ARTICLE OPEN

Methane emissions from groundwater pumping in the USA

J. T. Kulongoski¹ and P. B. McMahon²

Atmospheric methane accumulation contributes to climate change, hence quantifying methane emissions is essential to assess and model the impacts. Here, we estimate methane emissions from groundwater pumping in the Los Angeles Basin (LAB), north-eastern Pennsylvania, and the Principal aquifers of the USA using the average concentrations of methane in groundwater and annual groundwater pumping volumes. High average methane concentrations, 44.1 mg/L, and extensive groundwater pumping, $\sim 3.1 \times 10^{11}$ L/a in the LAB, result in the annual emission of $\sim 2.9 \times 10^{-3}$ Tg of microbial methane. Ethane emissions in the LAB were 3.5×10^{-6} Tg/a. Lower methane emissions estimated for NE Pennsylvania, $\sim 3.0 \times 10^{-6}$ Tg/a, reflect lower methane concentrations and groundwater pumping, 0.7 mg/L and 4.27×10^9 L/a, respectively. Methane concentrations and groundwater withdrawals, 1.06×10^{14} L/a, across the USA enabled the estimation of the total emissions of methane from Principal aquifers (92% of total pumping) of 0.044 Tg/a in the year 2000, which represents a small percentage ($\sim 0.2\%$) of the total annual US methane emissions, but a previously unquantified flux in the global methane budget. Globally, groundwater-pumping methane emissions were estimated to be 0.53 Tg/a, 0.2% of global methane emissions, by adopting a global estimate for groundwater extraction, and an average methane concentration in older groundwater of 0.44 mg/L.

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INTRODUCTION

Methane, a reduced form of carbon, is a minor component of the atmosphere at ~ 1840 parts per billion in the year 2016. Methane's atmospheric residence time is 12–17 years, and methane has a global warming potential of 25 over 100 years (GWP_{100} of 25), compared with carbon dioxide, which has a GWP_{100} of 1.¹ From 2000 to 2006, atmospheric concentrations of methane remained relatively constant, however, from 2007 to 2013, atmospheric methane increased by more than 5%, and in 2014 and 2015, concentrations increased by more than 10%,² and are approaching high greenhouse-gas scenarios, which could exacerbate climate change. Proposed drivers of methane emissions include growth in fossil fuel use, increased agricultural production, thawing arctic permafrost, increased precipitation and tropical flooding, and the decrease in hydroxyl radicals in the atmosphere. However, confirmation is difficult because of uncertainties in the global methane budget. Identification and quantification of previously unidentified sources of methane emissions is crucial for improving methane budget estimates, and modeling climate change.³

Methane gas is predominantly derived from organic matter and produced by either thermogenic or microbial processes.⁴ Thermogenic methane forms when organic matter is buried and heated, usually at considerable depths over long periods of time, and includes methane associated with coal, gas, and oil formations. Microbial methane formation follows two pathways: via acetate fermentation or CO_2 reduction, typically at shallower depths, by the actions of methanogenic organisms, members of the domain Archaea, on organic matter in anoxic environments, such as wetlands, landfills, and some aquifer sediments and coal deposits. Both thermogenic and microbial methane accumulate in groundwater as a result of generation, migration, and accumulation,^{5–10} with measured concentrations as high as 150 mg/L in the LAB.⁷

Groundwater pumping and the subsequent release of dissolved methane is potentially a significant source of methane emissions that has not been quantified in the global methane budget,¹¹ although methane emissions from groundwater in the UK have been estimated at 2.2×10^{-6} Tg/a, about 0.05% of total UK methane emissions.¹² Methane and other dissolved gases are typically removed from drinking-water distribution networks by several methods, included vented well caps, cascade, cone, and spray aerators, air stripping, or discharge into open or vented tanks.

While studying the sources and formation pathways for methane in LAB groundwater,⁷ the implications for the high methane concentrations and large volumes of annual groundwater pumping led to the estimation of methane emissions from the LAB, and a comparison with the Marcellus shale region of NE Pennsylvania. Further compilation of recent groundwater methane data,¹³ and annual groundwater pumping,¹⁴ enabled estimation of methane emissions from groundwater pumping in the Principal aquifers of the USA (Fig. 1).

