\psi} \mathbf{A}_1^T)^{-1} \mathbf{A}_1 \mathbf{y}_{meas} \quad (11)$$

Substituting Eq. (11) in Eq. (7) gives

$$\boldsymbol{\varepsilon} = \boldsymbol{\psi} \mathbf{A}_1^T (\mathbf{A}_1 \boldsymbol{\psi} \mathbf{A}_1^T)^{-1} \mathbf{A}_1 \mathbf{y}_{meas} \quad (12)$$

Substituting Eq. (12) in Eq. (1) gives the estimates of the process variables

$$\mathbf{y}_{esti} = \mathbf{y}_{meas} - \boldsymbol{\varepsilon} = \mathbf{y}_{meas} - \boldsymbol{\psi} \mathbf{A}_1^T (\mathbf{A}_1 \boldsymbol{\psi} \mathbf{A}_1^T)^{-1} \mathbf{A}_1 \mathbf{y}_{meas} \quad (13)$$

### 2. Gross Error Detection

Gross error detection identifies erroneous measurement from the measurement data (which has gross errors) coming from the process. Gross error exists only when the measurement value shows large deviation from the estimated value. Gross error can be found by calculating the relative error of each measurement, which is cal-

culated using the following equation:

$$\text{Relative error} = \frac{y_{meas} - y_{est}}{\sigma_{meas}} \quad (14)$$

where  $y_{meas}$  is the measured value of the process variable,  $y_{est}$  is the estimated (or model) value of the process variable obtained after carrying out data reconciliation,  $\sigma_{meas}$  is the standard deviation of the measurement.

We can say that the measurement is having gross error only when

$$\text{Relative error} > P_{95}$$

where  $P_{95}$  is a value of a normal distribution statistic calculated at 95% confidence interval, which is found to be 1.96. The measurement is said to have gross error only when the value of relative error exceeds 1.96. The gross error in the measurement does not exist, if the value of relative error is less than 1.96.

### 3. Principle of Closed-loop Mass Balance of WWTP

The overall mass balance of COD, nitrogen, phosphorous and GHG in a pilot-scale MBR plant is represented in Fig. 1. There are two main conversions involved in a treatment plant, one is from carbonaceous matter to gas, and the other is from nitrogenous matter to gas. As the amount of gas generated usually is not measured, this is estimated using mass balance of a plant.

While, total phosphorus (TP) does not have gas phase conversion, thereby all flows can be measured. Overall mass balance equations of individual components of WWTP are as follows [8]:

$$Q_{influent} - Q_{wastewater} - Q_{effluent} = 0 \quad (15)$$

$$TP_{influent} - TP_{wastewater} - TP_{effluent} = 0 \quad (16)$$

$$TN_{influent} - TN_{wastewater} - TN_{effluent} - N_{denitrified} = 0 \quad (17)$$

In this study, a closed-loop mass balance is used to estimate the amount of denitrified nitrogen ( $N_{denitrified}$ ). Using the closed-loop mass balance equation, mass balance based on total phosphorus (which involves no gas conversion) is used to calculate the amount of volatile suspended solid (VSS) in waste sludge stream. VSS of waste sludge can be calculated by the following equation (Eq. (18)).

$$VSS_{wastewater} = \frac{TP_{wastewater}}{TP/VSS} \quad (18)$$

where  $VSS_{wastewater}$  is the VSS of waste sludge,  $TP/VSS$  is the phosphorus fraction of waste sludge.

For calculating waste sludge TN, nitrogen fraction of waste sludge ( $TN/VSS$ ) is used. By using this value, TN of waste sludge can be calculated by the following equation (Eq. (19)):

$$TN_{wastewater} = VSS_{wastewater} \times TN/VSS \quad (19)$$

where  $TN_{wastewater}$  is the TN of waste sludge,  $TN/VSS$  is the nitrogen fraction of waste sludge. Hence, gas phase of TN can be calculated by Eq. (17), by using data of  $TN_{influent}$ ,  $TN_{effluent}$  and  $TN_{wastewater}$ .  $TN_{denitrified}$  is calculated from Eq. (19).

