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MEMORANDUM

TO: BoSS Permit Writing Staff

FROM: Danny Wong, Chief
Bureau of Stationary Sources DW

SUBJECT: Evaluation of AP-42 Emission Factors for Arsenic (As) and Cadmium (Cd) from Natural Gas Combustion

DATE: December 11, 2023

The purpose of this Memorandum is:

1) To evaluate the validity of the arsenic and cadmium emission factors listed in Table 1.4-4 "Emission Factors for Metal from Natural Gas Combustion (External Combustion Sources)" of USEPA Document AP-42; and
2) To determine how the arsenic (As) and cadmium (Cd) emission rates, and therefore health risks, from natural gas combustion should be analyzed.

As shown in Attachment 1 "Process Used by USEPA to Determine Arsenic and Cadmium Natural Gas Emission Factors," these AP-42 emission factors are based on limited stack test results and are questionable.

Attachment III "Characterization and Comparison of Trace Metal Compositions in Natural Gas, Biogas, and Biomethane (Characterization)" raises further questions on the validity of the AP-42 Emission Factors. The Characterization document presents the results of arsenic and cadmium concentrations in natural gas and has been peer-reviewed and accepted for publication.

The measured As and Cd concentrations listed in the Characterization document can be used to predict air contaminant emission factors more accurately than the AP-42 stack emissions test results for the following reasons:

1. Most of the stack tests used to determine AP-42 factors did not measure As and Cd over detection levels since there was insufficient As and Cd generated. The average, maximum, and two standard deviation levels of the As and Cd concentrations in the Characterization document were above the analytical method's detection limit of 10^{-1} ng/Nm^3.

2. The As and Cd analytical results in the Characterization document were based on the direct sampling of natural gas with a consistent analytical method. It can be assumed that all As and Cd are emitted since there are no air pollution controls for the metals. The AP-42 factors were based on stack test results, which have a higher potential for inaccuracy because of the additional sampling and analytical variables.

3. The Characterization document outlined the analytical results of four arsenic samples and 65 Cd samples. The As AP-42 factor was based on four boiler stack tests, one of which measured a non-detect concentration and the three others measured concentrations which were less than twice and more than the field value. The Cd AP-42 factor was based on the average of three stack tests of boilers with the following disparate capacities: 2.2 million British Thermal Units per hour (MMBTU/hr), 3,135 MMBTU/hr, 6,650 MMBTU/hr).

The following Table compares the AP-42 and Characterization document As and Cd emission factors:

Pollutant	AP-42 Emission Factor (lb/mmscf) - *	Characterization Document Emission Factor -** (lb/mmscf)
Arsenic	2.0E-04	5.98E-19
Cadmium	1.1E-03	1.27E-20

*- lb/mmscf is pounds per million cubic feet
**-Based on the maximum As and Cd concentrations in the Characterization document, 10.33 ng/Nm^3 and 0.22 ng/Nm^3, respectively.

Attachment II is "Input from California Air Quality Management Districts on Heavy Metal Emission Factors from Natural Gas Combustion." None of the listed California AQMD evaluates the As and Cd emission rates from External Combustion Sources.

It is the sole responsibility of the applicant to list in the permit application the emission rates of all air contaminants which have the potential to exceed their applicable reporting thresholds.

When evaluating the potential emission rates of As and Cd from natural gas combustion proposed by an applicant, the permit evaluator can consider the information outlined in this memorandum, which includes the following:

1. The problematic development of the As and Cd AP-42 emission factors listed in the above table;
2. The emission factors generated by the analytical results in the Characterization document; and
3. The California AQMD not regulating As and Cd from natural gas combustion.

Please note that there should be no differentiation when evaluating the potential As and Cd emissions from natural gas if the combustion unit is an external combustion unit, such as a boiler, or an internal combustion unit, such as a turbine or engine.

C: Ken Ratzman

ATTACHMENT I
PROCESS USED BY USEPA TO DETERMINE ARSENIC AND CADMIUM NATURAL GAS EMISSION FACTORS

BACKGROUND

The following references were used to determine the heavy metal emission factors for AP-42 Section 1.4 Natural Gas Combustion:

1. PICES Field Chemical Emissions Monitoring Project Site 120 Emissions Report. Carnot, Tustin, CA, December 1995 (Site 120)
2. PICES Field Chemical Emissions Monitoring Project Site 121 Emissions Report. Carnot, Tustin, CA, December 1995 (Site 121).
3. Gas-Fired Boiler and Turbine Air Toxics Summary Report. Prepared by Carnot Technical Services, Tustin, CA, For the Gas Research Institute and The Electric Power Research Institute, August 1996 (Carnot).
4. Source Test Report , Gibson Oil and Refining, Incorporated, May, 1990 (Gibson)

After reviewing References 1, 2, and 3, it was determined that Reference 3 listed the same testing results as those listed in References 1 and 2. Site 120 is a 750 MWe CE Tangentially-Fired boiler and Site 121 is a 330 MWe B&W Opposed-Fired boiler.

