

$^{14}\text{CH}_4$ EMISSIONS FROM NUCLEAR POWER PLANTS IN NORTHWESTERN EUROPE

ROOS EISMA,^{1,2} ALEX T. VERMEULEN² and KLAAS VAN DER BORG¹

ABSTRACT. We measured the ^{14}C content of atmospheric methane at a 200-m-high sampling station in The Netherlands. Combined with trajectories and a transport model, it is possible to estimate the $^{14}\text{CH}_4$ emissions from nuclear power plants in northwestern Europe. We demonstrate here two different methods of analyzing the data: forward modeling and an inverse method. Our data suggest that the emissions from pressurized water reactors are 260 ± 50 GBq per GW installed power per year, *ca.* 1.6 \pm 0.4 times higher than generally assumed. We also find that, in addition to the known nuclear sources of $^{14}\text{CH}_4$ (pressurized and boiling water reactors), there are two very strong sources of $^{14}\text{CH}_4$ (520 ± 200 and 1850 ± 450 GBq yr^{-1} , respectively), probably two test reactors near the sampling station.

INTRODUCTION

The ^{14}C content of atmospheric methane is an important parameter for estimating the contribution of methane from fossil origin to the total methane budget. It is determined by two counteractive effects: the ^{14}C -free methane released by the production and use of fossil fuels lowers the ^{14}C content, whereas the emission of $^{14}\text{CH}_4$ by nuclear power plants raises it. As a result, the ^{14}C content of atmospheric methane rose by *ca.* 1.4 pM per year in the period 1987–1989 (Quay *et al.* 1991), and by 0.8 pM per year in the period 1988–1992 (Brown *et al.* 1994). To obtain an accurate estimate of the fraction of methane from fossil origin, it is essential to have a good estimate of the $^{14}\text{CH}_4$ emissions from nuclear power plants. Two types of nuclear reactors are known to emit $^{14}\text{CH}_4$: pressurized water reactors (PWRs) and boiling water reactors (BWRs). The ^{14}C emission from PWRs is on the order of 274 GBq $\text{GW}^{-1} \text{yr}^{-1}$ (7.4 Ci $\text{GW}^{-1} \text{yr}^{-1}$), of which *ca.* 80% is in the form of methane ($^{14}\text{CH}_4$ emission 219 GBq $\text{GW}^{-1} \text{yr}^{-1}$); the ^{14}C emission from BWRs is 481 GBq $\text{GW}^{-1} \text{yr}^{-1}$, (13 Ci $\text{GW}^{-1} \text{yr}^{-1}$) of which *ca.* 5% is in the form of methane ($^{14}\text{CH}_4$ emission 24 GBq $\text{GW}^{-1} \text{yr}^{-1}$) (Kunz 1985; Hertelendi *et al.* 1989).

Emission factors, however, vary within several orders of magnitude, both between reactors, and within time for one individual reactor. The sparseness of data on the amount of ^{14}C released by nuclear power plants and the chemical form thereof leads to a large uncertainty in the estimate of the global $^{14}\text{CH}_4$ emission.

Because it is hardly possible to measure the emission of each reactor, a useful alternative is to determine the emission from a group of reactors simultaneously. Thus, we sample air on top of a high tower, and combine these measurements with trajectories and a transport model. Our sampling station is located in the middle of The Netherlands. Many PWRs and BWRs are located to the east and the south of the sampling station in Belgium, France and Germany. To the west and the north are the United Kingdom and the North Sea, where no $^{14}\text{CH}_4$ emissions are expected (Fig. 1). However, as reported previously, we also find high $^{14}\text{CH}_4$ values with air parcels coming from those directions. We present here more measurements and a method to determine the size of the $^{14}\text{CH}_4$ emissions from these data.