### 4. Calculation of Nitrous Oxide Emission

The amount of denitrified nitrogen ( $N_{denitrified}$ ) can be calculated by using a closed-loop mass balance of WWTP. The next step is to calculate the amount of nitrous oxide gas directly stripped from the liquid. In this study, experiment data from the WWTP and generation factors (ratio of  $N_2O$  produced to  $N_{denitrified}$ ) are used to estimate

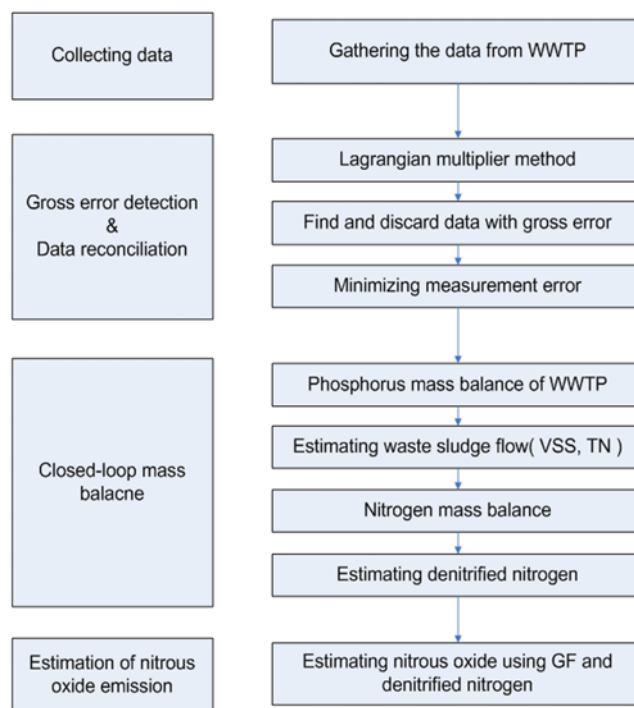


Fig. 2. Systematic method for estimation of  $N_2O$  emission in WWTP.

the amount of nitrous oxide released from a plant. Foley et al. [3] have carried out experiments which measure the amount of nitrous oxide emitted, using twenty samples and reported that the generation factor is  $0.013 \text{ kg } N_2O\text{-N/kg } N_{denitrified}$ . This factor is applied to estimate the direct emission of  $N_2O$  from WWTP by using the following equation [3]:

$$E_{N_2O} = N_{denitrified} \times GF \quad (20)$$

where  $E_{N_2O}$  is the emission of nitrous oxide from WWTP,  $GF$  is the generation factor of  $N_2O$  ( $\text{g } N_2O\text{-N/g } N_{denitrified}$ ).

In this study, a systematic method for estimating  $N_2O$  emission in WWTP is suggested (see Fig. 2). The first step of this method is to conduct GED and data reconciliation based on Lagrangian multiplier method. In this step, measurements with gross error are discarded and measurement (random) error is minimized. In the second step, a closed-loop mass balance is performed based on the reconciled data (results of data reconciliation). In this step, nitrogen of waste sludge flow is estimated by phosphorus mass balance. Then, denitrified nitrogen is estimated by nitrogen mass balance. In the final step,  $N_2O$  emission in WWTP is estimated by GF.

## RESULTS AND DISCUSSION

### 1. Process Description of WWTP

In this study, both pilot-scale (with the design value of flow rate is equal to  $500 \text{ m}^3/\text{d}$ ) and full-scale WWTP (with the design value of flow rate is equal to  $6,240 \text{ m}^3/\text{d}$ ) are considered for estimation of  $N_2O$  emission. We split the study into two cases. Case 1 is used for calculating the  $N_2O$  emission in pilot-scale wastewater treatment plant, while case 2 is used for full-scale wastewater treatment plant. In case 1, process data is obtained from pilot-scale WWTP located

