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# The missing carbon budget puzzle piece: shallow-water hydrothermal vents contribution to global CO<sub>2</sub> fluxes

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#### ABSTRACT

The release of  $CO_2$  gases from volcanoes and their secondary geothermal manifestations are an important contributor to the global carbon budget. While degassing from mid ocean ridges is relatively well-constrained, the contribution of shallow submarine volcanic degassing to the atmosphere is less clear. Shallow-water hydrothermal vents are common seafloor features present at depths shallower than 200 m near submarine volcanic areas, releasing a gas phase composed mainly of  $CO_2$  mixed with other trace gases. Despite their widespread distribution, a limited number of studies have investigated shallow-water vents  $CO_2$  flux to the atmosphere. Based on available data and through three different data expansion techniques, we estimate that shallow-water hydrothermal vents can contribute between 20 and 128 Mt  $CO_2$  yr<sup>-1</sup> globally, increasing previous estimates of global volcanic  $CO_2$  fluxes by ~9 to ~22 %. We conclude that shallow-water hydrothermal vents might be a significant, yet neglected contributor to the global carbon budget, and systematic studies are needed to increase the data available and better constrain their carbon contribution to the atmosphere.

#### **INTRODUCTION**

The geological carbon (C) cycle involves the movement of C through Earth's mantle, crust, and atmosphere. Carbon released through volcanism balances C consumed through the subduction of C-bearing sediments and carbonates to the deep mantle (Burton et al., 2013; Werner et al., 2019; Plank and Manning, 2019; Fischer et al., 2019; Bekaert et al., 2021). Active volcanoes release C mainly as  $CO_2$  through crater fumaroles and open vents, as well as by diffuse degassing from hot springs, volcanic flanks, and secondary geothermal features which altogether can be significant contributors to the total C volcanic flux (Werner et al., 2019). This is true for both subaerial and submarine volcanism, with the latter estimated to release approximately an order of magnitude less gas to the atmosphere (Hauri et al., 2019).

Direct emissions from terrestrial volcanoes contribute almost half of the total global estimates attributed to subaerial volcanism (~300 Mt yr<sup>-1</sup> of CO<sub>2</sub>) (Mörner and Etiope, 2002; Chiodini et al., 2006), of which active subaerial crater fumaroles and volcanic plumes release between 53 and 88 Mt yr<sup>-1</sup> (Fischer and Aiuppa, 2020). Diffuse degassing, although less characterized, is also thought to be an important contributor to global CO<sub>2</sub> (Wong et al., 2019), with estimated fluxes between 83 and 93 Mt yr<sup>-1</sup> that could rival CO<sub>2</sub> released by eruptive activity (Werner et al., 2019; Fischer et al., 2019; Fischer and Aiuppa, 2020). Submarine volcanism at spreading centers has been estimated to release a total CO<sub>2</sub> flux between 58 and 96.8 Mt yr<sup>-1</sup> (Marty and Tolstikhin, 1998; Hauri et al., 2019) with recent estimates reporting a flux of approximately 72.2 Mt CO<sub>2</sub> yr<sup>-1</sup> (Bekaert et al., 2021). However the ~100,000 year residence time of dissolved CO<sub>2</sub> in seawater likely buffers the short-term effect of MORs contribution to the global C budget despite their global extent (Hauri et al., 2019). However, if the system is exposed above sea level (e.g., Iceland today), where a significant delivery of  $CO_2$  from the mantle directly into the atmosphere is possible, MORs contributions have been estimated to be between 3.1 and 10.1 Mt CO<sub>2</sub> yr<sup>-1</sup> (Barry et al., 2014; Hauri et al., 2019), reflecting the high variability of CO<sub>2</sub> contributions depending on spreading rate, mantle C concentrations and magma flux.