¹R.J. van de Graaff Laboratory, Utrecht University, P.O. Box 80000, NL-3508 TA Utrecht, The Netherlands

²Netherlands Energy Research Foundation, P.O. Box 1, NL-1755 ZG Petten, The Netherlands

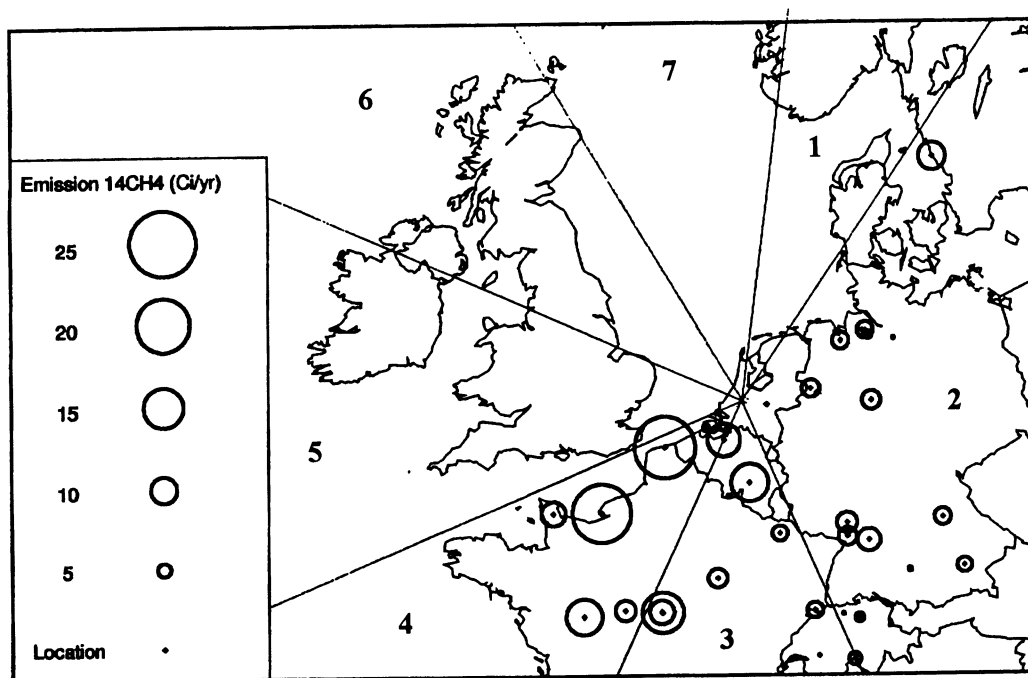


Fig. 1. Modeled $^{14}\text{CH}_4$ emissions from PWRs and BWRs in Ci per GW installed power (1 Ci=37 GBq). The size of the circle is proportional to the size of the emission; the dot in the center indicates the location of the reactor (or group of reactors). Europe is divided into the seven sectors used in the data analysis.

METHODS

Experimental

The Netherlands Energy Research Foundation (ECN) sampled air at the top of a 200-m-high tower in Cabauw, The Netherlands, pumping the air down through poly-flo tubing using oil-free pumps. Methane concentration is measured continuously using a gas chromatograph and occasionally a 3-h sample is taken for isotopic analysis. The sampled air is dried over silica gel, and pumped to 80 bar into stainless-steel cylinders. At the ECN laboratory, the methane is isolated using cold traps with charcoal and molecular sieve and a preparative gas chromatograph, and converted to CO_2 using a CuO oven at 1000°C . The stable isotope ratio is measured with a Finnegan Matt 251 mass spectrometer. At the Utrecht AMS facility, the CO_2 is converted into graphite and the ^{14}C content is measured. The sample size is in the order of 1 mg C, measured with a precision of 0.5–1% (van der Borg *et al.* 1987). The values are corrected to $\delta^{13}\text{C} = -25\text{‰}$ and age-corrected for decay of the standard, and expressed as percent modern (pM) (Stuiver and Polach 1977).