RESULTS

We estimate the emission of methane from the LAB at 2.9×10^{-3} Tg/a, by multiplying the annual groundwater abstraction for each aquifer (unit) by the average (arithmetic) methane concentration of each unit (Table 1), similar to approaches estimating the flux of nitrous oxide^{15,16} and methane from groundwater pumping.¹² According to the Water Replenishment District of Southern California, in the year 2000, 3.1×10^{11} L of groundwater was pumped for municipal and industrial supply in the LAB.^{17,18} The distribution of pumping varies by chronostratigraphic unit (Table 2), with most groundwater pumped from the Pacific A, Pacific, and Harbor units.^{17,19} However, emissions from the

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Fig. 1 Methane emissions resulting from pumping groundwater in the Principal aquifers of the USA. See Table 5 for aquifer names and values. Not shown but included in the total US groundwater pumping methane emissions are Alaska, Puerto Rico, Hawaii, and US Virgin Islands; *extrapolated estimate

Dominguez, Mesa, and Pacific units could not be estimated, since no wells in these units were sampled, and emission estimates were based only on the sampled units. This approach assumes all methane is completely degassed during pumping, treatment, and distribution of groundwater.^{12,15,16} Total ethane emissions also were calculated similarly, 3.5×10^{-6} Tg/a from the LAB aquifer systems.

DISCUSSION

For comparison, groundwater-pumping methane emissions for the LAB, an area of 1088 km², are ~0.7% of methane emitted annually from all sources in the South Coast Air Basin (SoCAB), an area of 17,469 km², which includes urbanized portions of Los Angeles, Orange, Riverside, and San Bernardino Counties, and ~3% of the methane released from the Aliso Canyon storage facility leak in 2015–2016 (Table 2). The ethane released from groundwater in the LAB is only ~0.02% of annual SoCAB emissions, and ~0.05% the Aliso release. While a relatively brief event, the Aliso Canyon gas storage facility leak near Los Angeles from 2015 to 2016 released over 0.1 Tg methane and 7.7×10^{-3} Tg ethane to the atmosphere.^{20,21} Annual emissions of methane since 2007 in the SoCAB have been $\sim 0.413 \pm 0.086$ Tg/a methane and ~0.023 Tg/a ethane.^{21,22} Methane emissions in the United States for various sectors including agriculture, energy, waste, industrial processes, land use change and forestry have been estimated as a total flux of ~29.03 Tg of methane²³ in the year 2000. Global emissions of methane are estimated at ~275 Tg/a of methane in 2010.²

High methane concentrations, those in excess of values expected from water equilibrating with the atmospheric ($\sim 5 \times 10^{-5}$ mg/L at 1 atm and 10 °C), have been identified in many aquifers in hydrocarbon-producing regions across the USA and the world e.g.^{24–27} The average methane concentration of 1701 Pennsylvania groundwater samples overlying the Marcellus is 0.7 mg/L²⁴ (less than detection-level values were assigned a value of zero, so this is a lower limit), the average concentration in

aquifers overlying the Bakken shale is 2.8 mg/L,²⁸ Eagle Ford shale is 1.3 mg/L,²⁹ Haynesville–Bossier shale is 2.6 mg/L, Fayetteville shale is 1.9 mg/L,²⁹ and in the entire UK is 0.045 mg/L.³⁰ The annual emissions of methane from the Pennsylvania groundwater overlying the Marcellus is 3.0×10^{-6} Tg/a, calculated using the average methane concentration (0.7 mg/L), and average annual withdrawal of 4.27×10^9 L/a in Susquehanna County <https://water.usgs.gov/watuse/data/2005/index.html> suggesting a relatively small contribution to the total US methane emissions from this area (Table 3). Future work is needed to quantify the withdrawal of groundwater in the Bakken, Eagle Ford, Haynesville–Bossier, and Fayetteville regions to calculate additional emissions of methane to the atmosphere from groundwater withdrawn from these hydrocarbon-producing regions. It should be noted that this is a coarse estimation of emissions from pumped groundwater to the atmosphere, based on a limited number of groundwater locations and samples that may be biased toward high-methane groundwater. Additional randomized sampling is needed for improved estimates.

