1 **Identifying key sources of uncertainty in the**

2 **modelling of greenhouse gas emissions from**

3 **wastewater treatment**

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8 **ABSTRACT**

9 This study investigates sources of uncertainty in the modelling

10 of greenhouse gas emissions from wastewater treatment,

11 through the use of local and global sensitivity analysis tools,

12 and contributes to an in-depth understanding of wastewater

13 treatment modelling by revealing critical parameters and

14 parameter interactions. One-factor-at-a-time sensitivity analysis

15 is used to screen model parameters and identify those with

16 significant individual effects on three performance indicators:

17 total greenhouse gas emissions, effluent quality and operational

18 cost. Sobol's method enables identification of parameters with

19 significant higher order effects and of particular parameter pairs

20 to which model outputs are sensitive. Use of a variance-based

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21 global sensitivity analysis tool to investigate parameter

22 interactions enables identification of important parameters not

23 revealed in one-factor-at-a-time sensitivity analysis. These

24 interaction effects have not been considered in previous studies

25 and thus provide a better understanding wastewater treatment

26 plant model characterisation. It was found that uncertainty in

27 modelled nitrous oxide emissions is the primary contributor to

28 uncertainty in total greenhouse gas emissions, due largely to the

29 interaction effects of three nitrogen conversion modelling

30 parameters. The higher order effects of these parameters are

31 also shown to be a key source of uncertainty in effluent quality.

32 *Keywords*: Benchmark model; greenhouse gas; model

33 identification; sensitivity; uncertainty; wastewater treatment

34 **1   INTRODUCTION**

35 Wastewater treatment can result in direct emissions of

36 greenhouse gases (GHGs) such as carbon dioxide (CO_2),

37 methane (CH_4) and nitrous oxide (N_2O), as well as indirect

38 emissions resulting from energy generation, chemical

39 manufacture and sludge disposal, amongst other sources.

40 Reduction of GHG emissions is a topic of global interest, and it

41 is recognised that appropriate design and operation of

42 wastewater treatment processes can play a significant role in

43 mitigating the effects of global warming (Gori et al., 2011).

44 Models used to estimate the magnitude of GHG emissions from

45 wastewater treatment plants (WWTPs) for inventories typically

46 utilise empirical emission factors (e.g. IPCC, 2006b), based on

47 the volume of wastewater treated, influent concentrations,

48 effluent concentrations or the mass of wastewater components

49 removed. These emission factors, however, have a high degree

50 of variability and uncertainty (Corominas et al., 2012): for

51 example, N_2O emissions in the range 0 - 90% of the nitrogen-

52 load were reported by Kampschreur et al. (2009). As such,

53 there has been increasing interest in the use of comprehensive

54 process models and mechanistic models to estimate dynamic

55 GHG emissions. Resulting from this, it has been highlighted

56 that significant variability can occur in GHG emissions from

57 WWTPs with different designs (Shahabadi et al., 2009) and

58 operating under different conditions (Flores-Alsina et al.,

59 2011).

60 As wastewater utilities face the challenge of simultaneously

61 reducing GHG emissions and improving treatment standards

62 due to increasing regulatory pressures, the importance of

63 including GHG emissions in addition to effluent quality and

64 operational costs when evaluating design alternatives is clear. It

65 has been shown that use of automatic control can reduce GHG

66 emissions (Corominas et al., 2010), but models used are

67 typically of hypothetical WWTPs and their results are not

68 always validated with real data (e.g. Hiatt and Grady, 2008;

3

69   Guo et al., 2012). As such, results are likely to be subject to a

70   high degree of uncertainty; and careful calibration is therefore

71   essential if applying the models and estimation methodologies

72   to a real WWTP for plant design or control strategy

73   development to reduce GHG emissions. Identification of the

74   most significant sources of uncertainty could aid efficient

75   calibration of models and reduce the complexity of future

76   uncertainty analyses, yet there has been little research into the

77   magnitude of uncertainty in GHG emission estimates resulting

78   from uncertainty in model parameters and emission factors.

79   Sensitivity analysis is a useful tool for identification of the key

80   parameters controlling model outputs (Tang et al., 2007a).

81   However, whilst sensitivity analyses of dynamic WWTP

82   models have previously been undertaken to investigate the

83   effects of uncertainty in model parameters (e.g. Pons et al.,

84   2008; Flores-Alsina et al., 2009; Ramin et al., 2012), design

85   and operational parameters (Benedetti et al., 2008; Pons et al.,

86   2008) and influent characteristics (Pons et al., 2008), no

87   detailed analyses for identification of key parameters affecting

88   GHG emissions have been carried out. Gori et al. (2011)

89   completed a sensitivity analysis to investigate the effects of

90   varying the pCOD/VSS ratio on the rate of GHG emissions

91   from different sources, but no other model parameters were

92   considered. Global sensitivity analyses (GSAs) of the

93   Benchmark Simulation Model No. 1 (BSM1) (Sin et al., 2011)

94   and the Benchmark Simulation Model No. 2 (BSM2)

95   (Benedetti et al., 2008), based on Monte Carlo experiments and

96   linear regression, enabled the identification of individual

97   parameters with significant effects on effluent quality and

98   operational cost, but did not consider GHG emissions.

99   However, interactions were not investigated and output

100 uncertainty was attributed to individual parameters only.

101 The aim of this research is to identify individual parameters and

102 parameter interactions which contribute significantly to

103 uncertainty in modelled GHG emissions from wastewater

104 treatment, as well as the more widely used performance

105 indicators of effluent quality and operational cost. Investigation

106 of the relative contributions of specific parameter interactions

107 to output uncertainty represents an advance in WWTP

108 modelling, as previous analyses have not enabled identification

109 of significant interactions. Sensitivity analysis of a revised

110 BSM2, with pre-defined layout, operating conditions and

111 influent characteristics, is carried out using the one-factor-at-a-

112 time (OAT) method, to identify significant individual (first

113 order) effects and inform the selection of parameters for

114 inclusion in further analysis. GSA is then carried out using a

115 variance-based method – Sobol's method (Saltelli, 2002) - to

116 investigate higher order effects (interactions). This tool has not,

117 as of yet, been extensively used in wastewater treatment, but

118 previous applications have revealed situations and modelling

119   scenarios in which calibration is likely to be most challenging

120   due to the greater presence of parameter interactions

121   (Massmann and Holzmann, 2012) and improved the efficiency

122   of multi-objective optimisation problems by identifying

123   important decision variable interactions (Fu et al., 2012). The

124   results enable identification of: a) parameters that have

125   negligible impact on uncertainty in key model outputs and can,

126   therefore, be excluded from future uncertainty analyses; and b)

127   parameters which contribute significantly to variance in any

128   key model output, due to first or higher order effects, and so

129   need to be accurately defined for model calibration and

130   application.

131   **2   MATERIALS AND METHODS**

132   **2.1   Model description**

133   *2.1.1   Model structure*

134   The WWTP model used for parameter sensitivity analysis,

135   which will be referred to as BSM2-e, is based on the

136   Benchmark Simulation Model No. 2: BSM2 (Jeppsson et al.,

137   2007), with modifications (outlined in Section 2.1.2) made to

138   enable dynamic modelling of the emissions shown in *Fig. 1*.

139   The plant layout and modelling of pre-treatment and sludge

140   treatment processes are unaltered from those of BSM2 (as

141   detailed by Jeppsson et al. (2007) and Nopens et al. (2010)), but

142   adjustments have been made to the activated sludge model to

143 enable calculation of N_2O emissions. A complete description of

144 all equations added and modifications made to the BSM2 is

145 provided as supplementary information.

146   Figure 1

147 ***2.1.2   Greenhouse gas emission modelling methodologies***

148 GHG emissions are modelled using previously published

149 estimation methodologies, which are implemented in BSM2.

150 Sources of GHG production and direct emissions from the

151 modelled processing units include:

152 • *Aerobic substrate utilisation (CO₂), biomass decay (CO₂)*

153 *and denitrification (CO₂ and N₂O) in activated sludge*

154 *reactors*

155 In BSM2, the reduction of nitrate to nitrogen is modelled as

156 a one-step process and dynamic production of N_2O (an

157 intermediate product) cannot be determined. Modifications

158 have therefore been made to include four-step denitrification

159 as detailed by Samie et al. (2011). Stripping of N_2O from

160 solution is then modelled using Henry's law. CO_2 emissions

161 resulting from nutrient removal are calculated using

162 emission factors derived from the stoichiometric

163 relationships for denitrification with and without an external

164 carbon source (Shahabadi et al., 2010).

165 Calculation of CO_2 emissions from substrate utilisation and

166 biomass decay is based upon the method detailed by

167   Monteith et al. (2005), with the suspended solids mass

168   balance equation adapted for non-steady state conditions.

169   Required concentrations and flow rates have been derived

170   from the BSM2 state variables and theoretical emission

171   factors, derived from stoichiometry, are applied.

172   • *Biogas leakage (CO_2 and CH_4) and combustion (CO_2)*

173   Dynamic CH_4 and CO_2 formation and stripping in the

174   anaerobic digester and the resultant biogas composition and

175   flow rate are modelled in BSM2. It is assumed in BSM2 that

176   all biogas is combusted for energy recovery. However, past

177   investigations (e.g. Shahabadi et al., 2009; Shahabadi et al.,

178   2010), have identified biogas leakage as a potential

179   contributor to total emissions. As it is impractical to

180   accurately measure or model small leaks, a fixed leakage

181   factor of 5% (Shahabadi et al., 2009) has been applied. It is

182   assumed that the remaining biogas is fully combusted and a

183   theoretical emission factor (Monteith et al., 2005) is used

184   calculate CO_2 production.

185   • *Stripping of dissolved gases (CH_4) in dewatering unit*

186   Dissolved CH_4 concentration in the digester effluent is

187   calculated using the BSM2 methodology. Given the

188   negligible partial pressure of CH_4 in the atmosphere, it is

189   assumed that all CH_4 is stripped from solution during

190   dewatering.

191 Additional direct emissions may result from poorly managed

192 treatment and unintentionally anaerobic conditions (Monteith et

193 al., 2005); these are not modelled, however, due to a lack of

194 reliable estimation techniques. Likewise, N_2O emissions

195 associated with nitrifier denitrification during nitrification are

196 omitted. There have been recent studies into the factors

197 influencing N_2O emissions (e.g. Foley et al., 2010; Law et al.,

198 2011; Rassamee et al., 2011), but there is little consensus on a

199 method which can be used to estimate emissions with any

200 degree of certainty and metabolic models of the nitrifier

201 denitrification pathway (Mampaey et al., 2011; Ni et al., 2011)

202 have been found unable to consistently reproduce experimental

203 N_2O emissions data (Law et al., 2012; Ni et al., 2013). The

204 significance of this omission is uncertain; heterotrophic

205 denitrification is the dominant nitrogen removal process, but

206 nitrifier denitrification yields greater N_2O emissions relative to

207 the nitrogen converted (Kampschreur et al., 2009). Incomplete

208 hydroxylamine oxidation can also result in N_2O emissions, but

209 it is unclear under what conditions this process becomes

210 dominant and current models are inadequate (Ni et al., 2013). If

211 nitrification modelling is included in future GHG emission

212 estimates, inclusion of the associated parameters in uncertainty

213 analysis is recommended.

