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Global methane emission through mud volcanoes and its past and present impact on the Earth's climate—a comment

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Introduction

The role of mud volcanoes (MVs) as a source of methane (CH₄) flux to the atmosphere and the ocean has been increasingly recognised in the last several years (Milkov 2000; Dimitrov 2002, 2003; Etiope and Klusman 2002; Kopf 2002, 2003; Milkov et al. 2003; Etiope and Milkov 2004). In one of the most recent papers, Kopf (2003) claims to report a reliable estimate of the global CH₄ emission from MVs. However, the significance and usefulness of the estimate presented by Kopf (2003) are rather poor. The used dataset is smaller than in previous studies (although the author makes a reverse claim), and some previously published works are misquoted and misinterpreted. Numerous arithmetic mistakes made during simple calculations and data manipulations lead to confusing results and conclusions. In this comment, we highlight some of the most significant problems with the estimates published by Kopf (2003).

Misquotations and misuse of data

We found that previously published results and datasets were misquoted and misused by Kopf (2003). On page 812, the author assigns a statement that “the deep-se-

ated, warm fluids triggering MVs may dissociate considerable volumes of massive clathrates” to the paper of Milkov (2000). However, no such suggestion was made in that paper. Instead, Milkov (2000) proposed that gas hydrates often are associated with deep-water MVs because MVs transport hydrocarbon gases and water into the gas hydrate stability zone. Furthermore, Milkov (2000) never suggested that there is a “positive correlation of mud volcanism and gas hydrate dissociation” as stated by Kopf (2003) (p. 806). Although some authors proposed that MVs may form as a result of gas hydrate decomposition (Reed et al. 1990; Van Rensbergen et al. 2002), such views were neither supported nor extensively discussed by Milkov (2000).

On page 813, Kopf (2003) writes: “In their less conservative estimate inferring an extra 5,000 deep-water mud cones, Milkov et al. (2003) propose that 15.9 Tg year⁻¹ (quiescence) and 17.1 Tg year⁻¹ (eruptions) of CH₄ are emitted into the atmosphere” (note that CH₄ masses are often given in Tg (1 Tg=10¹² g) in this comment). Instead, Milkov et al. (2003) suggested that 5,000 deep-water MVs may emit 13 Tg year⁻¹ (quiescence) and 14 Tg year⁻¹ (eruptions) of gas (predominantly CH₄) to the ocean (not to the atmosphere). The values 15.9 Tg year⁻¹ (quiescence) and 17.1 Tg year⁻¹ (eruptions) refer to the global emission from both onshore and offshore MVs both to the ocean and the atmosphere. The gas flux to the atmosphere from both quiescent activity and eruptions together was estimated at 6 Tg year⁻¹ and included gas flux from onshore and shallow (shelf) offshore MVs. Milkov et al. (2003) suggested that the global gas flux (33 Tg year⁻¹) is not equal to the atmospheric gas flux (6 Tg year⁻¹) because gas from deep-water MVs (27 Tg year⁻¹) is largely oxidized and sequestered at the seafloor and in the ocean. Unfortunately, Kopf (2003) does not acknowledge those conclusions and writes that in the study of Milkov et al. (2003) “it is still assumed that gas emitted at the seafloor may equally reach the atmosphere” (page 814).

On page 814, Kopf (2003) writes: “The fundamentally wrong conclusion of Milkov et al. (2003) is that

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they oppose their mud volcanic estimates with the seepage estimates instead of acknowledging that mud volcanism is one of many mechanisms for devolatilization and gas seepage". However, Milkov et al. (2003) simply compare the new estimate of gas flux from deep-water MVs with the previous estimate of global gas seepage from deep-water areas and conclude that these previous estimates may be too low because MVs alone may emit almost as much gas as previously suggested for the total seepage. Milkov et al. (2003) do not "oppose" MVs and the other seepage features; instead, the authors point out that MVs emit gases in addition to other fault and salt-related seeps and vents on continental margins.