To constrain emissions of methane from groundwater pumping across the USA, the average methane concentrations in 15 Principal aquifers were calculated using data from 833 sampled groundwater wells;¹³ less than reporting-level values were assigned a value of zero (Table 4). By treating values reported as less than the detection level as zero, the methane emissions calculated in this work are a minimum estimate. If the non-detections are assigned the value of one-half the detection level, the average methane concentrations in nine of fifteen aquifers, and the average of all samples, were the same as using a value of zero, while the other six aquifers were within 45%. Public-supply wells were selected for sampling using a randomized spatially distributed grid-cell network to provide statistical representation for the public-supply aquifers.¹³ The methane data are representative of methane emissions associated with pumping from public-supply wells. The 15 Principal aquifers sampled¹³ correspond to 15 of the 66 Principal aquifers identified by Maupin and

Table 1. Los Angeles Basin groundwater sample ID, well depth, perforation intervals, dissolved methane concentration, and model layer and chronostratigraphic unit

Sample ID	Well depth (m below LSD)	Perforation intervals (m below LSD)	Dissolved methane ⁷ (mg/L) LRL = 0.0001	Model layer and chronostratigraphic unit ¹⁹
LA_01	91	85–91	0.057	4-Pacific A
LA_02	332	296–302	28	8-Upper Wilmington A
LA_03	133	126–133	66	7-Bent Spring
LA_04	456	437–443	81	11-Long Beach A
LA_05	338	332–338	60	10-Lower Wilmington
LA_06	108	102–108	0.19	7-Bent Spring
LA_07	299	274–293	67	13-Long Beach C
LA_08	536	530–536	0.0015	6-Harbor
LA_09	158	152–158	0.25	9-Upper Wilmington B
LA_10	376	364–376	73	11-Long Beach A
LA_11	180	174–180	0.12	8-Upper Wilmington A
LA_12	168	162–168	21	7-Bent Spring
LA_13	424	405–424	110	13-Long Beach C
LA_14	419	389–407	86	11-Long Beach A
LA_15	192	186–192	0.29	8-Upper Wilmington A
LA_16	201	195–201	0.024	7-Bent Spring
LA_17	110	104–110	17	6-Harbor
LA_18	607	594–607	93	13-Long Beach C
LA_19	466	454–460	150	11-Long Beach A
LA_20	408	378–384	1.9	11-Long Beach A
LA_21	152	146–152	6.2	8-Upper Wilmington A
LA_22	219	213–219	4.8	9-Upper Wilmington B
LA_23	128	122–128	39	6-Harbor
LA_24	549	488–494	56	11-Long Beach A
LA_25	335	329–335	8.8	9-Upper Wilmington B
LA_26	591	579–591	37	13-Long Beach C
LA_27	389	383–389	50	12-Long Beach B
LA_28	171	165–171	58	8-Upper Wilmington A
LA_29	137	131–137	0.084	9-Upper Wilmington B
LA_30	427	421–427	30	13-Long Beach C
LA_31	427	360–366	94	11-Long Beach A
LA_32	149	143–149	20	8-Upper Wilmington A
LA_33	421	366–372	48	12-Long Beach B
LA_34	250	244–250	49	10-Lower Wilmington
LA_35	125	119–125	71	9-Upper Wilmington B
LA_36	314	290–296	74	12-Long Beach B
LA_37	236	230–236	130	11-Long Beach A

LSD land-surface datum, LRL lowest reporting level

Barber,¹⁴ who estimated groundwater withdrawals from the Principal aquifers of the USA. Total withdrawals from the Principal aquifers in the USA was 1.06×10^{14} L/a in 2000.¹⁴