Trajectories and Transport Model

A trajectory describes the route that an air parcel follows before sampling in the so-called mixing layer. The Royal Netherlands Meteorological Institute (KNMI) provides us with trajectories that are calculated from predicted wind fields. KNMI calculates daily a 12-h trajectory (*i.e.*, a trajectory that describes the route during the 12 h before sampling) for 12:00 GMT that day, a 24-h trajectory for the following 0:00 GMT, and a 36-h trajectory for 12:00 GMT the next day. The two predictions for the trajectories at 12:00 GMT can be used to determine the quality of the prediction. From these tra-

jectories, we calculated 36-h trajectories for every 3 h arrival time using spline interpolation. The trajectory data includes the location of the air parcel, the pressure, the temperature and cloud cover along the trajectory in 3-h steps. The trajectories are calculated for arrival point de Bilt and are translated by us for a distance of *ca.* 30 km to the sampling point Cabauw.

We use a transport model that follows an air parcel in the mixing layer and calculates the influence of sources along the trajectory and the concentration in the air parcel. The model differentiates between two vertical layers, the mixing layer and a reservoir layer. With the diurnal variation in mixing layer height, air is exchanged between these two layers. We assume that the mixing layer heights (daytime maximum and nighttime minimum) follow a sinusoidal seasonal variation, with an average of 1250 m for the daytime maximum and 850 m for the nighttime minimum, and an amplitude of, respectively, 400 m and 150 m. We calculate the diurnal variation using the pressure and temperature data.

The calculation starts with the air parcel at the beginning of the trajectory, with background concentrations in both the mixing layer and the reservoir layer. Then, the air parcel moves with a certain time step along the trajectory. The emissions from the sources at the earth surface are averaged over an area increasing in size with distance from the sampling station, which means that at the beginning of the trajectory, 36 h before sampling, sources in a circle with a large radius contribute to the air parcel, whereas near the sampling station only sources within a smaller circle contribute.

We apply the transport model in two ways to interpret our data: 1) forward modeling; and 2) an inverse method. In forward modeling, the transport model is combined with emission data to predict the atmospheric concentration at Cabauw for each trajectory, and the corresponding isotopic ratios. This can then be directly compared to the measurements. In the other (inverse) method, we calculate emissions from the measurements through a matrix inversion. The matrix coefficients are provided by the transport model.

Emission Data

We developed a rough emission database for use with the transport model. It includes emissions from cattle, landfills, mining, fossil fuels, wetlands and freshwater systems. The resolution of the data is rather large: for some sources a country scale, and for others a regional scale. The uncertainties in these data will have relatively little effect on the modeled $^{14}\text{CH}_4$ content, as the effects from nuclear power plants are an order of magnitude larger.

The $^{14}\text{CH}_4$ emissions from PWRs and BWRs were modeled using the data from World Nuclear Industry Handbook (1994) on the installed power in 1993 and the locations of the reactors. The geographical coordinates of those locations were determined from an atlas.

The emission factors quoted in the introduction are given relative to produced power rather than installed power. The average Load Factor (LF) in Western Europe in 1992 was *ca.* 72%. Therefore, adjusted values were used in the modeling of the emissions of $^{14}\text{CH}_4$: 160 GBq GW⁻¹ yr⁻¹ for PWRs, and 17 GBq GW⁻¹ yr⁻¹ for BWRs.

Inversion Method

Inversion methods have been used on a global scale to determine the contribution of different source types, or of different regions, using a global network of concentration measurements and a global circulation model (GCM) (*e.g.*, Enting *et al.* 1993). Measurements are described as a function of the parameters that need to be determined. This set of equations is then solved. In our study, we use a

similar method on a smaller scale in which the parameters are the emission factors for a several reactor types. The transport model is used to determine the contribution of each reactor type to the measured ^{14}C content for each sample.