In addition to the above misquotations, Kopf (2003) misuses previously presented data by assigning them inaccurate meaning. For example, Kopf (2003) reports in Table 2a that onshore small MVs emit from $5 \text{ m}^3 \text{ year}^{-1}$ to $3,413 \text{ m}^3 \text{ year}^{-1}$ of CH_4 . However, these fluxes are from single vents, not from the entire MV (Etiopie et al. 2002), which leads to problems in global extrapolations performed by Kopf (2003).

Problems with assumptions, calculations and extrapolations

Our analysis suggests that many conclusions of Kopf (2003) are based on inappropriate assumptions and erroneous calculations. We report here only the most significant problems, and the readers are encouraged to check the numbers themselves before using them in future research.

Kopf (2003) assumes that small MVs emit from $100 \text{ m}^3 \text{ year}^{-1}$ to $1,000 \text{ m}^3 \text{ year}^{-1}$ of CH_4 (Table 2c). This assumption is based on the measurements in Sicily, which the author misunderstood as discussed above. The total CH_4 flux from the Maccalube MV apparently classified by Kopf (2003) as "small" is about $560,000 \text{ m}^3 \text{ year}^{-1}$, which includes the flux from all vents and from soil microseepage (Etiopie et al. 2002). Kopf (2003) uses gas flux data from a single vent to calculate the global gas flux from small MVs. This extrapolation is inappropriate because numerous vents populate many small MVs, and the total gas flux from an individual small mud volcano may be several orders of magnitude higher than assumed in the calculations of Kopf (2003).

In the same Table 2c of Kopf (2003), the minimum and maximum CH_4 fluxes from mid-size onshore MVs are the same ($10,000 \text{ m}^3 \text{ year}^{-1}$). This is an apparent mistake, because the wider range is reported in Table 2a. A similar mistake is made for the large offshore MVs. These mistakes are then carried into Table 3, and the total calculated fluxes during quiescent periods are erroneous.

We found several mistakes made during data manipulation and conversion from one unit to another. For example, in Table 3, the total minimum CH_4 flux

from onshore MVs is reported to be $46,602,500 \text{ g year}^{-1}$ (second row from the bottom). However, this value represents the sum of the minimum quiescent and eruptive fluxes reported in the fourth row from the top, where fluxes are expressed in $\text{m}^3 \text{ year}^{-1}$. The appropriate value to report in the third row from the bottom and use in the following analysis would be $0.033 \text{ Tg year}^{-1}$. Similarly, the sum of maximum fluxes from onshore MVs during quiescent periods and eruptions ($3.28 \times 10^{11} \text{ m}^3 \text{ year}^{-1}$, implying that 99.9% of total flux is from eruptions) is reported in the second row from the bottom, where units are gram per year. We recalculated that the appropriate value to report is 234 Tg year^{-1} . However, this maximum flux is clearly too high because MVs emit predominantly ^{14}C -free CH_4 , and only $96\text{--}144 \text{ Tg year}^{-1}$ ($\sim 20\%$) of total atmospheric CH_4 flux ($\sim 600 \text{ Tg year}^{-1}$) is ^{14}C -free (Lelieveld et al. 1998; IPCC 2001). The bottom part of Table 3 reports a global minimum flux of $0.197 \text{ Tg year}^{-1}$ for all onshore and offshore MVs. However, the sum of values from the eleventh row of Table 3 is $0.226 \text{ Tg year}^{-1}$ (after appropriate conversion of units). Similarly, the maximum total flux reported is 123 Tg year^{-1} , but adding values from the eleventh row produces 611 Tg year^{-1} .