Reference 3 (Carnot) also included stack testing results for two gas fired utility turbines. These were designated as: 1) Site 123 - 55/73 MWe Westinghouse 501AA Turbine; and 2) Site 124 – 150 MWe GE Frame 7 Turbine. Although AP-42, Section 1.4 focuses on external combustion sources, the data generated from Sites 123 and 124 can be used since it includes natural gas samples that were analyzed for arsenic and stack test results for arsenic and cadmium, whose emission levels are not impacted by the type of combustion.

For Sites 120, 121, 123, and 124, stack testing for 15 elements was conducted while burning natural gas and a natural gas fuel analysis was done for the following elements: arsenic, cobalt, copper, lead, mercury, nickel, selenium, and phosphorous.

The Gibson boiler, which has a capacity of 2.2 million BTU/hr was stack tested while combusting natural gas for the following elements: arsenic, beryllium, cadmium, chromium, copper, lead, manganese, nickel, selenium, zinc. No analysis of the natural gas was done in the Gibson Boiler report.

ANALYSIS OF THE CADMIUM DATA

Initially, References 1, 2, and 3 were evaluated to determine how the cadmium emission factor in Table 1.4-4 was calculated. After it was determined that there were inconsistencies between the References 1, 2, and 3 and Table 1.4-4, the USEPA Office of Air Quality Planning and Standards (OAQPS) was contacted. The OAQPS explained that a fourth reference, “Source Test Report – Gibson Oil and Refining, Incorporated (Gibson)” was also used to arrive at the cadmium emission factor and provided the following table (Table 1) to show how the cadmium emission factor was derived:

OAQPS - TABLE 1
BOILERS CADMIUM EMISSION FACTORS

Site	Heat Input (mmbtu/hr)	Load (%)	Emission Factor, (lb/mmscf)
120	6650	97	1.49 E-05
121	3135	101	6.80 E-05
Gibson	2.2	100	3.23 E-03
Average - *			1.10 E-03

* - The average is the AP-42 emission factor.

Table 2 lists the cadmium stack emission results for the three test runs for Site 120, Site 121, and Gibson and the average gas flow rate during the stack emission tests.

TABLE 2
BOILERS STACK TEST CADMIUM EMISSIONS

Boiler	Run 1 -*	Run 2 -*	Run 3 -*	Average gas flow rate-*
Site 120	ND(0.04)	ND(0.05)	ND(0.05)	1,202,000
Site 121	0.11	NR	ND(0.04)	629,896
Gibson	BL	BL	7.52E-06 -**	13

*- Site 120 and 121 units - micrograms per cubic meter at standard conditions.
Gibson unit – pounds per hour
ND – Not detected at less than the reporting limit.
NR – Not reported.
BL – instinguishable from the blank
Average gas flow rate – cubic feet per minute
**- Converting Gibson hourly emissions to emission factor lb/mmscf:
(7.52E-06 lb/hr) * (hr/2.2E+06 mmBTU) *(1020 BTU/scf) * (10^6 scf/10^6 scf) =
3.4E-03 lb/mmscf, similar to AP-42 factor

The cadmium emissions measured at Site 123 (55/73 MWe Turbine) were below the detection limit of 0.01 lb/1012 BTU and the cadmium emissions measured at Site 124 (124/150 MWe Turbine) were below the detection limit of 0.07 lb/1020 BTU.

No natural gas fuel analysis was done for cadmium.

The 1.10E-03 lb/mmscf cadmium emission factor in Table 1.4-4 is questionable for the following reasons:

1. As presented in Table 1 above, the cadmium emission factors for Sites 120 and 121 are approximately two orders of magnitude lower than the Gibson stack test results. This skews the Table 1.1-4 cadmium emission factor to a much higher value since there are only three data points being evaluated.
2. The capacities of the Site 120 and 121 boilers are orders of magnitude higher than the Gibson boiler. This creates another problem in averaging the three emission factors in Table 1 since the Site 120 and 121 results have a lower margin for error than the Gibson results given the larger sampling volume analyzed for cadmium content.
3. Of the nine stack test runs in Table 2, only two had measurable quantities of cadmium.

4. The emission factors for Site 120 and Site 121 were calculated using the detection limits when the cadmium test result was “ND – Not detected at less than the reporting limit.”
5. Two of the three Gibson cadmium tests had results which were “instinguishable from the blank.”
6. The cadmium emissions for the two Turbines at Sites 123 and 124 were below detectable levels.
7. USEPA AP-42 Sections 3.1 “Stationary Gas Turbines” and 3.2 “Natural Gas-Fired Reciprocating Engine” do not include an emission factor for cadmium. This is significant since the cadmium emissions could only result from cadmium in the natural gas or being stripped from the interior of the combustion equipment.
8. In Table 1.4-4, cadmium has an Emission Factor Rating of “D.” A description of all USEPA AP-42 Emission Factor Ratings is at the end of this attachment.