214 Indirect emissions result from:

215 • *Generation of energy imported*

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216   Energy required for pumping, aeration, heating and mixing

217   is modelled using the original BSM2 methodologies; energy

218   recovery from biogas combustion is also calculated using

219   the BSM2 methodology, but with allowance for biogas

220   leakage incorporated. GHG emissions associated with net

221   energy import are affected by the electricity generation mix,

222   as emissions differ between energy sources. However, as

223   electricity grid composition varies locally and nationally and

224   the model is not linked to a specific location, a single

225   emission factor of 0.245 kg CO_2e/kWh (Gori et al., 2011) is

226   used but defined as uncertain.

227   • *Manufacture of chemicals*

228   Indirect emissions due to chemical addition have been

229   calculated using the carbon source flow rate for each tank, as

230   modelled in BSM2, and an emission factor of

231   1.54 kg CO_2e/kg MeOH (Shahabadi et al., 2010).

232   • *Offsite degradation of effluent*

233   Indirect CO_2 emissions are modelled based on the

234   assumption that all BOD_5 remaining in the effluent degrades

235   aerobically, as detailed by Shahabadi et al. (2010). Indirect

236   N_2O emissions are calculated using an emission factor of

237   0.005 kg N_2O-N/kg N (IPCC, 2006b).

238   • *Transport and offsite degradation of sludge*

239   Emissions resulting from the transport of sludge are

240   estimated using a fixed emission factor (Shahabadi et al.,

241   2010). Emissions of CO_2 and CH_4 resulting from the

242   degradation of biosolids remaining in the sludge are

243   modelled as detailed by Shahabadi et al. (2009), based on

244   the theoretical stoichiometric equation for biomass decay in

245   an anaerobic environment. Dynamic N_2O emissions are

246   calculated using the modelled sludge nitrogen content and

247   an emission factor of 0.01 kg N_2O-/kg N (IPCC, 2006a).

248 All emissions are converted to CO_2 equivalent (CO_2e) units,

249 using global warming potentials (GWPs) of 21 and 310 for CH_4

250 and N_2O respectively (IPCC, 1996), to enable comparison of

251 the magnitude of emissions from each source.

252 *2.1.3   Simulation strategy and performance assessment*

253 The performance of control strategies in the BSM2 is typically

254 assessed using a 609 day simulation, incorporating stabilisation

255 and evaluation periods, with predefined dynamic influent data.

256 Initial values should be determined by simulation with 200

257 days of constant influent data to allow the model to reach

258 steady state (Jeppsson et al., 2007). In order to carry out a GSA

259 of model parameters, however, it is necessary to significantly

260 reduce the computational demand. Based on analysis of the

261 effects of modifications in stabilisation and evaluation periods

262 on the OAT sensitivity analysis parameter rankings, a reduced

263 dynamic simulation period (consisting of 14 days stabilisation

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264   and 14 days evaluation, using days 322-350 of the BSM2

265   dynamic influent data) has been selected to follow the 200 day

266   steady state initialisation. Whilst this shortened simulation does

267   not reproduce the model outputs obtained with full length

268   stabilisation and evaluation, it has been found to be suitable for

269   assessment of the relative importance of parameters, enabling

270   correct identification of the most sensitive model parameters in

271   OAT sensitivity analysis and resulting in an average change in

272   rank of just 1.1 for all 70 parameters across the three key

273   outputs when compared with analysis using the full dynamic

274   simulation period (609 days).

275   Performance indicators used include an effluent quality index

276   (EQI) and an operational cost index (OCI), calculated using the

277   BSM2 methodology (Jeppsson et al., 2007). EQI is a weighted

278   sum of average effluent concentrations; OCI is a measure of the

279   average energy demand, energy recovery, carbon source dosage

280   and sludge production for disposal. Average GHG emissions

281   per unit of wastewater treated are also calculated, and the

282   contribution of each gas and direct and indirect emissions to

283   total GHG emissions are modelled to allow a more in-depth

284   investigation into the most significant sources of uncertainty.

285   *2.1.4   Model validation*

286   The magnitude of GHG emissions per unit of treated

287   wastewater reported in the literature differs significantly, even

288   for WWTPs with the same or similar treatment processes and

289   control. Total emissions in the range 19,554 – 22,920

290   kg CO_2e/d (equivalent to 0.947 – 1.110 kg CO_2e/m^3, based on

291   specified flow rate) were reported by Corominas et al. (2012) in

292   an investigation into the effects of different GHG modelling

293   approaches for the BSM2 plant. The BSM2-e emissions model

294   gives total GHG emissions of 1.077 kg CO_2e/m^3 when using

295   the default BSM2 evaluation period, which is within this range.

296   **2.2   Sensitivity analysis methodology**

297   153 BSM2 parameters are used in the model (excluding those

298   relating to the plant design and operation), and a further 64 are

299   used for the incorporated denitrification and emissions

300   modelling. Given the large number of evaluations required for

301   GSA, it is not practical to include every parameter. Therefore,

302   OAT sensitivity analysis, which requires significantly fewer

303   model evaluations, is used to provide an indication of the

304   importance of each parameter and identify parameters with

305   negligible effect on uncertainty in model outputs.

306   OAT sensitivity analysis enables changes in model outputs to

307   be clearly attributed to a specific parameter, with no ambiguity,

308   but does not explore the effects of varying two or more

309   parameters simultaneously and is unable to identify any

310   significant interactions. As such, it is followed by GSA to

311   obtain an understanding of second (and higher) order effects

312   and allow exploration of the full parameter space.

2.2.1 Parameter screening

2.2.1.1 Parameter selection and definitions

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314

315 Selection of BSM2 parameters is guided by the results of

316 previous GSA by Benedetti et al. (2008): those identified as

317 being not significant for EQI, OCI and effluent NH_4 violations

318 in terms of both the standard regression coefficient and the

319 partial correlation coefficient are excluded from this analysis.

320 Henry's law coefficients used to model dissolution and

321 stripping of CO_2 and CH_4 in the anaerobic digester, however,

322 are added to the analysis, as they may affect emissions despite

323 not having significant effects on previously considered model

324 outputs.

325 All half-saturation constants added for the modelling of

326 nitrogen conversions are included in the sensitivity analysis,

327 because these parameters have a high degree of uncertainty

328 (Reichert and Vanrolleghem, 2001) and affect modelled N_2O

329 production, which has been shown to be a major contributor to

330 GHG emissions from WWTPs (Rodriguez-Garcia et al., 2012).

331 Also, other half-saturation constants were found to be

332 significant by Benedetti et al. (2008).

333 It is assumed that median values for each parameter are equal

334 to the BSM2 default values (where applicable). For all other

335 parameters, median values are assumed to be those reported in

336 the literature on which the calculations are based. Parameters

337   for which no feasible range is specified in the literature are

338   classified according to the system defined by Reichert and

339   Vanrolleghem (2001) (summarised in *Table 1*) and adopted in

340   later sensitivity and uncertainty analyses (Rousseau et al., 2001;

341   Benedetti et al., 2008).

342   Table 1

343   Full details of parameters selected for screening are given in

344   *Table 2* and *Table 3*. Parameters 1-26 are BSM2 parameters,

345   27-39 are nitrogen conversion modelling parameters and 40-70

346   are emissions modelling parameters.

347   Table 2

348   Table 3

349   *2.2.1.2 One-factor-at-a-time sensitivity analysis*

350   To carry out OAT sensitivity analysis, a simulation is first

351   conducted with all parameters set at their default values; this

352   represents the base case. Further simulations are carried out

353   with each parameter individually set to its upper and lower

354   bound values in turn, whilst all others are held at their default

355   values. Percentage change in each model output with respect to

356   the base case is calculated for each simulation, to determine

357   which parameters cause the greatest variation in model outputs

358   when individually varied within their feasible range.

359   **2.2.2   Global sensitivity analysis**

360   Sobol's method (2001) is selected for GSA despite being

361   computationally expensive, as it enables first, second and

362   higher order effects to be distinguished through the calculation

363   of first, second and total order sensitivity indices for each

364   parameter or parameter pair. It also provides more robust

365   sensitivity rankings and a more detailed description of the

366   impact of individual parameters and their interactions on model

367   performance than other GSA methods such as analysis of

368   variance (Tang et al., 2007b), and requires significantly fewer

369   model evaluations than factorial design given the large number

370   of parameters under investigation.

371   The total variance (D) of model outputs, resulting from samples

372   of the feasible parameter space, is decomposed and attributed to

373   specific parameters and their interactions as follows, assuming

374   parameters are independent (Tang et al., 2007b):

$$D = \sum_i D_i + \sum_{i<j} D_{ij} + \sum_{i<j<k} D_{ijk} + \cdots + D_{12\ldots p} \tag{1}$$

375   where D_i = output variance resulting from the ith parameter; D_{ij}

376   = output variance resulting from interaction between ith and jth

377   parameters; p = total number of parameters.

378   First and second order sensitivity indices S_i and S_{ij} represent

379   the percentage contribution of the ith parameter alone and the

380   interaction between the ith and jth parameters to total variance,

381   respectively; total order index S_{Ti} represents the percentage

382   contribution related to the ith parameter, including the

383   interactions of any order, as defined below:

$$S_i = \frac{D_i}{D} \tag{2}$$

$$S_{ij} = \frac{D_{ij}}{D} \tag{3}$$

$$S_{Ti} = 1 - \frac{D_{\sim i}}{D} \tag{4}$$

384   where $D_{\sim i}$ = output variance resulting from all parameters

385   except ith parameter. A high first order sensitivity index

386   indicates a parameter whose individual uncertainty provides a

387   large contribution to output variance, whereas a low first order

388   index and high total order index indicates a parameter whose

389   interactions result in significant output variance, but

390   individually has little effect.

391   Sobol's method is implemented here as follows:

392   1. Specify upper and lower bounds of parameters for

393   analysis.

394   2. Generate $2n$ random parameter samples within the

395   specified bounds, with quasi-Monte Carlo sampling

396   using Sobol's sequence generator.

397   3. Resample parameters using Saltelli's (2002) extension

398   to Sobol's method, holding one fixed at a time, to

399   generate $n(2p+2)$ parameter sets.

400   4. Run model with each parameter set in turn, recording

401   values of model outputs.

402   5. Compute first order, total order and second order

403   sensitivity indices, and rankings for each parameter as

404   detailed by Tang et al. (2007b).

405   6. Calculate 95% bootstrap confidence intervals for all

406   sensitivity indices.

407 **3   RESULTS AND DISCUSSION**

408 **3.1   One-factor-at-a-time sensitivity analysis**

409 OAT sensitivity analysis results are presented in Tornado

410 diagrams, which show the percentage change in each model

411 output with respect to the base case when each model

412 parameter is individually set to its respective upper and lower

413 bounds. Parameters are ranked by the greatest range of

414 percentage change for any model output and results for the

415 most sensitive parameters are presented in *Fig. 2*. For clarity,

416 only the 28 parameters with a corresponding range of change of

417 at least 5% in one or more model output are shown.

418 Figure 2

419 Variation of a single parameter within its feasible range can

420 have particularly significant effects on modelled GHG

421 emissions; setting the half saturation constant for readily

422 biodegradable substrate for N_2O reduction (parameter 30) to its

423 upper bound, for example, results in a 244% increase in

424 reported GHG emissions. Individual variation of a further eight

425 parameters is shown to result in a range of at least 25% change

426 in GHG emissions.

427 A maximum range of variation in total GHG emissions of

428 260%, resulting from uncertainty in just one parameter (No.