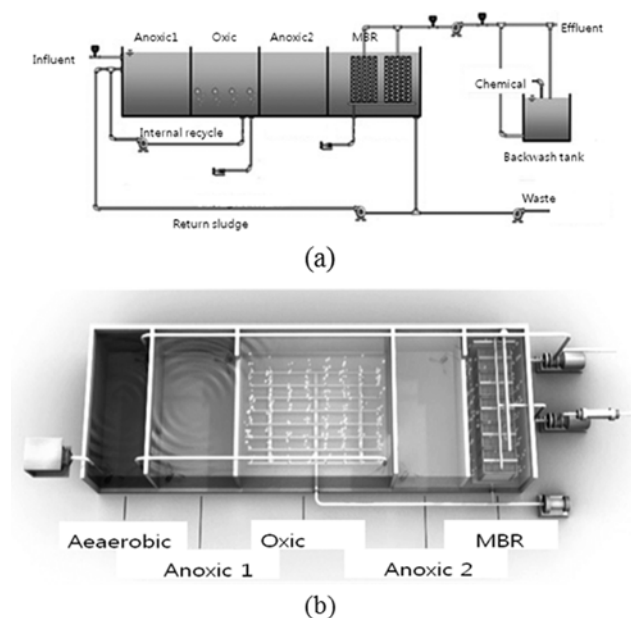


Fig. 3. Lay out of (a) pilot-scale and (b) full-scale MBR plants.

in Y-city, Korea. The reactors present in MBR process are anoxic1 reactor, oxidic (aerobic) reactor, anoxic2 reactor and submerged membrane bioreactor. The layout of the plant is shown in Fig. 3(a). In case 2, process data is obtained from full-scale WWTP located in G-city, Korea. The layout of this is shown in Fig. 3(b). It consists of an anaerobic, anoxic1, oxidic (aerobic), anoxic2 and MBR.

These two WWTPs have similar layout, except the presence of anaerobic reactor in full-scale WWTP. There are two recycle streams. One is an internal recycle stream which connects from the oxidic reactor to the first reactor (anoxic1 reactor in case of pilot-scale plant, anaerobic reactor in case of full-scale WWTP) for recycling nitrate to enhance the efficiency of the denitrification process. The other recycle stream is a return sludge which connects from the MBR to the first reactor for maintaining the mixed liquor suspended solid (MLSS).

In the WWTP, simultaneous nitrification and denitrification take place for the nitrogen removal. The nitrification process oxidizes ammonia into nitrites and nitrates, while denitrification converts nitrites and nitrate into nitrogen gas.  $N_2O$  emission from the WWTP is caused by these two processes. Thus, most  $N_2O$  emission from WWTP takes place in the activated sludge compartment, such as anaerobic, anoxic, oxidic and MBR reactors.

## 2. Estimation of $N_2O$ Emission in Pilot-scale WWTP (Case 1)

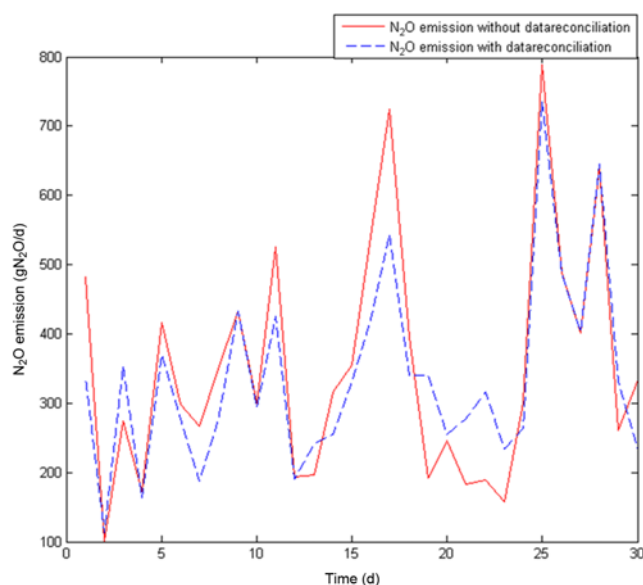
Thirty days (from 7 November 2008 to 6 December 2008) data (flow rate, TP and TN) are used in this study. In case 1, for carrying out the mass balance, each component measurement data of a stream (TP and TN in mg/L) is to be converted from mg/L to mass flow rate (g/d) by multiplying each measurement data (concentration in mg/L) with the value of flow rate ( $m^3/d$ ). In this study, data reconciliation of flow rates (influent, effluent and waste sludge streams) was performed to reduce the errors in measurements of flow rates. The data reconciliation results for case 1 are summarized in Table 1. It is clear that the values of relative errors of flow rate for all streams (influent, effluent, waste sludge) are less than 1.96, hence, we can