ANALYSIS OF THE ARSENIC DATA

Table 3 presents the results of the arsenic natural gas fuel analysis for Sites 120, 121, 123, and 124.

TABLE 3
ARSENIC CONCENTRATION LEVELS IN NATURAL GAS

Site	Concentration of Arsenic in Natural Gas -*
120	ND<2
121	4
123	ND<2
124	ND<2

*- micrograms per cubic meter
ND – Non-detect

Table 4 lists the arsenic stack emission results for the three test runs for Site 120, Site 121, Site 123, Site 124, and the Gibson boiler.

TABLE 4
ARSENIC STACK TEST RESULTS DURING NATURAL GAS COMBUSTION

Boiler	Run 1 -*	Run 2 -*	Run 3 -*
Site 120	0.73	0.21F	0.23F
Site 121	0.24F	NR	0.31F
Site 123	ND	ND	ND
Site 124	2.1F	2.7	2.9
Gibson	BL	BL	BL

*- Units - micrograms per cubic meter at standard conditions.
ND – Not detected at less than the reporting limit.
NR – Not reported.
BL – instinguishable from the blank
F – Field blank exceeded 50% of uncorrected result.

NOTE: A Field Blank is a sample used to identify and estimate contamination immediately before and after sampling (evaluation of protocols), during sample shipment, and for samples awaiting measurement in the laboratory.

Table 5 lists the Arsenic Emission factors determined from the stack emission testing.

TABLE 5
ARSENIC EMISSION FACTORS DETERMINED BY STACK TESTING

Site	Arsenic emission factor (lb/10^{12} BTU)	Arsenic emission factor (lb/10^6 scf)
120	0.23-*	2.3E-04
121	0.2 -*	2.0E-04
123	ND<0.10	1.0E-04
124	0.18-*	1.8E-04

*- Figure shown is less than twice and more than the field blank level.

Table 1.4-4 lists an arsenic emission factor for natural gas combustion of 2.3E-04 lb/10^6 scf.

The 2.0E-04 lb/10^6 scf arsenic emission factor in Table 1.4-4 is questionable for the following reasons:

1. Three out of the four natural gas samples analyzed for arsenic content had results which were below the detection limit.
2. Of the fifteen stack test runs to measure arsenic during natural gas combustion, three were non-detect, three were instinguishable from the blank, five had results in which the field blank exceeded 50% of uncorrected result, and one result was not reported.
3. In Table 1.4-4, arsenic has an Emission Factor Rating of "E." A description of all USEPA AP-42 Emission Factor Ratings is at the end of this attachment.
4. USEPA AP-42 Sections 3.1 "Stationary Gas Turbines" and 3.2 "Natural Gas-Fired Reciprocating Engine" do not include an emission factor for arsenic. This is significant since the arsenic emissions could only result from arsenic in the natural gas or being stripped off of the interior of the combustion equipment.

NATURAL GAS SAMPLING RESULTS

A peer-reviewed and accepted for publication paper "Characterization and Comparison of Trace Metal Compositions in Natural Gas, Biogas, and Biomethane (Characterization) Attachment III" summarizes the sampling and analysis of natural gas for heavy metal content. The average and maximum results of four natural gas samples for arsenic and 65 natural gas samples for cadmium are provided. The following table compares arsenic and cadmium natural gas emission factors based on the Characterization with the AP-42 Emission Factors.

Source of emission Factor	Arsenic Emission Factor (lb/10^6 ft3)	Cadmium Emission Factor (lb/10^6 ft3)
Paper-*	5.98E-19	1.27E-20
AP-42	2.3E-04	1.1E-03

* - Based on the maximum measured concentrations

USEPA AP-42 Emission Factor Ratings

- A = Excellent. Emission factor is developed primarily from A and B rated source test data taken from many randomly chosen facilities in the industry population. The source category population is sufficiently specific to minimize variability.
- B = Above average. Emission factor is developed primarily from A or B rated test data from a moderate number of facilities. Although no specific bias is evident, is not clear if the facilities tested represent a random sample of the industry. As with the A rating, the source category population is sufficiently specific to minimize variability.
- C = Average. Emission factor is developed primarily from A, B, and C rated test data from a reasonable number of facilities. Although no specific bias is evident, it is not clear if the facilities tested represent a random sample of the industry. As with the A rating, the source category population is sufficiently specific to minimize variability.
- D = Below average. Emission factor is developed primarily from A, B and C rated test data from a small number of facilities, and there may be reason to suspect that these facilities do not represent a random sample of the industry. There also may be evidence of variability within the source population.
- E = Poor. Factor is developed from C and D rated test data from a very few number of facilities, and there may be reason to suspect that the facilities tested do not represent a random sample of the industry. There also may be evidence of variability within the source category population.

