Corrections

PERSPECTIVE

Correction for "Theory of mass-independent fractionation of isotopes, phase space accessibility, and a role of isotopic symmetry," by Rudolph A. Marcus, which appeared in issue 44, October 29, 2013, of *Proc Natl Acad Sci USA* (110:17703–17707; first published June 28, 2013; 10.1073/pnas.1213080110).

The author notes that, on page 1, middle column, lines 11–16 "Fewer accidental resonances mean less energy sharing and so less statistical behavior with a consequence that they are in equilibrium with the population of accessible states of O_3^* at low pressures, as discussed later." should instead appear as "Fewer accidental resonances mean less energy sharing and so less statistical behavior with a consequence of a shorter lifetime of O_3^* at low pressures, as discussed later."

On page 2, middle column, first full paragraph, lines 11–14 "This major difference in the pressure effect indicates a difference in the role of the collisions in these two distant phenomena." should instead appear as "This major difference in the pressure effect indicates a difference in the role of the collisions in these two distinct phenomena."

On page 3, middle column, first paragraph, lines 4–7 "The overall deviation from statistical theory for the recombination rate constant was (N. Ghaderi) perhaps a factor of 2." should instead appear as "The overall deviation from statistical theory for the recombination rate constant was (N. Ghaderi) less than a factor of 2."

On page 3, middle column, first full paragraph, lines 22–26 "Any chaos in the form of higher-order resonances within a volume element h^N would be coarse gained and so presumably contribute to quantum chaos." should instead appear as "Any chaos in the form of higher-order resonances within a volume element h^N would be coarse gained and so presumably not contribute to quantum chaos."

Both the online article and the print article have been corrected.

www.pnas.org/cgi/doi/10.1073/pnas.1315099110

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Correction for "Measurements of methane emissions at natural gas production sites in the United States," by David T. Allen, Vincent M. Torres, James Thomas, David W. Sullivan, Matthew Harrison, Al Hendler, Scott C. Herndon, Charles E. Kolb, Matthew P. Fraser, A. Daniel Hill, Brian K. Lamb, Jennifer Miskimins, Robert F. Sawyer, and John H. Seinfeld, which appeared in issue 44, October 29, 2013, of *Proc Natl Acad Sci USA* (110:17768–17773; first published September 16, 2013; 10.1073/pnas.1304880110).

The authors note that upon publication their conflict of interest statement was not complete. The updated disclosure statement is as follows, "Jennifer Miskimins holds a joint appointment with Barree & Associates and the Colorado School of Mines. She has also served as an advisor to Nexen in 2012. David T. Allen served as a consultant for the Eastern Research Group and ExxonMobil in 2012, and is the current chair of the Science Advisory Board for the EPA. John H. Seinfeld has served as a consultant for Shell in 2012. David T. Allen, Matthew Harrison, Charles E. Kolb, and Robert F. Sawyer variously serve as members of scientific advisory panels for projects supported by Environmental Defense Fund and companies involved in the natural gas supply chain. These projects are led at Colorado State University (on natural gas gathering and processing), Washington State University (on local distribution of natural gas), and the University of West Virginia (on CNG fueling and use in heavy duty vehicles)."

Both the online article and print article have been corrected.

www.pnas.org/cgi/doi/10.1073/pnas.1318658110

Correction for "mitoBK$_{Ca}$ is encoded by the *Kcnma1* gene, and a splicing sequence defines its mitochondrial location," by Harpreet Singh, Rong Lu, Jean C. Bopassa, Andrea L. Meredith, Enrico Stefani, and Ligia Toro, which appeared in issue 26, June 25, 2013, of *Proc Natl Acad Sci USA* (110:10836–10841; first published June 10, 2013; 10.1073/pnas.1302028110).

PNAS notes that a conflict of interest statement was omitted during publication. PNAS declares that "The editor, Ramon Latorre, is a recent coauthor with the authors of this publication, having published a paper with them in 2012."

Additionally, the authors note:

"Although Figs. 1 and S1 display the same sequence template, the analyses of LC/MS/MS data were performed against the respective databases, rat for Fig. 1, and mouse for Fig. S1. Sequence alignment of rat (NCBI:Q62976.3; UniProtKB: Q62976-1 V.3, which differs by 3 amino acids near the N terminus with that of Figs. 1 and S1) and mouse (NCBI: NP_001240298.1) isoforms show 98.9% amino acid identity with differences circumscribed to the extreme N and C termini. Peptides identified by LC/MS/MS have the exact sequence in rat and mouse as shown in Figs.1 and S1."