The problem then consists of M linear equations, with N unknowns. M is the number of measurements and N the number of parameters. To compensate for uncertainties in the data (caused by errors in the measurements and the calculation with the transport model), there should be more measurements than parameters ($M > N$). The solution is taken to be a least squares fit through the data. The matrix T contains the coefficients that have been calculated with the transport model, T_{ij} gives the contribution of the j th source (reactor type in our case) to the ^{14}C content of the i th sample. This gives the set of equations

$$m_i = \sum T_{ij}e_j \quad (1)$$

with m_i ($i = 1 \dots M$) the series of measurements, and e_j ($j = 1 \dots N$) the emission factors to be determined. This problem is then solved by inversion of the matrix T through singular value decomposition (SVD) (Press *et al.* 1992). This decomposition of the matrix T makes it possible to identify ill-defined components of the problem, and to remove those terms.

RESULTS

Forward Modeling

From January to August 1993, we took 64 air samples with the 3-h sampling time centering around midnight or noon. ^{14}C ranges from 124.3 to 467.4 pM. The model was run with a time step of 30 min. The radius of the source area was 75 km at the beginning of the 36-h trajectory and 15 km near the arrival point. The background concentration was taken according to the seasonal variation found at the U.S. National Oceanographic and Atmospheric Administration (NOAA) station "Ocean Station M" (Steele *et al.* 1987), and is assumed to have a ^{14}C content of 126.5 pM (Quay *et al.* 1991).

Figure 2 shows part of the time series of atmospheric $^{14}\text{CH}_4$ calculated with the transport model and emission data. The sharp peaks result from the fact that nuclear power plants are strong $^{14}\text{CH}_4$ sources. A small change in the direction of the trajectory can therefore have a very large effect on the ^{14}C content of the air parcel.

Sensitivity to input parameters, combined with the observed variability of the $^{14}\text{CH}_4$ emissions from nuclear power plants (Kunz 1985) and the sensitivity to a small uncertainty in the direction of the trajectory, make it likely that there will be a large spread of the measurements around the modeled ^{14}C concentrations. Thus, reliable conclusions can be drawn only from a significant amount of data. A list of all uncertainties in the modeling and the interpretation is given in the next section.

Figure 3 shows the relation between the measured ^{14}C values and the modeled values. Error bars around the modeled values indicate uncertainties (as explained in the following section). Error bars around the measured values are too small to show in the figure. The correlation is reasonable for about half of the data, but high values were found for a large group of points where a low ^{14}C content was expected. Table 1 compares modeled values and measurements for seven sectors shown in Figure 1. Expected background ^{14}C concentrations were found for Sectors 1 and 6 (north and northern UK). In Sectors 2, 3 and 4 (east to southwest), where contributions from nuclear power plants are expected, we generally find somewhat higher values than expected.