429 30), is observed, whereas maximum changes in EQI and OCI

430 are significantly lower at 22.0% (No. 12) and 17.9% (No. 64)

431 respectively. This confirms that accurate calibration of the

432 model with regards to GHG emissions modelling is extremely

433 important. The nine parameters shown to have greatest

434 individual effects on GHG emissions are all used in the

435 modelling of nitrogen conversions, suggesting that uncertainty

436 in GHG emissions corresponds primarily to uncertainty in the

437 rate of N_2O production. The three parameters to which GHG

438 emissions are shown to be most sensitive result in negligible

439 change in EQI and OCI and ought, therefore, to be relatively

440 simple to calibrate if significant higher order effects are not

441 identified in GSA.

19

442 The greatest changes in EQI arise due to uncertainty in the

443 original BSM2 parameters, and nitrogen modelling parameters

444 have comparatively little impact. Uncertainty in emissions

445 modelling parameters has no effect on EQI. Uncertainty in

446 BSM2 parameters contributes to uncertainty in all three of the

447 key model outputs, although OCI is affected to a lesser degree

448 (maximum 3.2% change, compared with 22.0% and 19.0% for

449 EQI and GHG emissions respectively). It is, therefore,

450 important to take into account the effects of BSM2 parameter

451 values on GHG emissions as well as on conventional

452 performance assessment measures when calibrating the model.

453 The OCI is affected predominantly by uncertainty in the

454 oxygen transfer efficiency (parameter 64) during OAT

455 sensitivity analysis, suggesting that this is particularly

456 important to consider when carrying out uncertainty analyses

457 with regard to operational costs.

458 **3.2   Sobol's method global sensitivity analysis**

459 GSA was carried out using the highlighted parameters in *Table*

460 *1* and *Table 2*, selected based on OAT sensitivity analysis

461 screening results. In addition to the 28 parameters shown in

462 Fig. 2, these include a further 11 of the highest ranked

463 parameters. First order, second order and total order sensitivity

464 indices computed using a sample size of 4,000 are presented,

465 and parameters are classified as either 'not sensitive',

466   'sensitive' or 'highly sensitive' based on their contribution to

467   output variance. A threshold of 1% contribution to output

468   variance (i.e. a sensitivity index of at least 0.01) is used to

469   define sensitive parameters, and a 10% contribution (i.e. a

470   sensitivity index of at least 0.1) for highly sensitive parameters.

471   It is known that small numerical errors can result from the

472   truncation of Monte Carlo approximations used in Sobol's

473   method for calculation of integrals (Tang et al., 2007b), so

474   slightly negative indices are assumed to equal zero. Instances in

475   which the total order index is slightly greater than one or the

476   total order index is less than the sum of the first and second

477   order indices are also attributed to such errors. For the OCI,

478   total order indices sum to less than one; this apparent error,

479   however, is fully accounted for by the 95% confidence

480   intervals.

481   Bootstrapped confidence intervals, calculated using 1,000

482   resamples, are presented for all first and total order indices

483   greater than 0.01. It is noted that some sensitivity indices have

484   a high degree of uncertainty, with the greatest confidence

485   interval being 0.501 ± 0.099. The number of samples generated

486   for analysis was quadrupled from preliminary analyses in an

487   attempt to reduce confidence intervals, but further increase in

488   the number of samples is impractical due to the high

489   computational demand. Large uncertainties are not unexpected

490   for Sobol's method, however, due to random number

491   generation effects (Tang et al., 2007b), and confidence intervals

492   in excess of 20% of the corresponding sensitivity indices have

493   been reported for previous analyses (Tang et al., 2007a; Tang et

494   al., 2007b). Despite large confidence intervals, the sensitivity

495   indices can still be used to provide an indication of the relative

496   significance of uncertainty in each modelling parameter in

497   terms of its effects on model output uncertainties.

498   ***3.2.1   Sensitivity indices based on EQI, OCI and total GHG***
499   ***emissions***

500   *3.2.1.1 First and total order indices*

501   First and total order sensitivities calculated based on EQI, OCI

502   and total GHG emissions are presented in *Fig. 3*.

503   Figure 3

504   The EQI is shown to be sensitive or highly sensitive to twenty

505   BSM2 and nitrogen modelling parameters, with emissions

506   modelling parameters (predictably) having no effect.

507   Uncertainty in the BSM2 parameters results primarily in first

508   order effects, but it is shown that higher order effects are

509   dominant for nitrogen modelling parameters, and that some

510   important parameters cannot be identified based on their

511   individual effects alone. For example, OAT sensitivity analysis

512   suggests that EQI is not sensitive to parameters 28 and 29

513   (ranked 11th and 25th), but investigation into their interactions

514   using Sobol's method shows that they are the greatest

515   contributors to output variance.

516   The effects of parameter interactions on OCI uncertainty are

517   negligible, and there is only one highly sensitive parameter: the

518   oxygen transfer efficiency (parameter 64). OCI is also sensitive

519   to three BSM2 parameters, although their contribution to output

520   variance is insignificant in comparison.

521   All parameters classed as highly sensitive based on GHG

522   emissions are used in the modelling of N_2O production and

523   emission, supporting the earlier suggestion that, due to their

524   high GWP, uncertainty in the rate of N_2O emissions is a

525   significant contributor to uncertainty in total GHG emissions.

526   Variance in modelled GHG emissions is predominantly due to

527   interactions, although first order effects are still significant for

528   some nitrogen modelling parameters: parameter 28, for

529   example, contributes 50.1% of output variance to total output

530   variance, with 10.9% from the parameter itself and 39.2% from

531   its interactions with other parameters. It would, therefore, be

532   beneficial to investigate the effects of specific interactions, to

533   ensure that suitable allowance is made in future analyses and

534   model calibration.

535   It can be seen that there is only one parameter to which all three

536   key model outputs are sensitive (parameter 8), although both

537   EQI and GHG emissions are highly sensitive to the half

538   saturation coefficients for readily biodegradable substrate for

539   NO_3, NO_2 and NO reduction. Fourteen parameters are not

540   classed as sensitive based on any of the three key outputs; it is

541   suggested that these need not be included in future uncertainty

542   analyses.

543   *3.2.1.2 Second order indices*

544   Second order sensitivity indices calculated based on output

545   GHG emissions and EQI are presented in *Fig. 4* (second order

546   indices based on OCI are not calculated since it has been shown

547   that the effect of interactions is negligible): the shade of grey

548   represents the sensitivity index magnitude for the

549   corresponding parameter pair. Whilst no interactions due to

550   individual parameter pairs can be classed as highly sensitive,

551   there are numerous parameter pairs which have a significant

552   impact on output variance in GHG emissions and EQI (index $\geq$

553   0.01, shown with a circle).

554   Figure 4

555   Not all parameters identifiable as having significant

556   interactions, based on the difference between their total and

557   first order sensitivity indices, are found to have sensitive

558   parameter pairs, and the second order effects of some

559   parameters account for only a small proportion of total output

560   variance resulting from their interactions. Second order effects

561   involving parameter 28, for example, contribute to 3.1% of

562   variance in total GHG emissions, but all interactions with this

563   parameter contribute 39.2% of output variance, showing that

564   higher order interactions are significant; calibration of such

565   parameters is, therefore, likely to be challenging.

566   In terms of both GHG emissions and EQI, all sensitive

567   parameter pairings include at least one nitrogen modelling

568   parameter and the most significant second order interactions are

569   between two nitrogen modelling parameters. This provides

570   further support to the earlier suggestion that careful calibration

571   of nitrogen modelling parameters is vital if model output

572   uncertainty is to be reduced.

573   ***3.2.2   Sensitivity indices based on component GHG***
574   ***emissions***

575   Having identified parameters to which total GHG emissions are

576   sensitive, the effects of uncertainty in these parameters on

577   emissions of different gases and from different sources are

578   explored, and the contribution of uncertainty in different

579   emission components to uncertainty in total GHG emissions is

580   investigated.

581   The characteristics of GHG emissions resulting from the

582   160,000 parameter sets modelled for GSA are summarised in

583   *Table 4*, from which it can be seen that variance in direct N_2O

584   emissions contributes greatly to variance in total GHG

585   emissions. Indirect emissions provide a comparatively small

586   (12%) contribution to mean total GHG emissions, but are the

587   second greatest contributor to total variance. Variance in direct

588   CO_2 and CH_4 emissions provides negligible contribution to

589   total variance, despite contributing 33% of mean total GHG

590   emissions. This suggests that, unless uncertainty in direct N_2O

591   emissions is significantly reduced by reduction of relevant

592   parameter uncertainties, inclusion of parameters to which only

593   direct CO_2 and CH_4 emissions are sensitive is unnecessary

594   when calculating uncertainty in total GHG emissions. Further

595   GSA therefore focuses on sources of uncertainty in direct N_2O

596   and total indirect emissions.

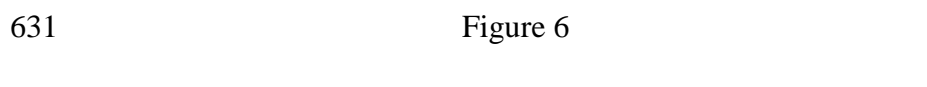597   Table 4

598   First and total order sensitivity indices based on emission

599   components are presented in *Fig. 5*. There is negligible

600   difference between those based on total GHG emissions and

601   those based on direct N_2O emissions only, confirming that

602   reducing uncertainty in N_2O emissions is key to reducing

603   uncertainty in total GHG emissions.

604   Figure 5

605   Uncertainty in indirect GHG emissions is primarily attributed

606   to first order effects of the oxygen transfer efficiency and

607   emission factors for carbonaceous BOD removal and N_2O from

608   the WWTP effluent and sludge (parameters 64, 65 and 68). A

609   further five sensitive parameters are also identifiable. Given

610   that the effects of interactions are negligible and the highly

611   sensitive parameters are not classed as sensitive based on any

612   other model output, calibration with regards to indirect

613   emissions ought to be straightforward.

614   As parameter interactions are shown to contribute significantly

615   to variance in direct N_2O emissions, second order sensitivity

616   indices are calculated and are shown in *Fig. 6*. Again, the

617   indices based on direct N_2O emissions are very similar to those

618   based on total GHG emissions, although there are differences:

619   whilst all sensitive parameter pairs still include at least one

620   nitrogen modelling parameter, nine pairs involving the half

621   saturation coefficient for NO_2 for heterotrophs (parameter 32)

622   are no longer classified as sensitive. This suggests that their

623   second order interactions impact primarily on other GHG

624   emissions. All emissions modelling parameters are involved in

625   significant second order interactions with parameters 29, 36, 37

626   and 38 and are, therefore, particularly important to reduce

627   uncertainty in and consider simultaneously during calibration.

628   Also important is the interaction between parameters 28 and 27,

629   which alone contributes 2% of variance in direct N_2O

630   emissions.

631   Figure 6

632   **3.3   Key sources of uncertainty and comparison of results**

633   Model parameters to which at least one of the key model

634   outputs (EQI, OCI and total GHG emissions) is sensitive, based

635　　on the corresponding sensitivity indices, are detailed in *Table 5*.

636　　Shading is used to distinguish sensitive and highly sensitive

637　　parameters for each output, and rankings based on OAT

638　　sensitivity analysis results as well as first and total order indices

639　　are provided. The maximum specific hydrolysis rate (parameter

640　　8) is classified as sensitive based on all three key model

641　　outputs, showing that it is necessary to simultaneously consider

642　　its impacts on each output during calibration. A further ten

643　　parameters are classified as sensitive based on both EQI and

644　　OCI; their effects on both effluent concentrations and GHG

645　　emissions must be taken into account during calibration. The

646　　remaining fourteen parameters are classified as sensitive based

647　　on just one model output.