"In published Fig. 7, panels *E* and *F* show slices of the same heart in each condition; to better display the infarcted vs. healthy portions, these images were scaled to approximately the same size. We noticed that some data points in panel *G* were slightly moved during figure preparation. The revised Fig. 7 now shows heart slices at their original magnification (*E* and *F*) and the correct panel *G*. The corrected figure and its legend appear below."

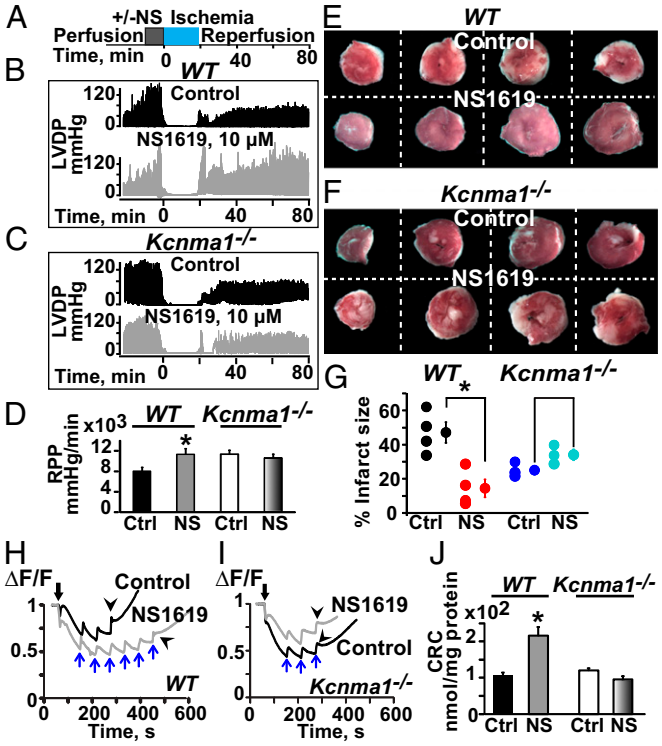

Fig. 7. BK$_{Ca}$ protects the heart from ischemic injury. (*A*) Ischemia/reperfusion protocol. (*B* and *C*) Function traces of hearts preconditioned with vehicle (DMSO, control) or with NS1619 (10 μM) in WT and *Kcnma1*$^{-/-}$ mice. (*D*) NS1619 significantly improved mean RPP in WT but not in *Kcnma1*$^{-/-}$ mice. (*E* and *G*) WT hearts preconditioned with NS1619 exhibited less infarct size (white) compared with the control. (*F* and *G*) In *Kcnma1*$^{-/-}$, infarct size was not reduced with NS1619. (*H–J*) Mitochondrial Ca^{2+} uptake. NS1619 preconditioning increased the amount of Ca^{2+} needed to induce a large Ca^{2+} release in WT but not in *Kcnma1*$^{-/-}$samples. Black arrows, addition of mitochondria. Blue arrows, 40 nmol Ca^{2+} pulses. Arrowheads, massive release of Ca^{2+}. *$P < 0.05$ vs. control (Ctrl); CRC, Ca^{2+} retention capacity.

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Measurements of methane emissions at natural gas production sites in the United States

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Edited by Susan L. Brantley, Pennsylvania State University, University Park, PA, and approved August 19, 2013 (received for review March 20, 2013)

Engineering estimates of methane emissions from natural gas production have led to varied projections of national emissions. This work reports direct measurements of methane emissions at 190 onshore natural gas sites in the United States (150 production sites, 27 well completion flowbacks, 9 well unloadings, and 4 workovers). For well completion flowbacks, which clear fractured wells of liquid to allow gas production, methane emissions ranged from 0.01 Mg to 17 Mg (mean = 1.7 Mg; 95% confidence bounds of 0.67–3.3 Mg), compared with an average of 81 Mg per event in the 2011 EPA national emission inventory from April 2013. Emission factors for pneumatic pumps and controllers as well as equipment leaks were both comparable to and higher than estimates in the national inventory. Overall, if emission factors from this work for completion flowbacks, equipment leaks, and pneumatic pumps and controllers are assumed to be representative of national populations and are used to estimate national emissions, total annual emissions from these source categories are calculated to be 957 Gg of methane (with sampling and measurement uncertainties estimated at ±200 Gg). The estimate for comparable source categories in the EPA national inventory is ∼1,200 Gg. Additional measurements of unloadings and workovers are needed to produce national emission estimates for these source categories. The 957 Gg in emissions for completion flowbacks, pneumatics, and equipment leaks, coupled with EPA national inventory estimates for other categories, leads to an estimated 2,300 Gg of methane emissions from natural gas production (0.42% of gross gas production).

greenhouse gas emissions | hydraulic fracturing

Methane is the primary component of natural gas and is also a greenhouse gas (GHG). In the US national inventories of GHG emissions for 2011, released by the Environmental Protection Agency (EPA) in April 2013 (1), 2,545 Gg of CH_4 emissions have been attributed to natural gas production activities. These published estimates of CH_4 emissions from the US natural gas industry are primarily based on engineering estimates along with average emission factors developed in the early 1990s (2, 3). During the past two decades, however, natural gas production processes have changed significantly, so the emission factors from the 1990s may not reflect current practices. This work presents direct measurements of methane emissions from multiple sources at onshore natural gas production sites incorporating operational practices that have been adopted or become more prevalent since the 1990s.