Annual methane emissions (Table 4) calculated for the 15 Principal aquifers discussed in McMahon et al.¹³, represent only ~50% of the groundwater withdrawal in the USA. To calculate the methane emissions from all 66 Principal aquifers, they were grouped into six Principal aquifer systems by lithology: carbonate rock, crystalline rock, sandstone, semi-consolidated sand, glacial unconsolidated sand and gravel, and nonglacial unconsolidated sand and gravel aquifer systems. Withdrawals from aquifers not included in one of the 66 Principal aquifers were reported in an “other” aquifers group.¹⁴ The emissions from all six Principal aquifer systems were calculated by assuming that the average methane concentration for the aquifers with data in a Principal aquifer system were representative of other aquifers in the same lithologic group without data. The methane concentration for each of the six aquifer systems were assumed to be the average of

the aquifers within it. In some cases, such as the Sandstone Principal Aquifer System, there was only one aquifer¹³ methane concentration to base the value on. The “other” aquifers group was assigned the average methane concentration for all Principal aquifers systems (0.44 mg/L).

The annual emissions from the six aquifer systems and “other” aquifers were 0.041 Tg/a (Table 4). Subtracting the 2.3×10^{-6} Tg/a calculated from this method with the Maupin and Barber¹⁴ data for the LAB (included in the California Coastal Plain PAS), and adding the 2.9×10^{-3} Tg/a estimated from this study for the LAB, total annual methane emissions from the Principal aquifers in the USA are 0.044 Tg/a (Table 4), a small part (~0.2%) of the US total. However, groundwater-pumping methane emissions in the USA are similar to the emissions of methane from leaking oil and gas wells,³¹ or industrial processes (Table 3). Most of the groundwater methane in the USA is emitted from Semi-Consolidated Sand and Gravel Principal Aquifer Systems (Fig. 1). Better constraints on the methane concentrations and groundwater pumping in the three

Table 2. Groundwater-pumping methane and ethane emissions from each chronostratigraphic unit in the Los Angeles Basin, including the annual volume of groundwater pumped from each unit and percent of total pumping for each unit, average methane concentration of each unit, average ethane concentration of each unit, annual methane emissions and annual ethane emissions from each unit

Model layer and chronostratigraphic unit ¹⁹	Pumped groundwater (L/a) (x10 ⁸)	% annual pumping	Average methane concentration (mg/L)	Average ethane concentration (mg/L)	Methane emissions (x10 ⁻⁶ Tg/a)	Ethane emissions (x10 ⁻⁶ Tg/a)
2-Dominguez	125	4.1	nd	nd	nd	nd
3-Mesa	472	15.3	nd	nd	nd	nd
4-Pacific A	515	16.7	0.057	nd	2.9	nd
5-Pacific	707	22.9	nd	nd	nd	nd
6-Harbor	694	22.5	18.7	0.0253	1295	1.76
7-Bent Spring	210	6.8	21.7	0.0009	457	0.019
8-Upper Wilmington A	218	7.1	18.8	0.0736	409	1.60
9-Upper Wilmington B	21	0.69	17.0	0.0037	36.2	0.008
10-Lower Wilmington	87	2.82	54.5	0.008	474	0.073
11-Long Beach A	0	0.01	84.0	0.0283	2.7	0.0009
12-Long Beach B	28	0.92	57.3	0.0122	162	0.034
13-Long Beach C	7	0.21	67.4	0.0392	43.9	0.025
Total: LA Basin	3084	na	na	na	2882	3.5
Aliso Canyon leak ²⁰	na	na	na	na	99,650	7700
South Coast Air Basin ²¹	na	na	na	na	413,000	23,000

nd no data, na not applicable

2014–2015 Aliso canyon leak data and South Coast Air basin data are presented for comparison

Table 3. Comparison of methane concentrations in groundwater in different study areas in the USA, annual groundwater withdrawal rates, and calculated annual methane emissions from groundwater pumping in oil and gas regions