ATTACHMENT II
INPUT FROM CALIFORNIA AIR QUALITY MANAGEMENT DISTRICTS ON HEAVY METAL EMISSION FACTORS FROM NATURAL GAS COMBUSTION

Ventura County Air Pollution Control District (VCAPCD)

VCAPCD does not include heavy metal emissions in permitted emission calculations for permitting of natural gas combustion emissions units. VCAPCD also does not require heavy metal emissions be included in a permit application.

Bay Area Air Quality Management District (BAAQMD)

In general, for combustion sources, BAAQMD collects annual data on fuel throughput, but does not require facilities to provide annual emissions data. The reported fuel throughput is used to calculate the emission inventory internally, and our internal calculations generally do not consider heavy metal emissions from natural gas combustion.

Site specific source test data is preferred instead of the old AP-42 or CATEF data, which have low quality ratings, but we do not have any recent source test data for boilers, so AP-42 data is used. BAAQMD source test data was used for gas turbines.

BAAQMD lists a cadmium emission factor from Turbines as 1.88E-04 lb/MMBTU, and an arsenic emission factor of 2.21E-05 lb/MMBTU. Note: Arsenic was non-detect and ½ of the reported detection limit was used. The key particulate Toxic Air Contaminants of concern are nickel, cadmium, and hexavalent chromium which may be present in the stainless steel used to make the turbine blades or in protective coating applied to the blades.

In the BAAQMD September 7, 2005 "Policy: Emission Factors for Toxic Air Contaminants from Miscellaneous Natural Gas Combustion Sources," the following is stated:

> AP-42 emission factors for metals are not used because:
> • they are based on a small number of tests;
> • they have poor EPA data quality ratings; and
> • Ventura and San Diego APCD do not use these factors.

South Coast Air Quality Management District (SCAQMD)

Comment issued by SCAQMD in response to Departments inquiry:
We currently don't consider metals emissions for natural gas fired external combustion equipment, and so far have not required the facilities to submit metals emission data during permitting of natural gas fired external combustion equipment. We do consider emissions of other toxics from natural gas combustion and use that in determining compliance with air toxics regulations, including Rule 1401.

San Diego Air Quality Management District (SDAQMD)

In the SDAPCD "Calculation Procedures," such as AO1- B12 - Boiler, Natural Gas Fired, >100 MMBTU/HR, PRE- NSPS, Uncontrolled, for natural gas combustion, the following is stated:

> "The AP-42 trace metal emission factors listed in Table 1.4-4 are NOT included since these values were based on insignificant and/or nondetectable test results."

ATTACHMENT III
CHARACTERIZATION AND COMPARISON OF TRACE METAL COMPOSITIONS IN NATURAL GAS, BIOGAS AND BIOMETHANE

energy&fuels

Characterization and comparison of trace metal compositions in natural gas, biogas and biomethane

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Characterization and comparison of trace metal compositions in natural gas, biogas and biomethane

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ABSTRACT

Biogases are a renewable energy source intended to facilitate the energy transition from natural gas in various domains such as heat and electricity production. The composition of biogas and biomethane is well known in terms of major compounds, which include methane, carbon dioxide and hydrogen sulphide. However, the trace element composition of these gases is poorly documented. For the first time, trace metal composition of biomethane produced from agricultural waste and biogas generated at a non-hazardous waste landfill and intended to produce electricity by cogeneration is presented in this work and is compared to the trace metal composition of natural gas. A dedicated high pressure bubbling sampler was used to sample gas at different operating pressures ranging from 1 to 40 bars. Multiple wide-ranging screenings of metals and metalloids were conducted regarding the elements Se, Cd, Ni, Sb, As, Zn, Pb, Sn, Cr, Ba, Al, V, Mo, Cu and Ag. The metal concentrations in the sampled natural gas and biomethane were found to be at the same order of magnitude and ranged from 10^{-1} to 10^{2} ng/Nm^3, although some differences in the details were observed. Compared with the metals in those two gases, the metals in the biogas were at higher concentrations, ranging from 1 to 10^3 ng/Nm^3.

1. INTRODUCTION

Energy transition is considered among the most important challenges of the twenty-first century. Compared with other fossil fuels, natural gas appears to be a good compromise for answering this challenge.