Horizontal drilling and hydraulic fracturing are among the practices that have become more widely used over the past two decades. During hydraulic fracturing, materials that typically consist of water, sand and, additives, are injected at high pressure into low-permeability formations. The injection of the hydraulic fracturing fluids creates channels for flow in the formations (often shale formations), allowing methane and other hydrocarbon gases and liquids in the formation to migrate to the production well. The well and formation is partially cleared of liquids in a process referred to as a completion flowback, after which the well is placed into production. Production of natural gas from shale formations (shale gas) accounts for 30% of US natural gas production, and this percentage is projected to grow to more than 50% by 2040 (4).

Multiple analyses of the environmental implications of gas production using hydraulic fracturing have been performed, including assessments of water contamination (5–8), criteria air pollutant and air toxics releases (9–11), and greenhouse gas emissions (11–18). Greenhouse gas emission analyses have generally been based on either engineering estimates of emissions or measurements made 100 m to a kilometer downwind of the well site. This work reports direct on-site measurements of methane emissions from natural gas production in shale gas production regions.

Significance

This work reports direct measurements of methane emissions at 190 onshore natural gas sites in the United States. The measurements indicate that well completion emissions are lower than previously estimated; the data also show emissions from pneumatic controllers and equipment leaks are higher than Environmental Protection Agency (EPA) national emission projections. Estimates of total emissions are similar to the most recent EPA national inventory of methane emissions from natural gas production. These measurements will help inform policymakers, researchers, and industry, providing information about some of the sources of methane emissions from the production of natural gas, and will better inform and advance national and international scientific and policy discussions with respect to natural gas development and use.

Author contributions: D.T.A. and M.H. designed research; D.T.A., V.M.T., J.T., D.W.S., M.H., A.H., and S.C.H. performed research; C.E.K., M.P.F., A.D.H., B.K.L., J.M., R.F.S., and J.H.S. analyzed data; and D.T.A. wrote the paper.

Conflict of interest statement: J.M. holds a joint appointment with Barree & Associates and the Colorado School of Mines. She has also served as an advisor to Nexen in 2012. D.T.A. served as a consultant for the Eastern Research Group and ExxonMobil in 2012, and is the current chair of the Science Advisory Board for the EPA. J.H.S. has served as a consultant for Shell in 2012. D.T.A., M.H., C.E.K., and R.F.S. variously serve as members of scientific advisory panels for projects supported by Environmental Defense Fund and companies involved in the natural gas supply chain. These projects are led at Colorado State University (on natural gas gathering and processing), Washington State University (on local distribution of natural gas), and the University of West Virginia (on CNG fueling and use in heavy duty vehicles).

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Methane emissions were measured directly at 190 natural gas production sites in the Gulf Coast, Midcontinent, Rocky Mountain, and Appalachian production regions of the United States. The sites included 150 production sites with 489 wells, all of which were hydraulically fractured. In addition to the 150 production sites, 27 well completion flowbacks, 9 well unloadings, and 4 well workovers were sampled; the sites were operated by nine different companies. The types of sources that were targeted for measurement account for approximately two-thirds of methane emissions from all onshore and offshore natural gas production, as estimated in the 2011 national greenhouse gas emission inventory (1). A summary of the scope of the study, along with a rationale for the inclusion or exclusion of sources for direct measurement efforts, is provided in *SI Appendix*. Sampling was conducted from May 2012 through December 2012 at sites throughout the United States (see *SI Appendix* for a map and for the number of sampling sites in each region). All nine companies that participated in the study provided sites for sampling, and at least three companies provided sites in each of the regions (*SI Appendix*).

The data presented in this report represent hundreds of measurements of methane emissions from several types of onshore natural gas production activities; however, the sites sampled still represent a small fraction of the total number of sites nationwide (Table 1). This dataset is designed to be representative of the participating companies' activities and practices, but not necessarily all activities and practices. Multiple methods were used to minimize the potential for bias in the sample set, as described in *SI Appendix*.

