СЕЛЕКТИВНОЕ ОПРЕДЕЛЕНИЕ УГАРНОГО ГАЗА ЕДИНИЧНЫМ МЕТАЛЛОКСИДНЫМ СЕНСОРОМ

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Полупроводниковые сенсоры часто используются для решения важной практической задачи – определения концентрации угарного газа в воздухе. Их недостатком является низкая селективность, которая может привести к ложному срабатыванию, когда в воздухе присутствуют другие газы-восстановители, например, пары аммиака или этанола. Для повышения селективности нами использовалась импульсная температурная модуляция в сочетании со специальным составом газочувствительного слоя сенсора. Использование импульсной температурной модуляции позволило выявить особенности аналита, связанные с кинетикой его сорбции на поверхности сенсора, с кинетикой химического взаимодействия между аналитами и хемосорбированным кислородом, а также с кинетикой десорбции продуктов химического взаимодействия. Однако, информация о качественном составе газовой среды содержится в экспериментальных данных в неявной форме, поскольку процедура качественного анализа с использованием низкоселективных сенсоров до сих пор не разработана. В этой статье мы предложили метод качественного анализа, основанный на модели степенной регрессии, связывающей концентрацию аналита с электрическим сопротивлением сенсора в различные моменты времени по измерительному циклу. Описанная в нашей работе экспериментальная процедура приводит к увеличению чувствительности количественного анализа на один – два порядка в зависимости от концентрации угарного газа.

Ключевые слова: металлоксидный сенсор, температурная модуляция, угарный газ, качественный анализ, количественный анализ

SELECTIVE DETERMINATION OF CARBON MONOXIDE BY SINGLE METAL OXIDE SENSOR

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Semiconductor sensors are often used to solve an important practical problem – the determination of the concentration of carbon monoxide in the air. Their disadvantage is the low selectivity, which can lead to false alarm when other reducing gases such as ammonia or ethanol vapor appear in the air. To increase the selectivity, we used pulsed temperature modulation in combination with a special composition of the gas sensitive layer of the sensor. The use of pulse temperature modulation has revealed the features of the analyte associated with the sorption kinetics at the surface of the sensor, with the kinetics of the chemical interaction between reductant analytes and chemisorbed oxygen, and the kinetics of desorption of chemical interaction products. However, information on the qualitative composition of the medium is contained in the experimental data in an implicit form, because the qualitative analysis procedure with the use of low selectivity sensors has so far remained undeveloped. In this paper, we proposed a qualitative analysis method based on the power-law regression model that relates the concentration of analyte gas to the electrical resistance of the sensor at various times during the measurement cycle. The experimental procedure shown in our work leads to an increase in the sensitivity of the quantitative analysis by one or two orders of magnitude depending on the concentration of carbon monoxide.

Key words: metal oxide sensor, temperature modulation, carbon monoxide, qualitative analysis, quantitative analysis

INTRODUCTION

Carbon monoxide is formed in all types of combustion reactions: when running automobile engines, heating boilers, in fires. In addition, it is formed and used in many chemical industries. This gas poses a serious danger to human life and health due to its high toxicity. An additional danger is the lack of odor and color of carbon monoxide. Effective health and safety enhancement require simple and compact devices that can signal the exceeding of the limit of the permissible concentration of carbon monoxide in the air. Semiconductor sensors are often used for the production of such devices, the advantages of which are simplicity and high sensitivity, and the disadvantage is low selectivity. Current devices based on semiconductor sensors can allow a false signal when other reductants, such as hydrogen or ethanol vapor, appear in the air. At the present time, there is an objective need for new generation gas analyzers – simple and compact, with autonomous power supply and capable of qualitative and quantitative air analysis.

Increasing the selectivity can be achieved by using multi-sensor systems such as "electronic nose", but increasing the number of sensors in the device increases the probability of failure in a geometric progression. In addition, the increase in the number of sensors increases the energy consumption, which reduces the operating time of the gas analyzer from an autonomous source. All this increases the importance of creating a compact, highly selective and sensitive carbon monoxide analyzer based on a single semiconductor sensor.