Shallow-water hydrothermal vents (SWHVs) are a particular class of hydrothermal vents commonly found along active plate margins and seafloor volcanic flanks (Figure 1A). They occur at depths shallower than ~200 m (Price and Giovannelli, 2017; Aiuppa et al., 2021), and are often dominated by gas phase emissions mainly composed of large amounts of  $CO_2$ 

mixed with other trace gasses like  $H_2S$  and  $CH_4$  (Figure 1B and 1C). Considering the abundance, global distribution and shallow depths of these vents (Price and Giovannelli, 2017), they could represent a major contributor to global  $CO_2$  degassing.



**Figure 1.** Global distribution of SWHVs (A) showing SWHVs with available gas flux information used in this work (yellow), the SWHVs present in the InterRidge database (v 3.4) or reported in the literature (teal), and the location of SWHVs reported by Price and Giovannelli (2017) (purple). Vigorous underwater degassing in (B) the Aeolian Archipelago, Italy (credits Giulia Bernardi); and (C) Milos Island, Greece (credits Costantino Vetriani/Rutgers University).

However, despite their potential importance, there is a lack of systematic and extensive characterization, and information regarding their spatial extent, structure, temporal evolution, and degassing flux is scarce (Price and Giovannelli, 2017; Martelat et al., 2020). Current data

on the gas composition and flux from SWHVs is limited to a handful of locations (Table 1). For example, SWHVs near Milos island (Greece) are among the most intensely studied vents in the world (Dando et al., 1995, 2014; Daskalopoulou et al., 2016; Price and Giovannelli, 2017; Minissale et al., 2019) with CO<sub>2</sub> emissions estimated to be between 1.5 and 7.5 Mt yr<sup>-1</sup>. These estimates are based on acoustic surveys (Dando et al., 1995, 2014), drone imagery, and gas chamber monitoring limited only to the hydrothermal emissions in Palechori Bay (Daskalopoulou et al., 2018; Khimasia et al., 2020, 2021) and extrapolated to a degassing area of approximately 70 km<sup>2</sup>, introducing significant uncertainties. Other well-studied shallow-water vent locations, such as those on the Aeolian Archipelago in Sicily (Italy) and the Gulf of Pozzuoli near Naples (Italy) are not well constrained with respect to C fluxes, and data is available from just a handful of sites (Italiano and Nuccio, 1991; Aiuppa et al., 2015, 2017, 2019, 2021).

The lack of flux estimates for the vast majority of known SWHVs can be attributed to several factors: difficulties associated with the measurements underwater; the large number of hydrothermal vents present (Price and Giovannelli, 2017); and the impossibility of using remote sensing techniques developed for subaerial degassing. Given the shallow nature of SWHVs, the abundance of gas-phase emissions, and the high number of shallow vents that occur globally, SWHVs might be a significant and yet neglected contributor to the global carbon budget. Here, we provide an overview of available data and use three independent statistical techniques to estimate the SWHVs contribution to the global C cycle.

#### **METHODS**

To estimate the contribution of SWHV degassing to global C fluxes we applied a three-step approach to obtain the average gas flux released by these features: (i) identify the SWHVs

with published gas flux data (Fig. 1A); (ii) apply three data expansion techniques to estimate the population mean, and (iii) multiply the obtained average gas flux by the number of SWHVs reported to constrain the amount of CO<sub>2</sub> (Mt CO<sub>2</sub> yr<sup>-1</sup>) that could potentially be delivered into the atmosphere. When compiling the data to be used for the downstream steps, we found a surprisingly low number of SWHVs with information regarding gas fluxes (Table S1). Nevertheless, this small dataset represents diverse locations and tectonic settings, potentially supporting their use as a representative subset of the global population of shallow vents. All statistical analyses were conducted on R (version 4.1.3, R Core Team, 2020). All data and code necessary to reproduce the analysis is available through a github repository released as a permanent doi <u>https://www.doi.org/10.5281/zenodo.7263267</u>.

The three data expansion techniques applied to overcome the bias associated with the small dataset size involved: oversampling (Approach 1); jackknife downsampling followed by 1,000 bootstrap resampling (Approach 2); and a synthetic minority oversampling technique (SMOTE) combined with bootstrapping (1,000 times) to increase our sample size by using feature vector nearest neighbor data generation (Chawla et al., 2002) and obtain a more robust estimate (see also Expanded Methods in the Supplemental Material).