Methane can originate from fossil fuels but can also be produced by methanization via anaerobic digestion of wet biomass. Producing biogas has multiple beneficial aspects and represents significant “greenhouse gas-saving potential”.[1] Biogas can be consumed directly at production sites or can be commercialized; its treatment depends on its final use. For injection into distribution networks, biogas requires purification steps to be upgraded into biomethane with a similar composition as that of natural gas. Concerning metals concentration, there is no specification except for Si concentration (Max 0.3 to 1 mgSi/m^3) according to technical standard NF EN 16723.[2]

In terms of the major gaseous compounds, the chemical compositions of natural gas and biomethane are similar.[3,4] They mainly consist of methane (80-98%vol) and gaseous inorganic compounds (total percentage between 3 and 15%vol) such as carbon dioxide, hydrogen sulphide, dinitrogen, and water.[3] In contrast, biogas composition differs drastically; depending on its origin and the optimization of the anaerobic digestion process,[5] biogas consists of 50 to 75% methane and 20 to 45% carbon dioxide.[3,4,6] Biogas can also consist of a high percentage of hydrogen sulphide (up to 16%), ammonia and other undesirable gaseous compounds.[3]

Trace levels of metals such as mercury, arsenic, zinc, nickel, tin, copper, and vanadium have also been found in natural gas[7-11]; the concentrations of these metals can range from 10^{-1} to 10^{5} ng/Nm^3, but in biogas, their concentrations can be higher depending on its origin. Pinel-Raffaitin et al.[12,13] reported arsenic and tin at concentrations ranging from 0.0016 to 18 μg/m^3 and from

0.12 to 23 µg/m^3, respectively, in landfill biogas. Moreover, Chottier reported the presence of solid deposits containing metals in engines using biogas.[14] These deposits were composed of at least 0.5%$_w$ antimony, zinc, arsenic, tin, aluminium, and titanium; these elements were found to originate from landfill biogas.

The metal concentrations in biogas, natural gas and biomethane are not currently subject to regulation. Therefore, very few studies on the metal content in these gas matrices have been conducted even though trace metals can be problematic from a health and environmental safety standpoint. These metals can also damage industrial installations that involve energetic gas-degrading treatment processes, such as aluminium heat exchange with mercury, and can cause other damage, including corrosion, amalgamations or deposit formations in pipes and engines.[9,15]

This paper explores for the first time in the same study the potential occurrence of metals in biogas produced on waste lanfill, biomethane produced from agricultural wastes, and natural gas sampled on the transmission grid. Sampling was conducted via a dedicated high pressure sampler, at different operating pressures from 1 to 40 bars.

2. EXPERIMENTAL SECTION

2.1. Gas sampling for total metal analysis. Natural gas, biomethane and biogas were sampled using a bubbling process to trap and preconcentrate the metals before analysis. The equipment and development of the high-pressure bubbling sampler are detailed elsewhere.[16] The high-pressure bubbling sampler was connected directly to the pipelines used, at operating pressures of 1 to 4 bar for biogas and treated biogas, and up to 40 bars for biomethane and natural gas. The bubbling traps were filled with a solution containing 10%$_w$ nitric acid and 5%$_w$ hydrogen peroxide for trapping the metals.

To assess the metal compositions at different time periods, two sampling campaigns were conducted for biomethane and biogas, and five were conducted for natural gas. The biogas was sampled on a non-hazardous waste landfill, who produces biogas for electricity. Biomethane was sampled on a biomethane plant that uses agricultural wastes, and produces biomethane for injection on the gas network. Finally natural gas was sampled on the French transmission grid. General chemical compositions of different kinds of gases are given in ESI Table 1. For each sampling campaign, bubbling was performed for 5 days at a flow rate of 20 L/min. A blank was implemented with nitrogen (Linde 5.0) before each sampling campaign. The bubbling solutions were stored at 4°C before being analysed.

2.2. Reagents. The trapping solutions were prepared in Millipore Milli-Q water (18.2 MΩ·cm). All of the reagents were of analytical grade or better. The metal trapping solution was prepared with Instra 70$\%_w$ nitric acid and 30$\%_w$ hydrogen peroxide.

2.3. Analytical procedure. The metals and metalloids in the nitric acid bubbling solutions were analysed by ICP-MS (Agilent 7500). The analytical parameters of the ICP-MS are presented in the supporting information. The calibration solutions, whose concentrations ranged from 0.05 to 25 µg/L, were prepared by successive mass dilutions at 1000 mg/L of all of the metals of interest – Se, Cd, Ni, Sb, As, Zn, Pb, Sn, Cr, Ba, Al, V, Mo, Cu and Ag – from metal standards (Conostans monoelemental standards from SCP Science (Baie D'urfé, Canada)).