Study area	Median methane conc. (mg/L)	Average methane conc. (mg/L)	Maximum methane conc. (mg/L)	Average withdrawal rates (L/a)	Calculated methane emissions (x10 ⁻⁶ Tg/a)
Los Angeles Basin, CA	39	44.1	150	3.10×10^{11}	2882
Marcellus, PA ²⁴	0.003	0.70	nd	4.27×10^9	3.00
Bakken ²⁸	0.006	2.8	32	nd	nd
Denver-Julesburg, CO ¹⁰	3.27/3.29	0.01/0.08	39	nd	nd
Eagle Ford ²⁹	0.003	1.3	24	nd	nd
Haynesville-Bossier ²⁹	0.014	2.6	22	nd	nd
Haynesville, TX ⁹	0.053	4.5	33	nd	nd
Fayetteville ²⁹	0.017	1.9	28	nd	nd
UK ^{12,29}	<0.00005	0.045	4.7	nd	2.2
USA-total in 2000 ²³					29.03×10^6
USA-Energy					12.9×10^6
USA-Agricultural					9.41×10^6
USA-Waste					6.38×10^6
USA-Land use					0.33×10^6
USA-Industrial processes					0.01×10

nd no data

Principal aquifers, High Plains, Central Valley, and Mississippi River aquifers, which comprise 48% of the groundwater pumping in the USA, would greatly improve these estimates.

Uncertainties associated with the Tier 1¹¹ emission estimates are at least 5%, which reflects the measurement uncertainty for methane, but do not account for temporal methane variability, incomplete accounting of groundwater pumping, or the inaccurate estimation of an aquifer's average methane concentration. Some temporal variability of methane resulting from sampling protocols³² or domestic wells³³ may be dismissed in this study, as

strict sampling protocols^{34,35} were used to sample public water-supply wells. However, significant variability in groundwater methane has been observed in samples (concentrations <0.3 mg/L) collected quarterly,³⁰ and sample pairs, which varied by up to 67%,¹⁰ representing significant uncertainty. Annual groundwater pumping uncertainties reflects either inaccurate reporting or missed pumping. Most large water purveyors are known and track pumping closely, so the uncertainty on reported pumping from public-supply wells is small, <5%. When aggregating pumping volumes, some small operators may fail to respond

Table 4. Comparison of methane concentrations in groundwater, annual groundwater withdrawal rates, and calculated annual methane fluxes from groundwater pumping from 15 Principal aquifers and the six Principal aquifer systems of the USA

Aquifer System	Principal aquifer	Minimum methane concentration ¹³ (mg/L)	Median methane concentration ¹³ (mg/L)	Average methane concentration ¹³ (mg/L)	Maximum methane concentration ¹³ (mg/L)	Average withdrawal rate ¹⁴ ($\times 10^{10}$ L/a)	Calculated minimum methane emissions ($\times 10^{-6}$ Tg/a)	Calculated median methane emissions ($\times 10^{-6}$ Tg/a)	Calculated average methane emissions ($\times 10^{-6}$ Tg/a)	Calculated maximum methane emissions ($\times 10^{-6}$ Tg/a)
Carbonate rock aquifer systems	Basin and Range carbonate rock (BNRC)	<0.001	<0.001	0.00037	0.005	10.1	0.0	174	6185	161,113
	Castle Hayne (CLHN)	<0.001	1.06	2.09	11.0	4.6	0.0	48	95	503
	Floridan (FLOR)	<0.001	0.025	0.60	16.5	503	0.0	125.7	3041	82,983
	Valley and Ridge, Piedmont, and Blue Ridge (VPDC)	<0.001	<0.001	0.005	0.196	36.9	0.0	0.0	1.7	72
	Total	<0.001	0.01	0.67	16.5	555	0.0	174	3138	83,559
Crystalline rock aquifer systems						648	0.0	0.0	14	220.3
Sandstone aquifer systems	Piedmont and Blue Ridge (PIED)	<0.001	<0.001	0.0021	0.034	20.2	0.0	0.0	0.43	6.9
	Cambrian-Ordovician (CMOR)	<0.001	0.006	0.14	3.67	284	0.0	17	409	10,410
Semiconsolidated sand and gravel aquifer systems						129	0.0	7.73	186	4726
	Coastal lowlands (CLOW)	<0.001	0.006	1.56	21.7	4628	0.5	322	30,528	1,148,404
	Mississippi Embayment (MISE)	<0.001	0.007	0.47	5.64	327	0.0	19.6	5101	71,059
	Northern Atlantic Coastal Plain (NACP)	<0.001	0.008	0.021	0.341	144	0.0	11.5	609	7372
	Southeastern Coastal Plain (SECP)	<0.001	0.006	0.103	3.47	119	0.0	7.1	122	4123
Glacial unconsolidated sand and gravel aquifer systems	Texas Coastal Uplands (TXCU)	0.001	0.009	0.99	17.6	52.6	0.53	4.7	519	9265
	Total		0.007	0.63	21.7	773	0.5	52.2	6381	92,309
	Glacial (GLAC)	<0.001	0.001	0.62	27.4	492	0.0	4.92	3073	134,774
Nonglacial unconsolidated sand and gravel aquifer systems						3349	0.0	0.0	17	498
	Basin and Range basin-fill (BNRF)	<0.001	<0.001	0.00092	0.038	777	0.0	0.0	7.2	295
	High Plains (HPAQ)	<0.001	<0.001	0.00037	0.008	2418	0.0	0.0	9.0	193
	Rio Grande (RGAQ)	<0.001	<0.001	0.0005	0.006	155	0.0	0.0	0.77	9.3
Select principal Aquifers total	Total	<0.001	<0.001	0.0006	0.038	5322	0.5	239	12,794	315,873
	Principal Aquifer systems total				0.44	10,571	0.6	626	40,931	1,467,901
	Aquifer systems total with Los Angeles Basin flux								43,620	
<0.001 assigned value of 0 for emissions calculations										