For selective analysis of gases, we need to accumulate a sufficiently large set of data on the gaseous medium, which is very difficult without the use of temperature modulation. The use of temperature modulation of the sensor substrate during the measurement increases the volume of significant data on the gas analyte, helps us to reveal its features associated with the chemisorption kinetics on the surface of the sensor, with the kinetics of the chemical interaction between reductant analytes and chemisorbed oxygen, with the kinetics of desorption of chemical interaction products. These features are implicitly contained in the data on the kinetics of the sensor resistance with temperature modulation. The authors of early works often used sinusoidal modulation of the sensor temperature [1-12], but pulse modulation [13-15] has many advantages, for example, lower energy consumption for the same range of temperatures. In addition, pulse modulation helps us under certain conditions to obtain additional extrema on the sensor resistance dependencies on time, which simplifies the qualitative analysis procedure.

Qualitative and quantitative analysis requires the chemometric processing of multidimensional data arrays. In most papers [1-15], the authors used methods such as fast Fourier transform, discrete wavelet transform, and the principal component method. However, the compression of information by these methods does

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not in itself guarantee a correct qualitative analysis, but more often it has a demonstration purpose. In addition, the use of complex information processing methods is not suitable for creating simple and compact devices based on the use of low-cost microcontrollers. In this paper, a different method is used to process multidimensional data, which combines a sufficiently high efficiency with the simplicity of software implementation.

METHODS AND EXPERIMENTS

As the basis of the gas-sensitive layer for the metal oxide sensor, we used a nanodispersed tin dioxide powder obtained from tin acid. To nanodispersed tin dioxide we added tetraammine palladium nitrate (+2). The resulting nanopowder was mixed with a viscous solution of methyl cellosolve in amyl alcohol to produce a paste. With this paste we covered a dielectric substrate containing platinum electrodes and a platinum heater. The substrate with a thin layer of paste was heated to a temperature of 750 °C, as a result of which the paste was converted into a nanodispersed gel. Palladium contained in the complex compound was partially reduced to the metal, and partially converted to oxides, mainly in PdO. The resulting gas sensitive layer included 97% SnO_2 and 3% Pd by weight. The synthesis of the gas sensitive layer determined its composition, which we checked with the help of X-ray microanalysis on a scanning electron microscope. After forming the gas sensitive layer, the sensor was soldered to the four-pin body.

We used a stainless steel flow cell with a volume of 1 cm^3 and a flow rate of 2 cm^3 per second. For the analysis, we used calibration gas mixtures with concentrations of carbon monoxide from 10 to 200 ppm and synthetic air. To create these mixtures, we used a Microgas-F device that mixes three streams: 1) a calibration gas mixture with a relative humidity (RH) of 0%; 2-3) synthetic air with RH 0 and 100%. The data presented in this paper were obtained for a gas mixture at RH 33%.

The oxide aluminum substrates included a platinum heating layer with a known value of the temperature coefficient of resistance. By controlling the resistance of the heating layer, we determined the sensor temperature with an error not exceeding 5 degrees.

Fig. 1 shows the temperature change for the sensor substrate of the SnO_2-based sensor with Pd nanoparticles and the change in the sensor resistance at 100 ppm methane (curve 2), at 100 ppm of carbon monoxide (curve 3), at 100 ppm ethanol (curve 4) over three measurement cycles. The duration of each cycle was 15 s, the first two seconds the sensor was heated to 450 °C, after which the sensor was cooled to 100 °C.
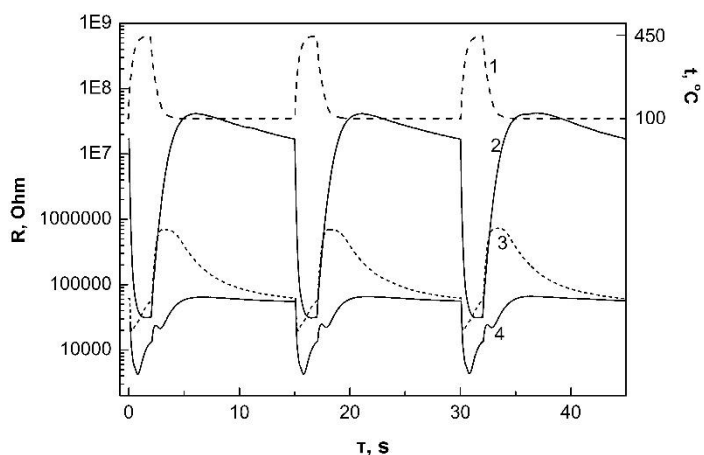