The ICP-MS analyses were verified by adding a 20 µg/L indium internal standard to each sample, and the addition of a certified reference material (ERMCA615) for As, Cd, Pb and Ni was analysed as a quality check. The certified values were 9.9 ± 0.7, 0.106 ± 0.011, 7.1 ± 0.6 and 25.3 ± 1.1 µg/L for As, Cd, Pb, and Ni, respectively. The measured concentrations in the certified reference material (and their bias compared with the concentrations of the bubbling solution samples) were 10.34 ± 0.08 (4%), 0.113 ± 0.003 (6%), 6.72 ± 0.06 (5%) and 26.1 ± 0.6 (3%) μg/L for As, Cd, Pb, and Ni, respectively.

The ICP-MS quantification limits were 10^{-1} μg/L for selenium, aluminium, zinc and copper; 10^{-2} μg/L for arsenic, antimony, tin, molybdenum, cadmium, barium, nickel and chromium; and 10^{-3} μg/L for silver, lead, and vanadium.

3. RESULTS AND DISCUSSION

3.1. Comparison of the metal concentrations between natural gas and biomethane. The metal compositions of the sampled gases were determined and compared. The metal concentrations for the three gases are presented in Table 1. The values represent the average concentrations of each campaign. Comparisons of the metal signatures are illustrated in Figure 1.

The metal compositions in the natural gas and biomethane ranged from 10^{-1} to 10^{2} ng/Nm^3. In detail, some differences were observed; relatively higher concentrations were observed in biomethane for most analysed metals, with the exceptions of arsenic and selenium, which were higher in the natural gas. Vanadium was detected at similar concentrations in both gases. Compared to concentrations reported in the literature, the metal concentrations observed in these samples are very low. Indeed, other studies have revealed that natural gas can contain metals at concentrations ranging from 10^{-1} to 10^{4} ng/Nm^3. Krupp et al.[9] identified arsenic compounds at concentrations of 10^{4} ng/m^3 in natural gas from offshore wells, and Duoyi et al.[11] measured metal concentrations ranging from 2 ng/m^3 (Ag) to 10^{5} ng/m^3 (Zn) in natural gas in China.

3.2. Comparison of the metal concentrations between natural gas and biogas. A biogas originating from a landfill disposal site and treated for cogeneration was also analysed. The gas purification treatment consisted of the removal of condensates via cooling with glycol and two different activated carbon sorption processes to remove hydrogen sulphide or siloxanes. The metal concentrations in the treated biogases were compared with those in the natural gas and the biomethane; the results are shown in Figure 2. Each metal value corresponds to the average concentration from multiple sampling campaigns.

The metal concentrations were drastically higher in the treated biogas than in the natural gas; the factors ranged from 10 (As, V) to 1000 (Cd) times higher. This result is not surprising, as volatile metals have often been found in biogas from landfill sites.[12,13,17]

3.3. Effect of the treatment of the biogas upon metal abatement

A comparison between the raw and treated biogases indicates a different metal signature. According to Figure 3, most of the metals (Al, Ni, Zn and Cd) are present in similar concentrations of approximately 1 $\mu g/Nm^3$ in both biogases. However, the concentrations of antimony, arsenic and tin were 100 to 1000 times higher in the raw biogas than in the treated biogas and reached concentrations of 10 $\mu g/Nm^3$ (Sn) and 100 $\mu g/Nm^3$ (Sb, As). These results indicate that the raw biogas treatment applied at this landfill, which usually aims to treat major compounds such as hydrogen sulphide, carbon dioxide, and siloxanes, is also partially effective for metals. We can also point out that selenium and silver concentrations were higher in the treated biogas than the raw biogas. This result can be explained by a possible release of these metals into the gas during the treatment process.

The various scrubbing and adsorption processes used in industrial sites are primarily designed to remove hydrogen sulphides and siloxanes from raw biogas. The ability of these cleaning processes to also remove the metals from biogas is interesting.

The metal content of the raw biogas depends on the composition of the biomass and on the anaerobic digestion process. In this study, the raw biogas analysed contained three major metals: tin, arsenic and antimony, with concentrations ranging from 10 to 100 $\mu g/m^3$ (Fig. 3).

4. CONCLUSION

Natural gas, biomethane and biogas were analysed to determine their metal compositions. The high pressure bubbling sampler allowed sampling of gas at different operating pressures from 1 to 40 bars. The metals were detected at concentrations ranging from 10^{-1} to 10^{2} ng/Nm^3 in the natural gas and biomethane and from 1 to 10^3 ng/Nm^3 in the biogas. The high-pressure bubbling sampler was successful to sample metals at concentrations as low as 10^{-1} ng/Nm^3. The ability to measure metals along this concentration scale can facilitate optimization of the performance of a treatment process or the selection of biomass to improve the biogas or biomethane chain.

The results of this study show that the metal content can vary drastically from one type of gas to another. Therefore, a regular monitoring of produced biogas and biomethane can help improving the data regarding biogas composition and exploring removal techniques for metals during treatment processes.