Results

Emission measurements were performed for 27 well completion flowbacks, 9 liquids unloadings, 4 well workovers, and 150 production sites with 489 hydraulically fractured wells (Table 1 and *SI Appendix*). Data are summarized here for the well completion flowbacks, liquids unloading, and production site emissions. *SI Appendix* provides additional details. The data on well workovers, collected for workovers without hydraulic fracturing, are not presented because the data set was small and emission estimates for workovers without fracturing represent less than 0.1% of national emission estimates.

Well Completion Flowbacks. After a well is drilled, the well is "completed." Completion is the process of making a well ready for continuous production. Specifically, after drilling and fracturing, before natural gas production can begin, the well must be cleaned of sand and liquid of various types that had been injected into the well. The recovery of these liquids is referred to as a flowback, and gas, including methane, can be dissolved or entrained in the flowback liquids. Some of the methane in the liquids can be sent to sales or emission control devices, but some can be emitted.

Measurements were made of methane emissions during 27 completion flowback events. Emissions data for each of the 27 events is provided in *SI Appendix*. Five of the flowbacks were in the Appalachian region, seven in the Gulf Coast region, five in the Midcontinent region, and 10 in the Rocky Mountain region. The durations of the completions ranged from 5 to 339 h (2 wk). Measured methane emissions over an entire completion flowback event ranged from less than 0.01 Mg to more than 17 Mg, with an average value of 1.7 Mg and a 95% confidence interval of 0.67–3.3 Mg. Measurement and sampling uncertainty are included in the confidence interval; uncertainties due to a limited sample size dominate the overall uncertainty estimate. Methods for determining the confidence intervals are described in *SI Appendix*.

The completions with the lowest emissions were those in which the flowback from the well was sent immediately, at the start of the completion, to a separator, and all of the gases from the separator were sent to sales. The only emissions from these completions were from methane dissolved in liquids (mostly water) sent from the separator to a vented tank. The completion flowback with the highest total emissions, 17 Mg, was the longest in duration (339 h) and had initial flowback into a vented tank with very high methane concentrations. Some of the other relatively high emission completion flowbacks (~3 Mg to 6 Mg of methane) involved large amounts of flared gas (up to 130 Mg of methane to the flare, which was assumed to combust the methane at 98% efficiency, *SI Appendix*). Another completion with emissions of 4 Mg of methane was one in which all gases, for the entire event, were vented to the atmosphere. This type of venting for the entire duration of the completion was observed in 9 of the 27 completions. However, the nine completions of this type showed a wide range of emissions (4 Mg of methane for one completion and 0.5 Mg of methane for another completion of this type for an adjacent well).

These data provide extensive measurements on methane emissions from well completions that can be used in national emission estimates. Current national inventories of methane emissions have been assembled, based on simple engineering models of the completion process. In the most recent EPA national greenhouse gas emission inventory (2011 inventory, released April 2013) (1), 8,077 well completions with hydraulic fracturing are estimated to result in 654 Gg per year of emissions, for an average of 81 Mg of methane per completion flowback (compared with 1.7 Mg per flowback for the events reported here). To understand the reasons for the much lower emissions per event reported in this work, it is useful to define a potential emission for each flowback. The potential of a flowback to emit is defined here, and in the EPA national inventory (1), as the methane that would be emitted if all of the methane leaving the wellhead during the flowback were vented to the atmosphere. Potential emissions for the wells in this work ranged from 0.2 Mg to more than 1 Gg methane, with an average of 124 Mg. The average from the EPA national inventory is slightly higher at 151 Mg. Net emissions are calculated, in the EPA national inventory, by reducing potential emissions by estimates of methane captured or controlled

Table 1. Comparison of sample set size to emission source populations

Source	No. of events/locations sampled	Total no. of events/locations
Well completions	27	8,077*
Gas well unloading	9	35,828[†]
Well workovers	4	1782 (11,663)[‡]
Wells	489	446,745[§]

*Completions, with hydraulic fracturing reported in the 2011 National GHG Emission Inventory (1).
[†]Wells without plunger lift that have unloading events (the type of event sampled in this work) reported in the 2011 National GHG Emission Inventory (1).
[‡]Workover events with (and without) hydraulic fracturing reported in the 2011 National GHG Emission Inventory (1).
[§]Gas wells with and without hydraulic fracturing reported in the 2011 National GHG Emission Inventory (1); 513,000 on-shore natural gas wells are reported by the Energy Information Administration (20); see *SI Appendix*.