Fig. 1. The dependence of the temperature (curve 1) and the MOX-sensor resistance (curves 2–4) on time for three measurement cycles at 100 ppm CH_4, CO, C_2H_5OH

Рис. 1. Зависимость температуры (кривая 1) и сопротивления MOX-сенсора (кривые 2–4) от времени для трёх измерительных циклов при 100 ppm CH_4, CO, C_2H_5OH

Fig. 2 shows the changes in the sensor resistance during one measurement cycle for air (curve 1), at 10 ppm CO (curve 2), at 20 ppm CO (curve 3), at 50 ppm CO (curve 4), at 100 ppm CO (curve 5). The circles in the figure indicate two sets of five sensor resistances at two different time points: 5 sec and 10 sec after the start of the cycle. The training sample includes 50 sets of sensor resistances of 7 values each, corresponding to seven different concentrations of carbon monoxide: 0 ppm (pure air), 2 ppm, 5 ppm, 10 ppm, 20 ppm, 50 ppm and 100 ppm. The sensor resistance value sets differ in time after the start of the cycle (shown in Fig. 1).
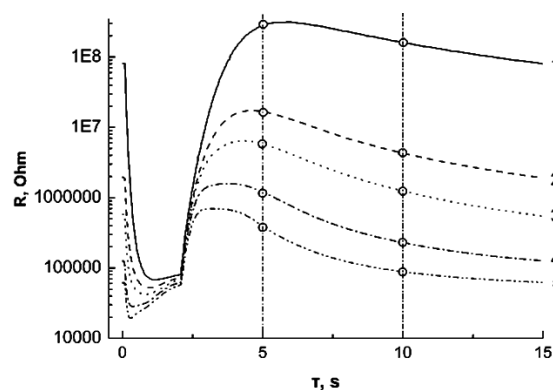

Fig. 2. The dependence of the MOX-sensor resistance on time during one measurement cycle at 0, 10, 20, 50, and 100 ppm CO (curves 1–5)

Рис. 2. Зависимость сопротивления MOX-сенсора от времени в течении одного измерительного цикла для 0, 10, 20, 50 и 100 ppm CO (кривые 1–5)

Fig. 3 shows the dependence of the concentration of carbon monoxide from the sensor resistance after 5 s from the start of the measurement cycle. We determined the empirical coefficients *a* and *b* in the

power-law regression model [16-20] that connects the concentration of the analyte gas ϕ_i with the resistance of the sensor R_i at various times during the measurement cycle (shown in Fig. 2):

$$\phi_i = a \cdot (R_i)^b \cdot \varepsilon_i, \qquad (1)$$

where ε_i is a lognormally distributed error minimized by least squares $\sum(\varepsilon_i)^2 \to \min$ for $i = 1, 2, \ldots, 7$. Transformation of the sample of sensor resistances into the sample of model coefficients (1) allowed us not only to compress the training sample, but also to present it in a more visible form.
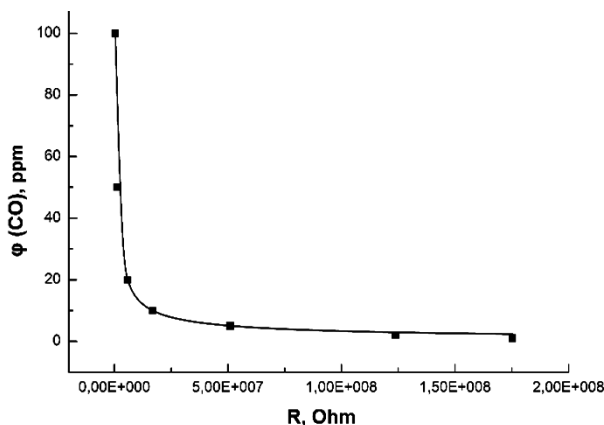

Fig. 3. The dependence of the CO concentration on the sensor resistance obtained after 5 s after start of the measurement cycle
Рис. 3. Зависимость концентрации CO от сопротивления сенсора, измеренного через 5 с от начала измерительного цикла

To test the proposed analysis method, data not included in the training sample was used. For each test analysis, we selected 50 sensor resistances corresponding to different time points during the measurement cycle. According to the power-law model (1) with the previously found coefficients a and b for each of the 50 tested sensor resistances R, we found 50 concentrations of the analyte gas ϕ, while the coefficients and the sensor resistance corresponded to the same time points.