Table 5. Principal aquifer number, name, and methane emissions

Map no.	Principal aquifer	Average withdrawal rate ¹⁴ ($\times 10^{10}$ L/a)	Calculated methane emissions (Tg/a $\times 10^{-6}$)
Semiconsolidated sand and gravel aquifer systems			
3	California Coastal Basin aquifers	475	2978*
4	Pacific Northwest basin-fill aquifers	120	749*
5	Columbia Plateau basin-fill aquifers	20	124*
6	Snake River Plain basin-fill aquifers	65	408*
7	Puget Sound aquifer system	36	225*
8	Willamette Lowland basin-fill aquifers	58	363*
9	Northern Rocky Mountains Intermontane Basins aquifer system	52	327*
10	Central Valley aquifer system	1355	8492*
12	Pecos River Basin alluvial aquifer	17	107*
13	Mississippi River Valley alluvial aquifer	1284	8042*
14	Seymour aquifer	23	147*
15	Surficial aquifer system	90	563*
16 [^]	Unconsolidated-deposit aquifers (Alaska)	4.6	29*
17 [^]	South Coast aquifer (Puerto Rico)	6.0	37*
18	Coastal lowlands aquifer system	327	5101
19	Texas coastal uplands aquifer system	53	519
20	Mississippi embayment aquifer system	131	609
21	Southeastern coastal plain aquifer system	119	122
22	Northern Atlantic coastal plain aquifer system	144	30
71	Alluvial aquifers	249	1558*
Glacial unconsolidated sand and gravel aquifer systems			
70	Glacial aquifer system	492	3073
Nonglacial unconsolidated sand and gravel aquifer systems			
1	Basin and Range basin-fill aquifers	777	7.2
2	Rio Grande aquifer system	155	0.8
11	High Plains aquifer	2418	9.0
Carbonate rock aquifer systems			
50	Floridan aquifer system	503	3041
68	Valley and Ridge carbonate-rock aquifers	37	1.7
42	Basin and Range carbonate-rock aquifers	10	0.04
54	Castle Hayne aquifer	4.6	95
53	Piedmont and Blue Ridge carbonate-rock aquifers	4.1	0.2*
51	Biscayne aquifer	112	756*
43	Roswell Basin aquifer system	53	359*
47	Silurian-Devonian aquifers	34	229*
44	Ozark Plateaus aquifer system	23	154*
55 [^]	North Coast Limestone aquifer system (Puerto Rico)	8.1	55*
52	New York and New England carbonate-rock aquifers	6.4	43*
45	Blaine aquifer	6.1	41*