Table 1. Overall mass balance of COD, nitrogen, phosphorus and GHGs in a pilot-scale MBR plant

| No. | Reconciled data   |                   |                   | Relative error |       |          |
|-----|-------------------|-------------------|-------------------|----------------|-------|----------|
|     | Influent          | Waste             | Effluent          | Influent       | Waste | Effluent |
|     | m <sup>3</sup> /d | m <sup>3</sup> /d | m <sup>3</sup> /d | -              | -     | -        |
| 1   | 548.2             | 1.3               | 546.9             | 0.37           | 0.01  | 0.37     |
| 2   | 284.4             | 6.5               | 277.9             | 0.39           | 0.00  | 0.39     |
| 3   | 622.5             | 1.8               | 620.7             | 0.40           | 0.01  | 0.40     |
| 4   | 338.0             | 6.5               | 331.5             | 0.38           | 0.00  | 0.38     |
| 5   | 745.2             | 18.5              | 726.6             | 0.38           | 0.00  | 0.39     |
| 6   | 354.2             | 13.1              | 341.2             | 0.38           | 0.00  | 0.38     |
| 7   | 401.9             | 9.3               | 392.6             | 0.38           | 0.00  | 0.39     |
| 8   | 406.4             | 7.7               | 398.8             | 0.37           | 0.00  | 0.38     |
| 9   | 670.1             | 26.5              | 288.4             | 0.39           | 0.00  | 0.39     |
| 10  | 615.4             | 19.1              | 596.2             | 0.38           | 0.00  | 0.39     |
| 11  | 520.2             | 21.3              | 499.0             | 0.41           | 0.00  | 0.42     |
| 12  | 373.6             | 15.4              | 358.2             | 0.41           | 0.00  | 0.42     |
| 13  | 433.2             | 24.8              | 408.5             | 0.40           | 0.00  | 0.41     |
| 14  | 478.4             | 6.9               | 471.5             | 0.41           | 0.00  | 0.41     |
| 15  | 592.3             | 12.8              | 579.5             | 0.43           | 0.00  | 0.44     |
| 16  | 572.4             | 15.3              | 557.1             | 0.44           | 0.00  | 0.45     |
| 17  | 538.7             | 4.3               | 534.4             | 0.46           | 0.00  | 0.47     |
| 18  | 557.1             | 11.6              | 545.5             | 0.56           | 0.00  | 0.57     |
| 19  | 413.1             | 16.4              | 396.7             | 0.42           | 0.00  | 0.43     |
| 20  | 487.0             | 4.8               | 482.2             | 0.46           | 0.01  | 0.46     |
| 21  | 443.1             | 1.4               | 441.6             | 0.51           | 0.01  | 0.51     |
| 22  | 523.6             | 3.2               | 520.4             | 0.80           | 0.01  | 0.80     |
| 23  | 433.0             | 5.0               | 427.9             | 0.49           | 0.00  | 0.50     |
| 24  | 591.6             | 5.1               | 586.5             | 0.43           | 0.01  | 0.43     |
| 25  | 770.7             | 10.7              | 760.1             | 0.49           | 0.00  | 0.50     |
| 26  | 599.3             | 6.1               | 593.2             | 0.51           | 0.00  | 0.51     |
| 27  | 444.7             | 5.3               | 439.4             | 0.49           | 0.00  | 0.50     |
| 28  | 784.3             | 14.6              | 769.7             | 0.63           | 0.00  | 0.64     |
| 29  | 498.1             | 9.2               | 488.9             | 0.52           | 0.00  | 0.53     |
| 30  | 403.2             | 16.2              | 387.0             | 0.60           | 0.00  | 0.61     |

conclude that the measurement data is not having gross errors. From a practical point of view, the reconciled flowrate value can be used for checking the accuracy of the existing flowrate field measurements and deciding the time for a measurement (sensor) calibration. Plant supervision and monitoring can be efficiently carried out by using the data reconciled model.

Furthermore, we could get the reconciled value of influent, effluent and waste sludge flow rate. So, the reliable and accurate estimation of mass flow rate of TP is possible using data reconciliation. The mass flow rate of TN in the waste sludge stream is calculated by using the reconciled value of TP, Eq. (18) and (19). To calculate the values of VSS and TN of waste sludge stream, values of TP/VSS and TN/VSS are needed. In case 1 study, 0.02 gP/gCOD (0.03 gP/gVSS) and 0.07 gN/gCOD (0.10 gN/gVSS), which are used in activated sludge model no.2d (ASM2d) are applied here again [4].  $N_{denitrified}$  is estimated by TN mass balance, and emission of  $N_2O$  is calculated using a generation factor. As a result, the amounts of  $N_2O$  emitted during thirty days are estimated and represented in Fig. 4.