ASSOCIATED CONTENT

Supporting Information

ICP-MS analytical parameters used in metal/metalloid analyses in the trapping solution (Table 1) (PDF)

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Notes

The authors have no conflicts of interest to declare

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Figure captions

Figure 1. Metal concentrations (in ng/Nm^3*)* presented using a logarithmic scale for natural gas and biomethane.

Figure 2. Metal concentrations (in ng/Nm^3) presented using a logarithmic scale for natural gas and treated biogas.

Figure 3. Metal concentrations (in ng/Nm^3) presented using a logarithmic scale for treated biogas and raw biogas.

Table legends

Table 1. Average metal concentrations, standard deviation (in ng/Nm^3) and standard deviation (in %) in natural gas, biomethane and biogas from several analysis campaigns (* no standard deviation due to only one analysis for this element in biomethane and biogas))

Tables

Table 1. Average metal concentrations, standard deviation (in ng/Nm^3) and standard deviation (in %) in natural gas, biomethane and biogas from several analysis campaigns (* no standard deviation due to only one analysis for this element in biomethane and biogas))

ng/Nm^3	Natural gas		Biomethane		Biogas	
Al	129 ± 134	(104)	322 ± 6	(2)	3925 ± 787	(20)
Se	34.2 ± 24	(24)	1.96 ± 1.96	(117)	4524 ± 4400	(98)
Zn	25.1 ± 20	(20)	41.1 ± 10.5	(26)	1362 ± 1150	(84)
Cr	6.43 ± 4	(4)	22.5 ± 0.5	(2)	446 ± 140	(32)
As	6.33 ± 4	(4)	0.70 ± 0.01	(1)	50.2 ± 60	(120)
Ni	5.97 ± 4	(4)	20.7 ± 6.5	(31)	2840 ± 2600	(93)
Sn	2.92 ± 3	(101)	22.8 ± 1.0	(4)	487 ± 170	(35)
Cu	2.67 ± 2	(62)	63.7 ± 79.3	(125)	312 ± 255	(82)
Sb	1.56 ± 0.4	(27)	13.5 ± 9.19	(68)	1439 ± 1950	(136)
Ba	1.43 ± 1.9	(27)	6.96 ± 1.06	(15)	89.5 ± 78	(87)
V	0.96 ± 0.6	(60)	0.78 ± 0.06	(8)	7.71 ± 3	(43)
Mo	0.62 ± 0.5	(78)	2.86 ± 1.14	(40)	30.4 ± 34	(111)
Pb	0.52 ± 0.3	(57)	2.06 ± 0.57	(27)	61.1 ± 70	(118)
Ag	0.37 ± 0.1	(41)	18.4*		25.7*	
Cd	0.12 ± 0.1	(65)	0.21 ± 0.08	(36)	779 ± 62	(8)

Figures

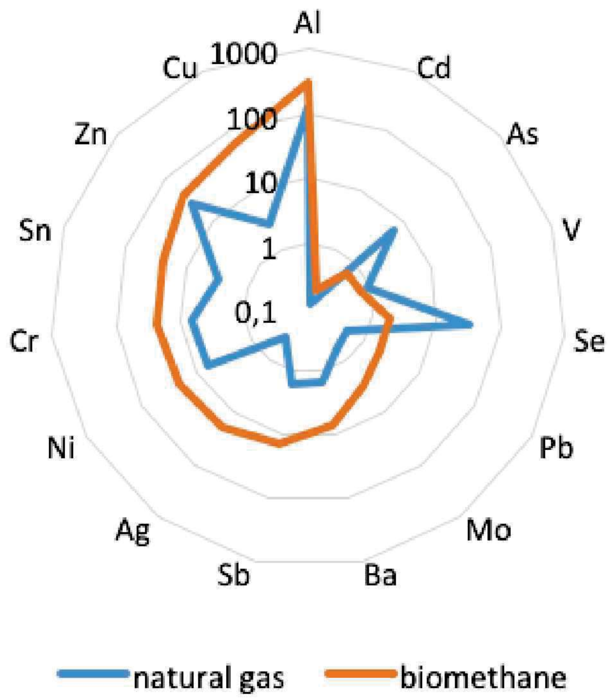

Fig. 1. Metal concentrations (in ng/Nm3) presented using a logarithmic scale for natural gas and biomethane