Global degassing estimates were calculated by considering: (i) the minimum number of known SWHVs (*n*=77), equal to the number of shallow-water vents reported in the InterRidge database (InterRidge Database, Ver. 3.4 accessed January 2022, <u>https://vents-data.interridge.org</u>); (ii) the maximum number of estimated SWHVs (*n*=487), equal to the global estimate of shallow vent numbers made by Price and Giovannelli (2017); and (iii) a more realistic and yet conservative estimate of the global number of SWHVs

(n=282), derived from the average of the two previous numbers. Average fluxes as well as degassing estimates obtained are summarized in Table 1.



Figure 2. Average gas composition of SWHVs reported in the literature (see Supplemental References).

#### **RESULTS AND DISCUSSION**

Statistical approaches to globally extrapolate C data have been applied previously by Burton et al. (2013), Shinohara (2013), and Aiuppa et al. (2019) to either obtain estimates of  $CO_2$  fluxes from different geological settings through field  $CO_2$  measurements or to estimate  $CO_2$  fluxes from volcanoes for which no data is available. In particular, Aiuppa et al. (2019) applied Monte Carlo permutations to a  $CO_2$  flux dataset from actively degassing volcanoes, running a simulation of random variation 100 times within the mean  $\pm$  standard deviation value of the fluxes and extrapolating available  $SO_2$  fluxes and  $CO_2/SO_2$  data to: estimate  $CO_2$  fluxes from volcanoes for which no data was available, and the total amount of  $CO_2$  that could be released by volcanic degassing. Fischer et al. (2019) applied a similar approach to

extrapolate the  $CO_2$  fluxes that could be released by unmeasured volcanoes that likely have undergone hydrothermal or magmatic degassing. However, as both groups acknowledge, regardless of the approach followed to obtain the  $CO_2$  flux, the size of the dataset (*i.e.*, total number of degassing SWHVs to be considered) and the definition of what will be considered as a representative flux are issues that will have an impact in the reliability of the estimations.

In our case, two major sources of uncertainty are present when attempting to estimate the global flux of SWHVs: i) the mean CO<sub>2</sub> flux from each vent location; and ii) their global abundance. Ideally, the average flux per unit area is known for a representative number of vents, and this can be extrapolated to a global flux using the global area of shallow vents, similarly to what has been successfully applied to obtain MOR estimates using the global length of MORs (Marty and Tolstikhin, 1998; Wong et al., 2019; Bekaert et al., 2021). However, the global number and distribution of SWHVs is not an easy function of geological features (like for MORs) and it is more difficult to estimate. Price and Giovannelli (2017) used the location of known Holocene volcanoes to estimate the global number of possible shallow vents locations, obtaining approximately 500 locations. This is about one order of magnitude higher than the number of known shallow vents (n=77) present in the latest release of the InterRidge database (Beaulieu and Szafranski, 2020), which is most certainly an underestimation of the global number of vents. For instance, the database lists only 2 locations in the Gulf of Naples, while an acoustic survey performed in 2014 confirmed 54 locations at depths between 71 and 158 m (Passaro et al., 2014). As we have previously stated, the number of available CO<sub>2</sub> flux measurements for SWHVs is very limited (Table S1), and accurate estimates of the mean SWHVs degassing are difficult and associated with large uncertainties. For example, for the Milos shallow vent area, the annual CO<sub>2</sub> flux estimates of 2.24 Mt of CO<sub>2</sub> (Dando et al., 1995) was used instead of the 4.50 Mt of CO<sub>2</sub> yr<sup>-1</sup>

reported more recently (Dando et al., 2014) since this value is considered an overestimation of the  $CO_2$  output of the island by more recent studies (Daskalopoulou et al., 2018). The same situation is also plausible for a number of other published estimates used in this work, hence additional direct measurements to better constrain the outliers are needed to reduce the associated uncertainties.