648　　　　　　　　　　　　　　Table 5

649　　OAT sensitivity analysis results provide a good indication of

650　　the most significant individual sources of uncertainty in output

651　　EQI and OCI: parameters classified as highly sensitive based

652　　on their first order indices are also the highest ranked in OAT

653　　sensitivity analysis. For GHG emissions, however, OAT

654　　sensitivity analysis did not enable correct identification of any

655　　parameters classified as highly sensitive in GSA and there are

656　　significant discrepancies between the first order index rankings

657　　and OAT sensitivity analysis rankings for all parameters. This

658　　shows that a full GSA is an important tool even when

659　　identification of only significant first order effects is required.

660   GSA using Sobol's method also enables identification of

661   parameters involved in interactions with significant effects on

662   uncertainty in the model output. As such, highly sensitive

663   parameters have been identified which have comparatively low

664   first order sensitivity indices and contribute to output

665   uncertainty primarily through higher order effects. These are

666   not all identifiable by OAT sensitivity analysis – uncertainty in

667   parameter 28, for example, provides the greatest contribution to

668   uncertainty in output EQI, but is ranked only 11th based on the

669   results of OAT sensitivity analysis. This highlights the

670   importance of including the effects of interactions when

671   identifying and prioritising sources of uncertainty.

672   **4   CONCLUSIONS**

673   This research uses sensitivity analysis tools to assess the

674   contribution of uncertain parameters in the modelling of GHG

675   emissions from wastewater treatment to uncertainty in model

676   outputs, and to identify parameters to which the outputs are

677   most sensitive. Sensitivity analyses are carried out using both

678   the OAT method (also used for screening) and Sobol's method

679   (to enable identification of significant interactions), from which

680   the following conclusions can be drawn:

681   •   Parameters used in the modelling of nitrogen

682   conversions have negligible first order (individual)

683   effects on the EQI and, based on OAT sensitivity

684	analysis, have a low significance rank. Use of Sobol's
685	method, however, enables identification of parameters
686	involved in interactions that contribute greatly to
687	uncertainty in EQI. This highlights the importance of
688	considering parameter interactions using a variance-
689	based global sensitivity analysis method such as Sobol's
690	method.
691	• Uncertainty in total GHG emissions from the modelled
692	WWTP result primarily from uncertainty in direct N_2O
693	emissions, due to their high GWP. Key sources of
694	uncertainty in direct N_2O emissions include the half
695	saturation coefficients for readily biodegradable
696	substrate for NO_3, NO_2 and NO reduction. As such,
697	further work to reduce uncertainty in these parameter
698	values would be beneficial in order to reduce
699	uncertainty in total GHG emissions.
700	• GSA reveals that parameters used in the modelling of
701	nitrogen conversions are key sources of uncertainty in
702	both EQI and total GHG emissions – therefore, when
703	calibrating the model, it is important to consider the
704	effects on both of these outputs.
705	• Uncertainty in the OCI is shown to be predominantly
706	due to first order effects resulting from uncertainty in
707	the oxygen transfer efficiency. Neither EQI or GHG
708	emissions are sensitive to this parameter, thus

30

709   calibration of model outputs used in calculation of the

710   OCI is expected to be relatively straightforward if this

711   knowledge is taken into account.

712 In summary, this study has enabled the identification of

713 parameters that contribute significantly to uncertainty in one or

714 more model outputs and require careful calibration, as well as

715 those that provide negligible contribution and can be omitted

716 from future uncertainty analyses.

717 **ACKNOWLEDGEMENTS**

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922

923 **FIGURE CAPTIONS**

924 *Fig. 1 – Schematic diagram of the modified BSM2 plant and*

925 *sources of modelled GHG emissions (adapted from Nopens et*

926 *al., 2010).*

927 *Fig. 2 – Percentage change in model output resulting from*

928 *variation of individual parameter values*

929 *Fig. 3 – First and total order sensitivity indices calculated*

930 *using Sobol's method*

931 *Fig. 4 – Second order sensitivity indices calculated using*

932 *Sobol's method*

933 *Fig. 5 – First and total order sensitivity indices based on direct*

934 *N_2O emissions and total indirect GHG emissions*

935 *Fig. 6 – Second order sensitivity indices calculated using*

936 *Sobol's method, based on direct N_2O emissions*

937 **FIGURES**

938 *Fig. 1 – Schematic diagram of the modified BSM2 plant and sources of modelled GHG*

939 *emissions (adapted from Nopens et al., 2010).*

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941   *Fig. 2 – Percentage change in model output resulting from variation of individual parameter*

942   *values*

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944   *Fig. 3 – First and total order sensitivity indices calculated using Sobol's method*
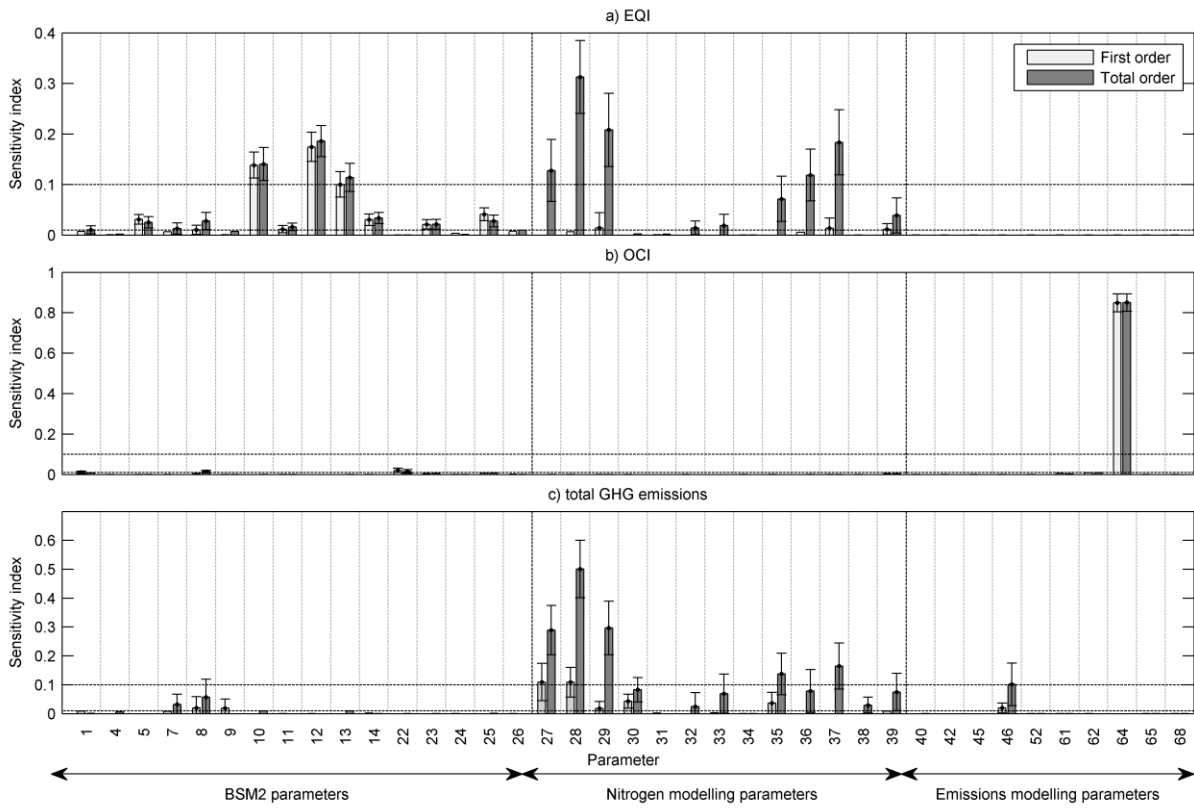
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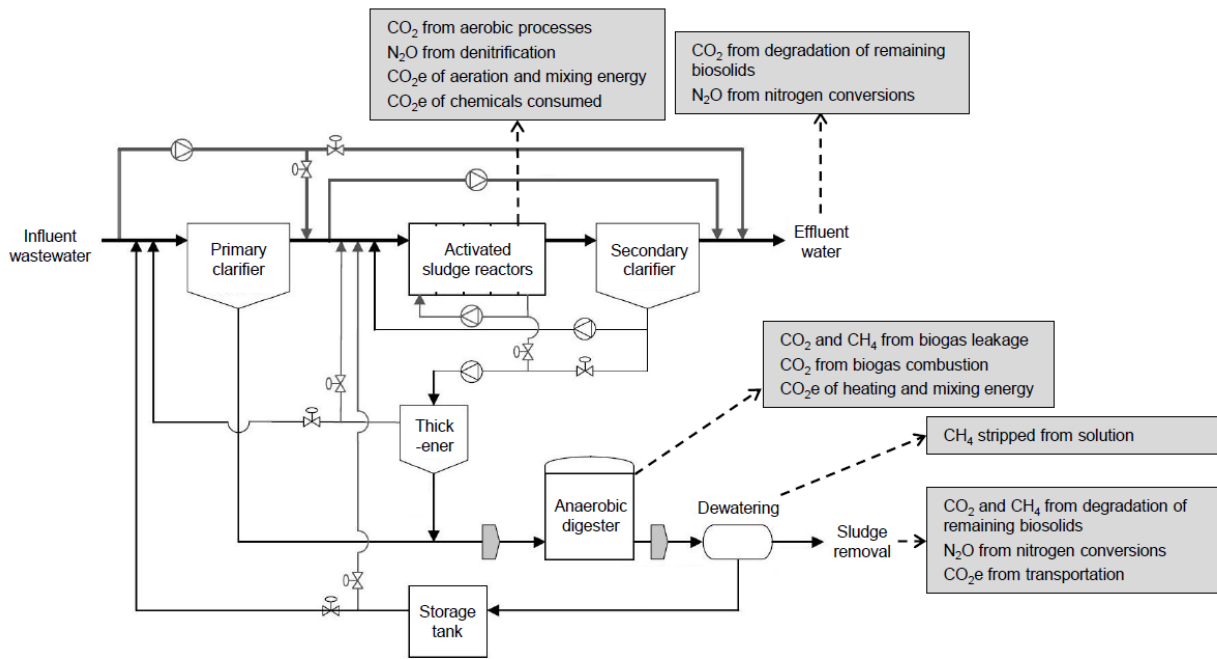946   *Fig. 4 – Second order sensitivity indices calculated using Sobol's method*
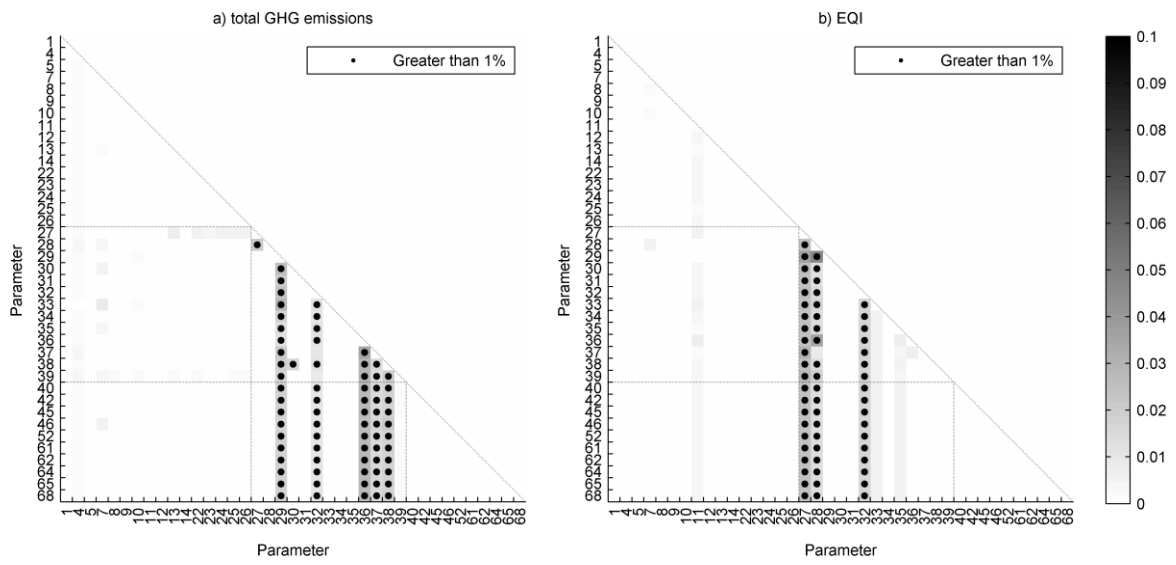
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948   *Fig. 5 – First and total order sensitivity indices based on direct N₂O emissions and total*