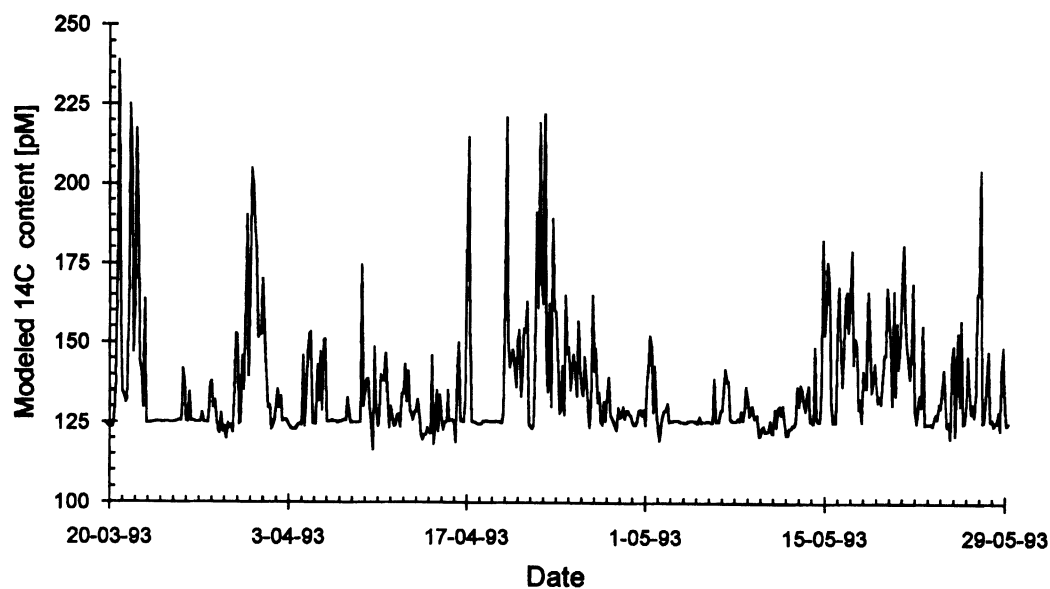


Fig. 2. ^{14}C content of atmospheric methane at Cabauw as a function of time, calculated from modeled emissions using a transport model and trajectories

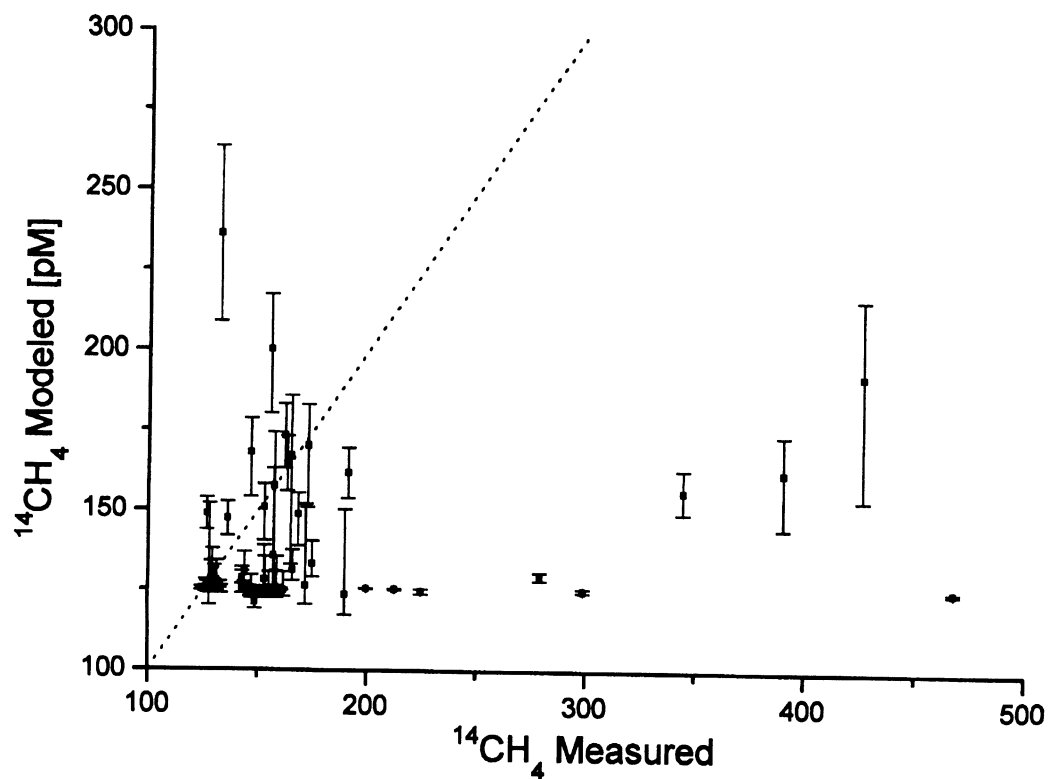


Fig. 3. The relation between modeled and measured ^{14}C content of atmospheric methane. ----- = 1:1 relation.