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because of regulatory or voluntary emission reductions. In the current national inventory, emission reductions are roughly one-half of potential emissions (*SI Appendix*). In this work, net or measured emissions for the total of all 27 completions are 98% less than potential emissions. This large difference between the net emissions measured in this work and the net emissions estimated in the national inventory is due to several factors. First, consistent with emerging regulatory requirements (21) and improved operating practices, 67% of the wells sent methane to sales or control devices. Second, for those wells with methane capture or control, 99% of the potential emissions were captured or controlled. Finally, the wells with uncontrolled releases had much lower than average potential to emit. Of the nine wells in this work that had uncontrolled venting of methane, the average potential to emit was 0.83 Mg, which is 0.55% of the average potential to emit in the national inventory. The relative importance of these factors is discussed in *SI Appendix*.

Unloadings. Gas wells often produce liquid hydrocarbons and water along with natural gas. In most new wells, the velocity of natural gas up the production tubing of the well is sufficient to lift any produced water out of the well with the gas. As gas production declines, the velocity may no longer be sufficient to lift the liquids, which begin to accumulate in the wellbore and eventually restrict gas flow from the producing formation. Liquids accumulation therefore needs to be removed to allow the well to continue to produce gas at optimal rates.

There are multiple methods of unloading a gas well, some of which do not result in emissions. In this work, sampling was performed for unloadings in which an operator manually bypasses the well's separator. Unlike automated plunger lift methods, these manual unloading events could be scheduled, allowing the study team adequate time to install measurement equipment. As the flow to the separator, which typically operates at pressures of multiple atmospheres, is bypassed, flow is diverted to an atmospheric pressure tank. This diversion allows the well to flow to a lower pressure destination (the atmospheric pressure tank, rather than the pressurized separator). This lower pressure end point allows more gas to flow, increasing velocity in the production tubing and lifting the liquids out of the well. Gas is discharged from the tanks through the tank vent, unless the tanks have an emissions control system such as a combustor.

The nine unloading events reported in this work were varied in their characteristics. Methane emissions ranged from less than 0.02 Mg to 3.7 Mg. Some unloadings lasted 2 h (or more) and had relatively uninterrupted flow. Other unloadings were as short as 10–15 min with uninterrupted flow, and still others had intermittent flow for short periods and periods of no flow for much of the unloading period. Some of the wells sampled only unloaded once over the current life of the well, whereas others were unloaded monthly. The average emission per unloading event was 1.1 Mg of methane (95% confidence limits of 0.32–2.0 Mg). If the emissions per event for each well are multiplied by the event frequency (events per year) reported by the well operators, the average emission per well per year was 5.8 Mg (an average of 5.9 events per unloaded well per year). The sampled population reflected a wide range of emission rates, with a population of high emitting wells and a population of low emitting wells. When emissions are averaged per event, emissions from four of the nine events contribute more than 95% of the total emissions. *SI Appendix* provides more information about individual unloading events.

Because the characteristics of the unloading events sampled in this work are highly variable, and because the number of events sampled is small, extrapolating the results to larger populations should be done with caution. One source of data on larger populations of wells with unloadings, to which the population sampled in this work can be compared, is a survey reported by the American Petroleum Institute and America's Natural Gas Alliance (API/ANGA) (22). In this survey, more than 20 companies provided data and well characteristics for 40,000–60,000 wells (with the number in the sample depending on the type of emission event). These API/ANGA data were used by the EPA to arrive at 2011 national inventory emission estimates for 35,828 wells without plunger lift and 22,866 with plunger lift, which vent for unloading. Unloading emissions for the wells in the API/ANGA survey were estimated based on well characteristics such as well bore volume, well pressure, venting time, and gas production rate (3). For the unloading events without plunger lift, 100 of the 2,901 wells (3%) in the survey account for 50% of the estimated emissions. Ninety percent of the estimated emissions in the API/ANGA survey are due to one-half of the wells. Because a small population of wells (3%) accounts for one-half of the emissions, if this relatively small population of high emitting wells is not adequately sampled, it is not possible to accurately estimate national emissions. The wells sampled in this work unloaded relatively infrequently. In contrast, some wells in the API/ANGA survey, including some of the highest emitting wells, unload with a daily or weekly frequency. An average frequency of unloading for the wells in the API/ANGA survey is 32.57 events per year, compared with an average observed in this work of 5.9.

Because a small number of unloading events accounts for a large fraction of emissions in the API/ANGA survey (22), and because some of these wells had frequencies of unloading higher than any of the events observed in this work, the sample set of nine events reported in this work is not sufficient for accurately estimating emissions from unloading at a national scale. Nevertheless, the data reported here provide valuable insights for the design of future sampling campaigns.