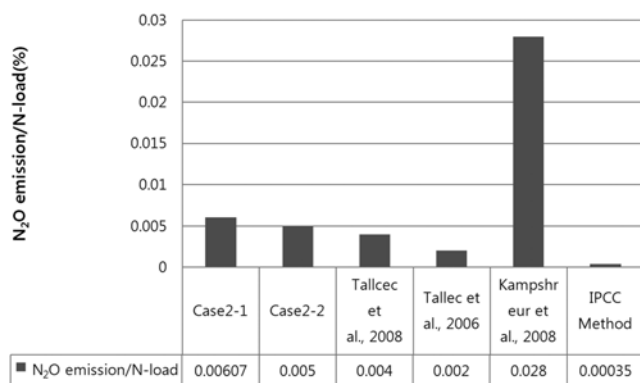


**Fig. 4. Result of estimation of  $N_2O$  emitted with & without data reconciliation.**

Results of data reconciliation of flow rates are used in the estimation of  $N_2O$  emission. It is considered that the estimation of  $N_2O$  emission with data reconciliation is more appropriate than the case without data reconciliation, because it gives reliability on the data of flow rates of the process. This reliability gives the accurate estimation of  $N_2O$  emission.

### 3. Estimation $N_2O$ Emission in Full-scale WWTP (Case 2)

Thirty-seven days (from 6 December 2010 to 31 March 2011) data (flow rate, TP and TN) obtained from the full-scale WWTP are used in this study. The values of each measurement and their standard deviations are essential to carry out data reconciliation. However, sufficient process data from full-scale WWTP could not be obtained. Thus, data reconciliation was not performed in the case 2 study. To increase accuracy of estimating  $N_2O$  emission, phosphorus and nitrogen contents of waste sludge, which are used in Eqs. (18) and (19), were measured. Phosphorus and nitrogen contents of waste sludge are 0.05 gP/g VSS and 0.12 g N/g VSS respec-



**Fig. 5.  $N_2O$  emission in WWTPs. Case2-1 :  $N_2O$  estimation using experiment data (N and P contents of waste sludge), Case2-2 :  $N_2O$  estimation using reference data (N and P contents of waste sludge).**

tively. In case 2,  $N_2O$  estimation using the values of the measured and reference data (N and P content of waste sludge which are used in case 1) of N and P contents of waste sludge is obtained. To see the accuracy of estimation of  $N_2O$  emission in this study, the value of  $N_2O$  emitted is compared with the values obtained using IPCC method and the recent studies as shown in Fig. 5.  $N_2O$  emission of the case 2 study gives a higher value of  $N_2O$  than does the IPCC method. This is because IPCC guidelines [9] assume that  $N_2O$  emission from WWTP is a minor source, while the major source is the river. Furthermore,  $N_2O$  emission factor, which is suggested by IPCC guidelines 2006, is based on one specific study in small BOD from a removal WWTP [10]. Thus,  $N_2O$  emission estimated using IPCC guidelines has quite a small value. If IPCC guideline is applied for estimation of  $N_2O$  emission in advanced WWTP, it can cause under-estimation of  $N_2O$  emission.

In this study, estimation of  $N_2O$  emission for case 2-1 is more accurate than estimation result of case 2-2 because precise N and P content data is used in case 2-1. Emission data shows variation with the fraction of nitrogen emitted as  $N_2O$  (see Fig. 5) because it depends on the operational condition. Thus, it is considered that by finding the optimal condition for minimizing  $N_2O$  emission, it is possible to reduce the emission. In this study, for estimating the  $N_2O$  emission GF is used. However, because this GF factor is a reference value, estimation data may have some error. Thus, the necessity for experimentation to estimate GF was found.

In this study, an attempt has been made to estimate the  $N_2O$  emission precisely. From the result, it can be concluded that reconciliation estimation of nitrogen and phosphorus content of waste sludge and experiment data of GF are essential for more precise estimation of  $N_2O$  emission in WWTP.