Table 5 continued

Map no.	Principal aquifer	Average withdrawal rate ¹⁴ ($\times 10^{10}$ L/a)	Calculated methane emissions (Tg/a $\times 10^{-6}$)
49	Upper carbonate aquifer	1.3	8.9*
48	Ordovician aquifers	0.8	5.4*
46	Arbuckle-Simpson aquifer	0.6	3.9*
56 [^]	Kingshill aquifer (Virgin Islands)	0.1	0.7*
Sandstone and carbonate rocks aquifer systems			
38	Edwards-Trinity aquifer system	102	689*
72 [^]	Intermediate aquifer system (Florida)	49	330*
40	Mississippian aquifers	40	266*
39	Valley and Ridge aquifers	13	88*
41	Paleozoic aquifers	2.5	17*
Crystalline rock aquifer systems			
59	Snake River Plain basaltic-rock aquifers	361	7.7*
60	Columbia Plateau basaltic-rock aquifers	129	2.8*
58	Pacific Northwest volcanic-rock aquifers	66	1.4*
61 [^]	Volcanic-rock aquifers (Hawaii)	59	1.3*
57	Southern Nevada volcanic-rock aquifers	0	0*
62	Piedmont and Blue Ridge crystalline-rock aquifers	20	0.4
73	New York and New England crystalline-rock aquifers	13	0.3*
Sandstone aquifer systems			
33	Cambrian-Ordovician aquifer system	129	186
25	Lower Cretaceous aquifers	44	63*
74 [^]	Northern Great Plains aquifer system	14	20*
23	Colorado Plateaus aquifers	27	39*
31	Pennsylvanian aquifers	18	26*
29	Early Mesozoic basin aquifers	18	26*
26	Rush Springs aquifer	7.8	11*
30	New York sandstone aquifers	7.7	11*
32	Marshall aquifer	7.4	11*
24	Denver Basin aquifer system	5.0	7.2*
27	Central Oklahoma aquifer	4.4	6.3*
28	Ada-Vamoosa aquifer	0.6	0.8*
34	Jacobsville aquifer	0.4	0.6*
37	Wyoming Tertiary aquifers	0.2	0.3*
Other			
75	Other aquifers	160	705*

*Extrapolated value; ^ not shown in Fig. 1

or may be missed, such that their pumping was not included. These operators would represent a small portion of the groundwater pumping and as such, the uncertainty on unaccounted pumping is ~5%. In total, the uncertainty associated with annual groundwater pumping is estimated to be ~10%. The average methane concentrations estimated for each aquifer have the largest uncertainties, as calculations may be skewed depending on which wells were selected to sample. A randomized well selection process^{13,36} ensures that samples are representative of

the concentrations in the aquifers being pumped. However, if studies do not collect enough samples to be representative, or their selection is not randomized, then the uncertainty could be up to 500% based on averaging sample concentrations in an aquifer. For the USGS Principal aquifer data,²⁹ a randomization process was applied to available public-supply wells in the aquifers, and the uncertainty on the average methane concentrations in the public-supply aquifers was reduced to ~25%. The overall uncertainty on emissions estimates, based largely on possible temporal variability of methane is ~80%.

While small compared with total global emissions,¹¹ methane emissions resulting from groundwater abstraction in the USA represent an important source to be quantified and should be included in the global methane budget. Emissions may be significant locally, where groundwater methane concentrations are high. Also, of local significance, methane, as a precursor to ozone formation, could represent an unaccounted for and potentially significant contribution to low-level ozone formation. More detailed analyses of correlations between methane concentrations and groundwater age, carbon system indicators, aquifer redox conditions, Eh potentials, as well as lithology and sediment age may help to better estimate methane occurrence and concentrations in groundwater.^{13,37} Within a given lithology group, methane concentrations are typically higher in younger sediments than in older sediments,¹³ and higher in older groundwater (pre 1950s) than recently recharged groundwater.^{7,13} Previous studies noted that sediment age can be important with respect to redox processes due to the preferential consumption of the most reactive components of sedimentary organic carbon by microbes over time.^{38–40} In support of this hypothesis, McMahon et al.¹³ found that for aquifers composed of similar lithologies, concentrations of methane, dissolved organic carbon, and ammonium were higher in the aquifers with younger sediments than in aquifers with older sediments.