TABLE 1. A Comparison Between Modeled and Measured ^{14}C Content of Atmospheric Methane

Region	Name	No. of samples	Average ratio		Modeled range (pM)	Measured range (pM)
			$\frac{^{14}\text{C}_{(\text{meas})}}{^{14}\text{C}_{(\text{mod})}}$	Standard deviation		
1	North	8	1.01	0.003	125.4–128.6	126.2–128.7
2	East	14	1.21	0.14	121.3–133.4	129.2–189.6
3	South	6	1.47	0.66	148.8–168.1	146.4–390.0
4	Southwest	15	1.15	0.46	125.1–236.2	124.3–426.5
5	Southern UK	17	1.61	0.92	124.0–125.1	127.1–467.1
6	Northern UK	6	1.00	0.004	125.2–125.8	125.4–127.0
7	Northwest	4	1.74	0.466	125.3–125.7	160.7–298.7

In Sectors 5 and 7 (west and northwest), background values are expected, and we found high to very high values. This indicates the presence of two additional sources of $^{14}\text{CH}_4$ to the west and northwest of the sampling station. Significant sources of enriched methane can only be nuclear installations, the closest of which are two test reactors, located in Delft (a high flux reactor, *ca.* 30 km to the west) and Petten (a high flux and a low flux reactor, *ca.* 90 km to the northwest). In the following analysis, we assume that those reactors are the additional sources. In the future, we will undertake measurements at these sites to confirm this.

Forward modeling is useful mainly for determining the degree of agreement between modeled emissions and measurements, but not for quantitative adjustments therein. The inversion method described below is more appropriate.

Uncertainties

Several uncertainties should be considered in interpreting the measurements:

1. The precision of the ^{14}C measurement (*ca.* 1 pM, no large effect on the results).
2. The effect of an error in the estimate of the ^{14}C content of excess methane in the air sample, due to uncertainty about the fossil fraction. We assume that this error is proportional to the excess concentration. A significant effect is seen only for samples with high methane concentration and relatively low ^{14}C content.
3. The ^{14}C content in background air. At the beginning of the trajectory, the air in the air parcel is assumed to be clean, that is, having the background methane concentration and isotope ratios. This will be correct for trajectories that arrive from a westerly direction (marine air), but it is clearly not valid for trajectories from an easterly direction (continental air) when the air has been above land for an undefined length of time before sampling.

Model runs showed that up to 50% of excess concentration at the beginning of the trajectory will still be present upon sampling, but this will not have a significant effect on the ^{14}C content: a) excess methane concentration (with a realistic fossil-fuel percentage therein) has a relatively small effect on the ^{14}C content of the samples; and b) a large amount of nuclear ^{14}C is unlikely, as almost all trajectories start 36 h before sampling outside the region shown in Figure 1, and there are just a few scattered PWRs and BWRs to be found in Finland and Eastern Europe. There are several large PWRs in Ukraine and Russia, but they are >2000 km away from Cabauw. At that distance, the radius of the source area causes the emissions to be very diluted.

4. A combination of the uncertainty in the trajectory and the “severity” thereof. The uncertainty has been determined by the rate of change with time of the direction of consecutive trajectories,

and from a comparison between the two predictions of the noon trajectory. The severity takes into account the effect of a small change in direction. In some cases, this has hardly any effect on the ^{14}C content, whereas in other cases, it may result in including a nuclear power plant in the source area or not.

5. The uncertainty of the transport model in determining the peak heights. The height of the peaks was found to be rather sensitive to the input parameters of the model, such as mixing layer height and size of the source area. The mixing layer height determines the volume in which the emission is mixed and, therefore, directly determines the height of the peak. The radius of the source area determines the size of the area over which the emissions are averaged; a larger width leads to lower, wider peaks. This term is taken to be proportional to the amount of excess $^{14}\text{CH}_4$ in the sample.

Inversion Methods

$^{14}\text{CH}_4$ in the sample has three sources: 1) background concentration; 2) excess methane in the air sample; and 3) emissions from nuclear power plants. To calculate the latter, we assumed the ^{14}C content of the background methane was 126.5 pM, and the ^{14}C content of the excess methane 100 pM, which corresponds to *ca.* 15% fossil methane.