**Table 1.** Estimated  $CO_2$  fluxes for shallow-water hydrothermal vents using the three different approaches and the resulting average flux

	Approach 1 (Mt CO <sub>2</sub> yr <sup>-1</sup> )	Approach 2 (Mt CO <sub>2</sub> yr <sup>-1</sup> )	Approach 3 (Mt CO <sub>2</sub> yr <sup>-1</sup> )	Average (Mt CO <sub>2</sub> yr <sup>-1</sup> )
Minimum SWHVs global $CO_2$ flux <sup>*</sup>	$21.1 \pm 0.5$	21.9 ± 1.2	$17.8 \pm 0.2$	$20.2 \pm 2.5$
Conservative SWHVs global $CO_2$ flux <sup>†</sup>	66.7 ± 1.5	$69.2 \pm 3.8$	$56.2 \pm 0.7$	$64.1 \pm 7.8$
Maximum SWHVs global $CO_2$ flux <sup>§</sup>	133.4 ± 2.9	$138.5 \pm 7.5$	$112.5 \pm 1.3$	$128.1 \pm 15.6$

\* Obtained after multiplying the vents registered at the InterRidge database (n=77) by the average flux obtained after each approach.

<sup>†</sup>Obtained after multiplying the average number of vents (n=282) times the average flux obtained in each approach. <sup>§</sup>Results after multiplying the maximum number of vents (n=487) by the average flux obtained in each approach.

To overcome the above mentioned limitations we used three different statistical approaches. The first two approaches relied on oversampling (Approach 1) or downsampling coupled with oversampling (Approach 2) to estimate the population mean. This was designed to reduce biases associated with the small dataset and reduce the bias introduced by outliers (Babu, 2011). Approach 3, involved generating artificial data points to fill in the gaps in the population estimate (SMOTE), a technique successfully applied to generate reliable population data (*i.e.*, Deng et al., 2017). The flux estimates obtained using Approach 3 show lower values (interpreted as more conservative estimates) compared to Approach 1 and 2, with confidence intervals more similar to the ones obtained with Approach 2. Each flux

estimate was then multiplied by the number of SWHVs to obtain what we defined as minimum, conservative and maximum fluxes from the global vents. The minimum flux resulted from the multiplication of the number of vents reported on the InterRidge Database (n=77) by the average obtained after each approach; the maximum flux was the result of multiplying the averages of each approach by the number of putative vents reported by Price and Giovannelli (2017) (n=487); the average between these two numbers (n=282) was used to obtain what we considered a more conservative and yet realistic number of vents.



**Figure 3**. Comparison of the estimated  $CO_2$  flux (in Mt  $CO_2$  yr<sup>-1</sup>) from different geological sources compared with the estimates for SWHVs obtained from this work. Fluxes from other geological features were taken from the literature (see Supplemental References).

Regardless of the approach considered, for each scenario (minimum, conservative and maximum flux from SWHVs) contributions to the  $CO_2$  fluxes were similar (Table 1) and are very close to simple linear expansion obtained by multiplying the average flux associated with the 10 sites reported (Table S1).

Published estimates of the amount of CO<sub>2</sub> released to the oceans and atmosphere by volcanic activity are between 158 and 637 Mt CO<sub>2</sub> yr<sup>-1</sup>, including that released into the oceans from mid-ocean ridges (Mörner and Etiope, 2002; Burton et al., 2013; Hauri et al. 2019; Werner et al. 2019; Bekaert et al., 2021). If we consider the number of putative SWHVs (n=487) proposed by Price and Giovanelli (2017) and we combine it with the average gas flux obtained in this work (maximum estimate scenario), the amount of CO<sub>2</sub> that could be released annually by SWHVs could represent between 6 to 30% of the CO<sub>2</sub> flux reported in the literature for subaerial volcanic degassing. Our results suggest that SWHVs emissions might be very high (Fig. 3), and comparable in size to the emissions produced by actively degassing volcanoes (Aiuppa et al., 2017, 2019; Werner et al., 2019; Fischer et al., 2019; Fischer and Aiuppa, 2020), and could even surpass the ones associated with MORs (21-72.2 Mt  $CO_2$  yr<sup>-1</sup>; (Hauri et al., 2019; Wong et al., 2019; Bekaert et al., 2021), In addition to this, when compared to the total CO<sub>2</sub> flux released by subaerial volcanism estimated through indirect methods, our results represent a fifth of the total flux reported in the literature (Burton et al., 2013; Werner et al., 2019; Aiuppa et al., 2019; Fischer et al., 2019). If instead, we consider the minimum estimate obtained based on the number of known and reported SWHVs (n=77), the amount of  $CO_2$  that could potentially be released into the oceans is similar to the one released by Mt. Etna, one of the major volcanic contributors globally (Aiuppa et al., 2015, 2017, 2019). Our conservative estimate instead, obtained using an intermediate number of SWHVs (n=282), is comparable to the degassing estimates from the East African Rift (Lee et