One important result from the measurements reported here is that current EPA estimation methods overpredict measured emissions. If the emission estimation method (3) used in the API/ANGA survey is applied to the events sampled in this work, estimates are 5 times higher than measured emissions. Estimates of the emissions for the nine events are 5.2 Mg per event versus measured emissions of 1.1 Mg per event. Emissions were overestimated for every event. The percentage by which emissions are overestimated increases as emissions per event decrease (*SI Appendix*). Possible causes of the overestimate include the assumptions in the estimation method that the entire well bore volume is released in an unloading and that the gas flow during an unloading is continuous.

Overall, the implication of all of these issues is a large uncertainty bound in the national emissions from gas well unloading. If the per well annual emissions from this work are used, a national emission estimate based on counts of wells that undergo unloading is in reasonable agreement with emissions in the EPA national inventory (1). In contrast, another estimate of unloading emissions, based on the per event emissions observed in this work and an estimate of national unloading events (22), would lead to a national estimate five times the estimate based on well counts. This estimate is not supported by the available data, given that the national event count is dominated by high frequency unloading events and the wells observed here unloaded far less frequently with much higher emission estimates per event. A lower estimate of unloading emissions could be suggested based on national well counts, emission estimates, and the finding that emission estimation methods, used in many EPA inventory estimates, overestimate observations made in this work by a factor of 5. All of these methods, however, assume a single scalar value represents a wide range of unloadings; the data presented in this work and in the API/ANGA survey (22) suggest that refined emission estimation methods, taking into account well and unloading characteristics, will be required. Additional measurements of unloading emissions are needed, both to resolve the

Table 2. National emission estimates for the natural gas production sector, based on this work and the 2011 national inventory

Category	2011 EPA GHG inventory net emissions,* Gg of methane/yr	Emission estimates from this report,† Gg of methane/yr	Comments
Sources with emissions measurements from this work used to generate national emission estimates			
Completion flowbacks from wells with hydraulic fracturing	654*	18‡ (5–27)§	Decrease in national emission estimate
Chemical pumps	34*	68 (35–100)§	Increase in national emission estimate
Pneumatic controllers	355*	580‡ (518–826)§	Increase in national emission estimate; if national emission factors derived from this work are used, this estimate becomes 790 Gg (*SI Appendix*)
Equipment leaks	172–211*,¶	291‡ (186–396)§	Increase in national emission estimate; this comparison is based on equivalent categories of equipment, not all equipment leaks¶ (*SI Appendix*)
Subtotal, national emissions, estimated based on this work	1215–1254†#	957 ± 200 #	Decrease of ~250 Gg for national emission estimate
Sources with limited measurements; national emissions not estimated			
Unloadings (nonplunger lift)	149* (EPA inventory)		Highly diverse events; small data set collected in this work; preliminary national emission estimates have a broad range of values (25–206 Gg; see text)
Workovers (without hydraulic fracturing)	0.3* (EPA inventory)		Measurements in this work included only one recompletion and three swabbing events (see text)
Other sources, not measured in this work			
Unloadings (plunger lift)	108* (EPA inventory)		No measurements made in this work
Workovers (with hydraulic fracturing)	143* (EPA inventory)		No measurements made in this work; equipment configurations are similar to completion flowbacks for wells with hydraulic fracturing; if emissions per event are comparable to completion flowbacks, current inventories may overestimate emissions
Other sources, not measured in this work	891–930*,¶ (EPA inventory)		Includes potential emissions of sources not measured less prorated regulatory and voluntary emission reductions*
Total methane, Gg	2,545	2,300	Decrease of ~250 Gg for estimate
Methane emissions,*,** % [percent of gross gas production]	0.47% [0.59%]	0.42% [0.53%]	Brackets: gross gas emitted/gross gas produced (assuming produced gas is 78.8% methane)

*Emissions from EPA national inventory are based on reported potential emissions less reductions; when reductions are reported for combined source categories, identical percentage reductions of potential emissions are assumed to apply across source categories (*SI Appendix*, section S5).

†Emission factors used to estimate national inventories are designed to be representative of the participating companies' activities and practices, but not necessarily all activities and practices.

‡National emissions based on a regionally weighted average (*SI Appendix*, section S5).

§Ranges are based on 95% confidence bounds of emission factors; activity factors are identical to those used in EPA inventory. Uncertainties in activity factors (e.g., device counts) are not included. Uncertainties associated with whether regional or national averaging is performed are included in the uncertainty estimate (*SI Appendix*, section S5.4).

¶Sampling in this work included compressors on well sites, but not all gathering compressors. Well site and gathering compressors are combined in the national inventory. Range reported for national inventory for equipment leaks and "other" sources reflect uncertainty in attributing compressor emissions from national inventory to a specific source category.

#Uncertainty bound assumes uncertainties for completion flowbacks, pneumatic pumps and controllers and leaks are independent, and consequently, the combined uncertainty is the square root of the sum of the squares of the individual uncertainties.