We ran the model to determine the contribution from PWRs, BWRs (both as a function of installed power) and the two test reactors. A fit was then made as described above with $M=64$ (measurements) and $N=4$ (emission factors). The weights and base vectors computed in the matrix decomposition showed that the emission factor for BWRs cannot be determined from this set because the contribution from BWRs is small compared to the other sources, and because the BWRs have approximately the same geographical distribution as the PWRs. Thus, the emission factor for BWRs was assumed to be the literature value and was excluded from the fit. The effect of the error sources listed in the previous section was studied by performing several model runs and matrix inversions while varying all parameters within reasonable ranges. This resulted in the average values and standard deviations shown in Table 2.

TABLE 2. Emission factors for three reactor types, calculated with the inversion method. The second fit is the average of several fits made with variations in the input parameters of the transport model.

Reactor type	Emission factor	Standard deviation
PWR	260 GBq GW ⁻¹ yr ⁻¹	50
Delft	520 GBq yr ⁻¹	200
Petten	1850 GBq yr ⁻¹	450

The emission factor for PWRs (260 ± 50 GBq GW⁻¹ yr⁻¹) is scaled here relative to the installed power of the nuclear power plants. However, the $^{14}\text{CH}_4$ emission is proportional to the produced power (219 GBq GW⁻¹ yr⁻¹, see Introduction).

It is difficult to compare these emission factors exactly, as that would require more knowledge about ^{14}C emissions on an hourly/daily basis. For a rough conversion, we used the average (averaged over all European PWRs) load factor. This is the produced energy as a percentage of the energy that could have been produced (installed power \times 1 year). This factor was 72% in 1992. As a result, the emission factor for PWRs found here is 1.6 ± 0.4 times higher than the literature value.

Unexpected Sources

Forward modeling indicates that two test reactor sites, Delft and Petten, near the sampling station are significant sources of $^{14}\text{CH}_4$. Inverse calculations gave emission factors of $520 \pm 200 \text{ GBq yr}^{-1}$ for Delft and $1850 \pm 450 \text{ GBq yr}^{-1}$ for Petten. The calculated emissions are very high, comparable to a PWR of several GW. Many test reactors of different types and sizes are distributed over Europe (and the rest of the world). If some of these reactors emit such a large amount of $^{14}\text{CH}_4$, they can form a substantial contribution to the global budget. Other (test) reactors located near PWRs in the rest of Europe may be responsible for part of the high emission factor calculated for PWRs. Nothing is known about ^{14}C emissions from the two test reactors, but we assume that some emissions are likely.

There are no other options for the observed high ^{14}C values from (north)western directions. Other nuclear installations in the UK include a fuel reprocessing plant in Sellafield, and graphite reactors distributed throughout the UK. Sellafield lies in Sector 6 (Fig. 1) with no high values observed. Similarly, low values from graphite reactors in Sectors 5 and 6 do not correspond with the high values in Sector 7.

CONCLUSION

Forward modeling is useful in determining the nature of the problem as well as the general agreement between modeled emissions and measurements. The results from forward modeling indicate higher emissions from nuclear power plants. Inversion methods are more suited to make a quantitative analysis. However, due to the scattering of the data, the number of fitted parameters must be much smaller than the number of measurements. Further data are needed to determine additional, and more accurate, emission factors. An emission factor for PWRs was calculated with the inverse method, as well as emission factors for two test reactors, but it was not possible to determine an emission factor for BWRs this way.

All methods to determine a methane budget from our measurements are limited by the fact that nuclear reactors are strong point sources and the emissions are known to be very variable in time. Both methods could be improved by the input of actual meteorological data to determine the mixing layer height and the width of the source area, which is determined by the meteorological stability. The errors caused by the uncertainty in the trajectories we use can be reduced by using trajectories that are calculated afterwards instead of predicted, and that go back >36 h. In general, the methods demonstrated here are useful local-source and intermediate global-scale measurements.

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