al., 2016; Hunt et al., 2017; Wong et al., 2019). We believe that this estimation  $(56.2 \pm 0.7 \text{ Mt} \text{CO}_2 \text{ yr}^{-1})$  is a more realistic one, given that just for the Gulf of Naples area, there are more vents present than the ones reported on the databases available (Passaro et al., 2014).

Although our results are exceptionally high, and possibly represent a large overestimate of the true contribution of SWHVs degassing to the global C budget, we strongly believe that SWHVs contribution to global degassing should not be ignored, especially if we consider that they could be releasing nearly as much  $CO_2$  as the East African Rift and three times as much as an actively degassing volcano like Mt. Etna. Shallow water hydrothermal vents are globally distributed, and given their shallow depths, their influence on atmospheric  $CO_2$  concentrations as well as local hydrogeochemical conditions (*e.g.*, ions and metals released in seawater) are probably higher than deep-sea vents associated with MOR. More systematic studies on degassing are needed to better constrain the role of SWHVs and reduce the uncertainties associated with their contribution to the global carbon flux.

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#### DATA AVAILABILITY

Data and codes used to obtain the estimations is available at the GitHub repository <u>https://github.com/giovannellilab/Shallow\_vent\_degassing\_paper\_2022</u> and released under doi <u>https://www.doi.org/10.5281/zenodo.7263267</u>.

#### AUTHOR CONTRIBUTIONS

DG and JMM conceived the idea, AB, MC, AC and DG performed the analysis. All authors equally contributed to the data interpretation and writing of this manuscript.

#### **CONFLICT OF INTEREST STATEMENT**

The authors have no conflicts of interest to declare.

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**Supplemental Material.** Supplemental Material containing the list of the shallow-water hydrothermal vent  $CO_2$  flux data with the associated references used in the manuscript, as well as an extended methods section is available online.

#### SUPPLEMENTAL MATERIAL

Site	Tectonic setting	Depth range (m)	Temperature (°C)	Flux (t CO <sub>2</sub> yr <sup>-1</sup> )	Reference
El Hierro Volcano (Canary Islands, Spain)	Intraplate volcano	-	38	219,000	Santana-Casiano et al. (2016)
Ischia Island (Gulf of Naples, Italy)	Volcanic ridge	0-10	15	1,228.38	D'Antonio et al. (2007)
Milos Shallow vents (Aegean Islands, Greece)	Arc Volcano	0-200	123	2,244,000	Dando et al. (2014)
Champagne Hot Springs (Dominica Island, Lesser Antilles)	Arc Volcano	1-5	71	0.198	Johnson and Cronan (2001)
Panarea hydrothermal field (Aeolian Islands, Italy)	Arc Volcano	7-200	130	6,600	Italiano and Nuccio (1991)
Kraternaya Bight, Yankich Island (Central Kurile Arc, Russia)	Arc Volcano	0-60	15	1.13	Zhirmunsky and Tarasov (1990)
Tutum Bay, Ambitle Island (Papua New Guinea)	Arc Volcano	5-10	98	8,000	Licence et al. (1987)
Espalamanca, Faial (Azores, Portugal)	Intraplate volcano	5-50	35	5,240.1	Giovannelli, (unpublished)
Secca delle Fumose, Campi Flegrei (Gulf of Naples, Italy)	Volcanic-ridge	4-20	82	18,905.8	Di Napoli et al. (2016)
Average CO <sub>2</sub> flux				310,508.7	

Table S1. Shallow-water hydrothermal vent  $CO_2$  flux data used in the manuscript.