949   *indirect GHG emissions*
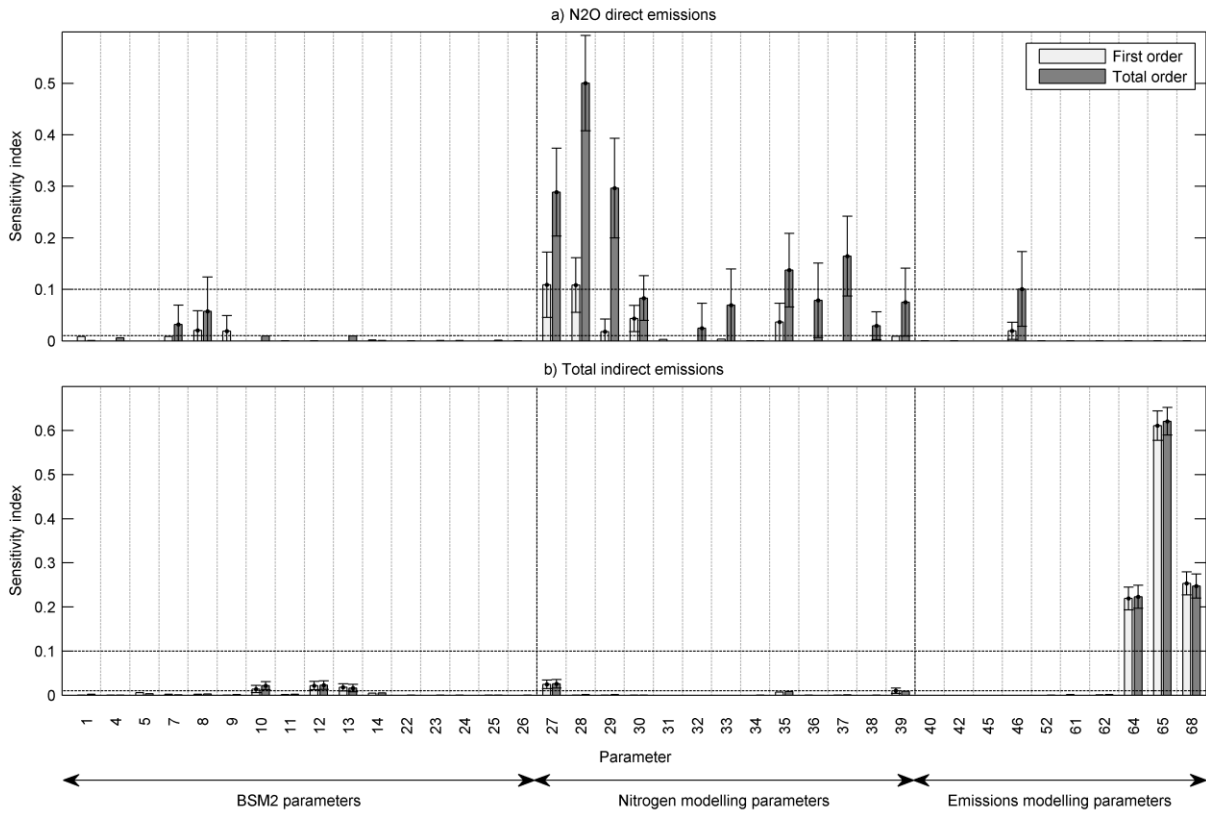
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951   *Fig. 6 – Second order sensitivity indices calculated using Sobol's method, based on direct*
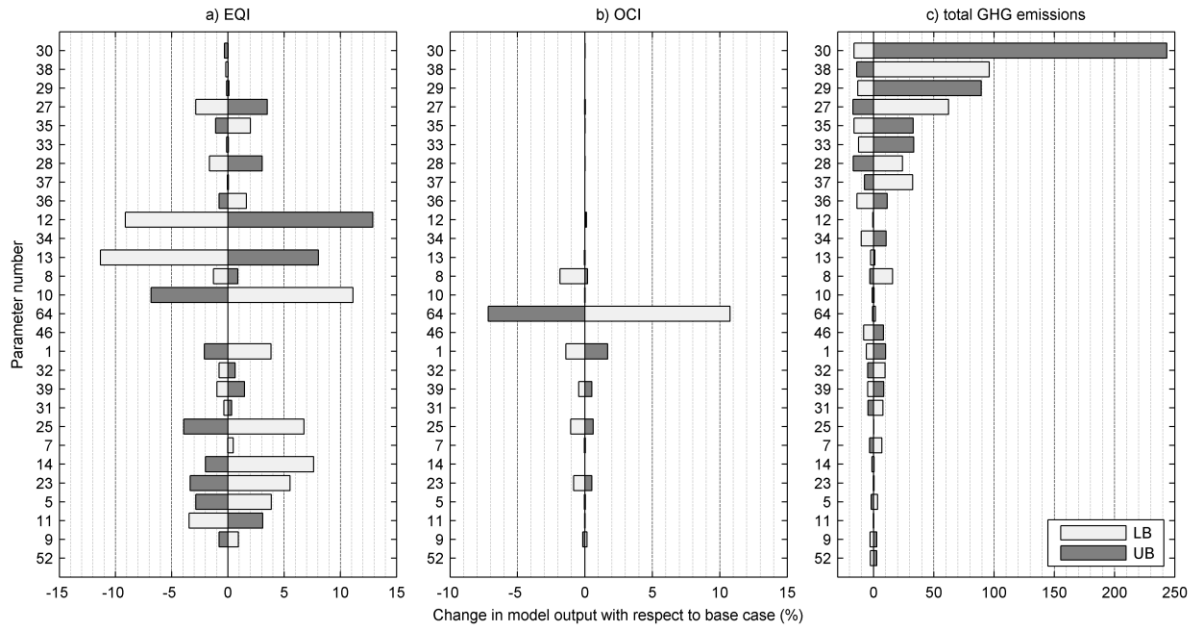
952   *N$_2$O emissions*
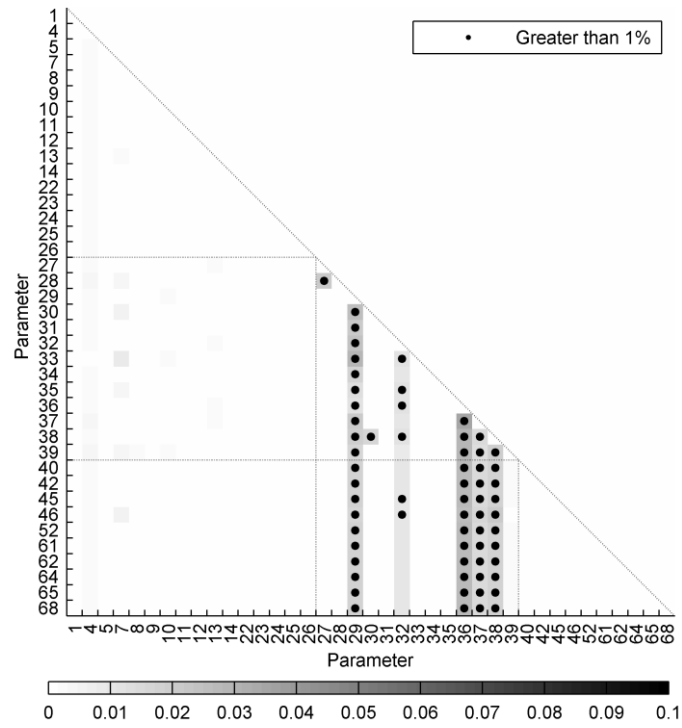
953

954 **TABLE CAPTIONS**

955 *Table 1 – Parameter uncertainty classes*

956 *Table 2 – BSM2 and nitrogen modelling parameters selected*

957 *for sensitivity analysis screening and global sensitivity analysis*

958 *(highlighted); HSC = half saturation coefficient*

959 *Table 3 – Emissions modelling parameters selected for*

960 *sensitivity analysis screening and global sensitivity analysis*

961 *(highlighted); EF = emission factor*

962 *Table 4 – Characteristics of total and component GHG*

963 *emission results used for Sobol's method sensitivity analysis*

964 *Table 5 – Ranking of model parameters to which at least one*

965 *key model output is sensitive*

966 **TABLES**

967 *Table 1 – Parameter uncertainty classes*

Class	Description	Uncertainty (%)	Examples
1	Accurately known parameters	5	External and input parameters
2	Intermediate	20	Growth rates; temperature dependence coefficients
3	Very poorly known parameters	50	Kinetic parameters, except those listed in Class 2; half-saturation concentrations; specific death and respiration rates

Table 2 – BSM2 and nitrogen modelling parameters selected for sensitivity analysis

screening and global sensitivity analysis (highlighted); HSC = half saturation coefficient