**US total gross gas production (oil and coal bed, gas, and shale, onshore and offshore): 547,000 Gg.

differences between estimates and measurements and to better characterize the population of wells with unloading emissions.

Finally, it is also clear from the data that properly accounting for unloading emissions will be important in reconciling emission inventories with regional ambient measurements. Average methane emission rates for a single unloading ranged from roughly 100 g/min to in excess of 30,000 g/min. These rates are much larger than emission rates for production sites (typically tens of grams of methane per minute per well) or from completions (typically a few hundred grams per event per minute). At these emission rates, a single unloading event could, during the short period that it is occurring, result in emissions that are the equivalent of just a few wells in routine production to the equivalent of up to several thousand wells in routine production. Therefore, reconciliation between instantaneous ambient measurements and emission inventories will need to carefully represent the emissions from unloadings.

Well Sites in Routine Production. A well site contains one or more wellheads and may contain separators, pneumatic controllers, water tanks, hydrocarbon tanks (oil or condensate), and possibly other devices such as dehydrators, compressors, and flares. In this work, measurements were made from pneumatic controllers and pumps, because these devices release methane as part of their routine operation, and from equipment leaks detected by using an infrared camera (*SI Appendix*) at well sites.

Emissions for equipment on well sites, in routine production, that were targeted for measurements had much narrower uncertainty bounds than well completion flowbacks or well unloadings. Emissions from pneumatic chemical injection pumps measured in this work averaged 3.7 ± 1.6 g of methane per minute per pump, 9% lower than the EPA emission factor (*SI Appendix*, section S2). Intermittent and low bleed pneumatic devices measured in this work averaged 5.9 ± 2.4 and 1.7 ± 1.0 g

Table 3. Measurement methods used in the study

Source	Direct measurement methods	Mobile downwind sampling
Well completions	Measurements from flowback tanks made by using enclosures and temporary stacks with measurements of flow rate and composition	Downwind tracer ratio methods: Metered release of C_2H_2 and N_2O on site and downwind measurements of methane to C_2H_2 and methane to N_2O concentration ratios
Gas well unloading	Temporary stack with measurements of flow rate and composition	
Well workovers	Measurements from flowback tanks made by using enclosures and temporary stacks with measurements of flow rate and composition	
Production sites	Infrared (FLIR) camera surveys of sites and flow rate measurements using a HiFlow device	Metered release of C_2H_2 and N_2O on site and downwind measurements of methane to C_2H_2 and methane to N_2O concentration ratios

of natural gas per device per minute, 29% and 270% higher than EPA emission factors, respectively (*SI Appendix*, section S2). No high bleed pneumatic devices were identified at the sampling sites, and the average emission rate for the population of pneumatic controllers sampled in this work was 3.36 ± 0.65 g of methane per min (3.8 ± 0.69 g of natural gas per min). Equipment leaks measured in this work averaged 1.23 ± 0.44 g of methane per minute per well, which can be compared with an EPA estimate of potential emissions (no regulatory or voluntary emission reductions) of 1.37–1.67, derived from EPA's inventory for similar equipment types (wellheads, separators, heaters, meters/piping, and dehydrator fugitives), with the range reflecting whether small compressors are added to the comparison (*SI Appendix*, section S5). Comparing to net emissions is challenging because EPA does not assign emission reductions to specific equipment categories. Additional information is provided in *SI Appendix*.

There was significant geographical variability in the emissions rates from pneumatic pumps and controllers, but these regional differences were not as pronounced for equipment leaks. Emissions per pump from the Gulf Coast are statistically significantly different and roughly an order of magnitude higher than from pumps in the Midcontinent. Emissions per controller from the Gulf Coast are highest and are statistically significantly different from controller emissions in the Rocky Mountain and Appalachian regions. Emissions per controller in the Rocky Mountain region are lowest and an order of magnitude less than the national average (*SI Appendix*).

Implications for National Emission Estimates. If the average emissions reported in this work for well completion flowbacks, pneumatic devices, and equipment leaks are assumed to be representative of national populations and are applied to national counts of completions, pneumatic devices, and wells in EPA's national inventory, emissions from these source categories would be calculated as 957 Gg (with sampling and measurement uncertainties estimated at ±200 Gg), compared with 1,211–1,250 Gg methane per year in the 2011 EPA national inventory (1) for the same source categories. A large emissions decrease associated with completion flowbacks is partially offset by emission increases from pneumatic controllers and equipment leaks. Reasons for these differences are described in *SI Appendix*.