Reality check and comparison with the previous estimates

It follows from the above analysis that the final total and onshore CH_4 fluxes reported in Table 3 and throughout the text were calculated with numerous arithmetic mistakes and are clearly erroneous. Therefore, it is not surprising that some implications from the presented results are not scientifically sound. For example, Kopf (2003) suggests that "the total amount of CH_4 is derived equally from the onshore and offshore features" (page 809). However, this is not consistent with the results in Table 3 (and also in Table 5) where the average total CH_4 flux from onshore and offshore MVs is $61.5 \text{ Tg year}^{-1}$, while CH_4 flux from onshore MVs is $0.164 \text{ Tg year}^{-1}$ or two orders of magnitude lower. Accepting the results reported in the bottom part of Table 3, it should be concluded that on average 99.8% of the global CH_4 flux is from offshore MVs, and the onshore MVs emit globally only from ~ 0.00005 to $\sim 0.33 \text{ Tg year}^{-1}$. The lower value is clearly illogical because it is more than ten times less than the CH_4 flux from just one mud volcano (for example, in Sicily, eastern Azerbaijan, and eastern Romania, Etiopie et al. 2002, 2004a, b). The upper value of the flux from onshore MVs is one order of magnitude lower than estimated in other studies (Table 1 in this comment).

The results presented by Kopf (2003) are inconsistent with the text, tables and figures, which leads to confusing conclusions. For example, the author states that the "onshore emission from mud volcanism is approximately on average 0.3% of annual CH_4 of all sources"

Table 1 Estimates of CH₄ flux from MVs (to the atmosphere and global) (Tg year⁻¹)

Study	Flux to the atmosphere during both quiescent activity and eruptions	Global flux to atmosphere and oceans
Dimitrov (2002)	10.3–12.6	–
Etiopie and Klusman (2002)	5–10 ^a	–
Kopf (2002)	–	0.08–1.39
Milkov et al. (2003)	6 ^b	33 ^b
Kopf (2003)	0.00005–0.328 ^a (~0.03–234) ^c	0.2–123 (~0.3–611) ^c
Dimitrov (2003)	5	–
Etiopie and Milkov (2004)	> 6–9	–

^aFlux from onshore MVs only

^bThe estimate includes minor contribution of non-CH₄ gases

^cThe range in parentheses is recalculated in this comment because errors in the original calculations and unit conversions were found

(page 810). However, the ratio of contributions from MVs and from all CH₄ sources in the atmosphere is reported to be 0.0003 (Table 4a), which implies 0.03% of CH₄ contributed by MVs. This result then contradicts Fig. 3a, where the relative significance of CH₄ emission from MVs is given at 10%. It appears that the author uses in Fig. 3a the value of 61 Tg year⁻¹, which is the average total gas flux from both onshore and offshore MVs as follows from the bottom of Table 3. However, using this number is inconsistent with the discussion that deep-water MVs do not contribute much CH₄ into the atmosphere. Fig. 3a implies that all global gas flux from MVs reaches the atmosphere which is not an appropriate assumption (Milkov et al. 2003). It is not clear what contribution of MVs to the atmospheric CH₄ budget (0.03%, 0.3% or 10% of total sources) presented by Kopf (2003) should be compared with ~1% estimated by Milkov et al. (2003).

Conclusions

Published estimates of CH₄ fluxes (global and to the atmosphere) from MVs are summarised in Table 1 of this comment. The estimates of Etiopie and Klusman (2002), Milkov et al. (2003), Dimitrov (2002; 2003) and Etiopie and Milkov (2004) are similar, and suggest that the total CH₄ flux from MVs (located mainly onshore) to the atmosphere is in a range of 5–13 Tg year⁻¹. The estimate of Kopf (2003) is ~0.00005–0.328 Tg year⁻¹,

which is significantly lower than suggested in the other studies. We found that this range was calculated erroneously because the proper unit conversion was not applied in the bottom part of Table 3. The range calculated from the upper part of Table 3 (0.03–234 Tg year⁻¹) varies over four orders of magnitude. The upper value of that range exceeds the total atmospheric flux of ¹⁴C-free CH₄ and is clearly not possible. It is unfortunate that the numerous misquotations and mistakes were not revealed during the review process.

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