Table 1 shows two examples of values for the coefficients a and b of the power-law regression model, the sensor resistances R measured during the air test with a relative humidity of 33% and an admixture of 28 ppm CO, and the carbon monoxide concentrations ϕ^* predicted by model (1). Despite the fact that the test values were not included in the training sample, the calculated values differ little from the true ones. For 50 calculated concentrations, we determined the mean value (for quantitative analysis) and the relative standard deviation (for qualitative analysis).

In Table 2 shows the relative standard deviation (RSD) values used for qualitative analysis. If the relative standard deviation was less than 0.5, then we assumed that the analyte is carbon monoxide, and otherwise – some other gas. As shown in the third column

of Table 2, for all carbon monoxide tests the relative standard deviation was less than 0.5, and for all test analyzes of other analytes it was more than 0.5. Thus, we realized a qualitative analysis of the carbon monoxide admixture in the air, without false results in cases when different concentrations of hydrogen, hydrogen sulfide, methane or ethanol entered the test chamber. The carbon monoxide concentrations ϕ^* predicted by the power-law regression model (shown in the third column of Table 2) were close to the true concentrations ϕ_0 (shown in the second column of Table 2).

Table 1

Calculation of the carbon monoxide concentration for two samples of sensor resistances R at different times of the same measurement cycle
***Таблица 1.** Вычисление концентрации угарного газа для двух выборок сопротивлений сенсора R в различные моменты времени одного измерительного цикла*

τ, s	$a \times 10^{-6}$	b	R, МΩ	ϕ^*, ppm
5	0.268	−0.613	3.028	28.9
10	0.147	−0.642	0.786	28.0

Table 2

Values and relative standard deviations of carbon monoxide concentrations for qualitative analysis
***Таблица 2.** Значения и относительные стандартные отклонения концентрации угарного газа для качественного анализа*

Analyte	ϕ_0, ppm	ϕ^*, ppm	RSD
CO	7.0	7.7	0.36
CO	15.4	14.0	0.12
CO	28.0	28.6	0.04
CO	75.0	72.1	0.08
C_2H_5OH	14.0	–	2.35
C_2H_5OH	60.0	–	2.81
C_2H_5OH	80.0	–	2.93
H_2S	7.0	–	1.85
H_2S	11.7	–	1.83
H_2S	35.0	–	2.59
H_2	7.4	–	0.78
H_2	15.6	–	1.03
H_2	29.0	–	1.23
H_2	77.4	–	1.65
CH_4	200.0	–	3.84
CH_4	500.0	–	4.02
CH_4	1000.0	–	4.40

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The sensor response S is the ratio of sensor resistances in the reference medium (in air) R_0 and in the test medium R:

$$S = R_0/R. \qquad (2)$$

The use of pulse heating of the sensor increased not only the selectivity of the analysis, but also its sensitivity. Line 1 in Figure 4 shows the sensor response at 300 °C constant temperature, and line 2 – the sensor response with pulse temperature modulation. As our experiments show, pulse heating leads to an increase in the sensor responses by one or two orders of magnitude in the concentration range from 10 to 100 ppm of the analyte. For metal oxide sensors, a good response to the reducing gases corresponds approximately to the gas concentration in ppm. Thus, the greatest response of the sensor at 100 ppm of carbon monoxide should reach 100 relative units, but in our case it reaches 50 relative units.
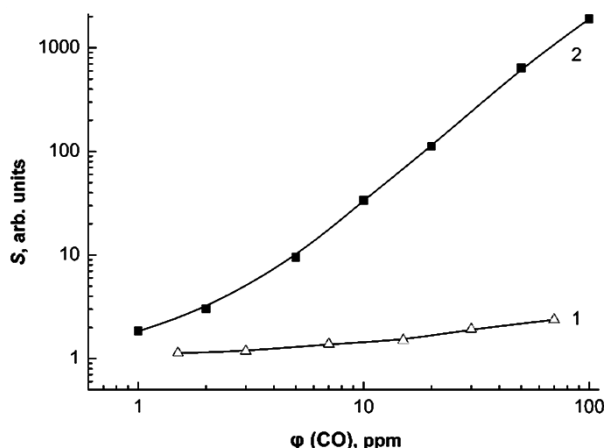