If 78–99% of groundwater in the upper 2 km of the continental crust is older than 50 years,^{41,42} then groundwater methane may represent a significant source of methane, given increased rates of groundwater depletion (1500 km³/a).⁴³ If 80% of the 1500 km³/a extracted is old groundwater with elevated methane concentrations (0.44 mg/L methane), then annual global groundwater-pumping methane emissions would be ~0.53 Tg/a, over three times the annual emissions from the metropolis of Los Angeles, California, but only 0.2% of global methane emissions. However, this estimate fails to capture the emissions of methane naturally/passively degassing from shallow methanogenic groundwater⁸ or from streams receiving methanogenic groundwater discharge,⁴⁴ both of which could represent significant annual emissions. Further constraint of these processes is needed to better estimate extracted and natural methane groundwater emissions. Although expensive, given the number of groundwater wells, capturing the methane at the largest wells pumping groundwater with the highest methane concentrations could greatly reduce emissions. For example, in the Los Angeles Basin, capturing methane at 17 wells, which each pump more than 2.5 × 10⁹ L annually, could reduce methane emissions by nearly a fifth.

METHODS

The LAB is located within a northwest trending alluviated plain on the southern California coast, and contains deep sequences of petroliferous sediments and traps overlain by organic-rich marine and alluvial water-bearing sediments.^{19,45} Thirteen chronostratigraphic water-bearing units were identified using sequence stratigraphy to subdivide and link sedimentary deposits into unconformity-bound units.¹⁹ Wells were associated with chronostratigraphic unit based on well-screen depth and location (Table 1). Methane concentrations from 37 LAB groundwater samples ranged in concentration from 0.002 mg/L to 150 mg/L (Table 1), with an average value of 44.1 mg/L. Sample selection for the LAB was not

randomized, and as a result, LAB methane emissions have a larger uncertainty (500%) than those of the Principal aquifers of the USA (80%), and thus may overestimate methane emissions. While thermogenic methane was detected locally in the shallow subsurface in conjunction with some of the historic explosions that occurred in the LAB,⁴⁶ the methane distribution and isotopic systematics, and groundwater age results indicate that most excess methane in LA groundwater originates from microbial production in anoxic or suboxic conditions in the shallow aquifer systems, rather than the migration of deeper thermogenic methane in the hydrocarbon-bearing formations associated with oil fields in the basin.⁷

Groundwater samples were collected in accordance with the protocols established by the USGS National Water-Quality Assessment (NAWQA)³⁴ and the USGS National Field Manual³⁵ after purging the equivalent of three casing-volumes from each well with a submersible pump. Samples were analyzed for a suite of inorganic, organic, and isotopic constituents; for a complete description of the sampling, analytical methods, quality assurance, and data.⁴⁷ Samples for analysis for concentration and isotopic composition of hydrocarbon gases were collected by attaching sampling tubing to a hose bib and flushing groundwater through the tubing before the flow was partially restricted with a control valve. An evacuated pouch containing a bactericide capsule was attached to the tubing and filled with 600–700 mL of sample water. The hydrocarbon gas concentrations and isotopic values were measured using gas chromatography and isotope ratio mass spectrometry, respectively. Methane concentration measurement uncertainty is ± 0.0001 mg/L⁷, and the statistics on the methane measurements have been previously presented.^{7,13}

DATA AVAILABILITY

All data used for calculations in this work are included in Tables 1–5. In addition, methane data for the LAB⁴⁷ may be downloaded at: <https://doi.org/10.3133/ofr20161181>. Methane data for the Principal aquifer¹³ may be downloaded at <https://doi.org/10.5066/F7377766>. Groundwater-pumping data for the Principal Aquifers of the USA¹⁴ are available for download at: <https://pubs.usgs.gov/circ/2005/1279>.

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AUTHOR CONTRIBUTIONS

J.T.K.: conceived, researched, collected and analyzed data, and wrote this paper. P.B.M.: researched, collected data, provided guidance, and editing.

ADDITIONAL INFORMATION

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