Parameter number/name	Description	Default value		Class	Bounds		
		Value	Ref.		Lower	Upper	Ref.
1/Y_H	Heterotrophic biomass yield (g COD/g COD)	0.67	a	1	0.6365	0.7035	c
2/f_P	Fraction of biomass yielding particulate products	0.08	b	1	0.076	0.084	c
3/i_XB	Biomass nitrogen/COD mass ratio (g N/g COD)	0.08	a	1	0.076	0.084	c
4/mu_H	Heterotrophic max specific growth rate (/d)	4	a	2	3.2	4.8	c
5/K_OH	Oxygen HSC for heterotrophic biomass (g(-COD)/m^3)	0.2	a	3	0.1	0.3	c
6/ny_g	Correction factor for anoxic heterotroph growth	0.8	a	2	0.64	0.96	c
7/ny_h	Correction factor for anoxic hydrolosis	0.8	a	2	0.64	0.96	N/A
8/k_h	Max specific hydrolosis rate (g COD/g COD/d)	3	a	3	1.5	4.5	N/A
9/K_X	HSC of slowly biodegradable substrate (g COD/g COD)	0.1	a	3	0.05	0.15	N/A
10/mu_A	Autotrophic max specific growth rate (/d)	0.5	a	2	0.4	0.6	c
11/K_NH	Ammonia HSC for autotrophs (g NH$_3$-N/m^3)	1	a	3	0.5	1.5	c
12/b_A	Decay coefficient for autotrophic biomass (/d)	0.05	a	3	0.025	0.075	N/A
13/K_OA	Oxygen HSC for autotrophic biomass (g (-COD)/m^3)	0.4	a	3	0.2	0.6	c
14/k_a	Ammonification rate (m^3/g COD/d)	0.05	a	3	0.025	0.075	N/A
15/F_TSS_COD	TSS fraction of total COD (g TSS/g COD)	0.75	a	1	0.7125	0.7875	N/A
16/k_hyd_ch	Hydrolosis influence coefficient for carbohydrates (/d)	10	a	N/A	6.25	12.5	Derived from c
17/k_hyd_pr	Hydrolosis influence coefficient for proteins (/d)	10	a	N/A	6.36	13.64	Derived from c
18/k_hyd_li	Hydrolosis influence coefficient for lipids (/d)	10	a	N/A	6.36	13.64	Derived from c
19/K_S_ac	Monod HSC for acetate (kg COD/m^3)	0.15	a	3	0.075	0.225	N/A
20/K_H_co2	Henry's law coefficient for CO$_2$ (M$_{liq}$/bar)	0.035	a	2	0.028	0.042	N/A
21/K_H_ch4	Henry's law coefficient for CH$_4$ (M$_{liq}$/bar)	0.0014	a	2	0.00112	0.00168	N/A
22/frxs_adm	Anaerobically degradable fraction biomass	0.68	a	1	0.646	0.714	N/A
23/v0	Maximum Vesilind settling velocity (m/d)	474	a	2	379.2	568.8	c
24/r_h	Hindered zone settling parameter (m^3/g SS)	5.76E-04	a	2	0.00046	0.00069	c
25/r_p	Flocculent zone settling parameter (m^3/g SS)	0.00286	a	2	0.00229	0.00343	c
26/f_ns	Non-settleable fraction	0.00228	a	2	0.00182	0.00274	c
27/K_S2	HSC for S_S for NO$_3$- reduction (g COD/m^3)	20	d	3	10	30	N/A
28/K_S3	HSC for S_S for NO$_2$- reduction (g COD/m^3)	20	d	3	10	30	N/A
29/K_S4	HSC for S_S for NO reduction (g COD/m^3)	20	d	3	10	30	N/A
30/K_S5	HSC for S_S for N$_2$O- reduction (g COD/m^3)	40	d	3	20	60	N/A
31/K_NO3	HSC for SNO$_3$ for heterotrophs (g N/m^3)	0.2	d	3	0.1	0.3	N/A
32/K_NO2	HSC for SNO$_2$ for heterotrophs (g N/m^3)	0.2	d	3	0.1	0.3	N/A
33/K_NO	HSC for SNO for heterotrophs (g N/m^3)	0.05	d	3	0.025	0.075	N/A
34/K_N2O	HSC for SN$_2$O for heterotrophs (g N/m^3)	0.05	d	3	0.025	0.075	N/A
35/ny_g2	Anoxic growth factor for NO$_3$- reduction	0.28	d	2	0.224	0.336	N/A
36/ny_g3	Anoxic growth factor for NO$_2$- reduction	0.16	d	2	0.128	0.192	N/A
37/ny_g4	Anoxic growth factor for NO reduction	0.35	d	2	0.28	0.42	N/A
38/ny_g5	Anoxic growth factor for N$_2$O reduction	0.35	d	2	0.28	0.42	N/A
39/ny_Y	Anoxic yield factor for heterotrophs	0.9	d	1	0.855	0.945	N/A

[a] Alex et al. (2008)
[b] Henze et al. (1987)
[c] Benedetti et al. (2008)
[d] Hiatt and Grady (2008)

Table 3 – Emissions modelling parameters selected for sensitivity analysis screening and

global sensitivity analysis (highlighted); EF = emission factor

Parameter number/name	Description	Default value		Class	Bounds		
		Value	Ref.		Lower	Upper	Ref.
40/f	Ratio of BOD_5 to BODu (g BOD_5/g BODu)	0.68	e	Class	0.646	0.714	N/A
41/EF_AerOxi	EF for aerobic oxidation of BOD (kg CO_2/kg O_2)	1.1	e	1	1.045	1.155	N/A
42/EF_AerAutoOxi	EF for endogenous respiration of VSS (kg CO_2/kg VSS)	1.947	e	1	1.850	2.044	N/A
43/EF_CO2denitWCarb	EF for CO_2 emissions from denitrification with external carbon source (g CO_2/g N_2-N)	2.62	Derived from f	1	2.489	2.751	N/A
44/EF_CO2denitWOCarb	EF for CO_2 emissions from denitrification without external carbon source (g CO_2/g N_2-N)	2.83	Derived from f	1	2.689	2.972	N/A
45/K_H_n2o_base	Henry's law constant for N_2O (mol/l/bar)	0.025	g	2	0.02	0.03	N/A
46/kLa_n2o	Gas transfer coefficient for N_2O (/d)	2	h	3	1	3	N/A
47/pgas_n2o	Partial pressure of N_2O in atmosphere (bar)	3.20E-07	i	2	2.56E-07	3.84E-07	N/A
48/EF_AnaerBODremCH4	CH_4 emissions from anaerobic carbonaceous substrate utilisation (g CH_4/g BOD)	0.25	f	1	0.238	0.263	N/A
49/EF_AnaerBODremCO2	CO_2 emissions from anaerobic carbonaceous substrate utilisation (g CO_2/g BOD)	0.27	f	1	0.257	0.284	N/A
50/EF_AnaerVSSdecCH4	CH_4 emissions from anaerobic biomass decay (g CH_4/g VSS)	0.35	f	1	0.333	0.368	N/A
51/EF_AnaerVSSdecCO2	CO_2 emissions from anaerobic biomass decay (g CO_2/g VSS)	0.58	f	1	0.551	0.609	N/A
52/leak_frac	Fraction of biogas leaked	0.05	j	3	0.025	0.075	N/A
53/CH4toCO2_combust	Combustion emission factor (g CO_2/g CH_4)	2.75	e	1	2.613	2.888	N/A
54/CH4_conversioneff	Energy conversion efficiency for heating	0.5	k	2	0.4	0.6	N/A
55/PF_Qintr	Pumping energy factor, internal AS recirculation (kWh/m^3)	0.004	a	2	0.0032	0.0048	N/A
56/PF_Qr	Pumping energy factor, AS sludge recycle (kWh/m^3)	0.008	a	2	0.0064	0.0096	N/A
57/PF_Qw	Pumping energy factor, AS wastage flow (kWh/m^3)	0.05	a	2	0.04	0.06	N/A
58/PF_Qpu	Pumping energy factor, pumped underflow from primary clarifier (kWh/m^3)	0.075	a	2	0.06	0.09	N/A
59/PF_Qtu	Pumping energy factor, pumped underflow from thickener (kWh/m^3)	0.06	a	2	0.048	0.072	N/A
60/PF_Qdo	Pumping energy factor, pumped underflow from dewatering unit (kWh/m^3)	0.004	a	2	0.0032	0.0048	N/A
61/mixenergyunitreac	Energy for activated sludge mixing (kW/m^3)	0.005	a	2	0.004	0.006	N/A
62/mixenergyunitAD	Energy for anaerobic digester mixing (kW/m^3)	0.005	a	2	0.004	0.006	N/A
63/cp	Specific heat capacity for water (Wd/gC)	4.84E-05	a	1	4.60E-05	5.09E-05	N/A
64/O2TransferEff	Aeration oxygen transfer efficiency (kg O_2/kWh)	1.80	l	2	1.44	2.16	N/A
65/EF_Elec	EF for electricity generation (kg CO_2e/kWh)	0.245	k	2	0.196	0.294	N/A
66/EF_EmbodiedCarb	EF for methanol usage (kg CO_2e/kg)	1.54	f	2	1.232	1.848	N/A
67/EF_SludgeTransport	EF for transport of sludge (kg CO_2e/tonne)	24	f	2	19.2	28.8	N/A
68/EF_SludgeN2O	EF for sludge applied to managed soils (kg N_2O/kg N)	0.016	m	2	0.013	0.019	N/A
69/EF_AerBODreml	EF for carbonaceous BOD removal (kg CO_2/kg COD)	0.33	f	1	0.314	0.347	N/A
70/EF_EffN2O	EF for N_2O emissions from effluent (kg N_2O/kg N)	0.008	n	2	0.006	0.009	N/A

[a]Alex et al. (2008)
[e]Monteith et al. (2005)
[f]Shahabadi et al. (2010)
[g]Lide and Frederiske (1995)
[h]Samie et al. (2011)
[i]European Environment Agency (2011)
[j]Shahabadi et al. (2009)
[k]Gori et al. (2011)
[l]Nopens et al. (2010)
[m]IPCC (2006a)
[n]IPCC (2006b)

972   *Table 4 – Characteristics of total and component GHG emission results used for Sobol's*

973   *method sensitivity analysis*

	Direct CO_2	Direct CH_4	Direct N_2O	Total indirect	Total GHGs
Base case (kg CO_2e/m^3)	0.4795	0.0595	0.1426	0.1872	0.8688
Mean (kg CO_2e/m^3)	0.4736	0.0596	1.1725	0.1913	1.8970
Variance ((kg $CO_2e/m^3)^2$)	0.0006	0.0003	9.6585	0.2047	9.7978

Table 5 – Ranking of model parameters to which at least one key model output is sensitive

Parameter number	Sensitivities based on EQI			Sensitivities based on OCI			Sensitivities based on total GHG emissions		
	GSA sensitivity rank		OAT rank	GSA sensitivity rank		OAT rank	GSA sensitivity rank		OAT rank
	First order	Total order		First order	Total order		First order	Total order	
1		20	10						
5	5	14	7						
7		19	25					12	17
8	12	12	17	3		4	6	11	11
10	2	5	3						
11	10	17	8						
12	1	3	1						
13	3	8	2						
14	6	11	5						
22				2	2	2			
23	7	15	6						
25	4	13	4						
27		6	9				1	3	4
28		1	11				2	1	7
29	8	2	25				7	2	3
30							3	7	1
32		18	19					14	14
33		16	30					10	6
35		9	13				4	5	5
36		7	15					8	9
37	9	4	28					4	8
38								13	2
39	11	10	14					9	15
46							5	6	12
64				1	1	1			

Light grey shading denotes sensitive parameters, based on corresponding index
Dark grey shading denotes highly sensitive parameters, based on corresponding index

975 # **Supplementary Information**

976

977 **Identifying key sources of uncertainty in the modelling of greenhouse gas**

978 **emissions from wastewater treatment**

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BSM2 additions and modifications to enable modelling of

greenhouse gas emissions in BSM2-e

982

983

984 **5 DIRECT EMISSIONS**

985 **5.1 Activated sludge reactors**

986 *5.1.1 Substrate utilisation*

987 The suspended solids mass balance given by Monteith et al. (2005) is modified for

988 application to each tank as follows, to enable calculation of biomass formed in each reactor

989 from substrate utilisation:

$$V\frac{dX}{dt} = Q_{in}X_{in} - Q_{out}X_{out} + VYr_s - Vk_dX \qquad (1)$$

990 where:

V	=	reactor volume [m^3]
dX/dt	=	rate of change of biomass concentration in reactor [g VSS/m^3/d]
$Q_{in}X_{in}$	=	biomass entering reactor in influent [g VSS/d]
$Q_{out}X_{out}$	=	biomass leaving reactor in effluent [g VSS/ d]
VYr_s	=	biomass formed in reactor from substrate utilisation [g VSS/d]
Vk_dX	=	biomass decay in reactor [g VSS/d]