Fig. 4. The dependence of the sensor response on the CO concentration at a constant temperature (curve 1) and at a pulse modulation of temperature (curve 2)
Рис. 4. Зависимость отклика сенсора от концентрации CO при постоянной температуре (кривая 1) и при импульсной температурной модуляции (кривая 2)

RESULTS AND DISCUSSION

What is the reason for the outstanding sensitivity values shown in our work? A decrease in the temperature of the gas-sensitive layer leads to an increase in the sorption of the analyzed gas, but at low temperatures the molecules do not go into the active state necessary for chemical processes. At a high temperature, the carbon monoxide molecules are activated and can interact with the oxygen anions O^-, O_2^-, and O^{2-} located on the surface of the gas-sensitive layer:

$$CO + O^- \rightarrow CO_2 + e^-. \qquad (3)$$
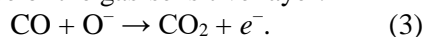
However, the increase in temperature reduces the sorption of the analyzed gas. Thus, maximizing the sensor response at a constant temperature of the sensor requires a search for a compromise – increasing the temperature reduces sorption, and lowering the temperature passivates the catalyst and reduces the number of active molecules.

Using pulse mode of sensor heating allows us to combine advantages of different temperatures of gas-sensitive layer. At the beginning of the measuring cycle, the sensor is cooled and the amount of carbon monoxide sorption is maximal. Heating the sensor to 450 °C activates the catalyst nanoparticles, which changes the state of a large number of carbon monoxide molecules to an active one and forces them to interact with oxygen anions (3). Sharp heating of the gas-sensitive layer allows the carbon monoxide molecules to activate and interact with the oxygen anions before they desorb from the surface. This, in our opinion, explains the anomalous increase in the response when sharp pulsed heating is used. Such an increase in the sensor response was not observed by us using a smooth sinusoidal heating.

CONCLUSION

The above results show the principal possibility of qualitative and quantitative analysis of gases using a single, low-selectivity sensor. This result was achieved by combining impulse heating in the measuring cycle of the sensor with an appropriate gas-sensitive layer and efficient processing of multidimensional data. Sensitivity of the sensor in the pulsed temperature mode increases by one or two orders of magnitude compared to the mode of constant temperature.

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REFERENCES
ЛИТЕРАТУРА

1. **Ionescu R., Llobet E., Brezmes J., Vilanova X., Correig X.** Dealing with humidity in the qualitative analysis of CO and NO2 using a WO3 sensor and dynamic signal processing. *Sens. Actuators B.* 2003. V. 95. P. 177–182. DOI: 10.1016/S0925-4005(03)00411-8.
2. **Ding H., Ge H., Liu J.** High performance of gas identification by wavelet transform-based fast feature extraction from temperature modulated semiconductor gas sensors. *Sens. Actuators B.* 2005. V. 107. P. 749–755. DOI: 10.1016/j.snb.2004.12.009.
3. **Ge H., Liu J.** Identification of gas mixtures by a distributed support vector machine network and wavelet decomposition from temperature modulated semiconductor gas sensor. *Sens. Actuators B.* 2006. V. 117. P. 408–414. DOI: 10.1016/j.snb.2005.11.037.
4. **Huang X.-J., Choi Y.-K., Yun K.-S., Yoon E.** Oscillating behaviour of hazardous gas on tin oxide gas sensor: Fourier and wavelet transform analysis. *Sens. Actuators B.* 2006. V. 115. P. 357–364. DOI: 10.1016/j.snb. 2005.09.022.
5. **Nakata S., Okunishi H., Nakashima Y.** Distinction of gases with a semiconductor sensor depending on the scanning profile of a cyclic temperature. *Analyst.* 2006. V. 131. P. 148–154. DOI: 10.1039/b509996j.

6. **Kato Y., Mukai T.** A real-time intelligent gas sensor system using a nonlinear dynamic response. *Sens. Actuators B.* 2007. V. 120. P. 514–520. DOI: 10.1016/j.snb.2006. 03.021.