## CONCLUSION

$N_2O$  generated in WWTP was estimated by using a newly proposed estimation method, based on data reconciliation and closed-loop mass balance. First (case 1), after performing data reconciliation on flow rates,  $N_2O$  emission was estimated more accurately based on plant mass balances. Second (case 2), the effect of difference for N and P contents of waste sludge and reference data was studied. The study showed that the estimation of  $N_2O$  emission with experimental data (N and P content of waste sludge) has more accuracy. Because the suggested method for  $N_2O$  estimation of WWTP is simple and easy to apply, it could be a useful shortcut method of estimation of GHG emissions from wastewater treatment plant when one needs to calculate the direct emission of nitrous oxide in full-scale plants. For more accurate quantification of  $N_2O$  emission in full-scale WWTP, other systematic full-scale measurement strategy, i.e., on line measurements over several days, is needed.

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## NOMENCLATURE

- $A_1$  : process matrix (balance equation) [-]  
 $E_{N_2O}$  : emission of nitrous oxide from WWTP [g]  
 $GF$  : generation factor of  $N_2O$  [ $gN_2O-N/gN_{denitrified}$ ]  
 $L$  : lagrangian [-]  
 $N_{denitrified}$  : denitrified nitrogen [g]  
 $P_{95}$  : value of a normal distribution statistic calculated at 95% confidence interval [-]  
 $Q_{influent}$  : flow rate of influent stream [ $m^3/d$ ]  
 $Q_{wastewater}$  : flow rate of waste stream [ $m^3/d$ ]  
 $Q_{effluent}$  : flow rate of effluent stream [ $m^3/d$ ]  
 $TP_{influent}$  : total phosphorus of influent stream [gP/d]  
 $TP_{wastewater}$  : total phosphorus of waste stream [g/d]  
 $TP_{effluent}$  : total phosphorus of effluent stream [g/d]  
 $TN_{influent}$  : total nitrogen of influent stream [g/d]  
 $TN_{wastewater}$  : total nitrogen of waste stream [g/d]  
 $TN_{effluent}$  : total nitrogen of effluent stream [g/d]  
 $TP/VSS$  : phosphorus fraction of waste sludge [-]  
 $TN/VSS$  : nitrogen fraction of waste sludge [-]  
 $VSS_{wastewater}$  : VSS of waste sludge [g/d]  
 $y_{meas}$  : vector of measurement values of n process variables [-]  
 $y_{model}$  : vector of model values of n process variables [-]  
 $y_{esti}$  : estimated (or model) value of the process variable obtained after carrying out data reconciliation [-]

## Greek Letters

- $\varepsilon$  : vector of random measurement errors [-]

- $\Psi$  : weight matrix [-]  
 $\lambda$  : vector of n Lagrangian multipliers [-]  
 $\sigma_{meas}$  : standard deviation of the measurement [-]

## REFERENCES

1. X. Liu, Y. Peng, C. Wu, T. Akio and Y. Peng, *J. Environ. Sci.*, **20**, 614 (2008).
2. P. Czepiel, P. Crill and R. Harriss, *Environ. Sci. Technol.*, **29**, 2352 (1995).
3. J. Foley, D. de Haas, Z. Yuan and P. Lant, *Water Res.*, **44**, 831 (2010).
4. O. Nowak, A. Franz, K. Svardal, V. Muller and V. Kuhn, *Water Sci. Technol.*, **39**, 133 (1999).
5. J. A. Romagnoli and M. C. Sanchez, *Data processing and reconciliation for chemical process operation*, Academic Press, USA (2000).
6. S. C. F. Meijer, H. van der Spoel, S. Susanti, J. J. Heijnen and M. C. M. van Loosdrecht, *Water Sci. Technol.*, **45**, 145 (2002).
7. L. Rieger, I. Takacs, K. Villez, H. Siegrist, P. Lessard, P. A. Vanrolleghem and Y. Comeau, *Water Environ. Res.*, **82**, 426 (2010).
8. S. Puig, M. C. M. van Loosdrecht, J. Colprim and S. C. F. Meijer, *Water Res.*, **40**, 4645 (2008).
9. 2006 IPCC Guidelines for national greenhouse gas inventories, Japan (2006).
10. M. J. Kampschreur, H. Temmink, R. Kleerebezem, M. S. M. Jetten and M. C. M. Loosdrecht, *Water Res.*, **43**, 4093 (2009).