#### **Expanded Methods**

When constructing the dataset to run the simulations, two considerations were made: (i) if a range was provided in the original publication, the mean value was taken; and (ii) values that were considered in the literature as overestimations and thus, capable of further skewing the mean distribution were discarded. Approach 1 involved oversampling by first creating a dataset of n=50 with the function "sample" and then running a 1000 bootstrap (allowing data replacement) using the function "bootstrap". Both operations were carried out using the R package BOOTSTRAP (Shao and Tu, 1995). Approach 2, more conservative, involved downsampling the dataset before oversampling to reduce the effect of possible outliers. This approach involved applying a jackknife resampling, followed by 1000 bootstrap permutations. The jackknife resampling was carried out using the function "rsamp" from the R package SAMPLER (Baldassaro, 2019). Approach 3, consisted in applying a synthetic minority oversampling technique, SMOTE, to increase our sample size by using feature vector nearest neighbor data generation (Chawla et al., 2002); an approach originally developed to generate missing data in unbalanced datasets for machine learning. SMOTE data generation was then combined with bootstrapping to get more robust estimates (Aborujilah et al., 2021). The function "SmoteClassif" present in the R package UBL (Branco et al., 2016) was used to perform the SMOTE data expansion. As a first step in this approach, the mean and standard deviation of flux data obtained after performing a balanced SMOTE to a starting dataset composed of the vents reported on the InterRidge Database that shared a common variable (i.e., temperature) was used to create a bigger and balanced dataset. This data was then reclassified using the function "SmoteClassif" and bootstrapped 1,000 times to obtain the final dataset, used for calculating the C flux emissions estimates.

#### Chemical composition of emissions from shallow water hydrothermal vents reported in

#### Figure 2

Champagne Island (Dominica): Johnson and Cronan (2001)

Bahia Concepcion (Gulf of Mexico): Forrest et al. (2005)

Espalamanca, Azores (Portugal): Munaro et al. (2010)

Ischia Island (Italy): D'Antonio et al. (2007)

Kagoshima Bay (Japan): Hashimoto et al. (1995)

Kolumbo Submarine Volcanoes (Greece): Rizzo et al. (2019)

Kueishan tao (Taiwan): (Kuo, 2001)

Kraternaya Bay, Central Kurile Arc (Russia): Zhirmunsky and Tarasov (1990)

Luise Harbor and Lihir Island (Papua New Guinea): Pichler et al. (1999)

Matupi Harbor and Rabaul Caldera (Papua New Guinea): Tarasov et al. (1999)

Milos Island (Greece): Dando et al. (2014)

Panarea Island (Italy): Italiano and Nuccio (1991)

Pozzuoli, Miseno Cape (Italy): Orlando et al. (2011)

San Felipe (Gulf of Mexico): Barragán et al. (2001)

Taupo Volcanic Zone (New Zealand): Giggenbach (1995)

Tor Caldara (Italy): Patwardhan et al. (2018)

Whale Island (New Zealand): Tarasov et al. (1999)

Wakamiko Caldera, Kagoshima Bay (Japan): Ishibashi et al. (2008)

CO2 fluxes reported from different geological settings used to construct Figure 3.

Arc Volcanoes data obtained from Sano and Williams (1996); Active Subaerial Volcanoes

from Burton et al. (2013) and Fischer et al. (2019); East African Rift from Lee et al., (2016);

Mt. Etna from Aiuppa et al. (2017); Mid ocean ridges from Varekamp et al. (1992); Marty

and Tolstikhin (1998); Hauri et al. (2019); and Bekaert et al. (2021); Volcanic Lakes from Perez et al. (2011); Hydrothermal systems data from Werner et al., (2019).

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