The estimated uncertainty in the national emission estimates based on this work is ~20% (200 Gg). The sources of uncertainty include measurement uncertainty, uncertainty introduced by the selection of sites, and uncertainty due to choices in performing regional or national averaging of equipment counts and emission factors. These components of the quantified uncertainty are described in *SI Appendix*. The uncertainty estimate does not include factors such as uncertainty in national counts of wells or equipment and the issue of whether the companies that provided sampling sites are representative of the national population.

The 957 ± 200 Gg in emissions for completion flowbacks, pneumatics, and equipment leaks, coupled with national inventory estimates for other categories, leads to an estimated 2,300 Gg of methane emissions from natural gas production (0.42% of gross gas production). A summary is provided in Table 2, and details of the calculations are available in *SI Appendix*.

Total emissions estimated based on measurements in this work (2,300 Gg) are comparable with the most recent EPA national GHG inventory (2,545 Gg in the 2011 inventory, released in April 2013) (1). Table 2 also compares emissions in specific source categories, estimated based on the measurements made in this work, to EPA estimates of the same categories in the national inventory (1). For some emission categories, such as completion flowbacks and pneumatic controllers, conclusions can be drawn from the comparisons. Specifically, measured emissions from completion flowbacks are roughly 600 Gg lower than the completion flowback emissions in the current inventory; measured emissions from pneumatic controllers are 150–500 Gg higher than in the current inventory. For other emission categories, such as equipment leaks and pneumatic pumps, however, drawing conclusions is more difficult. For these source categories, the national inventory reports potential emissions for each category, but aggregates emission reductions, creating uncertainty in the net emissions in these categories (see *SI Appendix*, section S5.5 for more details).

It should also be noted that the national inventory has changed in recent years based on evolving regulations (21) and understanding of emission sources. In this work, comparisons are made to the most recent release of the inventory (2011 final version, released in April 2013) and back casts to previous years by using consistent calculation methodologies. Emissions were estimated as 2,545 Gg in 2011, compared with 2,948 Gg in 2009 and 2,724 Gg in 2010. The work presented here suggests practices such as combusting or capturing emissions from completion flowbacks, as required by New Source Performance Standards subpart OOOO and the revised National Emission Standards for Hazardous Air Pollutants subpart HH (21), are resulting in reduced methane emissions. Other source categories require more data to produce national emission estimates, and adjustments in the inventory may emerge as more emission measurements are performed. Emission estimates may be adjusted downward if workovers with hydraulic fracturing are found to have emissions per event that are similar to completion flowbacks and may be adjusted either upward or downward as more emissions data are collected for liquids unloading or pneumatic devices.

Finally, an emissions intensity of 0.42% is reported in Table 2. The intensity expresses a methane emission per unit of gross gas production. This intensity should be interpreted with caution, because it includes only production operations and implicitly attributes all methane emissions from natural gas wells to natural gas production, although natural gas wells produce substantial amounts of natural gas liquids and oil. The intensity is reported here because it facilitates comparisons with other analyses that have appeared in the literature (23).

Methods

Multiple independent and complementary techniques were used to measure methane emissions. The primary procedures involved direct measurements of CH_4 emissions at their source. A variety of different procedures were used for direct source measurements, depending on the type of source being sampled and the type of natural gas production equipment being used. Table 3 summarizes the direct source methods used in the study; detailed descriptions of the methods are provided in *SI Appendix*.

In addition to direct source measurements, tracer ratio measurements, designed to estimate the total methane emissions from a site, were made at 20% of the well completion flowbacks and 13% of the production sites. The tracer release method was developed in the 1990s to quantify methane emissions from a wide range of natural gas system components (24, 25). Sites for tracer releases were selected for their steady, moderate winds and downwind access. Measurements for sites without downwind access could not be made. Table 3 also summarizes these measurement methods, which are described in detail in *SI Appendix*. In brief, tracer compounds were released at a known rate on-site; downwind measurements of methane (minus background) and the tracer (minus background) were assumed to be equal to the ratio of emission rates, allowing methane emissions to be estimated. These measurements were performed for a subset of the sampling locations that had relatively open terrain and steady winds, producing well-defined emission plumes downwind of the sites. The tracer studies allowed for an independent measurement of emissions that were also measured by using direct source methods. For completion flowbacks, emission estimates based on the downwind measurements were generally within a factor of 2 of the direct source measurements, supporting the conclusion that emissions from completion flowbacks are roughly 97% below the most recent national estimates and that emissions from completion flowbacks without methane control or recovery equipment, observed in this work, are well below the average potential emissions in current national inventories (1). For the production sites, emissions estimated based on the downwind measurements were also comparable to total on-site measurements; however, because the total on-site emissions were determined by using a combination of measurements and estimation methods, it is difficult to use downwind measurements to confirm the direct source measurements. Tracer study results are summarized in *SI Appendix*.

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