991 The rate of change of biomass concentration (*dX/dT* in Eq. 1) in each reactor is estimated

992 from states modelled in BSM2, based on the output values at the current (t_i) and subsequent

993 (t_{i+1}) time steps, using Eq. 2:

$$\frac{dX}{dt} = \frac{\left(\frac{(X_{B,H,} + X_{B,A})_{i+1}}{1.42} - \frac{(X_{B,H,} + X_{B,A})_i}{1.42}\right)}{t_{i+1} - t_i} \quad (2)$$

994   where:

$X_{B,H}$ =   active heterotrophic biomass [g COD/m^3]

$X_{B,A}$ =   Active autotrophic biomass [g COD/m^3]

1.42   =   conversion factor [COD/g VSS]

995   Biomass entering and leaving each reactor ($Q_{in}X_{in}$ and $Q_{out}X_{out}$ in Eq. 1) is calculated using

996   Eq. 3:

$$\text{biomass mass flow rate [g VSS/d]} = Q\frac{X_{B,H} + X_{B,A}}{1.42} \quad (3)$$

997   The rate of biomass decay (Vk_dX in Eq. 1) is calculated using the biomass concentration

998   derived from the BSM2 outputs and the reactor volume, as shown in Eq. 4:

$$\text{rate of biomass decay [g VSS/d]} = Vk_{d,T}\frac{X_{B,H} + X_{B,A}}{1.42} \quad (4)$$

999   where:

$k_{d,T}$ =   endogenous decay coefficient at temperature T

1000   Temperature dependency of k_d is modelled as for the heterotrophic decay coefficient in

1001   BSM2, using a base value of 0.05 d^{-1} (b_H, defined in BSM2) and the current activated sludge

1002   temperature (T_{as}) output from the model:

$$k_{\mathrm{d,T}} = b_H \exp\left(\left(\frac{\ln\left(\frac{b_H}{0.2}\right)}{5}\right)(T_{as} - 15)\right) \qquad (5)$$

1003   The rate of biomass formation in each reactor (VYr_s) is then derived from Eq. 1. The

1004   heterotrophic cell yield coefficient, Y, defined in BSM2 (0.67 g VSS/g COD) is used to

1005   calculate the aeration BOD_5 removal rate (r_s) and the oxygen removal rate due to the

1006   oxidation of substrate is then calculated using Eq. 6 (Monteith et al., 2005). A theoretical

1007   emission factor of 1.1 g CO_2/g O_2 (EF_{AerOxi}) (Monteith et al., 2005), derived from

1008   stoichiometry, is applied to calculate CO_2 production from aerobic oxidation:

$$r_{O2} = \frac{Vr_s}{f} - 1.42 Vr_s Y \qquad (6)$$

$$CO2_{AS,BOD} = \sum_{i=1}^{5} EF_{AerOxi} \times r_{O2,i} \qquad (7)$$

1009   Where:

r_{O2} = oxygen removal rate due to substrate oxidation [g O_2/ d]

Vr_s/f = total rate of BOD_u removal in reactor (due to both substrate oxidation

and biosynthesis) [g BOD_u/d]

$1.42Vr_sY$ = BODu removal due to biosynthesis (in which no CO_2 is formed)

[g COD/d]

f = conversion factor, set to 0.68 g BOD_5/g BOD_u (Monteith et al., 2005)

Y = cell yield coefficient [g VSS/g COD]

i = tank number

5.1.2 Biomass decay

1010

1011 The rate of CO_2 production due to biomass decay is modelled for each reactor using a

1012 theoretical emission factor of 1.947 kg CO_2/kg VSS ($EF_{AerAutoOxi}$) (Monteith et al., 2005). The

1013 total rate of CO_2 production (g CO_2/d) due to biomass decay in the activated sludge process is

1014 therefore calculated using Eq. 8.

(8)

$$CO2_{AS,VSS} = \sum_{i=1}^{5} EF_{AerAutoOxi} \times (Vk_d X)_i$$

5.1.3 Denitrification

1015

1016 The activated sludge model has been modified to include four-step denitrification as detailed

1017 by Samie et al. (2011), to enable dynamic modelling of CO_2 and N_2O production during

1018 denitrification. All processes and process rates in the model are detailed in Table SI-1 and

1019 reactions are detailed in Table SI-2. Processes A-D replace the single step in BSM2 for

1020 anoxic growth of heterotrophs and the single variable used in BSM2 for 'nitrate and nitrite

1021 nitrogen' (S_{NO}) is replaced with separate variables for nitrate (S_{NO3}), nitrite (S_{NO2}), nitric

1022 oxide (S_{NO}) and nitrous oxide nitrogen (S_{NO}).

1023 *Table SI-1: Modified ASM1 process rates, adapted from Samie et al. (2011) and Alex et al.*
1024 *(2008)*

	Process	Process rate
1	Aerobic growth of heterotrophs	$\mu_{HT} \left(\dfrac{S_S}{K_S + S_S} \right) \left(\dfrac{S_O}{K_{O,H} + S_O} \right) X_{B,H}$
A	Anoxic growth of heterotrophs on nitrate	$\mu_{HT} \left(\dfrac{S_S}{K_{S2} + S_S} \right) \left(\dfrac{K_{O,H2}}{K_{O,H2} + S_O} \right) \left(\dfrac{S_{NO3}}{K_{NO3} + S_{NO3}} \right) \eta_{g2} X_{B,H}$

B	Anoxic growth of heterotrophs on nitrite	$\mu_{HT}\left(\dfrac{S_S}{K_{S3}+S_S}\right)\left(\dfrac{K_{O,H3}}{K_{O,H3}+S_O}\right)\left(\dfrac{S_{NO2}}{K_{NO2}+S_{NO2}}\right)\left(\dfrac{K_{13NO}}{K_{13NO}+S_{NO}}\right)\eta_{g3}X_{B,H}$
C	Anoxic growth of heterotrophs on nitric oxide	$\mu_{HT}\left(\dfrac{S_S}{K_{S4}+S_S}\right)\left(\dfrac{K_{O,H4}}{K_{O,H4}+S_O}\right)\left(\dfrac{S_{NO}}{K_{NO}+S_{NO}+\dfrac{S_{NO}^2}{K_{14NO}}}\right)\eta_{g4}X_{B,H}$
D	Anoxic growth of heterotrophs on nitrous oxide	$\mu_{HT}\left(\dfrac{S_S}{K_{S5}+S_S}\right)\left(\dfrac{K_{O,H5}}{K_{O,H5}+S_O}\right)\left(\dfrac{S_{N2O}}{K_{N2O}+S_{N2O}}\right)\left(\dfrac{K_{15NO}}{K_{15NO}+S_{NO}}\right)\eta_{g5}X_{B,H}$
3	Aerobic growth of autotrophs	$\mu_{AT}\left(\dfrac{S_{NH}}{K_{NH}+S_{NH}}\right)\left(\dfrac{S_O}{K_{O,A}+S_O}\right)X_{B,A}$
4	Decay of heterotrophs	$b_{HT}X_{B,H}$
5	Decay of autotrophs	$b_{HT}X_{B,A}$
6	Ammonification of soluble organic nitrogen	$k_{aT}S_{ND}X_{B,H}$
7	Hydrolosis of entrapped organics	$k_{hT}\dfrac{X_S/X_{B,H}}{K_X+(X_S/X_{B,H})}\left(\left(\dfrac{S_O}{K_{O,H}+S_O}\right)+\eta_h\left(\dfrac{K_{O,H}}{K_{O,H}+S_O}\right)\left(\dfrac{S_{NO3}+S_{NO2}}{K_{NO}+S_{NO3}+S_{NO2}}\right)\right)X_{B,H}$
9	Hydrolosis of entrapped organic nitrogen	$k_{hT}\dfrac{X_S/X_{B,H}}{K_X+(X_S/X_{B,H})}\left(\left(\dfrac{S_O}{K_{O,H}+S_O}\right)+\eta_h\left(\dfrac{K_{O,H}}{K_{O,H}+S_O}\right)\left(\dfrac{S_{NO3}+S_{NO2}}{K_{NO}+S_{NO3}+S_{NO2}}\right)\right)X_{B,H}\left(\dfrac{X_{ND}}{X_S}\right)$
10	Stripping of N_2O to atmosphere	$kLa_{N2O}\left(S_{N2Os}-28K_{H,N2O}P_{N2O}\right)$

1025   *Table SI-2: Modified ASM1 stoichiometry matrix, adapted from Samie et al. (2011) and Alex et al. (2008)*

Process													Model component			
	S_I	S_S	X_I	X_S	$X_{B,H}$	$X_{B,A}$	X_P	S_{O2}	S_{NO3}	S_{NH}	S_{ND}	X_{ND}	S_{ALK}	S_{NO2}	S_{NO}	S_{N2O}
1		$-\dfrac{1}{Y_H}$			$+1$			$-\dfrac{1-Y_H}{Y_H}$		$-i_{XB}$			$-\dfrac{i_{XB}}{14}$			
A		$-\dfrac{1}{Y_H\eta_Y}$			$+1$				$-\dfrac{1-Y_H\eta_Y}{1.143Y_H\eta_Y}$	$-i_{XB}$			$-\dfrac{i_{XB}}{14}$	$+\dfrac{1-Y_H\eta_Y}{1.143Y_H\eta_Y}$		
B		$-\dfrac{1}{Y_H\eta_Y}$			$+1$					$-i_{XB}$			$+\dfrac{1-Y_H\eta_Y}{14\times0.571Y_H\eta_Y}$	$-\dfrac{i_{XB}}{14}\dfrac{1-Y_H\eta_Y}{0.571Y_H\eta_Y}$	$+\dfrac{1-Y_H\eta_Y}{0.571Y_H\eta_Y}$	
C		$-\dfrac{1}{Y_H\eta_Y}$			$+1$					$-i_{XB}$			$-\dfrac{i_{XB}}{14}$		$-\dfrac{1-Y_H\eta_Y}{0.571Y_H\eta_Y}$	$+\dfrac{1-Y_H\eta_Y}{0.571Y_H\eta_Y}$
D		$-\dfrac{1}{Y_H\eta_Y}$			$+1$					$-i_{XB}$			$-\dfrac{i_{XB}}{14}$			$-\dfrac{1-Y_H\eta_Y}{0.571Y_H\eta_Y}$
3						$+1$		$-\dfrac{4.57-Y_A}{Y_A}$	$+\dfrac{1}{Y_A}$	$-i_{XB}-\dfrac{1}{Y_A}$			$-\dfrac{i_{XB}}{14}-\dfrac{1}{7Y_A}$			
4			$+1-f_p$	-1			$+f_p$					$+i_{XB}-f_P i_{XP}$				

56

Process														
5			$+1 - f_P$		-1	$+f_P$						$+i_{XB} - f_P i_{XP}$		
6									$+1$	-1			$+\dfrac{1}{14}$	
7		$+1$	-1											
8										$+1$	-1			
9														-1
Units	COD						- COD	N					Mole	N

1026   Stripping of N_2O emission from solution is modelled using Eq. 9. Temperature dependency

1027   of the Henry's law constant is modelled in accordance with the ADM1 methodology for CO_2

1028   and CH_4 stripping, using a base value of 0.025 mol/l/atm at 298.15 K (Lide and Frederiske,

1029   1995; quoted in NIST, 2012).