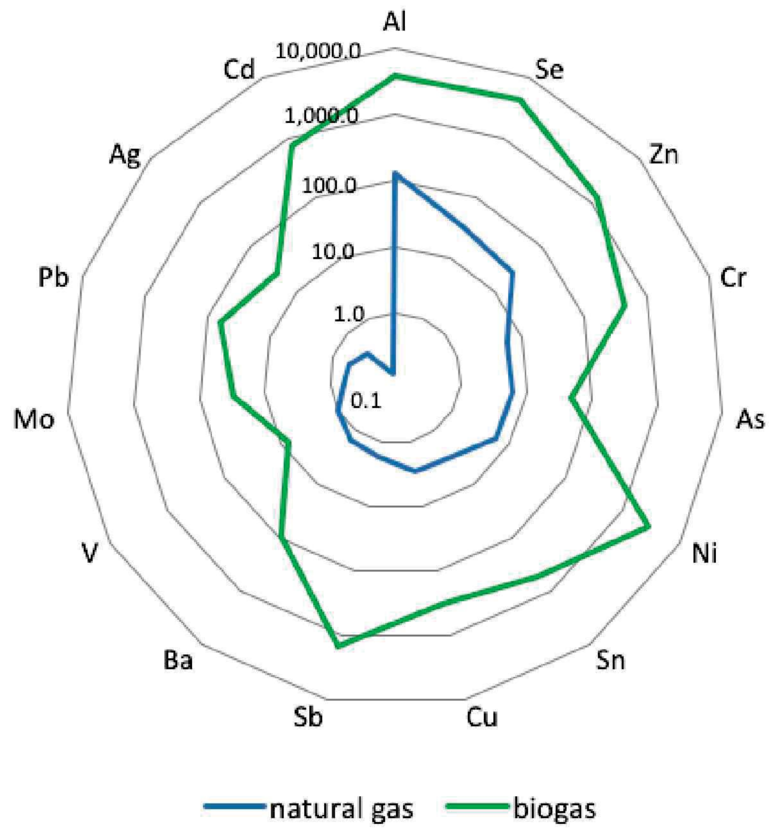

Fig. 2 Metal concentrations (in ng/Nm^3) presented using a logarithmic scale for natural gas and treated biogas.

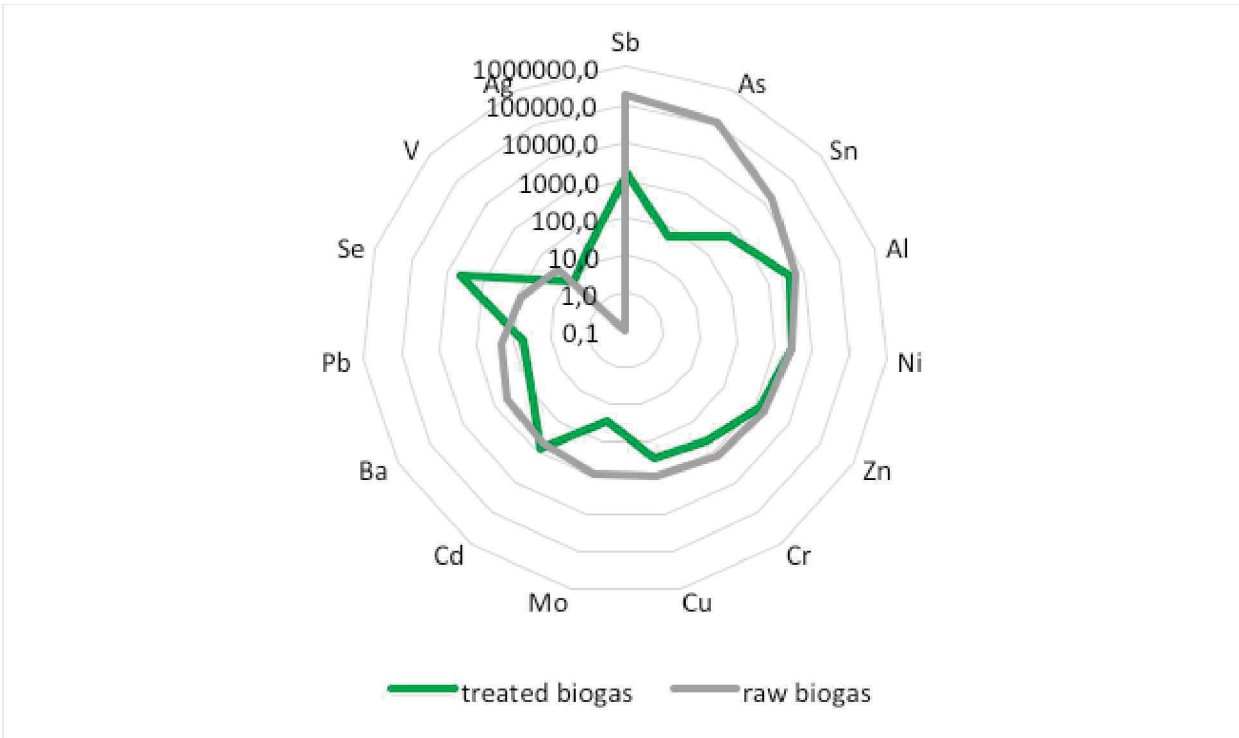

Fig. 3. Metal concentration (in ng/Nm^3) presented using a logarithmic scale for treated biogas and raw biogas