7. **Vergara A., Llobet E., Brezmes J., Ivanov P., Cane C., Gracia I., Vilanova X., Correig X.** Quantitative gas mixture analysis using temperaturemodulated micro-hotplate gas sensors: selection and validation of the optimal modulating frequencies. *Sens. Actuators B.* 2007. V. 123. P. 1002–1016. DOI: 10.1016/j.snb.2006.11.010.

8. **Vergara A., Llobet E., Brezmes J., Vilanova X., Ivanov P., Gracia I., Cane C., Correig X.** Optimized Temperature Modulation of Micro-Hotplate Gas Sensors Through Pseudorandom Binary Sequences. *IEEE Sens. J.* 2005. V. 5. N 6. P. 1369–1378. DOI: 10.1109/jsen.2005.855605.

9. **Vergara A., Llobet E., Martinelli E., Di Natale C., D'Amico A., Correig X.** Feature extraction of metal oxide gas sensors using dynamic moments. *Sensors and Actuators B.* 2007. V. 122. P. 219–226. DOI: 10.1016/j.snb. 2006.05.028.

10. **Martinelli E., Polese D., Catini A., D'Amico A., Di Natale C.** Self-adapted temperature modulation in metal-oxide semiconductor gas sensors. *Sens. Actuators B.* 2012. V. 161. P. 534–541. DOI: 10.1016/j.snb.2011.10.072.

11. **Herrero-Carron F., Yanez D.J., Rodriguez F., Varona P.** An active, inverse temperature modulation strategy for single sensor odorant classification. *Sensors and Actuators B. 2015.* V. 206. P. 555–563. DOI: 10.1016/ j.snb.2014.09.085.

12. **Fernandez L., Guney S., Gutierrez-Galvez A., Marco S.** Calibration transfer in temperature modulated gas sensor arrays. *Sens. Actuators B.* 2016. V. 231. P. 276–284. DOI: 10.1016/j.snb.2016.02.131.

13. **Samotaev N.N., Vasiliev A.A., Podlepetsky B.I., Sokolov A.V., Pisliakov A.V.** The mechanism of the formation of selective response of semiconductor gas sensor in mixture of $CH_4/H_2/CO$ with air. *Sens. Actuators B.* 2007. V. 127. P. 242–247. DOI: 10.1016/j.snb.2007.07.022.

14. **Shaposhnik A., Zviagin A., Sizask E., Ryabtsev S., Vasiliev A., Shaposhnik D.** Acetone and ethanol selective detection by a single MOX-sensor. *Proced. Eng.* 2014. V. 87. P. 1051–1054. DOI: 10.1016/j.proeng. 2014.11.343.

15. **Shaposhnik A., Moskalev P., Zviagin A., Chegereva K., Ryabtsev S., Vasiliev A., Shaposhnik P.** Selective gas detection by a single MOX-sensor. *MDPI Proceed.* 2017. V. 1. N 4. P. 594. DOI: 10.3390/proceedings 1040594.

16. **Cox D.R.** Regression models and life-tables. In Breakthroughs in statistics. New York: Springer. 1992. P. 527–541.

17. **Yu W., Wu B., Huang T., Li X., Williams K., Zhao H.** Statistical methods in proteomics. In Springer handbook of engineering statistics. London: Springer. 2006. P. 623–638.

18. **Jeirani Z., Jan B.M., Ali B.S., Noor I.M., See C.H., Saphanuchart W.** Correlations between interfacial tension and cumulative tertiary oil recovery in a triglyceride microemulsion flooding. *J. Indust. Eng. Chem.* 2013. V. 19. P. 1310–1314. DOI: 10.1016/j.jiec.2012. 12.033.

19. **Voit E.O., Martens H.A., Omholt S.W.** 150 years of the mass action law. *PLoS Comput. Biol.* 2015. V. 11. P. e1004012. DOI: 10.1371/jour-nal.pcbi.1004012.

20. **Abdul Aziz O.I., Ishtiaq K.S., Tang J., Moseman Valtierra S., Kroeger K.D., Gonneea M.E., Mora J., Morkeski K.** Environmental controls, emergent scaling, and predictions of greenhouse gas (GHG) fluxes in coastal salt marshes. *J. Geophys. Res.: Biogeosci.* 2018. V. 123. DOI: 10.1029/2018JG004556.