(9)
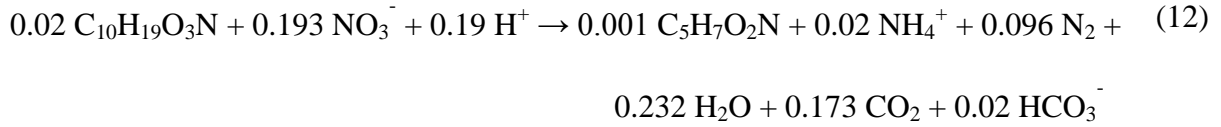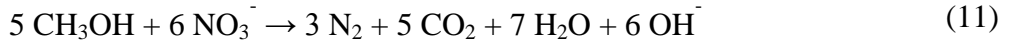$$r_{N2Og} = 3.14 kLa_{N2O} \times \max\left(0, \left(S_{N2Os} - 28 \times 1000 K_{H,N2O} Pgas_{N2O}\right)\right)$$

1030   where:

r_{N2Og} =   rate of N_2O emissions [g $N_2O/m^3/d$]

3.14   =   conversion factor from g N to g N_2O [g N_2O/g N]

kLa_{N2O} = N_2O gas transfer coefficient, set to 2 d^{-1} (Samie et al., 2011)

28   =   conversion factor [g N/mol N_2O]

1000   =   conversion factor [l/m^3]

$K_{H,N2O}$ =   Henry's law constant for N_2O [mol N_2O/kg/atm]

$Pgas_{N2O}$ =   partial pressure of N_2O in atmosphere, set to 3.2×10^{-7} atm (European

Environment Agency, 2011)

1031   The total rate of N_2O emission from the five activated sludge tanks at each time step is

1032   therefore calculated using Eq. 10.

(10)
$$N2O_{AS,deni} = \sum_{i=1}^{5} r_{N2Og,i} V_i$$

1033 CO_2 emissions resulting from nutrient removal are calculated using the stoichiometric

1034   relationships given by Shahabadi el. (2010) for denitrification with and without an external

1035   carbon source:

$$5 \text{ CH}_3\text{OH} + 6 \text{ NO}_3^- \rightarrow 3 \text{ N}_2 + 5 \text{ CO}_2 + 7 \text{ H}_2\text{O} + 6 \text{ OH}^- \tag{11}$$

$$0.02 \text{ C}_{10}\text{H}_{19}\text{O}_3\text{N} + 0.193 \text{ NO}_3^- + 0.19 \text{ H}^+ \rightarrow 0.001 \text{ C}_5\text{H}_7\text{O}_2\text{N} + 0.02 \text{ NH}_4^+ + 0.096 \text{ N}_2 + \tag{12}$$

$$0.232 \text{ H}_2\text{O} + 0.173 \text{ CO}_2 + 0.02 \text{ HCO}_3^-$$

1036 Given that these relationships are for complete denitrification and some nitrate removed in

1037 the model may be only partially denitrified, emission factors are derived to enable calculation

1038 of CO_2 emissions from denitrification based on the mass of nitrogen (N_2) produced instead of

1039 the mass of nitrate removed. This yields factors of 2.62 g CO_2/g N_2-N ($EF_{CO2denitWCarb}$) and

1040 2.83 g CO_2/g N_2-N ($EF_{CO2denitWOCarb}$) for denitrification with and without an external source

1041 respectively. Production of N_2 at each time step is modelled as follows:

$$r_{N2} = \left(\frac{1 - Y_H \eta_Y}{0.571 Y_H \eta_Y}\right) procD \tag{13}$$

1042 where:

$$r_{N2} \quad = \quad \text{rate of N}_2 \text{ production [g N/m}^3\text{/d]}$$

$$Y_H \quad = \quad \text{heterotrophic biomass yield [g COD/g COD]}$$

$$\eta_Y \quad = \quad \text{anoxic yield factor for heterotrophs}$$

$$procD \quad = \quad \text{process rate D, defined in Table SI-1}$$

1043 It is assumed that the emission factor for denitrification with an external carbon source is

1044 valid even for very low carbon source flow rates (Q_{carb}), provided that $Q_{carb} > 0$. The total

1045 rate of CO_2 emissions resulting from denitrification in the activated sludge is given by Eq. 14:

$$CO2_{AS,deni} = \sum_{i=1}^{5} E_i r_{N2,i} V_i \tag{14}$$

1046   where:

$$E_i \quad = \quad CO_2 \text{ emission factor } (EF_{CO2denitWCarb} \text{ when } Q_{carb} > 0, \text{ else}$$

$$EF_{CO2denitWOCarb})$$

5.2   Biogas leakage and combustion

1048   Dynamic CH_4 and CO_2 formation and stripping in the anaerobic digester and the resultant

1049   biogas composition and flow rate are modelled in BSM2. It is assumed that 5% of biogas

1050   produced is leaked to the atmosphere (Shahabadi et al., 2009) and the remaining biogas is

1051   fully combusted in accordance with Eq. 15, which yields an emission factor of

1052   2.75 g CO_2/g CH_4 (Monteith et al., 2005).

$$CH_4 + 2\ O_2 \rightarrow CO_2 + 2\ H_2O \tag{15}$$

1053   Total emissions of CH_4 ($CH4_{AD}$) and CO_2 ($CO2_{AD}$) to the atmosphere from the anaerobic

1054   digester are, therefore, calculated using Eq. 16 and Eq. 17 respectively.

$$CH4_{AD} = 0.05 \times CH4_{AD,biogas} \tag{16}$$

$$CO2_{AD} = CO2_{AD,biogas} + 2.75 \times 0.95 \times CH4_{AD,biogas} \tag{17}$$

1055   where

$$CH4_{AD,biogas} \quad = \quad \text{total } CH_4 \text{ content of biogas [kg } CH_4/d]$$

$$CO2_{AD,biogas} \quad = \quad \text{total } CO_2 \text{ content of biogas [kg } CO_2/d]$$

5.3   Stripping of dissolved gases in dewatering unit

1057   Dissolved CH_4 in sludge entering the dewatering unit is assumed to be equal to that in sludge

1058   leaving the anaerobic digester at the corresponding time step. Given that the partial pressure

1059   of CH_4 in the atmosphere is negligible, it is expected that no CH_4 would remain in solution.

1060   The CH_4 mass flow rate ($CH4_{dewatering}$) from the dewatering unit at each time step is therefore

1061   modelled using Eq. 18:

(18)

$$CH4_{dewatering} = \frac{16}{64} \times S_{ch4}\, Q$$

1062   where:

      16 = conversion factor [g CH_4/mol CH_4]

      64 = conversion factor [g COD/mol CH_4]

    S_{ch4} = dissolved CH_4 concentration [g COD/m^3]

     Q = sludge flow rate [m^3/d]

1063   The gas transfer rate is not taken into account as it is assumed that all dissolved CH_4 will be

1064   stripped eventually, and it would therefore have no effect on net emissions.

6   INDIRECT EMISSIONS

6.1   Generation of energy imported

Energy required for pumping, aeration, heating and mixing (E_{total}) is quantified in BSM2.

Energy credit from biogas combustion is reduced by 5% with respect to the BSM2 value to account for the 5% biogas leakage:

$$E_{credit} = 0.95 \times CH4_{AD,biogas} \times \frac{50014}{3600} \times CF \tag{19}$$

where:

50014 = theoretical CH_4 energy content [J/kg]

3600 = conversion factor [J/kWh]

CF = energy conversion efficiency (0.50 (Gori et al., 2011) for heating and 0.43 for electricity generation (Flores-Alsina et al., 2011))

GHG emissions associated with generation of energy imported are calculated based on net energy import and an emission factor of 0.245 kg CO_2e/kWh (Gori et al., 2011):

$$CO2e_{energy} = 0.245\big(\max(0, E_{total} - E_{credit})\big) \tag{20}$$

6.2   Manufacture of chemicals

Indirect emissions due to chemical addition are calculated using the carbon source flow rate for each tank, as modelled in BSM2, and an emission factor of 1.54 kg CO_2e/kg MeOH (Shahabadi et al., 2010):

$$CO2e_{methanol} = \sum_{i=1}^{5} \frac{Q_{C,i} \times 400}{1.5} \times 1.54 \tag{21}$$

1077   where:

Q_C =   carbon source flow rate [m^3/d]

400   =   carbon source concentration [kg COD/m^3]

1.5   =   theoretical oxygen demand of methanol [g COD/g MeOH]

1078   **6.3   Offsite degradation of effluent**

1079   Indirect CO_2 emissions from the reactor effluent are modelled using Eq. 22, based on the

1080   assumption that all BOD_5 remaining in the effluent degrades aerobically in accordance with

1081   the stoichiometric equation given by Shahabadi et al. (2010), which yields an emission factor

1082   of 0.33 g CO_2/g BOD ($EF_{AerBODreml}$). Effluent BOD (BOD_{eff}) is calculated using the BSM2

1083   methodology.

$$CO2_{eff} = BOD_{eff} \times EF_{AerBODreml} \tag{22}$$

1084   The rate of indirect N_2O emissions from the reactor effluent are calculated using the total

1085   effluent nitrogen concentration (N_{eff}) modelled in BSM2 and an emission factor of

1086   0.005 kg N_2O-N/kg N (IPCC, 2006b), as shown in Eq. 23.

$$N2O_{eff} = 0.005 \times \frac{44}{28} \times N_{eff}Q \tag{23}$$

1087   where:

$44/28$ =   conversion factor [g N_2O/g N_2O-N]

1088   **6.4   Transport and offsite degradation of sludge**

1089   Dynamic simulation of emissions resulting from sludge disposal is based on digester effluent

1090   concentrations and flow rates modelled in BSM2. Emissions resulting from the transport of

1091   sludge produced for disposal at each time step are estimated using Eq. 24, with an emission

1092   factor of 24 kg CO_2e/tonne solids (Shahabadi et al., 2010).

$$CO2e_{sludge,trans} = 24 \times TSS \times Q \tag{24}$$

1093   Indirect emissions resulting from the degradation of biosolids remaining in the sludge are

1094   modelled using the method detailed by Shahabadi et al. (2009), based on the theoretical

1095   stoichiometric equation for biomass decay in an anaerobic environment. It is assumed that the

1096   degradable suspended solids in the sludge can be represented by the readily biodegradable

1097   substrate (S_s) modelled in BSM2; the rates of CO_2 and CH_4 emissions resulting from the

1098   degradation of sludge produced at each time step are, therefore, calculated using Eq. 25 and

1099   Eq. 26 respectively.

$$CO2_{sludge} = EF_{AnaerVSSdecCO2} \times \frac{S_s}{1.42} Q \tag{25}$$

$$CH4_{sludge} = EF_{AnaerVSSdecCH4} \times \frac{S_s}{1.42} Q \tag{26}$$

1100   where:

| $EF_{AnaerVSSdecCO2}$ | = | theoretical CO_2 emission factor, set to 0.58 g CO_2/g VSS (Shahabadi et al., 2010) |
| $EF_{AnaerVSSdecCH4}$ | = | theoretical CH_4 emission factor, set to 0.35 g CH_4/g VSS (Shahabadi et al., 2010) |

1101 N_2O emissions resulting from sludge produced for disposal at each time step are calculated

1102   using the total nitrogen content modelled in BSM2 and an emission factor of

1103   0.01 kg N_2O-/kg N, as recommended by the IPCC (2006a) for application of sludge to

1104   managed soils:

(27)

$$N2O_{sludge} = 0.01 \times \frac{44}{28} \times N_{effluent,total}Q$$

1105

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